Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information:

Synthesis and Characterization of Uniform PCL-PEG Block Copolymers

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Contents:

1. Materials

1,5,7-Triazabicyclo[4.4.0]dec-5-ene (TBD, >98.0%, TCI), 1,8-diazabicyclo[5.4.0]undec-7-en (DBU, >98.0% (GC), TCI), 3,4-dihydro-2*H*-pyran (DHP, 99%, Acros Organics), acetone (99.5%, Bernd Kraft), acetonitrile (MeCN, HPLC Gradient grade, Fisher Chemical), acetic acid (96%, Carl Roth), ammonium chloride (technical grade, BASF), anhydrous *N*,*N*-Dimethylformamide (DMF, extra dry, 99.8%, stored over molecular sieve, AcroSeal, Fisher Scientific), benzyl bromide (98%, Sigma-Aldrich), calcium chloride (94%, Carl Roth), Celite® 545 (particle size 0.02-0.1 mm, Merck), chloroform (Fisher Chemical, analytical reagent grade stabilized with amylene), chloroform-*d* ($CDCl_3$, 99.80 atom-% D stabilized with silver foils, Eurisotop®), citric acid (99%, Sigma-Aldrich), copper(II) sulfate ($CuSO_4$, ≥99.8%, Sigma Aldrich), cyclohexane (HPLC grade, VWR), dichloromethane (DCM, ≥99.8%, HPLC grade, Fisher Chemical), dicyclohexylcarbodiimide (DCC), diethyl ether (technical grade, VWR), dimethyl sulfoxide-d_6 (DMSO-d_6, 99.80 atom-% D, Eurisotop®), ε-caprolactone (>99%, TCI), ethyl acetate (EA, HPLC grade, VWR), hydrochloric acid (HCl, 37 % solution in water, Acros Organics), hydrogen gas (99.999%, Alphagaz™, H_2, Air Liquide), 1*H*-imidazole (≥99%, Carl Roth), methanol (HPLC-Gradient grade, VWR Chemicals; anhydrous 99.8% Sigma Aldrich), mono methoxy polyethylene glycol ($mPEG_{750}$, M_n = 750, Sigma Aldrich), methyl iodide (contains copper as stabilizer, 99%, Sigma-Aldrich), methyl *tert*-butyl ether (MTBE, 99%, ABCR), *N*,*N*-diisopropylethylamine (DIPEA, ≥99%, Sigma-Aldrich), *N*,*N*-dimethylpyridin-4-amine (DMAP, ≥99%, Sigma-Aldrich), palladium on activated carbon (10 wt% Pd basis, Sigma-Aldrich), potassium *tert*-butoxide (KO*t*Bu, 98+%, pure, Acros Organics), *p*-toluenesulfonic acid monohydrate (99% extra pure, Acros Organics), *p*-toluenesulfonyl chloride (>99%, TCI), pyridine (analytical reagent grade, Fisher Chemical), ruthenium(III) chloride trihydrate (reagent plus, Sigma Aldrich), silica gel (technical grade, pore size 60 Å, 230-400 mesh particle size, 40-63 µm particle size), sodium carbonate (Na_2CO_3, food quality, Solvay), sodium chloride (NaCl, >99.5%, Fisher Scientific), sodium hydride (NaH, 60% dispersion in mineral oil, SigmaAldrich), sodium hydrogencarbonate ($NaHCO_3$, laboratory reagent grade, Fisher Scientific), sodium hydroxid (NaOH, Bernd Kraft, for analysis), sodium iodide (NaI, ≥99.5%, Sigma-Aldrich), sodium periodate ($NaIO_4$, ≥99%, Sigma-Aldrich), sodium sulfate (Na_2SO_4, Bernd Kraft, pure), *tert*-butyldimethylsilylchloride (TBDMS-Cl), tetrabutylammoniumfluoride (TBAF), tetra(ethylene glycol) (≥99.5%, Sigma Aldrich),

tetrahydrofuran (THF, for HPLC, Sigma Aldrich; anhydrous ≥99.9%, inhibitor-free, Sigma Aldrich), thionyl chloride (≥99%, Sigma-Aldrich), toluene (>99.7%, for synthesis, Bernd Kraft; extra dry, 99.8%, stored over molecular sieve, AcroSeal, Fisher Scientific), triethylamine (TEA, 99.5%, Carl Roth), tri(ethylene glycol) (≥98%, for synthesis, Carl Roth), triphenylmethyl chloride (≥95.0% (HPLC), Fluka). Water was deionized by passing through columns packed with ion exchange resins.

ε-Caprolactone was stirred over night over CaH_2 and distilled at 105 °C at 10^{-2} mbar. Afterwards, it was stored over activated molecular sieve (3 and 4 Å) and under argon atmosphere for not longer than two days. Mono methoxy poly(ethylene glycol) ($mPEG_{750}$, M_n = 750) was dissolved in toluene and stirred for one week at 120 °C in a Dean-Stark apparatus. Right before usage, it was dried *via* azeotropic distillation of toluene (3 ×) at 70 °C and 100 to 8 mbar. The macroinitiator was stored under argon atmosphere. TBD was dried at room temperature at 10^{-2} mbar for 24 hours and stored under argon atmosphere. All ring opening polymerizations were performed in flame dried young flasks under inert conditions.

2. Instrumentation

2.1. Nuclear Magnetic Resonance (NMR) spectroscopy

NMR spectra were recorded using the following spectrometer hardware.

Bruker AVANCE 300

^{1}H NMR (300 MHz), ^{13}C-NMR (75 MHz)

Bruker AVANCE 400

^{1}H NMR (400 MHz), ^{13}C-NMR (101 MHz)

Bruker AVANCE 500

^{1}H NMR (500 MHz), ^{13}C-NMR (126 MHz)

DMSO–d_6 and $CDCl_3$ were used as solvents and their respective resonance signals served as reference for the chemical shift δ in parts per million: ^{1}H: $CDCl_3$ = 7.26 ppm, DMSO-d_6 = 2.50 ppm; ^{13}C: $CDCl_3$ = 77.2 ppm, DMSO-d_6 = 39.5 ppm. The spin multiplicity and corresponding signal patterns were abbreviated as follows: s = singlet, d = doublet, t = triplet, q = quartet, quint. = quintet, m = multiplet. Coupling constants *J* were noted in Hz. Furthermore, 2D NMR methods (*e.g.*, heteronuclear single quantum coherence (HSQC), heteronuclear multiple bond correlation (HMBC) and correlated spectroscopy (COSY)) were carried out, if necessary, for signal assignment and structure elucidation. Diffusion-Ordered NMR Spectroscopy (DOSY) measurements were carried out for validation of the product purity.

2.2. Thin Layer Chromatography (TLC)

All thin layer chromatography (TLC) experiments were performed on silica-gel-coated aluminum foil (silica gel 60 F_{254}, layer thickness: 0.25 mm, Sigma-Aldrich). Compounds were visualized by irradiation with a UV lamp (λ = 254 and 365 nm), by staining with Seebach solution (mixture of 5.00 g phosphomolybdic acid hydrate, 2.00 g cerium(IV)-sulfate, 16.0 mL concentrated sulfuric acid and 200 mL water) or vanillin staining solution (mixture of 8.60 g vanillin and 2.50 mL concentrated sulfuric acid and 200 mL ethanol), or $KMnO_4$ staining solution (1.50 g $KMnO_4$, 10.0 g K_2CO_3, 1.25 mL 10% NaOH and 200 mL water).

Infrared (IR) spectroscopy

IR spectra were recorded on a Bruker alpha-p instrument in a frequency range of 3997.41 to 373.828 cm^{-1} applying KBr- and ATR-technology.

2.3. Size Exclusion Chromatography (SEC)

System I Ethylene glycol oligomers were characterized on a Shimadzu Size Exclusion Chromatography (SEC) system equipped with a Shimadzu isocratic pump model LC-20AD, a Shimadzu refractive index detector (24 °C) model RID-20A, a Shimadzu autosampler model SIL-20A and a Varian column oven model 510 (50 °C). For separation, a three-column setup was used with one SDV 3 µm, 8 × 50 mm precolumn and two SDV 3 µm, 1000 Å, 3 × 300 mm columns supplied by PSS, Germany. Anhydrous tetrahydrofuran (THF) stabilized with 250 ppm butylated hydroxytoluene (BHT, ≥99.9%) supplied by Sigma Aldrich was used at a flow rate of 1.0 mL min^{-1}. For calibration, linear poly(methyl methacrylate) standards (Agilent) ranging from 875 Da to 1677 kDa were used. The peak around 20.15 min. is a system peak and does not belong to any impurities. Dispersity *Đ* was determined by integration of the peak in LabSolution software. The program calculates M_w/M_n, which are obtained *via* the calibration.

System II: A PSS SECcurity^2 SEC system based on the Agilent infinity 1260 II hardware was used for the measurements. The system is equipped with a refractive index detector SECcurity² RI, a column oven "(Bio)SECcurity² column compartment TCC6500", a "standard SECcurity²" autosampler, isocratic pump "SECcurity² isocratic pump", and anhydrous tetrahydrofuran (THF) stabilized with 250 ppm butylated hydroxytoluene (BHT, ≥99.9%) supplied by Sigma Aldrich was used at a flow rate of 1.0 mL min^{-1} and at 30 °C as mobile phase. The analysis was performed on the following column system: Two columns PSS SDV analytical (3 µm, 300 × 8.0 mm^2, 1000 Å) with a PSS SDV analytical precolumn (3 µm, 50 × 8.0 mm^2). For the calibration, narrow linear poly(methyl methacrylate) standards (Polymer Standards Service, PPS, Germany) ranging from 102 to 62200 Da were used.

For the preparation of the samples, 1.5 mg of analyte was dissolved in 1.5 mL anhydrous tetrahydrofuran (THF) stabilized with 250 ppm butylated hydroxytoluene (BHT, ≥99.9%) supplied by Sigma Aldrich. All samples were filtered by syringe filter prior to use, to avoid plugging of the injection setup or the column.

2.4. Orbitrap Electrospray Ionization-Mass Spectrometry (ESI-MS)

Mass spectra were recorded on a Q Exactive (Orbitrap) mass spectrometer (Thermo Fisher Scientific, San José, CA, USA) equipped with an atmospheric pressure ionization source operating in the nebulizer assisted electrospray mode. The

instrument was calibrated in the *m*/*z*-range 150-2000 using a standard containing caffeine, Met-Arg-Phe-Ala acetate (MRFA) and a mixture of fluorinated phosphazenes (Ultramark 1621, all from Sigma Aldrich). A constant spray voltage of 3.5 kV, a dimensionless sheath gas of 6, and a sweep gas flow rate of 2 were applied. The capillary voltage and the S-lens RF level were set to 68.0 V and 320 °C, respectively. For the interpretation of the spectra, molecular peaks $[M]^+$, peaks of pseudo molecules $[M+H]^+$, $[M+NH_4]^+$, $[M+Na]^+$ and $[M+K]^+$ and characteristic fragment peaks are indicated with their mass to charge ratio (*m/z*) and their intensity in percent, relative to the most intense peak (100%).

2.5. Size Exclusion Chromatography coupled to Electrospray Ionization-Mass spectrometry (SEC-ESI-MS)

SEC-ESI-MS spectra were recorded on a Q Exactive (Orbitrap) mass spectrometer (Thermo Fisher Scientific, San Jose, CA, USA) equipped with a HESI II probe. The instrument was calibrated in the m/z range 74-1822 using premixed calibration solutions (Thermo Scientific). A constant spray voltage of 4.6 kV, a dimensionless gasflow rate of 8, and a dimensionless auxiliary gas flow rate of 2 were applied. The capillary temperature and the S-lens RF level were set to 320 °C and 62.0 V, respectively. The Q Exactive was coupled to an UltiMate 3000 UHPLC System (Dionex, Sunnyvale, CA, USA) consisting of a pump (LPG 3400SD), an autosampler (WPS 3000TSL), and a thermostatic column department (TCC 3000SD). Separation was performed on two mixed bed size exclusion chromatography columns (Polymer Laboratories, Mesopore 250 × 4.6 mm, particle diameter 3 µm) with precolumn (Mesopore 50 × 4.6 mm) operating at 30 °C. THF at a flow rate of 0.30 mL min^{-1} was used as eluent. The mass spectrometer was coupled to the column in parallel to a RI detector (RefractoMax520, ERC, Japan). 0.27 mL min^{-1} of the eluent were directed through the RI-detector and 30 µL min^{-1} infused into the electrospray source after postcolumn addition of a 100 µM solution of sodium iodide in methanol at 20 µL min^{-1} by a micro-flow HPLC syringe pump (Teledyne ISCO, Model 100DM). A 20 µL aliquot of a polymer solution with a concentration of 1 mg mL^{-1} was injected onto the HPLC system.

2.6. Gas Chromatography – Flame Ionization Detector (GC-FID)

GC chromatograms were recorded on a Bruker 430 GC instrument equipped with capillary column FactorFour™ VF-5ms (30.0 m × 0.25 mm × 0.25 µm), using flame ionization detection (FID). The oven temperature program was: initial temperature

95 °C, hold for 1 min, ramp at 15 °C min^{-1} to 200 °C, hold for 4 min, ramp at 15°C min^{-1} to 300 °C, hold for 2 min. Measurements were performed in split-split mode using nitrogen as the carrier gas (flow rate 30 mL min^{-1}) and were recorded for 20 min in total.

2.7. Differential Scanning Calorimetry (DSC)

The DSC experiments were caried out using a Mettler Toledo DSC star$_e$ system. The DSC experiments are carried out under nitrogen atmosphere using 40 µl aluminium crucibles and a sample mass of 5.5 or 6.5 mg. The BCP were analyzed with the following heating program with two cycles: first heating cycle: isotherm at 25 °C for 5 min; cooling: 25 °C to -15 °C in -10 K min^{-1}, heating: -15 °C to 70 °C in 20 K min^{-1}; cooling: 70 °C to -15 °C in -10 K min^{-1}; second heating cycle: -15 °C to 70 °C in 20 K min^{-1}, cooling: 70 °C to -15 °C in -10 K min^{-1}.

2.8. Fast Atom Bombardment (FAB)

FAB mass spectra were recorded on a Finnigan MAT 95 instrument. The protonated molecule ion is expressed by the term: $[M+H]^+$.

2.9. Small-Angle X-ray Scattering (SAXS)

For the investigation of the BCP SA, a SAXS laboratory camera Xeuss 2.0 Q-Xoom (Xenocs SA, Grenoble, France) was used. The camera is equipped with the X-ray micro focus source Genix3D Cu ULC (Ultra Low divergence) of Cu-k-alpha with an energy of 8.04 keV and a wavelength of 1.5406 Å. Prior the measurement, the samples were self-assembled directly on Kapton® foil *via* thermal or solvent vapor annealing. The sample-to-detector distance was set to 1000 mm and the exposure time to 30 min without a beam stop using the Pilatus3 R 300K detector (Dectris Ltd., Baden, Switzerland).

2.10. Self-assembly of the uniform and non-uniform BCPs

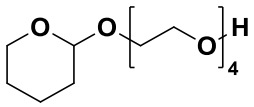
Thermal annealing: 2 mg of the respective BCP was placed directly on Kapton® foil and the sample was heated to 70 °C under vacuum, kept at that temperature for three hours and subsequently cooled to room temperature overnight.

Solvent vapor annealing: 5 mg of the respective polymer was dissolved in 30 µL acetone, one drop was added onto the Kapton® foil and put into a chamber with acetone saturated atmosphere. The solvent was allowed to evaporate over four days.

3. Synthesis

Mono(tetrahydropyranyl) tetra(ethylene glycol) – THP(EG)$_4$OH

Procedure according to BAKER *et al.*[1]



Chemical Formula: $C_{13}H_{26}O_6$
Exact Mass: 278.1729 Da
Molecular Weight: 278.3450 Da

3,4-Dihydro-2*H*-pyran (1.00 mL, 930 mg, 11.1 mmol, 1.00 equiv.) was added dropwise to a mixture of tetra(ethylene glycol) (8.30 mL, 9.34 g, 48.1 mmol, 4.35 equiv.) and *p*-toluenesulfonic acid monohydrate (27.4 mg, 0.14 mmol, 0.013 equiv.) dissolved in dry DCM (17 mL). The reaction mixture was stirred for 24 hours at room temperature. Half of the solvent was evaporated under reduced pressure. Afterwards, the mixture was washed with water (1 × 18 mL) and aqueous NaCl solution (6 × 10 mL) and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure, yielding the crude product as a colorless oil (2.30 g, 74.4%), which was further dried under high vacuum and used without additional purification. ^{1}H NMR analysis indicated a contamination with 12% of the doubly protected product. A full characterization of **THP(EG)$_4$OH** was performed for another batch after purification *via* column chromatography resulting in a decreased yield.

HRMS (ESI) of $C_{13}H_{26}O_6$ $[M+H]^+$ *m/z* calc. 279.1803, detected 279.1798; $[M+Na]^+$ *m/z* calc. 301.1623, detected 301.1616; $[M+NH_4]^+$ *m/z* calc. 296.2068, detected 296.2063; $[M+K]^+$ *m/z* calc. 317.1356, detected 317.1356.

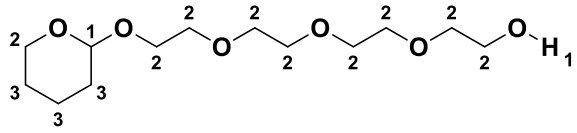
The mass of the tetra(ethylene glycol) was also detected. $C_8H_{18}O_5$ $[M+H]^+$ *m/z* calc. 195.1211, detected 195.1225.

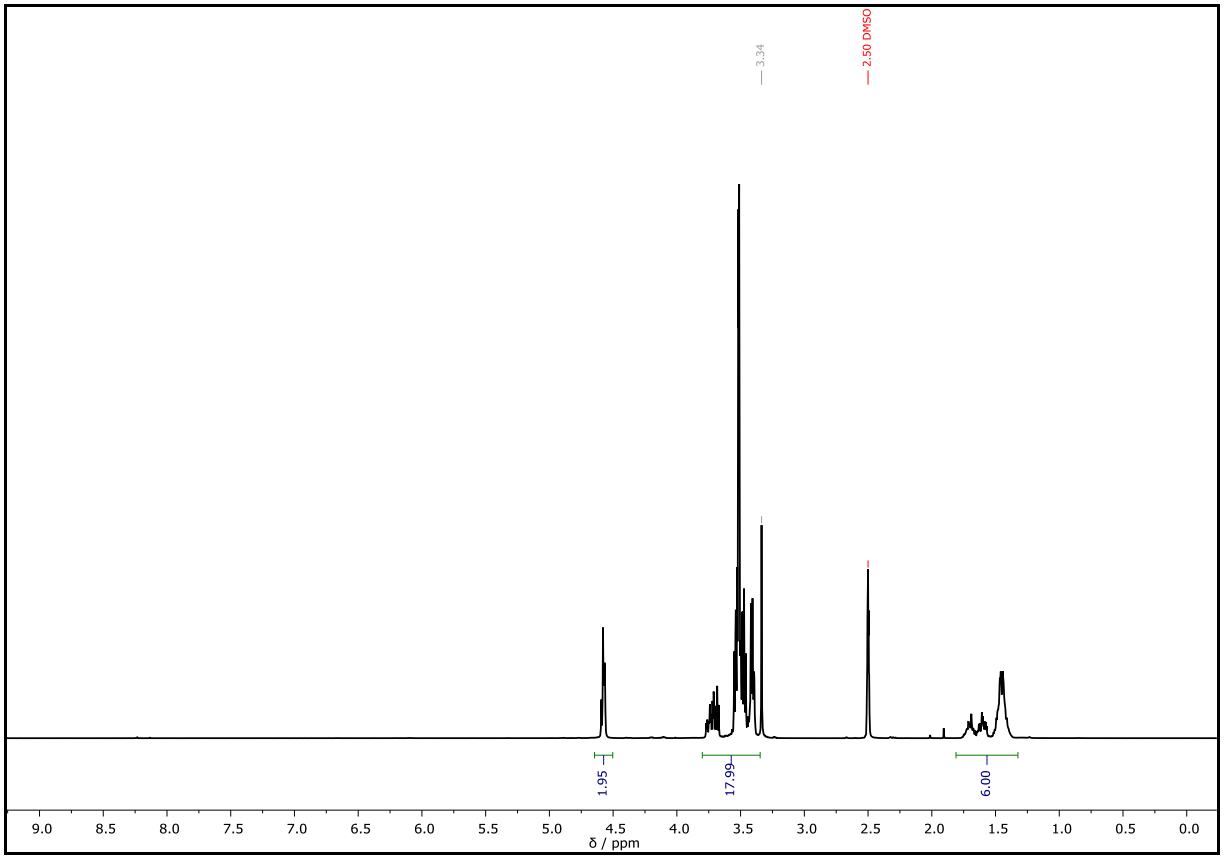
IR (ATR platinum diamond) $\tilde{\nu}$ / cm^{-1} = 3429.8, 2868.8, 1643.6, 1454.5, 1349.0, 1323.5, 1284.8, 1258.4, 1201.5, 1120.1, 1071.1, 1031.9, 985.7, 930.0, 906.9, 871.5, 812.7, 521.1, 428.9.

R_f = 0.17 (EA)

Đ (System I) = 1.00

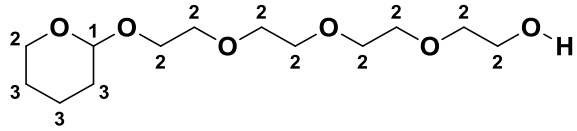
^{1}H NMR (400 MHz, DMSO-d_6): δ / ppm = 4.63 – 4.51 (m, 2H, CH^1 and OH^1), 3.80 – 3.37 (m, 18H, CH_2^2), 1.79 – 1.35 (m, 6H, CH_2^3).

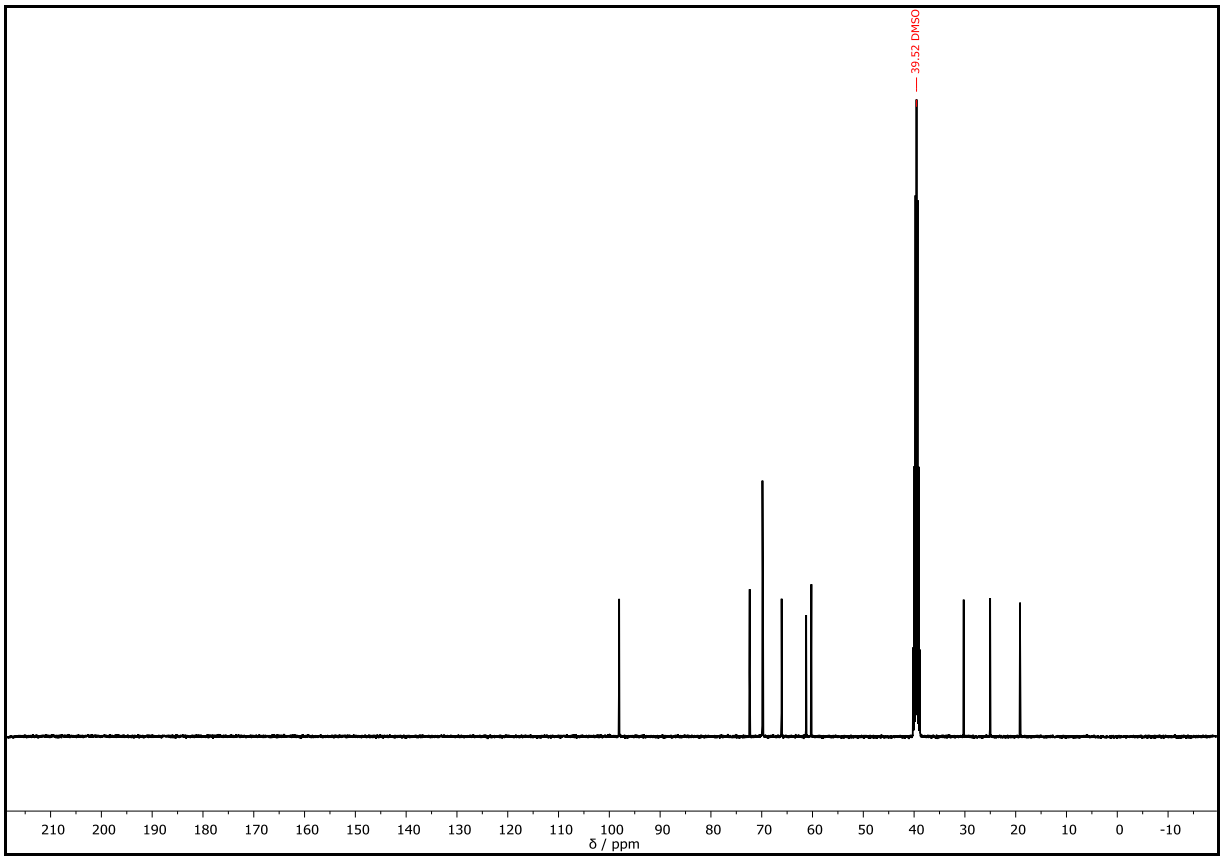




Supplementary Figure 1: ^{1}H NMR spectrum of **THP(EG)$_4$OH** recorded at 400 MHz in DMSO-d_6.

^{13}C NMR (101 MHz, DMSO-d_6): δ / ppm = 98.07 (CH^1), 72.37 (CH_2^2), 69.85 (CH_2^2), 69.81 (CH_2^2), 69.74 (CH_2^2), 66.08 (CH_2^2), 61.25 (CH_2^2), 60.22 (CH_2^2), 30.23 (CH_2^3), 25.03 (CH_2^3), 19.14 (CH_2^3).

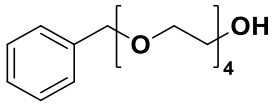




Supplementary Figure 2: ^{13}C NMR spectrum of **THP(EG)$_4$OH** recorded at 101 MHz in DMSO-d_6.

Monobenzyl tetra(ethylene glycol) – Bn(EG)$_4$OH

Procedure according to BRUCE *et al*.[2]



Chemical Formula: $C_{15}H_{24}O_5$
Exact Mass: 284.1624 Da
Molecular Weight: 284.3520 Da

Tetra(ethylene glycol) (69.1 mL, 77.7 g, 400 mmol, 4.00 equiv.) was added to a suspension of sodium hydride (60% dispersion in mineral oil, 16.0 g, 400 mmol, 4.00 equiv.) in dry THF (500 mL). The mixture was refluxed at 80 °C and a solution of benzyl bromide (11.9 mL, 17.1 g, 100 mmol, 1.00 equiv.) in dry THF (80 mL) was added dropwise. The reaction mixture was refluxed for another three hours. After cooling, methanol was slowly added to decompose the remaining excess of sodium hydride. The solvent was evaporated under reduced pressure and the obtained residue was redissolved in 5 wt% aqueous hydrochloric acid (200 mL). The product was extracted with chloroform (8 × 200 mL) and washed with water (1 × 100 mL). The combined organic layers were dried over anhydrous sodium sulfate, filtered, and concentrated *in vacuo*. Purification of the crude product *via* column chromatography (EA) yielded the monobenzylated tetra(ethylene glycol) **Bn(EG)$_4$OH** (23.7 g, 83.4 mmol, 83.4%) as a colorless oil. The product was dried under high vacuum before further use.

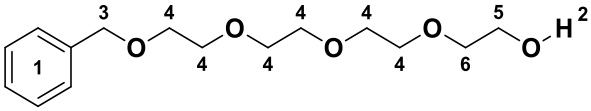
HRMS (ESI) of $C_{15}H_{24}O_5$ $[M+H]^+$ *m/z* calc. 285.1698, detected 285.1692; $[M+NH_4]^+$ *m/z* calc. 302.1963, detected 302.1957; $[M+Na]^+$ *m/z* calc. 307.1517, detected 307.1510; $[M+K]^+$ *m/z* calc. 323.1251, detected 323.1249.

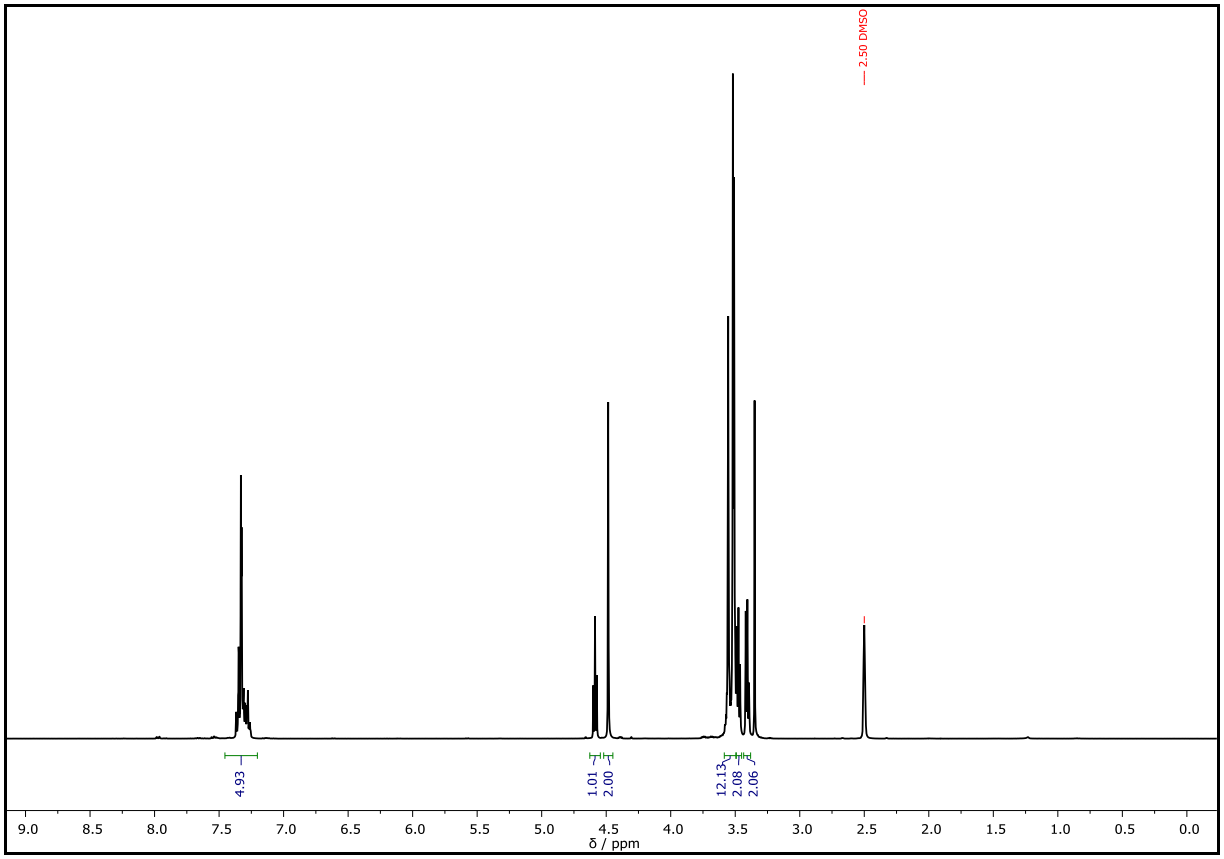
IR (ATR platinum diamond) $\tilde{\nu}$ / cm^{-1} = 3435.0, 2865.9, 1718.7, 1641.8, 1453.5, 1350.3, 1276.8, 1249.4, 1092.7, 940.4, 885.0, 846.5, 738.6, 698.4, 606.1, 526.9.

R_f = 0.25 (EA)

Đ (System I) = 1.00

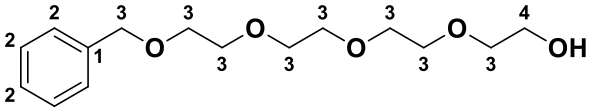
^{1}H NMR (400 MHz, DMSO-d_6): δ / ppm = 7.48 – 7.16 (m, 5H, H_{Ar}^1), 4.58 (t, *J* = 5.4 Hz, 1H, OH^2), 4.48 (s, 2H, CH_2^3), 3.59 – 3.37 (m, 12H, CH_2^4), 3.48 (t, *J* = 5.3 Hz, 2H, CH_2^5), 3.41 (t, *J* = 5.4 Hz, 2H, CH_2^6).

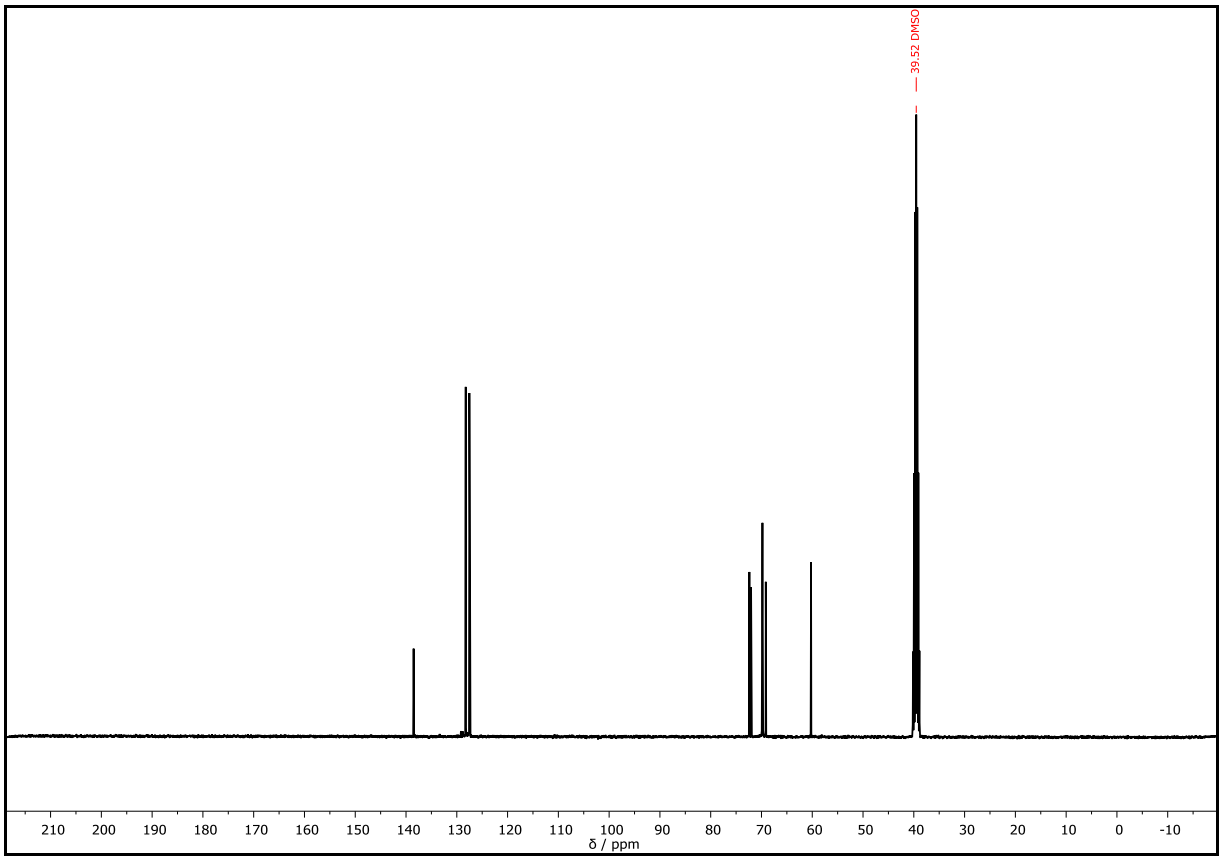




Supplementary Figure 3: ^{1}H NMR spectrum of **Bn(EG)$_4$OH** recorded at 400 MHz in DMSO-d_6.

^{13}C NMR (101 MHz, DMSO-d_6): δ / ppm = 138.50 (C_q^1), 128.24 (C_{Ar}^2), 127.51 (C_{Ar}^2), 127.39 (C_{Ar}^2), 72.37 (CH_2^3), 72.04 (CH_2^3), 69.87 (CH_2^3), 69.86 (CH_2^3), 69.83 (CH_2^3), 69.80 (CH_2^3), 69.79 (CH_2^3), 69.15 (CH_2^3), 60.23 (CH_2^4).

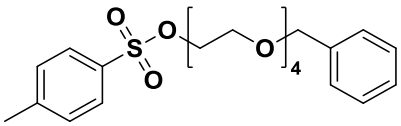




Supplementary Figure 4: ^{13}C NMR spectrum of **Bn(EG)$_4$OH** recorded at 101 MHz in DMSO-d_6.

Monobenzyl tetra(ethylene glycol) tosylate – Bn(EG)$_4$Ts

Procedure according to BRUCE *et al*.[2]



Chemical Formula: $C_{22}H_{30}O_7S$
Exact Mass: 438.1712 Da
Molecular Weight: 438.5350 Da

Monobenzyl tetra(ethylene glycol) **Bn(EG)$_4$OH** (2.00 g, 7.03 mmol, 1.00 equiv.) was dissolved in THF (5.00 mL) and added dropwise to a solution of sodium hydroxide (984 mg, 24.6 mmol, 3.50 equiv.) in water (5.00 mL) at 0 °C. Then, a solution of *p*-toluenesulfonyl chloride (1.61 g, 8.44 mmol, 1.20 equiv.) dissolved in THF (5.00 mL) was added dropwise, after which the reaction mixture was allowed to warm to room temperature and stirred for 15 hours. Subsequently, 1M HCl was slowly added to neutralize the excess of NaOH while cooling in an ice bath. The solvent was evaporated under reduced pressure and the product was extracted with DCM (3 × 75 mL). The combined organic layers were washed with 10% aqueous Na_2CO_3 (2 × 60 mL) and water (4 × 60 mL), dried over anhydrous sodium sulfate, filtered, and concentrated *in vacuo*. Purification of the crude product *via* column chromatography (cyhex:EA = 1:1) yielded the monobenzyl tetra(ethylene glycol) tosylate **Bn(EG)$_4$Ts** (2.96 g, 6.75 mmol, 96.2%) as a colorless oil. The product was dried under high vacuum, stored under argon atmosphere, and shielded from light until further use.

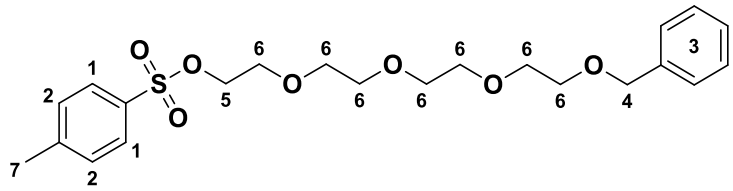
HRMS (ESI) of $C_{22}H_{30}O_7S$ $[M+H]^+$ *m/z* calc. 439.1780, detected 439.1762.

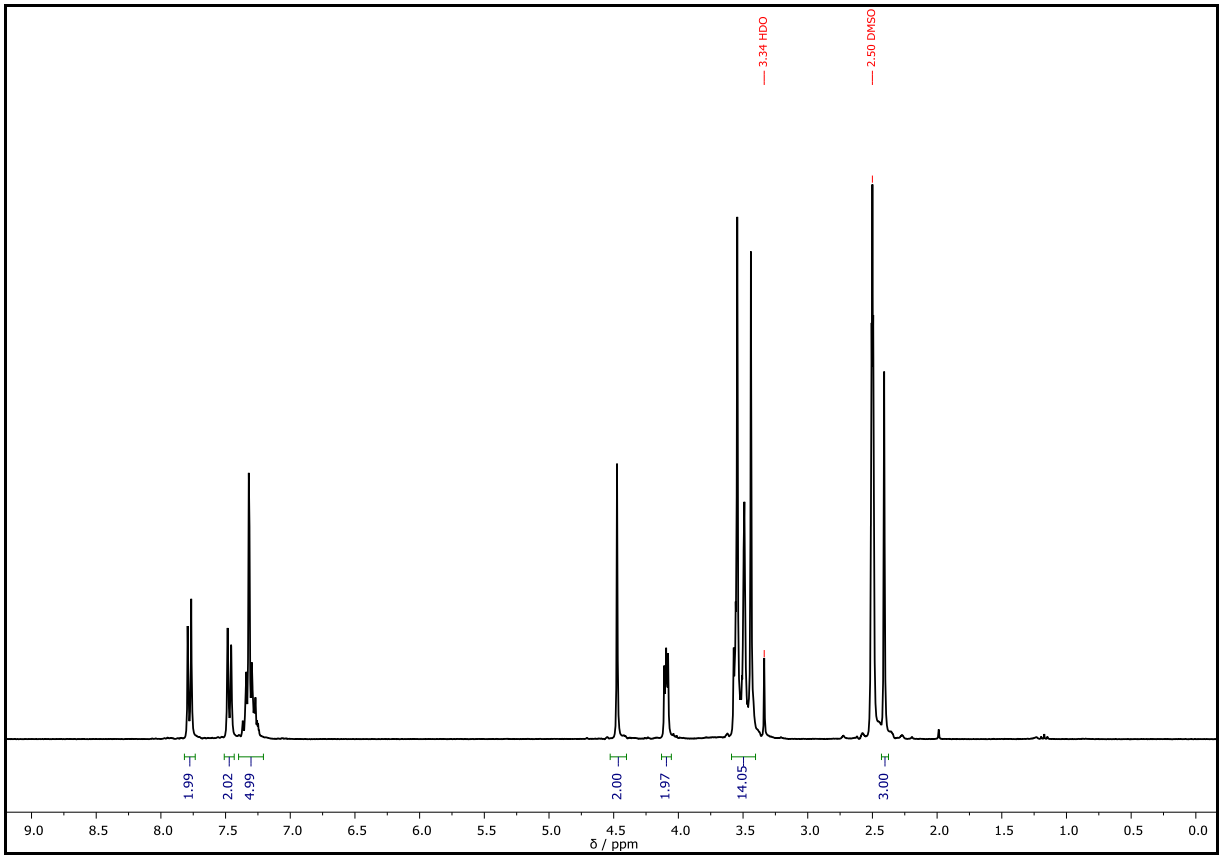
IR (ATR platinum diamond) $\tilde{\nu}$ / cm^{-1} = 2865.6, 1597.8, 1495.4, 1453.2, 1353.2, 1292.0, 1248.8, 1188.7, 1175.0, 1094.6, 1016.3, 916.8, 815.3, 774.0, 740.4, 698.6, 662.0, 582.3, 552.9, 465.4.

