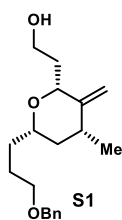


4H), 1.06 (s, 9H)ppm;  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$ =151.9, 138.8, 135.7, 135.6, 134.2, 129.6, 128.4, 127.8, 127.7, 127.6, 104.3, 77.4, 74.9, 72.9, 70.5, 60.8, 43.4, 36.0, 34.7, 32.8, 27.0, 26.2, 19.4, 18.2 ppm; HRMS (ESI-TOF) calcd for  $\text{C}_{35}\text{H}_{46}\text{O}_3\text{SiNa}^+$   $[\text{M}+\text{Na}]^+$  565.3108; Found 565.3111.

**2-((2*R*,4*R*,6*S*)-6-[3-(Benzyloxy)propyl]-4-methyl-3-methylidenetetrahydro-2*H*-pyran-2-yl)ethanol**

**(S1):** To a stirred solution of olefin derivative **19a** (500 mg, 0.921 mmol, 1.0 equiv) in THF (20 mL) at 0 °C

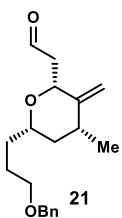


was added dropwise tetra-*n*-butylammonium fluoride (1 M in THF, 0.920 mL, 0.920 mmol, 1.0 equiv), and the reaction mixture was allowed to warm to 23 °C. After 2.5 h, the reaction mixture was quenched by the addition of saturated aqueous  $\text{NH}_4\text{Cl}$  solution (15 mL). The aqueous layer was extracted with EtOAc ( $3 \times 15$  mL) and the combined organic layers were

dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated under reduced pressure. The obtained residue was purified by flash column chromatography ( $\text{SiO}_2$ , 10  $\rightarrow$  40% EtOAc in hexanes) to afford pure alcohol **S1** (264 mg, 0.866 mmol, 94% yield) as a colorless oil. **S1**:  $R_f$ =0.40 ( $\text{SiO}_2$ , hexanes/EtOAc 3:2, v/v);  $[\alpha]_D^{23}$ =+8.10 ( $c$ =2.0,  $\text{CH}_2\text{Cl}_2$ ); FT-IR (film)  $\nu_{\text{max}}$ =3431, 2954, 2850, 1650, 1454, 1364, 1312, 1091, 1058, 903, 736  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ =7.36–7.32 (m, 4H), 7.30–7.26 (m, 1H), 4.87 (d,  $J$ =1.6 Hz, 1H), 4.82 (d,  $J$ =1.6 Hz, 1H), 4.49 (s, 2H), 3.95–3.89 (m, 1H), 3.84 (dd,  $J$ =6.0, 4.9 Hz, 2H), 3.66–3.57 (m, 1H), 3.53–3.41 (m, 2H), 2.31–2.23 (m, 1H), 2.02–1.91 (m, 2H), 1.81–1.61 (m, 3H), 1.56 (td,  $J$ =7.6, 6.1 Hz, 2H), 1.13–1.06 (m, 4H)ppm;  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$ =150.9, 138.7, 128.5, 127.8, 127.6, 105.0, 79.4, 77.7, 73.0, 70.3, 61.8, 42.6, 35.6, 33.5, 32.8, 26.1, 18.1 ppm; HRMS (ESI-TOF) calcd for  $\text{C}_{19}\text{H}_{28}\text{O}_3\text{Na}^+$   $[\text{M}+\text{Na}]^+$  327.1931; Found 327.1930.

**{(2*R*,4*R*,6*S*)-6-[3-(Benzyloxy)propyl]-4-methyl-3-methylidenetetrahydro-2*H*-pyran-2-yl}acet-**

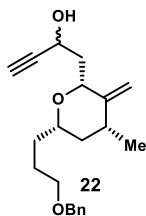
**aldehyde (21):** To a stirred solution of alcohol **S1** (200 mg, 0.657 mmol, 1.0 equiv) in  $\text{CH}_2\text{Cl}_2$  (10 mL) at



23 °C was added DMP (418 mg, 0.985 mmol, 1.5 equiv) portion wise. After 0.5 h, the reaction mixture was quenched by the addition of saturated aqueous  $\text{Na}_2\text{S}_2\text{O}_3$  solution (20 mL) and the obtained suspension was further stirred for 2 h. The aqueous layer was extracted with  $\text{CH}_2\text{Cl}_2$  ( $3 \times 10$  mL) and the combined organic layers were washed with saturated aqueous  $\text{NaHCO}_3$

solution (10 mL), dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated under reduced pressure. The obtained residue was purified by flash column chromatography ( $\text{SiO}_2$ , 10  $\rightarrow$  30% EtOAc in hexanes) to afford pure aldehyde **21** (179 mg, 0.591 mmol, 90% yield) as a colorless foam. **21**:  $R_f$ =0.80 ( $\text{SiO}_2$ , hexanes/EtOAc 3:2, v/v);  $[\alpha]_D^{23}$ =+17.0 ( $c$ =2.0,  $\text{CH}_2\text{Cl}_2$ ); FT-IR (film)  $\nu_{\text{max}}$ =3004, 2848, 2725, 1725, 1650, 1454, 1363, 1087, 1028, 904, 735  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ =9.81 (dd,  $J$ =2.7, 2.0 Hz, 1 H), 7.36–7.32 (m, 4 H), 7.30–7.26 (m, 1 H), 4.84 (dd,  $J$ =1.9, 0.6 Hz, 1 H), 4.75 (d,  $J$ =1.9 Hz, 1 H), 4.49 (s, 2 H), 4.29–4.22 (m, 1 H), 3.62–3.54 (m, 1 H), 3.47 (ddt,  $J$ =26.7, 9.3, 6.5 Hz, 2 H), 2.79–2.65 (m, 2 H), 2.36–2.28 (m, 1 H), 1.84–1.68 (m, 2 H), 1.67–1.59 (m, 1 H), 1.57–1.47 (m, 2 H), 1.14–1.07 (m, 4 H) ppm;  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$ =201.9, 150.2, 138.7, 128.4, 127.8, 127.6, 105.4, 77.7, 74.4, 72.9, 70.3, 45.7, 42.6, 35.6, 32.5, 26.0, 18.0 ppm; HRMS (ESI-TOF) calcd for  $\text{C}_{19}\text{H}_{26}\text{O}_3\text{Na}^+$   $[\text{M}+\text{Na}]^+$  325.1774; Found 325.1771.

**1-((2*R*,4*R*,6*S*)-6-[3-(Benzyloxy)propyl]-4-methyl-3-methylidenetetrahydro-2*H*-pyran-2-yl)but-3-yn-2-ol (**22**):** To a stirred solution of aldehyde **21** (600 mg, 1.98 mmol, 1.0 equiv) in THF (15 mL) at  $-78^\circ\text{C}$

