Electronic Supplementary Material (ESI) for ChemComm.
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Supplementary Information

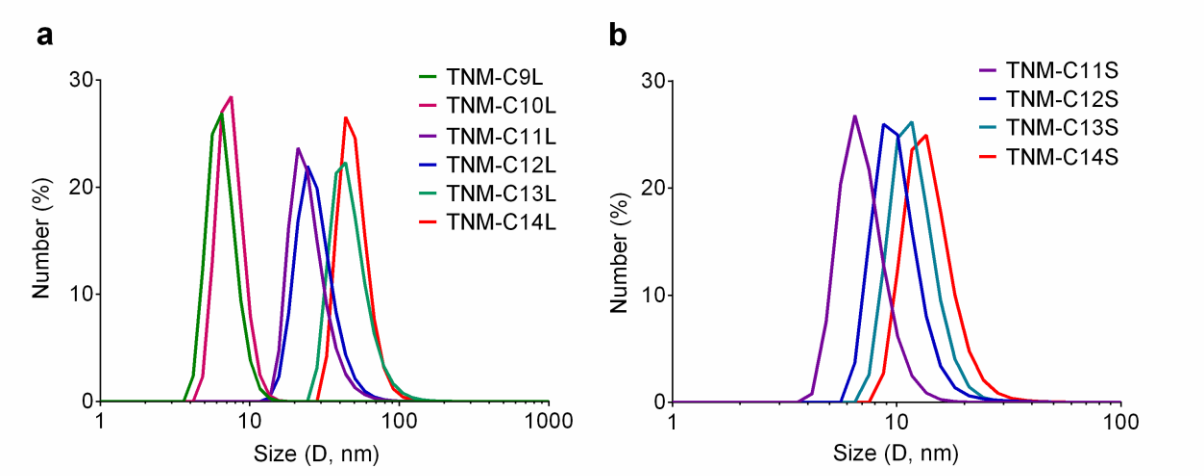


Figure S1. Dynamic light scattering (DLS) profiles of micelles formed by (a) TNM-Ls and (b) TNM-Ss. Micelle size was obtained by number-based analysis. All the TNMs showed a single set of populations in their micelle size when used at 0.5 wt %. Time-dependent fluctuation in the scattered light intensity was analyzed by autocorrelation, giving the translational diffusion coefficient (D). The hydrodynamic radii (R_h) of detergent micelles were correlated with the diffusion constant via the Stokes-Einstein equation.

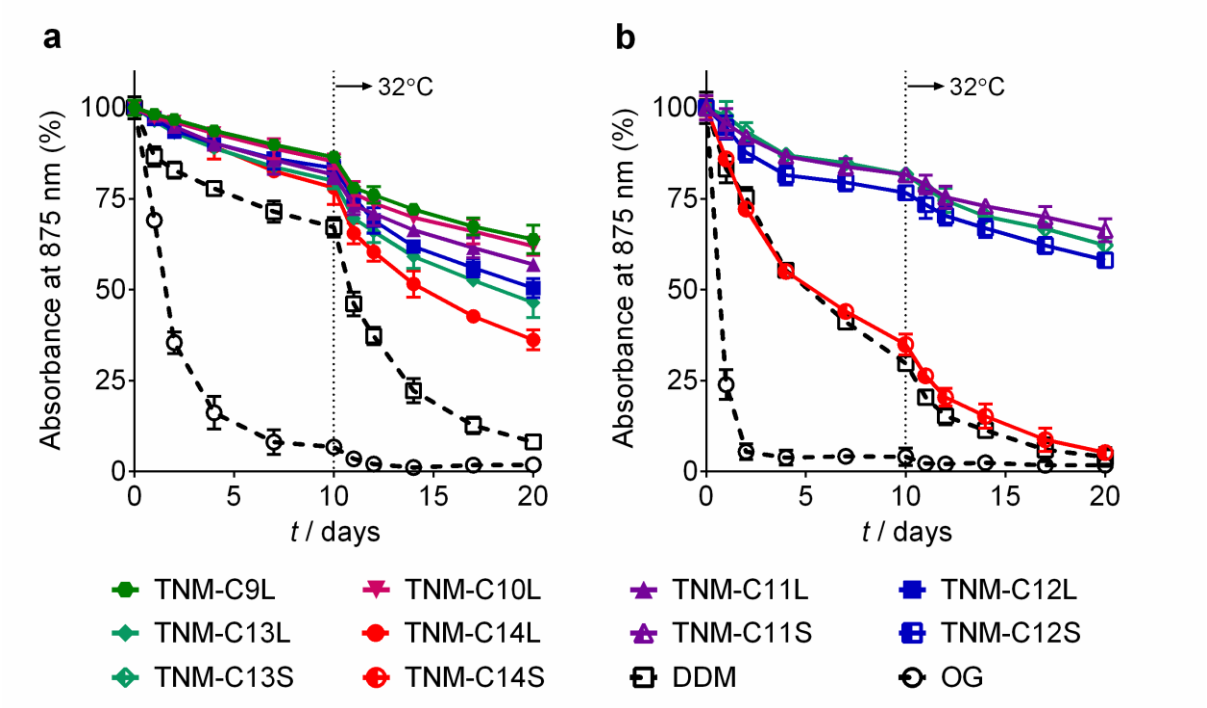


Figure S2. Long-term stability of LHI-RC complexes solubilized in novel agents (TNM-Ls (a) and TNM-Ss (b)) and conventional detergents (DDM and OG). The native conformation of the complexes strongly absorb light at 875 nm, which was used to assess protein stability. The protein stability was monitored at regular intervals during the incubation. The protein samples was incubated at 15℃ for TNM-Ls or 20℃ for TNM-Ss for 10 days, followed by a further 10 day incubation at 32℃. The temperature change indicated by the dotted lines on the graphs. Error bars, SEM, n = 2.

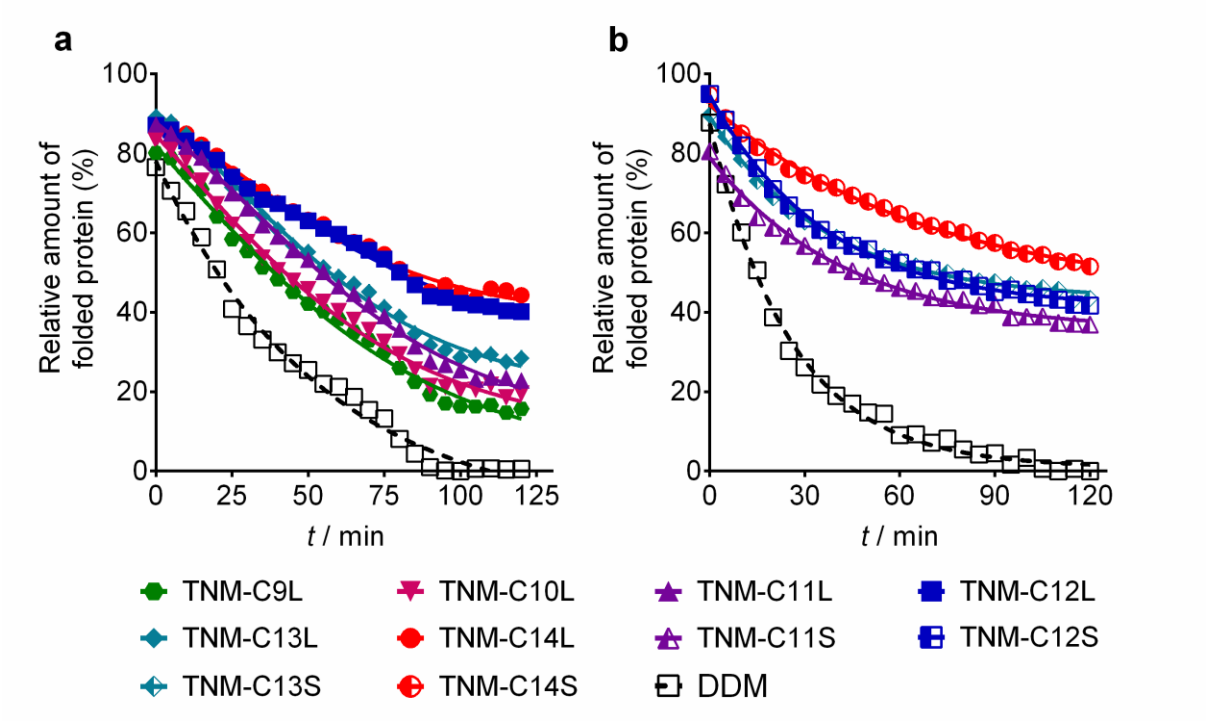


Figure S3. Thermal denaturation profile of UapA solubilized in individual TNMs (TNM-Ls (a) and TNM-Ss (b)) and a conventional detergent (DDM). Detergents were used at CMC+0.04 wt%. The relative amount of folded protein was monitored using the CPM assay over the course of a 120 min incubation at 40℃. The data is representative of three independent experiments.

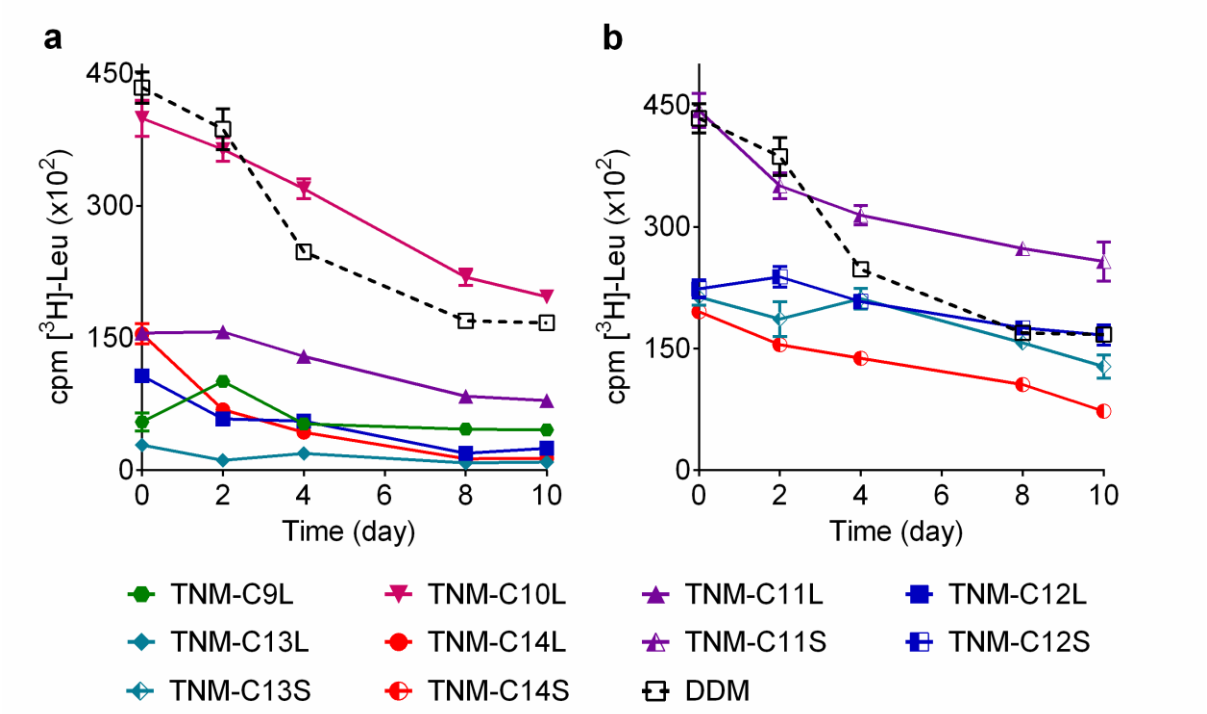


Figure S4. Long-term substrate binding activity for LeuT solubilized in individual TNMs (TNM-Ls (a) and TNM-Ss (b)) and a conventional detergent (DDM). All detergents were tested at CMC+0.2 wt%. Protein activity was measured via scintillation proximity assay (SPA) using a radio-labelled substrate ([^{3}H]-Leucine) during a 10-day incubation at room temperature. Error bars, SEM, n = 3.

