Supplementary Material for Organic & Biomolecular Chemistry

Supporting Information

Highly Efficient and Stereoselective Synthesis of β-Glycolipids

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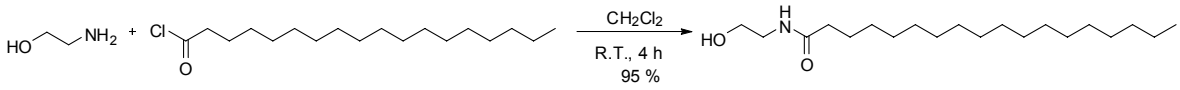
General methods. All reactions were conducted under a dried argon stream. Solvents (CH_2Cl_2 99.9%, toluene 99.9%) were purchased in capped Pure Solv System-4® bottles and used without further purification and stored under argon. Yields refer to the chromatographically and spectroscopically (^1H and ^{13}C) homogeneous materials, unless otherwise stated. TMSI was stored at –15°C under desiccated atmosphere. All other solvents and reagents were used without further purification. The sphingosine was purchased from Avanti Polar Lipids Inc (Alabaster, AL) and azidosphingosine was synthesized using a literature procedure.[1] All glassware utilized was flame-dried before use. Reactions were monitored by TLC carried out on 0.25 mm E. Merck silica gel plates. Developed TLC plates were visualized under a short-wave UV lamp and by heating plates that were dipped in ethanol/H_2SO_4 (15:1). Flash column chromatography (FCC) was performed using flash silica gel (32–63 μm) and employed a solvent polarity correlated with TLC mobility. Melting points, determined with Reichert apparatus, are uncorrected. Optical rotations were measured at 598 nm on a Jasco DIP-370 digital polarimeter using a 100 mm cell. NMR experiments were conducted on a Varian 400

[1] Duclos, R.I. *Chem. Phys. Lipids* **2001**, *111*, 111.

MHz instrument using $CDCl_3$ (99.9% D) as the solvent, with chemical shifts (δ) reference to internal standards $CDCl_3$ (7.26 ppm ^1H, 77.23 ppm ^{13}C) or Me_4Si as an internal reference (0.00 ppm) Chemical shifts are relative to the deuterated solvent peak and are in parts per million (ppm).

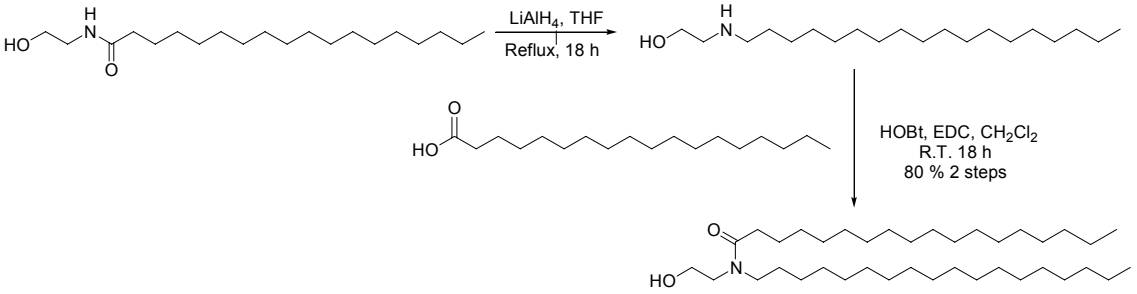
Experimental Procedures.

