Supplementary Information for:

Supramolecular polymerisation in water; elucidating the role of hydrophobic and hydrogen-bond interactions

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Contents

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. Cy3-*N*-hydroxy succinimide (NHS) and Cy5-NHS were purchased from Lumiprobe. 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 while triethyl amine 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 Millipore Milli-Q Integral Water Purification System. Reactions were followed by thin-layer chromatography (precoated 0.25 mm, 60-F254 silica gel plates from Merck).

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.

LC-MS was recorded on a system consisting of the following components: Shimadzu SCL-10 A VP system controller with Shimadzu LC-10AD VP liquid chromatography pumps (with an Alltima C18 3 u (50 × 2.1 mm) reversed-phase column and gradients of water–acetonitrile supplemented with 0.1% formic acid, a Shimadzu DGU 20A3 prominence degasser, a Thermo Finnigan surveyor auto sampler, a Thermo Finnigan surveyor PDA detector and a Thermo Scientific LCQ Fleet.

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. Variable temperature IR was recorded on a Bruker Tensor 27 equipped with a PIKE GladiATR. Solution FT-IR measurements were performed using a CaF_2 Liquid Cell with 0.05 mm pathlength purchased from New Era Enterprises.

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, excitation wavelength was 520 nm.

Cryogenic transmission electron microscopy was performed on samples with a concentration of 0.5 mg/mL. Vitrified films were prepared in a ‘Vitrobot’ instrument (PC controlled

vitrification robot, patent applied, Frederik et al 2002, patent licensed to FEI) at 22°C and a humidity of 100%. In the preparation chamber of the 'Vitrobot' a 3 µL sample was applied on a Quantifoil grid (R 2/2, Quantifoil Micro Tools GmbH), which was surface plasma treated just prior to use (Cressington 208 carbon coater operating at 5 mA for 40 s). Excess sample was removed by blotting using filter paper for 2s at –2 mm, and the thin film thus formed was shot (acceleration about 3 g) into liquid ethane just above its freezing point. The vitrified film was transferred to a cryoholder (Gatan 626) and observed at –170 °C in a Tecnai Sphera microscope operating at 200 kV. Microscopy images were taken at low dose conditions and at a defocus of 10 µm (magnification: 25000).

DLS measurements were recorded on an ALV/CGS-3 MD-4 compact goniometer system equipped with a multiple tau digital real time correlator (ALV-7004) and a solid state laser (λ = 532 nm; 40 mW).

Optical microscope images were acquired using a Nikon Ti-E microscope configured for TIRF imaging. Cy5-labelled samples were illuminated by the 647-nm laser lines built into the microscope. Fluorescence was collected by means of a Nikon 100x, 1.4 NA oil immersion objective and passed through a quad-band-pass dichroic filter (97335 Nikon). Frames were recorded onto a 128 x 128 pixel region of an EMCCD camera (ixon3, Andor).

Methods

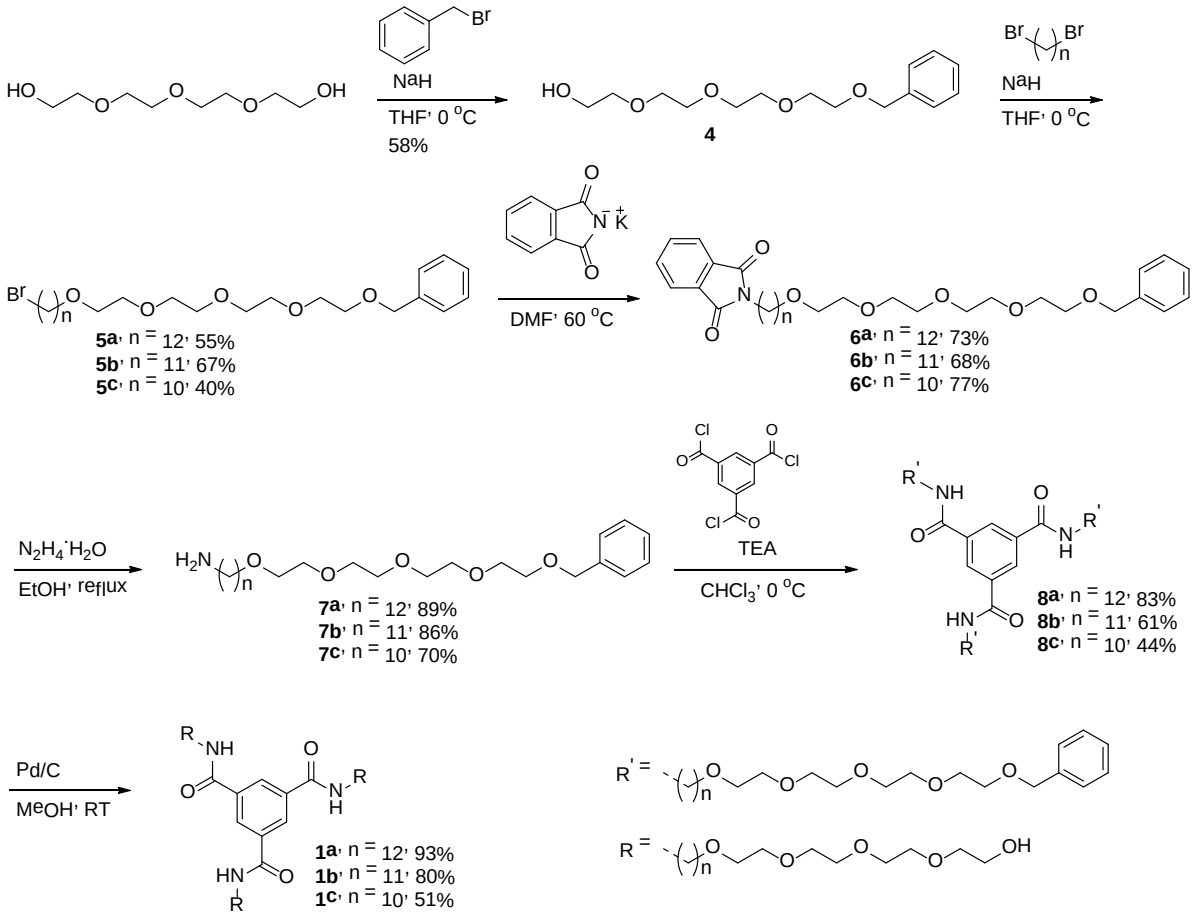
UV-Vis and fluorescence measurements were performed using quartz cuvettes (1 cm). Aqueous samples were prepared as follows: a stock solution of the desired BTA derivative was prepared in methanol and 5 µL was injected into 2.5 mL water (milliQ) obtaining the desired final concentration (c = 1 × 10^{-5} M or c = 5 × 10^{-5} M). Samples were allowed to anneal overnight and if needed heated to 50 °C and allowed to cool to room temperature prior to measuring.

Samples for solution FT-IR were prepared by addition of D_2O (0.208 ml) to **1a** (10.41 g) in a closed vial and heating the mixture to above 80 °C. The turbid suspension was allowed to cool down to room temperature upon which it became a slightly hazy, transparent, viscous solution. This solution was allowed to equilibrate overnight. Then it was injected into the FT-IR Cell (pathlength 0.05 mm) with a syringe.

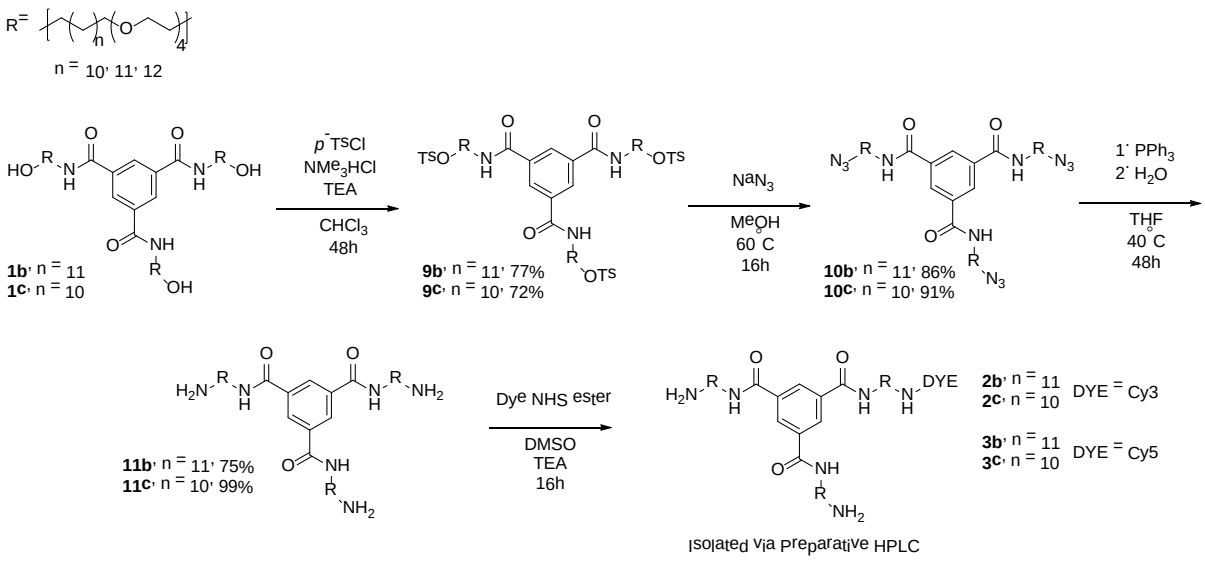
Samples for optical microscopy imaging were prepared at a concentration of c = 1 × 10^{-5} M with 5 % incorporation of the corresponding Cy5–labelled **3a**–**c** and allowed to equilibrate for 3 days. Prior to imaging the solutions were diluted to reduce the fibre density in the solution to c_{BTA} = 1 × 10^{-6} M and immediately imaged.

Synthesis

The synthesis of **1a** and all its intermediates has been reported elsewhere.[1] The synthesis of **1b** and **1c** was carried out analogously. The synthesis of **2a** and **3a** has been reported previously.[2] The synthesis of **2b**, **2c**, **3b**, and **3c** was carried out analogously.



Scheme S1: Synthetic approach for the formation of **1a-c**.



Scheme S2: Synthetic approach for the formation of **2a-c** and **3a-c**.

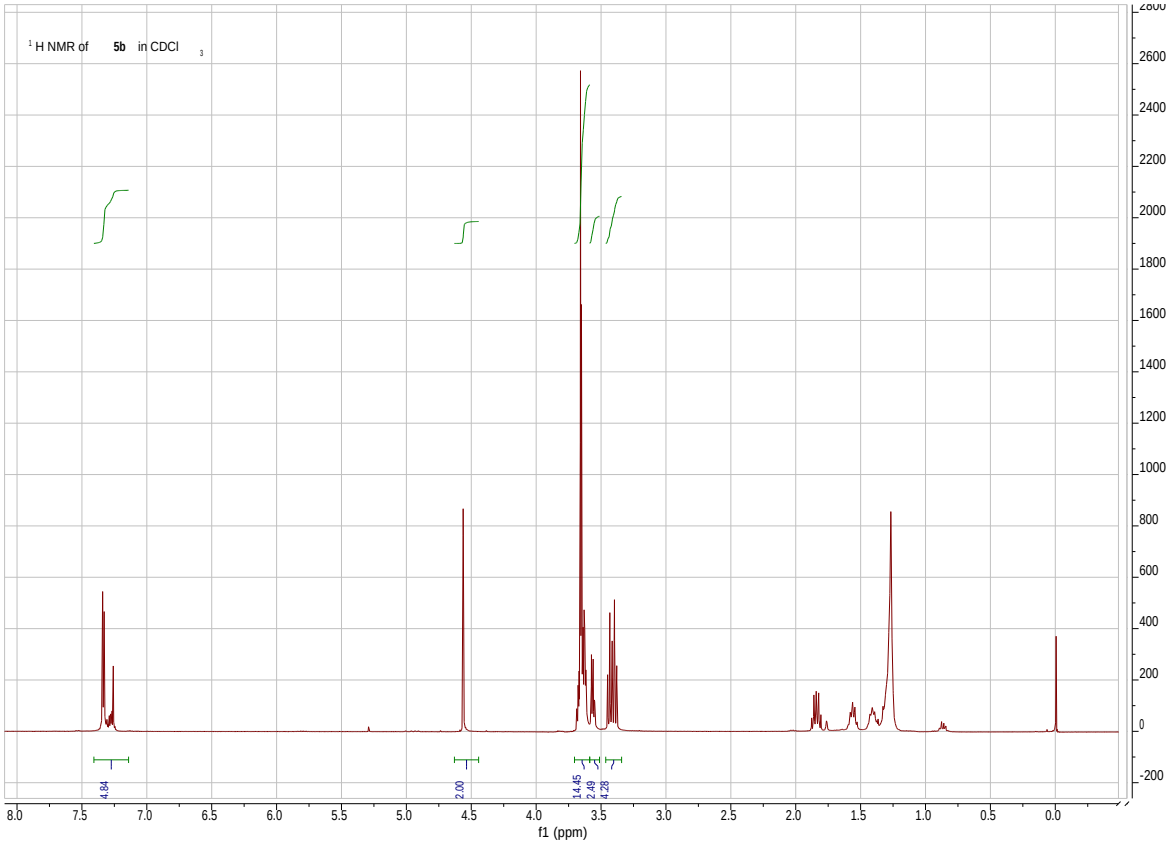
Synthetic procedures

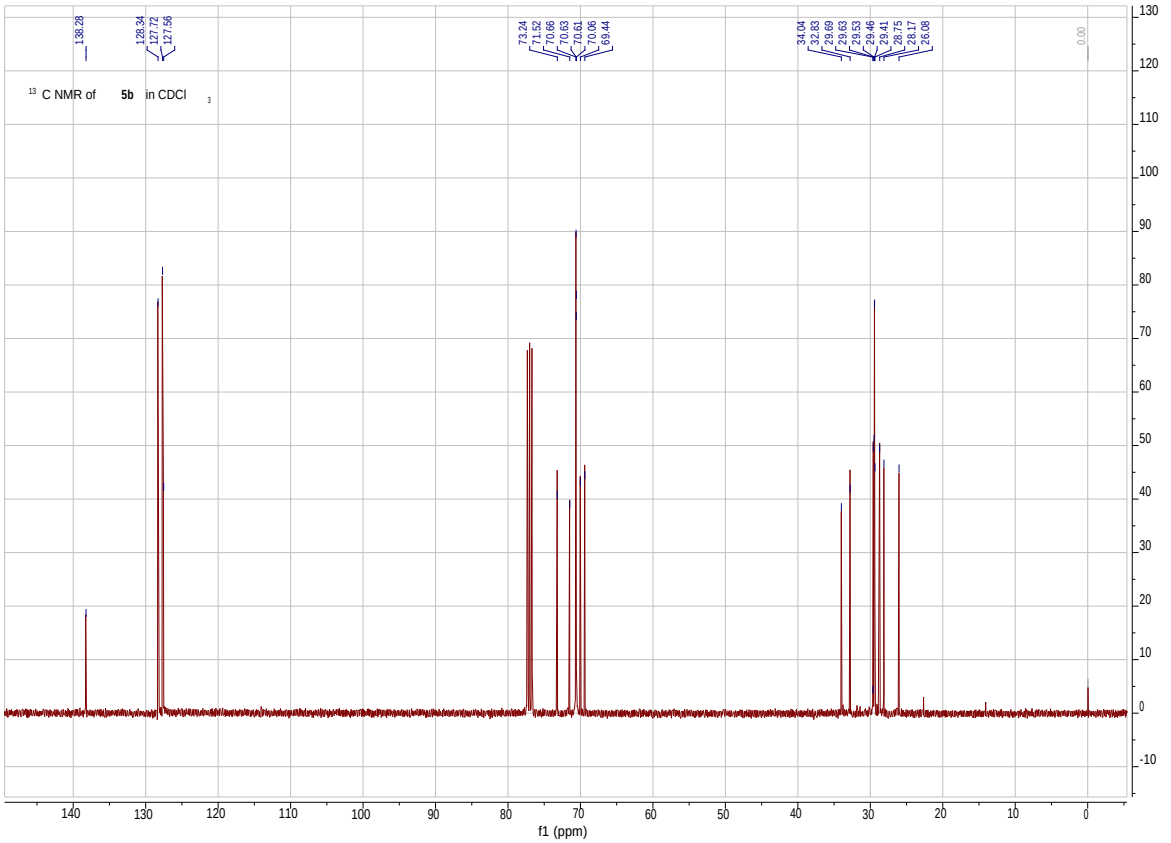
*General procedure for the synthesis of **5a-c**.*

A round bottom flask (250 mL, dried at 140 °C) was charged with dry THF (20 mL) and tetraethylene glycol benzyl ether **2** (3.125 g, 11 mmol). The solution was cooled to 0°C under an atmosphere of dry argon 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 neutralised with H_2O (20 mL) and extracted with diethyl ether (3 x 40 mL). The organic layers were combined, dried with magnesium sulphate, filtered and concentrated *in vacuo*. The material was purified by column chromatography (eluent heptane/ethyl acetate 80/20-50/50 v/v) yielding **5a** as a colourless oil (3.2 g, 55%).

*Tetraethylene glycol monobenzyl mono-11-bromoundecyl ether (**5b**).*

The synthesis of **5b** was performed following the general procedure yielding **5b** as a colourless oil (1.373 g, 67%). ^{1}H NMR (400 MHz, $CDCl_3$ δ): 7.38-7.47 (m, 5H, Ar), 4.56 (s, 2H, Ar-C$\underline{H}_2$-O), 3.61-3.69 (m, 14H, O-(C$\underline{H}_2$)$_2$-O), 3.59-3.55 (m, 2H, O-(C$\underline{H}_2$)$_2$-O), 3.43 (t, *J* = 7 Hz, 2H, $CH_2CH_2C\underline{H}_2O$), 3.4 (t, *J* = 7 Hz, 2H, $CH_2CH_2C\underline{H}_2$-Br), 1.88-1.81 (m, 2H, C$\underline{H}_2CH_2$-Br), 1.56 (p, *J* = 6.9 Hz, 2H, $CH_2C\underline{H}_2CH_2$-O), 1.45-1.37 (m, 2H, C$\underline{H}_2CH_2CH_2$-O), 1.33-1.23 (m, 12H, aliphatic). ^{13}C NMR (100 MHz, $CDCl_3$ δ): 138.27, 128.33, 127.71, 127.56, 73.23, 71.52, 70.7-70.55, 70.05, 69.43, 34.02, 32.81, 29.61, 29.51, 29.44, 29.44, 29.39, 28.73, 28.15, 26.06. MALDI-TOF-MS: (m/z) calc for $C_{26}H_{45}BrO_5$ 516.25, observed 539.22 $[M+Na]^+$. FT-IR (ATR) ν (cm^{-1}): 2924, 2854, 1496, 1454, 1351, 1294, 1249, 1208, 1101, 1041, 1028, 990, 946, 879, 852, 735, 698, 644, 607, 560, 463.

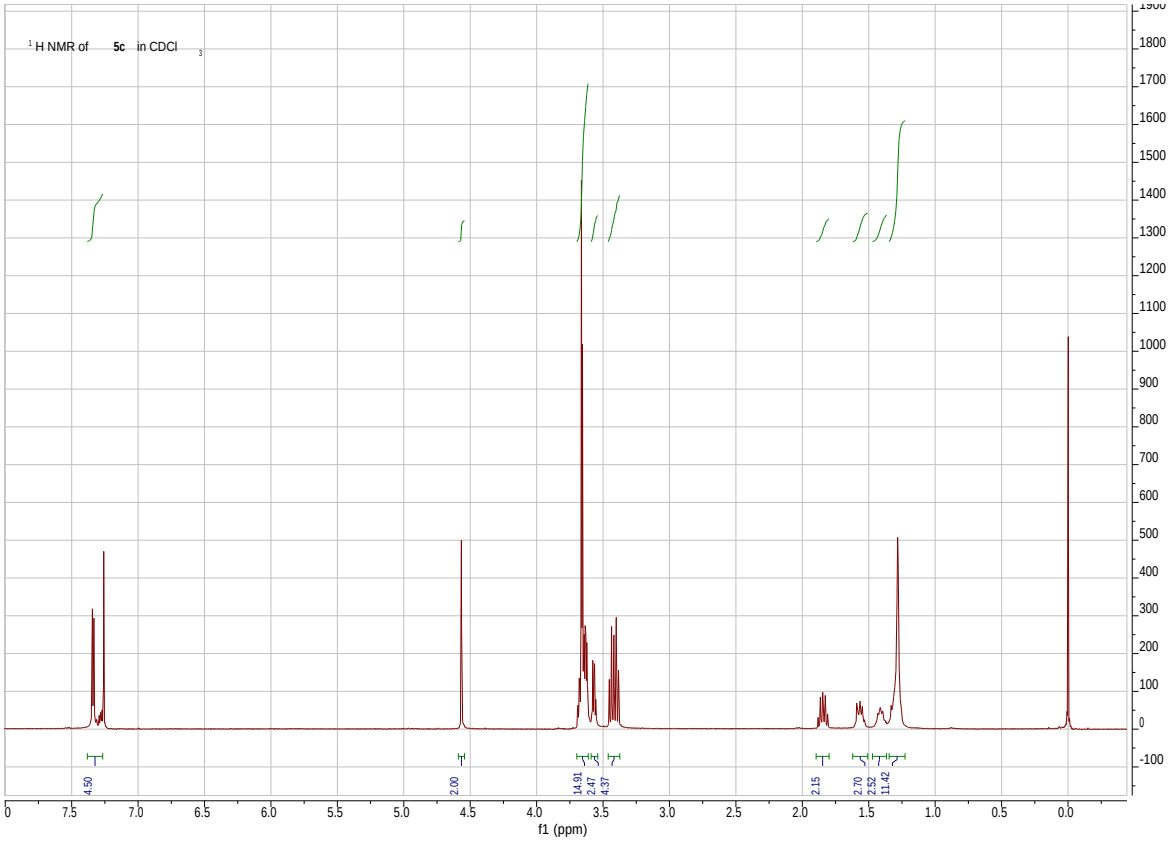


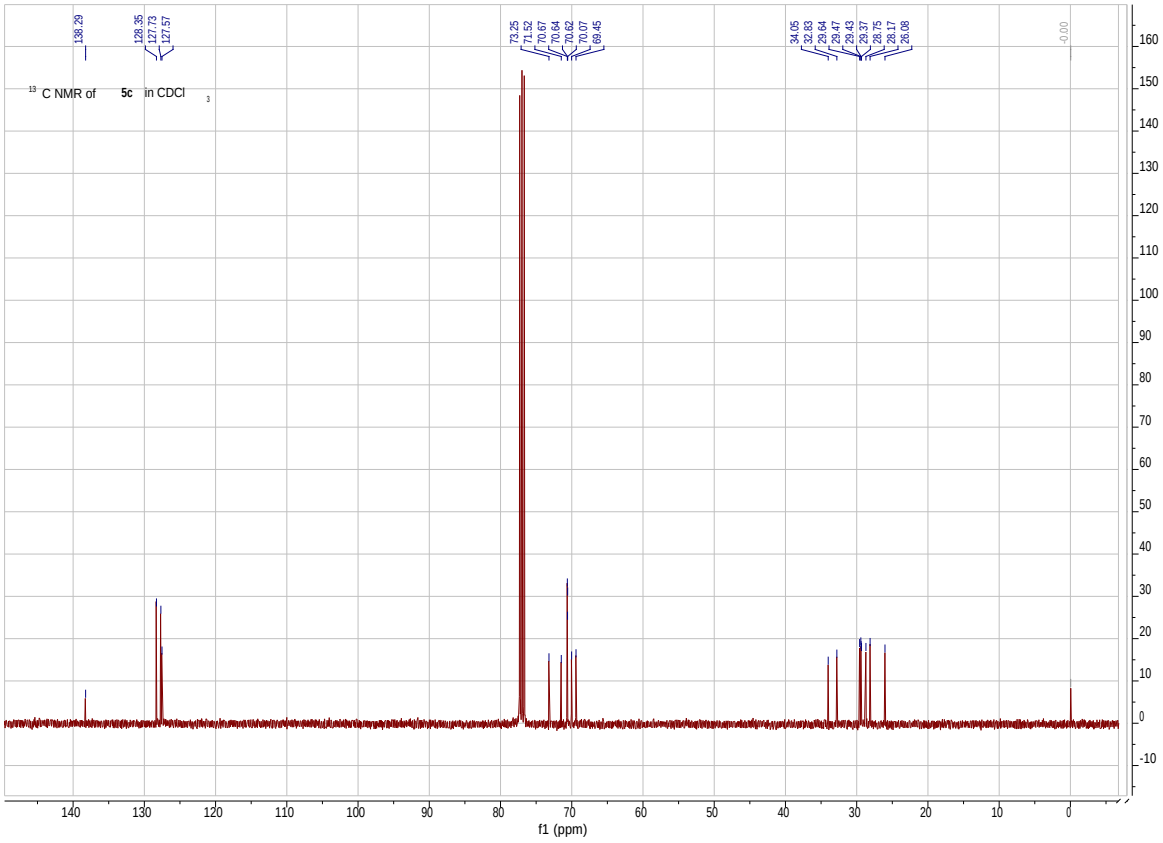


*Tetraethylene glycol monobenzyl mono-10-bromodecyl ether (**5c**).*

The synthesis of **5c** was performed following the general procedure yielding **5c** as a colourless oil (1.621 g, 40%). ^{1}H NMR (400 MHz, $CDCl_3$ δ): 7.35-7.47 (m, 5H, Ar), 4.56 (s,

2H, Ar-C$\underline{H_2}$-O), 3.61-3.69 (m, 14H, O-(C$\underline{H_2}$)$_2$-O), 3.59-3.55 (m, 2H, O-(C$\underline{H_2}$)$_2$-O), 3.43 (t, *J* = 6.8 Hz, 2H, CH$_2$CH$_2$C$\underline{H_2}$O), 3.4 (t, *J* = 6.8 Hz, 2H, CH$_2$CH$_2$C$\underline{H_2}$-Br), 1.88-1.81 (m, 2H, C$\underline{H_2}$CH$_2$-Br), 1.60-1.53 (m, 2H, CH$_2$C$\underline{H_2}$CH$_2$-O), 1.45-1.37 (m, 2H, C$\underline{H_2}$CH$_2$CH$_2$-O), 1.33-1.23 (m, 10H, aliphatic). ^{13}C NMR (100 MHz, $CDCl_3$ δ): 138.29, 128.35, 127.73, 127.57, 73.25, 71.52, 70.7-70.58, 70.07, 69.45, 34.05, 32.83, 29.64, 29.47, 29.43, 29.37, 28.75, 28.17, 26.08. MALDI-TOF-MS: (m/z) calc for $C_{25}H_{43}BrO_5$ 502.23 observed 525.24 $[M+Na]^+$. FT-IR (ATR) ν (cm^{-1}): 2925, 2855, 1496, 1454, 1351, 1296, 1248, 1207, 1100, 1041, 1028, 991, 945, 880, 852, 736, 698, 644, 610, 561, 464.





