SUPPORTING INFORMATION

Structure Assignment, Total Synthesis, and Antiviral Evaluation of Cycloviracin B_1

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General. All reactions were carried out under Ar. The solvents used were purified by distillation over the drying agents indicated and were transferred under Ar: THF, Et_2O (Mg-anthracene), CH_2Cl_2 (P_4O_{10}), MeCN, Et_3N, pyridine, DMF (CaH_2), MeOH (Mg), hexane, toluene (Na/K). Flash chromatography: Merck silica gel 60 (230-400 mesh). NMR: Spectra were recorded on a DPX 300, AV 400 or DMX 600 spectrometer (Bruker) in the solvents indicated; chemical shifts (δ) are given in ppm relative to TMS, coupling constants (J) in Hz. IR: Nicolet FT-7199 spectrometer, wavenumbers in cm^{-1}. MS (EI): Finnigan MAT 8200 (70 eV), HRMS: Finnigan MAT 95, Bruker APEX III FT-ICR-MS (7 T magnet). Melting points: Büchi melting point apparatus (uncorrected). Elemental analyses: H. Kolbe, Mülheim/Ruhr. All commercially available compounds (Lancaster, Fluka, Aldrich) were used as received unless stated otherwise.

Ketoester 4. *n*-BuLi (1.6 M in hexane, 89 mL, 142.4 mmol) is slowly added to a solution of diisopropylamine (20 mL, 142.7 mmol) in THF (200 mL) at 0 °C. After stirring at 0 °C for 30 min, the resulting LDA solution is cooled to –78 °C before *tert*-butyl acetate (19.5 mL, 144 mmol) is added dropwise, and stirring is continued at that temperature for 60 min. A solution of lactone **3** (13.7 g, 57 mmol) in THF (10 mL) is then slowly added over 15 min at –40 °C, the reaction mixture is allowed to stir for another 2 h at that temperature before the cooling bath is removed and the reaction is quenched with sat. aq. NH_4Cl and EtOAc. The organic layer is successively washed with aq. HCl (0.1 M) and sat. aq. $NaHCO_3$, is dried over $MgSO_4$, the solvent is evaporated and the crude product is purified by flash chromatography to give ketoester **4** as a colorless syrup which contains some double addition product (15.6 g, product ratio ≈ 5:1 (HPLC), corresponds to 61% of pure **4**). This product was used in the next step without further purification. Characteristic data of compound **4**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.56 (2H, t), 3.26 (2H, s), 2.45 (2H, t), 1.50 (2H, m), 1.46 (9H, s), 1.20-1.30 (22H, bm). ^{13}C NMR (75 MHz, $CDCl_3$): δ 203.5, 166.5, 81.8, 63.0, 50.6, 42.9, 32.7, 29.6-29.4, 28.3, 28.0, 27.9.

Compound (*R*)-5. To a solution of $[RuCl_2(COD)]_n$ (56 mg, 0.20 mmol) and (*R*)-BINAP (144 mg, 0.23 mmol) in toluene (12 mL) is added Et_3N (0.4 mL, 0.29 mmol) and the resulting mixture is stirred for 4 h at 140 °C. The solvent is removed and the residue is dissolved in THF (30 mL). This catalyst solution is added to a solution of ketoester **4** (crude product as described above, 4.41 g) in MeOH (100 mL) and the resulting mixture is stirred in an autoclave under H_2 (15 atm) for 15 h at 70 °C. After the autoclave has been vented, the solvent is evaporated and the residue is purified by flash chromatography (hexane/ethyl acetate, 8:1) to give the desired diol (*R*)-**5** (3.1 g, 88%) which exhibits the following analytical and spectroscopic data: $[\alpha]_D^{20} = -11.0$ (c = 2.00, $CDCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.95 (1H, m), 3.63 (2H, t), 2.47 (1H, dd, J = 5.4, 10 Hz), 2.31 (1H, dd, J = 6.6, 10.0 Hz), 1.56 (4H, m), 1.46 (9H, s), 1.20-1.40 (22H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.6, 81.2, 68.2, 63.1, 42.4, 36.5, 32.8, 29.7-29.4, 28.2, 25.8, 24.5. IR: 3398, 2924, 2852, 713, 1368, 1154, 1055 cm^{-1}. MS (ESI): *m/z* 381 ($[M+Na]^+$). Anal. *calcd.* for $C_{21}H_{42}O_4$: C 70.35, H 11.81, *found* C 70.39, H 11.89.

Compound 6. *tert*-Butyldiphenylchlorosilane (2.37 g, 8.6 mmol) and imidazole (0.67 g, 9.8 mmol) are added to a solution of the diol **5** (3.10 g, 8.6 mmol) in DMF (80 mL). After stirring for 4 h at ambient temperature, the solution is concentrated to ca. the half of its volume. CH_2Cl_2 and water are then added, the organic layer is successively washed with aq. HCl (0.1 M at 0 °C) and sat. aq. $NaHCO_3$ before it is dried over $MgSO_4$. The solvent is evaporated and the residue is purified by flash chromatography (hexane/ethyl acetate, 20:1) to give product (*R*)-**6** as a colorless syrup (4.2 g, 81%). The enantiomeric excess (ee = 98%) is determined by HPLC by comparison with the racemate (98%, 250 mm Chiralcel OD-H, ∅ 4.6 mm, n-heptane:2-propanol = 99:1, 0.5 mL/min, 298 K, 2.3 Mpa, UV, 220 nm). $[\alpha]_D^{20} = -6.9$ (c = 1.00, $CHCl_3$). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.65-7.68 (4H, m), 7.5-7.3 (6H, m), 3.95 (1H,

m), 3.66 (2H, t), 2.33 (1H, dd, J = 3.3, 10.0 Hz), 2.31 (1H, dd, J = 8.9, 10.0 Hz), 1.56 (4H, m), 1.44 (9H, s), 1.20-1.40 (22H, m), 1.04 (9H, s). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 172.8, 136.3, 134.6, 129.8, 127.9, 81.2, 68.5, 64.4, 42.8, 37.0, 33.0, 30.0, 28.2, 27.5, 26.1, 25.7, 19.7. IR: 3440, 3071, 2929, 2855, 1708, 1589, 1428, 1368, 1153, 1112, 702 cm^{-1}. MS (ESI): *m/z* 619 ([M+Na]$^+$). Anal. *calcd.* for $C_{37}H_{58}O_4Si$: C 74.70, H 9.83, *found* C 74.58, H 10.01.

Compound 8. Laevoglucosane **7** (16.60 g, 102 mmol) is slowly added to a suspension of NaH (11.29 g, 470 mmol) in DMF (300 mL) at 0 °C and the resulting mixture is stirred for 1 h at ambient temperature until the evolution of gas has ceased. BnBr (75 mL, 631 mmol) is then slowly introduced over a period of ca. 1 h and stirring is continued until TLC shows complete conversion. The reaction is quenched by careful addition of MeOH (100 mL). Most of the DMF is removed under reduced pressure, EtOAc (300 mL) and water (100 mL) are added, the aqueous layer is extracted with EtOAc, the combined organic layers are washed with sat. aq. $NaHCO_3$ and brine, dried over $MgSO_4$, evaporated, and the residue is purified by flash chromatography (hexane/ethyl acetate, 10:1 $\rightarrow$ 4:1) to yield compound **8** (34.0 g, 77%). The analytical and spectroscopic data of the product thus obtained are in full agreement with those reported in the literature.[1] $[\alpha]_D^{20} = -31.4$ (c = 2, $CHCl_3$).

Compound 9. NaOAc (5.6 g, 68.3 mmol) is added to a solution of 1,6-anhydro-2,3,4-tri-*O*-benzyl-β-D-glucopyranoside **8** (28.0 g, 65.6 mmol) in Ac_2O (150 mL) and the resulting mixture is warmed to 36 °C. H_2SO_4 conc. (3 mL) is then added, the mixture is stirred for 5 min before water (1 L) is introduced, and stirring is continued for 2 h. For work-up, the mixture is extracted with EtOAc, the combined organic layers are washed with sat. aq. $NaHCO_3$ before being dried over $MgSO_4$. Evaporation of the solvent gives compound **9** as a yellow oil (mixture of anomers, 33.4 g, 95%) which is used without further purification in the next step. The ^{1}H and ^{13}C NMR data are consistent with those previously reported.[1]

Compound 10. A solution of 1,6-di-*O*-acetyl-2,3,4-tri-*O*-benzyl-D-glucopyranoside **9** (18.00 g, 33.7 mmol) and $H_2NNH_2{\cdot}AcOH$ (3.65 g, 39.5 mmol) in DMF (200 mL) is stirred at ambient temperature until TLC analysis shows complete conversion (~5 h). EtOAc and brine are added, the aqueous layer is extracted with EtOAc and the combined organic layers are successively washed with sat. aq. $NaHCO_3$ and brine. Drying over $MgSO_4$ and evaporation of the solvent gives a viscous oil which is purified by flash chromatography (hexane/ethyl acetate, 5:2) to yield compound **10** as a colorless oil (13.5 g, 81%). Its ^{1}H and ^{13}C NMR data are consistent with those previously reported in the literature.[2]

Trichloroacetimidate 11. To a solution of 6-*O*-acetyl-2,3,4-tri-*O*-benzyl-D-glucopyranose **10** (13.5 g, 27.4 mmol) in trichloroacetonitrile (12 mL) and CH_2Cl_2 (140 mL) is added NaH (140 mg, 0.2 eq.). Additional 275 mg of NaH (0.4 eq.) are added after 1 h. After 2 h reaction time,

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[1] Bourke, D. G.; Collins, D. J.; Hibberd, A. I; McLeod, M. D. *Aust. J. Chem.* **1996**, *49*, 425-434.
[2] Hoch, M.; Heinz, E.; Schmidt, R. R. *Carbohydr. Res.* **1989**, *191*, 21-28.

the mixture is filtered through Celite, the solvents are evaporated, and the residue is purified by flash chromatography (hexane/ethyl acetate, 4:1) to give compound **11** as a pale yellow oil (13.0 g, 74%). Its ^{1}H and ^{13}C NMR data are consistent with those previously reported in the literature.[2]

Compound 12. A mixture of 6-*O*-acetyl-2,3,4-tri-*O*-benzyl-α-D-glucopyranosyl trichloroacetimidate (**11**) (172 mg, 0.27 mmol), alcohol **6** (120 mg, 0.20 mmol), and molecular sieves 4Å in CH_2Cl_2 (3 mL) is stirred for 30 min at ambient temperature. The solution is then cooled to −78 °C prior to the addition of $BF_3{\cdot}Et_2O$ (3.5 μL) and stirring is continued at −40 °C for 2 h. The cooling bath is removed and the mixture is stirred for 30 min before it is filtered through a pad of Celite. The filtrate is diluted with CH_2Cl_2 and washed with sat. aq. $NaHCO_3$, the organic layer is dried over $MgSO_4$ and evaporated, and the crude product is purified by flash chromatography (hexane/ethyl acetate, 10:1) to give product **12** (141 mg, 62%) as a colorless syrup. Moreover, 30 mg of alcohol **6** can be recovered. Data of glycoside **12**: $[\alpha]_D^{20} = +8.1$ (c = 2.25, $CHCl_3$). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.73-7.68 (4H, m), 7.50-7.20 (21H, m), 4.94 (2H, t, J = 11.0 Hz), 4.84 (1H, d, J = 10.9 Hz), 4.79 (1H, d, J = 11.0 Hz), 4.72 (1H, d, J = 11.1 Hz), 4.56 (1H, d, J = 10.9 Hz), 4.51 (1H, d, J = 7.8 Hz), 4.30 (1H, dd, J = 14.0, 1.7 Hz), 4.22 (1H, dd, J = 14.0, 4.4 Hz), 4.06 (1H, m), 3.68 (2H, t, J = 6.5 Hz), 3.65 (1H, t, J = 9.0 Hz), 3.55-3.45 (2H, m), 3.37 (1H, dd, = J 7.8, 9.1 Hz), 2.70 (1H, dd, J = 5.5, 15.0 Hz), 2.40 (1H, dd, J = 7.7, 15.0 Hz), 2.04 (3H, s), 1.58 (4H, m), 1.43 (9H, s), 1.40-1.20 (22H), 1.04 (9H, s). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 170.6, 170.5, 138.9, 138.8, 138.3, 135.6, 134.4, 129.6-127.6, 103.1, 84.9, 82.3, 80.2, 77.8, 77.3, 75.6, 74.9, 74.7, 72.9, 64.2, 63.2, 42.2, 34.5, 32.7, 29.9-29.5, 27.9, 26.8, 25.9, 25.5, 20.7, 19.2. IR: 3068, 2928, 2855, 1743, 1730, 1604, 1497, 1454, 1154, 1110, 1093, 1073, 739, 701 cm^{-1}. MS (ESI) *m/z* 1093 ($[M+Na]^+$). Anal. *calcd.* for $C_{66}H_{90}O_{10}Si$: C 73.98, H 8.47, *found* C 74.06, H 8.41.

Hydroxy Acid 13. A solution of glycoside **12** (875 mg, 8.2 mmol) and F_3CCOOH (1.5 mL) in CH_2Cl_2 (10 mL) is stirred for 1 h at 0 °C and then at ambient temperature for another 2 h. After evaporation of the solvents, a saturated solution of NH_3 in MeOH (30 mL) is added and stirring is continued overnight. Removal of the solvents and purification of the residue by flash chromatography (hexane/ethyl acetate/acetic acid, 300:100:1) affords hydroxy acid **13** as a colorless solid (585 mg, 74%). $[\alpha]_D^{20} = +9.8$ (c = 1.50, $CHCl_3$). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.75-7.68 (4H, m), 7.5-7.30 (21H, m), 4.94 (1H, AB, J = 11.0 Hz), 4.90 (1H, AB, J = 11.0 Hz), 4.82 (1H, AB, J = 11.0 Hz), 4.79 (1H, AB, J = 11.0 Hz), 4.72 (1H, AB, J = 11.0 Hz), 4.58 (1H, AB, J = 11.0 Hz), 4.52 (1H, d, J = 7.8 Hz), 4.12 (1H, m), 3.88 (1H, d, J = 11.4), 3.68 (2H, t, J = 6.5 Hz), 3.65-3.55 (2H, m), 3.42-3.37 (3H, m), 2.59 (1H, dd, J = 8.0, 15.3 Hz), 2.52 (1H, dd, J = 3.3, 15.3 Hz), 1.61 (2H, m), 1.45-1.15 (24H, m), 1.05 (9H, s). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 175.0, 138.9, 138.8, 138.4, 135.6, 134.4, 129.6-127.6, 103.7, 84.7, 82.4, 78.6, 78.2, 75.6, 75.5, 74.9, 74.8, 64.2, 62.5, 41.5, 36.1, 32.7, 29.9-29.5, 26.8, 25.9, 25.4, 19.2. IR: 3440, 3068, 2926, 2853, 1711, 1497, 1454, 1391, 1354, 1095, 1093, 737,

699 cm^{-1}. MS (ESI): *m/z* 995 ($[M+Na]^+$). Anal. *calcd.* for $C_{60}H_{80}O_9Si$: C 74.04, H 8.28, *found* C 74.18, H 8.19.

Compound 15. KH (5 mg, 0.12 mmol) is added at 0 °C to a solution of compound **13** (59 mg, 0.06 mmol) and 2-chloro-1,3-dimethylimidazolinium chloride **14** (25 mg, 0.15 mmol) in CH_2Cl_2 (3.5 mL) and the resulting mixture is stirred for 1 h at that temperature. DMAP (17 mg, 14 mmol) is then introduced and stirring is continued for 15 h at ambient temperature. For work-up, the mixture is filtered through a pad of Celite, the filtrate is evaporated, and the residue is purified by flash chromatography (hexane/ethyl acetate, 10:1) to give the monomeric lactone **18** (12 mg, 21%) and the desired lactide **15** (41 mg, 71%) as colorless syrups each. Data of compound **18**: $[\alpha]_D^{20}$ = +31.6 (*c* = 2.00, $CHCl_3$). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.73-7.68 (4H, m), 7.5-7.25 (21H, m), 4.97 (1H, d, *J* = 11.2 Hz), 4.93 (1H, dd, *J* = 11.7, 3.1 Hz), 4.83 (1H, s), 4.70 (2H, s), 4.67 (1H, d, *J* = 11.2 Hz), 4.63 (1H, d, *J* = 10.6 Hz), 4.54 (1H, d, *J* = 11.6 Hz), 4.28 (1H, t, *J* = 10.1 Hz), 3.91 (1H, d, *J* = 11.7 Hz), 3.81 (1H, d, *J* = 3.8 Hz), 3.78 (1H, m), 3.74 (1H, m), 3.73 (1H, dd, *J* = 3.8, 10.1 Hz), 3.69 (2H, t, *J* = 6.5), 2.54 (1H, t, *J* = 11.3 Hz), 2.39 (1H, dd, *J* = 2.1, 11.3 Hz), 1.61 (4H, m), 1.40-1.20 (22H, m), 1.06 (9H, s). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 174.1, 138.5, 137.7, 135.6, 134.3, 129.6-127.6, 102.2, 84.2, 84.0, 81.2, 76.1, 75.1, 73.5, 72.9, 71.7, 64.1, 63.2, 43.6, 37.4, 32.7, 29.9-29.5, 26.7, 25.9, 25.9, 19.1. IR: 2927, 2854, 1747, 1589, 1497, 1454, 1110, 1091, 738, 700 cm^{-1}. MS (ESI): *m/z* 977 ($[M+Na]^+$).

Data of lactide **15**: $[\alpha]_D^{20}$ = +26.0 (*c* = 2.00, $CHCl_3$). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.73-7.68 (8H, m), 7.50-7.25 (42H, m), 4.96 (2H, d, *J* = 11.1 Hz), 4.92 (2H, d, *J* = 11.0), 4.82 (2H, d, *J* = 11.1 Hz), 4.78 (2H, d, *J* = 11.0 Hz), 4.73 (2H, d, *J* = 11.1 Hz), 4.55 (2H, d, *J* = 11.1 Hz), 4.47 (2H, d, *J* = 7.9 Hz), 4.30 (2H, d, *J* = 11.3), 4.07-4.00 (4H, m), 3.68 (4H, t, *J* = 6.5 Hz), 3.64 (2H, t, *J* = 8.9 Hz), 3.52 (2H, t, *J* = 9.8 Hz), 3.51 (2H, m), 3.41 (2H, dd, *J* = 7.9, 9.0 Hz), 2.89 (2H, dd, *J* = 6.1, 16.0 Hz), 2.35 (2H, dd, *J* = 5.8, 16.0 Hz), 1.7-1.35 (8H, m), 1.40-1.10 (44H), 1.04 (9H, s); ^{13}C NMR (100 MHz, CD_2Cl_2): δ 171.4, 138.9, 138.8, 138.3, 135.6, 134.4, 124.4-127.6, 105.3 (104.9 in $CDCl_3$), 84.8, 82.3, 79.3, 77.8, 75.6, 74.9, 74.8, 72.4, 64.2, 63.6, 41.6, 36.2, 32.7, 29.9-29.5, 26.8, 25.9, 25.4, 19.2. IR: 2927, 2854, 1737, 1589, 1497, 1428, 1110, 1087, 1070, 737, 700 cm^{-1}. MS (ESI) *m/z* 1931 ($[M+Na]^+$). Anal. *calcd.* for $C_{120}H_{156}O_{16}Si$: C 75.43, H 8.23, *found* C 75.27, H 8.21.

