Supplementary Information

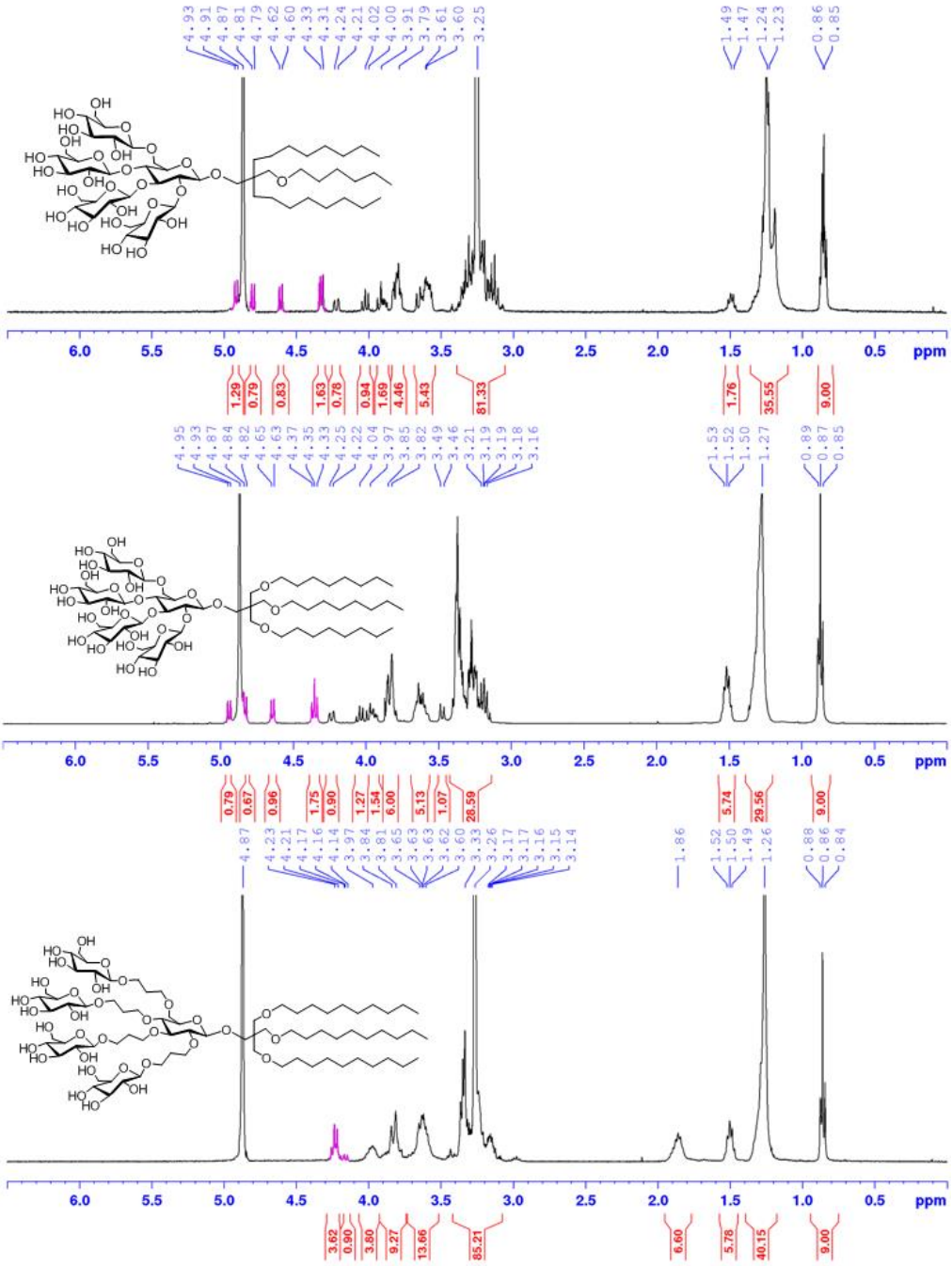


Fig. S1. A full range of ^{1}H NMR spectra of representative TPSs (TPS-A8 (a), TPS-E8 (b) and TPS-E10L (c)) dissolved in CD_3OD. The anomeric proton peaks were well dispersed in the range of 4.25 to 4.95 ppm for TPS-A6 and TPS-E8 while the corresponding peaks of TPS-E10L were collapsed into a small region (4.15~4.30 ppm). The anomeric peaks were indicated in purple and the other peaks were in black.

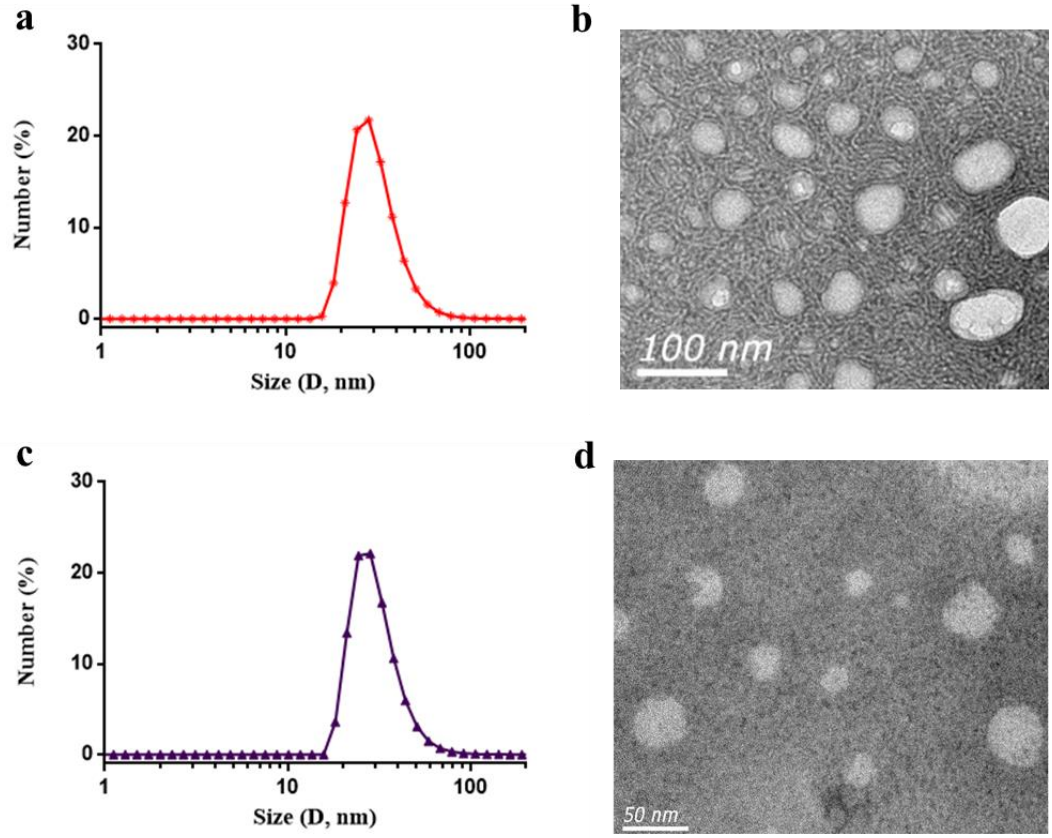


Fig. S2. Hydrodynamic diameter distributions measured by dynamic light scattering (DLS) (a, c) and negative staining TEM images (b, d) of TPS-E8 and TPS-E11L dissolved in water. Detergent samples for EM analysis were stained with 2 % phosphotungstic acid.

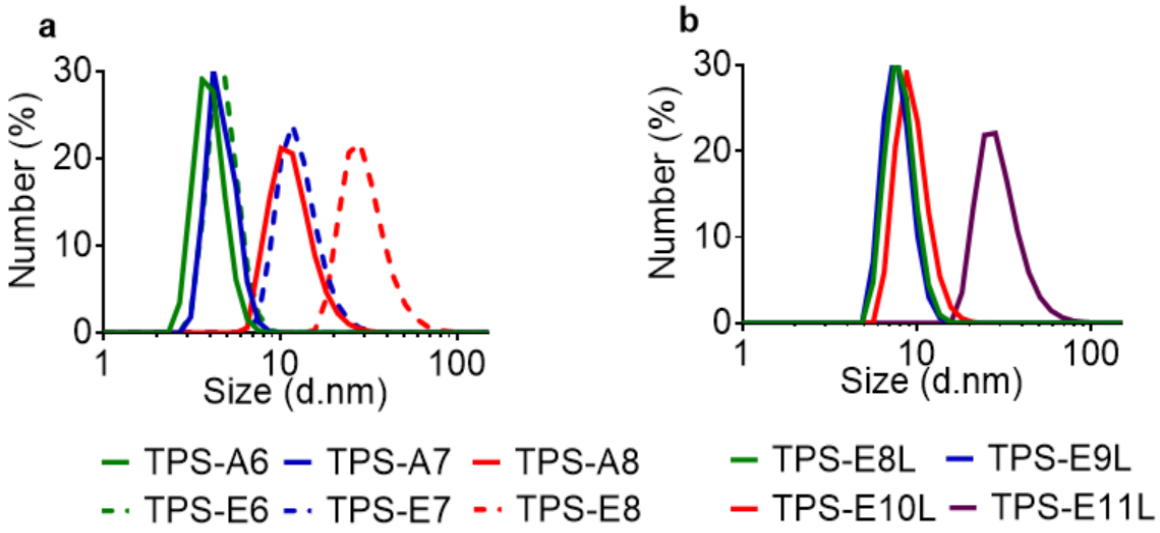


Fig. S3. Micellar profiles of individual novel agents (TPS-A/Es (a) and TPS-ELs (b)) estimated by dynamic light scattering (DLS). Detergents include TPSs (TPS-A6, TPS-A7, TPS-A8; TPS-E6, TPS-E7, TPS-E8) and TPS-ELs (TPS-E8L, TPS-E9L, TPS-E10L, TPS-E11L) and were tested at 1.0 wt% for this measurement. Based on scattered light intensity, the time scale of micelle movements was analyzed, which gives micellar distribution in term of the hydrodynamic diameter (R_h). All these agents tend to form a single set of micelles.

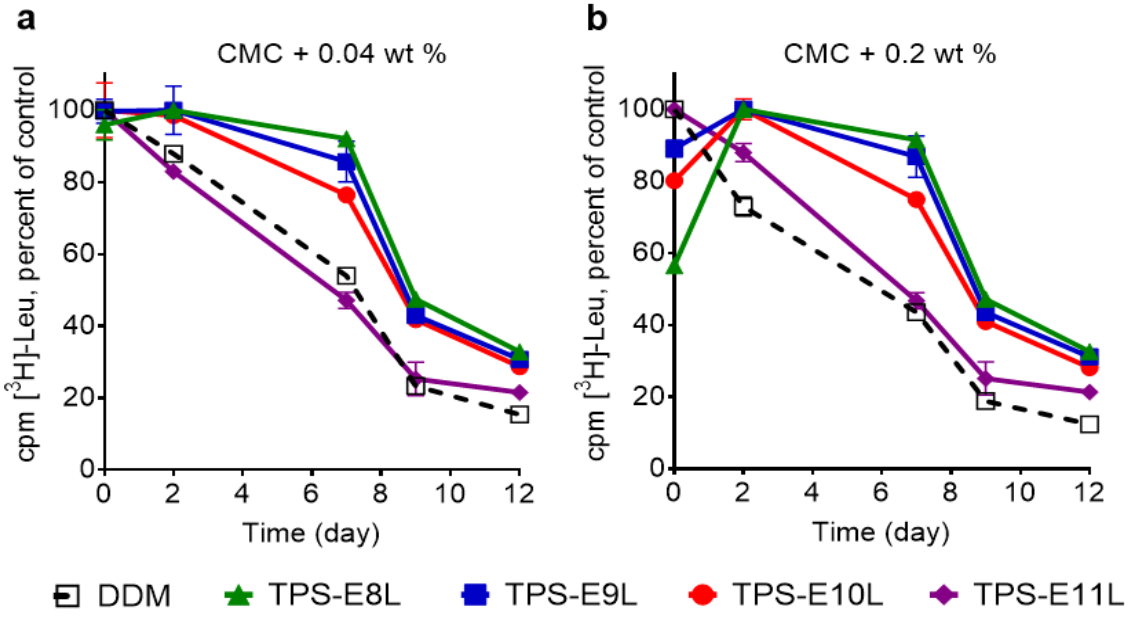


Fig. S4 Long-term stability of LeuT solubilized in DDM or a TPS-EL (TPS-E8L, TPS-E9L, TPS-E10L, or TPS-E11L). The detergents were tested at CMC + 0.04 wt% (a) or CMC + 0.2 wt% (b). DDM-purified transporter was mixed with individual detergent-containing solutions and then incubated for 12 days at room temperature. During the incubation, LeuT stability was monitored at regular intervals by measuring the ability to bind radio-labeled substrate ([^{3}H]-Leu) *via* scintillation proximity assay (SPA). Errors, SEM; $n = 3$.