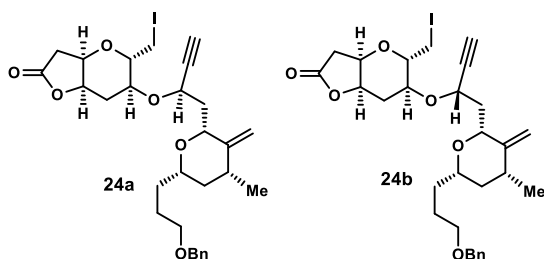


was added ethynylmagnesium bromide (0.5 M in THF, 9.92 mL, 4.96 mmol, 2.5 equiv), and the reaction mixture was warmed to  $-10^\circ\text{C}$ . After 15 min, the reaction mixture was quenched by the addition of saturated aqueous  $\text{NH}_4\text{Cl}$  solution (30 mL). The aqueous layer was extracted with EtOAc ( $3 \times 20$  mL) and the combined organic layers were dried over

anhydrous  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated under reduced pressure. The obtained residue was purified by flash column chromatography ( $\text{SiO}_2$ , 5  $\rightarrow$  20% EtOAc in hexanes) to afford alcohol **22** (mixture of diastereomers, 1.5:1 *dr*, 520 mg, 1.58 mmol, 80% yield) as a colorless foam. **22**:  $R_f$ =0.35 ( $\text{SiO}_2$ , hexanes/EtOAc 5:1, v/v);  $[\alpha]_D^{23}$ =+21.3 ( $c$ =3.0,  $\text{CH}_2\text{Cl}_2$ ); FT-IR (film)  $\nu_{\text{max}}$ =3415, 3297, 2956, 2850, 1650, 1454, 1365, 1312, 1206, 1089, 1062, 903, 697  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ =7.36–7.31 (m, 4 H), 7.29–7.26 (m, 1 H), 4.87 (d,  $J$ =1.5 Hz, 0.6 H), 4.84 (d,  $J$ =1.6 Hz, 0.4 H), 4.83 (d,  $J$ =1.6 Hz, 1 H), 4.67 (tdt,  $J$ =7.3, 5.2, 2.4 Hz, 1 H), 4.51–4.47 (m, 2 H), 4.34–4.28 (m, 0.4 H), 3.98–3.93 (m, 0.6 H), 3.66 (dddd,  $J$ =11.2, 7.3, 5.5, 2.1 Hz, 0.4 H), 3.62–3.57 (m, 0.6 H), 3.54–3.43 (m, 2 H), 2.46 (d,  $J$ =2.1 Hz, 1 H), 2.45 (d,  $J$ =2.1 Hz, 1 H), 2.35–2.23 (m, 1 H), 2.21–2.09 (m, 1.6 H), 2.05 (ddd,  $J$ =14.4, 5.9, 2.7 Hz, 0.4 H), 1.83–1.61 (m, 3 H), 1.59–1.50 (m, 2 H), 1.15–1.08 (m, 4 H) ppm;  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$ =150.5, 150.3, 138.7, 138.6,

128.5, 127.8, 127.7, 127.6, 127.5, 105.3, 105.1, 84.8, 84.6, 78.5, 77.8, 77.7, 76.7, 73.0, 72.9, 72.6, 70.2, 70.1, 62.0, 60.9, 42.5, 39.2, 37.3, 35.6, 35.5, 32.7, 32.6, 26.1, 26.0, 18.1, 18.0 ppm; HRMS (ESI-TOF) calcd for C<sub>21</sub>H<sub>28</sub>O<sub>3</sub>Na<sup>+</sup> [M+Na]<sup>+</sup> 351.1931; Found 351.1935.

**(3a*R*,5*S*,6*S*,7a*R*)-6-{[(2*R*)-1-{(2*R*,4*R*,6*S*)-6-[3-(Benzyloxy)propyl]-4-methyl-3-methylidenetetrahydro-2*H*-pyran-2-yl}but-3-yn-2-yl]oxy}-5-(iodomethyl)hexahydro-2*H*-furo[3,2-*b*]pyran-2-one (24a) and (3a*R*,5*S*,6*S*,7a*R*)-6-{[(2*S*)-1-{(2*R*,4*R*,6*S*)-6-[3-(benzyloxy)propyl]-4-methyl-3-methylidenetetrahydro-2*H*-pyran-2-yl}but-3-yn-2-yl]oxy}-5-(iodomethyl)hexahydro-2*H*-furo[3,2-*b*]pyran-2-one (24b):**

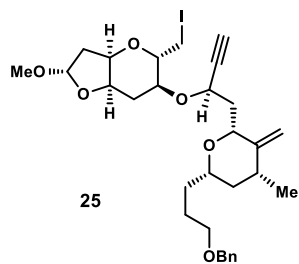


To a stirred solution of alkyne **22** (200 mg, 0.609 mmol, 1.0 equiv) in CH<sub>2</sub>Cl<sub>2</sub> (5 mL) at 23 °C was added Co<sub>2</sub>(CO)<sub>8</sub> (250 mg, 0.731 mmol, 1.2 equiv) in one portion. After 20 min, a solution of iodide **23**<sup>5</sup> (363 mg, 1.22 mmol, 2.0 equiv) in CH<sub>2</sub>Cl<sub>2</sub> (8 mL) was added. The reaction mixture was cooled to 0 °C, and BF<sub>3</sub>·Et<sub>2</sub>O (151 μL, 1.22 mmol, 2.0 equiv) was added dropwise. After 0.5 h, the reaction mixture was carefully quenched by the addition of saturated aqueous NaHCO<sub>3</sub> solution (20 mL), and allowed to warm to 23 °C. The aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 20 mL) and the combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure.

To a stirred solution of the so-obtained crude residue in acetone (20 mL) was added portion wise diammonium cerium(IV) nitrate (CAN) (1.67 g, 3.04 mmol, 5.0 equiv) at 0 °C. The resulting mixture was allowed to warm to 23 °C and stirred for 1 h before it was quenched by the addition of water (60 mL). The aqueous layer was extracted with EtOAc (3 × 30 mL) and the combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure. The obtained residue was purified by flash column chromatography (SiO<sub>2</sub>, 10 → 40% ethyl acetate in hexanes) to afford pure *cis*-isomer **24a** (185 mg, 0.304 mmol, 50% yield overall) and *trans*-isomer **2b** (59.0 mg, 0.097 mmol, 16% yield overall) as colorless oils (3:1 *dr*). **24a** (*cis*-isomer): R<sub>f</sub>=0.50 (SiO<sub>2</sub>, 40% EtOAc in hexanes); [α]<sub>D</sub><sup>23</sup>=+108.3 (*c*=0.6, CH<sub>2</sub>Cl<sub>2</sub>); FT-IR (film) ν<sub>max</sub>=3283, 3030, 2929, 2854, 1781, 1454, 1365, 1095, 1050, 904, 698 cm<sup>-1</sup>; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ=7.36–7.31 (m, 4H), 7.30–7.26 (m, 1H), 4.80 (d, *J*=1.5 Hz, 1H), 4.77 (d,