Compound 16. A solution of compound **15** (450 mg, 0.236 mmol) and tetrabutylammonium fluoride trihydrate (158 mg, 0.50 mmol) in THF (5 mL) is stirred at ambient temperature for 30 min. For work-up, the solvent is evaporated and the residue is purified by flash chromatography (hexane/ethyl acetate, 1:1) to give diol **16** as an amorphous solid (310 mg, 92%). mp 129-131 °C. ^{1}H NMR (CD_2Cl_2): δ 7.4-7.20 (30H, m), 4.98 (2H, d, *J* = 11.2 Hz), 4.93 (2H, d, *J* = 11.1 Hz), 4.84 (2H, d, *J* = 11.2 Hz), 4.80 (2H, d, *J* = 11.1 Hz), 4.75 (2H, d, *J* = 11.2 Hz), 4.56 (2H, d, *J* = 11.2 Hz), 4.49 (2H, d, *J* = 7.9 Hz), 4.32 (2H, d, *J* = 11.3 Hz), 4.05 (4H, m), 3.66 (2H, t, *J* = 8.9 Hz), 3.58 (4H, t, *J* = 6.6 Hz), 3.54 (2H, t, *J* = 9.5 Hz), 3.51 (2H,

dd, J = 9.5, 1.7 Hz), 3.43 (2H, dd, J = 7.9, 9.0 Hz), 2.90 (2H, dd, J = 6.0, 16.0 Hz), 2.37 (2H, dd, J = 5.9, 16.0 Hz), 1.7-1.45 (8H, m), 1.4-1.1 (44H). ^{13}C NMR (CD_2Cl_2): δ 171.4, 138.9, 138.8, 138.3, 128.4-127.6, 105.3 (104.9 in $CDCl_3$), 84.8, 82.3, 79.2, 77.7, 75.6, 74.9, 74.8, 72.4, 63.6, 62.9, 41.6, 36.2, 33.0, 29.8-29.6, 25.9, 25.4. MS (ESI): *m/z* 1455 ($[M+Na]^+$). Anal. *calcd.* for $C_{88}H_{120}O_{16}$: C 73.71, H 8.44, *found* C 73.80, H 8.31.

Compound 17. A solution of diol **16** (360 mg, 0.25 mmol) in CH_2Cl_2 (3 mL) is treated with *tert*-butyldiphenylsilyl chloride (70 µL, 0.26 mmol), triethylamine (60 µL, 0.50 mmol) and a few crystals of DMAP at ambient temperature for 1 h. The solvent is evaporated and the residue is purified by flash chromatography (hexane/ethyl acetate, 2:1) to yield a mixture containing the disilylated derivative **15** (22%), the desired mono-silylated compound **17** (240 mg, 52%), and recovered starting diol **16** (21%) which are separated by flash chromatography. Analytical and spectroscopic data of compound **17**: $[\alpha]_D^{20}$ = +28.8 (c = 1.00, $CHCl_3$). mp 74-75 °C. ^{1}H NMR (400 MHz, $CDCl_3$). δ 7.67-7.65, 7.37-7.23 (40H, m), 4.99-4.53 (12H, 6AB), 4.46 (2H, d, J = 7.8 Hz), 4.34 (2H, dd, J = 1.8, 11.7 Hz), 3.99 (2H, m), 3.67-3.62 (6H, m), 3.49 (2H, ddd, J = 1.9, 6.2, 9.7 Hz), 3.44 (2H, t, J = 8.7 Hz), 3.40 (2H, dd, J = 8.0, 9.1 Hz), 2.93 (2H, dd, J = 5.2, 15.9 Hz), 2.36 (2H, dd, J = 7.1, 15.9 Hz), 1.80-1.15 (64H, m), 1.04 (9H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.3, 138.4, 138.3, 137.8, 135.6, 134.2, 129.4, 128.4-127.5, 104.9, 84.8, 82.3, 78.7, 77.8, 75.7, 75.0, 74.9, 72.2, 64.0, 63.5, 63.0, 41.4, 35.9, 32.8, 32.6, 29.7-29.4, 26.9, 25.8, 25.7, 25.4, 19.2. IR: 3525, 3031, 2923, 2852, 1732, 1717, 1068 cm^{-1}. Anal. *calcd.* for $C_{104}H_{138}O_{16}Si$: C 74.70, H 8.32, *found* C 74.76, H 8.25.

Compound 19. The synthesis of the (*S*)-enantiomer follows the same procedure as in case of (*R*)-**6** using (*S*)-BINAP as the ligand, $[\alpha]_D^{20}$ = +7.1 (c = 1.00, $CHCl_3$). HRMS (ESI): *calcd.* for $C_{37}H_{60}O_4Si$ (596.96): 597.4339, *found* 597.4338 ($[M+H]^+$).

Glycoside 20. TMSOTf (15 µL) is added to a solution of alcohol (*S*)-**19** (500 mg, 0.83 mmol) and trichloroacetimidate **11** (800 mg, 1.25 mmol) in CH_2Cl_2 (20 mL) and CH_3CN (20 mL) at –50 °C and the reaction mixture is stirred for 30 min before it is allowed to warm to ambient temperature. For work-up, the reaction is neutralised with Et_3N, the solvents are evaporated and the residue is purified by flash chromatography (hexane/ethyl acetate, 15:1). The first compound to be eluded is the desired β-anomer **20** which is obtained as a colorless oil (570 mg, 63%): $[\alpha]_D^{20}$ = +8.0 (c = 1.10, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60-7.15 (m, 25H), 4.93-4.53 (3AB, 6H), 4.50 (1H, d, J = 7.8 Hz), 4.32 (1H, d, J = 11.8 Hz), 4.38 (1H, dd, J = 4.8, 11.7 Hz), 4.10 (1H, m), 3.65 (2H, t, J = 6.6 Hz), 3.62 (1H, m), 3.49 (2H, m), 3.39 (1H, dd, J = 7.8, 9.1 Hz), 2.59 (1H, dd, J = 6.3, 15.6 Hz), 2.39 (1H, dd, J = 6.5, 15.6 Hz), 2.01 (3H, s) 1.60-1.24 (26 H, m), 1.41 (9H, s), 1.04 (9H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.7, 138.5, 138.4, 137.8, 135.6, 134.2, 129.4, 128.5, 128.3, 1283-128.1, 127.9, 127.8, 127.5, 102.3, 84.8, 82.1, 80.7, 77.7, 76.1, 75.6, 74.9, 74.7, 72.7, 64.0, 63.3, 41.3, 35.4, 32.6, 29.7-29.6, 29.4, 28.1, 26.9, 25.7, 25.0, 20.8, 19.2. IR: 2928, 2855, 1744, 1731, 1454, 1235,

1071 cm^{-1}. MS (ESI): *m/z* 1093 ($[M+Na]^+$). Anal. *calcd.* for $C_{66}H_{90}O_{10}Si$: C 73.98, H 8.47, *found* C 73.85, H 8.45.

The second fraction is the corresponding α-anomer (170 mg, 19%) which shows the following spectroscopic and analytical properties. Syrup, $[\alpha]_D^{20} = +34.6$ (*c* = 0.75, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ 7.80-7.20 (m, 25H), 4.96 (1H, d, *J* = 3.0 Hz), 4.99-4.54 (6H, 3×AB), 4.27 (2H, m), 4.03-3.94 (2H, m), 3.65 (2H, t, *J* = 6.6 Hz), 3.65 (1H, dd, *J* = 3.7, 9.7 Hz), 3.46 (1H, dd, *J* = 8.9, 10.1 Hz), 2.63 (1H, dd, *J* = 6.7, 15.5 Hz), 2.39 (1H, dd, *J* = 6.2, 15.5 Hz), 2.00 (3H, s), 1.65-1.24 (26H, m), 1.42 (9H, s), 1.04 (9H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.7, 138.7, 138.1, 135.5, 134.2, 129.4, 128.4-127.5, 95.8, 81.9, 80.6, 80.1, 77.4, 75.6, 75.3, 74.2, 73.1, 68.8, 64.0, 63.1, 41.3, 33.6, 32.6, 29.7-29.6, 29.4, 28.1, 26.9, 25.8, 24.9, 20.8, 19.2. IR: 2928, 2855, 1743, 1732, 1110 cm^{-1}. MS (ESI): *m/z* 1093 ($[M+Na]^+$). Anal. *calcd.* for $C_{66}H_{90}O_{10}Si$: C 73.98, H 8.47, *found* C 73.82, H 8.51.

Compound 23. Glycoside **20** (300 mg, 0.28 mmol) is treated with a saturated methanolic solution of ammonia (10 mL) overnight. All volatiles are then removed *in vacuo* and the residue is purified by flash chromatography (hexane/ethyl acetate, 10:1) to give alcohol **23** as a colorless syrup (240 mg, 83%): $[\alpha]_D^{20} = +7.0$ (*c* = 0.75, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.75-7.20 (25H, m), 4.92-4.60 (6H, 3×AB), 4.54 (1H, d, *J* = 7.8 Hz), 4.14 (1H, m), 3.83 (1H, dd, *J* = 2.7, 11.8 Hz), 3.69-3.61 (4H, m), 3.51 (1H, dd, *J* = 9.1, 9.5 Hz), 3.36 (2H, m), 2.57 (1H, dd, *J* = 6.6, 15.6 Hz), 2.38 (1H, dd, *J* = 6.3, 15.7 Hz), 1.85 (bs, 1H, OH), 1.60-1.24 (26 H, m), 1.42 (9H, s), 1.04 (9H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.8, 138.6, 138.5, 138.0, 135.6, 134.2, 129.4, 129.0, 128.4, 128.3, 128.2, 128.1, 128.0, 127.8, 127.50, 101.6, 84.7, 82.3, 80.8, 77.0, 75.7, 75.5, 75.0, 74.8, 74.9, 64.0, 62.2, 41.3, 35.2, 32.6, 29.7-29.6, 29.4, 28.1, 26.9, 25.8, 25.1, 19.2. IR: 3480, 2927, 2855, 1729, 1367, 1091 cm^{-1}. MS (ESI) *m/z*: 1051 ($[M+Na]^+$). Anal. *calcd.* for $C_{69}H_{88}O_9Si$: C 74.67, H 8.62, *found* C 74.88, H 8.61.

Hydroxy Acid 21. Trifluoroacetic acid (0.2 mL) is added to a solution of glycoside **23** (60 mg, 0.06 mmol) in CH_2Cl_2 (2 mL) at 0 °C. The ice bath is removed and the solution is stirred at ambient temperature for 10 h. For work-up, the solvent is evaporated and the crude product is purified by flash chromatography (hexane/ethyl acetate/acetic acid, 300:100:1) to give compound **21** as a colorless syrup (20 mg, 35% yield). ^1H NMR (400 MHz, CD_2Cl_2): δ 7.72-7.68 (4H, m), 7.5-7.30 (21H, m), 4.89 (2H, d, *J* = 11.0 Hz), 4.85 (2H, d, *J* = 11.0 Hz), 4.80 (1H, d, *J* = 11.0 Hz), 4.70 (1H, d, *J* = 11.3 Hz), 4.62 (1H, d, *J* = 11.3 Hz), 4.60 (1H, d, *J* = 7.8 Hz), 4.19 (1H, m), 3.84 (1H, dd, *J* = 2.6, 11.4), 3.68 (2H, t, *J* = 6.5 Hz), 3.65-3.55 (2H, m), 3.50 (1H, t, *J* = 9.0 Hz), 3.39 (1H, m), 3.36 (1H, dd, *J* = 7.9, 9.0 Hz), 2.64 (1H, dd, *J* = 7.4, 16.0 Hz), 2.54 (1H, dd, *J* = 5.2, 16.0 Hz), 1.58 (2H, m), 1.45-1.2 (24H), 1.05 (9H, s). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 175.0, 138.9, 138.8, 138.5, 135.7, 134.4, 129.6-127.6, 101.7, 84.7, 82.2, 78.0, 75.7, 75.56, 75.3, 74.9, 74.8, 64.2, 62.2, 39.6, 35.3, 32.7, 29.8-29.5, 26.8,

25.9, 25.3, 19.2. MS (ESI): *m/z* 995 ([M+Na]$^+$). Anal. *calcd.* for $C_{60}H_{80}O_9Si$: C 74.04, H 8.28, *found* C 74.09, H 8.16.

Macrodiolide 22. KH (2 mg, 0.05 mmol) is added to a solution of hydroxy acid **21** (20 mg, 0.02 mmol) and 2-chloro-1,3-dimethylimidazolium chloride **14** (15 mg, 0.08 mmol) in CH_2Cl_2 (3 mL) at 0 °C and stirring is continued for 1 h. DMAP (12 mg, 0.09 mmol) is then introduced and the reaction is stirred for 15 h. For work-up, the mixture is filtered through a pad of Celite, the solvent is evaporated, and the residue is purified by flash chromatography (hexane/ethyl acetate, 10:1) to yield lactide **22** (8 mg, 41%) as a colorless syrup. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.66 (8H, m), 7.50-7.25 (42H, m), 4.92 (2H, d, *J* = 11.1 Hz), 4.86 (2H, d, *J* = 11.0 Hz), 4.85 (2H, d, *J* = 11.1 Hz), 4.77 (2H, d, *J* = 11.1 Hz), 4.67 (2H, d, *J* = 11.1 Hz), 4.56 (2H, d, *J* = 11.1 Hz), 4.50 (2H, d, *J* = 7.8 Hz), 4.33 (2H, dd, *J* = 1.8, 11.3), 4.18 (2H, m), 3.93 (2H, dd, *J* = 10.1, 11.3 Hz), 3.66 (2H, t, *J* = 9.0 Hz), 3.65 (4H, t, *J* = 6.5 Hz), 3.62 (2H, dt, *J* = 1.8, 10.0, 10.0 Hz), 3.38 (2H, dd, *J* = 7.8, 9.0 Hz), 3.30 (2H, dd, *J* = 9.0, 10.0 Hz, H-4), 2.85 (2H, dd, *J* = 3.9, 13.7 Hz), 2.36 (2H, dd, *J* = 10.9, 13.7 Hz), 1.6-1.5 (8H, m), 1.40-1.10 (44H), 1.04 (s, 18H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 170.4, 139.1, 138.9, 138.3, 135.9, 134.6, 129.8-127.8, 100.3, 85.1, 82.4, 78.9, 75.9, 75.3, 75.0, 73.7, 73.3, 65.1, 64.4, 39.7, 35.3, 33.0, 30.4-29.5, 27.0, 26.2, 24.8, 19.4. MS (ESI): *m/z* 1931 ([M+Na]$^+$).

Compound 25. To a solution of alcohol **23** (215 mg, 0.20 mmol), acid **24** (see below, 200 mg, 0.24 mmol) and DMAP (32 mg, 0.26 mmol) in CH_2Cl_2 (5 mL) is added DIC (0.51 mmol, 0.51 mL of a 1M solution in CH_2Cl_2) at 0 °C. The mixture is allowed to warm to ambient temperature while stirring overnight. Evaporation of the solvent left a syrup which is purified by flash chromatography (hexane/ethyl acetate, 15:1) to give ester **25** as a colorless oil (320 mg, 83%). $[\alpha]_D^{20}$ = +8.4 (*c* = 1.00, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70-7.20 (40H, m), 5.86-5.75 (1H, m), 5.04-4.52 (14H, m), 4.50 (1H, d, *J* = 7.8 Hz), 4.47 (1H, d, *J* = 7.8 Hz), 4.34 (1H, d, *J* = 11.9 Hz), 4.22 (1H, dd, *J* = 4.6, 11.6 Hz), 4.12-4.05 (2H, m), 3.84-3.76 (2H, m), 3.64 (2H, t, *J* = 6.6 Hz), 3.62-3.58 (3H, m), 3.50-3.46 (2H, m), 3.38-3.31 (2H, m), 3.23 (1H, m), 2.96 (1H, dd, *J* = 4.6, 16.1 Hz), 2.58 (1H, dd, *J* = 6.2, 15.4 Hz), 2.51 (1H, dd, *J* = 8.4, 16.3 Hz), 2.39 (1H, dd, *J* = 6.4, 15.6 Hz), 2.04 (2H, m), 1.60-1.24 (50 H, m), 1.41 (9H, s), 1.04 (9H, s), 0.88 (9H, s), 0.07 and 0.04 (2s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.0, 170.7, 139.2, 138.7, 138.6, 138.5, 137.8, 135.6, 134.2, 129.4, 128.5, 128.4-128.3, 128.1, 127.9, 127.8, 127.7, 127.5-127.4, 114.07, 103.8, 102.3, 84.7, 82.6, 82.2, 80.7, 78.0, 77.5, 77.2, 76.0, 75.5, 75.7, 75.6, 74.1, 74.9, 74.8, 74.7, 72.8, 64.0, 63.1, 62.1, 41.1, 40.1, 33.8, 35.4, 35.1, 32.6, 29.9-29.4, 28.1, 26.9, 25.9, 25.3, 24.9, 19.2, 18.3, –5.0, –5.4. IR: 3066, 3031, 2926, 2854, 1734, 1454, 1071 cm^{-1}. MS (ESI) *m/z*: 1877 ([M+Na]$^+$). Anal. *calcd.* for $C_{115}H_{162}O_{16}Si_2$: C 74.39, H 8.80, *found* C 74.51, H 8.87.