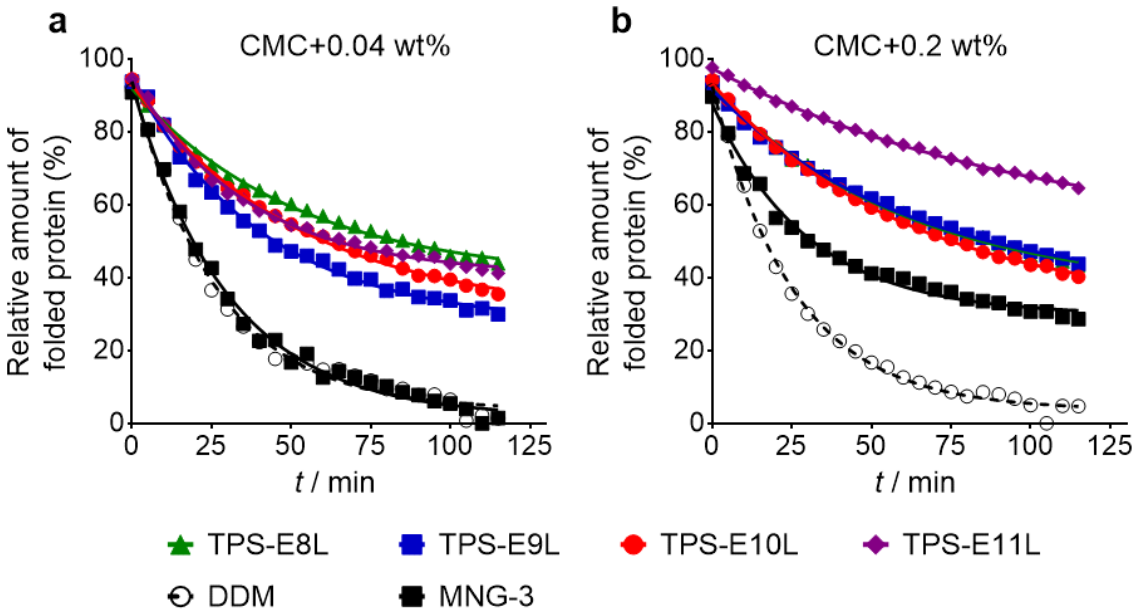


Fig. S5 Thermal denaturation profile of UapA purified in DDM, MNG-3, and a TPS-EL (TPS-E8L, TPS-E9L, TPS-E10L, or TPS-E11L). DDM-purified transporter was diluted into solutions containing individual detergents to reach a final detergent concentration of CMC + 0.04 wt% (a) or CMC + 0.2 wt% (b). Thermal stability of the transporter was monitored by CPM assay performed at 40 °C for 120 min. The relative amounts of folded protein were normalized relative to the most destabilizing condition in this experiment, that is, protein denaturation in DDM or MNG-3 after 120-min incubation. The data is a representative of three experiments.

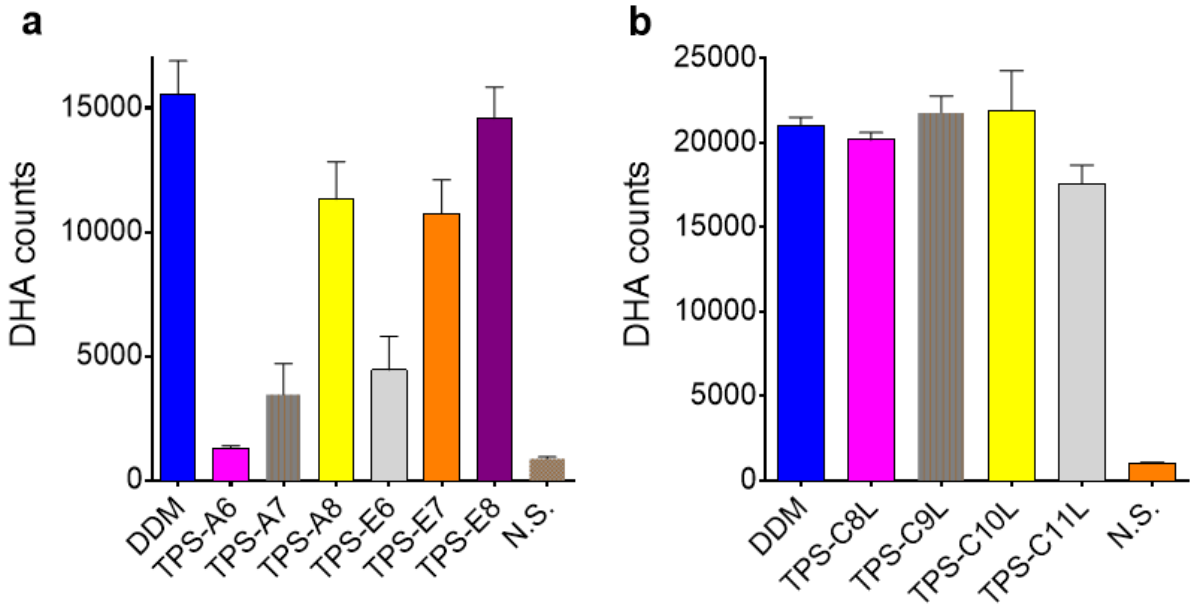


Fig. S6 Ligand binding activity for β_2AR solubilized in DDM, a TPS-A/E (TPS-As: TPS-A6, TPS-A7 and TPS-A8; TPS-Es: TPS-E6, TPS-E7 and TPS-E8) (a) or a TPS-EL (TPS-E8L, TPS-E9L, TPS-E10L, or TPS-E11L) (b). DDM-purified β_2AR was diluted to each detergent solution to give a final detergent concentration of 0.2 wt%. Receptor activity solubilized in individual detergents was measured using the antagonist ([^{3}H]-dihydroalprenolol (DHA)) *via* radiolabeled ligand-binding assay. N.S. represents a nonspecific binding. Errors, SEM; $n = 3$.

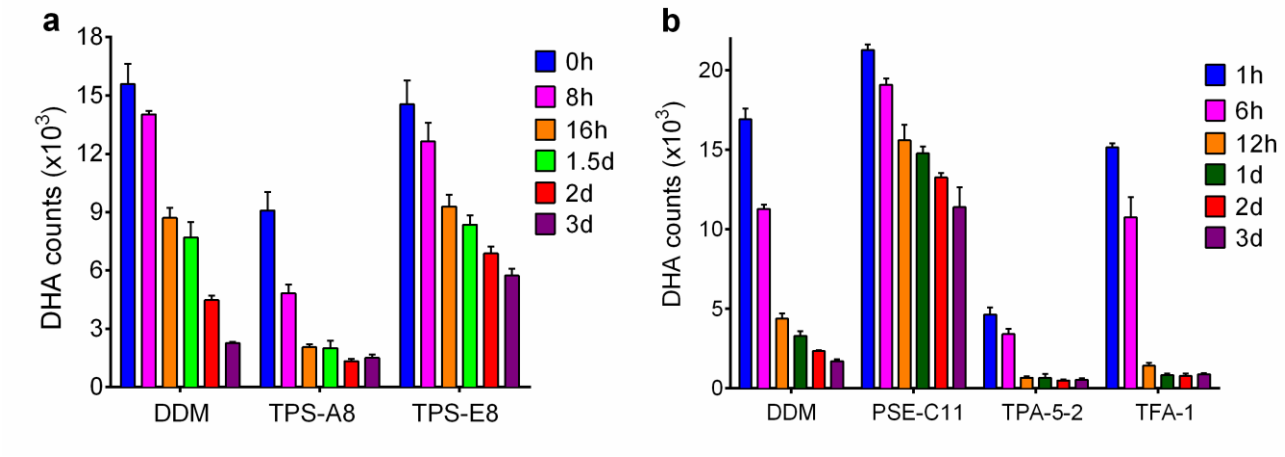


Fig. S7 Long-term stability of β_2AR solubilized in DDM, TPS-A8 and TPS-E8 (a) as well as previously developed novel agents (PSE-C11, TPA-5-2 and TFA-1) (b). 0.1% DDM-purified β_2AR was diluted into the individual detergent solutions. All the detergents were tested at 0.2%. Receptor activity was monitored at regular intervals during a 3-day incubation at room temperature, by measuring the ability to bind the antagonist **(**[^{3}H]-dihydroalprenolol (DHA)**)** *via* radiolabeled ligand-binding assay. Errors, SEM; $n = 3$.

Critical micelle concentration (CMC) determination by diphenylhexatriene (DPH) encapsulation

Critical micelle concentration (CMC) of TPSs detergents was determined by Synergy Mx Monochromator Based Multi-Mode Microplate reader. Aqueous solutions of TPSs agents with concentration 5.0 mM stock solutions were prepared in deionized water. A series of detergent solutions were prepared with a range of concentrations from the stock solutions. 200 µL of each detergent sample was transferred to a 96-well plate in duplicate. A DPH stock solution was prepared by dissolving 3.0 mg DPH in 5.0 mL THF. 50 µL of the stock solution was added into 950 µL of distilled water to prepare a DPH working solution. To each of the solutions 2.0 µL DPH work solution was added into each well containing a detergent solution for dye encapsulation. After 15 ~ 20 min incubation at room temperature, fluorescence intensities were measured at 430 nm following excitation at 358 nm. Detergent CMC values were determined by plotting florescence intensities as a function of detergent concentrations.

Micelle size measurement by dynamic light scattering (DLS)

The dynamic light scattering (DLS) measurements were carried out by using a Malvern Zeta Sizer Nano ZS90 particle analyzer with a maximum power of 5 MW, a He-Ne laser set at 633 nm was used as the light source. The scattered light was collected at an angle of 90°. The hydrodynamic diameter (D_h) of the detergent micelles were measured at 1.0 wt% concentration in deionized water. All the samples were filtered by a syringe filter with a pore size of 0.22 µm. The translational diffusion coefficient and was calculated by autocorrelation analysis on time-dependent scattered light intensity. Hydrodynamic diameter (D_h) values for micelles formed by individual detergents were expressed as mean ± SD (n = 5).

Detergent sample preparation for the transmission electron microscopy (TEM) analysis

Transmission electron microscopy (TEM) imaging for detergents micellar size was carried out with a copper grid coated with an ultrathin layer carbon (Ted Pella Inc., USA) using a JEM-2100F field emission scanning TEM (JEOL, Germany). Detergent solutions were prepared with a concentration of 1.0 wt% in deionized water. Then, a drop of the detergent solutions was put into the copper grid coated with a carbon film and after that it was stained with 2% phosphotungstic acid in water. The excess water was dried gently using a filter paper. The samples were used for TEM analysis at different magnification levels.

Detergent evaluation with membrane proteins

LeuT stability assay

The wild type of leucine transporter (LeuT) from *Aquifex aeolicus* was purified according to the protocol described previously.[1] LeuT was expressed in *E. coli* C41 (DE3) transformed with pET16b encoding C-terminally 8xHis-tagged transporter (expression plasmid was kindly provided by Dr E. Gouaux, Vollum Institute, Portland, Oregon, USA). Briefly, the transporter was bound to Ni^{2+}-NTA resin (Life Technologies, Denmark) after bacterial membranes containing LeuT was treated with 1 % DDM. The resin-bound transporter was eluted in 20 mM Tris-HCl (pH 8.0), 1 mM NaCl, 199 mM KCl, 0.05 % DDM and 300 mM imidazole. Subsequently, approximately 1.5 mg/ml protein stock was diluted 10 times in an identical buffer without DDM and imidazole, but supplemented with DDM (control), a TPS-A (TPS-A6, TPS-A7, or TPS-A8), a TPS-E (TPS-E6, TPS-E7, or TPS-E8) or a TPS-EL (TPS-E8L, TPS-E9L, TPS-E10L, or TPS-E11L) to give a final concentrations of CMC + 0.04 wt% or CMC + 0.2 wt %. The protein samples were stored at room temperature and were centrifuged at the indicated time points. Protein activity was determined by measuring [^{3}H]-Leu binding using scintillation proximity assay (SPA).[2] Shortly, SPA was performed with 5 µL of the respective protein samples, 20 nM [^{3}H]-Leu and 1.25 mg/ml copper chelate (His-Tag) YSi beads (both from Perkin Elmer, Denmark) in buffer containing 450 mM NaCl and the respective test detergents at above-mentioned concentrations. [^{3}H]-Leu binding was determined using a MicroBeta liquid scintillation counter (Perkin Elmer).

