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RCM-Based Synthesis of a Variety of β -C-Glycosides and their *In Vitro* Anti-Solid Tumor Activity

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Supporting Information

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All proton NMR assignments were established through with the aid of the corresponding GCOSY and proton decoupling experiments. In general, a diagnostic proton was identified by its chemical shift and then that signal was correlated with adjacent protons. See included 2-D spectra for compounds **1d**, **3g** and **6g** for details.

RCM Examples

ENTRY 1

3,4,6-tri-*O*-benzyl-1,2-dideoxy-5-*O*-(2-methoxyphenylacetyl)-D-arabino-hex-1-enitol (**3a**):¹ 1'-(3, 4, 6-tri-*O*-benzyl- β -D-glucosyl)-2-methoxytoluene (**6a**):²

Acetylation of **6a** gave the corresponding 2-acetyl derivative that exhibited a signal for *H*-2 at 4.94 ppm (dd, 1 H, *J* = 8.8, 8.8 Hz, CHOAc) indicating an axial relationship between *H*-1, *H*-2 and *H*-3 thus confirming the stereochemical assignment.

ENTRY 2

Triflate (**8b**)

To a stirring solution of the phenol (450 mg, 1.46 mmol), triethylamine (0.22 mL, 1.61 mmol), and CH_2Cl_2 (6.0 mL) cooled to 0 °C was added Tf_2O (0.27 mL, 1.61 mmol) dropwise. After the addition was complete, 4-DMAP (30 mg, 0.25 mmol) was added, and stirred for 1 h at room temperature. The reaction mixture was poured into H_2O (15 mL), and extracted with Et_2O (3 x 25 mL), washed with H_2O (15 mL), 10% HCl (2 x 15 mL), H_2O (15 mL), and brine (15 mL). The organic extracts were dried over MgSO_4 , filtered and concentrated *in vacuo* to give **8b** (622 mg, 97%). The product **8b** was used without further purification (R_f = 0.42, TLC, silica, 10% Et_2O -hexanes; ^1H NMR, 500 MHz) ^1H NMR (500 MHz, CDCl_3 , rotamers) δ 7.31 (d, 1 H, *J* = 8.5 Hz, Ar*H*), 7.26 (d, 1 H, *J* = 8.5 Hz, Ar*H*), 7.21 (d, 1 H, *J* = 8.5 Hz, Ar*H*), 7.18 (d, 1 H, *J* = 9.0 Hz, Ar*H*), 4.09 (dddd, 1 H, *J* = 3.5, 3.5, 3.5, 3.5 Hz, *H*-2), 3.84-3.79 (m, 1 H, *H*-1), 3.71 (d, 1 H, *J* = 9.5 Hz, *H*-1), 3.17 (dd, 1 H, *J* = 13.0, 2.5 Hz, *H*-3), 2.77-2.69 (m, 1 H, *H*-3), 1.61 (s, 3 H, CH_3), 1.50 (s, 9 H, 3 x CH_3), 1.45 (s, 3 H, CH_3); ^{13}C NMR (125 MHz, CDCl_3 , rotamers) δ 152.1, 148.2, 139.1, 131.2, 121.3, 117.4, 93.7, 80.3, 65.8, 58.8, 38.0, 28.4, 27.4, 24.4.

Styrene (**9b**)

¹ For full experimental and spectral data listing for this compound please see the supporting information corresponding to: Postema, M. H. D.; Piper, J. L. *Org. Lett.* **2003**, *5*, 1721-1723.

Crude **8b** (600 mg, 1.36 mmol) was re-dissolved in THF (15 mL) and charged into a round bottom flask containing LiCl (177 mg, 4.18 mmol), $(\text{Ph}_3\text{P})_4\text{Pd}$ (31 mg, 27.2 μmol), tributyl(vinyl)tin (0.4 mL, 1.36 mmol) and THF (10 mL). The reaction mixture was degassed for 20 min and then heated to reflux for 11 h, at which point TLC indicated complete conversion of the starting material. The mixture was cooled to room temperature and poured into ice-cold pentane (25 mL). The organic phase was washed with water (10 mL), 10% ammonium hydroxide (10 mL), water (10 mL), brine (10 mL), dried over MgSO_4 , filtered and concentrated to give a viscous yellow oil. Flash chromatography of the residue over silica using 10 $\rightarrow$ 15% Et_2O -hexanes gave **9b** (350 mg, 76% over 2 steps) as a pure (R_f = 0.35, TLC, silica, 15% Et_2O -hexanes; ^1H NMR, 500 MHz) white solid: m.p. = 84-85 $^\circ\text{C}$; $[\alpha]_D^{26}$ = -14.5 (c = 1.00, CHCl_3); FT-IR (neat) 2978, 2933, 2873, 1697, 1387, 1365, 1257, 1173, 1092, 1054, 856 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3 , all rotamer peaks reported) δ 7.38-7.32 (m, 2 H, 2 x ArH), 7.21 (d, 1 H, J = 8.0 Hz, ArH), 7.15 (d, 1 H, J = 7.5 Hz, ArH), 6.68 (ddd, 1 H, J = 17, 10.5, 3.5 Hz, H -4), 5.72 (dd, 1 H, J = 17.5, 2.5 Hz, H -5), 5.34-5.21 (dd, 1 H, J = 5.5, 5.5 Hz, H -5), 4.01 (dd, 1 H, J = 5.0, 5.0 Hz, 0.5 H, H -2), 3.96 (dd, 1 H, J = 5.0, 5.0 Hz, 0.5 H, H -2), 3.79-3.73 (m, 2 H, 2 x H -1), 3.21 (dd, 0.5 H, J = 11, 4.0 Hz, H -3), 2.65 (dd, 0.5 H, J = 12.5 Hz, H -3), 1.64 (s, 1.5 H, $\text{C}(\text{CH}_3)_2$), 1.55 (s, 1.5 H, $\text{C}(\text{CH}_3)_2$), 1.53 (s, 9 H, $\text{C}(\text{CH}_3)_3$), 1.50 (s, 1.5 H, $\text{C}(\text{CH}_3)_2$), 1.46 (s, 1.5 H, $\text{C}(\text{CH}_3)_2$); ^{13}C NMR (125 MHz, CDCl_3 , data for only one rotamer reported) δ 151.6, 138.1, 136.4, 135.9, 129.4, 126.4, 113.5, 94.0, 79.7, 66.0, 59.1, 39.3, 29.7, 28.5, 26.9, 23.2; HRMS (FAB) calcd for $\text{C}_{19}\text{H}_{27}\text{NO}_3\text{Na}$ (M) $^+$ 340.1883, found 340.1887.

Alcohol (10b)

9-BBN (8.7 mL, 4.35 mmol, 0.5 M in THF) was added dropwise over 30 min to a cool (0 $^\circ\text{C}$) THF (10 mL) solution of **9b** (230 mg, 0.73 mmol) and stirred for 1 h, warmed to room temperature and stirred was for an additional 4 h. The solution was cooled to 0 $^\circ\text{C}$ and NaOH (10 mL, 1 M solution, 10 mmol) was added followed by H_2O_2 (10 mL, 0.1 mmol, 30% in H_2O). After warming to room temperature and an additional 2 h at room temperature, the biphasic mixture was treated with saturated $\text{Na}_2\text{S}_2\text{O}_3$ (3 mL) and most of the THF was removed *in vacuo*. The aqueous mixture was then extracted with EtOAc (3 x 25 mL) and the combined organic extracts were washed with brine, dried over MgSO_4 and filtered. Flash chromatography of the residue over silica using 25 $\rightarrow$ 35% EtOAc -hexanes gave alcohol **10b** (225 mg, 93%) as a pure (R_f = 0.30, TLC, silica, 35% EtOAc -hexanes; ^1H NMR, 400 MHz) white solid: m.p. = 66-67 $^\circ\text{C}$; $[\alpha]_D^{26}$ = -20.8 (c = 1.00, CHCl_3); FT-IR (neat) 3430 (br), 2978, 2932, 2872, 1696, 1454, 1389, 1365, 1257, 1172, 1093, 1052, 855, 768 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , rotamers) δ 7.22-7.11 (m, 4 H, 4 x ArH), 3.98-3.92 (m, 1 H, H -2), 3.87-3.81 (m, 2 H, 2 x H -5), 3.79-3.72 (m, 2 H, 2 x H -4), 3.09-3.03 (m, 1 H, H -1), 2.87-2.80 (m, 2 H, 2 x H -3), 2.67-2.58 (m, 1 H, H -1), 1.63 (s, 3 H, $\text{C}(\text{CH}_3)_2$), 1.52 (s, 9 H, $\text{C}(\text{CH}_3)_3$), 1.49 (s, 3 H, $\text{C}(\text{CH}_3)_2$); ^{13}C NMR (125 MHz, CDCl_3 , rotamers) δ 136.6, 129.7, 129.5, 129.3, 129.1, 94.4, 94.0, 79.7, 66.0, 63.6, 59.2, 39.2, 38.7, 28.6, 26.9, 23.2; HRMS (FAB) calcd for $\text{C}_{19}\text{H}_{29}\text{NO}_4\text{Na}$ (M) $^+$ 358.1989, found 358.1987.

Acid (2b)

Dess-Martin periodane (704 mg, 1.66 mmol) was added in one portion to a solution of alcohol **10b** (186 mg, 0.55 mmol) in CH_2Cl_2 (9 mL) at ambient temperature. After 1 h, the reaction mixture was treated with saturated NaHSO_3 (0.2 mL) followed by NaHCO_3 (10 mL) and the aqueous layer was extracted with Et_2O (3 x 10 mL). The combined organic extracts were dried over MgSO_4 , filtered and concentrated to give a crude oil (183 mg, 0.55 mmol, ~100%) that was taken up in *t*-BuOH (7.5 mL) and H_2O (0.75 mL). 2-Methyl-2-butene (310 μL , 3.69 mmol), NaClO_2 (65 mg, 0.72 mmol) and KH_2PO_4 (86 mg, 0.72 mmol) were then sequentially added to this suspension and stirring was continued for 12 h at ambient temperature. The organic phase was removed *in vacuo* and the aqueous phase acidified using 1 N HCl (2 mL, 2 mmol), extracted with EtOAc (5 x 15 mL), washed with brine, dried over MgSO_4 and concentrated. Flash chromatography of the residue over silica using 40 $\rightarrow$ 45% EtOAc -hexanes-0.5% AcOH gave acid **2b** (178 mg, 93% over 2 steps) as a pure (R_f = 0.25, TLC, silica, 40% EtOAc -hexanes (0.5% AcOH); ^1H NMR, 500 MHz) white solid: m.p. = 89-90 $^\circ\text{C}$; $[\alpha]_D^{26}$ = -9.3 (c = 1.00, CHCl_3); FT-IR (neat) 3200-3000 (br) 2978, 2925, 1703, 1407, 1390, 1257, 1168, 1094, 1016, 742 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3 , only set of rotamer signals reported) δ 10.30 (bs, 1 H, CO_2H), 8.05 (d, 1 H, J = 7.5, ArH), 7.44 (dd, 1 H, J = 7.5, 1.0 Hz, ArH), 7.22-7.16 (m, 2 H, ArH), 4.00-3.94 (m, 1 H, H -3), 3.80-3.74 (m, 2 H, 2 x H -4), 3.69-3.63 (m, 2 H, 2 x H -1), 3.08 (dd, 1 H, J = 13.0, 1.0 Hz, H -2), 2.69-2.62 (m, 1 H, H -2), 1.65 (s, 3 H, $\text{C}(\text{CH}_3)_2$), 1.52 (s, 9 H, $\text{C}(\text{CH}_3)_3$), 1.50 (s, 3 H, $\text{C}(\text{CH}_3)_2$); ^{13}C NMR (125 MHz, CDCl_3 , only one set of rotamer signals reported) δ 171.1, 153.0, 141.9, 137.6, 133.4, 129.7, 129.6, 128.0, 94.6, 66.1, 59.1, 40.7, 29.7, 28.6, 26.9, 23.2; HRMS (FAB) calcd for $\text{C}_{19}\text{H}_{27}\text{NO}_5\text{Na}$ (M) $^+$ 372.1781, found 372.1789.

DCC-mediated esterification exemplified by the preparation of ester (**3b**)

4-DMAP (44 mg, 0.36 mmol) and DCC (223 mg, 1.08 mmol) were added in one portion to a dry solution of acid **2b** (300 mg, 0.86 mmol) and olefin alcohol **1a**² (300 mg, 0.72 mmol) in dry CH_2Cl_2 (5 mL). The resulting solution was then stirred for 18 h at ambient temperature, at which point TLC (25% Et_2O -hexanes) showed the reaction was complete. The reaction mixture was diluted with ether (20 mL) and filtered by gravity through cotton to remove most of the formed dicyclohexylurea. The resulting organic solution was washed with NH_4Cl (1 x 30 mL), dried and concentrated under reduced pressure. Flash chromatography of the residue over silica using 15 $\rightarrow$ 25% Et_2O -hexanes gave **3b** (502 mg, 93%) as a pure (R_f = 0.41, TLC, silica, 25% Et_2O -hexanes; ^1H NMR (400 MHz, CDCl_3)) yellow oil: $[\alpha]_D^{26}$ = -20.0 (c = 1.00, CHCl_3); FT-IR (neat) 2978, 2930, 2868, 1736, 1697, 1388, 1255 1092, 1072, 737, 698 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , only set of rotamer signals reported) δ 7.29-7.23 (m, 4 H, ArH), 7.19-7.00 (m, 14 H, ArH), 6.94-6.90 (m, 1 H, ArH), 5.84 (ddd, 1 H, J = 18, 10.5, 7.5 Hz, H -2), 5.61 (br d, 1 H, J = 5.2 Hz, H -5), 5.09 (d, 1 H, J = 18 Hz, H -1), 5.01 (d, 1 H, J = 10.8 Hz, H -1), 4.59 (d, 1 H, J = 11.2 Hz, OCH_2Ph), 4.50 (d, 1 H, J = 11.2 Hz, OCH_2Ph), 4.42 (d, 1 H, J = 12 Hz, OCH_2Ph), 4.25-4.14 (m, 2 H, 2 x OCH_2Ph), 4.06 (d, 1 H, J = 11.2 Hz, OCH_2Ph), 3.91-3.82 (m, 2 H, H -3, H -4), 3.81-3.75 (m, 2 H, 2 x H -6), 3.74-3.68 (m, 1 H, H -9), 3.54 (br d, 1 H, J = 9.0 Hz, H -7), 3.41-3.26 (m, 3 H, H -7, 2 x H -10), 3.02 (dd, 1 H, J = 10.5, 1.0 Hz, H -8), 2.57 (ddd, 1 H, J = 23, 13.5, 12 Hz, H -8), 1.78 (s, 3 H, $\text{C}(\text{CH}_3)_2$), 1.53 (s, 3 H, $\text{C}(\text{CH}_3)_2$), 1.43 (s, 9 H, $\text{C}(\text{CH}_3)_3$); ^{13}C NMR (100 MHz, CDCl_3) δ 170.7, 129.7, 129.6, 129.5, 129.4, 128.4, 128.4, 128.3, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 127.5, 119.0, 80.4, 80.2, 75.0, 74.1,

² Freeman, F.; Robarge, K. D. *Carbohydr. Res.* **1987**, *171*, 1-11.

73.3, 73.2, 73.0, 70.8, 70.6, 70.3, 67.9, 59.2, 41.0, 28.6, 28.4, 23.2; HRMS (FAB) calcd for $C_{46}H_{55}O_8Na$ (M)⁺ 772.3820, found 772.3825.

