Supporting Online Material for

Supramolecular polymerization in water harnessing both hydrophobic effects and hydrogen bond formation

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Experimental Details

Materials

Unless stated otherwise, all reagents and chemicals were obtained from commercial sources at the highest purity available and used without further purification. (*S*)-Citronellol was obtained from Takasago, (*e.e.* = 98.4%). All solvents were of AR quality and purchased from Biosolve. Dry, degassed THF was obtained after passage through an activated alumina solvent column system. Deuterated chloroform was dried over 4Å molsieves and triethylamine was stored on KOH pellets. Flash chromatography was performed on a Biotage flash chromatography system using 200–425 mesh silica gel (Type 60A Grade 633). Water was purified on an EMD Milipore Mili-Q Integral Water Purification System. Reactions were followed by thin-layer chromatography (precoated 0.25 mm, 60-F254 silica gel plates from Merck). All reactions were performed under an atmosphere of dry argon unless stated otherwise.

Instrumentation

^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Varian Mercury Vx 400 MHz (100 MHz for ^{13}C) or a Varian Mercury Plus 200 MHz (50 MHz for ^{13}C) NMR spectrometer. Chemical shifts are given in ppm (δ) values relative to residual solvent or tetramethylsilane (TMS). Splitting patterns are labelled as s, singlet; d, doublet; dd, double doublet; t, triplet; q, quartet; quin, quintet; m, multiplet and b stands for broad.

Matrix assisted laser desorption/ionisation mass spectra were obtained on a PerSeptive Biosystems Voyager DE-PRO spectrometer or a Bruker autoflex speed spectrometer using α-cyano-4-hydroxycinnamic acid (CHCA) and 2-[(2E)-3-(4-tert-butylphenyl)-2-methylprop-2-enylidene]malononitrile (DCTB) as matrices.

Infrared spectra were recorded on a Perkin Elmer Spectrum One 1600 FT-IR spectrometer or a Perkin Elmer Spectrum Two FT-IR spectrometer, equipped with a Perkin Elmer Universal ATR Sampler Accessory.

CD measurements were performed on a Jasco J-815 spectropolarimeter where the sensitivity, time constant and scan rate were chosen appropriately. Corresponding temperature dependent measurements were performed with a Jasco PTC-348WI Peltier-type temperature controller, with a temperature range of 263-383 K and adjustable temperature slope.

Ultraviolet-visible (UV-vis) absorbance spectra were recorded on and a Jasco V-650 UV-vis spectrometer with a Jasco ETCT-762 temperature controller.

Fluorescence data were recorded on a Varian Cary Eclipse fluorescence spectrometer.

Samples for cryogenic transmission electron microscopy (cryo-TEM) were prepared in a 'Vitrobot' instrument (PC controlled vitrification robot, patent applied, Frederik et al 2002, patent licensed to FEI) at room temperature and a relative humidity >95%. In the preparation chamber of the 'Vitrobot' a 3µl sample was applied on a Quantifoil grid (R 2/2, Quantifoil Micro Tools GmbH; freshly glow discharged just prior to use), excess liquid was blotted away for 2s at -2mm and the thin film thus formed was shot (acceleration about 3 g) into liquid ethane. The vitrified film was transferred to a cryoholder (Gatan 626) and observed at -170 °C in a Tecnai Sphera microscope operating at 200 kV. Micrographs were taken at low dose conditions.

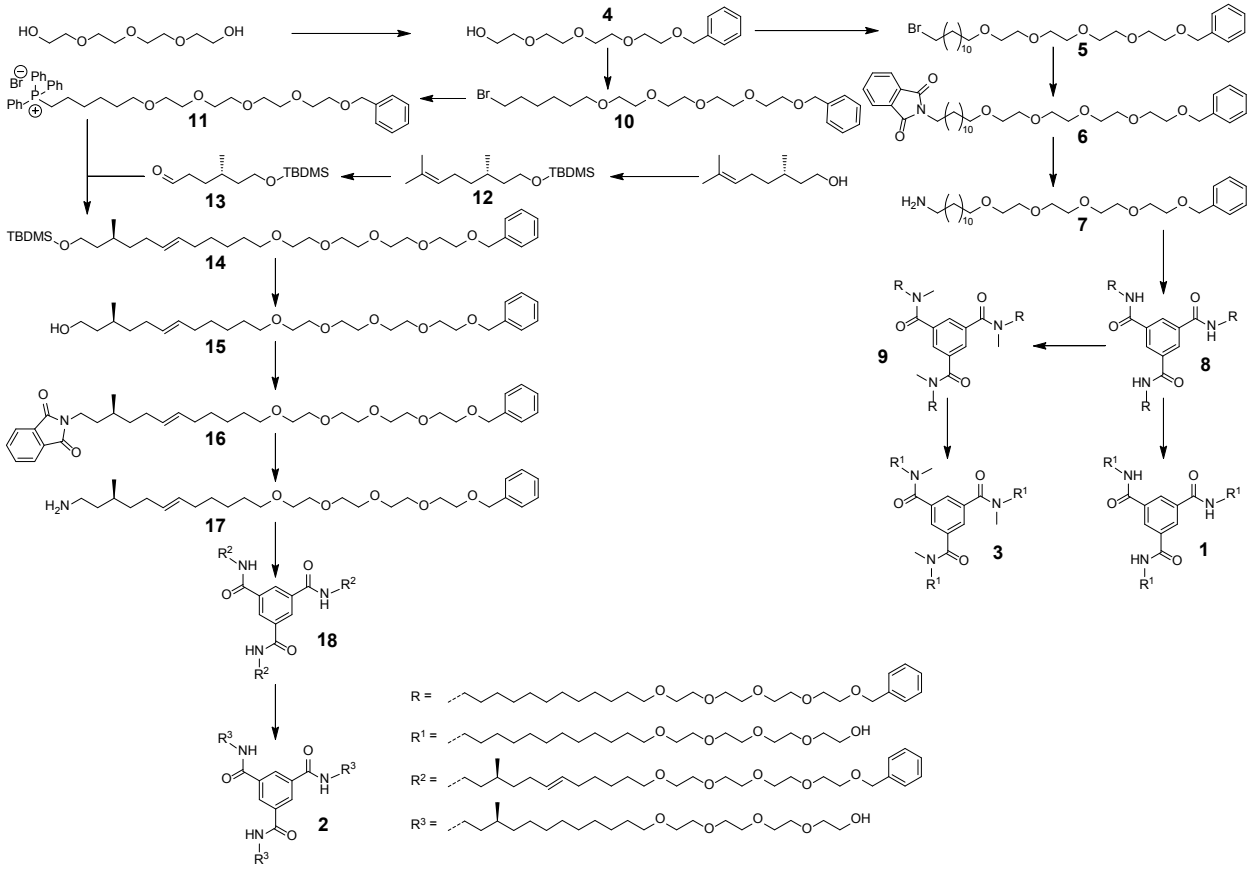
Ozonolysis was performed using an in-situ ozone generator from Ozone Tech Systems.

Methods

UV-Vis and CD measurements were performed using quartz cuvettes (1 cm). A stock solution of **1** in water was prepared by measuring out the desired amount of material, addition of water (miliQ) and heating the mixture to above the LCST upon which the mixture became opaque. Upon cooling, a clear solution was obtained which was then completed to obtain the correct concentration ($c = 1x10^{-5}$M or $c = 5 x10^{-5}$M). For the time dependent measurements, stock solutions of **1** in methanol were prepared and 5 µl

was injected into 2.5 ml water (miliQ) obtaining the desired concentration (c = 1x10^{-5}M or c = 5 x10^{-5}M) Stock solutions of (*S*)-**2** in methanol were prepared, and by injecting 5 µl into 2.5 ml water (miliQ) solutions of the desired concentration were obtained (c = 1x10^{-5}M or c = 5 x10^{-5}M).

Synthesis

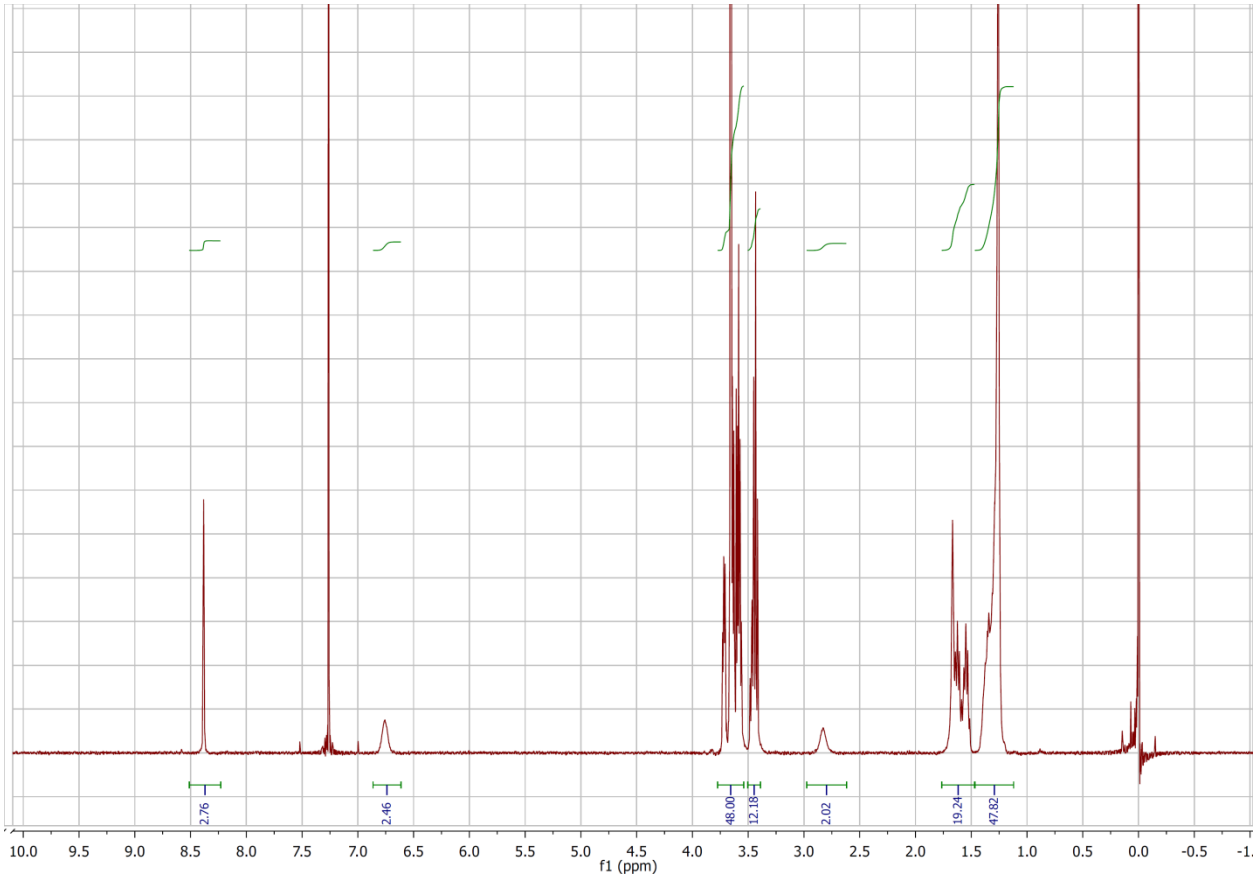


Scheme S1: Synthetic approach for the formation of **1**, **2** and **3.**

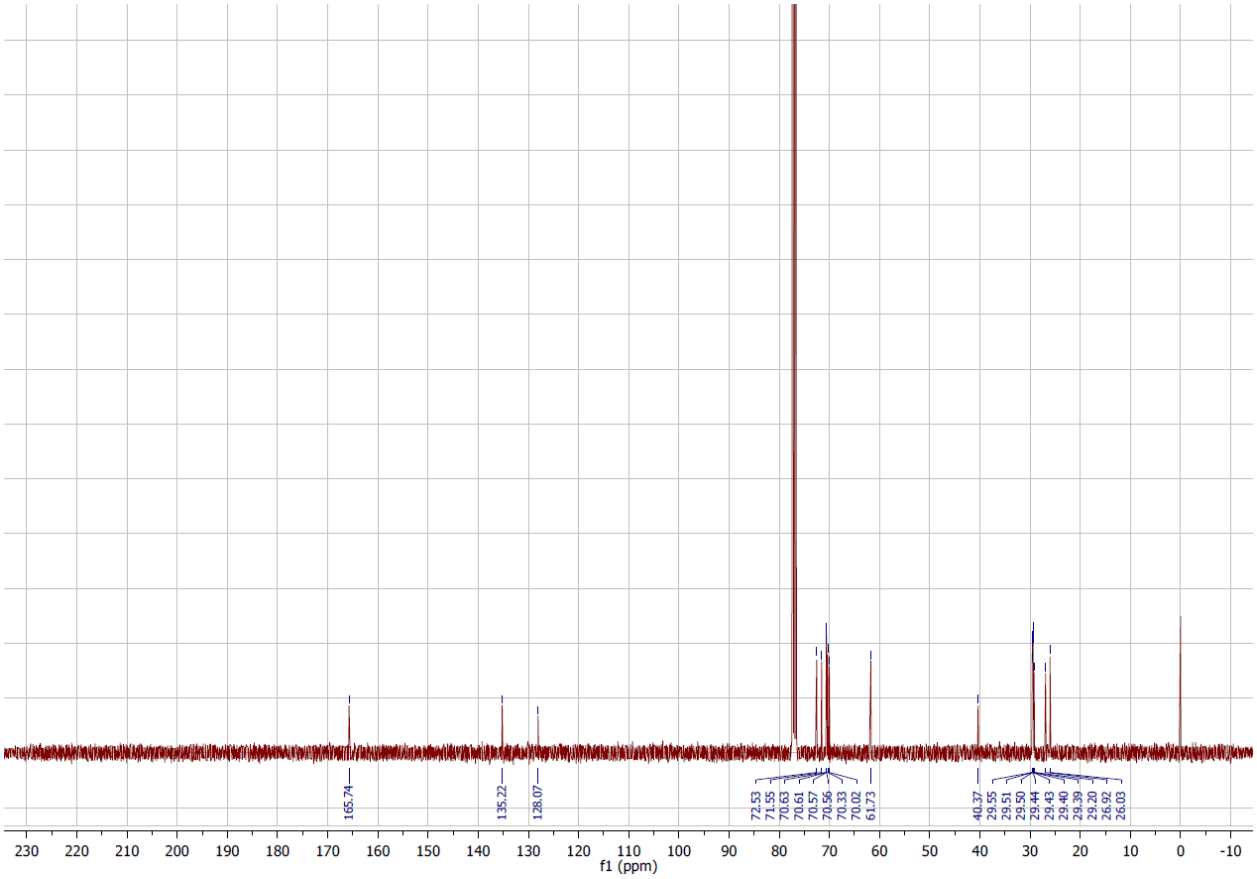
Synthetic procedures

N^1,N^3,N^5-Tris(1-hydroxy-3,6,9,12-tetraoxatetracosan-24-yl)benzene-1,3,5-tricarboxamide (**1**). A round bottom flask (10 ml) was charged with N^1,N^3,N^5-tris(1-phenyl-2,5,8,11,14-pentaoxahexacosan-26-yl)benzene-1,3,5-tricarboxamide **8** (0.10 mmol, 0.15 g), methanol (3 ml) and N_2(g) was led through the stirred solution for 10 minutes. Subsequently, Pd/C (catalytic amount) was added and a balloon filled with H_2(g) was connected. The reaction mixture was stirred under H_2(g) atmosphere overnight at room temperature. The reaction mixture was filtered over celite and concentrated *in vacuo* yielding **1** as a colorless oil which solidified upon standing. Yield = 0.12 g, 93%. ^{1}H NMR (400 MHz, $CDCl_3$ δ): 8.38 (s, 3H, Ar), 6.76 (b, 3H, C=ONHCH$_2$), 3.76 – 3.54 (m, 48H, O-(CH$_2$)$_2$-O), 3.45 (m, 12H, CH$_2$CH$_2$NHC=O, CH$_2$CH$_2$CH$_2$O), 2.83 (b, 3H, CH$_2$CH$_2$OH), 1.76 – 1.47 (m, 12H, CH$_2$CH$_2$CH$_2$O, CH$_2$CH$_2$CH$_2$O), 1.47 – 1.12 (m, 48H, aliphatic). ^{13}C NMR (100 MHz, $CDCl_3$ δ): 165.74, 135.22, 128.07, 72.53, 71.55, 70.63, 70.61, 70.57, 70.56, 70.33, 70.02, 61.73, 40.37, 29.55, 29.51, 29.50, 29.44, 29.43, 29.40, 29.39, 29.20, 26.92, 26.03. MALDI-TOF-MS: calculated M_w = 1287.93 g/mol, observed m/z = 1288.87 [MH$^+$], 1310.95 [Na$^+$ adduct]. FT-IR (ATR) ν (cm^{-1}): 3239, 3069, 2918, 2851, 1641, 1562, 1468, 1350, 1294, 1114, 937, 885, 722, 693.

^{1}H NMR (400 MHz), solvent is $CDCl_3$.

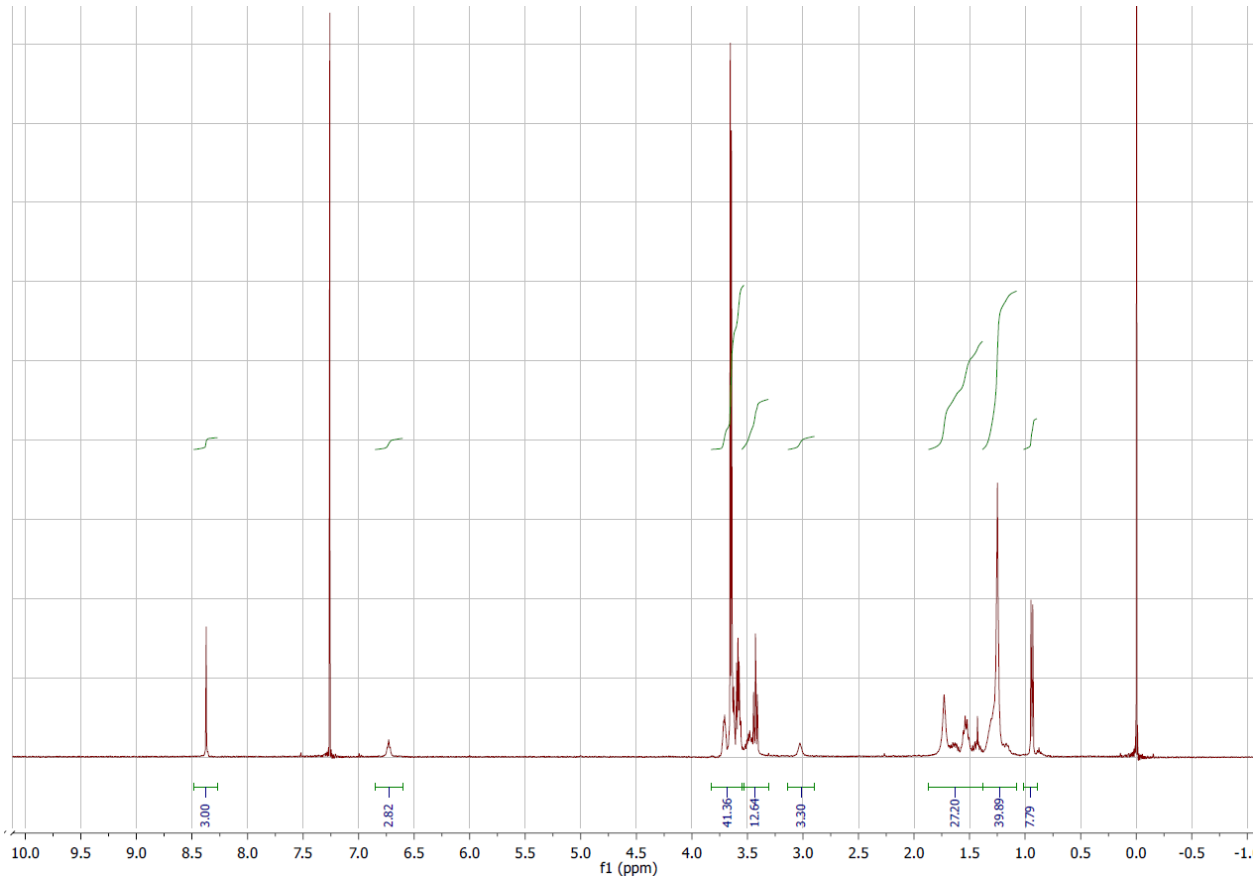


^{13}C NMR (100 MHz), solvent is $CDCl_3$.

