Supporting Information:

Efficient, One-Pot Syntheses of Biologically Active α Anomeric Glycolipids**

*Wenjun Du, Suvarn S. Kulkarni and Jacquelyn Gervay-Hague**

Department of Chemistry, University of California, Davis,

One Shields Avenue, Davis, CA, 95616 (USA)

Fax number: 530-754-6915

Email: gervay@chem.ucdavis.edu

General Experimental. All reactions were conducted under a dried argon stream. Solvents (CH_2Cl_2 99.8%, benzene 99.8%) were purchased in capped DriSolv™ bottles and used without further purification and stored under argon. TMSI was stored at -15 °C under desiccated atmosphere. All other solvents and reagents were purchased from commercial sources and used without further purification. All glassware utilized was flame-dried before use. Glass-backed TLC plates (Silica Gel 60 with a 254 nm fluorescent indicator) were used without further manipulation and stored over desiccant. Acceptor **6** was purchased from Avanti Polar Lipids Inc (Alabaster, AL). Developed TLC plates were visualized under a short-wave UV lamp, stained with an I_2-SiO_2 mixture, and /or by heating plates that were dipped in ammonium molybdate/cerium (IV) sulfate solution. Silica gel column chromatography was performed using flash silica gel (32-63 μm) and employed a solvent polarity correlated with TLC mobility. 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 600 MHz instrument using $CDCl_3$ (99.9% D) or CD_3OD (99.9%) or pyridine-

d_5 (99.9% D) as the solvent. Chemical shifts are relative to the deuterated solvent peak and are in parts per million (ppm). Mass spectra were acquired using a Qtrap LC/MS instrument. The microwave-assisted reaction was conducted in a Discover Labmate® (CEM Co., Matthews, NC) microwave reactor.

(*2S, 3R, 4E*)-2-(N-stearoylamino)-4-octadecene-1,3-diol (8): To a solution of sphingosine (100 mg, 0.33 mmol) in CH_2Cl_2 (3 mL) was added EDCI (128 mg, 0.66 mmol) and DMAP (cat.). Under stirring, stearic acid (95 mg, 0.33 mmol in 10 mL CH_2Cl_2) was added dropwise over a period time of 16 h. The reaction was stirred under argon for 24 h at rt. Solvent was evaporated and the residue was applied to silica gel column chromatography ($CHCl_3$:MeOH = 9:1, R_f = 0.43) to afford **8** as a white powder (140 mg, 75%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.88 (t, *J* = 6.8 Hz, 6H), 1.26-1.40 (m, 50H), 1.64 (t, *J* = 7.2 Hz, 2H), 2.06 (dd, *J* = 14.4, 7.2 Hz, 2H), 2.24 (t, *J* = 7.2 Hz, 2H), 3.71 (m, 1H), 3.91-3.97 (m, 2H), 4.32 (m, 1H), 5.42 (dd, *J* = 15.6, 6.6 Hz, 1H), 5.79 (dt, *J* = 15.6, 6.6 Hz, 1H), 6.28 (d, *J* = 7.2 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 14.3, 22.9, 26.0, 29.4, 29.5, 29.6, 29.7, 29.8, 29.9, 32.2, 32.6, 54.7, 62.8, 74.9, 129.0, 134.6, 174.2. ESIMS calc'd for $C_{36}H_{71}NNaO_3$ $[M+Na]^+$ 588.53, found: 588.18.

(*2S, 3R, 4R*)-2-(N-stearoylamino)-octadecane-1,3,4-triol (9): To a solution of phytosphingosine (99 mg, 0.31 mmol) in pyridine (3 mL) was added EDCI (128 mg, 0.66 mmol) and DMAP (cat.). Under stirring, stearic acid (90 mg, 0.31 mmol, in 15 mL CH_2Cl_2) was added dropwise over a period time of 16 h. The reaction was stirred under argon for 24 h at rt. Solvent was evaporated and the residue was applied to silica gel column chromatography ($CHCl_3$:MeOH = 88:12, R_f = 0.35) to afford **9** as a white powder (120 mg,