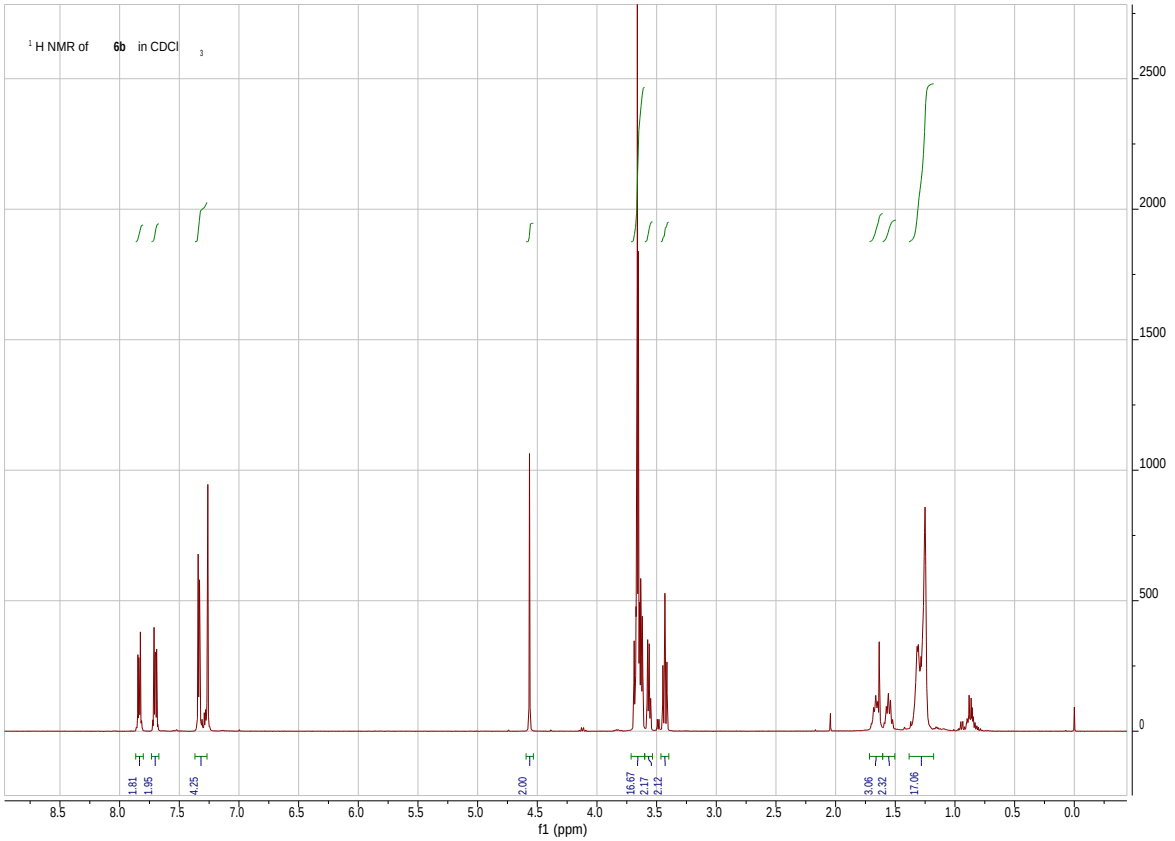
*General procedure for the synthesis of **6a-c**.*

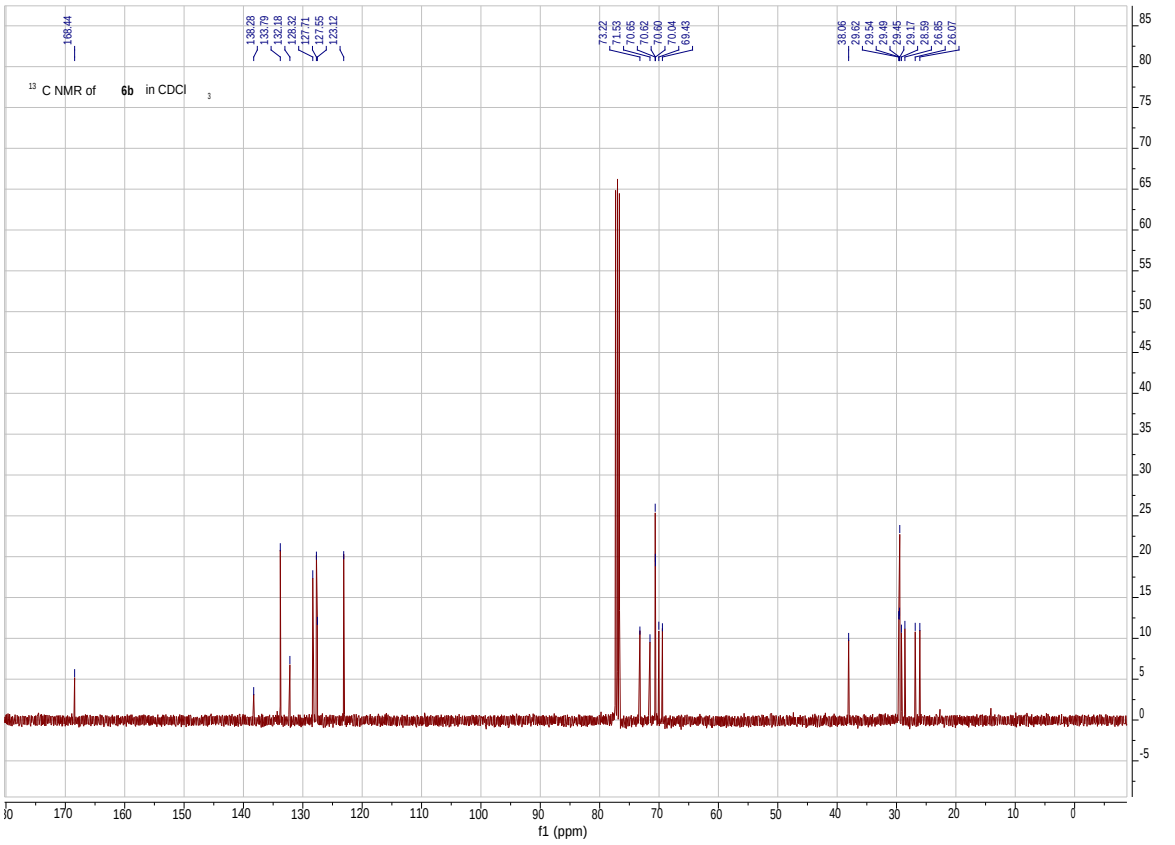
A round bottom flask (100 mL) was charged with tetraethylene glycol monobenzyl mono-12-bromododecyl ether **5a** (6.4 mmol, 3.4 g), DMF (10 mL) and potassium phthalimide (9.0 mmol, 1.7 g). The mixture was heated to 60 °C under an atmosphere of dry argon and stirred for 2 hours. Then ethyl acetate (50 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) yielding **6a** as a colourless oil (2.8 g, 73%).

*2-(1-Phenyl-2,5,8,11,14-pentaoxapentacosan-25-yl)isoindoline-1,3-dione (**6b**).*

The synthesis of **6b** was performed following the general procedure yielding **6b** as a colourless oil (1.491 gr, 68%). ^{1}H NMR (400 MHz, $CDCl_3$ δ): 7.84 (dd, *J* = 5.4, 3.0 Hz, 2H, phthalimide), 7.70 (dd, *J* = 5.5, 3.1 Hz, 2H, phthalimide), 7.35-7.27 (m, 5H, Ar), 4.56 (s, 2H, Ar-C$\underline{H}_2$-O), 3.69-3.60 (m, 16H, O-(C$\underline{H}_2$)$_2$-O, $CH_2C\underline{H}_2$N), 3.58-3.55 (m, 2H, O-(C$\underline{H}_2$)$_2$-O), 3.43 (t, *J* = 6.8 Hz, 2H,$CH_2CH_2C\underline{H}_2$-O), 1.66 (p, *J* = 7.5 2H, $CH_2C\underline{H}_2CH_2$O), 1.56 (p, *J* = 7.1 2H, C$\underline{H}_2CH_2CH_2$O), 1.43-1.24 (m, 14H, aliphatic). ^{13}C NMR (100 MHz, $CDCl_3$ δ): 168.44, 138.28, 133.79, 132.18, 128.32, 127.71, 127.55, 123.12, 73.22, 71.53, 70.67-70.58, 70.04, 69.43, 38.06, 29.62, 29.54, 29.49, 29.45, 29.45, 29.17, 28.59, 26.85, 26.07. MALDI-TOF-MS: (m/z) calc for $C_{34}H_{49}NO_7$ 583.35 observed 606.32 $[M+Na]^+$. FT-IR (ATR) ν (cm^{-1}):

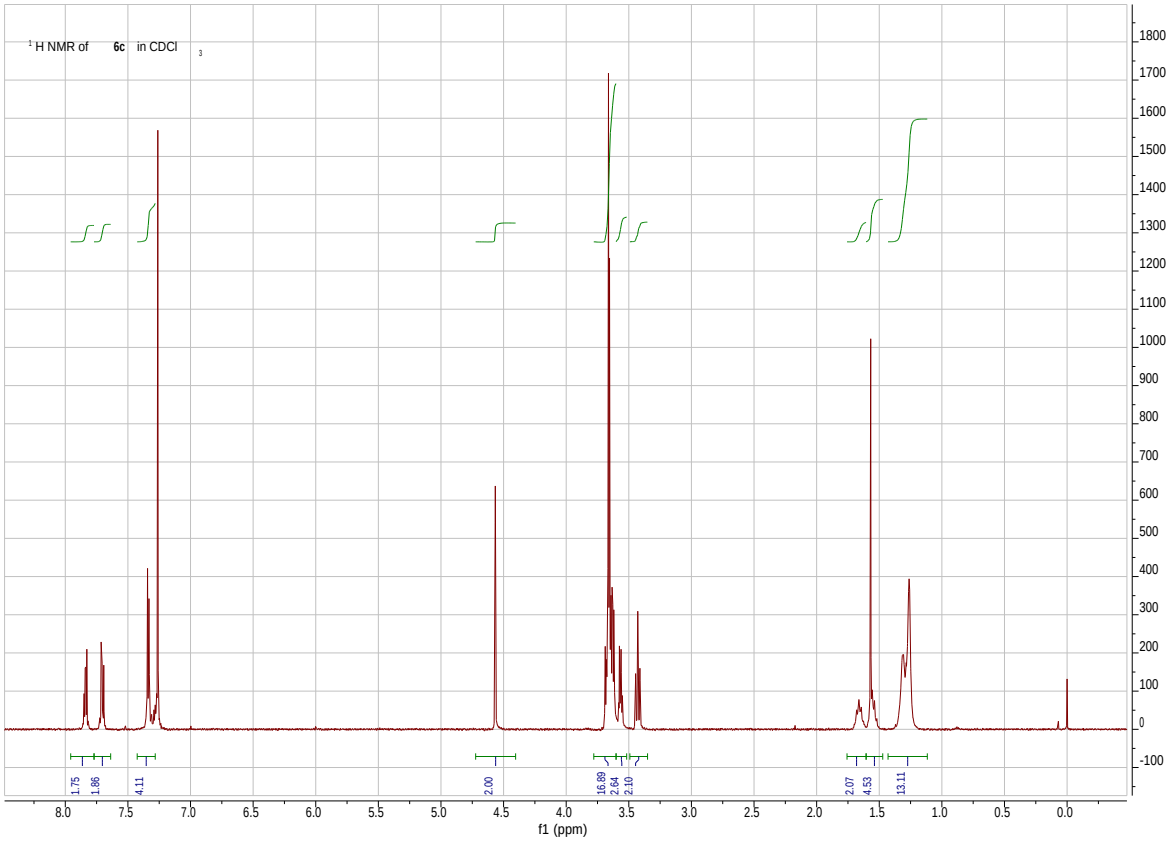
2925, 2855, 1772, 1710, 1615, 1467, 1454, 1437, 1395, 1363, 1300, 1248, 1100, 1043, 945, 879, 794, 720, 698, 620, 530.

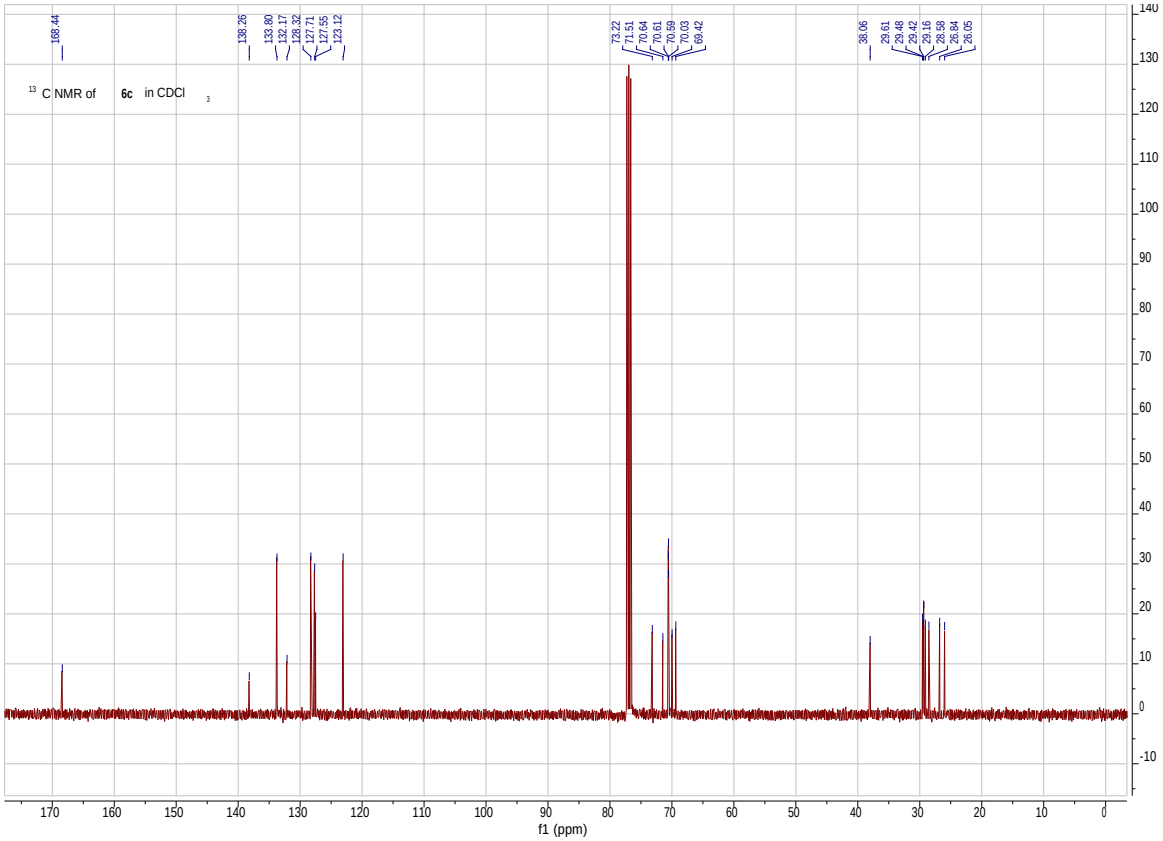




*2-(1-Phenyl-2,5,8,11,14-pentaoxatetracosan-24-yl)isoindoline-1,3-dione (**6c**).*

The synthesis of **6c** was performed following the general procedure yielding **6c** as a colourless oil (1.378 g, 77%). ^{1}H NMR (400 MHz, $CDCl_3$ δ): 7.84 (dd, *J* = 5.4, 3.1 Hz, 2H, phthalimide), 7.77 (dd, *J* = 5.4, 3.0 Hz, 2H, phthalimide), 7.35-7.27 (m, 5H, Ar), 4.58-4.54 (m, 2H, Ar-C$\underline{H}_2$-O), 3.69-3.60 (m, 16H, O-(C$\underline{H}_2$)$_2$-O, $CH_2C\underline{H}_2N$), 3.58-3.55 (m, 2H, O-(C$\underline{H}_2$)$_2$-O), 3.43 (t, *J* = 6.8 Hz, 2H,$CH_2CH_2C\underline{H}_2$-O), 1.70-1.63 (m, 2H, $CH_2C\underline{H}_2CH_2$-O), 1.58-1.53 (m, 2H, C$\underline{H}_2CH_2CH_2$-O), 1.43-1.24 (m, 12H, aliphatic). ^{13}C NMR (100 MHz, $CDCl_3$ δ): 168.44, 138.27, 133.80, 132.17, 128.32, 127.72, 127.55, 123.12, 73.22, 71.52, 70.67-70.57, 70.03, 69.43, 38.06, 29.61, 29.48, 29.42, 29.41, 29.16, 28.58, 26.84, 26.05. MALDI-TOF-MS: (m/z) calc for $C_{33}H_{47}NO_7$ 569.34 observed 592.34 $[M+Na]^+$. FT-IR (ATR) ν (cm^{-1}): 2926, 2856, 2246, 1772, 1710, 1615, 1496, 1467, 1454, 1437, 1395, 1362, 1300, 1250, 1205, 1188, 1099, 1043, 992, 947, 913, 876, 795, 720, 698, 647, 620, 604, 530, 464.



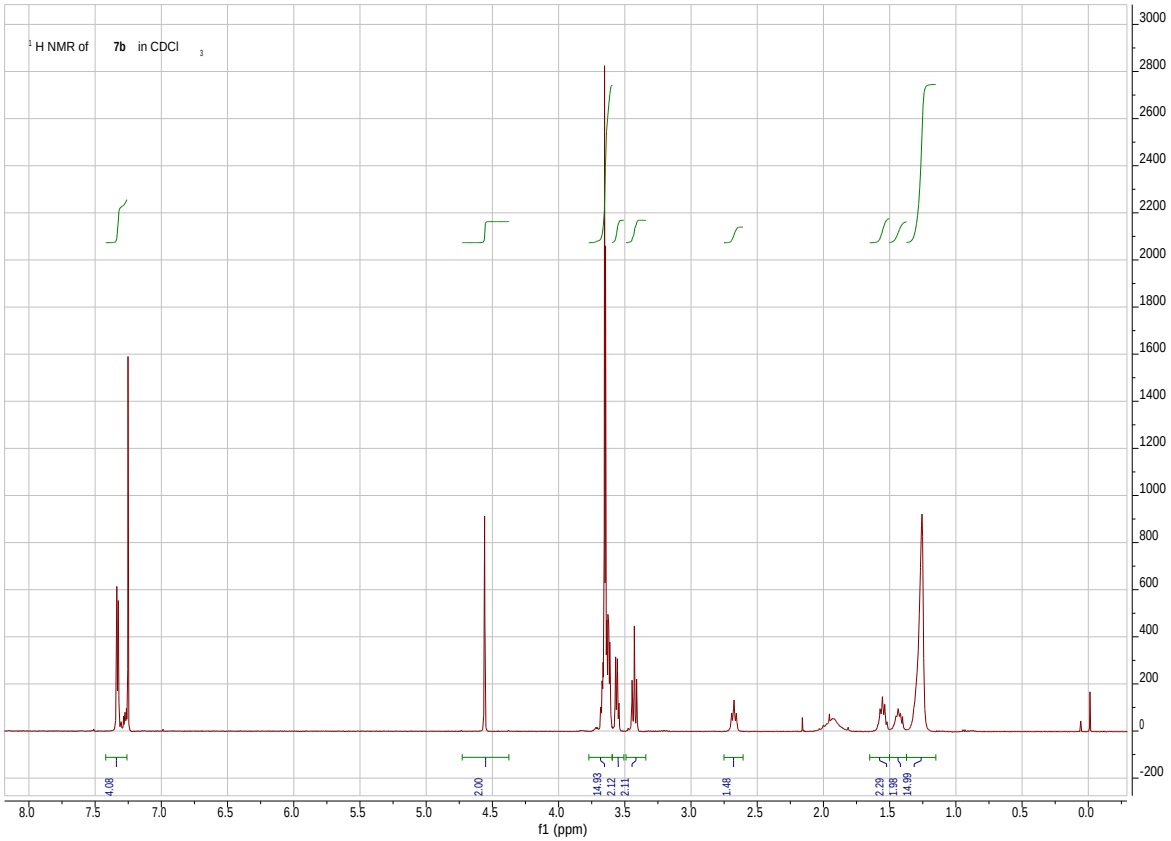


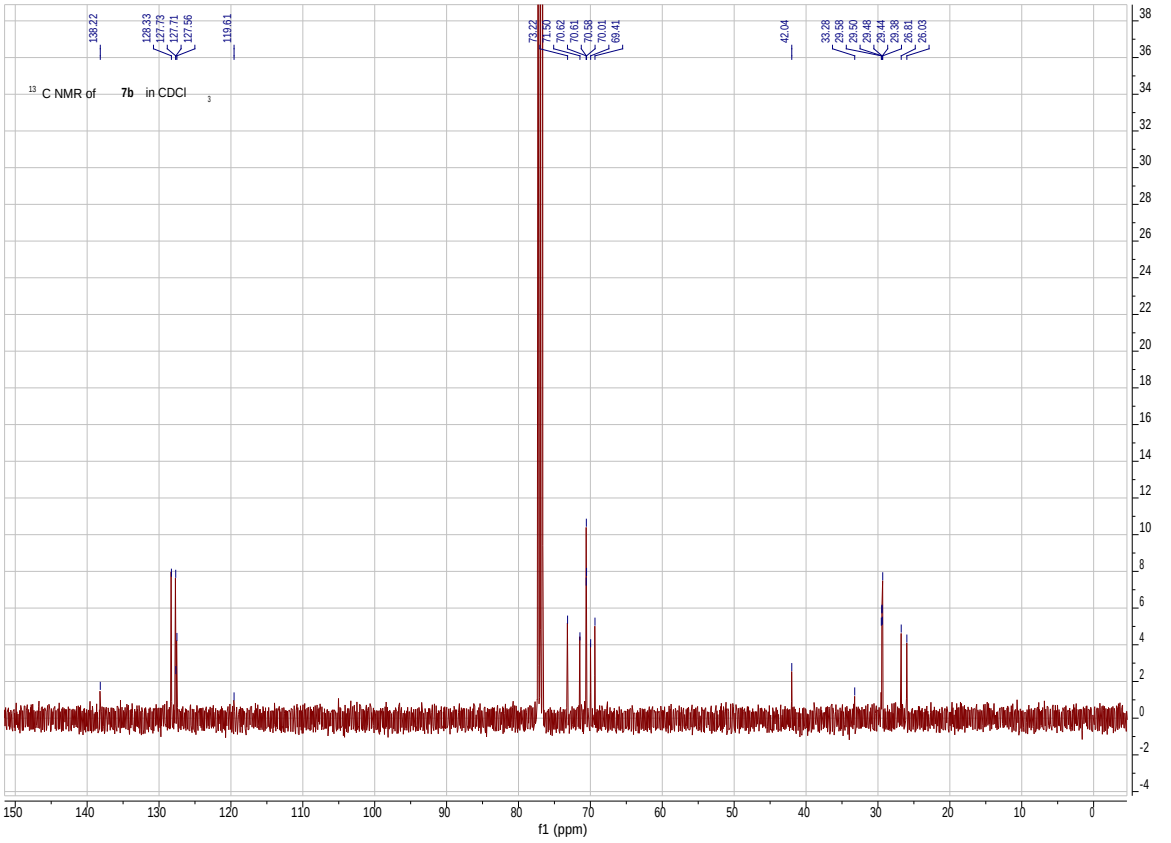
*General procedure for the synthesis of **7a-c**.*

To a stirred solution of 2-(1-phenyl-2,5,8,11,14-pentaoxahexacosan-26-yl)isoindoline-1,3-dione **6a** (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/isopropyl amine 90/10 v/v) yielding **7a** as a slightly yellow oil (0.182 g, 89%).