Synthesis of *N*-(2-hydroxyethyl)stearamide



A solution of stereoyl chloride (50 g 0.165 mol) in 250 mL of dry CH_2Cl_2 was cooled to 0 °C. To this solution 2-amino ethanol (100.78 g, 1.65 mol) was added in a slow drop-wise manner over a period of 30 min, resulting in the precipitation of a white solid. The reaction was stirred for 4 h at room temperature and then the mixture was filtered. The solid was washed with hexane and diethyl ether and dried *in vacuo*. The resulting crystalline material was recrystallized from CH_2Cl_2 to give 51.26 g of pure *N*-(2-hydroxyethyl)stearamide (95%) as a white solid[2] that was homogeneous. TLC (Hexane-AcOEt-MeOH 60:30:10) R_f 0.25; m.p. 53–55 °C; ^1H NMR (400 MHz, $CDCl_3$): δ. 5.94 (1H, br. s), 3.72 (2H, t, *J*=5.2 Hz), 3.42 (2H, q, *J*=5.2, 1 Hz), 2.18 (2H, t, *J*=7.2 Hz), 1.62 (2H, quint, *J*=7.2 Hz), 1.28 (28H, m), 0.87 (3H, t, *J*=6.8 Hz); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 172.6, 61.0, 41.6, 36.5, 31.8, 29.5, 28.6, 25.6, 22.7, 14.1. Anal. Calcd. for $C_{20}H_{41}NO_2$: C, 73.34; H, 12.62; N, 4.28. Found: C, 73.30; H, 12.69; N, 4.20.

Synthesis of *N*-(2-hydroxyethyl)-*N*-octadecylstearamide[3]

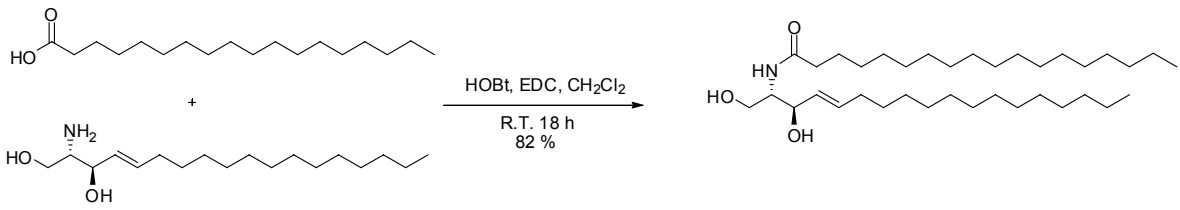


[2] Eliash, R.; Weissbuch, I.; Weygand, M.J.; Kjaer, K.; Leiserowitz, L.; Lahav, M. *J. Phys. Chem. B,* **2004**, *108*, 7228.
[3] Wilson, C.V.; Stenberg, J.F.*Org. Synth. Coll. Vol. 4,* 564.

A 250 mL, three-necked, roundbottomed flask was fitted with a heating bath, mechanical stirrer, reflux condenser with drying tube, and a stoppered, pressure-equalizing dropping funnel, flushed with nitrogen or argon, and charged with 75 mL of dry THF, and $LiAlH_4$ (1.45 g, 38.22 mmol). A mixture of 75 mL of THF and *N*-(2-hydroxyethyl)stearamide (10 g, 30.58 mmol) was added, with stirring, at a rate sufficient to reach and maintain refluxing. After the addition was completed, the reaction mixture was kept boiling for 18 h. The flask was immersed in an ice bath, and 30 mL of water, 15 mL of 10% aqueous potassium hydroxide, and again 30 mL of water were added cautiously with very vigorous stirring. The reaction mixture was stirred for an additional 1h, filtered with suction, and the solid was washed with several 100-mL portions of ethyl acetate. The two layers were separated, and the aqueous phase was extracted with ethyl acetate (3 x 100 mL). The combined organic layers were dried over anhydrous sodium sulphate and concentrated *in vacuo* to get crude residue of 2-(ocatadecylamino) ethanol as a white solid (6.7 g, 70%).