UapA thermal denaturation assay

UapAG411V$_{\Delta 1\text{-}11}$ was expressed as a fusion protein with C-terminal GFP in *Saccharomyces cerevisiae* strain FGY217 and isolated as described previously in sample buffer (20 mM Tris (pH 7.5), 150 mM NaCl, 0.03% DDM, 1 mM xanthine).[3] The transporter was concentrated to approximately 10 mg/ml using a 100 kDa molecular weight cut off filter (Millipore). The transporter was diluted 1:150 into buffer containing either a TPS-A (TPS-A6, TPS-A7, or TPS-A8), a TPS-E (TPS-E6, TPS-E7, or TPS-E8), a TPS-EL (TPS-E8L, TPS-E9L, TPS-E10L, or TPS-E11L), MNG-3 or DDM (control) at concentrations of CMC + 0.04 wt% or CMC + 0.2 wt% in Greiner 96-well plates. The CPM dye (Invitrogen), stored in DMSO (Sigma), was diluted in dye buffer (20 mM Tris (pH 7.5), 150 mM NaCl, 0.03% DDM, 5 mM EDTA). 3 µl of the diluted dye solution was added to individual protein samples. The reaction mixtures were incubated for 120 min at 40 °C. During the incubation, the fluorescence emission intensity was monitored using a microplate spectrofluorometer set at excitation and emission wavelengths of 387 and 463 nm, respectively. A maximum value in fluorescence intensity was used to calculate the percentage of relative folded transporter during the incubation period. The relative amounts of folded transporters were plotted against time using GraphPad Prism.

β_2AR stability assay

Long-term stability measurement: β_2AR was purified using 0.1% DDM. The DDM-purified β_2AR was diluted into buffer solutions containing DDM, DDM/CHS or individual novel agents (TPS-As: TPS-

A6, TPS-A7, and TPS-A8; TPS-Es; TPS-E6, TPS-E7, and TPS-E8; TPS-ELs: TPS-E8L, TPS-E9L, TPS-E10L, and TPS-E11L) to reach a final detergent concentration of CMC + 0.2 wt%. β_2AR in each detergent was stored for 3-5 days at room temperature and its ligand binding capacity was measured at regular intervals by incubating with 10 nM of radioactive [^{3}H]-dihydroalprenolol (DHA) for 30 min at room temperature. The mixture was loaded onto a G-50 column and collected the flow-through with certain amount of binding buffer (20 mM HEPES pH 7.5, 100 mM NaCl, supplemented with 0.5 mg/ml BSA), and further filled with 15 ml scintillation fluid. Receptor-bound [^{3}H]-DHA was measured with a scintillation counter (Beckman). The binding capacity of each TPS-solubilized β_2AR for [^{3}H]-DHA was expressed as a column graph.

Purification and stability measurement on β_2AR-G_s complex in TPS-E10L: 100 μM β_2AR in 0.1% DDM was mixed with 120 μM G_s heterotrimer for 30 min at room temperature. 0.5 unit apyrase (NEB) and 2 mM $MgCl_2$ was added to facilitate complex formation and the solution incubated for a further 1 hr. 1% TPS-E10L was then added to give a final concentration of 0.8% and the sample incubated for a further 30 min to initiate detergent exchange from DDM to TPS-E10L. The protein solution was loaded onto an M1 Flag column, washed with a series of buffers with different molar ratios of 0.1% DDM buffer to 0.5% TPS-E10L buffer to allow complete detergent exchange from DDM to TPS-E10L, and the protein finally eluted with 0.05% TPS-E10L buffer. A preparative gel filtration was carried out to purify the β_2AR-G_s complex with running buffer (20mM HEPES pH 7.5, 100 mM NaCl, 0.005% TPS-E10L, 1 μM BI, 100 μM TCEP). To measure the stability of the β_2AR-G_s complex in TPS-E10L, analytical gel filtrations were performed at regular intervals (0 and 7 days) with the same formulation of running buffer as above-mentioned.

Negative stain EM analysis of β_2AR-G_s solubilized in TPS-E10L: β_2AR-G_s was prepared for electron microscopy using the conventional negative staining protocol,[4] and imaged at room temperature with a Tecnai T12 electron microscope operated at 120 kV using low-dose procedures. Images were recorded at a magnification of 71,138x and a defocus value of ~ 1.4 μm on a Gatan US4000 CCD camera. All images were binned (2x2 pixels) to obtain a pixel size of 4.16 Å at the specimen level. Particles were manually excised using e2boxer (part of the EMAN2 software suite).[5] 2D reference-free alignment and classification of particle projections was performed using ISAC.[6] 23035 projections of β_2AR-G_s were subjected to ISAC, producing 19 classes consistent over two-way matching and accounting for 5401 particle projections.

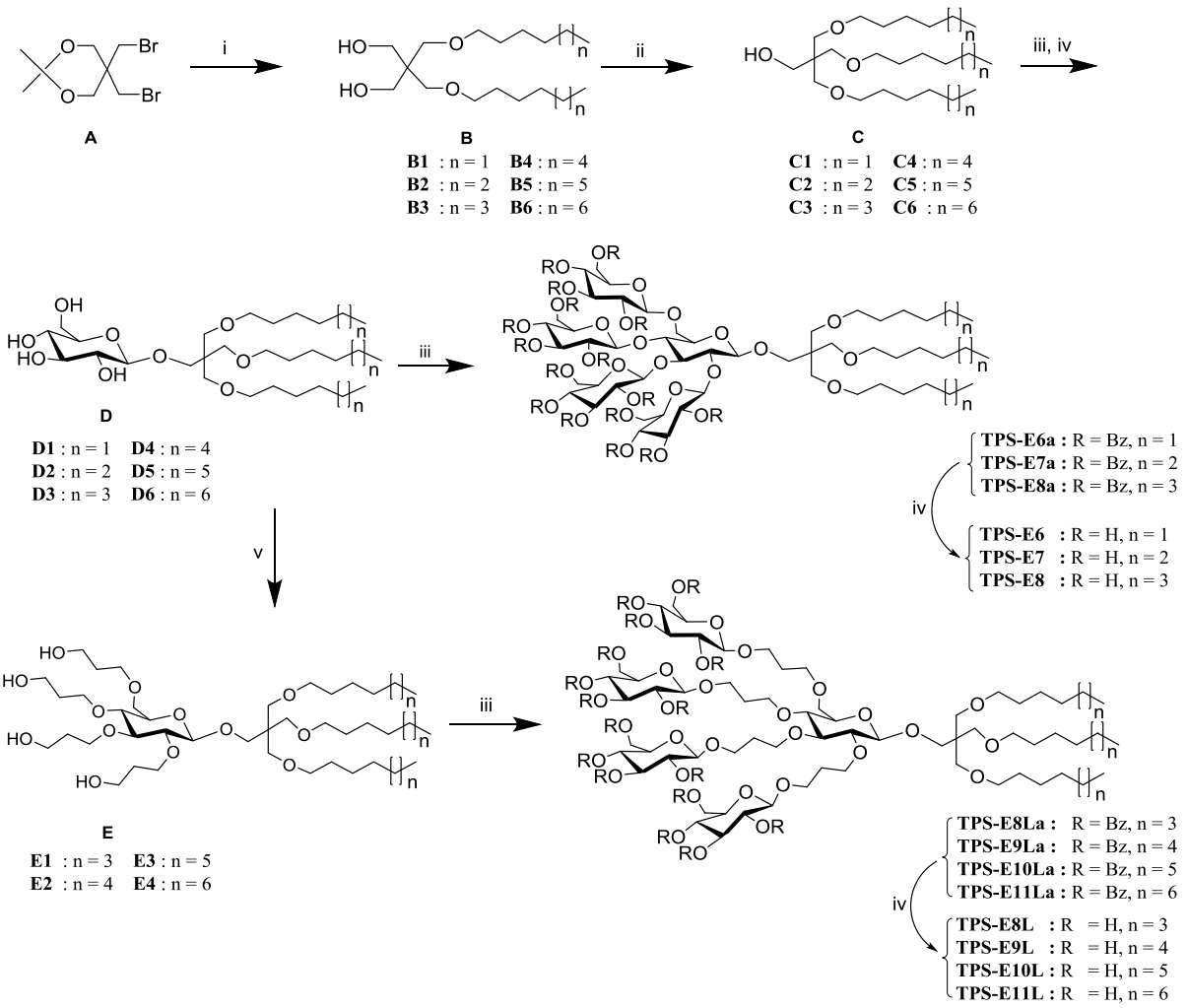
$MelB_{st}$ solubilization and thermal stability assay

A published protocol was used to evaluate stability of MelB from *Salmonella typhimurium* ($MelB_{St}$) with DDM and representative TPSs.[7] The plasmid pK95ΔAHB/WT $MelB_{St}$/CH10 encoding the wild-type $MelB_{St}$ with a C-terminal 10-His tag was expressed in DW2 cells (*ΔmelB* and *ΔlacZY*). Cell growth and membrane preparation were carried out as reported.[8] Protein assays were carried out with a Micro BCA kit (Thermo Scientific). For the measurement of thermostability, membrane samples containing $MelB_{St}$ (a final protein concentration was 10 $mg.mL^{-1}$) were incubated with a solubilization buffer (20 mM sodium phosphate, pH 7.5, 200 mM NaCl, 10% glycerol, 20 mM melibiose) and 1.5 wt% of DDM or individual TPSs (TPS-A8, TPS-E6, TPS-E7, TPS-E8 and TPS-E10L) at six different

temperatures (0, 25, 35, 45, 55, and 65 °C) for 90 minutes. Following ultracentrifugation at 355,590 g in a Beckman Optima^{TM} MAX Ultracentrifuge using a TLA-100 rotor for 45 min at 4 °C, 20 μg of each protein sample was separated by SDS-16% PAGE, followed by immunoblotting with a Penta-His-HRP antibody (Qiagen). $MelB_{St}$ was detected using SuperSignal West Pico chemiluminescent substrate by the ImageQuant LAS 4000 Biomolecular Imager (GE Healthcare Life Science).

Preparation of RSO vesicles and Trp→D^2G FRET assay. RSO membrane vesicles were prepared via osmotic lysis from *E. coli* DW2 cells containing $MelB_{St}$ or $MelB_{Ec}$.[9-11] The RSO membrane vesicles in a buffer (pH 7.5) containing 100 mM KP_i and 100 mM NaCl at a protein concentration of 1 mg/ml were treated with 1.0 % DDM or a TPS (TPS-A8 and TPS-E7) at 23 °C for 30 min and subjected to ultracentrifugation using TLA 120.2 rotor at >300,000 g for 45 min at 4 ºC. The supernatants were applied for Trp→D^2G FRET experiments using an Amico-Bowman Series 2 (AB2) Spectrofluorometer. Trp residues were excited at 290 nm and FRET (Trp→D^2G) was recorded at 490 and 465 nm m for $MelB_{St}$ and $MelB_{Ec}$, respectively.[11] On a time trace, 10 μM D^2G was added into the MelB solutions at 1-min time points and excess melibiose or equal volume of water was added into the solutions at 2-min time points.

Supplementary scheme I



i) NaH, ROH, DMF, 120 °C; *p*-TSA, MeOH, CH_2Cl_2, room temperature; ii) NaH, 1-bromoalkane (RBr), DMF, 100 °C; iii) AgOTf, 2,4,6-collidine, CH_2Cl_2, perbenzoylated glucosylbromide, -45 °C to room temperature; iv) NaOMe, MeOH, room temperature; v) allyl bromide, NaH, DMF, room temperature; 9-BBN, THF, 3M NaOH, 30% H_2O_2 room temperature .

General procedure for the synthesis of dialkylated diol ***(A→B; step i)***

In a dry, two neck flask, a solution of NaH (0.17 mmol) in DMF at 0 °C under N_2 atmosphere, was treated with respective alcohol (17 mmol) and stirred it at room temperature for 0.5 h. The reaction mixture was heated to 120 °C, after addition of 5,5-bis-(bromomethyl)-2,2-dimethyl-[1,3]dioxane (**A**)[7] (4.3 mmol), and left for 15 h at this temperature. After cooling to room temperature, the reaction mixture was quenched with ice-cold water and extracted with diethyl ether three times. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4 and then concentrated by rotary evaporation. After complete evaporation, the residue dissolved in 1:1 mixture of CH_2Cl_2 and MeOH was added with *p*-toluenesulfonic acid (*p*-TSA) monohydrate (catalytic amount) and left stirring at room temperature for 2 h. The reaction mixture was neutralized with a saturated aqueous $NaHCO_3$

solution and the volume of solvent was reduced by rotary evaporation. The reaction mixture was partitioned between CH_2Cl_2 and H_2O. The separated organic layer was washed with brine, dried over anhydrous Na_2SO_4, and then concentrated *in vacuo*. Flash column chromatography (EtOAc/hexane) affords an ether-containing diol (**B1-6**) as a white solid (92-94 % (two steps)).