*1-Phenyl-2,5,8,11,14-pentaoxapentacosan-25-amine (**7b**).*

The synthesis of **7b** was performed following the general procedure yielding **7b** as a slightly yellow oil (1.004 gr, 86%). ^{1}H NMR (400 MHz, $CDCl_3$ δ): 7.43-7.25 (m, 5H, Ar), 4.56 (s, 2H, Ar-C$\underline{H}_2$-O), 3.72-3.63 (m, 14H, O-(C$\underline{H}_2$)$_2$-O), 3.56-3.53 (m, 2H, O-(C$\underline{H}_2$)$_2$-O), 3.44 (t, 2H,$CH_2CH_2C\underline{H}_2$-O), 2.67 (t, 2H, $CH_2C\underline{H}_2$-NH_2) 1.63-1.52 (m, 2H, $CH_2C\underline{H}_2CH_2$-O), 1.50-1.38 (m, 2H, C$\underline{H}_2CH_2CH_2$-O), 1.39-1.24 (m, 16H, aliphatic). ^{13}C NMR (100 MHz, $CDCl_3$ δ): 138.27, 128.35, 127.73, 127.57, 73.24, 71.54, 70.65-70.55, 70.05, 69.44, 42.19, 33.67, 29.70, 29.64, 29.60, 29.57, 29.53, 29.47, 26.88, 26.09. MALDI-TOF-MS: (m/z) calc for $C_{26}H_{47}NO_5$ 453.35 observed 454.35 $[M+H]^+$. FT-IR (ATR) ν (cm^{-1}): 2923, 2853, 1586, 1496, 1455, 1351, 1299, 1249, 1206, 1100, 1041, 1028, 990, 944, 878, 849, 736, 698, 609, 463.

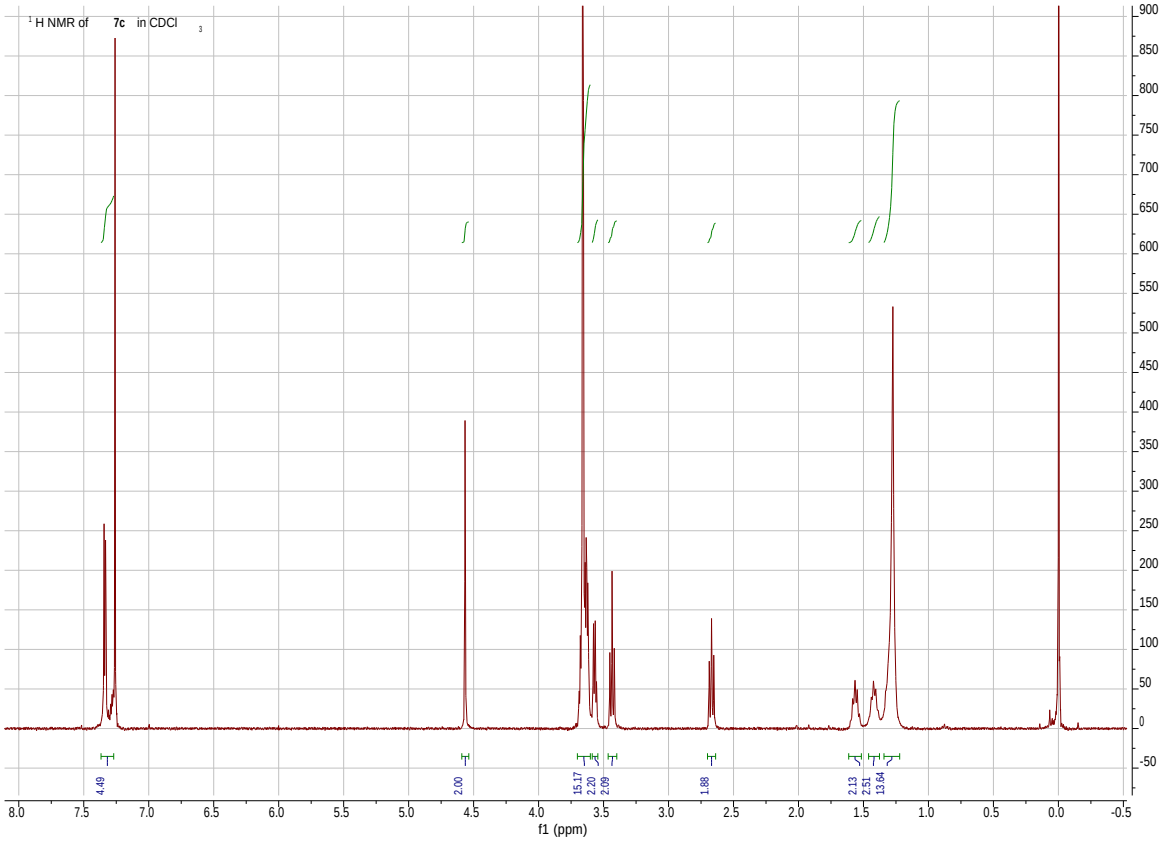


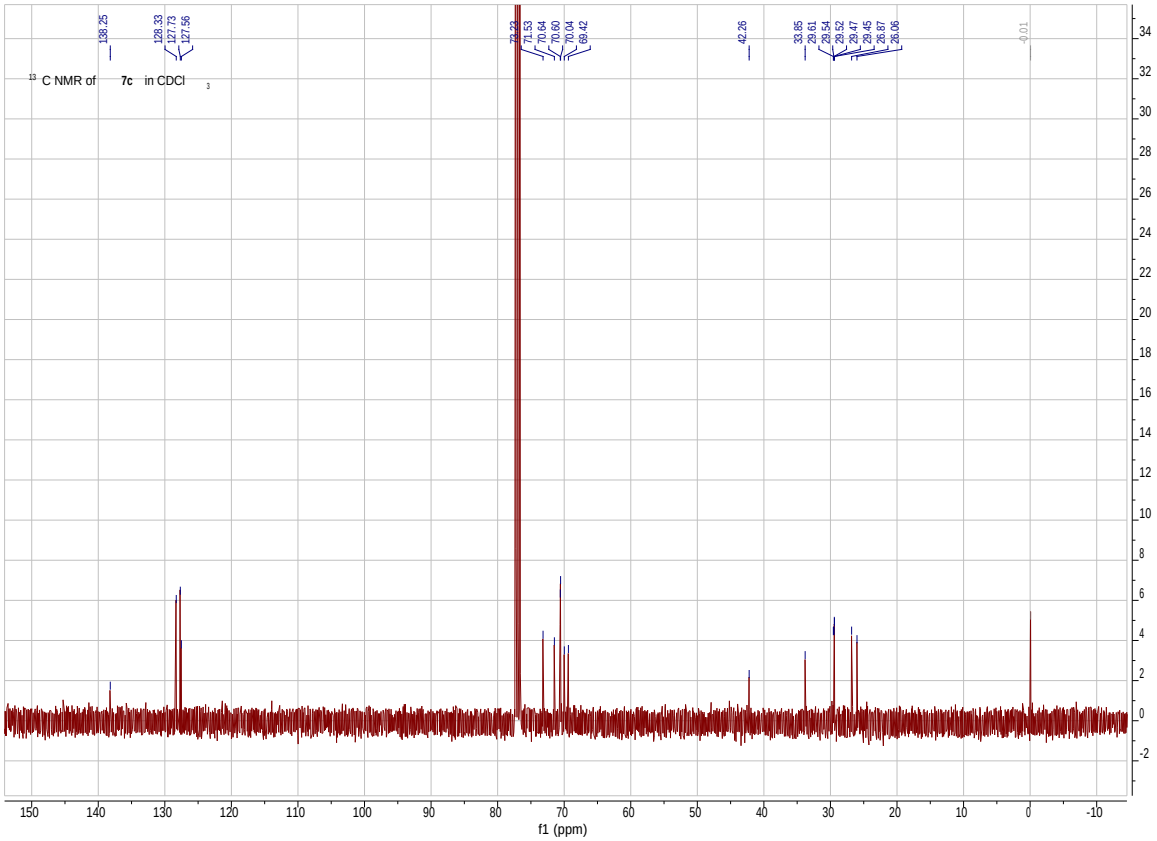


*1-Phenyl-2,5,8,11,14-pentaoxatetracosan-24-amine (**7c**).*

The synthesis of **7c** was performed following the general procedure yielding **7c** as a slightly yellow oil (0.749 gr, 70%). ^{1}H NMR (400 MHz, $CDCl_3$ δ): 7.40-7.28 (m, 5H, Ar), 4.57 (s,

2H, Ar-C$\underline{H_2}$-O), 3.71-3.60 (m, 14H, O-(C$\underline{H_2}$)$_2$-O), 3.57-3.52 (m, 2H, O-(C$\underline{H_2}$)$_2$-O), 3.44 (t, 2H,$CH_2CH_2C\underline{H_2}$-O), 2.67 (t, 2H, $CH_2C\underline{H_2}$-NH_2) 1.63-1.52 (m, 2H, $CH_2C\underline{H_2}CH_2$-O), 1.49-1.38 (m, 2H, C$\underline{H_2}CH_2CH_2$-O), 1.40-1.25 (m, 16H, aliphatic). ^{13}C NMR (100 MHz, $CDCl_3$ δ): 138.26, 128.35, 127.74, 127.58, 73.25, 71.54, 70.68-70.57, 70.05, 69.44, 42.28, 33.87, 29.63, 29.56, 29.54, 29.49, 29.47, 26.89, 26.08. MALDI-TOF-MS: (m/z) calc for $C_{25}H_{45}NO_5$ 439.33 g/mol observed 440.35 $[M+H]^+$. FT-IR (ATR) ν (cm^{-1}): 2923, 2854, 1574, 1454, 1383, 1349, 1303, 1249, 1207, 1100, 1041, 1028, 992, 945, 879, 850, 819, 736, 698, 613, 464.





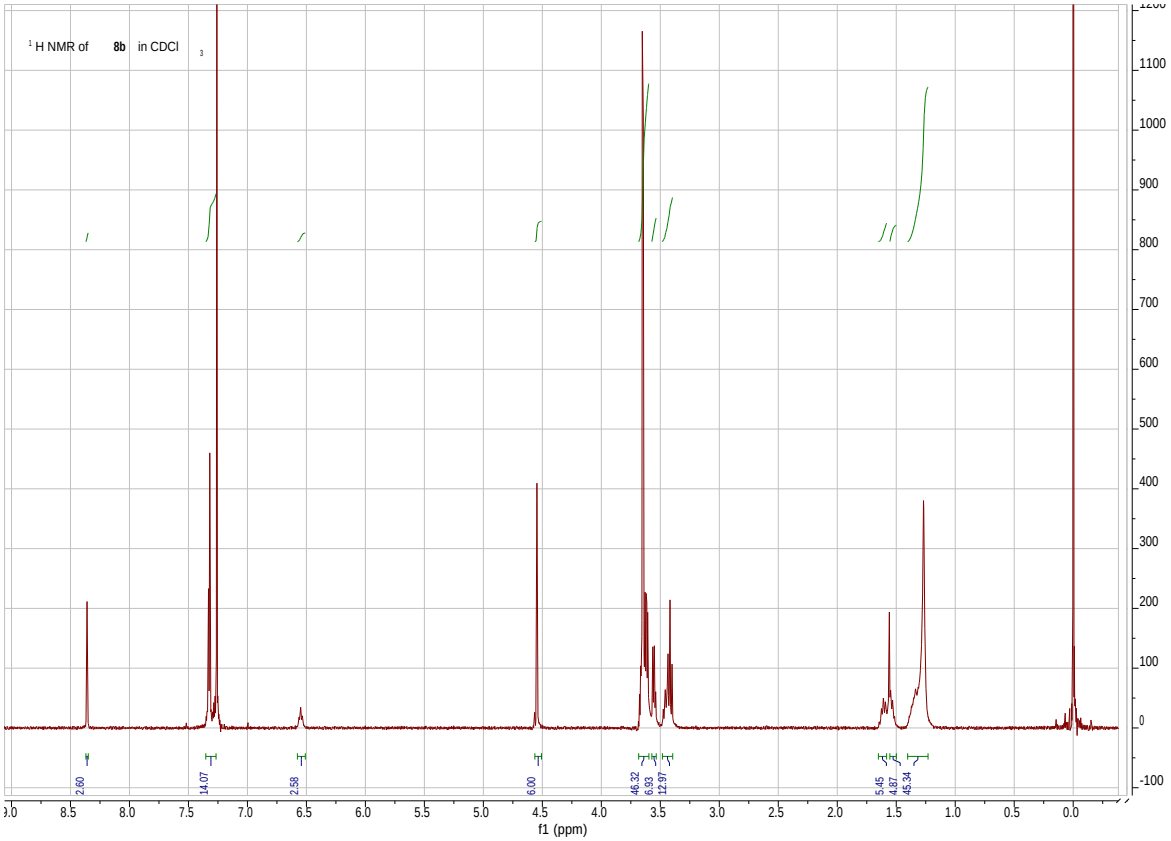
*General procedure for the synthesis of **8a-c**.*

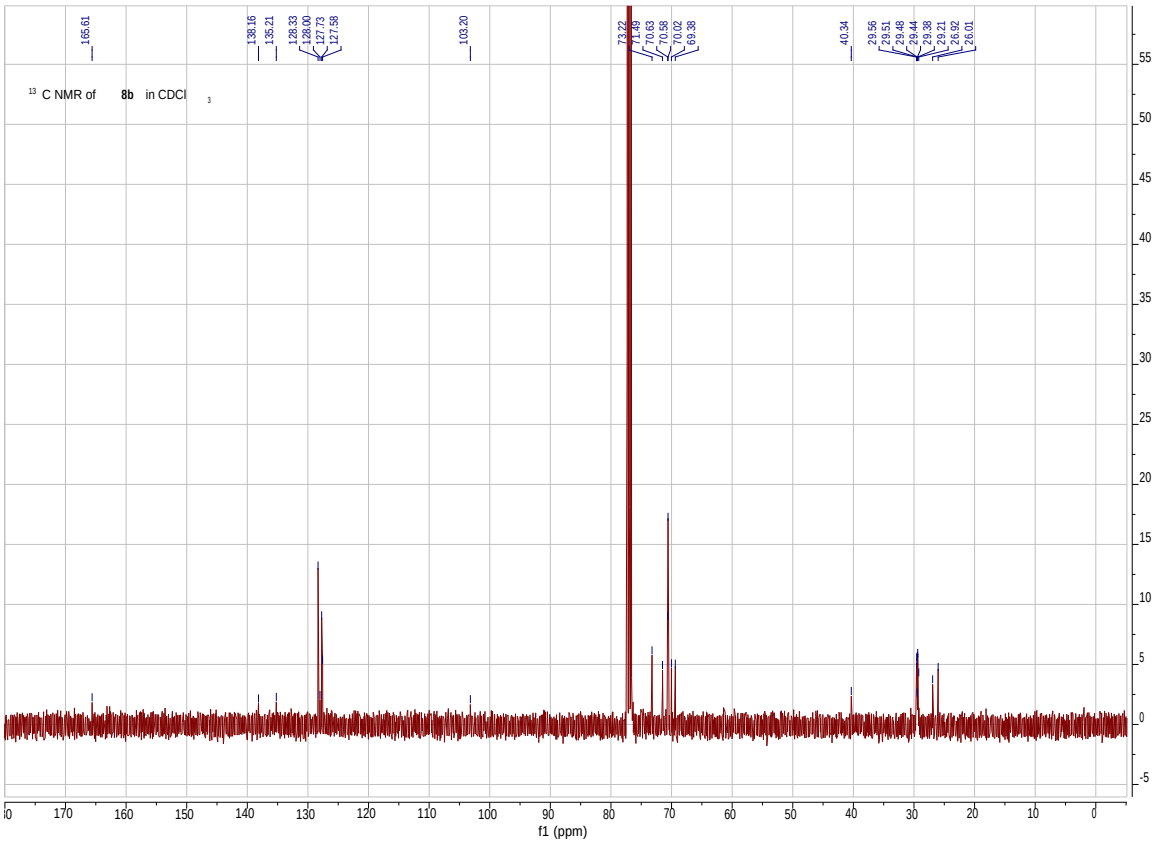
A two neck round bottom flask (10 mL, dried at 140 °C) was charged with 1-phenyl-2,5,8,11,14-pentaoxahexacosan-26-amine **7a** (0.39 mmol,0.182 g), dry chloroform (1 mL) and triethyl amine (0.99 mmol, 0.100 g) under an atmosphere of dry argon. The mixture was stirred at 0 °C and a solution of 1,3,5-benzenetricarbonyl 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) yielding **8a** as a colourless oil that solidified upon standing (0.156 g, 83.4%).

*N^1,N^3,N^5-Tris(1-phenyl-2,5,8,11,14-pentaoxapentacosan-25-yl)benzene-1,3,5-tricarboxamide (**8b**).*

The synthesis of **8b** was performed following the same procedure as described for **8a** yielding **8b** as a colourless oil that solidified upon standing (0.533 gr, 61%). ^{1}H NMR (400 MHz, $CDCl_3$ δ): 8.37 (s, 3H, Ar, benzenetricarboxamide), 7.34-7.29 (s, 15H, Ar) 6.61-6.58 (t, 3H, C=ON$\underline{H}$$CH_2$), 4.57 (s, 6H, Ar-C$\underline{H}_2$-O), 3.68-3.61 (m, 42H, O-(C$\underline{H}_2$)$_2$-O), 3.58- 3.54 (m, 6H, O-(C$\underline{H}_2$)$_2$-O) , 3.48-3.40 (m, 12H, CH_2C$\underline{H}_2$NHC=O, CH_2CH_2C$\underline{H}_2$O) 1.65-1.48 (M, 12h, CH_2C$\underline{H}_2CH_2$O, C$\underline{H}_2CH_2CH_2$O), 1.40-1.25 (m, 42H, aliphatic). ^{13}C NMR (100 MHz, $CDCl_3$ δ): 165.61, 138.16, 135.21, 128.33, 128.00, 127.73, 127.58, 73.22, 71.49, 70.65-70.56, 70.02, 69.38, 40.34, 29.56, 29.51, 29.48, 29.44, 29.38, 29.37, 29.21, 26.92, 26.01. MALDI-TOF-MS: (m/z) calc for $C_{87}H_{141}N_3O_{18}$ 1516.02 observed 1539.01 $[M+Na]^+$. FT-IR (ATR) ν (cm^{-1}):

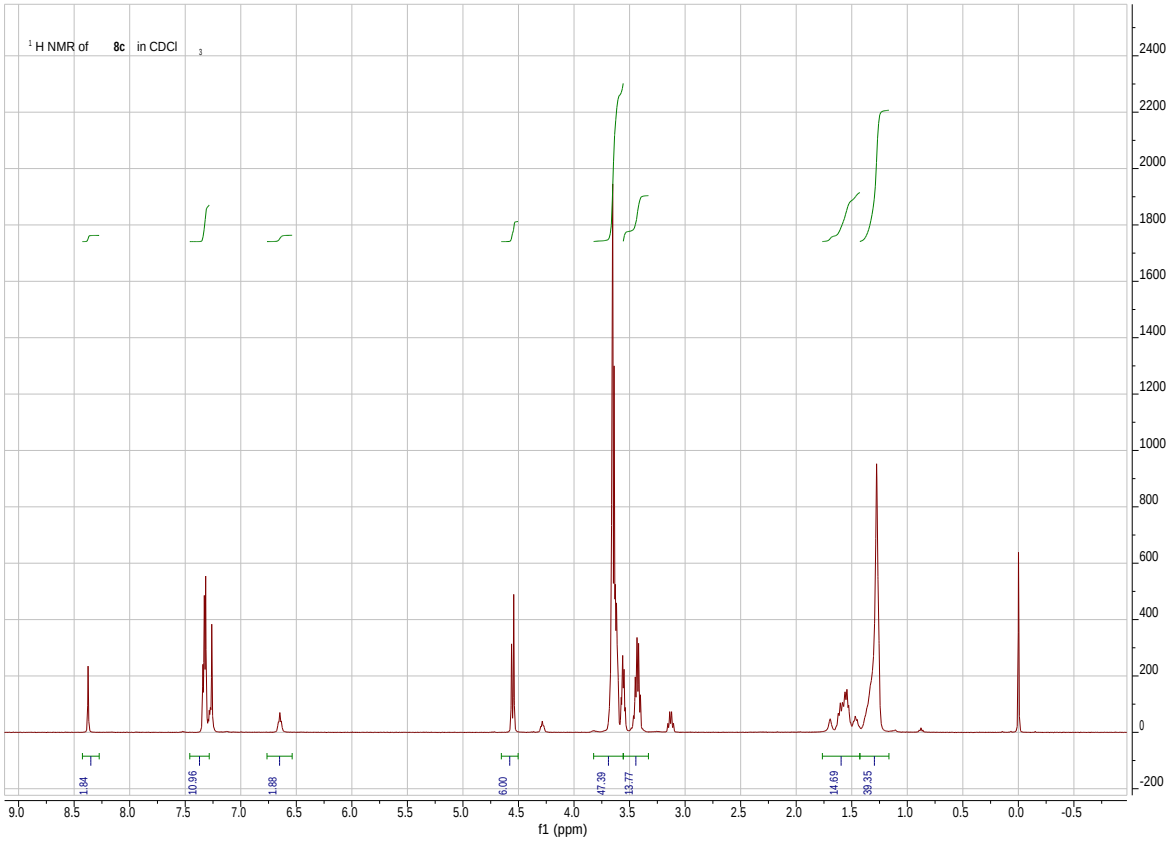
3334, 3065, 3031, 2924, 2854, 2111, 1644, 1536, 1496, 1454, 1350, 12887, 1206, 1099, 1041, 1028, 946, 880, 850, 736, 698, 607, 555, 464.

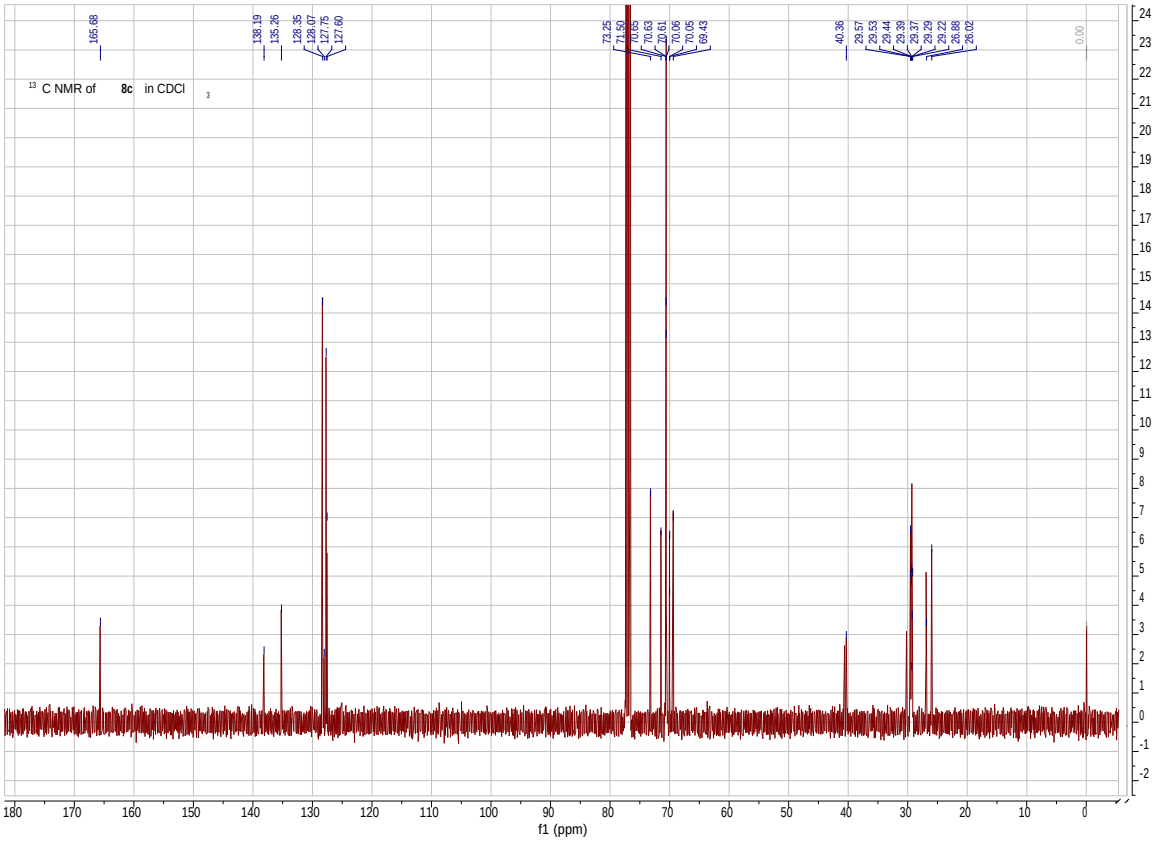




*N^1,N^3,N^5-Tris(1-phenyl-2,5,8,11,14-pentaoxatetracosan-24-yl)benzene-1,3,5-tricarboxamide (**8c**).*

The synthesis of **8c** was performed following the same procedure as described for **8a** yielding **8c** as a colourless oil (0.351 gr, 44%). ^{1}H NMR (400 MHz, $CDCl_3$ δ): 8.37 (s, 3H, Ar, benzenetricarboxamide), 7.34-7,27 (s, 15H, Ar) 6.66-6,63 (t, 3H, C=ON<u>H</u>CH_2), 4.57 (d, 6H, Ar-C<u>H_2</u>-O), 3.68-3.61 (m, 36H, O-(C<u>H_2</u>)$_2$-O), 3.58- 3.54 (m, 6H, O-(C<u>H_2</u>)$_2$-O) , 3.48-3.40 (m, 12H, CH_2C<u>H_2</u>NHC=O, CH_2CH_2C<u>H_2</u>O) 1.65-1.45 (M, 12h, CH_2C<u>H_2</u>CH_2O, C<u>H_2</u>CH_2CH_2O), 1.39-1.26 (m, 44H, aliphatic). ^{13}C NMR (100 MHz, $CDCl_3$ δ): 165.68, 138.19, 135.26, 128.35, 128.07, 127.75, 127.60, 73.25, 71.50, 70.69-70.58, 70.06, 69.43, 40.36, 29.57, 29.53, 29.44, 29.39, 29.37, 29.22, 26.88, 26.02. FT-IR (ATR) ν (cm^{-1}): 3336, 3063, 3031, 2922, 2853, 1662, 1536, 1496, 1453, 1348, 1284, 1247, 1102, 1039, 1028, 959, 883, 851, 737, 697, 613, 550, 466.