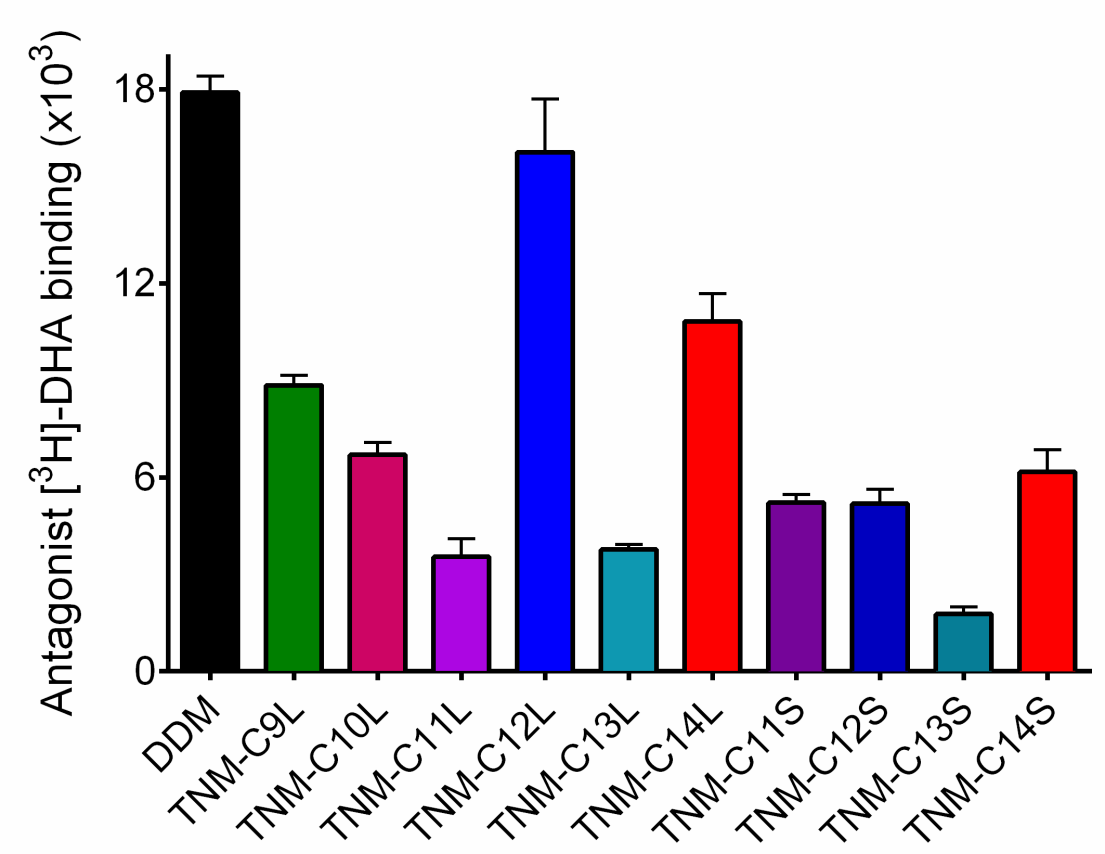


Figure S5. Ligand binding activity of β_2AR solubilized in DDM and individual TNMs (TNM-Ls and TNM-Ss). 0.1% DDM-purified β_2AR was diluted into buffer solutions containing individual detergents and receptor activity was measured at regular intervals using the antagonist [^{3}H]-dihydroalprenolol (DHA) over the course of four-day incubation at room temperature. The final detergent concentration was CMC+0.2 wt%. Error bars, SEM, *n* = 3.

Table S1. Molecular weights (MWs) and critical micelle concentrations (CMCs) of novel agents (TNM-Ls and TNM-Ss) and a conventional detergent (DDM), and hydrodynamic radii (R_h; n = 5) of their micelles.

Detergent	*M.W.*[a]	CMC (μM)	CMC (wt%)	R_h (nm)[b]
TNM-C9L	1646.9	~2.0	~0.00033	4.5 ± 0.2
TNM-C10L	1689.0	~1.5	~0.00025	4.5 ± 0.1
TNM-C11L	1731.1	~1.0	~0.00017	29.5 ± 1.6
TNM-C12L	1773.2	~0.8	~0.00016	33.8 ± 0.8
TNM-C13L	1815.2	~0.6	~0.00011	45.9 ± 2.7
TNM-C14L	1857.3	~0.4	~0.00007	48.1 ± 1.1
TNM-C11S	1690.0	~2.5	~0.00042	5.7 ± 0.2
TNM-C12S	1732.1	~1.5	~0.00026	6.5 ± 0.6
TNM-C13S	1774.2	~1.0	~0.00018	9.8 ± 1.7
TNM-C14S	1816.3	~0.8	~0.00015	11.6 ± 0.2
DDM	510.1	~170	~0.0087	3.4 ± 0.0

[a] Molecular weight of detergents. [b] Hydrodynamic radius of detergents measured at 1.0 wt% by dynamic light scattering.

Protein stability evaluation

***R. capsulatus* superassembly stability assay**

The superassembly was solubilized and purified from specialized photosynthetic membranes obtained from an engineered strain of *Rhodobacter capsulatus* according to the reported protocol.[1] A 10 ml aliquot of the frozen membranes was homogenized using a glass tissue homogenizer and was incubated with mild agitation at 32℃ for 30 mins. The resulting homogenized membranes were treated with DDM at 1.0 wt% for 30 min at 32℃. Following ultracentrifugation, the supernatant containing the solubilized LHI-RC complexes was collected and incubated with Ni^{2+}-NTA resin at 4℃ for one hour. The resin-containing solution was loaded into 10 His-SpinTrap columns (GE healthcare) and the resin was washed twice with 500 μl binding buffer (10 mM Tris (pH 7.8), 100 mL NaCl, 1×CMC DDM). Binding buffer containing 1M imidazole (2×300 μl) was used to elute DDM-purified LHI-RC complex. 80 μl of the protein sample was diluted into 920 μL of individual detergent solutions (TNM-Ls (TNM-C9L, TNM-C10L, TNM-C11L, TNM-C12L, TNM-C13L and TNM-C14L), TNM-Ss (TNM-C11S, TNM-C12S, TNM-C13S and TNM-C14S), DDM and OG). The final detergent concentration was CMC+0.04 wt% or CMC+0.2 wt%. The resulting LHI-RC complex in each detergent was incubated over 20 days (the first 10 days at either 15 or 20℃ and then 10 days at 32℃. Protein stability was measured at regular intervals during the incubation by taking UV-Visible spectra of the samples in the range of 650 nm to 950 nm. Protein integrity was assessed by monitoring 875 nm absorbance (A_{875}).

UapA thermal denaturation assay

$UapAG411V_{\Delta 1\text{-}11}$ was expressed as a GFP fusion 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).[2] The protein was concentrated to approximately 10 mg/ml using a 100 kDa molecular weight cut off filter (Millipore). The protein was diluted 1:150 into buffer containing either DDM, a TNM-L (TNM-C9L, TNM-C10L, TNM-C11L, TNM-C12L, TNM-C13L, or TNM-C14L) or a TNM-S (TNM-C11S, TNM-C12S, TNM-C13S, or TNM-C14S) 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) and 3 μl of the diluted dye was added to individual protein samples. The reaction mixture was incubated for 120 min at 40 ℃. The fluorescence emission was monitored using a microplate spectrofluorometer set at excitation and emission wavelengths of 387 nm and 463 nm, respectively. The maximum fluorescence value was used to calculate the percentage of relative folded protein during this incubation period. The relative amounts of folded proteins were plotted against time using GraphPad Prism.

LeuT stability assay

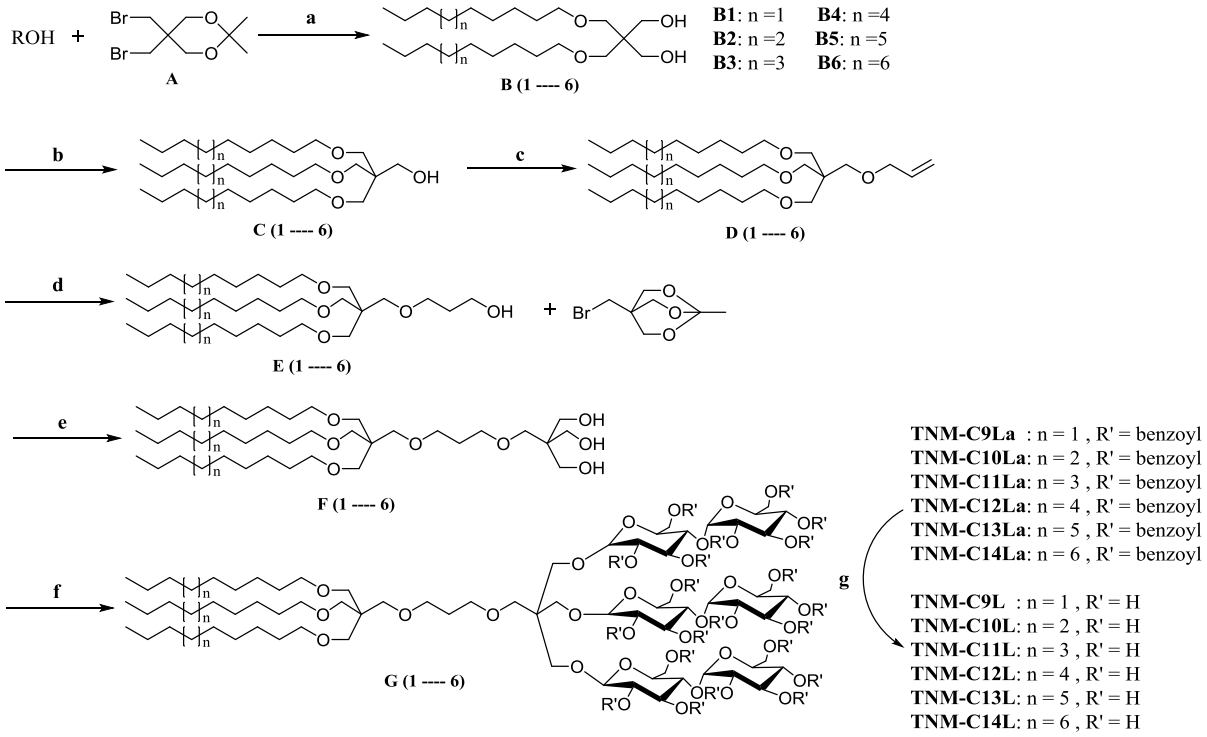
Purification of the wild type leucine transporter (LeuT) from *Aquifex aeolicus* was performed according to the protocol described previousely.[3] LeuT was expressed in *E. coli* C41(DE3) transformed with pET16b encoding C-terminally 8xHis-tagged transporter (expression plasmid was kindly provided by Dr. E. Gouaux, Vollum Institute, Portland, Oregon, USA). After isolation of bacterial membranes, the protein was solubilized by treatment of 1.0 % DDM. The DDM-solubilized protein was bound to Ni^{2+}-NTA resin (Life Technologies, Denmark) and eluted in 20 mM Tris-HCl (pH 8.0), 1 mM NaCl, 199 mM KCl, 0.05 % DDM and 300 mM imidazole. Subsequently, approx. 1.5 mg/ml protein stock was diluted ten-fold in identical buffer without DDM and imidazole, but supplemented with a TNM-L (TNM-C9L, TNM-C10L, TNM-C11L, TNM-C12L, TNM-C13L, or TNM-C14L), a TNM-S (TNM-C11S, TNM-C12S, TNM-C13S, or TNM-C14S), or DDM (control). The final detergent concentration was either CMC + 0.04 wt% or CMC + 0.2 wt%. Protein samples were stored for 10 days at room temperature and, at the indicated time points, were centrifuged and the ligand binding activity of the transporter determined via scintillation proximity assay (SPA) using [^{3}H]-Leucine.[4] The assay was performed with buffer containing 450 mM NaCl and the respective TNMs at the concentrations indicated above. The SPA reaction was carried out in the presence of 20 nM [^{3}H]-Leu and 1.25 mg/ml copper chelate (His-Tag) YSi beads (both from PerkinElmer, Denmark). Total [^{3}H]-Leu binding for the respective samples was measured using a MicroBeta liquid scintillation counter (PerkinElmer).