$J=1.5$  Hz, 1 H), 4.56–4.45 (m, 5 H), 3.97 (dt,  $J=11.0$ , 1.6 Hz, 1 H), 3.83 (dt,  $J=6.4$ , 4.8 Hz, 1 H), 3.74 (dddd,  $J=11.2$ , 7.4, 5.3, 2.1 Hz, 1 H), 3.59 (ddd,  $J=7.7$ , 6.3, 3.9 Hz, 1 H), 3.53–3.43 (m, 3 H), 3.28 (dd,  $J=10.8$ , 7.8 Hz, 1 H), 2.76 (dd,  $J=18.5$ , 6.3 Hz, 1 H), 2.67 (dd,  $J=18.4$ , 1.6 Hz, 1 H), 2.42 (d,  $J=2.0$  Hz, 1 H), 2.39–2.30 (m, 1 H), 2.21–2.10 (m, 2 H), 2.06 (dt,  $J=14.9$ , 4.9 Hz, 1 H), 1.96 (ddd,  $J=14.2$ , 11.1, 2.2 Hz, 1 H), 1.86–1.74 (m, 2 H), 1.73–1.65 (m, 1 H), 1.59–1.49 (m, 2 H), 1.08–1.01 (m, 4 H) ppm;  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta=175.0$ , 151.5, 138.8, 128.5, 127.8, 127.7, 104.2, 83.4, 76.7, 76.0, 74.5, 73.5, 73.1, 72.9, 70.6, 69.4, 63.3, 53.6, 43.3, 38.3, 35.7, 35.6, 32.8, 26.6, 26.4, 18.1, 5.5 ppm; HRMS (ESI-TOF) calcd for  $\text{C}_{29}\text{H}_{37}\text{O}_6\text{INa}^+$   $[\text{M}+\text{Na}]^+$  631.1527; Found 631.1528. **24b** (*trans*-isomer):  $R_f=0.4$  ( $\text{SiO}_2$ , hexanes/EtOAc 3:2,  $\nu/\nu$ );  $[\alpha]_D^{23}=+22.6$  ( $c=0.50$ ,  $\text{CH}_2\text{Cl}_2$ ); FT-IR (film)  $\nu_{\text{max}}=3285$ , 2929, 2852, 1781, 1454, 1364, 1194, 1092, 1049, 904, 698  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta=7.36$ –7.31 (m, 4 H), 7.30–7.27 (m, 1 H), 4.85 (brs, 1 H), 4.81 (d,  $J=1.9$  Hz, 1 H), 4.63–4.55 (m, 2 H), 4.51 (AB quart,  $J=11.5$  Hz, 2 H), 4.46 (ddd,  $J=10.3$ , 4.9, 2.1 Hz, 1 H), 3.90 (dd,  $J=10.6$ , 3.0 Hz, 1 H), 3.73–3.64 (m, 1 H), 3.56 (td,  $J=6.7$ , 4.0 Hz, 1 H), 3.49 (dddd,  $J=15.8$ , 13.2, 9.0, 6.5 Hz, 3 H), 3.36 (dd,  $J=10.9$ , 4.0 Hz, 1 H), 3.30 (dd,  $J=10.9$ , 6.7 Hz, 1 H), 2.79–2.63 (m, 2 H), 2.56 (ddd,  $J=14.4$ , 6.1, 4.7 Hz, 1 H), 2.48 (d,  $J=2.0$  Hz, 1 H), 2.35–2.23 (m, 1 H), 2.19–2.09 (m, 2 H), 2.04 (ddd,  $J=13.2$ , 10.3, 3.1 Hz, 1 H), 1.79 (dddd,  $J=17.2$ , 9.2, 6.8, 4.3 Hz, 2 H), 1.71–1.61 (m, 1 H), 1.55–1.48 (m, 2 H), 1.11–1.05 (m, 4 H) ppm;  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta=174.7$ , 150.7, 138.7, 128.5, 127.8, 127.7, 104.8, 82.8, 77.5, 76.2, 75.2, 74.9, 74.0, 73.1, 73.0, 70.4, 69.2, 67.9, 43.2, 37.9, 35.8, 34.7, 32.5, 30.3, 26.2, 18.1, 6.0 ppm; HRMS (ESI-TOF) calcd for  $\text{C}_{29}\text{H}_{37}\text{O}_6\text{INa}^+$   $[\text{M}+\text{Na}]^+$  631.1527; Found 631.1528.

**Methyl 3,7-anhydro-6-*O*-[(2*R*)-1-[(2*R*,4*R*,6*S*)-6-[3-(benzyloxy)propyl]-4-methyl-3-methylidenetetrahydro-2*H*-pyran-2-yl]but-3-yn-2-yl]-2,5,8-trideoxy-8-iodo- $\alpha$ -D-*altro*-octofuranoside (25):** To a stirred

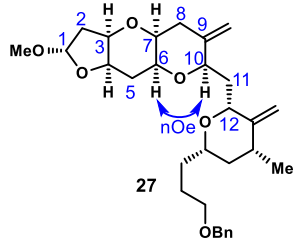


solution of lactone **24b** (200 mg, 0.329 mmol, 1.0 equiv) in  $\text{CH}_2\text{Cl}_2$  (10 mL) at  $-78^\circ\text{C}$  was added dropwise DIBAL-H (1.0 M in toluene, 395  $\mu\text{L}$ , 0.395 mmol, 1.2 equiv). The resulting mixture was warmed to  $-20^\circ\text{C}$  and stirred for 1 h before it was diluted with ethyl acetate (20 mL) and quenched by the addition of saturated aqueous solution of Rochelle salt solution (40 mL), allowed to

warm to 23 °C, and stirred for 2 h until the reaction mixture became a clear solution. The aqueous layer was extracted with EtOAc (3 × 10 mL), and the combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure.

The so-obtained crude residue was dissolved in MeOH (8 mL) and *p*-TsOH·H<sub>2</sub>O (11.2 mg, 0.0658 mmol, 0.2 equiv) was added at 23 °C. After 0.5 h, the reaction mixture was quenched by the addition of saturated aqueous NaHCO<sub>3</sub> (6 mL) and diluted with water (6 mL). The aqueous layer was extracted with EtOAc (3 × 10 mL), and the combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure. The obtained residue was purified by flash column chromatography (SiO<sub>2</sub>, 5 → 20% EtOAc in hexanes) to afford pure acetal **25** (154 mg, 0.247 mmol, 75% yield overall) as a colorless oil. **25**: R<sub>f</sub>=0.60 (SiO<sub>2</sub>, hexanes/EtOAc 2:1, v/v); [α]<sub>D</sub><sup>23</sup>=+86.2 (*c*=1.5, CH<sub>2</sub>Cl<sub>2</sub>); FT-IR (film) ν<sub>max</sub>=3286, 2927, 2853, 1454, 1366, 1211, 1114, 1093, 1057, 904, 698 cm<sup>-1</sup>; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ=7.36–7.31 (m, 4H), 7.30–7.27 (m, 1H), 5.13 (dd, *J*=4.3, 3.1 Hz, 1H), 4.83 (d, *J*=1.8 Hz, 1H), 4.79 (d, *J*=1.8 Hz, 1H), 4.50 (s, 2H), 4.48 (q, *J*=5.2 Hz, 1H), 4.44 (dt, *J*=11.0, 2.2 Hz, 1H), 4.13 (q, *J*=4.5 Hz, 1H), 4.02–3.96 (m, 1H), 3.71–3.60 (m, 2H), 3.55–3.42 (m, 4H), 3.29 (s, 3H), 3.22 (dd, *J*=10.5, 8.1 Hz, 1H), 2.39 (d, *J*=2.0 Hz, 1H), 2.30–2.21 (m, 3H), 2.14 (ddd, *J*=14.1, 11.1, 2.1 Hz, 1H), 2.06–1.90 (m, 3H), 1.87–1.79 (m, 1H), 1.77 (ddd, *J*=12.8, 4.6, 2.1 Hz, 1H), 1.68 (ddq, *J*=12.8, 9.5, 6.7 Hz, 1H), 1.55 (ddd, *J*=8.8, 7.3, 4.3 Hz, 2H), 1.11–1.05 (m, 4H) ppm; <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ=151.1, 138.6, 128.5, 127.7, 127.6, 104.5, 104.1, 83.8, 74.4, 73.2, 73.1, 73.0, 72.9, 72.6, 63.1, 54.9, 43.3, 40.0, 38.3, 35.9, 33.0, 27.3, 26.4, 18.1, 7.9 ppm; HRMS (ESI-TOF) calcd for C<sub>30</sub>H<sub>41</sub>O<sub>6</sub>Na<sup>+</sup> [M+Na]<sup>+</sup> 647.1840; Found 647.1842.

**(2*S*,3*aR*,4*aS*,7*R*,8*aS*,9*aR*)-7-({(2*R*,4*R*,6*S*)-6-[3-(Benzyloxy)propyl]-4-methyl-3-methylidenetetrahydro-2*H*-pyran-2-yl}methyl)-2-methoxy-6-methylidenedecahydrofuro[3,2-*b*]pyrano[2,3-*e*]pyran (**27**):**



To a stirred solution of **25** (108 mg, 0.173 mmol, 1.0 equiv) in THF (5 mL) at 0 °C was added KO*t*-Bu (38.8 mg, 0.346 mmol, 2.0 equiv). The resulting mixture was allowed to warm to 23 °C and stirred for 10 min before it was diluted with hexanes (30 mL) and EtOAc (15 mL) and filtered through a pad of SiO<sub>2</sub>. The filtrate was concentrated under reduced pressure to give crude

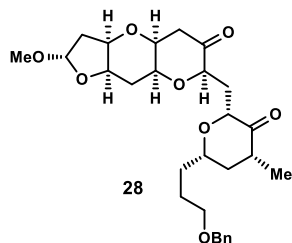
exocyclic olefin **26** (90.2 mg, 0.173 mmol, quantitative yield), which was used in the next step without further purification.