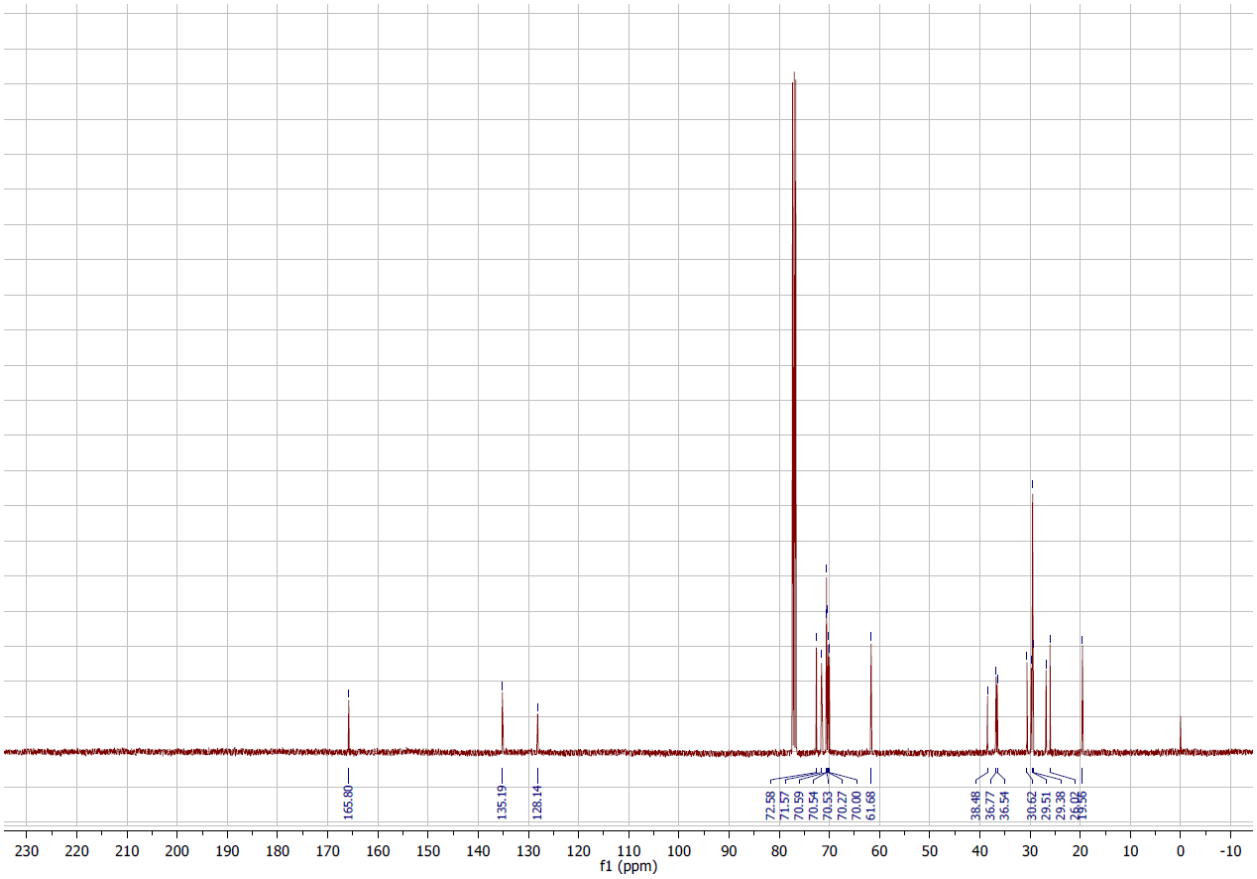


N^1,N^3,N^5-Tris((S)-1-hydroxy-22-methyl-3,6,9,12-tetraoxatetracosan-24-yl)benzene-1,3,5-tricarboxamide (**2**). A round bottom flask (10 ml) was charged with N^1,N^3,N^5-tris((*S*)-24-methyl-1-phenyl-2,5,8,11,14-pentaoxahexacos-20-en-26-yl)benzene-1,3,5-tricarboxamide **18** (0.123 mmol, 196 mg) and methanol (5 ml) was added. After N_2(g) was led through the stirred solution for 10 minutes, Pd/C (catalytic amount) was added and a balloon filled with H_2(g) was connected. The reaction mixture was stirred under H_2(g) atmosphere overnight at room temperature. The reaction mixture was filtered over celite and concentrated *in vacuo*, yielding **2** as a slightly yellow waxy material. Yield = 0.161 g, 98 %. ^{1}H NMR (400 MHz, $CDCl_3$ δ): 8.37 (s, 3H, Ar), 6.73 (t, *J* = 5.2 Hz, 3H, C=ONHCH$_2$), 3.74 – 3.53 (m, 48H, O-(CH$_2$)$_2$-O), 3.52 – 3.45 (m, 6H, CH$_2$CH$_2$NHC=O), 3.43 (t, *J* = 6.8 Hz, 6H, CH$_2$CH$_2$CH$_2$O), 3.03 (b, 3H, CH$_2$CH$_2$OH), 1.69 – 1.10 (m, 57H, aliphatic), 0.94 (d, *J* = 6.5 Hz, 9H, CH$_2$CH(CH$_3$)CH$_2$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.80, 135.19, 128.14, 72.58, 71.57, 70.59, 70.59, 70.54, 70.53, 70.27, 70.00, 61.68, 38.48, 36.77, 36.54, 30.62, 29.78, 29.51, 29.51, 29.38, 26.81, 26.02, 19.56. MALDI-TOF-MS: calculated M_w = 1329.97 g/mol, observed m/z = 1352.98 [Na^+ adduct]. FT-IR (ATR) ν (cm^{-1}): 3349, 3244, 3072, 2922, 2854, 1641, 1538, 1457, 1349, 1294, 1261, 1102, 939, 884, 837, 721, 691.

^{1}H NMR (400 MHz), solvent is $CDCl_3$.

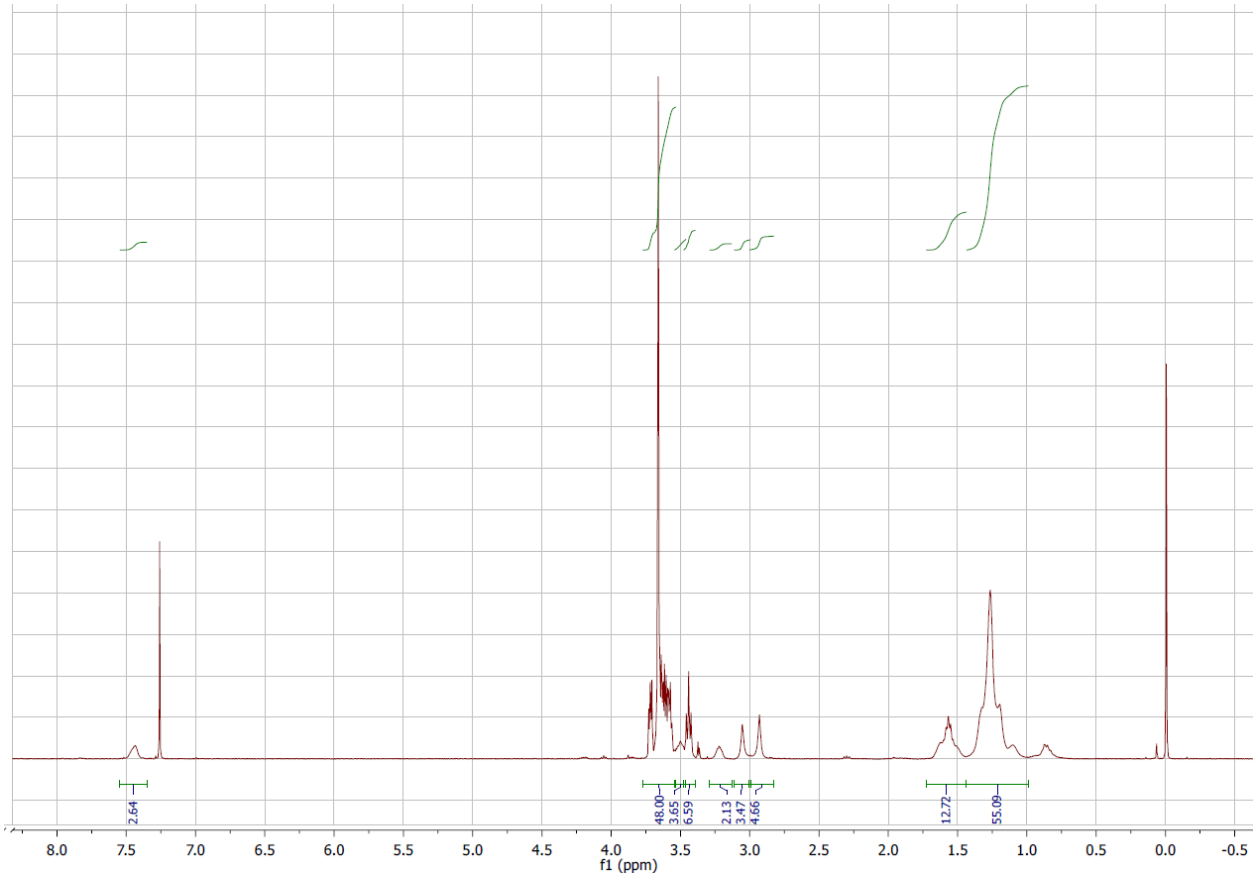


^{13}C NMR (100 MHz), solvent is $CDCl_3$.

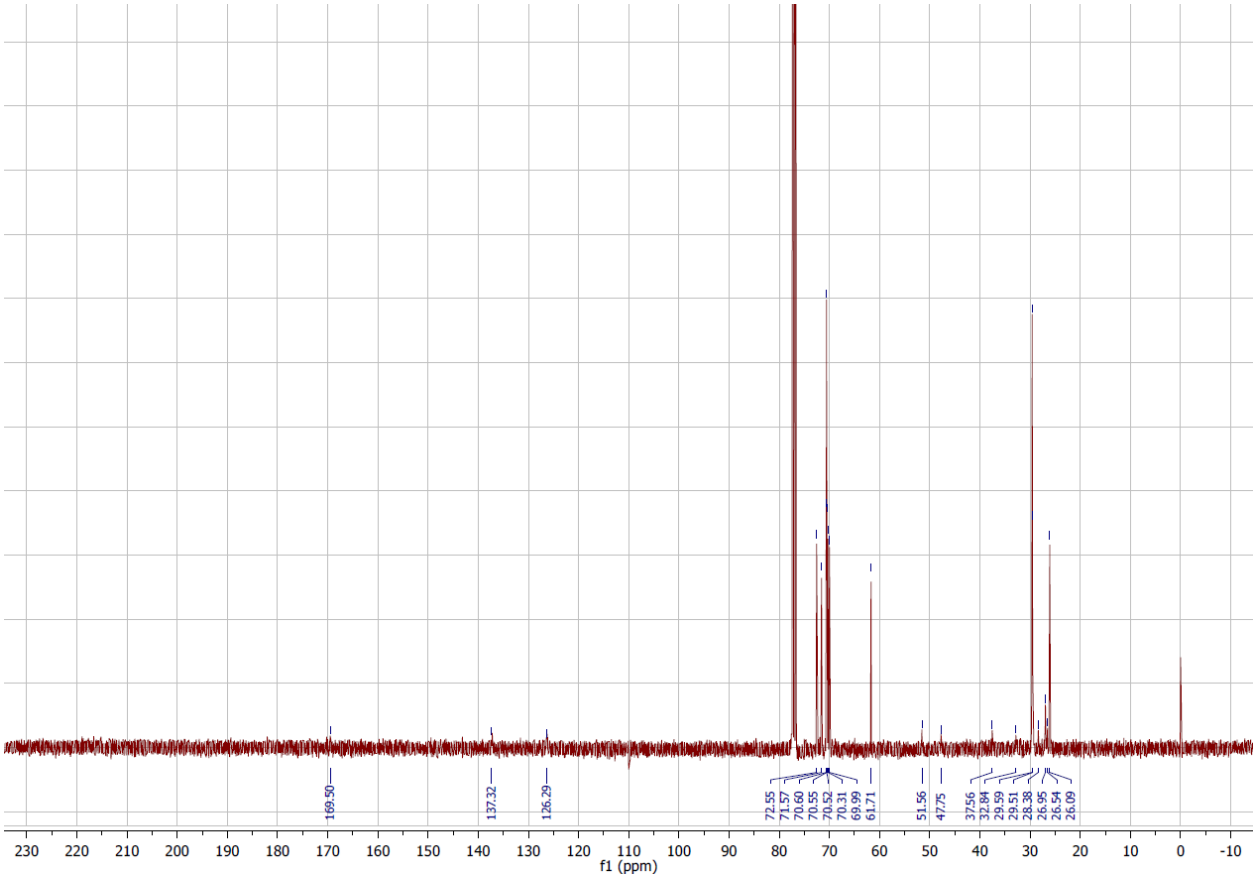


N^1,N^3,N^5-tris(1-hydroxy-3,6,9,12-tetraoxatetracosan-24-yl)-N^1,N^3,N^5-trimethylbenzene-1,3,5-tricarboxamide (**3**). A round bottom flask (25 ml) was charged with N^1,N^3,N^5-trimethyl-N^1,N^3,N^5-tris(1-phenyl-2,5,8,11,14-pentaoxahexacosan-26-yl)benzene-1,3,5-tricarboxamide **9** (0.069 mmol, 0.11 g) and methanol (10 mL) was added. N_2(g) was led through the stirred solution for 10 minutes. Subsequently, Pd/C (catalytic amount) was added and a balloon filled with H_2(g) was connected. The mixture was stirred under H_2(g) atmosphere overnight at room temperature. The reaction mixture was filtered over celite and the solvent was removed *in vacuo* yielding **3** as a slightly yellow waxy material. Yield = 0.046 g, 50%. ^{1}H NMR (400 MHz, $CDCl_3$ δ): 7.44 (bs, 3H, Ar), 3.76 – 3.54 (m, 48H, O-(C$\underline{H}_2$)$_2$-O), 3.50 (b, 6H, N-C$\underline{H}_2$, *trans*), 3.44 (t, *J* = 6.8 Hz, 6H, $CH_2CH_2C\underline{H}_2O$), 3.22 (b, 6H, N-C$\underline{H}_2$, *cis*), 3.05 (s, 9H, N-C-$\underline{H}_3$, *cis*), 2.93 (s, 9H, N-C$\underline{H}_3$, *trans*), 1.69 – 1.46 (m, 12H, $CH_2C\underline{H}_2CH_2O$, $C\underline{H}_2CH_2CH_2O$), 1.42 – 1.02 (m, 48H, aliphatic). ^{13}C NMR (100 MHz, $CDCl_3$ δ): 169.50, 137.32, 126.29, 72.55, 71.57, 70.68-70.46, 70.31, 69.99, 61.71, 51.56, 47.75, 37.56, 32.84, 29.80-29.25, 28.38, 26.95, 26.54, 26.09. MALDI-TOF-MS: calculated M_w = 1329.97g/mol, observed m/z = 1352.95 [Na^+ adduct]. FT-IR (ATR) ν (cm^{-1}): 3438, 2923, 2854, 1636, 1457, 1400, 1351, 1298, 1252, 1107, 942, 888, 738, 644, 529.

^{1}H NMR (400 MHz), solvent is $CDCl_3$.

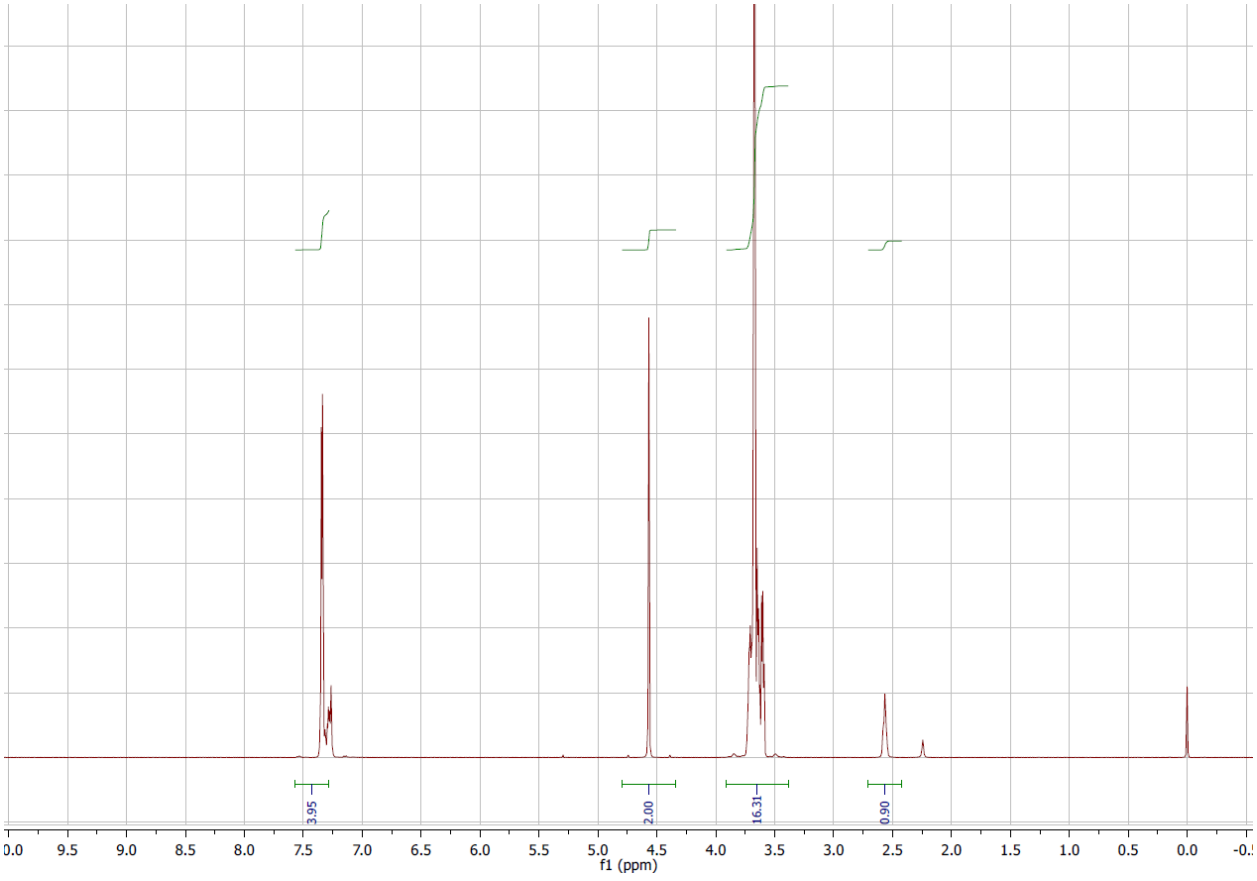


^{13}C NMR (100 MHz), solvent is $CDCl_3$.