Compound 26. A solution of compound **25** (200 mg, 0.11 mmol) in CH_2Cl_2 (10 mL) is treated with trifluoroacetic acid (1 mL) at ambient temperature for 30 min. All volatiles are then evaporated by repeated azeotropic distillation with toluene and the residue is purified by

flash chromatography (hexane/acetone, 9:1) to give hydroxy acid **26** as a colorless solid (140 mg, 77%). mp 70-71 °C. $[\alpha]_D^{20}$= +6.6 (*c* = 0.80, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70-7.20 (40H, m), 5.86-5.76 (1H, m), 5.01-4.45 (14H, m), 4.54 (1H, d, *J* = 7.7 Hz), 4.44 (1H, d, *J* = 7.8 Hz), 4.39 (1H, dd, *J* = 2.3, 11.7 Hz), 4.22 (1H, m), 4.12 (1H, dd, *J* = 6.5, 11.7 Hz), 4.08 (1H, m), 3.78 (1H, dd, *J* = 2.2, 12.1 Hz), 3.65 (2H, t, *J* = 6.6 Hz), 3.69-3.61 (2H, m), 3.57-3.52 (2H, m), 3.45-3.35 (5H, m), 2.70 (1H, dd, *J* = 7.5, 15.4 Hz), 2.60 (1H, dd, *J* = 7.3, 15.9 Hz), 2.50 (1H, dd, *J* = 4.7, 15.9 Hz), 2.40 (1H, dd, *J* = 4.4, 15.4 Hz), 2.04 (2H, m), 1.75-1.23 (50 H, m), 1.04 (9H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.9, 173.6, 139.2, 138.7, 138.4, 138.4, 137.9, 137.7, 135.6, 134.2, 129.4, 128.4-128.3, 128.0-127.8, 127.8-127.5, 114.4, 103.5, 101.2, 84.8, 84.7, 82.3, 82.1, 78.3, 78.1, 77.8, 75.3, 75.3, 75.7, 75.0-74.9, 74.8, 72.8, 64.0, 63.7, 62.3, 41.2, 39.3, 33.8, 35.8, 35.3, 32.6, 29.8-29.4, 29.2, 29.0, 26.9, 25.7, 25.2, 25.1, 19.2. IR: 3515, 3065, 2921, 2852, 1956, 1728, 1697, 1453, 1087 cm^{-1}. MS (ESI): *m/z* 1708 ([M+Na]$^+$).

Lactide 27. Triethylamine (16 µL, 0.120 mmol) is added to a solution of acid **26** (100 mg, 0.06 mmol) in THF (5 mL) at ambient temperature. After 10 min, the mixture is treated with 2,4,6-trichlorobenzoyl chloride (12 µL, 0.078 mmol) and stirring is continued for 2 h. The resulting mixture is diluted with toluene (50 mL) and added dropwise over a period of 3 h to a refluxing solution of DMAP (150 mg, 1.20 mmol) in toluene (100 mL). Once the addition is complete, reflux is continued for 1 h prior to evaporation of all volatiles and flash chromatography of the residue (hexane/acetone, 95:5). This affords macrolactone **27** as a colorless solid (88 mg, 89%). mp 90-91 °C. $[\alpha]_D^{20}$= +16.4 (*c* = 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70-7.22 (40H, m), 5.86-5.76 (1H, m), 5.01-4.54 (14H, m), 4.56 (1H, dd, *J* = 2.4, 11.3 Hz), 4.51 (1H, d, *J* = 7.9 Hz), 4.45 (1H, d, *J* = 7.7 Hz), 4.34 (1H, dd, *J* = 2.0, 11.2 Hz), 4.17 (1H, m), 4.09 (1H, dd, *J* = 9.6, 11.1 Hz), 4.01 (1H, m), 3.81 (1H, dd, *J* = 9.1, 11.5 Hz), 3.65 (2H, t, *J* = 6.6 Hz), 3.70-3.60 (2H, m), 3.60-3.51 (2H, m), 3.43 (1H, dd, *J* = 8.4, 8.6 Hz), 3.39 (1H, dd, *J* = 8.2, 9.2 Hz), 3.34 (1H, dd, *J* = 9.1, 9.4 Hz), 3.27 (1H, t, *J* = 9.3 Hz), 3.40 (1H, dd, *J* = 3.7, 15.3 Hz), 2.86 (1H, dd, *J* = 4.7, 13.9 Hz), 2.52 (1H, dd, *J* = 10.7, 15.3 Hz), 2.32 (1H, dd, *J* = 10.4, 13.7 Hz), 2.02 (2H, m), 1.75-1.19 (50H, m), 1.04 (9H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.5, 170.4, 139.2, 138.5, 138.3, 138.2, 137.7, 137.4, 135.6, 134.2, 129.4, 128.5, 128.4, 128.4-128.3, 128.1, 128.0, 127.8-127.5, 114.1, 104.5, 99.1, 84.9, 84.6, 82.2, 82.1, 78.5, 78.5, 78.2, 75.8, 75.6, 75.2, 75.1, 74.8, 73.1, 72.6, 72.4, 64.5, 64.0, 63.6, 41.4, 39.2, 33.8, 35.3, 34.3, 32.6, 29.8-29.4, 29.2, 29.9, 26.9, 25.8, 25.1, 24.8, 19.2. IR: 3066, 3030, 2923, 2852, 1882, 1734, 1497, 1071 cm^{-1}. MS (ESI): *m/z* 1689 ([M+Na]$^+$).

Compound 30. Zinc chloride (1.5 eq. of a 1M solution in diethyl ether) is added to a solution of the (*R*)-2-hexanol (152 µL, 1.0 mmol) and the 1,2-anhydro glucose derivative **29**[3] (400 mg, 1.0 mmol) in dry THF (10 mL) at –78 °C. The reaction is allowed to reach ambient temperature and stirring is continued overnight. The reaction is then diluted with MTBE and

[3] Belluci, G.; Chiappe, C.; D'Andrea, F. *Tetrahedron: Asymmetry* **1995**, *6*, 221-230.

washed with water and brine. Filtration through short silica gel column (hexan-ethyl acetate, 4:1) affords glycoside **30** as a colorless syrup (160 mg, 32%). $[\alpha]_D^{20} = -12.1$ (c =1.50, $CHCl_3$). ^1H NMR (400 MHz, $CHCl_3$): δ 7.38-7.18 (15H, m), 4.96-4.53 (6H, 3AB), 4.29 (1H, d, J = 7.6 Hz), 3.88-3.80 (1H, m), 3.73 (1H, dd, J = 2.0, 10.9 Hz), 3.68 (1H, dd, J = 4.7, 10.8 Hz), 3.62-3.42 (4H, m), 2.35-2.20 (1H, bs), 1.67-1.58 (1H, m), 1.50-1.25 (5H, m), 1.16 (3H, d, J = 6.2 Hz), 0.89 (3H, bt, J = 6.9 Hz). ^{13}C NMR (100 MHz, $CHCl_3$): δ 138.7, 138.3, 138.2, 128.3-127.5, 100.7, 84.6, 77.7, 75.3, 75.0, 74.9, 74.9, 74.9, 74.7, 73.5, 69.1, 36.8, 27.6, 22.6, 19.7, 14.0. IR: 3457, 2956, 2869, 1454, 1108, 1063 cm^{-1}. HRMS (EI): *calcd.* for $C_{33}H_{42}O_6$: 534.2981, *found* 534.2980.

Compound 31. To a stirred solution of **30** (40 mg, 0.075 mmol) in dry DMF (5 mL) are added NaH (8 mg, 0.30 mmol, 4 eq.) and methyl iodide (20 µL, 0.30 mmol, 4 eq.) at 0 °C and the resulting mixture is stirred at ambient temperature for 1 h. For work-up, residual sodium hydride is destroyed with a few drops of methanol. The reaction mixture is diluted with MTBE, washed with water and brine, the organic phase is dried and evaporated. The crude product is filtered through a short column of silica (hexane/ethyl acetate, 10:1) to give the corresponding 2'-*O*-methyl ether derivative which shows the following spectroscopic properties: ^1H NMR (400 MHz, $CHCl_3$): δ 7.37-7.17 (15 H, m), 4.92-4.52 (6H, 3AB), 4.33 (1H, d, J 7.8 Hz), 3.72 (1H, dd, J 1.9, 10.9 Hz), 3.66 (1H, dd, J 5.0, 10.9 Hz), 3.60 (3H, s), 3.58-3.49 (2H, m), 3.46-3.38 (1H, m), 3.12 (1H, t, J = 7.9 Hz), 1.70-1.25 (6H, m), 1.19 (3H, d, J = 6.2 Hz), 0.89 (bt, 3H, J = 6.9 Hz). ^{13}C NMR (100 MHz, $CHCl_3$): δ 138.9, 138.4, 138.3, 128.3-127.4, 101.6, 85.1, 84.3, 77.8, 75.4, 75.3, 74.9, 73.5, 69.2, 60.4, 37.0, 27.5, 22.7, 19.6, 14.1.

To a solution of this methyl ether in ethyl acetate (1 mL) and ethanol (2 mL) is added Pd-C (10%, 10 mg) and the resulting suspension is vigorously stirred under an atmosphere of H_2 for 12 h. The mixture is filtered through a pad of Celite and the filtrate is concentrated to give compound **31** (27 mg, 66 %) as a white solid: mp 64-65 °C. $[\alpha]_D^{20} = -31.0$ (c = 0.60, MeOH). ^1H NMR (400 MHz, pyridine-d_5): δ 4.78 (1H, d, J = 7.8 Hz), 4.48 (1H, dd, J = 2.5, 11.7 Hz), 4.30 (1H, dd, J = 5.4, 11.7 Hz), 4.18-4.05 (2H, m), 4.02-3.96 (1H, m), 3.85-3.79 (1H, m), 3.74 (3H, s), 3.38 (1H, t, J = 8.1 Hz), 1.70-1.60 (1H, m), 1.50-1.40 (1H, m), 1.45-1.20 (4H, m), 1.19 (3H, d, J = 6.1 Hz), 0.79 (3H, t, J = 7.3 Hz). ^{13}C NMR (100 MHz, pyridine-d_5): δ 101.9, 85.1, 78.1, 77.7, 74.2, 71.8, 62.8, 60.6, 37.4, 27.7, 23.0, 19.6, 14.2. IR: 3334, 2932, 1074 cm^{-1}. HRMS (EI) *calcd.* for ($C_{13}H_{26}O_6$+H): 279.1807, *found* 279.1806 ($[M+H]^+$).

Compound 32. Prepared as described above using (*S*)-2-hexanol (36%). $[\alpha]_D^{20} = -17.3$ (c = 1.20, $CHCl_3$). ^1H NMR (400 MHz, $CHCl_3$): δ 7.38-7.17 (15H, m), 4.96-4.35 (6H, 3AB), 4.30 (1H, d, J = 7.4 Hz), 3.75-3.53 (7H, m), 2.40-2.20 (1H, bs), 1.65-1.55 (1H, m), 1.50-1.25 (5H, m), 1.27 (3H, d, J = 6.2 Hz), 0.89 (3H, bt, J = 6.8 Hz). ^{13}C NMR: δ 138.7, 138.3, 138.2, 128.3-127.5, 102.5, 84.6, 77.7, 77.2, 75.1, 75.0, 74.9, 73.4, 69.1, 34.4, 27.6, 22.7, 21.7, 14.0.

IR: 3359, 2931, 1724, 1703, 1453, 1059 cm^{-1}. HRMS (EI) *calcd.* for $C_{33}H_{42}O_6$ *m/z* 534.2981; *found* 534.2978.

Compound 33. NaH (8 mg, 0.30 mmol, 4 eq.) and methyl iodide (20 μL, 0.30 mmol, 4 eq.) are added to a stirred solution of compound **32** (40 mg, 0.075 mmol) in DMF (5 mL) at 0 °C. After stirring for 1 h, the remaining sodium hydride is destroyed with a few drops of methanol. The reaction mixture is diluted with MTBE, the organic layer is washed with water and brine, dried and evaporated. The crude product is passed through a short column of silica (hexane/ethyl acetate, 10:1) to give the corresponding 2'-*O*-methyl ether derivative which shows the following spectroscopic properties: ^{1}H NMR (400 MHz, $CHCl_3$): δ 7.32-7.24 (15 H, m), 4.92-4.50 (6H, 3AB), 4.33 (1H, d, *J* = 7.8 Hz), 3.70 (1H, m), 3.65-3.63 (1H, m), 3.60 (3H, s), 3.55-3.48 (2H, m), 3.45-3.40 (1H, m), 3.13 (1H, t, *J* 7.9 Hz), 1.63-1.58 (1H, m), 1.49-1.25 (5H, m), 1.27 (3H, d, *J* 6.2 Hz), 0.90 (3H, bt, *J* = 6.9 Hz). ^{13}C NMR (100 MHz, $CHCl_3$): δ 138.8, 138.3, 138.2, 128.3-127.4, 103.4, 85.1, 84.4, 77.8, 77.5, 75.5, 74.9, 74.7, 73.4, 69.3, 60.6, 36.5, 27.4, 22.7, 21.8, 14.0.

To a solution of this methyl ether in ethyl acetate (1 mL) and ethanol (2 mL) is added Pd-C (10%, 10 mg) and the resulting suspension is vigorously stirred under H_2 for 12 h. The mixture is filtered through a pad of Celite and the filtrate is concentrated to give the product **33** (30 mg, 70%) as a white solid: mp 46-47 °C. $[\alpha]_D^{20}$ = –26.2 (*c* = 1.00, MeOH). ^{1}H NMR (400 MHz, pyridine-d_5): δ 4.49 (1H, d, *J* = 7.8 Hz), 4.48 (1H, dd, *J* = 2.5, 11.6 Hz), 4.30 (1H, dd, *J* = 5.4, 11.6 Hz), 4.19-4.05 (2H, m), 3.93-3.89 (1H, m), 3.83-3.80 (1H, m), 3.93-3.89 (1H, m), 3.83-3.80 (1H, m), 3.76 (3H, s), 3.38 (1H, t *J* = 8.5 Hz), 1.70-1.62 (1H, m), 1.50-1.20 (5H, m), 1.30 (3H, d, *J* = 6.2 Hz), 0.84 (3H, t, *J* = 7.2 Hz). ^{13}C NMR (100 MHz, pyridine-d_5): δ 103.7, 85.3, 78.1, 77.8, 76.3, 71.7, 62.8, 60.7, 36.7, 27.6, 23.0, 22.0, 14.2. IR: 3365, 2932, 1379, 1172, 1080, 1028 cm^{-1}. HRMS (EI) *calcd.* for ($C_{13}H_{26}O_6$+H): 279.1807, *found* 279.1809 ($[M+H]^+$).

4-Bromo-1-(*tert*-butyldimethylsilyloxy)butane (34). A solution of 4-bromo-1-butanol[4] (6.1 g, 40 mmol), *tert*-butyldimethylsilyl chloride (7.2 g, 48 mmol), triethylamine (11.1 mL, 80 mmol) and DMAP (50 mg) in dry CH_2Cl_2 (50 mL) is stirred at ambient temperature overnight. The solvent is evaporated and the residue is purified by flash chromatography (hexane/ethyl acetate, 6:1) to give compound **34** as a colorless oil (8.5 g, 80%). All analytical and spectroscopic data are in agreement with those previously reported in the literature.[5]

(6*R*)-6-*O*-Benzyl-1-*O*-(*tert*-butyldimethylsilyl)-1,6-heptanediol (35). Magnesium turnings (365 mg, 15 mmol) are activated overnight with a few crystals of iodine under Ar before they are suspended in THF (10 mL). A solution of bromobutane **34** (4.0 g, 15 mmol) in THF (5 mL) is slowly added to this suspension and the resulting mixture is refluxed for 2 h. The

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Grignard reagent thus obtained is cooled to –40 °C and diluted with THF (50 mL). CuCl(COD) (150 mg, 0.7 mmol) is introduced before a solution of (*R*)-propenoxide (0.5 mL, 7.0 mmol) in THF (5 mL) is added dropwise and the resulting mixture is stirred for 3 h while the temperature is allowed to rise to –10 °C. For work-up, the reaction is quenched with sat. aq. NH_4Cl, diluted with MTBE and successively washed with aq. sat. NH_4Cl and brine. The organic phase is dried and concentrated and the crude product is purified by flash chromatography (hexane/ethyl acetate, 4:1) to give desired alcohol (2.3 g, 70%) as a colorless oil which shows the following spectroscopic properties: $[\alpha]_D^{20} = -4.7$ (c = 1.30, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ 3.76 (1H, m), 3.56 (2H, t, J = 6.5 Hz), 1.53-1.27 (9H, m), 1.14 (3H, d, J = 6.1 Hz), 0.85 (9H, s), 0.05, 0.01 (6H, 2s). ^{13}C NMR (75 MHz, $CDCl_3$): δ 68.1, 63.2, 39.4, 32.8, 25.9, 25.8, 25.6, 23.5, 18.4, –5.25. IR: 3356, 2930, 2858, 1472, 1255, 1099, 836 cm^{-1}. HRMS (ESI): *calcd.* for ($C_{13}H_{31}O_2Si$+H): 247.2093, *found* 247.2094 ($[M+H]^+$).

To a stirred solution of this alcohol (1.6 g, 6.94 mmol) in DMF (30 mL) are successively added NaH (340 mg, 14.0 mmol) and benzyl bromide (1.2 mL, 10 mmol) at 0 °C and the resulting mixture is stirred overnight. Excess NaH is destroyed by adding a few drops of methanol before the reaction mixture is diluted with MTBE, washed with water and brine. The organic layers are dried and evaporated and the residue is purified by flash chromatography (hexane/ethyl acetate, 50:1) to give product **35** (1.6 g, 73%) as a colorless oil. $[\alpha]_D^{20} = -12.1$ (c = 1.08, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ 7.28 (5H, m), 4.48 (2H, AB, J = 11.7, 33.0 Hz), 3.49 (2H, t, J = 6.5 Hz), 3.47 (1H, m), 1.60-1.22 (8H, m), 1.14 (3H, d, J = 6.2 Hz), 0.84 (9H, s), 0.01, 0.00 (6H, 2s). ^{13}C NMR (75 MHz, $CDCl_3$): δ 139.2, 128.29-127.35, 74.9, 70.3, 63.2, 36.7, 32.8, 25.9, 25.8, 25.3, 19.6, 18.4, –5.24. IR: 2930, 2857, 1471, 1387, 1255, 1097 cm^{-1}. HRMS (ESI): *calcd.* for ($C_{20}H_{37}O_2Si$+H): 337.2562, *found* 337.2561 ($[M+H]^+$).

(6*R*)-6-*O*-Benzyl-1,6-heptanediol (36). A solution of compound **35** (1.30 g, 3.86 mmol) and tetra-*n*-butylammonium fluoride trihydrate (1.26 g, 4.0 mmol) in THF (30 mL) is stirred at ambient temperature for 30 min. Evaporation of the solvent followed by flash chromatography (hexane/ethyl acetate, 2:1) of the residue affords alcohol **36** as a colorless oil (800 mg, 93%). $[\alpha]_D^{20} = -22.6$ (c = 1.50, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ 7.28 (5H, m), 4.48 (2H, AB, J = 11.8 Hz), 3.64 (2H, t, J = 6.6 Hz), 3.50 (1H, m), 1.65-1.32 (9H, m), 1.18 (3H, d, J = 6.1 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 139.1, 128.3-127.3, 74.7, 70.3, 62.9, 36.6, 32.7, 25.8, 25.3, 19.6. IR: 3383, 3088, 2933, 2860, 1454, 1374, 1068 cm^{-1}. HRMS (ESI): *calcd.* for ($C_{14}H_{23}O_2$+H): 223.1698, *found* 223.1698 ($[M+H]^+$).