68%). ^{1}H NMR (600 MHz, $CDCl_3$:CD_3OD = 90:10) δ 0.74 (t, *J* = 7.2 Hz, 6H), 1.11-1.64 (m, 52), 1.31-1.58 (m, 4H), 2.07 (d, *J* = 7.8 Hz, 2H), 3.40 (m, 2H), 3.55 (dd, *J* = 11.4, 5.4 Hz, 1H), 3.64 (dd, *J* = 11.4, 3.6 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$:CD_3OD = 90:10) δ 13.9, 22.6, 25.8, 25.9, 29.3, 29.4, 29.5, 29.6, 29.7, 29.8, 29.9, 31.9, 33.1, 36.6, 52.1, 61.2, 72.6, 75.8, 174.7. ESIMS calc'd for $C_{36}H_{73}NNaO_4$ $[M+Na]^+$ 606.54, found: 606.54.

1-*O*-Palmitoyl-2-*O*-oleoyl-3-*O*-α-D-galactopyranosyl-*sn*-glycerol (BbGL-II, 1a): To a solution of 1,2,3,4,6-penta-*O*-trimethylsilyl-D-galactopyranose (**4**, 81 mg, 0.15 mmol) in CH_2Cl_2 (3 mL) at 0 °C was added TMSI (30 mg, 0.15 mmol). The reaction was stirred under argon at 0 °C for 20 min. The reaction was stopped by adding 15 mL of anhydrous benzene and solvent was evaporated under reduced pressure. The slightly yellow oil **5** was dissolved in CH_2Cl_2 (1.5 mL) and kept under argon. In a separate flask, molecular sieves (MS, 4 Å, 50 mg), TBAI (220 mg, 0.60 mmol), **6** (29 mg, 0.050 mmol) and DIPEA (58 mg, 0.45 mmol) were added into CH_2Cl_2 (1.5 mL). The mixture was stirred under argon at rt. The glycosyl iodide **5** was added dropwise and the reaction mixture was stirred at rt for 24 h. Solvent was evaporated. MeOH (15 mL) and Dowex® 50WX8-200 ion exchange resin (1 g) were added and the reaction was stirred at rt for 4 h. Resin was removed by filtration. The solvent was removed *in vacuo* and the resulting residue was purified by silica gel chromatography ($CHCl_3$:MeOH = 10:1, R_f = 0.36) to afford **1a** as a white powder (31 mg, 81%). $[\alpha]_D^{25}$ +29^o (c = 1.0, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.87 (t, *J* = 6.8 Hz, 6H), 1.24-1.40 (m, 44 H), 1.67 (dd, *J* = 11.4, 7.2 Hz, 4H), 2.00 (dd, *J* = 12.0, 6.0 Hz, 4H), 2.31 (dt, *J* = 7.8, 5.4 Hz, 4H), 2.45 (s, 1H), 2.94 (s, 1H), 3.10 (s, 1H), 3.63 (m, dd, *J* = 10.8, 6.0 Hz, 1H, H-3a), 3.70-3.90 (m, 6H, H-2', H-4', H-5', H6a', H6b', H-3b), 4.05-4.08 (m, 1H,

H-3'), 4.13 (dd, *J* = 6.0, 12.0 Hz, 1H, H-1b), 4.37 (dd, *J* = 3.6, 12.0 Hz, 1H, H-1a), 4.92 (d, *J* = 3.6 Hz, 1H, H-1'), 5.24 (dt, *J* = 9.6, 5.4 Hz, 1H, H-2), 5.34 (dt, *J* = 15.6, 6.8 Hz, 2H, CH=CH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 14.1, 22.67, 22.68, 24.9, 27.16, 27.21, 29.12, 29.19, 29.28, 29.31, 29.32, 29.35, 29.49, 29.52, 29.63, 29.65, 29.66, 29.69, 29.74, 31.90, 31.92, 34.1, 34.3, 62.1, 63.1, 66.6, 69.3, 69.8, 70.0, 70.2, 70.8, 99.3, 129.7, 130.0, 173.3, 173.6; ESIMS calc'd for $C_{43}H_{80}NaO_{10}$ $[M+Na]^+$ 779.56, found: 779.52.