General procedure for the three-step protocol exemplified by the preparation of C-glycoside (6b)

A solution of titanium tetrachloride (1.19 mL, 2 M in CH_2Cl_2 , 2.38 mmol) was added to cool ($0^\circ C$) THF (2 mL). The resulting mixture was stirred for 30 minutes at which point TMEDA (0.69 mL, 4.59 mmol) was added in one portion. The resulting yellow-brown suspension was allowed to warm to ambient temperature and stirred for 30 minutes. At this point, zinc dust (339 mg, 5.18 mmol) and lead (II) chloride (4 mg, 0.014 mmol) were added in one portion and stirring at ambient temperature was continued for 10 min. A solution of ester **3b** (100 mg, 0.14 mmol) and dibromomethane (91 μL , 1.3 mmol) in THF (2 mL) was then added *via* cannula to the reaction flask in one portion. The mixture was stirred at $60^\circ C$ for 1 hour, cooled to $0^\circ C$ and then quenched by the addition of saturated potassium carbonate (1.0 mL). The resulting mixture was stirred for 30 minutes (while warming to ambient temperature), diluted with ether (20 mL) and stirred vigorously for 15 minutes. The resulting mixture was filtered through basic alumina using 3% triethylamine-ether as the eluent. The greenish-blue precipitate that resulted was crushed (mortar and pestle) and thoroughly extracted by vigorous stirring over diethyl ether (15-20 mL) for 30 minutes. The combined ethereal extracts were concentrated *in vacuo*, azeotroped with benzene (3 x 20 mL) and re-dissolved in dry toluene (14 mL). After the crude enol ether was degassed thoroughly under nitrogen atmosphere for 20 minutes, the first aliquot (1/4) of catalyst **7** (30 mg, 0.158 mmol, 25 mol%) was added and heated to $60^\circ C$. The remaining catalyst was added in three more portions over the next three hours and upon completion, the solution was cooled to $0^\circ C$, $BH_3 \cdot THF$ (1.4 mL, 1 M in THF, 1.4 mmol) was added to the cooled solution and the resulting mixture was stirred at this temperature for three hours until TLC indicated the reaction was complete. NaOH (10 mL, 1 M) and hydrogen peroxide (10 mL, 30% in water) were added sequentially dropwise, and the solution was allowed to warm to room temperature over 2 hours at which point TLC showed a clean product spot. The solution was extracted with ether (3 x 15 mL) and the combined ethereal extracts were washed with brine (1 x 20 mL), dried over magnesium sulfate, filtered and concentrated *in vacuo*. Flash chromatography of the residue over silica using 10 $\rightarrow$ 20% EtOAc-hexanes gave **6b** (59 mg, 59% over 3 steps) as a pure (R_f = 0.32, TLC, silica, 20% EtOAc-hexanes; ^1H NMR (400 MHz, $CDCl_3$)) oil: $[\alpha]_D^{26} = +5.2$ (c = 1.00, $CHCl_3$); FT-IR (neat) 3463, 2979, 2929, 2868, 1695, 1453, 1388, 1364, 1257, 1106, 1094, 855, 734, 697 cm^{-1} ; ^1H NMR (400 MHz, $CDCl_3$, rotamers) δ 7.40-7.20 (m, 17 H, ArH), 7.18-7.04 (m, 2 H, ArH), 4.96 (d, 1 H, J = 11.2 Hz, OCH_2Ph), 4.79 (d, 1 H, J = 10.4 Hz, OCH_2Ph), 4.73 (d, 1 H, J = 11.2 Hz, OCH_2Ph), 4.62 (d, 1 H, J = 10.8 Hz, OCH_2Ph), 4.58-4.48 (m, 2 H, 2 x OCH_2Ph), 3.97 (m, 1 H, H-9), 3.78-3.66 (m, 4 H, 2 x H-6, 2 x H-10), 3.59 (dd, 1 H, J = 9.6, 9.6 Hz, H-4), 3.49 (dd, 1 H, J = 8.8, 8.8 Hz, H-3), 3.44-3.37 (m, 2 H, H-1, H-5), 3.32 (dd, 1 H, J = 9.2, 9.2 Hz, H-2), 3.20-3.02 (m, 2 H, H-7, H-8), 2.84-2.72 (m, 1 H, H-7), 2.61 (dd, 1 H, J = 11.2, 11.2 Hz, H-8), 1.65 (s, 3 H, $C(CH_3)_2$), 1.53 (s, 9 H, $C(CH_3)_3$), 1.50 (s, 3 H, $C(CH_3)_2$); ^{13}C NMR (125 MHz, $CDCl_3$, rotamers) δ 151.6, 138.3, 138.0, 136.5, 136.2, 130.1, 128.9, 128.7, 128.4, 127.9, 127.8, 127.6, 127.5, 93.9, 86.7, 79.7, 79.1, 78.4, 74.7, 73.4, 72.9, 68.8, 66.0, 59.2, 39.2, 37.3, 28.5, 26.9, 23.2; HRMS (FAB) calcd for $C_{46}H_{54}O_8Na$ (M)⁺ 760.3820, found 760.3833.

ENTRY 3
Vinyl (9c)

Triflyl chloride (54 μ L, 0.51 mmol) was added dropwise to a stirred and cooled (0 $^{\circ}$ C) solution of 3-deoxyestrone³ (120 mg, 0.47 mmol) and triethylamine (72 μ L, 0.51 mmol) in CH_2Cl_2 (1.5 mL). After the addition was complete, 4-DMAP (3 mg, 24.6 μ mol) was added and stirring was continued for 1 h at ambient temperature. The reaction mixture was poured into water (5 mL), extracted with Et_2O (3 x 10 mL), washed with H_2O (5 mL), 10% HCl (2 x 5 mL), H_2O (5 mL) and brine (5 mL). The organic extracts were dried, filtered and concentrated *in vacuo* to provide a pale yellow oil (172 mg, 84% crude yield). A solution of the crude product in THF (1 mL) was added to a THF (2 mL) solution of LiCl (56 mg, 1.32 mmol), $(\text{Ph}_3\text{P})_4\text{Pd}$ (10 mg, 8.75 μ mol) and tributyl(vinyl)tin (0.13 mL, 0.43 mmol). The reaction mixture was degassed for 20 min and heated to reflux for 11 h, at which point TLC indicated complete conversion. The mixture was cooled to room temperature and poured into ice-cold pentane (10 mL). The organic phase was washed with water (5 mL), 10% ammonium hydroxide (5 mL), water (5 mL), brine (5 mL), dried, filtered and concentrated to give a viscous yellow oil. Flash chromatography of the residue over silica gel using 10 $\rightarrow$ 20% Et_2O -hexanes gave **9c** (95 mg, 76% over 2 steps) as a pure (R_f = 0.30, TLC, silica, 15% Et_2O -hexanes; ^1H NMR, 500 MHz) white solid: m.p. = 44-45 $^{\circ}$ C; $[\alpha]_D^{25}$ = +102.4 (c = 1.00, CHCl_3); FT-IR (neat) 2922, 2866, 1706, 1498, 1451, 1376, 988, 897, 830 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.29 (d, 1 H, J = 8.0 Hz, ArH), 7.22 (d, 1 H, J = 8.0 Hz, ArH), 7.15 (s, 1 H, ArH), 6.69 (dd, 1 H, J = 17.5, 11.0 Hz, C=C-H), 5.72 (d, 1 H, J = 17.5 Hz, C=CH-H), 5.20 (d, 1 H, J = 10.5 Hz, C=CH-H), 2.94-2.86 (m, 2 H, 2 x CH), 2.36-2.24 (m, 2 H, 2 x CH), 1.99-1.88 (m, 2 H, 2 x CH), 1.84-1.75 (m, 1 H, CH), 1.75-1.63 (m, 2 H, 2 x CH), 1.60-1.50 (m, 2 H, 2 x CH), 1.46-1.34 (m, 3 H, 3 x CH), 1.34-1.23 (m, 2 H, 2 x CH), 1.22-1.14 (m, 1 H, CH), 0.77 (s, 3 H, CH_3); ^{13}C NMR (125 MHz, CDCl_3) δ 140.6, 136.9, 136.7, 134.8, 126.8, 125.5, 123.4, 112.8, 53.7, 44.6, 41.0, 40.5, 39.0, 38.8, 29.7, 28.1, 26.6, 25.2, 20.6, 17.5; HRMS (FAB) calcd for $\text{C}_{20}\text{H}_{26}$ (M)⁺ 266.2035, found 266.2036.

Alcohol (10c)

9-BBN (4.5 mL, 2.25 mmol, 0.5 M in THF) was added dropwise over 30 min to a cool (0 $^{\circ}$ C) THF solution of the vinyl estrone derivative **9c** (500 mg, 1.88 mmol) dissolved in THF (15 mL) and the reaction was stirred for 1 h before warming to room temperature. Stirring was continued for an additional hour and NaOH (10 mL, 10 mmol, 1 M solution), followed by H_2O_2 (10 mL, 30% in H_2O) were added dropwise. After 2 h at room temperature, the biphasic mixture was treated with saturated Na_2SO_3 (3 mL) and the organic phase was removed *in vacuo*. The aqueous mixture was extracted with EtOAc (3 x 25 mL), washed with brine, dried, filtered and concentrated. Flash chromatography of the residue over silica using 30% Et_2O -hexanes gave **10c** (508 mg, 95%) as pure (R_f = 0.33, TLC, silica 30% Et_2O -hexanes; ^1H NMR, 500 MHz) white needles: m.p. = 82-83 $^{\circ}$ C; $[\alpha]_D^{25}$ = +71.5 (c = 1.00, CHCl_3); FT-IR (neat) 3330 (br),

³ Huang-Minlon, *J. Am. Chem. Soc.* **1949**, *71*, 3301-3303.

2925, 2867, 1713, 1500, 1451, 1376, 1045, 829, 755, 692 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.26 (d, 1 H, $J = 8.0$ Hz, ArH), 7.00 (d, 1 H, $J = 7.5$ Hz, ArH), 6.95 (s, 1 H, ArH), 3.88-3.82 (app t, 2 H, 2 x OCH), 2.92-2.84 (m, 2 H, 2 x CH), 2.84-2.78 (m, 2 H, 2 x CH), 2.34-2.20 (m, 2 H, 2 x CH), 1.96-1.85 (m, 2 H, 2 x CH), 1.81-1.72 (m, 1 H, CH), 1.72-1.60 (m, 2 H, 2 x CH), 1.60-1.46 (m, 3 H, 3 x CH), 1.44-1.30 (m, 2 H, 2 x CH), 1.32-1.20 (m, 2 H, 2 x CH), 1.20-1.11 (m, 1 H, CH), 0.75 (s, 3 H, CH_3); ^{13}C NMR (125 MHz, CDCl_3) δ 139.0, 137.0, 135.3, 129.6, 126.2, 125.7, 63.7, 53.6, 44.4, 41.1, 40.5, 39.0, 38.8, 38.6, 29.7, 28.1, 26.6, 25.2, 20.6, 17.5; HRMS (FAB) calcd for $\text{C}_{20}\text{H}_{28}\text{ONa}$ (M) $^+$ 307.2032, found 307.2037.

Acid (2c)

Dess-Martin periodane (210 mg, 0.5 mmol) was added in one portion to a stirred CH_2Cl_2 (8 mL) solution of alcohol **10c** (94 mg, 0.33 mmol) at ambient temperature. After 1 h, the reaction mixture was treated sequentially with saturated NaHSO_3 (0.5 mL) and NaHCO_3 (10 mL) and the aqueous layer was extracted with Et_2O (3 x 10 mL). The combined organic extracts were dried, filtered and concentrated to give a crude oil (90 mg, 0.32 mmol, 96%) that was taken up in *t*-BuOH (4.3 mL) and H_2O (0.43 mL). 2-Methyl-2-butene (185 μL , 2.2 mmol), NaClO_2 (39 mg, 0.43 mmol) and KH_2PO_4 (52 mg, 0.43 mmol) were then sequentially added to this suspension and stirring was continued for 12 h at ambient temperature. The organic phase was removed *in vacuo* and the aqueous phase acidified with 1 N HCl (2 mL), extracted with EtOAc (5 x 10 mL), washed with brine, dried over MgSO_4 and concentrated. Flash chromatography of the residue over silica using 25% EtOAc -hexanes-0.5% AcOH gave **2c** (90 mg, 91% over 2 steps) as a pure ($R_f = 0.24$, TLC, silica 25% EtOAc -hexanes (0.5% AcOH); ^1H NMR, 500 MHz) white solid: m.p. = 127-128 $^\circ\text{C}$; $[\alpha]_D^{26} = +64.4$ ($c = 1.00$, CHCl_3); FT-IR (neat) 3400-2700 (br) 2930, 2866, 1704, 1499, 1450, 1431, 1408, 1376, 1358, 1296, 1217, 1154, 940 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.28 (d, 1 H, $J = 8.0$ Hz, ArH), 7.04 (d, 1 H, $J = 7.5$ Hz, ArH), 7.01 (s, 1 H, ArH), 3.60 (app s, 2 H, 2 x C(=O)OCH $_2$ -), 2.92-2.85 (m, 2 H, 2 x CH), 1.97-1.87 (m, 2 H, 2 x CH), 1.82-1.74 (m, 1 H, CH), 1.74-1.63 (m, 2 H, 2 x CH), 1.59-1.50 (m, 2 H, 2 x CH), 1.46-1.33 (m, 3 H, 3 x CH), 1.33-1.22 (m, 2 H, 2 x CH), 1.20-1.13 (m, 1 H, CH), 0.75 (s, 3 H, CH_3); ^{13}C NMR (125 MHz, CDCl_3) δ 178.3, 139.9, 137.2, 130.2, 129.8, 126.5, 125.7, 53.6, 44.3, 41.0, 40.6, 40.5, 38.8, 38.8, 29.6, 28.0, 26.5, 25.2, 20.5, 17.5; HRMS (FAB) calcd for $\text{C}_{20}\text{H}_{26}\text{O}_2\text{Na}$ (M) $^+$ 321.1825, found 321.1827.

Ester (3c)

The general method for esterification was followed using: alcohol **1a**⁴ (351 mg, 0.84 mmol), acid **2c** (300 mg, 1.01 mmol), DCC (260 mg, 1.26 mmol), 4-DMAP (51 mg, 0.42 mmol) and CH_2Cl_2 (6 mL). Flash chromatography of the residue over silica using 15 $\rightarrow$ 25% Et_2O -hexanes gave **3c** (490 mg, 82%) as a pure

⁴ Freeman, F.; Robarge, K. D. *Carbohydr. Res.* **1987**, *171*, 1-11.

(R_f = 0.35, TLC, silica, 25% diethyl ether-hexanes; ^1H NMR (500 MHz, CDCl_3)) yellow oil: $[\alpha]_D^{26} = +50.6$ (c = 1.00, CHCl_3); FT-IR (neat) 3063, 3030, 2920, 2866, 2360, 2342, 1732, 1497, 1453, 1251, 1066, 733, 696 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.40-7.28 (m, 15 H, ArH), 7.25 (d, 1 H, J = 7.5 Hz, ArH), 7.08 (d, 1 H, J = 8.0 Hz, ArH), 7.01 (s, 1 H, ArH), 5.92 (ddd, 1 H, J = 17.5, 10.5, 8.0 Hz, H -2), 5.35 (dd, 1 H, J = 10.5, 1.0 Hz, H -1), 5.33-5.27 (m, 2 H, H -1, H -5), 4.66 (d, 1 H, J = 11 Hz, OCH_2Ph), 4.58 (d, 1 H, J = 11 Hz, OCH_2Ph), 4.55 (d, 1 H, J = 12.0 Hz, OCH_2Ph), 4.52 (d, 1 H, J = 12 Hz, OCH_2Ph), 4.48 (d, 1 H, J = 12 Hz, OCH_2Ph), 4.20 (d, 1 H, J = 12.0 Hz, OCH_2Ph), 3.88 (dd, 1 H, J = 8.0, 5.0 Hz, H -3), 3.86-3.84 (m, 2 H, 2 x H -6), 3.83 (dd, 1 H, J = 5.0, 5.0 Hz, H -4), 3.55 (d, 1 H, J = 15 Hz, H -7), 3.50 (d, 1 H, J = 14.5 Hz, H -7), 2.84-2.79 (m, 2 H, 2 x CH), 2.34-2.27 (m, 1 H, CH), 2.27-2.20 (m, 1 H, CH), 1.95-1.89 (m, 2 H, 2 x CH), 1.85-1.66 (m, 3 H, 3 x CH), 1.60-1.46 (m, 2 H, 2 x CH), 1.43-1.26 (m, 6 H, 6 x CH), 1.21-1.13 (m, 1 H, CH), 0.77 (s, 3 H, CH_3); ^{13}C NMR (125 MHz, CDCl_3) δ 170.8, 139.5, 138.2, 138.1, 138.0, 136.9, 135.2, 130.8, 129.7, 128.2, 128.2, 128.1, 128.0, 127.9, 127.5, 127.5, 127.4, 126.4, 125.5, 119.2, 80.9, 80.5, 74.9, 73.0, 73.0, 70.3, 68.0, 53.5, 44.2, 41.1, 40.9, 40.4, 38.7, 38.7, 29.4, 27.9, 26.4, 25.1, 20.5, 17.5; HRMS (FAB) calcd for $\text{C}_{47}\text{H}_{54}\text{O}_5\text{Na}$ (M) $^+$ 721.3863, found 721.3849.