To a stirred solution of the obtained exocyclic olefin **26** (90.2 mg, 0.173 mmol, 1.0 equiv) in toluene (10 mL) at 23 °C were added *n*-Bu<sub>3</sub>SnH (100 μL, 0.346 mmol, 2.0 equiv) and AIBN (14.2 mg, 0.0865 mmol, 0.5 equiv). The resulting mixture was transferred and submerged into a preheated oil bath (90 °C) and stirred for 2 h before it was allowed to cool to 23 °C. The resulting mixture was concentrated under reduced pressure. Flash column chromatography (SiO<sub>2</sub>, hexanes/EtOAc 20:1, *v/v* → 2:1, *v/v*) of the residue afforded the corresponding organotin intermediate (80.1 mg, 0.102 mmol, 58% yield) as a colorless oil.

To a stirred solution of the residue obtained above (mixture of isomers, 80.1 mg, 0.102 mmol, 1.0 equiv) in MeOH (4 mL) at 23 °C was added *p*-TsOH·H<sub>2</sub>O (17.5 mg, 0.102 mmol, 1.0 equiv). The resulting mixture was stirred for 45 min and then diluted with saturated aqueous NaHCO<sub>3</sub> solution (10 mL). The aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organic layers were washed with brine (10 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure. Flash column chromatography (SiO<sub>2</sub>, 5 → 20% EtOAc in hexanes) of the residue afforded **27** (40.7 mg, 0.0816 mmol, 80% yield) as a colorless oil. NOE studies indicate the *cis*-relation between H6 and H10. **27**: R<sub>f</sub> = 0.20 (SiO<sub>2</sub>, hexanes/EtOAc 5:1, *v/v*);  $[\alpha]_D^{23} = +67.8$  (*c* = 2.0, CH<sub>2</sub>Cl<sub>2</sub>); FT-IR (film)  $\nu_{\max} = 2953, 2850, 1651, 1454, 1364, 1194, 1094, 1028, 897, 697 \text{ cm}^{-1}$ ; <sup>1</sup>H NMR (600 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  = 7.33 (dd, *J* = 7.4, 1.5 Hz, 2H), 7.19 (td, *J* = 7.6, 1.8 Hz, 2H), 7.11 (td, *J* = 7.2, 1.4 Hz, 1H), 5.02 (dd, *J* = 5.7, 2.8 Hz, 1H), 4.87 (brs, 1H), 4.84 (brs, 1H), 4.82 (brs, 1H), 4.73 (d, *J* = 1.9 Hz, 1H), 4.37 (s, 2H), 4.34 (d, *J* = 10.5 Hz, 1H), 4.28–4.23 (m, 1H), 3.73 (dt, *J* = 5.4, 3.3 Hz, 1H), 3.66 (ddd, *J* = 5.7, 3.2, 1.8 Hz, 1H), 3.40 (dddd, *J* = 15.4, 9.0, 6.4, 2.8 Hz, 3H), 3.31 (ddd, *J* = 5.5, 3.6, 2.1 Hz, 1H), 3.15 (s, 3H), 2.95 (td, *J* = 4.4, 2.0 Hz, 1H), 2.54 (dd, *J* = 14.0, 4.1 Hz, 1H), 2.36 (dt, *J* = 15.0, 3.6 Hz, 1H), 2.31–2.23 (m, 3H), 2.13 (ddd, *J* = 13.5, 10.7, 2.4 Hz, 1H), 2.06 (ddd, *J* = 14.1, 6.1, 2.8 Hz, 1H), 1.99 (ddt, *J* = 12.6, 6.3, 3.3 Hz, 1H), 1.90 (dddd, *J* = 15.9, 8.5, 4.6, 1.7 Hz, 1H), 1.77 (dtd, *J* = 13.3, 6.6, 3.0 Hz, 1H), 1.69 (dt, *J* = 14.9, 5.4 Hz, 1H), 1.61 (dtt, *J* = 13.9, 9.2, 4.0 Hz, 1H), 1.49 (dddd, *J* = 13.7, 10.1, 6.3, 4.2 Hz, 1H), 1.40 (ddd, *J* = 12.5, 4.6, 2.1 Hz, 1H), 1.05–0.99 (m, 1H), 0.96 (d, *J* = 6.5 Hz, 3H) ppm; <sup>13</sup>C NMR (151 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  = 152.6, 144.8, 139.5, 128.6, 128.4, 127.7, 108.9, 104.7,

104.0, 77.1, 77.0, 74.9, 74.4, 73.4, 73.0, 72.3, 70.8, 70.6, 55.1, 43.4, 41.4, 38.3, 36.0, 35.2, 33.0, 30.6, 26.7, 18.2 ppm; HRMS (ESI-TOF) calcd for  $C_{30}H_{42}O_6Na^+$   $[M+Na]^+$  521.2874; Found 521.2874.

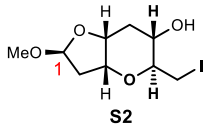
**Methyl (16*S*)-3,7:6,10:12,16-trianhydro-16-[3-(benzyloxy)propyl]-2,5,8,11,14,15-hexadeoxy-14-methyl-D-xylo- $\beta$ -L-galactadecofuranoside-9,13-diulose (**28**):** Through a stirred solution of olefin **27**



(30.0 mg, 0.0602 mmol, 1.0 equiv) in  $CH_2Cl_2$  (6 mL) at  $-78^\circ C$  was bubbled freshly generated ozone. After the color of the reaction mixture changed to light blue (ca. 5 min), the resulting mixture was quenched by the addition of dimethyl sulfide (44.0  $\mu L$ , 0.602 mmol, 10.0 equiv), and allowed to warm to  $23^\circ C$ . After stirring for 10 h, the solvent was removed under reduced pressure, and the

obtained residue was purified by flash column chromatography ( $SiO_2$ , 20  $\rightarrow$  40% ethyl acetate in hexanes) to afford pure diketone **28** (28.4 mg, 0.0566  $\mu mol$ , 94% yield) as a colorless oil. **3**:  $R_f$ =0.40 ( $SiO_2$ , hexanes/EtOAc 2:1,  $v/v$ );  $[\alpha]_D^{23}$ =+74.2 ( $c$ =0.60,  $CH_2Cl_2$ ); FT-IR (film)  $\nu_{max}$ =2928, 2854, 1724, 1454, 1362, 1262, 1094, 1046, 740  $cm^{-1}$ ;  $^1H$  NMR (600 MHz,  $C_6D_6$ )  $\delta$  7.17–6.98 (m, 4 H), 6.95–6.79 (m, 1 H), 4.75 (dd,  $J$ =5.6, 2.9 Hz, 1 H), 4.18 (s, 2 H), 3.85 (ddd,  $J$ =9.9, 3.8, 1.0 Hz, 1 H), 3.77 (dd,  $J$ =9.5, 3.9 Hz, 1 H), 3.48 (dt,  $J$ =5.3, 3.8 Hz, 1 H), 3.32 (dddt,  $J$ =11.2, 8.9, 5.0, 2.9 Hz, 1 H), 3.21–3.13 (m, 3 H), 2.96 (dt,  $J$ =5.0, 2.5 Hz, 1 H), 2.94 (s, 3 H), 2.76 (td,  $J$ =4.9, 2.3 Hz, 1 H), 2.39 (dd,  $J$ =15.5, 4.4 Hz, 1 H), 2.35–2.28 (m, 2 H), 2.04 (dt,  $J$ =14.6, 4.3 Hz, 1 H), 1.96–1.89 (m, 2 H), 1.81 (ddd,  $J$ =14.2, 6.2, 2.9 Hz, 1 H), 1.64–1.53 (m, 2 H), 1.47–1.38 (m, 2 H), 1.37–1.31 (m, 1 H), 1.26 (ddd,  $J$ =13.1, 6.2, 1.9 Hz, 1 H), 1.24–1.21 (m, 1 H), 0.98 (td,  $J$ =12.9, 11.0 Hz, 1 H), 0.74 (d,  $J$ =6.6 Hz, 3 H) ppm;  $^{13}C$  NMR (151 MHz,  $C_6D_6$ )  $\delta$  207.4, 205.8, 139.4, 129.9, 128.7, 127.8, 104.7, 79.0, 77.7, 77.1, 76.6, 73.7, 73.1, 72.2, 70.32, 70.26, 55.2, 43.4, 42.39, 42.37, 41.1, 32.3, 30.4, 30.1, 26.6, 14.6 ppm; HRMS (ESI-TOF) calcd for  $C_{28}H_{38}O_8Na^+$   $[M+Na]^+$  525.2459; Found 525.2462.