1-*O*-Oleoyl-2-*O*-Palmitoyl-3-*O*-α-D-galactopyranosyl-*sn*-glycerol (BbGL-II, 1b): To a solution of 1,2,3,4,6-penta-*O*-trimethylsilyl-D-galactopyranose (**4**, 55 mg, 0.10 mmol) in CH_2Cl_2 (1.5 mL) at 0 °C was added TMSI (22 mg, 0.11 mmol). The reaction was stirred under argon at 0 °C for 20 min. The reaction was stopped by adding 15 mL of anhydrous benzene and solvent was evaporated under reduced pressure. The slightly yellow oil **5** was dissolved in CH_2Cl_2 (1.5 mL) and kept under argon. In a separate flask, molecular sieves (MS, 4 Å, 50 mg), TBAI (114 mg, 0.30 mmol), **7** (20 mg, 0.034 mmol) and DIPEA (39 mg, 0.30 mmol) were added into CH_2Cl_2 (1.5 mL). The mixture was stirred under argon at rt. The glycosyl iodide **5** was added dropwise and the reaction mixture was stirred at rt for 36 h. Solvent was evaporated. MeOH (15 mL) and Dowex® 50WX8-200 ion exchange resin (0.5 g) were added and the reaction was stirred at rt for 4 h. Resin was removed by filtration. The solvent was removed *in vacuo* and the resulting residue was purified by silica gel chromatography ($CHCl_3$:MeOH = 10:1, R_f = 0.36) to afford **1b** as a white powder (18 mg, 72%). $[\alpha]_D^{27}$ +46° (c = 1.1, $CHCl_3$); IR ($CHCl_3$) ν 3458, 3397, 2915, 2852, 1734, 1656, 1462, 1378, 1242, 1150, 1073, 1054, 971, 799, 720 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.87 (t, *J* = 6.9 Hz, 6H, CH_3), 1.24-1.36 (m, 44 H, CH_2), 1.59 (dd, *J* = 6.9, 13.5 Hz, 4H,

CH_2), 2.00 (dd, *J* = 6.0, 12.0 Hz, 4H, CH_2), 2.31 (dt, *J* = 4.2, 5.4 Hz, 4H, CH_2), 2.80 (s, 2H, OH), 3.55 (s, 1H, OH), 3.61 (dd, *J* = 10.8, 6.0 Hz, 1H, H-3a), 3.74-3.94 (m, 6H, H-2', H-4', H-5', H-6a', H-6b', H-3b), 4.03-4.12 (m, 1H, H-3'), 4.13 (dd, *J* = 6.0, 12.0 Hz, 1H, H-1a), 4.36 (dd, *J* = 2.4, 12.0 Hz, 1H, H-1b), 4.92 (d, *J* = 2.4 Hz, 1H, H-1'), 5.24 (dt, 1H, *J* = 5.4, 10.2 Hz, H-2), 5.34 (ddd, *J* = 6.0, 11.4, 20.4 Hz, 2H, CH=CH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 14.1, 22.68, 22.69, 24.85, 24.90, 27.17, 27.21, 29.11, 29.13, 29.15, 29.21, 29.31, 29.36, 29.5, 29.66, 29.69, 29.71, 29.76, 31.90, 31.92, 34.1, 34.3, 62.2, 62.8, 66.6, 69.2, 69.8, 70.0, 70.2, 70.7, 99.3, 129.7, 130.0, 173.3, 173.6; HRMS MALDI calc'd for $C_{43}H_{80}NaO_{10}$ $[M+Na]^+$ 779.5614, found: 779.5434.