(6*R*)-6-*O*-Benzyl-1-iodo-6-heptanol (37). I_2 (3.20 g, 12.60 mmol) is added to a solution of triphenylphosphine (1.65 g, 6.30 mmol) and imidazole (860 mg, 12.60 mmol) in acetonitrile (20 mL) and THF (5 mL) at 0 °C. The mixture is stirred for 15 min at this temperature before a solution of alcohol **36** (700 mg, 3.15 mmol) in acetonitrile (5 mL) is added and the resulting mixture is stirred for 2 h. Dilution with MTBE, successive washing of the organic layer with

aq. $Na_2S_2O_3$, water and brine, followed by flash chromatography (hexane/ethyl acetate, 50:1) of the residue gives iodide **37** as a pale yellow oil (930 mg, 89%): $[\alpha]_D^{20} = -12.9$ (c = 1.00, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 (5H, m), 4.49 (2H, AB, J = 11.8 Hz), 3.51 (1H, m), 3.17 (2H, t, J = 7.0 Hz), 1.82 (2H, m), 1.65-1.55 (2H, m), 1.50-1.30 (6H, m), 1.19 (3H, d, J = 6.1 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.1, 128.3-127.4, 74.6, 70.3, 36.6, 33.5, 30.5, 24.4, 19.6, 7.07. IR: 3029, 2932, 2858, 1453, 1373, 1208, 1094, 1067 cm^{-1}. HRMS (ESI): *calcd.* for $C_{14}H_{21}OI$: 332.0637, *found* 332.0638.

Preparation of the Dialkylzinc Compound 38.[6] A Schlenk-flask is charged with iodide **37** (1.0 g, 3.0 mmol), CuCN (9 mg, 0.1 mmol) and diethylzinc (1.2 mL, 12 mmol) and the resulting mixture is stirred for 10 days at 50 °C under Ar. The progress of the reaction can be monitored by GC/MS or TLC control of hydrolyzed samples. Excess diethylzinc and the resulting ethyl iodide are pumped off in high *vacuo* within 2 h at ambient temperature. The dialkylzinc reagent **38** thus formed is dissolved in toluene (9 mL) and the resulting stock solution (1 mL contains ca. 0.15 mmol dialkylzinc derivative) is ready for use.

Compound 40. A flame-dried flask is charged with *trans*-(1*R*,2*R*)-bis(trifluoromethyl-sulfonylamido)-cyclohexane (**39**) (25 mg, 0.06 mmol), toluene (2 mL) and Ti(O*i*Pr)$_4$ (180 µL, 0.6 mmol) and the mixture is stirred at 40 °C for 30 min under Ar. After being cooled to –50 °C, a solution of the zinc reagent **38** (0.6 mmol) is added before a solution of dodecanal (100 µL, 0.44 mmol) in toluene (2 mL) is introduced and the resulting mixture is allowed to slowly warm (1 h) to –20 °C. The reaction is quenched by adding aq. sat. NH_4Cl before it is diluted with MTBE and washed with 1N HCl, water and brine. The organic phase is dried (Na_2SO_4) and concentrated and the residue is purified by flash chromatography (hexane/ethyl acetate, 9:3) to yield alcohol **40** as a colorless oil (112 mg, 65%). $[\alpha]_D^{20} = -9.3$ (c = 1.10 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35-7.23 (10H, m), 4.50 (2H, AB), 3.58-3.55 (1H, m), 3.52-3.47 (1H, m), 1.58-1.20 (36H, m), 1.18 (3H, d, J = 6.1 Hz), 0.87 (3H, t, J = 6.7 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.2, 129.5, 128.3, 127.6, 127.3, 74.9, 74.8, 72.0, 70.3, 37.5, 37.4, 36.6, 31.9, 29.7-29.3, 25.7, 25.6, 25.5, 22.6, 19.6. HRMS (EI): *calcd.* for ($C_{26}H_{46}O_2$+H): 391.3576, *found* 391.3578 ([M+H]$^+$).

3,4,6-Tri-*O*-benzyl-2-*O*-methyl-α-D-glucopyranose trichloroacetimidate (41). NaH (15 mg, 0.6 mmol) is added to a solution of 3,4,6-tri-*O*-benzyl-2-*O*-methyl-α-D-glucopyranose[7] (465 mg, 1.0 mmol) in CH_2Cl_2 (10 mL) and trichloroacetonitrile (0.5 mL). After 1 h the mixture is filtered through a pad of Celite, the filtrate is evaporated and the residue is purified by flash chromatography (hexane/ethyl acetate, 4:1) to give compound **41** as a pale yellow oil (900 mg, 69%). $[\alpha]_D^{20} = +56.8$ (c = 0.95, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.60 (1H, s), 7.31-7.26 (15H, m), 6.57 (1H, d, J = 3.5 Hz), 4.95-4.46 (6H, 3AB), 3.98 (1H, m), 3.97

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(1H, t, J = 9.3 Hz), 3.80-3.76 (2H, m), 3.68 (1H, dd, J = 1.9, 10.8 Hz), 3.55 (1H, dd, J = 3.5, 9.6 Hz), 3.50 (3H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.4, 138.7, 138.1, 137.9, 128.4-127.5, 94.0, 81.7, 81.3, 76.7, 75.4, 75.3, 73.4, 73.1, 68.1, 58.9. IR: 3338, 2926, 1734, 1671, 1074 cm^{-1}. MS (ESI): 630 ([M+Na]$^+$). HRMS (EI) *calcd.* 607.12952, *found* 607.12960.

Compound 42. Alcohol **40** (60 mg, 0.15 mmol) and trichloroacetimidate **41** (140 mg, 0.225 mmol, 1.5 eq.) are dissolved in CH_2Cl_2 and CH_3CN (3 mL each) and the resulting solution is cooled to –50 °C. TMSOTf (5 µL) is added and the mixture is stirred 30 min at that temperature. After neutralisation with triethylamine and evaporation of the solvents, the residue is purified by flash chromatography (hexane/ethyl acetate, 4:1) to give glycoside **42** as a viscous oil (80 mg, 92%). $[\alpha]_D^{20} = -16.2$ (c = 0.80, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37-7.17 (20H, m), 4.92-4.40 (8H, 4AB), 4.31 (1H, d, J = 7.8 Hz), 3.72-3.65 (2H, m), 3.65-3.58 (1H, m), 3.59 (3H, s), 3.55-3.50 (2H, m), 3.48-3.42 (1H, m), 3.42-3.38 (1H, m), 3.13-3.08 (1H, m), 1.62-1.22 (30H, m), 1.15 (3H, d, J = 6.1 Hz), 0.88 (3H, t, J = 6.8 Hz).^{13}C NMR: 139.2, 138.9, 135.5, 138.3, 128.3-127.3, 102.7, 85.2, 84.5, 80.2, 77.9, 75.5, 74.9, 73.5, 70.2, 69.3, 60.6, 36.7, 34.9, 34.0, 31.9, 29.9-29.3, 25.5, 25.2, 25.0, 22.7, 19.6, 14.1. IR: 2926, 2854, 1454, 1358, 1086 cm^{-1}. HRMS (EI) *calcd.* for ($C_{54}H_{76}O_7$+H): 837.56693, *found* 837.56741 ([M+H]$^+$).

Compound 43. Prepared as described above using *trans*-(1*S*,2*S*)-bis(trifluoromethyl-sulfonylamido)-cyclohexane as a catalyst in the dialkylzinc addition reaction. Viscous oil (80 mg, 91%). $[\alpha]_D^{20} = -17.2$ (c = 0.95, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27-7.07 (20H, m), 4.92-4.40 (8H, 4AB), 4.31 (1H, d, J = 7.8 Hz), 3.72-3.65 (2H, m), 3.65-3.58 (1H, m), 3.59 (3H, s), 3.55-3.50 (2H, m), 3.48-3.42 (1H, m), 3.42-3.38 (1H, m), 3.13-3.08 (1H, m), 1.62-1.22 (30H, m), 1.18 (3H, d, J = 6.1 Hz), 0.88 (3H, t, J = 6.8 Hz).^{13}C NMR (100 MHz, $CDCl_3$): 139.2, 138.9, 135.5, 138.3, 128.3-127.3, 103.0, 85.2, 84.5, 80.3, 77.9, 75.5, 74.8, 73.6, 70.3, 69.3, 60.6, 36.7, 34.9, 34.0, 31.9, 29.9-29.3, 25.5, 25.2, 25.0, 22.7, 19.6, 14.1. IR: 2926, 2854, 1454, 1358, 1086 cm^{-1}. HRMS *calcd.* for ($C_{54}H_{76}O_7$+H): 837.56693, *found* 837.56701 ([M+H]$^+$).

Compound 47. To a solution of diisopropylamine (22 mL, 157 mmol) in THF (200 mL) is slowly added n-BuLi (1.6 M in hexane, 98 mL, 157 mmol) at 0 °C. After stirring at 0 °C for 30 min the solution is cooled to –78 °C. Freshly distilled cycloheptanone (18.4 mL, 156 mmol) is added dropwise over 60 min and the resulting mixture is stirred for 30 min at –78 °C prior to the addition of MeI (13 mL, 209 mmol). The cooling bath is removed and the solution is allowed to reach ambient temperature while stirring for 15 h. The reaction is quenched with sat. aq. NH_4Cl and CH_2Cl_2, the organic layer is successively washed with aq. HCl (0.1 M) and sat. aq. $NaHCO_3$ and then dried over $MgSO_4$, the solvent is evaporated and the product is purified by distillation (64 °C, 10 mbar) to give 2-methylcycloheptanone **47** (16.5 g**,** 84%). ^{1}H NMR (300 MHz, $CDCl_3$): δ2.60 (1H, m), 2.47 (2H, m), 1.9-1.75 (4H, m), 1.74-1.25 (4H, m), 1.06 (3H, d, J = 6.9 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ216.6, 46.6, 42.6, 33.3, 29.8, 28.6,

24.5, 17.6. MS (GC-EI) *m/z* 126, 111, 98, 93, 83, 69, 55, 41, 39, 27. These data are consistent with those previously reported in the literature.[8]

Compound 48. A mixture containing 2-methylcycloheptanone (**47**) (16.3 g, 114 mmol) and an aq. suspension of *m*-CPBA (70-75%, 48 g, ca. 194-208 mmol) in CH_2Cl_2 (300 mL) is refluxed for 20 h. The reaction is quenched with sat. aq. $NaHCO_3$, the organic layer is washed twice with sat. aq. $Na_2S_2O_3$ and is dried over Na_2SO_4. Evaporation of the solvent followed by distillation of the residue (77 °C, 9.10^{-1} mbar) affords lactone **48** (13.54 g, 74%). This product contains traces of an unidentified by-product but can be used in the next step without further purification. An analytically pure sample is obtained by flash chromatography on silica gel (ethyl acetate/hexanes, 1:10) which exhibits the following spectroscopic properties: ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.75 (1H, m), 2.54 (2H, m), 1.95-1.40 (8H, m), 1.34 (3H, d, J = 6.9 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 176.6, 74.9, 38.9, 32.3, 28.8, 26.3, 24.0, 21.6. These data are consistent with those previously reported in the literature.[9]

Compound 49. Porcine liver esterase (PLE SIGMA, 300 mg, 19U/mg) is added to a vigorously stirred solution of lactone **48** (4.0 g, 28.1 mmol) in aq. NaH_2PO_4-buffer (100 mM, 50 mL). The pH-value of 7.2 is maintained throughout the reaction by an autotitrator (Mettler Toledo DL50) by adding aq. NaOH (2M) to the mixture. After a conversion of 40% (corresponding to the addition of 5.6 mL of the NaOH solution) Celite is added, the resulting mixture is stirred for 2 min, the Celite is filtered off and the aqueous filtrate is extracted with EtOAc. The combined organic layers are dried over Na_2SO_4 and evaporated to give enantiomerically enriched (*S*)-**48**. The remaining aqueous phase is acidified to pH = 2 by adding aq. HCl (2M) and is then repeatedly extracted with ethyl acetate. The combined organic phases are dried over Na_2SO_4 and evaporated to give enantiomerically pure (*R*)-7-hydroxyheptanoic acid (**49**) (1.7 g, ee = 95%). $[\alpha]_D^{20}$ = +11.7 (c = 2.00, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.06 (2H, bs), 3.81 (1H, m), 2.35 (2H, t, J = 7.4 Hz), 1.65 (2H, m), 1.55-1.20 (6H, m), 1.34 (3H, d, J = 6.2 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 179.1, 68.2, 38.9, 34.0, 29.0, 25.3, 24.6, 23.4. These data are consistent with those previously reported. [9]

Compound 51. Carbonyl diimidazole (2.68 g, 16.5 mmol) is added to a solution of (*R*)-7-hydroxyheptanoic acid **49** (1.97 g, 12.2 mmol) in THF (50 mL) at 0 °C and the resulting mixture is stirred for 4 h. After that time, the magnesium salt **50** (4.0 g, 12.7 mmol)[10] is introduced, the cooling bath is removed, and the reaction is stirred for 10-15 h. For work-up, the solvent is evaporated and the residue is re-dissolved in CH_2Cl_2. The organic phase is then successively washed with water and sat. aq. $NaHCO_3$, is dried over Na_2SO_4 and evaporated. A solution of the resulting syrup in THF (30 mL) is treated with aq. NaOH (2M, 4 mL) for 90

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min before adding sat. aq. NH_4Cl (20 mL) and CH_2Cl_2 (50 mL). The organic phase is dried over Na_2SO_4, the solvent is evaporated and the residue is purified by flash chromatography (hexane/ethyl acetate, 4:1) to give product **51** as a colorless oil (2.22 g, 74%). $[\alpha]_D^{20} = -6.2$ (c = 1.08, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ 5.05 (1H, m), 3.78 (1H, m), 3.39 (2H, s), 2.54 (2H, t, J = 7.3 Hz), 1.61 (2H, m), 1.50-1.25 (6H, m), 1.25 (6H, d, J = 6.2 Hz), 1.17 (3H, d, J = 6.2 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 203.0, 166.9, 69.0, 67.9, 49.7, 42.9, 39.1, 29.0, 25.5, 23.5, 23.4, 21.8. IR: 3442, 2979, 2934, 2859, 1736, 1713, 1643, 1466, 1375, 1312, 1269, 1106 cm^{-1}. HRMS (EI): *m/z calcd.* 245.175283, *found* 245.175194.

Compound 52. A solution of $[RuCl_2(COD)]_n$ (28 mg, 0.10 mmol) and (*R*)-BINAP (72 mg, 0.12 mmol) in toluene (6 mL) and Et_3N (0.2 mL, 0.15 mmol) is stirred for 4 h at 140 °C. The solvent is removed and THF (15 mL) is added. This catalyst solution is added to a solution of compound **51** (1.71 g, 7.0 mmol) in MeOH (40 mL) and the resulting mixture is stirred under an atmosphere of H_2 (20 bar) in an autoclave for 15 h at 65 °C. Evaporation of the solvent gives an orange solid which is purified by flash chromatography (hexane/ethyl acetate, 4:1) providing product **52** as a colorless syrup (1.72 g, 99%). $[\alpha]_D^{20} = -20.3$ (c = 0.60, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ 5.05 (1H, m), 3.98 (1H, m), 3.79 (1H, m), 2.47 (1H, dd, J = 3.2, 16.4 Hz), 2.37 (1H, dd, J = 8.9, 16.4 Hz), 2.22 (2H, bs), 1.6-1.3 (8H, m), 1.25 (6H, d, J = 6.2 Hz), 1.18 (3H, d, J = 6.2 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.6, 68.1, 68.0, 68.0, 41.6, 39.2, 36.4, 29.5, 25.6, 25.4, 23.5, 21.8; IR: 3420, 2978, 2933, 2859, 1713, 1643, 1466, 1375, 1285, 1180, 1108, 968 cm^{-1}. HRMS (EI): *m/z calcd.* 247.190933, *found* 247.191094.

Compound 54. A suspension of 2-*O*-acetyl-2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl trichloro acetimidate **53** (10.26 g, 16.1 mmol),[11] diol **52** (1.65 g, 6.70 mmol), and molecular sieves 4Å (5 g) in CH_2Cl_2 (300 mL) is stirred for 30 min at ambient temperature. The solution is cooled to –78 °C before TMSOTf (150 µL, 0.81 mmol) is added and stirring is continued for 150 min at that temperature. For work-up, the mixture is filtered through a pad of Celite, the filtrate is quenched with sat. aq. $NaHCO_3$, the organic layer is dried over $MgSO_4$ and evaporated, and the residue is purified by flash chromatography (hexane/ethyl acetate, 6:1 → 4:1) to give product **54** (6.6 g, 82%). $[\alpha]_D^{20} = +6.3$ (c = 1.01, $CHCl_3$) ^1H NMR (300 MHz, CD_2Cl_2): δ 7.40-7.15 (30H), 4.95 (1H, m), 4.87-4.75 (6H, m), 4.69-4.50 (8H, m), 4.45 (1H, d, J = 8.0 Hz), 4.40 (1H, d, J = 8.1 Hz), 3.97 (1H, m), 3.76-3.60 (9H, m), 3.50-3.40 (2H, m), 2.77 (1H, dd, J = 5.6, 15.6 Hz), 2.39 (1H, dd, J = 7.4, 15 Hz), 1.96 (3H, s), 1.95 (3H, s), 1.60-1.18 (16H, m), 0.90 (3H, d, J = 6.9 Hz). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 170.7, 169.4, 138.6, 138.6, 138.4, 138.4, 128.4-127.6, 101.5, 99.5, 83.1, 83.1, 78.3, 78.1, 77.8, 75.5, 75.2, 75.1, 75.1, 75.0, 74.9, 74.9, 73.5, 73.5, 73.4, 73.3, 69.1, 68.9, 67.7, 41.5, 37.1, 34.9, 29.7, 25.4, 25.1, 21.7, 20.9, 20.8, 19.5. IR: 3031, 2932, 2863, 1749, 1728, 1605, 1497, 1454, 1373, 1232, 1058, 736, 699 cm^{-1}. MS (ESI): *m/z* 1217 ($[M+Na]^+$).

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[11] Fürstner, A.; Konetzki, I. *Tetrahedron Lett*. **1998**, *39*, 5721.