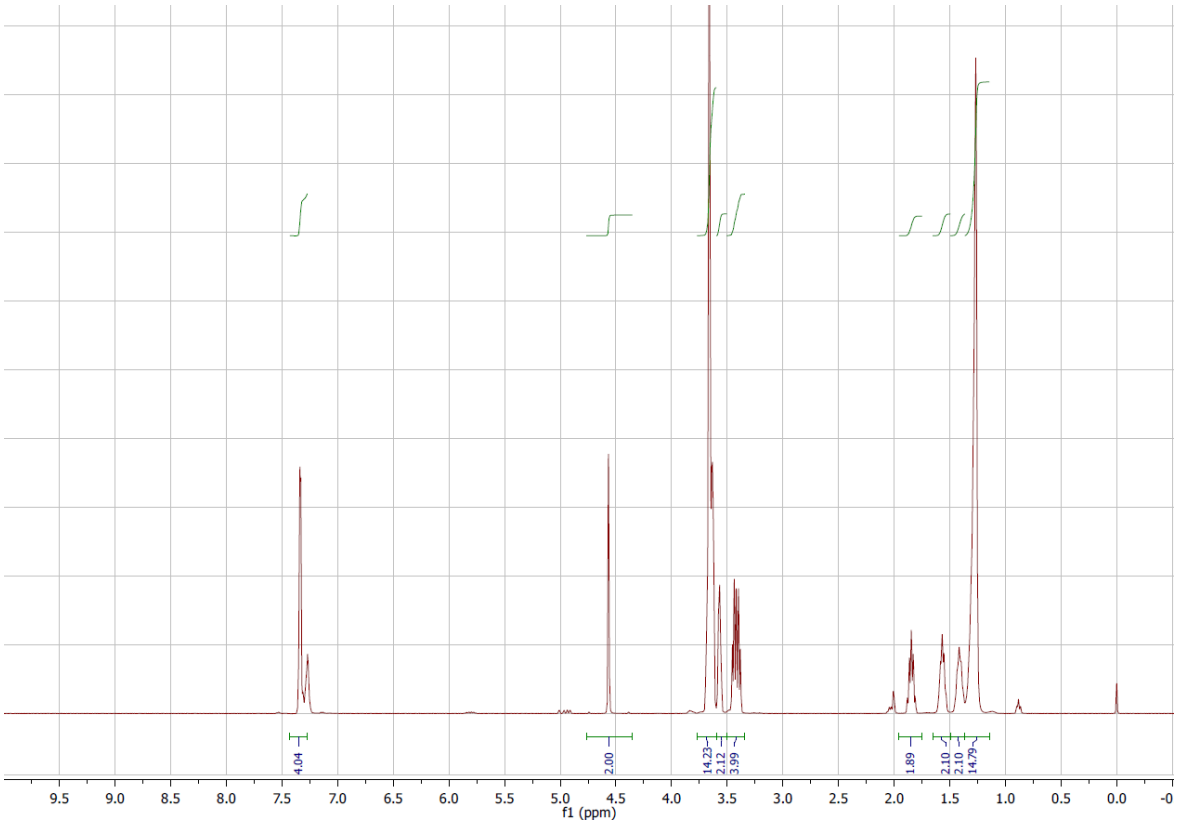
Tetraethylene glycol benzyl ether (**4**). A round bottom flask (1 L, dried at 145 °C) was charged with tetraethylene glycol (29.81 g, 0.153 mol) and dry THF (100 ml). The solution was stirred at 0 °C and sodium hydride (60% in mineral oil, 6.12 g, 0.153 mol) was added, upon which the mixture foamed vigorously. The ice bath was removed and after 30 minutes benzylbromide (15.8 g, 0.092 mol, 0.6 eq) was added, resulting in a turbid mixture, which was stirred overnight. Subsequently, deionized water (100 ml) was added and the mixture was extracted with diethylether (3x 100 ml). The organic fractions were combined, dried with magnesium sulfate, filtered and concentrated *in vacuo*. The material was purified by column chromatography (ethylacetate/heptane 60/40) yielding **4** as a colorless oil (15.17 g, 58%). ^{1}H NMR (400 MHz, $CDCl_3$ δ): 7.41 – 7.27 (m, 5H, Ar), 4.57 (s, 2H, Ar-C$\underline{H}_2$-O), 3.78 – 3.54 (m, 16H, O-(C$\underline{H}_2$)$_2$-O), 2.57 (b, 1H, $CH_2CH_2O\underline{H}$).

^{1}H NMR (400 MHz), solvent is $CDCl_3$.

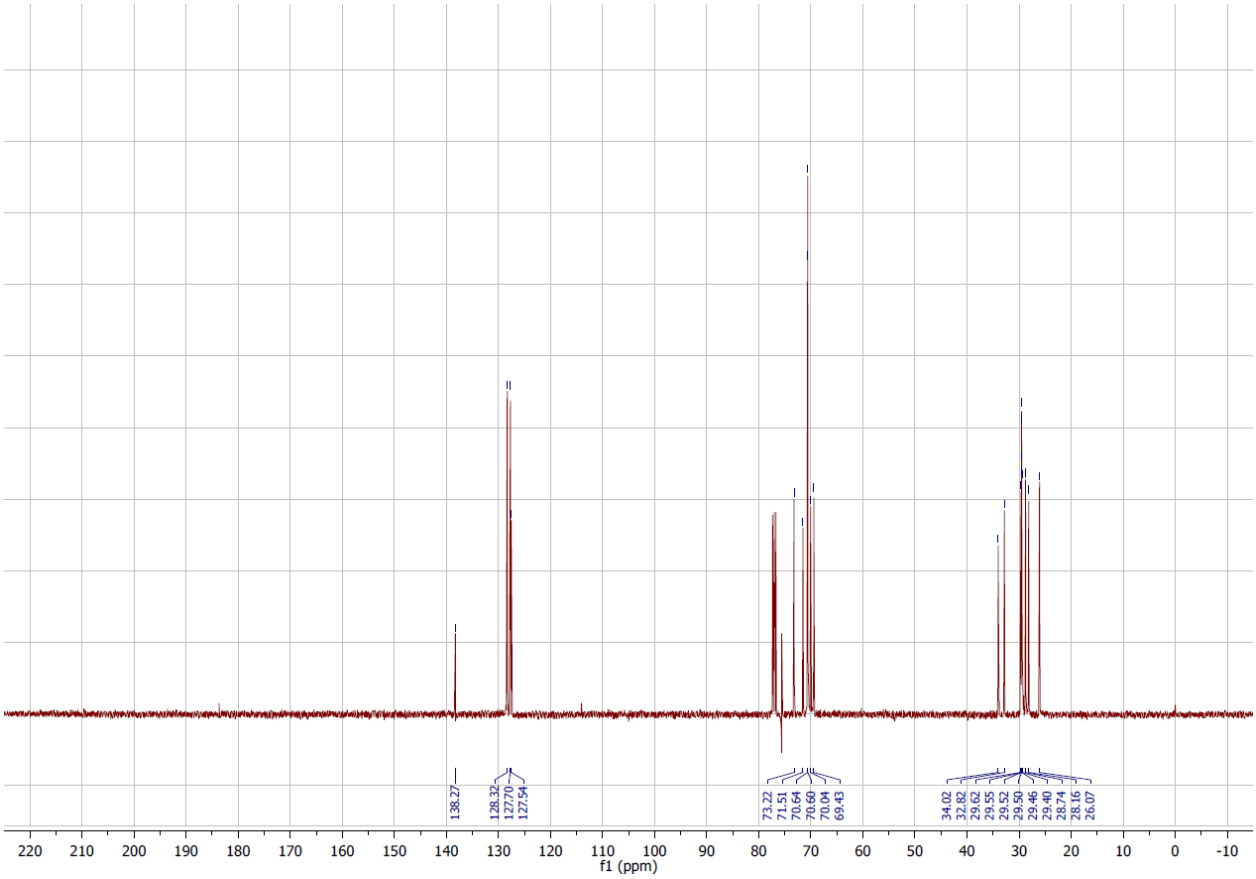


Tetraethylene glycol monobenzyl mono-12-bromododecyl ether (**5**). A round bottom flask (250 ml, dried at 140 °C) was charged with dry THF (20 ml) and tetraethylene glycol benzyl ether **4** (3.125 g, 11 mmol). The solution was cooled to 0 °C and sodium hydride (60% in mineral oil, 440 mg, 11 mmol) was added to the stirring solution, upon which the mixture foamed vigorously. The ice bath was removed and after 30 minutes 1,12-dibromododecane (10.88 g, 33 mmol) was added in one portion to the vigorously stirred mixture. Subsequently, the reaction mixture was stirred overnight. It was then neutralized with H_2O (20 ml) and extracted with diethylether (3x 40 ml). The organic layers were combined, dried with magnesium sulfate, filtered and concentrated *in vacuo*. The material was purified by column chromatography (eluent heptane/ethyl acetate 80/20-50/50 v/v) yielding **5** as a colorless oil. Yield = 3.2 g, 55%. ^{1}H NMR (400 MHz, $CDCl_3$ δ): 7.42 – 7.27 (m, 5H, Ar), 4.57 (s, 2H, Ar-C$\underline{H}_2$-O), 3.72 – 3.60 (m, 14H, O-(C$\underline{H}_2$)$_2$-O), 3.60 – 3.53 (m, 2H, O-(C$\underline{H}_2$)$_2$-O), 3.48 – 3.35 (m, 4H, $CH_2CH_2C\underline{H}_2O$, $CH_2C\underline{H}_2Br$), 1.85 (p, J = 6.8 Hz, 2H, C$\underline{H}_2CH_2Br$), 1.66 – 1.50 (m, 2H, $CH_2C\underline{H}_2CH_2O$), 1.50 – 1.36 (m, 2H, C$\underline{H}_2CH_2CH_2O$), 1.36 – 1.12 (m, 14H, aliphatic). ^{13}C NMR (100 MHz, $CDCl_3$ δ): 138.27, 128.32, 127.70, 127.54, 73.22, 71.51, 70.7-70.5, 70.04, 69.43, 34.02, 33.79, 32.82, 29.62, 29.55, 29.52, 29.50, 29.46, 29.40, 29.12, 28.74, 28.16, 26.07. FT-IR (ATR) ν (cm^{-1}): 2924, 2854, 1454, 1351, 1295, 1249, 1207, 1101, 1041, 1028, 992, 945, 879, 852, 735, 698, 644, 611, 561, 464.

^{1}H NMR (400 MHz), solvent is $CDCl_3$.

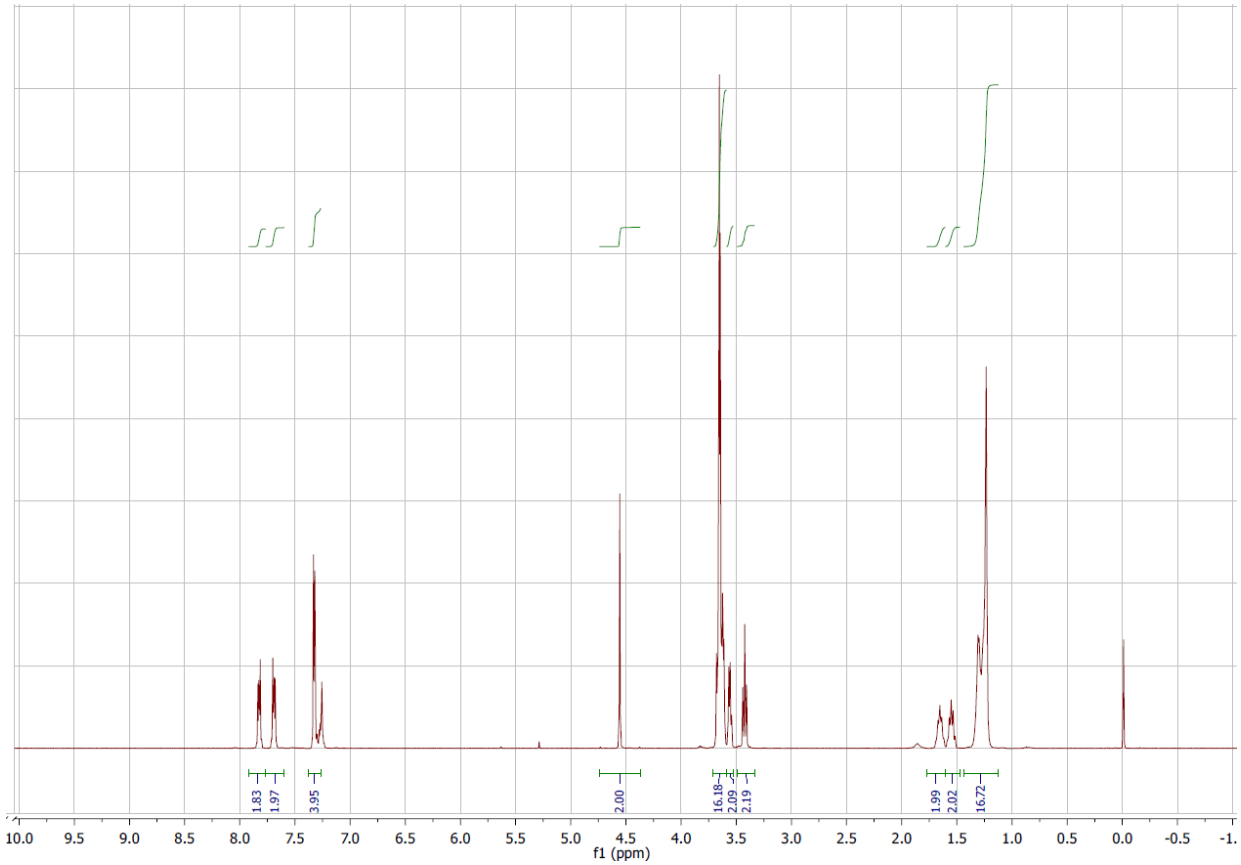


^{13}C NMR (100 MHz), solvent is $CDCl_3$.

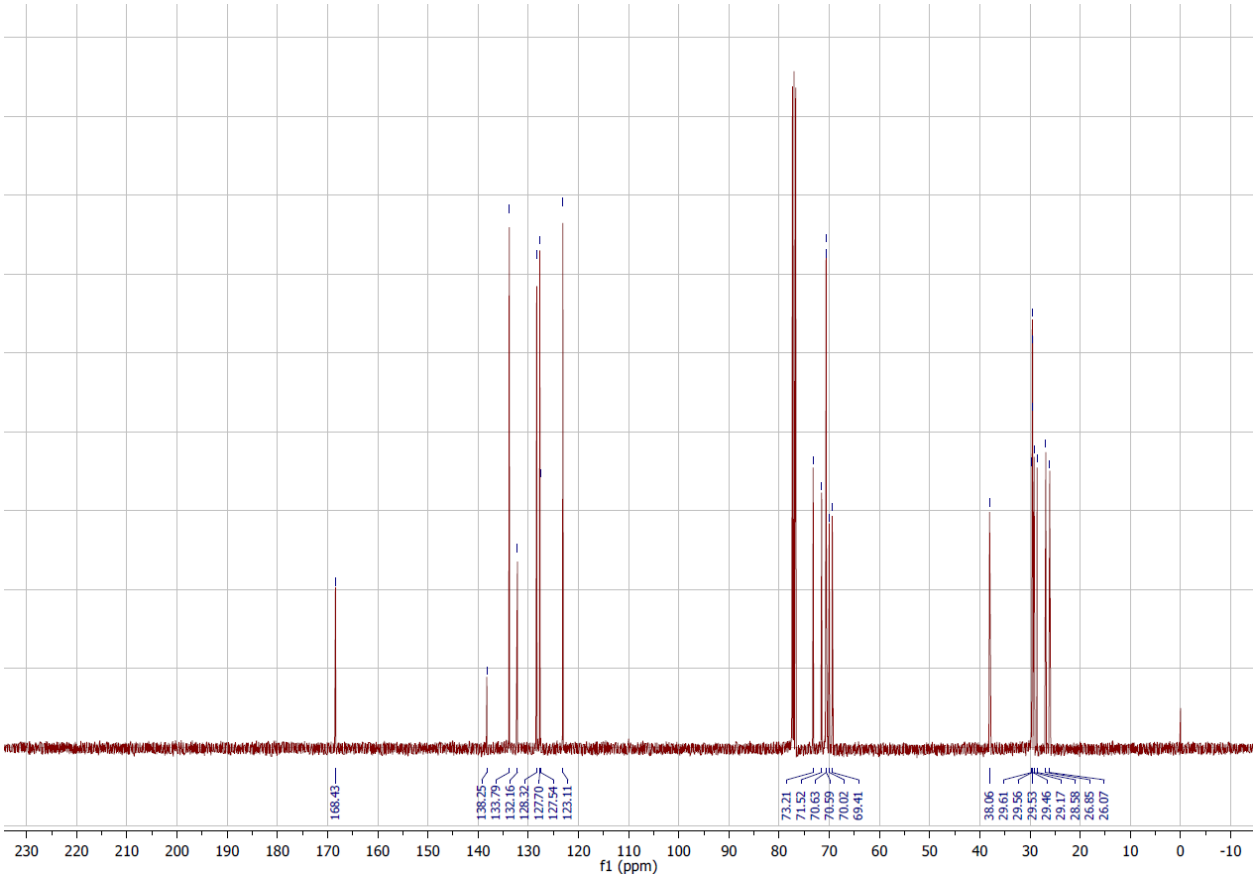


2-(1-Phenyl-2,5,8,11,14-pentaoxahexacosan-26-yl)isoindoline-1,3-dione (**6**). A round bottom flask (100 ml) was charged with tetraethylene glycol monobenzyl mono-12-bromododecyl ether **5** (6.4 mmol, 3.4 g), DMF (10 ml) and potassium phthalimide (9.0 mmol, 1.7 g). The mixture was heated to 60 °C and stirred for 2 hours. Then ethyl acetate (50 ml) was added and the solution was extracted with acidic H_2O (3x 30 ml, pH 3). The aqueous layers were extracted two times with ethyl acetate (25 ml). The organic fractions were combined and one equivalent DCM was added (100 ml). The mixture was dried with $MgSO_4$, filtered and the solvent was removed *in vacuo*. The material was purified by column chromatography (heptane/ethyl acetate 75/25 – 50/50 v/v). Yield = 2.8 g. 73%. ^{1}H NMR (400 MHz, $CDCl_3$ δ): 7.83 (dd, J = 5.5, 3.0 Hz, 2H, phthalimide), 7.70 (dd, J = 5.4, 3.0 Hz, 2H, phthalimide), 7.39 – 7.26 (m, 5H, Ar), 4.56 (s, 2H, Ar-C$\underline{H}_2$-O), 3.72 – 3.59 (m, 16H, O-(C$\underline{H}_2$)$_2$-O, $CH_2C\underline{H}_2N$), 3.59 – 3.53 (m, 2H, O-(C$\underline{H}_2$)$_2$-O), 3.43 (t, J = 6.8 Hz, 2H, $CH_2CH_2C\underline{H}_2O$), 1.73 – 1.61 (m, 2H, $CH_2C\underline{H}_2CH_2O$), 1.61 – 1.47 (m, 2H, $C\underline{H}_2CH_2CH_2O$), 1.42 – 1.09 (m, 16H, aliphatic). ^{13}C NMR (100 MHz, $CDCl_3$ δ): 168.43, 138.25, 133.79, 132.16, 128.32, 127.70, 127.54, 123.11, 73.21, 71.52, 70.7-70.5, 70.02, 69.41, 38.06, 29.65-29.42, 29.17, 28.58, 26.85, 26.07. FT-IR (ATR) ν (cm^{-1}): 2925, 2855, 1772, 1712, 1615, 1467, 1455, 1437, 1396, 1367, 1300, 1249, 1104, 1047, 948, 881, 795, 721, 699, 620, 530.

^{1}H NMR (400 MHz), solvent is $CDCl_3$.