1-*O*-Palmitoyl-2-*O*-stearoyl-3-*O*-α-D-galactopyranosyl-*sn*-glycerol (1c): BbGl-II (**1a**, 26 mg, 0.034 mmol) and Pd/C (26 mg, 100% w/w) was suspended in a solution of CH_2Cl_2 (2 mL) and MeOH (8 mL). The reaction mixture was placed on a hydrogenation shaker and subjected to hydrogenation under a pressure of 65 psi for 18 h. The reaction mixture was filtered through Celite and washed with copious amounts solvent of MeOH/CH_2Cl_2 (80/20, v/v). The filtrate was collected and concentrated under reduced pressure and the resulting residue was purified with silica gel chromatography ($CHCl_3$:MeOH = 10:1, R_f = 0.36) to afford **1c** (24 mg, 93%) as a white powder. $[\alpha]_D^{25}$ +35° (c = 0.5, pyridine). ^{1}H NMR (600 MHz, C_5D_5N) δ 0.88 (t, *J* = 6.6 Hz, 6H), 1.27-1.39 (m, 52H), 1.68-1.72 (m, 4H), 2.43-2.49 (m, 4H), 3.95 (dd, *J* = 10.2, 6.0 Hz, 1H), 4.30 (dd, *J* = 10.2, 6.0 Hz, 1H), 4.47-4.51 (m, 3H), 4.55-4.58 (m, 2H), 4.67 (d, *J* = 2.4 Hz, 1H), 4.72 (dd, *J* = 9.6, 3.6 Hz, 1H), 4.77 (dd, *J* = 11.4, 3.6 Hz, 1H), 5.44 (d, *J* = 3.6 Hz, 1H), 5.70 (m, 1H). ^{13}C NMR (150 MHz, C_5D_5N) δ 14.7, 23.4, 25.7, 29.8, 30.0, 30.1, 30.2, 30.3, 30.4, 30.5, 32.6, 34.7, 34.9, 63.0, 63.4, 66.7,

70.8, 71.2, 71.4, 71.9, 73.6, 101.7, 173.6, 173.8. ESIMS calc'd for $C_{43}H_{82}NaO_{10}$ $[M+Na]^+$ 781.58, found: 781.32.

(***2S, 3R, 4E*)-1-*O*-(α-D-Galactopyranosyl)-2-(*N*-octadecanosylamino)-4-1,3-octadecenediol** (**2**): To a solution of 1,2,3,4,6-penta-*O*-trimethylsilyl-D-galactopyranose (**4**, 108 mg, 0.20 mmol) in CH_2Cl_2 (3 mL) at 0 °C was added TMSI (40 mg, 0.20 mmol). The reaction was stirred under argon for 15 min. and was stopped by adding 15 mL of anhydrous benzene. Solvent was evaporated under reduced pressure and the slightly yellow oil **5** was dissolved in CH_2Cl_2 (10 mL) and kept under argon. In a separate flask, molecular sieves (MS, 4 Å, 50 mg), TBAI (220 mg, 0.60 mmol), **8** (38 mg, 0.066 mmol) and DIPEA (77 mg, 0.60 mmol) were added into CH_2Cl_2 (1.5 mL). The mixture was stirred under argon at rt. The glycosyl iodide **5** was added dropwise and the reaction mixture was stirred at rt for 48 h. Solvent was evaporated. MeOH (15 mL) and Dowex® 50WX8-200 ion exchange resin (1 g) were added and the reaction was stirred at rt for 4 h. Resin was removed by filtration. The solvent was removed *in vacuo* and the resulting residue was purified by silica gel chromatography ($CHCl_3$:MeOH = 87:13, R_f = 0.35). The slightly yellow powder was washed with small amount of cold EtOAc (1 mL) to afford **2** as a white powder (37 mg, 77%). $[\alpha]_D^{25}$ +29° (c = 1.0, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3/CD_3OD$ = 9:1) δ 0.82 (t, *J* = 7.2 Hz, 6H), 1.20-1.35 (m, 50 H), 1.54 (t, *J* = 7.8 Hz, 2H), 1.98 (dd, *J* = 14.4, 7.2 Hz, 2H), 2.13 (t, *J* = 7.2 Hz, 2H), 3.61 (dd, *J* = 10.8, 4.8 Hz, 1H), 3.66-3.78 (m, 6H), 3.91-3.93 (m, 2H), 4.03 (d, *J* = 6 Hz, 1H), 4.81 (d, *J* = 3.6 Hz, 1H), 5.38 (dd, *J* = 15.6, 6.6 Hz, 1H), 5.74 (dt, *J* = 15.6, 6.6 Hz, 1H), 6.98 (d, *J* = 9.0 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3/CD_3OD$ = 9:1) δ 14.2, 22.8, 26.0, 29.4, 29.5, 29.6, 29.7, 29.8, 29.9, 32.1, 32.5, 36.7,