R_f = 0.45 (cyhex:EA = 1:1).

Đ (System I) = 1.00

^{1}H NMR (300 MHz, DMSO-d_6): δ / ppm = 7.83 – 7.71 (m, 2H, CH_{Ar}^{1}), 7.53 – 7.42 (m, 2H, CH_{Ar}^{2}), 7.40 – 7.23 (m, 5H, H_{Ar}^{3}), 4.47 (s, 2H, CH_2^{4}), 4.16 – 4.03 (m, 2H, CH_2^{5}), 3.62 – 3.40 (m, 14H, CH_2O^{6}), 2.41 (s, 3H, CH_3^{7}).

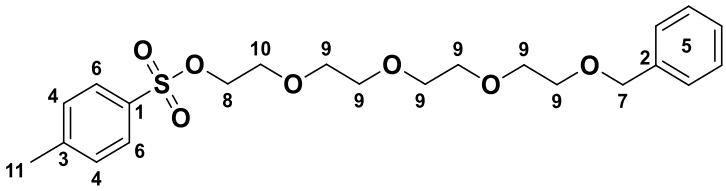


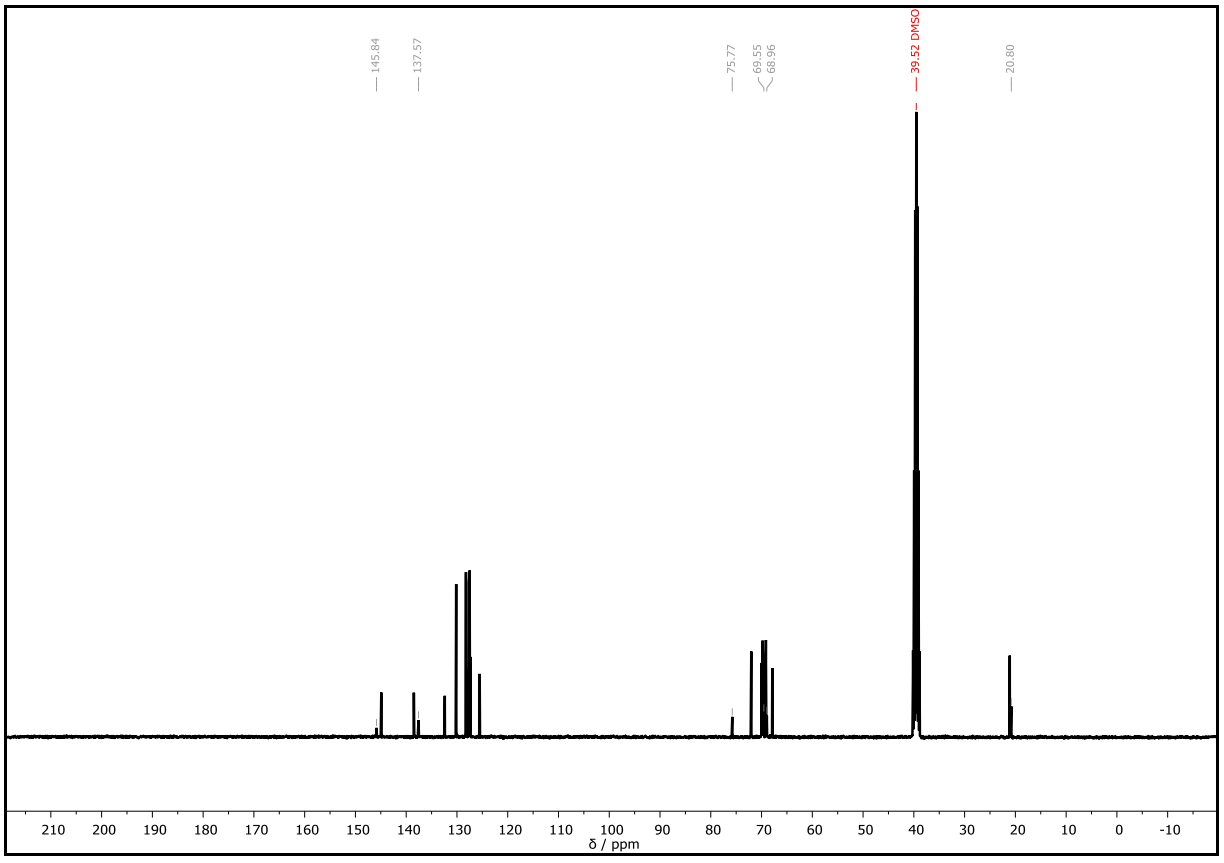


Supplementary Figure 5: ^{1}H NMR spectrum of **Bn(EG)$_4$Ts** recorded at 300 MHz in DMSO-d_6.

^{13}C NMR (101 MHz, DMSO-d_6): δ / ppm = 144.84 (C_q^1), 138.42 (C_q^2), 132.33 (C_q^3), 130.08 (CH_{Ar}^4), 128.21 (CH_{Ar}^5), 127.99 (CH_{Ar}^5), 127.58 (CH_{Ar}^6), 127.47 (CH_{Ar}^5), 71.97 (CH_2^7), 69.94 (CH_2^8), 69.76 (CH_2^9), 69.74 (CH_2^9), 69.71 (CH_2^9), 69.68 (CH_2^9), 69.65 (CH_2^9), 69.61 (CH_2^9), 69.08 (CH_2^{10}), 21.05 (CH_3^{10}).

Please note: the product partially degraded in the time between the ^{1}H and the ^{13}C NMR measurement. The impurities are marked in the ^{13}C NMR spectrum (Supplementary Figure 6)

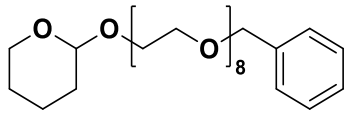




Supplementary Figure 6: ^{13}H NMR spectrum of **Bn(EG)$_4$Ts** recorded at 101 MHz in DMSO-d_6.

α-Benzyl-ω-tetrahydropyranyl octa(ethylene glycol) – THP(EG)$_8$Bn

Procedure according to BAKER *et al*.[1]



Chemical Formula: $C_{28}H_{48}O_{10}$
Exact Mass: 544.3247 Da
Molecular Weight: 544.6820 Da

Mono(tetrahydropyranyl) tetra(ethylene glycol) **THP(EG)$_4$OH** (500 mg, 1.80 mmol, 1.00 equiv.) dissolved in dry THF (1.50 mL) was added to sodium hydride (60% dispersion in mineral oil, 144 mg, 3.60 mmol, 2.00 equiv.) and sodium iodide (14.0 mg, 94.4 µmol, 0.05 equiv.) in dry THF (10.5 mL). The reaction mixture was cooled to 0 °C with an ice bath and a solution of monobenzyl tetra(ethylene glycol) monotosylate **Bn(EG)$_4$Ts** (868 mg, 1.98 mmol, 1.10 equiv.) in dry THF (2.14 mL) was added dropwise over one hour. Purification of the crude product *via* column chromatography (DCM:MeOH = 40:1) afforded the α-benzyl-ω-tetrahydropyranyl octa(ethylene glycol) **THP(EG)$_8$Bn (A)** as a colorless oil (671 mg, 1.23 mmol, 68.4%). The product was dried under high vacuum until further use.

HRMS (ESI) of $C_{28}H_{48}O_{10}$ $[M+Na]^+$ *m/z* calc. 567.3142, detected 567.3126; $[M+K]^+$ *m/z* calc. 583.2876, detected 583.2864.

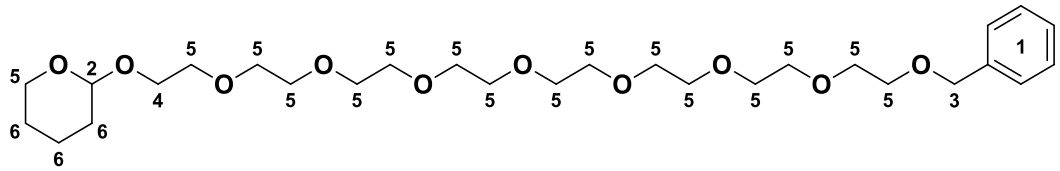
The mass of the α-benzyl-ω-tetrahydropyranyl hepta(ethylene glycol) was also detected. $[M+Na]^+$ *m/z* calc. 523.2880, detected 523.2866; $[M+K]^+$ *m/z* calc. 539.2614, detected 539.2606.

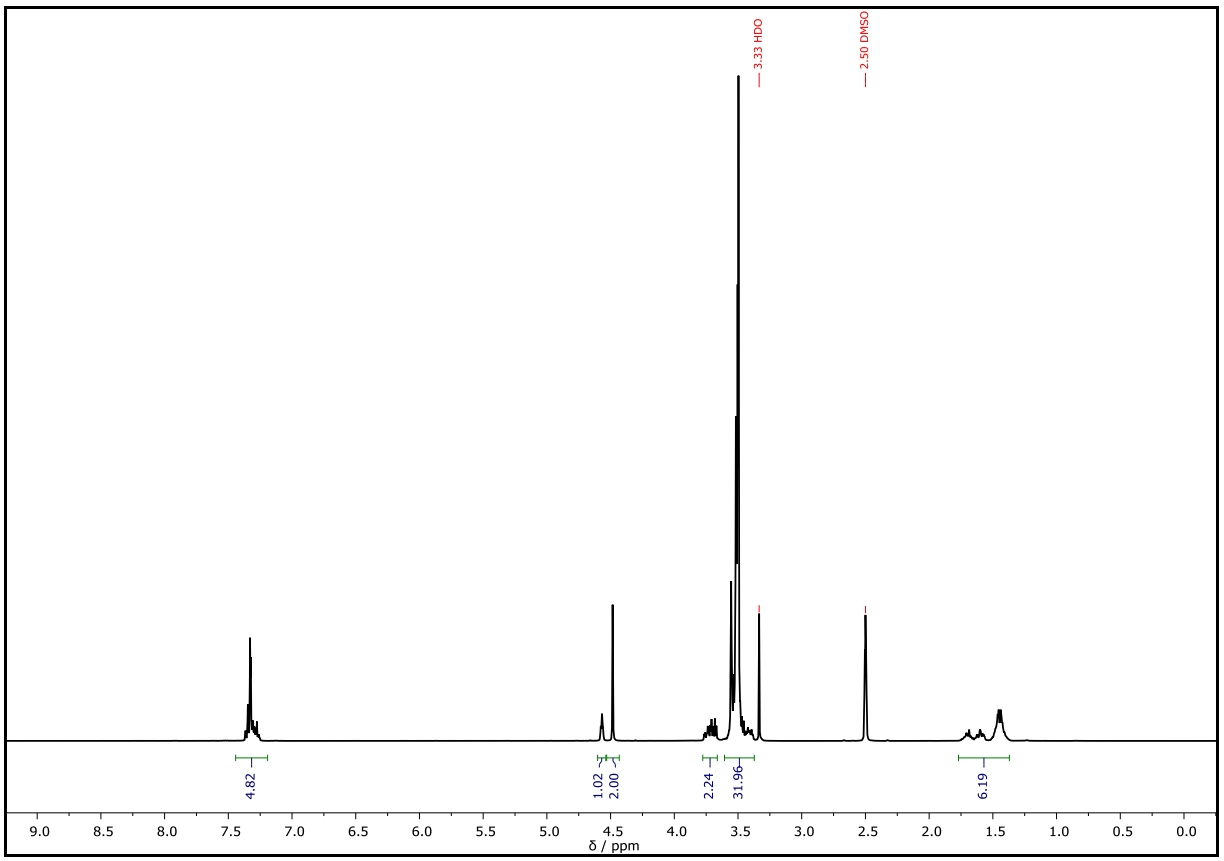
IR (ATR platinum diamond) $\tilde{\nu}$ / cm^{-1} = 2865.7, 1453.9, 1349.5, 1287.0, 1250.0, 1201.5, 1098.1, 1032.7, 987.0, 871.5, 813.8, 739.0, 698.9, 536.8, 428.9.

R_f = 0.18 (EA)

Đ (System I) = 1.00

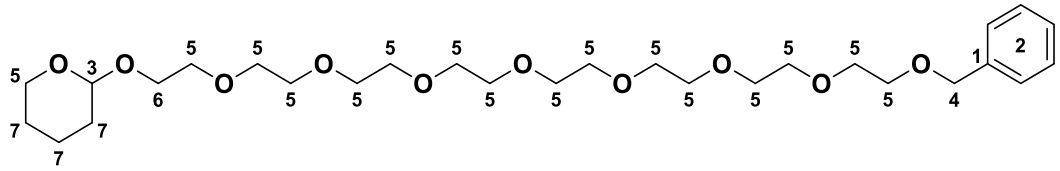
^{1}H NMR (400 MHz, DMSO-d_6): δ / ppm = 7.43 – 7.21 (m, 5H, H_{Ar}^{1}), 4.57 (d, J = 3.7 Hz, 1H, CH^{2}), 4.49 (d, J = 2.3 Hz, 2H, CH_2^{3}), 3.79 – 3.64 (m, 2H, CH_2^{4}), 3.63 – 3.35 (m, 32H, CH_2O^{5}), 1.78 – 1.35 (m, 6H, CH_2^{6}).

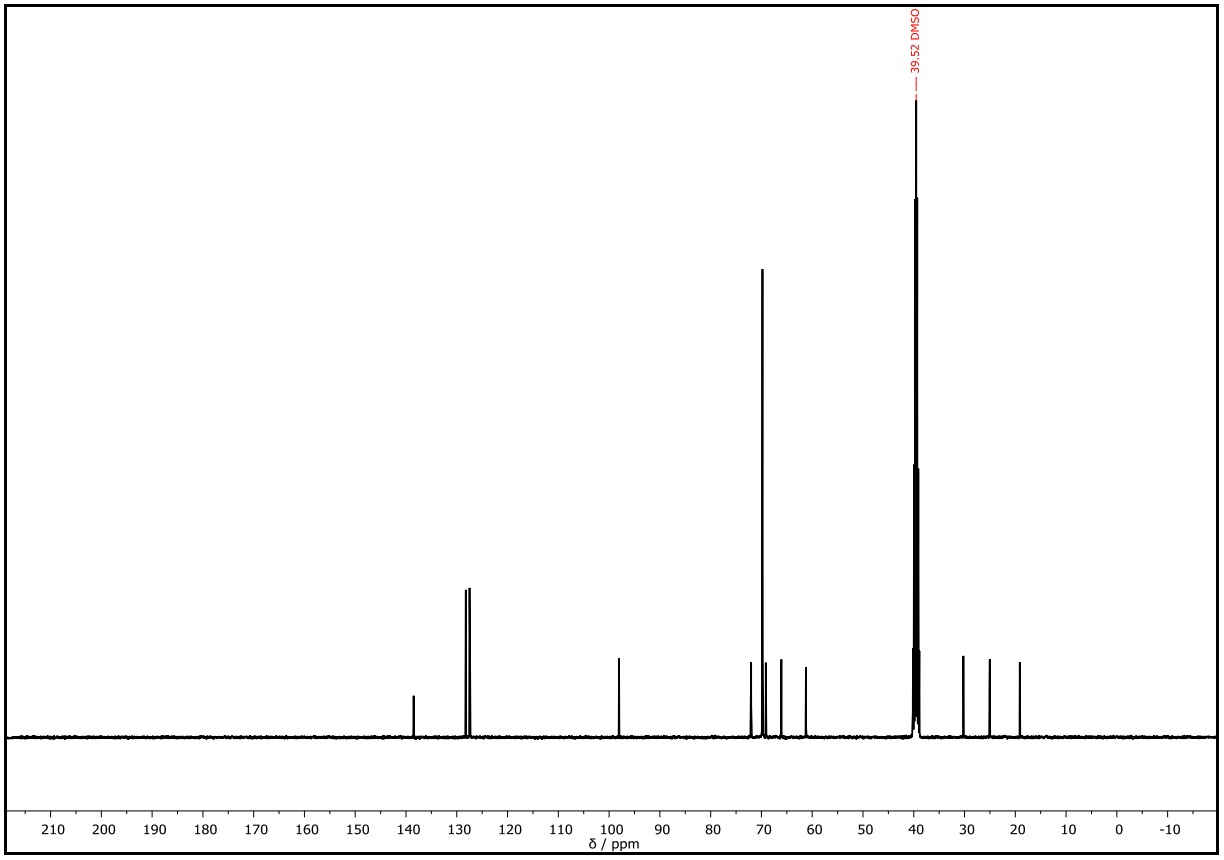




Supplementary Figure 7: ^{1}H NMR spectrum of **THP(EG)$_8$Bn (A)** recorded at 400 MHz in DMSO-d_6.

^{13}C NMR (101 MHz, DMSO-d_6): δ / ppm = 138.49 (C_q^1), 128.21 (CH_{Ar}^2), 127.48 (CH_{Ar}^2), 127.36 (CH_{Ar}^2), 98.04 (CH^3), 72.02 (CH_2^4), 69.85 (CH_2^5), 69.81 (CH_2^5), 69.79 (CH_2^5), 69.73 (CH_2^5), 69.14 (CH_2^5), 66.07 ($CH_2^{5,6}$), 61.23 ($CH_2^{5,6}$), 30.22 (CH_2^7), 25.03 (CH_2^7), 19.12 (CH_2^7).





Supplementary Figure 8: ^{13}C NMR spectrum of **THP(EG)$_8$Bn (A)** recorded at 101 MHz in DMSO-d_6.

Procedure according to Bruce *et al*.[2]

The synthesis of product **THP(EG)$_8$Bn** was repeated according to the procedure of Bruce *et al*. using mono(tetrahydropyranyl) tetra(ethylene glycol) **THP(EG)$_4$OH** (261 mg, 0.94 mmol, 1.00 equiv.), KO*t*Bu (145 mg, 1.29 mmol, 1.37 equiv.), monobenzyl tetra(ethylene glycol) monotosylate **THP(EG)$_4$Ts** (530 mg, 1.21 mmol, 1.29 equiv.). Here, water instead of 1M aqueous HCl was added to quench the reaction. The crude product was analyzed *via* SEC-ESI-MS and the calculated and detected masses of the formed molecules are summarized in Supplementary Table 1. Purification of the crude product *via* column chromatography (EA:methanol = 1:0 → 9:1) yielded the α-benzyl-ω-tetrahydropyranyl octa(ethylene glycol) **THP(EG)$_8$Bn (B)** (243 mg, 0.45 mmol, 47.6%) as a yellowish oil. The product was dried under high vacuum before further use.

The analytical data is consistent with the one of **THP(EG)$_8$Bn (A)**.

Supplementary Table 1: SEC-ESI-MS results of **THP(EG)8Bn (B)**.

Formular	M calc. / Da[1]	M detected / Da
$[Bn(EG)_{16}OH+H]^+$	813.4845	813.4807
$[THP(EG)_{16}OH+H]^+$	807.4951	807.4912
$[Bn(EG)_{12}Bn+Na]^+$	749.4086	749.4064
$[THP(EG)_{12}Bn+Na]^+$	743.4191	743.4171
$[THP(EG)_{12}THP+Na]^+$	737.4297	737.4277
$[Bn(EG)_{12}OH+H]^+$	637.3796	637.3781
$[THP(EG)_{12}OH+H]^+$	631.3902	631.3831
$[THP(EG)_8Bn+Na]^+$	567.3142	567.3127
$[Bn(EG)_8OH+H]^+$	461.2747	461.2737
$[Bn(EG)_4Ts+Na]^+$	461.1599	461.1594
$[Bn(EG)_4Ts+H]^+$	439.1780	439.1775

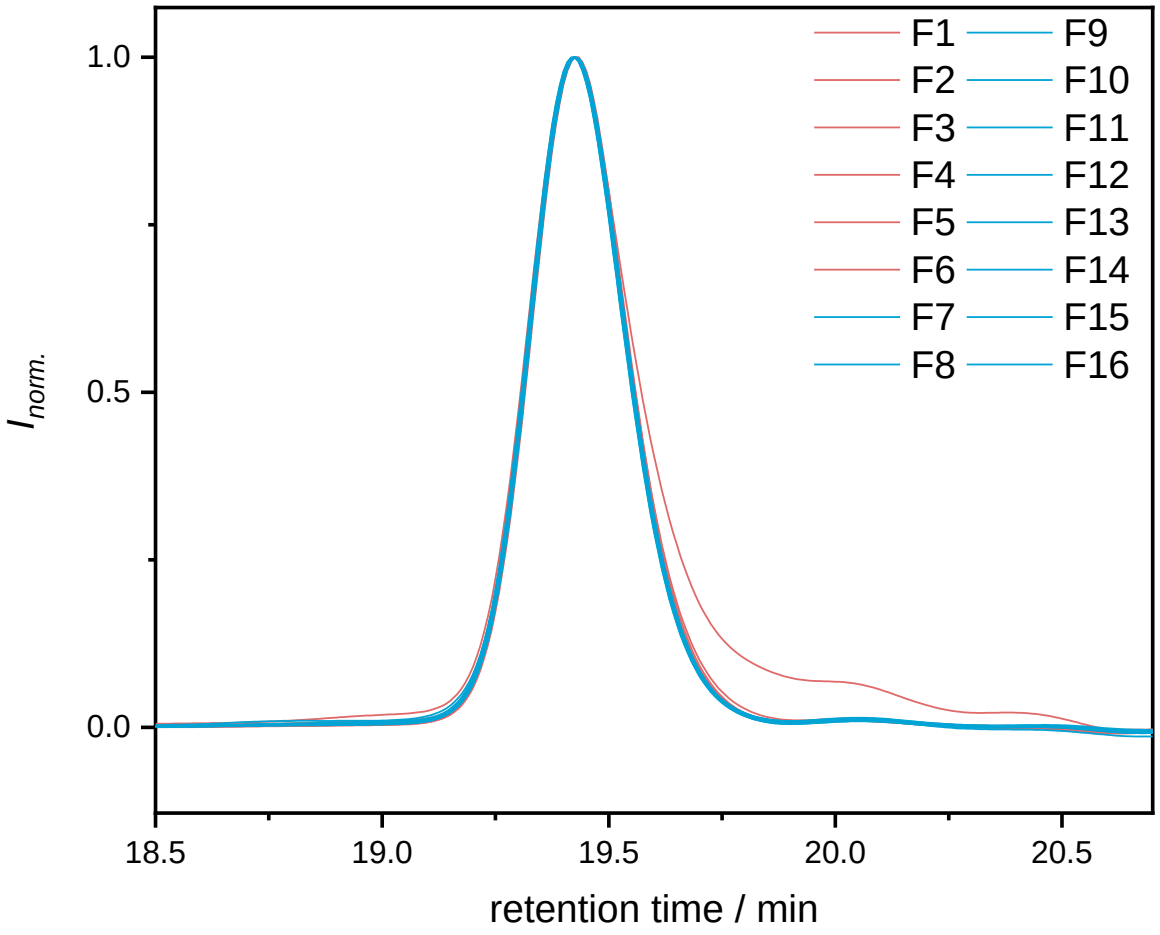
[1] mMass Version 5.5.0 was used for the mass calculations

The synthesis of **THP(EG)$_8$Bn (B)** was repeated on a 58.7 g scale and the purification *via* column chromatography is reported in the following.

Supplementary Table 2: SEC results of the first purification of **THP(EG)$_8$Bn (B)**.

cc	*m* / g	M_n / Da	M_w / Da	M_z / Da	*Đ*	purity / %
F1	14.6	650	650	650	1.00	98
F2	6.67	700	700	700	1.00	97
F3	5.11	700	700	700	1.00	97
F4	4.36	700	700	700	1.00	98
F5	3.63	700	700	700	1.00	98
F6	2.84	700	700	700	1.00	98
F7	2.10	700	700	700	1.00	>99
F8	1.68	700	700	700	1.00	>99
F9	1.05	700	700	700	1.00	>99
F10	0.89	700	700	700	1.00	>99
F11	0.57	700	700	700	1.00	>99
F12	0.85	700	700	700	1.00	>99
F13	0.55	700	700	700	1.00	>99
F14	0.58	700	700	700	1.00	>99
F15	0.49	700	700	700	1.00	>99

eluent: DCM:Acetone = 4:1 → EA:MeOH = 9:1; Yellow: product containing fractions with insufficient purity; green: fractions containing only product **THP(EG)$_8$Bn (B)**.



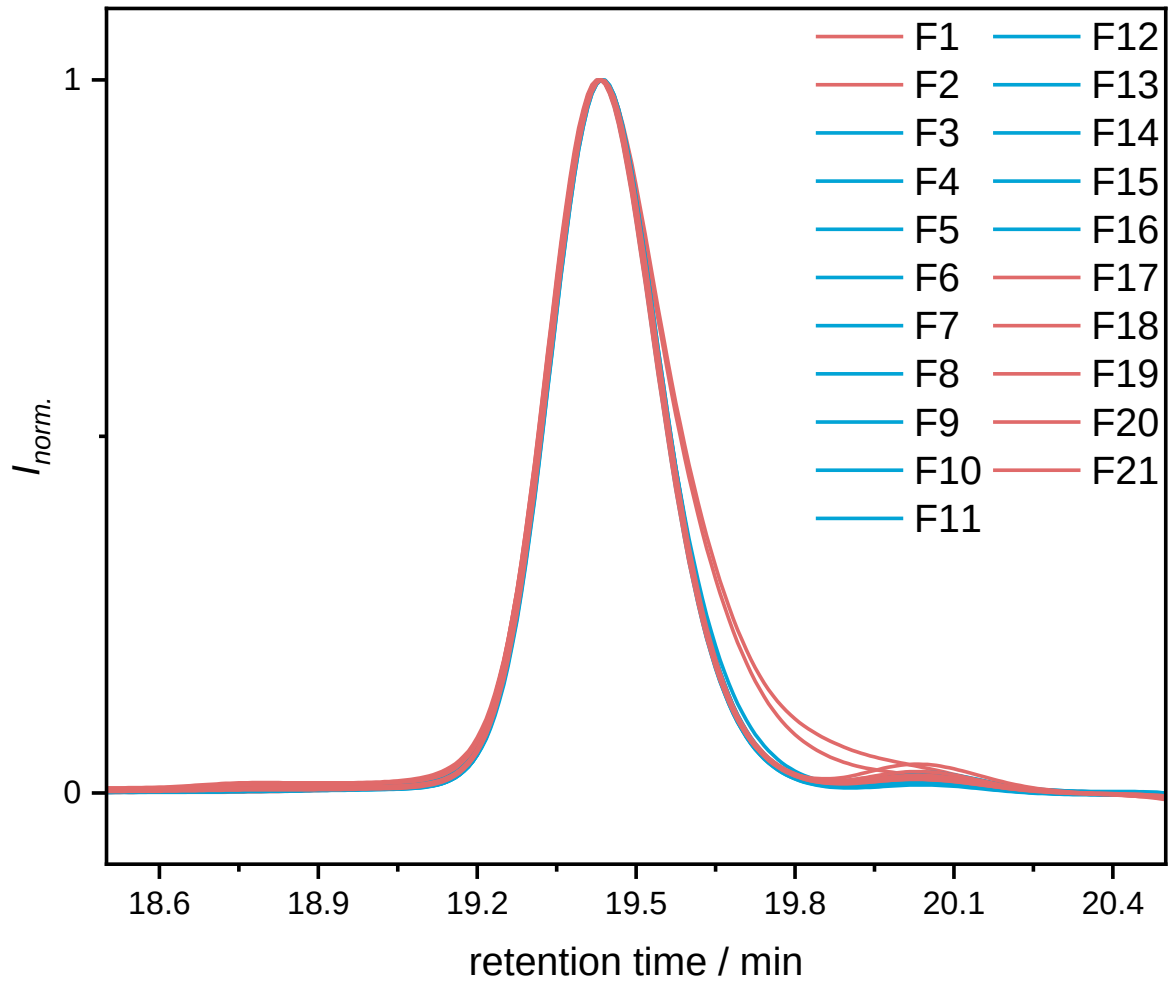
Supplementary Figure 9: SEC traces of the individual fractions obtained from the purification *via* column chromatography (cc1) of **THP(EG)$_8$Bn (B)**.

The product fractions of the first column with insufficient purity (Supplementary Table 2, highlighted in yellow) were purified again *via* column chromatography.

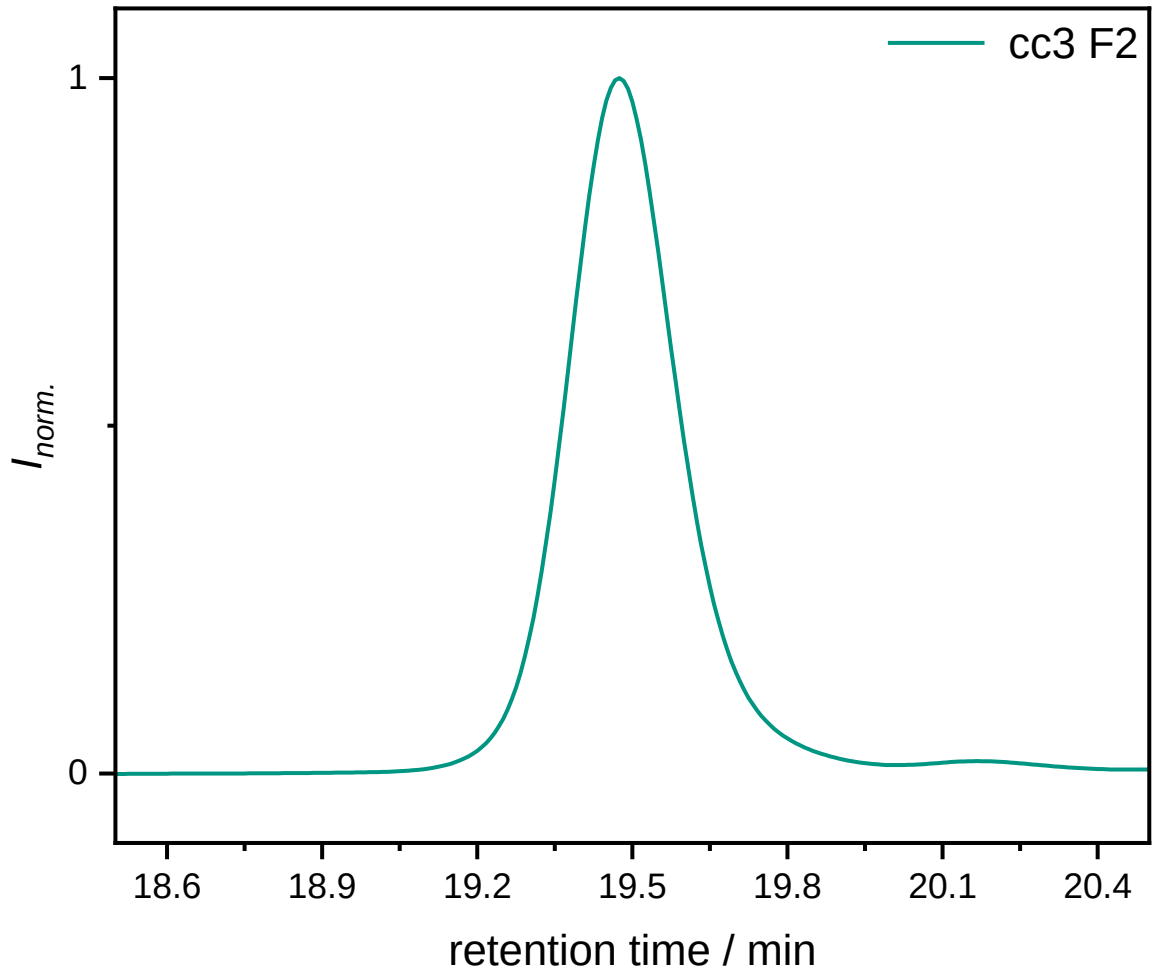
Supplementary Table 3: SEC results of the second purification of **THP(EG)$_8$Bn (B)**.

cc 2	*m* / g	M_n / Da	M_w / Da	M_z / Da	*Đ*	purity / %
F1	5.62	650	650	650	1.00	>99*
F2	5.43	650	650	650	1.00	>99*
F3	1.23	700	700	700	1.00	95
F4	1.40	700	700	700	1.00	99
F5	0.95	700	700	700	1.00	98
F6	0.68	700	700	700	1.00	98
F7	0.73	700	700	700	1.00	98
F8	0.69	700	700	700	1.00	98
F9	0.77	700	700	700	1.00	96
F10	0.69	700	700	700	1.00	96
F11	0.56	700	700	700	1.00	95
F12	0.51	700	700	700	1.00	97
F13	0.49	650	700	700	1.00	97
F14	0.40	700	700	700	1.00	94
F15	0.51	700	700	700	1.00	96
F16	0.49	700	700	700	1.00	96
F17	0.31	700	700	700	1.00	94
F18	0.27	650	700	700	1.00	95
F19	0.27	650	650	700	1.00	94
F20	0.47	650	650	700	1.00	93
F21	0.48	650	650	700	1.00	94

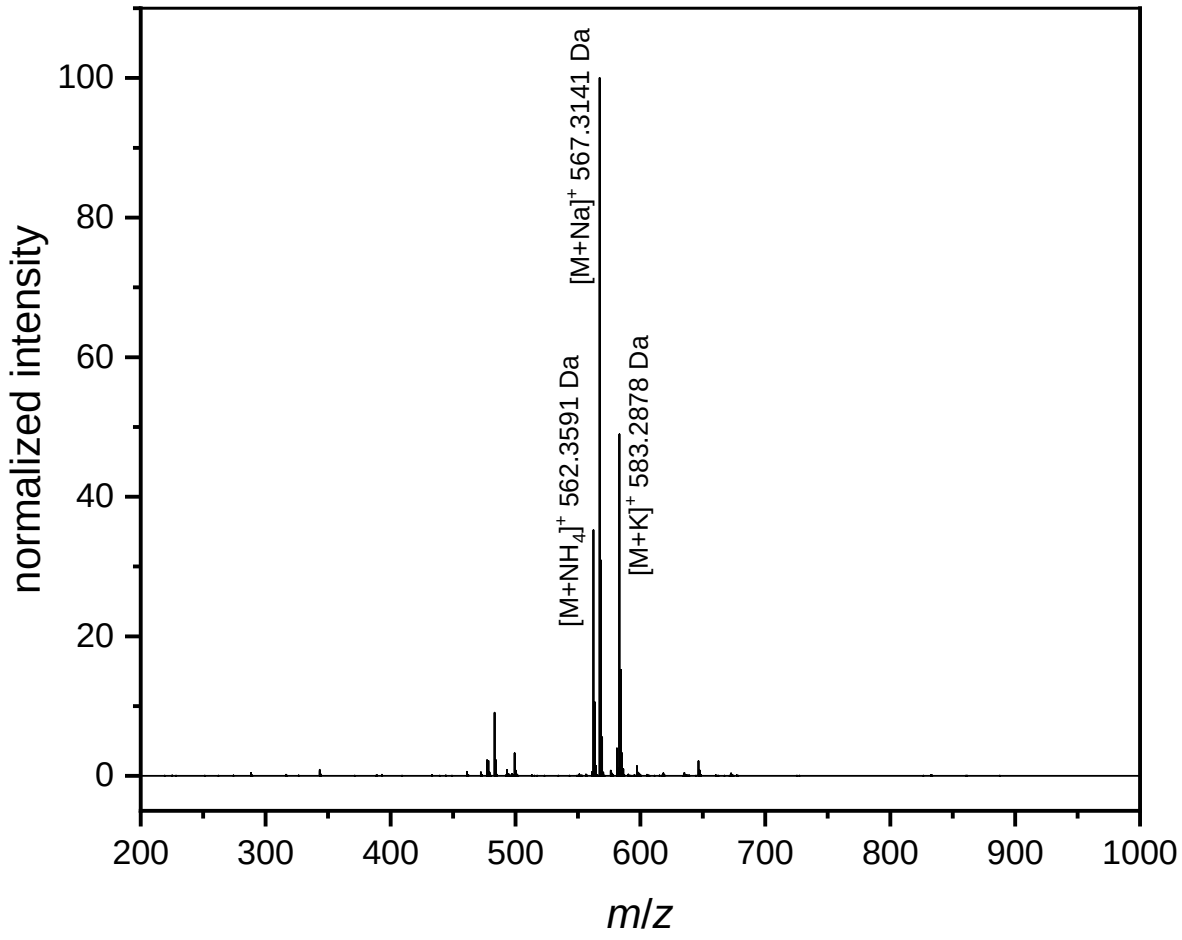
eluent: DCM:Acetone = 4:1 → EA:MeOH = 9:1; red: fractions were discarded; yellow: product containing fractions with insufficient purity; green: fractions containing only product **THP(EG)$_8$Bn (B)**. *purity was determined *via* integration of the single broad peak, thus the real purity is lower than specified and the fractions were not used for further synthesis.



Supplementary Figure 10: SEC traces of the individual fractions obtained from the purification *via* column chromatography (cc2) of **THP(EG)$_8$Bn (B)**.

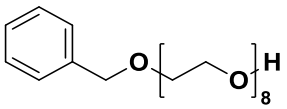


Supplementary Figure 11: SEC trace of the fraction obtained from the purification of **THP(EG)$_8$Bn (B) cc2 F4** *via* column chromatography (cc3) of **THP(EG)$_8$Bn (B)**.



Supplementary Figure 12: ESI-MS spectrum of **THP(EG)$_8$Bn (B)**.

Monobenzyl octa(ethylene glycol) – Bn(EG)$_8$OH



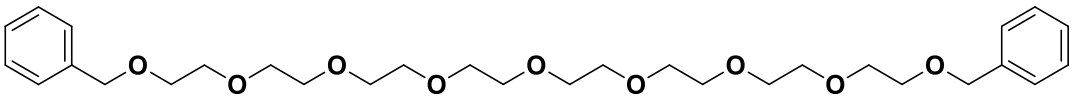
Chemical Formula: $C_{23}H_{40}O_9$
Exact Mass: 460.2672 Da
Molecular Weight: 460.5640 Da

The synthesis was performed according to a procedure of BAKER *et al*.[1] α-Benzyl-ω-tetrahydropyranyl octa(ethylene glycol) **THP(EG)$_8$Bn** (4.00 g, 7.34 mmol, 1.00 eq) was added to a solution of *p*-toluenesulfonic acid monohydrate (12.6 mg, 73.2 µmol, 0.01 equiv.) in anhydrous methanol (7 mL). After stirring the reaction mixture for 36 hours at room temperature, the solvent was evaporated under reduced pressure. The residue was dissolved in DCM (50 mL) and washed with aqueous NaCl/HCl solution (50 mL). The phases were separated, and the organic layer was dried over anhydrous sodium sulfate, filtered and concentrated *in vacuo* to afford the monobenzyl octa(ethylene glycol) **Bn(EG)$_8$OH** as a colorless oil (3.30 g, 7.17 mmol, 97.7%).

HRMS (ESI) of $C_{23}H_{40}O_9$ $[M+H]^+$ *m/z* calc. 461.2747, detected 461.2746; $[M+NH_4]^+$ *m/z* calc. 478.3012, detected 478.3013; $[M+Na]^+$ *m/z* calc. 483.2566, detected 438.2565; $[M+K]^+$ *m/z* calc. 499.2301, detected 499.2303.

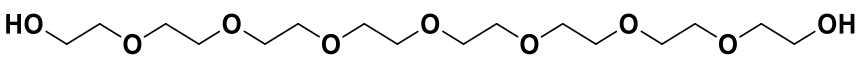
The mass of the α-benzyl-ω-tetrahydropyranyl octa(ethylene glycol) **THP(EG)$_8$Bn** was also detected. $C_{28}H_{48}O_{10}$ $[M+NH_4]^+$ *m/z* calc. 562.3588, detected 562.3583; $[M+Na]^+$ *m/z* calc. 567.3142, detected 567.3139.

The mass of the bis-benzyl octa(ethylene glycol) was also detected. $C_{30}H_{46}O_9$ $[M+H]^+$ *m/z* calc. 573.3037, detected 573.3032.



Chemical Formula: $C_{30}H_{46}O_9$
Exact Mass: 550.3142 Da

The mass of the octa(ethylene glycol) was also detected. $C_{16}H_{34}O_9$ $[M+H]^+$ *m/z* calc. 371.2277, detected 371.2275.