2,2-bis((hexyloxy)methyl)propane-1,3-diol (**B1**) was prepared in 92 % yield according to the general procedure for the preparation of dialkylated diol. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 3.65 (d, *J* = 4.0 Hz, 4H), 3.51 (s, 4H), 3.42 (t, *J* = 4.0 Hz, 4H), 2.85 (t, *J* = 4.0 Hz, 2H), 1.56 (quin, *J* = 4.0 Hz, 4H), 1.38-1.21 (m, 12H), 0.87 (t, *J* = 8.0 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 72.1, 71.8, 44.7, 31.5, 29.4, 25.7, 22.5, 14.0.

2,2-bis((heptyloxy)methyl)propane-1,3-diol (**B2**) was prepared in 92 % yield according to the general procedure for the preparation of dialkylated diol. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 3.65 (d, *J* = 4.0 Hz, 4H), 3.51 (s, 4H), 3.42 (t, *J* = 4.0 Hz, 4H), 2.85 (t, *J* = 4.0 Hz, 2H), 1.56 (quin, *J* = 4.0 Hz, 4H), 1.38-1.21 (m, 16H), 0.87 (t, *J* = 8.0 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 72.2, 71.8, 44.7, 31.9, 29.6, 29.4, 26.3, 22.6, 14.0.

2,2-bis((octyloxy)methyl)propane-1,3-diol (**B3**) was prepared in 94 % yield according to the general procedure for the preparation of dialkylated diol. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 3.65 (d, *J* = 4.0 Hz, 4H), 3.51 (s, 4H), 3.42 (t, *J* = 8.0 Hz, 4H), 2.85 (t, *J* = 4.0 Hz, 2H), 1.56 (quin, *J* = 4.0 Hz, 4H), 1.38-1.21 (m, 20H), 0.87 (t, *J* = 8.0 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 72.2, 71.8, 44.7, 31.9, 29.6, 29.5, 29.3, 26.3, 22.8, 14.2.

2,2-bis((nonyloxy)methyl)propane-1,3-diol (**B4**) was prepared in 92 % yield according to the general procedure for the preparation of dialkylated diol. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 3.65 (d, *J* = 4.0 Hz, 4H), 3.51 (s, 4H), 3.42 (t, *J* = 4.0 Hz, 4H), 2.85 (t, *J* = 4.0 Hz, 2H), 1.56 (quin, *J* = 4.0 Hz, 4H), 1.28-1.26 (m, 24H), 0.88 (t, *J* = 7.2 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 73.4, 72.2, 65.7, 44.6, 32.1, 29.8, 29.7, 29.5, 26.3, 22.9, 14.1.

2,2-bis((decyloxy)methyl)propane-1,3-diol (**B5**) was prepared in 92 % yield according to the general procedure for the preparation of dialkylated diol. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 3.65 (d, *J* = 4.0 Hz, 4H), 3.51 (s, 4H), 3.42 (t, *J* = 4.0 Hz, 4H), 2.85 (t, *J* = 4.0 Hz, 2H), 1.56 (quin, *J* = 4.0 Hz, 4H), 1.28-1.26 (m, 28H), 0.88 (t, *J* = 7.2 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 73.4, 72.2, 65.7, 44.6, 32.1, 29.8, 29.7, 29.5, 26.2, 22.9, 14.1.

2,2-bis((undecyloxy)methyl)propane-1,3-diol (**B6**) was prepared in 94 % yield according to the general procedure for the preparation of dialkylated diol. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 3.65 (d, *J* = 4.0 Hz, 4H), 3.51 (s, 4H), 3.42 (t, *J* = 8.0 Hz, 4H), 2.85 (t, *J* = 4.0 Hz, 2H), 1.56 (quin, *J* = 4.0 Hz, 4H), 1.28-1.25 (m, 32H), 0.88 (t, *J* = 7.2 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 73.5, 72.3, 65.7, 44.6, 32.1, 29.8, 29.7, 29.6, 29.5, 26.3, 22.8, 22.9, 14.1.

General procedure for the synthesis of trialkylated mono-ol ***(B→C; step ii)***

In a dry, two neck flask, charged with argon, a stirred solution of NaH (212.0 mmol) in dry DMF was treated with a solution of diol derivative (**B1-6**) (212.0 mmol) in dry DMF. After 20 min, a 1-bromoalkane (RBr) (330.0 mmol) was added to the mixture and the temperature was increased up to 100 °C. The reaction mixture was left at this temperature for 4 h, then cooled to room temperature and quenched with H_2O. The reaction mixture was extracted with CH_2Cl_2 two times, washed with brine and dried over anhydrous Na_2SO_4. The reaction mixture was purified by silica gel column chromatography (EtOAc/hexane) providing a trialkyl-containing mono-ol (**C1-6**) as an oily liquid (85 to 90 %).

3-(hexyloxy)-2,2-bis((hexyloxy)methyl)propan-1-ol (**C1**) was prepared in 87 % yield according to the general procedure for the preparation of trialkylated mono-ol. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 3.72 (d, *J* = 8.0 Hz, 2H), 3.44 (s, 6H), 3.39 (t, *J* = 8.0 Hz, 6H), 3.17 (t, *J* = 4.0 Hz, 1H), 1.54 (quin, *J* = 4.0 Hz, 6H), 1.40-1.21 (m, 18H), 0.87 (t, *J* = 8.0 Hz, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 71.6, 71.3, 66.3, 44.7, 31.6, 29.5, 25.8, 22.6, 14.1.

3-(heptyloxy)-2,2-bis((heptyloxy)methyl)propan-1-ol (**C2**) was prepared in 90 % yield according to the general procedure for the preparation of trialkylated mono-ol. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 3.72 (d, *J* = 8.0 Hz, 2H), 3.44 (s, 6H), 3.40 (t, *J* = 8.0 Hz, 6H), 3.19 (t, *J* = 8.0 Hz, 1H), 1.54 (quin, *J* = 8.0 Hz, 6H), 1.40-1.21 (m, 24H), 0.87 (t, *J* = 8.0 Hz, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 71.6, 71.3, 66.3, 44.7, 31.8, 29.6, 29.1, 26.1, 22.6, 14.1.

3-(octyloxy)-2,2-bis((octyloxy)methyl)propan-1-ol (**C3**) was prepared in 85 % yield according to the general procedure for the preparation of trialkylated mono-ol. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 3.71 (d, *J* = 8.0 Hz, 2H), 3.44 (s, 6H), 3.40 (t, *J* = 8.0 Hz, 6H), 3.21 (t, *J* = 8.0 Hz, 1H), 1.54 (quin, *J* = 8.0 Hz, 6H), 1.40-1.21 (m, 30H), 0.87 (t, *J* = 8.0 Hz, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 71.6, 71.3, 66.3, 44.7, 31.8, 29.6, 29.5, 29.1, 26.2, 22.6, 14.1.

3-(nonyloxy)-2,2-bis((nonyloxy)methyl)propan-1-ol (**C4**) was prepared in 87 % yield according to the general procedure for the preparation of trialkylated mono-ol. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 3.71 (d, *J* = 8.0 Hz, 2H), 3.43 (s, 6H), 3.38 (t, *J* = 8.0 Hz, 6H), 3.17 (t, *J* = 4.0 Hz, 1H), 1.53 (quin, *J* = 4.0 Hz, 6H), 1.30-1.26 (m, 36H), 0.88 (t, *J* = 7.2 Hz, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 71.6, 71.3, 66.3, 44.7, 31.6, 29.5, 25.8, 22.6, 14.1.

3-(decyloxy)-2,2-bis((decyloxy)methyl)propan-1-ol (**C5**) was prepared in 90 % yield according to the general procedure for the preparation of trialkylated mono-ol. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 3.71 (d, *J* = 8.0 Hz, 2H), 3.44 (s, 6H), 3.36 (t, *J* = 8.0 Hz, 6H), 3.17 (t, *J* = 8.0 Hz, 1H), 1.52 (quin, *J* = 8.0 Hz, 6H), 1.28-1.26 (m, 42H), 0.88 (t, *J* = 7.2 Hz, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 71.6, 71.3, 66.3, 44.7, 31.8, 29.6, 29.1, 26.1, 22.6, 14.1.

3-(undecyloxy)-2,2-bis((undecyloxy)methyl)propan-1-ol (**C6**) was prepared in 85 % yield according to the general procedure for the preparation of trialkylated mono-ol. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 3.71 (d, *J* = 8.0 Hz, 2H), 3.43 (s, 6H), 3.38 (t, *J* = 8.0 Hz, 6H), 3.16 (t, *J* = 8.0 Hz, 1H), 1.53 (quin, *J* = 8.0

Hz, 6H), 1.28-1.26 (m, 48H), 0.88 (t, *J* = 7.2 Hz, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 71.7, 71.4, 62.9, 45.1, 32.1, 29.9, 29.7, 29.5, 26.4, 22.7, 14.2.

General procedure for glycosylation and de-O-benzoylation under Zemplén's condition ***(C→D; step iii & iv)***

This reaction was carried out according to a literature method[12] with some modifications. Briefly, a mixture of mono-ol derivative (**C1-6**), AgOTf (1.2 or 4.5 equiv.), 2,4,6-collidine (0.7 or 2.0 equiv.) in anhydrous CH_2Cl_2 was stirred at -45 °C. Then perbenzoylated glucosylbromide (1.2 or 4.5 equiv.) in CH_2Cl_2 was transferred *via* cannula to a solution over time of 0.5 h. The reaction was left to warm to 0 °C for 1.5 h. The reaction was monitored by TLC. After completion of reaction (as detected by TLC), pyridine was added to the reaction mixture. The reaction mixture was diluted with CH_2Cl_2 before being filtered over celite. The filtrate was washed successively with a 1 M aqueous $Na_2S_2O_3$ solution, a 0.1 M aqueous HCl solution, and brine. Then the organic layer was dried with anhydrous Na_2SO_4 and the solvent was removed by rotary evaporation. The glycosylated product was dissolved in MeOH and then treated with the required amount of a methanolic solution of 0.5 M NaOMe such that the final concentration of NaOMe was 0.05 M. The reaction mixture was left stirring for 6 h at room temperature, and then neutralized with amberlite IR-120 (H^+ form) resin. The resin was removed by filtration and washed with MeOH, and solvent was removed from the combined filtrate *in vacuo*. The residue was purified by silica gel column chromatography (MeOH/CH_2Cl_2) to give a product as a white solid (**D1-6**) (88 to 90 % (two steps)).

A compound (**D1**) was prepared in 88 % yield according to the general procedure for glycosylation and de-*O*-benzoylation. **^{1}H NMR** (400 MHz, CD_3OD): δ 4.21 (d, *J* = 8.0 Hz, 1H), 3.85 (quint, *J* = 8.0 Hz, 2H), 3.70-3.65 (m, 1H), 3.51 (d, *J* = 8.0 Hz, 1H), 3.45-3.36 (m, 12H), 3.32-3.28 (m, 2H), 3.26-3.15 (m, 2H), 1.59-1.50 (m, 6H), 1.40-1.22 (m, 18H), 0.90 (t, *J* = 8.0 Hz, 9H); **^{13}C NMR** (100 MHz, CD_3OD): δ 105.5, 78.1, 77.9, 75.2, 72.6, 71.6, 70.6, 70.5, 62.8, 46.7, 33.0, 30.8, 27.2, 23.8, 14.6.

A compound (**D2**) was prepared in 89 % yield according to the general procedure for glycosylation and de-*O*-benzoylation. **^{1}H NMR** (400 MHz, CD_3OD): δ 4.21 (d, *J* = 8.0 Hz, 1H), 3.85 (quint, *J* = 8.0 Hz, 2H), 3.70-3.65 (m, 1H), 3.51 (d, *J* = 8.0 Hz, 1H), 3.45-3.36 (m, 12H), 3.32-3.28 (m, 2H), 3.26-3.15 (m, 2H), 1.59-1.50 (m, 6H), 1.40-1.22 (m, 24H), 0.90 (t, *J* = 8.0 Hz, 9H); **^{13}C NMR** (100 MHz, CD_3OD): δ 105.5, 78.1, 77.9, 75.2, 72.6, 71.6, 70.6, 70.5, 62.8, 46.7, 33.2, 30.9, 30.4, 27.5, 23.8, 14.7.