C-Glycoside (6c)

The general procedure for the three step protocol was followed using: Titanium tetrachloride (1.19 mL, 2 M in CH_2Cl_2 , 2.38 mmol), THF (2 mL), TMEDA (0.69 mL, 4.59 mmol), zinc dust (339 mg, 5.18 mmol), lead (II) chloride (4 mg, 0.014 mmol), ester **3c** (100 mg, 0.14 mmol), dibromomethane (91 μL , 1.3 mmol), catalyst **7** (30 mg, 0.158 mmol, 25 mol%), toluene (14 mL), $\text{BH}_3 \cdot \text{THF}$ (1.4 mL, 1 M in THF, 1.4 mmol), NaOH (10 mL, 1 M, 10 mmol) and hydrogen peroxide (10 mL, 30% in water, 0.05 mol). After the usual work-up, flash chromatography of the residue over silica using 10 $\rightarrow$ 20% EtOAc-hexanes gave **6c** (52 mg, 52% over 3 steps) as a pure (R_f = 0.32, TLC, silica, 20% EtOAc-hexanes; ^1H NMR (500 MHz, CDCl_3)) oil: $[\alpha]_D^{26} = +34.3$ (c = 1.00, CHCl_3); FT-IR (neat) 3441, 3063, 3030, 2919, 2865, 1607, 1497, 1453, 1359, 1047, 1027, 908, 831, 731, 697 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.41-7.30 (m, 13 H, Ph), 7.29-7.25 (m, 2 H, Ph), 7.22 (d, 1 H, J = 8.0 Hz, ArH), 7.12 (d, 1 H, J = 8.0 Hz, ArH), 7.05 (s, 1 H, ArH), 5.00 (d, 1 H, J = 12.4 Hz, OCH_2Ph), 4.84 (d, 1 H, J = 10.4 Hz, OCH_2Ph), 4.77 (d, 1 H, J = 11.6 Hz, OCH_2Ph), 4.66 (d, 1 H, J = 11.2 Hz, OCH_2Ph), 4.64 (d, 1 H, J = 12.8 Hz, OCH_2Ph), 4.58 (d, 1 H, J = 12 Hz, OCH_2Ph), 3.78-3.74 (m, 2 H, 2 x H -6), 3.65 (dd, 1 H, J = 9.2, 9.2 Hz, H -4), 3.53 (dd, 1 H, J = 8.8, 8.8 Hz, H -3), 3.48-3.39 (m, 2 H, H -1, H -2, H -5), 3.10 (dd, 1 H, J = 14.8, 2.4 Hz, H -7), 2.90-2.75 (m, 3 H, H -7, 2 x CH), 2.36-2.22 (m, 2 H, CH, OH), 1.95-1.88 (m, 2 H, 2 x CH), 1.84-1.78 (m, 1 H, CH), 1.76-1.63 (m, 2 H, 2 x CH), 1.44-1.34 (m, 3 H, 3 x CH), 1.34-1.24 (m, 3 H, 3 x CH), 1.22-1.02 (m, 1 H, CH), 0.78 (s, 3 H, CH_3); ^{13}C NMR (125 MHz, CDCl_3) δ 138.5, 138.4, 138.0, 136.3, 135.3, 130.3, 128.6, 128.4, 128.3, 127.9, 127.8, 127.7, 127.7, 127.5, 127.1, 125.0, 86.8, 79.9, 79.1, 78.4, 75.1, 74.7, 73.5, 73.3, 68.9, 53.6, 44.3, 41.0, 40.5, 38.9, 38.8, 37.4, 29.6, 28.1, 26.5, 25.2, 20.5, 17.5; HRMS (FAB) calcd for $\text{C}_{46}\text{H}_{54}\text{O}_5\text{Na}$ (M) $^+$ 709.3863, found 709.3840.

ENTRY 4

Benzyl 3-adamantyl-2-propenoate (10d)

Alcohol **8d** (1.1 g, 6.66 mmol) was dissolved in CH_2Cl_2 (150 mL) and Dess-Martin periodane (4.22 g, 9.98 mmol) was added portion-wise over 2 min. After the usual work-up, the residue **9d** ($R_f = 0.25$, TLC silica, 10% EtOAc-hexanes; ^1H NMR, 500 MHz) was dissolved in benzene and (carbobenzyloxymethyl)triphenylphosphorane (5.7 g, 13.99 mmol) was added in one portion. Stirring was continued for 8 h, after which point no starting material remained (TLC silica, 10% EtOAc-hexanes). The solvent was removed *in vacuo* and the solid residue was subjected to flash chromatography over silica gel using 10 $\rightarrow$ 15% EtOAc-hexanes to afford benzyl ester **10d** (1.73 g, 88% combined yield over 2 steps) as a 12:1 (*E*:*Z*) mixture of separable isomers. Major (*E*) isomer: ($R_f = 0.41$, TLC, silica, 15% EtOAc-hexanes); FT-IR (neat) 2910, 2848, 2359, 2336, 1717, 1647, 1453, 1302, 1160, 989, 748, 696 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.40-7.30 (m, 5 H, ArH), 5.77 (d, 1 H, $J = 13.0$ Hz, C=C-H), 5.69 (d, 1 H, $J = 13.0$ Hz, C=C-H), 5.19 (s, 2 H, OCH_2Ph), 1.98 (s, 3 H, 3 x CH), 1.84 (s, 6 H, 3 x CH_2), 1.68 (s, 6 H, 3 x CH_2); ^{13}C NMR (125 MHz, CDCl_3) δ 166.7, 155.1, 135.9, 128.5, 128.4, 128.2, 118.0, 66.1, 40.9, 36.5, 28.4; HRMS (FAB) calcd for $\text{C}_{20}\text{H}_{24}\text{O}_2\text{Na}$ (M) $^+$ 319.1668, found 319.1669.

3-Adamantyl-2-propanoic acid (2d)

Pd/C (10%, 20 mg) was added to an EtOAc (10 mL) solution of ester **10d** (800 mg, 2.69 mmol) that was then shaken under an atmosphere of H_2 (50 psi) for 12 h. The solution was filtered through Celite using EtOAc as eluent (100 mL) and concentrated to a yellow oil. Flash chromatography over silica gel using 20 $\rightarrow$ 35% Et_2O -hexanes-0.5% AcOH gave adamantyl acid **2d** (500 mg, 89%) as a pure ($R_f = 0.41$, TLC, silica, 30% Et_2O -hexanes; ^1H NMR (300 MHz, CDCl_3)) white solid: m.p. = 134-135 $^\circ\text{C}$; FT-IR (neat) 2898, 2846, 2657, 1696, 1451, 1421, 1307, 1103, 940, 735 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 11.70 (bs, 1 H, COOH), 2.35-2.27 (m, 2 H, 2 x CH), 1.95 (s, 3 H, 3 x CH), 1.70 (d, 3 H, $J = 11.7$ Hz, 3 x CH), 1.61 (d, 3 H, $J = 11.4$ Hz, 3 x CH), 1.48-1.39 (m, 8 H, 4 x CH_2); ^{13}C NMR (125 MHz, CDCl_3) δ 181.6, 42.0, 38.6, 37.0, 31.9, 28.5, 27.9; HRMS (FAB) calcd for $\text{C}_{13}\text{H}_{20}\text{O}_2$ (M) $^+$ 208.1458, found 208.1447.

(3,4,6-tri-*O*-benzyl-1,2-dideoxy-D-arabino-hex-1-enyl) 3-adamantyl-2-propanoate (3d)

The general method for esterification was followed using: alcohol **1a**⁵ (500 mg, 1.20 mmol), acid **2d** (300 mg, 1.44 mmol), DCC (371 mg, 1.80 mmol), 4-DMAP (73 mg, 0.6 mmol) and CH_2Cl_2 (10 mL). Flash chromatography of the residue over silica using 15 $\rightarrow$ 25% Et_2O -hexanes gave **3d** (678 mg, 93%) as a pure ($R_f = 0.41$, TLC, silica, 25% Et_2O -hexanes; ^1H NMR (500 MHz, CDCl_3)) yellow oil: $[\alpha]_D^{26} = -8.0$ ($c = 1.00$, CHCl_3); FT-IR (neat) 3029, 2900, 2846, 2118, 1734, 1452, 1098, 1028, 734, 696 cm^{-1} ; ^1H NMR

⁵ Freeman, F.; Robarge, K. D. *Carbohydr. Res.* **1987**, *171*, 1-11.

(500 MHz, CDCl_3) δ 7.34-7.26 (m, 15 H, ArH), 5.90 (ddd, 1 H, $J = 17.5, 10.0, 7.5$ Hz, H-2), 5.32 (dd, 1 H, $J = 10.0, 1.5$ Hz, H-1), 5.28 (dd, 1 H, $J = 18.5, 1.0$ Hz, H-1), 5.21 (ddd, 1 H, $J = 4.5, 4.5, 4.5$ Hz, H-5), 4.72 (d, 1 H, $J = 11$ Hz, OCH_2Ph), 4.65 (d, 1 H, $J = 11.5$ Hz, OCH_2Ph), 4.60 (d, 1 H, $J = 11.5$ Hz, OCH_2Ph), 4.49 (d, 1 H, $J = 12$ Hz, OCH_2Ph), 4.46 (d, 1 H, $J = 12.5$ Hz, OCH_2Ph), 4.32 (d, 1 H, $J = 12$ Hz, OCH_2Ph), 3.91 (dd, 1 H, $J = 8.0, 5.0$ Hz, H-3), 3.80 (dd, 1 H, $J = 5.0, 5.0$ Hz, H-4), 3.79-3.77 (m, 2 H, 2 x H-6), 2.18 (ddd, 1 H, $J = 16, 9.0, 9.0$ Hz, H-7), 2.08 (ddd, 1 H, $J = 16.5, 9.5, 9.5$ Hz, H-7), 1.95 (s, 3 H, 3 x CH), 1.70 (app d, 3 H, $J = 12.0$ Hz, 3 x CH), 1.61 (app d, 3 H, $J = 12.0$ Hz, 3 x CH), 1.43 (app d, 6 H, $J = 2.0$ Hz, 3 x CH_2), 1.35 (app dd, 2 H, $J = 9.0, 9.0$ Hz, 2 x H-8); ^{13}C NMR (125 MHz, CDCl_3) δ 174.0, 138.6, 138.4, 138.3, 135.5, 128.6, 128.5, 128.5, 128.3, 128.3, 127.9, 127.9, 127.8, 119.6, 80.7, 80.6, 75.0, 73.0, 72.3, 70.3, 68.1, 42.0, 38.7, 37.0, 31.8, 28.5, 28.1; HRMS (FAB) calcd for $\text{C}_{40}\text{H}_{48}\text{O}_5\text{Na}$ (M)⁺ 631.3394, found 631.3380.

2'-(3, 4, 6-tri-*O*-benzyl- β -D-glucosyl)-1-ethyladamantane (6d):

The general procedure for the three step protocol was followed using: Titanium tetrachloride (1.4 mL, 2 M in CH_2Cl_2 , 2.79 mmol), THF (3 mL), TMEDA (0.8 mL, 5.37 mmol), zinc dust (400 mg, 6.07 mmol), lead (II) chloride (5 mg, 0.016 mmol), ester **3d** (100 mg, 0.16 mmol), dibromomethane (107 μL , 1.53 mmol), catalyst **7** (28 mg, 0.033 mmol, 20 mol%), toluene (16 mL), $\text{BH}_3\cdot\text{THF}$ (1.64 mL, 1 M in THF, 1.64 mmol), NaOH (10 mL, 1 M, 10 mmol) and hydrogen peroxide (10 mL, 30% in water, 0.05 mol). After the usual work-up, flash chromatography of the residue over silica using 10→20% EtOAc-hexanes gave **6d** (57 mg, 0.096 mmol, 60% over 3 steps) as a pure ($R_f = 0.45$, TLC, silica, 35% Et₂O-hexanes; ^1H NMR (500 MHz, CDCl_3) oil: $[\alpha]_D^{26} = -7.3$ ($c = 1.00$, CHCl_3); FT-IR (neat) 3272, 2900, 2846, 1750, 1496, 1452, 1359, 1229, 1132, 1101, 1070, 1028, 734, 697 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.41-7.30 (m, 13 H, ArH), 7.27-7.24 (m, 2 H, ArH), 5.00 (d, 1 H, $J = 12$ Hz, OCH_2Ph), 4.84 (d, 1 H, $J = 11.5$ Hz, OCH_2Ph), 4.76 (d, 1 H, $J = 12$ Hz, OCH_2Ph), 4.68 (d, 1 H, $J = 12.5$ Hz, OCH_2Ph), 4.65 (d, 1 H, $J = 10$ Hz, OCH_2Ph), 4.62 (d, 1 H, $J = 12.5$ Hz, OCH_2Ph), 3.77 (dd, 1 H, $J = 11.5, 2.0$ Hz, H-6), 3.73 (dd, 1 H, $J = 11.0, 4.0$ Hz, H-6), 3.66 (dd, 1 H, $J = 9.5, 9.5$ Hz, H-4), 3.48 (dd, 1 H, $J = 9.5, 9.5$ Hz, H-3), 3.42 (ddd, 1 H, $J = 10, 4.5, 2.0$ Hz, H-5), 3.34 (ddd, 1 H, $J = 9.5, 9.5$ Hz, H-2), 3.12 (ddd, 1 H, $J = 9.0, 9.0, 2.5$ Hz, H-1), 2.15 (bs, 1 H, OH), 1.96 (s, 3 H, 3 x CH), 1.86-1.78 (m, 1 H, H-7), 1.73 (app d, 3 H, $J = 12$ Hz, 3 x CH), 1.65 (d, 3 H, $J = 11.5$ Hz, 3 x CH), 1.51 (s, 6 H, 3 x CH_2), 1.49-1.39 (m, 2 H, H-7, H-8), 1.09 (ddd, 1 H, $J = 12.5, 12.5, 3.0$ Hz, H-8); ^{13}C NMR (125 MHz, CDCl_3) δ 138.6, 138.3, 138.0, 128.7, 128.4, 128.3, 127.9, 127.8, 127.7, 127.7, 127.5, 86.9, 80.1, 79.1, 78.6, 75.1, 74.7, 74.0, 73.3, 68.8, 42.4, 39.9, 37.2, 32.0, 28.7, 24.8; HRMS (FAB) calcd for $\text{C}_{39}\text{H}_{48}\text{O}_5\text{Na}$ (M)⁺ 619.3394, found 619.3373.

ENTRY 5

Acid (2e)

LiOH (1.08 g, 25.8 mmol) was added to a cool (0 °C) solution of the steroidal ethyl ester⁶ (550 mg, 1.29 mmol) in THF (11 mL). After 10 minutes, water (11 mL) was added and the resulting suspension was vigorously stirred at 0 °C for 1 h, allowed to warm to ambient temperature and then stirred overnight. The mixture was cooled to 0 °C and acidified by the addition of HCl (10 mL, 2 M) until litmus red was obtained. The resulting solution was extracted with EtOAc (5 x 25 mL), dried over MgSO₄ and concentrated *in vacuo*. Flash chromatography of the residue over silica gel using 10→15% EtOAc-hexanes-0.5% AcOH gave the steroid-based acid **2e** (500 mg, 97%) as a pure (R_f = 0.33, TLC, silica, 15% EtOAc-hexanes (0.5% AcOH); ¹H NMR (500 MHz, CDCl₃)) white solid: m.p. = 162-164 °C; $[\alpha]_D^{26}$ = +19.4 (c = 1.00, CHCl₃); FT-IR (neat) 3400-2800 (br), 2929, 2867, 2850, 1716, 1466, 1445, 1384, 1305, 1153, 929 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 2.24-2.20 (m, 2 H, CH₂), 1.98-1.93 (m, 1 H, CH), 1.84-1.75 (m, 2 H, 2 x CH), 1.71-1.44 (m, 6 H, 6 x CH), 1.38-0.94 (m, 23 H, 23 x CH), 0.90 (d, 3 H, J = 23 Hz, CH-CH₃), 0.85 (app d, 6 H, 2 x CH-CH₃), 0.76 (s, 3 H, CH₃), 0.64 (s, 3 H, CH₃); ¹³C NMR (125 MHz, CDCl₃) δ 179.3, 56.5, 56.3, 54.5, 46.4, 42.6, 41.8, 40.1, 39.5, 38.3, 36.2, 35.8, 35.7, 35.5, 35.2, 35.1, 32.1, 29.7, 28.8, 28.5, 28.2, 28.0, 24.2, 23.8, 22.8, 22.6, 21.0, 18.7, 12.3, 12.1; HRMS (FAB) calcd for C₂₉H₅₀O₂Na (M)⁺ 430.3811, found 430.3815.