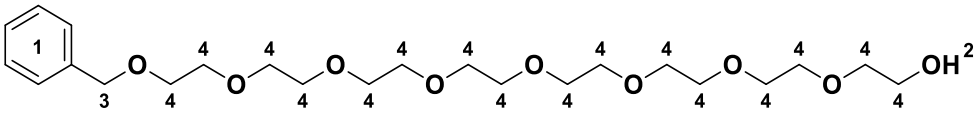
Chemical Formula: $C_{16}H_{34}O_9$
Exact Mass: 370.2203 Da

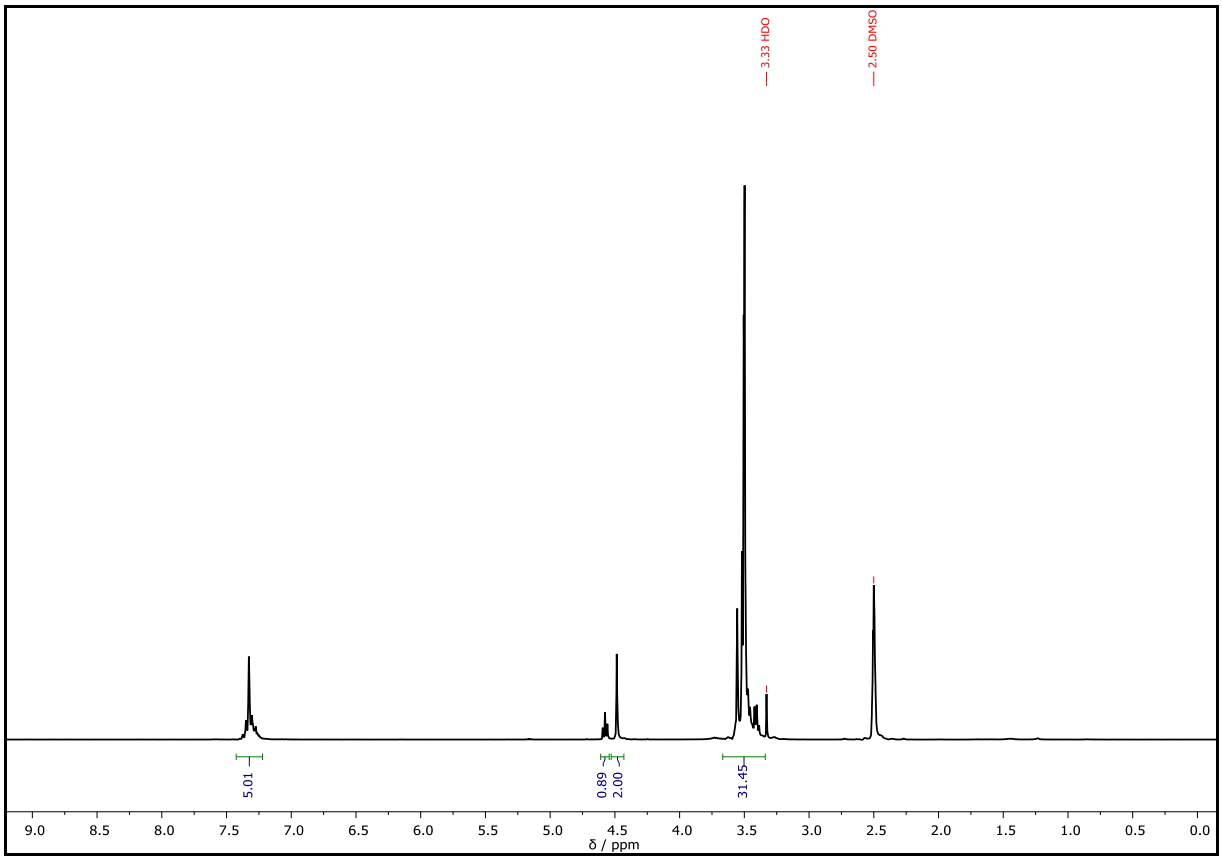
IR (ATR platinum diamond) $\tilde{\nu}$ / cm^{-1} = 3475.1, 2865.4, 1719.4, 1453.6, 1349.6, 1276.0, 1250.5, 1094.0, 944.6, 848.3, 740.0, 716.8, 699.3, 527.3.

R_f = 0.11 (EA).

Đ (System I) = 1.00

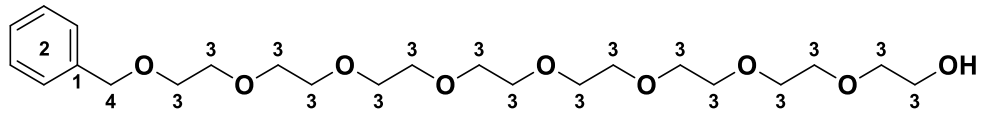
^{1}H NMR (300 MHz, DMSO-d_6): δ / ppm = 7.46 – 7.19 (m, 5H, H_{Ar}^1), 4.58 (t, J = 5.4 Hz, 1H, OH^2), 4.49 (s, 2H, CH_2^3), 3.69 – 3.36 (m, 32H, CH_2^4).

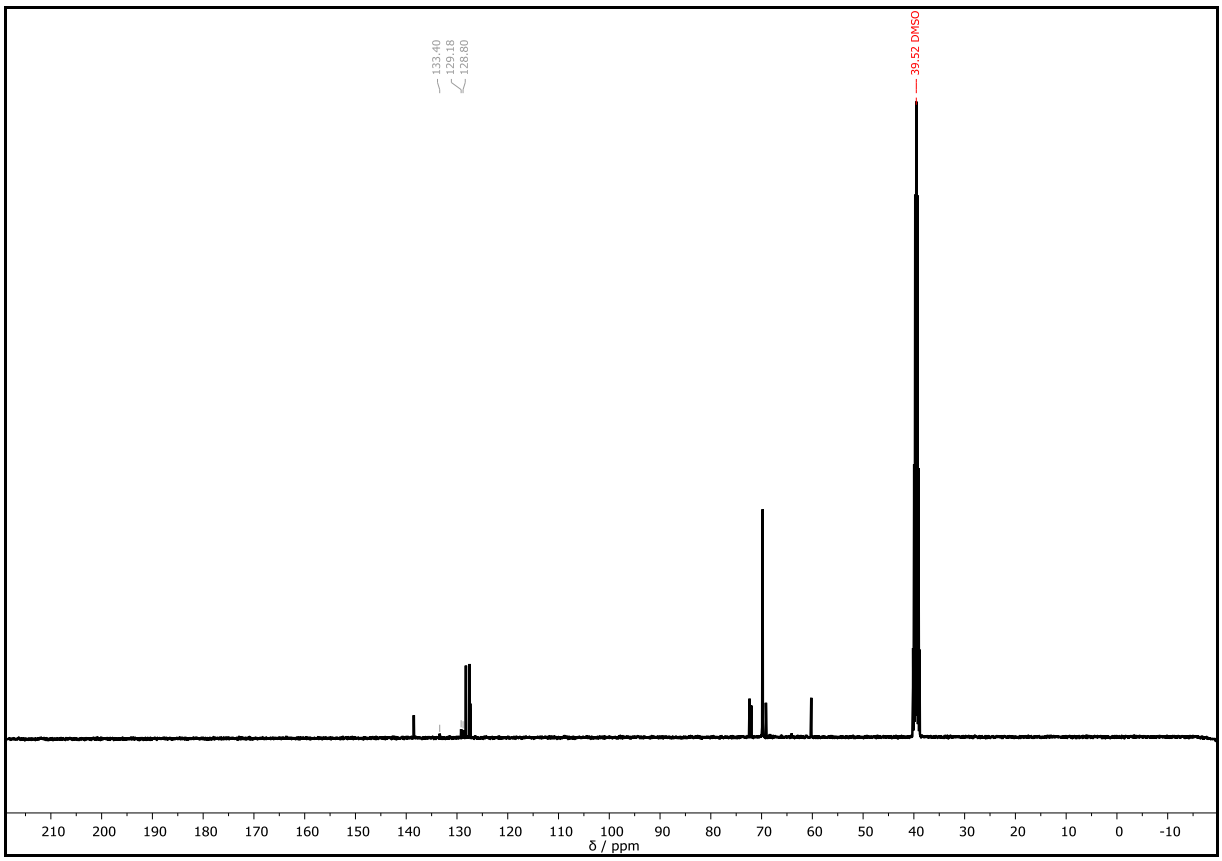




Supplementary Figure 13 ^{1}H NMR spectrum of **Bn(EG)$_8$OH** recorded at 300 MHz in DMSO-d_6.

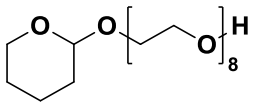
^{13}C NMR (101 MHz, DMSO-d_6): δ / ppm = 138.49 (C_q^1), 128.23 (CH_{Ar}^2), 127.50 (CH_{Ar}^2), 127.39 (CH_{Ar}^2), 72.36 (CH_2^3), 72.03 (CH_2^4), 69.85 (CH_2^3), 69.80 (CH_2^3), 69.14 (CH_2^3), 60.22 (CH_2^3).





Supplementary Figure 14 ^{13}C NMR spectrum of **Bn(EG)$_8$OH** recorded at 101 MHz in DMSO-d_6.

Mono(tetrahydropyranyl) octa(ethylene glycol) – THP(EG)$_8$OH

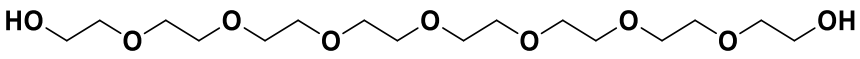


Chemical Formula: $C_{21}H_{42}O_{10}$
Exact Mass: 454.2778 Da
Molecular Weight: 454.5570 Da

Palladium on carbon (400 mg, 10 wt%) was added to a solution of α-benzyl-ω-tetrahydropyranyl octa(ethylene glycol) **THP(EG)$_8$Bn** (4.00 g, 7.34 mmol, 1.00 eq) dissolved in EA (35 mL). The reaction mixture was stirred overnight at reflux under hydrogen atmosphere (balloon). After cooling to room temperature, the mixture was filtered through a pad of celite to remove the Pd/C. The organic phase was dried over anhydrous sodium sulfate and the solvent was removed under reduced pressure affording the product **THP(EG)$_8$OH** as a colorless oil (3.30 g, 7.26 mmol, 98.9%).

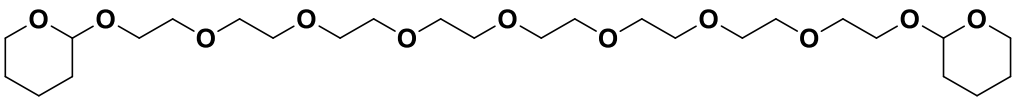
HRMS (ESI) of $C_{21}H_{42}O_{10}$ $[M+H]^+$ *m/z* calc. 455.2852, detected 455.2851; $[M+NH_4]^+$ *m/z* calc. 472.3117, detected 472.3119; $[M+Na]^+$ *m/z* calc. 477.2671, detected 477.2670; $[M+K]^+$ *m/z* calc. 493.2406, detected 493.2408.

The mass of the octa(ethylene glycol) was also detected. $C_{16}H_{34}O_9$ $[M+H]^+$ *m/z* calc. 371.2277, detected 371.2275; $[M+Na]^+$ *m/z* calc. 393.2096, detected 393.2092.



Chemical Formula: $C_{16}H_{34}O_9$
Exact Mass: 370.2203 Da

The mass of the bis-tetrahydropyranyl octa(ethylene glycol) was also detected. $C_{26}H_{50}O_{11}$ $[M+Na]^+$ *m/z* calc. 561.3247, detected 561.3243.



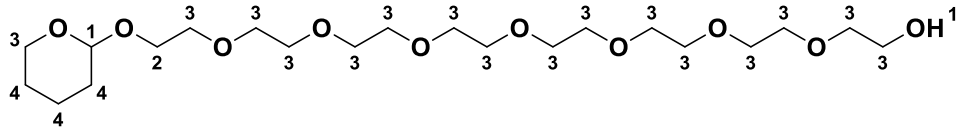
Chemical Formula: $C_{26}H_{50}O_{11}$
Exact Mass: 538.3353 Da

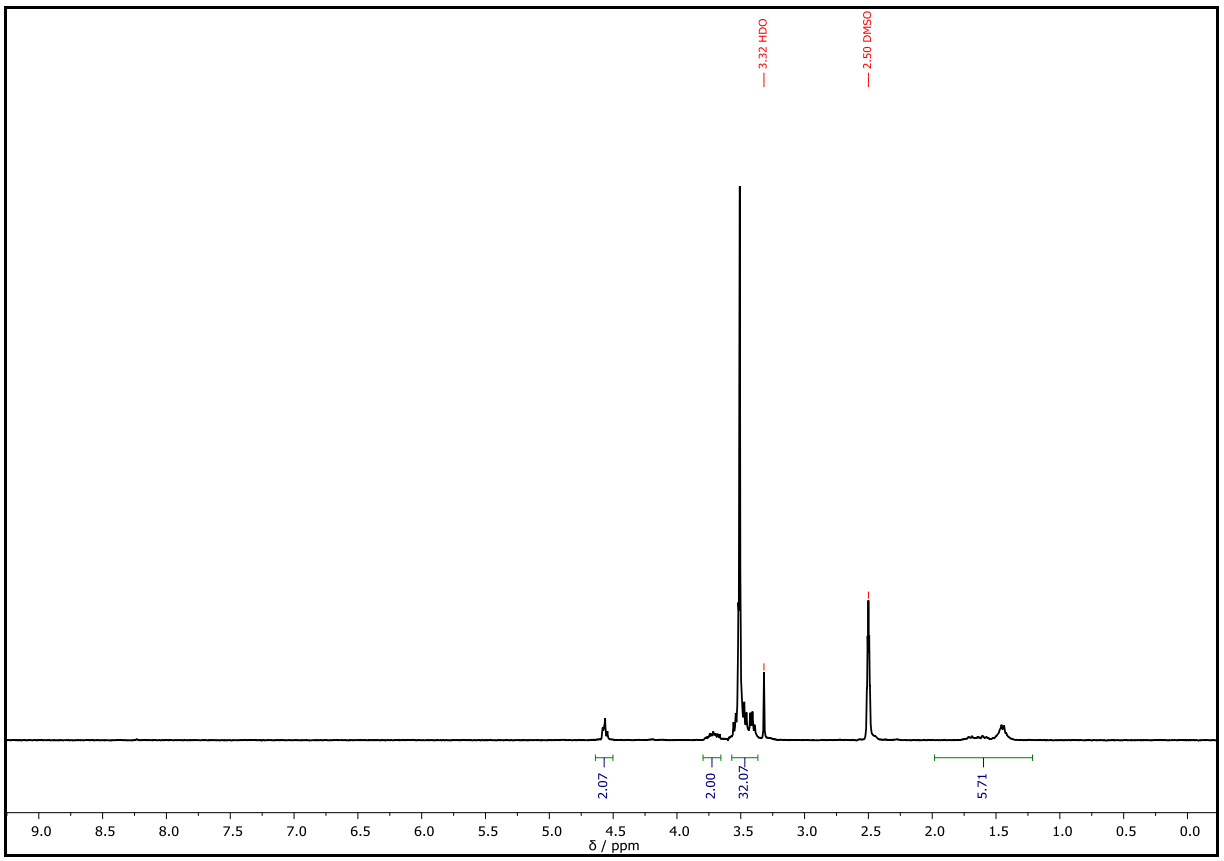
IR (ATR platinum diamond) $\tilde{\nu}$ / cm^{-1} = 3439.5, 2868.5, 1731.0, 1454.3, 1349.5, 1248.5, 1201.4, 1096.9, 1033.0, 988.2, 942.2, 871.3, 524.2.

R_f = 0.03 (EA)

Đ (System I) = 1.00

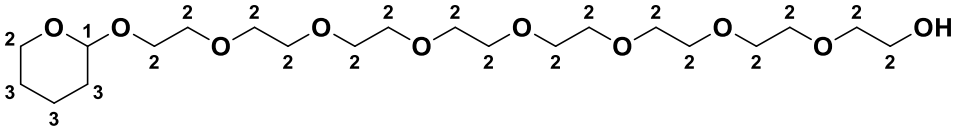
^{1}H NMR (300 MHz, DMSO-d_6): δ / ppm = 4.64 – 4.51 (m, 2H, OH^1 and CH^1), 3.86 – 3.64 (m, 2H, CH_2^2), 3.64 – 3.35 (m, 32H, CH_2^3), 1.83 – 1.34 (m, 6H, CH_2^4).

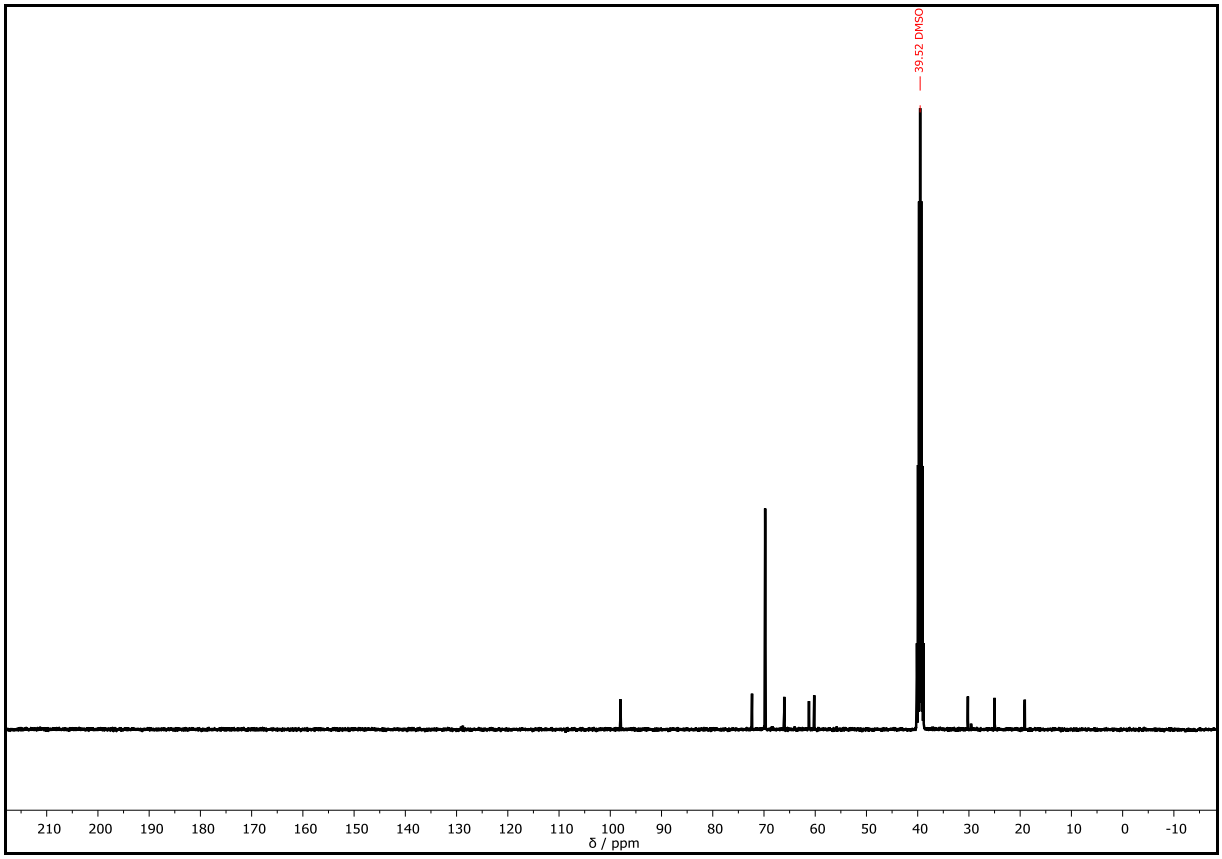




Supplementary Figure 15: ^{1}H NMR spectrum of **THP(EG)$_8$OH** recorded at 300 MHz in DMSO-d_6.

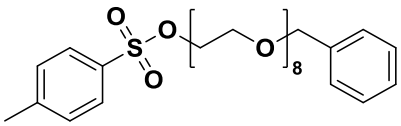
^{13}C NMR (101 MHz, DMSO-d_6): δ / ppm = 98.06 (CH^1), 72.36 (CH_2^2), 69.83 (CH_2^2), 69.80 (CH_2^2), 69.74 (CH_2^2), 66.08 (CH_2^2), 61.25 (CH_2^2), 60.22 (CH_2^2), 30.23 (CH_2^3), 25.04 (CH_2^3), 19.14 (CH_2^3).





Supplementary Figure 16: ^{13}C NMR spectrum of **THP(EG)$_8$OH** recorded at 101 MHz in DMSO-d_6.

α-Benzyl-ω-tosyl octa(ethylene glycol) – Bn(EG)$_8$Ts



Chemical Formula: $C_{30}H_{46}O_{11}S$
Exact Mass: 614.2761 Da
Molecular Weight: 614.7470 Da

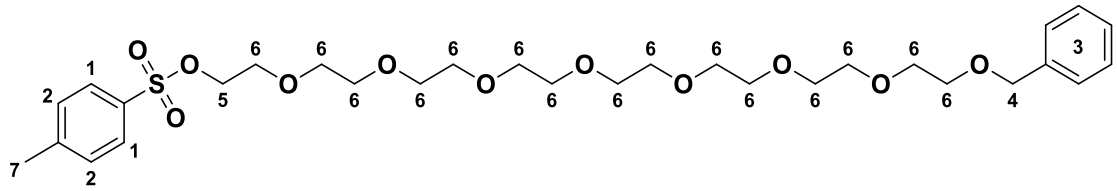
The monobenzyl octa(ethylene glycol) tosylate **Bn(EG)$_8$Ts** was prepared according to the procedure of BRUCE *et al.*[2] Monobenzyl octa(ethylene glycol) (2.75 g, 5.97 mmol, 1.00 equiv.), sodium hydroxide (836 mg, 20.9 mmol, 3.50 equiv.), *p*-toluenesulfonyl chloride (1.37 g, 7.16 mmol, 1.20 equiv.) were used. Purification of the crude product *via* column chromatography (EA) yielded the monobenzyl octa(ethylene glycol) tosylate **Bn(EG)$_8$Ts** (1.87 g, 3.04 mmol, 50.9%) as a colorless, oil. The product was dried under high vacuum, stored under argon atmosphere, and shielded from light until further use.

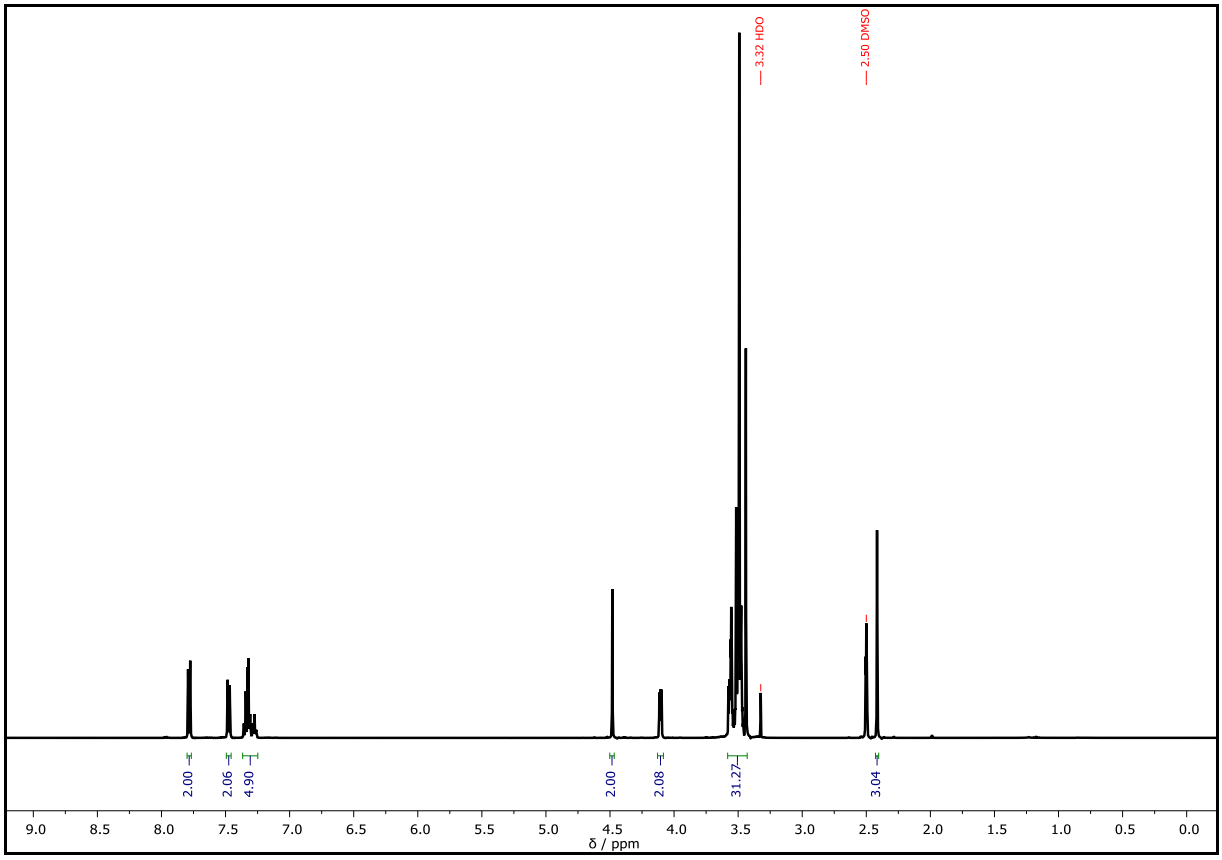
HRMS (FAB) of $C_{30}H_{47}O_{11}S_1$ $[M+H]^+$ calcd. 615.2839, detected 615.2841.

IR (ATR platinum diamond) $\tilde{\nu}$ / cm^{-1} = 2864.8, 1597.3, 1452.6, 1352.3, 1292.0, 1248.4, 1175.9, 1095.9, 1017.7, 920.2, 816.8, 747.5, 699.4, 663.4, 554.7.

R_f = 0.31 (EA).

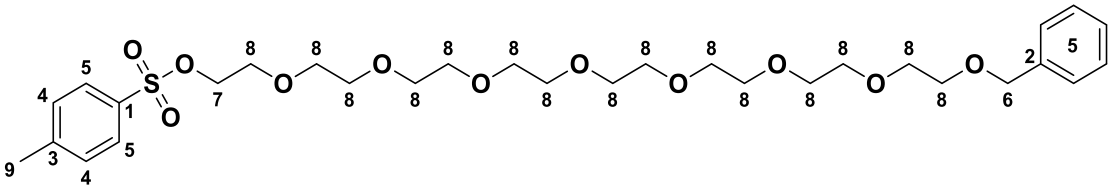
^{1}H NMR (400 MHz, DMSO-d_6): δ / ppm = 7.78 (d, J = 8.3 Hz, 2H, CH_{Ar}^1), 7.48 (d, J = 8.1 Hz, 1H, CH_{Ar}^2), 7.38 – 7.24 (m, 5H, CH_{Ar}^3), 4.48 (s, 2H, CH_2^4), 4.13 – 4.06 (m, 2H, CH_2^5), 3.59 – 3.42 (m, 30H, CH_2^6), 2.42 (s, 3H, CH_3^7).

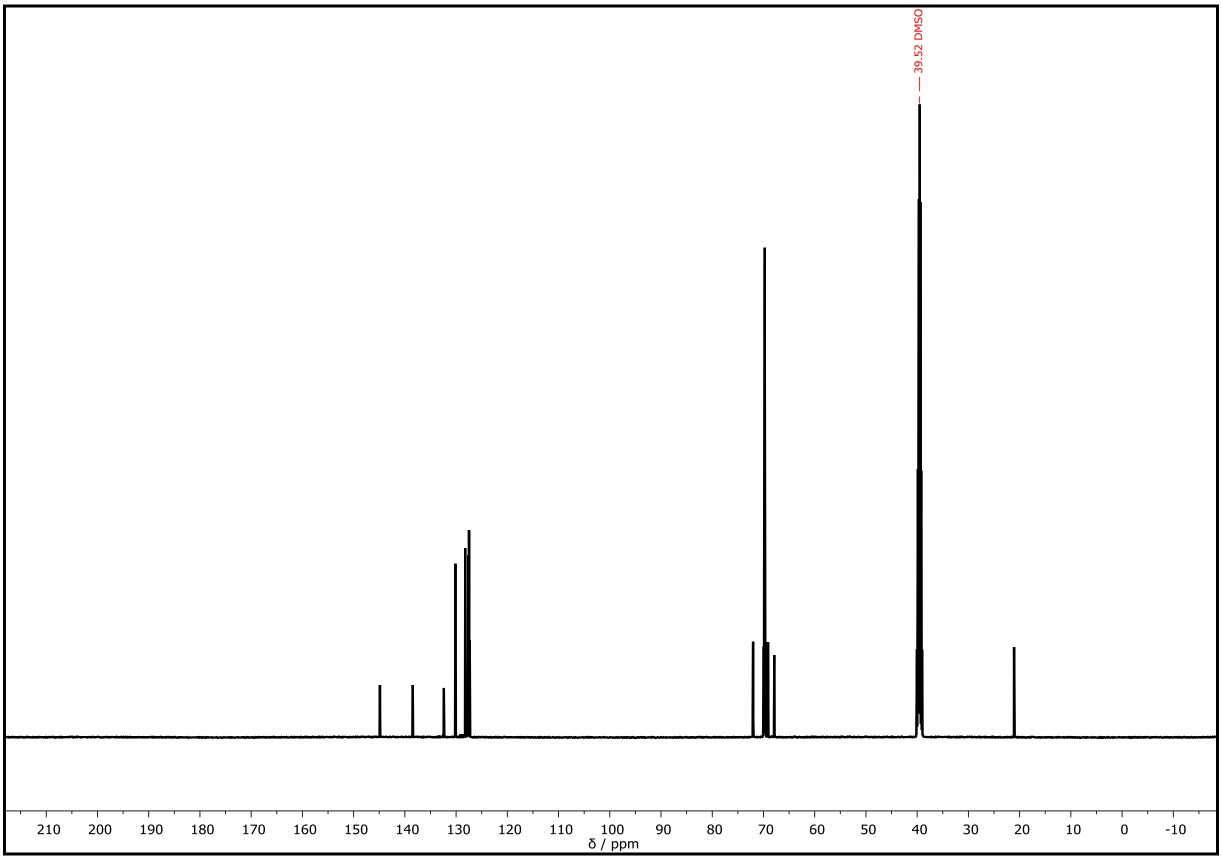




Supplementary Figure 17: ^{1}H NMR spectrum of **Bn(EG)$_8$Ts** recorded at 400 MHz in DMSO-d_6.

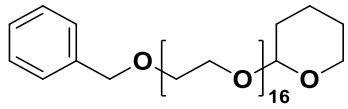
^{13}C NMR (101 MHz, DMSO-d_6): δ / ppm = 144.87 (C_q^1), 138.48 (C_q^2), 132.41 (C_q^3), 130.12 (CH^4), 128.19 (CH^5), 127.61 (CH^5), 127.46 (CH^5), 127.34 (CH^5), 72.01 (CH_2^6), 69.97 (CH_2^7), 69.83 (CH_2^8), 69.76 (CH_2^8), 69.69 (CH_2^8), 69.64 (CH_2^8), 69.12 (CH_2^8), 67.87 (CH_2^8), 21.07 (CH_3^9).





Supplementary Figure 18 ^{13}C NMR spectrum of **Bn(EG)$_8$Ts** recorded at 101 MHz in DMSO-d_6.

α-Benzyl-ω-tetrahydropyranyl hexadeca(ethylene glycol) – THP(EG)$_{16}$Bn

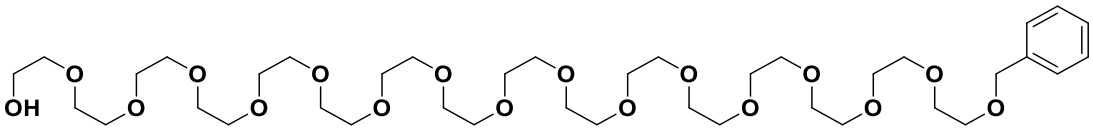


Chemical Formula: $C_{44}H_{80}O_{18}$
Exact Mass: 896.5345 Da
Molecular Weight: 897.1060 Da

The doubly protected hexadeca(ethylene glycol) **THP(EG)$_{16}$Bn** was prepared using the procedure described above for the synthesis of the doubly protected octa(ethylene glycol) **THP(EG)$_8$Bn**.[2] The reaction was performed in a 15.6 mmol scale using the monobenzyl octa(ethylene glycol) tosylate **Bn(EG)$_8$Ts** and the mono(tetrahydropyranyl) octa(ethylene glycol) **THP(EG)$_8$OH**. Purification of the crude product *via* column chromatography (DCM:acetone = 6:1 → 1:1) yielded the product **THP(EG)$_{16}$Bn** as a yellowish solid (6.01 g, 6.70 mmol, 43.0%).

HRMS (ESI) of $C_{44}H_{80}O_{18}$ $[M+NH_4]^+$ *m/z* calc. 914.5683, detected 914.5454; $[M+Na]^+$ *m/z* calc. 919.5208, detected 919.5237; $[M+K]^+$ *m/z* calc. 935.4976, detected 935.4952.

The mass of the α-benzyl-ω-hydroxy hexadeca(ethylene glycol) was detected as most intensive signal. $C_{39}H_{72}O_{17}$ $[M+H]^+$ *m/z* calc. 813.4842, detected 913.4815.



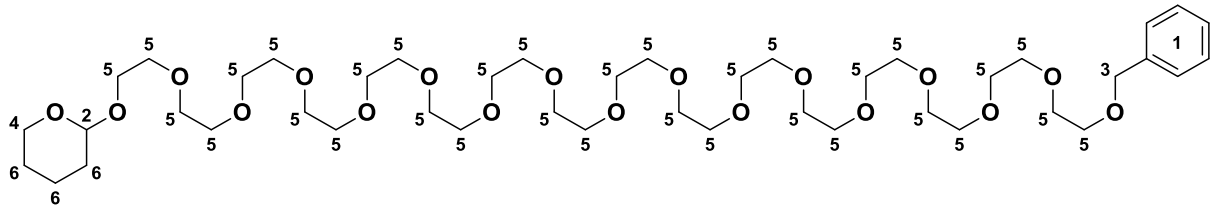
Chemical Formula: $C_{39}H_{72}O_{17}$
Exact Mass: 812.4770 Da

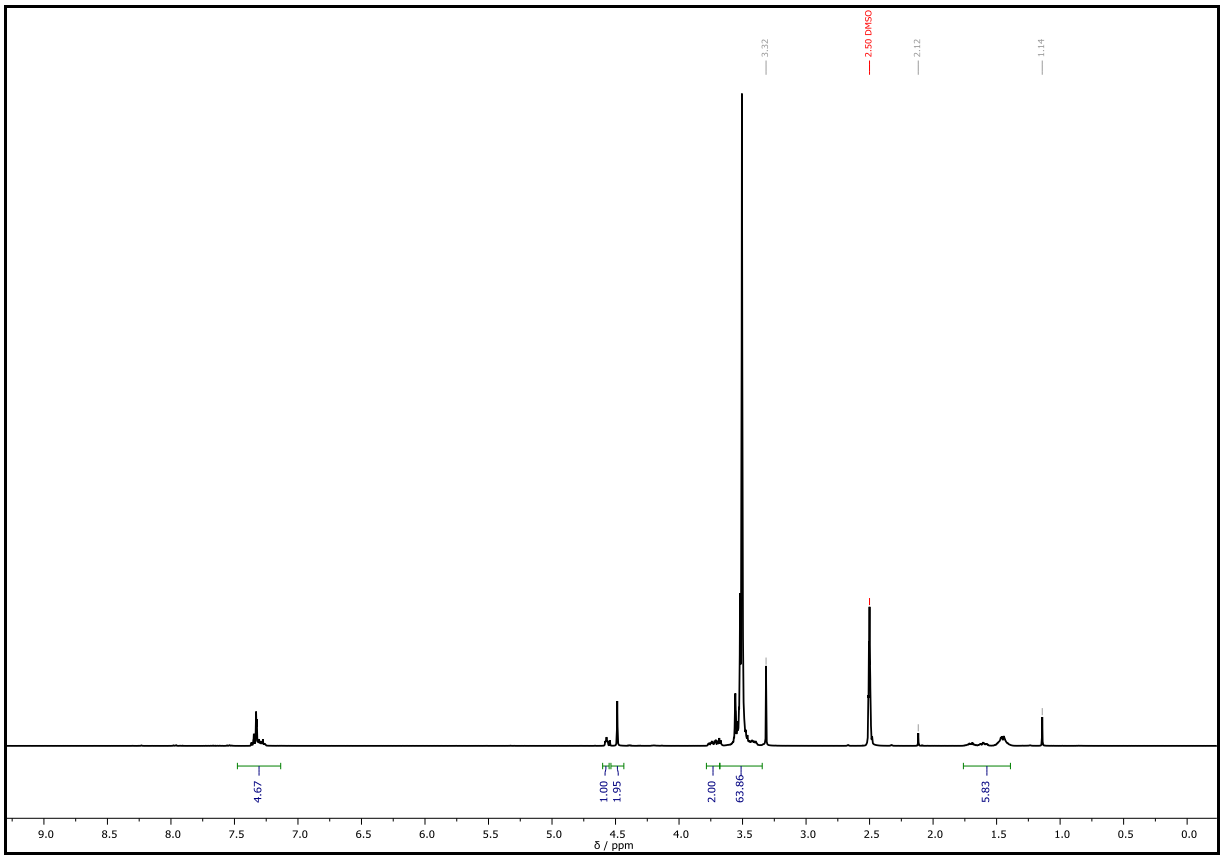
IR (ATR platinum diamond) $\tilde{\nu}$ / cm^{-1} = 2864.7, 1720.4, 1454.0, 1349.0, 1293.7, 1250.0, 1201.4, 1095.5, 1032.9, 987.8, 945.8, 870.5, 814.0, 741.2, 699.7, 520.0.

R_f = 0.29 (EA:MeOH = 9:1).

Đ (System I) = 1.00

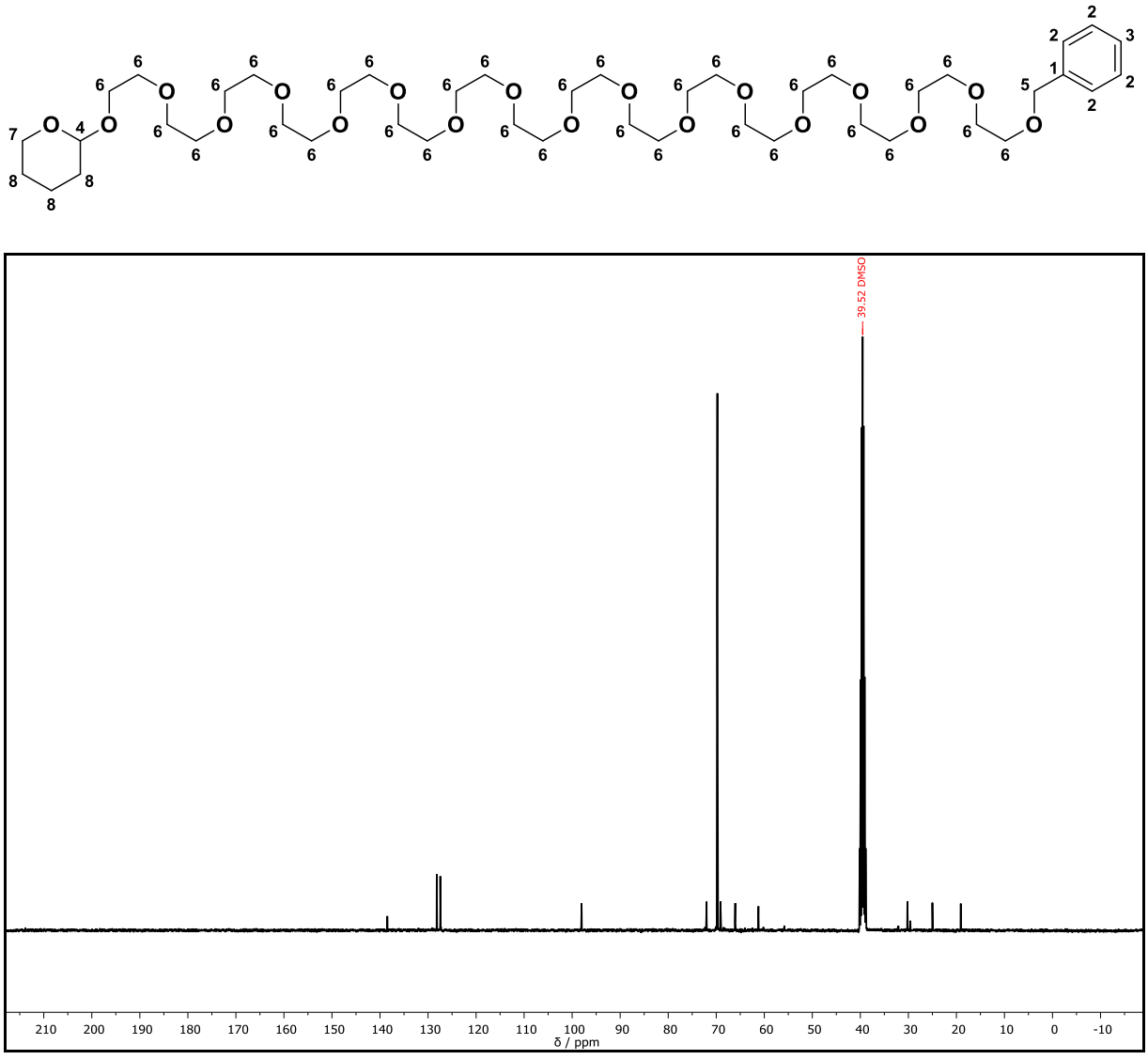
^{1}H NMR (400 MHz, DMSO-d_6): δ / ppm = 7.39 – 7.22 (m, 5H, CH_{Ar}^1), 4.57 (t, J = 3.8 Hz, 1H, CH^2), 4.49 (s, 2H, CH_2^3), 3.79 – 3.66 (m, 2H, CH_2^4), 3.60 – 3.38 (m, 64H, CH_2^5), 1.77 – 1.39 (m, 6H, CH_2^6).





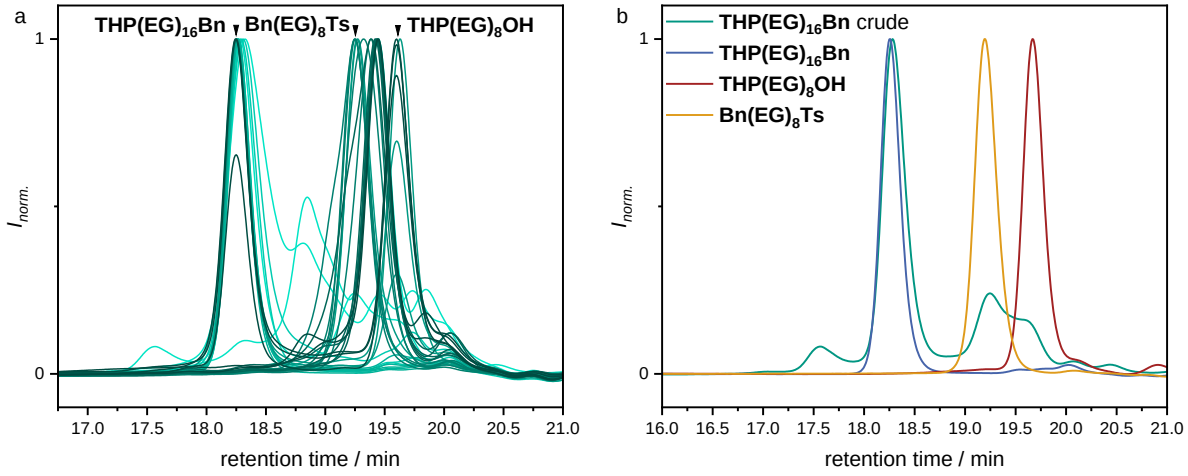
Supplementary Figure 19: ^{1}H NMR spectrum of **THP(EG)$_{16}$Bn** recorded at 400 MHz in DMSO-d_6.