A compound (**D3**) was prepared in 90 % yield according to the general procedure for glycosylation and de-*O*-benzoylation. **^{1}H NMR** (400 MHz, CD_3OD): δ 4.21 (d, *J* = 8.0 Hz, 1H), 3.85 (quint, *J* = 8.0 Hz 2H), 3.70-3.65 (m, 1H), 3.51 (d, *J* = 8.0 Hz, 1H), 3.45-3.36 (m, 12H), 3.32-3.28 (m, 2H), 3.26-3.15 (m, 2H), 1.59-1.50 (m, 6H), 1.40-1.22 (m, 30H), 0.90 (t, *J* = 8.0 Hz, 9H); **^{13}C NMR** (100 MHz, CD_3OD): δ 105.5, 78.1, 77.9, 75.2, 72.6, 71.6, 70.6, 70.5, 62.8, 46.7, 33.2, 30.9, 30.7, 30.6, 27.5, 23.9, 14.7.

A compound (**D4**) was prepared in 88 % yield according to the general procedure for glycosylation

and de-*O*-benzoylation. **^{1}H NMR** (400 MHz, CD_3OD): δ 4.21 (d, *J* = 8.0 Hz, 1H), 3.85 (quint, *J* = 8.0 Hz, 2H), 3.70-3.65 (m, 1H), 3.51 (d, *J* = 8.0 Hz, 1H), 3.45-3.36 (m, 12H), 3.32-3.28 (m, 2H), 3.26-3.15 (m, 2H), 1.59-1.50 (m, 6H), 1.40-1.22 (m, 36H), 0.90 (t, *J* = 8.0 Hz, 9H); **^{13}C NMR** (100 MHz, CD_3OD): δ 105.5, 78.1, 77.9, 75.2, 72.6, 71.6, 70.6, 70.5, 62.8, 46.7, 33.2, 31.0, 30.9, 30.8, 30.7, 27.6, 23.9, 14.7.

A compound (**D5**) was prepared in 88 % yield according to the general procedure for glycosylation and de-*O*-benzoylation. **^{1}H NMR** (400 MHz, CD_3OD): δ 4.22 (d, *J* = 8.0 Hz, 1H), 3.85 (quint, *J* = 8.0 Hz, 2H), 3.70-3.65 (m, 1H), 3.51 (d, *J* = 8.0 Hz, 1H), 3.45-3.36 (m, 12H), 3.32-3.28 (m, 2H), 3.26-3.15 (m, 2H), 1.59-1.50 (m, 6H), 1.40-1.22 (m, 42H), 0.88 (t, *J* = 8.0 Hz, 9H); **^{13}C NMR** (100 MHz, CD_3OD): δ 105.5, 78.1, 77.9, 75.2, 72.6, 71.6, 70.6, 70.5, 62.8, 46.7, 33.2, 30.1, 30.9, 30.8, 30.6, 27.5, 23.9, 14.7.

A compound (**D6**) was prepared in 88 % yield according to the general procedure for glycosylation and de-*O*-benzoylation. **^{1}H NMR** (400 MHz, CD_3OD): δ 4.22 (d, *J* = 8.0 Hz, 1H), 3.85 (quint, *J* = 8.0 Hz, 2H), 3.70-3.65 (m, 1H), 3.51 (d, *J* = 8.0 Hz, 1H), 3.45-3.36 (m, 12H), 3.32-3.28 (m, 2H), 3.26-3.15 (m, 2H), 1.59-1.50 (m, 6H), 1.40-1.22 (m, 48H), 0.88 (t, *J* = 8.0 Hz, 9H); **^{13}C NMR** (100 MHz, CD_3OD): δ 105.5, 78.1, 77.9, 75.2, 72.6, 71.6, 70.6, 70.5, 62.8, 46.7, 33.2, 30.1, 30.9, 30.8, 30.7, 30.6, 27.5, 23.9, 14.7.

TPS-E6a was synthesized according to the general procedure for glycosylation. Yield: 80 %; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.24 (d, *J* = 8.0 Hz, 2H), 8.15-7.78 (m, 24H), 7.72-7.67 (m, 5H), 7.66-7.59 (m, 3H), 7.58-7.12 (m, 46H), 5.96 (t, *J* = 8.0 Hz, 1H), 5.92-5.82 (m, 3H), 5.71-5.69 (m, 2H), 5.61-5.42 (m, 6H), 5.01 (d, *J* = 8.0 Hz, 1H), 4.98-4.92 (m, 2H), 4.88-4.79 (m, 2H), 4.77-4.65 (m, 2H), 4.58-4.42 (m, 3H), 4.36-4.29 (m, 1H), 4.26-4.13 (m, 2H), 4.12-4.05 (m, 2H), 4.03-3.95 (d, *J* = 8.0 Hz, 1H), 3.91-3.71 (m, 4H), 3.37-3.18 (m, 14H), 2.85 (br s, 1H), 2.75 (br s, 1H), 1.59-1.45 (m, 6H), 1.38-1.19 (m, 18H), 0.84 (t, *J* = 8.0 Hz, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 166.2, 166.1, 166.0, 165.9, 165.8, 165.6, 165.2, 165.1, 164.9, 164.4, 133.4, 133.1, 130.1, 129.9, 129.8, 129.7, 129.5, 129.4, 129.3, 129.2, 129.1, 129.0, 128.9, 128.6, 128.5, 128.4, 128.3, 128.2, 101.7, 101.5, 99.9, 99.8, 74.9, 73.4, 72.8, 72.7, 72.6, 72.5, 72.4, 71.6, 71.3, 70.6, 70.3, 70.2, 69.4, 68.8, 63.7, 63.5, 45.6, 31.8, 29.8, 26.0, 22.8, 14.2.

TPS-E7a was synthesized according to the general procedure for glycosylation. Yield: 78 %; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.24 (d, *J* = 8.0 Hz, 2H), 8.15-7.78 (m, 24H), 7.72-7.67 (m, 5H), 7.66-7.59 (m, 3H), 7.58-7.12 (m, 46H), 5.96 (t, *J* = 8.0 Hz, 1H), 5.92-5.82 (m, 3H), 5.71-5.69 (m, 2H), 5.61-5.42 (m, 6H), 5.01 (d, *J* = 8.0 Hz, 1H), 4.98-4.91 (m, 2H), 4.88-4.79 (m, 2H), 4.77-4.65 (m, 2H), 4.59-4.42 (m, 3H), 4.36-4.29 (m, 1H), 4.26-4.13 (m, 2H), 4.12-4.05 (m, 2H), 4.03-3.95 (d, *J* = 8.0 Hz, 1H), 3.91-3.71 (m, 4H), 3.37-3.18 (m, 14H), 2.85 (br s, 1H), 2.75 (br s, 1H), 1.59-1.45 (m, 6H), 1.40-1.18 (m, 24H), 0.84 (t, *J* = 8.0 Hz, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 166.2, 166.1, 166.0, 165.9, 165.8, 165.6, 165.2, 165.1, 164.9, 164.4, 133.4, 133.1, 130.1, 129.9, 129.8, 129.7, 129.5, 129.4, 129.3, 129.2, 129.1, 129.0, 128.9, 128.6, 128.5, 128.4, 128.3, 128.2, 101.7, 101.5, 99.9, 99.8, 74.9, 73.4, 72.8, 72.7, 72.6, 72.5, 72.4, 71.6, 71.3, 70.6, 70.3, 70.2, 69.4, 68.8, 63.7, 63.5, 45.6, 32.1, 29.9, 29.4, 26.3, 22.8, 14.3.

TPS-E8a was synthesized according to the general procedure for glycosylation. Yield: 76 %; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.24 (d, *J* = 8.0 Hz, 2H), 8.15-7.78 (m, 24H), 7.72-7.67 (m, 5H), 7.66-7.59 (m, 3H), 7.58-7.12 (m, 46H), 5.96 (t, *J* = 8.0 Hz, 1H), 5.92-5.82 (m, 3H), 5.71-5.69 (m, 2H), 5.61-5.42 (m, 6H), 5.01 (d, *J* = 8.0 Hz, 1H), 4.98-4.92 (m, 2H), 4.88-4.79 (m, 2H), 4.77-4.65 (m, 2H), 4.59-4.41 (m, 3H), 4.36-4.29 (m, 1H), 4.26-4.13 (m, 2H), 4.12-4.05 (m, 2H), 4.03-3.95 (d, *J* = 8.0 Hz, 1H), 3.91-3.71 (m, 4H), 3.37-3.18 (m, 14H), 2.85 (br s, 1H), 2.75 (br s, 1H), 1.59-1.45 (m, 6H), 1.40-1.19 (m, 30H), 0.84 (t, *J* = 8.0 Hz, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 166.2, 166.1, 166.0, 165.9, 165.8, 165.6, 165.2, 165.1, 164.9, 164.4, 133.4, 133.1, 130.1, 129.9, 129.8, 129.7, 129.5, 129.4, 129.3, 129.2, 129.1, 129.0, 128.9, 128.6, 128.5, 128.4, 128.3, 128.2, 101.7, 101.5, 99.9, 99.8, 74.9, 73.4, 72.8, 72.7, 72.6, 72.5, 72.4, 71.6, 71.3, 70.6, 70.3, 70.2, 69.4, 68.8, 63.7, 63.5, 45.6, 32.0, 29.9, 29.8, 26.4, 22.8, 14.3.

TPS-E6 was synthesized according to the general procedure for de-*O*-benzoylation. Yield: 94 %; **^{1}H NMR** (400 MHz, CD_3OD): δ 4.95 (d, *J* = 8.0 Hz, 1H), 4.85 (d, *J* = 8.0 Hz, 1H), 4.66 (d, *J* = 8.0 Hz, 1H), 4.38 (t, *J* = 8.0 Hz, 2H), 4.25 (d, *J* = 10.4 Hz, 1H), 4.12-3.95 (m, 3H), 3.90-3.82 (m, 6H), 3.75-3.59 (m, 6H), 3.46-3.18 (m, 28H), 1.60-1.51 (m, 6H), 1.40-1.28 (m, 18H), 0.89 (t, *J* = 8.0 Hz, 9H); **^{13}C NMR** (100 MHz, CD_3OD): δ 104.7, 104.0, 103.4, 102.9, 102.6, 80.3, 80.2, 78.4, 78.0, 77.9, 77.8, 77.6, 76.0, 75.4, 75.2, 75.1, 72.5, 72.1, 71.7, 71.5, 71.3, 70.8, 70.2, 69.2, 63.3, 62.9, 62.7, 62.5, 46.8, 32.9, 30.8, 27.2, 23.8, 14.6; **HRMS (EI)**: calcd. for $C_{53}H_{98}O_{29}$ $[M+Na]^+$ 1221.6091, observed 1221.6095.

TPS-E7 was synthesized according to the general procedure for de-*O*-benzoylation. Yield: 92 %; **^{1}H NMR** (400 MHz, CD_3OD): δ 4.95 (d, *J* = 8.0 Hz, 1H), 4.85 (d, *J* = 8.0 Hz, 1H), 4.66 (d, *J* = 8.0 Hz, 1H), 4.38 (t, *J* = 8.0 Hz, 2H), 4.25 (d, *J* = 10.4 Hz, 1H), 4.12-3.95 (m, 3H), 3.90-3.82 (m, 6H), 3.75-3.59 (m, 6H), 3.46-3.18 (m, 28H), 1.60-1.51 (m, 6H), 1.39-1.28 (m, 24H), 0.90 (t, *J* = 8.0 Hz, 9H); **^{13}C NMR** (100 MHz, CD_3OD): δ 104.7, 104.0, 103.4, 102.9, 102.6, 80.3, 80.2, 78.4, 78.0, 77.9, 77.8, 77.6, 76.0, 75.4, 75.2, 75.1, 72.5, 72.1, 71.7, 71.5, 71.3, 70.8, 70.2, 69.2, 63.3, 62.9, 62.7, 62.5, 46.8, 33.1, 30.8, 30.4, 27.5, 23.8, 14.6; **HRMS (EI)**: calcd. for $C_{56}H_{104}O_{29}$ $[M+Na]^+$ 1263.6561, observed 1263.6556.