Ester (**3e**)

The general method for esterification was followed using: alcohol **1a7** (436 mg, 1.05 mmol), acid **2e** (500 mg, 1.25 mmol), DCC (324 mg, 1.58 mmol), 4-DMAP (64 mg, 0.53 mmol) and CH₂Cl₂ (8 mL). Flash chromatography of the residue over silica gel using 10→20% EtOAc-hexanes gave ester **3e** (762 mg, 91%) as a pure (R_f = 0.61, TLC, silica, 20% EtOAc-hexanes; ¹H NMR (500 MHz, CDCl₃)) yellow oil: $[\alpha]_D^{26}$ = +8.4 (c = 1.00, CHCl₃); FT-IR (neat) 2924, 2849, 1732, 1712, 1604, 1540, 1453, 1361, 1219, 1093, 1068, 734, 696 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.33-7.24 (m, 15 H, ArH), 5.88 (ddd, 1 H, J = 17.5, 10.0, 8.0 Hz, H-2), 5.32 (dd, 1 H, J = 10.5, 1.0, Hz, H-1), 5.28 (d, 1 H, J = 18 Hz, H-1), 5.23 (ddd, 1 H, J = 4.5, 4.5, 4.5 Hz, H-5), 4.71 (d, 1 H, J = 11 Hz, OCH₂Ph), 4.64 (d, 1 H, J = 11.5 Hz, OCH₂Ph), 4.57 (d, 1 H, J = 12 Hz, OCH₂Ph), 4.49-4.43 (m, 2 H, 2 x OCH₂Ph), 4.31 (d, 1 H, J = 11.5 Hz, OCH₂Ph), 3.91 (dd, 1 H, J = 8.0, 5.0 Hz, H-3), 3.79 (dd, 1 H, J = 5.0, 5.0 Hz, H-4), 3.78-3.76 (m, 2 H, 2 x H-6), 2.12-2.02 (m, 2 H, 2 x H-7), 1.98-1.93 (m, 1 H, 1 x CH), 1.85-1.70 (m, 2 H, 2 x CH), 1.65-1.58 (m, 2 H, 2 x CH), 1.56-1.50 (m, 2 H, 2 x CH), 1.50-1.43 (m, 1 H, CH), 1.36-0.93 (m, 20 H, 20 x CH), 0.92-0.85 (m, 3 H, 3 x CH), 0.90 (d, 3 H, J = 7.0 Hz, CHCH₃), 0.87 (d, 3 H, J = 6.5 Hz, CHCH₃), 0.86 (d, 3 H, J = 6.5 Hz, CHCH₃), 0.72 (s, 3 H, CH₃), 0.64 (s, 3 H, CH₃); ¹³C NMR (125 MHz, CDCl₃) δ 172.2, 138.1, 138.1, 138.1, 135.2, 128.3, 128.3, 128.2, 128.0, 127.6, 127.6, 127.5, 119.4, 81.0, 80.9, 75.0, 73.0, 72.3, 70.4, 68.1, 56.6, 56.3, 54.5, 46.3, 42.6, 42.2, 40.0, 39.5, 38.2, 36.2, 35.8, 35.5, 35.3, 32.0, 28.8, 28.5, 28.2, 28.0, 24.2, 23.8, 22.8, 22.6, 21.0, 18.7, 12.3, 12.1; HRMS (FAB) calcd for C₅₆H₇₈O₅Na (M)⁺ 853.5741, found 853.5735.

⁶ Golebiewski, W. M.; Keyes, R. F.; Cushman, M. *Bioorg. Med. Chem.* **1996**, *4*, 1637-1648.

⁷ Freeman, F.; Robarge, K. D. *Carbohydr. Res.* **1987**, *171*, 1-11.

C-Glycoside (6e)

The general procedure for the three step protocol was followed using: Titanium tetrachloride (1.02 mL, 2 M in CH_2Cl_2 , 2.04 mmol), THF (2 mL), TMEDA (0.59 mL, 3.94 mmol), zinc dust (290 mg, 4.44 mmol), lead (II) chloride (3 mg, 0.012 mmol), ester **3e** (100 mg, 0.12 mmol), dibromomethane (78 μL , 1.12 mmol), catalyst **7** (20 mg, 0.024 mmol, 20 mol%), toluene (12 mL), $\text{BH}_3 \cdot \text{THF}$ (1.2 mL, 1 M in THF, 1.2 mmol), NaOH (10 mL, 1 M, 10 mmol) and hydrogen peroxide (10 mL, 30% in water, 0.05 mol). After the usual work-up, flash chromatography of the residue over silica using 10 $\rightarrow$ 20% EtOAc-hexanes gave **6e** (47 mg, 50% over 3 steps) as a pure (R_f = 0.42, TLC, silica, 20% EtOAc-hexanes; ^1H NMR (500 MHz, CDCl_3)) white solid: m.p. = 42-43 $^\circ\text{C}$; $[\alpha]_D^{26} = +19.2$ (c = 1.00, CHCl_3); FT-IR (neat) 3489 (br), 2916, 2850, 1454, 1343, 1162, 1120, 1063, 902, 816, 699, 668 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.38-7.27 (m, 13 H, ArH), 7.24-7.21 (m, 2 H, ArH), 4.96 (d, 1 H, J = 11.5 Hz, OCH_2Ph), 4.81 (d, 1 H, J = 10.5 Hz, OCH_2Ph), 4.72 (d, 1 H, J = 11.5 Hz, OCH_2Ph), 4.64 (d, 1 H, J = 12 Hz, OCH_2Ph), 4.61 (d, 1 H, J = 11.5 Hz, OCH_2Ph), 4.57 (d, 1 H, J = 12 Hz, OCH_2Ph), 3.75 (dd, 1 H, J = 11.0, 2.0 Hz, H -6), 3.69 (dd, 1 H, J = 11.5, 5.0 Hz, H -6), 3.61 (dd, 1 H, J = 9.5, 9.5 Hz, H -4), 3.46 (dd, 1 H, J = 9.0, 9.5 Hz, H -3), 3.40 (ddd, 1 H, J = 10.0, 4.0, 2.0 Hz, H -5), 3.29-3.22 (m, 2 H, H -1, H -2), 1.99-1.93 (m, 1 H, CH), 1.86-1.74 (m, 2 H, 2 x CH), 1.69-1.46 (m, 8 H, 8 x CH), 1.42-1.08 (m, 18 H, 18 x CH), 0.92-0.85 (m, 4 H, 4 x CH), 0.90 (d, 3 H, J = 8.0 Hz, CHCH_3), 0.87 (d, 3 H, J = 9.0 Hz, CHCH_3), 0.86 (d, 3 H, J = 8.0 Hz, CHCH_3), 0.74 (s, 3, CH_3), 0.64 (s, 3 H, CH_3); ^{13}C NMR (100 MHz, CDCl_3) δ 138.6, 138.2, 138.1, 128.7, 128.5, 128.4, 128.3, 128.0, 127.9, 127.8, 127.8, 127.7, 127.6, 87.0, 79.0, 78.6, 77.2, 75.2, 74.7, 74.4, 73.4, 69.0, 55.6, 56.2, 54.6, 46.4, 42.6, 40.1, 39.5, 39.4, 38.6, 36.2, 36.0, 35.8, 35.5, 35.0, 34.2, 32.1, 29.8, 29.0, 28.3, 28.0, 24.2, 23.8, 22.8, 22.6, 21.0, 18.7, 12.3, 12.1; HRMS (FAB) calcd for $\text{C}_{55}\text{H}_{78}\text{O}_5\text{Na}$ (M) $^+$ 841.5741, found 841.5753.

ENTRY 6

Ester (3f)

The general method for esterification was followed using: alcohol **1b**⁸ (500 mg, 1.19 mmol), acid **2f**⁹ (250 mg, 1.43 mmol), DCC (368 mg, 1.79 mmol), 4-DMAP (73 mg, 0.60 mmol) and CH_2Cl_2 (5 mL). Flash chromatography of the residue over silica using 20 $\rightarrow$ 25% Et₂O-hexanes gave **3f** (662 mg, 97%) as a pure (R_f = 0.30, TLC, silica, 20% EtOAc-hexanes; ^1H NMR (500 MHz, CDCl_3)) yellow oil: $[\alpha]_D^{26} = -16.9$ (c =

⁸ Pearson, W. H., Hines, J. V. *Tetrahedron Lett.* **1991**, 32, 5513-5516.

⁹ Siddiqui, M. A.; Marquez, V. E.; Driscoll, J. S. Barchi, Jr., J. J., *Tetrahedron Lett.* **1994**, 35, 3263-3266.

1.00, CHCl_3); FT-IR (neat) 2916, 2868, 1736, 1496, 1454, 1369, 1249, 1209, 1154, 1062, 996, 932, 856, 736, 697 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.34–7.25 (m, 15 H, ArH), 5.92 (ddd, 1 H, $J = 17.5, 10.5, 8.0$, $H-2$), 5.39 (ddd, 1 H, $J = 5.5, 5.5, 5.5$ Hz, $H-5$), 5.38 (dd, 1 H, $J = 10.5, 1.5$ Hz, $H-1$), 5.31 (d, 1 H, $J = 17, 1.5$ Hz, $H-1$), 4.74 (d, 1 H, $J = 11$ Hz, OCH_2Ph), 4.56 (m, 1 H, $J = 11$ Hz, OCH_2Ph), 4.56 (m, 1 H, $J = 11$ Hz, OCH_2Ph), 4.48 (d, 1 H, $J = 12$ Hz, OCH_2Ph), 4.43 (d, 1 H, $J = 11.5$ Hz, OCH_2Ph), 4.30 (d, 1 H, $J = 12$ Hz, OCH_2Ph), 4.05 (dddd, 1 H, $J = 12.5, 12.5, 6.0, 6.0$ Hz, $H-9$), 3.97 (dd, 1 H, $J = 7.5, 6.0$ Hz, $H-10$), 3.88 (dd, 1 H, $J = 6.5, 6.5$ Hz, $H-3$), 3.83 (dd, 1 H, $J = 6.0, 4.0$ Hz, $H-4$), 3.59–3.53 (m, 2 H, 2 x $H-6$), 3.49 (dd, 1 H, $J = 7.0, 7.0$ Hz, $H-10$), 2.42 (ddd, 1 H, $J = 17.0, 7.5, 7.5$ Hz, $H-7$), 2.30 (ddd, 1 H, $J = 15.5, 7.5, 7.5$ Hz, $H-7$), 1.83–1.77 (m, 2 H, 2 x $H-8$), 1.39 (s, 3 H, $\text{C}(\text{CH}_3)_2$), 1.31 (s, 3 H, $\text{C}(\text{CH}_3)_2$); ^{13}C NMR (125 MHz, CDCl_3) δ 172.5, 138.2, 138.1, 137.8, 135.5, 128.3, 128.3, 128.2, 128.0, 127.9, 127.7, 127.7, 127.6, 127.5, 108.9, 80.0, 79.2, 74.8, 74.5, 73.1, 71.6, 70.2, 69.0, 68.0, 30.6, 28.8, 27.2, 25.9; HRMS (FAB) calcd for $\text{C}_{35}\text{H}_{42}\text{O}_7\text{Na}$ (M) $^+$ 597.2823, found 597.2799.

C-Glycoside (6f)

The general procedure for the three step protocol was followed using: Titanium tetrachloride (7.4 mL, 2 M in CH_2Cl_2 , 14.8 mmol), THF (23 mL), TMEDA (4.3 mL, 28.5 mmol), zinc dust (2.1 g, 32.2 mmol), lead (II) chloride (24 mg, 0.09 mmol), ester **3f** (500 mg, 0.87 mmol), dibromomethane (0.57 mL, 8.09 mmol), catalyst **7** (148 mg, 0.17 mmol, 20 mol%), toluene (100 mL), $\text{BH}_3\cdot\text{THF}$ (8.7 mL, 1 M in THF, 8.7 mmol), NaOH (50 mL, 1 M, 50 mmol) and hydrogen peroxide (50 mL, 30% in water, 0.40 mol). After the usual work-up, flash chromatography of the residue over silica using 20→25% EtOAc-hexanes gave **6f** (278 mg, 57% over 3 steps) as a pure ($R_f = 0.28$, TLC, silica, 20% EtOAc-hexanes; ^1H NMR (500 MHz, CDCl_3) oil: $[\alpha]_D^{26} = -21.0$ ($c = 1.00$, CHCl_3); FT-IR (neat) 3420 (br), 2920, 2865, 1454, 1368, 1210, 1156, 1073, 911, 848, 734, 697 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.38–7.25 (m, 15 H, ArH), 4.85 (d, 1 H, $J = 11.5$ Hz, OCH_2Ph), 4.73 (d, 1 H, $J = 11.5$ Hz, OCH_2Ph), 4.63 (d, 1 H, $J = 11.5$ Hz, OCH_2Ph), 4.51 (d, 1 H, $J = 11.5$ Hz, OCH_2Ph), 4.48 (d, 1 H, $J = 11.5$ Hz, OCH_2Ph), 4.46 (d, 1 H, $J = 12.5$ Hz, OCH_2Ph), 4.11 (ddd, 1 H, $J = 13.0, 13.0, 6.5, 6.5$ Hz, $H-9$), 4.04–4.00 (m, 2 H, $H-10$, $H-4$), 3.77 (dd, 1 H, $J = 9.5, 9.5$ Hz, $H-2$), 3.61–3.55 (m, 3 H, 2 x $H-6$, $H-5$), 3.53 (dd, 1 H, $J = 7.5, 7.5$ Hz, $H-10$), 3.37 (dd, 1 H, $J = 9.5, 3.0$ Hz, $H-3$), 3.17 (ddd, 1 H, $J = 9.0, 9.0, 2.0$ Hz, $H-1$), 2.40 (bs, 1 H, OH), 1.96–1.85 (m, 2 H, $H-7$, $H-8$), 1.67–1.53 (m, 2 H, $H-7$, $H-8$), 1.40 (s, 3 H, $\text{C}(\text{CH}_3)_2$), 1.34 (s, 3 H, $\text{C}(\text{CH}_3)_2$); ^{13}C NMR (125 MHz, CDCl_3) δ 138.5, 137.8, 137.7, 128.6, 128.4, 128.2, 128.1, 127.9, 127.9, 127.7, 127.7, 127.6, 108.5, 84.1, 79.6, 77.1, 75.8, 74.3, 73.5, 72.5, 71.5, 70.5, 69.3, 68.8, 29.4, 27.8, 26.9, 25.7; HRMS (FAB) calcd for $\text{C}_{34}\text{H}_{42}\text{O}_7\text{Na}$ (M) $^+$ 585.2823, found 585.2793.

Diol (15f)

The usual method for benzylation was followed using: alcohol **6f** (200 mg, 0.36 mmol), NaH (50 mg, 1.24 mmol), BnBr (0.13 mL, 1.07 mmol) and DMF (2 mL). Flash chromatography of the residue over

silica using 20→25% EtOAc-hexanes gave the product (207 mg, 90%) as a pure (R_f = 0.35, TLC, silica, 20% EtOAc-hexanes; ^1H NMR (500 MHz, CDCl_3), (HRMS (FAB) calcd for $\text{C}_{41}\text{H}_{48}\text{O}_7\text{Na}$ (M) $^+$ 675.3292, found 675.3273)) clear oil that was taken to the next step without further characterization. *p*-TsOH (5 mg) was added to a $\text{MeOH-CH}_2\text{Cl}_2$ (1:1, 3 mL) solution of the acetonide (150 mg, 0.23 mmol) and the resulting mixture was stirred for 12 h at ambient temperature. The reaction was quenched with Et_3N (1 mL) and concentrated. Flash chromatography of the residue over silica using 2→4% $\text{MeOH-CH}_2\text{Cl}_2$ gave **15f** (112 mg, 80%, 72% over 2 steps) as a pure (R_f = 0.40, TLC, silica, 5% $\text{MeOH-CH}_2\text{Cl}_2$; ^1H NMR (500 MHz, CDCl_3) white solid: m.p. = 79–80 °C; $[\alpha]_D^{26} = +38.3$ (c = 1.00, CHCl_3); FT-IR (neat) 3386 (br), 3063, 3030, 2915, 2862, 1497, 1453, 1359, 1209, 1063, 909, 735, 697 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.40–7.28 (m, 20 H, ArH), 4.97 (d, 1 H, J = 10.5 Hz, OCH_2Ph), 4.95 (d, 1 H, J = 11.5 Hz, OCH_2Ph), 4.76 (d, 1 H, J = 11.5 Hz, OCH_2Ph), 4.76 (d, 1 H, J = 12 Hz, OCH_2Ph), 4.71 (d, 1 H, J = 11.5 Hz, OCH_2Ph), 4.63 (d, 1 H, J = 11.5, OCH_2Ph), 4.48 (d, 1 H, J = 11.5 Hz, OCH_2Ph), 4.41 (d, 1 H, J = 11.5 Hz, OCH_2Ph), 3.72–3.66 (m, 2 H, H -9, H -2), 3.63–3.48 (m, 5 H, H -10, 2 x H -6, H -5, H -4), 3.44–3.34 (m, 2 H, H -10, H -2), 3.27 (ddd, 1 H, J = 9.0, 9.0, 1.5 Hz, H -1), 2.16 (bs, 1 H, OH) 2.12–2.05 (m, 1 H, H -8), 1.68–1.56 (m, 2 H, H -7, H -8), 1.51 (dddd, 1 H, J = 6.5, 6.5, 6.5, 6.5 Hz, H -7); ^{13}C NMR (125 MHz, CDCl_3) δ 138.4, 138.2, 138.1, 137.6, 128.5, 128.4, 128.2, 128.1, 128.0, 127.8, 127.8, 127.7, 127.5, 84.7, 80.3, 78.6, 77.1, 75.5, 74.4, 73.6, 73.5, 72.3, 72.0, 69.4, 66.8, 30.6, 28.3.; HRMS (FAB) calcd for $\text{C}_{38}\text{H}_{44}\text{O}_7\text{Na}$ (M) $^+$ 635.2979, found 635.2983.