β_2AR stability assay

The β_2AR was purified by the use 0.1% DDM as previously described.[5] Briefly, the receptor was expressed in Sf9 insect cells infected with baculovirus and solubilized in 1% DDM. The DDM-solubilized receptor was purified by alprenolol sepharose in the presence of 0.01% cholesteryl succinate (CHS). The DDM-purified β_2AR was diluted into buffer solutions containing DDM or TNM-C12L to reach a detergent concentration of CMC + 0.2 wt%. β_2AR in each detergent was stored for 4 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 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) was collected. A further 15 ml scintillation fluid was added. Receptor-bound [^{3}H]-DHA was measured with a scintillation counter (Beckman).

Preparation of Tandem Neopentyl Glycol Maltosides (TNMs)

Supplementary scheme I



a) i) NaH, ROH, DMF, 120℃; ii) *p*-TSA, MeOH, CH_2Cl_2, RT; b) NaH, 1-bromoalkane (RBr), DMF, 100℃; c) NaH, Allyliodide, THF, 60℃; d) 1M BH_3 in THF, 3M NaOH, 30% H_2O_2, THF, RT; e) i) NaH, DMF:THF (1:1), 100˚C; (ii) CH_2Cl_2: MeOH (1:1), HCl, NaOH; f) perbenzoylated maltosylbromide, AgOTf, CH_2Cl_2 , RT; g) NaOMe, MeOH, RT.

*General procedure for the synthesis of dialkylated diols **(step a)***

To a solution of NaH (4.0 equiv.) in DMF, a respective alcohol (3.0 equiv.) was added dropwise at 0℃ under N_2 atmosphere and the resulting mixture was stirred at room temperature for 15 min. After addition of 5,5-bis-bromomethyl-2,2-dimethyl-[1,3]dioxane (**A**)[6] (1.0 equiv.), the reaction mixture was warmed to 120℃ and left for 15 h at this temperature. After cooling to room temperature, the reaction 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 of the solvent, the residue was dissolved in 1:1 mixture of CH_2Cl_2 and MeOH and *p*-toluenesulfonic acid (*p*-TSA) monohydrate (catalytic amount) was then added and left stirring at room temperature for 2 hrs. 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 collected organic layer was washed with brine, dried over anhydrous Na_2SO_4, and then concentrated *in vacuo*. Flash column chromatography (EtOAc/hexane) afforded ether-containing diol (**B1–B6**)) as a white solid (92-94 % (two steps)).

*General procedure for the synthesis of trialkylated mono-ol **(step b)***

To a suspension of NaH (1.3 equiv.) in dry DMF was added dropwise a solution of diols derivatives **(B1–B6)** (1.0 equiv.) in dry DMF at 0℃ under argon. After 15 min stirring, 1-bromoalkane (RI) (1.3 equiv.) was added to the mixture and the temperature was increased up to 100℃. The reaction mixture left at this temperature for 4 hrs, and then was cooled down 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 organic layer was concentrated *in vacuo* and the resulting residue was purified by silica gel column chromatography (EtOAc/hexane) providing trialkyl-containing mono-ol (**C1–C6**) as an oily liquid (85 to 90 %).

*General procedure for allylation **(step c)***

To a suspension of NaH (2.0 equiv.) in dry THF was added dropwise a solution of trialkylated mono-ol derivative (**C1–C6**) (1.0 equiv.) at 0℃ under Ar. After 15 min stirring, the allyl iodide (1.5 equiv.) was added to the mixture and the temperature was increased up to 60℃. The reaction mixture left at this temperature for 4 hrs, and then was cooled down 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 organic layer was concentrated *in vacuo* and the resulting residue was purified by silica gel column chromatography (EtOAc/hexane) providing the trialkylated allyl compound (**D1–D6**) as an oily liquid (90 to 95 %).

*General procedure for hydroboration **(step d)***

This reaction was carried out according to a literature method with some modifications.[7] Briefly, freshly distilled dry THF (3 ml) and an allylated compound (**D1–D6**) (1.65 g, 2.77 mmol) were placed in a dry round bottomed flask under N_2 and then cooled to 0℃ in an ice bath. 1 M BH_3 solution in THF (3 ml) was added slowly to this mixture and the reaction mixture was then allowed to stir at 0℃ for 10 hrs. The reaction mixture was then quenched with 3 M NaOH solution (2 ml) and stood with stirring for 20 min, followed by addition of 30% H_2O_2 solution (2 ml). The mixture was stirred at room temperature for 2 hrs. After being saturated with K_2CO_3, the reaction mixture was extracted with diethyl ether. The organic layer was dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The resulting mixture was purified by silica gel column chromatography (EtOAc/hexane) providing trialkylated hydroboration compound (**E1–E6**) as an oily liquid (55 to 60 %).

*General procedure for the synthesis of trialkylated tri-ol **(step e)***

To a solution of trialkylated mono-ol (**E1–E6**) (1.0 equiv.) in DMF (10 ml) was added NaH (3.0 equiv.) at 0℃ under Ar and the reaction mixture was stirred for 12 min. 4-(bromomethyl)-l-methyl-2,6,7-trioxabicyclo[2.2.2]-octane (3.0 equiv.)[8] dissolved in THF (3 ml) was added dropwise. The resulting mixture was heated at 100℃ for 24 hrs. After quenching with water, the solvents were removed under reduced pressure. The solid residue was dissolved in diethyl ether, washed with brine and dried over anhydrous Na_2SO_4. After concentrating organic layer by rotary evaporation, the residue was dissolved in DCM/MeOH (10 ml/10 ml) mixture. To this solution was added a few drops of conc. HCl and the resulting mixture was heated at 50℃ for 4 hrs. After neutralization with NaOH and concentration of the reaction mixture, the resulting residue was purified by column chromatography

(EtOAc/hexane), providing the trialkylated tri-ol (**F1–F6**) as an oily liquid (45 to 50 %).

General procedure for glycosylation reaction[9] ***(step f)***

Under N_2 atmosphere, a mixture of a tri-ol derivative **(F1–F6)** (1.0 equiv.), AgOTf (4.5 equiv.), 2,4,6-collidine (1.0 equiv.) in anhydrous CH_2Cl_2 was stirred at room temperature. A solution of perbenzoylated maltosylbromide (4.0 equiv.) in CH_2Cl_2 was added dropwise to this suspension. Stirring was continued for 10 min at room temperature. After completion of reaction (as detected by TLC), pyridine was added to the reaction mixture, and the resulting solution was diluted with CH_2Cl_2 before being filtered over celite. The filtrate was washed successively with 1 M aqueous $Na_2S_2O_3$ solution, 0.1 M aqueous HCl solution, and brine. The organic layer was collected and dried with anhydrous Na_2SO_4 and followed by rotary evaporation. The resulting residue was purified by silica gel column chromatography (EtOAc/hexane), providing the glycosylated product (**G1–G6**) as a white solid (45 to 75 %).

General Procedure for the de-O-benzoylations under Zemplén's condition[9] ***(step g)***

The *O*-benzoylated compounds (**G1–G6**) were dissolved in MeOH and then treated with 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 hrs 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) providing the fully deprotected compounds as a white solid (90 to 95 %).

2,2-bis((nonyloxy)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), 1.28-1.26 (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 **(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), 1.28-1.26 (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, 26.3, 22.9, 14.1.

2,2-bis((undecyloxy)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), 1.28-1.25 (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, 22.9, 14.1.

2,2-bis((dodecyloxy)methyl)propane-1,3-diol **(B4)** was prepared in 94 % yield according to the general procedure for the preparation of dialkylated diol. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 3.64 (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), 1.55 (quin, *J* = 4.0 Hz, 4H),

1.28-1.25 (m, 36H), 0.88 (t, *J* = 7.2 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 73.6, 72.4, 65.8, 44.6, 32.1, 30.2, 29.9, 29.8, 29.5, 26.3, 22.9, 14.2.

2,2-bis((tridecyloxy)methyl)propane-1,3-diol **(B5)** 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, 40H), 0.88 (t, *J* = 7.2 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 73.6, 72.5, 65.8, 44.6, 32.1, 30.3, 29.9, 29.7, 29.6, 26.3, 22.9, 14.2.

2,2-bis((tetradecyloxy)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, 44H), 0.88 (t, *J* = 7.2 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 73.6, 72.5, 65.8, 44.6, 32.1, 30.3, 29.9, 29.7, 29.6, 26.4, 22.9, 14.3.

3-(nonyloxy)-2,2-bis((nonyloxy)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 3.71 (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 **(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 3.71 (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 **(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), 3.43 (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.

3-(dodecyloxy)-2,2-bis((dodecyloxy)methyl)propan-1-ol (**C4)** 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), 3.17 (t, *J* = 8.0 Hz, 1H), 1.53 (quin, *J* = 8.0 Hz, 6H), 1.30-1.26 (m, 54H), 0.88 (t, *J* = 7.2 Hz, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 71.8, 71.4, 70.2, 62.9, 45.1, 32.1, 29.9, 29.7, 29.6, 26.4, 22.7, 14.2.

3-(trideyloxy)-2,2-bis((trideyloxy)methyl)propan-1-ol **(C5)** 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), 3.17 (t, *J* = 8.0 Hz, 1H), 1.53 (quin, *J* = 8.0 Hz, 6H), 1.28-1.25 (m, 60H), 0.88 (t, *J* = 7.2 Hz, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 71.7, 71.4, 70.2, 62.9, 45.1, 32.1, 29.9, 29.7, 29.6, 26.4, 22.7, 14.2.

3-(tetradecyloxy)-2,2-bis((tetradecyloxy)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), 1.28-1.25 (m, 66H), 0.88 (t, *J* = 7.2 Hz, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 71.7, 71.4, 70.3, 62.9, 45.1, 32.1, 31.9, 29.9, 29.7, 29.5, 26.4, 22.7, 14.2.

1-(3-(allyloxy)-2,2-bis((nonyloxy)methyl)propoxy)nonane **(D1)** was prepared in 92 % yield according to the general procedure for the preparation of allyl compound. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 5.93-5.83 (m, 1H), 5.28-5.22 (m, 1H), 5.14-5.11 (m, 1H), 3.95-3.93 (m, 2H), 3.42 (s, 2H), 3.38 (s, 6H), 3.35 (t, *J* = 8.0 Hz, 6H), 1.52 (quin, *J* = 8.0 Hz, 6H), 1.28-1.26 (m, 36H), 0.88 (t, *J* = 7.2 Hz, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 135.4, 116.1, 72.4, 72.1, 71.9, 71.7, 69.8, 69.7, 45.6, 32.1, 29.8, 29.5, 26.4, 26.3, 22.9, 14.2.