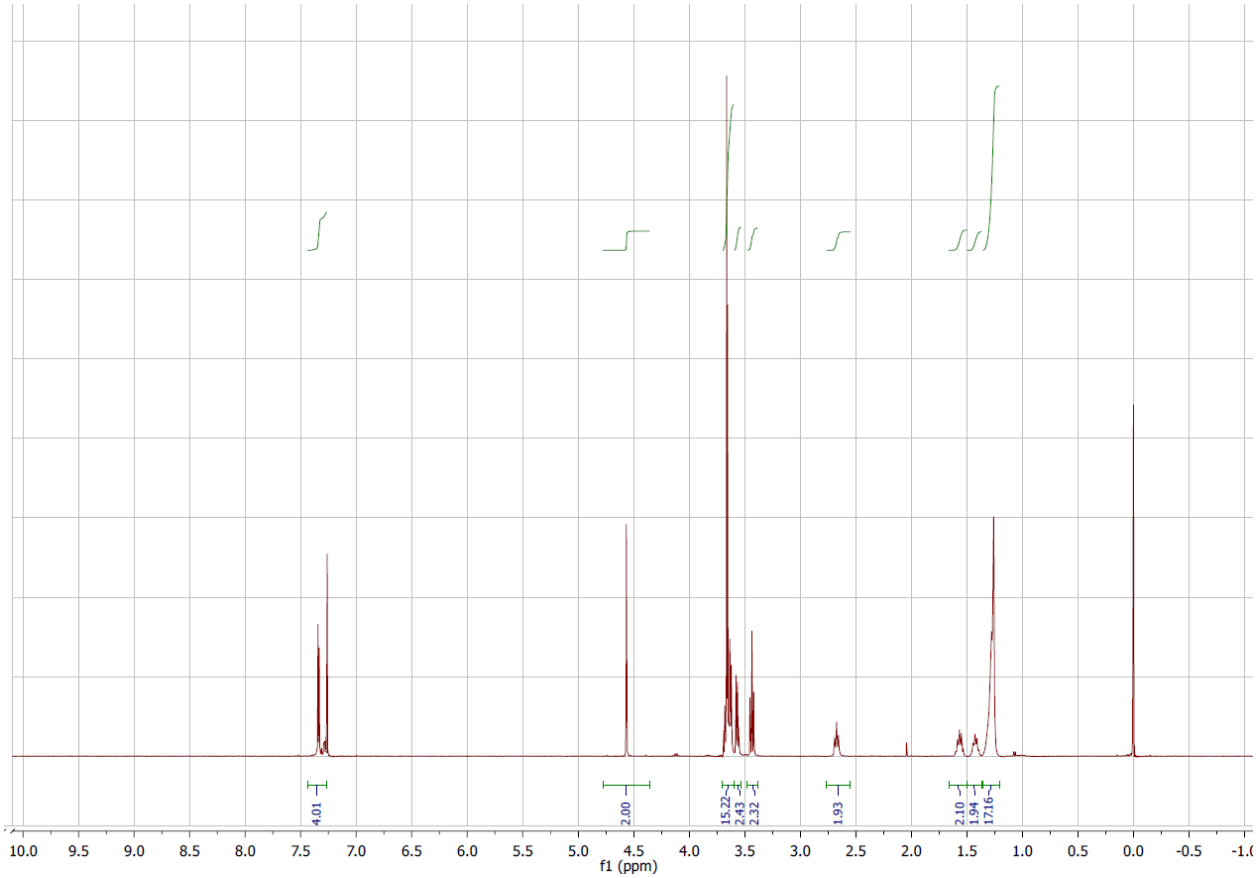


^{13}C NMR (100 MHz), solvent is $CDCl_3$.

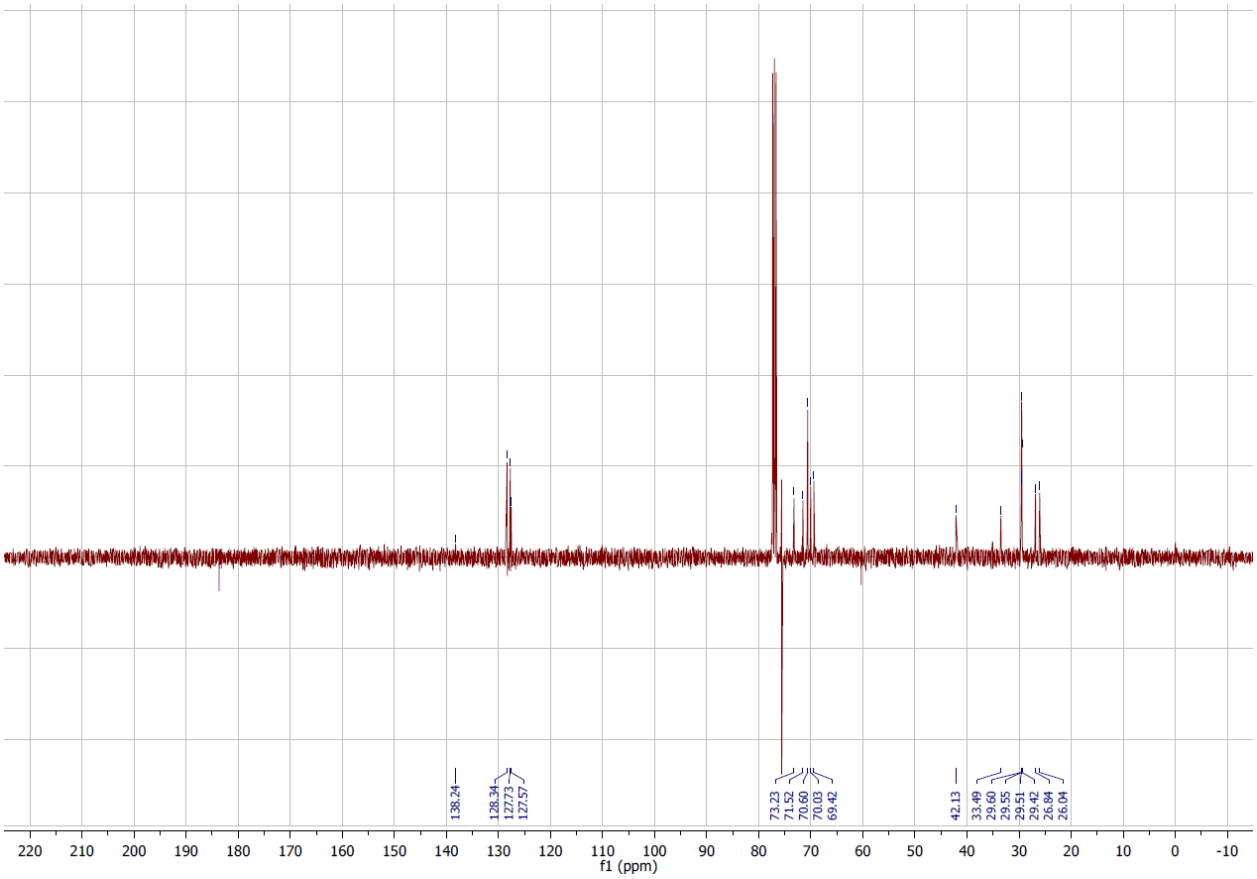


1-Phenyl-2,5,8,11,14-pentaoxahexacosan-26-amine (**7**). To a stirred solution of 2-(1-phenyl-2,5,8,11,14-pentaoxahexacosan-26-yl)isoindoline-1,3-dione **6** (0.44 mmol, 0.263 g) in ethanol (4 ml) hydrazine monohydrate (0.3 ml) was added and the mixture was allowed to stir overnight at reflux. The mixture was concentrated *in vacuo* and chloroform (10 ml) was added. The solution was extracted with NaOH solution (3x 10 ml, 1 M). The organic fraction was dried with $MgSO_4$, filtered and concentrated *in vacuo*. The obtained material was purified by silica filtration (Eluent: ethyl acetate followed by ethyl acetate/isopropylamine 90/10 v/v). Yield = 0.182 g, 89%. ^{1}H NMR (400 MHz, $CDCl_3$ δ): 7.42 – 7.27 (m, 5H, Ar), 4.57 (s, 2H, Ar-C$\underline{H}_2$-O), 3.71 – 3.61 (m, 14H, O-(C$\underline{H}_2$)$_2$-O), 3.59 – 3.53 (m, 2H, O-(C$\underline{H}_2$)$_2$-O), 3.44 (t, *J* = 6.8 Hz, 2H, $CH_2CH_2C\underline{H}_2O$), 2.67 (t, *J* = 6.9 Hz, 2H, $CH_2C\underline{H}_2NH_2$), 1.63 – 1.51 (m, 2H, $CH_2C\underline{H}_2CH_2O$), 1.48 – 1.37 (m, 2H, $C\underline{H}_2CH_2CH_2O$), 1.36 – 1.22 (m, 16H, aliphatic). ^{13}C NMR (100 MHz, $CDCl_3$ δ): 138.24, 128.34, 127.73, 127.57, 73.23, 71.52, 70.7-70.5, 70.03, 69.42, 42.13, 33.49, 29.65-29.35, 26.84, 26.04. MALDI-TOF-MS: calculated M_w = 467.36 g/mol, observed m/z = 468.44 [MH^+]. FT-IR (ATR) ν (cm^{-1}): 2920, 2853, 1648, 1568, 1487, 1466, 1455, 1386, 1349, 1320, 1303, 1250, 1205, 1107, 1043, 949, 880, 818, 736, 698, 615.

^{1}H NMR (400 MHz), solvent is $CDCl_3$.



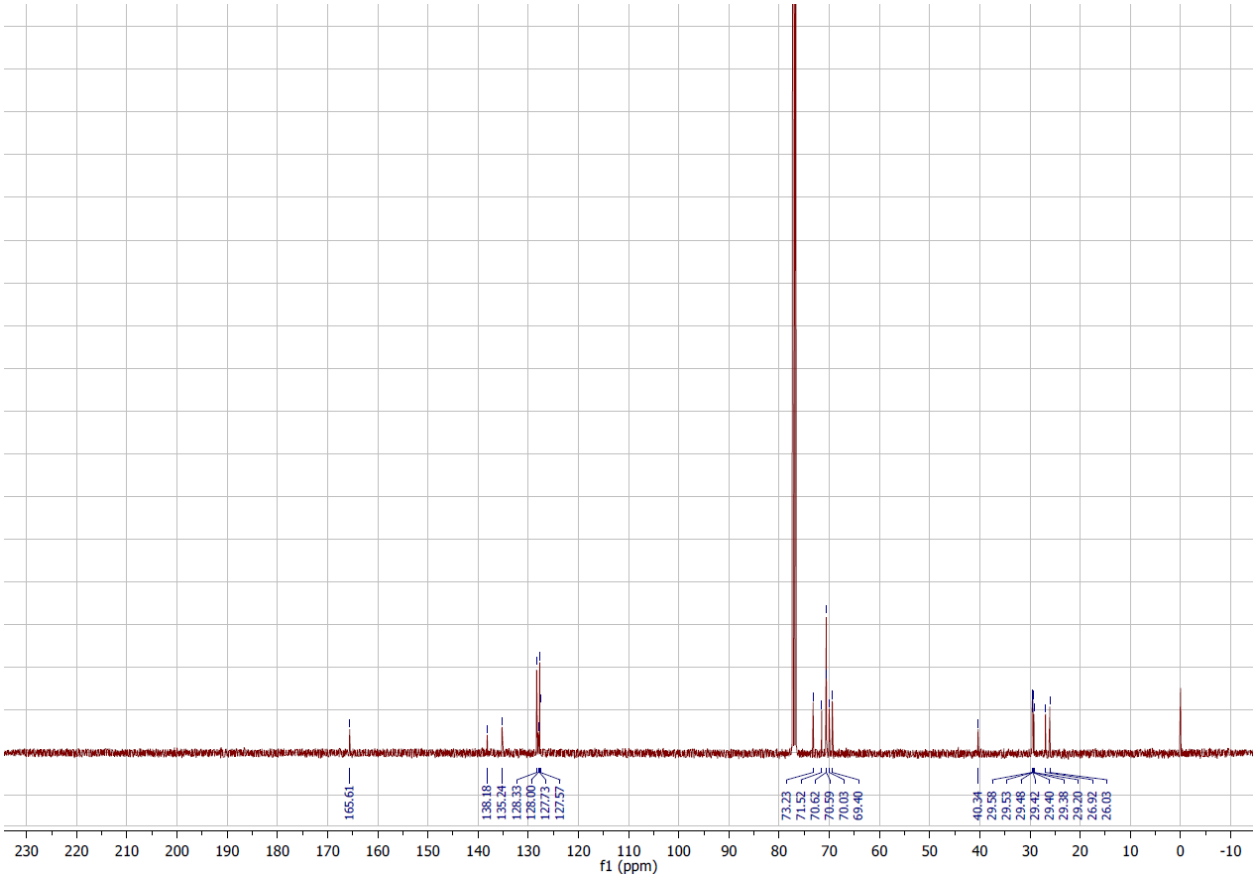
^{13}C NMR (100 MHz), solvent is $CDCl_3$.



N^1,N^3,N^5-Tris(1-phenyl-2,5,8,11,14-pentaoxahexacosan-26-yl)benzene-1,3,5-tricarboxamide (**8**). A two neck round bottom flask (10 ml, dried at 140 °C) was charged with 1-phenyl-2,5,8,11,14-pentaoxahexacosan-26-amine **7** (0.39 mmol,0.182 g), dry chloroform (1 ml) and triethylamine (0.99 mmol, 0.100 g). The mixture was stirred at 0 °C and a solution of 1,3,5-benzenetricarbonyl trichloride (0.12 mmol, 32.8 mg) in chloroform (0.2 ml) was added drop wise. After 15 minutes the reaction mixture was allowed to reach room temperature and stirred overnight. The reaction mixture was concentrated *in vacuo* and purified by column chromatography (eluent chloroform/methanol, 96/4, v/v). Yield = 0.156 g, 83.4%. ^{1}H NMR (400 MHz, $CDCl_3$ δ): 8.36 (s, 3H, Ar (benzene tricarboxamide)), 7.39 – 7.27 (m, 15H, Ar), 6.57 (t, *J* = 5.7 Hz, 3H, C=ONHCH$_2$), 4.55 (s, 6H, Ar-CH$_2$-O), 3.69 – 3.59 (m, 42H, O-(CH$_2$)$_2$-O), 3.59 – 3.53 (m, 6H, O-(CH$_2$)$_2$-O), 3.49 – 3.39 (m, 12H, CH$_2$CH$_2$NHC=O, CH$_2$CH$_2$CH$_2$O), 1.74 – 1.46 (m, 12H, CH$_2$CH$_2$CH$_2$O, CH$_2$CH$_2$CH$_2$O), 1.46 – 1.11 (m, 48H, aliphatic). ^{13}C NMR (100 MHz, $CDCl_3$ δ): 165.61, 138.18, 135.24, 128.33, 128.00, 127.73, 127.57, 73.23, 71.52, 70.65-70.57, 70.03, 69.40, 40.34, 29.58, 29.53, 29.48, 29.44, 29.42, 29.40, 29.38, 29.20, 26.92, 26.03. MALDI-TOF-MS: calculated M_w = 1558.07 g/mol, observed m/z = 1580.93 [Na^+ adduct]. FT-IR (ATR) ν (cm^{-1}): 3246, 3065, 2923, 2854, 1642, 1538, 1454, 1351, 1293, 1261, 1206, 1104, 1041, 1029, 946, 880, 851, 737, 698, 613.

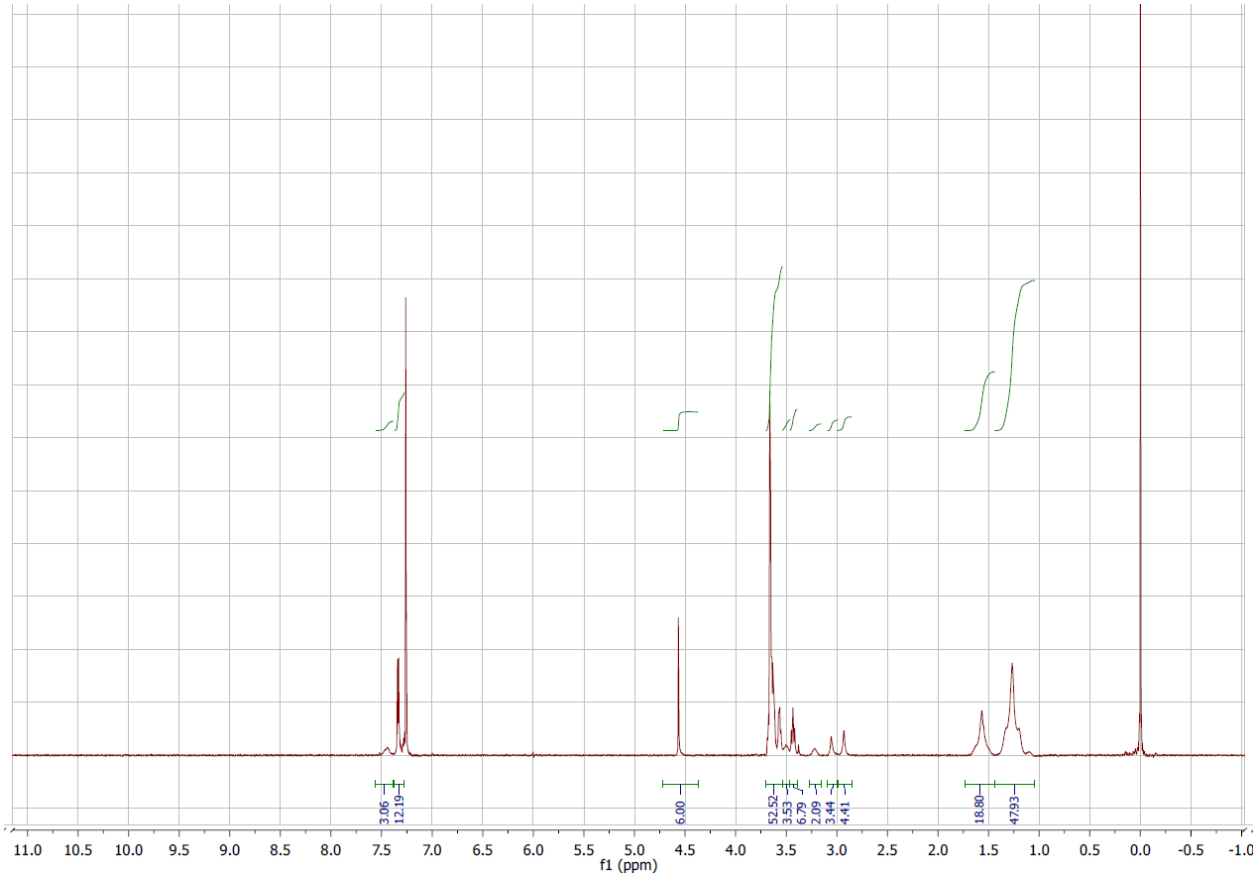
^{1}H NMR (400 MHz), solvent is $CDCl_3$.

^{13}C NMR (100 MHz), solvent is $CDCl_3$.