Compound 55. $LiAlH_4$ (580 mg, 15 mmol) is added in portions to a solution of compound **54** (2.9 g, 2.42 mmol) in THF (10 mL) at 0 °C. The mixture is stirred for 1 h at that temperature before the cooling bath is removed. Stirring is continued until TLC shows complete conversion. For work-up, sat. aq. Na_2SO_4 is added slowly to destroy the excess of $LiAlH_4$. The mixture is filtered and the remaining solid is carefully washed with ethyl acetate. The combined organic layers are washed with sat. aq. NH_4Cl and brine, are dried over Na_2SO_4, the solvent is evaporated, and the residue is purified by flash chromatography (hexane/ethyl acetate, 2:1) to give product **55** as a colorless syrup (2.1 g, 82%). $[\alpha]_D^{24} = -14.2$ (c = 0.40, $CHCl_3$). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.45-7.20 (30H, m), 4.97 (1H, d, J = 11.4 Hz), 4.96 (1H, d, J = 11.4 Hz), 4.86 (1H, d, J = 10.9 Hz), 4.84 (3H, d, J = 11.4 Hz), 4.63-4.50 (6H, m), 4.35 (1H, d, J = 7.7 Hz), 4.34 (1H, d, J = 7.7 Hz), 3.92-3.83 (3H, m), 3.63-3.43 (13H, m), 3.08 (1H, t, J = 6.4 Hz), 2.55 (1H, J = 2.3 Hz, OH), 2.48 (1H, J = 2.1 Hz, OH), 1.80-1.30 (12H, m), 1.20 (3H, d, J = 6.1 Hz). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 139.2, 139.0, 138.6, 138.4, 138.1, 128.5-127.5, 102.4, 100.7, 84.7, 84.6, 78.0, 77.8, 76.9, 75.2, 75.0, 74.9, 74.9, 74.9, 74.8, 74.7, 74.6, 73.5, 73.5, 69.6, 69.3, 58.4, 37.8, 37.2, 35.9, 29.9, 25.4, 25.3, 19.6. IR: 3442, 3089, 3062, 3030, 2928, 2863, 1496, 1453, 1360, 1314, 1264, 1218, 1110, 1062, 1028, 772, 752, 735, 698 cm^{-1}. MS (ESI): *m/z* 1077 ([M+Na]$^+$). Anal. *calcd.* for $C_{64}H_{78}O_{13}$: C 72.84, H 7.45, *found* C 72.91, H 7.40.

Compound 57. Tri-*n*-butylphosphine (789 µL, 3.2 mmol) is added dropwise to a solution of triol **55** (2.03 g, 1.9 mmol) and *o*-nitrophenyl selenocyanate (720 mg, 3.2 mmol, 1.65 µL) in THF (50 mL). After the reaction is stirred for 30 min, 4 mL of aq. H_2O_2 (30%, *w/w*) are added and the solution is stirred for 1 h at 0 °C and then at ambient temperature until TLC shows complete consumption of the intermediate selenide. Sat. aq. $Na_2S_2O_3$ is carefully added to destroy the excess H_2O_2 before the mixture is diluted with CH_2Cl_2 (50 mL) and stirring is continued for 15 h. The organic phase is separated, washed with sat. aq. $NaHCO_3$, dried over Na_2SO_4, the solvent is evaporated and the residue is purified by flash chromatography (hexane/ethyl acetate, 10:1) to yield the desired alkene as a pale yellow oil (1.80 g, 90%) which shows the following spectroscopic properties: $[\alpha]_D^{20} = -13.6$ (c = 0.35, $CHCl_3$). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.40-7.20 (30H, m), 5.89 (1H, ddd, J = 17.5, 10.5, 6.9 Hz), 5.21 (1H, bd, J = 17.0 Hz), 5.10 (1H, bd, J = 10.4 Hz), 4.94 (1H, d, J = 11.4 Hz), 4.94 (1H, d, J = 11.5 Hz), 4.84 (2H, d, J = 10.9 Hz), 4.83 (2H, d, J = 11.1 Hz), 4.64-4.50 (6H, m), 4.33 (1H, d, J = 7.6 Hz), 4.32 (1H, d, J = 7.7 Hz), 4.09 (1H, m), 3.85 (1H, m), 3.78-3.40 (12H, m), 2.41 (2H, bs, OH), 1.72-1.30 (10H, m), 1.18 (3H, d, J = 6.2 Hz). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 139.6, 139.2, 139.2, 138.7, 138.7, 128.4-127.6, 115.5, 102.0, 100.7, 84.7, 81.6, 77.8, 77.8, 75.3, 75.2, 75.1, 74.9, 74.9, 74.8, 74.8, 73.5, 73.4, 69.4, 69.2, 37.2, 34.8, 29.7, 25.4, 25.0, 19.6. IR: 3642, 3030, 2930, 2861, 1730, 1643, 1605, 1497, 1453, 1000, 736, 698 cm^{-1}. MS (ESI): *m/z* 1059 ([M+Na]$^+$).

NaH (16 mg, 0.67 mmol) is added to a solution of this alkene (95 mg, 0.091 mmol) and MeI (50 µL) in DMF (5 mL) at 0 °C. The cooling bath is removed and the mixture is stirred for 4 h

at 70 °C. Sat. aq. NH_4Cl is added to destroy the excess NaH, the aqueous phase is extracted with CH_2Cl_2 (10 mL), the organic layer is washed with brine, dried over Na_2SO_4 and evaporated. The residue is purified by flash chromatography (hexane/ethyl acetate, 10:1) to give compound **57** as a colorless syrup (77 mg, 78%). $[\alpha]_D^{20} = -19.3$ (c = 1.10, $CHCl_3$). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.40-7.20 (30H, m), 5.90 (1H, ddd, J = 17.3, 10.5, 6.9 Hz), 5.21 (1H, bd, J = 17.2 Hz), 5.10 (1H, bd, J = 10.5 Hz), 4.91 (2H, d, J = 11.2 Hz), 4.83 (2H, d, J = 11.4 Hz), 4.79 (2H, d, J = 11.1 Hz), 4.64-4.50 (6H, m), 4.37 (1H, d, J = 7.8 Hz), 4.36 (1H, d, J = 7.8 Hz), 4.08 (1H, m), 3.84 (1H, m), 3.77-3.64 (4H, m), 3.60 (3H, s), 3.59 (s, 3H), 3.58-3.50 (4H, m), 3.44-3.34 (2H, m), 3.15-3.05 (2H, m), 1.72-1.30 (10H, m), 1.20 (3H, d, J = 6.1 Hz). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 139.8, 139.3, 139.3, 138.8, 138.7, 128.4-127.5, 115.2, 102.5, 101.5, 85.0, 84.9, 84.6, 84.5, 81.6, 77.9, 77.9, 75.3, 75.2, 74.9, 74.9, 74.8, 74.8, 74.8, 73.5, 73.4, 69.4, 69.2, 60.5, 60.3, 37.4, 34.9, 29.9, 25.4, 25.0, 19.4. IR: 3030, 2930, 2860, 1496, 1453, 1076, 735, 697 cm^{-1}. MS (ESI): *m/z* 1087 ($[M+Na]^+$). Anal. *calcd.* for $C_{66}H_{80}O_{12}$: C 74.41, H 7.57, *found* C 74.52, H 7.56.

Aldehyde 58. O_3 is bubbled through a solution of alkene **57** (220 mg, 0.21 mmol) in CH_2Cl_2 (30 mL) at –78 °C. After the solution turned blue, the mixture is purged with argon for 5 min. Me_2S (250 μL, 3.4 mmol, 16 eq.) is then added and the mixture is stirred for 60 min at –78 °C. After warming to room temperature, all volatiles are evaporated and the residue is quickly passed through a short column of silica gel (hexane/ethyl acetate, 5:1) to yield aldehyde **58** as a colorless syrup (210 mg, 95%). $[\alpha]_D^{20} = +5.8$ (c = 0.80, $CHCl_3$). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 9.66 (1H, d, J = 2.8 Hz), 7.5-7.10 (30H, m), 4.95-4.45 (12H, m), 4.37 (1H, d, J = 7.2 Hz), 4.36 (1H, d, J = 7.6 Hz), 3.89-3.37 (18H, m), 3.22 (1H, t, J = 8.7 Hz), 3.08 (1H, m), 1.75-1.30 (10H, m), 1.20 (3H, d, J = 6.2 Hz). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 203.4, 139.3, 139.1, 138.8, 138.7, 138.6, 138.5, 128.4-127.5, 104.4, 101.5, 85.2, 84.9, 84.6, 84.5, 84.3, 77.9, 77.5, 75.4, 75.2, 75.0, 74.9, 74.8, 73.5, 69.4, 68.9, 60.5, 60.3, 37.3, 30.5, 29.6, 25.2, 24.8, 19.4. IR: 3030, 2930, 2860, 1731, 1605, 1496, 1453, 1075, 751, 698 cm^{-1}. MS (ESI): *m/z* 1089 ($[M+Na]^+$).

Compound 59. A solution of PPh_3 (49 mg, 0.187 mmol, 1.5 eq.) and 1-phenyl-5-mercapto tetrazole (34 mg, 0.187 mmol, 1.5 eq.) in THF (3 mL) is stirred at 0°C for 5 min before a solution of alcohol **12** (105 mg, 0.126 mmol) in THF (2 mL) is added. Diisopropyl azodicarboxylate (DIAD, 37 μg, 0.187 mmol, 1.5 eq.) is added dropwise to the resulting mixture which is allowed to stir for 4 h. For work-up, the solvent is evaporated and the residue is purified by flash chromatography (hexane/ethyl acetate, 6:1) to yield sulfide **59** as a syrup (101 mg, 85%). $[\alpha]_D^{20} = +6.3°$ (c = 1.00, $CHCl_3$). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.61-7.56 (5H, m), 7.38-7.22 (15H, m), 4.96 (2H, t, J = 11.5 Hz), 4.86 (1H, d, J = 11.0 Hz), 4.81 (1H, d, J = 11 Hz), 4.73 (1H, d, J = 11.1 Hz), 4.58 (1H, d, J = 11 Hz), 4.54 (1H, d, J = 7.8 Hz), 4.30 (1H, dd, J = 12.8, 1.8 Hz), 4.24 (1H, dd, J = 12.8, 4.6 Hz), 4.07 (1H, m), 3.67 (1H, t, J = 8.9 Hz), 3.55-3.48 (2H, m), 3.40 (2H, t, J = 7.3 Hz), 3.38 (1H, t, J = 8.0 Hz), 2.72 (1H, dd, J = 5.5, 15.0 Hz), 2.42 (1H, dd, J = 7.7, 15.0 Hz), 2.05 (3H, s), 1.83 (2H, m), 1.6 (2H, m),

1.46 (9H, s), 1.40-1.20 (22H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 170.6, 170.5, 138.9, 138.8, 138.3, 130.2, 129.9, 128.4-127.6, 124.0, 103.0, 84.8, 82.3, 80.2, 77.8, 77.2, 75.6, 74.9, 74.7, 72.9, 63.2, 42.2, 34.6, 33.5, 29.8-28.7, 28.0, 25.1, 20.7. IR: 2925, 2853, 1742, 1727, 1597, 1499, 1454, 1366, 1454, 1236, 1153, 1085, 757, 698 cm^{-1}. MS (ESI): *m/z* 1015 ([M+Na]$^+$). Anal. *calcd.* for $C_{57}H_{76}N_4O_9S$: C 68.92, H 7.71, N 5.64, *found* C 69.02, H 7.66, N 5.52.

Compound 60. To a stirred solution of sulfide **59** (280 mg, 0.281 mmol) in EtOH (6 mL) at rt is added dropwise a yellow solution of ammonium molybdate tetrahydrate (38 mg, 0.031 mmol) in aqueous hydrogen peroxide (0.36 mL, 30 wt%, 3.1 mmol)). The resulting mixture is vigorously stirred for 20 h and then partitioned between CH_2Cl_2 and aq. $Na_2S_2O_3$. The organic phase is dried with Na_2SO_4 and the solvent removed *in vacuo*. Purification by flash chromatography (hexane – ethyl acetate, 6:1) yields sulfone **60** as a colorless oil (280 mg, 97%). $[\alpha]_D^{20}$ = +7.0° (*c* = 1.00, $CHCl_3$). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.75-7.60 (5H, m), 7.40-7.35 (15H, m), 4.98 (2H, t, *J* = 12.1 Hz), 4.88 (1H, d, *J* = 11.0 Hz), 4.83 (1H, d, *J* = 11 Hz), 4.76 (1H, d, *J* = 11.2 Hz), 4.60 (1H, d, *J* = 10.9 Hz), 4.56 (1H, d, *J* = 7.8 Hz), 4.32 (1H, bd, *J* = 11 Hz), 4.26 (1H, dd, *J* = 12, 3.3 Hz), 4.08 (1H, m), 3.75-3.65 (3H, m), 3.55-3.50 (2H, bs), 3.41 (1H, dd, *J* = 7.8, 9.1 Hz), 2.74 (1H, dd, *J* = 5.6, 15 Hz), 2.44 (1H, dd, *J* = 7.7, 15 Hz), 2.06 (3H, s), 1.94 (2H, m), 1.63 (2H, m), 1.47 (9H, s), 1.40-1.20 (22H). ^{13}C NMR (400 MHz, CD_2Cl_2): δ 170.6, 170.5, 138.9, 138.8, 138.3, 131.5, 129.7, 128.4-127.6, 103.1, 84.8, 82.3, 80.2, 77.8, 77.2, 75.6, 74.9, 74.7, 72.9, 63.2, 56.2, 42.2, 34.6, 29.8-29.0, 29.6, 28.0, 25.1, 20.7. IR: 2925, 2854, 1742, 1728, 1596, 1498, 1454, 1366, 1233, 1152, 1069, 760, 698 cm^{-1}. MS (ESI): *m/z* 1047 ([M+Na]$^+$). Anal. *calcd.* for $C_{57}H_{76}N_4O_{11}S$: C 66.77, H 7.47, N 5.46, *found* C 66.88, H 7.56, N 5.30.

Compound 62. A solution of PPh_3 (110 mg, 0.420 mmol) and 1-phenyl-5-mercapto tetrazole (75 mg, 0.420 mmol) in THF (10 mL) is stirred at 0 °C for 5 min before a solution of alcohol **17** (470 mg, 0.281 mmol) in THF (6 mL) is added. Diisopropyl azodicarboxylate (DIAD, 84 µg, 0.420 mmol) is then added dropwise and the mixture is stirred for 4 h at ambient temperature. For work-up, the solvent is evaporated and the residue is purified by flash chromatography (hexane/ethyl acetate, 6:1) to yield sulfide **62** as a colorless oil (467 mg, 91%). $[\alpha]_D^{24}$ = +22.8 (*c* = 1.00, $CHCl_3$). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.70-7.20 (45H), 5.00 (2H, d, *J* = 11 Hz), 4.95 (2H, d, *J* = 11.0 Hz), 4.86 (2H, d, *J* = 11.2 Hz), 4.82 (2H, d, *J* = 11.0 Hz), 4.77 (2H, d, *J* = 11.2 Hz), 4.58 (2H, d, *J* = 11.1 Hz), 4.47 (2H, d, *J* = 7.8 Hz), 4.33 (2H, d, *J* = 10.8), 4.10-4.00 (4H, m), 3.71 (2H, t, *J* = 6.7 Hz), 3.67 (2H, t, *J* = 8.9 Hz), 3.58-3.50 (4H, m), 3.45 (2H, dd, *J* = 7.9, 9.0 Hz), 3.41 (2H, t, *J* = 7.4 Hz), 2.92 (2H, dd, *J* = 6.0, 16.0 Hz), 2.39 (2H, dd, *J* = 5.9, 16.0 Hz), 1.84 (2H, m), 1.65-1.10 (50H, m), 1.08 (9H, s). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 171.4, 138.9, 138.8, 138.3, 135.6, 134.4, 130.2-124.4, 105.3, 84.8, 82.3, 79.3, 77.8, 75.6, 74.9, 74.8, 72.4, 64.2, 63.6, 41.6, 36.2, 33.5, 32.7, 29.9-29.5, 26.8, 25.9, 25.4, 19.2. IR: 2926, 2854, 1735, 1109, 1070 cm^{-1}. Anal. *calcd.* for $C_{111}H_{142}N_4O_{15}SSi$: C 72.75, H 7.81, *found* C 72.63, H 7.65.

Compound 63. To a stirred solution of sulfide **62** (110 mg, 0.281 mmol) in EtOH/CH_2Cl_2 (3/2 *v/v*, 2.5 mL) is added dropwise a yellow solution of ammonium molybdate tetrahydrate (8 mg, 0.007 mmol) in aqueous hydrogen peroxide (30 wt%, 80 μL, 0.68 mmol). The resulting mixture is vigorously stirred for 20 h and is then partitioned between CH_2Cl_2 and aq. $Na_2S_2O_3$. The organic phase is dried over Na_2SO_4, the solvent is evaporated and the residue is purified by flash chromatography (hexane/ethyl acetate, 6:1) to give sulfone **63** as a colorless oil (75 mg, 67%). $[\alpha]_D^{20}$ = +23.2 (*c* = 0.80, $CHCl_3$). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.70-7.20 (45H), 4.97 (2H, d, *J* = 11.6 Hz), 4.93 (2H, d, *J* = 12.0 Hz), 4.83 (2H, d, *J* = 12.0 Hz), 4.79 (2H, d, *J* = 11.3 Hz), 4.74 (2H, d, *J* = 11.2 Hz), 4.55 (2H, d, *J* = 11.1 Hz), 4.48 (2H, d, *J* = 7.8 Hz), 4.30 (2H, d, *J* = 11.6), 4.10-4.00 (4H, m), 3.73-3.60 (6H, m), 3.58-3.50 (4H, m), 3.42 (2H, bt, *J* = 8.2 Hz), 2.89 (2H, dd, *J* = 6.0, 16.0 Hz), 2.35 (2H, dd, *J* = 5.6, 16.0 Hz), 1.92 (2H, m), 1.65-1.10 (50H, m), 1.05 (9H, s). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 171.5, 138.8, 138.7, 138.3, 135.6, 134.4, 131.6, 130.2-125.4, 105.3, 84.8, 82.3, 79.3, 77.7, 75.6, 74.9, 74.8, 72.3, 64.1, 63.6, 56.1, 41.6, 36.2, 32.7, 29.9-29.0, 26.7, 25.9, 25.4, 19.2; MS (ESI): *m/z* 1885 ([M+Na]$^+$). Anal. *calcd.* for $C_{111}H_{142}N_4O_{17}SSi$: C 71.51, H 7.68, *found* C 71.40, H 7.60.

Compound 65. LiHMDS (6.5 mg, 0.039 mmol) is added to a stirred solution of sulfone **63** (42 mg, 0.023 mmol) in freshly distilled DME (2 mL) at –78 °C and the resulting yellow solution is stirred for 10 minutes. A solution of aldehyde **58** (36 mg, 0.034 mmol, 1.5 eq.) in DME (1 mL) is then introduced and the mixture is stirred for 60 min at –78 °C before the cooling bath is removed and the reaction is quenched after another 30 min by adding sat. aq. NH_4Cl and CH_2Cl_2. The organic layer is dried over Na_2SO_4, the solvent is evaporated and the residue is purified by flash chromatography (hexane/ethyl acetate, 5:1) to give alkene **64** as a colorless syrup (37 mg, 61%, *E/Z* ~ 1:1).