1-(3-(allyloxy)-2,2-bis((decyloxy)methyl)propoxy)decane **(D2)** was prepared in 90 % yield according to the general procedure for the preparation of allyl compound. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 5.93-5.84 (m, 1H), 5.27-5.22 (m, 1H), 5.13-5.10 (m, 1H), 3.95-3.93 (m, 2H), 3.42 (s, 2H), 3.38 (s, 6H), 3.35 (t, *J* = 8.0 Hz, 6H), 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 135.5, 116.1, 72.4, 72.1, 71.9, 69.8, 69.7, 45.6, 32.1, 29.8, 29.5, 26.4, 26.3, 22.9, 14.2.

1-(3-(allyloxy)-2,2-bis((undecyloxy)methyl)propoxy)undecane **(D3)** was prepared in 94 % yield according to the general procedure for the preparation of allyl compound. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 5.95-5.85 (m, 1H), 5.27-5.22 (m, 1H), 5.14-5.11 (m, 1H), 3.95-3.93 (m, 2H), 3.42 (s, 2H), 3.38 (s, 6H), 3.35 (t, *J* = 8.0 Hz, 6H), 1.52 (quin, *J* = 8.0 Hz, 6H), 1.29-1.26 (m, 48H), 0.88 (t, *J* = 7.2 Hz, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 135.5, 116.1, 72.4, 72.1, 71.9, 70.0, 69.8, 69.7, 45.6, 32.1, 29.8, 29.5, 26.4, 26.3, 22.9, 14.2.

1-(3-(allyloxy)-2,2-bis((dodecyloxy)methyl)propoxy)dodecane **(D4)** was prepared in 94 % yield according to the general procedure for the preparation of allyl compound. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 5.93-5.83 (m, 1H), 5.27-5.22 (m, 1H), 5.14-5.11 (m, 1H), 3.95-3.93 (m, 2H), 3.42 (s, 2H), 3.38 (s, 6H), 3.35 (t, *J* = 8.0 Hz, 6H), 1.53 (quin, *J* = 8.0 Hz, 6H), 1.28-1.26 (m, 54H), 0.88 (t, *J* = 7.2 Hz, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 135.6, 116.2, 72.4, 72.1, 71.9, 69.9, 69.7, 45.6, 32.1, 29.8, 29.6, 26.4, 26.3, 22.9, 14.2.

1-(3-(allyloxy)-2,2-bis((tridecyloxy)methyl)propoxy)tridecane **(D5)** was prepared in 95 % yield according to the general procedure for the preparation of allyl compound. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 5.93-5.83 (m, 1H), 5.27-5.22 (m, 1H), 5.14-5.11 (m, 1H), 3.95-3.93 (m, 2H), 3.42 (s, 2H), 3.38 (s, 6H), 3.35 (t, *J* = 8.0 Hz, 6H), 1.52 (quin, *J* = 8.0 Hz, 6H), 1.28-1.26 (m, 60H), 0.88 ((t, *J* = 7.2 Hz, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 135.6, 116.1, 72.4, 72.1, 71.9, 69.8, 69.7, 45.6, 32.1, 29.9, 29.8, 29.7, 29.6, 26.4, 26.3, 22.9, 14.3.

1-(3-(allyloxy)-2,2-bis((tetradecyloxy)methyl)propoxy)tetradecane **(D6)** was prepared in 93 % yield according to the general procedure for the preparation of allyl compound. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 5.93-5.83 (m, 1H), 5.27-5.22 (m, 1H), 5.14-5.11 (m, 1H), 3.95-3.93 (m, 2H), 3.42 (s, 2H), 3.38 (s, 6H), 3.35 (t, *J* = 8.0 Hz, 6H), 1.52 (quin, *J* = 8.0 Hz, 6H), 1.28-1.26 (m, 66H), 0.88 (t, *J* = 7.2 Hz, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 135.7, 116.2, 72.5, 72.4, 72.1, 71.9, 71.7, 69.8, 69.7, 45.6, 32.1, 29.8, 29.5, 26.4, 26.4, 23.2, 14.3.

3-(3-(nonyloxy)-2,2-bis((nonyloxy)methyl)propoxy)propan-1-ol **(F1)** was prepared in 55 % yield according to the general procedure for the preparation of hydroboration compound. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 3.76 (t, *J* = 8.0 Hz, 2H), 3.60 (t, *J* = 8.0 Hz, 2H), 3.43 (s, 2H), 3.38 (s, 6H), 3.35 (t, *J* = 8.0 Hz, 6H), 2.88 (brs, 1H), 1.80 (quin, *J* = 8.0 Hz, 2H), 1.52 (quin, *J* = 8.0 Hz, 6H), 1.30-1.26 (m, 36H), 0.88 (t, *J* = 7.2 Hz, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 71.8, 71.4, 70.2, 62.9, 45.3, 32.1, 31.9, 29.9, 29.7, 29.8, 29.5, 26.4, 22.9, 14.2.

3-(3-(decyloxy)-2,2-bis((decyloxy)methyl)propoxy)propan-1-ol **(F2)** was prepared in 58 % yield according to the general procedure for the preparation of hydroboration compound. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 3.76 (t, *J* = 8.0 Hz, 2H), 3.59 (t, *J* = 8.0 Hz, 2H), 3.43 (s, 2H), 3.37 (s, 6H), 3.35 (t, *J* = 8.0 Hz, 6H), 2.88 (brs, 1H), 1.80 (quin, *J* = 8.0 Hz, 2H), 1.52 (quin, *J* = 8.0 Hz, 6H), 1.30-1.26 (m, 42H), 0.88 (t, *J* = 7.2 Hz, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 71.8, 71.4, 70.2, 62.9, 45.3, 32.1, 29.9, 29.8, 29.5, 26.4, 22.9, 14.2.

3-(3-(undecyloxy)-2,2-bis((undecyloxy)methyl)propoxy)propan-1-ol **(F3)** was prepared in 58 % yield according to the general procedure for the preparation of hydroboration compound. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 3.77 (t, *J* = 8.0 Hz, 2H), 3.60 (t, *J* = 8.0 Hz, 2H), 3.43 (s, 2H), 3.37 (s, 6H), 3.35 (t, *J* = 8.0 Hz, 6H), 2.90 (brs, 1H), 1.80 (quin, *J* = 8.0 Hz, 2H), 1.52 (quin, *J* = 8.0 Hz, 6H), 1.30-1.26 (m, 48H), 0.88 (t, *J* = 7.2 Hz, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 71.8, 71.5, 70.2, 63.0, 45.3, 32.1, 29.9, 29.8, 29.6, 29.5, 26.4, 22.9, 14.2.

3-(3-(dodecyloxy)-2,2-bis((dodecyloxy)methyl)propoxy)propan-1-ol **(F4)** was prepared in 57 % yield according to the general procedure for the preparation of hydroboration compound. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 3.77 (t, *J* = 8.0 Hz, 2H), 3.60 (t, *J* = 8.0 Hz, 2H), 3.43 (s, 2H), 3.37 (s, 6H), 3.35 (t, *J* = 8.0 Hz, 6H), 2.90 (brs, 1H), 1.80 (quin, *J* = 8.0 Hz, 2H), 1.52 (quin, *J* = 8.0 Hz, 6H), 1.30-1.25 (m, 54H), 0.88 (t, *J* = 7.2 Hz, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 71.9, 71.4, 70.2, 62.9, 45.3, 32.1, 29.9, 29.8, 29.6, 29.5, 26.4, 22.9, 14.3.

3-(3-(tridecyloxy)-2,2-bis((tridecyloxy)methyl)propoxy)propan-1-ol **(F5)** was prepared in 60 % yield according to the general procedure for the preparation of hydroboration compound. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 3.76 (t, *J* = 8.0 Hz, 2H), 3.61 (t, *J* = 8.0 Hz, 2H), 3.43 (s, 2H), 3.38 (s, 6H), 3.35 (t, *J* = 8.0 Hz, 6H), 2.90 (brs, 1H), 1.80 (quin, *J* = 8.0 Hz, 2H), 1.52 (quin, *J* = 8.0 Hz, 6H), 1.30-1.25 (m, 60H), 0.88 (t, *J* = 7.2 Hz, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 71.9, 71.4, 70.2, 62.9, 45.3, 32.1, 31.9, 30.1, 29.9, 29.8, 29.5, 26.4, 22.9, 14.3.

3-(3-(tetradecyloxy)-2,2-bis((tetradecyloxy)methyl)propoxy)propan-1-ol **(F6)** was prepared in 58 % yield according to the general procedure for the preparation of hydroboration compound. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 3.77 (t, *J* = 8.0 Hz, 2H), 3.60 (t, *J* = 8.0 Hz, 2H), 3.43 (s, 2H), 3.37 (s, 6H), 3.35 (t, *J* = 8.0 Hz, 6H), 2.89 (brs, 1H), 1.80 (quin, *J* = 8.0 Hz, 2H), 1.52 (quin, *J* = 8.0 Hz, 6H), 1.30-1.25 (m, 66H), 0.88 (t, *J* = 7.2 Hz, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 71.9, 71.4, 70.2, 62.9, 45.3, 32.2, 31.1, 29.9, 29.8, 29.7, 29.5, 26.5, 22.9, 14.3.

2-(hydroxymethyl)-2-((3-(3-(nonyloxy)-2,2-bis((nonyloxy)methyl)propoxy)propoxy)methyl)propane-1,3-diol **(G1)** was prepared in 45 % yield according to the general procedure for the preparation of trialkylated tri-ol. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 3.70 (s, 6H), 3.52 (t, *J* = 8.0 Hz, 2H) 3.50 (s, 2H), 3.46 (t, *J* = 8.0 Hz, 2H), 3.38 (quin, *J* = 8.0 Hz, 12H), 3.35 (s, 2H), 2.88 (br s, 3H), 1.79 (quin, *J* = 8.0

Hz, 2H), 1.52 (quin, *J* = 8.0 Hz, 6H), 1.31-1.26 (m, 36H), 0.88 (t, *J* = 7.2 Hz, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 73.1, 71.6, 69.9, 69.6, 68.8, 67.7, 64.9, 45.4, 31.9, 29.7, 29.6, 29.5, 29.4, 26.2, 22.7, 14.1.

2-(hydroxymethyl)-2-((3-(3-(decyloxy)-2,2-bis((decyloxy)methyl)propoxy)propoxy)methyl)propane-1,3-diol **(G2)** was prepared in 47 % yield according to the general procedure for the preparation of trialkylated tri-ol. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 3.67 (s, 6H), 3.51 (t, *J* = 8.0 Hz, 2H) 3.49 (s, 2H), 3.46 (t, *J* = 8.0 Hz, 2H), 3.36 (quin, *J* = 8.0 Hz, 12H), 3.35 (s, 2H), 2.68 (br s, 3H), 1.79 (quin, *J* = 8.0 Hz, 2H), 1.52 (quin, *J* = 8.0 Hz, 6H), 1.31-1.26 (m, 42H), 0.88 (t, *J* = 7.2 Hz, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 73.1, 71.6, 69.9, 68.8, 67.7, 64.9, 45.4, 31.9, 29.7, 29.6, 29.4, 26.2, 22.7, 14.1.