TPS-E8 was synthesized according to the general procedure for de-*O*-benzoylation. Yield: 92 **%; ^{1}H NMR** (400 MHz, CD_3OD): δ 4.95 (d, *J* = 8.0 Hz, 1H), 4.84 (d, *J* = 8.0 Hz, 1H), 4.65 (d, *J* = 8.0 Hz, 1H), 4.37 (t, *J* = 8.0 Hz, 2H), 4.25 (d, *J* = 10.4 Hz, 1H), 4.12-3.95 (m, 3H), 3.90-3.81 (m, 6H), 3.75-3.59 (m, 6H), 3.46-3.18 (m, 28H), 1.60-1.51 (m, 6H), 1.39-1.28 (m, 30H), 0.89 (t, *J* = 8.0 Hz, 9H); **^{13}C NMR** (100 MHz, CD_3OD): δ 104.7, 104.0, 103.4, 102.9, 102.6, 80.3, 80.2, 78.4, 78.0, 77.9, 77.8, 77.6, 76.0, 75.4, 75.2, 75.1, 72.5, 72.1, 71.7, 71.5, 71.3, 70.8, 70.2, 69.2, 63.3, 62.9, 62.7, 62.5, 46.9, 33.2, 30.9, 30.7, 30.6, 27.6, 23.9, 14.6; **HRMS (EI)**: calcd. for $C_{59}H_{110}O_{29}$ $[M+Na]^+$ 1305.7030, observed 1305.7032.

*General procedure for allylation and hydroboration **(D→E; step v)***

To a suspension of (**D3-6**) (13.1 mmol) in dry DMF (100 mL), NaH (99 mmol) and allyl bromide (96

mmol) were added and the reaction mixture was stirred overnight at room temperature. The reaction was quenched with ice water at 0 °C and CH_2Cl_2 (30 mL) was added. The organic phase was separated, consecutively washed with water (3x) and brine (2x), dried (Na_2SO_4), filtered, concentrated using rotary evaporation and dried overnight in high vacuum. Then, to a solution of allylated product (1.55 mmol) in dry THF (30 mL), 0.5 M 9-BBN-H solution in THF (28 mL, 14 mmol) was added and the reaction mixture was stirred at room temperature for 1.5 h. The excess reagent was destroyed by adding ice water. Oxidation was subsequently achieved by the simultaneous dropwise addition of 3 M aqueous NaOH (14 mL) and 30% H_2O_2 (14 mL), followed by stirring overnight at room temperature. The mixture was saturated with K_2CO_3 and the layers were separated. The aqueous layer was washed with EtOAc (3x) and the combined organic phases were concentrated and purified by flash chromatography to yield a target product (**E1-4**; 75-80% (two steps)).

A compound (**E1**) was prepared in 80 % yield according to the general procedure for allylation and hydroboration. **^{1}H NMR** (400 MHz, CD_3OD): δ 4.21 (d, *J* = 8.0 Hz, 1H), 3.85-3.80 (m, 6H), 3.71-3.58 (m, 14H), 3.48 (d, *J* = 8.0 Hz, 1H), 3.45-3.36 (m, 14H), 2.98 (t, *J* = 8.0 Hz, 1H), 1.85-1.79 (m, 8H), 1.56-1.50 (m, 6H), 1.40-1.22 (m, 30H), 0.88 (t, *J* = 8.0 Hz, 9H); **^{13}C NMR** (100 MHz, CD_3OD): δ 105.3, 86.1, 83.8, 79.4, 76.1, 72.6, 71.7, 71.1, 70.8, 70.7, 70.5, 70.0, 69.6, 60.4, 60.3, 60.2, 60.1, 46.6, 34.6, 34.4, 33.8, 33.2, 30.9, 30.8, 30.7, 27.6, 23.9, 14.8.

A compound (**E2**) was prepared in 76 % yield according to the general procedure for allylation and hydroboration. **^{1}H NMR** (400 MHz, CD_3OD): δ 4.21 (d, *J* = 8.0 Hz, 1H), 3.85-3.80 (m, 6H), 3.71-3.58 (m, 14H), 3.48 (d, *J* = 8.0 Hz, 1H), 3.45-3.36 (m, 14H), 2.98 (t, *J* = 8.0 Hz, 1H), 1.85-1.79 (m, 8H), 1.56-1.50 (m, 6H), 1.40-1.22 (m, 36H), 0.88 (t, *J* = 8.0 Hz, 9H); **^{13}C NMR** (100 MHz, CD_3OD): δ 105.3, 86.1, 83.7, 79.3, 76.1, 72.5, 71.6, 71.0, 70.8, 70.5, 70.0, 69.6, 60.4, 60.3, 60.2, 60.0, 46.6, 34.6, 34.4, 33.9, 32.8, 31.1, 31.0, 30.9, 30.8, 30.7, 30.2, 27.5, 23.9, 14.8.

A compound (**E3**) was prepared in 76 % yield according to the general procedure for allylation and hydroboration. **^{1}H NMR** (400 MHz, CD_3OD): δ 4.21 (d, *J* = 8.0 Hz, 1H), 3.85-3.80 (m, 6H), 3.71-3.58 (m, 14H), 3.48 (d, *J* = 8.0 Hz, 1H), 3.45-3.36 (m, 14H), 2.98 (t, *J* = 8.0 Hz, 1H), 1.85-1.79 (m, 8H), 1.56-1.50 (m, 6H), 1.40-1.22 (m, 42H), 0.88 (t, *J* = 8.0 Hz, 9H); **^{13}C NMR** (100 MHz, CD_3OD): δ 105.3, 86.0, 83.7, 79.3, 76.1, 72.5, 71.6, 71.0, 70.8, 70.5, 70.0, 69.6, 60.4, 60.3, 60.2, 60.0, 46.6, 34.6, 34.4, 33.8, 33.3, 31.1, 31.0, 30.9, 30.8, 30.7, 27.6, 23.9, 14.8.

A compound (**E4**) was prepared in 75 % yield according to the general procedure for allylation and hydroboration. **^{1}H NMR** (400 MHz, CD_3OD): δ 4.21 (d, *J* = 8.0 Hz, 1H), 3.85-3.80 (m, 6H), 3.71-3.58 (m, 14H), 3.48 (d, *J* = 8.0 Hz, 1H), 3.45-3.36 (m, 14H), 2.98 (t, *J* = 8.0 Hz, 1H), 1.85-1.79 (m, 8H), 1.56-1.50 (m, 6H), 1.40-1.22 (m, 48H), 0.89 (t, *J* = 8.0 Hz, 9H); **^{13}C NMR** (100 MHz, CD_3OD): δ 105.3, 86.1, 83.7, 79.3, 76.1, 72.5, 71.6, 71.0, 70.8, 70.5, 70.0, 69.6, 60.4, 60.3, 60.2, 60.0, 46.6, 34.6, 34.4, 33.8, 33.3, 31.1, 31.0, 30.9, 30.8, 30.7, 27.6, 23.9, 14.8.

TPS-E8La was synthesized according to the general procedure for glycosylation. Yield: 83 %; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.15-7.78 (m, 30H), 7.58-7.12 (m, 50H), 6.12-5.95 (m, 4 H), 5.80-5.75

(m, 4H), 5.65-5.55 (m, 4H), 4.95-4.85 (m, 3H), 4.72-4.65 (m, 4H), 4.62-4.53 (m, 4H), 4.25-4.15 (m, 4H), 3.98-3.76 (m, 6H), 3.72-3.48 (m, 6H), 3.42-3.21 (m, 18H), 2.85 (br s, 2H), 2.65 (br s, 1H), 1.85-1.68 (m, 8H), 1.53-1.48 (m, 6H), 1.35-1.22 (m, 30H), 0.86 (t, *J* = 8.0 Hz, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 166.1, 165.8, 165.2, 165.1, 133.4, 133.2, 129.8, 129.7, 129.6, 129.4, 128.9, 128.5, 128.4, 128.3, 101.4, 73.1, 72.1, 72.0, 71.5, 69.8, 69.5, 69.1, 68.0, 67.5, 63.2, 59.9, 45.3, 31.9, 30.4, 29.7, 29.5, 29.4, 26.3, 22.7, 14.2.

TPS-E9La was synthesized according to the general procedure for glycosylation. Yield: 84 %; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.15-7.78 (m, 30H), 7.58-7.12 (m, 50H), 6.12-5.95 (m, 4 H), 5.80-5.75 (m, 4H), 5.65-5.55 (m, 4H), 4.95-4.85 (m, 3H), 4.72-4.65 (m, 4H), 4.62-4.53 (m, 4H), 4.25-4.15 (m, 4H), 3.98-3.76 (m, 6H), 3.72-3.48 (m, 6H), 3.42-3.21 (m, 18H), 2.85 (br s, 2H), 2.65 (br s, 1H), 1.85-1.68 (m, 8H), 1.53-1.48 (m, 6H), 1.35-1.22 (m, 36H), 0.86 (t, *J* = 8.0 Hz, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 166.1, 165.8, 165.2, 165.1, 133.4, 133.2, 129.8, 129.7, 129.6, 129.4, 129.3, 128.9, 128.5, 128.4, 128.3, 101.5, 73.1, 72.1, 72.0, 71.5, 69.8, 69.5, 69.1, 68.0, 67.5, 63.2, 63.1, 59.9, 45.3, 32.0, 31.9, 30.4, 29.8, 29.7, 29.5, 29.4, 26.3, 22.7, 14.2.

TPS-E10La was synthesized according to the general procedure for glycosylation. Yield: 84 %; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.15-7.78 (m, 30H), 7.58-7.12 (m, 50H), 6.12-5.95 (m, 4 H), 5.80-5.75 (m, 4H), 5.65-5.55 (m, 4H), 4.95-4.85 (m, 3H), 4.72-4.65 (m, 4H), 4.62-4.53 (m, 4H), 4.25-4.15 (m, 4H), 3.98-3.76 (m, 6H), 3.72-3.48 (m, 6H), 3.42-3.21 (m, 18H), 2.85 (br s, 2H), 2.65 (br s, 1H), 1.85-1.68 (m, 8H), 1.53-1.48 (m, 6H), 1.35-1.22 (m, 42H), 0.86 (t, *J* = 8.0 Hz, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 166.1, 165.8, 165.2, 165.1, 133.4, 133.2, 129.8, 129.7, 129.6, 129.4, 129.3, 128.9, 128.5, 128.4, 128.3, 101.4, 73.1, 72.1, 72.0, 71.5, 69.8, 69.5, 69.1, 68.0, 67.5, 63.2, 63.1, 59.9, 45.3, 32.0, 31.9, 30.4, 29.7, 29.6, 29.5, 29.4, 26.3, 22.7, 14.2.

TPS-E11La was synthesized according to the general procedure for glycosylation. Yield: 82 %; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.15-7.78 (m, 30H), 7.58-7.12 (m, 50H), 6.12-5.95 (m, 4 H), 5.80-5.75 (m, 4H), 5.65-5.55 (m, 4H), 4.95-4.85 (m, 3H), 4.72-4.65 (m, 4H), 4.62-4.53 (m, 4H), 4.25-4.15 (m, 4H), 3.98-3.76 (m, 6H), 3.72-3.48 (m, 6H), 3.42-3.21 (m, 18H), 2.85 (br s, 2H), 2.65 (br s, 1H), 1.85-1.68 (m, 8H), 1.53-1.48 (m, 6H), 1.35-1.22 (m, 48H), 0.86 (t, *J* = 8.0 Hz, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 166.1, 165.8, 165.2, 165.1, 133.4, 133.2, 129.8, 129.7, 129.6, 129.4, 129.3, 128.9, 128.5, 128.4, 128.3, 101.4, 73.1, 72.1, 72.0, 71.5, 69.9, 69.8, 69.5, 69.1, 68.0, 67.5, 63.2, 63.1, 59.9, 45.3, 32.2, 32.0, 31.9, 30.4, 29.8, 28.7, 29.5, 29.4, 26.3, 22.8, 14.2.

TPS-E8L was synthesized according to the general procedure for de-*O*-benzoylation. Yield: 92 %; **^{1}H NMR** (400 MHz, CD_3OD): δ 4.23 (d, *J* = 8.0 Hz, 4H), 4.16 (d, *J* = 8.0 Hz, 1H), 4.02-3.99 (m, 4H), 3.92-3.80 (m, 10H), 3.73-3.55 (m, 17H), 3.42-3.15 (m, 32H), 1.92-1.80 (m, 8H), 1.55-1.50 (m, 6H), 1.41-1.25 (m, 30H), 0.89 (t, *J* = 8.0 Hz, 9H); **^{13}C NMR** (100 MHz, CD_3OD): δ 104.5, 78.1, 77.9, 75.1, 72.6, 71.7, 70.5, 69.6, 68.1, 62.9, 46.6, 33.2, 31.9, 30.9, 30.8, 30.7, 30.6, 27.6, 23.9, 14.7. **HRMS (EI)**: calcd. for $C_{71}H_{134}O_{33}$ $[M+Na]^+$ 1537.8705, observed 1537.8701.