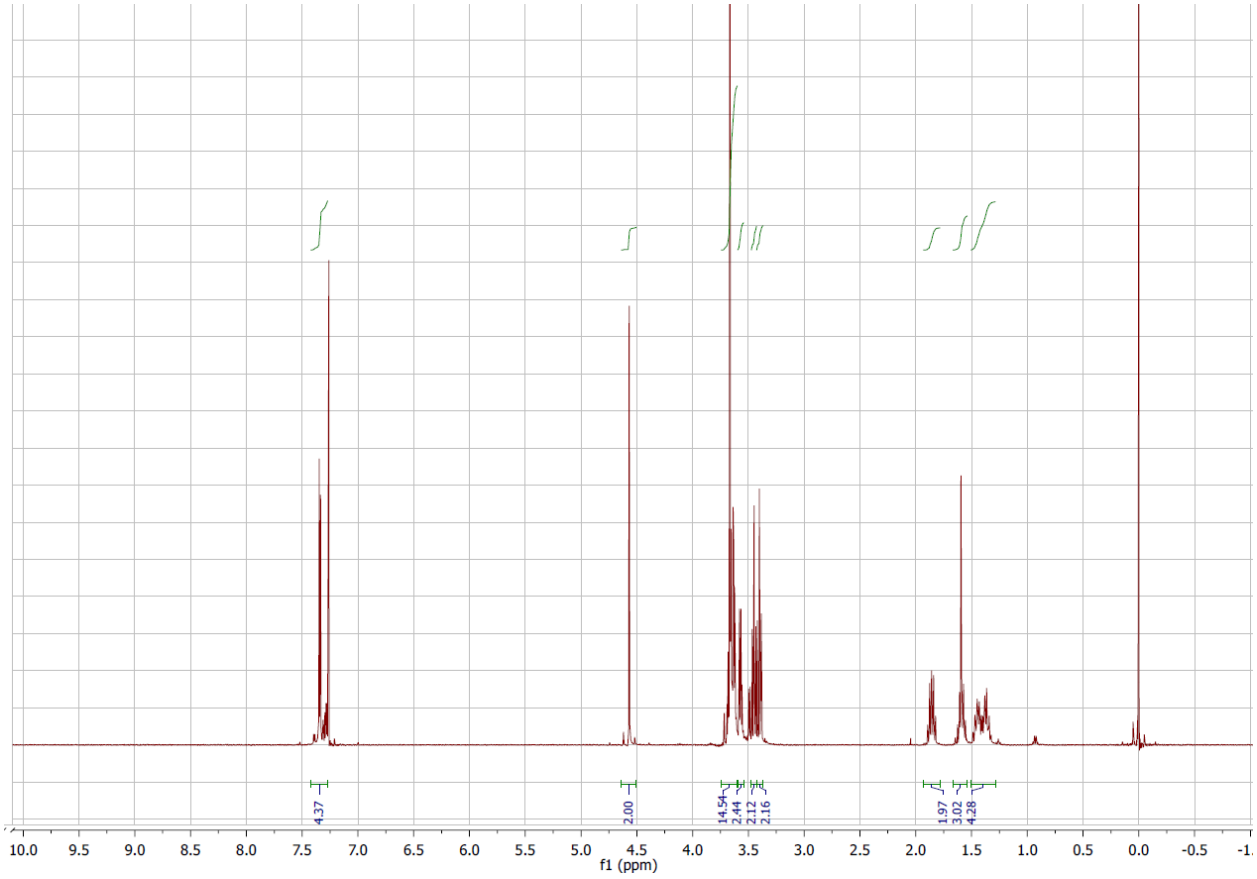
N^1,N^3,N^5-Trimethyl-N1,N3,N5-tris(1-phenyl-2,5,8,11,14-pentaoxahexacosan-26-yl)benzene-1,3,5-tricarboxamide (**9**). N^1,N^3,N^5-tris(1-phenyl-2,5,8,11,14-pentaoxahexacosan-26-yl)benzene-1,3,5-tricarboxamide **8** (0.13 mmol, 0.21 g) was dissolved in dry THF. The solution was stirred at 0 °C and sodium hydride (60% dispersion in mineral oil, 0.47 mmol, 0.011 g) was added. The ice bath was removed and the mixture was allowed to stir for 30 minutes at room temperature. Then, iodomethane (0.78 mmol, 0.11 g) was added and the mixture was stirred for 16 hours at reflux. The solvent was removed *in vacuo* and the obtained material was purified by column chromatography ($CHCl_3$/methanol 100/0-90/10 v/v) yielding **9** as a slightly yellow waxy material. Yield = 0.11 g, 53%. ^{1}H NMR (400 MHz, $CDCl_3$ δ): 7.44 (bs, 3H, Ar (benzene tricarboxamide)), 7.39 – 7.27 (m, 15H, Ar), 4.57 (s, 6H, Ar-C$\underline{H}_2$-O), 3.72 – 3.54 (m, 48H, O-(C$\underline{H}_2$)$_2$-O), 3.54 – 3.46 (b, 6H, N-C$\underline{H}_2$, *trans*), 3.43 (t, J = 6.8 Hz, 6H, $CH_2CH_2C\underline{H}_2O$), 3.29 – 3.15 (b, 6H, N-C$\underline{H}_2$, *cis*), 3.05 (s, 9H, N-C$\underline{H}_3$, *cis*), 2.93 (s, 9H, N-C$\underline{H}_3$, t*rans*), 1.71 – 1.44 (m, 12H, $CH_2C\underline{H}_2CH_2O$, $C\underline{H}_2CH_2CH_2O$), 1.44 – 1.04 (m, 48H, aliphatic). MALDI-TOF-MS: calculated M_w = 1601.12 g/mol, observed m/z = 1623.10 [Na^+ adduct].

^{1}H NMR (400 MHz), solvent is $CDCl_3$.



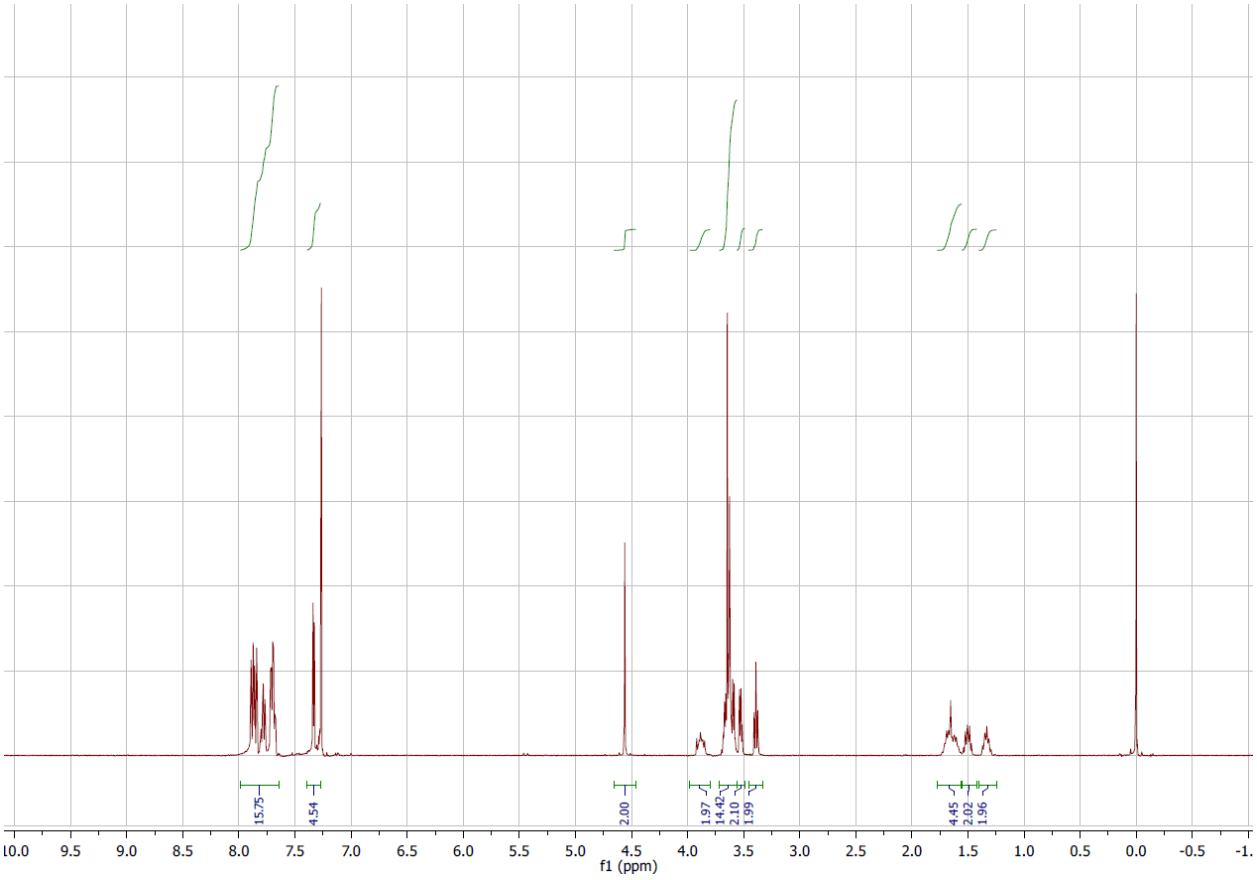
20-Bromo-1-phenyl-2,5,8,11,14-pentaoxaicosane (**10**). In a round bottom flask (1 L, dried at 140 °C) tetraethylene glycol benzyl ether **4** (7.05 g, 24.79 mmol) was dissolved in dry THF (25 ml) and the solution was stirred at 0 °C. Subsequently, sodium hydride (60% in mineral oil, 1.22g, 30.5 mmol) was added upon which the mixture foamed vigorously. The ice bath was removed and the mixture was stirred for 30 minutes. Subsequently, 1,6-dibromohexane (19 ml, 0.125 mol) was added and the mixture was allowed to stir overnight at room temperature. Deionized water was added (75 ml) and the mixture was extracted with diethylether (3 x 75 ml). The organic layers were combined, dried with magnesium sulfate, filtered and concentrated *in vacuo*. The obtained slightly yellow clear oil was purified by column chromatography (heptane/ethyl acetate 60/40) yielding **10** as a slightly yellow oil. Yield = 5.59 g, 50 %. ^{1}H NMR (400 MHz, $CDCl_3$ δ): 7.41 – 7.27 (m, 5H, Ar), 4.57 (s, 2H, Ar-C$\underline{H}_2$-O), 3.73 – 3.60 (m, 14H, O-(C$\underline{H}_2$)$_2$-O), 3.60 – 3.55 (m, 2H, O-(C$\underline{H}_2$)$_2$-O), 3.45 (t, J = 6.6 Hz, 2H, $CH_2C\underline{H}_2Br$), 3.40 (t, J = 6.8 Hz, 2H, $CH_2C\underline{H}_2O$), 1.94 – 1.77 (m, 2H, C$\underline{H}_2CH_2Br$), 1.67 – 1.53 (m, 2H, C$\underline{H}_2CH_2O$), 1.53 – 1.28 (m, 4H, aliphatic).

^{1}H NMR (400 MHz), solvent is $CDCl_3$.

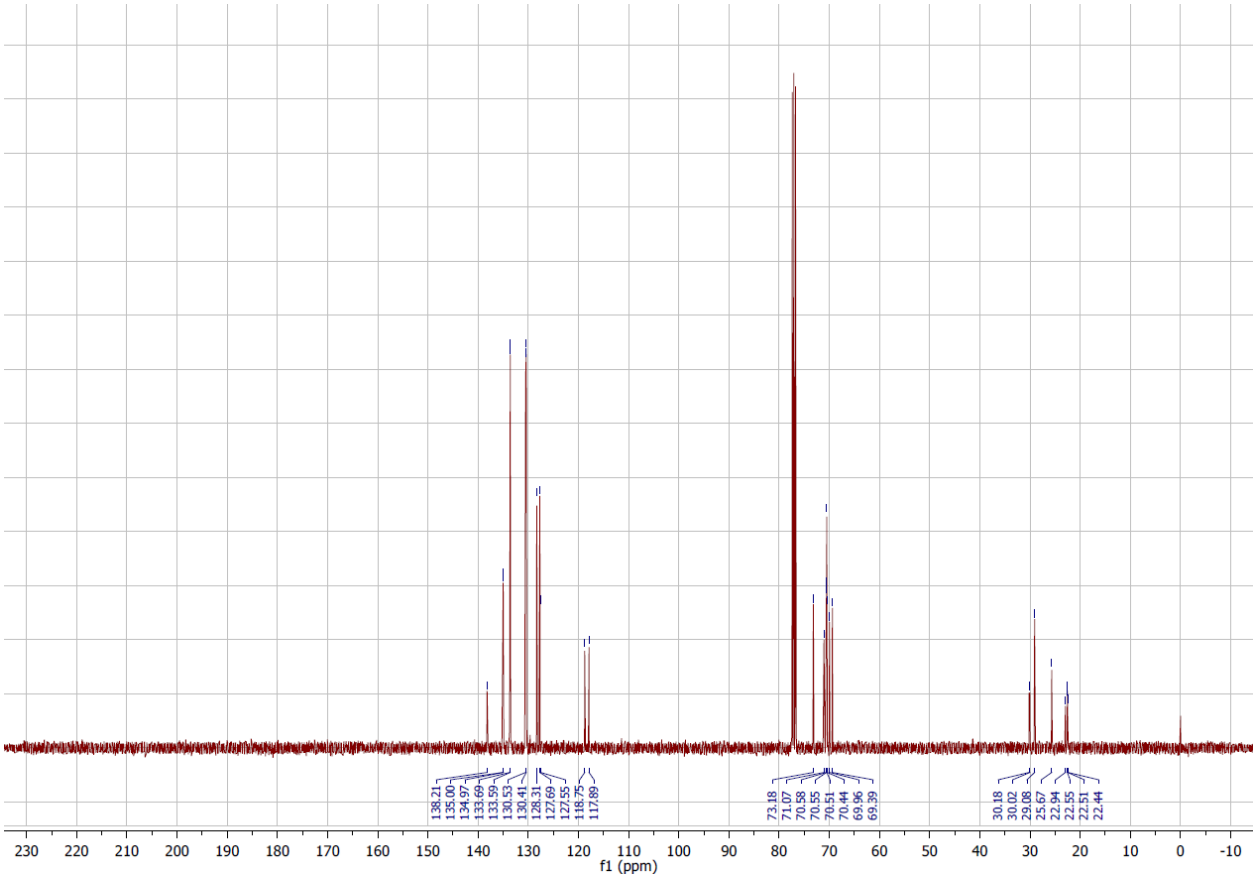


Triphenyl(1-phenyl-2,5,8,11,14-pentaoxaicosan-20-yl)phosphonium bromide (**11**). A round bottom flask (25 ml) was charged with 20-bromo-1-phenyl-2,5,8,11,14-pentaoxaicosane **10** (6.08 mmol, 2.72 g) and triphenylphosphine (9.12 mmol, 2.39 g) wass added. The reaction mixture was heated to 140 °C and the melt was stirred for 7 days. The reaction mixture was purified by column chromatography (eluent heptane/ethyl acetate 60/40 followed by chloroform/ methanol 94/6 v/v) obtaining the product as a slightly yellowish oil. Yield = 4.01 g, 93%. ^{1}H NMR (400 MHz, $CDCl_3$ δ): 7.96 – 7.63 (m, 15H, CH_2P-(Ar)$_3$), 7.42 – 7.27 (m, 5H, O-CH_2-Ar), 4.56 (s, 2H, O-CH_2-Ar), 3.97 – 3.79 (m, 2H, CH_2P-(Ar)$_3$), 3.72 – 3.56 (m, 14H, O-(CH_2)$_2$-O), 3.56 – 3.47 (m, 2H, O-(CH_2)$_2$-O), 3.39 (t, *J* = 6.5 Hz, 2H, $CH_2CH_2CH_2O$), 1.78 – 1.56 (m, 4H, P-$CH_2CH_2CH_2$, $CH_2CH_2CH_2O$), 1.56 – 1.42 (m, 2H, P-$CH_2CH_2CH_2$), 1.42 – 1.25 (m, 2H, $CH_2CH_2CH_2O$). ^{13}C NMR (100 MHz, $CDCl_3$ δ): 138.21, 135.00, 134.97, 133.69, 133.59, 130.53, 130.41, 128.31, 127.69, 127.55, 118.75, 117.89, 73.18, 71.07, 70.60-70.42, 69.96, 69.39, 30.18, 30.02, 29.08, 25.67, 22.94, 22.55, 22.51, 22.44. MALDI-TOF-MS: calculated M_w = 629.34 g/mol, observed m/z = 629.34 [M^+]. FT-IR (ATR) ν (cm^{-1}): 3055, 2861, 1715, 1623, 1587, 1485, 1453, 1438, 1349, 1279, 1249, 1110, 1028, 996, 942, 856, 789, 744, 722, 691, 531, 508, 494.

^{1}H NMR (400 MHz), solvent is $CDCl_3$.

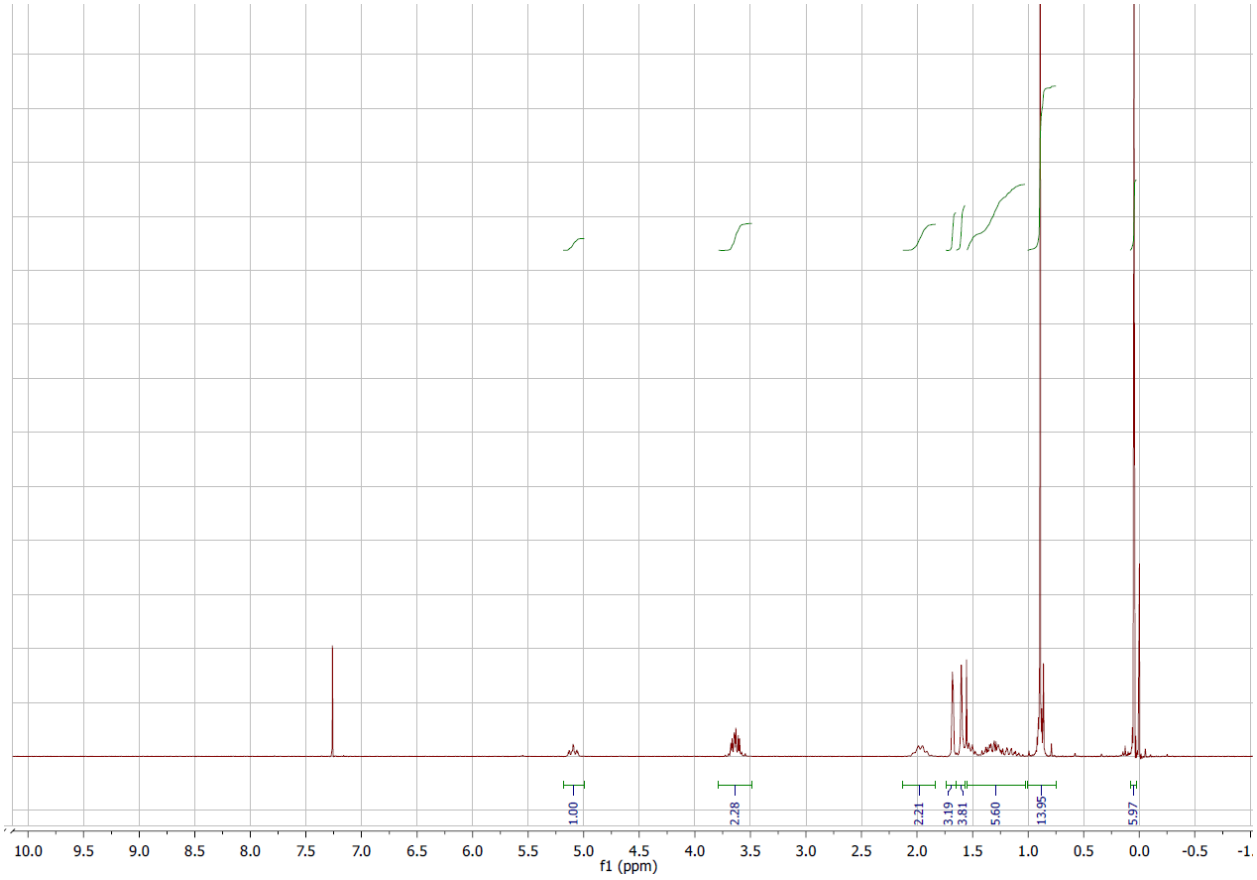


^{13}C NMR (100 MHz), solvent is $CDCl_3$.