Palladium on charcoal (10% w/w, 70 mg) is added to a solution of this compound (120 mg, 0.017 mmol) in ethyl acetate (10 mL) and the resulting mixture is stirred under H_2 (1 atm) for 6 h. The catalyst is then filtered off and is very carefully rinsed with ethyl acetate/hexane (1/1, 500 mL). The combined filtrates are evaporated to give product **65** as a colorless syrup (85 mg, 72%). $[\alpha]_D^{20}$ = +12.2 (*c* = 0.80, $CHCl_3$); ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.70-7.65 (4H, m), 7.45-7.20 (66H, m), 5.01-4.72 (16H, m), 4.64-4.52 (8H, m), 4.49 (2H, d, *J* = 7.8 Hz), 4.37 (1H, d, *J* = 7.8 Hz), 4.34 (1H, d, *J* = 7.7 Hz), 4.32 (2H, bd, *J* = 10.2), 4.10-4.00 (4H, m), 3.84 (1H, m), 3.77-3.48 (17H, m), 3.59 (6H, s), 3.43 (2H, bt, *J* = 9 Hz), 3.40 (2H, m), 3.10-3.04 (2H, m), 2.91 (2H, dd, *J* = 6.0, 16.0 Hz), 2.37 (2H, dd, *J* = 5.8, 16.0 Hz), 1.70-1.15 (69H, m), 1.06 (9H, s). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 171.4, 139.3, 138.9, 138.8, 138.7, 138.3, 135.7, 134.4, 129.6, 130.2-125.4, 105.3, 102.8, 101.5, 85.1, 84.9, 84.8, 84.7, 84.5, 82.3, 80.1, 79.3, 78.0, 77.8, 75.6, 75.3, 75.2, 75.0, 74.9, 74.9, 74.8, 73.6, 73.5, 72.4, 69.4, 64.2, 63.6, 60.5, 60.3, 41.6, 37.5, 36.2, 35.1, 34.2, 32.7, 29.9-29.0, 26.8, 25.9, 25.5 25.1, 19.4, 19.2.

Compound 66. A solution of compound **65** (75 mg, 0.028 mmol) and tetra-*n*-butylammonium fluoride trihydrate (28 μL of 1M solution in THF, 0.028 mmol) in THF (2 mL) is stirred at ambient temperature until TLC shows complete conversion (ca. 2 h). Evaporation of the solvent gives a viscous oil which is purified by flash chromatography (hexane/ethyl acetete, 2:1) to yield alcohol **66** as a colorless oil (65 mg, 95%); $[\alpha]_D^{20}$ = +15.1 (*c* = 0.50, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31-7.20 (60H, m), 4.96-4.52 (24 H, 12AB), 4.47 (2H, d, *J* = 7.8 Hz), 4.34 (2H, dd, *J* = 1.6, 11.6 Hz), 4.33 (1H, d, *J* = 7.7 Hz), 4.29 (1H, d, *J* = 7.8 Hz), 3.98 (4H, m), 3.82 (1H, m), 3.73-3.65 (4H, m), 3.64 (2H, vt), 3.61 (2H, t, *J* = 6.6 Hz), 3.60 (1H, m), 3.59 (3H, s), 3.57 (3H, s), 3.55-3.45 (6H, m), 3.45 (2H, vt), 3.40 (2+2H, m+t), 3.11 (2H, m), 2.93 (2H, dd, *J* = 5.1, 15.9 Hz), 2.38 (2H, dd, *J* = 7.1, 15.9 Hz), 1.70-1.15 (66H, m), 1.18 (3H, d, *J* = 7.7 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.3, 138.8-137.7 and 128.4-127.4, 104.9, 102.8, 101.5, 85.2, 85.0, 84.7, 84.4, 84.3, 82.3, 80.3, 78.6, 77.8, 77.7, 75.6, 75.4, 75.1, 75.0-74.8, 73.5, 73.4, 72.2, 69.2, 63.5, 63.0, 60.6, 60.5, 41.4, 37.3, 35.9, 34.9, 34.1, 32.8, 30.0-29.4, 25.7, 25.3, 25.0, 19.5. Anal. *calcd.* for $C_{153}H_{198}O_{27}$: C 74.42, H 8.08, *found* C 74.30, H 8.20.

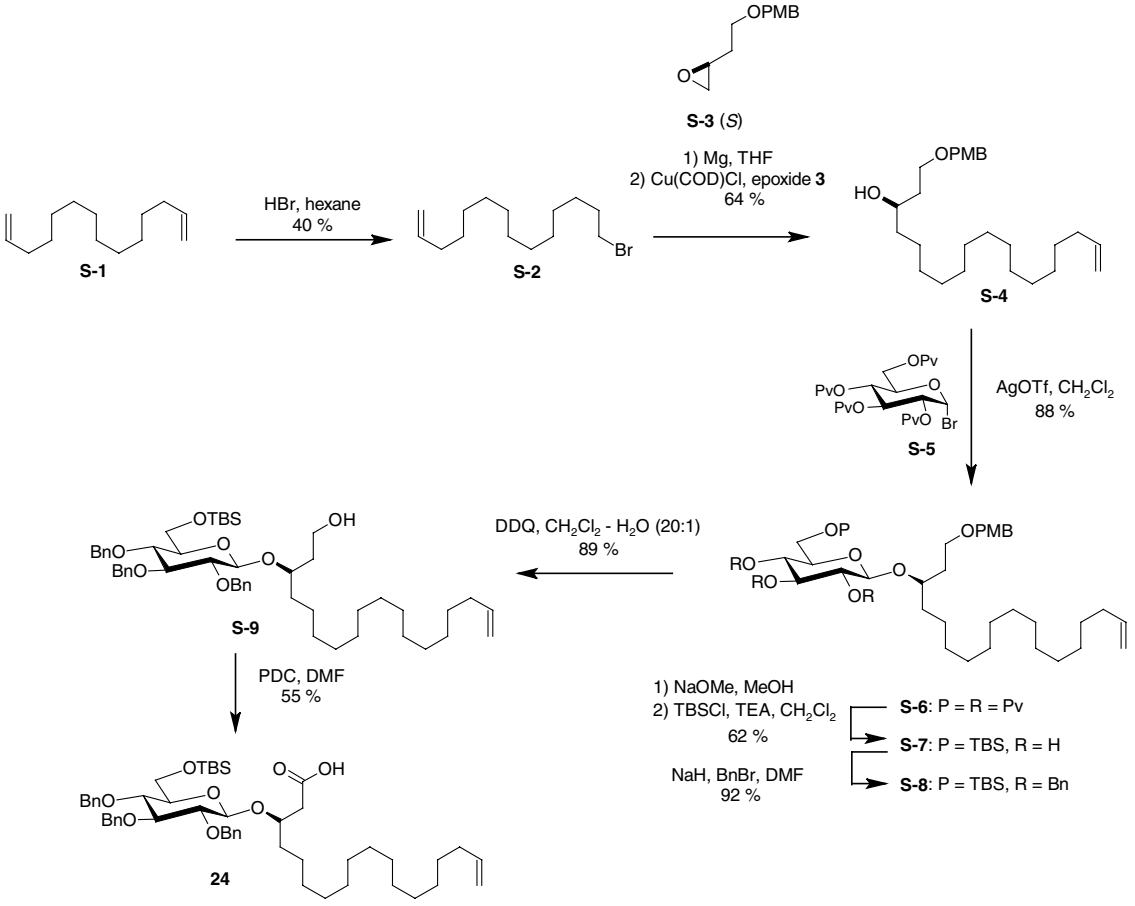
Compound 67. A mixture of PCC (11 mg, 0.05 mmol) and alcohol **66** (60 mg, 0.024 mmol) is stirred in dichloromethane (3 mL) for 1.5 h (TLC) before it is poured onto a short column of silica gel. Elution with hexane/ethyl acetate (4:1) gives aldehyde **67** (50 mg, 83%) which is directly used in the next step without further characterization.

Compound 68. A flame-dried flask is charged with *trans*-(1*S*,2*S*)-bis(trifluoromethyl-sulfonylamido)-cyclohexane **39** (4 mg, 0.01 mmol), toluene (1mL) and Ti(O*i*Pr)$_4$ (26 μL, 0.10 mmol) and the mixture is stirred at 40 °C for 30 min under argon. After being cooled to –50 °C, the zinc reagent **38** (0.10 mmol, 5 eq.) is added followed by a solution of aldehyde **67** (50 mg, 0.02 mmol) in toluene (2 mL). The resulting mixture is slowly (1 h) warmed to –20 °C before it is quenched with aq. sat. NH_4Cl and diluted with tert-butyl methyl ether. The organic phase is successively washed with HCl (1M), water and brine, is dried (Na_2SO_4) and evaporated, and the residue is purified by flash chromatography (hexane/ethyl acetate, 3:1) to give alcohol **68** as a colorless oil (40 mg, 81% over both steps). $[\alpha]_D^{20}$= +9.5 (*c* = 1.50, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31-7.24 (65H, m), 4.96-4.43 (26H, 13AB), 4.47 (2H, d, *J* = 7.8 Hz), 4.34 (2H, dd, *J* = 1.6, 11.6 Hz), 4.33 (1H, d, *J* = 7.7 Hz), 4.29 (1H, d, *J* = 7.8 Hz), 3.98 (4H, m), 3.83 (1H, m), 3.73-3.66 (4H, m), 3.64 (2H, vt), 3.60 (2H, m), 3.59 (3H, s), 3.58 (3H, s), 3.54-3.47 (6H, m), 3.44 (2H, vt), 3.40 (2H, m), 3.40 (2H, dd, *J* = 7.9, 9.1 Hz), 3.11 (2H, m), 2.93 (2H, dd, *J* = 5.1, 15.8 Hz), 2.38 (2H, dd, *J* = 7.0, 15.9 Hz), 1.62-1.12 (76H, m), 1.18 (6H, d, *J* = 6.1 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.3, 138.9-137.8, 128.5-127.3, 104.9, 102.8, 101.5, 85.2, 85.0, 84.7, 84.5, 84.3, 82.3, 80.3, 78.7, 77.9, 77.8, 75.7, 75.5, 75.1, 74.9-74.8, 73.5, 73.4, 72.2, 72.0, 70.2, 69.3, 63.5, 60.6, 60.5, 41.4, 37.5, 37.4, 37.3, 36.6, 35.9, 34.9, 34.1, 30.0-29.5, 25.7, 25.6, 25.3, 25.0, 19.6, 19.5. Anal. *calcd.* for $C_{167}H_{218}O_{28}$: C 75.03, H 8.22, *found* C 75.20, H 8.12.

Compound 69. TMSOTf (5 μL) is added to a solution of alcohol **68** (35 mg, 0.013 mmol) and trichloroacetimidate **41** (12 mg, 0.02 mmol) in CH_2Cl_2 (2 mL) and CH_3CN (2 mL) at –50 °C and stirring is continued for 30 min at –50 → –40 °C. After neutralization with triethylamine and evaporation of the solvent, the residue is purified by flash chromatography (hexane-ethyl acetate, 4:1) to give product **69** as a viscous oil (35 mg, 87%). $[\alpha]_D^{20} = +6.1$ (c = 1.50, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.31-7.24 (65H, m), 4.95-4.44 (32H, 16AB), 4.47 (2H, d, J = 7.4 Hz), 4.33 (3H, bd, J = 8 Hz), 4.31 (1H, d, J = 7.8 Hz), 4.29 (1H, d, J = 7.7 Hz), 3.98 (4H, m), 3.83 (1H, m), 3.73-3.65 (6H, m), 3.64 (2H, vt), 3.62 (2H, m), 3.59 (3H, s), 3.59 (3H, s), 3.58 (3H, s), 3.56-3.48 (9H, s), 3.45 (2H, vt), 3.42 (3H, m), 3.40 (2H, vt), 3.12 (3H, vt), 2.93 (2H, dd, J = 5.2, 15.9 Hz), 2.38 (2H, dd, J = 6.9, 15.9 Hz), 1.65-1.14 (76H, m), 1.18 (6H, d, J = 6.1 Hz). ^{13}C NMR (150 MHz, $CDCl_3$): δ 171.3, 139.1-137.7, 128.3-127.5, 104.9, 102.77, 102.76, 101.5, 85.2, 85.0, 84.7, 84.43, 84.42, 84.3, 82.3, 80.3, 78.8, 77.83, 77.82, 77.7, 75.7, 75.5, 75.4, 75.1, 74.9-74.9, 73.5, 73.4, 72.2, 70.2, 69.3, 69.2, 63.5, 60.60, 60.59, 60.5, 41.4, 37.2, 36.6, 35.9, 34.9, 34.1, 33.9, 30.0-29.5, 25.5, 25.4, 25.3, 25.3, 25.0, 25.0, 19.6, 19.5. Anal. *calcd.* for $C_{195}H_{248}O_{33}$: C 75.07, H 8.01, *found* C 75.22, H 8.10.

Cycloviracin B_1 (1). Palladium on charcoal (10% *w/w*, 10 mg) is added to a solution of compound **69** (25 mg, 0.008 mmol) in EtOAc (1 mL) and EtOH (2 mL) and the resulting mixture is stirred under H_2 (1 atm) overnight. The suspension is filtered through a plug of Celite and the filtrate is evaporated to give analytically pure cycloviracin **1** as an amorphous solid (12 mg, 89%). $[\alpha]_D^{20} = -14.1$ (c = 0.70, MeOH); [lit. $[\alpha]_D^{26} = -15.6$ (c = 0.5, MeOH)]; ^{1}H NMR (600 MHz, pyridine-d_5): δ 5.23 (3H, bd, J = 9.7 Hz), 4.89 (2H, d, J = 7.7 Hz), 4.85 and 4.84 (2H, 2d, J = 7.7 and 7.8 Hz), 4.81 (1H, d, J = 7.8 Hz), 4.56 (2H, dd, J = 8.4, 11.5 Hz), 4.50 (3H, bd, J = 14.9 Hz), 4.46 (2H, m), 3.37-4.32 (3H, m), 4.19-4.11 (10H, m), 4.05-3.92 (8H, m), 3.88-3.83 (3H, m), 3.816 (3H, s), 3.815 (3H, s), 3.77 (3H, s), 3.62 (2H, dd, J = 4.5, 15.8 Hz), 3.44-3.39 (3H, m), 2.79 (2H, dd, J = 9.1, 15.3 Hz), 1.80-1.20 (76H, m), 1.33 (2H, d, J = 6.1 Hz), 1.22 (3H, d, J = 6.1 Hz). ^{13}C NMR (150 MHz, pyridine-d_5): δ 171.73, 106.48, 103.19, 103.15, 101.84, 85.37, 85.15, 79.34, 79.33, 78.96, 78.35, 78.15, 78.02, 77.79, 77.68, 75.18, 74.62, 74.21, 72.15, 71.92, 71.82, 67.04, 65.42, 62.96, 62.88, 60.83, 60.81, 60.67, 42.49, 40.22, 37.82, 36.07, 35.42, 35.40, 34.26, 30.49, 30.42, 30.25, 30.24, 30.07-29.96, 26.48, 25.75, 25.71, 25.63, 25.64, 25.34, 25.25, 24.36, 19.56. These data are in excellent agreement with those of authentic cycloviracin B_1, cf. Table 2 in the Text. For copies of the ^{1}H and ^{13}C NMR spectra see the Supporting Information of our Communication published in *J. Am. Chem. Soc*. **2002**, *124*, 10274.

Scheme S-1. Preparation of the Building Block 24 Required for the Synthesis of the (3*R*,3'*S*)-Configured Macrodiolide 27 (Pv = Pivaloyl)



14-Brom-1-tetradecene (S-2). To a vigorously stirred solution of 1,13-tetradecene **S-1** (15 g, 77.3 mmol) and dibenzoylperoxide (100 mg) in hexane (200 mL) is slowly added a solution of HBr (6.1 g, 75 mmol) in ethyl ether at 0 °C. The mixture is warmed to ambient temperature and stirring is continued for 1 h. The reaction mixture is diluted with MTBE and carefully washed with aq. sat. $NaHCO_3$, water and brine. Evaporation of the solvents gives a syrup which is purified by distillation. After a fore-run (2-3 × 10^{-2} mbar, 55-81 °C) containing unreacted starting material (ca. 6.5 g), the desired monobromide **S-2** is collected (2-3 × 10^{-2} mbar, 97-110 °C) (8.5 g, 40%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.85-5.74 (m, 1H), 5.02-4.90 (m, 2H), 3.40 (t, 2H, J = 6.9 Hz), 2.07-2.00 (m, 2H), 1.90-1.80 (m, 2H), 1.60-1.25 (m, 16 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 139.2, 114.1, 34.0, 33.8, 32.9, 32.6, 29.6, 29.5-27.8, 26.5. HRMS (EI): *m/z calcd.* for $C_{14}H_{27}Br$ 274.12963, *found* 274.12968.

(*S*)-2-[2-(4-methoxy-benzyloxy)-ethyl]-oxirane (S-3): To a solution of 3-buten-1-ol (10.0 g, 138.67 mmol) in dry DMF (200 mL) is added sodium hydride (6.6 g, 278 mmol) at 0 °C under Ar. After stirring for 10 min, *p*-methoxybenzyl chloride (18.9 mL, 140 mmol) is introduced and the mixture is stirred at ambient temperature until TLC shows complete

conversion of the substrate. For work-up, a few drops of methanol are added to destroy excess sodium hydride before the mixture is diluted with MTBE and washed with water and brine. The organic layer is dried and the solvent is evaporated under reduced pressure. The crude product is redissolved in CH_2Cl_2 and *m*-chloroperbenzoic acid (48 g, 2 eq.) is added to the mixture which is allowed to stir overnight. Aq. sat. $Na_2S_2O_3$ is then added, the mixture is diluted with CH_2Cl_2 and is consecutively washed with aq. sat. $Na_2S_2O_3$ and brine. The organic phase is dried and concentrated to afford a orange-red syrup containing racemic epoxide (26.6 g, 92%) which was resolved as follows:

A 25 mL flask is charged with (1*S*,2*S*)-1,2-cyclohexanediamino-*N*,*N*'-bis(3,5-di-*t*-butyl-salicylidene)cobalt(II) (345 mg, 0.57 mmol),[12] the crude racemic epoxide **S-3** prepared above (5.5 g, 28.6 mmol), and acetic acid (32 μL, 0.57 mmol) and the resulting mixture is stirred for 1 h at ambient temperature. The mixture is then cooled to 0 °C before THF (5 mL) and water (280 μL, 15.73 mmol) are introduced. The reaction is stirred at ambient temperature for 48 h. Evaporation of the solvent under reduced pressure and Kugelrohr-distillation of the residue ($2\text{-}3 \times 10^{-2}$ mbar, 130-150 °C) affords pure *S*-epoxide **S-3** as a yellow oil: $[\alpha]_D^{20} = -10.6$ (*c* = 1.00, $CHCl_3$). ^{1}H NMR (300 MHz, $CHCl_3$): δ 7.24 (d, 2H, *J* = 8.9 Hz), 6.87 (d, 2H, *J* = 8.9 Hz), 4.45 (s, 2H), 3.80 (s, 3H), 3.56-3.63 (m, 2H), 3.06 (m, 1H), 2.77 (dd, 1H, *J* = 4.0, 5.1 Hz), 2.51 (dd, 1H, *J* = 2.7, 5.1 Hz), 1.93-1.73 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.2, 130.4, 129.2, 114.2, 72.7, 66.7, 55.9, 50.1, 47.1, 32.9. IR: 3483, 3045, 2860, 1613, 1514, 823 cm^{-1}. HRMS (EI): *m/z calcd.* for $C_{12}H_{16}O_3$: 208.1099, *found* 208.1098.