53.6, 62.2, 68.1, 69.1, 70.0, 70.4, 70.5, 72.9, 100.0, 128.9, 134.2, 174.7. ESIMS calc'd for $C_{42}H_{81}NNaO_8$ $[M+Na]^+$ 750.59, found: 750.66.

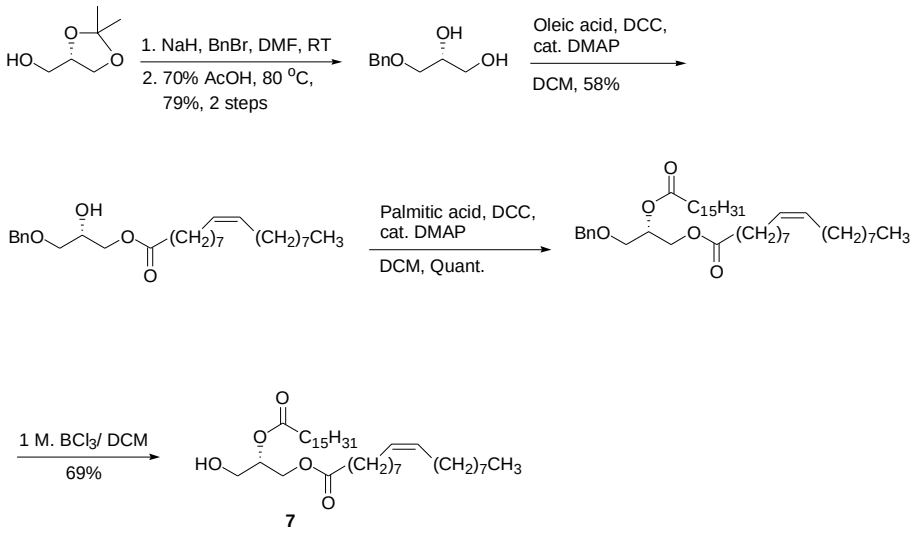
(*2S, 3S, 4R*)-1-*O*-(α-D-Galactopyranosyl)-2-(*N*-octadecanosylamino)-1,3,4-octadecanetriol (3): The synthetic protocol of **3** is the same as described for compound **2** as a white powder (15 mg, 30%). ^{1}H NMR (600 MHz, C_5D_5N) δ 0.88 (t, *J* = 6.8 Hz, 6H), 1.25-1.34, m, 50H), 1.68 (m, 1H), 1.82 (m, 2H), 1.88 (m, 2H), 2.35 (m, 1H), 2.46 (t, *J* = 7.2 Hz, 2H), 4.35 (m, 2H), 4.40-4.48 (m, 4H), 4.53-4.58 (m, 2H), 4.65-4.70 (m, 2H), 5.30 (m, 1H), 5.61 (d, *J* = 3.6 Hz, 1H), 8.54 (d, *J* = 9.2 Hz, 1H). ^{13}C NMR (150 MHz, C_5D_5N) δ 14.6, 23.3, 26.7, 26.9, 30.0, 30.1, 30.2, 30.23, 30.3, 30.4, 30.5, 30.7, 32.5, 34.7, 37.2, 51.9, 63.1, 69.1, 70.7, 71.4, 71.9, 72.9, 73.4, 77.1, 101.9, 173.6. ESIMS calc'd for $C_{42}H_{83}NO_9$ $[M+Na]^+$ 768.60, found: 768.78.