^{13}C NMR (101 MHz, DMSO-d_6): δ / ppm = 138.48 (C_q^1), 128.19 (CH_{Ar}^2), 127.45 (CH_{Ar}^2), 127.34 (CH_{Ar}^3), 98.03 (CH^4), 72.00 (CH_2^5), 69.83 (CH_2^6), 69.77 (CH_2^6), 69.71 (CH_2^6), 69.12 (CH_2^6), 66.05 (CH_2^7), 61.21 (CH_2^7), 30.20 (CH_2^8), 25.00 (CH_2^8), 19.09 (CH_2^8).



Supplementary Figure 20: ^{13}C NMR spectrum of **THP(EG)$_{16}$Bn** recorded at 101 MHz in DMSO-d_6.

The synthesis of **THP(EG)$_{16}$Bn** was repeated on a 14 g scale and the purification *via* column chromatography is shown in the following.



Supplementary Figure 21: **a** SEC of individual fractions obtained from the purification process of **THP(EG)$_{16}$Bn** *via* column chromatography; **b** comparison of the SEC traces of **THP(EG)$_{16}$Bn** before (green trace) and after purification (blue trace) and the starting materials **THP(EG)$_8$OH** (red trace) and **Bn(EG)$_8$Ts** (yellow trace).

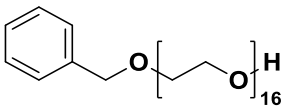
Supplementary Table 4 SEC data of **THP(EG)$_{16}$Bn**.

cc 1	*m* / mg	M_n / Da	M_w / Da	M_z / Da	$Đ$	purity / %
F1	652	*n.a.*	*n.a.*	*n.a.*	*n.a.*	*n.a.*
F2	64.0	*n.a.*	*n.a.*	*n.a.*	*n.a.*	*n.a.*
F3	90.5	*n.a.*	*n.a.*	*n.a.*	*n.a.*	*n.a.*
F4	111	*n.a.*	*n.a.*	*n.a.*	*n.a.*	*n.a.*
F5	189	*n.a.*	*n.a.*	*n.a.*	*n.a.*	*n.a.*
F6	87.0	*n.a.*	*n.a.*	*n.a.*	*n.a.*	*n.a.*
F7	70.9	*n.a.*	*n.a.*	*n.a.*	*n.a.*	*n.a.*
F8	64.4	*n.a.*	*n.a.*	*n.a.*	*n.a.*	*n.a.*
F9	58.6	*n.a.*	*n.a.*	*n.a.*	*n.a.*	*n.a.*
F10	80.0	*n.a.*	*n.a.*	*n.a.*	*n.a.*	*n.a.*
F11	57.6	*n.a.*	*n.a.*	*n.a.*	*n.a.*	*n.a.*
F12	41.2	*n.a.*	*n.a.*	*n.a.*	*n.a.*	*n.a.*
F13	36.8	*n.a.*	*n.a.*	*n.a.*	*n.a.*	*n.a.*
F14	80.3	*n.a.*	*n.a.*	*n.a.*	*n.a.*	*n.a.*
F15	39.6	n.a.	n.a.	n.a.	n.a.	n.a.
F16	48.1	1200	1200	1200	1.01	5.4

Supplementary Table 5 SEC data of **THP(EG)$_{16}$Bn**.						
cc 1	*m* / mg	M_n / Da	M_w / Da	M_z / Da	*Đ*	purity / %
F17	150	1100	1100	1100	1.01	56.2
F18	231	1100	1100	1100	1.01	71.8
F19	433	1100	1100	1100	1.01	83.3
F20	1581	1100	1100	1150	1.01	87.6
F21	1613	1150	1150	1150	1.00	>99
F22	1272	1150	1150	1150	1.00	>99
F23	1445	1150	1150	1150	1.00	>99
F24	978	1150	1150	1150	1.00	>99
F25	704	1150	1150	1150	1.00	>99
F26	459	1150	1150	1150	1.00	91.3
F27	590	1150	1150	1150	1.00	75.4
F28	232	1150	1150	1150	1.01	53.7
F29	160	1150	1150	1150	1.01	48.4
F30	133	1150	1150	1150	1.01	47.2
F31	317	1150	1150	1150	1.01	36.5

Chromatograms were recorded on SEC system I. Red: fractions containing only impurities; yellow: product containing fractions with insufficient purity; green: fractions containing only product **THP(EG)$_{16}$Bn**.

Monobenzyl hexadeca(ethylene glycol) – Bn(EG)$_{16}$OH



Chemical Formula: $C_{39}H_{72}O_{17}$
Exact Mass: 812.4770 Da
Molecular Weight: 812.9880 Da

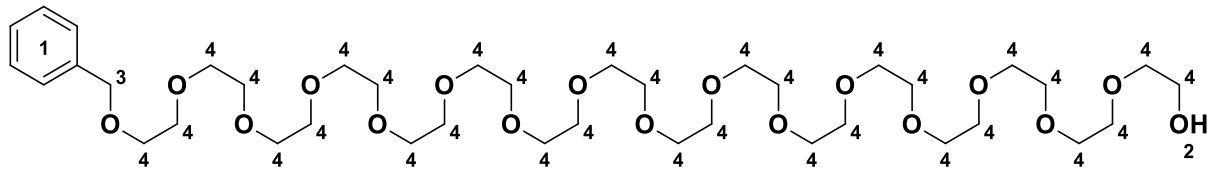
The monobenzyl protected hexadeca(ethylene glycol) **Bn(EG)$_{16}$OH** was prepared using the procedure described above for the synthesis of the monobenzyl protected octa(ethylene glycol) **Bn(EG)$_8$OH**.

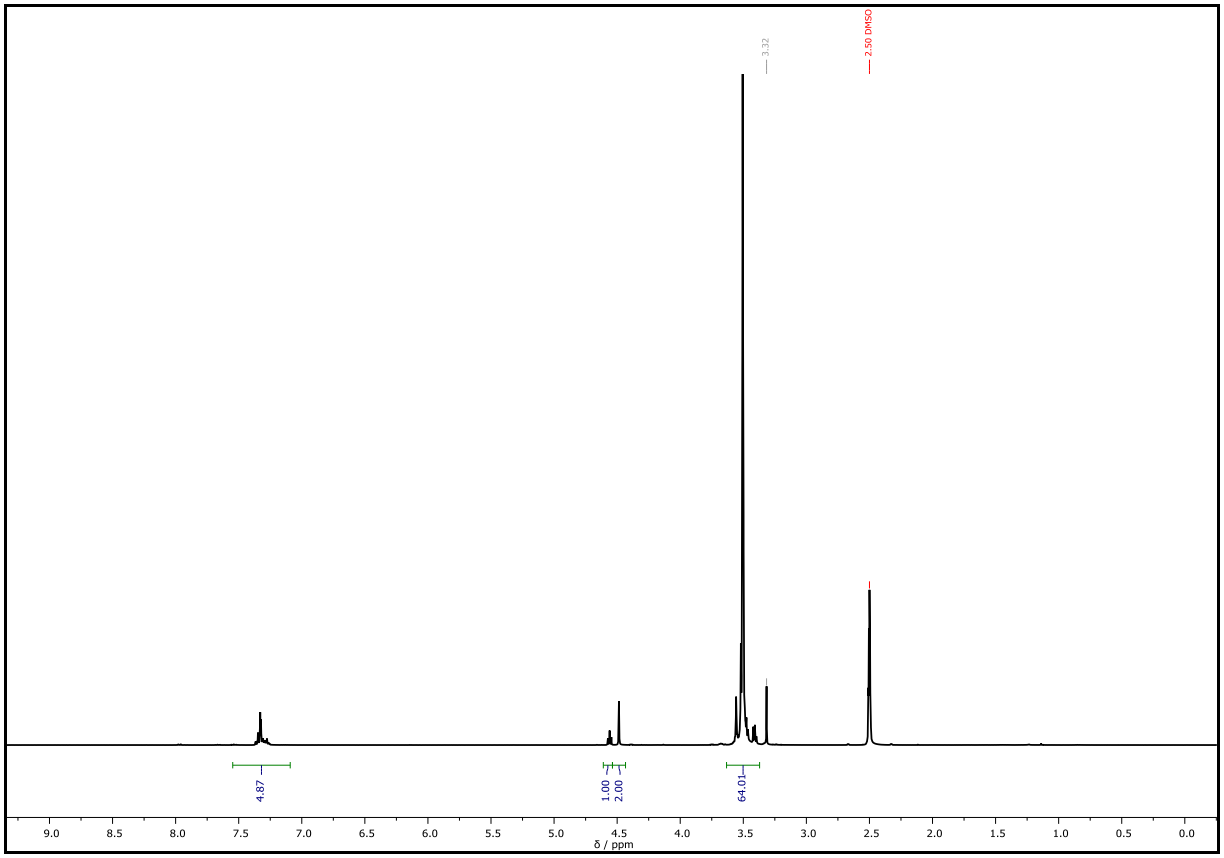
THP(EG)$_{16}$Bn	4.00 g, 4.46 mmol, 1.00 equiv.
TsOH	8.48 mg, 44.6 µmol, 0.01 equiv.
MeOH	5.00 mL
Yield	3.61 g, 4.44 mmol, 99.7%, yellowish solid
R_f	0.26 (EA/MeOH = 4:1).
Đ (system I)	1.00

HRMS (ESI) of $C_{39}H_{72}O_{17}$ $[M+NH_4]^+$ *m/z* calc. 830.5108, detected 830.5112; $[M+Na]^+$ *m/z* calc. 835.4662, detected 835.4664; $[M+K]^+$ *m/z* calc. 851.4401, detected 851.4398.

IR (ATR platinum diamond) $\tilde{\nu}$ / cm^{-1} = 3474.3, 2863.9, 1719.7, 1638.1, 1453.2, 1348.7, 1294.3, 1246.2, 1095.7, 946.6, 847.0, 741.8, 699.9, 535.9.

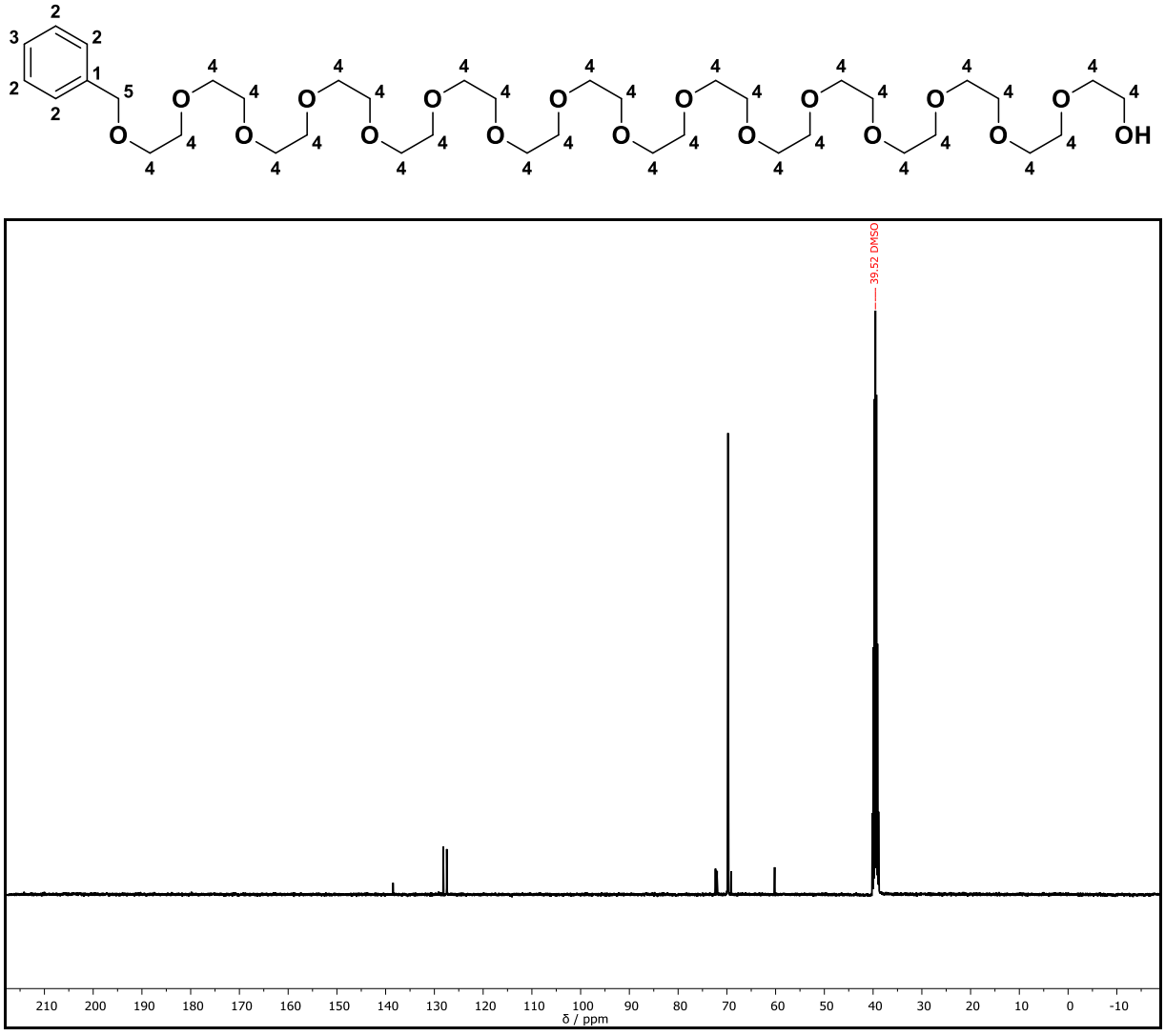
^{1}H NMR (400 MHz, DMSO-d_6): δ / ppm = 7.43 – 7.18 (m, 5H, CH_{Ar}^1), 4.56 (t, J = 5.5 Hz, 1H, OH^2), 4.49 (s, 2H, CH_2^3), 3.63 – 3.38 (m, 64H, CH_2^4).





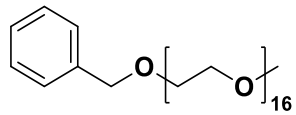
Supplementary Figure 22: ^{1}H NMR spectrum of **Bn(EG)$_{16}$OH** recorded at 400 MHz in DMSO-d_6.

^{13}C NMR (101 MHz, DMSO-d_6): δ / ppm = 138.48 (C_q^1), 128.19 (CH_{Ar}^2), 127.45 (CH_{Ar}^2), 127.34 (CH_{Ar}^3), 72.33 (CH_2^4), 72.00 (CH_2^5), 69.83 (CH_2^4), 69.77 (CH_2^4), 69.12 (CH_2^4), 60.20 (CH_2^4).



Supplementary Figure 23: ^{13}C NMR spectrum of **Bn(EG)$_{16}$OH** recorded at 101 MHz in DMSO-d_6.

α-Benzyl-ω-methyl hexadeca(ethylene glycol) – Bn(EG)$_{16}$OMe



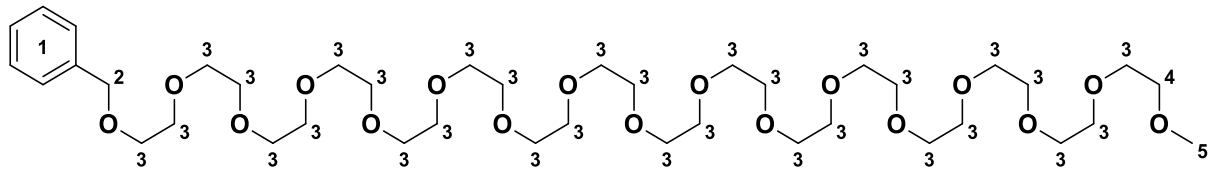
Chemical Formula: $C_{40}H_{74}O_{17}$
Exact Mass: 826.4926 Da
Molecular Weight: 827.0150 Da

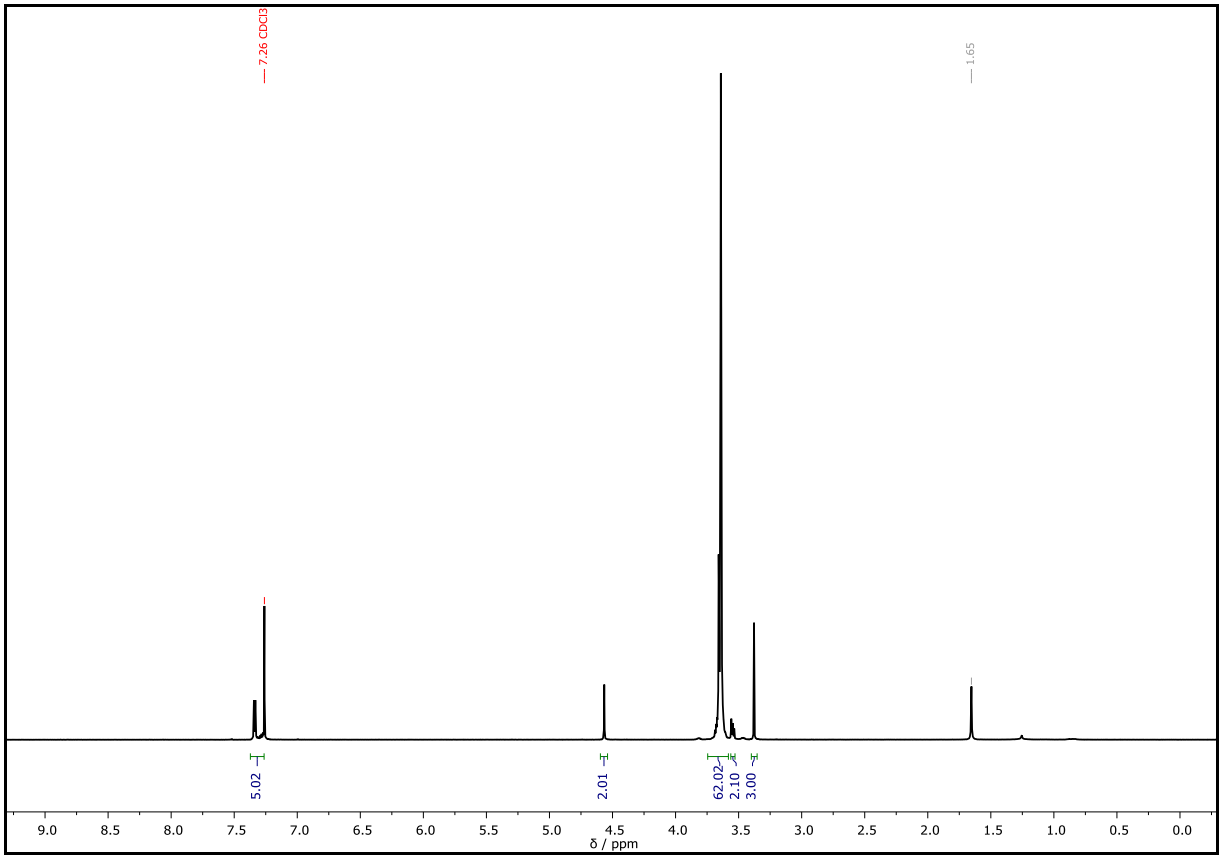
NaH (177 mg, 4.43 mmol, 1.20 equiv., dispersed in 60% mineral oil) was added to monobenzyl hexadeca(ethylene glycol) **Bn(EG)$_{16}$OH** (2.30 mL, 3.00 g, 3.69 mmol, 1.00 equiv.) dissolved in anhydrous THF (38 mL) at 0 °C under argon-atmosphere. Methyl iodide (5.24 g, 36.9 mmol, 10.0 equiv.) was added dropwise and the reaction mixture was stirred over night at room temperature. The solution was cooled to 0 °C and water (38 mL) was added to quench the excess of NaH. Subsequently, the mixture was extracted with EA, and the aqueous phase was further extracted with DCM (3 × 20 mL). The combined organic layers were dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. Purification of the crude product *via* column chromatography (EA:MeOH = 9:1) yielded the α-benzyl-ω-methyl hexadeca(ethylene glycol) **Bn(EG)$_{16}$OMe** as a yellowish solid in 29.7% (908 mg, 1.10 mmol).

HRMS (ESI) of $C_{40}H_{74}O_{17}$ $[M+H]^+$ *m/z* calc. 827.4999, detected 827.4978; $[M+NH_4]^+$ *m/z* calc. 844.5264, detected 844.5231; $[M+K]^+$ *m/z* calc. 865.4558, detected 865.4519.

R_f = 0.16 (EA:MeOH = 9:1).

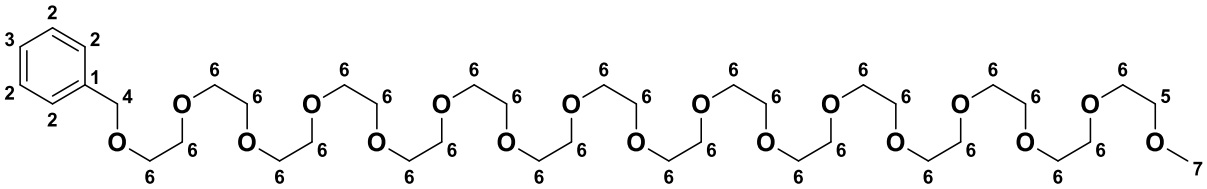
^{1}H NMR (400 MHz, $CDCl_3$): δ / ppm = ^{1}7.36 – 7.27 (m, 5H, CH_{Ar}^1), 4.57 (s, 2H, CH_2^2), 3.78 – 3.58 (m, 62H, CH_2^3), 3.57 – 3.53 (m, 2H, CH_2^4), 3.38 (s, 3H, CH_3^5).



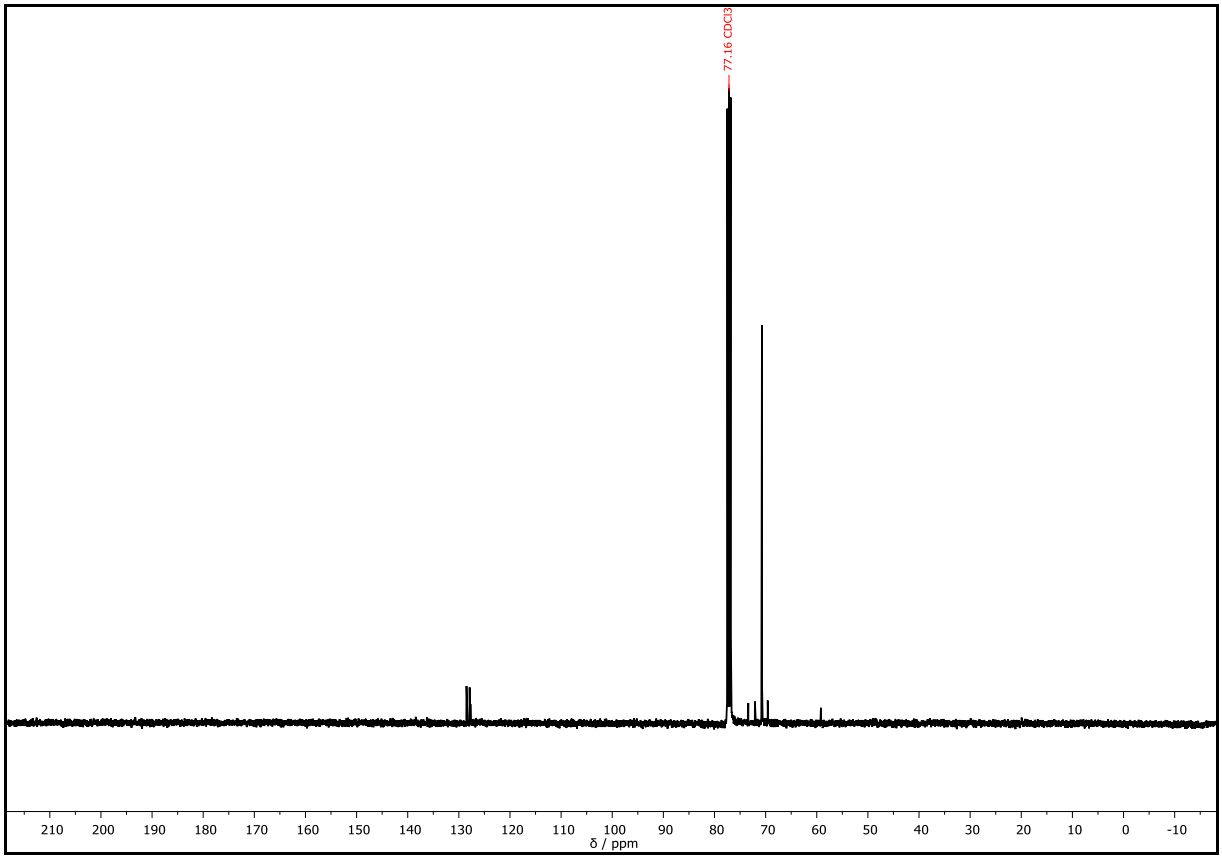


Supplementary Figure 24: ^{1}H NMR spectrum of **Bn(EG)$_{16}$OMe** recorded at 400 MHz in $CDCl_3$.

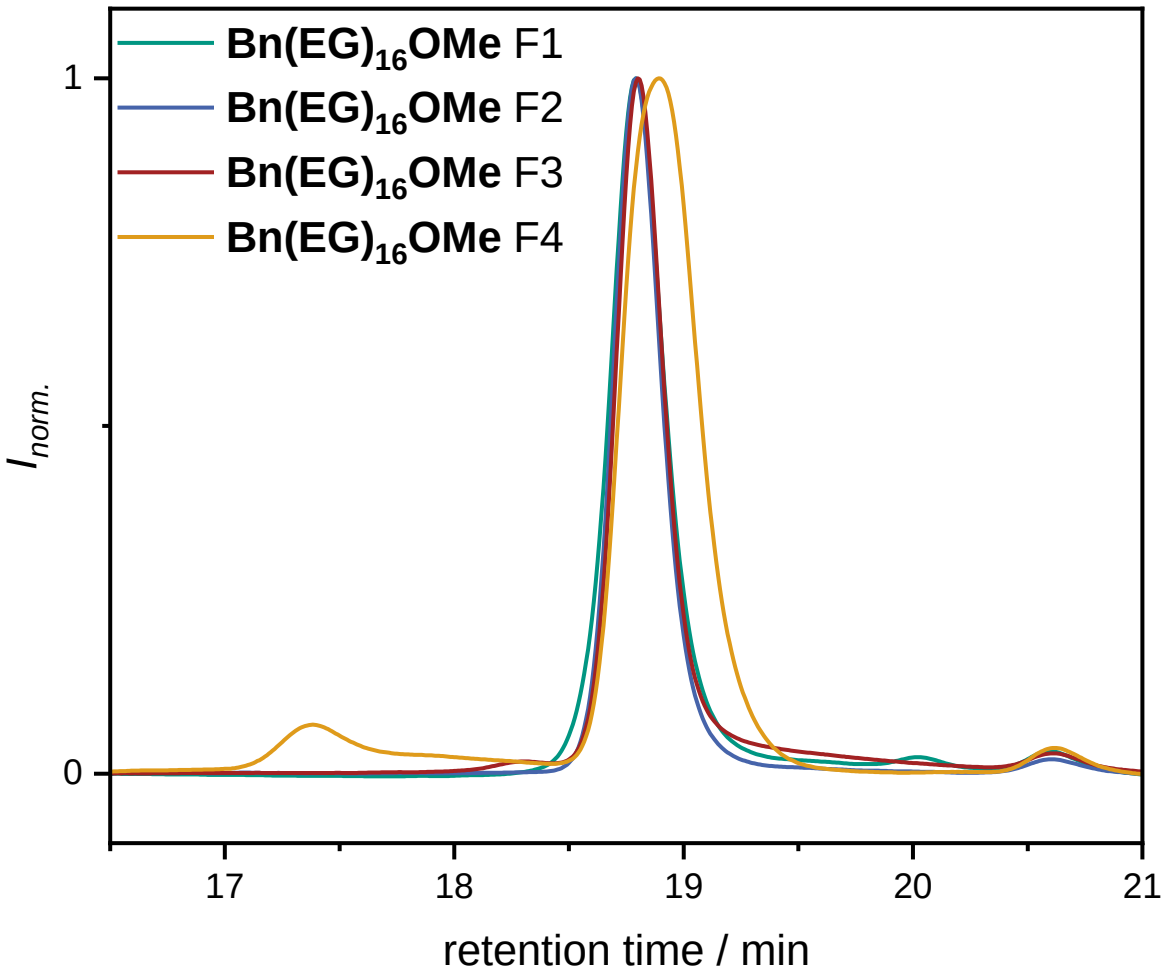
^{13}C NMR (101 MHz, $CDCl_3$): δ / ppm = 128.50 (CH_{Ar}^2), 127.89 (CH_{Ar}^2), 127.73 (CH_{Ar}^3), 73.39 (CH_2^4), 72.09 (CH_2^5), 70.76 (CH_2^6), 70.72 (CH_2^6), 69.59 (CH_2^6), 59.18 (CH_3^7).



Note that C_q^1 is not visible in the ^{13}C spectra due to low sample concentration.

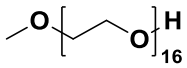


Supplementary Figure 25: ^{13}C NMR spectrum of **Bn(EG)$_{16}$OMe** recorded at 101 MHz in $CDCl_3$.



Supplementary Figure 26: SEC traces of **Bn(EG)$_{16}$OMe** after column chromatography. F2 showed the narrowest peak and was used for further synthesis. Compared to F1, F2 shows a broadening towards higher and lower retention times and a second peak around 20 min. The chromatogram for F3 exhibits an impurity signal towards lower and a tailing towards higher retention times. A broad impurity signal is observed in F4. Furthermore, the signal shows a higher distribution and is shifted towards higher retention times.

Monomethyl hexadeca(ethylene glycol) – HO(EG)$_{16}$OMe

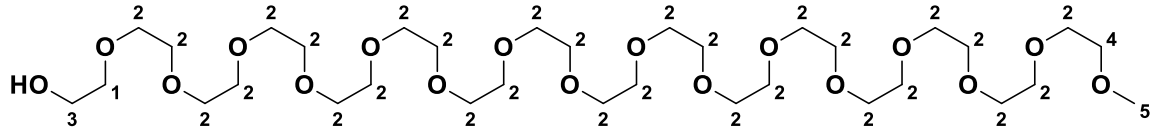


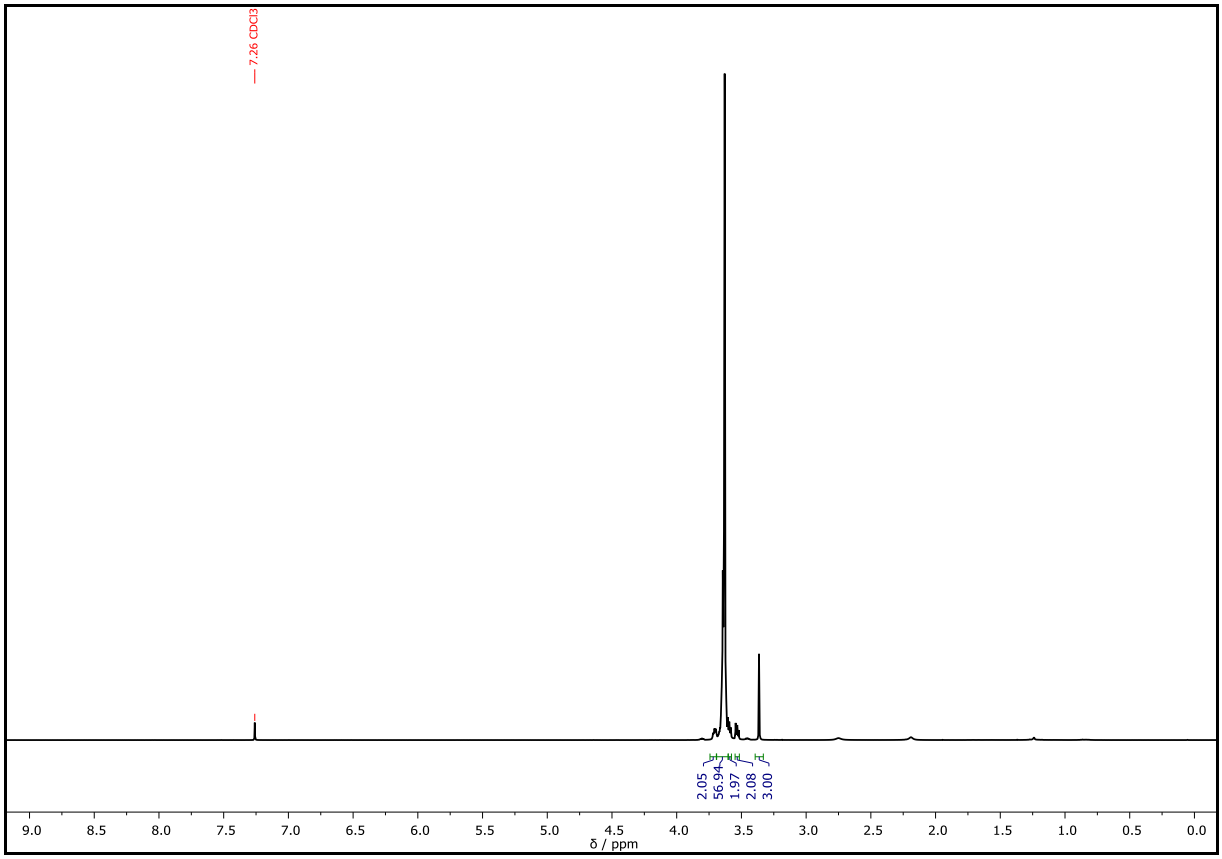
Chemical Formula: $C_{33}H_{68}O_{17}$
Exact Mass: 736.4457 Da
Molecular Weight: 736.8900 Da

α-Benzyl-ω-methyl hexadeca(ethylene glycol) **Bn(EG)$_{16}$OMe** (908 mg, 1.10 mmol, 1.00 equiv.) was dissolved in ethanol (20 mL) and palladium on carbon (90.8 mg, 10 wt%) was added. The reaction mixture was flushed with hydrogen (balloon) and stirred under hydrogen-atmosphere over night at room temperature. Afterwards, the mixture was filtered through a pad of Celite® to remove the heterogeneous catalyst and the filter cake was washed with methanol. The solvent was evaporated under reduced pressure yielding the monomethyl hexadeca(ethylene glycol) **HO(EG)$_{16}$OMe** as a yellowish solid (789 mg, 954 µmol, 97.6%).

HRMS (ESI) of $C_{33}H_{68}O_{17}$ $[M+Na]^+$ *m/z* calc. 759.4349, detected 759.4337; $[M+K]^+$ *m/z* calc. 775.4088, detected 775.4073.

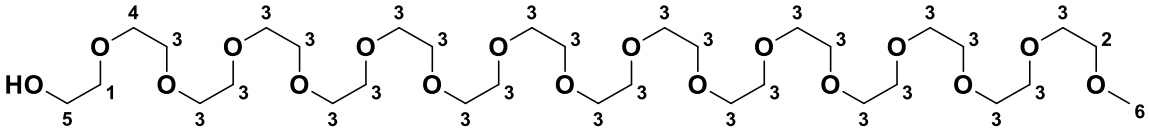
^{1}H NMR (400 MHz, $CDCl_3$): δ / ppm = 3.73 – 3.69 (m, 2H, CH_2^1), 3.67 – 3.61 (m, 58H, CH_2^2), 3.61 – 3.58 (m, 2H, CH_2^3), 3.55 – 3.51 (m, 2H, CH_2^4), 3.36 (s, 3H, CH_3^5).

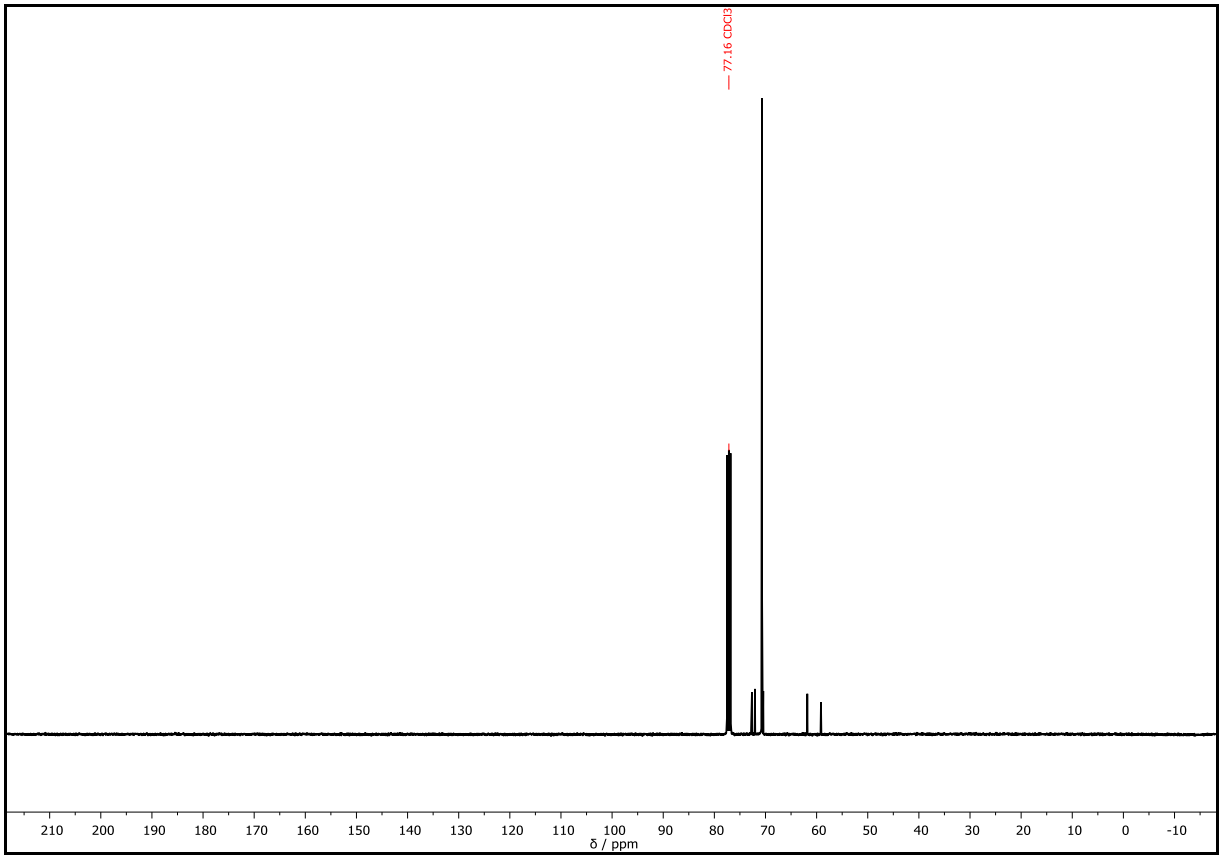




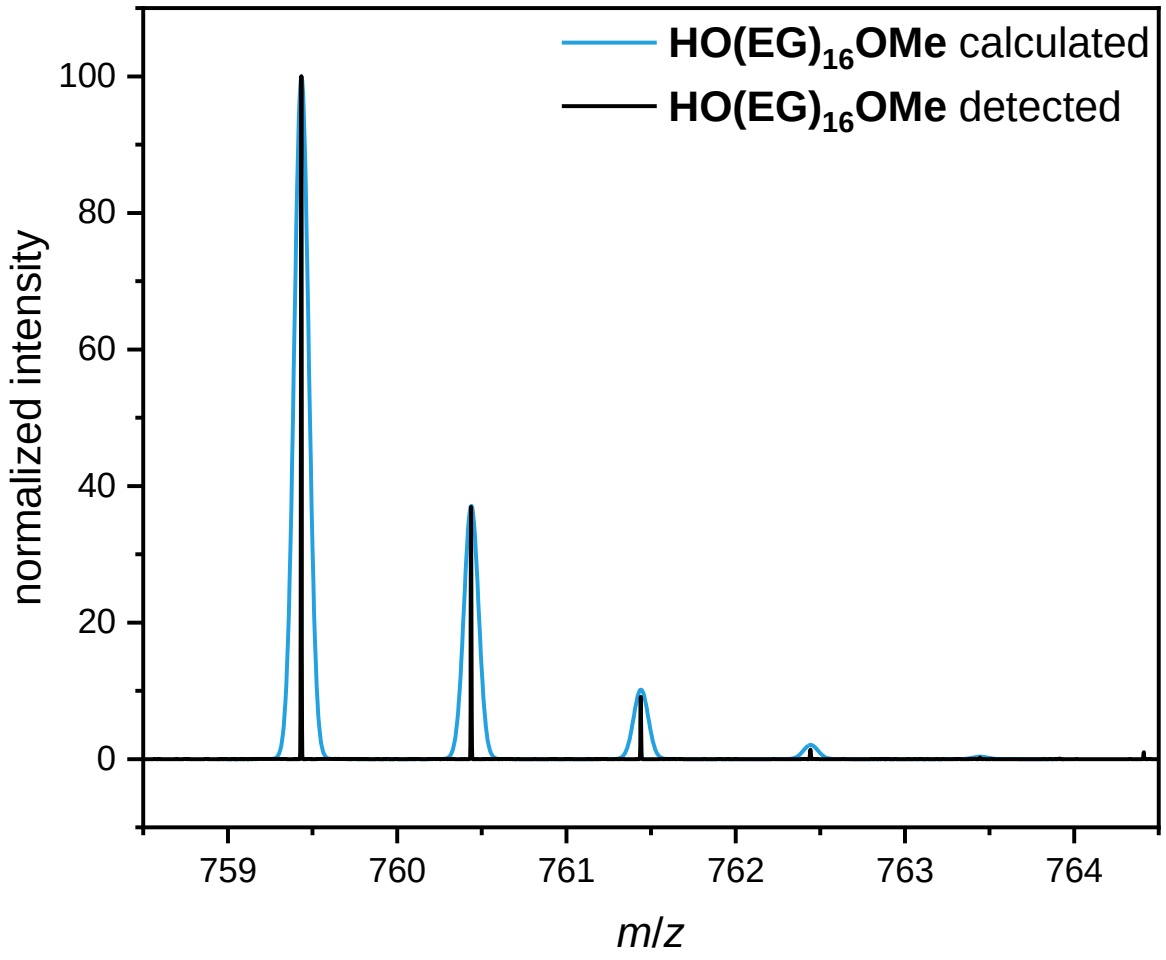
Supplementary Figure 27: ^{1}H NMR spectrum of **HO(EG)$_{16}$OMe** recorded at 400 MHz in $CDCl_3$.