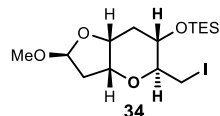
**Methyl 3,7-anhydro-2,5,8-trideoxy-8-iodo- $\alpha$ -D-altro-octofuranoside (**S2**):** To a stirred solution of **23**



(10.2 g, 34.2 mmol, 1.0 equiv) in  $CH_2Cl_2$  (300 mL) at  $-78^\circ C$  was added dropwise DIBAL-H (1.0 M in toluene, 85.5 mL, 85.5 mmol, 2.5 equiv). The resulting mixture was

allowed to slowly warm to  $-20^{\circ}\text{C}$  and stirred for 1 h. The mixture was acidified by addition of HCl (3 M in MeOH, 150 mL, 450 mmol, 13.2 equiv), the resulting mixture was allowed to warm to  $23^{\circ}\text{C}$  and stirred for 8 h before it was diluted with  $\text{H}_2\text{O}$  (200 mL). The layers were separated, and the aqueous layer was extracted with  $\text{CH}_2\text{Cl}_2$  ( $3 \times 300\text{ mL}$ ). The combined organic layers were washed with  $\text{NaHCO}_3$  solution (100 mL, sat. aq.), dried over  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated under reduced pressure. Flash column chromatography ( $\text{SiO}_2$ , hexanes/EtOAc 1:1,  $v/v \rightarrow 1:2$ ,  $v/v$ ) of the residue afforded **S2** (7.63 g, 24.3 mmol, 71% yield) and C1-*epi*-**S2** (1.51 g, 4.79 mmol, 14% yield) as colorless oils, respectively. The configurations of the newly generated stereocenters were confirmed by nOe studies (see spectrum part). **S2**:  $R_f=0.40$  ( $\text{SiO}_2$ , hexanes/EtOAc 1:1,  $v/v$ );  $[\alpha]_{\text{D}}^{23}=+97.1$  ( $c=1.0$ ,  $\text{CHCl}_3$ ); FTIR (film):  $\nu_{\text{max}}$  3504, 2926, 2831, 1430, 1368, 1345, 1248, 1212, 1184, 1140, 1096, 1055, 1038, 1018, 993, 969, 950, 916, 890, 846,  $800\text{ cm}^{-1}$ ;  $^1\text{H}$  NMR (600 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  4.74 (dd,  $J=6.0, 3.5\text{ Hz}$ , 1 H), 3.82 (dddd,  $J=9.4, 5.4, 2.8, 1.1\text{ Hz}$ , 1 H), 3.59–3.48 (m, 3 H), 3.44–3.32 (m, 1 H), 3.09 (s, 3 H), 2.66 (dd,  $J=10.7, 9.6\text{ Hz}$ , 1 H), 2.54 (dd,  $J=10.7, 5.3\text{ Hz}$ , 1 H), 2.15 (ddd,  $J=14.6, 6.0, 0.8\text{ Hz}$ , 1 H), 1.91 (ddt,  $J=15.3, 2.5, 1.1\text{ Hz}$ , 1 H), 1.83 (ddd,  $J=14.6, 5.2, 3.5\text{ Hz}$ , 1 H), 1.20 (dt,  $J=15.6, 3.7\text{ Hz}$ , 1 H). ppm;  $^{13}\text{C}$  NMR (151 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  104.5, 78.0, 73.7, 70.4, 65.3, 55.5, 41.4, 26.9, 3.6 ppm; HRMS (ESI-TOF)  $m/z$ :  $[\text{M}+\text{Na}]^+$  Calcd. for  $\text{C}_9\text{H}_{15}\text{IO}_4\text{Na}^+$  336.9907; Found 336.9903.

**Methyl 3,7-anhydro-2,5,8-trideoxy-8-iodo-6-O-(triethylsilyl)- $\alpha$ -D-*altro*-octofuranoside (34):** To a

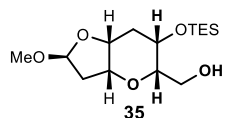


stirred solution of **S2** (7.60 g, 24.3 mmol, 1.0 equiv) in  $\text{CH}_2\text{Cl}_2$  (100 mL) at  $0^{\circ}\text{C}$  was added imidazole (3.31 g, 48.6 mmol, 2.0 equiv) and  $\text{TESCl}$  (4.00 mL, 31.6 mmol, 1.3 equiv). The resulting mixture was allowed to slowly warm to  $23^{\circ}\text{C}$  and stirred for 1 h before it was quenched by the addition of sat. aq.  $\text{NaHCO}_3$  solution (50 mL). The layers were separated, and the aqueous layer was extracted with  $\text{CH}_2\text{Cl}_2$  ( $3 \times 100\text{ mL}$ ). The combined organic layers were washed with brine (100 mL), dried over  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated under reduced pressure. Flash column chromatography ( $\text{SiO}_2$ , hexanes/EtOAc 20:1,  $v/v \rightarrow 2:1$ ,  $v/v$ ) of the residue afforded **34** (10.4 g, 24.3 mmol, quant. yield) as colorless oil. **34**:  $R_f=0.70$  ( $\text{SiO}_2$ , hexanes/EtOAc 5:1,  $v/v$ );  $[\alpha]_{\text{D}}^{23}=+93.5$  ( $c=1.0$ ,  $\text{CHCl}_3$ ); FTIR (film):  $\nu_{\text{max}}$  2954, 2911, 2877, 1458, 1369, 1343, 1212, 1177, 1118, 1100, 1043, 1018, 1002, 918, 878, 805, 744,  $728\text{ cm}^{-1}$ ;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  5.10 (dd,  $J=5.6, 1.7\text{ Hz}$ , 1 H), 4.52 (dt,  $J=7.3, 4.7\text{ Hz}$ ,



1 H), 4.15 (q,  $J=6.0$  Hz, 1 H), 3.63 (td,  $J=7.8, 5.7$  Hz, 1 H), 3.42 (dd,  $J=10.4, 3.0$  Hz, 1 H), 3.35 (ddd,  $J=7.9, 6.7, 3.0$  Hz, 1 H), 3.31 (s, 3 H), 3.24 (dd,  $J=10.4, 6.7$  Hz, 1 H), 2.29–2.20 (m, 2 H), 2.17 (ddd,  $J=14.4, 7.3, 1.7$  Hz, 1 H), 1.82 (ddd,  $J=13.8, 7.7, 6.2$  Hz, 1 H), 0.96 (t,  $J=8.0$  Hz, 9 H), 0.62 (qd,  $J=7.9, 1.4$  Hz, 6 H) ppm;  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ):  $\delta$  104.1, 75.3, 74.0, 73.6, 68.2, 55.0, 39.1, 34.2, 8.7, 7.0, 5.1 ppm; HRMS (ESI-TOF)  $m/z$ :  $[\text{M}+\text{Na}]^+$  Calcd. for  $\text{C}_{15}\text{H}_{29}\text{IO}_4\text{SiNa}^+$  451.0772; Found 451.0774.