ENTRY 7

See experimental section in article.

ENTRY 8¹⁰3-(2, 2-dimethyl-[1,3]dioxolan-4-yl)-propionic acid 2,3-bis-benzyloxy-1-benzyloxymethyl-pent-4-enyl ester (**3h**)¹¹ **C-Glycoside (**6h**)¹¹** **Diol (**15h**)¹¹**

¹⁰ Note that the configuration of C-9 was drawn incorrectly in our original communication (Postema, M. H. D.; Piper, J. L. *Org. Lett.* **2003**, *5*, 1721–1723). The correct configuration is as depicted here.

¹¹ For full experimental and spectral data listing for this compound please see the supporting information corresponding to: Postema, M. H. D.; Piper, J. L. *Org. Lett.* **2003**, *5*, 1721–1723.

ENTRY 9**Ester (3i)**

The general method for esterification was followed using: Alcohol **1c**¹² (580 mg, 1.14 mmol), acid **2f** (240 mg, 1.37 mmol), DCC (353 mg, 1.71 mmol) and 4-DMAP (70 mg, 0.57 mmol) in CH_2Cl_2 (4 mL). Flash chromatography of the residue over silica gel gave **3i** (659 mg, 87%) as a pure ($R_f = 0.30$, TLC, silica 40% EtOAc-hexanes, ^1H NMR (500 MHz, CDCl_3)) pale yellow oil: $[\alpha]_D^{26} = -12.0$ ($c = 1.00$, CHCl_3); FT-IR (neat) 2914, 2868, 1734, 1612, 1513, 1464, 1369, 1247, 1173, 1071, 1034, 821 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.23-7.17 (m, 6 H, ArH), 6.87-6.81 (m, 6 H, ArH), 5.86 (ddd, 1 H, $J = 18.5, 11.0, 8.5$ Hz, H-2), 5.31 (d, 1 H, $J = 10$ Hz, H-1), 5.26 (d, 1 H, $J = 17$ Hz, H-1), 5.18 (ddd, 1 H, $J = 4.5, 4.5, 4.5$ Hz, H-5), 4.60 (d, 1 H, $J = 11$ Hz, OCH_2Ar), 4.54 (d, 1 H, $J = 11$ Hz, OCH_2Ar), 4.52 (d, 1 H, $J = 11$ Hz, OCH_2Ar), 4.43 (d, 1 H, $J = 11.5$ Hz, OCH_2Ar), 4.38 (d, 1 H, $J = 12$ Hz, OCH_2Ar), 4.24 (d, 1 H, $J = 12$ Hz, OCH_2Ar), 4.65 (dddd, 1 H, $J = 12.5, 12.5, 6.5, 6.5$ Hz, H-9), 4.00 (dd, 1 H, $J = 8.0, 6.5$ Hz, H-10), 3.86 (dd, 1 H, $J = 7.5, 4.5$ Hz, H-3), 3.79 (s, 3 H, OCH_3), 3.78 (s, 6 H, 2 x OCH_3), 3.75-3.73 (m, 1 H, H-6), 3.73-3.71 (m, 2 H, H-4, H-6), 3.49 (dd, 1 H, $J = 15.0, 7.5$ Hz, H-10), 2.37 (ddd, 1 H, $J = 16.0, 6.5, 6.5$ Hz, H-7), 2.18 (ddd, 1 H, $J = 16.0, 7.0, 7.0$ Hz, H-7), 1.81-1.74 (m, 2 H, 2 x H-8), 1.40 (s, 3 H, CH_3), 1.32 (s, 3 H, CH_3); ^{13}C NMR (125 MHz) δ 172.1, 159.1, 159.0, 135.4, 130.3, 130.1, 130.0, 129.7, 129.6, 129.3, 119.0, 113.6, 113.5, 113.5, 108.8, 80.1, 79.9, 74.8, 74.5, 72.6, 72.4, 69.8, 69.0, 67.7, 55.1, 55.1, 30.4, 28.5, 26.8, 25.5; HRMS(FAB): calcd for $\text{C}_{38}\text{H}_{48}\text{O}_{10}\text{Na}$ (M)⁺ 687.3140, found 687.3163.

C-Glycoside (6i)

The general procedure for the three step protocol was followed using: Titanium tetrachloride (3.2 mL, 2 M in CH_2Cl_2 , 6.39 mmol), THF (10 mL), TMEDA (1.88 mL, 12.46 mmol), zinc dust (0.92 g, 14.06 mmol), lead (II) chloride (11 mg, 0.04 mmol), ester **3i** (250 mg, 0.38 mmol), dibromomethane (0.25 mL, 3.53 mmol), catalyst **7** (80 mg, 0.094 mmol, 25 mol%), toluene (37 mL), $\text{BH}_3 \cdot \text{THF}$ (3.8 mL, 1 M in THF, 3.8 mmol), NaOH (20 mL, 1 M, 20 mmol) and hydrogen peroxide (20 mL, 30% in water, 0.16 mol). After the usual work-up, flash chromatography of the residue over silica using 30→40% EtOAc-hexanes gave **6i** (124 mg, 50% over 3 steps) as a pure ($R_f = 0.26$, TLC, silica, 40% EtOAc-hexanes; ^1H NMR (500 MHz, CDCl_3)) white solid: m.p. = 81-82 °C; $[\alpha]_D^{26} = +32.7$ ($c = 1.00$, CHCl_3); FT-IR (neat) 3478, 2933, 2866, 1612, 1513, 1464, 1368, 1302, 1247, 1094, 1035, 821 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.30-

¹² Postema, M. H. D.; Piper, J. L. *Org. Lett.* **2003**, *5*, 1721-1723.

7.24 (m, 4 H, ArH), 7.13-7.08 (m, 2 H, ArH), 6.92-6.81 (m, 6 H, ArH), 4.90 (d, 1 H, $J = 12$ Hz, OCH₂Ar), 4.71 (d, 1 H, $J = 10.5$ Hz, OCH₂Ar), 4.65 (d, 1 H, $J = 11$ Hz, OCH₂Ar), 4.57 (d, 1 H, $J = 11.5$ Hz, OCH₂Ar), 4.49 (d, 1 H, $J = 10$ Hz, OCH₂Ar), 4.48 (d, 1 H, $J = 11.5$ Hz, OCH₂Ar), 4.11 (dddd, 1 H, $J = 12.5, 12.5, 6.5, 6.5$ Hz, H-9), 4.03 (dd, 1 H, $J = 7.5, 6.0$ Hz, H-10), 3.80 (s, 6 H, 2 x OCH₃), 3.79 (s, 3 H, OCH₃), 3.68-3.62 (m, 2 H, 2 x H-6), 3.55 (dd, 1 H, $J = 9.5, 9.5$ Hz, H-4), 3.52 (dd, 1 H, $J = 7.5, 7.5$ Hz, H-10), 3.41 (dd, 1 H, $J = 9.0, 9.0$ Hz, H-3), 3.36 (ddd, 1 H, $J = 9.5, 3.0, 3.0$ Hz, H-5), 3.27 (dd, 1 H, $J = 9.0, 9.0$ Hz, H-2), 3.14 (ddd, 1 H, $J = 8.5, 8.5, 1.5$ Hz, H-1), 2.16 (br s, 1 H, OH), 1.95-1.86 (m, 1 H, H-8), 1.86-1.78 (m, 1 H, H-7), 1.62-1.53 (m, 2 H, H-7, H-8), 1.40 (s, 3 H, CH₃), 1.34 (s, 3 H, CH₃); ¹³C NMR (125 MHz, CDCl₃) δ 159.3, 159.2, 159.2, 130.6, 130.1, 130.1, 129.6, 129.5, 114.1, 113.8, 113.7, 108.6, 86.3, 79.0, 78.1, 75.9, 74.7, 74.4, 73.7, 73.1, 69.4, 68.4, 55.2, 55.2, 29.3, 27.7, 26.9, 25.7; HRMS (FAB) calcd for C₃₇H₄₈O₁₀Na (M)⁺ 675.3140, found 675.3145.

Diol (15i)

To a stirred solution of KH (50 mg, 30% dispersion in mineral oil, 0.38 mmol) and DMF (3 mL) at 0 °C was added alcohol **6i** (70 mg, 0.11 mmol) dropwise over 5 minutes. After 10 minutes, PMBCl (45 μ L, 0.33 mmol) was added dropwise followed by tetrabutylammonium iodide (10 mg, 0.027 mmol). Stirring was continued for 30 minutes at 0 °C and then for 5 h at ambient temperature. The solution was quenched by dropwise addition of saturated NH₄Cl (10 mL) and extracted with EtOAc (3 x 10 mL). The combined organic layers were washed with brine (1 x 10 mL), dried over MgSO₄, filtered, and concentrated. Flash chromatography of the residue over silica using 25 $\rightarrow$ 30% EtOAc-hexanes gave the product (68 mg, 80%) as a pure ($R_f = 0.25$, TLC, silica, 30% EtOAc-hexanes; ¹H NMR (500 MHz, CDCl₃; HRMS (FAB) calcd for C₄₅H₅₆O₁₁Na (M)⁺ 795.3715, found 795.3682) oil which was taken to the next step without any further characterization. The usual procedure for acetonide deprotection was employed using: CH₂Cl₂ (2 mL), MeOH (2 mL), *p*-TsOH (5 mg, 0.026 mmol) and the acetonide sugar (50 mg, 0.065 mmol). After the usual work-up, flash chromatography of the residue over silica using 2 $\rightarrow$ 4% CH₂Cl₂-MeOH gave **15i** (43 mg, 90%) as a pure ($R_f = 0.20$, TLC, silica, 5% CH₂Cl₂-MeOH; ¹H NMR (500 MHz, CDCl₃)) white solid: m. p. = 104-105 °C; [α]_D²⁶ = +2.5 ($c = 1.00$, CHCl₃); FT-IR (neat) 3383, 3000, 2904, 2854, 1613, 1514, 1466, 1301, 1252, 1173, 1063, 1033, 820, 760 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.27 (app dd, 2 H, $J = 9.0$ Hz, ArH), 7.22 (app d, 2 H, $J = 8.5$ Hz, ArH), 6.88 (app dd, 3 H, $J = 2.5$ Hz, ArH), 6.86 (app dd, 3 H, $J = 3.0$ Hz, ArH), 6.82 (app d, 2 H, $J = 9.0$ Hz, ArH), 4.87-4.83 (m, 2 H, 2 x OCH₂Ar), 4.82 (d, 1 H, $J = 11$ Hz, OCH₂Ar), 4.74 (d, 1 H, $J = 10.5$ Hz, OCH₂Ar), 4.56 (d, 1 H, $J = 11$ Hz, OCH₂Ar), 4.51 (d, 1 H, $J = 11.5$ Hz, OCH₂Ar), 4.44 (d, 1 H, $J = 12$ Hz, OCH₂Ar), 4.43 (d, 1 H, $J = 11.5$ Hz, OCH₂Ar), 4.02 (dd, 1 H, $J = 7.5, 6.0$ Hz, H-10), 3.80 (s, 3 H, OCH₃), 3.80 (s, 3 H, OCH₃), 3.79 (s, 3 H, OCH₃), 3.79 (s, 3 H, OCH₃), 3.66 (dddd, 1 H, $J = 7.0, 7.0, 3.0, 3.0$ Hz, H-9), 3.65-3.61 (m, 2 H, 2 x H-6), 3.53 (dd, 1 H, $J = 11, 3.5$ Hz, H-10), 3.34 (ddd, 1 H, $J = 10, 4.5, 2.0$ Hz, H-5), 3.46-3.41 (m, 2 H, 2 x OCH), 3.26 ($J = 9.5, 9.5, 2.0$ Hz, H-1), 3.24-3.18 (dd, 1 H, $J = 9.5, 9.5$ Hz, OCH), 2.06-1.97 (m, 1 H, H-7), 1.64-1.56 (m, 1 H, H-8), 1.55-1.45 (m, 2 H, H-7, H-8); ¹³C NMR (125 MHz, CDCl₃) δ 159.3, 159.3, 159.3, 159.2, 130.7, 130.1, 130.0, 129.7, 129.7, 129.7, 129.6, 129.3, 113.8, 113.8, 113.7, 86.8, 81.6, 79.7, 78.4, 78.3, 75.2, 74.9, 74.6, 73.0, 72.2, 68.8, 66.8, 55.3, 55.2, 55.2, 30.4, 28.4; HRMS (FAB) calcd for C₄₂H₅₂O₁₁Na (M)⁺ 755.3402, found 755.3396.

ENTRY 10

C-Glycoside (6j)

The two-step protocol was followed using:

(a) Titanium tetrachloride (7.39 mL, 2 M in CH_2Cl_2 , 14.8 mmol), THF (23 mL), TMEDA (4.3 mL, 28.5 mmol), zinc dust (2.1 g, 32.2 mmol), lead (II) chloride (25 mg, 0.09 mmol), ester **3h** (500 mg, 0.87 mmol), dibromomethane (0.57 mL, 8.1 mmol) and THF (10 mL).

(b) Ruthenium-based metathesis catalyst **7** (221 mg, 0.26 mmol, 30 mol%), added in 5 portions over 2 hours to a dry and degassed toluene (87 mL) solution of the intermediate acyclic enol ether. After the usual work-up the solution was concentrated.

The material was carried an additional two steps:

(c) The crude glycal was re-dissolved in a solution of EtOAc-EtOH (12 mL, 5:1) and shaken under atmosphere of hydrogen gas (55 psi) for 6 h. The mixture was filtered through Celite and rinsed with 200 mL EtOAc-MeOH (5:2), concentrated *in vacuo* and taken up in DMF (15 mL).

(d) The product of the previous sequence was added dropwise to a stirring solution of rinsed (2 x 10 mL THF) NaH (44 mg, 1.84 mmol) in DMF (5 mL) at 0°C . The reaction was stirred for 15 minutes at which point PMBCl (0.28 mL, 2.1 mmol) was added, along with a catalytic amount of TBAI (5 mg). After 1 h, the solution was warmed to ambient temperature and stirring was continued for 5 additional h at which point TLC analysis deemed the reaction was complete. The mixture was diluted with Et_2O (20 mL), washed with water (1 x 20 mL), brine (1 x 20 mL), dried over MgSO_4 , filtered and concentrated to give an oil. Flash chromatography of the residue over silica using 20 $\rightarrow$ 25% EtOAc-hexanes gave **6j** (136 mg, 25% over 4 steps) as a pure (R_f = 0.29, TLC, silica, 20% EtOAc-hexanes; ^1H NMR (500 MHz, CDCl_3)) yellow oil: $[\alpha]_D^{26} = +8.5$ (c = 1.00, CHCl_3); FT-IR (neat) 2985, 2934, 2861, 1613, 1513, 1463, 1368, 1247, 1173, 1091, 1034, 820 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.28 (app dd, 4 H, J = 7.0, 7.0 Hz, ArH), 7.09 (app d, 2 H, J = 8.5 Hz, ArH), 6.87 (app dd, 2 H, J = 7.0 Hz, ArH), 6.86 (app dd, 2 H, J = 6.5 Hz, ArH), 6.82 (app dd, 2 H, J = 8.5 Hz, ArH), 4.80 (d, 1 H, J = 10.5 Hz, OCH_2Ar), 4.63 (d, 1 H, J = 11.5 Hz, OCH_2Ar), 4.57 (d, 1 H, J = 12 Hz, OCH_2Ar), 4.56 (d, 1 H, J = 11 Hz, OCH_2Ar), 4.47 (d, 1 H, J = 11.5 Hz, OCH_2Ar), 4.44 (d, 1 H, J = 10 Hz, OCH_2Ar), 4.11 (dddd, 1 H, J = 12.5, 12.5, 6.5, 6.5 Hz, H-9), 4.03 (dd, 1 H, J = 7.5, 6.0 Hz, H-10), 3.79 (s, 3 H, OCH_3), 3.78 (s, 3 H, OCH_3), 3.77 (s, 3 H, OCH_3), 3.69-3.57 (m, 3 H, H-1, 2 x H-6), 3.53 (dd, 1 H, J = 7.5, 7.5 Hz, H-10), 3.42 (dd, 1 H, J = 9.5, 9.5 Hz, H-4), 3.38-3.31 (m, 2 H, H-3, H-5), 2.11 (ddd, 1 H, J = 12.5, 5.0, 1.0 Hz, H-2), 1.82-1.69 (m, 2 H, H-7, H-8), 1.63-1.56 (m, 1 H, H-8), 1.55-1.47 (m, 1 H, H-7), 1.43-1.37 (m, 1 H, H-2), 1.41 (s, 3 H, CH_3), 1.35 (s, 3 H, CH_3); ^{13}C NMR (125 MHz, CDCl_3) δ 159.0, 130.6, 130.6, 130.2, 129.5, 129.4, 129.1, 113.6, 113.6, 113.5, 80.6, 78.8, 78.1, 75.5, 74.9, 74.4, 72.9, 70.9, 69.1, 68.9, 55.1, 55.0, 36.7, 31.2, 29.5, 26.8, 25.6; HRMS (FAB) calcd for $\text{C}_{37}\text{H}_{48}\text{O}_9\text{Na}$ (M) $^+$ 659.3191, found 659.3192.