^{13}C NMR (101 MHz, $CDCl_3$): δ / ppm = 72.65 (CH_2^1), 72.06 (CH_2^2), 70.73 (CH_2^3), 70.69 (CH_2^3), 70.67 (CH_2^3), 70.64 (CH_2^3), 70.44 (CH_2^4), 61.82 (CH_2^5), 59.15 (CH_3^6).

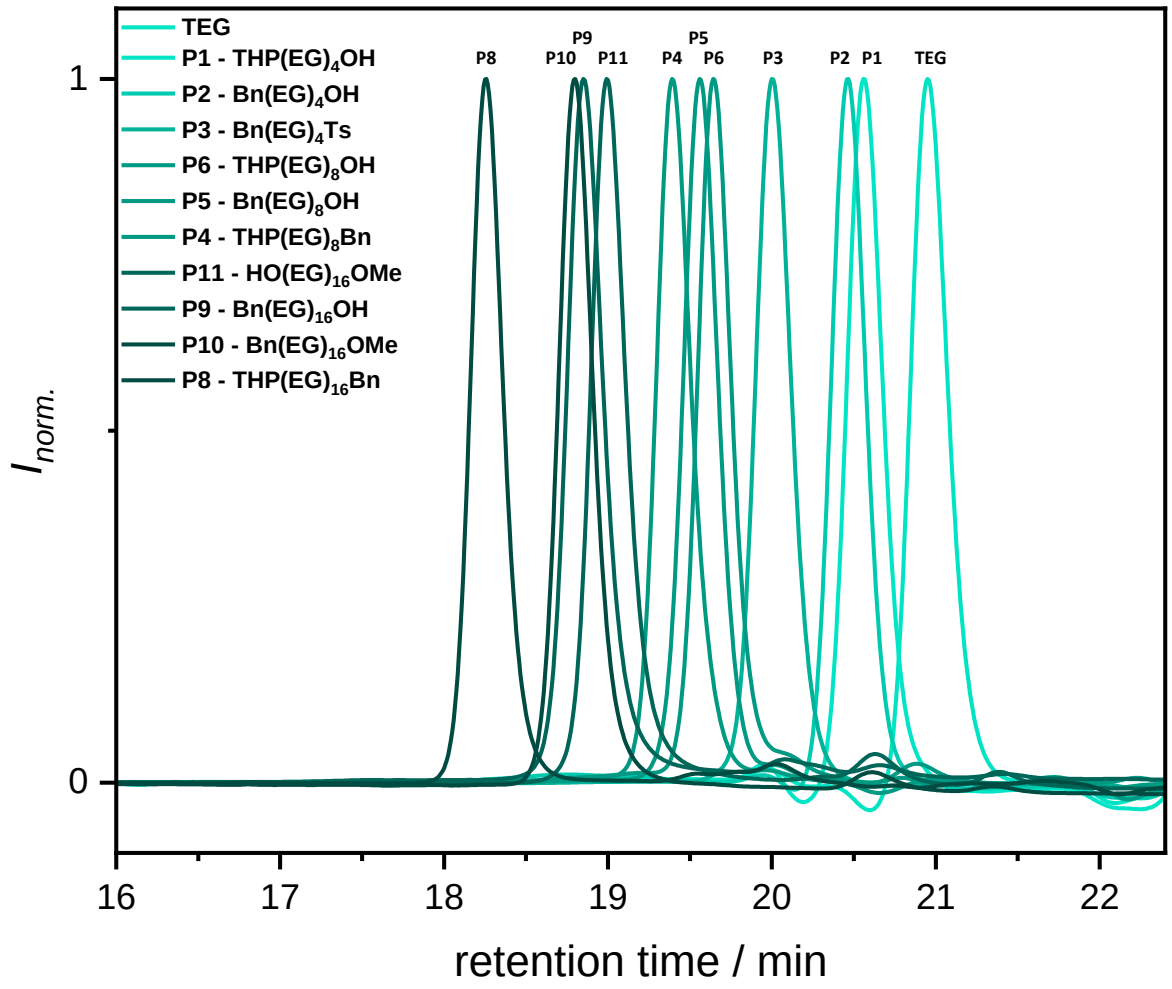




Supplementary Figure 28: ^{13}C NMR spectrum of **HO(EG)$_{16}$OMe** recorded at 101 MHz in $CDCl_3$.

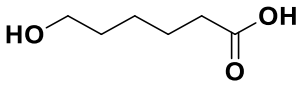


Supplementary Figure 29: Comparison of the calculated and measured isotopic pattern of the sodium adduct of **HO(EG)$_{16}$OMe** ([M+Na]$^+$ *m/z* calc. 759.4349, detected 759.4337).



Supplementary Figure 30: SEC overview of the synthesized PEGs. The SEC traces range from the starting material tetra(ethylene glycol) (**TEG**) at a retention time of 21.0 min in light green to the doubly protected hexadeca(ethylene glycol) **THP(EG)$_{16}$Bn** at 18.3 min in dark green.

6-Hydroxyhexanoic acid – HO(CL)$_1$CO$_2$H



Chemical Formula: $C_6H_{12}O_3$
Exact Mass: 132.0786 Da
Molecular Weight: 132.1590 Da

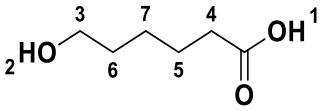
NaOH (21.0 g, 525 mmol, 2.00 equiv.) and *ε*-caprolactone (27.8 mL, 30.0 g, 263 mmol, 1.00 equiv.) were added in a round bottom flask, charged with 800 mL water. The mixture was stirred overnight at room temperature. Subsequently, the pH was adjusted to 2 using 3 M hydrochloride solution and the reaction mixture was extracted with 1500 mL diethyl ether by applying a liquid/liquid continuous extractor. The organic layers were dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure to give product **HO(CL)$_1$CO$_2$H** (32.8 g, 248 mmol, 94.3%) as a white solid.

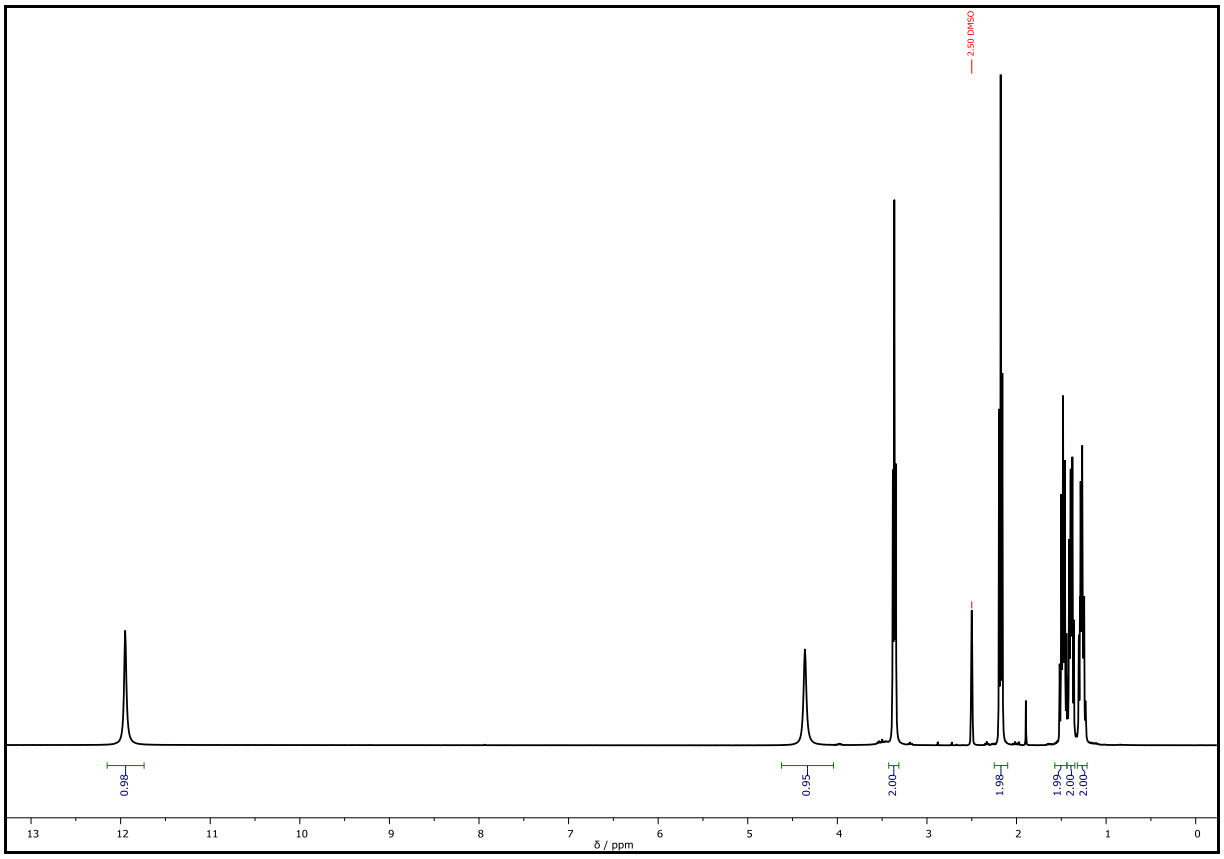
FAB of $C_6H_{12}O_3$ ($M+H^+$ = 133.1); HRMS (FAB) of $C_6H_{12}O_3$ $[M+H]^+$ calcd. 133.0865, detected 133.0865.

IR (ATR platinum diamond) $\tilde{\nu}$ / cm^{-1} = 3246.1, 2938.0, 2859.2, 2525.8, 1911.3, 1681.8, 1464.4, 1412.6, 1292.5, 1266.1, 1235.3, 1159.9, 1111.6, 1081.1, 1045.4, 984.1, 899.5, 841.9, 730.7, 675.6, 488.6.

R_f = 0.10 (cyhex/EA = 1:1).

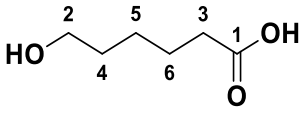
^{1}H NMR (DMSO-d_6, 400 MHz): δ / ppm = 11.96 (s, 1 H, CO_2H^1), 4.34 (t, J = 5.0 Hz, 1 H, OH^2), 3.26–3.43 (m, 2 H, CH_2^3), 2.18 (t, J = 7.3 Hz, 2 H, CH_2^4), 1.49 (dt, J = 14.8, 7.3 Hz, 2 H, CH_2^5), 1.39 (dd, J = 13.3, 6.5 Hz, 2 H, CH_2^6), 1.20–1.34 (m, 2 H, CH_2^7).

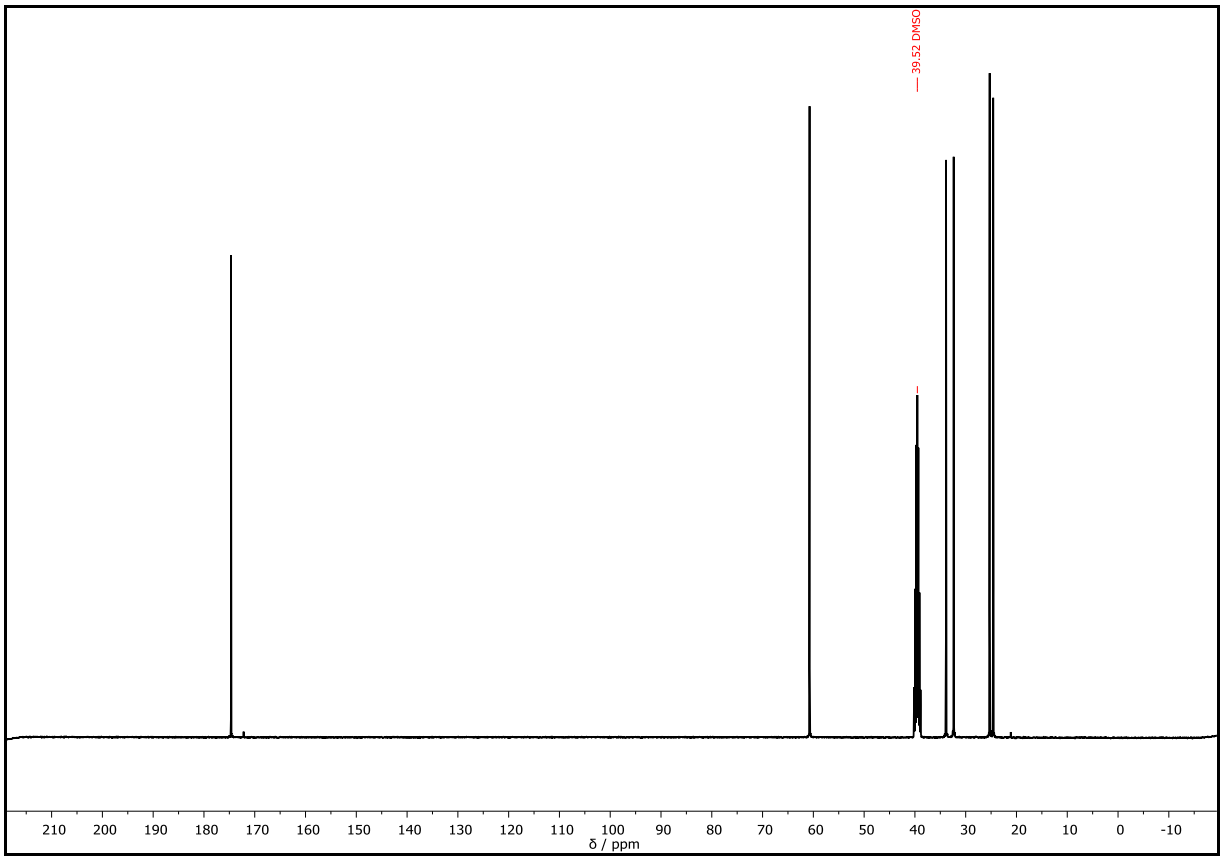




Supplementary Figure 31: ^{1}H NMR spectrum of **HO(CL)$_1$CO$_2$H**, recorded at 400 MHz in DMSO-d_6.

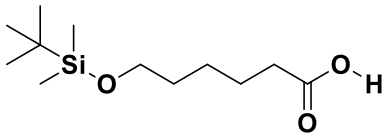
^{13}C NMR (DMSO-d_6, 101 MHz): δ / ppm = 174.46 (C_q^1), 60.54 (CH_2^2), 24.38 (CH_2^3), 33.66 (CH_2^4), 32.16 (CH_2^5), 25.07 (CH_2^6).





Supplementary Figure 32: ^{13}C NMR spectrum of **HO(CL)$_1$CO$_2$H**, recorded at 101 MHz in DMSO-d_6.

6-(*tert*-Butyldimethyl)siloxyhexanoic acid – TBDMS(CL)$_1$CO$_2$H



Chemical Formula: $C_{12}H_{26}O_3Si$
Exact Mass: 246.1651 Da
Molecular Weight: 246.4220 Da

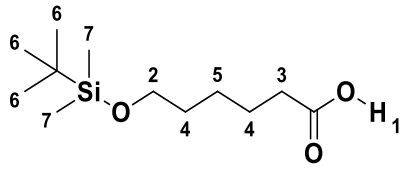
6-Hydroxyhexanoic acid **HO(CL)$_1$CO$_2$H** (16.5 g, 125 mmol, 1.00 equiv.) and imidazole (20.4 g, 300 mmol, 2.40 equiv.) were dissolved in 108 mL dry DMF. After stirring for 10 minutes at room temperature, *tert*-butyldimethylsilylchloride (24.5 g, 162 mmol, 1.30 equiv.) was added and the reaction mixture was stirred overnight at 50 °C under argon atmosphere. Subsequently, the solution was poured into a separation funnel, containing 250 mL of brine. The organic layer was separated, and the aqueous phase was extracted with diethyl ether (4 × 250 mL). The combined organic layers were dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. Purification of the crude product by column chromatography (cyhex/EA 1:1 → 1:3) yielded the product **TBDMS(CL)$_1$CO$_2$H** (26.2 g, 106 mmol, 85.3%) as a yellowish oil.

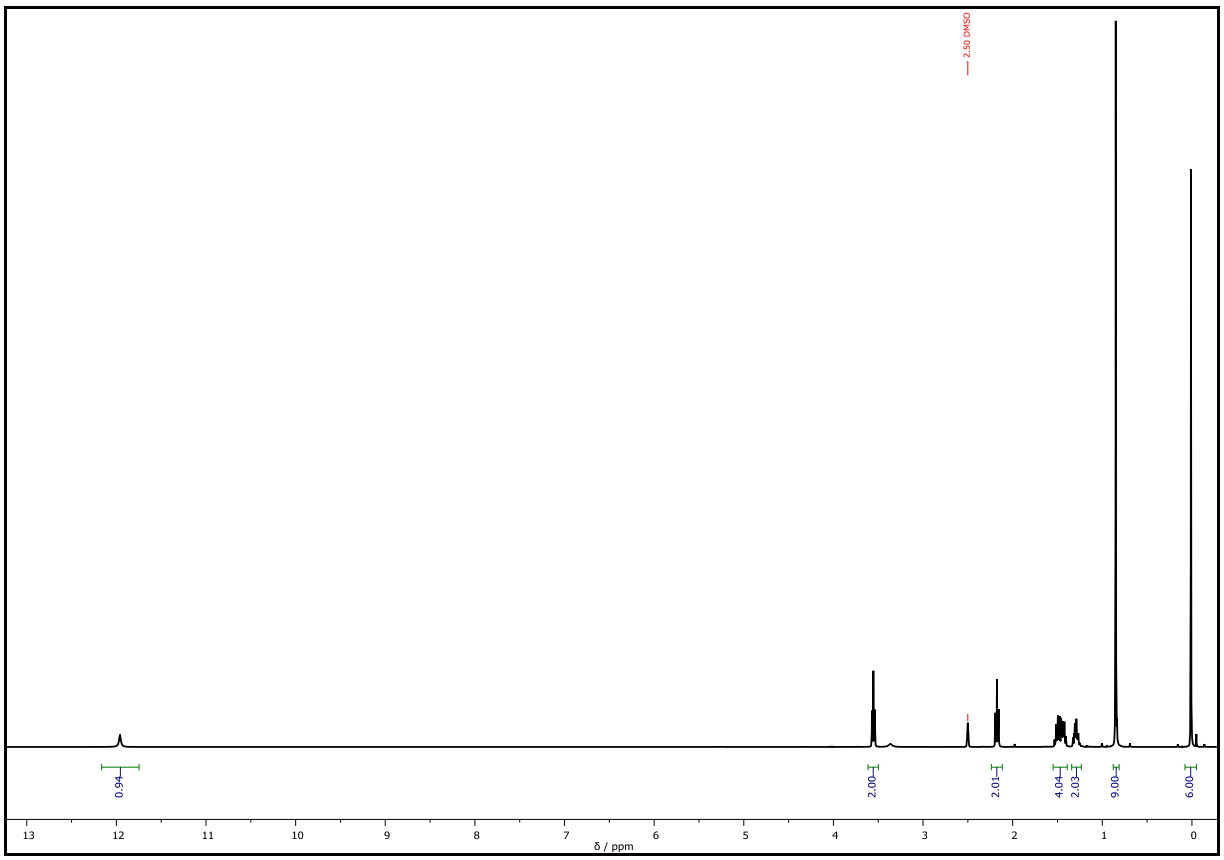
FAB of $C_{12}H_{26}O_3Si$ ($M+H^+$ = 247.2); HRMS (FAB) of $C_{12}H_{26}O_3Si$ $[M+H]^+$ calcd. 247.1729, detected 247.1731.

IR (ATR platinum diamond) $\tilde{\nu}$ / cm^{-1} = 2929.2, 2857.2, 1708.3, 1462.4, 1411.6, 1388.5, 1360.9, 1282.3, 1251.7, 1096.8, 1005.4, 982.6, 937.4, 832.3, 773.3, 661.0, 469.6, 403.0.

R_f = 0.52 (cyclohexane/EA = 5:1).

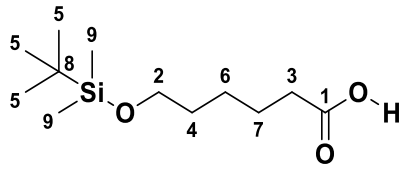
^{1}H NMR (DMSO-d_6, 400 MHz): δ / ppm = 11.96 (s, 1 H, CO_2H^1), 3.56 (t, J = 6.3, 2 H, CH_2^2), 2.18 (t, J = 7.3 Hz, 2 H, CH_2^3), 1.38-1.56 (m, 4 H, CH_2^4), 1.25–1.35 (m, 2 H, CH_2^5), 0.85 (s, 9 H, CH_3^6), 0.01 (s, 6 H, CH_3^7).

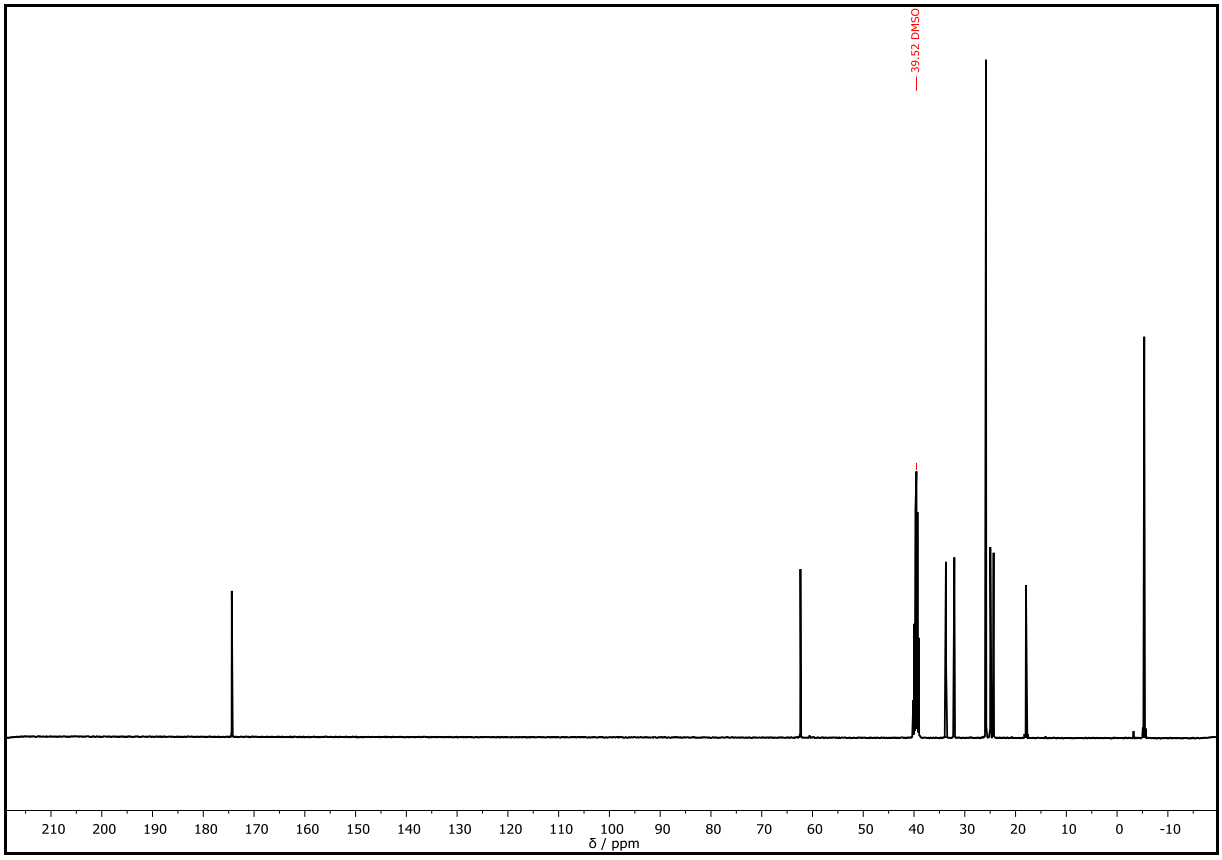




Supplementary Figure 33: ^{1}H NMR spectrum of **TBDMS(CL)$_1$CO$_2$H**, recorded at 400 MHz in DMSO-d_6.

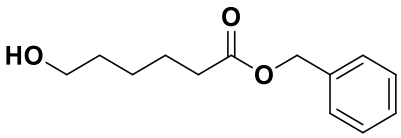
^{13}C NMR (DMSO-d_6, 101 MHz): δ / ppm = 174.39 (C_q^1), 62.37 (CH_2^2), 33.72 (CH_2^3), 32.06 (CH_2^4), 25.82 (CH_3^5), 24.97 (CH_2^6), 24.33 (CH_2^7), 17.95 (C_q^8), 5.35 (CH_3^9).





Supplementary Figure 34: ^{13}C NMR spectrum of **TBDMS(CL)$_1$CO$_2$H**, recorded at 101 MHz in DMSO-d_6.

Benzyl 6-hydroxyhexanoate – HO(CL)$_1$Bn



Chemical Formula: $C_{13}H_{18}O_3$
Exact Mass: 222.1256 Da
Molecular Weight: 222.2840 Da

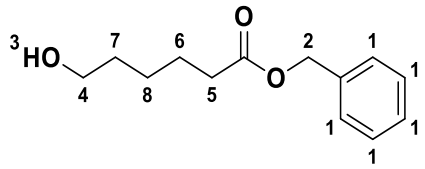
6-Hydroxyhexanoic acid **HO(CL)$_1$CO$_2$H** (16.8 g, 127 mmol, 1.00 equiv.) and DBU (19.3 g, 127 mmol, 1.00 equiv.) were dissolved in dichloromethane (76 mL). Benzyl bromide (18.1 mL, 26.1 g, 152 mmol, 1.20 equiv.) in dichloromethane (51 mL) was added dropwise to the solution. The reaction mixture was stirred overnight at room temperature. Subsequently, the mixture was washed with water (100 mL) and extracted with dichloromethane (2 × 100 mL). The combined organic layers were dried over anhydrous sodium sulfate, filtered, and the solvent was removed under reduced pressure. Purification of the crude product *via* column chromatography (cyhex/EA 5:1 → 1:3) yielded the benzyl-6-hydroxyhexanoate **HO(CL)$_1$Bn** (24.8 g, 112 mmol, 87.9%) as a yellowish oil.

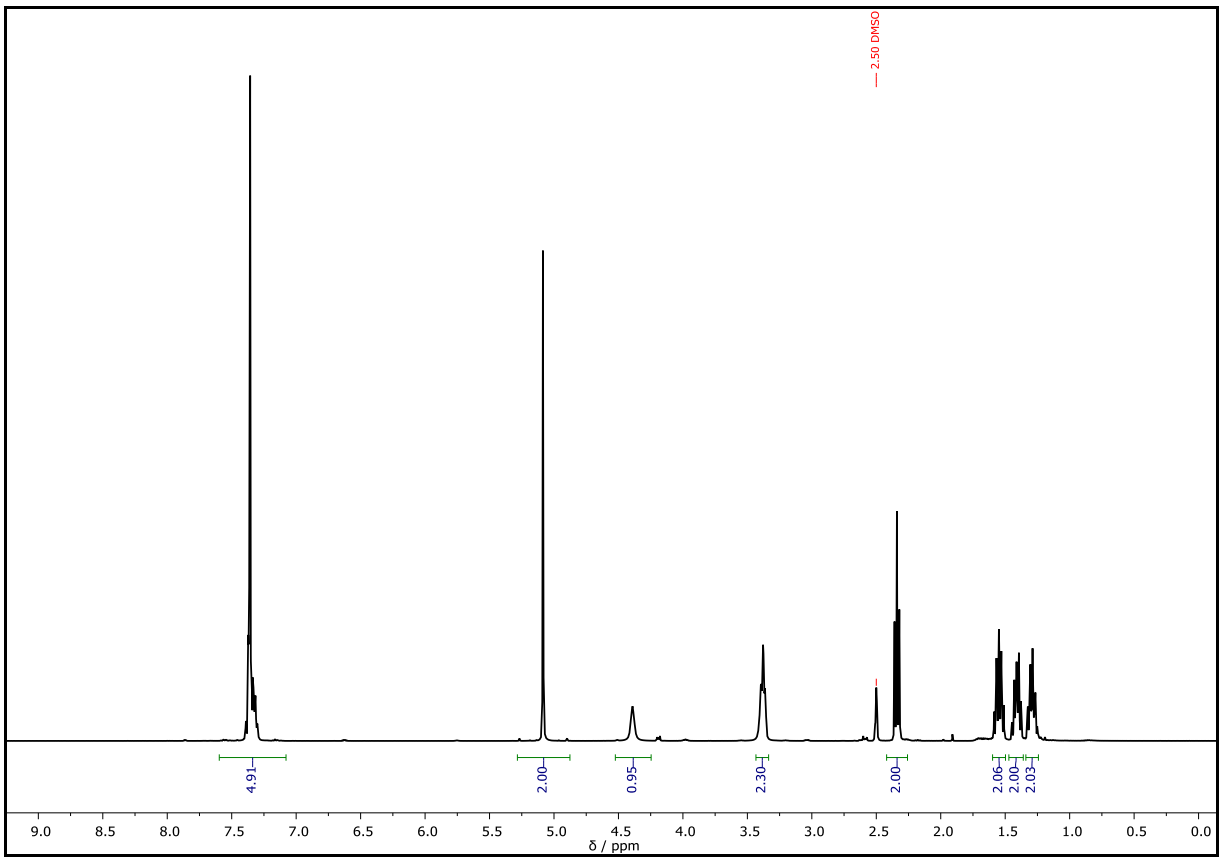
FAB of $C_{13}H_{18}O_3$ ($M+H^+$ = 222.2); HRMS (FAB) of $C_{13}H_{18}O_3$ $[M+H]^+$ calcd. 222.1256, detected 222.1255.

IR (ATR platinum diamond) $\tilde{\nu}$ / cm^{-1} = 3400.0, 3033.3, 2934.5, 2862.0, 1730.6, 1497.2, 1455.0, 1382.2, 1351.1, 1150.0, 1073.5, 1051.9, 1026.4, 736.3, 696.9, 578.2, 502.4.

R_f = 0.62 (cyhex/EA = 1:1).

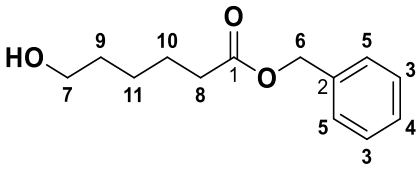
^{1}H NMR (DMSO-d_6, 400 MHz): δ / ppm = 7.29-7.42 (m, 5H, CH_{Ar}^{1}), 5.08 (s, 2H, CH_2^{2}), 4.35 (t, J =5.2 Hz, 1H, OH^{3}), 3.31-3.41 (m, 2H, CH_2^{4}), 2.34 (t, J = 7.4 Hz, 2H, CH_2^{5}), 1.48-1.60 (m, 2H, CH_2^{6}), 1.34-1.46 (m, 2H, CH_2^{7}), 1.24-1.34 (m, 2H, CH_2^{8}).

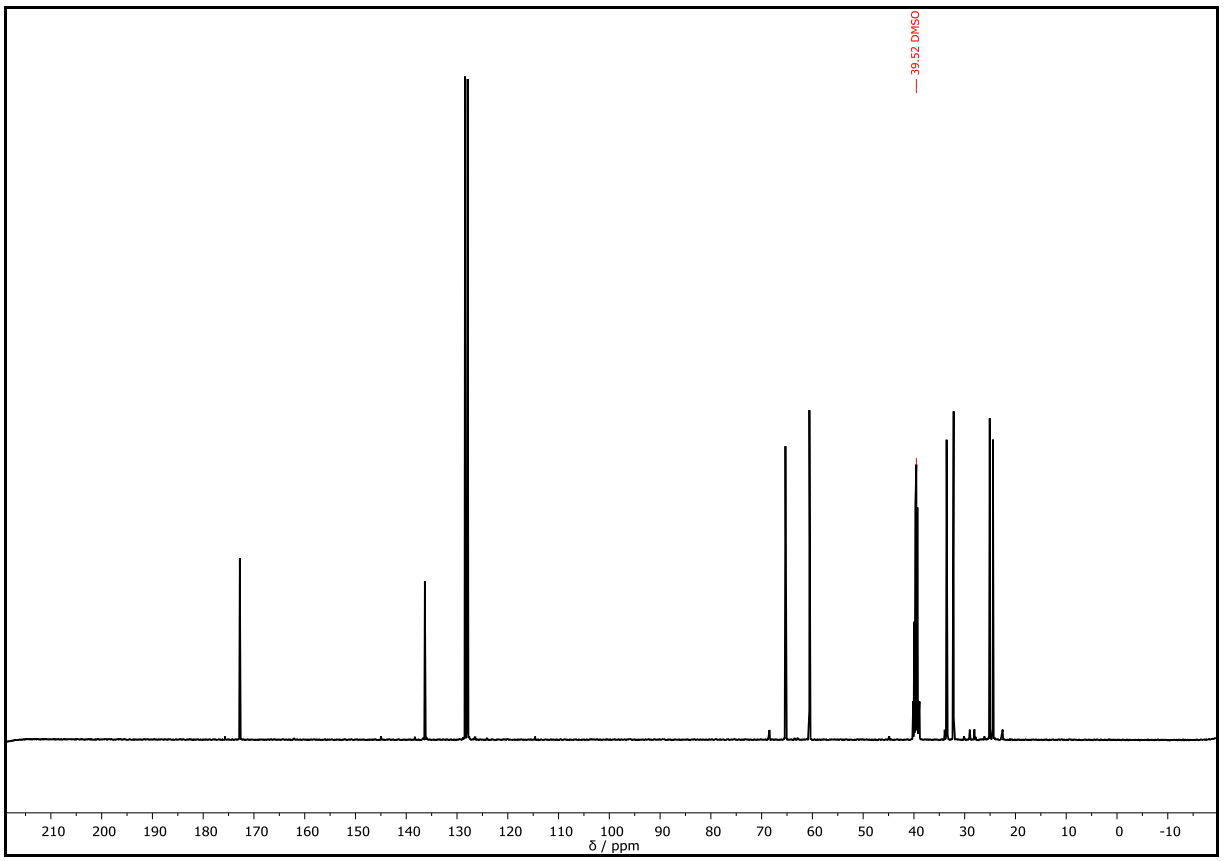




Supplementary Figure 35: ^{1}H NMR spectrum of **HO(CL)$_1$Bn**, recorded at 400 MHz in DMSO-d_6.

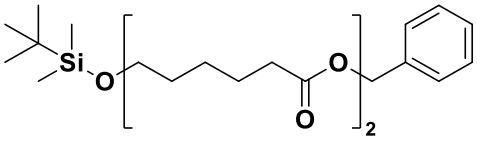
^{13}C NMR (DMSO-d_6, 101 MHz): δ / ppm = 172.79 (C_q^1), 136.33 ($C_{q,Ar}^2$), 128.42 ($CH_{Ar,ortho}^3$), 127.69 ($CH_{Ar,para}^4$), 127.92 ($CH_{Ar,meta}^5$), 65.31 (CH_2^6), 60.59 (CH_2^7), 33.57 (CH_2^8), 32.18 (CH_2^9), 25.08 (CH_2^{10}), 24.43 (CH_2^{11}).





Supplementary Figure 36: ^{13}C NMR spectrum of **HO(CL)$_1$Bn**, recorded at 101 MHz in DMSO-d_6.

Doubly protected dimer – TBDMS(CL)$_2$Bn



Chemical Formula: $C_{25}H_{42}O_5Si$
Exact Mass: 450.2802 Da
Molecular Weight: 450.6910 Da

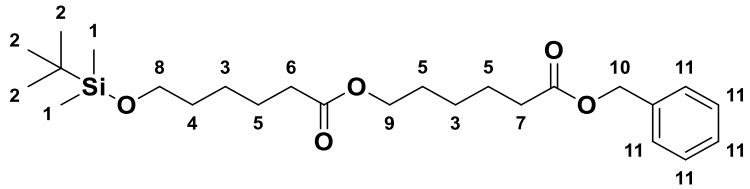
6-(*tert*-Butyldimethyl)siloxyhexanoic acid **TBDMS(CL)$_1$CO$_2$H** (11.1 g, 45.1 mmol, 1.00 equiv.), benzyl-6-hydroxyhexanoate **HO(CL)$_1$Bn** (10.0 g, 45.1 mmol, 1.00 equiv.), 1,3-dicyclohexylcarbodiimide (DCC) (11.2 g, 54.1 mmol, 1.10 equiv.) and 4-(dimethylamino)pyridine (DMAP) (6.60 g, 54.1 mmol, 1.10 equiv.) were dissolved in 108 mL dichloromethane. The solution was stirred overnight at room temperature until complete conversion of the starting materials was indicated by GC analysis. Subsequently, the reaction mixture was washed with 100 mL saturated $CuSO_4$-solution and twice with 100 mL of water. The organic layer was separated, dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. Purification of the crude product *via* column chromatography (cyhex/EA 20:1 → 8:1) yielded the doubly protected dimer **TBDMS(CL)$_2$Bn** (17.9 g, 39.8 mmol, 88.3%) as a colorless oil.

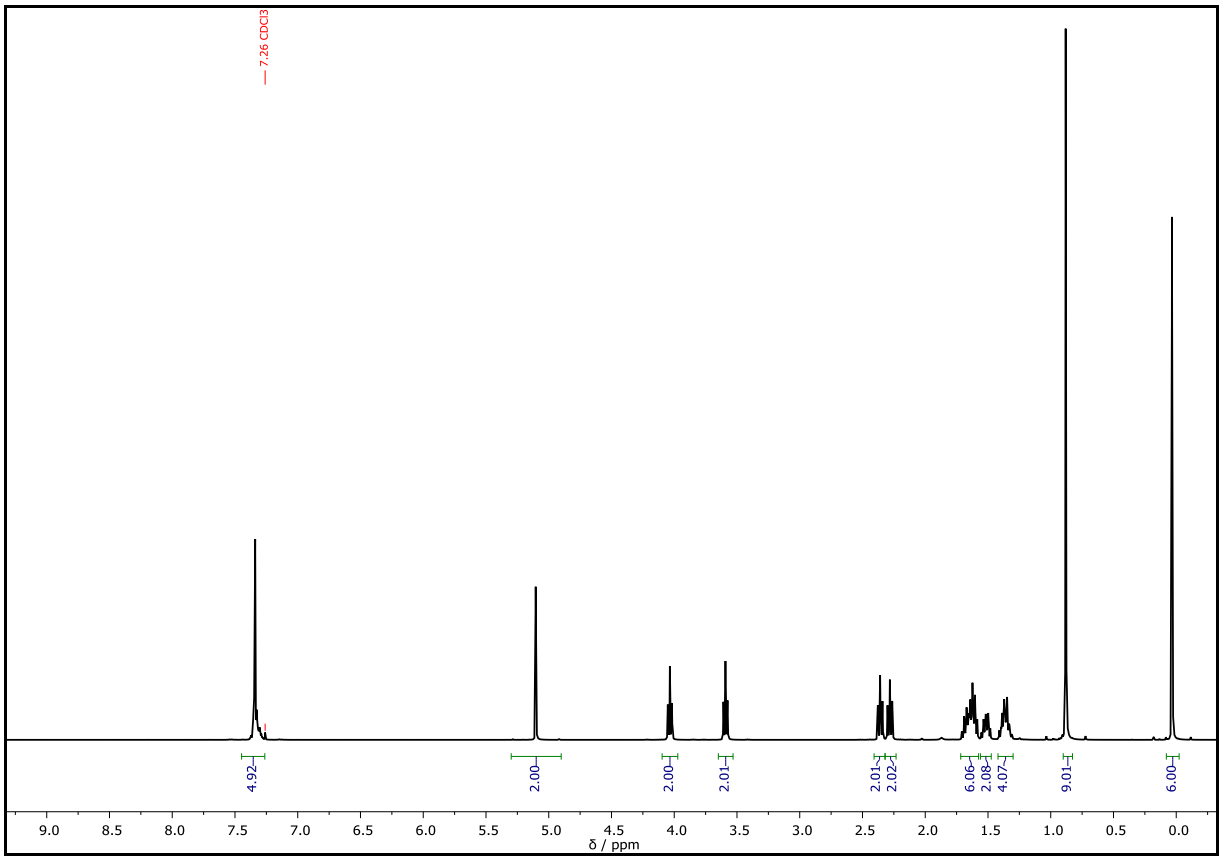
FAB of $C_{25}H_{42}O_5Si$ ($M+H^+$ = 451.3); HRMS (FAB) of $C_{25}H_{42}O_5Si$ $[M+H]^+$ calcd. 451.2880, detected 451.279.

IR (ATR platinum diamond) $\tilde{\nu}$ / cm^{-1} = 2930.2, 2857.2, 1733.5, 1461.5, 1386.4, 1359.6, 1253.1, 1155.7, 1094.7, 1005.0, 833.5, 774.4, 735.2, 696.8, 661.3, 577.3, 497.1, 400.2.

R_f = 0.50 (cyhex/EA = 5:1).

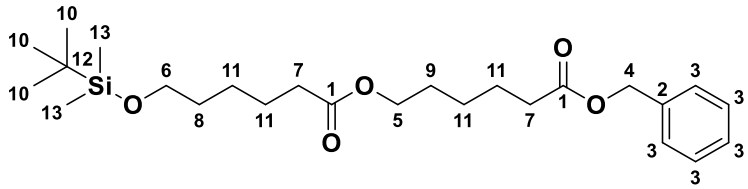
^{1}H NMR ($CDCl_3$, 400 MHz): δ / ppm = 7.35 (s, 5H, CH_{Ar}^{11}), 5.12 (s, 2H, CH_2^{10}), 4.04 (t, *J* = 6.6 Hz, 2H, CH_2^{9}), 3.60 (t, *J* = 6.4 Hz, 2H, CH_2^{8}), 2.36 (t, *J* = 7.5 Hz, 2H, CH_2^{7}), 2.28 (t, *J* = 7.6 Hz, 2H, CH_2^{6}), 1.58-1.71 (m, 6H, CH_2^{5}), 1.47-1.56 (m, 2H, CH_2^{4}), 1.28-1.45 (m, 4H CH_2^{3}), 0.89 (s, 9H, CH_3^{2}), 0.04 (s, 6H, CH_3^{1}).