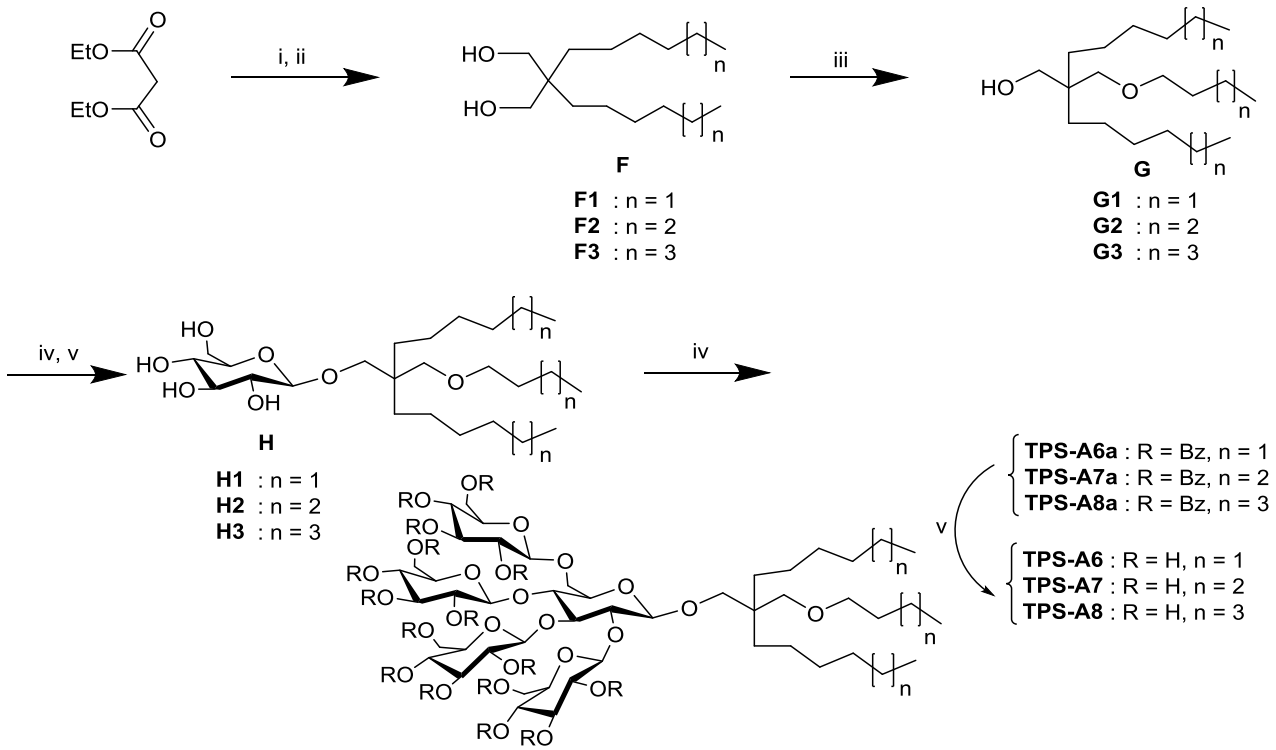
TPS-E9L was synthesized according to the general procedure for de-*O*-benzoylation. Yield: 92 %; **^{1}H NMR** (400 MHz, CD_3OD): δ 4.23 (d, *J* = 8.0 Hz, 4H), 4.16 (d, *J* = 8.0 Hz, 1H), 4.02-3.99 (m, 4H),

3.92-3.80 (m, 10H), 3.73-3.55 (m, 17H), 3.42-3.15 (m, 32H), 1.92-1.80 (m, 8H), 1.55-1.50 (m, 6H), 1.41-1.25 (m, 36H), 0.89 (t, J = 8.0 Hz, 9H); **^{13}C NMR** (100 MHz, CD_3OD): δ 104.5, 78.1, 77.9, 75.1, 72.6, 71.7, 70.5, 69.6, 68.1, 62.9, 46.6, 33.2, 31.9, 30.9, 30.8, 30.7, 30.6, 27.6, 23.9, 14.7; **HRMS (EI)**: calcd. for $C_{74}H_{140}O_{33}$ $[M+Na]^+$ 1579.9175, observed 1579.9180.

TPS-E10L was synthesized according to the general procedure for de-*O*-benzoylation. Yield: 92 %; **^{1}H NMR** (400 MHz, CD_3OD): δ 4.23 (d, J = 8.0 Hz, 4H), 4.16 (d, J = 8.0 Hz, 1H), 4.02-3.99 (m, 4H), 3.92-3.80 (m, 10H), 3.73-3.55 (m, 17H), 3.42-3.15 (m, 32H), 1.92-1.80 (m, 8H), 1.55-1.50 (m, 6H), 1.41-1.25 (m, 42H), 0.88 (t, J = 8.0 Hz, 9H); **^{13}C NMR** (100 MHz, CD_3OD): δ 104.5, 78.1, 77.9, 75.1, 72.6, 71.7, 70.5, 69.6, 68.1, 62.9, 46.6, 33.2, 31.9, 30.9, 30.8, 30.7, 30.6, 27.6, 23.9, 14.7; **HRMS (EI)**: calcd. for $C_{77}H_{146}O_{33}$ $[M+Na]^+$ 1621.9644, observed 1621.9640.

TPS-E11L was synthesized according to the general procedure for de-*O*-benzoylation. Yield: 92 %; **^{1}H NMR** (400 MHz, CD_3OD): δ 4.23 (d, J = 8.0 Hz, 4H), 4.16 (d, J = 8.0 Hz, 1H), 4.02-3.99 (m, 4H), 3.92-3.80 (m, 10H), 3.73-3.55 (m, 17H), 3.42-3.15 (m, 32H), 1.92-1.80 (m, 8H), 1.55-1.50 (m, 6H), 1.41-1.25 (m, 48H), 0.88 (t, J = 8.0 Hz, 9H); **^{13}C NMR** (100 MHz, CD_3OD): δ 104.5, 78.1, 77.9, 75.1, 72.6, 71.7, 70.5, 69.6, 68.1, 62.9, 46.6, 33.2, 31.9, 30.9, 30.8, 30.7, 30.6, 27.6, 23.9, 14.7; **HRMS (EI)**: calcd. for $C_{80}H_{152}O_{33}$ $[M+Na]^+$ 1664.0114, observed 1664.0107.

Supplementary scheme II



i) NaH, 1-iodoalkane (RI), THF, room temperature; ii) $LiAlH_4$, THF, RT; iii) NaH, 1-bromoalkane (RBr), DMF, 100 °C; iv) AgOTf, 2,4,6-collidine, CH_2Cl_2, perbenzoylated glucosylbromide, -45 °C to room temperature; v) NaOMe, MeOH, room

temperature.

General procedure for dialkylation and reduction ***(F; step i & ii)***

This reaction was performed according to a literature method[13] with slight modification. Diethyl malonate (6.9 mmol) in THF was treated with NaH (21 mmol) in THF at 0 °C and left stirring for 20 min. Then 1-iodoalkane (RI) (2.6 equiv.) was added to the reaction mixture. After complete addition, the reaction mixture was stirred at room temperature for 48 h, quenched by adding ice-cold saturated NH_4Cl and extracted with diethyl ether two times. The organic layer was washed with brine and dried with anhydrous Na_2SO_4. After complete evaporation of the solvent, $LiAlH_4$ (14.0 mmol) was added slowly to the residue dissolved in THF at 0 °C. The mixture was stirred at room temperature for 4 h, quenched with MeOH, water, a 1 N aqueous HCl solution successively at 0 °C and then extracted with diethyl ether twice. The combined organic layer was washed with brine and dried with anhydrous Na_2SO_4. The residue was purified by silica gel column chromatography (EtOAc/hexane) providing an alkyl-containing diol (**F1-3**) as a white solid (90 to 92 % (two steps)).

2,2-dihexyl-propane-1,3-diol (**F1**) was prepared in 92 % yield according to the general procedure for dialkylation and reduction. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 3.57 (s, 4H), 2.28 (s, 2H), 1.38-1.08 (m, 20H), 0.88 (t, *J* = 8.0 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 69.5, 41.2, 32.0, 31.1, 30.5, 29.9, 23.1, 22.9, 14.3.

2,2-diheptyl-propane-1,3-diol (**F2**) was prepared in 92 % yield according to the general procedure for dialkylation and reduction. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 3.57 (s, 4H), 2.28 (s, 2H), 1.38-1.08 (m, 24H), 0.88 (t, *J* = 8.0 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 69.5, 41.2, 32.1, 30.8, 29.8, 29.5, 23.1, 22.9, 14.3.

2,2-dioctyl-propane-1,3-diol (**F3**) was prepared in 90 % yield according to the general procedure for dialkylation and reduction. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 3.57 (s, 4H), 2.28 (s, 2H), 1.38-1.08 (m, 28H), 0.88 (t, *J* = 8.0 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 69.5, 41.2, 32.1, 30.9, 30.8, 29.8, 29.5, 23.1, 22.9, 14.3.

Compounds (**G1-3**) were synthesized according to the same synthetic protocol used for compounds (C1-6, step ii) as described in **supplementary scheme I**.

2-(butoxymethyl)-2-hexyloctan-1-ol (**G1**) was prepared in 90 % yield according to the general procedure for the preparation of trialkylated mono-ol. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 3.50 (d, *J* = 8.0 Hz, 2H), 3.39 (t, *J* = 8.0 Hz, 2H), 3.32 (s, 2H), 3.10 (t, *J* = 4.0 Hz, 1H), 1.54 (quin, *J* = 4.0 Hz, 2H), 1.40-1.19 (m, 22H), 0.88 (t, *J* = 8.0 Hz, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 79.0, 71.7, 70.2, 40.8, 32.0, 31.8, 31.5, 30.4, 23.0, 22.8, 19.5, 14.2, 14.0.

2-heptyl-2-((pentyloxy)methyl)nonan-1-ol (**G2**) was prepared in 90 % yield according to the general procedure for the preparation of trialkylated mono-ol. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 3.50 (d, *J* = 8.0 Hz, 2H), 3.39 (t, *J* = 8.0 Hz, 2H), 3.32 (s, 2H), 3.10 (t, *J* = 4.0 Hz, 1H), 1.55 (quin, *J* = 4.0 Hz, 2H),

1.40-1.19 (m, 28H), 0.88 (t, *J* = 8.0 Hz, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 79.1, 72.0, 70.3, 40.8, 32.1, 31.8, 31.5, 30.7, 29.7, 29.5, 26.0, 23.1, 22.8, 14.3, 14.1.

2-((hexyloxy)methyl)-2-octyldecan-1-ol (**G3**) was prepared in 88 % yield according to the general procedure for the preparation of trialkylated mono-ol. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 3.50 (d, *J* = 8.0 Hz, 2H), 3.39 (t, *J* = 8.0 Hz, 2H), 3.32 (s, 2H), 3.10 (t, *J* = 4.0 Hz, 1H), 1.54 (quin, *J* = 4.0 Hz, 2H), 1.40-1.19 (m, 34H), 0.88 (t, *J* = 8.0 Hz, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 79.1, 72.0, 70.3, 40.8, 32.1, 31.8, 31.5, 30.7, 29.7, 29.5, 26.0, 23.1,22.9, 22.8, 14.3, 14.2.

Compounds (**H1-3**) and (TPS-A6, TPS-A7 and TPS-A8) were synthesized according the general procedure used for glycosylation and de-*O*-benzoylation under Zemplén's conditions as described in **supplementary scheme I**.

A compound (**H1**) was prepared in 88 % yield according to the general procedure for glycosylation and de-*O*-benzoylation. **^{1}H NMR** (400 MHz, CD_3OD): δ 4.19 (d, *J* = 8.0 Hz, 1H), 3.87 (d, *J* = 8.0 Hz 1H), 3.84 (d, *J* = 8.0 Hz, 1H), 3.75-3.67 (m, 1H), 3.39-3.20 (m, 10H), 1.56-1.50 (m, 2H), 1.40-1.22 (m, 22H), 0.89 (t, *J* = 8.0 Hz, 9H); **^{13}C NMR** (100 MHz, CD_3OD): δ 105.4, 78.2, 77.9, 75.3, 74.3, 73.8, 72.1, 71.8, 62.9, 42.2, 33.1, 32.5, 31.4, 23.9, 23.8, 20.7, 14.6, 14.4.