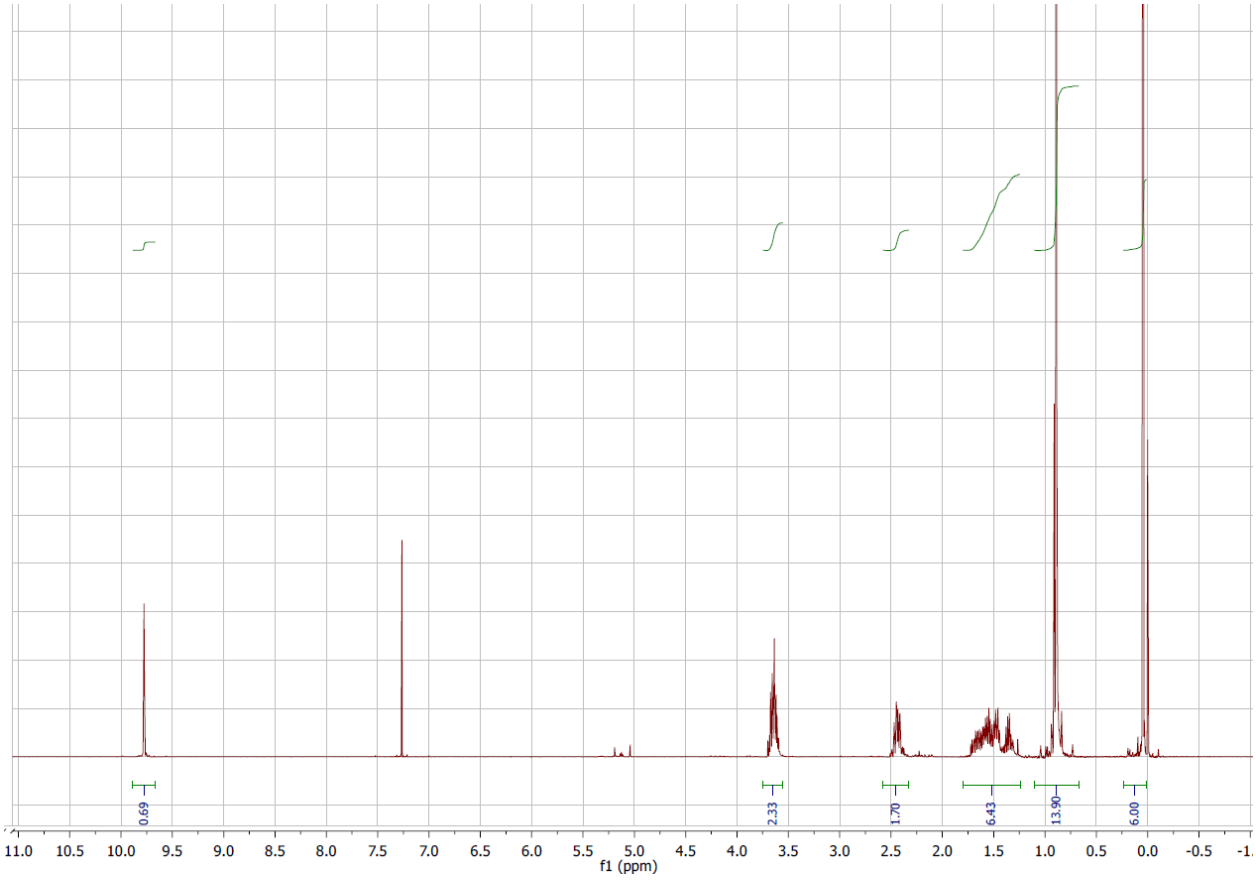
(S)-tert-Butyl((3,7-dimethyloct-6-en-1-yl)oxy)dimethylsilane (**12**). A round bottom flask (50 ml) was charged with (*S*)-3,7-dimethyloct-6-en-1-ol (32.0 mmol, 5.0 g), imidazole (35.64 mmol, 2.43 g) and dry DMF (10 ml). The mixture was stirred and after all solids dissolved the mixture was cooled to 0 °C and *tert*-butylchlorodimethylsilane (35.74 mmol, 5.34 g) was added in one portion. After 5 minutes the reaction mixture was allowed to reach room temperature and stirred overnight. 1M HCl solution (50 ml) was added and the mixture was extracted with chloroform (50 ml). The organic layer was extracted once more with HCl solution (50 ml, 1 M) and subsequently neutralized with saturated $NaHCO_3$ solution (50 ml). The organic layer was dried with $MgSO_4$, filtered and concentrated *in vacuo*. The obtained material was purified by silica filtration (eluent heptane/ethyl acetate, 70/30, v/v). Yield = 99 %. ^{1}H NMR (200 MHz, $CDCl_3$ δ): 5.23 – 4.97 (m, 1H, $(CH_3)_2C{=}C\underline{H}CH_2$), 3.79 – 3.44 (m, 2H, Si-O-$C\underline{H}_2CH_2$), 2.17 – 1.81 (m, 2H, $(CH_3)_2C{=}CHC\underline{H}_2$), 1.74 – 1.65 (m, 3H, $(C\underline{H}_3)_2C{=}CHCH_2$), 1.65 – 1.57 (m, 3H, $(C\underline{H}_3)_2C{=}CHCH_2$), 1.56 – 1.03 (m, 5H, $C\underline{H}_2C\underline{H}(CH_3)C\underline{H}_2$), 1.01 – 0.73 (m, 12H, Si-$C(C\underline{H}_3)_3$, $CH_2CH(C\underline{H}_3)CH_2$), 0.05 (s, 6H, Si-$(C\underline{H}_3)_2$). FT-IR (ATR) ν (cm^{-1}): 2956, 2929, 2858, 1463, 1378, 1254, 1093, 986, 897, 834, 774, 733, 662.

^{1}H NMR (400 MHz), solvent is $CDCl_3$.



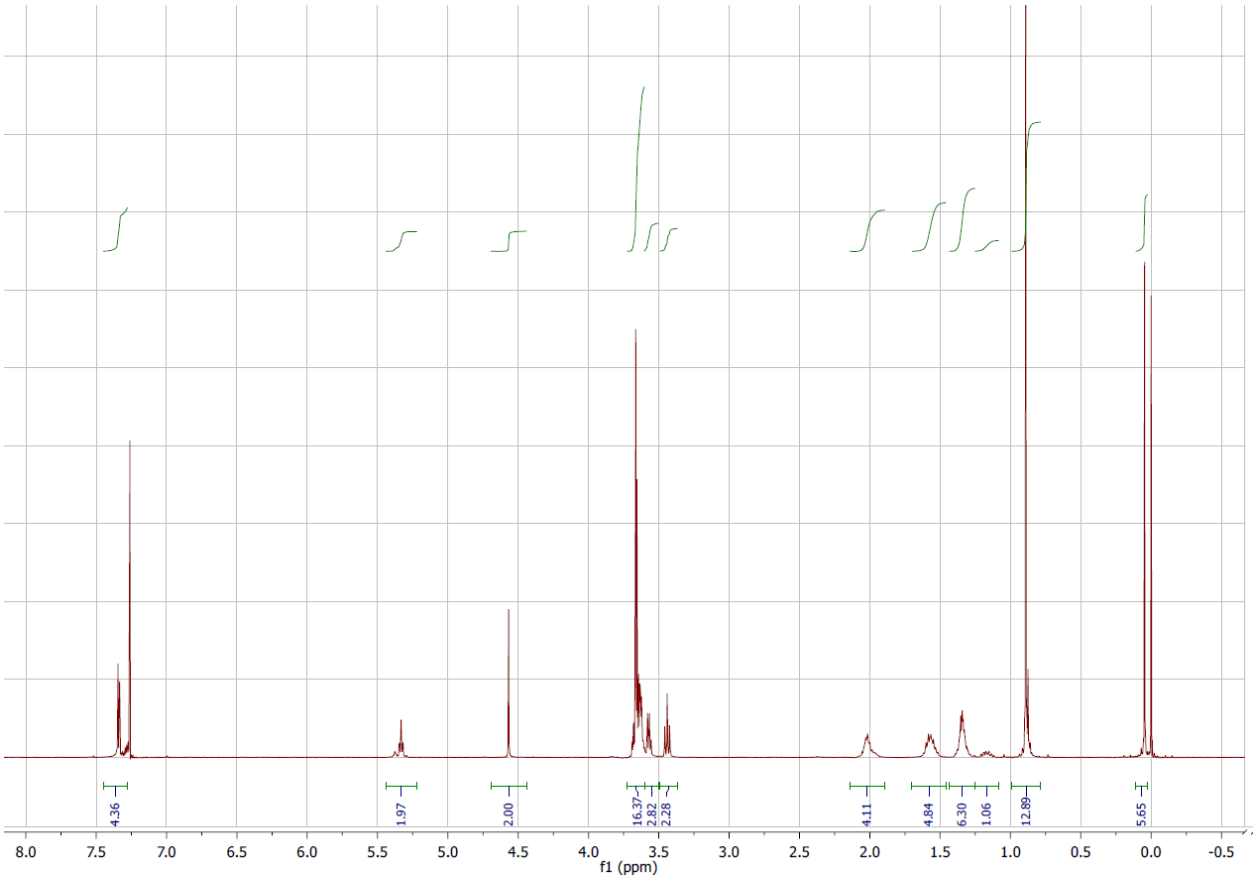
(S)-6-((tert-Butyldimethylsilyl)oxy)-4-methylhexanal (**13**). A three neck round bottom flask (100 ml, dried at 140 °C) was charged with (*S*)-*tert*-butyl((3,7-dimethyloct-6-en-1-yl)oxy)dimethylsilane **12** (7.40 mmol, 2.00 g) and dry DCM (70 ml) was added. The solution was flushed with $N_{2(g)}$ and cooled to -80 °C. Subsequently, ozone was led trough the stirring solution until the solution turned bright blue. At this point dimethyl sulfide (DMS, 82 mmol, 6 ml) was added upon which the reaction mixture immediately became colorless. The reaction mixture was allowed to reach room temperature and was subsequently stirred for one hour at 30 °C. The solvent and excess DMS were removed *in vacuo* and the obtained oil was redissolved in chloroform (20 ml) after which it was extracted two times with deionized water (20 ml). The organic layer was dried with $MgSO_4$, filtered and concentrated *in vacuo* yielding **13** as a colorless oil. Yield = 1.6 g, 91%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.78 (t, J = 1.9 Hz, 1H, $CH_2C\underline{H}$=O), 3.75 – 3.53 (m, 2H, O-$C\underline{H}_2CH_2$), 2.57 – 2.27 (m, 2H, $C\underline{H}_2$CH=O), 1.92 – 1.16 (m, 5H, , $C\underline{H}_2C\underline{H}(CH_3)C\underline{H}_2$), 1.13 – 0.61 (m, 12H, Si-$C(C\underline{H}_3)_3$, $CH_2CH(C\underline{H}_3)CH_2$), 0.04 (s, 6H, Si-$(C\underline{H}_3)_2$).

^{1}H NMR (400 MHz), solvent is $CDCl_3$.



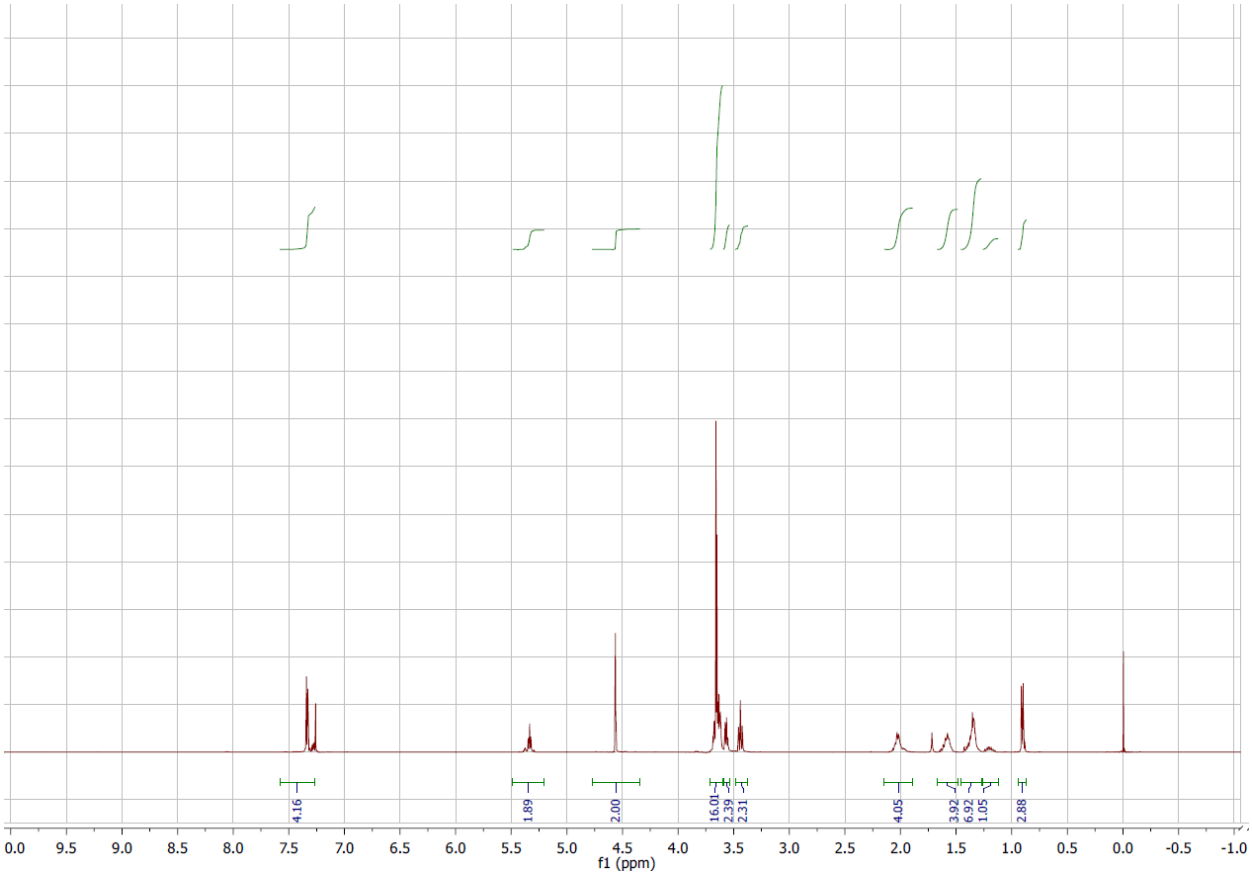
(S)-24,28,28,29,29-Pentamethyl-1-phenyl-2,5,8,11,14,27-hexaoxa-28-silatriacont-20-ene (**14**). A two neck round bottom flask (25 ml, dried at 140 °C) was charged with triphenyl(1-phenyl-2,5,8,11,14-pentaoxaicosan-20-yl)phosphonium bromide **11** and dry THF (16 ml). The mixture was slightly heated by use of a water bath (50 °C) to speed up the dissolution of the solids. Subsequently, the solution was cooled to -30 °C (acetonitrile and N_2(l)) and *n*-butyllithium (1.6 M solution in hexanes,1.26 mmol, 0.79 ml) was added dropwise. The reaction mixture turned bright orange, indicative for the formation of the corresponding ylid. The reaction mixture was stirred at -30 °C (acetonitrile and N_2(l)) for 30 minutes. Then, it was cooled to -78 °C (acetone and dry ice) and a solution of (*S*)-6-((tert-butyldimethylsilyl)oxy)-4-methylhexanal **13** (2.02 mmol, 0.493 g) in dry THF (1 ml) was added dropwise. Upon addition, the color immediately changed to faintly yellow and the reaction mixture became somewhat turbid. After 50 minutes at -78 °C the reaction mixture was allowed to reach -30 °C (acetonitrile and N_2(l)), upon which the mixture became a clear, faintly yellow solution. After 1.5 hours the reaction mixture was allowed to reach room temperature and was stirred for an additional 1.5 hours. The reaction was quenched with saturated NH_4Cl solution (50 ml) and the mixture was extracted three times with diethyl ether (50 ml) The organic layers were combined, dried with $MgSO_4$, filtered and the solvent was removed *in vacuo*. The material was purified by column chromatography (eluent heptane/ethyl acetate 80/20-70/30) yielding a mixture of the E and Z isomers. Yield = 0.45 g, 59%. ^{1}H NMR (400 MHz, $CDCl_3$ δ): 7.41 – 7.27 (m, 5H, Ar), 5.44 – 5.22 (m, 2H, $CH_2C\underline{H}$=$C\underline{H}$ CH_2, Z and E), 4.57 (s, 2H, Ar-$C\underline{H}_2$-O), 3.73 – 3.60 (m, 16H, O-($C\underline{H}_2$)$_2$-O, Si-O-$C\underline{H}_2CH_2$), 3.60 – 3.50 (m, 2H, O-($C\underline{H}_2$)$_2$-O), 3.44 (t, *J* = 6.8 Hz, 2H, $CH_2CH_2C\underline{H}_2O$), 2.14 – 1.89 (m, 4H, $C\underline{H}_2CH$=$CHC\underline{H}_2$), 1.67 – 1.47 (m, 4H, Si-O-$CH_2C\underline{H}_2$, $CH_2C\underline{H}_2CH_2O$), 1.43 – 1.25 (m, 6H, $C\underline{H}_2CH_2CH$=$CHCH_2C\underline{H}_2C\underline{H}_2$), 1.25 – 1.08 (m, 1H, $CH_2C\underline{H}(CH_3)CH_2$), 0.99 – 0.78 (m, 12H, Si-$C(C\underline{H}_3)_3$, $CH_2CH(C\underline{H}_3)CH_2$), 0.05 (s, 6H, Si-($C\underline{H}_3$)$_2$). MALDI-TOF-MS: calculated M_w = 594.43 g/mol, observed m/z = 617 [Na^+ adduct].

^{1}H NMR (400 MHz), solvent is $CDCl_3$.

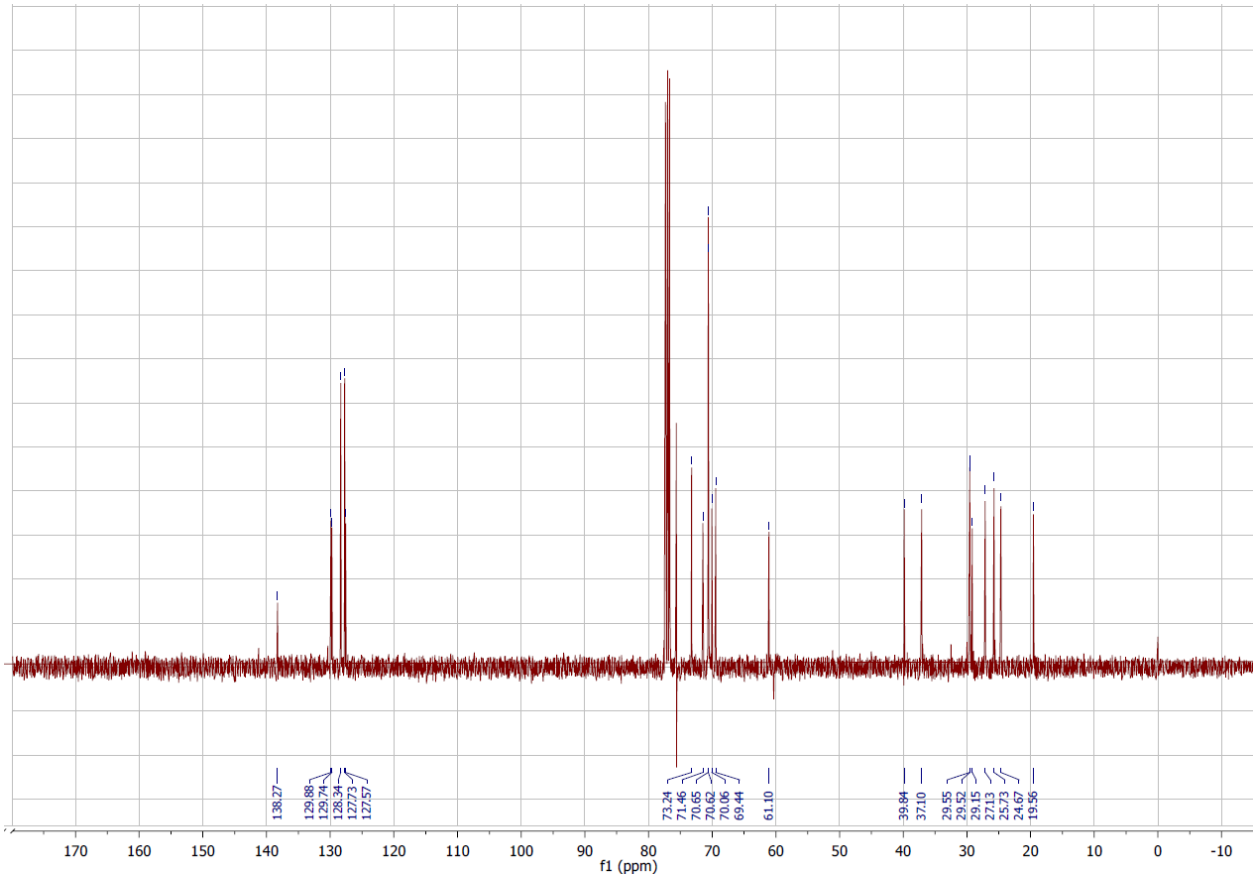


(S)-24-Methyl-1-phenyl-2,5,8,11,14-pentaoxahexacos-20-en-26-ol (**15**). A two neck round bottom flask (25 ml, dried at 140 °C) was charged with (*S*)-24,28,28,29,29-pentamethyl-1-phenyl-2,5,8,11,14,27-hexaoxa-28-silatriacont-20-ene **14** (1.21 mmol, 0.717 mg) and dry THF (6 ml). The solution was cooled to 0 °C and tetrabutylammonium fluoride (1M in THF, 1.8 ml) was added dropwise. The reaction mixture was allowed to reach room temperature and stirring was continued for 4.5 hours. The reaction was quenched with saturated NH_4Cl solution (30 ml) and the aqueous layer was extracted with diethyl ether (3x 30 ml). The organic layers were combined, dried with $MgSO_4$, filtered and concentrated *in vacuo*. The material was purified by column chromatography (eluent heptane/dimethoxyethane 100/0-50/50 v/v). Yield = 0.53 g, 91%. ^{1}H NMR (400 MHz, $CDCl_3$ δ): 7.42 – 7.27 (m, 5H, Ar), 5.48 – 5.22 (m, 2H, $CH_2C\underline{H}$=C$\underline{H}$ CH_2, Z and E), 4.57 (s, 2H, Ar-C$\underline{H}_2$-O), 3.71 – 3.60 (m, 16H, O-(C$\underline{H}_2$)$_2$-O, HO-C$\underline{H}_2$CH$_2$), 3.59 – 3.54 (m, 2H, O-(C$\underline{H}_2$)$_2$-O), 3.44 (t, *J* = 6.8 Hz, 2H, $CH_2CH_2C\underline{H}_2O$), 2.15 – 1.89 (m, 4H, C$\underline{H}_2$CH=CHC$\underline{H}_2$), 1.67 – 1.49 (m, 4H, HO-CH$_2$C$\underline{H}_2$, $CH_2C\underline{H}_2CH_2O$), 1.46 – 1.27 (m, 6H, C$\underline{H}_2CH_2$CH=CHCH$_2C\underline{H}_2C\underline{H}_2$), 1.27 – 1.12 (m, 1H, $CH_2C\underline{H}(CH_3)CH_2$), 0.91 (d, *J* = 6.6 Hz, 3H, $CH_2CH(C\underline{H}_3)CH_2$). ^{13}C NMR (100 MHz, $CDCl_3$ δ): 138.27, 129.88, 129.74, 128.34, 127.73, 127.57, 73.24, 71.46, 70.67-70.57, 70.06, 69.44, 61.10, 39.84, 37.10, 29.55, 29.52, 29.15, 27.13, 25.73, 24.67, 19.56. MALDI-TOF-MS: calculated M_w = 480.35 g/mol, observed m/z = 503.37 [Na^+ adduct], 519.34 [K^+ adduct]. FT-IR (ATR) ν (cm^{-1}): 2922, 2860, 1454, 1351, 1297, 1250, 1206, 1100, 849, 737, 698, 605, 532, 466.