Microwave-assisted glycosylation and one-pot synthesis of compound **3**:

To a solution of 1,2,3,4,6-penta-*O*-trimethylsilyl-D-galactopyranose (**4**, 33 mg, 0.051 mmol) in CH_2Cl_2 (3 mL) at 0 °C was added TMSI (12.4 mg, 0.051 mmol). The reaction was stirred at 0 °C for 20 min and was stopped by adding 15 mL of anhydrous benzene. Solvent was removed under reduced pressure and the slightly yellow oil **5** was dissolved in CH_2Cl_2 (3 mL) and was transferred into a 10 mL microwave reaction test tube. TBAI (19 mg, 0.051 mmol), **9** (30 mg, 0.051 mmol) and DIPEA (20 mg, 0.153 mmol) were added into the test tube and the tube was placed into a microwave reactor. The reaction was conducted at 130 ^{o}C for 90 min at 225 watts. The reaction mixture was transferred to a flask and solvent was removed under reduced pressure. MeOH (10 mL) and Dowex® 50WX8-200 ion exchange

resin (1 g) was added and the reaction was stirred at rt for 4 h. The work-up and purification was the same as mentioned above to afford **3** as white powder (37 mg, 67%).

Synthesis of lipid chain acceptor 7



3-*O*-Benzyl-*sn*-glycerol: To a solution of S(+) 2,2-dimethyl-1,3-dioxolane-4-methanol (0.48 g, 3.63 mmol) in DMF (5 mL) at 0 ^{o}C was added NaH (0.13 g, 5.45 mmol) portion wise, followed by benzyl bromide (0.68 g, 3.99 mmol). The reaction was allowed to reach rt and stirred overnight. It was quenched with addition of a few drops of methanol followed by Ethyl acetate (10 mL) and water (10 mL). The organic layer was separated and the aqueous layer was extracted with ethyl acetate (3 x 10 mL). Combined organic layer was dried on anhyd. sodium sulfate and concentrated *in vacuo* to get crude residue as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$), δ 1.36 (s, 3H, CH_3), 1.41 (s, 3H, CH_3), 3.46 (dd, J = 5.4, 10.4 Hz, 1H, CH_2), 3.55 (dd, J = 5.4, 10.4 Hz, 1H, CH_2), 3.73 (dd, J = 8.4, 6.6 Hz, 1H, CH_2), 4.05 (dd, J = 8.4, 6.6 Hz, 1H, CH_2), 4.30 (dt, J = 6.0, 12.0 Hz, 1H, CH), 4.55, 4.59 (ABq, J = 12.0 Hz, 2H, PhCH_2), 7.20-7.40 (m, 5H, Ar*H*); ^{13}C NMR (150 MHz, $CDCl_3$) δ 25.6, 27.0, 67.1, 71.3, 73.8, 75.0, 109.6, 127.87, 127.96, 127.98, 128.0, 128.6, 138.2.

This crude product was added with 70% aqueous AcOH solution (10 mL). The reaction mixture was heated at 80 ^{o}C for 30 min and concentrated *in vacuo*. Flash olumn chromatography (EtOAc; hexane 1:1 (*Rf* = 0.3)) afforded pure diol (0.52 g, 79% in 2 steps). IR ($CHCl_3$) ν 3366, 2896, 1496, 1453, 1365, 1209, 1073, 741, 698 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.78 (brs, 2H, OH), 3.46 (dd, *J* = 6.6, 9.6 Hz, 1H, CH_2OBn), 3.55 (dd, *J* = 5.4, 9.6 Hz, 1H, CH_2OBn), 3.60 (dd, *J* = 6.0, 12.0 Hz, 1H, CH_2OH), 3.68 (dd, *J* = 3.6, 12.0 Hz, 1H, CH_2OH), 3.88 (tt, *J* = 2.1, 3.9 Hz, 1H, CH), 4.58 (s, 2H, PhCH_2), 7.20-7.40 (m, 5H, Ar*H*); ^{13}C NMR (150 MHz, $CDCl_3$) δ 64.0, 70.7, 71.7, 73.5, 127.8, 127.9, 128.5, 137.6.