A solution of 2-(octadecylamino) ethanol (1 g, 3.194 mmol), HOBt (586 mg, 3.832 mmol), EDC (734 mg, 3.832 mmol) and DIPEA (494 mg, 3.832 mmol) in 30 mL of dry CH_2Cl_2 was cooled to 0 $^{\circ}$C. Stearic acid (908 mg, 3.194 mmol) in 20 mL of dry CH_2Cl_2 was added drop wise over 6 h at 0°C, and then the reaction was stirred under argon for 18 h at room temperature. The mixture was diluted with ethyl acetate (75 mL) and washed successively with HCl (10 % aqueous, 2 x 30 mL), $NaHCO_3$ (7 % aqueous, 2 x 30 mL), K_2CO_3 (7% aqueous, 2 x 30 mL), and brine (3 x 30 mL). The organic layer was dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel using hexane/AcOEt/MeOH (85:10:5) as the eluent to give 1.67 g of pure *N*-(2-hydroxyethyl)-*N*-octadecylstearamide (90 %). TLC (Hexane/AcOEt/MeOH 60:30:10) R_f 0.70; m.p. 50–52 $^{\circ}$C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.75 (2H, t, *J*=5.2 Hz), 3.52 (2H, t, *J*=5.2 Hz), 3.26 (2H, t, *J*=7.6 Hz), 2.32 (2H, t, *J*=7.6 Hz), 1.62-1.54 (4H, m), 1.25 (58H, m), 0.87 (6H, t, *J*=6.5 Hz); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 173.0, 58.9, 50.2, 47.3, 34.3, 31.8, 30.4, 29.6, 29.3, 28.9, 28.6, 27.7, 22.7, 14.1. Anal. Calcd. for $C_{38}H_{77}NO_2$: C, 78.69; H, 13.38; N, 2.41. Found: C, 78.73; H, 12.98, N, 2.45.

Synthesis of *N*-((2*S*,3*R*,4E)-1,3-dihydroxyoctadec-4-en-2-yl)stearamide[4]



A solution of sphingosine (100 mg, 0.333 mmol), HOBt (61 mg, 0.4 mmol), EDC (76 mg, 0.4 mmol) and DIPEA (77 mg, 0.6 mmol) in 20 mL of dry CH_2Cl_2 was cooled to 0 °C. Under stirring, stearic acid (94 mg, 0.333 mmol in 20 mL of dry CH_2Cl_2) was added drop wise over 6 h at 0°C, and then the reaction was stirred under argon for 18 h at room temperature. The mixture was diluted with ethyl acetate (75 mL) and washed successively with HCl (10% aqueous, 2 x 30 mL), $NaHCO_3$ (7% aqueous, 2 x 30 mL), K_2CO_3 (7% aqueous, 2 x 30 mL), and brine (3 x 30 mL). The organic layer was dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel using hexane-AcOEt-MeOH (85:10:5) as the eluent to give 154 mg of pure *N*-((2*S*,3*R*,E)-1,3-dihydroxyoctadec-4-en-2-yl)stearamide (82 %). TLC (Hexane-AcOEt-MeOH 60:30:10) R_f 0.70; m.p. 104–106 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.23 (1H, d, *J*=7.3 Hz), 5.77 (1H, dt, *J*=15.4, 6.7 Hz), 5.51 (1H, dd, *J*=15.4, 6.4 Hz), 4.3 (1H, dd, *J*=6.4, 3.4 Hz), 3.94 (1H, dd, *J*=11.3, 3.7 Hz), 3.89 (1H, dddd, *J*=7.3, 3.7, 3.4, 3.2 Hz), 3.69 (1H, dd, *J*=11.3, 3.2 Hz), 2.21 (2H, t, *J*=7.5 Hz), 2.03 (2H, dt, *J*=7.2, 6.7 Hz), 1.62 (2H, quint, *J*=7.5 Hz), 1.35 (2H, m), 1.34-1.20 (48H, m), 0.86 (6H, t, *J*=6.9 Hz); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 174.2, 134.6, 129, 74.9, 62.8, 54.7, 36.92, 32.2, 31.98, 29.9, 29.8, 29.7, 29.6, 29.5, 29.4, 26, 22.9, 14.3. Anal. Calcd. for $C_{36}H_{71}NO_3$: C, 76.40; H, 12.64; N, 2.47. Found: C, 76.59; H, 12.47, N, 2.59.