Diol (15j)

The usual acetonide deprotection was employed using: CH_2Cl_2 (2 mL), MeOH (2 mL), *p*-TsOH (9 mg, 0.047 mmol), and sugar acetonide (100 mg, 0.157 mmol). Typical work-up and flash chromatography of the residue over silica using 2 $\rightarrow$ 4% CH_2Cl_2 -MeOH gave **15j** (82 mg, 88%) as a pure (R_f = 0.25, TLC, silica, 2% CH_2Cl_2 -MeOH; ^1H NMR (500 MHz, CDCl_3)) white solid: m.p. = 43–44 °C; $[\alpha]_D^{26} = +6.0$ (c = 1.00, CHCl_3); FT-IR (neat) 3585 (br), 2934, 2864, 1613, 1513, 1299, 1246, 1174, 1086, 1035, 820, 788, 761 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.29–7.24 (m, 4 H, ArH), 7.10–7.07 (m, 2 H, ArH), 6.88–6.84 (m, 4 H, ArH), 6.84–6.80 (m, 2 H, ArH), 4.78 (d, 1 H, J = 10.5 Hz, OCH_2Ar), 4.61 (d, 1 H, J = 11.5 Hz, OCH_2Ar), 4.55 (d, 1 H, J = 11 Hz, OCH_2Ar), 4.50 (d, 1 H, J = 11.5 Hz, OCH_2Ar), 4.44 (d, 1 H, J = 11.5 Hz, OCH_2Ar), 4.42 (d, 1 H, J = 10.5 Hz, OCH_2Ar), 3.80 (s, 3 H, OCH_3), 3.80 (s, 3 H, OCH_3), 3.79 (s, 3 H, OCH_3), 3.72–3.63 (m, 2 H, H -3, H -9), 3.64–3.54 (m, 2 H, H -1, H -5), 3.51 (dd, 1 H, J = 10, 6.0 Hz, H -10), 3.43–3.35 (m, 3 H, 2 $\times$ H -6, H -10), 3.31 (dd, 1 H, J = 9.5, 9.5 Hz, H -4), 2.24–2.04 (m, 2 H, H -2, OH), 1.80–1.58 (m, 4 H, H -7, 2 $\times$ H -8, OH), 1.54–1.44 (m, 1 H, H -7), 1.45–1.38 (m, 1 H, H -2); ^{13}C NMR (125 MHz, CDCl_3) δ 159.2, 159.1, 130.6, 130.4, 130.0, 129.7, 129.7, 129.2, 113.8, 113.7, 80.5, 78.5, 78.2, 76.1, 74.6, 73.0, 72.1, 71.2, 69.2, 66.8, 55.3, 37.2, 32.6, 30.8; HRMS (FAB) calcd for $\text{C}_{34}\text{H}_{44}\text{O}_9\text{Na}$ (M) $^+$ 619.2878, found 619.2923.

ENTRY 11**Ester (3k)**

The general method for esterification was followed using: alcohol **1a**¹³ (256 mg, 0.61 mmol), acid **2k** (200 mg, 0.74 mmol), DCC (190 mg, 0.92 mmol), and 4-DMAP (37 mg, 0.3 mmol) in CH_2Cl_2 (4 mL). Flash chromatography of the residue over silica gel using 10 $\rightarrow$ 20% EtOAc-hexanes gave **3k** (402 mg, 85%) as a pure (R_f = 0.49, TLC, silica, 20% EtOAc-hexanes; ^1H NMR (500 MHz, CDCl_3)) yellow oil: $[\alpha]_D^{26} = +29.1$ (c = 1.00, CHCl_3); FT-IR (neat) 2976, 2918, 2870, 1735, 1692, 1454, 1387, 1364, 1247, 1167, 1097, 1070, 736, 697 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3 , 45 °C) δ 7.33–7.25 (m, 15 H, Ph), 5.90 (ddd, 1 H, J = 17.5, 10.5, 8.0 Hz, H -2), 5.35–5.27 (m, 2 H, 2 $\times$ H -1), 5.25 (ddd, 1 H, J = 5.5, 5.5, 3.5 Hz, H -5), 4.73 (d, 1 H, J = 11 Hz, OCH_2Ph), 4.66 (d, 1 H, J = 11.5 Hz, OCH_2Ph), 4.50 (d, 1 H, J = 12 Hz, OCH_2Ph), 4.46 (d, 1 H, J = 12.5 Hz, OCH_2Ph), 4.35 (d, 1 H, J = 11.5 Hz, OCH_2Ph), 3.94 (dd, 1 H, J = 5.0, 5.0 Hz, H -3), 3.88 (dd, 1 H, J = 8.5, 5.5 Hz, H -10), 3.86–3.80 (m, 1 H, H -9), 3.80–3.77 (m, 2 H, 2 $\times$ H -6), 3.72–3.65 (m, 1 H, H -10), 3.59 (d, 1 H, J = 6.0 Hz, H -4), 2.30–2.14 (m, 2 H, 2 $\times$ H -7), 2.06–1.92 (m, 1 H, H -8), 1.88–1.78 (m, 1 H, H -8), 1.58 (s, 3 H, CH_3), 1.47 (s, 12 H, 1 $\times$ CH_3 , 1 $\times$ $(\text{CH}_3)_3$); ^{13}C NMR (125 MHz, CDCl_3) δ 172.0, 152.3, 138.0, 135.3, 128.3, 128.3, 128.2, 128.1, 127.8, 127.7, 127.6, 119.3, 80.5, 75.0, 73.0, 70.3, 66.7, 56.6, 30.9, 28.7, 28.4, 28.2, 27.6, 26.7, 24.4, 23.1; HRMS (FAB) calcd for $\text{C}_{40}\text{H}_{51}\text{O}_8\text{Na}$ (M) $^+$ 696.3507, found 696.3498.

C-Glycoside (6k)

¹³ Freeman, F.; Robarge, K. D. *Carbohydr. Res.* **1987**, *171*, 1–11.

The general procedure for the three step protocol was followed using: Titanium tetrachloride (1.27 mL, 2 M in CH_2Cl_2 , 2.53 mmol), THF (2 mL), TMEDA (0.74 mL, 4.89 mmol), zinc dust (360 mg, 5.51 mmol), lead (II) chloride (4 mg, 0.015 mmol), ester **3k** (100 mg, 0.149 mmol), dibromomethane (97 μL , 1.39 mmol), catalyst **7** (31 mg, 0.037 mmol, 25 mol%), toluene (12 mL), $\text{BH}_3\cdot\text{THF}$ (1.5 mL, 1 M in THF, 1.5 mmol), NaOH (10 mL, 1 M, 10 mmol) and hydrogen peroxide (10 mL, 30% in water, 0.05 mol). After the usual work-up, flash chromatography of the residue over silica using 10 $\rightarrow$ 20% EtOAc-hexanes gave **6k** (49 mg, 50% over 3 steps) as a pure (R_f = 0.28, TLC, silica, 30% EtOAc-hexanes; ^1H NMR (500 MHz, CDCl_3)) white solid: m.p. = 39-40 $^\circ\text{C}$; $[\alpha]_D^{26}$ = + 36.7 (c = 1.00, CHCl_3); FT-IR (neat) 3456, 2924, 2865, 2359, 1694, 1454, 1390, 1364, 1255, 1219, 1173, 1093, 1028, 735, 697 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.29-7.24 (m, 3 H, ArH), 7.22-7.18 (m, 3 H, ArH), 7.17-7.08 (m, 7 H, ArH), 7.07-7.02 (m, 2 H, ArH), 4.84 (d, 1 H, J = 12 Hz, OCH_2Ph), 4.80-4.70 (m, 2 H, 2 x OCH_2Ph), 4.58 (d, 1 H, J = 11 Hz, OCH_2Ph), 4.45 (d, 1 H, J = 12.5 Hz, OCH_2Ph), 4.38 (d, 1 H, J = 12.5 Hz, OCH_2Ph), 3.98-3.75 (m, 1 H, H-9), 3.69-3.63 (m, 3 H, 2 x H-6, H-10), 3.61 (dd, 1 H, J = 9.5, 9.5 Hz, H-4), 3.59-3.54 (m, 1 H, H-10), 3.43 (dd 1 H, J = 8.5, 8.5 Hz, H-4), 3.34 (dd, 1 H, J = 9.5, 3.5, 3.5 Hz, H-5), 3.30 (dd, 1 H, J = 9.0, 9.0 Hz, H-2), 3.16-3.08 (m, 1 H, H-1), 2.16-2.06 (s, 1 H, OH), 1.90-1.82 (m, 1 H, H-8), 1.73-1.62 (m, 4 H, H-7, CH_3), 1.54-1.44 (m, 4 H, H-7, CH_3), 1.40 (s, 9 H, CH_3); ^{13}C NMR (125 MHz, CDCl_3) δ 139.7, 139.4, 128.6, 128.5, 128.5, 127.9, 127.7, 127.7, 127.6, 101.4, 87.7, 79.9, 79.2, 75.1, 74.8, 73.8, 70.1, 67.5, 57.9, 31.1, 30.1, 30.1, 28.9, 28.6, 27.6, 24.4; HRMS (FAB) calcd for $\text{C}_{39}\text{H}_{51}\text{O}_8\text{Na}$ (M) $^+$ 684.3507, found 684.3492.

Glycoglycerolipid Synthesis

ENTRY 1

C-Glycoglycerolipid (17a)

Stearic anhydride (172 mg, 0.31 mmol) was added in one portion to a 1:1 solution CH_2Cl_2 -pyridine (1:1, 2 mL) containing diol **15f** (32 mg, 0.052 mmol) and 4-DMAP (3 mg, 0.03 mmol) and the solution was stirred for 18 hrs at ambient temperature. The resulting orange solution was then concentrated and flash chromatography of the residue over silica using 10 $\rightarrow$ 20% EtOAc-hexanes gave the product **16a** (46 mg, 77%) as a pure (R_f = 0.34, TLC, silica, 20% EtOAc-hexanes; ^1H NMR (500 MHz, CDCl_3); m.p. = 34-35 $^\circ\text{C}$; HRMS (FAB) calcd for $\text{C}_{74}\text{H}_{112}\text{O}_9\text{Na}$ (M) $^+$ 1167.8199, found 1167.8196) white solid that was directly carried onto the next step. Pd/C (5 mg) was added in one portion to a solution of **16a** (15 mg, 13.0 μmol) in EtOAc-MeOH (1:1, 5 mL). The solution was degassed five times with H_2 and the resulting suspension shaken under an atmosphere of H_2 (60 psi) for 15 hours at ambient temperature. The reaction mixture was filtered through Celite using a mixture of MeOH- CH_2Cl_2 (1:1, 40 mL) as the eluent and the resulting solution concentrated. Flash chromatography of the residue over silica using 5 $\rightarrow$ 10% MeOH- CH_2Cl_2 gave **17a** (21 mg, 78%) as a pure (R_f = 0.24, TLC, silica, 10% MeOH- CH_2Cl_2 ; ^1H NMR (500 MHz, CDCl_3)) white solid: m.p. = 71-72 $^\circ\text{C}$; $[\alpha]_D^{26}$ = - 7.7 (c = 1.00, CHCl_3); FT-IR (neat) 3370 (br), 2958, 2859,

1729, 1704, 1468, 1379, 788, 724 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 5.07 (dddd, 1 H, $J = 7.5, 7.5, 7.5, 4.5$ Hz, $H-9$), 4.15 (dd, 1 H, $J = 12, 3.0$ Hz, $H-10$), 3.92 (dd, 1 H, $J = 12, 7.0$ Hz, $H-10$), 3.85-3.82 (m, 1 H, $H-4$), 3.70 (dd, 1 H, $J = 11.5, 6.0$ Hz, $H-6$), 3.61 (dd, 1 H, $J = 11.5, 5.0$, $H-6$), 3.35-3.26 (m, 3 H, $H-2, H-3, H-5$), 3.02 (ddd, 1 H, $J = 8.5, 8.5, 2.0$ Hz, $H-1$), 2.22-2.16 (m, 4 H, 2 x $-\text{C}(=\text{O})\text{CH}_2-$), 1.84-1.75 (m, 1 H, $H-7$), 1.75-1.68 (m, 1 H, $H-8$), 1.63-1.55 (m, 1 H, $H-8$), 1.54-1.45 (m, 4 H, 2 x CH_2), 1.45-1.38 (m, 1 H, $H-7$), 1.21-1.13 (bs, 56 H, 28 x CH_2), 0.77 (app t, 6 H, $J = 7.0$ Hz, 2 x CH_3); ^{13}C NMR (125 MHz, CDCl_3) δ 173.9, 79.2, 77.8, 74.9, 71.2, 71.1, 69.5, 64.9, 62.0, 34.3, 34.0, 31.7, 29.5, 29.5, 29.3, 29.2, 29.1, 29.0, 26.7, 26.6, 24.8, 24.7, 22.5, 13.9; HRMS (FAB) calcd for $\text{C}_{46}\text{H}_{88}\text{O}_9\text{Na}$ (M) $^+$ 807.6321, found 807.6357.

ENTRY 2**C-Glycoglycerolipid (17b)¹⁴** **ENTRY 3****C-Glycoglycerolipid (17c)**

The general method for DCC-mediated esterification was followed using: Diol **15f** (20 mg, 0.033 mmol), heneicosanoic acid (37 mg, 0.11 mmol), DCC (10.2 mg, 0.05 mmol), 4-DMAP (2 mg, 0.017 mmol) and CH_2Cl_2 (2 mL). After the usual work-up, flash chromatography of the residue over silica using 10 $\rightarrow$ 20% EtOAc-hexanes gave **16c** (31 mg, 76%) as a pure ($R_f = 0.32$, TLC, silica, 15% EtOAc-hexanes; ^1H NMR (500 MHz, CDCl_3), HRMS (FAB) calcd for $\text{C}_{80}\text{H}_{124}\text{O}_9\text{Na}$ (M) $^+$ 1251.9138, found 1251.9081) white solid. The product was then taken directly to the next step and the general method of hydrogenolysis was followed using **16c** (25 mg, 0.02 mmol), Pd/C (10 mg) and EtOAc (4 mL). The usual work-up followed by flash chromatography of the residue over silica using 5 $\rightarrow$ 10% MeOH- CH_2Cl_2 gave **17c** (13.4 mg, 79%) as a pure ($R_f = 0.22$, TLC, silica, 10% MeOH- CH_2Cl_2 ; ^1H NMR (500 MHz, CDCl_3)) white solid: m.p. = 75-76 $^\circ\text{C}$; $[\alpha]_D^{26} = -5.5$ ($c = 1.00$, CHCl_3); FT-IR (neat) 3404 (br), 2917, 2950, 1737, 1467, 1243, 1168, 1103, 721 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 5.16-5.10 (m, 1 H, $H-9$), 4.20 (dd, 1 H, $J = 11.5, 3.0$ Hz, $H-10$), 3.97 (dd, 1 H, $J = 12.0, 7.0$ Hz, $H-10$), 3.90 (app s, 1 H, $H-4$), 3.76 (dd, 1 H, $J = 11.5, 6.0$ Hz, $H-6$), 3.67 (dd, 1 H, $J = 11.5, 5.0$ Hz, $H-6$), 3.42-3.32 (m, 3 H, $H-2, H-3, H-5$), 3.09 (ddd, 1 H, $J = 9.0, 9.0, 2.0$ Hz, $H-1$), 2.27-2.21 (m, 4 H, 2 x $-\text{C}(=\text{O})\text{CH}_2-$), 1.89-1.81 (m, 1 H, $H-7$), 1.80-1.72 (m, 1 H, $H-8$), 1.68-1.58 (m, 1 H, $H-8$), 1.58-1.50 (m, 4 H, 2 x CH_2), 1.50-1.44 (m, 1 H, $H-7$), 1.26-1.19 (m, 68 H, 34 x CH_2), 0.82 (t, 6 H, $J = 7.0$ Hz, 2 x CH_3); ^{13}C NMR (125 MHz, CDCl_3) δ 174.0, 173.9, 79.2, 77.8, 75.0, 71.3, 71.2, 69.7, 64.9, 62.3, 34.4, 34.1, 31.8, 29.6, 29.5, 29.4, 29.4, 29.2, 29.2, 29.2, 29.0, 26.7, 24.9, 24.7, 22.6, 14.0; HRMS (FAB) calcd for $\text{C}_{52}\text{H}_{100}\text{O}_9\text{Na}$ (M) $^+$ 891.7260, found 891.7267.