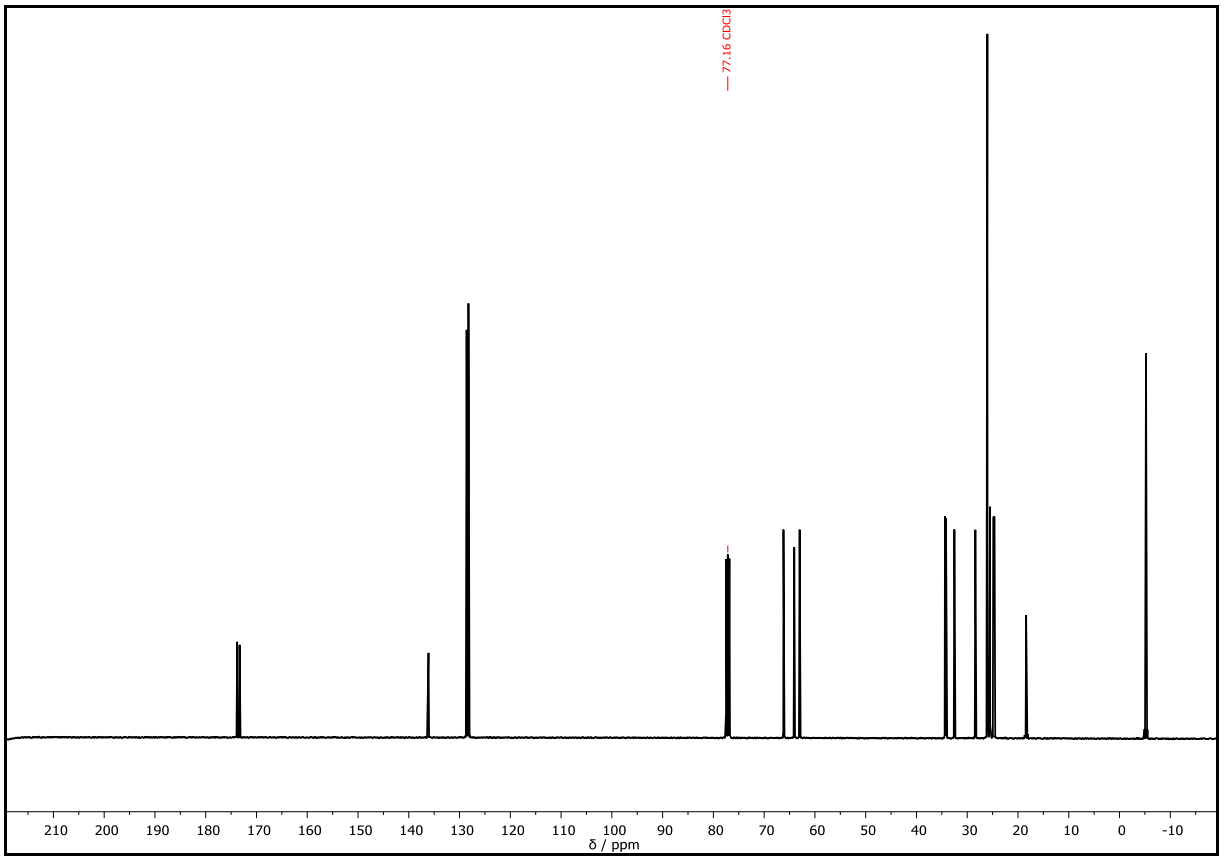




Supplementary Figure 37: ^{1}H NMR spectrum of **TBDMS(CL)$_2$Bn**, recorded at 400 MHz in $CDCl_3$.

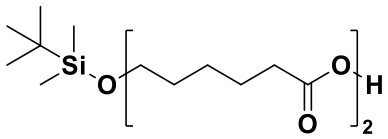
^{13}C NMR ($CDCl_3$, 101 MHz): δ / ppm = 173.80 (C_q^1), 173.33 (C_q^1), 136.12 ($C_{q,Ar}^2$), 128.61 (CH_{Ar}^3), 128.24 (CH_{Ar}^3), 66.19 (CH_2^4), 64.07 (CH_2^5), 63.01 (CH_2^6), 34.38 (CH_2^7), 34.18 (CH_2^7), 32.53 (CH_2^8), 28.40 (CH_2^9), 26.03 (CH_3^{10}), 25.58 (CH_2^{11}), 25.51 (CH_2^{11}), 24.87 (CH_2^{11}), 24.62 (CH_2^{11}), 18.40 (C_q^{12}), -5.22 (CH_3^{13}).





Supplementary Figure 38: ^{13}C NMR spectrum of **TBDMS(CL)$_2$Bn**, recorded at 101 MHz in $CDCl_3$.

Carboxyl–terminated Dimer – TBDMS(CL)$_2$CO$_2$H



Chemical Formula: $C_{18}H_{36}O_5Si$
Exact Mass: 360.2332 Da
Molecular Weight: 360.5660 Da

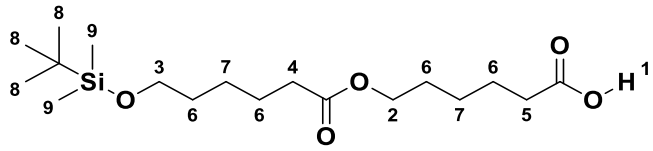
Doubly protected dimer **TBDMS(CL)$_2$Bn** (5.00 g, 11.1 mmol, 1.00 equiv.) was dissolved in 60 mL EA under argon atmosphere. Subsequently, palladium on activated carbon (10 wt%, 500 mg) was added to the solution and the reaction mixture was stirred for 45 min under hydrogen atmosphere using a balloon. After TLC indicated complete deprotection of the starting material, the mixture was filtered through a pad of celite. The residue was washed with EA (3 × 30 mL) and the combined filtrate was concentrated under reduced pressure yielding the carboxyl terminated dimer **TBDMS(CL)$_2$CO$_2$H** (3.96 g, 11.0 mmol, 99.0%) as a clear colorless oil.

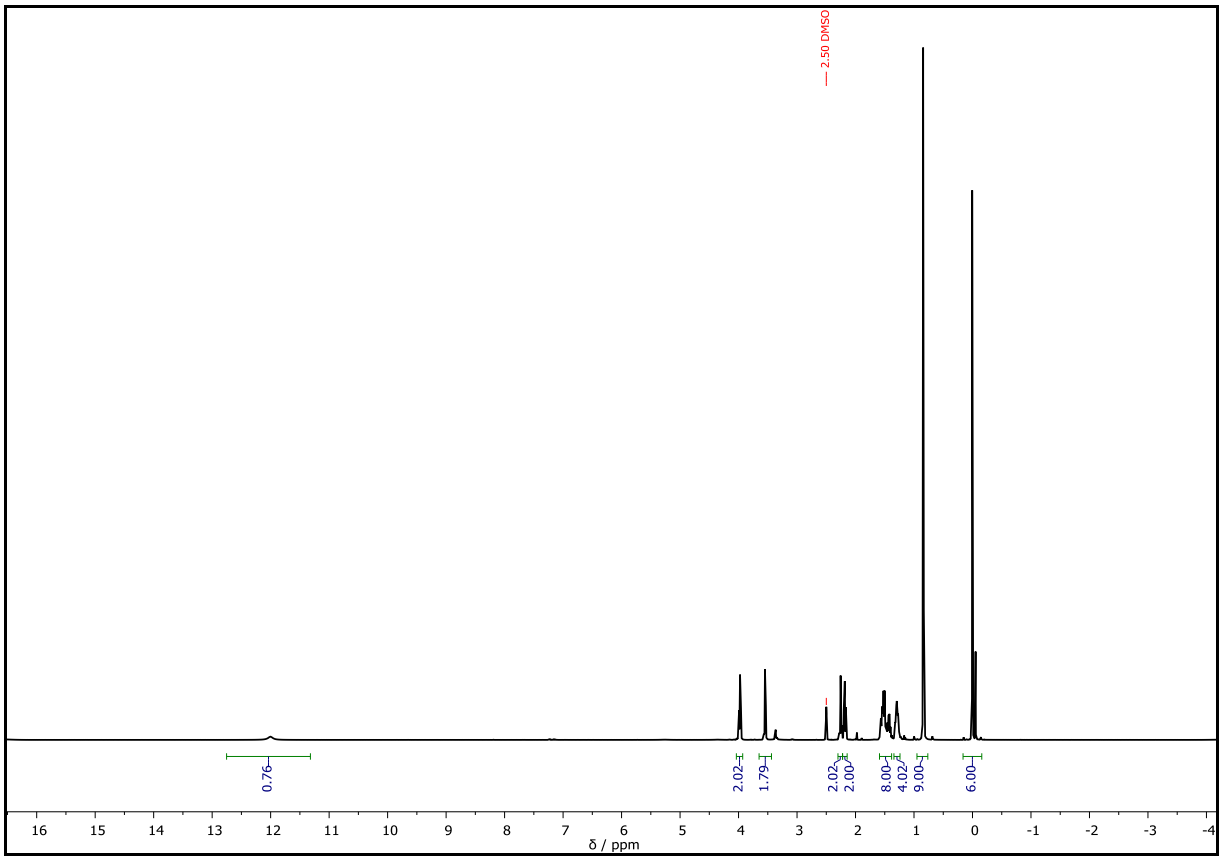
FAB of $C_{18}H_{36}O_5Si$ ($M+H^+$ = 361.3); HRMS (FAB) of $C_{18}H_{36}O_5Si$ $[M+H]^+$ calcd. 361.2410, detected 361.2409.

IR (ATR platinum diamond) ν / cm^{-1} = 2935.7, 2862.7, 1707.4, 1460.0, 1393.0, 1163.4, 1050.0, 835.4, 775.7, 732.2, 585.0.

R_f = 0.36 (cyhex/EA = 4:1).

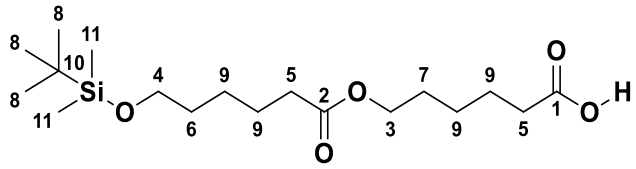
^{1}H NMR (DMSO-d_6, 300 MHz): δ / ppm = 12.00 (s, 1H, CO_2H^1), 3.98 (t, J = 6.6 Hz, 2H, CH_2^2), 3.55 (t, J = 6.2 Hz, 2H, CH_2^3), 2.27 (t, J = 7.3 Hz, 2H, CH_2^4), 2.19 (t, J = 7.3 Hz, 2H, CH_2^5), 1.37–1.62 (m, 8H, CH_2^6), 1.21–1.37 (m, 4H CH_2^7), 0.85 (s, 9H, CH_3^8), 0.01 (s, 6H, CH_3^9).

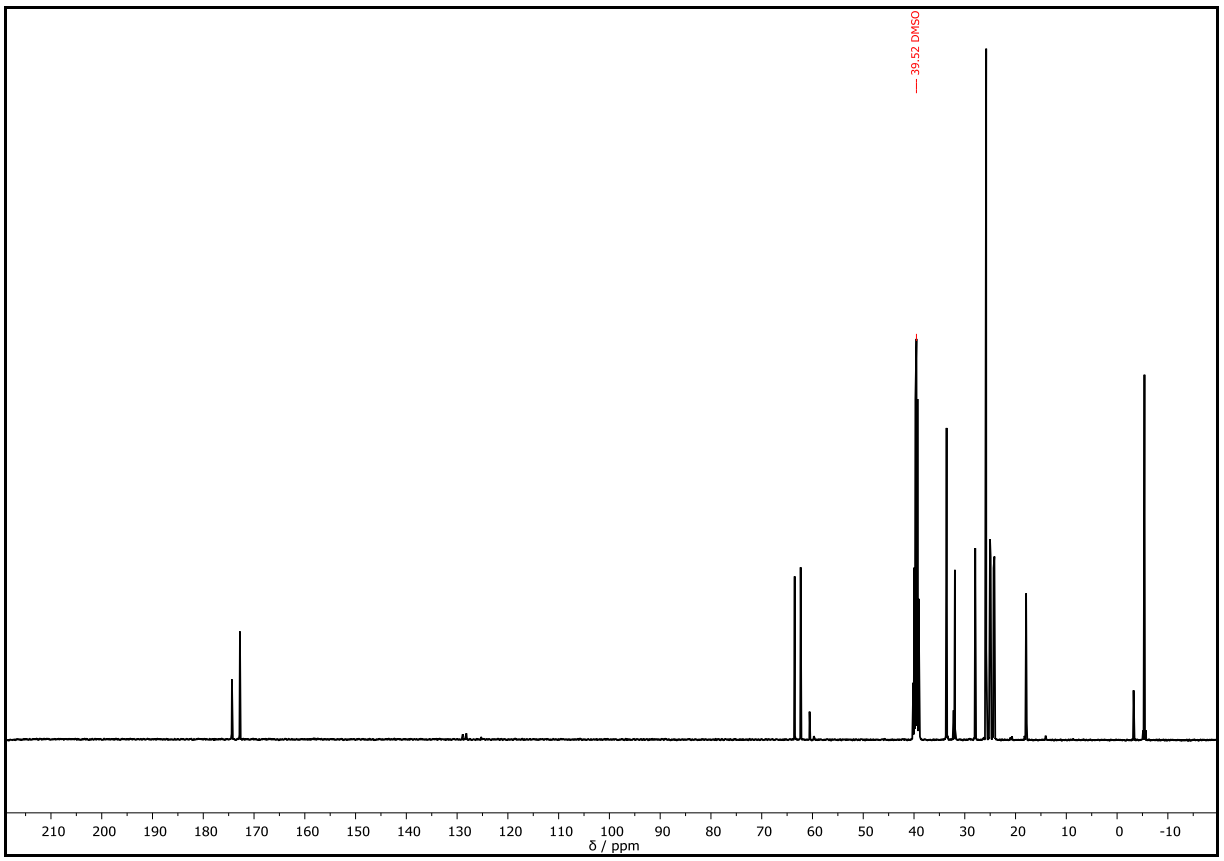




Supplementary Figure 39: ^{1}H NMR spectrum of **TBDMS(CL)$_2$CO$_2$H**, recorded at 300 MHz in DMSO-d_6.

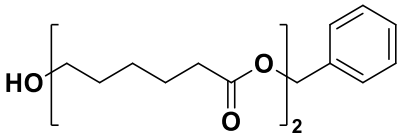
^{13}C NMR (DMSO-d_6, 101 MHz): δ / ppm = 174.36 (C_q^1), 172.78 (C_q^2), 63.50 (CH_2^3), 62.33 (CH_2^4), 33.58 (CH_2^5), 31.95 (CH_2^6), 27.94 (CH_2^7), 25.78 (CH_3^8), 25.03 (CH_2^9), 24.90 (CH_2^9), 24.33 (CH_2^9), 24.16 (CH_2^9), 17.92 (C_q^{10}), -5.39 (CH_3^{11}).





Supplementary Figure 40: ^{1}H NMR spectrum of **TBDMS(CL)$_2$CO$_2$H**, recorded at 101 MHz in DMSO-d_6.

Hydroxyl–terminated dimer – HO(CL)$_2$Bn



Chemical Formula: $C_{19}H_{28}O_5$
Exact Mass: 336.1937 Da
Molecular Weight: 336.4280 Da

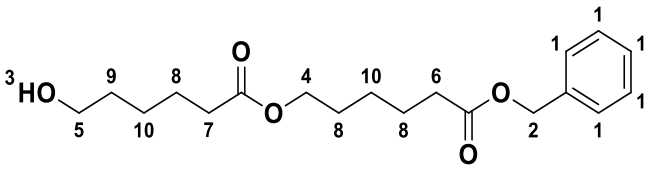
Tetrabutylammonium fluoride (TBAF) (17.5 g, 55.5 mmol, 2.00 equiv.) and glacial acetic acid (3.18 mL, 3.33 mg, 55.5 mmol, 2.00 equiv.) were dissolved in 56 mL THF and added to a solution of doubly protected dimer **TBDMS(CL)$_2$Bn** (12.5 g, 27.7 mmol, 1.00 equiv.) in THF (57 mL). The reaction mixture was stirred overnight at 50 °C and monitored *via* TLC until complete conversion of the starting material. Subsequently, the mixture was poured into a separation funnel containing dichloromethane (300 mL) and water (300 mL). The organic phase was separated and washed with saturated $NaHCO_3$ (2 × 200 mL), 5 wt% citric acid (2 × 200 mL) and water (1 × 200 mL). The combined organic layers were dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. Purification of the crude product *via* column chromatography (cyhex/EA = 1:1) yielded the hydroxyl-terminated dimer **HO(CL)$_2$Bn** (9.23 g, 27.4 mmol, 98.9%) as a colorless oil.

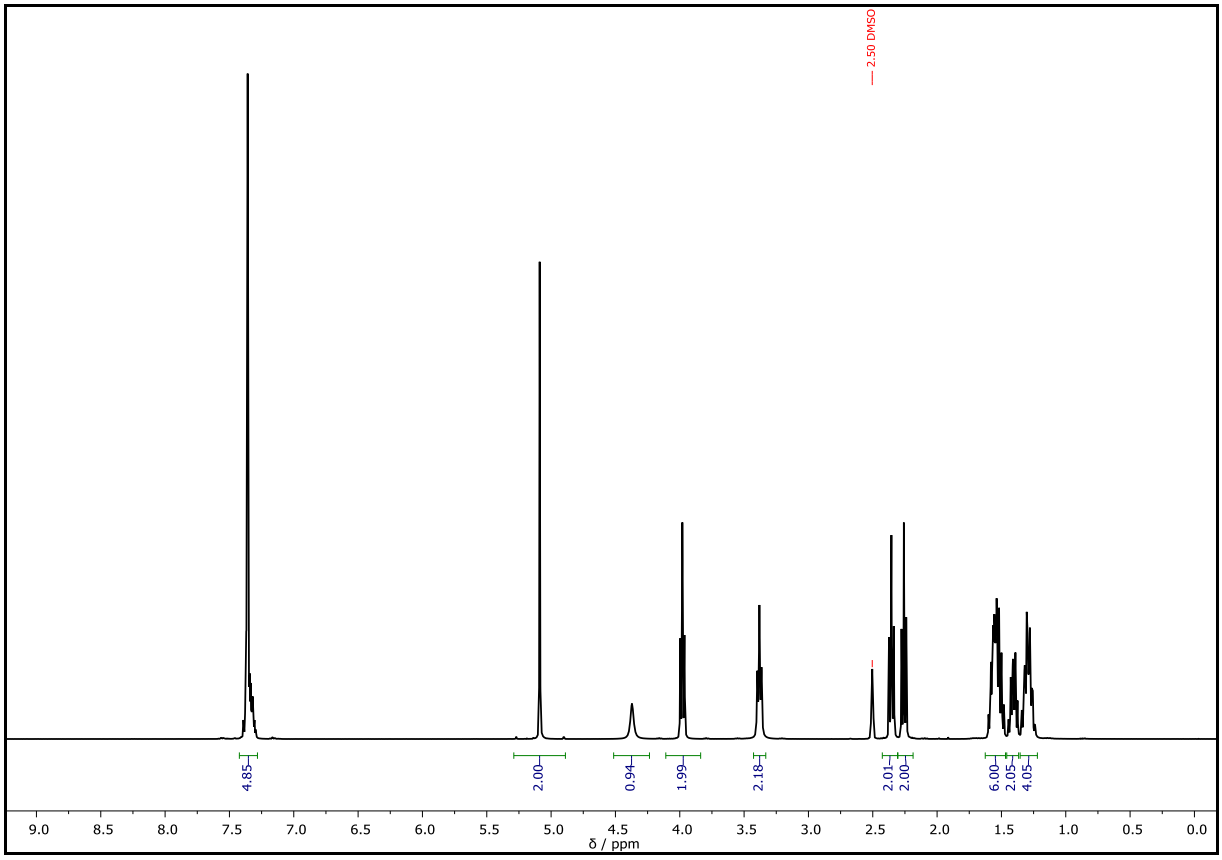
FAB of $C_{19}H_{28}O_5$ ($M+H^+$ = 337.2); HRMS (FAB) of $C_{19}H_{28}O_5$ $[M+H]^+$ calcd. 337.2015, detected 337.2014.

IR (ATR platinum diamond) $\tilde{\nu}$ / cm^{-1} = 3431.4, 2936.2, 2863.1, 1729.3, 1497.7, 1455.5, 1385.1, 1353.3, 1154.6, 1080.1, 736.3, 697.5, 579.8, 498.1.

R_f = 0.63 (cyhex/EA = 1:1).

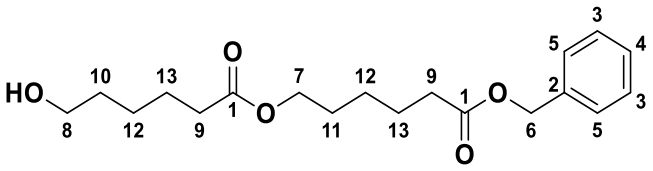
^{1}H NMR (DMSO-d_6, 300 MHz): δ / ppm = 7.27–7.39 (m, 5H, CH_{Ar}^1), 5.09 (s, 2H, CH_2^2), 4.37 (t, J =5.1 Hz, 1H, OH^3), 3.98 (t, J = 6.6, 2H, CH_2^4), 3.38 (t, J = 6.4 Hz, 2H, CH_2^5), 2.35 (t, J = 7.4, 2H, CH_2^6), 2.25 (t, J = 7.4, 2H, CH_2^7), 1.46-1.62 (m, 6H, CH_2^8), 1.35-1.46 (m, 2H, CH_2^9), 1.22-1.35 (m, 4H, CH_2^{10}).

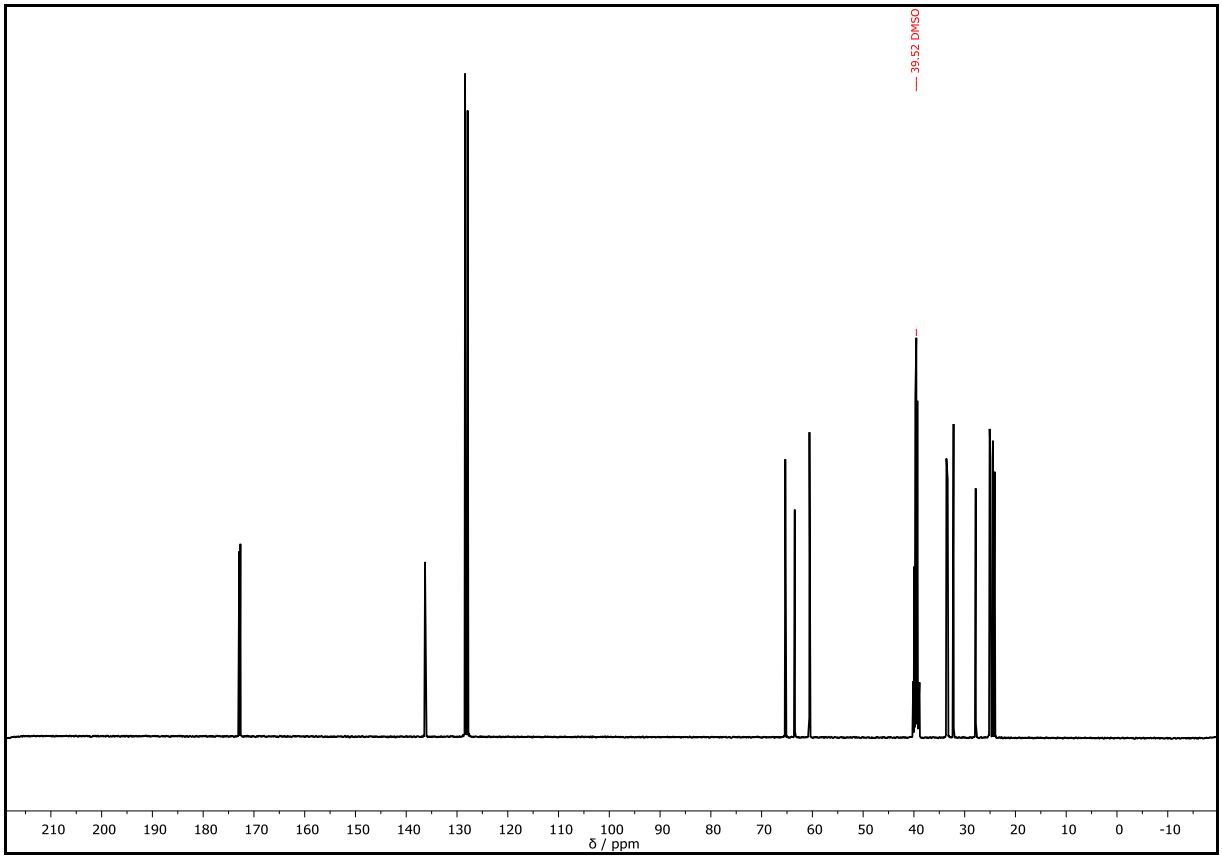




Supplementary Figure 41: ^{1}H NMR spectrum of **HO(CL)$_2$Bn**, recorded at 300 MHz in DMSO-d_6.

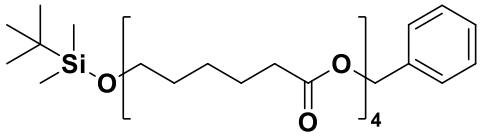
^{13}C NMR (DMSO-d_6, 101 MHz): δ / ppm = 172.89 (C_q^1), 172.66 (C_q^1), 136.30 ($C_{q,Ar}^2$), 128.40 ($CH_{Ar,meta}^3$), 127.96 ($CH_{Ar,para}^4$), 127.91 ($CH_{Ar,ortho}^5$), 65.33 (CH_2^6), 63.48 (CH_2^7), 60.58 (CH_2^8), 33.36 (CH_2^9), 33.34 (CH_2^9), 32.19 (CH_2^{10}), 27.83 (CH_2^{11}), 25.08 (CH_2^{12}), 24.91 (CH_2^{12}), 24.45 (CH_2^{13}), 24.10 (CH_2^{13}).





Supplementary Figure 42: ^{1}H NMR spectrum of **HO(CL)$_2$Bn**, recorded at 101 MHz in DMSO-d_6.

Doubly protected tetramer – TBDMS(CL)$_4$Bn



Chemical Formula: $C_{37}H_{62}O_9Si$
Exact Mass: 678.4163 Da
Molecular Weight: 678.9790 Da

The doubly protected tetramer **TBDMS(CL)$_4$Bn** was prepared using the procedure described above for the synthesis of the doubly protected dimer **TBDMS(CL)$_2$Bn**. The reaction was performed in two batches, which were combined and purified in one batch *via* column chromatography. Quantities of the starting materials and the yield are the sum of both reactions.

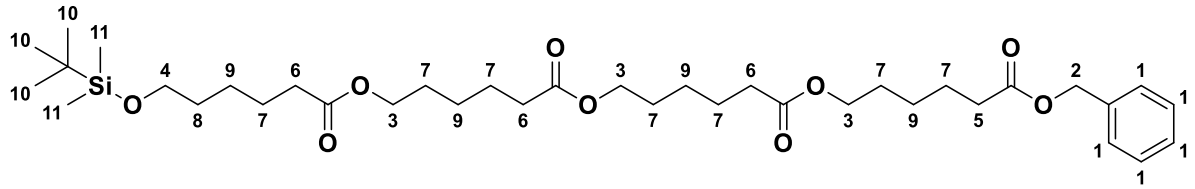
TBDMS(CL)$_2$CO$_2$H	31.0 g, 86.3 mmol, 1.00 equiv.
HO(CL)$_2$Bn	29.0 g, 86.3 mmol, 1.00 equiv.
DCC	19.6 g, 94.9 mmol, 1.10 equiv.
DMAP	11.6 g, 94.9 mmol, 1.10 equiv.
DCM	208 mL
eluent	cyhex/EA = 5:1
yield	51.5 g, 75.9 mmol, 87.9%, colorless oil
R_f	0.32 (cyhex/EA = 6:1).
Đ (system I)	1.00

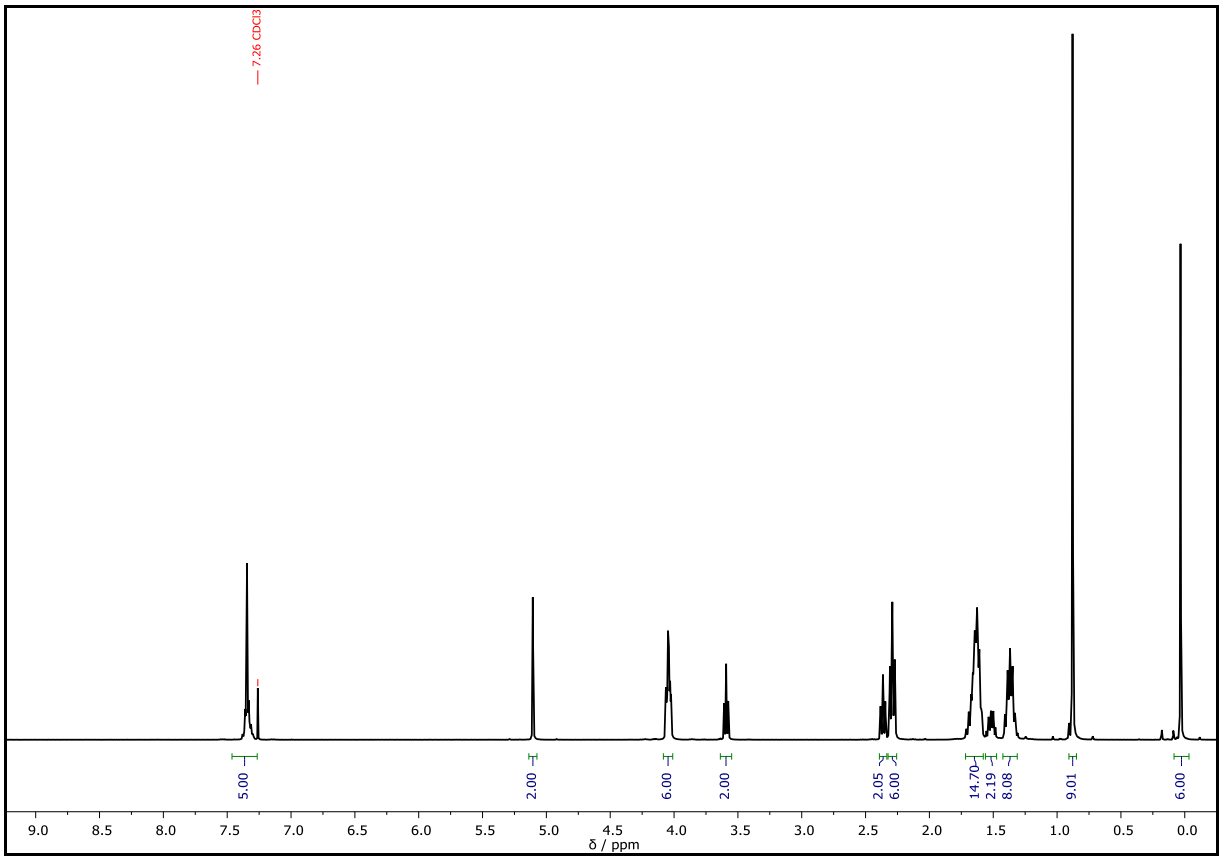
FAB of $C_{37}H_{62}O_9Si$ ($M+H^+$ = 679.4); HRMS (FAB) of $C_{37}H_{62}O_9Si$ $[M+H]^+$ calcd. 679.4241, detected 679.4242.

IR (ATR platinum diamond) $\tilde{\nu}$ / cm^{-1} = 2932.4, 2858.3, 1732.6, 1459.2, 1387.4, 1358.8, 1232.4, 1157.2, 1094.2, 833.8, 774.9, 736.3, 697.0, 500.8, 445.0.

***R*$_f$** = 0.32 (cyhex/EA = 6:1).

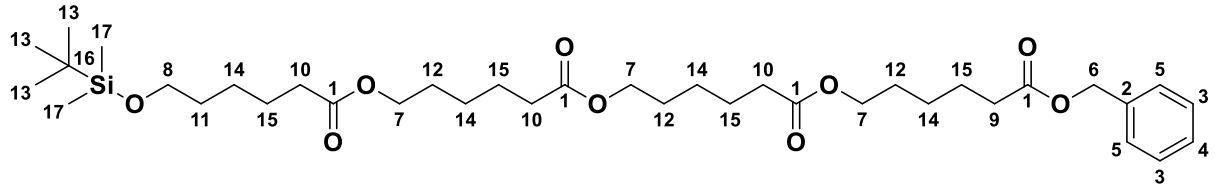
^{1}H NMR ($CDCl_3$, 300 MHz): δ / ppm = 7.34 (s, 5H, CH_{Ar}^1), 5.10 (s, 2H, CH_2^2), 4.04 (t, *J* = 6.6 Hz, 6H, CH_2^3), 3.59 (t, *J* = 6.4 Hz, 2H, CH_2^4), 2.35 (t, *J* = 7.5 Hz, 2H, CH_2^5), 2.28 (t, *J* = 7.6 Hz, 6H, CH_2^6), 1.55-1.73 (m, 14H, CH_2^7), 1.45-1.55 (m, 2H, CH_2^8), 1.28-1.43 (m, 8H CH_2^9), 0.87 (s, 9H, CH_3^{10}), 0.03 (s, 6H, CH_3^{11}).

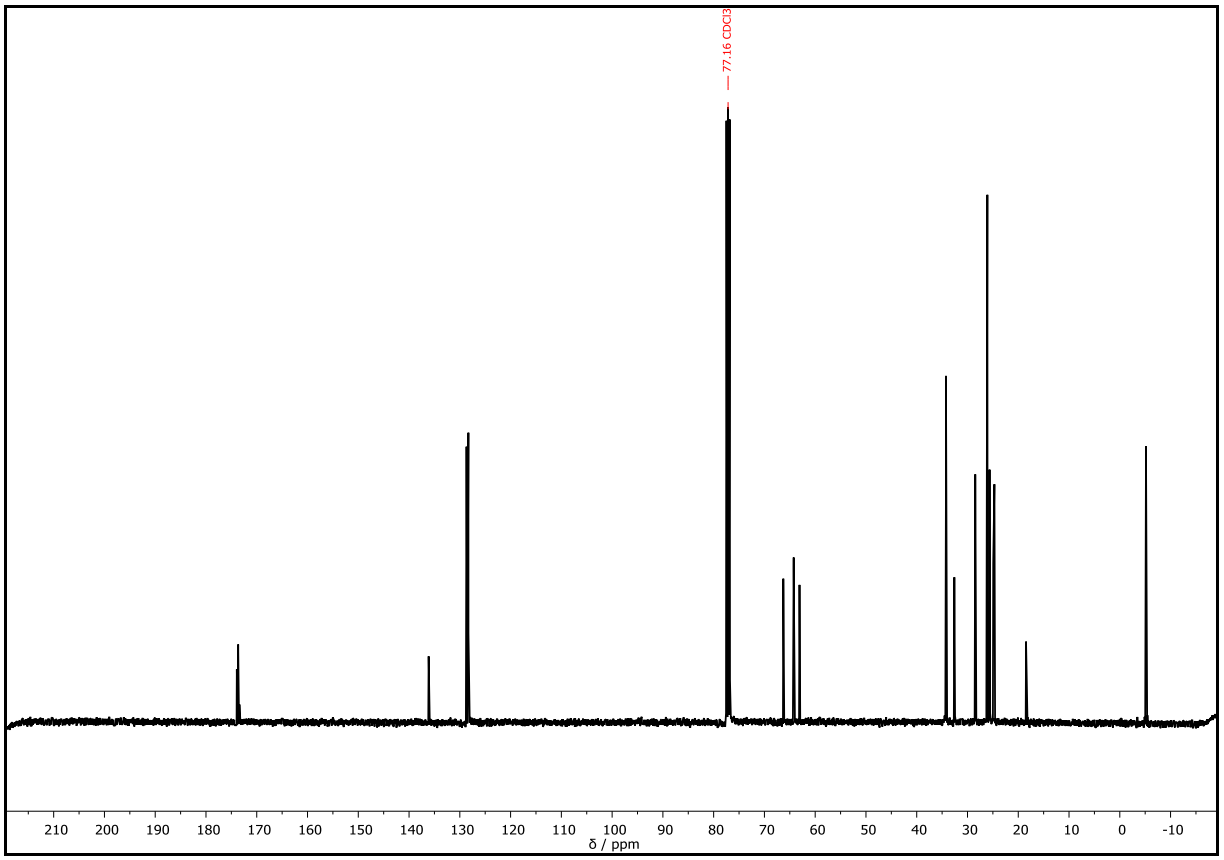




Supplementary Figure 43: ^{1}H NMR spectrum of **TBDMS(CL)$_4$Bn**, recorded at 300 MHz in $CDCl_3$.

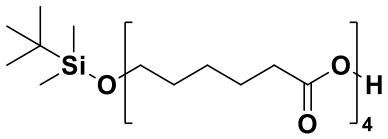
^{13}C NMR ($CDCl_3$, 101 MHz): δ / ppm = 173.92 (C_q^1), 173.66 (C_q^1), 173.43 (C_q^1), 136.14 ($C_{q,Ar}^2$), 128.68 ($CH_{Ar,meta}^3$), 128.34 ($CH_{Ar,para}^4$), 128.31 ($CH_{Ar,ortho}^5$), 66.28 (CH_2^6), 64.24 (CH_2^7), 64.17 (CH_2^7), 63.09 (CH_2^8), 34.45 (CH_2^9), 34.24 (CH_2^{10}), 32.59 (CH_2^{11}), 28.46 (CH_2^{12}), 28.44 (CH_2^{12}), 26.08 (CH_3^{13}), 25.65 (CH_2^{14}), 25.57 (CH_2^{14}), 24.93 (CH_2^{15}), 24.70 (CH_2^{15}), 24.67 (CH_2^{15}), 18.46 (C_q^{16}), -5.16 (CH_3^{17}).





Supplementary Figure 44: ^{13}C NMR spectrum of **TBDMS(CL)$_4$Bn**, recorded at 101 MHz in $CDCl_3$.

Carboxyl–terminated tetramer – TBDMS(CL)$_4$CO$_2$H



Chemical Formula: $C_{30}H_{56}O_9Si$
Exact Mass: 588.3694 Da
Molecular Weight: 588.8540 Da

The carboxyl-terminated tetramer **TBDMS(CL)$_4$CO$_2$H** was prepared using the procedure described above for the synthesis of the carboxyl-terminated dimer **TBDMS(CL)$_2$CO$_2$H**.

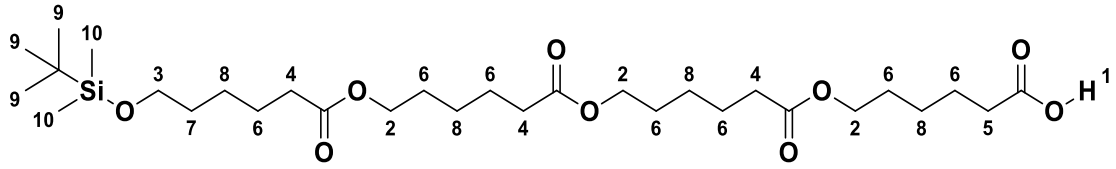
TBDMS(CL)$_4$Bn	10.0 g, 14.7 mmol, 1.00 equiv.
Pd/C	1.00 g, 10 wt%
EA	120 mL
yield	8.59 g, 14.6 mmol, 99.1%, colorless oil
Đ (system I)	1.00

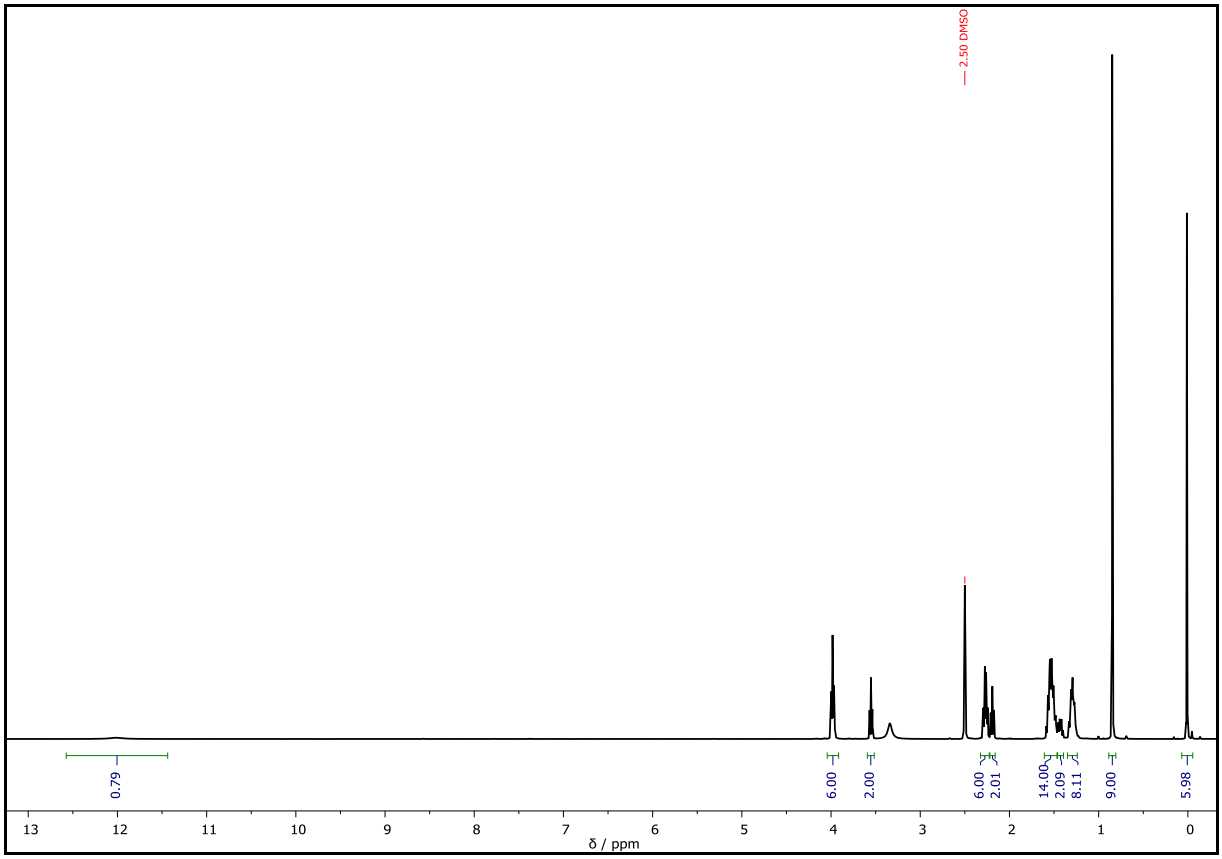
FAB of $C_{30}H_{56}O_9Si$ ($M+H^+ = 589.4$); HRMS (FAB) of $C_{30}H_{56}O_9Si$ $[M+H]^+$ calcd. 589.3772, detected 589.3773.