General procedures for the preparation of amide-derivative of stannyl ethers.

Preparation of 4, 8 and 13: A mixture of alcohol (0.305 mmol) and bis-(tributyltin) oxide (30 mg, 0.152 mmol) in 15 ml of dry toluene, was heated to reflux and was subjected to azeotropic dehydration using a Dean-Stark system or 4 Å molecular sieves

[4] Julina, R. ; Herzig, T. ; Bernet, B.; Vasella, A. *Helv. Chim. Acta*, **1986**, *69*, 368.

overnight. Removal of solvent under reduced pressure afforded the stannyl ethers **4**, **8**, and **13** which was used for the glycosylation reaction without further purification.

Preparation of 14 and 15: A mixture of sphingosine or ceramide (0.176 mmol) and dibutyltin oxide (0.176 mmol) in dry toluene (15 mL), was heated to reflux and was subjected to azeotropic dehydration using a Dean-Stark system or 4 Å molecular sieves overnight. Removal of solvent under reduced pressure afforded the stannyl acetals **14** and **15**, which was used for the glycosylation reaction without further purification.

General procedure for glycosylation.

The following protocol was followed prior to the glycosylation reaction: 1,2,3,4,6-penta-*O*-acetyl-β-D-galactopyranose and donor alcohol were separately dried by co-destillation with toluene (3 x 5 mL) in dried flasks and then were placed under vacuum for 1 h. TBAI was added to a dried flask with a magnetic stirring bar and was co-destilled with dry toluene (2 x 5 mL) in the dark. Activated 4 Å molecular sieves were added to the flask, and the mixture was co-destilled with toluene once more (5 mL) before being placed under vacuum for 1 h. Complete water exclusion is crucial to achieve good yields.

A solution of 1,2,3,4,6-penta-*O*-acetyl-β-D-galactopyranose previously dried (0.366 mmol) in CH_2Cl_2 (3 mL) was cooled to 0°C under argon atmosphere in the dark and TMSI (0.439 mmol) was added to the stirring mixture. The reaction was stirred for 20 min at 0°C. The reaction was stopped by adding 3 mL of dry toluene and co-destilling three times with dry toluene to obtain compound **3** as a slightly yellow oil, which was then dissolved in anhydrous toluene (5 mL) and kept under argon.

To a stirred mixture of TBAI (0.030 mmol) and 4Å molecular sieves (300 mg) in anhydrous toluene (5 mL) under argon at room temperature was added a solution of stannyl derivative (0.305 mmol) in dry toluene (5 mL) and a solution of **3** (0.25 mmol) in dry toluene (5 mL) *via* syringe. The reaction mixture was stirred at 80°C in the dark for 18 h and then diluted with AcOEt (15 mL) and cooled to 0°C. The white precipitate was removed by filtration through a pad of Celite. The organic layer was concentrated *in vacuo* to get the orthoester, which was co-destilled with dry toluene (3 x 5 mL) and placed under vacuum for 1 h before the next reaction.

A solution containing the orthoester in anhydrous CH_2Cl_2 (5 mL) was cooled to 0°C under argon atmosphere, and freshly distilled $BF_3{\cdot}EtO_2$ (0.915 mmol) was added to the stirring mixture. After, the resulting reaction mixture was stirred for 3 h at room temperature, it was quenched with saturated aqueous $NaHCO_3$ solution and 25 mL of AcOEt was added. The aqueous phase was extracted with AcOEt (2 x 15 mL), and the combined organic extract was washed with saturated aqueous $Na_2S_2O_3$ solution (2 x 10 mL) and brine (3 x 10 mL), dried with anhydrous Na_2SO_4, and concentrated *in vacuo*. The resulting residue was purified by flash column chromatography on silica gel using hexane/AcOEt/MeOH as eluent to give the product.