¹⁴ For full experimental and spectral data listing for this compound please see the supporting information corresponding to: Postema, M. H. D.; Piper, J. L. *Org. Lett.* **2003**, 5, 1721-1723.

ENTRY 4

C-Glycoglycerolipid (17d)

The general procedure for esterification was employed using **15h** (20 mg, 0.033 mmol), heneicosanoic acid (37 mg, 0.11 mmol), 4-DMAP (5 mg, 0.41 mmol), and DCC (10 mg, 49.5 μ mol). Flash chromatography of the residue on silica gel using 20% EtOAc-hexanes gave **16d** (31.0 mg, 77%) as a pure (R_f = 0.41, TLC, silica, 20% EtOAc-hexanes; ^1H NMR (500 MHz, CDCl_3); HRMS (FAB) calcd for $\text{C}_{80}\text{H}_{124}\text{O}_9\text{Na}$ (M) $^+$ 1251.9138, found 1251.9124) oil. The product was then taken onto the next step and the general procedure for hydrogenolysis was followed using: **16d** (25 mg, 20 μ mol), EtOAc-MeOH (1:1, 10 mL) and Pd/C (5 mg). After the usual work-up, flash chromatography of the residue over silica using 10% MeOH- CH_2Cl_2 gave **17d** (15.2 mg, 86%) as a pure (R_f = 0.25, TLC, silica, 10% MeOH- CH_2Cl_2 ; ^1H NMR (500 MHz, CDCl_3)] white solid: m.p. = 40–41 $^\circ\text{C}$; $[\alpha]_D^{26} = +30.1$ (c = 1.00, CH_2Cl_2); FT-IR (neat) 3451, 2920, 2851, 1714, 1612, 1513, 1360, 1092, 1036, 821 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 5.05 (dddd, 1 H, J = 8.0, 8.0, 8.0, 4.5 Hz, H -9), 4.15 (dd, 1 H, J = 12.5, 3.0 Hz, H -10), 3.91 (dd, 1 H, J = 11.5, 7.0 Hz, H -10), 3.69 (dd, 1 H, J = 12.5, 3.5 Hz, H -6), 3.61 (dd, 1 H, J = 12, 5.0 Hz, H -6), 3.28–3.22 (m, 2 H, H -3, H -4), 3.12–3.08 (m, 1 H, H -5), 3.06 (ddd, 1 H, J = 8.5, 8.5, 2.0 Hz, H -1), 3.02–2.96 (m, 1 H, H -2), 2.23–2.15 (m, 4 H, 2 $\times$ $\text{C}(=\text{O})\text{CH}_2$ -), 1.82–1.74 (m, 1 H, H -7), 1.74–1.66 (m, 1 H, H -8), 1.60–1.53 (m, 1 H, H -7), 1.53–1.44 (m, 4 H, 2 $\times$ CH_2), 1.41–1.33 (m, 1 H, H -7), 1.20–1.16 (m, 1 H, H -7), 1.30–1.22 (m, 52 H, 26 $\times$ CH_2), 0.76 (t, 6 H, J = 7.0 Hz, 2 $\times$ CH_3); ^{13}C NMR (125 MHz, CDCl_3) δ 174.0, 173.9, 79.2, 78.8, 78.5, 73.4, 71.1, 70.0, 65.1, 61.8, 34.5, 34.2, 31.9, 29.7, 29.7, 29.6, 29.6, 29.4, 29.2, 26.6, 26.6, 25.0, 24.8, 22.7, 14.1; HRMS (FAB) calcd for $\text{C}_{52}\text{H}_{100}\text{O}_9\text{Na}$ (M) $^+$ 891.7260, found 891.7260.

ENTRY 5

C-Glycoglycerolipid (17e)

The general method for DCC-mediated esterification was followed using: Diol **15f** (23 mg, 0.038 mmol), 4-DMAP (2.3 mg, 0.019 mmol), heptacosanoic acid (53 mg, 0.13 mmol) and DCC (11.8 mg, 0.057 mmol). Flash chromatography of the residue over silica using 10 $\rightarrow$ 20% EtOAc-hexanes gave **16e** (43 mg, 0.03 mmol, 81%) as a pure (R_f = 0.35, TLC, silica, 15% EtOAc-hexanes; ^1H NMR (500 MHz, CDCl_3); HRMS (FAB) calcd for $\text{C}_{92}\text{H}_{148}\text{O}_9\text{Na}$ (M) $^+$ 1421.1049, found 1421.1003) white solid. The product was then taken directly to the next step and the general method of hydrogenolysis was followed using **16e** (25 mg, 0.02 mmol), Pd/C (10 mg) and EtOAc (4 mL). After the usual work-up, flash chromatography of the residue over silica using 5 $\rightarrow$ 10% MeOH- CH_2Cl_2 gave **17e** (14 mg, 80%) as a pure (R_f = 0.33, TLC, silica, 10% MeOH- CH_2Cl_2 ; ^1H NMR (500 MHz, CDCl_3)) white solid: m.p. = 84–85 $^\circ\text{C}$; $[\alpha]_D^{26} = +12.1$ (c = 1.00, CHCl_3); FT-IR (neat) 3363, 2916, 2848, 1708, 1464, 1356, 1219, 1091, 720 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 5.21–5.15 (m, 1 H, H -9), 4.25 (dd, 1 H, J = 11.5, 3.5 Hz, H -10), 4.02 (dd, 1 H, J = 12.0, 7.0 Hz, H -10), 3.95 (dd, 1 H, J = 2.0, 2.0 Hz, H -4), 3.82 (dd, 1 H, J = 12.0, 6.0 Hz, H -6), 3.76 (ddd, 1 H, J = 10.5, 10.5, 3.5 Hz, H -6), 3.44 (dd, 1 H, J = 9.0, 9.0 Hz, H -2), 3.43–3.39 (m, 2 H, H -3, H -5),

3.14 (ddd, 1 H, $J = 8.0, 8.0, 2.5$ Hz, $H-1$), 2.31-2.26 (m, 4 H, 2 x CH_2), 1.95-1.86 (m, 1 H, $H-7$), 1.85-1.75 (m, 1 H, $H-8$), 1.75-1.67 (m, 1 H, $H-8$), 1.64-1.53 (m, 5 H, $H-7$, 2 x CH_2), 1.34-1.24 (m, 92 H, 46 x CH_2), 0.77 (t, 6 H, $J = 6.5$ Hz, 2 x CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.8, 173.7, 79.3, 77.9, 77.8, 75.3, 71.4, 70.3, 71.4, 70.3, 65.0, 62.9, 34.4, 34.1, 31.8, 29.6, 29.4, 29.4, 29.4, 29.3, 29.2, 29.2, 29.2, 29.1, 26.8, 24.9, 24.8, 23.9, 22.6, 13.9; HRMS (FAB) calcd for $C_{64}H_{124}O_9Na$ (M) $^+$ 1059.9138, found 1059.9124.

ENTRY 6**C-Glycoglycerolipid (17f)**

The general procedure for DCC-mediated esterification was followed using: diol **15h** (18 mg, 0.03 mmol), heptacosanoic acid (18 mg, 0.044 mmol), 4-DMAP (2 mg, 0.015 mmol) and DCC (9 mg, 0.044 mmol). Flash chromatography using 20% EtOAc-hexanes gave **16f** (33.0 mg, 81%) as a pure ($R_f = 0.40$, TLC, silica, 20% EtOAc-hexanes; ^1H NMR (500 MHz, $CDCl_3$); HRMS (FAB) calcd for $C_{92}H_{148}O_9Na$ (M) $^+$ 1421.1049, found 1421.1125) yellow oil. The product was then taken directly to the next step and the general method of hydrogenolysis was followed using: **16f** (10 mg, 6.6 μ mol) in EtOAc:MeOH (1:1, 5 mL) was added Pd/C (2 mg). After the usual work-up, flash chromatography of the residue over silica gel using 5 $\rightarrow$ 10% MeOH- CH_2Cl_2 gave **17f** (5 mg, 71%) as a pure ($R_f = 0.31$, TLC, silica, 10% MeOH- CH_2Cl_2 ; ^1H NMR (500 MHz, $CDCl_3$)] white solid: m.p. = 99-100 $^{\circ}C$; $[\alpha]_D^{26} = +2.9$ ($c = 1.00$, $CHCl_3$); FT-IR (neat) 3486 (br), 2916, 2850, 2361, 1713, 1612, 1513, 1465, 1360, 1247, 1219, 1090, 1035, 820 cm^{-1} ; ^1H NMR (500 MHz, $CDCl_3$) δ 5.18-5.12 (m, 1 H, $H-9$), 4.23 (dd, 1 H, $J = 12.5, 3.0$ Hz, $H-10$), 3.98 (dd, 1 H, $J = 12.0, 7.0$ Hz, $H-10$), 3.78 (dd, 1 H, $J = 12.5, 3.0$ Hz, $H-6$), 3.71 (dd, 1 H, $J = 12.0, 4.5$ Hz, $H-6$), 3.44-3.35 (m, 2 H, $H-3$, $H-4$), 3.24-3.18 (m, 2 H, $H-1$, $H-5$), 3.13 (dd, 1 H, $J = 8.5, 8.5$ Hz, $H-2$), 2.30-2.24 (m, 4 H, $C(O)CH_2$), 2.21-2.13 (m, 4 H, 4 x OH), 1.90-1.82 (m, 1 H, $H-7$), 1.80-1.71 (m, 1 H, $H-8$), 1.70-1.62 (m, 1 H, $H-8$), 1.62-1.52 (m, 4 H, 2 x CH_2), 1.52-1.43 (m, 1 H, $H-7$), 1.30-1.21 (m, 92 H, 46 x CH_2), 0.85 (t, 6 H, $J = 7.0$ Hz, 2 x CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.9, 173.9, 79.2, 78.7, 77.2, 77.2, 73.4, 64.8, 61.9, 34.3, 34.0, 31.7, 29.5, 29.3, 29.2, 29.1, 28.9, 26.7, 26.4, 24.8, 24.7, 22.5, 13.9; HRMS (FAB) calcd for $C_{64}H_{124}O_9Na$ (M) $^+$ 1059.9138, found 1059.9102.

ENTRY 7**C-Glycoglycerolipid (17g)**

1-Iodoheptadecane (50 μ L, 0.16 mmol) was added dropwise over 10 min to a DMF (1 mL) solution of diol **15h** (25 mg, 0.04 mmol) and washed NaH (2 mg, 0.09 mmol) at 0 $^{\circ}C$. After 10 min, the usual work-up was followed by flash chromatography over silica gel using 20% Et₂O-hexanes to give **16g** (8 mg, 7.53 μ mol, 19%) as a pure ($R_f = 0.40$, TLC, silica, 20% Et₂O-hexanes; ^1H NMR (500 MHz, $CDCl_3$); HRMS (FAB) calcd for $C_{70}H_{108}O_7Na$ (M) $^+$ 1083.7987, found 1083.8018) clear oil. The product was then taken directly to the next step and the general method of hydrogenolysis was followed using: **16g** (16 mg, 15.0 μ mol) in EtOAc:MeOH (1:1, 5 mL) was added Pd/C (10 mg). Flash chromatography of the residue over silica gel using 5 $\rightarrow$ 10% MeOH- CH_2Cl_2 gave **17g** (8 mg, 76%) as a pure ($R_f = 0.20$, TLC, silica, 10%

MeOH-CH₂Cl₂; ¹H NMR (500 MHz, CDCl₃) white solid: m.p. = 64-65 °C; [α]_D²³ = + 7.2 (*c* = 1.00, CH₂Cl₂); FT-IR (neat) 3353, 2921, 2851, 1730, 1462, 1376, 1248, 1102, 720 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 3.77 (dd, 1 H, *J* = 12.5, 3.5 Hz, *H*-6), 3.64 (dd, 1 H, *J* = 12, 5.0 Hz, *H*-6), 3.55 (ddd, 1 H, *J* = 9.5, 6.5 Hz, 6.5 Hz, *H*-9), 3.44-3.30 (m, 9 H, *H*-2, *H*-3, *H*-4, 2 x *H*-10, 4 x CH₂), 3.22-3.15 (m, 1 H, *H*-5), 3.12 (dd, 1 H, *J* = 10, 10 Hz, *H*-1), 2.65-2.62 (bs, 4 H, 4 x OH), 1.85-1.77 (m, 1 H, *H*-7), 1.64-1.47 (m, 7 H, *H*-7, *H*-8, 2 x CH₂), 1.29-1.18 (bs, 52 H, 26 x CH₂), 0.83 (t, 6 H, *J* = 7.0 Hz, 2 x CH₃); ¹³C NMR (125 MHz, CDCl₃) δ 79.0, 78.9, 78.6, 78.3, 73.3, 73.2, 71.7, 70.6, 70.5, 62.3, 31.8, 30.0, 29.6, 29.6, 29.5, 29.4, 29.4, 29.3, 27.3, 27.2, 26.0, 22.6, 14.0; HRMS (FAB) calcd for C₄₂H₈₄O₇Na (*M* + Na)⁺ 723.6109, found 723.6068.

ENTRY 8**C-Glycoglycerolipid (17h)**

The same procedure for alkylation was followed using: diol **15h** (30 mg, 48.9 μ mol), DMF (2 mL), NaH (8 mg, 0.2 mmol, 60% dispersion in mineral oil), bromoeicosane (105 mg, 0.29 mmol), and tetrabutylammonium iodide (2 mg, 4.9 μ mol). After the usual work-up, flash chromatography over silica gel using 20% Et₂O-hexanes; ¹H NMR (500 MHz, CDCl₃); HRMS (FAB) calcd for C₇₈H₁₂₄O₇Na (*M*)⁺ 1195.9239, found 1195.9268. The product was then taken directly to the next step and the general method of hydrogenolysis was followed using: **16h** (12 mg, 10.0 μ mol) in EtOAc:MeOH (1:1, 5 mL) was added Pd/C (10 mg). Flash chromatography of the residue over silica gel using 5→10% MeOH-CH₂Cl₂ gave **17h** (6.5 mg, 76%) as a pure (*R*_f = 0.27, TLC, silica, 10% MeOH-CH₂Cl₂; ¹H NMR (500 MHz, CDCl₃) white solid: m.p. = 70-71 °C; [α]_D²⁶ = + 8.9 (*c* = 1.00, CH₂Cl₂); FT-IR (neat) 3426 (b), 2914, 2861, 1612, 1513, 1463, 1362, 1301, 1247, 1173, 1085, 1033, 820 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 3.76 (dd, 1 H, *J* = 12.0, 3.0 Hz, *H*-6), 3.63 (dd, 1 H, *J* = 12.0, 5.0 Hz, *H*-6), 3.54 (ddd, 1 H, *J* = 9.5, 7.5 Hz, 7.5 Hz, *H*-9), 3.43-3.35 (m, 4 H, 2 x *H*-10, OCH₂), 3.35-3.28 (m, 5 H, *H*-2, *H*-3, *H*-4, OCH₂), 3.20-3.13 (m, 1 H, *H*-5), 3.10 (dd, 1 H, *J* = 9.0, 9.0 Hz, *H*-1), 2.27-2.22 (m, 1 H, *H*-7), 1.85-1.78 (m, 1 H, *H*-8), 1.63-1.44 (m, 6 H, *H*-7, *H*-8, 2 x CH₂), 1.26-1.18 (bs, 68 H, 34 x CH₂), 0.82 (t, 6 H, *J* = 7.0 Hz, 2 x CH₃); ¹³C NMR (125 MHz, CDCl₃) δ 79.1, 78.9, 78.6, 78.3, 73.2, 73.2, 71.6, 70.6, 70.5, 62.2, 31.8, 30.0, 29.6, 29.5, 29.5, 29.4, 29.4, 29.2, 27.3, 26.0, 22.6, 14.0; HRMS (FAB) calcd for C₅₀H₁₀₀O₇Na (*M*)⁺ 835.7361, found 835.7396.