(*R*)-1-*O*-*para*-Methoxybenzyl-octadec-17-ene-1,3-diol (S-4). Magnesium (365 mg, 15 mmol) is activated overnight with a few crystals of iodine under Ar before it is suspended in THF (10 mL). A solution of bromide **S-2** (4.10 g, 15 mmol) in THF (5 mL) is slowly added to this suspension at 70 °C and the resulting mixture is refluxed for 2 h. The Grignard reagent thus obtained is cooled to –40 °C and diluted with THF (50 mL). CuCl(COD) (1 mmol) is introduced before a solution of epoxide **S-3** (2.0 g, 9.6 mmol) in THF (5 mL) is added dropwise and the resulting mixture is stirred for 3 h while the temperature is allowed to rise to –10 °C. The reaction is quenched with sat. aq. NH_4Cl, is diluted with MTBE and successively washed with aq. NH_4Cl and brine. The organic phase is dried and concentrated, and the residue is purified by flash chromatography (hexane/ethyl acetate, 4:1) to give alcohol **S-4** (2.5 g, 64%) as a colorless solid: mp 37-38 °C. $[\alpha]_D^{20} = +6.6$ (*c* = 1.00, $CHCl_3$). ^{1}H NMR (300 MHz, $CHCl_3$): δ 7.25 (d, 2H, *J* = 8.9 Hz), 6.85 (d, 2H, *J* = 8.7 Hz), 5.90-5.70 (m, 1H), 5.05-4.90 (m, 2H), 4.45 (s, 3H), 3.70-3.55 (m, 4H), 2.10-2.00 (m, 2H), 1.75-1.65 (m, 2H), 1.50-1.20 (m, 24H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.2, 139.2, 130.0, 129.3, 114.0, 113.8, 72.9,

[12] (a) Tokunaga, M.; Larrow, J. F.; Kakiuchi, F.; Jacobsen, E. N. *Science* **1997**, *277*, 936. (b) Furrow, M. E.; Schaus, S. E.; Jacobsen, E. N. *J. Org. Chem.* **1998**, *63*, 6776. (c) Keith, J. M.; Larrow, J. F.; Jacobsen, E. N. *Adv. Synth. Catal.* **2001**, *343*, 5.

71.5, 69.0, 55.2, 37.4, 36.3, 33.7, 29.7-28.9, 25.6. IR: 3340, 2917, 2849, 1614, 1515, 1251, 818 cm $^{-1}$. HRMS (EI): *m/z calcd.* for $C_{26}H_{44}O_3$: 404.3290, *found* 404.3288.

(3*R*)-1-*O*-*para*-Methoxybenzyl-3-(2,3,4,6-tetra-*O*-pivaloyl-β-D-glucopyranosyl)-octadec-17-ene-1,3-diol (S-6): A solution of 2,3,4,6-tetra-O-pivaloyl-α-D-glucopyranosyl bromide **S-5** (4.0 g, 6.0 mmol)[13] in CH_2Cl_2 (20 mL) is added to a mixture of alcohol **S-4** (2.2 g, 5.44 mmol), silver triflate (2.8 g, 11.0 mmol) and 2,6-di-*tert*-butylpyridine (5.0 mL, 22.0 mmol) in CH_2Cl_2 (80 mL) at –40 °C under Ar. The reaction is stirred at this temperature for 0.5 h and then at –20 °C for an additional hour. For work-up, the mixture is diluted with CH_2Cl_2 before it is filtered through a pad of Celite. Evaporation of the filtrate gives a syrup which is purified by flash chromatography (hexane/ethyl acetate, 4:1) to give glycoside **S-6** (4.3 g, 88%) as a colorless oil. $[\alpha]_D^{20} = -11.5$ (c = 0.95, $CHCl_3$). ^{1}H NMR (300 MHz, $CHCl_3$): δ 7.25 (d, 2H, J = 8.9 Hz), 6.85 (d, 2H, J = 8.7 Hz), 5.88-5.75 (m, 1H), 5.30 (t, 1H, J = 9.4 Hz), 5.11 (t, 1H, J = 9.9 Hz), 5.03-4.72 (m, 2H), 4.28 (d, 1H, J = 7.9 Hz), 4.44-4.34 (AB, 2H), 4.19 (dd, 1H, J = 1.7, 12.3 Hz), 4.02 (dd, 1H, J = 5.3, 12.2 Hz), 3.80 (s, 3H), 3.80-3.74 (m, 1H), 3.66 (ddd, 1H, J = 1.7, 5.2, 10.1 Hz), 3.53 (t, 1H, J = 6.7 Hz), 2.07-2.00 (m, 2H), 1.80-1.73 (m, 2H), 1.50-1.20 (m, 24H), 1.20, 1.15, 1.14, 1.11 (4s, 12H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 178.0, 177.2, 176.4, 176.3, 159.1, 139.2, 130.8, 129.1, 114.0, 113.7, 99.4, 76.4, 72.7, 72.6, 72.0, 71.5, 68.1, 66.9, 61.9, 55.2, 38.8, 38.7, 38.7, 34.8, 34.5, 33.8, 29.8, 29.6-29.5, 29.1, 28.9, 27.1-27.0, 25.2; IR: 2971, 2927, 2854, 1745, 1613, 1480, 1141 cm^{-1}. HRMS (ESI): *m/z calcd.* for ($C_{52}H_{86}O_{12}$+Na): 925.6017; *found* 925.6013 ([M+Na]$^+$).

(3*R*)-1-*O*-*para*-Methoxybenzyl-3-[6-*O*-(*tert*-butyldimethylsilyl)-β-D-glucopyranosyl]-octadec-17-ene-1,3-diol (S-7). A solution of glycoside **S-6** (4.30 g, 4.76 mmol) in MeOH (50 mL) is reacted overnight with NaOMe (1.54 g, 28.56 mmol) before it is diluted with ethyl acetate and successively washed with water (3 times) and brine. The organic layer is dried and evaporated. To a solution of the residue in CH_2Cl_2 (50 mL) and triethylamine (0.84 mL, 6 mmol) are added *tert*-butyldimethylsilyl chloride (755 mg, 5 mmol) and 4-dimethylaminopyridine (10 mg) and the resulting mixture is stirred overnight. Evaporation of all volatiles followed by flash chromatography of the crude material on silica gel (hexane/ethyl acetate, 1:1) gives compound **S-7** as a colorless oil (2.0 g, 62%). $[\alpha]_D^{20} = -29.9$ (c = 1.17, $CHCl_3$); ^{1}H NMR (300 MHz, $CHCl_3$): δ 7.25 (d, 2H, J = 8.9 Hz), 6.86 (d, 2H, J = 8.7 Hz), 5.90-5.75 (m, 1H), 5.05-4.90 (m, 2H), 4.41 (AB, 2H), 4.31 (d, 1H, J = 7.7 Hz), 3.90 (dd, 1H, J = 5.0, 10.5 Hz), 3.80-3.70 (m, 2H), 3.80 (s, 3H), 3.60-3.50 (m, 4H), 3.38-3.30 (m, 2H), 2.08-2.00 (m, 2H), 1.85-1.75 (m, 2H), 1.60-1.20 (m, 26H), 0.88 (s, 3H), 0.07, 0.06 (2s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.1, 139.2, 130.7, 129.1, 114.1, 113.7, 101.2, 76.2, 73.9, 73.6, 73.2, 72.6, 66.9, 64.8, 55.3, 34.9, 23.4, 33.8, 29.8-28.9, 25.8, 25.2, 18.2, -5.5. IR: 3430, 2925, 2835, 1514, 1247, 1033 cm^{-1}. Anal. *calcd*. for $C_{38}H_{68}O_8Si$: C 67.02, H 10.06, *found* C 67.00, H 9.98.

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[13] Kunz, H.; Harreus, A. *Liebigs Ann. Chem*. **1982**, 41.

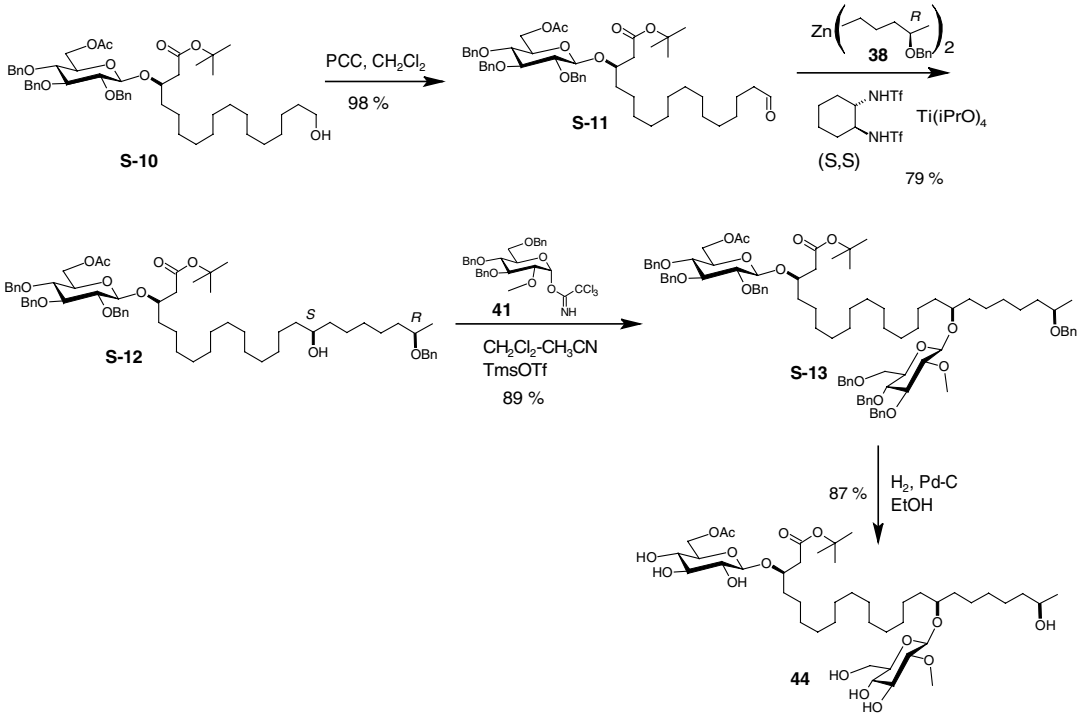
(3*R*)-1-*O*-*para*-Methoxybenzyl-3-[2,3,4-tri-*O*-benzyl-6-*O*-(*tert*-butyldimethylsilyl)-β-D-glucopyranosyl]-octadec-17-ene-1,3-diol (S-8). To a stirred solution of compound **S-7** (1.8 g, 2.64 mmol) in dry DMF (50 mL) are added NaH (760 mg, 31.6 mmol) and benzyl bromide (2.5 mL, 21 mmol) at 0 °C. The reaction mixture is stirred at ambient temperature for 3 h before residual NaH is destroyed with a few drops of methanol. The reaction mixture is diluted with MTBE, washed with water and brine, the organic phase is dried and evaporated. Purification of the residue by flash chromatography (hexane/ethyl acetate, 15:1) provides product **S-8** (2.3 g, 92%) as a colorless oil. $[\alpha]_D^{20} = -1.9$ (c = 1.13, $CHCl_3$). ^{1}H NMR (300 MHz, $CHCl_3$): δ 7.30-7.24 (m, 17 H), 6.86 (d, 2H, J = 8.7 Hz), 5.90-5.70 (m, 1H), 4.96-4.77 (m, 8H), 4.42 (m, 3H), 3.85-3.77 (m, 3H), 3.83 (s, 3H), 3.65-3.55 (m, 4H), 3.36-3.32 (m, 1H), 3.25-3.20 (m, 1H), 2.10-1.88 (m, 2H), 1.95-1.80 (m, 2H), 1.62-1.10 (m, 26H), 0.89 (s, 3H), 0.07, 0.05 (2s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.1, 129.3, 138.7, 138.6, 129.1-127.5, 114.1, 113.7, 102.1, 84.9, 82.6, 77.6, 76.6, 75.8, 75.7, 75.0, 74.9, 72.5, 67.5, 55.2, 34.3, 33.8, 29.9-29.0, 25.9, 25.1, 18.3, -4.9, -5.3. IR: 2926, 2854, 1513, 1094, 1071 cm^{-1}. MS (ESI): *m/z* 973 ([M+Na]$^+$). Anal. *calcd.* for $C_{59}H_{86}O_8Si$: C 74.48, H 9.11, *found* C 74.40, H 8.98;

(3*R*)-3-[2,3,4-Tri-*O*-benzyl-6-*O*-(*tert*-butyldimethylsilyl)-β-D-glucopyranosyl]-octadec-17-ene-1,3-diol (S-9). To a stirred solution of compound **S-8** (2.3 g, 2.42 mmol) in CH_2Cl_2/H_2O (100 mL, 20:1) is added DDQ (775 mg, 3.4 mmol, 1.4 eq.) at 5 °C. The reaction is stirred for 2 h at ambient temperature before it is quenched with sat. aq. $NaHCO_3$. The mixture is diluted with MTBE, washed with aq. sat. $NaHCO_3$ and brine, and the organic layer is dried and evaporated. Purification of the residue by flash chromatography (hexane/ethyl acetate, 20:1 and 10:1) provides product **S-9** (1.8 g, 89%) as a colorless oil. $[\alpha]_D^{20} = +1.4$ (c = 1.00, $CHCl_3$). ^{1}H NMR (300 MHz, $CHCl_3$): δ 7.30-7.24 (m, 15 H), 5.88-5.74 (m, 1H), 5.03-4.58 (m, 8H), 4.44 (d, 1H, J = 7.8 Hz), 3.89-3.80 (m, 3H), 3.71-3.58 (m, 3H), 3.48 (t, 1H, J = 9.6 Hz), 3.40 (dd, 1H, J = 7.8, 9.1 Hz), 3.33 (m, 1H), 2.07-2.00 (m, 2H), 1.60-1.10 (m, 26H), 0.89 (s, 3H), 0.08, 0.06 (2s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 139.2, 138.6, 138.5, 128.4, 128.3, 128.2, 128.0, 127.9, 127.8, 127.8, 127.6, 127.6, 114.0, 102.9, 84.8, 82.4, 77.7, 75.8, 75.0, 74.9, 62.6, 58.6, 36.1, 33.8, 29.9-28.9, 25.9, 25.4, -5.4, -5.5. IR: 3539, 2926, 2854, 1640, 1070 cm^{-1}. MS (ESI): *m/z* 853 ([M+Na]$^+$). Anal. *calcd.* for $C_{51}H_{78}O_7Si$: C 73.69, H 9.46, *found* C 73.77, H 9.39.

(3*R*)-3-[2,3,4-Tri-*O*-benzyl-6-*O*-(*tert*-butyldimethylsilyl)-β-D-glucopyranosyl]oxy-octadec-17-enoic acid (24). A suspension of alcohol **S-9** (1.6 g, 1.93 mmol) and PDC (4.4 g, 11.58 mmol, 6 eq.) in dry DMF (10 mL) is stirred overnight (15 h) under Ar. After this time the reaction is diluted with ethyl acetate, the resulting solution is washed with sat. aq. $NaHCO_3$ and brine before it is dried, filtered and evaporated. The residue is subjected to flash chromatography (hexane/acetone, 4:1) to give acid **24** as a colorless solid (900 mg, 55%). mp 43-44 °C. $[\alpha]_D^{20} = +18.5$ (c = 1.05, $CHCl_3$). ^{1}H NMR (300 MHz, $CHCl_3$): δ 7.30-7.24 (m, 15H), 5.87-5.74 (m, 1H), 5.04-4.61 (m, 8H), 4.47 (d, 1H, J = 7.8 Hz), 4.05 (m, 1H), 3.82 (dd, 1H, J = 1.4, 11.2 Hz), 3.73 (dd, 1H, J = 5.2, 11.3 Hz), 3.64 (t, 1H, J = 9.1 Hz), 3.51 (t, 1H, J =

9.1 Hz), 3.41 (dd, 1H, *J* = 7.9, 9.3 Hz), 3.33 (ddd, 1H, *J* = 1.4, 5.0, 9.7 Hz), 2.67 (m, 2H), 2.3 (m, 2H), 1.60-1.10 (m, 24H), 0.89 (s, 3H), 0.07, 0.06 (2s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.7, 138.9, 138.1, 138.1, 138.0, 137.8, 114.1, 103.9, 84.7, 82.3, 78.4, 77.4, 76.2, 45.7, 75.0, 75.0, 62.5, 41.1, 35.0, 29.6-29.9, 25.8, 25.4, 18.3, –5.3, –5.5. IR: 3031, 2926, 2854, 1733, 1709, 1070 cm^{-1}. HRMS (ESI): *calcd.* for ($C_{51}H_{76}O_8Si$+Na): 867.5207, *found* 867.5211 ([M+Na]$^+$).

Scheme 2. Preparation of the Model Compounds 44 and 45



(3*R*)-*tert*-Butyl [3-(6-*O*-acetyl-2,3,4-tri-*O*-benzyl-β-D-glucopyranosyl)oxy]heptadecanoate (S-10). A solution of compound **12** (1.0 g, 1.30 mmol) and tetrabutylammonium fluoride trihydrate (440 mg, 1.40 mmol) in THF (10 mL) is stirred at ambient temperature until TLC shows complete conversion of the substrate (ca. 2 h). Evaporation of the solvent gives a viscous oil which is purified by flash chromatography (hexane/ethyl acetate, 4:1) to yield alcohol **S-10** as a colorless oil (1.0 g, 92%). $[\alpha]_D^{20}$ = +12.2 (*c* = 1.00, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28-7.20 (m, 15H), 4.96-4.53 (3AB, 6H), 4.49 (d, 1H, *J* = 7.8 Hz), 2.28 (d, 1H, *J* = 10.8 Hz), 4.20 (dd, 1H, *J* = 4.5, 11.6 Hz), 4.04 (m, 1H), 3.65 (m, 1H), 3.63 (t, 2H, *J* = 6.6 Hz), 3.48 (m, 2H), 3.40 (dd, 1H, *J* = 7.9, 9.1 Hz), 2.74 (dd, 1H, *J* = 5.4, 15.1 Hz), 2.42 (dd, 1H, *J* = 8.0, 15.2 Hz), 2.02 (s, 3H), 1.65-1.15 (m, 26H), 1.44 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.7, 138.4, 138.3, 137.8, 128.4-127.6, 103.1, 84.8, 82.2, 80.3, 77.6, 77.4,

75.7, 74.9, 74.8, 72.7, 63.3, 63.1, 42.2, 34.6, 32.8, 29.7-29.4, 28.1, 25.7, 25.1, 20.8. IR: 3438, 2926, 2854, 1744, 1728, 1367, 1070 cm^{-1}. MS (ESI): *m/z* 855 ($[M+Na]^+$). Anal. *calcd.* for $C_{50}H_{72}O_{10}$ (833.05): C 72.08, H 8.71, *found* C 72.14, H 8.63.