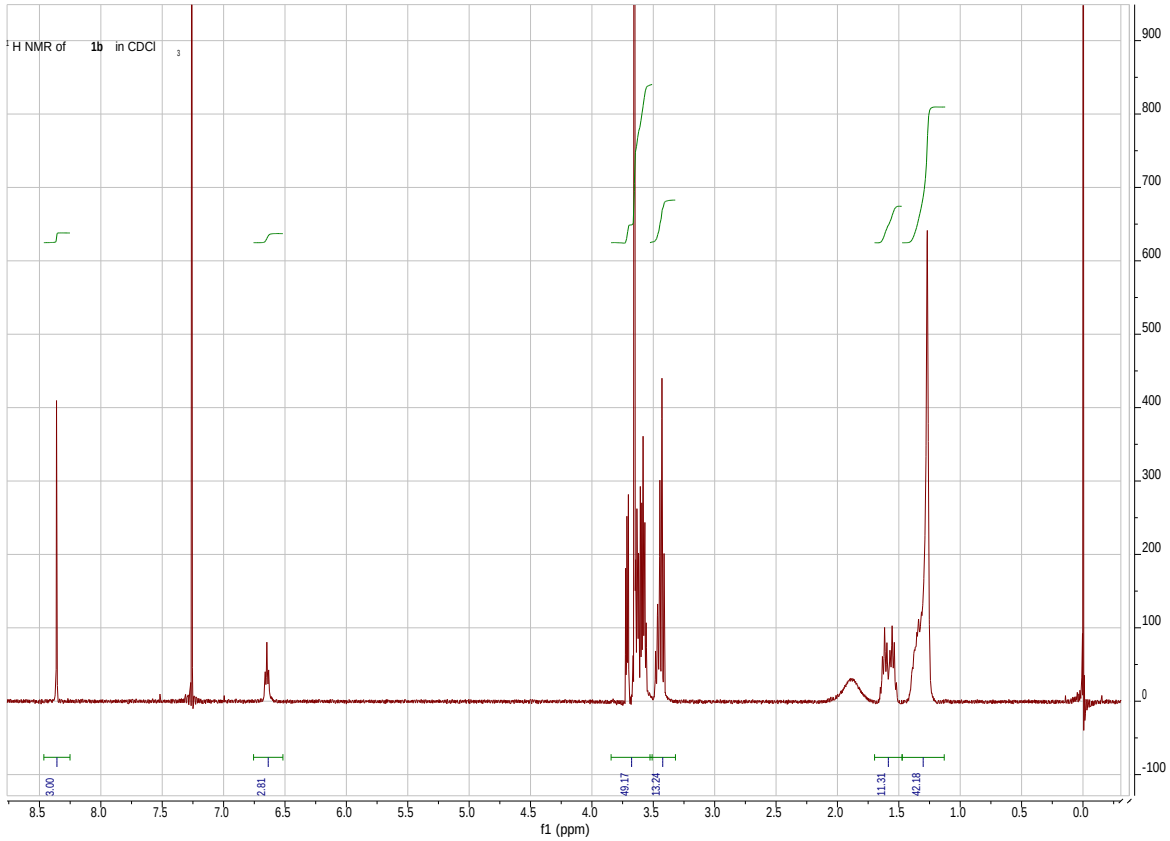


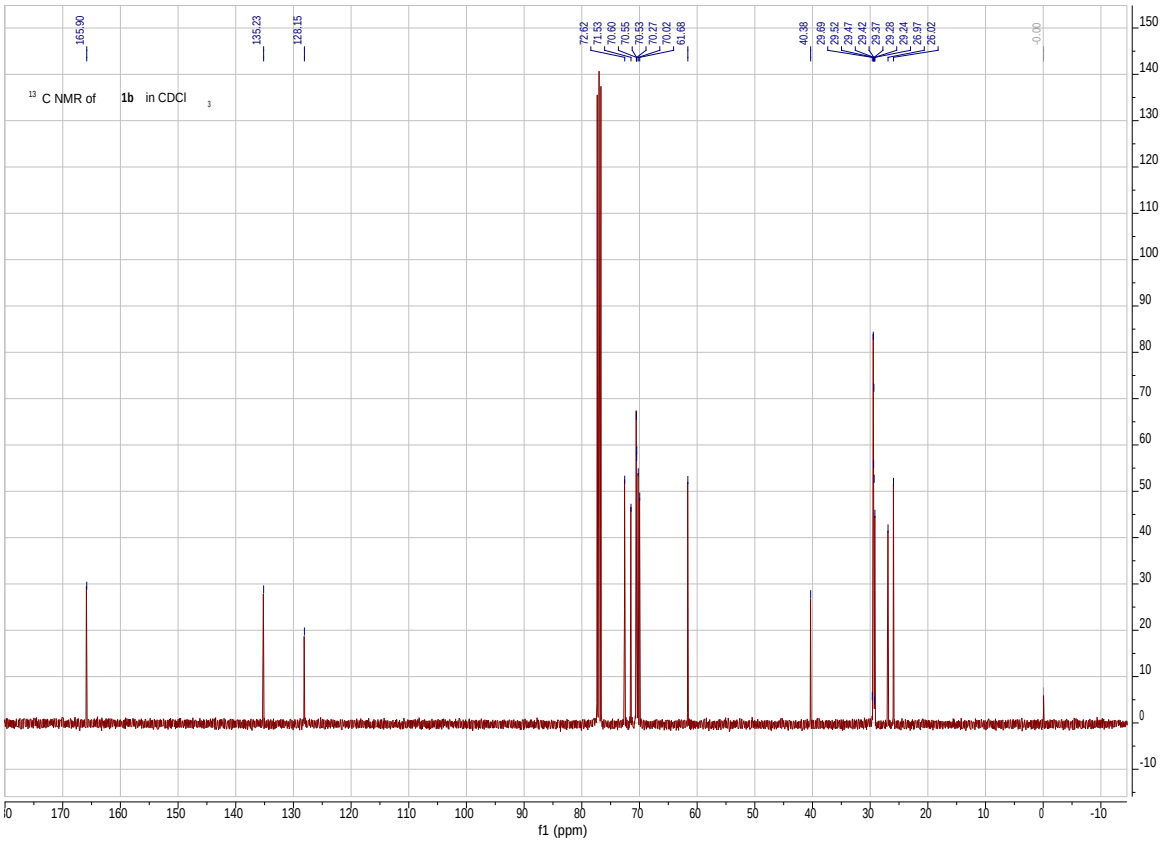
*General procedure for the synthesis of **1a-c**.*

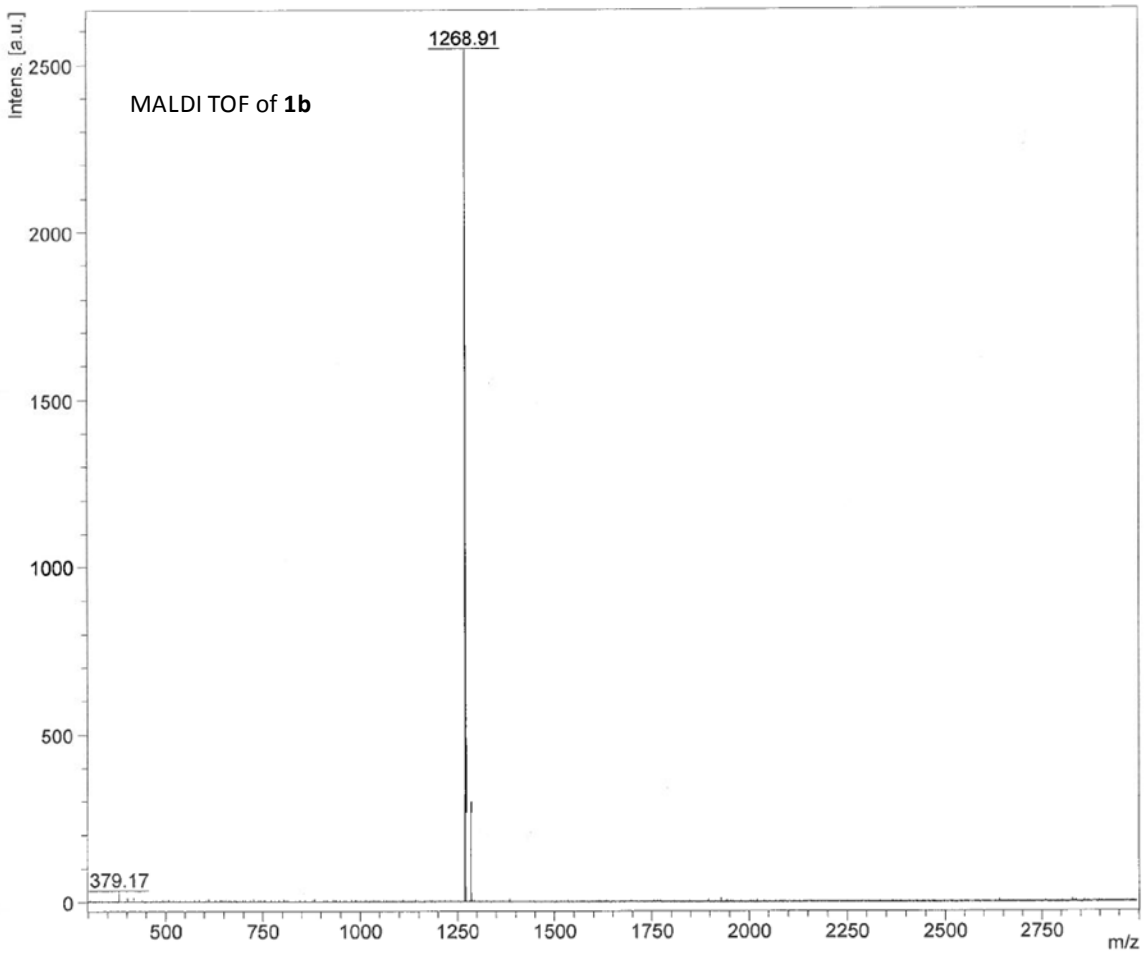
A round bottom flask (10 mL) was charged with N^1,N^3,N^5-tris(1-phenyl-2,5,8,11,14-pentaoxahexacosan-26-yl)benzene-1,3,5-tricarboxamide **8a** (0.10 mmol, 0.15 g), methanol (3 mL) and N_2(g) was led through the stirred solution for 10 minutes. Subsequently, Pd/C (catalytic amount) was added and a balloon 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 **1a** as a colourless oil which solidified upon standing (0.12 g, 93%).

*N^1,N^3,N^5-Tris(1-hydroxy-3,6,9,12-tetraoxatricosan-23-yl)benzene-1,3,5-tricarboxamide (**1b**).*

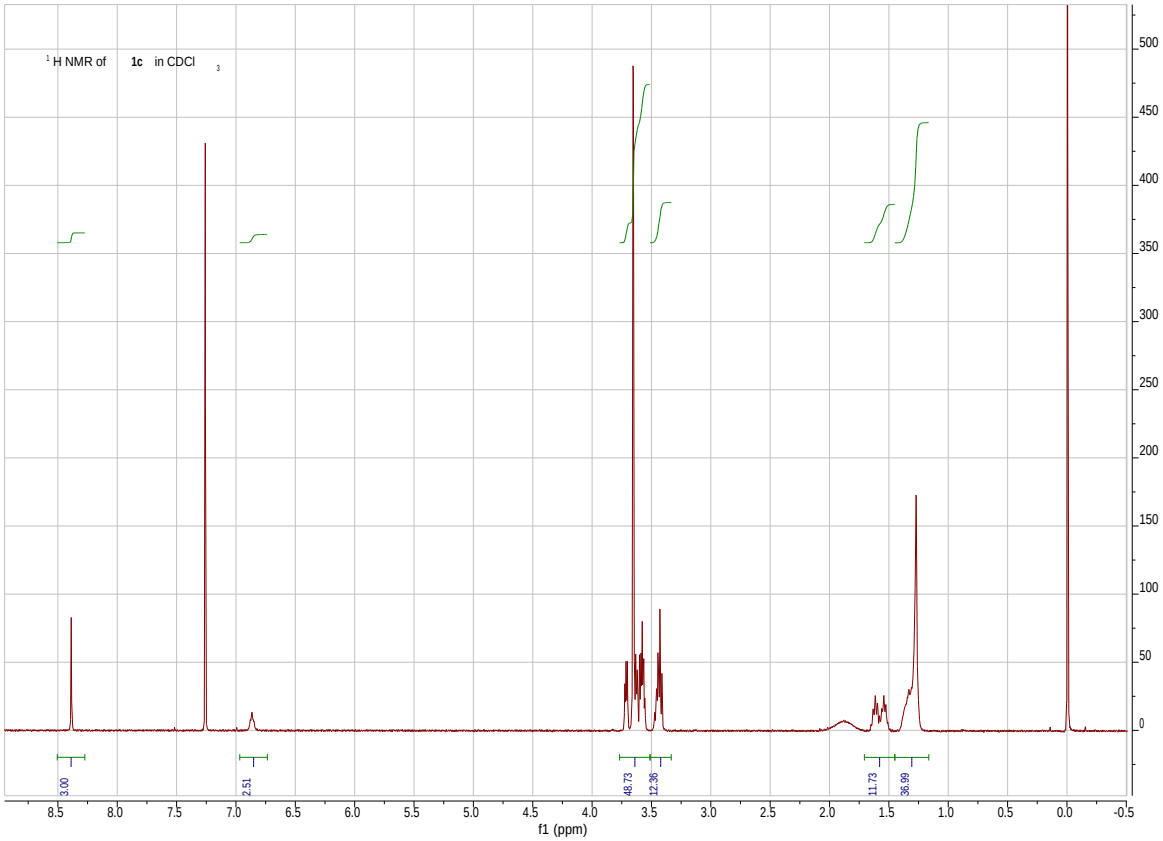
The synthesis of **1b** was performed following the general procedure yielding **1b** as a colourless oil that solidified upon standing (0.341 g, 80%). ^{1}H NMR (400 MHz, $CDCl_3$ δ): 8.38 (s, 3H, Ar), 6.85-6.82 (t, 3H, C=ONHCH$_2$), 3.74-3.56 (m, 48H, O-(CH$_2$)$_2$-O), 3.50-3.41 (m, 12, CH$_2$CH$_2$NHC=O, CH$_2$CH$_2$CH$_2$O), 1.65-1.44 (m, 12H, CH$_2$CH$_2$CH$_2$O, CH$_2$CH$_2$CH$_2$O), 1.42-1.23 (m, 46H, aliphatic). ^{13}C NMR (100 MHz, $CDCl_3$ δ): 165.90, 135.23, 128.15, 72.62, 71.53, 70.60, 70.59, 70.55, 70.53, 70.27, 70.02, 61.68, 40.38, 29.52, 29.51, 29.47, 29.43, 29.42, 29.37, 29.24, 26.97, 26.02. MALDI-TOF-MS: (m/z) calc for $C_{66}H_{123}N_3O_{18}$ 1245.88 observed 1268.90 $[M+Na]^+$. FT-IR (ATR) ν (cm^{-1}): 3348, 3308, 3258, 2916, 2851, 1659, 1647, 1634, 1549, 1466, 1352, 1292, 1103, 942, 886, 835, 704, 576.

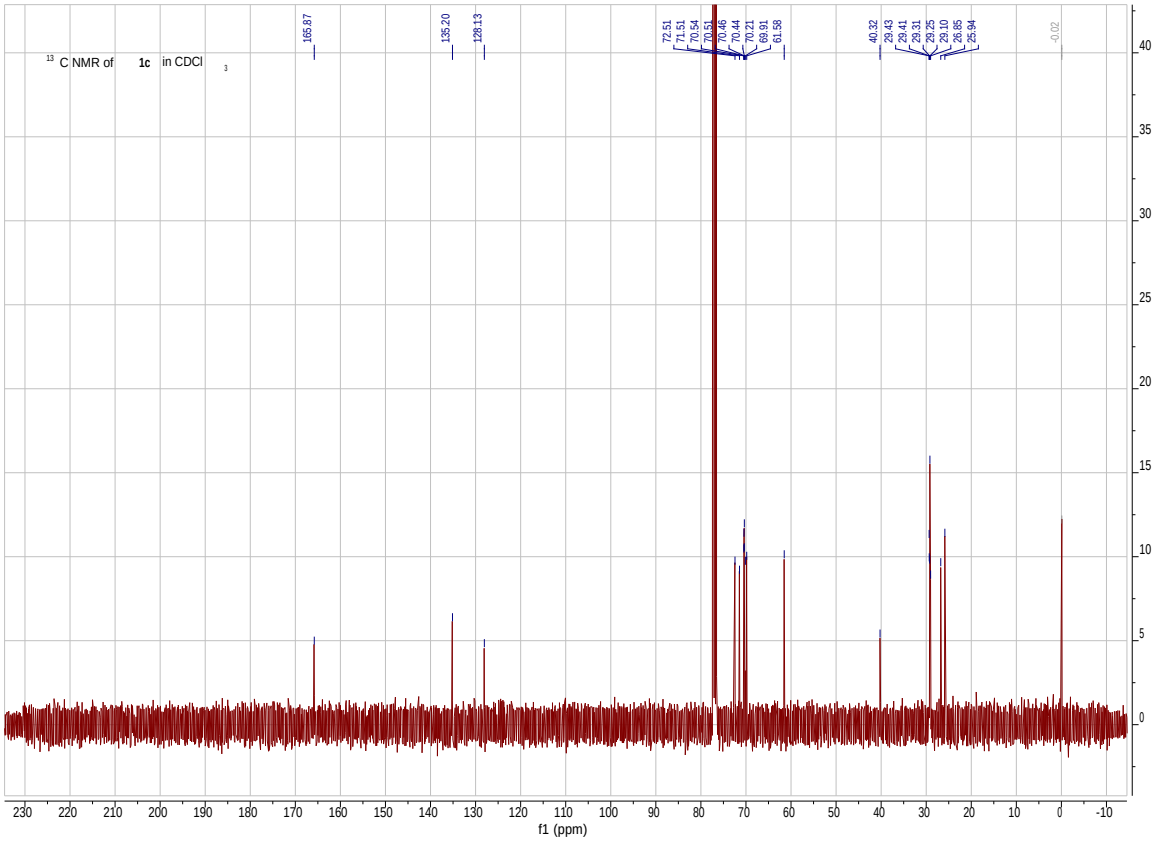

H NMR of 1b in CDCl3
3.00
2.81
49.17
13.24
11.31
42.18
f1 (ppm)

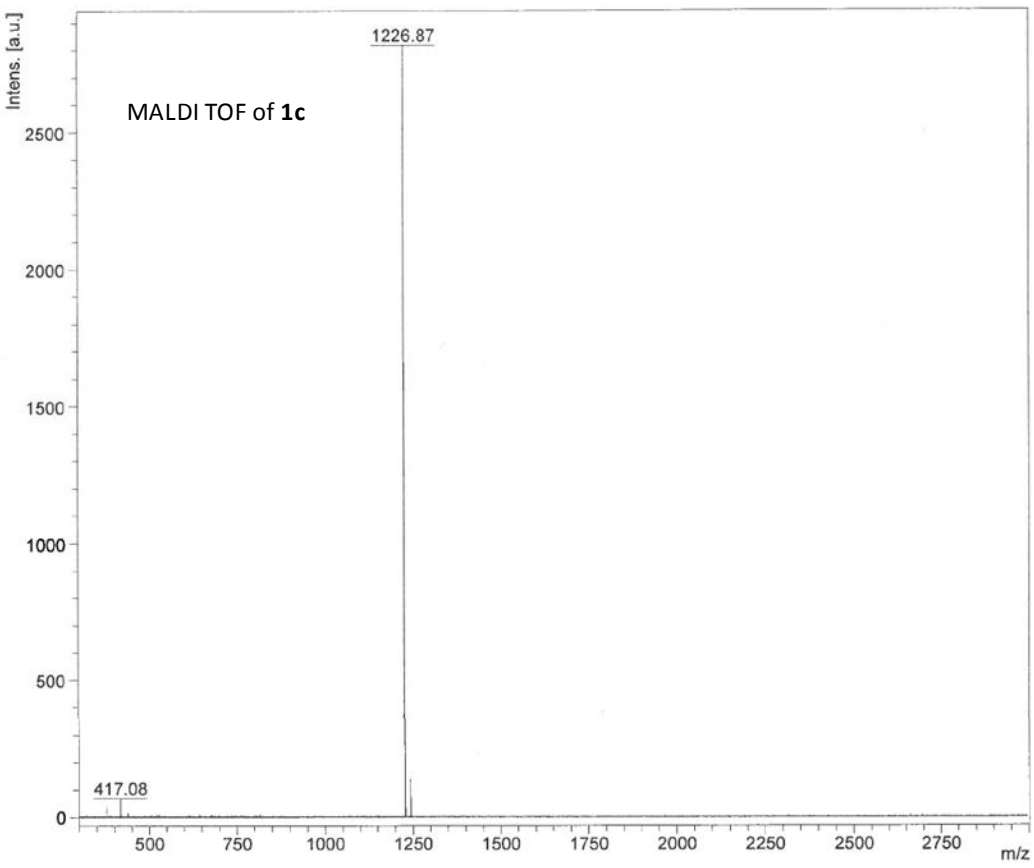

C NMR of 1b in CDCl3
165.90
135.23
128.15
72.62
71.53
70.60
70.35
70.53
70.27
70.02
61.68
40.38
29.69
29.52
29.47
29.42
29.37
29.28
29.14
26.97
26.02
f1 (ppm)



*N^1,N^3,N^5-Tris(1-hydroxy-3,6,9,12-tetraoxadocosan-22-yl)benzene-1,3,5-tricarboxamide (**1c**).*
The synthesis of **1c** was performed following the general procedure yielding **1c** as a colourless oil (0.136 gr, 51%). ^{1}H NMR (400 MHz, $CDCl_3$ δ): 8.39 (s, 3H, Ar), 6.84-6.81 (t, 3H, C=ON<u>H</u>CH_2), 3.73-3.56 (m, 48H, O-($C\underline{H}_2$)$_2$-O), 3.48-3.42 (m, 12, $CH_2C\underline{H}_2$NHC=O, $CH_2CH_2C\underline{H}_2$O), 1.65-1.44 (m, 12H, $CH_2C\underline{H}_2CH_2O$, $C\underline{H}_2CH_2CH_2O$), 1.39-1.27 (m, 44H, aliphatic). ^{13}C NMR (100 MHz, $CDCl_3$ δ): 165.87, 135.20, 128.13, 72.51, 71.51, 70.54, 70.51, 70.46, 70.44, 70.21, 69.91, 61.58, 40.32, 29.43, 29.41, 29.31, 29.26, 29.25, 29.10, 26.85, 25.94. MALDI-TOF-MS: (m/z) calc for $C_{63}H_{117}N_3O_{18}$ 1203.83 observed 1226.83 $[M+Na]^+$. FT-IR (ATR) ν (cm^{-1}): 3341, 2924, 2854, 1649, 1539, 1458, 1350, 1288, 1250, 1101, 941, 885, 835, 705, 573.