**Methyl 3,7-anhydro-2,5-dideoxy-6-*O*-(triethylsilyl)- $\beta$ -L-galacto-octofuranoside (35):** To a stirred



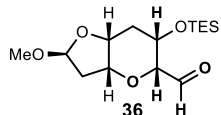
solution of **34** (9.30 g, 21.7 mmol, 1.0 equiv) in THF (60 mL) at 0 °C was added KO $t$ -Bu (3.65 g, 32.6 mmol, 1.5 equiv). The resulting mixture was allowed to warm to

23 °C and stirred for 5 min before it was diluted with hexanes (100 mL) and EtOAc (30 mL), and filtered through a pad of  $\text{SiO}_2$ . The filtrate was concentrated under reduced pressure to give crude exocyclic olefin **26** (6.50 g, 21.7 mmol, quantitative yield), which was used in the next step without further purification.

To a stirred solution of the above obtained olefin intermediate (6.50 g, 21.7 mmol, 1.0 equiv) in THF (100 mL) at 0 °C were added  $\text{BH}_3\cdot\text{Me}_2\text{S}$  (2.0 M in THF; 12.0 mL, 23.9 mmol, 1.1 equiv), the resulting mixture was allowed to warm to 23 °C and stirred for 0.5 h before it was quenched by the addition of  $\text{H}_2\text{O}$  (150 mL). To this mixture was added  $\text{NaBO}_3$  (9.46 g, 95.6 mmol, 4.4 equiv) and the resulting mixture was further stirred for 6 h. The reaction mixture was then extracted with EtOAc ( $3 \times 100$  mL), the combined organic extracts were washed with brine (100 mL), dried over  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated under reduced pressure. Flash column chromatography ( $\text{SiO}_2$ , hexanes/EtOAc 10:1,  $v/v \rightarrow 1:2, v/v$ ) afforded **35** (5.32 g, 16.7 mmol, 77% yield for the two steps) as a colorless oil. **35**:  $R_f=0.40$  ( $\text{SiO}_2$ , hexanes/EtOAc 1:1,  $v/v$ );  $[\alpha]_D^{23}=+75.3$  ( $c=1.0$ , EtOAc); FT-IR (film):  $\nu_{\text{max}}$  3473, 2953, 2911, 2877, 1459, 1419, 1374, 1238, 1181, 1143, 1097, 1022, 926, 867, 783, 741,  $726\text{ cm}^{-1}$ ;  $^1\text{H}$  NMR (600 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  5.15 (dd,  $J=5.8, 3.7$  Hz, 1 H), 3.86 (dd,  $J=11.1, 7.2$  Hz, 1 H), 3.72 (dt,  $J=5.1, 2.6$  Hz, 1 H), 3.66–3.56 (m, 2 H), 3.51–3.40 (m, 1 H), 3.25 (s, 3 H), 3.03 (ddd,  $J=7.2, 4.6, 1.8$  Hz, 1 H), 2.26 (ddt,  $J=14.3, 5.8, 0.8$  Hz, 1 H), 2.07 (dt,  $J=15.1, 2.9$  Hz, 1 H), 2.01 (ddd,  $J=14.3, 5.6, 3.7$  Hz, 1 H), 1.82 (d,  $J=6.8$  Hz, 1 H), 1.34 (ddd,  $J=15.1, 4.8, 4.1$  Hz, 1 H), 1.02 (t,  $J=7.9$  Hz, 9 H), 0.59 (qd,  $J=7.9, 5.9$  Hz, 6 H) ppm;  $^{13}\text{C}$  NMR (151 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  105.1, 78.7, 77.2, 73.1, 64.4, 63.6, 55.2, 41.7, 32.9, 7.1, 5.4 ppm; HRMS (ESI-TOF)  $m/z$ :  $[\text{M}+\text{Na}]^+$  Calcd. for  $\text{C}_{15}\text{H}_{30}\text{O}_5\text{SiNa}^+$

341.1755; Found 341.1760.

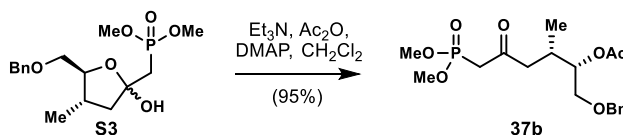
**Methyl (8S)-2,6-anhydro-4,7-dideoxy-3-O-(triethylsilyl)-D-galacto-octodialdo-8,5-furanoside (36):** To



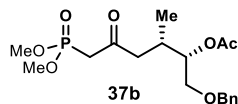
a stirred solution of alcohol **35** (4.70 g, 14.7 mmol, 1.0 equiv) in dry CH<sub>2</sub>Cl<sub>2</sub> (50 mL) at 0 °C was added Dess–Martin periodinane (9.37 g, 22.1 mmol, 1.5 equiv). The

resulting mixture was allowed to warm to 23 °C and stirred for 1 h before it was quenched by the addition of sat. aq. NaHCO<sub>3</sub> solution (30 mL) and a sat. aq. Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution (50 mL). The layers were separated, and the aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 50 mL). The organic layer was washed with brine (50 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure. Flash column chromatography (SiO<sub>2</sub>, hexanes/EtOAc 10:1, v/v → 1:1, v/v) afforded aldehyde **10** (3.86 g, 12.2 mmol, 83% yield) as a colorless oil. **36**: R<sub>f</sub>=0.70 (SiO<sub>2</sub>, hexanes/EtOAc 1:1, v/v); [α]<sub>D</sub><sup>23</sup>=+130.0 (c=1.0, EtOAc); FT-IR (film): ν<sub>max</sub> 2954, 2912, 2878, 1740, 1461, 1411, 1370, 1296, 1182, 1142, 1123, 1099, 1021, 985, 886, 862, 785, 728 cm<sup>-1</sup>; <sup>1</sup>H NMR (600 MHz, C<sub>6</sub>D<sub>6</sub>): δ 9.68 (brs, 1 H), 5.16 (dd, J=5.8, 3.8 Hz, 1 H), 3.93 (dt, J=4.2, 2.2 Hz, 1 H), 3.63 (dt, J=4.7, 2.3 Hz, 1 H), 3.45 (dd, J=5.4, 2.5 Hz, 1 H), 3.24 (s, 3 H), 3.07 (dd, J=1.9, 0.9 Hz, 1 H), 2.32 (ddt, J=14.4, 5.9, 0.8 Hz, 1 H), 2.05–1.89 (m, 2 H), 1.22–1.12 (m, 1 H), 1.02 (t, J=7.9 Hz, 9 H), 0.60 (qd, J=7.9, 2.3 Hz, 6 H) ppm; <sup>13</sup>C NMR (151 MHz, C<sub>6</sub>D<sub>6</sub>): δ 202.1, 105.0, 82.5, 76.9, 72.5, 65.2, 55.3, 41.5, 32.3, 7.0, 5.3 ppm; HRMS (ESI-TOF) m/z: [M+Na]<sup>+</sup> Calcd. for C<sub>15</sub>H<sub>28</sub>O<sub>5</sub>SiNa<sup>+</sup> 339.1597; Found 339.1598.