2-(hydroxymethyl)-2-((3-(3-(undecyloxy)-2,2-bis((undecyloxy)methyl)propoxy)propoxy)methyl) propane-1,3-diol **(G3)** was prepared in 47 % yield according to the general procedure for the preparation of trialkylated tri-ol. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 3.67 (s, 6H), 3.50 (t, *J* = 8.0 Hz, 2H) 3.48 (s, 2H), 3.45 (t, *J* = 8.0 Hz, 2H), 3.36 (quin, *J* = 8.0 Hz, 12H), 3.35 (s, 2H), 3.29 (brs, 3H), 1.79 (quin, *J* = 8.0 Hz, 2H), 1.52 (quin, *J* = 8.0 Hz, 6H), 1.31-1.26 (m, 48H), 0.88 (t, *J* = 7.2 Hz, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 73.1, 71.6, 69.9, 69.6, 68.8, 67.7, 64.9, 45.4, 44.8, 31.9, 29.7, 29.6, 29.4, 26.2, 22.7, 14.2.

2-(hydroxymethyl)-2-((3-(3-(dodecyloxy)-2,2-bis((dodecyloxy)methyl)propoxy)propoxy)methyl) propane-1,3-diol **(G4)** was prepared in 50 % yield according to the general procedure for the preparation of trialkylated tri-ol. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 3.70 (s, 6H), 3.52 (t, *J* = 8.0 Hz, 2H) 3.50 (s, 2H), 3.46 (t, *J* = 8.0 Hz, 2H), 3.36 (quin, *J* = 8.0 Hz, 12H), 3.35 (s, 2H), 2.91 (br s, 3H), 1.79 (quin, *J* = 8.0 Hz, 2H), 1.52 (quin, *J* = 8.0 Hz, 6H), 1.31-1.26 (m, 54H), 0.88 (t, *J* = 7.2 Hz, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 73.2, 71.6, 69.9, 68.9, 68.8, 67.7, 65.1, 45.4, 44.9, 31.9, 29.7, 29.6, 29.4, 26.2, 22.7, 14.2.

2-(hydroxymethyl)-2-((3-(3-(tridecyloxy)-2,2-bis((tridecyloxy)methyl)propoxy)propoxy)methyl) propane-1,3-diol **(G5)** was prepared in 49 % yield according to the general procedure for the preparation of trialkylated tri-ol. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 3.70 (s, 6H), 3.52 (t, *J* = 8.0 Hz, 2H) 3.50 (s, 2H), 3.46 (t, *J* = 8.0 Hz, 2H), 3.36 (quin, *J* = 8.0 Hz, 12H), 3.35 (s, 2H), 2.67 (brs, 3H), 1.79 (quin, *J* = 8.0 Hz, 2H), 1.52 (quin, *J* = 8.0 Hz, 6H), 1.31-1.25 (m, 60H), 0.88 (t, *J* = 7.2 Hz, 9H);**^{13}C NMR** (100 MHz, $CDCl_3$): δ 73.14 ,71.6, 69.9, 68.8, 67.7, 65.1, 45.5, 31.9, 29.7, 29.6, 29.4, 26.2, 22.7, 14.2.

2-(hydroxymethyl)-2-((3-(3-(tetradecyloxy)-2,2-bis((tetradecyloxy)methyl)propoxy)propoxy)methyl) propane-1,3-diol **(G6)** was prepared in 50 % yield according to the general procedure for the preparation of trialkylated tri-ol. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 3.70 (s, 6H), 3.52 (t, *J* = 8.0 Hz, 2H) 3.50 (s, 2H), 3.46 (t, *J* = 8.0 Hz, 2H), 3.36 (quin, *J* = 8.0 Hz, 12H), 3.35 (s, 2H), 2.65 (br s, 3H), 1.79 (quin, *J* = 8.0 Hz, 2H), 1.52 (quin, *J* = 8.0 Hz, 6H), 1.31-1.25 (m, 66H), 0.88 (t, *J* = 7.2 Hz, 9H);**^{13}C NMR** (100 MHz, $CDCl_3$): δ 73.14 ,71.6, 69.9, 68.8, 67.7, 65.1, 45.5, 32.1, 31.9, 29.7, 29.7, 29.4, 26.2, 22.7, 14.3.

TNM-C9La was prepared in 52% yield according to the general procedure for glycosylation reaction. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.08 (d, *J* = 8.0 Hz, 6H), 7.98 (d, *J* = 8.0 Hz, 6H), 7.92-7.83 (m, 12H), 7.79-7.66 (m, 12H), 7.65-7.20 (m, 69H), 6.10 (t, *J* = 18.2 Hz, 3H), 5.75-5.62 (m, 3H), 5.43 (t, *J* = 16.4

Hz, 3H), 5.19-5.10 (m, 6H), 4.57 (t, *J* = 3.2 Hz, 6H), 4.34-4.26 (dd, *J* = 8.0, 12.0 Hz, 9H), 4.18 (d, *J* = 8.0 Hz, 3H), 3.70 (t, *J* = 20.0 Hz, 6H), 3.37 (quin, *J* = 18.4 Hz, 12H), 3.23-2.98 (m, 14H), 1.79 (quin, *J* = 8.0 Hz, 2H), 1.52 (quin, *J* = 8.0 Hz, 6H), 1.31-1.25 (m, 36H), 0.87 (t, *J* = 7.2 Hz, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 166.0, 165.7, 165.5, 165.0, 164.7, 133.4, 133.1, 129.9, 129.8, 129.7, 129.6, 29.4, 129.3, 128.9, 128.8, 128.7, 128.6, 128.4, 128.2, 100.8, 95.7, 72.1, 72.0, 71.5, 71.2, 69.7, 68.9, 68.8, 63.3, 62.3, 45.3, 31.9, 29.7, 29.5, 29.4, 26.2, 22.7, 14.2

TNM-C10La was prepared in 45% yield according to the general procedure for glycosylation reaction. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.08 (d, *J* = 8.0 Hz, 6H), 7.98 (d, *J* = 8.0 Hz, 6H), 7.92-7.83 (m, 12H), 7.79-7.66 (m, 12H), 7.65-7.20 (m, 69H), 6.12 (t, *J* = 18.2 Hz, 3H), 5.75-5.63 (m, 3H), 5.44 (t, *J* = 16.4 Hz, 3H), 5.20-5.11 (m, 6H), 4.58 (t, *J* = 3.2 Hz, 6H), 4.34-4.26 (dd, *J* = 8.0, 12.0 Hz, 9H), 4.18 (d, *J* = 8.0 Hz, 3H), 3.70 (t, *J* = 20.0 Hz, 6H), 3.36 (quin, *J* = 18.4 Hz, 12H), 3.24-2.99 (m, 14H), 1.79 (quin, *J* = 8.0 Hz, 2H), 1.53 (quin, *J* = 8.0 Hz, 6H), 1.31-1.25 (m, 42H), 0.87 (t, *J* = 7.2 Hz, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 166.0, 165.7, 165.5, 165.0, 164.7, 133.4, 133.1, 129.9, 129.8, 129.7, 129.6, 129.4, 129.3, 128.9, 128.8, 128.6, 128.4, 128.3, 100.8, 95.7, 72.1, 72.0, 71.5, 71.2, 69.7, 68.8, 63.3, 62.3, 45.3, 31.9, 29.7, 29.5, 29.4, 26.3, 22.7, 14.2

TNM-C11La was prepared in 48% yield according to the general procedure for glycosylation reaction. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.08 (d, *J* = 8.0 Hz, 6H), 7.98 (d, *J* = 8.0 Hz, 6H), 7.92-7.85 (m, 12H), 7.79-7.67 (m, 12H), 7.65-7.22 (m, 69H), 6.11 (t, *J* = 20 Hz, 3H), 5.75-5.63 (m, 6H), 5.44 (t, *J* = 16.4 Hz, 3H), 5.20-5.10 (m, 6H), 4.57 (t, *J* = 3.2 Hz, 6H), 4.34-4.26 (dd, *J* = 8.0, 12.0 Hz, 9H), 4.19 (d, *J* = 8.0 Hz, 3H), 3.70 (t, *J* = 20.0 Hz, 6H), 3.37 (quin, *J* = 18.4 Hz, 12H), 3.23-2.98 (m, 14H), 1.79 (quin, *J* = 8.0 Hz, 2H), 1.51 (quin, *J* = 8.0 Hz, 6H), 1.30-1.25 (m, 48H), 0.87 (t, *J* = 7.2 Hz, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 166.1, 165.8, 165.5, 165.1, 164.7, 133.4, 133.1, 129.9, 129.8, 129.7, 129.6, 129.4, 129.3, 128.9, 128.8, 128.7, 128.6, 128.4, 128.2, 100.8, 95.7, 72.1, 72.0, 71.5, 71.2, 69.7, 68.9, 68.8, 63.3, 62.4, 45.3, 31.9, 29.7, 29.5, 29.4, 26.3, 22.7, 14.2

TNM-C12La was prepared in 70% yield according to the general procedure for glycosylation reaction. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.09 (d, *J* = 8.0 Hz, 6H), 7.98 (d, *J* = 8.0 Hz, 6H), 7.92-7.83 (m, 12H), 7.79-7.66 (m, 12H), 7.65-7.20 (m, 69H), 6.11 (t, *J* = 18.2 Hz, 3H), 5.75-5.63 (m, 6H), 5.44 (t, *J* = 16.4 Hz, 3H), 5.20-5.11 (m, 6H), 4.57 (t, *J* = 3.2 Hz, 6H), 4.34-4.26 (dd, *J* = 8.0, 12.0 Hz, 9H), 4.18 (d, *J* = 8 Hz, 3H), 3.70 (t, *J* = 20.0 Hz, 6H), 3.36 (quin, *J* = 18.4 Hz, 12H), 3.23-2.98 (m, 14H), 1.79 (quin, *J* = 8.0 Hz, 2H), 1.53 (quin, *J* = 8.0 Hz, 6H), 1.34-1.25 (m, 54H), 0.87 (t, *J* = 7.2 Hz, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 166.0, 165.7, 165.5, 165.0, 164.7, 133.4, 133.1, 129.9, 129.8, 129.7, 129.6, 129.4, 129.3, 128.9, 128.7, 128.6, 128.4, 128.2, 100.8, 95.7, 72.1, 72.0, 71.5, 71.2, 69.7, 68.9, 68.8, 63.3, 62.3, 45.4, 31.9, 29.8, 29.6, 29.4, 26.3, 22.7, 14.2

TNM-C13La was prepared in 65% yield according to the general procedure for glycosylation reaction. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.09 (d, *J* = 8.0 Hz, 6H), 7.96 (d, *J* = 7.2Hz, 6H), 7.90-7.83 (m, 12H), 7.79-7.66 (m, 12H), 7.65-7.20 (m, 69H), 6.08 (t, *J* = 18.2 Hz, 3H), 5.75-5.63 (m, 6H), 5.41 (t, *J* = 16.4 Hz, 3H), 5.20-5.10 (m, 6H), 4.56 (t, *J* = 3.2 Hz, 6H), 4.34-4.26 (dd, *J* = 8.0, 12.0 Hz, 9H), 4.18 (d, *J* = 8 Hz, 3H), 3.70 (t, *J* = 20.0 Hz, 6H), 3.36 (quin, *J* = 18.4 Hz, 12H), 3.20-2.96 (m, 14H), 1.60 (quin, *J* = 8.0 Hz, 2H), 1.50 (quin, *J* = 8.0 Hz, 6H), 1.34-1.21 (m, 60H), 0.87 (t, *J* = 7.2 Hz, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 166.2, 165.8, 165.5, 165.0, 164.7, 133.4, 133.1, 129.9, 129.8, 129.7, 129.6, 129.4, 129.3, 128.9, 128.8, 128.7, 128.6, 128.4, 128.2, 100.8, 95.7, 72.1, 72.0, 71.5, 71.2, 69.7,