1 H NMR of 1c in CDCl 3
3.00
2.51
48.73
12.96
11.73
36.99
f1 (ppm)

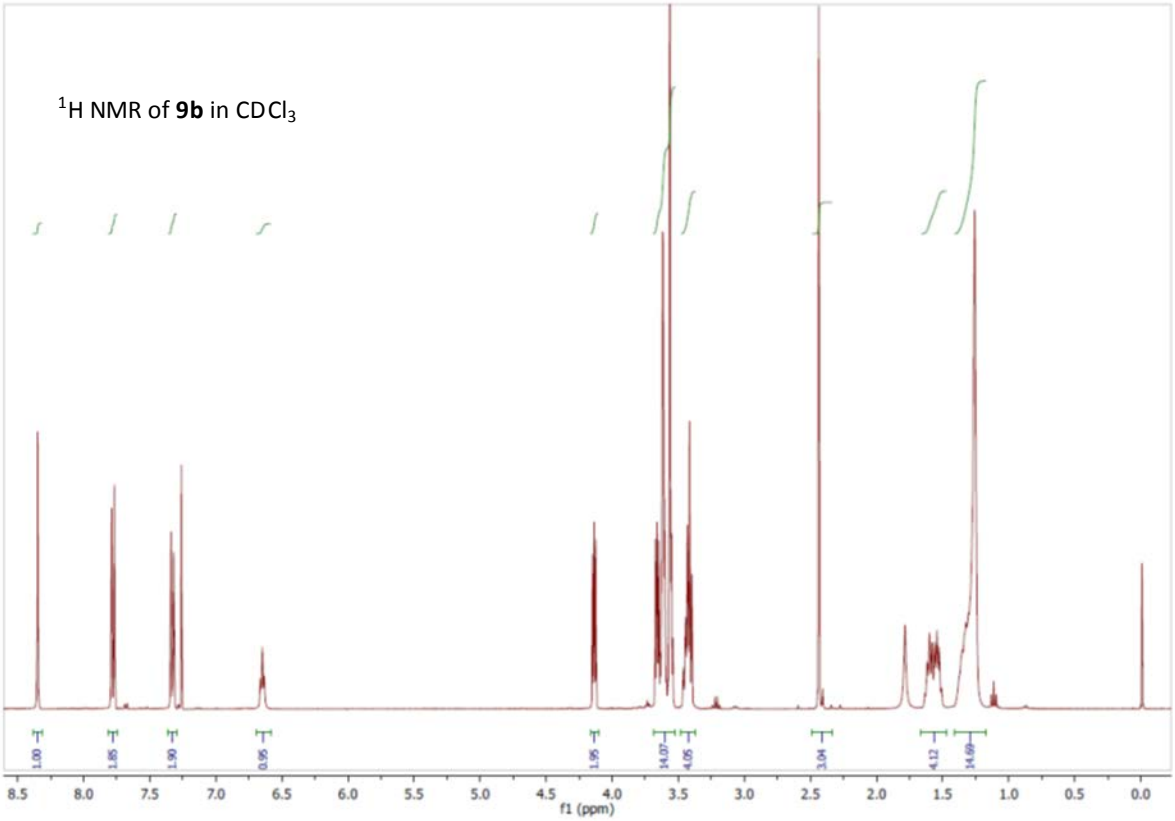

13 C NMR of 1c in CDCl 3
165.87
135.20
128.13
72.51
71.51
70.54
70.51
70.46
70.44
70.21
69.91
61.58
40.32
29.43
29.41
29.31
29.25
29.10
26.85
25.94
-0.02
f1 (ppm)



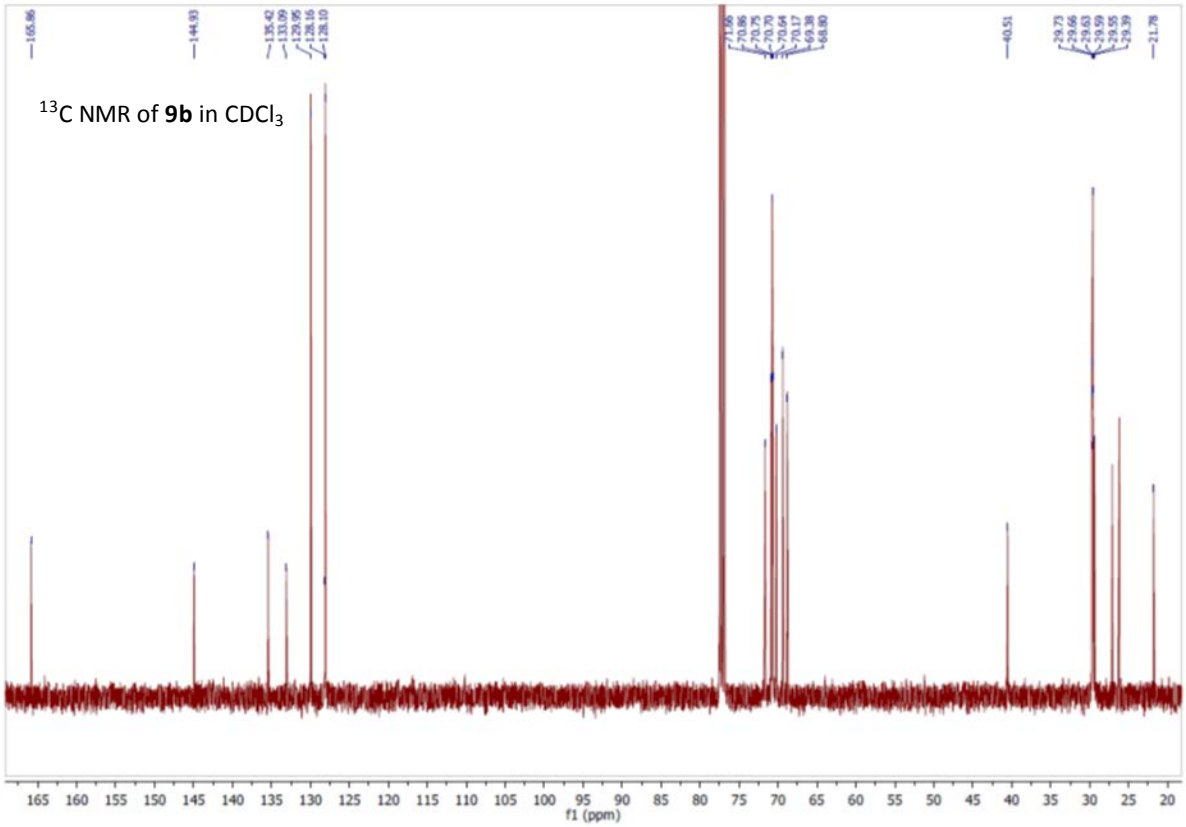
*1,1',1''-(Benzene-1,3,5-triyl)tris(1-oxo-14,17,20,23-tetraoxa-2-azapentacosane-25,1-diyl) tris(4-methylbenzenesulfonate)(**9b**).*

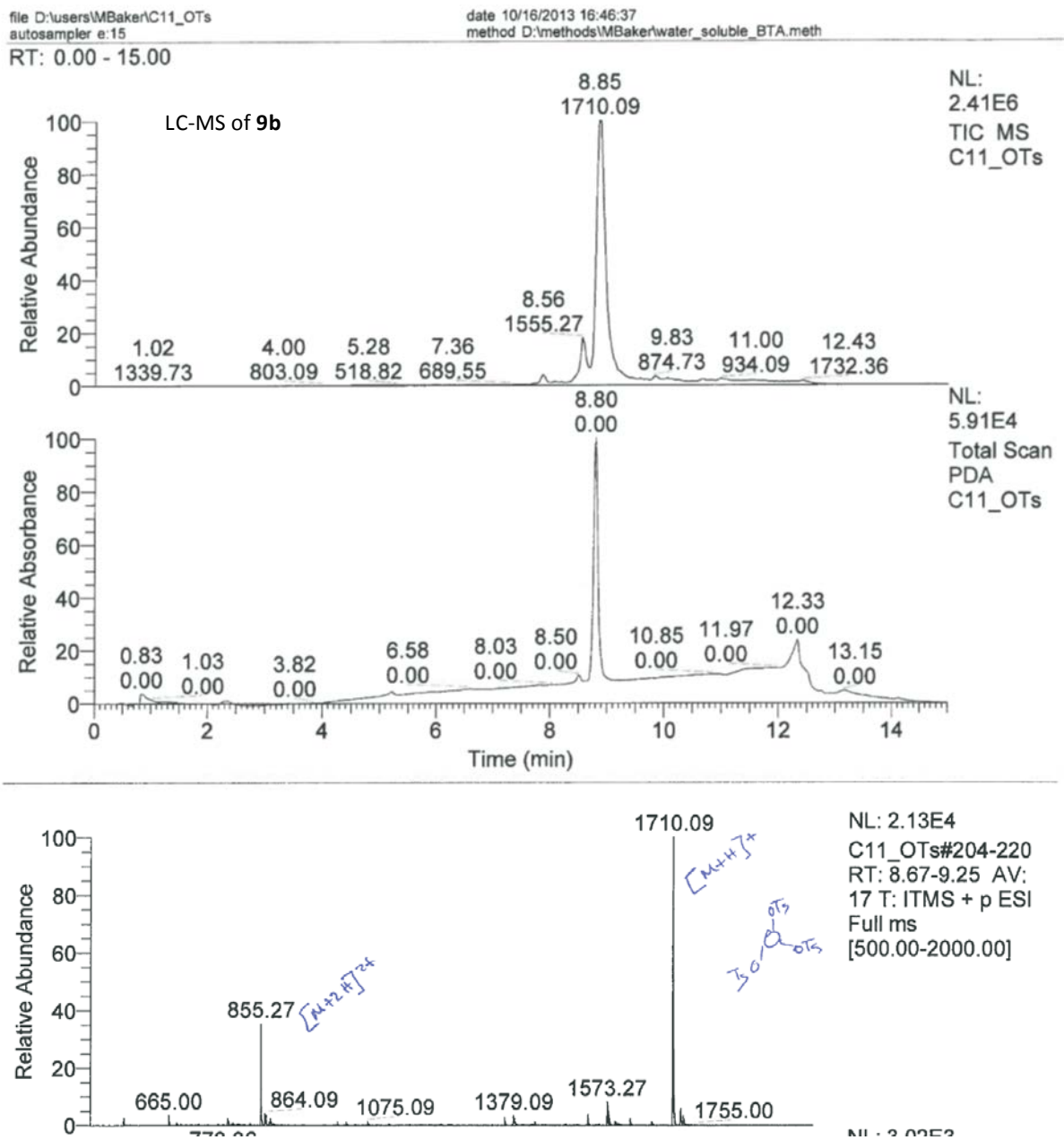
In a round bottom flask (10 mL) **1b** (20 mg, 0.016 mmol), and trimethylamine hydrochloride (1.533 mg, 0.016 mmol) were dissolved in chloroform (2 mL) to give a colorless solution. The reaction vessel was then purged with dry argon, and triethylamine (0.013 ml, 0.096 mmol) was added dropwise. Then, the reaction was cooled to 0 °C and a solution of *p*-toluenesulfonyl chloride (15.29 mg, 0.080 mmol) in chloroform (1 mL) was added dropwise. The reaction was stirred overnight, and the next day another equivalent of TsCl and TMAHCl along with a few drops of TEA was added to push the reaction to completion. The solvent was removed under a N_2 stream, and the crude reaction mixture was purified directly via column chromatograph (SiO_2). Chloroform was used to wash all of the TsCl off the column, and then the solvent system was switched to 6% MeOH/$CHCl_3$ (R_f ~ 0.4) to isolate **9b** (21 mg, 77% yield) as a colorless oil that slowly solidified over time. ^{1}H NMR (400 MHz, $CDCl_3$ δ): 8.35 (s, 3H, Ar), 7.78 (d, *J*=8.3 Hz, 6H, Ar), 7.32 (d, *J*=8.3 Hz, 6H, Ar), 6.65 (t, *J*=5.8 Hz, 3H), 4.14 (m, 6H, C$\underline{H}_2$-OTs), 3.68–3.53 (m, 42H, ethylene glycol and aliphatic), 3.43, (m, 12H), 2.44 (s, 9H, C$\underline{H}_3$-Ar), 1.65–1.50 (m, 12H), 1.42–1.20 (m, 42H, aliphatic) ^{13}C NMR (100 MHz, $CDCl_3$ δ): 165.86, 144.93, 135.42, 133.09, 129.95, 128.16, 128.10, 71.66, 70.86, 70.75, 70.70, 70.64, 70.17, 69.38, 68.80, 40.51, 29.73, 29.66, 29.63, 29.59, 29.55, 29.39, 27.10, 26.19, 21.78. HPLC-MS (ESI): (m/z) calc for $C_{87}H_{141}N_3O_{24}S_3$ 1708.91, observed 1710.09$[M+H]^+$.

^{1}H NMR of **9b** in $CDCl_3$



^{13}C NMR of **9b** in $CDCl_3$

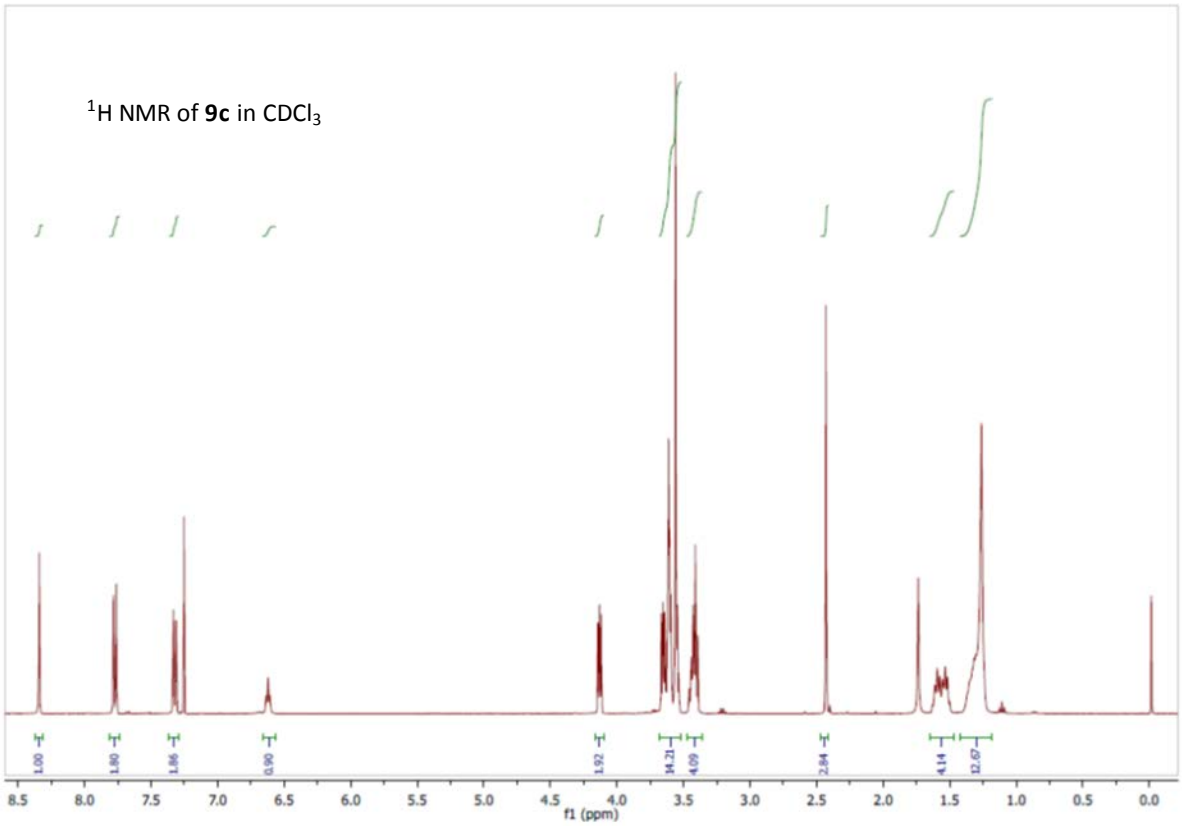




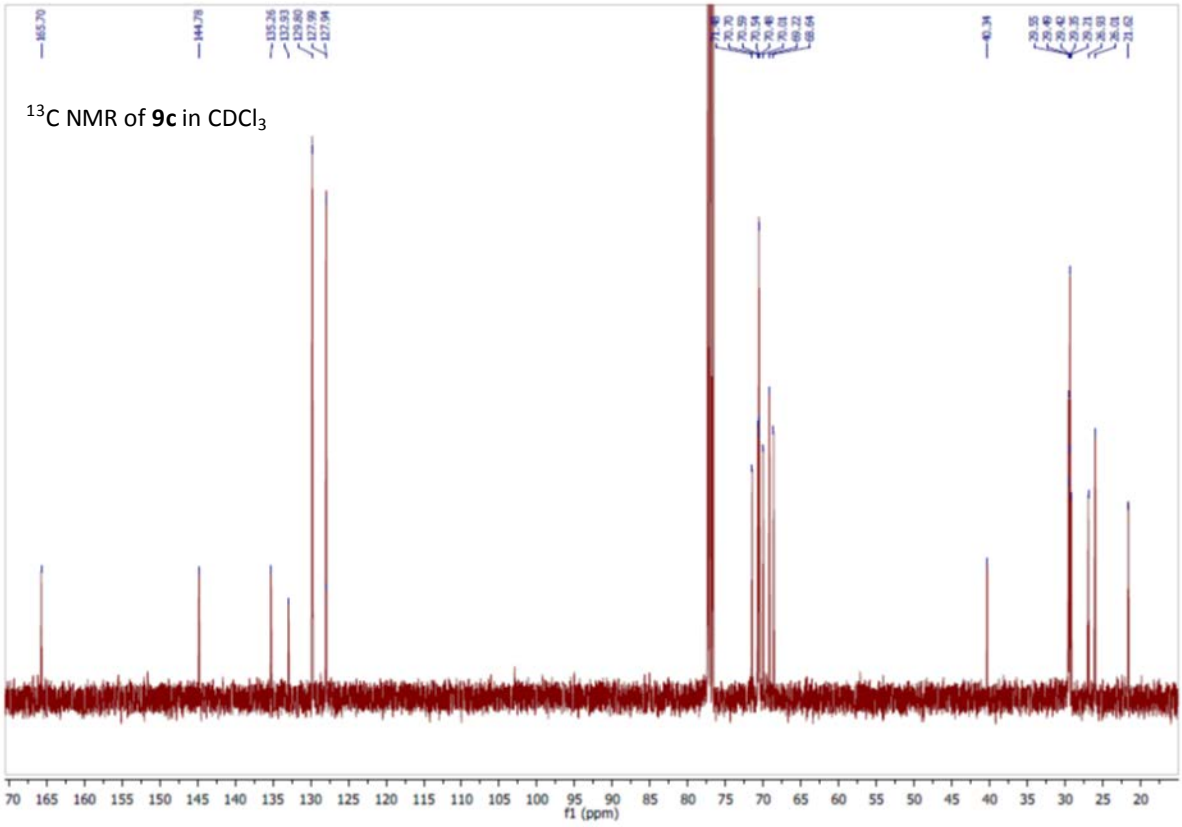
*1,1',1''-(Benzene-1,3,5-triyl)tris(1-oxo-13,16,19,22-tetraoxa-2-azatetracosane-24,1-diyl) tris(4-methylbenzenesulfonate) (**9c**).*

In a round bottom flask (10 mL) **1c** (20 mg, 0.017 mmol), and trimethylamine hydrochloride (1.587 mg, 0.017 mmol) were dissolved in chloroform (2 ml) to give a colorless solution. The reaction vessel was then purged with dry argon, and triethylamine (0.014 ml, 0.100 mmol) was added dropwise. Then, the reaction was cooled to 0 °C and a solution of *p*-toluenesulfonyl chloride (15,83 mg, 0,083 mmol) in chloroform (1 mL) was added dropwise. The reaction was allowed to stir overnight, and the next day another equivalent of TsCl and TMAHCl along with a few drops of TEA was added to push the reaction to completion. The solvent was removed under a N_2 stream, and the crude reaction mixture was purified directly via column chromatograph (SiO_2). Chloroform was used to wash all of the TsCl off the column, and then the solvent system was switched to 6%

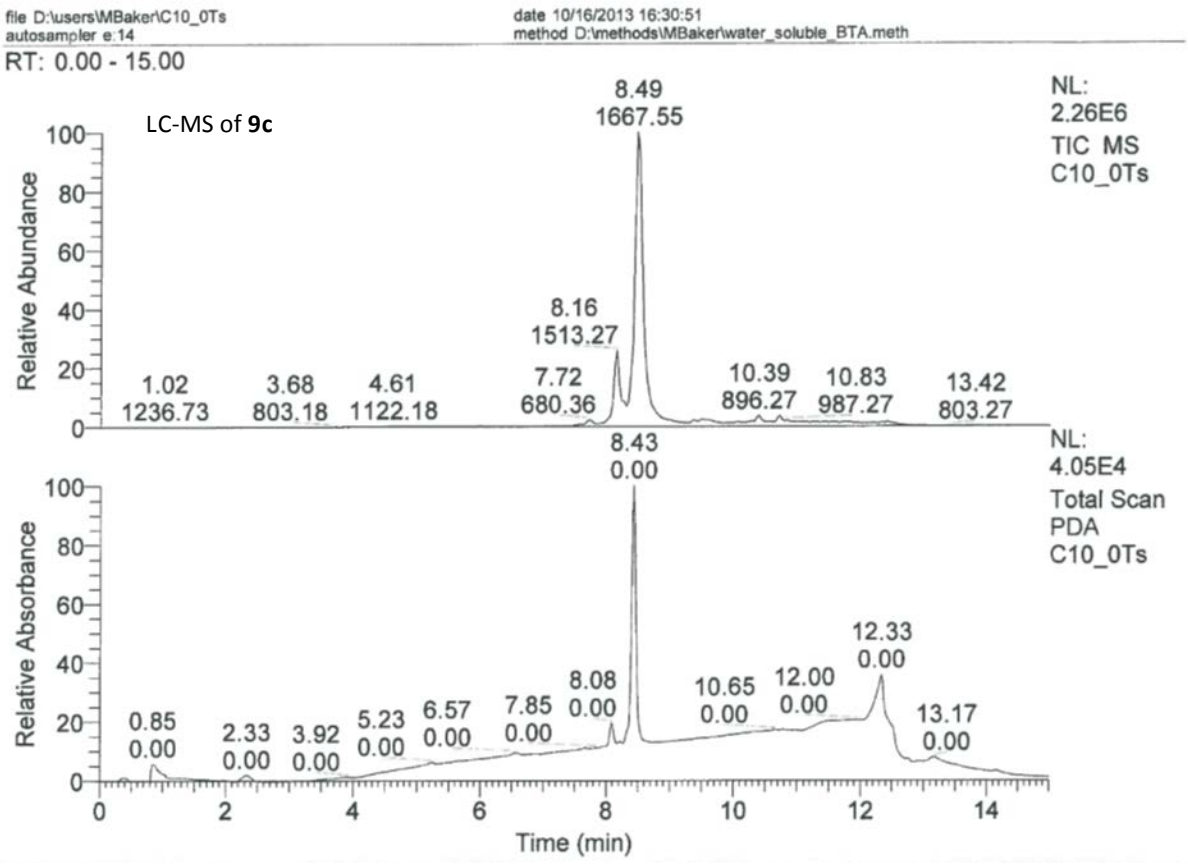
MeOH/$CHCl_3$ (R_f ~ 0.4) to isolate **9c** (20 mg, 72% yield) as a colorless oil that slowly solidified over time. ^{1}H NMR (400 MHz, $CDCl_3$ δ): 8.34 (s, 3H, Ar), 7.77 (d, *J*=8.3 Hz, 6H, Ar), 7.32 (d, *J*=8.1 Hz, 6H, Ar), 6.62 (t, *J*=5.7 Hz, 3H), 4.14 (m, 6H, C<u>H</u>$_2$-OTs), 3.69–3.52 (m, 42H, ethylene glycol and aliphatic), 3.42, (m, 12H), 2.43 (s, 9H, C<u>H</u>$_3$-Ar), 1.65–1.50 (m, 12H), 1.42–1.20 (m, 36H, aliphatic) ^{13}C NMR (100 MHz, $CDCl_3$ δ): 165.70, 144.78, 135.26, 132.93, 129.80, 127.99, 127.94, 71.48, 70.70, 70.59, 70.54, 70.48, 70.01, 69.22, 68.64, 40.34, 29.55, 29.49, 29.42, 29.35, 29.21, 26.93, 26.01, 21.62. HPLC-MS (ESI): (m/z) calc for $C_{84}H_{135}N_3O_{24}S_3$ 1666.86, observed 1668.00 $[M+H]^+$.