**Preparation of 37b**



**(2S,3S)-1-(Benzyloxy)-6-(dimethoxyphosphoryl)-3-methyl-5-oxohexan-2-yl acetate (37b):** To a stirred

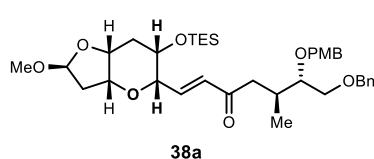


solution of ketal **S3**<sup>5</sup> (6.30 g, 18.3 mmol, 1.0 equiv) in CH<sub>2</sub>Cl<sub>2</sub> (50 mL) were added Et<sub>3</sub>N (5.10 mL, 36.6 mmol, 2.0 equiv), Ac<sub>2</sub>O (2.59 mL, 27.4 mmol, 1.5 equiv) and

*N,N*-dimethylpyridin-4-amine (DMAP, 220 mg, 1.83 mmol, 0.1 equiv) at 0 °C. The resulting mixture was allowed to warm to 23 °C and stirred for 15 h before it was quenched by the addition of MeOH (2 mL) and

a sat. aq. NaHCO<sub>3</sub> solution (30mL). The layers were separated, and the aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3×50mL). The combined organic layers were washed with brine (20 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure. Flash column chromatography (SiO<sub>2</sub>, hexanes/EtOAc 1:1, v/v → 1:3, v/v) of the residue afforded phosphonate **37b** (8.07 g, 17.4 mmol, 95% yield) as a colorless oil. **37b**: R<sub>f</sub>=0.40 (SiO<sub>2</sub>, 100% EtOAc);  $[\alpha]_D^{23} = -6.1$  (*c*=0.87, CHCl<sub>3</sub>); FT-IR (film):  $\nu_{\max}$  3643, 2957, 2856, 1716, 1454, 1402, 1372, 1236, 1158, 1104, 1023, 808, 740, 699 cm<sup>-1</sup>; <sup>1</sup>H NMR (600 MHz, CD<sub>3</sub>CN):  $\delta$  7.41–7.23 (m, 5 H), 4.86 (ddd, *J*=6.7, 5.5, 4.0 Hz, 1 H), 4.59–4.34 (m, 2 H), 3.70 (s, 3 H), 3.68 (s, 3 H), 3.58–3.51 (m, 2 H), 3.18–2.99 (m, 2 H), 2.69 (dd, *J*=17.7, 4.2 Hz, 1 H), 2.52–2.44 (m, 1 H), 2.43–2.33 (m, 1 H), 2.00 (s, 3 H), 0.89 (d, *J*=6.8 Hz, 3 H) ppm; <sup>13</sup>C NMR (151 MHz, CD<sub>3</sub>CN):  $\delta$  202.23 (d, *J*=6.1 Hz), 171.3, 139.5, 129.3, 128.6, 128.5, 76.2, 73.6, 70.3, 53.49 (d, *J*=6.5 Hz), 47.43 (d, *J*=1.9 Hz), 47.42, 42.1, 41.3, 30.6, 21.3, 16.7 ppm; HRMS (ESI-TOF) *m/z*: [M+Na]<sup>+</sup> Calcd. for C<sub>18</sub>H<sub>27</sub>O<sub>7</sub>PNa<sup>+</sup> 409.1387; Found 409.1390.

**Methyl (8*E*)-3,7-anhydro-14-*O*-benzyl-2,5,8,9,11,12-hexadeoxy-13-*O*-(4-methoxybenzyl)-12-methyl-6-*O*-(triethylsilyl)-D-threo-β-L-galacto-tetradec-8-enofuranosid-10-ulose (38a):** To a stirred solution of

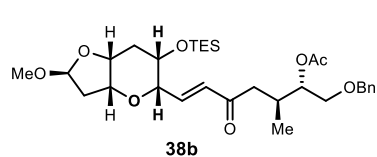


aldehyde **36** (1.10 g, 3.47 mmol, 1.0 equiv) and phosphonate **37a** (2.09 g, 4.51 mmol, 1.3 equiv) in MeCN (30 mL) at 0 °C was added LiCl (441 mg, 10.4 mmol, 3.0 equiv) and Et<sub>3</sub>N (2.42 mL, 17.3 mmol, 5.0 equiv). The

resulting mixture was allowed to warm to 23 °C and stirred for 1.5 h before it was quenched by the addition of sat. aq. NH<sub>4</sub>Cl solution (20mL). The layers were separated, and the aqueous layer was extracted with EtOAc (3×50 mL). The combined organic layers were washed with brine (30 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure. Flash column chromatography (SiO<sub>2</sub>, hexanes/EtOAc 10:1, v/v → 2:1, v/v) of the residue afforded enone **38a** (1.93 g, 2.95 mmol, 85% yield) as a colorless oil. **38a**: R<sub>f</sub>=0.70 (SiO<sub>2</sub>, hexanes/EtOAc 2:1, v/v);  $[\alpha]_D^{23} = +30.7$  (*c*=0.40, EtOAc); FT-IR (film):  $\nu_{\max}$  2954, 2910, 2876, 1696, 1637, 1613, 1513, 1455, 1368, 1301, 1247, 1180, 1140, 1097, 1054, 1028, 983, 889, 820, 740, 699 cm<sup>-1</sup>; <sup>1</sup>H NMR (600 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  7.34–7.17 (m, 5 H), 7.13–7.00 (m, 2 H), 6.86 (d, *J*=4.6 Hz, 1 H), 6.84–6.78 (m, 2 H), 6.50 (dd, *J*=16.0, 1.5 Hz, 1 H), 5.18 (dd, *J*=5.8, 3.8 Hz, 1 H), 4.66 (d, *J*=11.3 Hz, 1 H), 4.46 (d, *J*=11.3 Hz, 1 H), 4.33 (s, 2 H), 3.75–3.69 (m, 1 H), 3.59 (dd, *J*=5.5, 2.6 Hz, 1 H), 3.53–3.44

(m, 3 H), 3.43–3.37 (m, 2 H), 3.32 (s, 3 H), 3.26 (s, 3 H), 2.82 (dd,  $J=16.6, 4.3$  Hz, 1 H), 2.75–2.64 (m, 1 H), 2.47 (dd,  $J=16.6, 8.8$  Hz, 1 H), 2.33 (dd,  $J=14.3, 5.8$  Hz, 1 H), 2.09 (d,  $J=15.1$  Hz, 1 H), 2.04 (ddd,  $J=14.3, 5.5, 3.8$  Hz, 1 H), 1.34 (dt,  $J=15.2, 4.4$  Hz, 1 H), 1.09–0.85 (m, 12 H), 0.62–0.55 (m, 6 H).ppm;  $^{13}\text{C}$  NMR (151 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  198.5, 159.6, 143.5, 139.2, 131.8, 130.5, 129.6, 128.6, 127.79, 127.78, 127.69, 114.0, 105.1, 81.7, 77.7, 77.1, 73.4, 72.5, 72.5, 71.8, 66.1, 55.3, 54.8, 43.7, 41.7, 33.0, 31.8, 17.1, 7.1, 5.4 ppm; HRMS (ESI-TOF)  $m/z$ :  $[\text{M}+\text{Na}]^+$  Calcd. for  $\text{C}_{37}\text{H}_{54}\text{O}_8\text{SiNa}^+$  677.3480; Found 677.3479.