A compound (**H2**) was prepared in 88 % yield according to the general procedure for glycosylation and de-*O*-benzoylation. **^{1}H NMR** (400 MHz, CD_3OD): δ 4.20 (d, *J* = 8.0 Hz, 1H), 3.86 (d, *J* = 8.0 Hz 1H), 3.83 (d, *J* = 8.0 Hz, 1H), 3.75-3.67 (m, 1H), 3.39-3.20 (m, 10H), 1.54-1.51 (m, 2H), 1.40-1.22 (m, 28H), 0.89 (t, *J* = 8.0 Hz, 9H); **^{13}C NMR** (100 MHz, CD_3OD): δ 105.4, 78.2, 77.9, 75.2, 74.3, 73.8, 72.3, 71.7, 62.9, 42.2, 33.2, 32.4, 31.7, 30.6, 30.5, 29.9, 23.9, 23.8, 23.7, 14.8, 14.7.

A compound (**H3**) was prepared in 86 % yield according to the general procedure for glycosylation and de-*O*-benzoylation. **^{1}H NMR**(400 MHz, CD_3OD): δ 4.19 (d, *J* = 8.0 Hz, 1H), 3.86 (d, *J* = 8.0 Hz 1H), 3.84 (d, *J* = 8.0 Hz, 1H), 3.75-3.67 (m, 1H), 3.39-3.20 (m, 10H), 1.54-1.50 (m, 2H), 1.40-1.22 (m, 34H), 0.89 (t, *J* = 8.0 Hz, 9H); **^{13}C NMR** (100 MHz, CD_3OD): δ 105.4, 78.2, 77.9, 75.3, 74.3, 73.8, 72.4, 71.8, 62.9, 42.2, 33.2, 32.5, 31.8, 30.9, 30.8, 30.6, 27.3, 24.0, 23.9, 23.8, 23.7,14.8, 14.7.

TPS-A6a was synthesized according to the general procedure for glycosylation. Yield: 80 %; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.24 (d, *J* = 8.0 Hz, 2H), 8.15-7.80 (m, 24H), 7.72-6.67 (m, 5H), 7.66-7.59 (m, 3H), 7.58-7.12 (m, 46H), 5.94 (t, *J* = 8.0 Hz, 1H), 5.91-5.82 (m, 3H), 5.71-5.69 (m, 2H), 5.61-5.42 (m, 6H), 5.01 (d, *J* = 8.0 Hz, 1H), 4.98-4.92 (m, 2H), 4.88-4.79 (m, 2H), 4.77-4.65 (m, 2H), 4.58-4.42 (m, 1H), 4.41-4.39 (m, 2H), 4.38-4.36 (m, 1H), 4.29-4.06 (m, 5H), 3.72-3.39 (m, 4H), 3.65 (t, *J* = 8.0 Hz, 1H), 3.58 (d, *J* = 8.0 Hz, 1H), 3.41-3.35 (m, 2H), 3.29-3.26 (br s, 1H), 3.18 (d, *J* = 8.0 Hz, 1H), 3.08 (t, *J* = 8.0 Hz, 2H), 2.75 (br s, 1H), 2.63 (br s, 1H), 1.56-1.50 (m, 2H), 1.40-1.15 (m, 22H), 0.84 (t, *J* = 8.0 Hz, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 166.2, 166.1, 166.0, 165.9, 165.6, 165.3, 165.2, 165.1, 164.9, 164.5, 164.4, 133.4, 133.2, 133.1, 130.1, 130.0, 129.9, 129.8, 129.7, 129.5, 129.4, 129.3, 129.2, 129.1, 129.0, 128.6, 128.5, 128.4, 128.3, 128.2, 101.6, 99.9, 73.4, 72.8, 72.6, 72.3, 71.8, 71.4, 71.2, 70.4, 63.7, 41.0, 32.2, 32.1, 32.0, 30.5, 30.4, 26.1, 23.0, 22.9, 22.6, 19.6, 14.3, 14.2.

TPS-A7a was synthesized according to the general procedure for glycosylation. Yield: 82 %; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.24 (d, *J* = 8.0 Hz, 2H), 8.15-7.80 (m, 24H), 7.72-6.67 (m, 5H), 7.66-7.59 (m, 3H), 7.58-7.12 (m, 46H), 5.94 (t, *J* = 8.0 Hz, 1H), 5.91-5.82 (m, 3H), 5.71-5.69 (m, 2H), 5.61-5.42 (m, 6H), 5.01 (d, *J* = 8.0 Hz, 1H), 4.98-4.92 (m, 2H), 4.88-4.79 (m, 2H), 4.77-4.65 (m, 2H), 4.58-4.42 (m, 1H), 4.41-4.39 (m, 2H), 4.38-4.36 (m, 1H), 4.29-4.06 (m, 5H), 3.72-3.39 (m, 4H), 3.65 (t, *J* = 8.0 Hz, 1H), 3.58 (d, *J* = 8.0 Hz, 1H), 3.41-3.35 (m, 2H), 3.29-3.26 (br s, 1H), 3.18 (d, *J* = 8.0 Hz, 1H), 3.08 (t, *J* = 8.0 Hz, 2H), 2.75 (br s, 1H), 2.63 (br s, 1H), 1.56-1.50 (m, 2H), 1.40-1.15 (m, 28H), 0.84 (t, *J* = 8.0 Hz, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 166.2, 166.1, 166.0, 165.9, 165.6, 165.3, 165.2, 165.1, 164.9, 164.5, 164.4, 133.4, 133.2, 133.1, 130.1, 130.0, 129.9, 129.8, 129.7, 129.5, 129.4, 129.3, 129.2, 129.1, 129.0, 128.6, 128.5, 128.4, 128.3, 128.2, 101.6, 99.9, 73.4, 72.8, 72.6, 72.3, 71.8, 71.4, 71.2, 70.4, 63.7, 41.0, 32.1, 30.8, 30.7, 29.9, 29.7, 29.6, 26.1, 22.8, 22.7, 14.3, 14.2.

TPS-A8a was synthesized according to the general procedure for glycosylation. Yield: 78 %; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.24 (d, *J* = 8.0 Hz, 2H), 8.15-7.80 (m, 24H), 7.72-6.67 (m, 5H), 7.66-7.59 (m, 3H), 7.58-7.12 (m, 46H), 5.94 (t, *J* = 8.0 Hz, 1H), 5.91-5.82 (m, 3H), 5.71-5.69 (m, 2H), 5.61-5.42 (m, 6H), 5.01 (d, *J* = 8.0 Hz, 1H), 4.98-4.92 (m, 2H), 4.88-4.79 (m, 2H), 4.77-4.65 (m, 2H), 4.58-4.42 (m, 1H), 4.41-4.39 (m, 2H), 4.38-4.36 (m, 1H), 4.29-4.06 (m, 5H), 3.72-3.39 (m, 4H), 3.65 (t, *J* = 8.0 Hz, 1H), 3.58 (d, *J* = 8.0 Hz, 1H), 3.41-3.35 (m, 2H), 3.29-3.26 (br s, 1H), 3.18 (d, *J* = 8.0 Hz, 1H), 3.08 (t, *J* = 8.0 Hz, 2H), 2.75 (br s, 1H), 2.63 (br s, 1H), 1.56-1.50 (m, 2H), 1.40-1.15 (m, 34H), 0.84 (t, *J* = 8.0 Hz, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 166.2, 166.1, 166.0, 165.9, 165.6, 165.3, 165.2, 165.1, 164.9, 164.5, 164.4, 133.4, 133.2, 133.1, 130.1, 130.0, 129.9, 129.8, 129.7, 129.5, 129.4, 129.3, 129.2, 129.1, 129.0, 128.6, 128.5, 128.4, 128.3, 128.2, 101.6, 99.9, 73.4, 72.8, 72.6, 72.3, 71.8, 71.4, 71.2, 70.4, 63.7, 41.0, 32.2, 32.1, 31.9, 30.8, 30.7, 29.9, 29.7, 29.6, 26.1, 22.8, 22.6, 14.3, 14.2.

TPS-A6 was synthesized according to the general procedure for de-*O*-benzoylation. Yield: 94 %; **^{1}H NMR** (400 MHz, CD_3OD): δ 4.93 (d, *J* = 8.0 Hz, 1H), 4.81 (d, *J* = 8.0 Hz, 1H), 4.62 (d, *J* = 8.0 Hz, 1H), 4.33 (d, *J* = 8.0 Hz, 2H), 4.24 (d, *J* = 10.0 Hz, 1H), 4.02 (t, *J* = 8.0 Hz, 1H), 3.91-3.85 (m, 2H), 3.87-3.82 (m, 5H), 3.68-3.63 (m, 6H), 3.48-3.19 (m, 22H), 1.52-1.46 (m, 2H), 1.38-1.18 (m, 22H), 0.86 (t, *J* = 8.0 Hz, 9H); **^{13}C NMR** (100 MHz, CD_3OD): δ 104.8, 103.8, 103.3, 103.0, 102.5, 78.4, 78.1, 78.0, 77.8, 77.7, 76.1, 76.0, 75.3, 75.1, 75.0, 74.2, 74.0, 72.2, 71.7, 71.5, 71.4, 69.4, 63.4, 62.9, 62.8, 62.5, 42.3, 33.2, 33.1, 32.3, 32.2, 31.4, 23.8, 20.7, 14.6, 14.5; **HRMS (EI)**: calcd. for $C_{49}H_{90}O_{27}$ $[M+Na]^+$ 1133.5567, observed 1133.5564.

TPS-A7 was synthesized according to the general procedure for de-*O*-benzoylation. Yield: 94 %; **^{1}H NMR** (400 MHz, CD_3OD): δ 4.93 (d, *J* = 8.0 Hz, 1H), 4.81 (d, *J* = 8.0 Hz, 1H), 4.62 (d, *J* = 8.0 Hz, 1H), 4.33 (d, *J* = 8.0 Hz, 2H), 4.24 (d, *J* = 10.0 Hz, 1H), 4.02 (t, *J* = 8.0 Hz, 1H), 3.91-3.85 (m, 2H), 3.87-3.82 (m, 5H), 3.68-3.63 (m, 6H), 3.48-3.19 (m, 22H), 1.52-1.46 (m, 2H), 1.38-1.18 (m, 28H), 0.85 (t, *J* = 8.0 Hz, 9H); **^{13}C NMR** (100 MHz, CD_3OD): δ 104.8, 103.8, 103.3, 103.0, 102.5, 78.4, 78.1, 78.0, 77.8, 77.7, 76.1, 76.0, 75.3, 75.1, 75.0, 74.2, 74.0, 72.2, 71.7, 71.5, 71.4, 69.4, 63.4, 62.9, 62.8, 62.5, 42.3, 33.2, 33.1, 32.2, 32.1, 31.7, 30.6, 30.5, 27.9, 24.1, 23.7, 14.6, 14.5; **HRMS (EI)**: calcd. for $C_{52}H_{96}O_{27}$ $[M+Na]^+$ 1175.6037, observed 1175.6033.

TPS-A8 was synthesized according to the general procedure for de-*O*-benzoylation. Yield: 93 %; **^{1}H NMR** (400 MHz, CD_3OD): δ 4.93 (d, *J* = 8.0 Hz, 1H), 4.81 (d, *J* = 8.0 Hz, 1H), 4.62 (d, *J* = 8.0 Hz, 1H), 4.33 (d, *J* = 8.0 Hz, 2H), 4.24 (d, *J* = 10.0 Hz, 1H), 4.02 (t, *J* = 8.0 Hz, 1H), 3.91-3.85 (m, 2H), 3.87-3.82 (m, 5H), 3.68-3.63 (m, 6H), 3.48-3.19 (m, 22H), 1.52-1.46 (m, 2H), 1.38-1.18 (m, 34H), 0.86 (t, *J* = 8.0 Hz, 9H); **^{13}C NMR** (100 MHz, CD_3OD): δ 104.8, 103.8, 103.3, 103.0, 102.5, 78.4, 78.1, 78.0, 77.8, 77.7, 76.1, 76.0, 75.3, 75.1, 75.0, 74.2, 74.0, 72.2, 71.7, 71.5, 71.4, 69.4, 63.4, 62.9, 62.8, 62.5, 42.3, 33.2, 33.0, 32.3, 32.2, 31.7, 30.9, 30.8, 30.6, 30.5, 29.9, 23.8, 23.7, 14.6, 14.5; **HRMS (EI)**: calcd. for $C_{55}H_{102}O_{27}$ $[M+Na]^+$ 1217.6506, observed 1217.6509.

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