^{1}H NMR (400 MHz), solvent is $CDCl_3$.



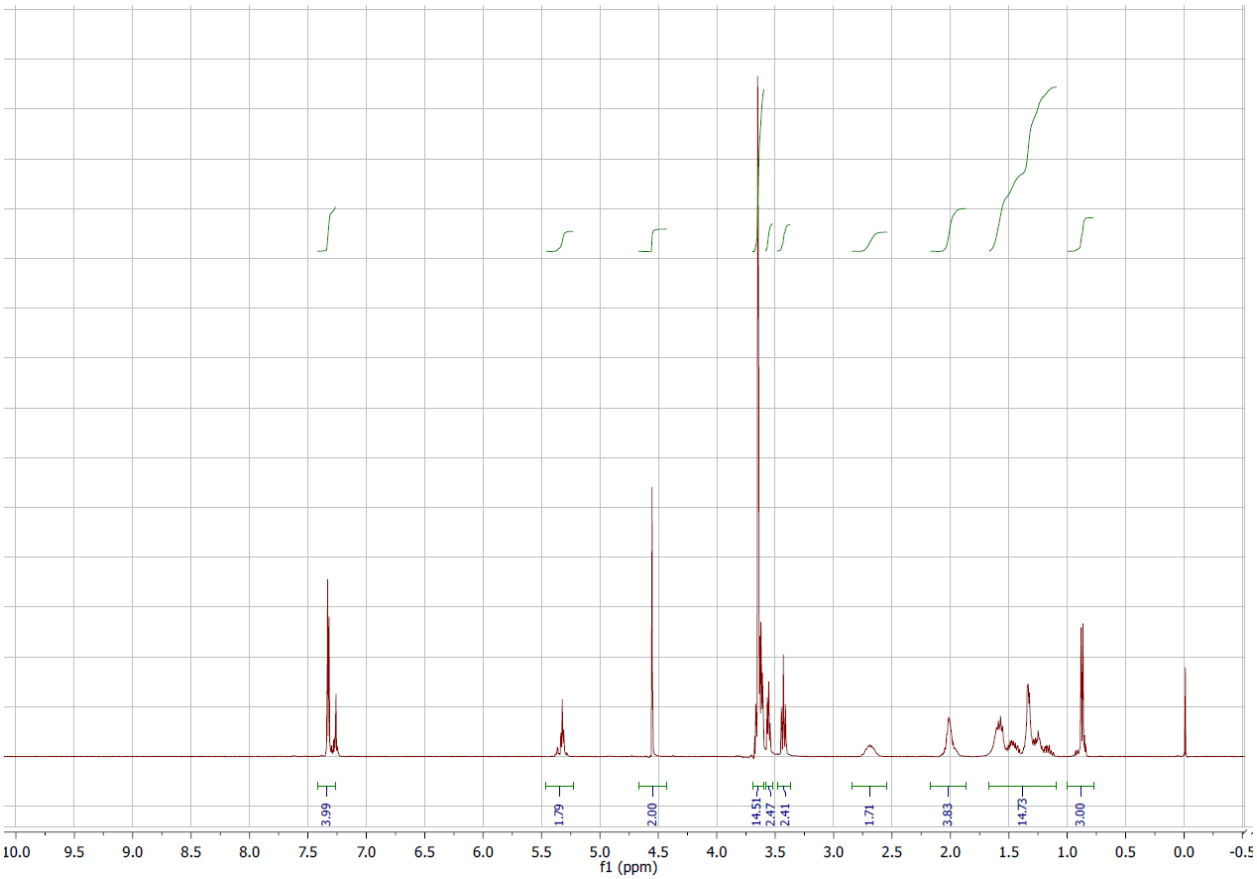
^{13}C NMR (100 MHz), solvent is $CDCl_3$.



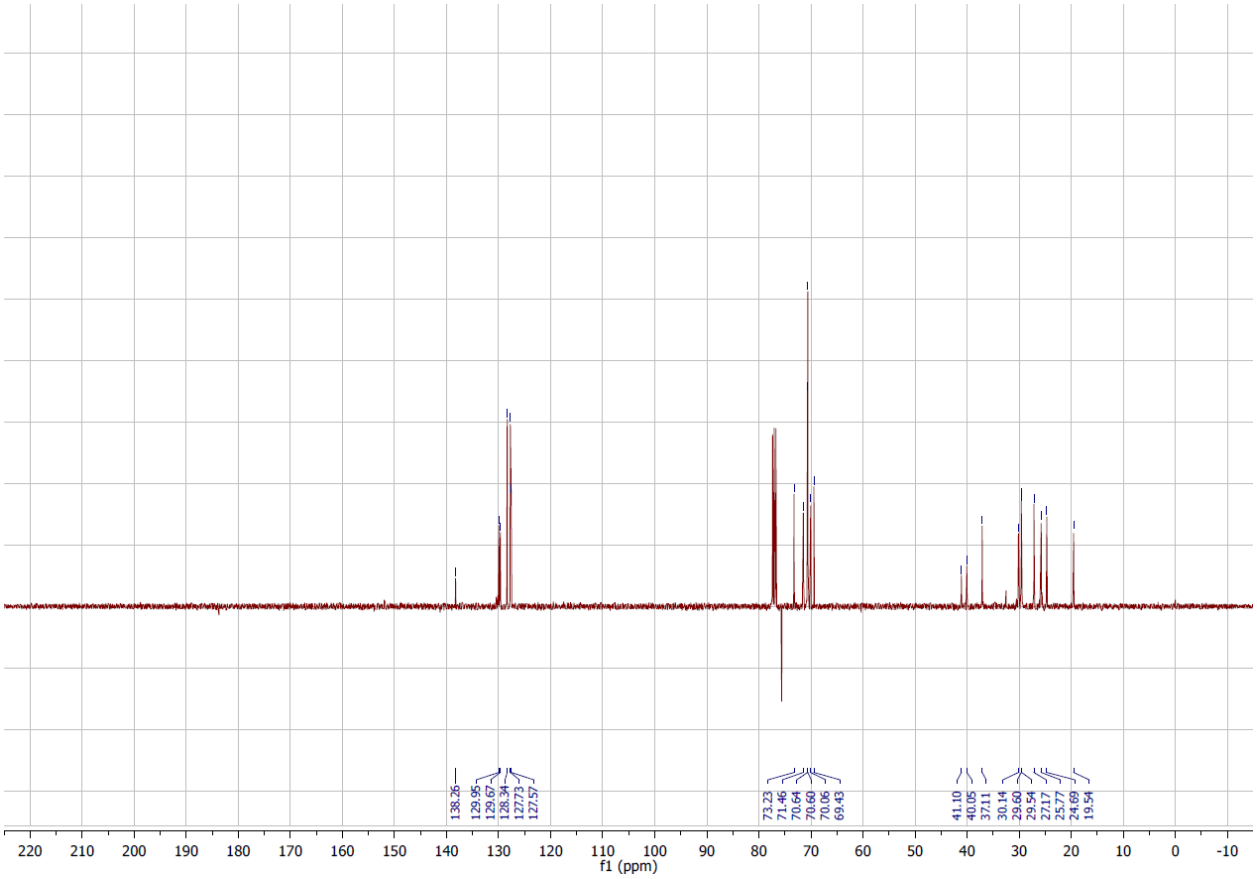
(S)-2-(24-Methyl-1-phenyl-2,5,8,11,14-pentaoxahexacos-20-en-26-yl)isoindoline-1,3-dione (**16**). A two neck round bottom flask (25 ml, dried at 140 °C) was charged with (*S*)-24-methyl-1-phenyl-2,5,8,11,14-pentaoxahexacos-20-en-26-ol **15** (1.08 mmol, 0.52g), diethyl ether (10 ml), phthalimide (2.18 mmol, 0.321 g) and triphenylphosphine (2.16 mmol, 0.567 g). The heterogeneous reaction mixture was stirred at 0 °C and diisopropyl azodicarboxylate (DIAD) (2.23 mmol, 0.44 ml) was added dropwise. Subsequently, the reaction mixture was allowed to reach room temperature and was stirred overnight. The reaction mixture was filtered over a glass filter and the solids were washed three times with diethyl ether (15 ml). The filtrate was concentrated *in vacuo* at high vacuum for 2 hours. The obtained material was directly used in the subsequent step.

(S)-24-methyl-1-phenyl-2,5,8,11,14-pentaoxahexacos-20-en-26-amine (**17**). A round bottom flask (100 ml) was charged with (*S*)-2-(24-methyl-1-phenyl-2,5,8,11,14-pentaoxahexacos-20-en-26-yl)isoindoline-1,3-dione **16** and ethanol (15 ml) was added. To the stirring solution hydrazine monohydrate (0.5 ml) was added. The reaction mixture was stirred overnight at reflux. The reaction mixture was concentrated *in vacuo*, redissolved in chloroform (25 ml) and extracted with NaOH solution (3x 25 ml, 1 M). The organic layer was dried with $MgSO_4$, filtered and concentrated *in vacuo*. The material was purified by filtration over silica (eluent: ethyl acetate/methanol 95/5 followed by ethyl acetate/isopropylamine 9/1). Yield = 0.417 g, 81%. ^{1}H NMR (400 MHz, $CDCl_3$ δ): 7.39 – 7.27 (m, 5H, Ar), 5.45 – 5.24 (m, 2H, $CH_2C\underline{H}$=C$\underline{H}$ CH_2, Z and E), 4.57 (s, 2H, Ar-C$\underline{H}_2$-O), 3.71 – 3.60 (m, 14H, O-(C$\underline{H}_2$)$_2$-O), 3.60 – 3.51 (m, 2H, O-(C$\underline{H}_2$)$_2$-O), 3.44 (t, *J* = 6.8 Hz, 2H, $CH_2CH_2C\underline{H}_2O$), 2.83 – 2.58 (m, 2H, $CH_2C\underline{H}_2NH_2$), 2.16 – 1.91 (m, 4H, C$\underline{H}_2$CH=CHC$\underline{H}_2$), 1.66 – 1.09 (m, 11H, aliphatic), 0.89 (d, *J* = 6.5 Hz, 3H, $CH_2CH(C\underline{H}_3)CH_2$). ^{13}C NMR (100 MHz, $CDCl_3$ δ): 138.26, 129.95, 129.67, 128.34, 127.73, 127.57, 73.23, 71.46, 70.66-70.56, 70.06, 69.43, 41.10, 40.05, 37.11, 30.14, 29.60, 29.54, 27.17, 25.77, 24.69, 19.54. MALDI-TOF-MS: calculated M_w = 479.36 g/mol, observed m/z = 480.39 [MH^+], 502.37 [Na^+ adduct]. FT-IR (ATR) ν (cm^{-1}): 2920, 2858, 1583, 1454, 1350, 1300, 1250, 1206, 1100, 1040, 985, 945, 877, 851, 820, 736, 698, 612, 524, 466.

^{1}H NMR (400 MHz), solvent is $CDCl_3$.

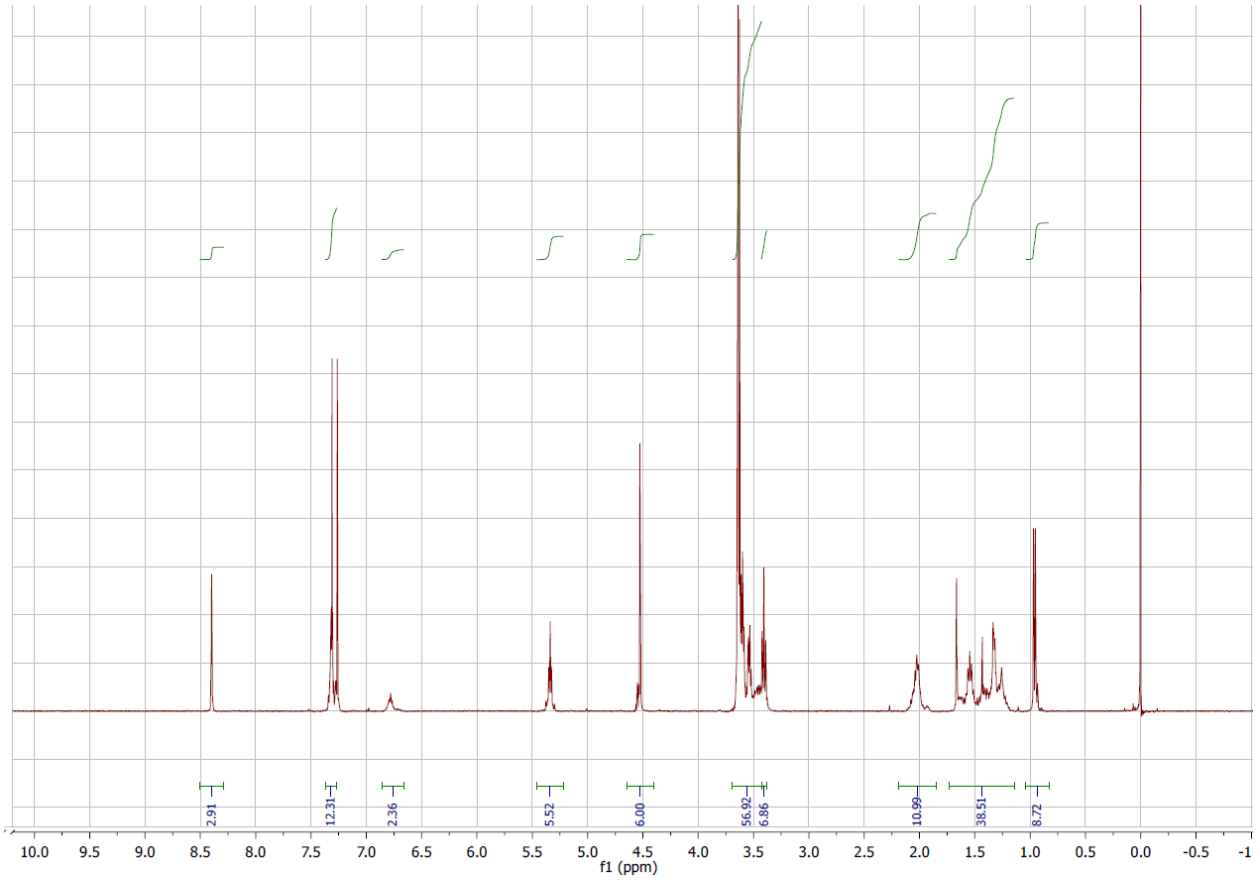


^{13}C NMR (100 MHz), solvent is $CDCl_3$.

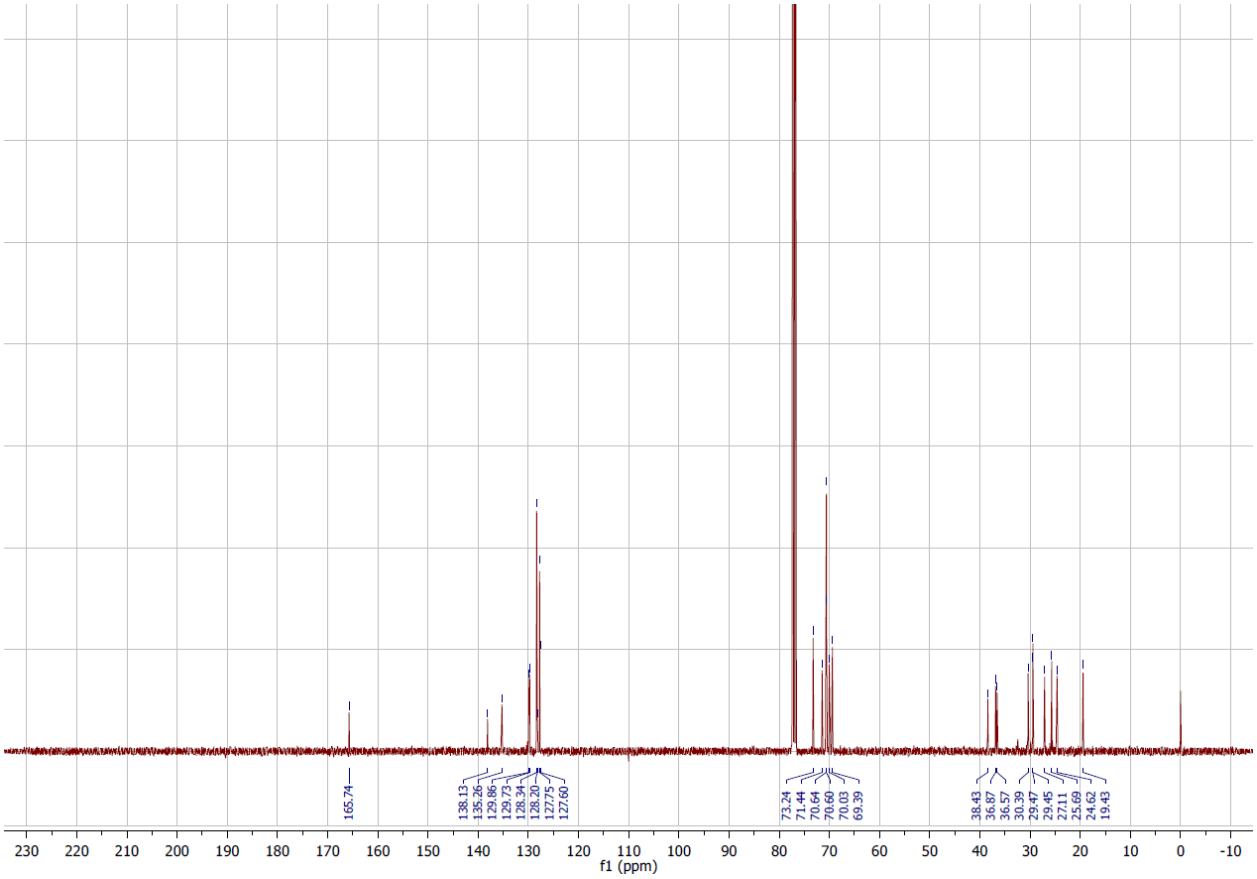


N^1,N^3,N^5-tris((S)-24-methyl-1-phenyl-2,5,8,11,14-pentaoxahexacos-20-en-26-yl)benzene-1,3,5-tricarboxamide (**18**). A two neck round bottom flask (25 ml, dried at 140 °C) was charged with (*S*)-24-methyl-1-phenyl-2,5,8,11,14-pentaoxahexacos-20-en-26-amine **17** (0.534 mmol, 0.256 g) and dry chloroform (1.5 ml). To the stirred solution was added triethylamine (1.0 mmol, 0.14 ml) and the mixture was cooled to 0 °C. Subsequently, 1,3,5-benzenetricarbonyl trichloride (0.167 mmol, 44.17 mg) was dissolved in dry chloroform (0.5 ml) and added dropwise to the reaction mixture. The reaction mixture was allowed to reach room temperature and was stirred for an additional 4 hours. The solvent was removed *in vacuo* and the material was purified by column chromatography (eluent, heptane/dimethoxyethane 50/50, v/v). Yield = 0.21 g, 77%. ^{1}H NMR (400 MHz, $CDCl_3$ δ): 8.40 (s, 3H, Ar (benzenetricarboxamide), 7.37 – 7.27 (m, 15H, Ar), 6.86 – 6.65 (b, 3H, C=ON<u>H</u>CH_2), 5.34 (m, 6H, CH_2C<u>H</u>=C<u>H</u> CH_2, Z and E), 4.53 (s, 6H, Ar-C<u>H</u>$_2$-O), 3.69 – 3.43 (m, 54H, O-(C<u>H</u>$_2$)$_2$-O, CH_2C<u>H</u>$_2$NHC=O), 3.41 (t, *J* = 6.7 Hz, 6H, CH_2CH_2C<u>H</u>$_2$O), 2.16 – 1.87 (m, 12H, C<u>H</u>$_2$CH=CHC<u>H</u>$_2$), 1.76 – 1.13 (m, 33H, aliphatic), 0.96 (d, *J* = 6.5 Hz, 9H, $CH_2CH(C$<u>H</u>$_3)CH_2$). ^{13}C NMR (100 MHz, $CDCl_3$ δ): 165.74, 138.13, 135.26, 129.86, 129.73, 128.34, 128.20, 127.75, 127.60, 73.24, 71.44, 70.67-70.56, 70.03, 69.39, 38.43, 36.87, 36.57, 30.39, 29.47, 29.45, 27.11, 25.69, 24.62, 19.43. MALDI-TOF-MS: calculated M_w = 1594.07 g/mol, observed m/z = 1617.04 [Na^+ adduct], 1633.03 [K^+ adduct]. FT-IR (ATR) ν (cm^{-1}): 3237, 3066, 2923, 2859, 1640, 1561, 1454, 1351, 1300, 1252, 1105, 1041, 946, 906, 853, 736, 697, 613.