68.9, 68.8, 63.3, 62.3, 45.4, 32.0, 29.7, 29.5, 29.4, 26.2, 22.8, 14.3

TNM-C14La was prepared in 75% yield according to the general procedure for glycosylation reaction. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.08 (d, *J* = 8.0 Hz, 6H), 7.98 (d, *J* = 8.0 Hz, 6H), 7.88-7.84 (m, 12H), 7.79-7.66 (m, 12H), 7.65-7.20 (m, 69H), 6.10 (t, *J* = 18.2 Hz, 3H), 5.75-5.62 (m, 6H), 5.43 (t, *J* = 16.4 Hz, 3H), 5.19-5.12 (m, 6H), 4.57 (t, *J* = 3.2 Hz, 6H), 4.34-4.26 (dd, *J* = 8.0, 12.0 Hz, 9H), 4.18 (d, *J* = 8.0 Hz, 3H), 3.69 (t, *J* = 20.0 Hz, 6H), 3.32 (quin, *J* = 18.4 Hz, 12H), 3.23-2.98 (m, 14H), 1.65 (quin, *J* = 8.0 Hz, 2H), 1.51 (quin, *J* = 8.0 Hz, 6H), 1.31-1.21 (m, 66H), 0.87 (t, *J* = 7.2 Hz, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 166.2, 165.8, 165.5, 165.1, 165.0, 164.7, 133.4, 133.1, 129.9, 129.8, 129.7, 129.6, 129.4, 129.3, 128.9, 128.8, 128.7, 128.6, 128.4, 128.2, 100.8, 95.7, 72.1, 72.0, 71.5, 71.2, 69.7, 68.9, 68.8, 63.3, 62.3, 45.4, 32.0, 29.7, 29.5, 29.4, 26.2, 22.8, 14.3

TNM-C9L was prepared in 90% yield according to the general procedure for deprotection reaction. **^{1}H NMR** (400 MHz, CD_3OD): δ 5.15 (d, *J* = 4.0 Hz, 3H), 4.35 (d, *J* = 8.0 Hz, 3H), 3.98 (d, *J* = 12.0 Hz, 3H), 3.84-3.78 (m, 6H), 3.70-3.58 (m, 15H), 3.55-3.22 (m, 45H), 1.81 (quin, *J* = 12.0 Hz, 2H), 1.56 (quin, *J* = 12.0 Hz, 6H), 1.34-1.29 (m, 36H), 0.89 (t, *J* = 7.2 Hz, 9H); **^{13}C NMR** (100 MHz, CD_3OD): δ 105.1, 103.1, 81.5, 77.9, 76.6, 75.2, 74.8, 74.3, 72.6, 71.5, 70.6, 62.8, 46.7, 46.6, 33.3, 31.0, 30.8, 30.6, 27.6, 23.9, 14.7; **HRMS (EI)**: calcd. for $C_{76}H_{142}O_{38}$ $[M+Na]^+$ 1685.9077, found 1685.9081.

TNM-C10L was prepared in 95% yield according to the general procedure for de-*O*-benzoylation under Zemplén's condition. **^{1}H NMR** (400 MHz, CD_3OD): δ 5.15 (d, *J* = 4.0 Hz, 3H), 4.35 (d, *J* = 8.0 Hz, 3H), 3.98 (d, *J* = 12.0 Hz, 3H), 3.82-3.78 (m, 6H), 3.70-3.58 (m, 15H), 3.55-3.22 (m, 45H), 1.79 (quin, *J* = 12.0 Hz, 2H), 1.54 (quin, *J* = 19.6 Hz, 6H), 1.34-1.29 (m, 42H), 0.90 (t, *J* = 7.2 Hz, 9H); **^{13}C NMR** (100 MHz, CD_3OD): δ 105.1, 103.1, 81.5, 77.8, 76.6, 75.1, 74.9, 74.3, 72.6, 71.5, 70.6, 62.8, 46.7, 33.3, 31.0, 30.9, 30.8, 30.7, 27.6, 23.9, 14.7; **HRMS (EI)**: calcd. for $C_{79}H_{148}O_{38}$ $[M+Na]^+$ 1727.9546, found 1727.9548.

TNM-C11L was prepared in 94% yield according to the general procedure for de-*O*-benzoylation under Zemplén's condition. **^{1}H NMR** (400 MHz, CD_3OD): δ 5.15 (d, *J* = 4.0 Hz, 3H), 4.34 (d, *J* = 8.0 Hz, 3H), 3.97 (d, *J* = 10.0 Hz, 3H), 3.84-3.78 (m, 6H), 3.70-3.58 (m, 15H), 3.55-3.22 (m, 45H), 1.79 (quin, *J* = 12.8 Hz, 2H), 1.54 (quin, *J* = 12.0 Hz, 6H), 1.34-1.29 (m, 48H), 0.90 (t, *J* = 7.2 Hz, 9H); **^{13}C NMR** (100 MHz, CD_3OD): δ 105.1, 103.1, 81.5, 77.8, 76.6, 75.1, 74.8, 74.2, 72.6, 71.5, 70.6, 70.0, 62.8, 62.2, 46.7, 46.6, 33.3, 31.0, 30.8, 30.7, 27.6, 23.9, 14.7; **HRMS (EI)**: calcd. for $C_{82}H_{154}O_{38}$ $[M+Na]^+$ 1770.0016, found 1770.0011.

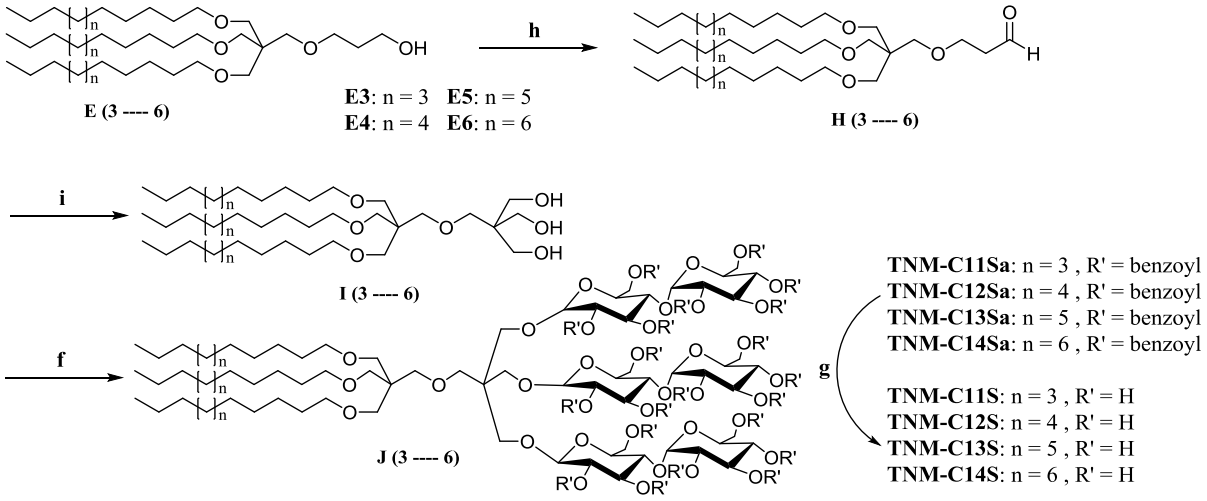
TNM-C12L was prepared in 95% yield according to the general procedure for de-*O*-benzoylation under Zemplén's condition. **^{1}H NMR** (400 MHz, CD_3OD): δ 5.15 (d, *J* = 4.0 Hz, 3H), 4.35 (d, *J* = 8.0 Hz, 3H), 3.98 (d, *J* = 12.0 Hz, 3H), 3.84-3.78 (m, 6H), 3.70-3.58 (m, 15H), 3.55-3.22 (m, 45H), 1.80 (quin, *J* = 12.0 Hz, 2H), 1.55 (quin, *J* = 12.0 Hz, 6H), 1.34-1.29 (m, 54H), 0.90 (t, *J* = 7.2 Hz, 9H); **^{13}C NMR** (100 MHz, CD_3OD): δ 105.1, 103.1, 81.5, 77.8, 76.6, 75.1, 74.9, 74.2, 72.6, 71.5, 70.6, 62.8, 46.7, 46.6, 33.3, 31.0, 30.8, 30.7, 27.6, 23.9, 14.7; **HRMS (EI)**: calcd. for $C_{85}H_{160}O_{38}$ $[M+Na]^+$ 1812.0485, found 1812.0480.

TNM-C13L was prepared in 93% yield according to the general procedure for de-*O*-benzoylation under Zemplén's condition. **^{1}H NMR** (400 MHz, CD_3OD): δ 5.15 (d, *J* = 4.0 Hz, 3H), 4.34 (d, *J* = 8.0

Hz, 3H), 3.97 (d, *J* = 10.0 Hz, 3H), 3.86-3.78 (m, 6H), 3.70-3.57 (m, 15H), 3.55-3.20 (m, 45H), 1.79 (quin, *J* = 12.4 Hz, 2H), 1.54 (quin, *J* = 12.0 Hz, 6H), 1.34-1.28 (m, 60H), 0.90 (t, *J* = 7.2 Hz, 9H); **^{13}C NMR** (100 MHz, CD_3OD): δ 105.1, 103.1, 81.5, 77.8, 76.7, 75.1, 74.8, 74.2, 72.6, 71.5, 70.6, 70.0, 62.8, 46.7, 46.6, 33.3, 31.0, 30.8, 30.7, 27.6, 23.9, 14.7; **HRMS (EI)**: calcd. for $C_{88}H_{166}O_{38}$ $[M+Na]^+$ 1855.0989, found 1855.1305.

TNM-C14L was prepared in 95% yield according to the general procedure for de-*O*-benzoylation under Zemplén's condition. **^{1}H NMR** (400 MHz, CD_3OD): δ 5.15 (d, *J* = 4.0 Hz, 3H), 4.34 (d, *J* = 7.6 Hz, 3H), 3.97 (d, *J* = 10.0 Hz, 3H), 3.84-3.78 (m, 6H), 3.70-3.58 (m, 15H), 3.55-3.22 (m, 45H), 1.79 (quin, *J* = 12.8 Hz, 2H), 1.54 (quin, *J* = 12.0 Hz, 6H), 1.34-1.28 (m, 66H), 0.90 (t, *J* = 7.2 Hz, 9H); **^{13}C NMR** (100 MHz, CD_3OD): δ 103.1, 81.5, 77.9, 74.9, 72.5, 71.5, 70.6, 62.8, 54.9, 46.6, 33.3, 30.8, 30.7, 27.6, 24.3, 23.9, 14.7; **HRMS (EI)**: calcd. for $C_{91}H_{172}O_{38}$ $[M+Na]^+$ 1897.1459, found 1897.1396.

Supplementary scheme II



h) pyridinium chlorochromate (PCC), CH_2Cl_2, celite; i) formaldehyde, EtOH, KOH; f) perbenzoylated maltosylbromide, AgOTf, CH_2Cl_2 , RT; g) NaOMe, MeOH, RT.

General procedure for alcohol oxidation ***(step h)***

To the solution of pyridinium chlorochromate (PCC) (2.0 equiv.) and celite (1:1) in CH_2Cl_2 trialkylated hydroboration compound (**E3–E6**) (1.0 equiv.) was added dropwise. The resulting mixture was stirred at RT for 1 day. The solution was diluted in CH_2Cl_2 followed by filtration over a short pad of celite. The residue obtained after removal of solvent at low pressure was subsequently purified by silica gel column chromatography (EtOAc/hexane), providing the trialkylated aldehyde compound (**H3–H6**) as an oily liquid (90 to 95 %).