ENTRY 9**C-Glycoglycerolipid (17i)**

The general method for esterification was followed using: diol **15i** (40 mg, 0.055 mmol), oleoyl chloride (0.1 mL, 0.33 mmol), and 4-DMAP (3 mg, 0.027 mmol) in CH₂Cl₂ (2 mL). Flash chromatography of the residue over silica using 15-30% EtOAc-hexanes gave **16i** (48 mg, 80%) as a pure (*R*_f = 0.35, TLC, silica, 30% EtOAc-hexanes; ¹H NMR (500 MHz, CDCl₃); HRMS (FAB) calcd for C₇₈H₁₁₆O₁₃Na (*M*)⁺ 1283.8308, found 1283.8390) yellow oil. The product was then taken directly to the next step and a

solution of **16i** (40 mg, 0.032 mmol) in CH_2Cl_2 (2.4 mL) and H_2O (0.1 mL) was treated with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (29 mg, 0.127 mmol). The reaction was stirred for 1 h at ambient temperature, diluted with H_2O (2 mL) and CH_2Cl_2 (2 mL), the aqueous phase was extracted with CH_2Cl_2 (3 x 10 mL). The organic extracts were dried with MgSO_4 , filtered and concentrated *in vacuo* to give a crude oil. Flash chromatography of the residue over silica using 5 $\rightarrow$ 10% CH_2Cl_2 -MeOH gave **17i** (18 mg, 73%) as a pure (R_f = 0.22, TLC, silica, 5% CH_2Cl_2 -MeOH; ^1H NMR (400 MHz, CDCl_3)) white solid: m.p. = 99-100 $^\circ\text{C}$; $[\alpha]_D^{26}$ = -16.2 (c = 1.00, CHCl_3); FT-IR (neat) 3390, 2924, 2854, 1738, 1464, 1378, 1174, 1089, 1013, 723 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 5.34-5.24 (m, 4 H, 4 x =C-H), 5.15-5.08 (m, 1 H, *H*-9), 4.21 (dd, 1 H, J = 11.5, 2.5 Hz, *H*-10), 3.95 (dd, 1 H, J = 12, 7.0 Hz, *H*-10), 3.75 (dd, 1 H, J = 12.0, 2.4 Hz, *H*-6), 3.67 (dd, 1 H, J = 12, 4.8 Hz, *H*-6), 3.38-3.29 (m, 1 H, *H*-4), 3.20-3.12 (m, 2 H, *H*-3, *H*-5), 3.09 (dd, 1 H, J = 6.0, 6.0 Hz, *H*-2), 3.07 (dd, 1 H, J = 7.2, 7.2 Hz, *H*-1), 3.04-2.70 (m, 4 H, 4 x OH), 2.28-2.22 (m, 4 H, 2 x CH_2), 1.99-1.92 (m, 8 H, 4 x CH_2), 1.89-1.78 (m, 1 H, *H*-7), 1.78-1.68 (m, 1 H, *H*-8), 1.67-1.59 (m, 1 H, *H*-8), 1.61-1.50 (m, 4 H, 2 x CH_2), 1.50-1.38 (m, 1 H, *H*-7), 1.32-1.19 (m, 36 H, 18 x CH_2), 0.83 (t, 6 H, J = 5.6 Hz, 2 x CH_3); ^{13}C NMR (125 MHz, CDCl_3) δ 173.9, 173.8, 129.9, 129.6, 79.2, 78.7, 78.3, 73.3, 71.2, 70.2, 64.9, 62.0, 45.9, 34.3, 34.0, 31.8, 29.6, 29.6, 29.2, 29.1, 29.0, 29.0, 27.1, 27.1, 26.7, 26.5, 24.9, 24.7, 22.6, 14.0; HRMS (FAB) calcd for $\text{C}_{46}\text{H}_{84}\text{O}_9\text{Na}$ (M) $^+$ 803.6008, found 803.6077.

ENTRY 10

See experimental section in paper.

ENTRY 11**C-Glycoglycerolipid (17k)**

The general method for esterification was followed using: diol **15j** (26 mg, 0.044 mmol), oleoyl chloride (86 μL , 0.26 mmol), and 4-DMAP (3 mg, 0.022 mmol) in pyridine (1.5 mL). Flash chromatography of the residue over silica using 25 $\rightarrow$ 30% EtOAc-hexanes gave **16k** (41 mg, 85%) as a pure (R_f = 0.52, TLC, silica, 30% EtOAc-hexanes; ^1H NMR (500 MHz, CDCl_3)) yellow oil. The product was then taken directly to the next step and TFA (5 drops) was added to a solution of **16k** (25 mg, 0.022 mmol) in CH_2Cl_2 (2.0 mL) and the reaction was stirred for 1 h at ambient temperature. At this point TLC analysis (silica, first 30% EtOAc-hexanes then 5% MeOH- CH_2Cl_2) indicated the reaction was almost complete and upon concentration *in vacuo* the reaction went to completion. Flash chromatography of the residue over silica gel using 3 $\rightarrow$ 5% MeOH- CH_2Cl_2 gave **17k** (14.5 mg, 85%) as a pure (R_f = 0.33, TLC, silica, 5% MeOH- CH_2Cl_2 ; ^1H NMR (400 MHz, CDCl_3)) clear oil: $[\alpha]_D^{26}$ = +4.9 (c = 1.00, CH_2Cl_2); FT-IR (neat) 3390 (b), 2921, 2852, 1736, 1463, 1376, 1245, 1168, 1088, 1052, 722 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 5.32-5.20 (m, 4 H, 4 x C=C-H), 5.10-5.00 (m, 1 H, *H*-9), 4.25 (dd, 1 H, J = 11.6, 3.2 Hz, *H*-10), 3.99 (dd, 1 H, J = 12.4, 6.8 Hz, *H*-10), 3.71 (dd, 1 H, J = 12.0, 4.5 Hz, *H*-6), 3.44-3.35 (m, 2 H, *H*-3, *H*-4), 3.24-3.18 (m, 2 H, *H*-1, *H*-5), 3.13 (dd, 1 H, J = 8.5, 8.5 Hz, *H*-2), 2.30-2.24 (m, 4 H, C(=O) CH_2 -), 2.21-2.13 (m, 4 H, 4 x OH), 1.90-1.82 (m, 1 H, *H*-7), 1.80-1.71 (m, 1 H, *H*-8), 1.70-1.62 (m, 1 H, *H*-8), 1.62-1.52 (m, 4 H, 2 x CH_2), 1.52-1.43 (m, 1 H, *H*-7), 1.30-1.21 (m, 92 H, 46 x CH_2), 0.85 (t, 6 H, J = 7.0 Hz, 2 x

CH_3); ^{13}C NMR (125 MHz, CDCl_3) δ 173.6, 173.6, 130.0, 130.0, 129.7, 129.7, 78.9, 77.2, 75.0, 72.8, 72.7, 70.8, 64.9, 62.5, 55.2, 38.6, 34.4, 34.1, 31.9, 30.5, 29.7, 29.7, 29.5, 29.3, 29.2, 29.1, 29.1, 27.2, 27.2, 26.8, 25.0, 24.8, 22.7, 14.1; HRMS (FAB) calcd for $\text{C}_{46}\text{H}_{84}\text{O}_8\text{Na}$ (M) $^+$ 787.6058, found 787.6573.

O-Glycoside Examples

The known corresponding β -O-glycoglycerolipid **171** was prepared in a straightforward manner from the known tetraacetate **18**¹⁵ as delineated in Scheme S-1.

Scheme S-1. Preparation of β -O-glycoglycerolipid **171**

PMB-Acetonide (**19**)

A catalytic amount of pre-washed NaH (~5 mg) was added in one portion to a methanol (50 mL) solution of tetraacetate **18** (448 mg, 0.97 mmol). The resulting solution was stirred for 1 h at ambient temperature and the reaction was then quenched by the addition of acetic acid (0.5 mL) and the resulting solution concentrated *in vacuo* and then azeotroped with benzene (20 mL). The resulting oil was pumped under vacuum (0.5 mm Hg) for 6 hours and then dissolved in DMF (20 mL) and the resulting solution cooled to 0 °C and PMBCl (4.85 mL, 4.85 mmol, 5 eq.), TBAI (36 mg, 97 μmol , 0.1 eq) and sodium hydride (195 mg, 4.85 mmol, 5 eq) were added sequentially to the cool solution. The resulting mixture was then allowed to warm to ambient temperature over 1 h and then heated to 80 °C for 12 hours. The solution was cooled and carefully quenched by the addition of MeOH (10 mL). The solution was concentrated *in vacuo* and the residue dissolved in ether (100 mL). The ethereal fraction was washed with saturated ammonium chloride (1 x 30 mL), brine (1 x 30 mL), dried and concentrated. Flash chromatography of the residue over silica using 20 $\rightarrow$ 40% ether-hexanes gave **19** (641 mg, 85% over 2 steps) as a pure (^1H NMR (500 MHz, CDCl_3) oil: $[\alpha]_D^{26} = 6.91$ ($c = 1.00$, CHCl_3); FT-IR (neat) 2916, 2848, 1612, 1514, 1472, 1462, 1248, 1173, 1071, 1036, 820, 720 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.26-7.18 (m, 7 H, ArH), 7.02-7.00 (m, 2 H, ArH), 6.85-6.76 (m, 7 H, ArH), 4.81 (d, 1 H, $J = 10.5$ Hz, OCH_2Ar), 4.80 (d, 1 H, $J = 11$ Hz, OCH_2Ar), 4.69 (d, 1 H, $J = 10$ Hz, OCH_2Ar), 4.68 (d, 1 H, $J = 10.5$ Hz, OCH_2Ar), 4.61 (d, 1 H, $J = 10.5$ Hz, OCH_2Ar), 4.52 (d, 1 H, $J = 12$ Hz, OCH_2Ar), 4.44 (d, 1 H, $J = 12$ Hz, OCH_2Ar), 4.38 (d, 1 H, $J = 10.5$ Hz, OCH_2Ar), 4.36 (d, 1 H, $J = 8.0$ Hz, $H-1$), 4.32 (dddd, 1 H, $J = 4.0, 4.0, 4.0, 4.0$ Hz, $H-8$), 4.05 (dd, 1 H, $J = 8.0, 6.0$ Hz, $H-7$ or $H-9$), 3.98 (dd, 1 H, $J = 10, 4.5$ Hz, $H-7$ or $H-9$), 3.84 (dd, 1 H, $J = 8.5, 6.0$ Hz, $H-7$ or $H-9$), 3.78 (s, 3 H, OCH_3), 3.77 (s, 3 H, OCH_3), 3.76 (s, 6 H, 2 x OCH_3), 3.64 (dd, 1 H, $J = 10.5, 1.5$ Hz, $H-6$), 3.60-3.54 (m, 2 H, $H-6, H-7$ or $H-9$), 3.54 (dd, 1 H, $J = 8.5, 8.5$ Hz, $H-4$), 3.48 (dd, 1

¹⁵ van Boeckel, C. A. A.; Visser, G. M.; van Boom, J. H. *Tetrahedron* **1985**, *41*, 4557-4565.

H, $J = 9.5, 9.5$ Hz, $H-3$), 3.38 (dd, 1 H, $J = 8.5, 8.5$ Hz, $H-2$), 3.38-3.35 (m, 1 H, $H-5$), 1.39 (s, 3 H, $C(CH_3)_2$), 1.34 (s, 3 H, $C(CH_3)_2$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 130.9, 130.6, 130.3, 130.2, 129.8, 129.6, 129.5, 113.8, 103.9, 84.4, 81.8, 77.5, 75.3, 74.9, 74.6, 74.5, 74.3, 73.1, 70.3, 68.4, 67.0, 55.3, 26.9, 25.4; HRMS (FAB) calcd for $C_{44}H_{54}O_{12}Na$ (M) $^+$ 797.3507, found 797.3536.

PMB-Diol (20)

The usual procedure for acetonide deprotection was employed using: CH_2Cl_2 (4 mL), MeOH (4 mL), p -TsOH (15 mg, 0.007 mmol) and the acetonide sugar **19** (200 mg, 0.258 mmol). After the usual work-up, flash chromatography of the residue over silica using 3 $\rightarrow$ 5% MeOH- CH_2Cl_2 gave **20** (138 mg, 73%) as a pure ($R_f = 0.23$, TLC, silica, 5% CH_2Cl_2 -MeOH; ^1H NMR (500 MHz, $CDCl_3$)) white solid: $[\alpha]_D^{26} = +21.2$ ($c = 1.00$, $CHCl_3$); FT-IR (neat) 3450 (br), 2916, 2851, 1612, 1513, 1463, 1302, 1248, 1173, 1068, 1034, 820 cm^{-1} ; ^1H NMR (500 MHz, $CDCl_3$) δ 7.28-7.21 (m, 6 H, ArH), 7.05 (app d, 2 H, $J = 8.0$ Hz, ArH), 6.89-6.80 (m, 8 H, ArH), 4.84 (d, 1 H, $J = 11$ Hz, OCH_2Ar), 4.79 (d, 1 H, $J = 10.5$ Hz, OCH_2Ar), 4.73 (d, 1 H, $J = 11.5$ Hz, OCH_2Ar), 4.71 (d, 1 H, $J = 10$ Hz, OCH_2Ar), 4.67 (d, 1 H, $J = 10.5$ Hz, OCH_2Ar), 4.50 (d, 1 H, $J = 11.5$ Hz, OCH_2Ar), 4.45 (d, 1 H, $J = 11.5$ Hz, OCH_2Ar), 4.40 (d, 1 H, $J = 11.5$ Hz, OCH_2Ar), 4.37 (d, 1 H, $J = 8.0$ Hz, $H-1$), 3.96 (dd, 1 H, $J = 11.5, 2.5$ Hz, OCH), 3.88 (m, 1 H, OCH), 3.80 (s, 3 H, OCH_3), 3.80 (s, 3 H, OCH_3), 3.79 (s, 3 H, OCH_3), 3.79 (s, 3 H, OCH_3), 3.78-3.73 (m, 1 H, OCH), 3.70-3.61 (m, 2 H, 2 x OCH), 3.59 (dd, 1 H, $J = 8.5, 8.5$ Hz, $H-3$), 3.54 (dd, 1 H, $J = 11, 5.5$ Hz, OCH), 3.51-3.43 (m, 3 H, 3 x OCH), 3.41 (dd, 1 H, $J = 8.5, 8.5$ Hz, $H-2$), 2.30 (br s, 1 H, OH); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.3, 159.2, 159.2, 159.2, 130.6, 130.4, 130.0, 129.7, 129.7, 129.5, 113.8, 113.8, 104.4, 84.3, 81.8, 77.5, 75.3, 74.6, 74.4, 74.0, 73.1, 71.2, 68.5, 63.3, 55.2; HRMS (FAB) calcd for $C_{41}H_{50}O_{12}Na$ (M) $^+$ 757.3194, found 757.3167.

O-Glycoside Oleoyl Lipid (17I)

The general method for esterification was followed using: diol **20** (60 mg, 0.082 mmol), oleoyl chloride (162 μ L, 0.49 mmol), and 4-DMAP (10 mg) in pyridine (3 mL). Flash chromatography of the residue over silica using 20% EtOAc-hexanes gave the fully protected β -O-glycoglycerolipid (75 mg, 73%) as a pure ($R_f = 0.65$, TLC, silica, 20% EtOAc-hexanes; ^1H NMR (500 MHz, $CDCl_3$), HRMS (FAB) calcd for $C_{77}H_{114}O_{14}Na$ (M) $^+$ 1285.8101, found 1285.8119) yellow oil. The product was then taken directly to the next step and TFA (5 drops) was added to a solution of the fully protected β -O-glycoglycerolipid (50 mg, 0.039 mmol) in CH_2Cl_2 (2.0 mL) and the reaction was stirred for 1 h at ambient temperature. At this point TLC analysis (20% MeOH- CH_2Cl_2) indicated the reaction was almost complete and upon concentration *in vacuo* the reaction went to completion. Flash chromatography of the residue over silica gel using 5 $\rightarrow$ 10%

MeOH-CH₂Cl₂ gave **17l** (22 mg, 72%) as a pure (R_f = 0.35, TLC, silica, 10% MeOH-CH₂Cl₂; ¹H NMR (400 MHz, CDCl₃)) clear oil whose spectral and physical data matched that from the literature.¹⁶

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¹⁶ (a) van Boeckel, C. A. A.; Visser, G. M.; van Boom, J. H. *Tetrahedron* **1985**, *41*, 4557-4565. (b) Shirahashi, H.; Murakami, N.; Watanabe, M.; Nagatsu, A.; Sakakibara, J.; Tokuda, H.; Nishino, H.; Iwashima, A. *Chem. Pharm. Bull.* **1993**, *41*, 1664-1666. (c) Nagatsu, A.; Watanabe, M.; Ikemoto, K.; Hashimoto, M.; Murakami, N.; Sakakibara, J.; Tokuda, H.; Nishino, H.; Iwashima, A.; Yazawa, K. *Bioorg. Med. Chem. Lett.* **1994**, *4*, 1619-1622.

Unity 500 spectrometer

Unity 500 spectrometer

Unity 500 spectrometer

Unity 500 spectrometer

Mercury 400 spectrometer

Unity 500 spectrometer

S34

Unity 500 spectrometer

Unity 500 spectrometer

S36

10-30
11-76

Unity 500 spectrometer

S37

Unity 500 spectrometer

Mercury 400 spectrometer

S39

Unity 500 spectrometer

540