^{1}H NMR (400 MHz), solvent is $CDCl_3$.

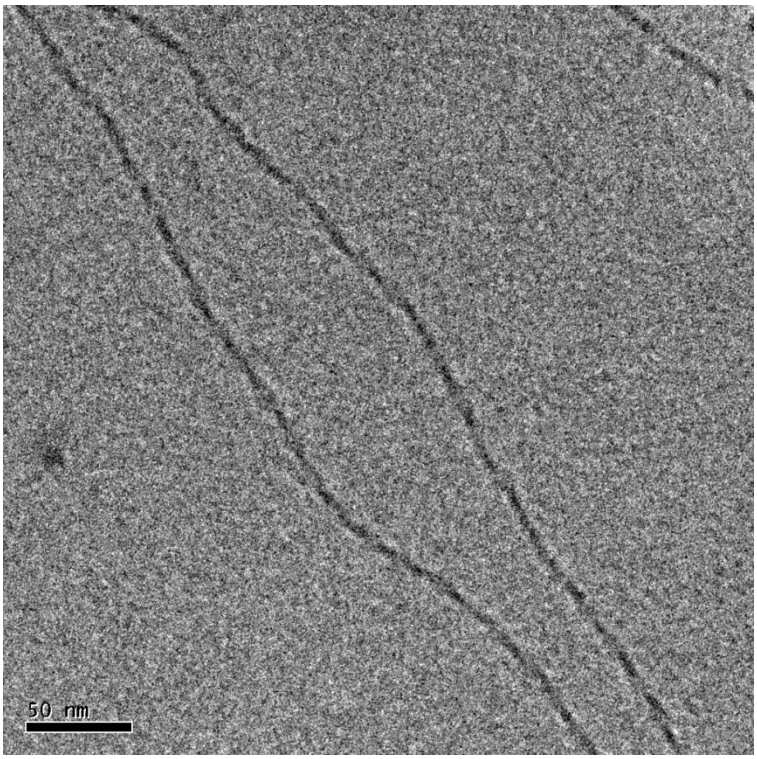


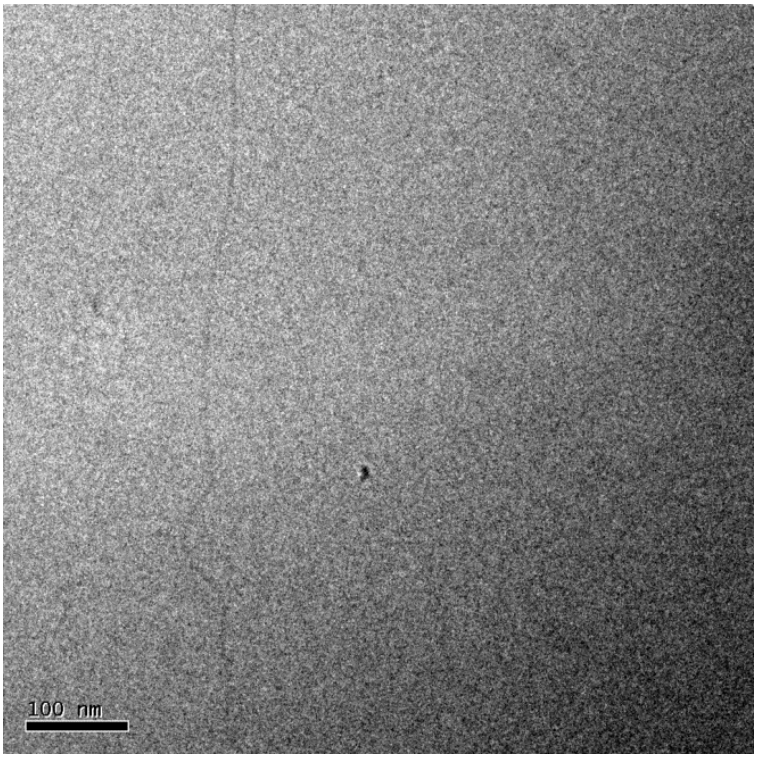
^{13}C NMR (100 MHz), solvent is $CDCl_3$.



Electronic Supplementary Material (ESI) for Chemical Communications

Supporting data





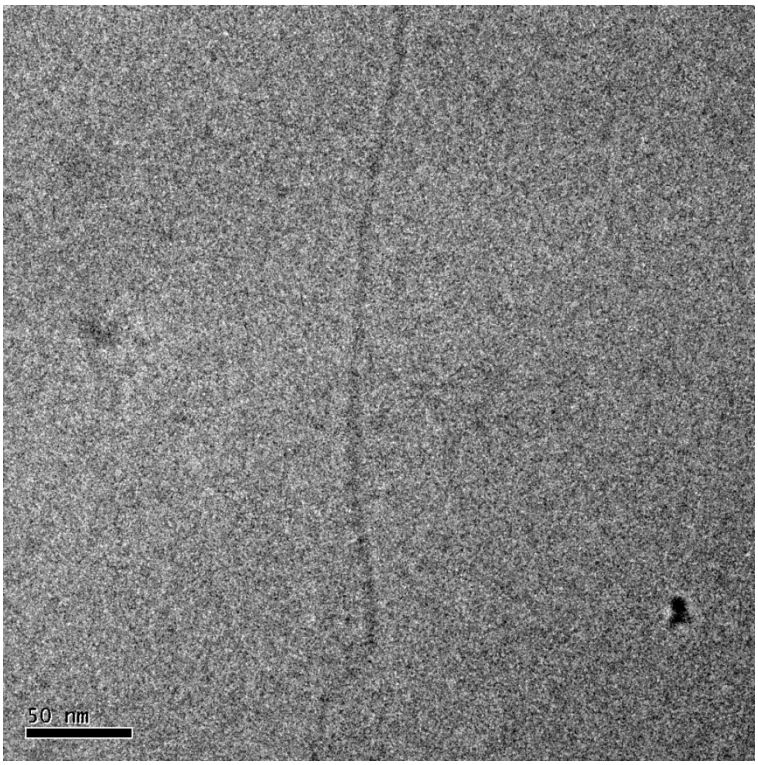


Figure S1: Top) Cryo-TEM of **1** (c = 0.5 mg/ml in pure water), displaying thin twisted fibers. Middle) Cryo-TEM of **2** (c = 0.5 mg/ml in water/methanol 9/1 v/v), displaying a thin fiber more than 700 nm in length. bottom) Cryo-TEM of **2** (c = 0.5 mg/ml in water/methanol 9/1 v/v), displaying a thin fiber of a uniform diameter.

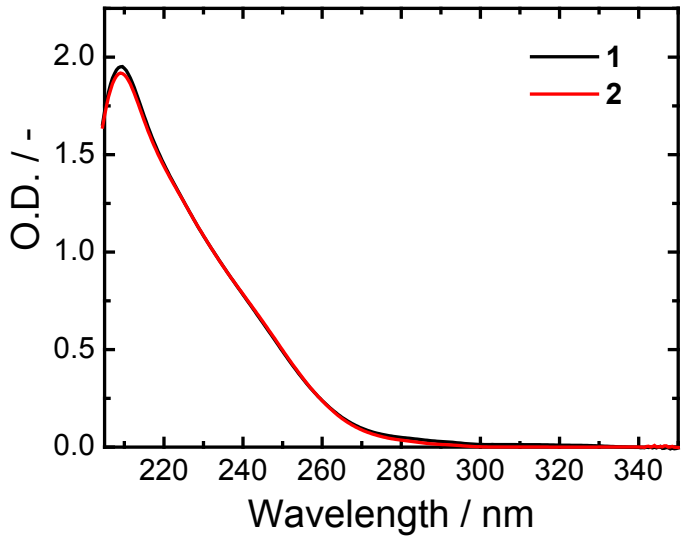


Figure S2: UV-Vis spectra of **1** (black) and **2** (red) in methanol at 20 °C (c = $5x10^{-5}$M), displaying an absorption maximum at 209 nm, typical for the molecularly dissolved state.

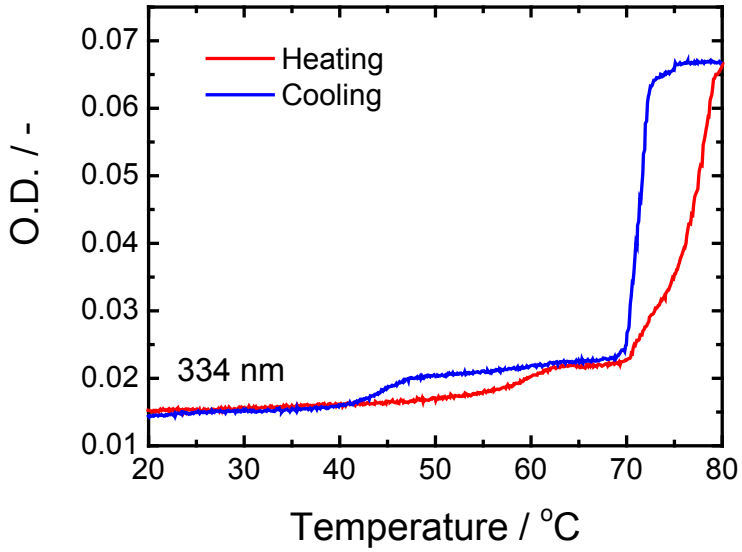


Figure S3: LCST determination of **1** in water (c = $1x10^{-5}$M) : The optical density was recorded as a function of temperature at 334 nm, where **1** does not absorb. The large increase in optical density above 70 °C represents the LCST of **1**.

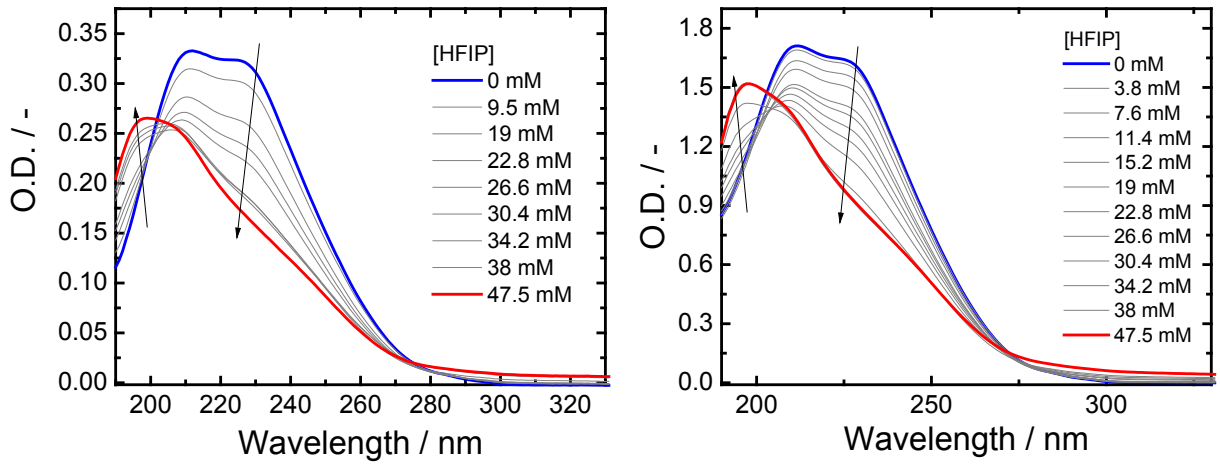


Figure S4: UV-Vis spectra of **1** in water at 20 °C as a function of HFIP concentration, Left: c = $1x10^{-5}$M Right: c = $5x10^{-5}$M. Upon addition of HFIP a transition from the aggregated state to a non-aggregated state is observed. The arrows indicate the diminishing of the absorption band at 226 nm and the emergence of a new absorption maximum resulting from solvation by HFIP (See Figure S5).

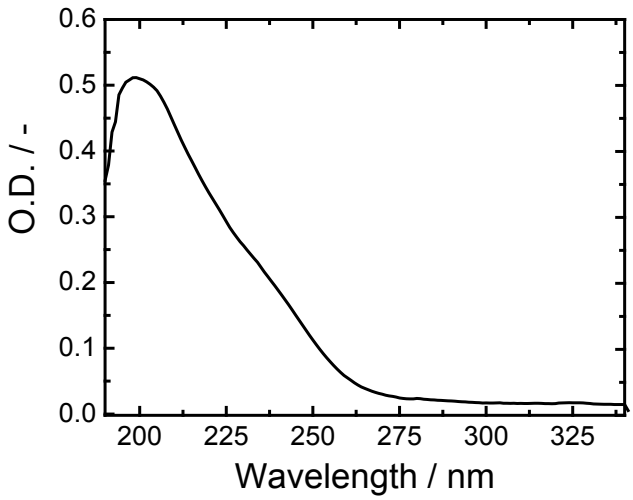


Figure S5: UV-Vis spectrum of **1** (c = $1x10^{-5}$M) in pure HFIP at 20 °C.

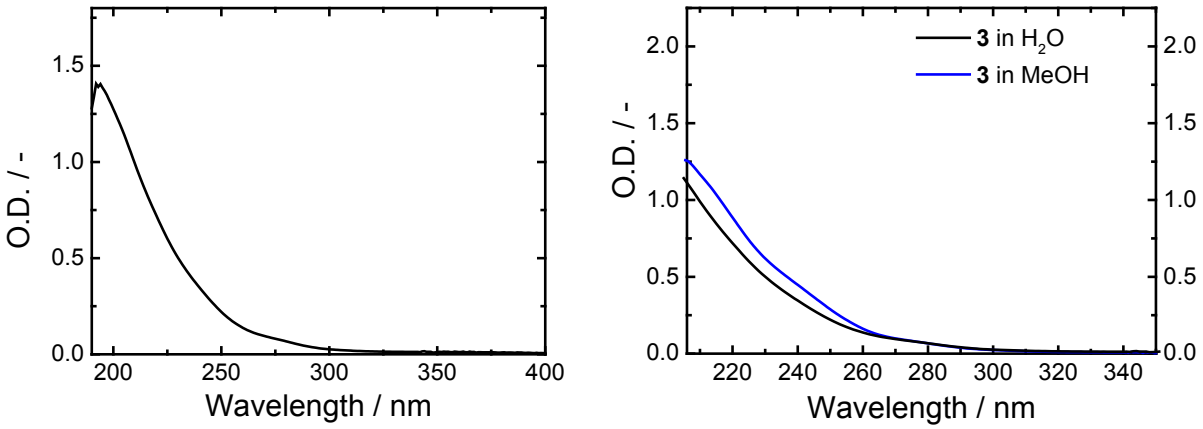


Figure S6: Left) UV-Vis spectrum of **3** in water at 20 °C (c = $5x10^{-5}$M). Right) overlay of UV-Vis spectrum of **3** in water at 20 °C (black, c = $5x10^{-5}$M) and **3** in methanol at 20 °C (blue, c = $5x10^{-5}$M).

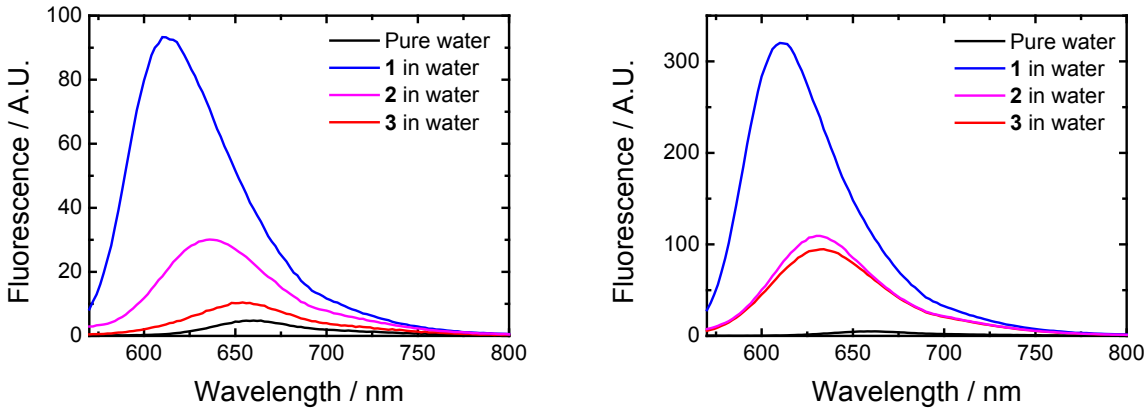


Figure S7: Fluorescence measurements of Nile Red at 20 °C. Left) Concentrations of **1**, **2** and **3** are $1x10^{-5}$M. Black: pure water, Blue: solution of **1** in water, pink: solution of **2** in water,red: solution of **3** in water. Right) Concentrations of **1**, **2** and **3** are $5x10^{-5}$M. black: pure water, Blue: solution of **1** in water, pink: solution of **2** in water, red: solution of **3** in water.

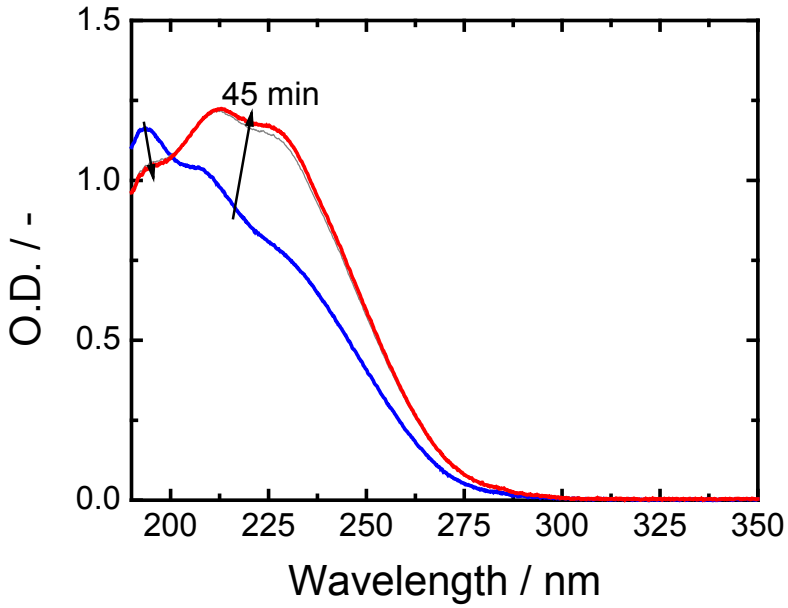


Figure S8: UV-vis absorption of **1** in water (c = $5x10^{-5}$M) injected from methanol (c = $2.5x10^{-2}$ M, 5 µl was injected into 2.5 ml water) and followed in time (grey curve is after 15 minutes, red curve is after 45 minutes).