General procedure for the synthesis of trialkylated *tri-ol* ***(step i)***

This reaction was carried out according to a literature method with some modifications.[10] To the solution of an trialkylated aldehyde **(H3–H6)** in 50% aqueous alkaline EtOH (KOH 30%), formaldehyde solution was added. The resulting mixture was stirred at RT for 2 hrs and then heated at 60℃ for 2 days. After removal of EtOH by rotary evaporator, the resulting mixture was extracted with

diethyl ether. The organic layer was dried over anhydrous Na_2SO_4 followed by purification by silica gel column chromatography (EtOAc/hexane) providing trialkylated tri-ol compound **(I3–I6)** as an oily liquid (30 to 40 %).

3-(3-(undecyloxy)-2,2-bis((undecyloxy)methyl)propoxy)propanal **(H3)** was prepared in 90 % yield according to the general procedure for alcohol oxidation. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.69 (s, 1H), 3.68 (t, *J* = 8.0 Hz, 2H), 3.35 (s, 6H), 3.28 (t, *J* = 8.0 Hz, 6H), 2.54-2.50 (m, 2H) 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 202.0, 71.7, 70.4, 69.7, 65.4, 45.5, 44.0, 32.1, 29.9, 29.8, 29.7, 29.5, 26.4, 22.9, 14.3.

3-(3-(dodecyloxy)-2,2-bis((dodecyloxy)methyl)propoxy)propanal **(H4)** was prepared in 93 % yield according to the general procedure for alcohol oxidation. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.69 (s, 1H), 3.68 (t, *J* = 8.0 Hz, 2H), 3.35 (s, 6H), 3.28 (t, *J* = 8.0 Hz, 6H), 2.54-2.50 (m, 2H) 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 202.0, 71.7, 70.4, 69.7, 65.4, 45.5, 44.0, 32.1, 29.9, 29.7, 29.5, 26.4, 22.9, 14.3.

3-(3-(tridecyloxy)-2,2-bis((tridecyloxy)methyl)propoxy)propanal **(H5)** was prepared in 95 % yield according to the general procedure for alcohol oxidation. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.69 (s, 1H), 3.68 (t, *J* = 8.0 Hz, 2H), 3.36 (s, 6H), 3.28 (t, *J* = 8.0 Hz, 6H), 2.55-2.51 (m, 2H) 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 202.0, 71.7, 70.4, 69.7, 65.4, 45.5, 44.0, 32.1, 29.9, 29.8, 29.7, 29.5, 26.4, 22.9, 14.3.

3-(3-(tetradecyloxy)-2,2-bis((tetradecyloxy)methyl)propoxy)propanal **(H6)** was prepared in 95 % yield according to the general procedure for alcohol oxidation. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.69 (s, 1H), 3.68 (t, *J* = 8.0 Hz, 2H), 3.36 (s, 6H), 3.28 (t, *J* = 8.0 Hz, 6H), 2.55-2.51 (m, 2H) 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 202.0, 71.7, 70.4, 69.7, 65.4, 45.5, 44.0, 32.1, 29.9, 29.8, 29.7, 29.5, 26.4, 22.9, 14.3.

2-(hydroxymethyl)-2-((3-(undecyloxy)-2,2-bis((undecyloxy)methyl)propoxy)methyl)propane-1,3-diol **(I3)** was prepared in 37 % yield according to the general procedure for the preparation of trialkylated tri-ol. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 3.67 (s, 6H), 3.46 (s, 2H) 3.42 (s, 2H), 3.36 (quin, *J* = 8.0 Hz, 12H), 2.75 (brs, 3H), 1.52 (quin, *J* = 8.0 Hz, 6H), 1.31-1.26 (m, 48H), 0.88 (t, *J* = 7.2 Hz, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 73.5, 72.5, 72.0, 70.6, 65.2, 45.4, 32.1, 29.9, 29.7, 29.5, 26.4, 22.9, 14.3.

2-(hydroxymethyl)-2-((3-(dodecyloxy)-2,2-bis((dodecyloxy)methyl)propoxy)methyl)propane-1,3-diol **(I4)** was prepared in 30 % yield according to the general procedure for the preparation of trialkylated tri-ol. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 3.67 (s, 6H), 3.46 (s, 2H) 3.42 (s, 2H), 3.36 (quin, *J* = 8.0 Hz, 12H), 2.82 (brs, 3H), 1.52 (quin, *J* = 8.0 Hz, 6H), 1.31-1.26 (m, 54H), 0.88 (t, *J* = 7.2 Hz, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 73.5, 72.5, 72.0, 70.6, 65.2, 45.4, 32.1, 29.9, 29.7, 29.5, 26.4, 22.9, 14.3.

2-(hydroxymethyl)-2-((3-(tridecyloxy)-2,2-bis((tridecyloxy)methyl)propoxy)methyl)propane-1,3-diol **(I5)** was prepared in 35 % yield according to the general procedure for the preparation of trialkylated tri-ol. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 3.67 (s, 6H), 3.47 (s, 2H) 3.42 (s, 2H), 3.36 (quin, *J* = 8.0 Hz, 12H), 2.90 (brs, 3H), 1.52 (quin, *J* = 8.0 Hz, 6H), 1.31-1.26 (m, 60H), 0.88 (t, *J* = 7.2 Hz, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 73.5, 72.5, 72.0, 70.6, 65.2, 45.4, 32.1, 30.0, 29.9, 29.7, 29.5, 26.4, 22.9, 14.3.

2-(hydroxymethyl)-2-((3-(tetradecyloxy)-2,2-bis((tetradecyloxy)methyl)propoxy)methyl)propane-1,3-diol **(I6)** was prepared in 40 % yield according to the general procedure for the preparation of trialkylated tri-ol. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 3.67 (s, 6H), 3.47 (s, 2H) 3.42 (s, 2H), 3.36 (quin, *J* = 8.0 Hz, 12H), 2.85 (brs, 3H), 1.52 (quin, *J* = 8.0 Hz, 6H), 1.31-1.26 (m, 66H), 0.88 (t, *J* = 7.2 Hz, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 73.5, 72.5, 72.0, 70.6, 65.2, 45.4, 32.1, 30.0, 29.9, 29.7, 29.5, 26.4, 22.9, 14.3.

TNM-C11Sa was prepared in 45% yield according to the general procedure for glycosylation reaction. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.07 (d, *J* = 8.0 Hz, 6H), 7.97 (d, *J* = 8.0 Hz, 6H), 7.90-7.83 (m, 12H), 7.78-7.72 (m, 12H), 7.66-7.22 (m, 69H), 6.11 (t, *J* = 20.0 Hz, 3H), 5.75-5.63 (m, 6H), 5.44 (t, *J* = 16.4 Hz, 3H), 5.20-5.10 (m, 6H), 4.57 (t, *J* = 3.2 Hz, 6H), 4.34-4.26 (dd, *J* = 8.0, 12.0 Hz, 9H), 4.19 (d, *J* = 8.0 Hz, 3H), 3.70 (t, *J* = 20.0 Hz, 4H), 3.37 (quin, *J* = 18.4 Hz, 12H), 3.23-2.98 (m, 12H), 1.79 (quin, *J* = 8.0 Hz, 2H), 1.51 (quin, *J* = 8.0 Hz, 6H), 1.30-1.25 (m, 48H), 0.87 (t, *J* = 7.2 Hz, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 166.2, 165.9, 165.6, 165.2, 165.1, 164.8, 133.5, 133.2, 130.1, 130.0, 129.9, 129.7, 129.6, 129.5, 129.1, 129.0, 128.9, 128.8, 128.5, 128.4, 101.2, 96.0, 72.3, 71.5, 71.3, 70.0, 69.5, 69.1, 45.7, 32.1, 29.9, 29.8, 29.5, 26.4, 22.9, 14.3.

TNM-C12Sa was prepared in 58% yield according to the general procedure for glycosylation reaction. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.07 (d, *J* = 8.0 Hz, 6H), 7.97 (d, *J* = 8.0 Hz, 6H), 7.90-7.83 (m, 12H), 7.78-7.72 (m, 12H), 7.66-7.22 (m, 69H), 6.11 (t, *J* = 20.0 Hz, 3H), 5.75-5.63 (m, 6H), 5.44 (t, *J* = 16.4 Hz, 3H), 5.20-5.10 (m, 6H), 4.57 (t, *J* = 3.2 Hz, 6H), 4.35-4.27 (dd, *J* = 8.0, 12.0 Hz, 9H), 4.19 (d, *J* = 8.0 Hz, 3H), 3.70 (t, *J* = 20.0 Hz, 4H), 3.37 (quin, *J* = 18.4 Hz, 12H), 3.23-2.98 (m, 12H), 1.79 (quin, *J* = 8.0 Hz, 2H), 1.51 (quin, *J* = 8.0 Hz, 6H), 1.30-1.25 (m, 54H), 0.87 (t, *J* = 7.2 Hz, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 166.2, 165.9, 165.6, 165.2, 165.1, 164.8, 133.5, 133.2, 130.1, 130.0, 129.9, 129.7, 129.6, 129.5, 129.1, 129.0, 128.9, 128.8, 128.7, 128.5, 128.4, 101.2, 96.0, 72.3, 71.5, 71.3, 70.0, 69.5, 69.1, 45.7, 32.1, 29.9, 29.8, 29.5, 26.4, 22.9, 14.3

TNM-C13Sa was prepared in 60% yield according to the general procedure for glycosylation reaction. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.07 (d, *J* = 8.0 Hz, 6H), 7.97 (d, *J* = 8.0 Hz, 6H), 7.90-7.83 (m, 12H), 7.78-7.72 (m, 12H), 7.66-7.22 (m, 69H), 6.11 (t, *J* = 20.0 Hz, 3H), 5.75-5.63 (m, 6H), 5.44 (t, *J* = 16.4 Hz, 3H), 5.20-5.10 (m, 6H), 4.57 (t, *J* = 3.2 Hz, 6H), 4.35-4.27 (dd, *J* = 8.0, 12.0 Hz, 9H), 4.19 (d, *J* = 8.0 Hz, 3H), 3.71 (t, *J* = 20.0 Hz, 4H), 3.37 (quin, *J* = 18.4 Hz, 12H), 3.23-2.98 (m, 12H), 1.79 (quin, *J* = 8.0 Hz, 2H), 1.51 (quin, *J* = 8.0 Hz, 6H), 1.30-1.25 (m, 60H), 0.87 (t, *J* = 7.2 Hz, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 166.2, 165.9, 165.6, 165.2, 165.1, 164.9, 133.5, 133.2, 130.1, 130.0, 129.9, 129.7, 129.6, 129.5, 129.1, 129.0, 128.9, 128.8, 128.5, 128.4, 101.2, 96.0, 72.3, 71.5, 71.3, 70.0, 69.5, 69.1, 45.7, 32.1, 29.9, 29.8, 29.5, 26.4, 22.9, 14.3