IR (ATR platinum diamond) $\tilde{\nu}$ / cm^{-1} = 2931.5, 2858.3, 1732.2, 1708.8, 1461.8, 1389.6, 1359.8, 1232.9, 1159.0, 1094.1, 1006.0, 833.9, 774.9, 661.5, 398.2.

R_f = 0.26 (cyhex/EA = 2:1).

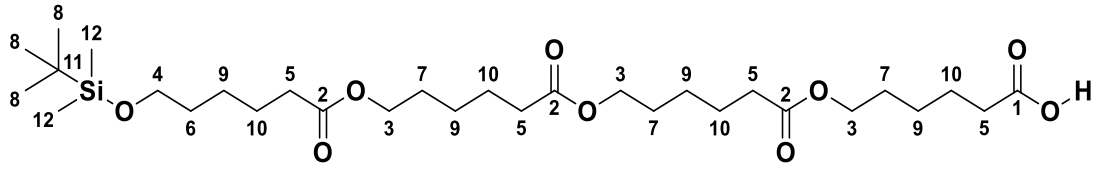
^{1}H NMR (DMSO-d_6, 400 MHz): δ / ppm = 12.00 (s, 1H, CO_2H^1), 3.98 (t, J = 6.5 Hz, 6H, CH_2^2), 3.55 (t, J = 6.2 Hz, 2H, CH_2^3), 2.27 (td, J = 7.3, 3.8 Hz, 6H, CH_2^4), 2.19 (t, J = 7.3 Hz, 2H, CH_2^5), 1.46-1.62 (m, 14H, CH_2^6), 1.38–1.46 (m, 2H, CH_2^7), 1.22–1.36 (m, 8H CH_2^8), 0.85 (s, 9H, CH_3^9), 0.01 (s, 6H, CH_3^{10}).

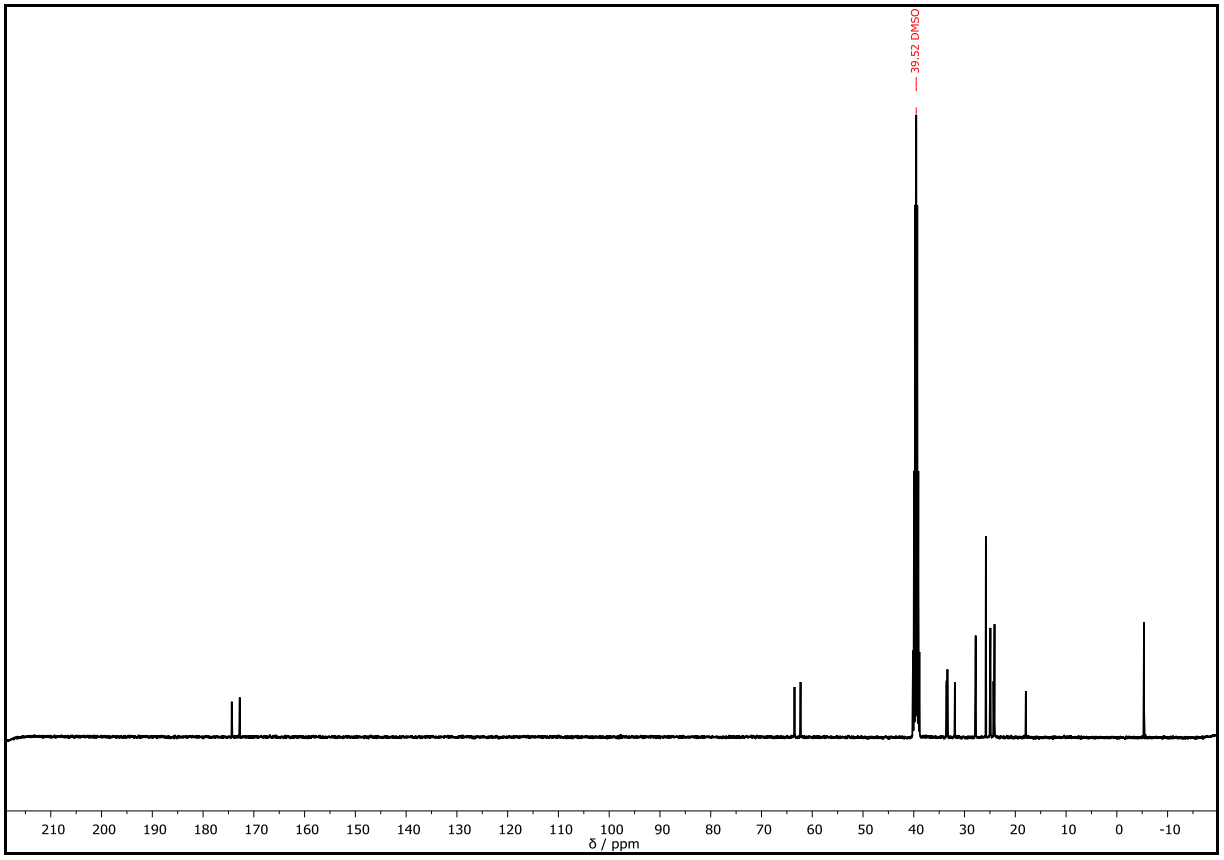




Supplementary Figure 45: ^{1}H NMR spectrum of **TBDMS(CL)$_4$CO$_2$H**, recorded at 400 MHz in DMSO-d_6.

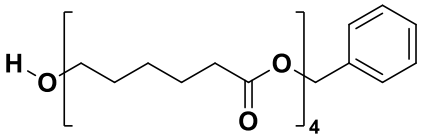
^{13}C NMR (DMSO-d_6, 101 MHz): δ / ppm = 174.35 (C_q^1), 172.83 (C_q^2), 172.77 (C_q^2), 172.76 (C_q^2), 63.50 (CH_2^3), 62.30 (CH_2^4), 33.57 (CH_2^5), 33.52 (CH_2^5), 33.37 (CH_2^5), 31.90 (CH_2^6), 27.88 (CH_2^7), 27.81 (CH_2^7), 25.80 (CH_3^8), 24.98 (CH_2^9), 24.90 (CH_2^9), 24.86 (CH_2^9), 24.30 (CH_2^{10}), 24.09 (CH_2^{10}), 17.92 (C_q^{11}), -5.35 (CH_3^{12}).





Supplementary Figure 46: ^{13}C NMR spectrum of **TBDMS(CL)$_4$CO$_2$H**, recorded at 101 MHz in DMSO-d_6.

Hydroxyl–terminated tetramer – HO(CL)$_4$Bn



Chemical Formula: $C_{31}H_{48}O_9$
Exact Mass: 564.3298 Da
Molecular Weight: 564.7160 Da

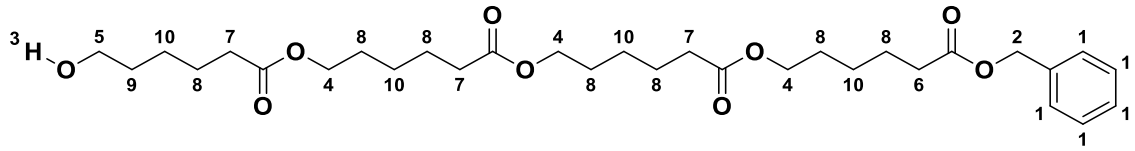
The hydroxyl-terminated tetramer **HO(CL)$_4$Bn** was prepared according to the procedure described above for the synthesis of the hydroxyl-terminated dimer **HO(CL)$_2$Bn**.

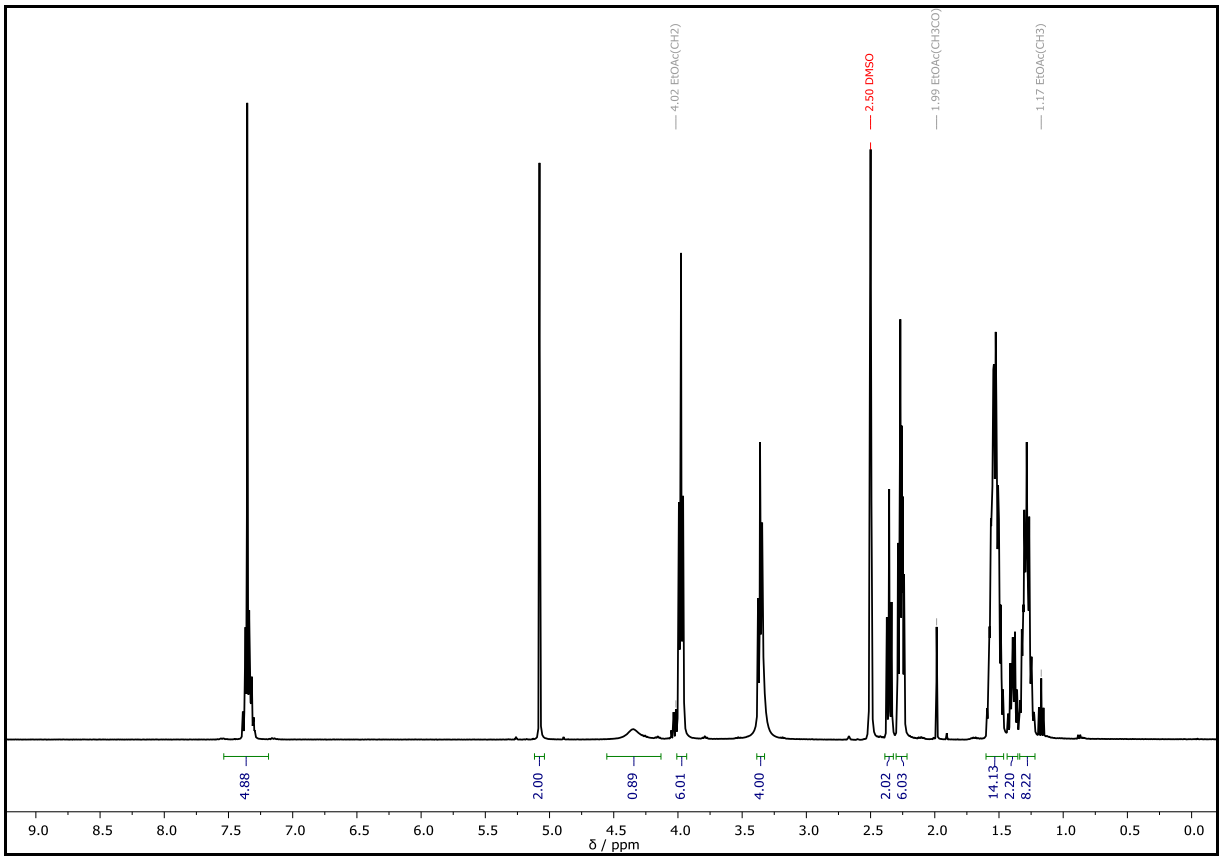
TBDMS(CL)$_4$Bn	6.00 g, 8.84 mmol, 1.00 equiv.
TBAF	16.0 g, 17.7 mmol, 2.00 equiv.
glacial acetic acid	1.01 mL, 1.06 g, 17.7 mmol, 2.00 equiv.
total THF	35.0 mL
eluent	cyclohexane/EA = 1:1
yield	4.98 g, 8.82 mmol, 99.8%, colorless oil
R_f	0.42 (cyhex/EA = 1:1).
Đ (system I)	1.00

FAB of $C_{31}H_{48}O_9$ ($M+H^+$ = 565.3); HRMS (FAB) of $C_{31}H_{48}O_9$ $[M+H]^+$ calcd. 565.3377, detected 565.3375.

IR (ATR platinum diamond) $\tilde{\nu}$ / cm^{-1} = 3528.8, 2936.8, 2863.0, 1730.0, 1455.7, 1388.0, 1354.3, 1158.8, 1090.7, 738.0, 698.3, 580.7, 387.8.

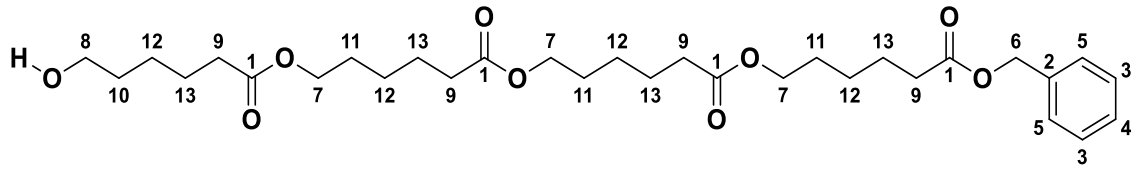
^{1}H NMR (DMSO-d_6, 300 MHz): δ / ppm = 7.26–7.42 (m, 5H, CH_{Ar}^{1}), 5.08 (s, 2H, CH_2^{2}), 4.37 (s, 1H, OH^{3}), 3.98 (t, J = 6.5, 6H, CH_2^{4}), 3.35 (t, J = 6.4 Hz, 2H, CH_2^{5}), 2.36 (t, J = 7.3 Hz, 2H, CH_2^{6}), 2.26 (m, 6H, CH_2^{7}), 1.46-1.62 (m, 14H, CH_2^{8}), 1.36-1.45 (m, 2H, CH_2^{9}), 1.20-1.36 (m, 8H, CH_2^{10}).

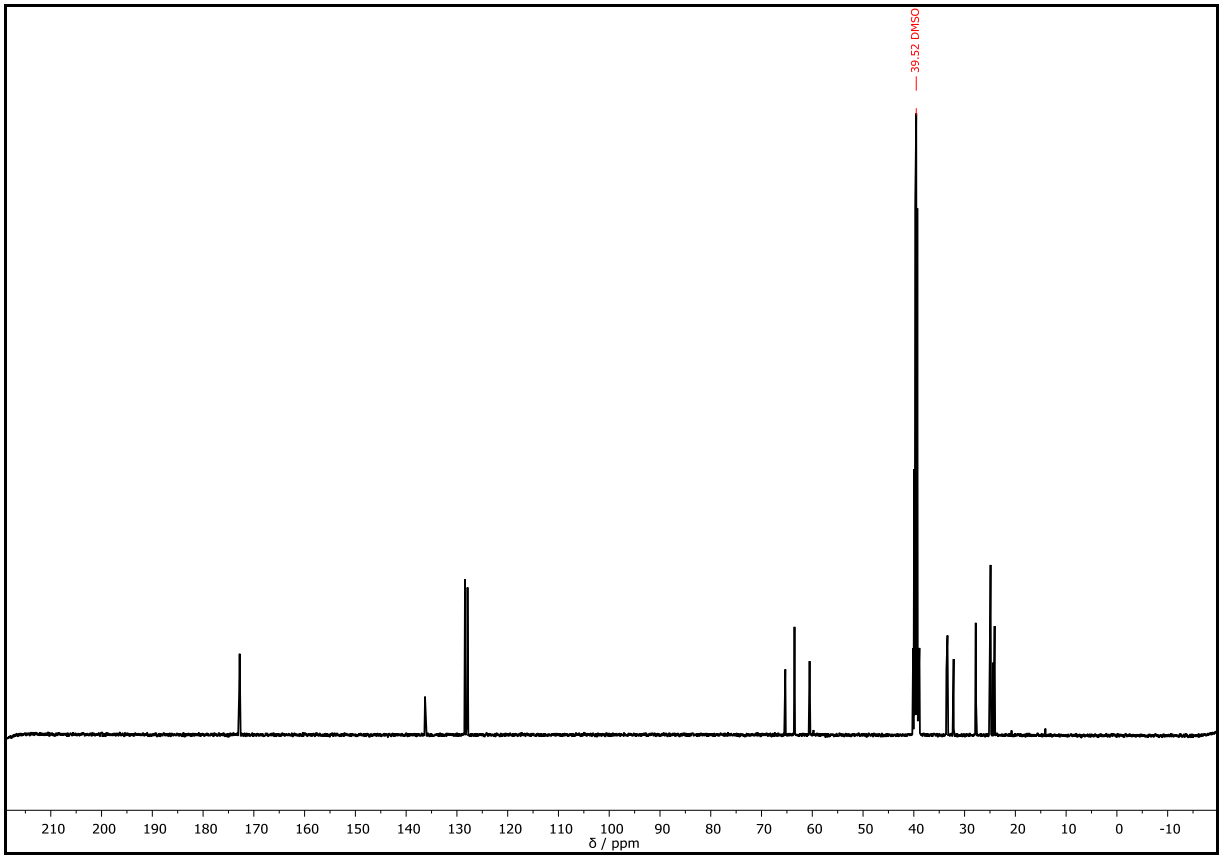




Supplementary Figure 47: ^{1}H NMR spectrum of **HO(CL)$_4$Bn**, recorded at 300 MHz in DMSO-d_6.

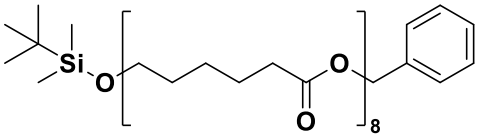
^{13}C NMR (DMSO-d_6, 101 MHz): δ / ppm = 172.90 (C_q^1), 172.80 (C_q^1), 172.67 (C_q^1), 136.28 ($C_{q,Ar}^2$), 128.41 ($CH_{Ar,meta}^3$), 127.97 ($CH_{Ar,para}^4$), 127.91 ($CH_{Ar,ortho}^5$), 65.31 (CH_2^6), 63.50 (CH_2^7), 63.46 (CH_2^7), 60.53 (CH_2^8), 33.58 (CH_2^9), 33.37 (CH_2^9), 33.32 (CH_2^9), 32.16 (CH_2^{10}), 27.80 (CH_2^{11}), 25.05 (CH_2^{12}), 24.89 (CH_2^{12}), 24.42 (CH_2^{13}), 24.09 (CH_2^{13}), 24.07 (CH_2^{13}).





Supplementary Figure 48: ^{13}C NMR spectrum of **HO(CL)$_4$Bn**, recorded at 101 MHz in DMSO-d_6.

Doubly protected octamer – TBDMS(CL)$_8$Bn



Chemical Formula: $C_{61}H_{102}O_{17}Si$
Exact Mass: 1134.6886 Da
Molecular Weight: 1135.5550 Da

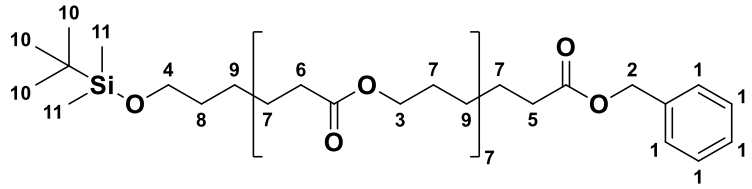
The doubly protected octamer **TBDMS(CL)$_8$Bn** was prepared using the procedure described above for the synthesis of the doubly protected dimer **TBDMS(CL)$_2$Bn**. 0.20 equiv. DPTS was used instead of 1.10 equiv. DMAP.

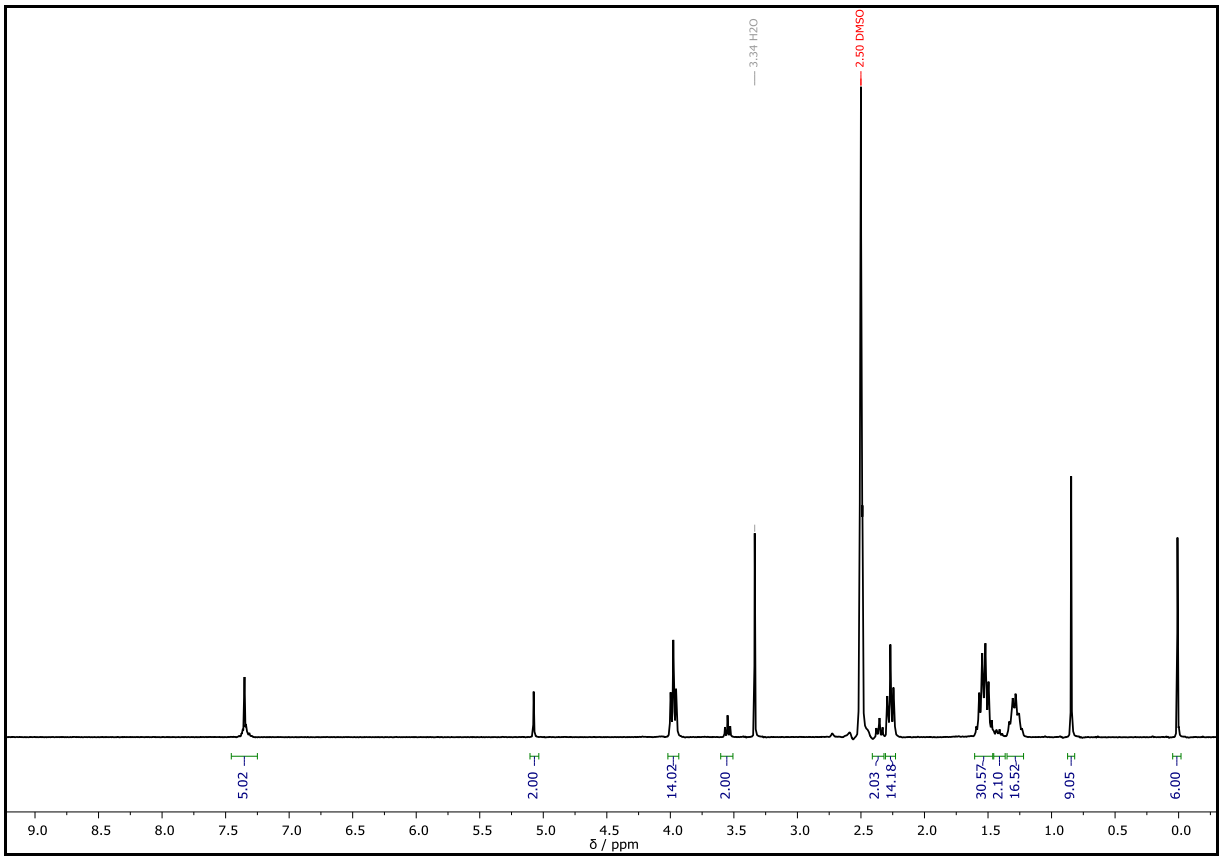
TBDMS(CL)$_4$CO$_2$H	24.5 g, 41.5 mmol, 1.00 equiv.
HO(CL)$_4$Bn	23.5 g, 41.5 mmol, 1.00 equiv.
DCC	9.43 g, 45.7 mmol, 1.10 equiv.
DPTS	2.45 g, 8.31 mmol, 0.20 equiv.
DCM	100 mL
eluent	cyhex/EA = 3:1
yield	44.5 g, 39.2 mmol, 94.4%, white solid
R_f	0.50 (cyhex/EA = 2:1).
Đ (system I)	1.00

HRMS (ESI) of $C_{61}H_{102}O_{17}Si$ $[M+H]^+$ calcd. 1135.6959, detected 1135.6947; $[M+Na]^+$ calcd. 1157.6778, detected 1157.6758; $[M+K]^+$ calcd. 1173.6518, detected 1173.6498.

IR (ATR platinum diamond) ν / cm^{-1} = 2934.0, 2859.1, 1730.5, 1458.3, 1358.0, 1157.6, 1094.6, 835.2, 776.0, 737.0, 698.3.

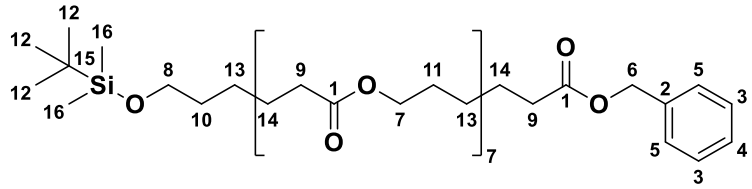
^{1}H NMR (DMSO-d_6, 400 MHz): δ / ppm = 7.41 – 7.30 (m, 5H, CH_{Ar}^1), 5.08 (s, 2H, CH_2^2), 3.98 (t, J = 6.4 Hz, 14H, CH_2^3), 3.55 (t, J = 6.2 Hz, 2H, CH_2^4), 2.35 (t, J = 7.3 Hz, 2H, CH_2^5), 2.26 (t, J = 7.4 Hz, 14H, CH_2^6), 1.64 – 1.45 (m, 30H, CH_2^7), 1.41 (t, J = 6.9 Hz, 2H, CH_2^8), 1.36 – 1.22 (m, 16H, CH_2^9), 0.85 (s, 9H, CH_3^{10}), 0.01 (s, 6H, CH_3^{11}).

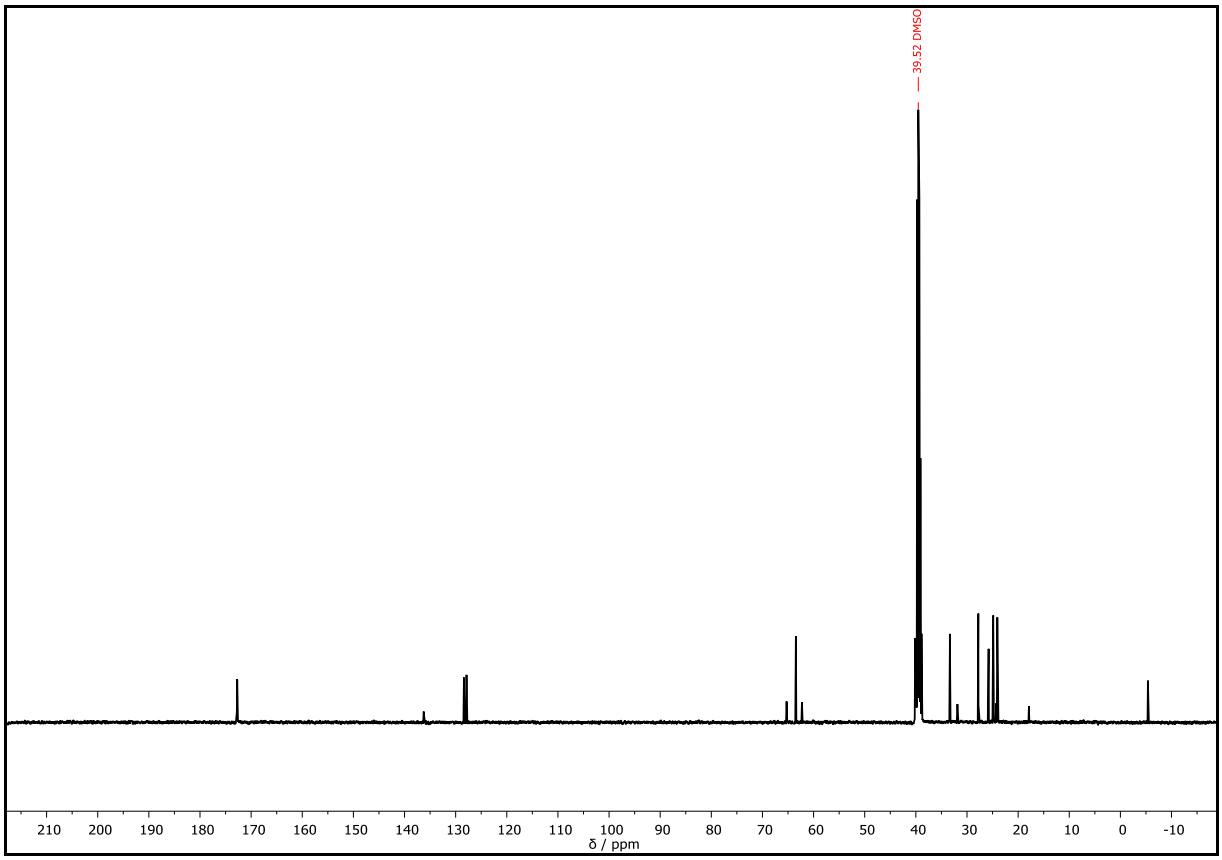




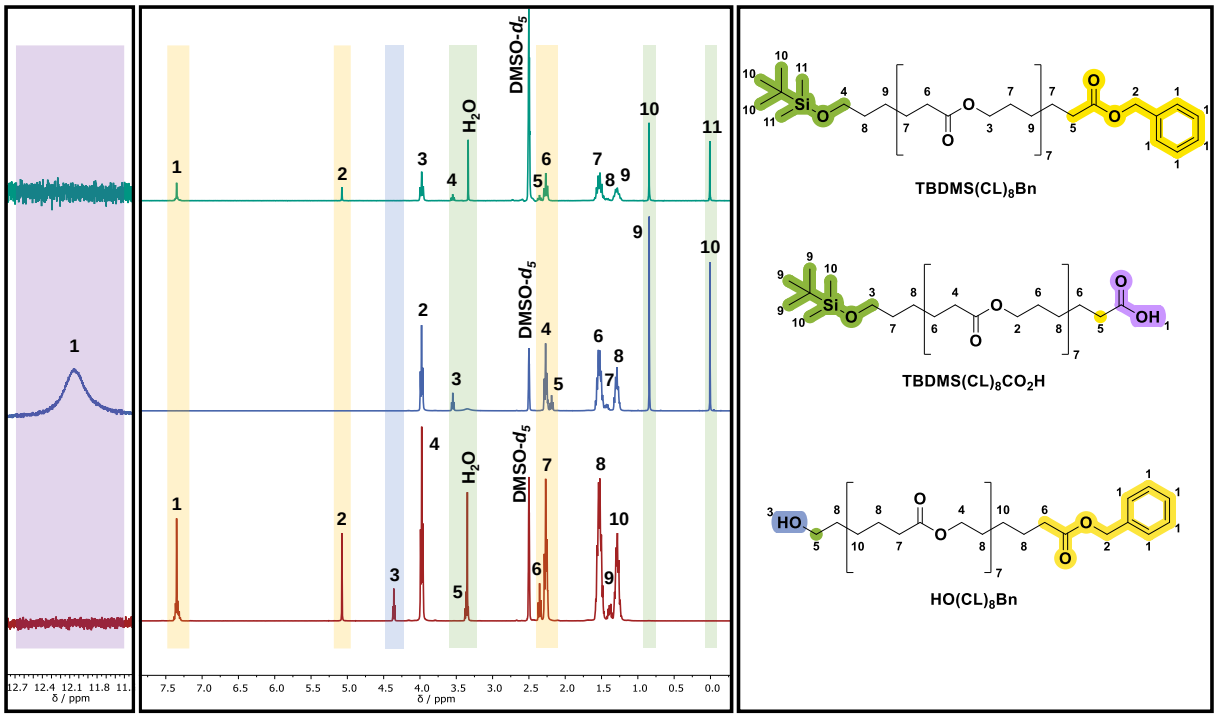
Supplementary Figure 49: ^{1}H NMR spectrum of **TBDMS(CL)$_8$Bn**, recorded at 400 MHz in DMSO-d_6.

^{13}C NMR (DMSO-d_6, 101 MHz): δ / ppm = 172.79(C_q^1), 172.73 (C_q^1), 172.62 (C_q^1), 136.26 ($C_{q,Ar}^2$), 128.38 ($CH_{Ar,meta}^3$), 127.94 ($CH_{Ar,para}^4$), 127.87 ($CH_{Ar,ortho}^5$), 65.28 (CH_2^6), 63.47 (CH_2^7), 63.43 (CH_2^7), 62.28 (CH_2^8), 33.54 (CH_2^9), 33.35 (CH_2^9), 33.30 (CH_2^9), 31.87 (CH_2^{10}), 27.78 (CH_2^{11}), 25.77 (CH_3^{12}), 24.87 (CH_2^{13}), 24.83 (CH_2^{13}), 24.27 (CH_2^{14}), 24.07 (CH_2^{14}), 24.05 (CH_2^{14}), 17.89 (C_q^{15}), -5.38 (CH_3^{16}).

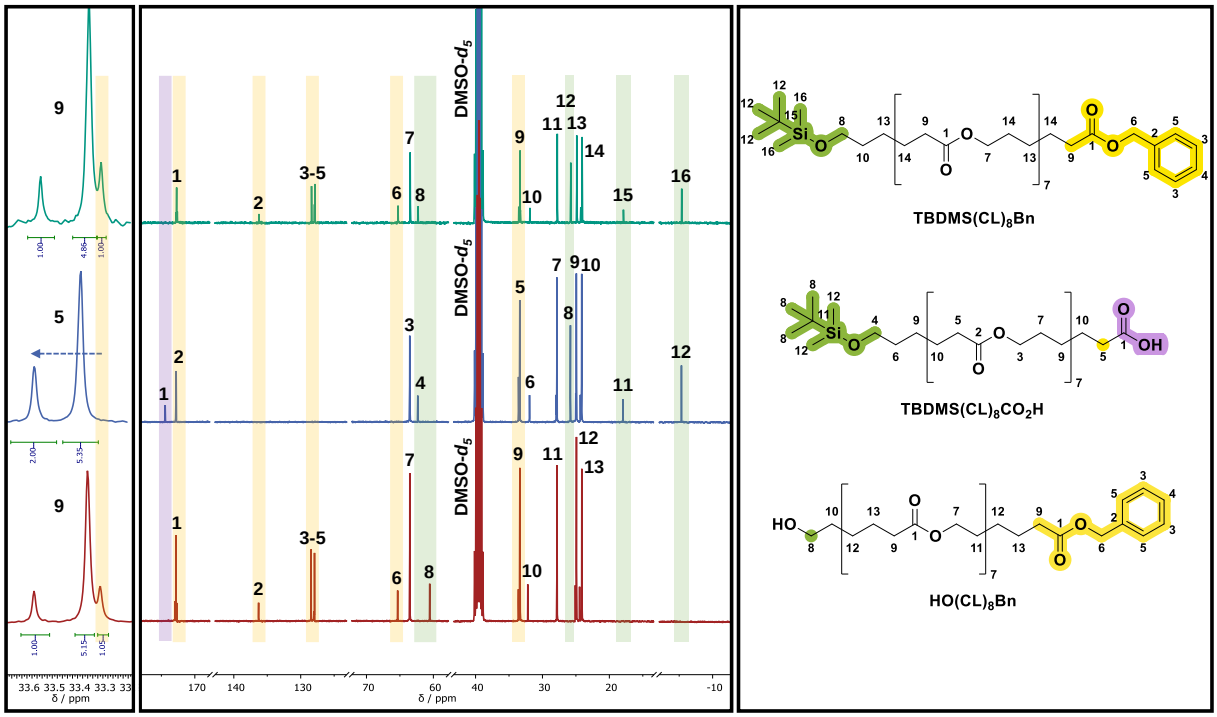




Supplementary Figure 50: ^{13}C NMR spectrum of **TBDMS(CL)$_8$Bn**, recorded at 101 MHz in DMSO-d_6.

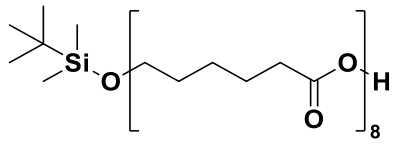


Supplementary Figure 51: Comparison of ^{1}H NMR spectra of octa(ε-caprolactone) derivatives. The green spectrum on the top shows the characteristic signals of the doubly protected octamer **TBDMS(CL)$_8$Bn**. The specific peaks **10** and **11** for the TBDMS protecting group are highlighted in green at 0.01, 0.85 ppm, and for the α-methylene group **4** at 3.55 ppm, and for the benzyl ester in yellow, at 7.35 ppm for the aromatic protons (signal **1**), at 5.08 ppm for the benzyl methylene group (signal **2**) and the α-methylene group **5** at 2.35 ppm. After reductive hydrogenation of the benzyl ester, the corresponding peaks completely vanished and a signal at 12.1 ppm is observed for the carboxylic acid (signal highlighted in purple, blue spectrum in the middle of compound **TBDMS(CL)$_8$CO$_2$H**). The α-methylene group next to the carboxylic acid shifted to 2.19 ppm. In the case of TBDMS cleavage (red spectrum on the bottom of **HO(CL)$_8$Bn**), the corresponding peaks highlighted in green completely vanished, and the α-methylene group next to the resulted alcohol (at 4.36 ppm) function shifted to 3.36 ppm. These spectra are representative for all coupling and deprotection products obtained during the IEG.



Supplementary Figure 52: Comparison of ^{13}C NMR spectra of octa(ε-caprolactone) derivatives. The green spectrum on the top shows the characteristic signals of the doubly protected octamer **TBDMS(CL)$_8$Bn**. The specific peaks of the benzyl protection group highlighted in yellow are completely vanished after the reductive hydrogenation (compare blue spectrum of **TBDMS(CL)$_8$CO$_2$H**). Further, the CH_2-group in α-position to the ester and the quaternary carbon of the carboxylic acid is shifted downfield to 33.6 ppm and overlaps with another backbone signal (detailed section **a**), and 174.4 ppm (signal **1** of **TBDMS(CL)$_8$CO$_2$H**, highlighted in purple), respectively. In the case of the TBDMS cleavage (red spectrum on the bottom of **HO(CL)$_8$Bn**), the corresponding peaks, highlighted in green, completely vanished and the α-methylene group next to the resulting alcohol is shifted upfield from 62.3 to 60.6 ppm. These spectra are representative for all coupling and deprotection products obtained during the IEG. A full characterization for each of them is provided in the experimental section.

Carboxyl–terminated octamer – TBDMS(CL)$_8$CO$_2$H



Chemical Formula: $C_{54}H_{96}O_{17}Si$
Exact Mass: 1044.6417 Da
Molecular Weight: 1045.4300 Da

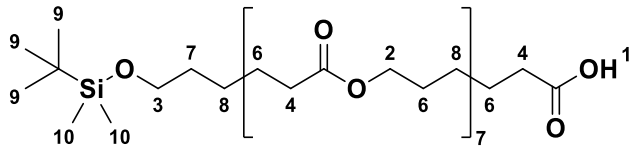
The carboxyl-terminated octamer **TBDMS(CL)$_8$CO$_2$H** was prepared using the procedure described above for the synthesis of the carboxyl-terminated dimer **TBDMS(CL)$_2$CO$_2$H**.

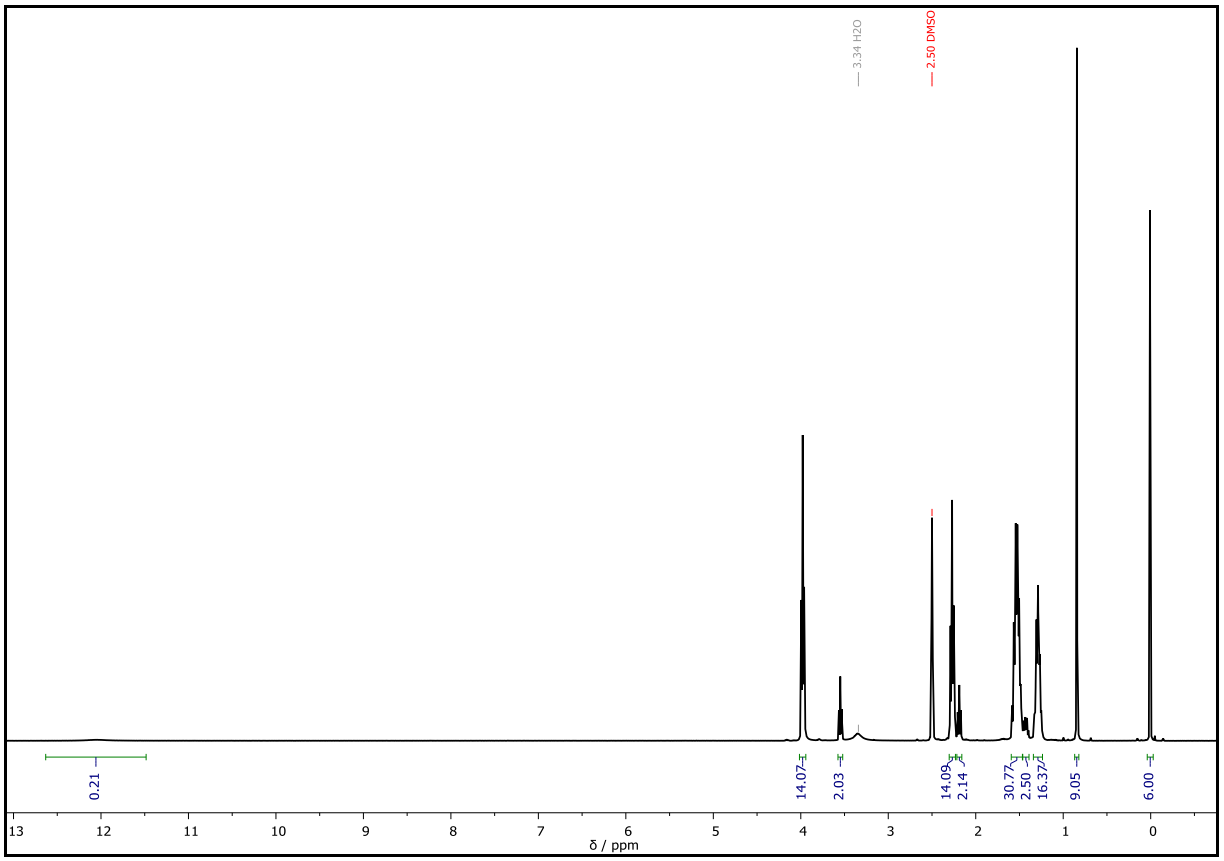
TBDMS(CL)$_8$Bn	3.00 g, 2.64 mmol, 1.00 equiv.
Pd/C	300 mg, 10 wt%
EA	42 mL
yield	2.76 g, 2.64 mmol, quant. yield, white solid
Đ (system I)	1.00

HRMS (ESI) of $C_{54}H_{96}O_{17}Si$ $[M+H]^+$ calcd. 1045.6490, detected 1045.6477; $[M+NH_4]^+$ calcd. 1062.6755, detected 1062.6742.