3-*O*-Benzyl-1-*O*-oleyl-*sn*-glycerol: A solution of 3-*O*-benzyl-*sn*-glycerol (400 mg, 2.20 mmol) in dry CH_2Cl_2 (12 mL) was cooled to 0 ^{o}C. An 8 mL solution of DCC (906 mg, 4.39 mmol), DMAP (10 mg, 0.07 mmol) and oleic acid (620 mg, 2.19 mmol) in CH_2Cl_2 was added to it in a slow drop-wise manner over a period of 1 h. The reaction was stirred for 12 h at rt. The mixture was filtered over Celite, washed with saturated aqueous sodium bicarbonate solution and brine, dried on anhyd. sodium sulfate and concentrated *in vacuo*. The residue was purified by flash column chromatography using silica gel (Hexane: EtOAc = 4:1, R_f = 0.35) to get monoacylated product (568 mg, 58%) as colorless oil. $[\alpha]_D^{28}$ +1^{o} (C = 1.1, $CHCl_3$); IR ($CHCl_3$) ν 3448, 3004, 2923, 2854, 1734, 1656, 1456, 1369, 1253, 1175, 1096, 1021, 735, 697 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.88 (t, *J* = 7.2 Hz, 3H, CH_3), 1.24-1.36 (m, 20H, CH_2), 1.60 (dt, *J* = 7.2, 14.4 Hz, 2H, CH_2), 2.02 (dd, *J* = 6.6, 13.2 Hz, 4H, CH_2), 2.31 (t, *J* = 7.8 Hz, 2H, CH_2), 2.60 (s, 1H, OH), 3.46 (dd, *J* = 6.0, 9.0 Hz, 1H, CH_2OBn), 3.55 (dd, *J* = 4.8, 9.6 Hz, 1H, CH_2OBn), 4.00-4.06 (m, 1H, *CH*OH), 4.13 (dd, *J* = 6.6, 11.4 Hz, 1H, CH_2OAcyl), 4.18 (dd, *J* = 4.2, 11.4 Hz, 1H, CH_2OAcyl), 4.58 (s, 1H,

Ph*CH*$_2$), 5.35 (ddd, *J* = 6.0, 11.4, 15.6 Hz, 2H, CH=CH), 7.20-7.40 (m, 5H, Ar*H*); ^{13}C NMR (150 MHz, $CDCl_3$) δ 14.1, 22.6, 24.9, 27.1, 27.2, 29.0, 29.1, 29.3, 29.5, 29.6, 29.7, 31.9, 34.1, 65.3, 68.9, 70.8, 73.5, 127.7, 127.8, 128.4, 129.7, 130.0, 137.6, 173.9; EMSI calc'd for $C_{28}H_{46}NaO_4$ $[M+Na]^+$ 469.33, found: 469.50.

3-*O*-Benzyl-1-*O*-oleyl-2-*O*-palmitoyl-*sn*-glycerol: A 4 mL solution of DCC (111 mg, 0.54 mmol), DMAP (3 mg, 0.02 mmol) and palmitic acid (86 mg, 0.34 mmol) in CH_2Cl_2 was cooled to 0 ^{o}C. A solution of 3-*O*-Benzyl-1-*O*-oleyl-*sn*-glycerol (100 mg, 0.228 mmol) in CH_2Cl_2 (2 mL) was added to it in a drop-wise manner and stirred for 12 h at rt. The mixture was filtered over Celite, washed with saturated aqueous sodium bicarbonate solution and brine, dried on anhydrous sodium sulfate and concentrated *in vacuo*. The residue was purified by flash column chromatography using silica gel (Hexane:EtOAc = 15:1, R_f = 0.35) to get the product (154 mg, quantitative) as colorless oil. $[\alpha]_D^{28}$ +5^o (c = 2.0, $CHCl_3$); IR ($CHCl_3$) ν 2924, 2854, 1742, 1651, 1460, 1369, 1241, 1164, 1109, 1028, 733, 698 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.88 (t, *J* = 7.2 Hz, 6H, CH_3), 1.22-1.38 (m, 44H, CH_2), 1.52 (dt, *J* = 7.2, 14.4 Hz, 4H, CH_2), 1.94 (dd, *J* = 6.6, 12.6 Hz, 4H, CH_2), 2.20 (t, *J* = 7.8 Hz, 2H, CH_2), 2.24 (t, *J* = 7.8 Hz, 2H, CH_2), 3.51 (ddd, *J* = 5.0, 10.2, 15.6 Hz, 2H, *CH*$_2$OBn), 4.11 (dd, *J* = 5.4, 12.0 Hz, 1H, *CH*$_2$OAcyl), 4.27 (dd, *J* = 3.6, 12.0 Hz, 1H, *CH*$_2$OAcyl), 4.44, 4.48 (ABq, *J* = 12.0 Hz, 2H, Ph*CH*$_2$), 4.06 (dt, *J* = 4.2, 9.0 Hz, 1H, CH), 5.35 (ddd, *J* = 6.0, 11.4, 15.6 Hz, 2H, CH=CH), 7.20-7.32 (m, 5H, Ar*H*); ^{13}C NMR (150 MHz, $CDCl_3$) δ 14.1, 22.65, 22.66, 24.8, 24.9, 27.1, 27.2, 29.06, 29.09, 29.16, 29.27, 29.29, 29.33, 29.46, 29.50, 29.61, 29.63, 29.67, 29.74, 31.88, 31.90, 34.1, 34.3, 62.6, 68.2, 70.0,