Compound S-12 [being (*S*)-Configured at C-17]. A mixture of PCC (430 mg, 2.0 mmol) and alcohol **S-10** (830 mg, 1.0 mmol) is stirred in dichloromethane (20 mL) at room temperature for 1.5 h before it is poured onto a short column of silica gel. Elution with hexane/ethyl acetate (4:1) provides aldehyde **S-11** (810 mg, 98 %) which is used directly to the next step. Characteristic data: $[\alpha]_D^{20}$ = +13.0 (*c* = 0.60, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ 9.75 (t, 1H, *J* = 1.9 Hz), 7.30-7.20 (m, 15H), 4.96-4.53 (3AB, 6H), 4.49 (d, 1H, *J* = 7.8 Hz), 4.30 (d, 1H, *J* = 11.8 Hz), 4.21 (dd, 1H, *J* = 4.5, 11.5 Hz), 4.65 (m, 1H), 3.49 (m, 2H), 3.40 (dd, 1H, *J* 7.9, 9.1 Hz), 2.73 (dd, 1H, *J* = 5.4, 15.1 Hz), 2.44-2.34 (m, 3H), 2.02 (s, 3H), 1.65-1.15 (m, 26H), 1.44 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 202.9, 170.7, 170.6, 138.4, 137.7, 128.4-127.6, 103.1, 84.8, 82.2, 80.4, 77.7, 77.4, 77.3, 75.7, 74.9, 74.8, 72.7, 63.3, 43.9, 42.2, 34.6, 28.8-29.2, 28.1, 25.1, 22.1, 20.8. IR: 2926, 2854, 2717, 1743, 1727, 1070 cm^{-1}. MS (ESI): *m/z* 853 ($[M+Na]^+$).

A flame-dried flask is charged with *trans*-(1*S*,2*S*)-bis(trifluoromethyl-sulfonylamido)-cyclohexane **39** (113 mg, 0.3 mmol), toluene (4mL) and $Ti(O^iPr)_4$ (700 µL, 3.0 mmol) and the resulting mixture is stirred at 40 °C for 30 min. After being cooled to –50 °C, the organozinc reagent **38** (3 mmol) and a solution of aldehyde **S-11** (1 mmol) in toluene (2 mL) are successively added and the resulting mixture is slowly (1 h) warmed to –20 °C. The reaction is quenched by adding aq. sat. NH_4Cl before it is diluted with MTBE and successively washed with HCl (1N), water and brine. The organic phase is dried (Na_2SO_4) and concentrated, and the residue is purified by flash chromatography (hexane/ethyl acetate, 7:3) to yield alcohol **S-12** as a colorless oil (800 mg, 77% over both steps). $[\alpha]_D^{20}$ = +5.3 (*c* = 1.10, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ 7.28-7.15 (m, 20H), 4.96-4.43 (4AB, 8H), 4.48 (d, 1H, *J* = 7.7 Hz), 4.29 (d, 1H, *J* = 10.7 Hz), 4.20 (dd, 1H, *J* = 4.5, 11.7 Hz), 4.01 (m, 1H), 3.69-3.44 (m, 5H), 3.40 (dd, 1H, *J* = 7.8, 9.1 Hz), 2.74 (dd, 1H, *J* = 5.4, 15.1 Hz), 2.40 (dd, 1H, *J* = 8.0, 15.1 Hz), 2.02 (s, 3H), 1.62-1.17 (m, 36H), 1.43 (s, 9H), 1.18 (d, 3H, *J* = 6.1 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.6, 138.4, 138.3, 137.8, 128.4-127.3, 103.1, 84.8, 82.3, 80.3, 77.7, 77.4, 75.7, 74.9, 74.9, 74.8, 72.7, 72.2, 70.3, 63.3, 42.2, 37.5, 37.4, 36.6, 34.6, 29.8-29.4, 28.1, 25.6, 25.6, 25.5, 25.1, 20.8, 19.6. IR: 3477, 2927, 2854, 1744, 1728, 1070 cm^{-1}. MS (ESI): *m/z*: 1059 ($[M+Na]^+$). Anal. *calcd.* for $C_{64}H_{92}O_{11}$: C 74.10, H 8.94, *found* C 73.86, H 8.89.

Compound S-13. Alcohol **S-12** (60 mg, 0.058 mmol) and trichloroacetimidate **41** (53 mg, 0.087 mmol) are dissolved in CH_2Cl_2 and CH_3CN (1:1, 8 mL) and the resulting solution is cooled to –50 °C before TMSOTf (5 µL) is added. The reaction mixture is stirred for 30 min at –40 °C before it is neutralized (triethylamine) and evaporated. The residue is purified by flash chromatography (hexane/ethyl acetate, 9:1) to give glycoside **S-13** as a viscous oil (76

mg, 89%): $[\alpha]_D^{20} = -1.7$ (c = 1.00, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31-7.24 (m, 35H), 4.95-4.43 (7AB, 14H), 4.50 (d, 1H, J = 7.8 Hz), 4.31 (d, 1H, J = 7.7 Hz), 4.29 (d, 1H, J = 9.8 Hz), 4.20 (dd, 1H, J = 3.7, 10.7 Hz), 4.03 (m, 1H), 3.72-3.46 (m, 9H), 3.58 (s, 3H), 3.43-3.38 (m, 2H), 3.14-3.09 (td, 1H, J = 2.4, 8.1 Hz), 2.72 (dd, 1H, J = 5.4, 15.1 Hz), 2.40 (dd, 1H, J = 7.9, 15.1 Hz), 2.02 (s, 3H), 1.63-1.16 (m, 36H), 1.43 (s, 9H), 1.19 (d, 3H, J = 6.1 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.7, 170.6, 138.9, 138.4, 138.4, 138.3, 138.2, 137.7, 128.4-127.3, 103.1, 102.7, 85.1, 84.3, 84.4, 82.2, 80.3, 80.2, 77.8, 77.6, 77.4, 75.7, 75.4, 74.9, 74.8, 73.5, 72.7, 70.2, 69.2, 63.3, 60.5, 42.2, 36.6, 34.9, 34.6, 34.0, 29.9-29.5, 28.0, 25.5, 25.3, 25.1, 25.0. IR: 2927, 2855, 1740, 1367, 1240, 1072 cm^{-1}. MS (ESI): *m/z*: 1505 ([M+Na]$^+$). Anal. *calcd.* for $C_{92}H_{122}O_{16}$: C 74.46, H 8.29, *found* C 74.50, H 8.22.

Compound 44: To a solution of disaccharide **S-13** (40 mg, 0.026 mmol) in EtOAc (1 mL) and ethanol (2 mL) is added palladium on charcoal (10% w/w, 20 mg) and the resulting suspension is stirred under hydrogen atmosphere overnight. The catalyst is filtered off through a short pad of Celite and the filtrate is evaporated to give compound **44** as a colorless syrup (20 mg, 87%). $[\alpha]_D^{20} = -17.1$ (c = 1.50, MeOH). ^{1}H NMR (400 MHz, pyridine-d_5): δ 4.92 (d, 1H, J = 7.8 Hz), 4.86 (dd, 1H, J = 1.4, 12.8 Hz), 4.83 (d, 1H, J = 7.8 Hz), 4.73 (dd, 1H, J = 5.8, 11.6 Hz), 4.52-4.42 (m, 2H), 4.31 (dd, 1H, J = 5.3, 11.9 Hz) 4.21-4.06 (m, 3H), 4.04-3.90 (m, 5H), 3.83 (m, 1H), 3.82 (s, 3H), 3.41 (t, 1H, J = 8.2 Hz), 3.14 (dd, 1H, J = 5.6, 15.0 Hz), 2.69 (dd, 1H, J = 7.8, 15.0 Hz), 2.02 (s, 3H), 1.80-1.15 (m, 36H), 1.48 (s, 9H), 1.34 (d, 3H, J = 6.1 Hz). ^{13}C NMR (100 MHz, pyridine-d_5): δ 170.9, 170.8, 104.4, 103.1, 85.4, 80.1, 79.4, 78.3, 78.0, 77.8, 77.2, 75.1, 75.0, 72.0, 71.5, 67.0, 64.8, 63.0, 60.8, 49.2, 42.9, 40.2, 35.4, 35.1, 34.3, 30.5, 30.2, 30.0, 29.9-29.8, 28.1, 27.0, 26.4, 25.6, 25.4, 25.3, 24.4, 20.8.

Compound S-12 [with (*R*)-Configuration at C-17]. Prepared as described above for the (*S*)-configured analogue. $[\alpha]_D^{20} = +5.7$ (c = 1.20, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33-7.25 (m, 20H), 4.96-4.43 (4AB, 8H), 4.49 (d, 1H, J = 7.8 Hz), 4.30 (d, 1H, J = 11.3 Hz), 4.20 (dd, 1H, J = 3.6, 10.7 Hz), 4.03 (m, 1H), 3.67-3.42 (m, 5H), 3.40 (t, 1H, J = 7.9 Hz), 2.75 (dd, 1H, J = 5.4, 15.1 Hz), 2.40 (dd, 1H, J = 8.0, 15.1 Hz), 2.02 (s, 3H), 1.60-1.15 (m, 36H), 1.43 (s, 9H), 1.18 (d, 3H, J = 6.1 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.7, 170.6, 139.1, 138.4, 138.3, 137.7, 128.4-127.3, 103.1, 84.8, 82.3, 80.3, 77.6, 77.4, 75.7, 74.9, 74.8, 74.8, 72.7, 71.9, 70.2, 63.3, 42.1, 37.5, 37.4, 36.3, 34.6, 29.7-29.4, 28.1, 25.7, 25.6, 25.5, 25.1, 20.7, 19.6. IR: 2927, 2854, 1744, 1728, 1367, 1236, 1069 cm^{-1}. MS (ESI): *m/z* 1060 ([M+Na]$^+$). Anal. *calcd.* for $C_{64}H_{92}O_{11}$: C 74.10, H 8.94, *found* C 74.15, H 8.99.

Compound S-13 (C17-*R*). Prepared as described above for the (*S*)-configured analogue. (76 mg, 89%). $[\alpha]_D^{20} = +5.2$ (c = 1.00, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34-7.18 (m, 35H), 4.95-4.41 (7AB, 14H), 4.49 (d, 1H, J = 7.8 Hz), 4.32 (d, 1H, J = 7.8 Hz), 4.29 (d, 1H, J = 10.5 Hz), 4.20 (dd, 1H, J = 3.7, 10.5 Hz), 4.04 (m, 1H), 3.70-3.53 (m, 11H), 3.68 (s, 3H), 3.10 (t, 1H, J = 7.8 Hz), 2.77 (dd, 1H, J = 5.4, 15.1 Hz), 2.41 (dd, 1H, J = 7.9, 15.1 Hz), 2.01 (s, 3H), 1.60-1.15 (m, 36H), 1.42 (s, 9H), 1.16 (d, 3H, J = 6.1 Hz). ^{13}C NMR (100 MHz,

$CDCl_3$): δ 170.7, 170.6, 138.9, 138.4, 138.4, 138.3, 138.3, 137.8, 128.4-127.4, 103.1, 102.7, 85.1, 84.8, 84.5, 82.3, 80.3, 80.2, 77.8, 77.6, 77.4, 75.7, 75.5, 74.9, 74.9, 74.8, 73.5, 72.7, 70.2, 69.3, 63.3, 60.6, 42.2, 36.7, 34.8, 34.6, 34.0, 29.9-29.5, 28.1, 25.6, 25.3, 25.1, 20.8, 19.6; IR: 2927, 2855, 1728, 1454, 1366, 1071 cm^{-1}. MS (ESI): *m/z* 1506 ($[M+Na]^+$). Anal. *calcd.* for $C_{92}H_{122}O_{16}$: C 74.46, H 8.29, *found* C 74.29, H 8.33.

Compound 45: Prepared as described above for the (*S*)-configured analogue (15 mg, 96%). $[\alpha]_D^{20} = -17.2$ (*c* = 1.50, MeOH). ^1H NMR (400 MHz, pyridine-d_5): δ 4.92 (d, 1H, *J* = 7.8 Hz), 4.88 (dd, 1H, *J* = 1.4, 11.6 Hz), 4.84 (d, 1H, *J* = 7.8 Hz), 4.74 (dd, 1H, *J* = 5.7, 11.6 Hz), 4.50-4.45 (m, 2H), 4.33 (dd, 1H, *J* = 5.3, 11.9 Hz) 4.18-4.09 (m, 3H), 4.02-3.92 (m, 5H), 3.84 (m, 1H), 3.82 (s, 3H), 3.42 (t, 1H, *J* = 8.3 Hz), 3.14 (dd, 1H, *J* = 5.6, 15.0 Hz), 2.70 (dd, 1H, *J* = 7.8, 15.0 Hz), 2.02 (s, 3H), 1.82-1.20 (m, 36H), 1.48 (s, 9H), 1.31 (d, 3H, *J* = 6.1 Hz). ^{13}C NMR (100 MHz, pyridine-d_5): δ 170.9, 170.8, 104.4, 103.5, 85.4, 80.1, 79.4, 78.3, 78.0, 77.8, 77.2, 75.1, 75.0, 72.0, 71.5, 71.2, 67.0, 64.8, 63.0, 60.8, 49.2, 42.9, 40.2, 35.4, 35.1, 34.4, 30.3, 30.0-29.9, 28.1, 26.4, 25.6, 25.4, 25.3, 24.3, 20.8, 19.2.

Spectroscopic Properties of the Compounds Used in the Antiviral Assays

Compound 70. $[\alpha]_D^{20} = +6.8$ (*c* = 0.60, MeOH). ^1H NMR (400 MHz, CD_3OD): δ 4.45 (dd, *J* = 1.9, 11.7 Hz, 2H), 4.31 (d, *J* = 7.8 Hz, 2H), 4.00 (m, 2H), 3.97 (dd, *J* = 7.9, 11.7 Hz, 2H), 3.51 (m, 4H), 3.44 (m, 2H), 3.32 (t, *J* = 8.9 Hz, 2H), 3.20 (t, 2H), 3.14 (dd, *J* = 7.8, 8.9 Hz, 2H), 3.95 (dd, *J* = 5.1, 15.3 Hz, 2H), 2.42 (dd, *J* = 8.2, 15.3 Hz, 2H) 1.60-1.25 (m, 52H). ^{13}C NMR (100 MHz, CD_3OD): δ 172.9, 105.6, 79.0, 77.9, 75.2, 74.8, 72.1, 65.4, 63.0, 42.7, 36.3, 33.6, 30.7-30.6, 26.9, 26.2. IR: 3421, 2921, 2851, 1735, 1083 cm^{-1}. HRMS (ESI): *m/z calcd.* for ($C_{46}H_{84}O_{16}$+Na): 915.5657, *found* 915.5665 ($[M+Na]^+$).

Compound 71. mp 117-118 °C. $[\alpha]_D^{20} = +2.3$ (*c* = 1.20, MeOH). ^1H NMR (400 MHz, CD_3OD): δ 4.31 (d, *J* = 7.8 Hz, 1H), 4.06 (m, 1H), 3.81 (dd, *J* = 2.4, 12.0 Hz, 1H), 3.65 (s, 3H), 3.62 (dd, *J* = 5.6, 12.1 Hz, 1H), 3.62 (t, *J* = 6.6 Hz, 2H), 3.34-3.18 (m, 3H), 3.12 (dd, *J* = 7.9, 9.0 Hz, 1H), 2.71 (dd, *J* = 6.4, 15.4 Hz, 1H), 2.50 (dd, *J* = 5.5, 15.4 Hz, 1H), 1.70-1.15 (m, 26H). ^{13}C NMR (100 MHz, CD_3OD): δ 174.3, 104.2, 78.0, 77.9, 77.7, 75.2, 71.7, 63.0, 62.9, 52.1, 41.9, 35.9, 33.7, 30.7-30.6, 26.9, 26.1. IR: 3349, 2922, 2851, 1734, 1086, 1047 cm^{-1}. HRMS (ESI): *m/z calcd.* for ($C_{24}H_{46}O_9$+Na): 501.3039, *found* 501.3040 ($[M+Na]^+$).

Compound 72. mp 113-114 °C; $[\alpha]_D^{20} = +3.0$ (*c* = 1.10, MeOH); ^1H NMR (400 MHz, CD_3OD): δ 4.91 (dd, *J* = 3.2, 11.5 Hz, 1H), 4.60 (s, 1H), 4.05 (t, *J* = 10.1 Hz, 1H), 4.01 (d, *J* = 11.6 Hz, 1H), 3.71 (d, *J* = 4.4 Hz, 1H), 3.66 (m, 1H), 3.56 (dd, *J* = 3.0, 9.8 Hz, 1H), 3.53 (t, *J* = 6.7 Hz, 2H), 3.40 (dd, *J* = 4.4, 10.3 Hz, 1H), 2.47 (t, *J* = 11.2 Hz, 1H), 2.36 (dd, *J* = 2.1, 11.3 Hz, 1H), 1.60-1.25 (m, 26H). ^{13}C NMR (100 MHz, CD_3OD): δ 176.2, 107.7, 81.2, 79.3, 78.9, 78.3, 67.1, 64.2, 63.0, 44.3, 38.5, 33.7, 30.7-30.5, 26.9, 26.6. IR: 3412, 2918, 2850,

1699, 1070, 1057, 1030 cm^{-1}. HRMS (ESI): *m/z calcd.* for ($C_{23}H_{42}O_8$+Na): 469.2777, *found* 469.2776 ([M+Na]$^+$).

Compound 73. mp 92-93 °C. $[\alpha]_D^{20}$= –27.5 (*c* = 0.45, MeOH). ^{1}H NMR (400 MHz, CD_3OD): δ 4.37 (d, *J* = 7.9 Hz, 1H), 4.35 (d, *J* = 7.9 Hz, 1H), 3.89 (m, 1H), 3.82 (m, 2H), 3.67-3.60 (m, 3H), 3.56 (s, 3H), 3.55 (s, 3H), 3.35 (dd, *J* = 1.1, 8.9 Hz, 2H), 3.26 (dd, *J* = 2.8, 8.9 Hz, 2H), 3.19 (m, 2H), 2.81 (m, 2H), 1.65-1.25 (m, 12H), 1.16 (d, *J* = 6.2 Hz, 3H), 0.91 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, CD_3OD): δ 103.7, 102.3, 85.2, 84.9, 82.0, 77.8, 77.7, 75.7, 71.8, 62.9, 61.1, 61.0, 38.4, 34.4, 31.0, 28.7, 26.3, 26.0, 19.7, 9.9. IR: 3433, 2931, 1460, 1374, 1079, 1062, 1021 cm^{-1}. HRMS (ESI): *m/z calcd.* for ($C_{24}H_{46}O_{12}$+Na): 549.2887, *found* 549.2889 ([M+Na]$^+$).