Synthesis of 11. Following the general procedure, the reaction was carried out starting from penta-*O*-acetyl-galactopyranose (142 mg, 0.366 mmol), TMSI (88 mg, 0.839 mmol), TBAI (11 mg, 0.030 mmol) and **8** (188 mg, 0.305 mmol). When the reaction was finished the reaction crude was purified by flash column chromatography on silica gel using hexane-AcOEt-MeOH (85:10:5) as eluent to give 186 mg (93%) of **11** as a unique anomer. TLC (hexane/AcOEt/MeOH 60:30:10) R_f 0.40; m.p. 136–138°C; $[\alpha]_D^{25}$ −5 (c = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.85 (1H, t, *J*=5.2 Hz), 5.39 (1H, d, *J*=3.2 Hz), 5.19 (1H, dd, *J*=10.8, 8.4 Hz), 5.01 (1H, dd, *J*=10.8, 3.6 Hz), 4.46 (1H, d, *J*=8.4 Hz), 4.16-4.13 (2H, m), 3.91 (1H, t, *J*=6.4 Hz), 3.87 (1H, ddd, *J*=10.4, 6.4, 4.0 Hz), 3.67 (1H, ddd, *J*=10.4, 6.8, 3.6 Hz), 3.51 (2H, q, *J*=5.2 Hz), 2.17 (2H, t, *J*=7.2 Hz), 2.07 (3H, s), 2.06 (3H, s), 2.04 (3H, s), 1.98 (3H, s), 1.61 (2H, quint, *J*=7.2, Hz), 1.33 (2H, sex, *J*=7.6, Hz); 1.25 (26H, m), 0.87 (3H, t, *J*=7.2 Hz); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 172.0, 170.2, 170.0, 169.9, 168.8, 100.0, 71.8, 70.9, 68.2, 67.0, 61.2, 61.0, 41.6, 36.5, 31.8, 29.5, 28.6, 25.6, 22.7, 20.7, 20.5 14.1. Anal. Calcd. for $C_{34}H_{59}NO_{11}$: C, 62.08; H, 9.04; N, 2.11. Found: C, 62.02; H, 9.08; N, 2.21.

Synthesis of 16. Following the general procedure, the reaction was carried out starting from penta-*O*-acetyl-galactopyranose (80 mg, 0.206 mmol), TMSI (49 mg, 0.247 mmol), TBAI (6 mg, 0.017 mmol) and **13** (149 mg, 0.172 mmol). When the reaction was finished the reaction crude was purified by flash column chromatography on silica gel using hexane-AcOEt-MeOH (85:10:5) as eluent to give 145 mg (93%) of **16** as a unique anomer. TLC (Hexane/AcOEt/MeOH 60:30:10) R_f 0.50; m.p. 136–138 °C; $[\alpha]_D^{25}$ −11 (c = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz $CDCl_3$): δ 5.37 (1H, d, *J*=3.2 Hz), 5.17

(1H, dd, *J*=10.4, 8.0 Hz), 5.0 (1H, dd, *J*=10.4, 3.2 Hz), 4.47 (1H, d, *J*=8.0 Hz), 4.17-4.01 (2H, m), 3.96 (1H, t, *J*=6.4 Hz), 3.9 (1H, ddd, *J*=10.0, 6.0, 4.0 Hz), 3.77 (1H, ddd, *J*=10.0, 6.4, 3.6 Hz), 3.52 (2H, q, *J*=5.0 Hz), 3.27 (2H, t, *J*=7.2 Hz), 2.32 (2H, t, *J*=7.2 Hz), 2.09 (3H, s), 2.04 (3H, s), 2.02 (3H, s), 1.01 (3H, s), 1.62-1.54 (4H, m), 1.25 (58H, m), 0.87 (6H, t, *J*=7.2 Hz); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 173.0, 170.9, 170.8, 170.5, 170.0, 169.0, 100.1, 72, 71, 68.8, 67.1, 61.5, 58.9, 50.2, 47.3, 34.3, 31.8, 30.4, 29.6, 29.3, 28.9, 28.6, 27.7, 22.7, 20.8, 20.6, 14.1. Anal. Calcd. for $C_{52}H_{95}NO_{11}$: C, 68.61; H, 10.52; N, 1.54. Found: C, 68.59; H, 10.55, N, 1.49.