TNM-C14Sa was prepared in 55% yield according to the general procedure for glycosylation reaction. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.07 (d, *J* = 8.0 Hz, 6H), 7.97 (d, *J* = 8.0 Hz, 6H), 7.90-7.83 (m, 12H), 7.78-7.72 (m, 12H), 7.66-7.22 (m, 69H), 6.11 (t, *J* = 20.0 Hz, 3H), 5.75-5.63 (m, 6H), 5.44 (t, *J* = 16.4 Hz, 3H), 5.20-5.10 (m, 6H), 4.57 (t, *J* = 3.2 Hz, 6H), 4.35-4.27 (dd, *J* = 8.0, 12.0 Hz, 9H), 4.19 (d, *J* = 8.0 Hz, 3H), 3.71 (t, *J* = 20.0 Hz, 4H), 3.37 (quin, *J* = 18.4 Hz, 12H), 3.23-2.98 (m, 12H), 1.79 (quin, *J* = 8.0 Hz, 2H), 1.51 (quin, *J* = 8.0 Hz, 6H), 1.30-1.25 (m, 66H), 0.87 (t, *J* = 7.2 Hz, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 166.2, 165.9, 165.6, 165.2, 165.1, 164.9, 133.5, 133.2, 130.1, 130.0, 129.9, 129.7, 129.6, 129.5, 129.1, 129.0, 128.8, 128.5, 128.4, 101.2, 96.0, 72.3, 71.5, 71.3, 70.0, 69.5, 69.1,

45.7, 32.1, 29.9, 29.8, 29.5, 26.4, 22.9, 14.3

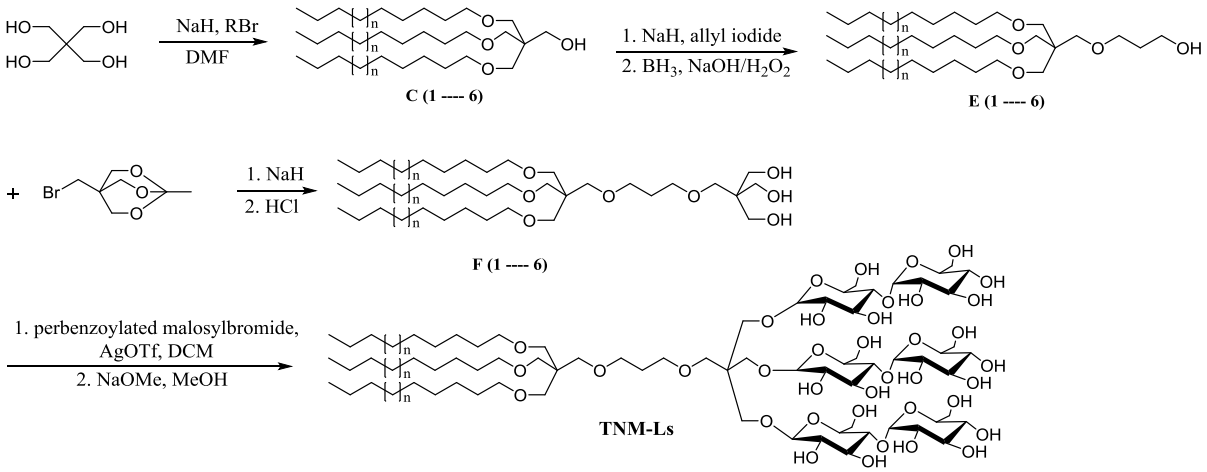
TNM-C11S was prepared in 94% yield according to the general procedure for the de-*O*-benzoylation under Zemplén's condition. **^{1}H NMR** (400 MHz, CD_3OD): δ 5.15 (d, *J* = 4.0 Hz, 3H), 4.35 (d, *J* = 8.0 Hz, 3H), 3.98 (d, *J* = 10.0 Hz, 3H), 3.87-3.79 (m, 6H), 3.70-3.58 (m, 13H), 3.55-3.22 (m, 43H), 1.54 (quin, *J* = 12.0 Hz, 6H), 1.34-1.29 (m, 48H), 0.90 (t, *J* = 7.2 Hz, 9H); **^{13}C NMR** (100 MHz, CD_3OD): δ ; **HRMS (EI)**: calcd. for $C_{79}H_{148}O_{37}$ $[M+Na]^+$ 1711.9597, found 1711.9594.

TNM-C12S was prepared in 90% yield according to the general procedure for de-*O*-benzoylation under Zemplén's condition. **^{1}H NMR** (400 MHz, CD_3OD): δ 5.15 (d, *J* = 4.0 Hz, 3H), 4.35 (d, *J* = 8.0 Hz, 3H), 3.98 (d, *J* = 10.0 Hz, 3H), 3.87-3.79 (m, 6H), 3.70-3.58 (m, 13H), 3.56-3.23 (m, 43H), 1.54 (quin, *J* = 12.0 Hz, 6H), 1.34-1.29 (m, 54H), 0.90 (t, *J* = 7.2 Hz, 9H); **^{13}C NMR** (100 MHz, CD_3OD): δ ; **HRMS (EI)**: calcd. for $C_{82}H_{154}O_{37}$ $[M+Na]^+$ 1754.0067, found 1754.0071.

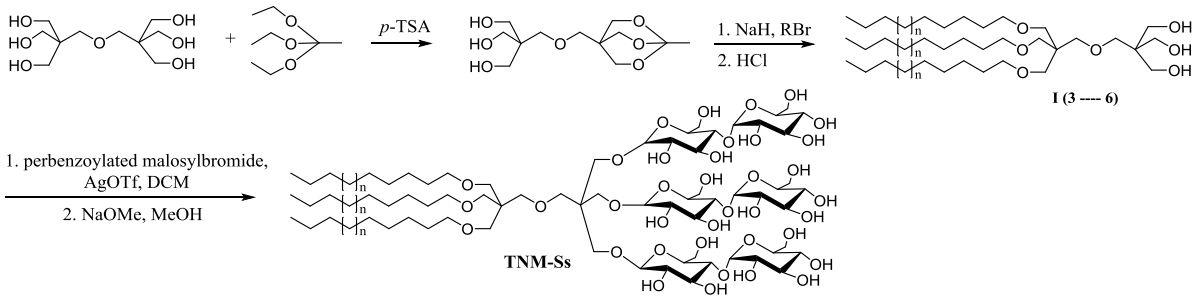
TNM-C13S was prepared in 93% yield according to the general procedure for de-*O*-benzoylation under Zemplén's condition. **^{1}H NMR** (400 MHz, CD_3OD): δ 5.15 (d, *J* = 4.0 Hz, 3H), 4.35 (d, *J* = 8.0 Hz, 3H), 3.98 (d, *J* = 10.0 Hz, 3H), 3.87-3.79 (m, 6H), 3.70-3.58 (m, 13H), 3.55-3.22 (m, 43H), 1.55 (quin, *J* = 12.0 Hz, 6H), 1.34-1.29 (m, 60H), 0.90 (t, *J* = 7.2 Hz, 9H); **^{13}C NMR** (100 MHz, CD_3OD): δ ; **HRMS (EI)**: calcd. for $C_{85}H_{160}O_{37}$ $[M+Na]^+$ 1796.0536, found 1796.0541.

TNM-C14S was prepared in 95% yield according to the general procedure for de-*O*-benzoylation under Zemplén's condition. **^{1}H NMR** (400 MHz, CD_3OD): δ 5.15 (d, *J* = 4.0 Hz, 3H), 4.35 (d, *J* = 8.0 Hz, 3H), 3.98 (d, *J* = 10.0 Hz, 3H), 3.87-3.79 (m, 6H), 3.70-3.58 (m, 13H), 3.56-3.23 (m, 43H), 1.55 (quin, *J* = 12.0 Hz, 6H), 1.34-1.29 (m, 66H), 0.90 (t, *J* = 7.2 Hz, 9H); **^{13}C NMR** (100 MHz, CD_3OD): δ ; **HRMS (EI)**: calcd. for $C_{88}H_{166}O_{37}$ $[M+Na]^+$ 1839.1040, found 1839.0858.

***Hypothetical* synthetic scheme I**



***Hypothetical* synthetic scheme II**



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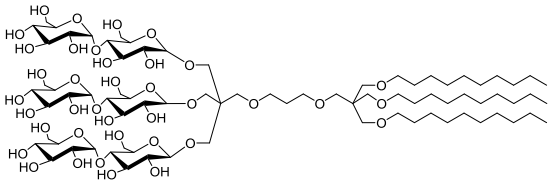
TNM-C10L



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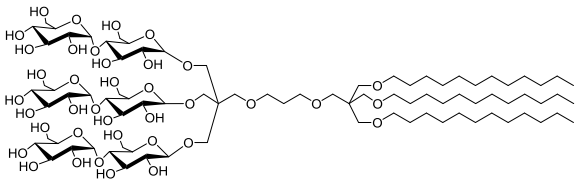

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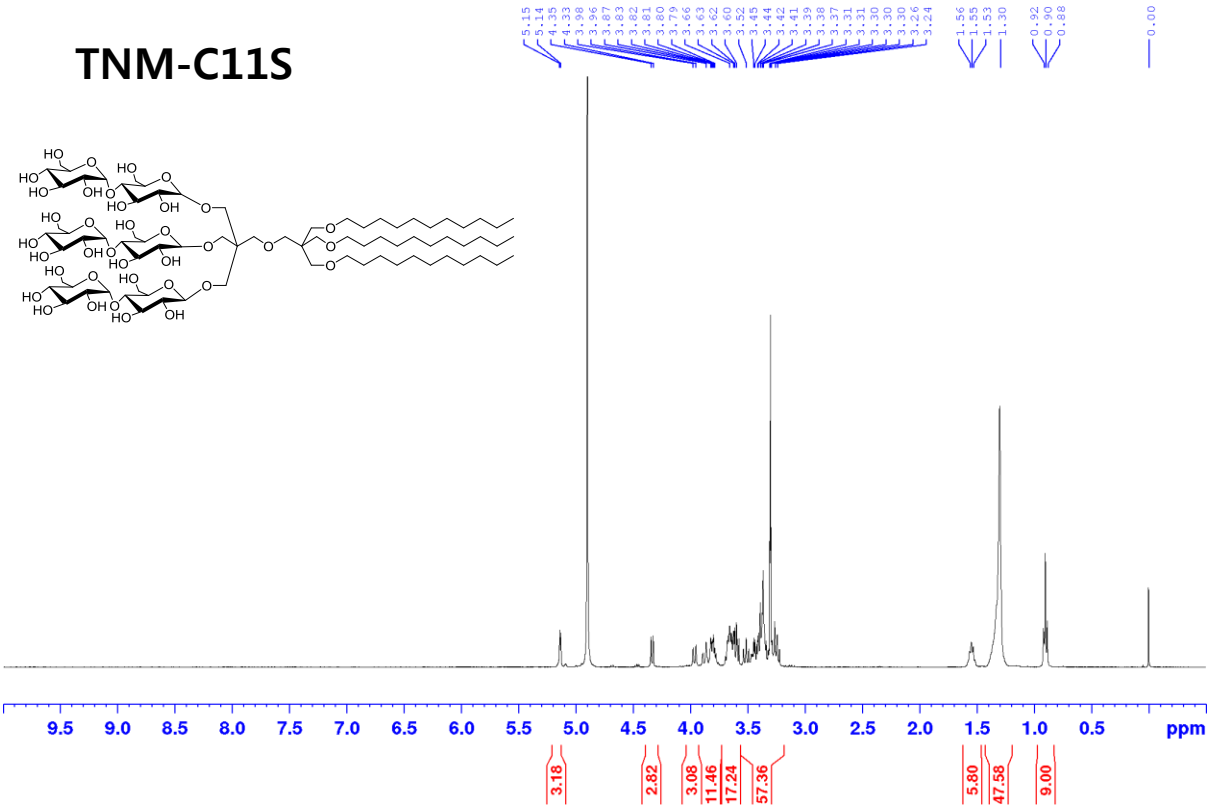
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