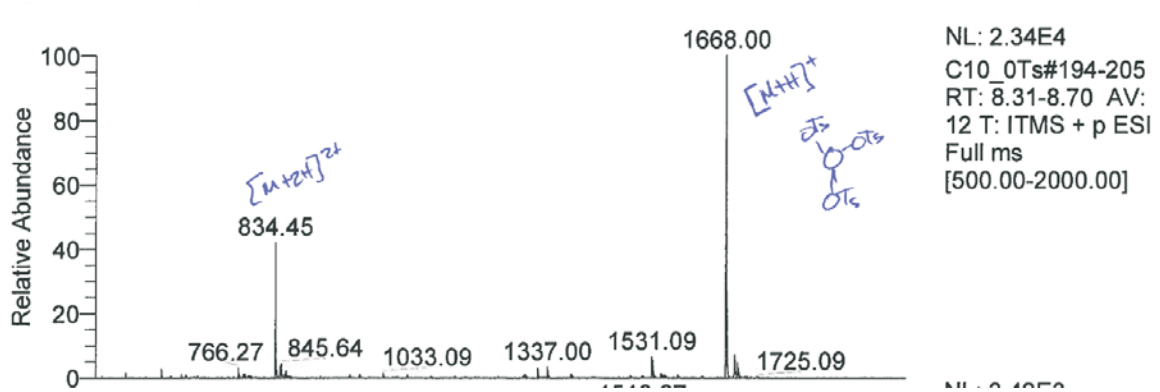


^{13}C NMR of **9c** in $CDCl_3$



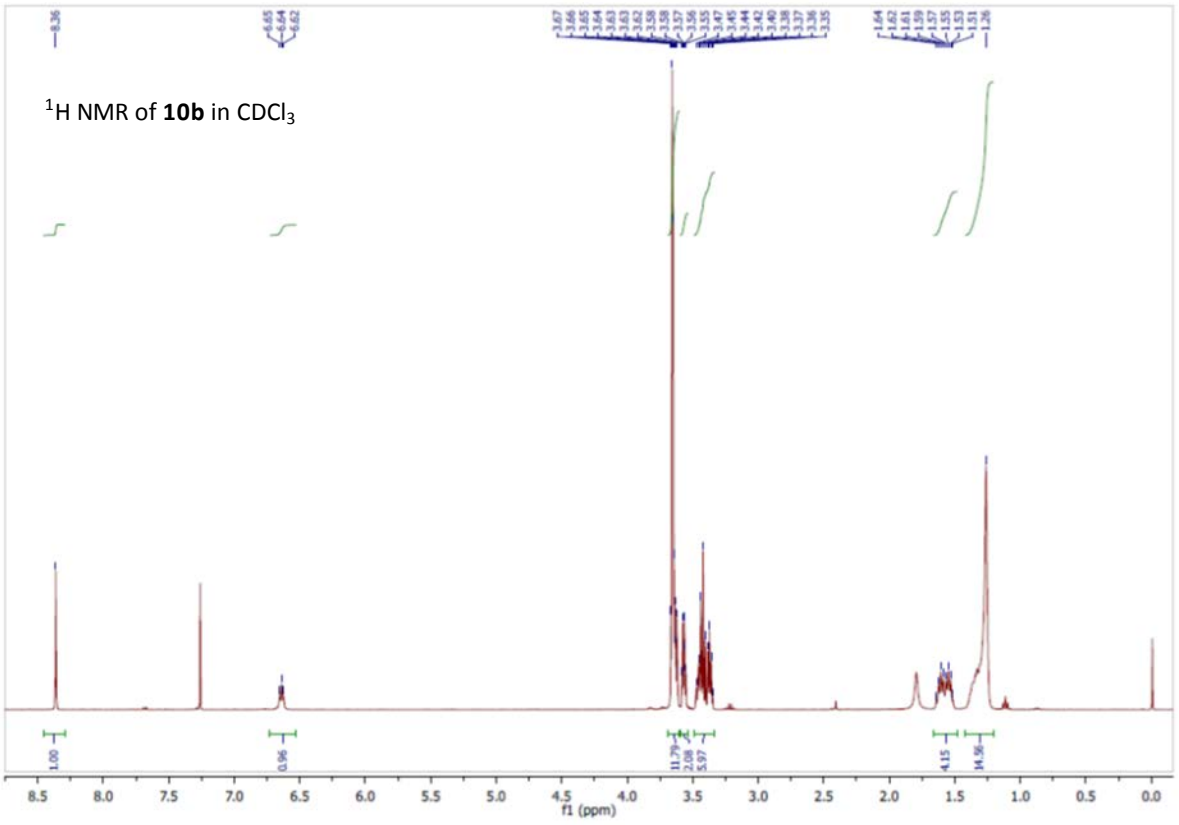
LC-MS of **9c**



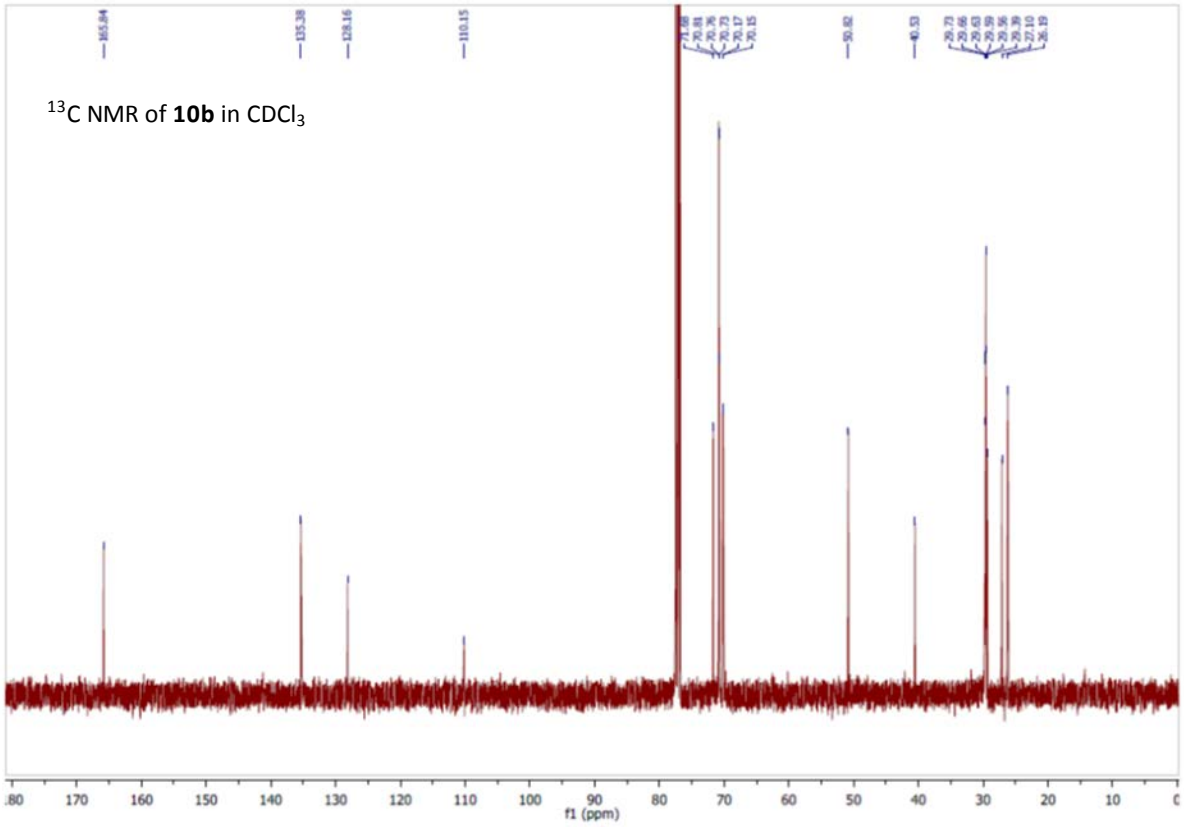


*N1,N3,N5-Tris(1-azido-3,6,9,12-tetraoxatricosan-23-yl)benzene-1,3,5-tricarboxamide (**10b**).*

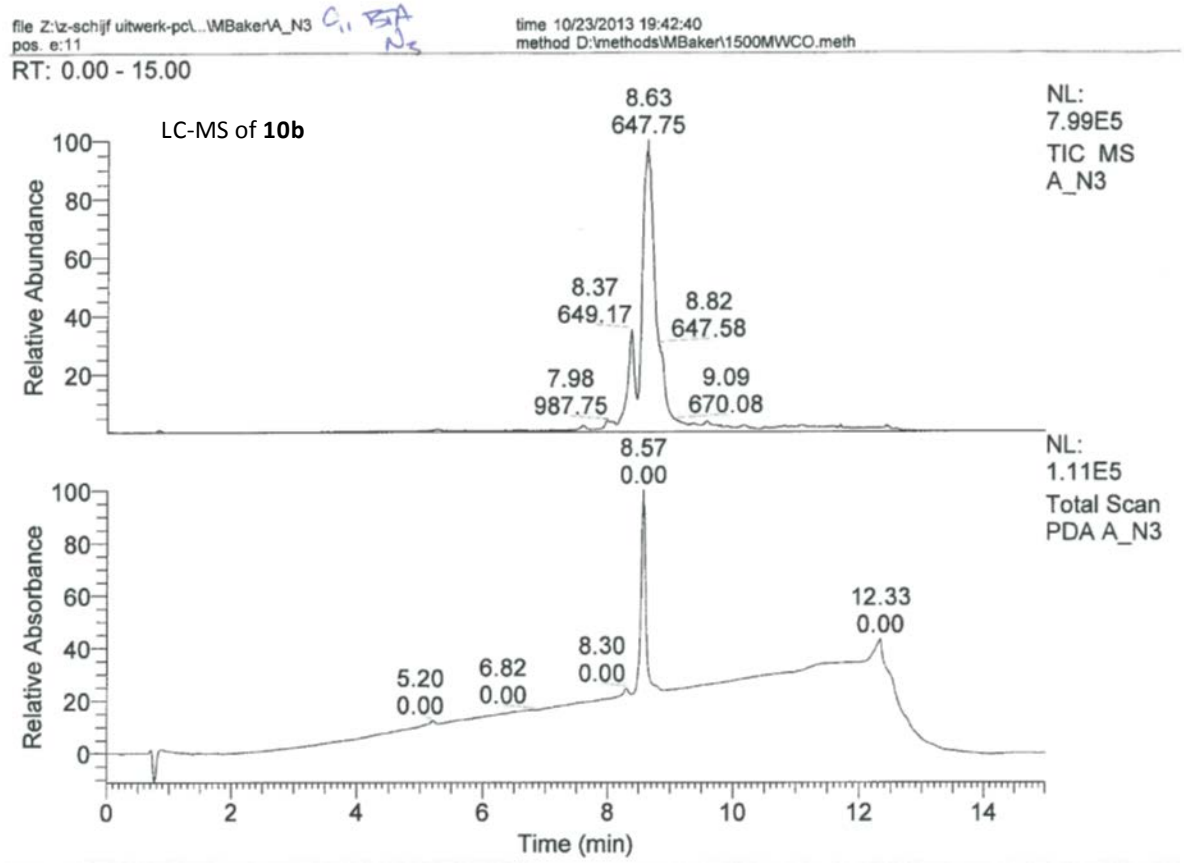
A vial (5 mL) was charged with **9b** (18 mg, 10.53 µmol) and sodium azide (20 mg, 0.308 mmol) in methanol (2 mL) to give a yellow suspension. The vial was then sealed and the suspension was stirred at 60 °C over two nights. The reaction was then allowed to cool to room temperature, the solids were suspended in chloroform and directly loaded for column chromatography (SiO_2), running from pure chloroform to 5% MeOH in $CHCl_3$. This yielded **10b** (12 mg, 86% yield) as a colorless residue. ^{1}H NMR (400 MHz, $CDCl_3$ δ): 8.36 (s, 3H, Ar), 6.64 (t, *J*=5.6 Hz, 3H), 3.69–3.60 (m, 36H, ethylene glycol and aliphatic), 3.56 (m, 6H), 3.43, (m, 18H), 1.65–1.50 (m, 12H), 1.42–1.20 (m, 42H, aliphatic). ^{13}C NMR (100 MHz, $CDCl_3$ δ): 165.84, 135.38, 128.16, 71.68, 70.81, 70.76, 70.73, 70.17, 70.15, 50.82, 40.53, 29.73, 29.66, 29.63, 29.59, 29.56, 29.39, 27.10, 26.19. HPLC-MS (ESI): (m/z) calc for $C_{66}H_{120}N_{12}O_{15}$ 1320.90, observed 1321.75 $[M+H]^+$.

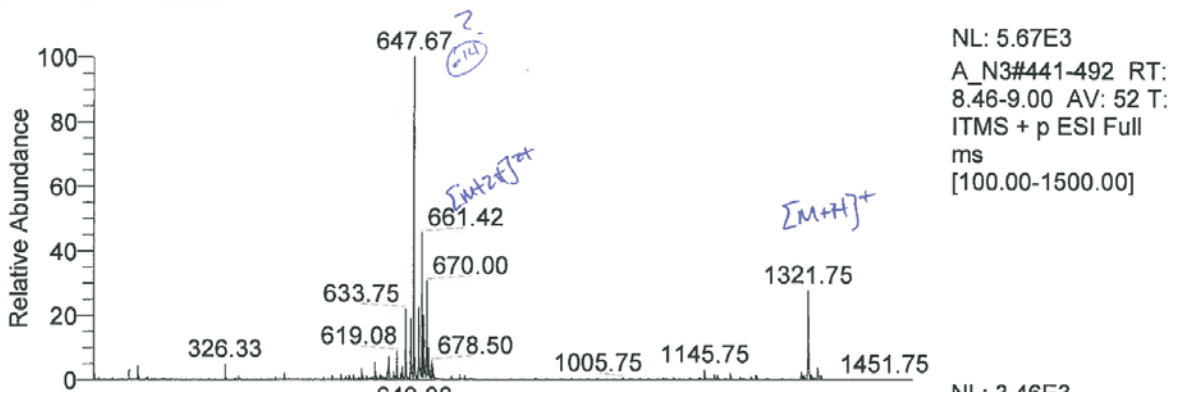


^{13}C NMR of **10b** in $CDCl_3$



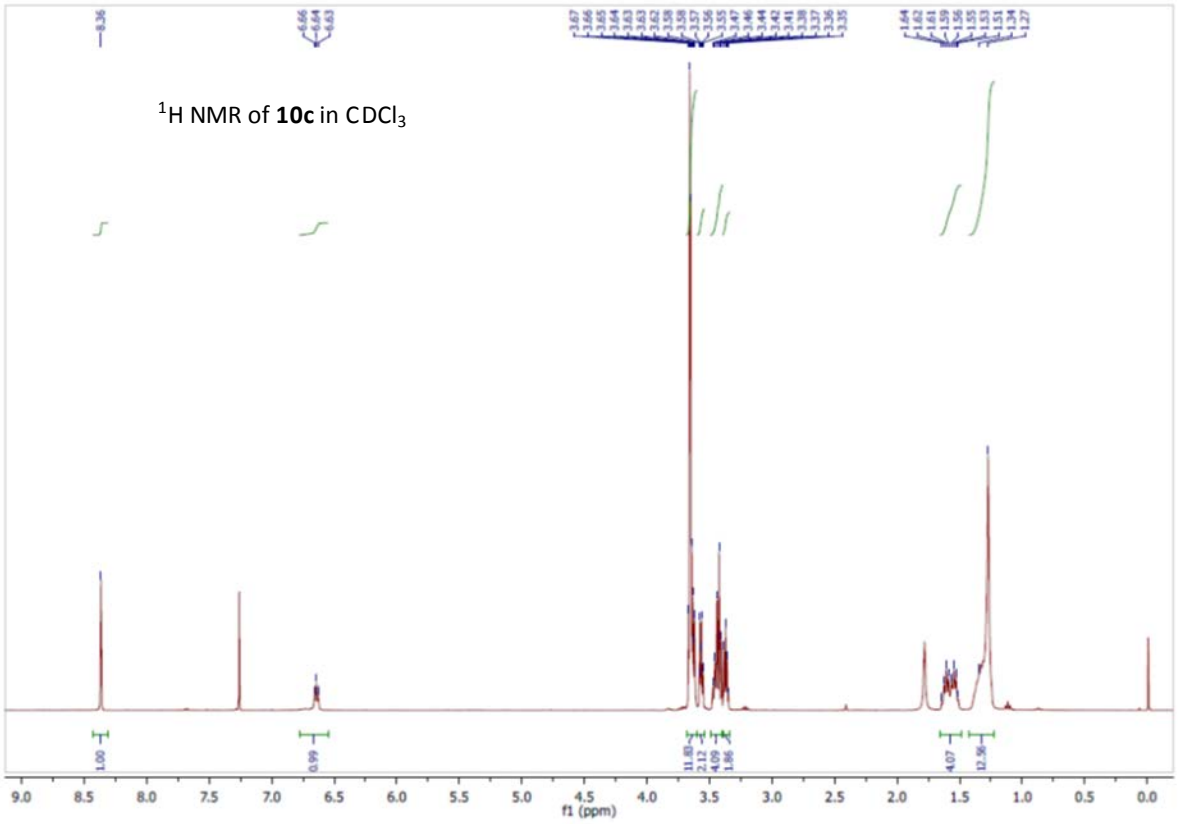
LC-MS of **10b**

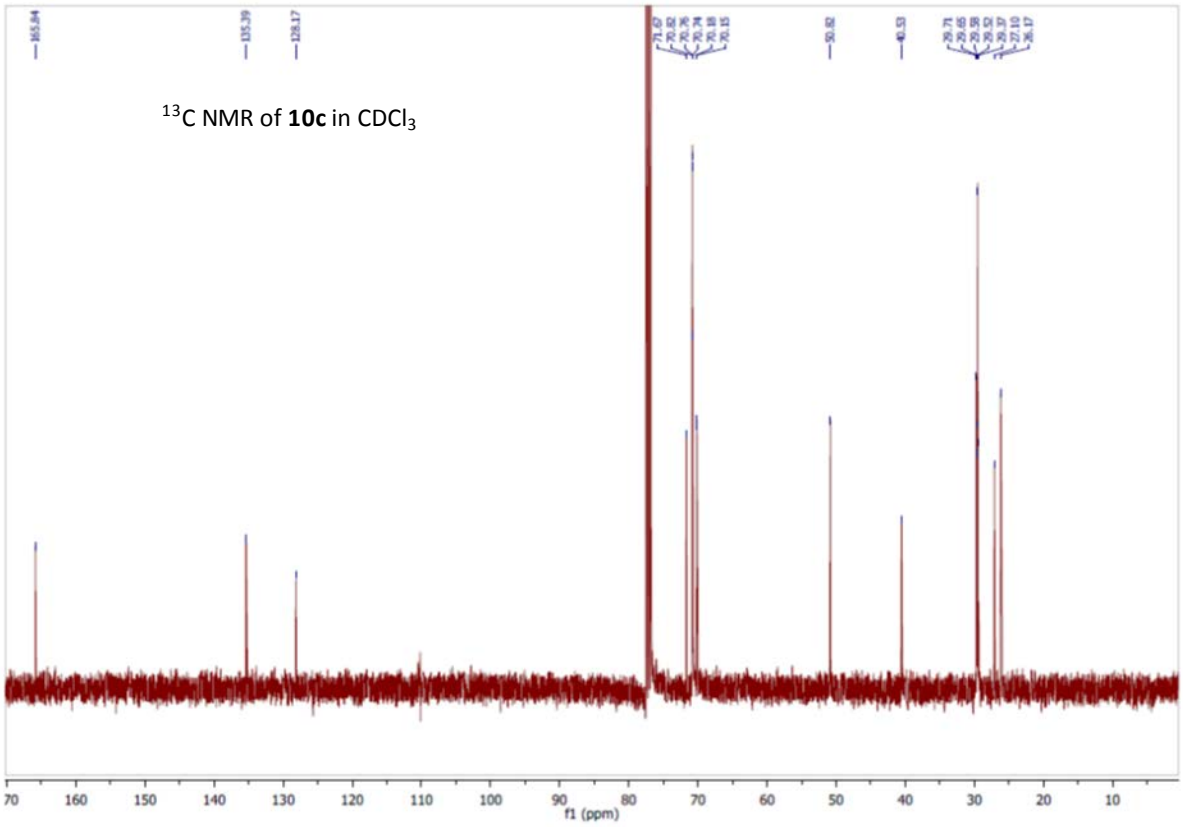




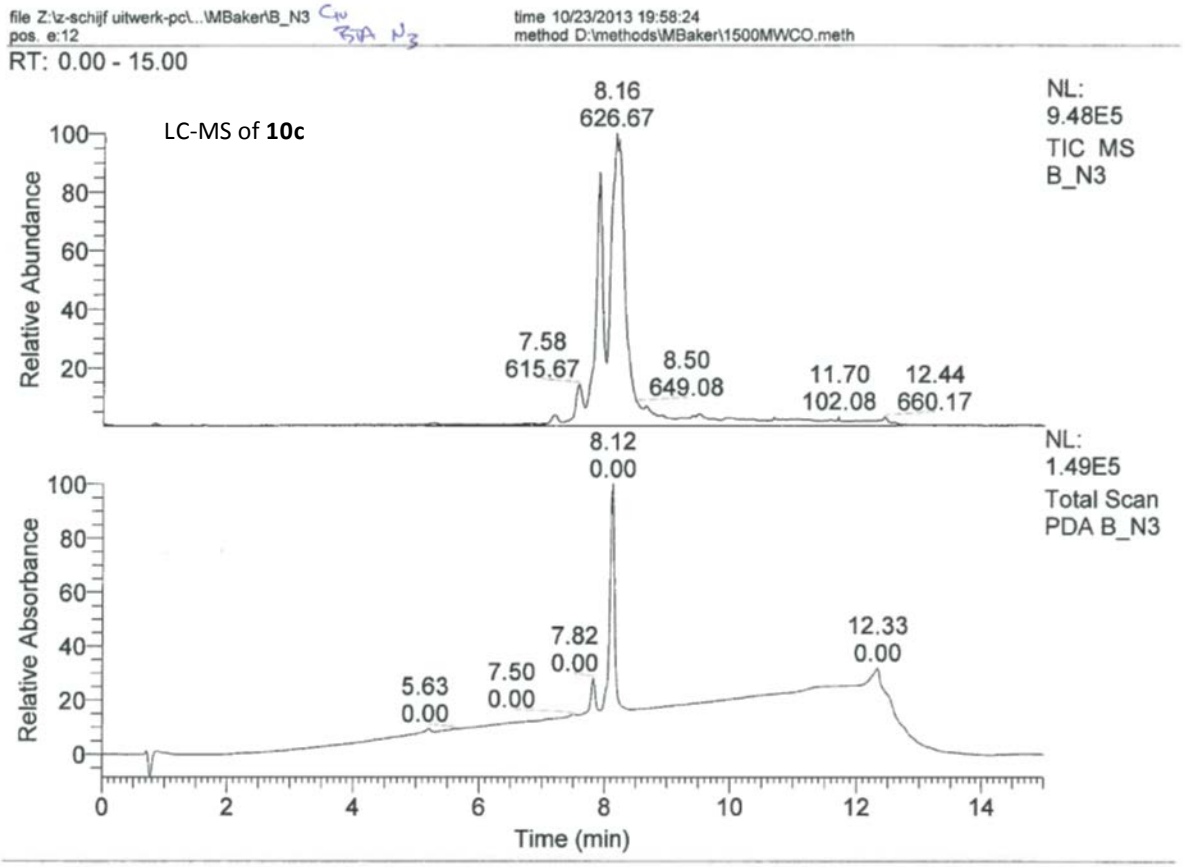
*N1,N3,N5-Tris(1-azido-3,6,9,12-tetraoxadocosan-22-yl)benzene-1,3,5-tricarboxamide (**10c**).*

A vial (5 mL) was charged with **9c** (20 mg, 0.012 mmol) and sodium azide (20 mg, 0.308 mmol) in methanol (2 mL) to give a yellow suspension. The vial was then sealed and the suspension was stirred at 60 °C over two nights. The reaction was then allowed to cool to room temperature, the solids were suspended in chloroform and directly loaded for column chromatography (SiO_2), running from pure chloroform to 5% MeOH in $CHCl_3$. This yielded **10c** (14 mg, 91% yield) as a colorless residue. ^{1}H NMR (400 MHz, $CDCl_3$ δ): 8.36 (s, 3H, Ar), 6.64 (t, *J*=5.6 Hz, 3H), 3.69–3.60 (m, 36H, ethylene glycol and aliphatic), 3.56, (m, 6H), 3.49–3.34 (m, 18H), 1.65–1.50 (m, 12H), 1.42–1.20 (m, 36H, aliphatic) ^{13}C NMR (100 MHz, $CDCl_3$ δ): 165.84, 135.39, 128.17, 71.67, 70.82, 70.76, 70.74, 70.18, 70.15, 50.82, 40.53, 29.71, 29.65, 29.58, 29.52, 29.37, 27.10, 26.17. HPLC-MS (ESI): (m/z) calc for $C_{63}H_{114}N_{12}O_{15}$ 1278.85, observed 1279.83 $[M+H]^+$.