**Methyl (8E)-13-O-acetyl-3,7-anhydro-14-O-benzyl-2,5,8,9,11,12-hexadeoxy-12-methyl-6-O-(triethylsilyl)-D-threo- $\beta$ -L-galacto-tetradec-8-enofuranosid-10-ulose (38b):** To a stirred solution of the aldehyde

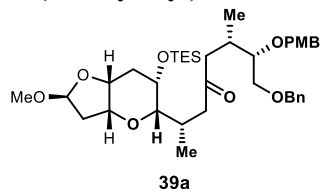


**36** (3.10 g, 9.80 mmol, 1.0 equiv) and phosphonate **37b** (4.92 g, 12.7 mmol, 1.3 equiv) in MeCN (50 mL) at 0 °C were added LiCl (1.25 g, 29.4 mmol, 3.0 equiv) and  $\text{Et}_3\text{N}$  (6.83 mL, 49.0 mmol, 5.0 equiv). The

resulting mixture was allowed to warm to 23 °C and stirred for 1.5 h before it was quenched by the addition of sat. aq.  $\text{NH}_4\text{Cl}$  solution (50 mL). The layers were separated, and the aqueous layer was extracted with EtOAc ( $3 \times 50$  mL). The combined organic layers were washed with brine (20 mL), dried over  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated under reduced pressure. Flash column chromatography ( $\text{SiO}_2$ , hexanes/EtOAc 10:1,  $v/v \rightarrow 2:1, v/v$ ) of the residue afforded enone **38b** (5.03 g, 8.72 mmol, 89% yield) as a colorless oil. **38b**:  $R_f=0.60$  ( $\text{SiO}_2$ , hexanes/EtOAc 2:1,  $v/v$ );  $[\alpha]_D^{23}=+30.3$  ( $c=2.0$ , EtOAc); FT-IR (film):  $\nu_{\text{max}}$  2953, 2910, 2876, 1740, 1697, 1675, 1637, 1455, 1415, 1371, 1238, 1181, 1139, 1127, 1097, 1053 1023, 982, 887, 739, 699  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (600 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  7.35–7.27 (m, 4 H), 7.23–7.13 (m, 1 H), 6.76 (dd,  $J=16.0, 5.0$  Hz, 1 H), 6.31 (dd,  $J=16.0, 1.6$  Hz, 1 H), 5.19 (dd,  $J=5.7, 3.9$  Hz, 1 H), 4.95 (ddd,  $J=6.4, 5.4, 4.4$  Hz, 1 H), 4.61–4.37 (m, 2 H), 4.09 (dd,  $J=5.4, 2.7$  Hz, 1 H), 3.99–3.96 (m, 1 H), 3.94 (dt,  $J=5.1, 1.9$  Hz, 1 H), 3.84 (td,  $J=3.6, 2.0$  Hz, 1 H), 3.58–3.49 (m, 2 H), 3.36 (s, 3 H), 2.66 (dd,  $J=16.6, 3.7$  Hz, 1 H), 2.55 (ddq,  $J=13.2, 6.6, 3.6$  Hz, 1 H), 2.42 (dd,  $J=16.6, 9.5$  Hz, 1 H), 2.38 (dd,  $J=14.5, 5.8$  Hz, 1 H), 2.24 (dt,  $J=15.1, 3.0$  Hz, 1 H), 2.09–2.03 (m, 4 H), 1.93 (dt,  $J=15.1, 4.4$  Hz, 1 H), 0.93 (t,  $J=7.9$  Hz, 9 H), 0.89 (d,  $J=6.8$  Hz, 3 H), 0.59–0.55 (m, 6 H) ppm;  $^{13}\text{C}$  NMR (151 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  198.8, 170.8, 143.9, 138.1, 130.2, 128.5, 127.8, 127.7, 104.8, 77.8, 77.1, 75.8, 73.2, 72.6, 69.5, 66.0, 55.6, 43.0, 41.2, 32.9, 30.1, 21.2, 16.7, 6.9, 5.0 ppm;

HRMS (ESI-TOF)  $m/z$ :  $[M+Na]^+$  Calcd. for  $C_{31}H_{48}O_8SiNa^+$  599.3011; Found 599.3009.

**Methyl 3,7-anhydro-14-*O*-benzyl-2,5,8,9,11,12-hexadeoxy-13-*O*-(4-methoxybenzyl)-8,12-dimethyl-6-*O*-(triethylsilyl)-D-arabino- $\beta$ -L-galacto-tetradecofuranosid-10-ulose (**39a**):** To a stirred solution of



CuCN (349 mg, 3.90 mmol, 3.0 equiv) in THF (50 mL) was added MeLi (1.6 M in Et<sub>2</sub>O, 4.87 mL, 7.80 mmol, 6.0 equiv) at  $-78^\circ\text{C}$ . The resulting mixture was stirred at  $-40^\circ\text{C}$  for 10 min and then cooled to  $-78^\circ\text{C}$ . Then, TMSCl (990  $\mu\text{L}$ ,

7.80 mmol, 6.0 equiv) and **38a** (850 mg, 1.30 mmol, 1.0 equiv) in THF (10 mL) were added. The resulting mixture was allowed to warm to  $-40^\circ\text{C}$  and stirred for additional 0.5 h before it was quenched by the addition of sat. aq.  $\text{NH}_4\text{Cl}$  solution (30 mL). The mixture was allowed to warm to  $23^\circ\text{C}$  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 ( $3 \times 30\text{ mL}$ ). The combined organic layers were washed with aq. HCl (0.05 M, 30 mL),  $\text{NaHCO}_3$  (30 mL, sat. aq.), dried over  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated under reduced pressure. Flash column chromatography ( $\text{SiO}_2$ , hexanes/EtOAc 10:1,  $v/v \rightarrow 2:1$ ,  $v/v$ ) of the residue afforded ketone **39a** (706 mg, 1.05 mmol, 81% yield) as a colorless oil. **39a**:  $R_f=0.80$  ( $\text{SiO}_2$ , hexanes/EtOAc 2:1,  $v/v$ );  $[\alpha]_D^{23}=+14.8$  ( $c=0.50$ , EtOAc); FT-IR (film):  $\nu_{\text{max}}$  2953, 2910, 2876, 1709, 1613, 1514, 1456, 1414, 1369, 1302, 1248, 1183, 1139, 1098, 1029, 972, 943, 824, 738  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (600 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  7.36–7.18 (m, 5H), 7.13–6.97 (m, 2H), 6.83 (d,  $J=8.6\text{ Hz}$ , 2H), 5.18 (dd,  $J=5.8, 3.9\text{ Hz}$ , 1H), 4.68 (d,  $J=11.3\text{ Hz}$ , 1H), 4.47 (d,  $J=11.3\text{ Hz}$ , 1H), 4.35 (d,  $J=1.7\text{ Hz}$ , 2H), 3.73 (dt,  $J=4.6, 2.0\text{ Hz}$ , 1H), 3.63 (brs, 1H), 3.58 (dd,  $J=5.4, 2.5\text{ Hz}$ , 1H), 3.53–3.46 (m, 2H), 3.45 (td,  $J=5.3, 4.0\text{ Hz}$ , 1H), 3.32 (s, 3H), 3.27 (s, 3H), 2.74 (dd,  $J=16.1, 4.0\text{ Hz}$ , 1H), 2.68–2.52 (m, 4H), 2.33–2.12 (m, 4H), 2.02 (ddd,  $J=14.2, 5.4, 3.8\text{ Hz}$ , 1H), 1.31 (dt,  $J=15.3, 4.4\text{ Hz}$ , 1H), 1.09 (t,  $J=7.9\text{ Hz}$ , 9H), 1.00 (d,  $J=6.6\text{ Hz}$ , 3H), 0.92 (d,  $J=6.5\text{ Hz}$ , 3H), 0.75–0.60 (m, 6H).ppm;  $^{13}\text{C}$  NMR (151 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  209.0, 159.7, 139.2, 131.8, 129.7, 128.6, 127.8, 127.7, 114.0, 105.1, 81.9, 81.8, 77.6, 73.4, 72.9, 72.5, 71.8, 63.5, 55.2, 54.8, 47.1, 46.1, 41.8, 33.4, 31.6, 30.7, 17.1, 16.5, 7.3, 5.7 ppm; HRMS (ESI-TOF)  $m/z$ :  $[M+Na]^+$  Calcd. for  $\text{C}_{38}\text{H}_{58}\text{O}_8\text{SiNa}^+$  693.3793; Found 693.3794.