73.3, 127.6, 127.7, 128.4, 129.7, 130.0, 137.7, 173.0, 173.3; EMSI calc'd for $C_{44}H_{76}NaO_5$ $[M+Na]^+$ 707.56, found: 707.50.

1-*O*-Oleyl-2-*O*-palmitoyl-*sn*-glycerol 7: To a solution of 3-*O*-Benzyl-1-*O*-oleyl-2-*O*-palmitoyl-*sn*-glycerol (110 mg, 0.16 mmol) in 2 mL CH_2Cl_2 at -78 ^oC, boron trichloride (0.35 mL, 0.35 mmol) (1 M in CH_2Cl_2) was added over a period of 15 min. The reaction was stirred for 30 min under argon. The contents of the flask were then poured over ice water, the aqueous layer separated and extracted with CH_2Cl_2 (10 mL x 3), dried over anhydrous sodium sulfate and concentrated *in vacuo*. The crude product was purified using silica gel column chromatography (Hexane:EtOAc = 19:1~7:1 (R_f = 0.35) gradient) to get the alcohol (66 mg, 69%) as colorless oil. $[\alpha]_D^{27}$ -3^o (C = 1.1, $CHCl_3$); IR ($CHCl_3$) ν 3442, 2911, 2853, 1736, 1652, 1460, 1374, 1239, 1167, 1116, 1094, 1053, 722, 700 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 0.88 (t, *J* = 7.2 Hz, 6H, CH_3), 1.22-1.36 (m, 44H, CH_2), 1.52 (dt, *J* = 7.2, 14.4 Hz, 4H, CH_2), 1.94 (dd, *J* = 6.0, 12.0 Hz, 4H, CH_2), 2.05 (s, 1H, OH), 2.20 (t, *J* = 7.8 Hz, 2H, CH_2), 2.24 (t, *J* = 7.8 Hz, 2H, CH_2), 3.72 (s, 2H, *CH_2*OH), 4.25 (dd, *J* = 6.0, 12.0 Hz, 1H, *CH_2*OAcyl), 4.31 (dd, *J* = 4.8, 12.0 Hz, 1H, *CH_2*OAcyl), 4.00-4.06 (dt, *J* = 4.8, 10.2 Hz, 1H, CH), 5.35 (ddd, *J* = 6.0, 10.8, 16.2 Hz, 2H, CH=CH);^{13}C NMR (150 MHz, $CDCl_3$) δ 14.1, 22.66, 22.67, 24.78, 24.82, 24.84, 24.91, 27.14, 27.19, 29.06, 29.08, 29.15, 29.25, 29.30, 29.46, 29.50, 29.60, 29.63, 29.66, 29.67, 29.71, 29.74, 31.83, 31.88, 31.90, 34.1, 34.3, 61.5, 62.0, 72.1, 129.7, 130.0, 173.4, 173.8; EMSI calc'd for $C_{37}H_{70}NaO_5$ $[M+Na]^+$ 617.51, found: 617.60.