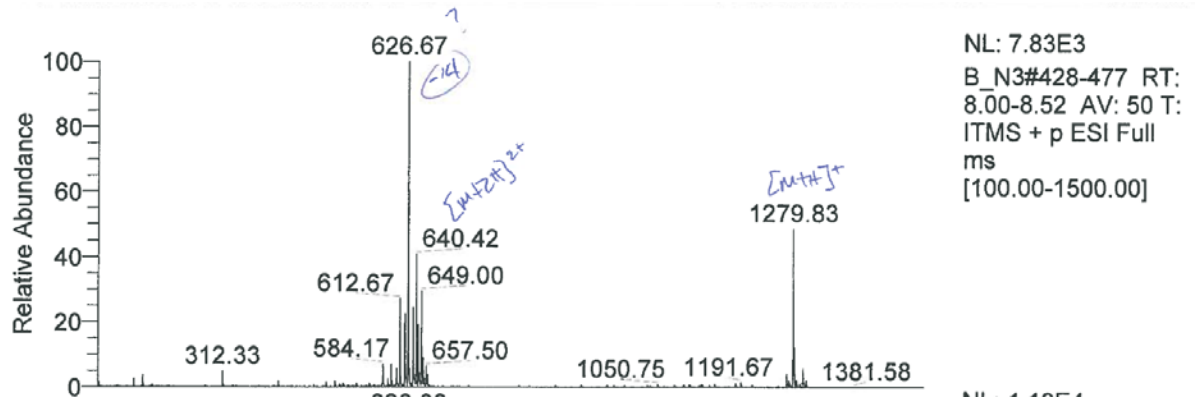




^{13}C NMR of **10c** in $CDCl_3$

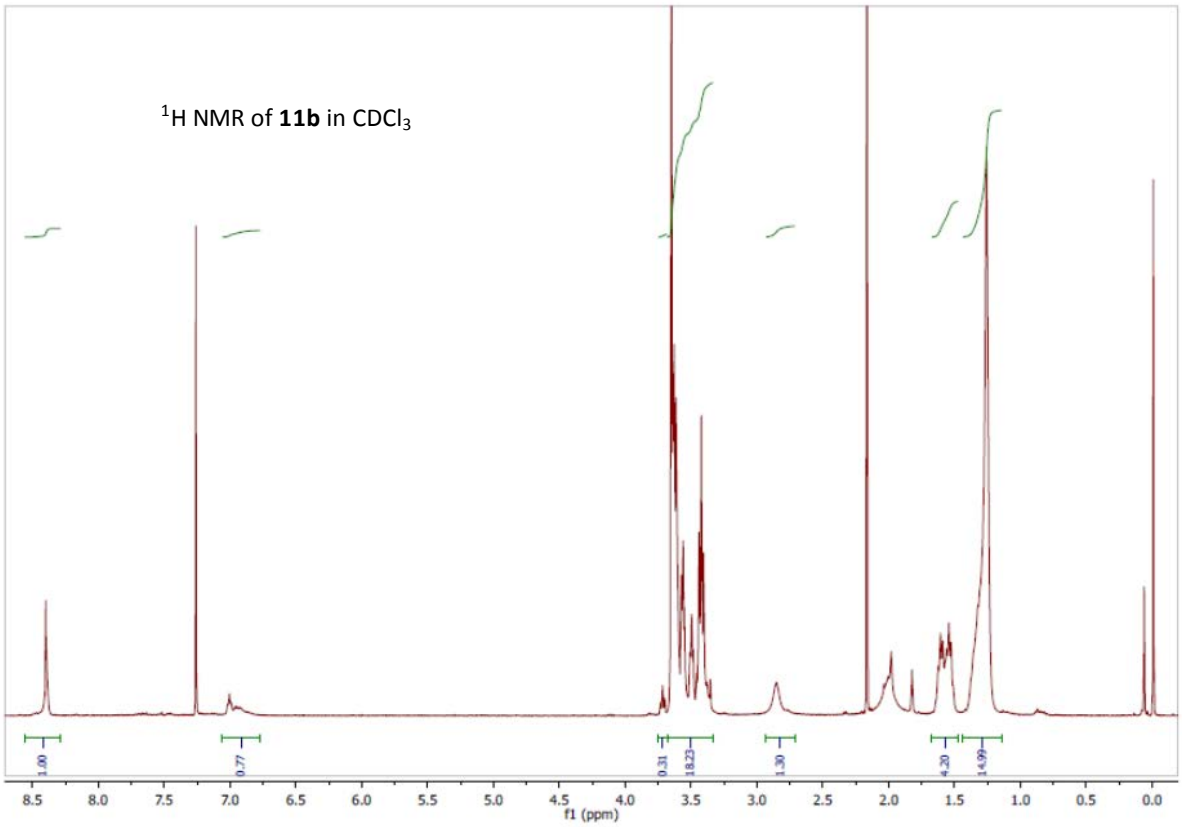


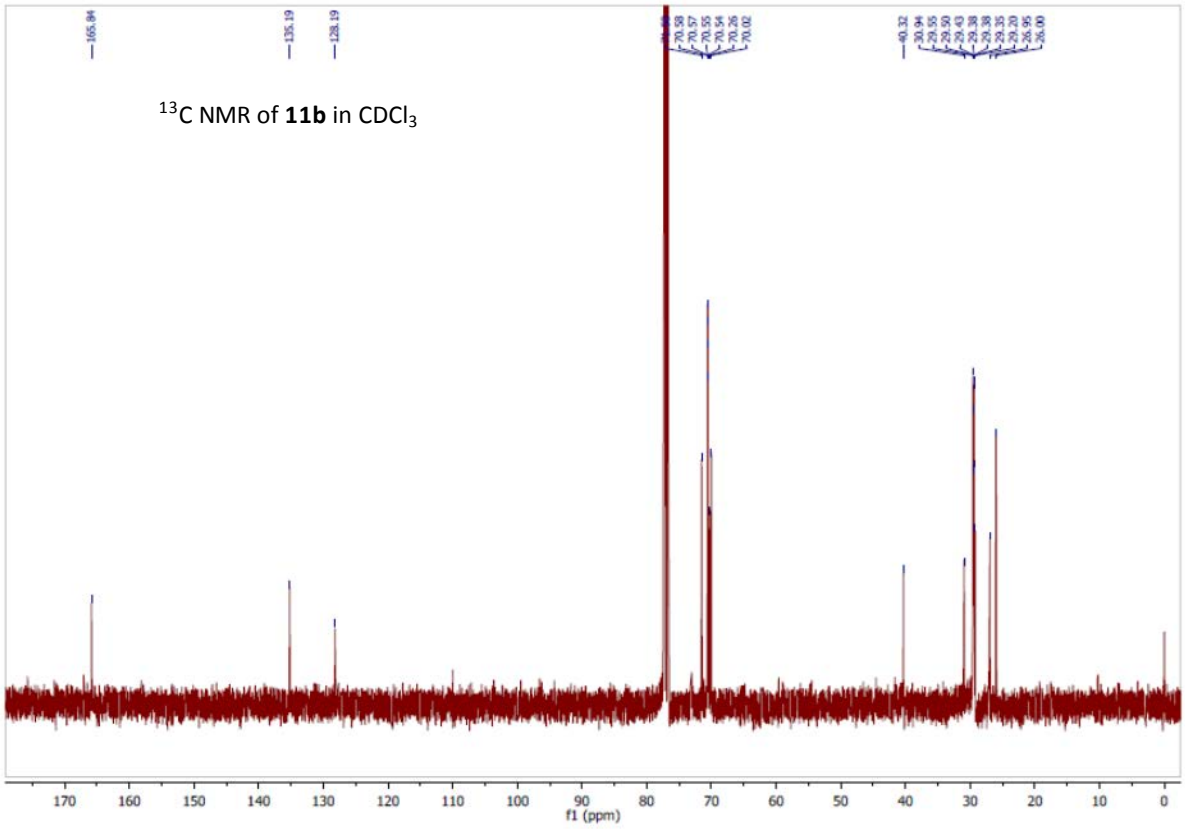
LC-MS of **10c**



*N1,N3,N5-Tris(1-amino-3,6,9,12-tetraoxatricosan-23-yl)benzene-1,3,5-tricarboxamide (**11b**).*

To a dry NMR tube was added **10b** (12 mg, 9.08 μmol) and triphenylphosphine (14.2 mg, 54.48 μmol) along with dry *d*8-THF (0.7 mL). The NMR tube was sealed and placed in a 40 °C oil bath overnight and conversion was tracked via NMR. The next day 150 μL of D_2O was added to the NMR tube and let react over another night at 40 °C. Solvents were removed in vacuo and the residue was taken up in chloroform and loaded for column chromatography (SiO_2); running the column in 5% MeOH in $CHCl_3$ allowed the removal of residual triphenylphosphine and triphenylphosphine oxide, while switching to 5% (3:1 MeOH:*i*-$PrNH_2$) in $CHCl_3$ eluted **11b** and solvent removal facilitated isolation of **11b** (8.5 mg, 75% yield). ^{1}H NMR (400 MHz, $CDCl_3$ δ): 8.40 (s, 3H, Ar), 7.07–6.88 (m, 3H), 3.71–3.29 (m, 54H, ethylene glycol and aliphatic), 3.56 (m, 6H), 2.85 (s br, 6H) 1.65–1.50 (m, 12H), 1.42–1.20 (m, 42H, aliphatic). ^{13}C NMR (100 MHz, $CDCl_3$ δ): 165.84, 135.19, 128.19, 71.50, 70.58, 70.57, 70.55, 70.54, 70.26, 70.02 40.32, 30.94, 29.55, 29.50, 29.43, 29.38, 29.38, 29.35, 29.20, 26.95, 26.00.

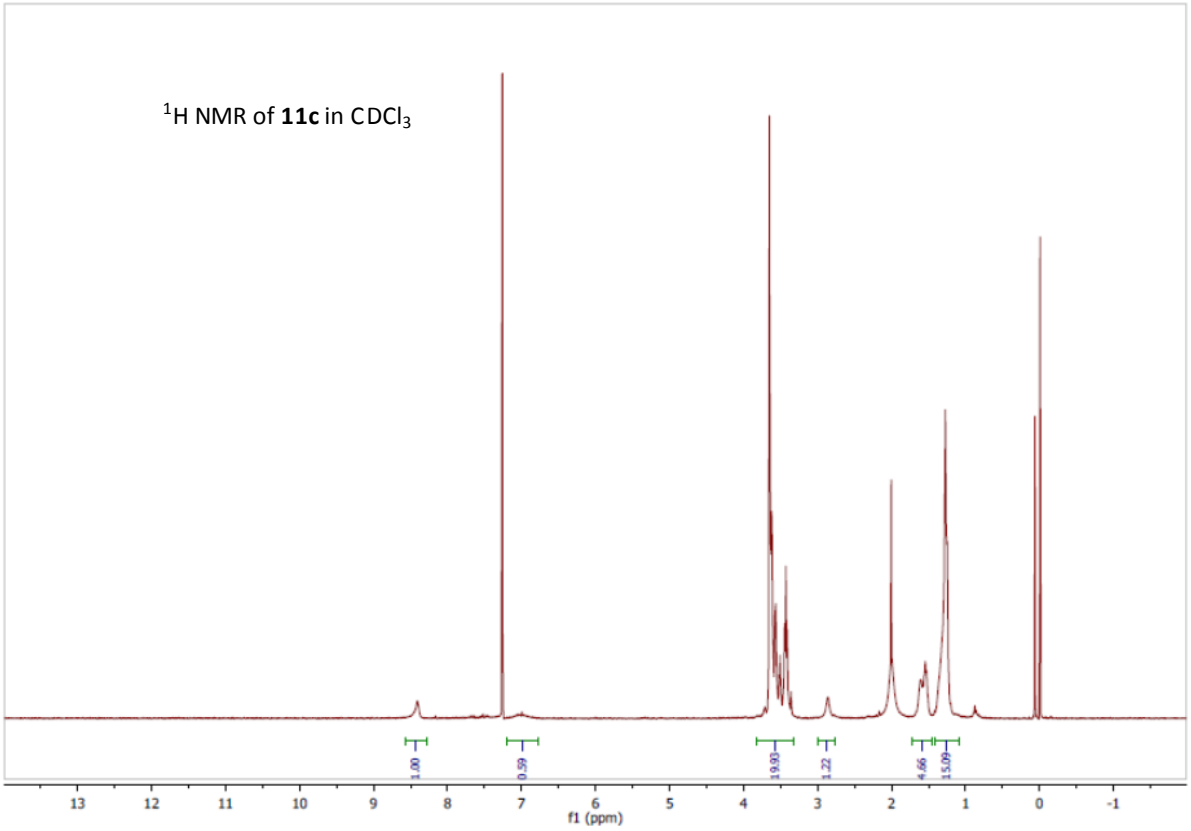


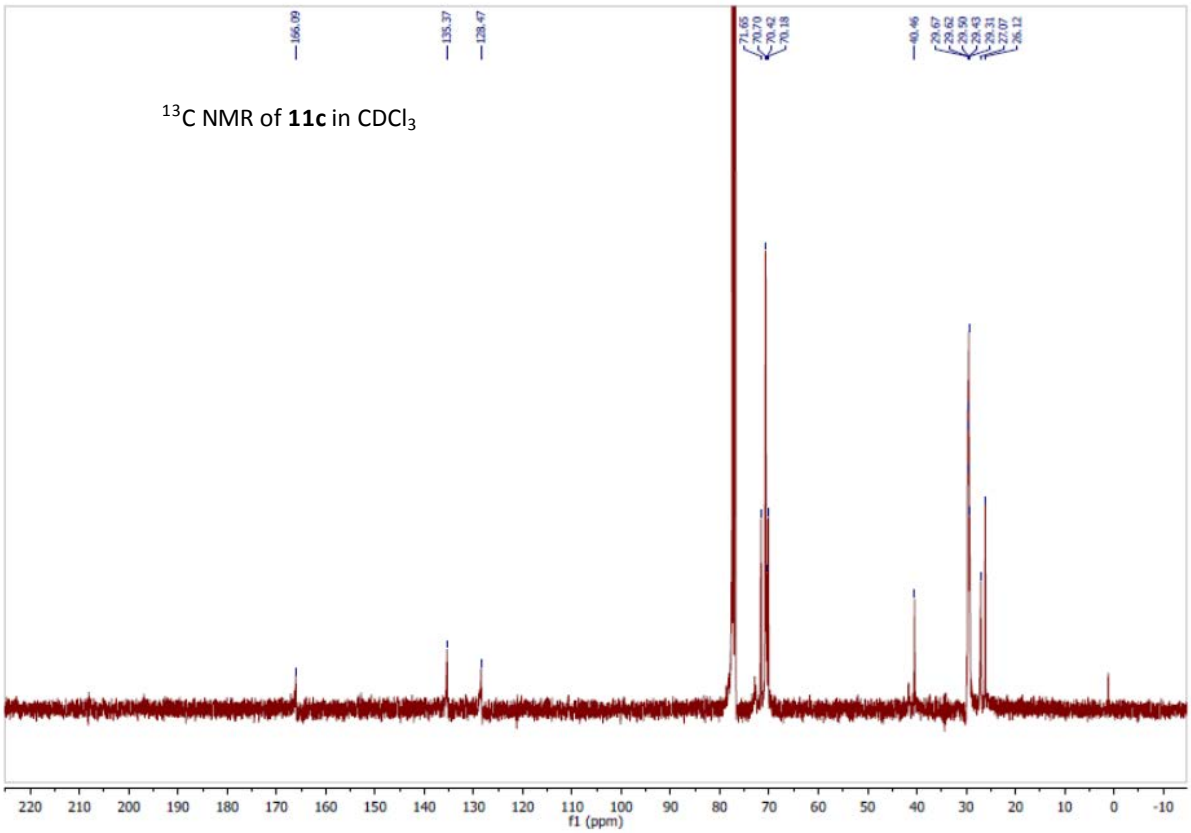


*N1,N3,N5-Tris(1-amino-3,6,9,12-tetraoxadocosan-22-yl)benzene-1,3,5-tricarboxamide (**11c**).*

To a dry NMR tube was added **10c** (14 mg, 10.94 μmol) and triphenylphosphine (20.0 mg, 0.076 mmol) along with dry *d*8-THF (0.7 mL). The NMR tube was sealed and placed in a 40

°C oil bath overnight and conversion was tracked via NMR. The next day 150 µL of D_2O was added to the NMR tube and let react over another night at 40 °C. Solvents were removed in vacuo and the residue was taken up in chloroform and loaded for column chromatography (SiO_2); running the column in 5% MeOH in $CHCl_3$ allowed the removal of residual triphenylphosphine and triphenylphosphine oxide, while switching to 5% (3:1 MeOH:*i*-$PrNH_2$) in $CHCl_3$ eluted **11c** and solvent removal facilitated isolation of **11c** (13.1 mg, quant. yield). ^{1}H NMR (400 MHz, $CDCl_3$ δ): 8.41 (s, 3H, Ar), 7.21–6.72 (m, 3H), 3.84–3.18 (m, 60H, ethylene glycol and aliphatic), 2.86 (s br, 6H) 1.65–1.50 (m, 12H), 1.42–1.20 (m, 36H, aliphatic). ^{13}C NMR (100 MHz, $CDCl_3$ δ): 166.09, 135.37, 128.47, 71.65, 70.70, 70.42, 70.18, 40.46, 29.67, 29.62, 29.50, 29.43, 29.31, 27.07, 26.12.

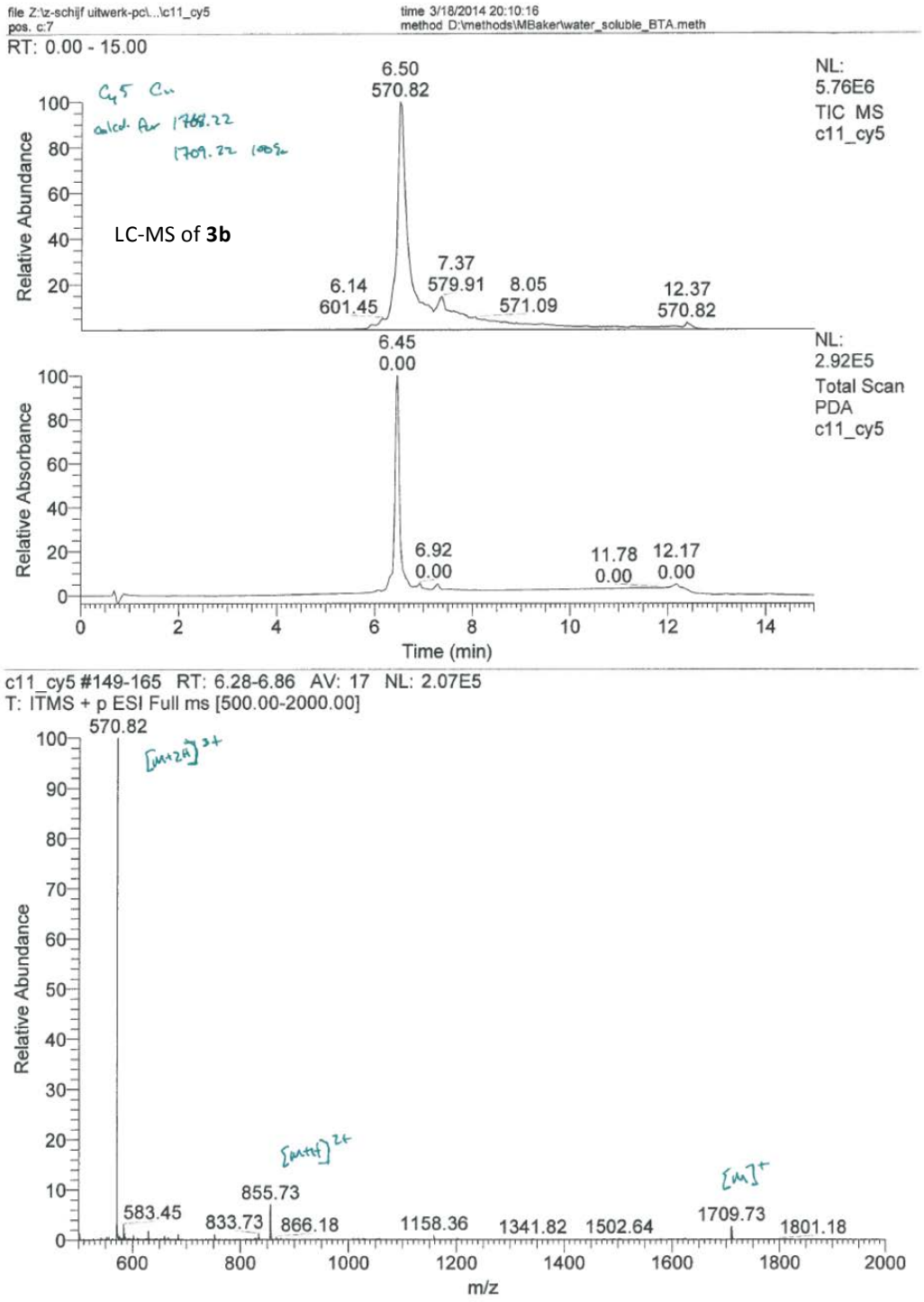




General procedure for dye conjugation to NH_2-terminated BTAs. Synthesis of Cy5-C11-BTA conjugate.

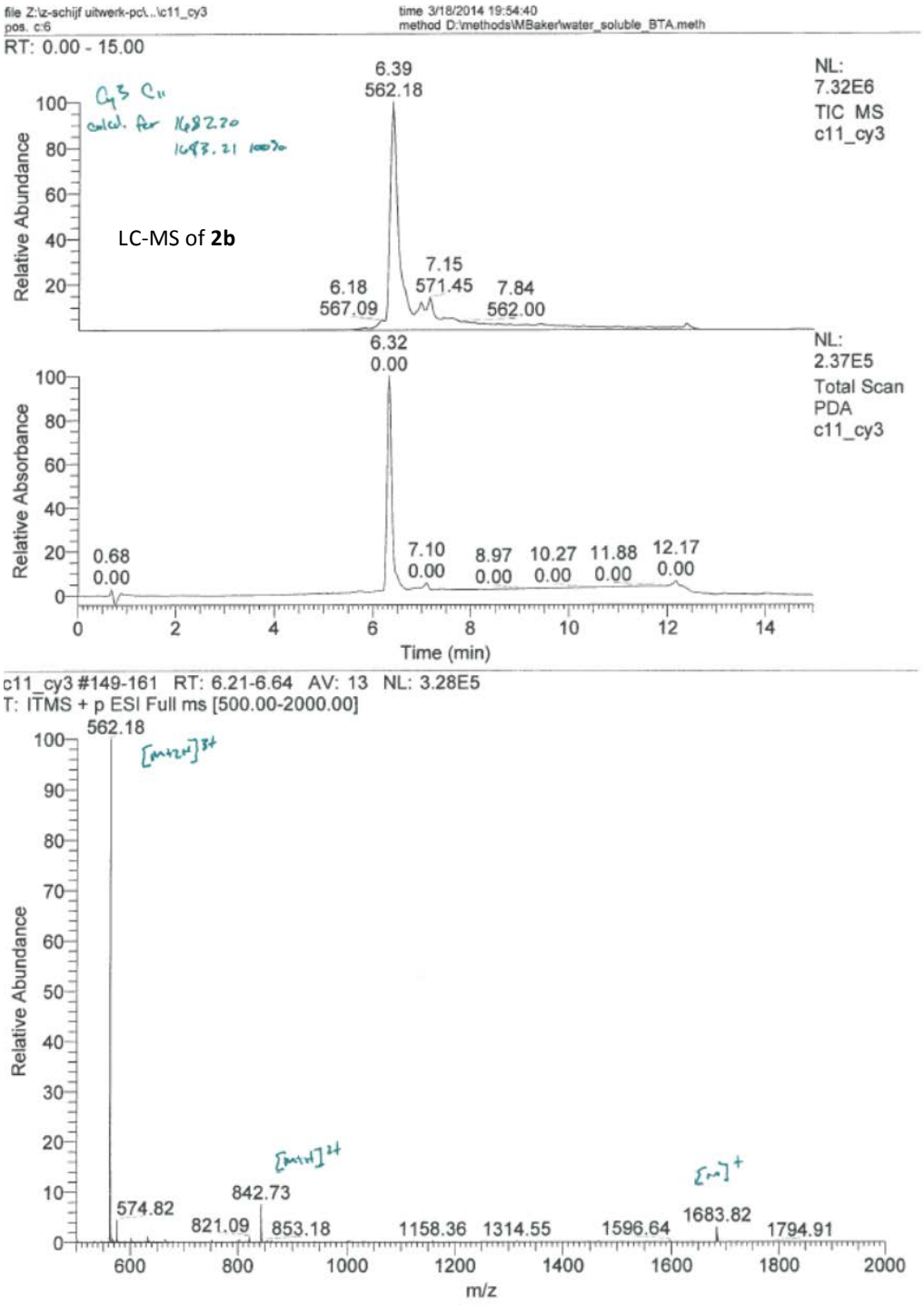
*1-(1-(3,5-Bis((1-amino-3,6,9,12-tetraoxatricosan-23-yl)carbamoyl)phenyl)-1,27-dioxo-14,17,20,23-tetraoxa-2,26-diazadotriacontan-32-yl)-3,3-dimethyl-2-((1E,3E,5E)-5-(1,3,3-trimethylindolin-2-ylidene)penta-1,3-dien-1-yl)-3H-indol-1-ium (**3b**).*

To a small vial with stirbar, was added **11b** (3.85 mg, 3.10 µmol), 20 µL of trimethylamine, and 500 µL of DMSO. To this mixture was added Cy5-NHS (1.907 mg, 3.10 µmol) dissolved in another 500 µL of DMSO. The vial was purged with argon, sealed, and allowed to react overnight away from light. The next day, the reaction mixture was put in a dialysis tube (MWCO 1000) and dialyzed against deionised H_2O for 1 hour to remove a bulk of DMSO. The recovered contents were then purified using preparative HPLC with customized gradients of H_2O (0.01% TFA) and MeCN (0.01% TFA); between 60% MeCN and 70% MeCN required for elution of the target compound. Starting material and twice reacted compounds could be recovered in most cases. Lyophilization yielded **3b** as a blue amorphous solid. In most cases, the yield was well below 20%. HPLC-MS (ESI): (m/z) calc for $C_{98}H_{163}N_8O_{16}^+$ 1709.22 g/mol, observed 1709.73 $[M]^+$.