Synthesis of 17. Following the general procedure, the reaction was carried out starting from penta-*O*-acetyl-galactopyranose (143 mg, 0.368 mmol), TMSI (88 mg, 0.441 mmol), TBAI (11 mg, 0.030 mmol) and **14** (171 mg, 0.307 mmol). When the reaction was finished the reaction crude was purified by flash column chromatography on silica gel using hexane-AcOEt-MeOH (85:10:5) as eluent to give 188 mg (94%) of **17** as a unique anomer. TLC (Hexane/AcOEt/MeOH 60:30:10) R_f 0.60; m.p. 50–52 °C; $[\alpha]_D^{25}$ –21 (c = 1.0, $CHCl_3$).^{1}H NMR (400 MHz, $CDCl_3$): δ 5.8 (1H, dt, *J*=15.6, 6.4 Hz), 5.48 (1H, dd, *J*=15.6, 7.2 Hz), 5.37 (1H, d, *J*=3.2 Hz), 5.19 (1H, dd, *J*=10.5, 7.5 Hz), 5.0 (1H, dd, *J*=10.5, 3.2 Hz), 4.5 (1H, d, *J*=8.0 Hz), 4.25 (1H, dd, *J*=6.8, 6.0 Hz), 4.2-4.06 (2H, m), 3.96 (1H, t, *J*=6.4 Hz), 3.93 (1H, dd, *J*=12.8, 6.0 Hz), 3.69 (1H, dd, *J*=10.4, 4.4 Hz), 3.45 (1H, m), 2.06 (2H, q, *J*=7.2 Hz), 2.05 (3H, s), 2.04 (3H, s), 2.03 (3H, s), 1.96 (3H, s), 1.36 (2H, m), 1.25 (20H, m), 0.87 (3H, t, *J*=7.2 Hz); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 170.2, 169.3, 169.2, 165.0, 139.0, 122.7, 100.5, 72.8, 72.5, 72.0, 71.0, 68.3, 68.1, 63.5, 61.8, 32.4, 31.9, 29.6-28.7, 22.7, 20.6, 20.5, 14.0. Anal. Calcd. for $C_{32}H_{53}N_3O_{11}$: C, 58.61; H, 8.15; N, 6.41. Found: C, 58.80; H, 8.17; N, 6.28.

Synthesis of 18. Following the general procedure, the reaction was carried out starting from penta-*O*-acetyl-galactopyranose (82 mg, 0.211 mmol), TMSI (50 mg, 0.253 mmol), TBAI (6 mg, 0.017 mmol) and **15** (140 mg, 0.176 mmol). When the reaction was finished the reaction crude was purified by flash column chromatography on silica gel using hexane-AcOEt-MeOH (85:10:5) as eluent to give 139 mg (90%) of **18** as a unique anomer. TLC (Hexane/AcOEt/MeOH 60:30:10) R_f 0.60; m.p. 50–52 °C; $[\alpha]_D^{25}$ –13.5 (c = 1.0, $CHCl_3$). ^{1}H NMR (400, MHz $CDCl_3$): δ 5.89 (1H, d, *J*=7.0 Hz), 5.75