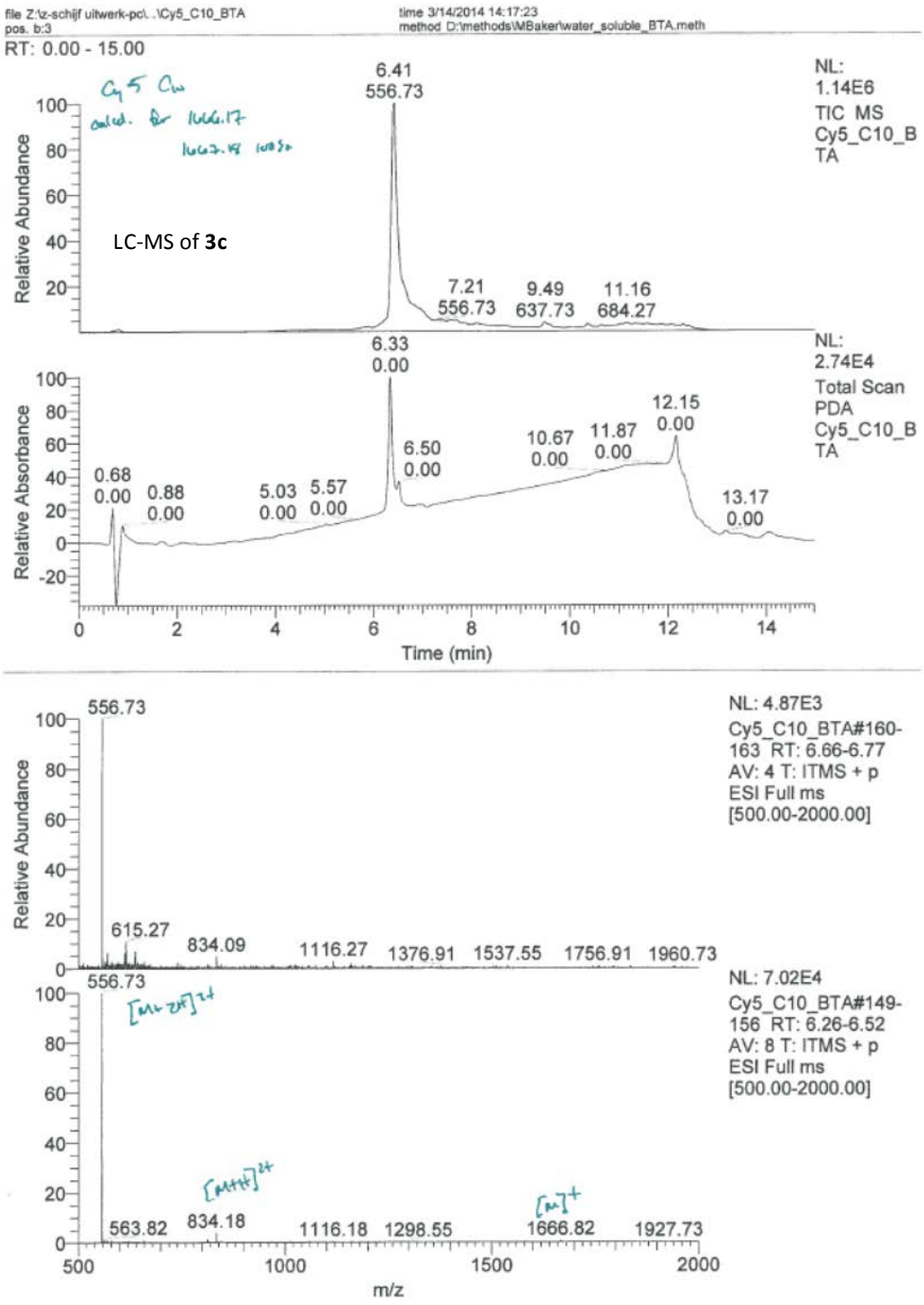
*1-(1-(3,5-Bis((1-amino-3,6,9,12-tetraoxatricosan-23-yl)carbamoyl)phenyl)-1,27-dioxo-14,17,20,23-tetraoxa-2,26-diazadotriacontan-32-yl)-3,3-dimethyl-2-((1E,3E)-3-(1,3,3-trimethylindolin-2-ylidene)prop-1-en-1-yl)-3H-indol-1-ium (**2b**).*

2b was synthesized using the procedure above with **11b** (3.85 mg, 3.10 µmol), Cy3 NHS ester (1.83 mg, 3.10 µmol), and 20 µL of trimethylamine. **2b** was obtained as an amorphous red solid. HPLC-MS (ESI): (m/z) calc for $C_{96}H_{161}N_8O_{16}^+$ 1683.21, observed 1683.82 $[M]^+$.



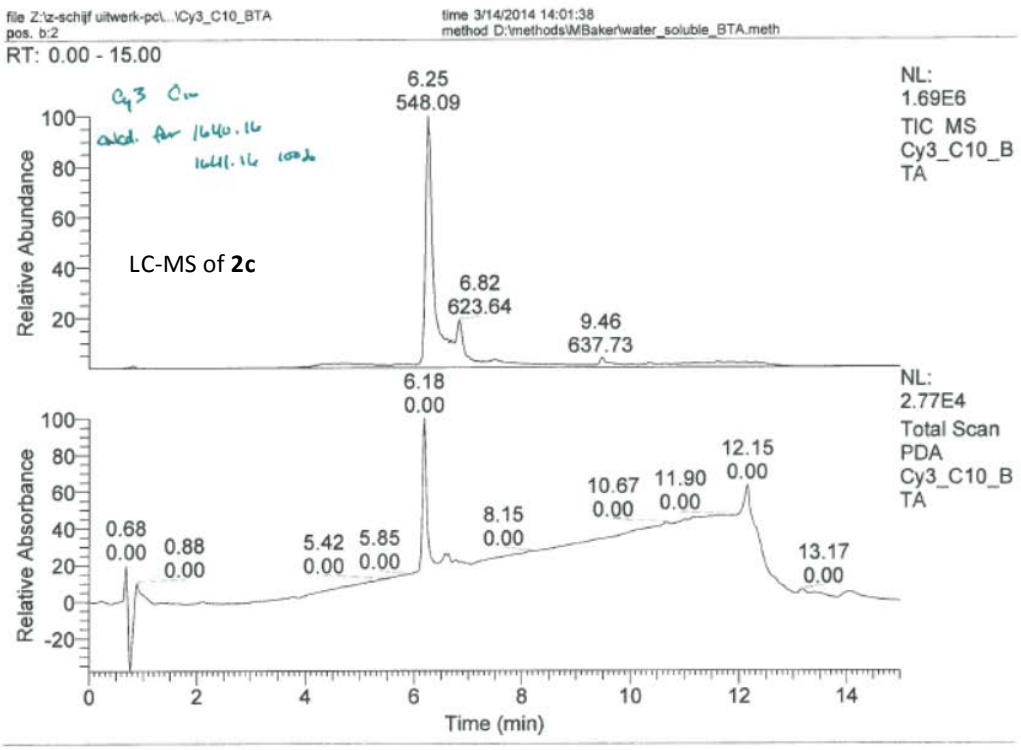
*1-(1-(3,5-Bis((1-amino-3,6,9,12-tetraoxadocosan-22-yl)carbamoyl)phenyl)-1,26-dioxo-13,16,19,22-tetraoxa-2,25-diazahentriacontan-31-yl)-3,3-dimethyl-2-((1E,3E,5E)-5-(1,3,3-trimethylindolin-2-ylidene)penta-1,3-dien-1-yl)-3H-indol-1-ium (**3c**).*

3c was synthesized using the procedure above with **11c** (2.5 mg, 2.08 µmol), Cy5 NHS ester (1.28 mg, 2.08 µmol), and 20 µL of trimethylamine. **3c** was obtained as an amorphous blue solid. HPLC-MS (ESI): (m/z) calc for $C_{98}H_{157}N_8O_{16}^+$ 1667.18, observed 1666.82 $[M]^+$.



*1-(1-(3,5-bis((1-amino-3,6,9,12-tetraoxadocosan-22-yl)carbamoyl)phenyl)-1,26-dioxo-13,16,19,22-tetraoxa-2,25-diazahentriacontan-31-yl)-3,3-dimethyl-2-((1E,3E)-3-(1,3,3-trimethylindolin-2-ylidene)prop-1-en-1-yl)-3H-indol-1-ium (**2c**).*

2c was synthesized using the procedure above with **11c** (2.5 mg, 2.08 µmol), Cy3 NHS ester (1.28 mg, 2.08 µmol), and 20 µL of trimethylamine. **2c** was obtained as an amorphous red solid. HPLC-MS (ESI): (m/z) calc for $C_{93}H_{155}N_8O_{16}^+$ 1641.16, observed 1641.73 $[M]^+$.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time 3/14/2014 14:01:38
method D:\methods\MBaker\water_soluble_BTA.meth
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Cy3 Cl-
calcd. for 1640.16
1641.16 100%
6.25
548.09
6.82
623.64
9.46
637.73
NL:
1.69E6
TIC MS
Cy3_C10_B
TA
Relative Abundance
LC-MS of 2c
6.18
0.00
NL:
2.77E4
Total Scan
PDA
Cy3_C10_B
TA
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0.00
0.88
0.00
5.42
0.00
5.85
0.00
8.15
0.00
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0.00
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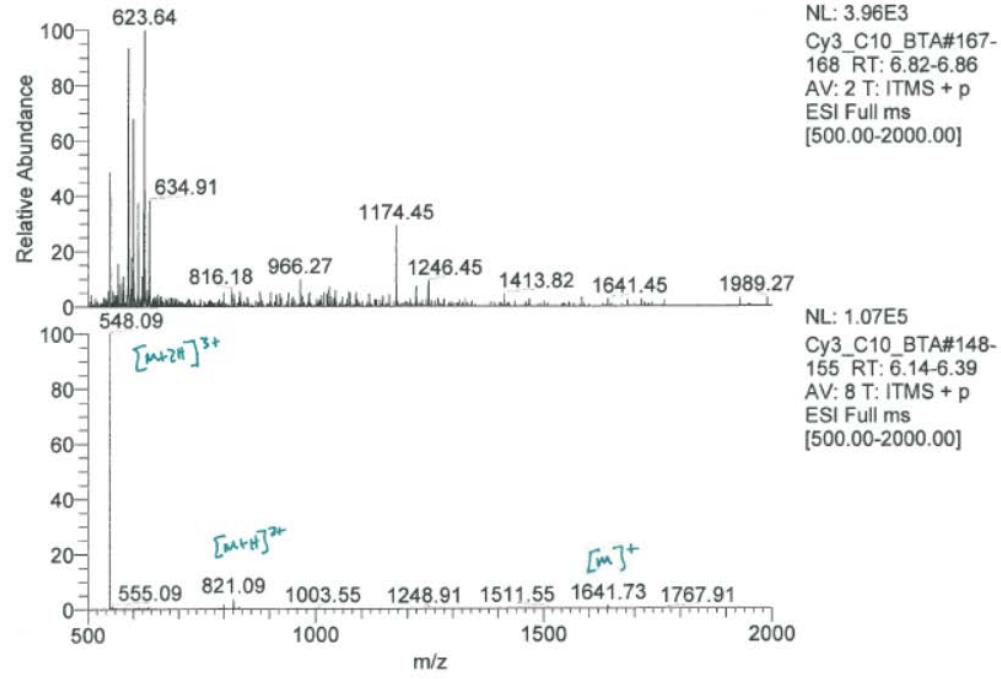
0.00
12.15
0.00
13.17
0.00
Relative Absorbance
Time (min)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966.27
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1413.82
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1989.27
NL: 3.96E3
Cy3_C10_BTA#167-
168 RT: 6.82-6.86
AV: 2 T: ITMS + p
ESI Full ms
[500.00-2000.00]
Relative Abundance
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[M+2H]3+
[M+H]2+
[M]+
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821.09
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1641.73
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[500.00-2000.00]
m/z

Supporting data

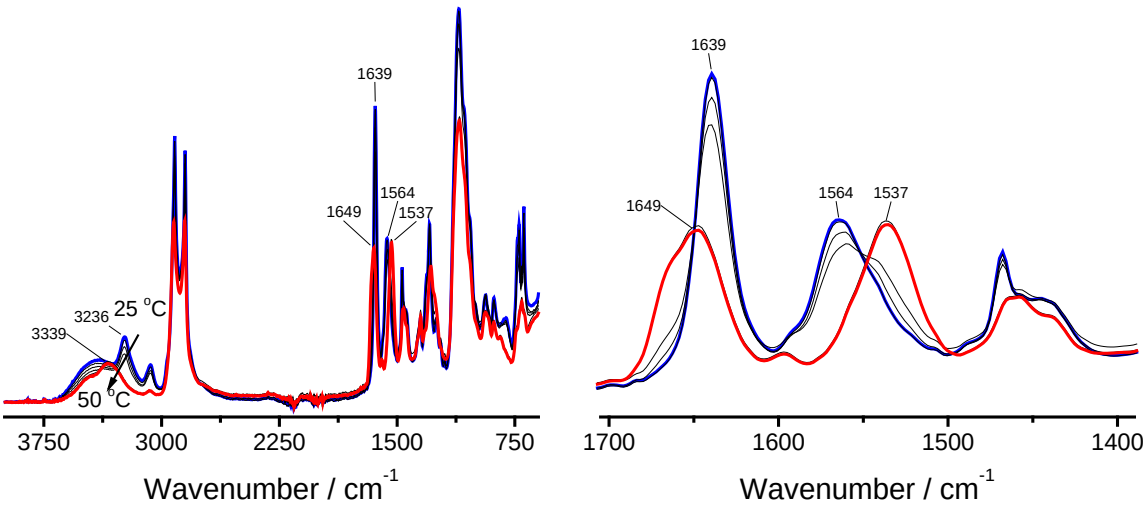

Figure S1: Left: IR spectrum of **1a** in the solid state at different temperatures displaying vibrations indicative for threefold hydrogen bonding at 25 °C (blue) and vibrations typical for the absence of hydrogen bonds at 50 °C (red). Right: zoom of the amide I and amide II vibrations.

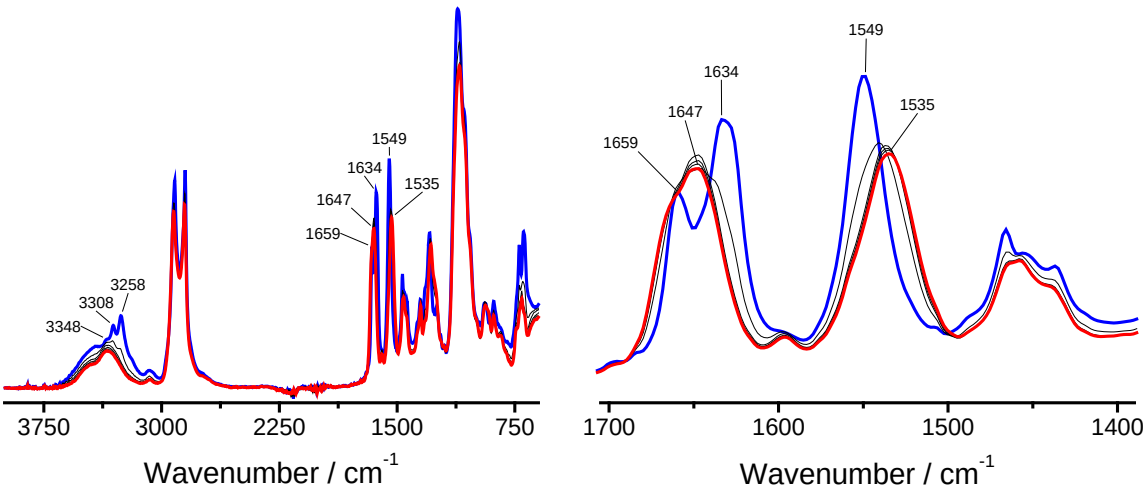

Figure S2: Left: FT-IR spectrum of **1b** in the solid state at different temperatures displaying vibrations indicating the presence of different packing modes at 25 °C (blue) and vibrations typical for the absence of hydrogen bonds at 50 °C (red). Right: zoom of the amide I and amide II vibrations.

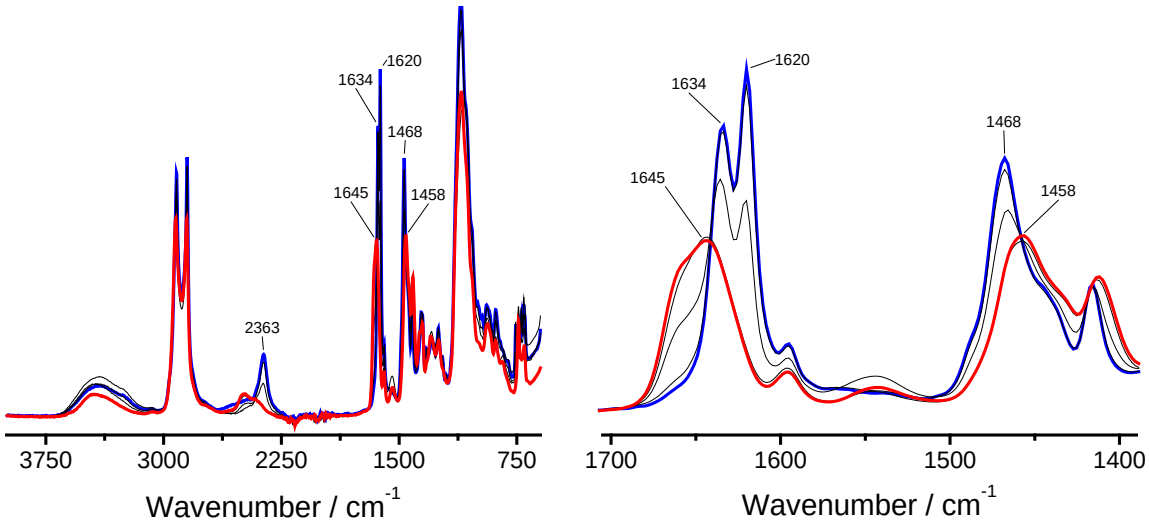

Figure S3: Left: FT-IR spectrum of **1a**-*d6* in the solid state at different temperatures displaying vibrations indicative for threefold hydrogen bonding at 25 °C (blue) and vibrations typical for the absence of hydrogen bonds at 50 °C (red). Right: zoom of the amide I and amide II vibrations.

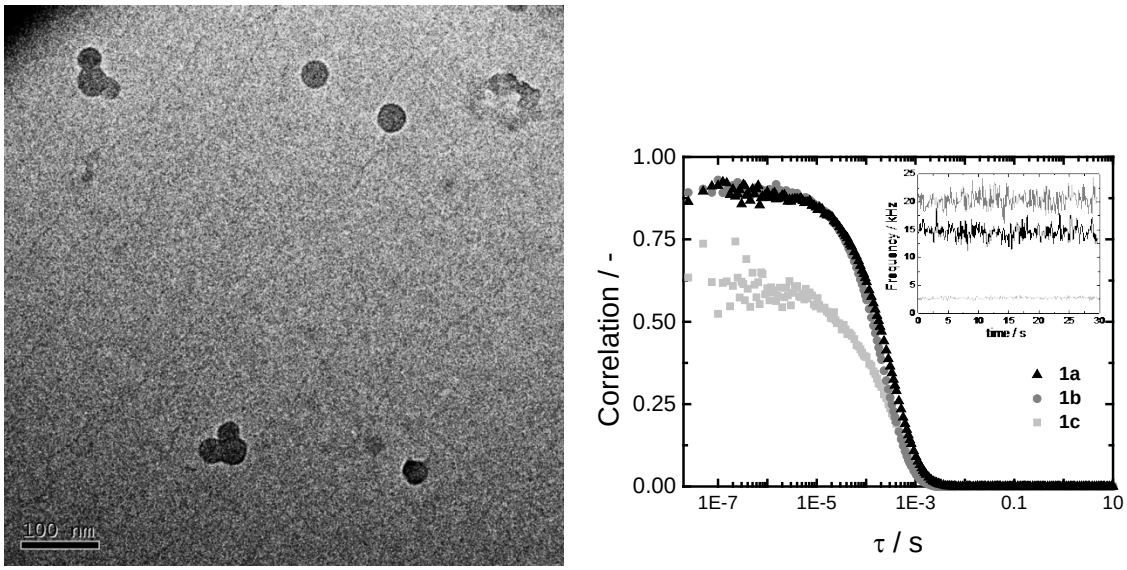

Figure S4: Left: a digitally enhanced image of the cryoTEM of **1b** shows the fibres formed more clearly. Right: Correlation functions of **1a-c** at 90 ° angle and 20 °C (c = 5×10^{-5}M) displaying comparable decay times. Inset: Count rates of **1a-c** where the low count rate of **1c** indicates a low amount of scattering objects.

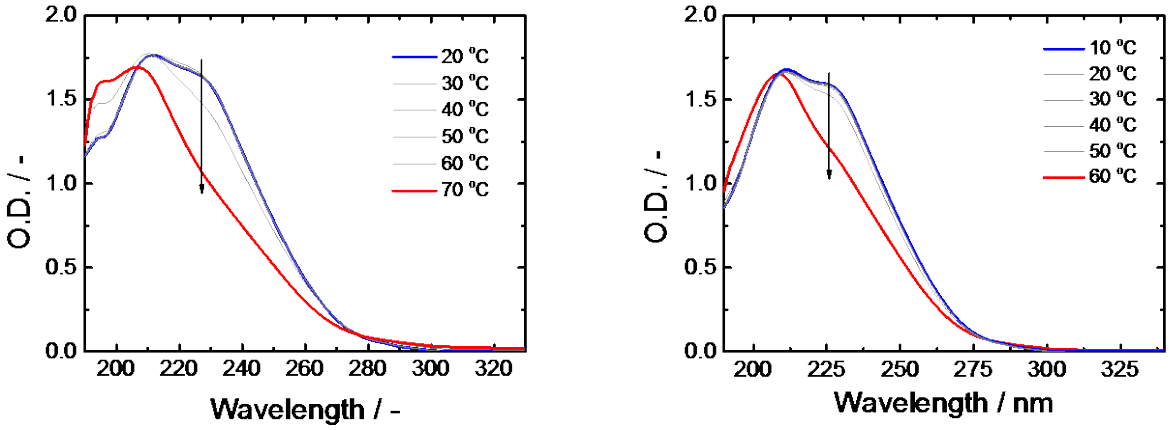

Figure S5: A) UV-vis spectra of **1a** at different temperatures in H_2O (c = 5 × 10^{-5} M). B) UV-vis spectra of **1b** at different temperatures in H_2O (c = 5 × 10^{-5} M).

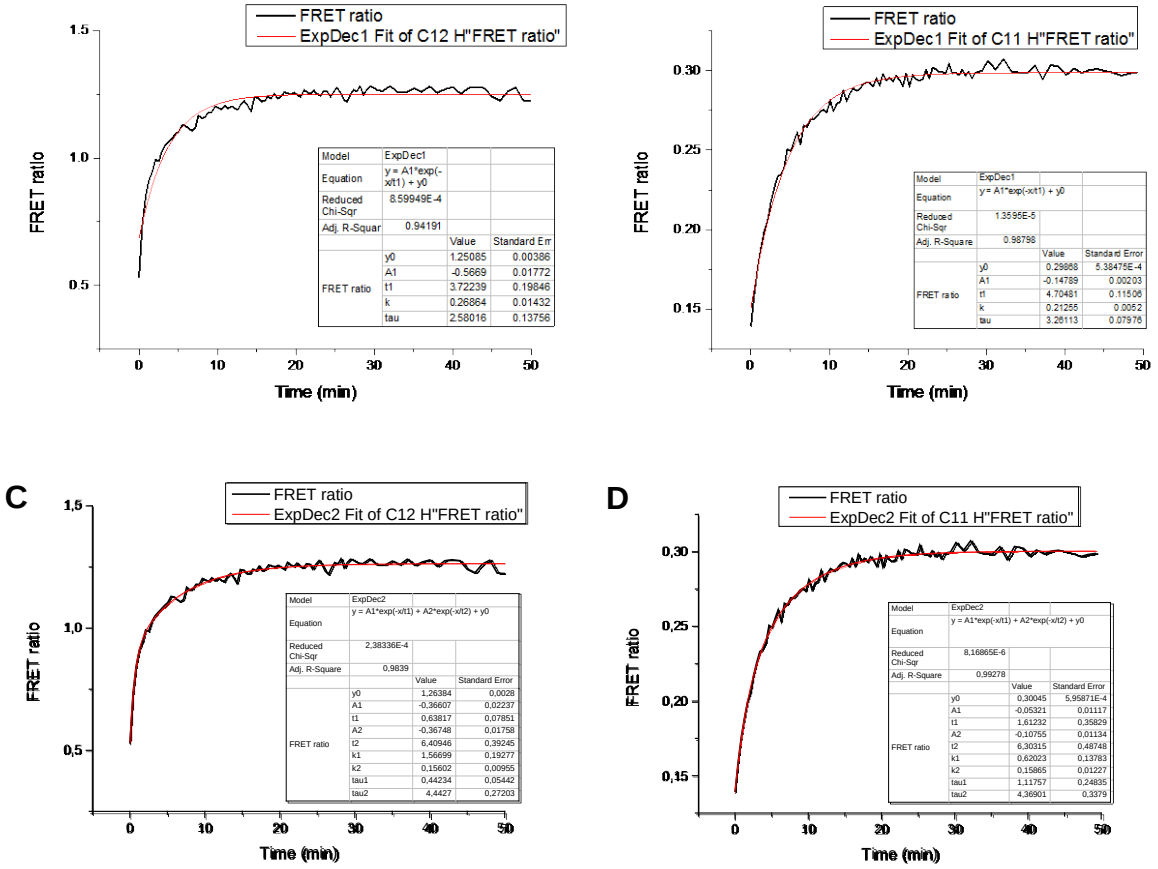

Figure S6: Fitting of FRET experiments was done by a single (A,B) and biexponential curve fit (C.D). The exchange kinetics are similar in both cases although the R^2 values are slightly better for the biexponential fit. Single exponential fit: A) **1a**, t_1 = 3.72 ± 0.20, R^2 = 0.94**.** B) **1b**, t_1 = 4.70 ± 0.12 R^2 = 0.98; Biexponential fit: C) **1a** t_1 = 6.41 ± 0,39, t_2 = 0.64 ± 0,08, R^2 = 0.98; D) **1b** t_1 = 6.30 ± 0.49; t_2 = 1.61 ± 0,36; R^2 = 0.99. In all cases, c_{BTA} = 1 × 10^{-5} M.

1. C. M. A. Leenders, L. Albertazzi, T. Mes, M. M. E. Koenigs, A. R. A. Palmans and E. W. Meijer, *Chem. Commun.*, 2013, **49**, 1963-1965.

2. M. B. Baker, L. Albertazzi, I. K. Voets, C. M. A. Leenders, A. R. A. Palmans, G. M. Pavan and E. W. Meijer, *Nat Commun*, 2015, **6**.