(1H, dt, *J*=15.3, 6.7 Hz), 5.49 (1H, dd, *J*=15.3, 7.5 Hz), 5.38 (1H, d, *J*=3.2 Hz), 5.20 (1H, dd, *J*=10.6, 8 Hz), 5.0 (1H, dd, *J*=10.6, 3.6 Hz), 4.47 (1H, d, *J*=8 Hz), 4.25 (1H, dd, *J*=7.5, 3.4 Hz), 4.16 (1H, dd, *J*=10.0, 4.6 Hz), 4.15-3.99 (3H, m), 3.92 (1H, t, *J*=6.4 Hz), 3.65 (1H, dd, *J*=10.0, 3.2 Hz), 2.20 (2H, t, *J*=7.5 Hz), 2.05 (3H, s), 2.04 (3H, s), 2.03 (2H, dt, *J*=7.2, 6.7, Hz), 2.03 (3H, s), 1.99 (3H, s), 1.61 (2H, quint, *J*=7.5 Hz), 1.35 (2H, m), 1.34-1.20 (48H, m), 0.87 (6H, t, *J*=6.9, Hz); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 174.3, 170.2, 170.1, 169.9, 168.8, 133.9, 128.8, 101.0, 71.9, 71.7, 71.0, 68.2, 68.1, 67.1, 61.3, 53.0, 36.0, 31.9, 31.5, 29.0, 29-28.8, 25.5, 21.2, 20.6, 20.5, 13.4. Anal. Calcd. for $C_{49}H_{87}NO_{12}$: C, 66.7; H, 9.94; N, 1.59. Found: C, 66.97; H, 9.63, N, 1.38.

Synthesis of 19. Following the general procedure, the reaction was carried out starting from octa-*O*-acetyl-lactose (143 mg, 0.211 mmol), TMSI (50 mg, 0.253 mmol), TBAI (6 mg, 0.017 mmol) and **15** (140 mg, 0.176 mmol). When the reaction was finished the reaction crude was purified by flash column chromatography on silica gel using hexane-AcOEt-MeOH (85:10:5) as eluent to give 184 mg (90%) of **19** as a unique anomer. TLC (Hexane/AcOEt/MeOH 60:30:10) R_f 0.35; m.p. 50–52 °C; $[\alpha]_D^{25}$ −12.2 (c = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.97 (1H, d, *J*=7.0 Hz), 5.88 (1H, dt, *J*=15.3, 6.7 Hz), 5.53 (1H, dd, *J*=15.3, 7.5 Hz), 5.33 (1H, d, *J*=2.6 Hz), 5.17 (1H, dd, *J*=10.4, 9.2 Hz), 5.08 (1H, dd, *J*=10.4, 8.0 Hz), 4.94 (1H, dd, *J*=10.4, 3.4 Hz), 4.87 (1H, dd *J*=9.6, 8.0 Hz), 4.49 (1H, d, *J*=8.0 Hz), 4.48 (1H, d, *J*=8 Hz), 4.35 (1H, dd, *J*=9.6, 1 Hz), 4.16-4.01 (2H, m), 4.02-3.93 (3H, m), 3.88 (1H, t, *J*=6.4 Hz), 3.81 (1H, t, *J*=9.6 Hz), 3.62 (1H, dd, *J*=10.0, 3.2 Hz), 3.55 (1H, m) 2.20 (2H, t, *J*=7.5 Hz), 2.14 (3H, s), 2.07 (3H, s), 2.05 (3H, s), 2.02 (3H, s), 2.03 (2H, dt, *J*=7.2, 6.7, Hz), 2.01 (3H, s), 1.96 (3H, s), 1.95 (3H, s), 1.61 (2H, quint, *J*=7.5 Hz), 1.35 (2H, m), 1.34-1.20 (48H, m), 0.87 (6H, t, *J*=6.9 Hz); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 173.1, 170.7, 170.6, 170.5, 170.2, 170.1, 169.9, 169.6, 133.5, 128.8, 101.0, 100.7, 76.5, 74.5, 73.1, 73.0, 72.2, 71.4, 71.1, 69.4, 67.9, 67.0, 62.3, 61.2, 52.2, 36.1, 31.9, 31.6, 21.2, 14.1. Anal. Calcd. for $C_{61}H_{103}NO_{20}$: C, 62.59; H, 8.87; N, 1.2. Found: C, 62.87; H, 8.69, N, 1.39.