IR (ATR platinum diamond) ν / cm^{-1} = 2935.2, 2860.3, 1730.3, 1461.4, 1390.2, 1359.3, 1157.9, 1094.1, 834.9, 776.0, 736.9.

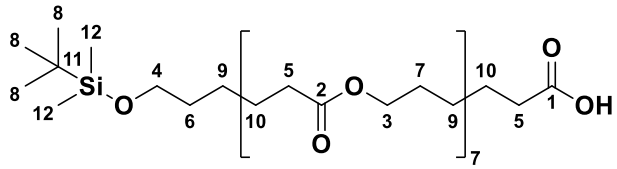
^{1}H NMR (DMSO-d_6, 400 MHz): δ / ppm = 12.05 (br, 1H, CO_2H^{1}), 3.98 (t, J = 6.7 Hz, 14H, CH_2^{2}), 3.55 (t, J = 6.3 Hz, 2H, CH_2^{3}), 2.32 – 2.23 (m, 14H, CH_2^{4}), 2.19 (t, J = 7.3 Hz, 2H, CH_2^{5}), 1.60 – 1.46 (m, 30H, CH_2^{6}), 1.46 – 1.39 (m, 2H, CH_2^{7}), 1.35 – 1.24 (m, 16H, CH_2^{8}), 0.84 (s, 9H, CH_3^{9}), 0.01 (s, 6H, CH_3^{10}).

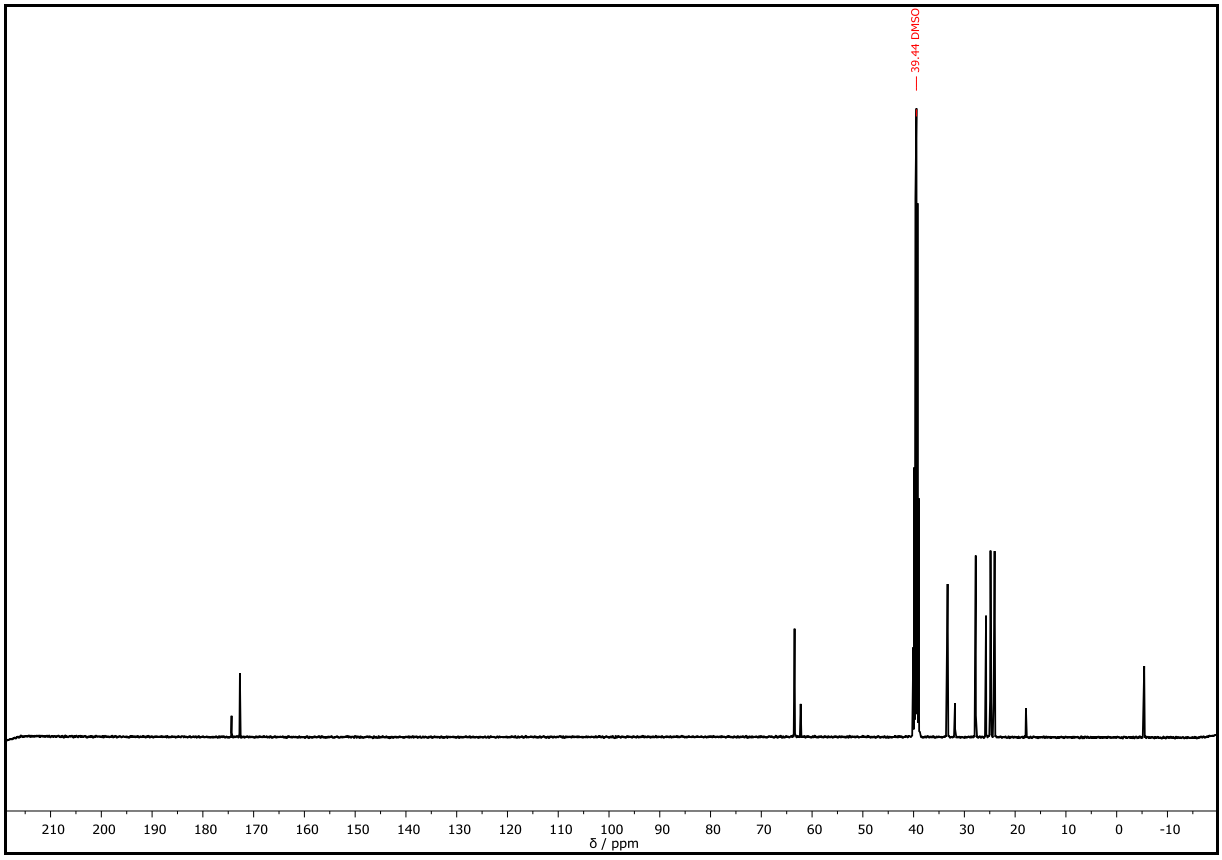




Supplementary Figure 53: ^{1}H NMR spectrum of **TBDMS(CL)$_8$CO$_2$H**, recorded at 400 MHz in DMSO-d_6.

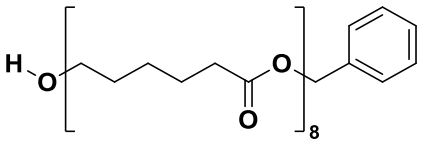
^{13}C NMR ($CDCl_3$, 101 MHz): δ / ppm = 174.35 (C_q^1), 172.77 (C_q^2), 172.74 (C_q^2), 172.71 (C_q^2), 63.50 (CH_2^3), 63.45 (CH_2^3), 63.41 (CH_2^3), 62.25 (CH_2^4), 33.50 (CH_2^5), 33.31 (CH_2^5), 31.85 (CH_2^6), 27.84 (CH_2^7), 27.76 (CH_2^7), 25.74 (CH_3^8), 24.94 (CH_2^9), 24.85 (CH_2^9), 24.81 (CH_2^9), 24.25 (CH_2^{10}), 24.08 (CH_2^{10}), 24.05 (CH_2^{10}), 17.87 (C_q^{11}), -5.42 (CH_3^{12}).





Supplementary Figure 54: ^{13}C NMR spectrum of **TBDMS(CL)$_8$CO$_2$H**, recorded at 101 MHz in DMSO-*d*$_6$.

Hydroxyl–terminated octamer – HO(CL)$_8$Bn



Chemical Formula: $C_{55}H_{88}O_{17}$
Exact Mass: 1020.6022 Da
Molecular Weight: 1021.2920 Da

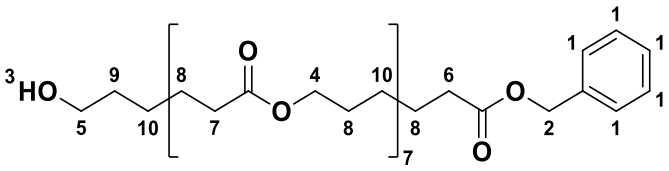
The hydroxyl-terminated tetramer **HO(CL)$_8$Bn** was prepared according to the procedure described above for the synthesis of the hydroxyl-terminated dimer **HO(CL)$_2$Bn**.

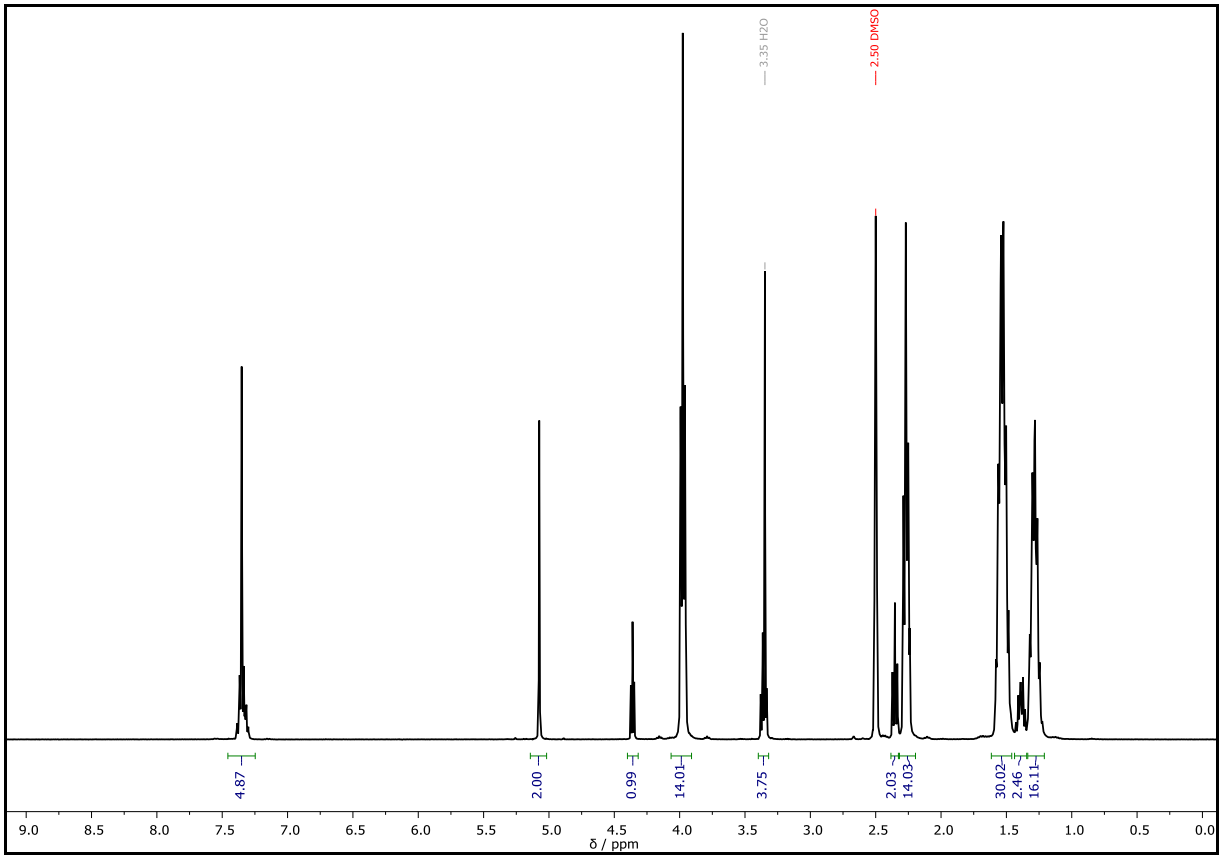
TBDMS(CL)$_8$Bn	3.00 g, 2.64 mmol, 1.00 equiv.
TBAF	1.67 g, 6.39 mmol, 2.42 equiv.
glacial acetic acid	305 µL, 320 mg, 5.33 mmol, 2.02 equiv.
total THF	10.6 mL
eluent	cyhex/EA = 1:1
yield	2.62 g, 2.57 mmol, 97.3%, white solid
R_f	0.53 (cyhex/EA = 1:1).
Đ (system I)	1.00

HRMS (ESI) of $C_{55}H_{88}O_{17}$ $[M+H]^+$ calcd. 1021.6094, detected 1021.6075; $[M+NH_4]^+$ calcd. 1038.6360, detected 1038.6328.

IR (ATR platinum diamond) $\tilde{\nu}$ / cm^{-1} = 2943.5, 2864.6, 1719.0, 1470.7, 1417.8, 1397.3, 1364.8, 1292.2, 1238.0, 1177.1, 1107.4, 1043.4, 959.5, 933.5, 840.1, 730.6, 697.4, 580.8, 453.0.

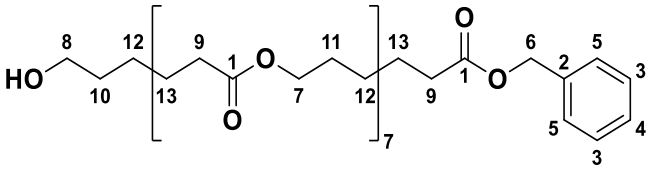
^{1}H NMR (DMSO-d_6, 400 MHz): δ / ppm = 7.40 – 7.28 (m, 5H, CH_{Ar}^{1}), 5.07 (s, 2H, CH_2^{2}), 4.36 (t, J = 5.1 Hz, 1H, OH^{3}), 3.97 (t, J = 6.5 Hz, 14H, CH_2^{4}), 3.36 (t, J = 6.5 Hz, 2H, CH_2^{5}), 2.35 (t, J = 7.4 Hz, 2H, CH_2^{6}), 2.30 – 2.21 (m, 14H, CH_2^{7}), 1.61-1.46 (m, 30H, CH_2^{8}), 1.44 – 1.35 (m, 2H, CH_2^{9}), 1.35 – 1.22 (m, 16H, CH_2^{10}).

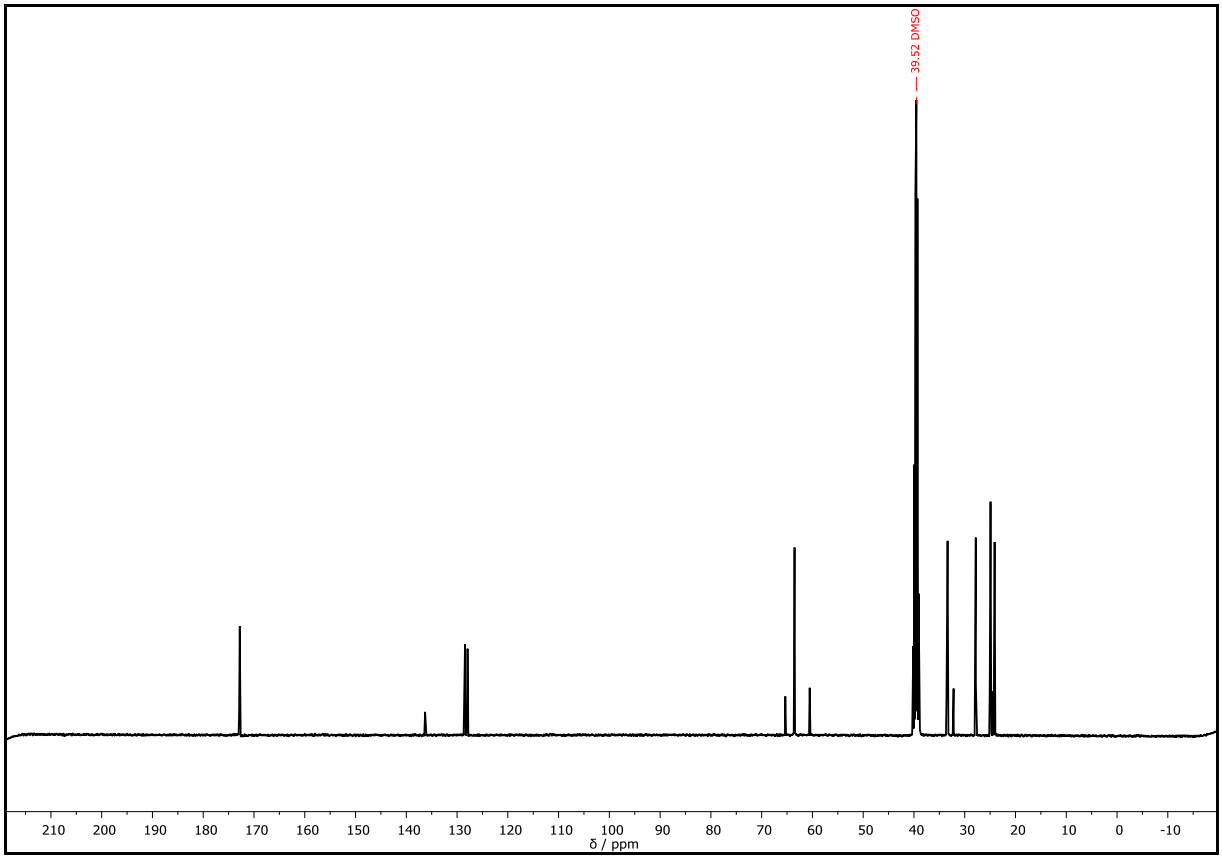




Supplementary Figure 55: ^{1}H NMR spectrum of **HO(CL)$_8$Bn**, recorded at 400 MHz in DMSO-d_6.

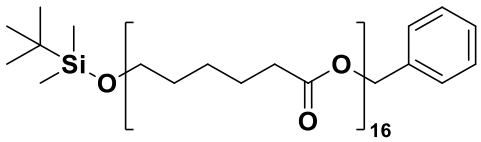
^{13}C NMR (DMSO-d_6, 101 MHz): δ / ppm = 172.92 (C_q^1), 172.81 (C_q^1), 172.69 (C_q^1), 136.29 ($C_{q,Ar}^2$), 128.43 ($CH_{Ar,meta}^3$), 128.00 ($CH_{Ar,para}^4$), 127.94 ($CH_{Ar,ortho}^5$), 65.33 (CH_2^6), 63.52 (CH_2^7), 60.55 (CH_2^8), 33.59 (CH_2^9), 33.38 (CH_2^9), 32.19 (CH_2^{10}), 27.83 (CH_2^{11}), 25.08 (CH_2^{12}), 24.92 (CH_2^{12}), 24.45 (CH_2^{13}), 24.12 (CH_2^{13}).





Supplementary Figure 56: ^{13}C NMR spectrum of **HO(CL)$_8$Bn**, recorded at 101 MHz in DMSO-d_6.

Doubly protected hexadecamer – TBDMS(CL)$_{16}$Bn



Chemical Formula: $C_{109}H_{182}O_{33}Si$
Exact Mass: 2047.2333 Da
Molecular Weight: 2048.7070 Da

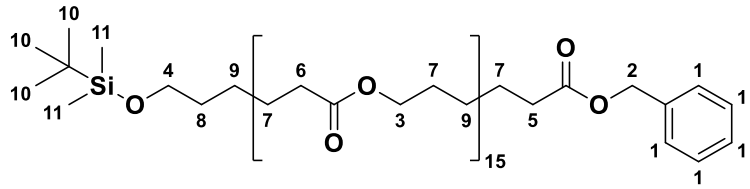
The doubly protected hexadecamer **TBDMS(CL)$_{16}$Bn** was prepared using the procedure described above for the synthesis of the doubly protected dimer **TBDMS(CL)$_2$Bn**. The reaction was performed in two batches, which were combined and purified *via* column chromatography. Quantities of the starting materials and the yield are the sum of both reactions. 0.20 equiv. DPTS was used instead of 1.10 equiv. DMAP.

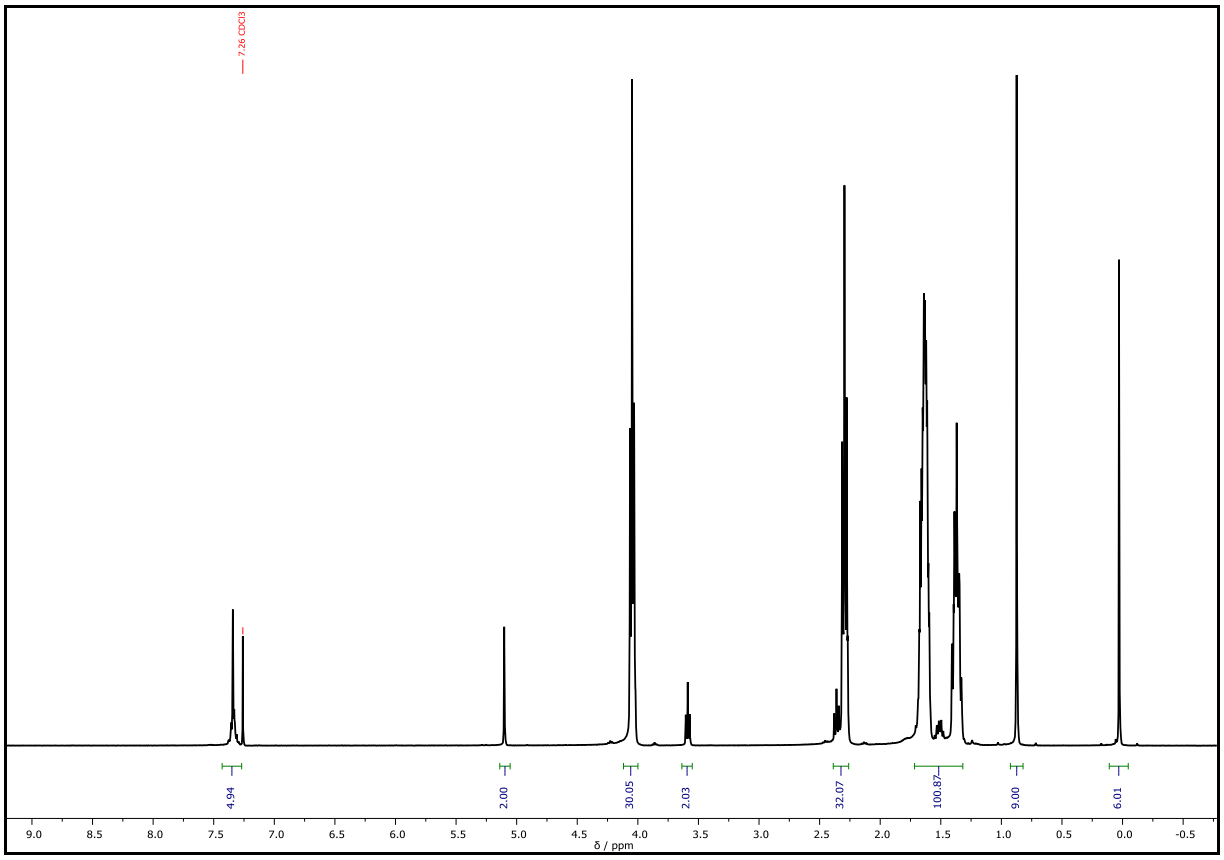
TBDMS(CL)$_8$CO$_2$H	2.00 g, 1.92 mmol, 1.00 equiv.
HO(CL)$_8$Bn	1.95 g, 1.92 mmol, 1.00 equiv.
DCC	434 mg, 2.10 mmol, 1.10 equiv.
DPTS	112 mg, 380 µmol, 0.20 equiv.
DCM	10.0 mL
eluent	cyhex/EA = 2:1
yield	3.82 g, 1.86 mmol, 97.1%, white solid
R_f	0.49 (cyhex/EA = 3:1).
Đ (system I)	1.00

HRMS (ESI) of $C_{109}H_{182}O_{33}Si$ $[M+H]^+$ calcd. 2048.2405, detected 2048.2424.

IR (ATR platinum diamond) $\tilde{\nu}$ / cm^{-1} = 3323.7, 2928.7, 2851.3, 1721.6, 1624.8, 1569.1, 1470.8, 1419.3, 1364.6, 1293.4, 1239.9, 1160.5, 1087.7, 1044.2, 960.4, 891.7, 836.3, 775.9, 731.5, 614.6, 453.2, 416.9.

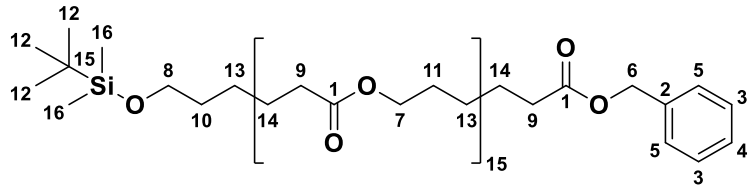
^{1}H NMR ($CDCl_3$, 400 MHz): δ / ppm = 7.41 – 7.30 (m, 5H, CH_{Ar}^{1}), 5.11 (s, 2H, CH_2^{2}), 4.05 (t, *J* = 6.7 Hz, 30H, CH_2^{3}), 3.59 (t, *J* = 6.4 Hz, 2H, CH_2^{4}), 2.49 – 2.21 (m, 32H, CH_2^{5}, CH_2^{6}), 1.77 – 1.25 (m, 96H, CH_2^{7}, CH_2^{8} and CH_2^{9}), 0.88 (s, 9H, CH_3^{10}), 0.03 (s, 6H, CH_3^{11}).

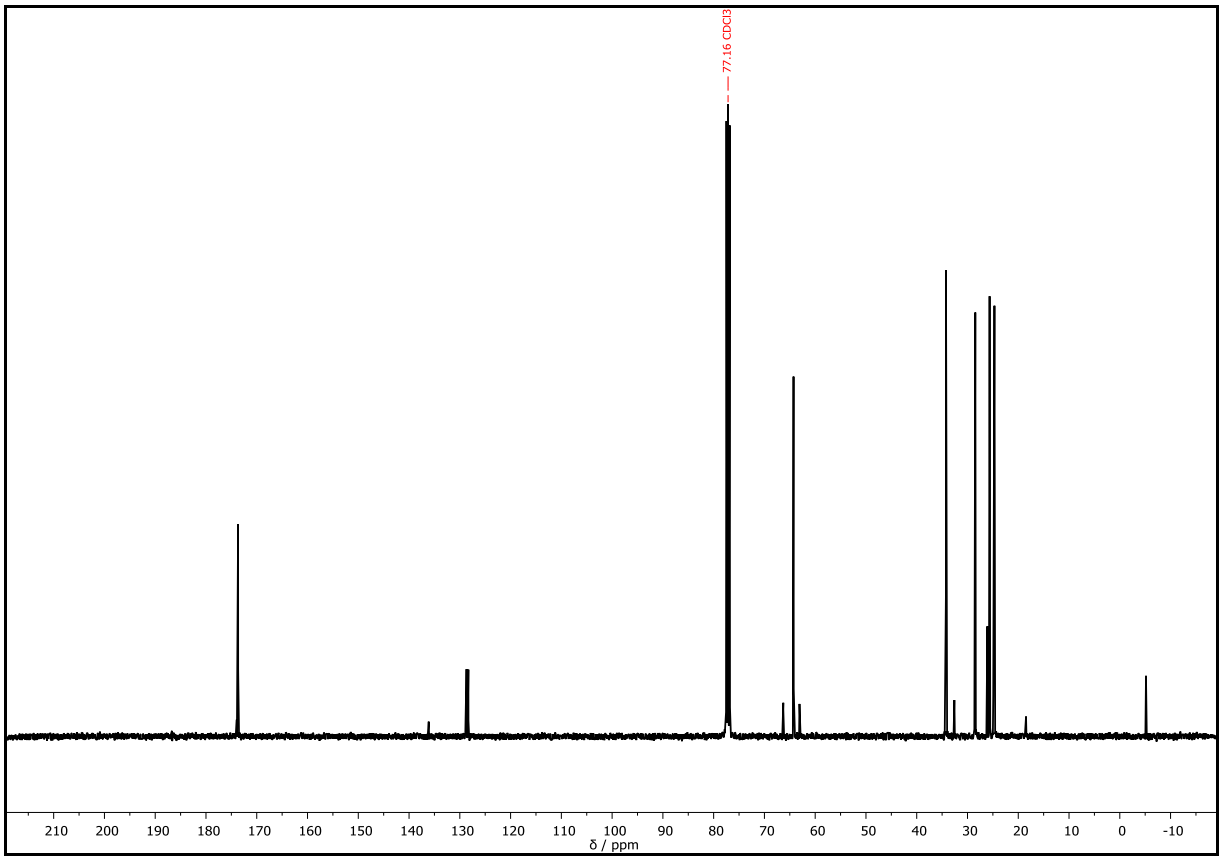




Supplementary Figure 57: ^{1}H NMR spectrum of **TBDMS(CL)$_{16}$Bn**, recorded at 400 MHz in $CDCl_3$.

^{13}C NMR ($CDCl_3$, 101 MHz): δ / ppm = 173.94 (C_q^1), 173.68 (C_q^1), 173.44 (C_q^1), 136.13 ($C_{q,Ar}^2$), 128.68 ($CH_{Ar,meta}^3$), 128.34 ($CH_{Ar,para}^4$), 128.31 ($CH_{Ar,ortho}^5$), 66.28 (CH_2^6), 64.26 (CH_2^7), 63.09 (CH_2^8), 34.45 (CH_2^9), 34.23 (CH_2^9), 32.59 (CH_2^{10}), 28.46 (CH_2^{11}), 26.08 (CH_3^{12}), 25.65 (CH_2^{13}), 24.93 (CH_2^{14}), 24.69 (CH_2^{14}), 18.47 (C_q^{15}), -5.16 (CH_3^{16}).





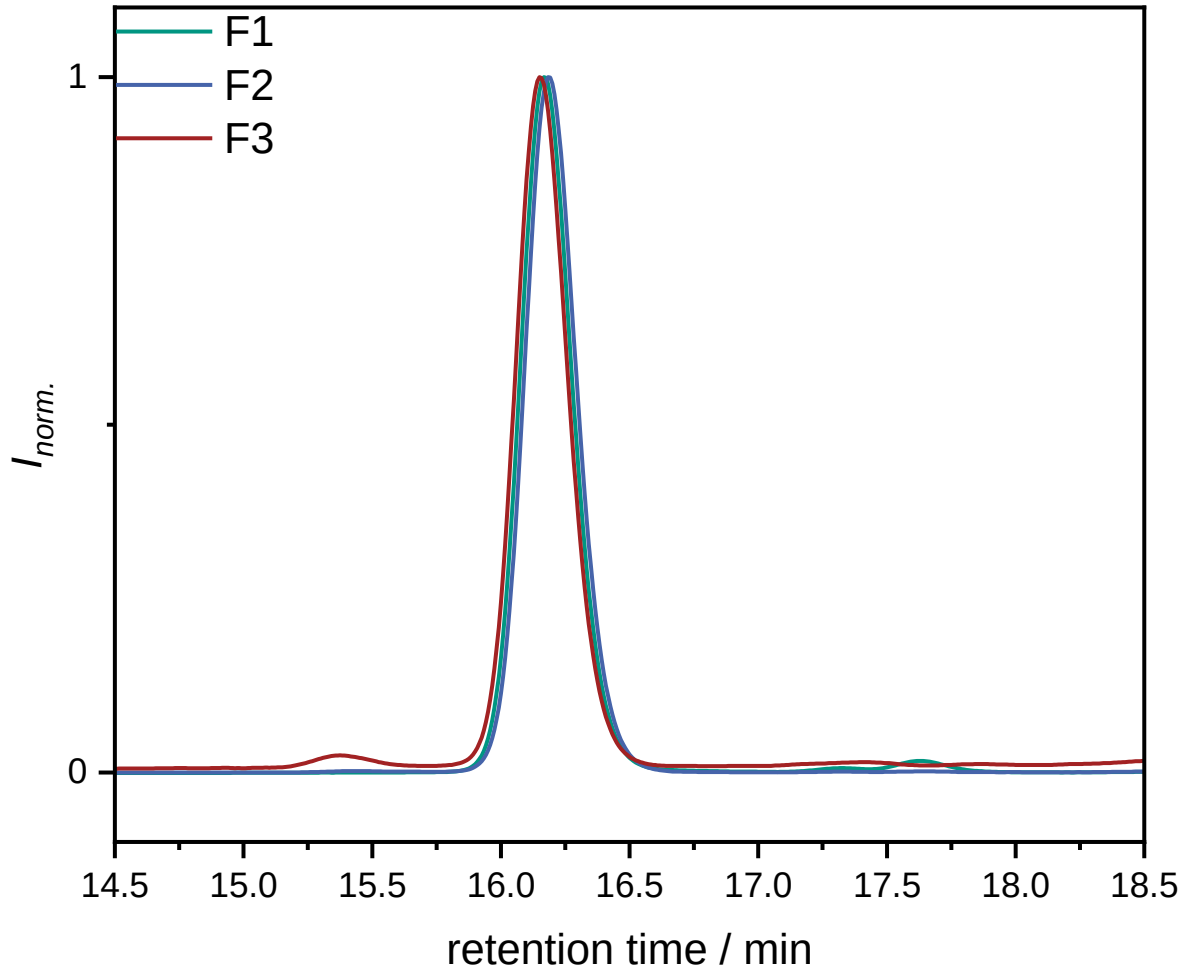
Supplementary Figure 58: ^{13}C NMR spectrum of **TBDMS(CL)$_{16}$Bn**, recorded at 101 MHz in $CDCl_3$.

In a second approach, the reaction was performed in a 15.5 mmol scale. The crude product (38.8 g) was purified *via* column chromatography for four times. In total 46 fractions were collected. The respective amounts, the analysis *via* GPC (system I) and the chromatograms are given in the following. The ones highlighted in green were used for further synthesis. The ones in yellow were purified *via* another column chromatography and the ones marked in red were discarded.

Supplementary Table 6: SEC results of the first purification of **TBDMS(CL)$_{16}$Bn**.

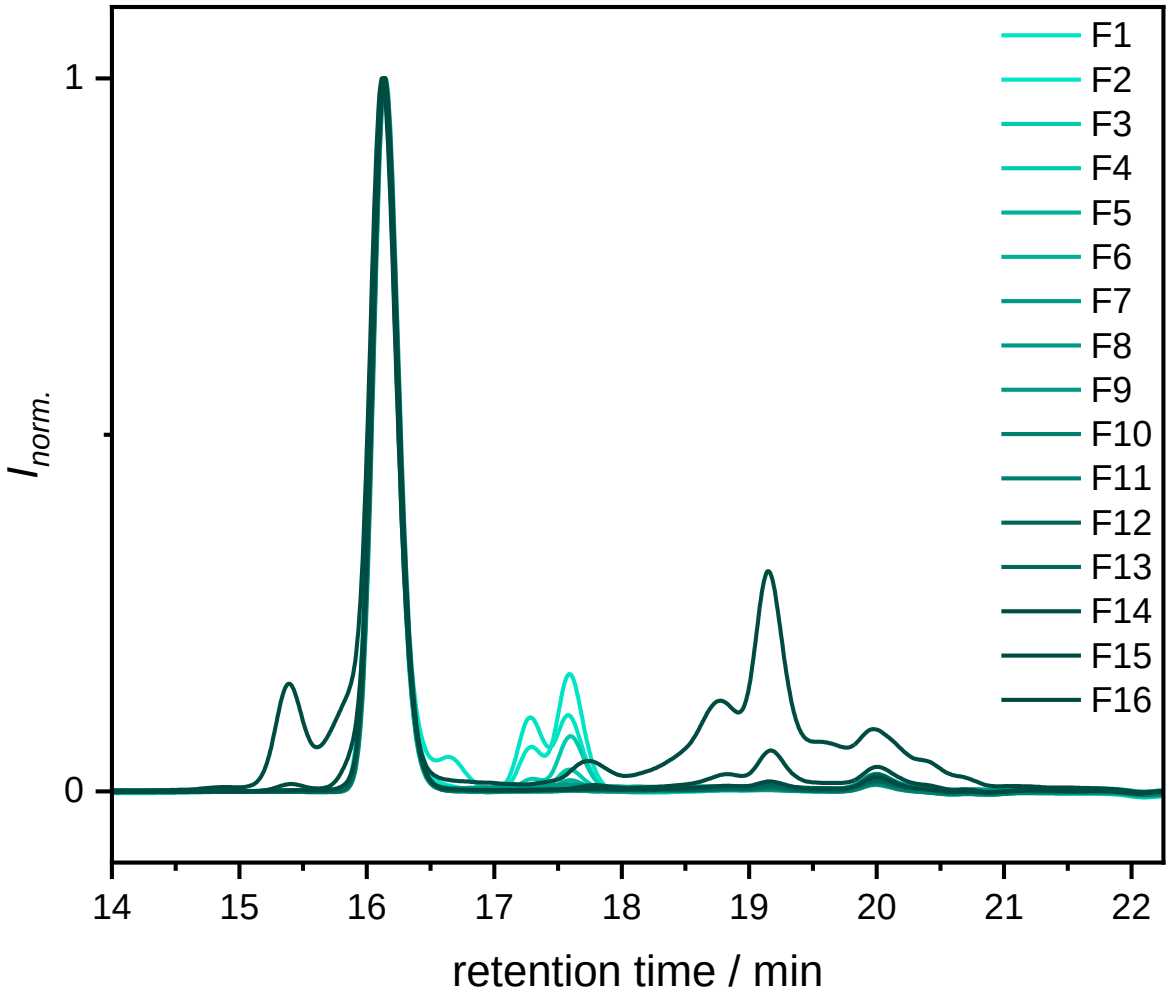
cc 1	*m* / g	M_n / Da	M_w / Da	M_z / Da	*Đ*	purity / %
F1	29.8	3800	3850	3850	1.00	98.5
F2	1.54	3800	3800	3850	1.00	>99
F3	0.32	3850	3900	3900	1.00	98.4

eluent: cyhex:EA = 2:1 → 1:1; in total 31.7 g of product with a purity of 98.6%.



Supplementary Figure 59: SEC traces of the individual fractions obtained from the first purification *via* column chromatography of **TBDMS(CL)$_{16}$Bn**.

Supplementary Table 7: SEC results of the second purification of **TBDMS(CL)$_{16}$Bn**.						
cc 2	*m* / g	M_n / Da	M_w / Da	M_z / Da	*Đ*	purity / %
F1	0.61	3900	3900	3950	1.00	81.0
F2	0.12	3900	3900	3900	1.00	82.2
F3	0.49	3900	3900	3900	1.00	91.6
F4	0.84	3900	3900	3950	1.00	97.2
F5	7.64	3900	3900	3900	1.00	98.8
F6	5.83	3900	3900	3950	1.00	99.4
F7	6.02	3900	3900	3950	1.00	>99
F8	3.87	3900	3900	3950	1.00	>99
F9	2.48	3850	3900	3900	1.00	>99
F10	1.09	3900	3900	3900	1.00	>99
F11	1.81	3900	3900	3900	1.00	>99
F12	1.15	3900	3900	3900	1.00	>99
F13	0.80	3900	3900	3900	1.00	>99
F14	0.48	3900	3900	3900	1.00	>99
F15	0.09	3900	3900	3950	1.00	92.5
F16	0.03	4000	4050	4050	1.01	53.2
eluent: cyhex:EA = 3:1 → 2:1 → 1:1 → 0:1.						

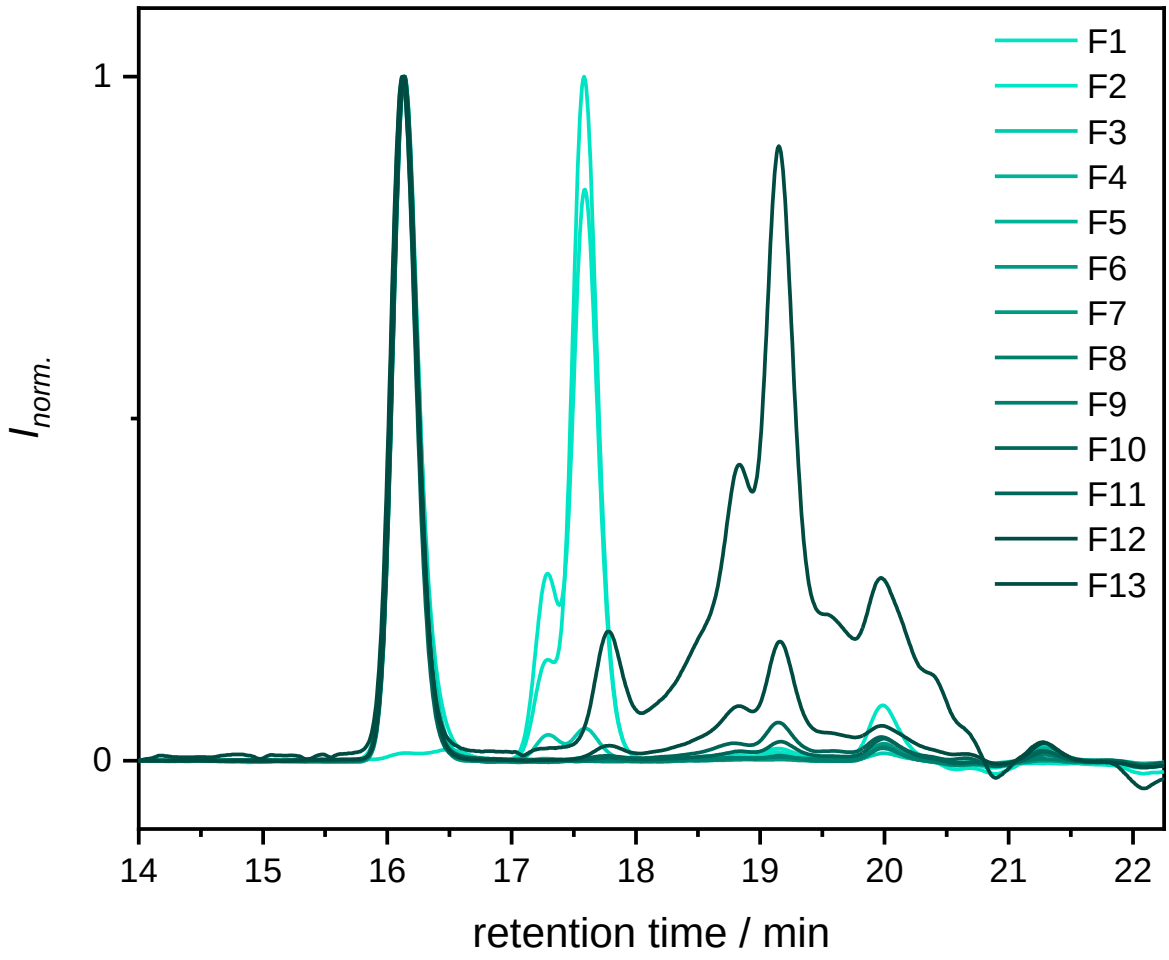


Supplementary Figure 60: SEC traces of the individual fractions obtained from the second purification *via* column chromatography of **TBDMS(CL)$_{16}$Bn**.

Supplementary Table 8: SEC results of the third purification of **TBDMS(CL)$_{16}$Bn**.

cc 3	*m* / mg	M_n / Da	M_w / Da	M_z / Da	*Đ*	purity / %
F1	246	*n.a.*[1]	*n.a.*[1]	*n.a.*[1]	*n.a.*[1]	*n.a.*[1]
F2	512	3850	3900	3900	1.00	50.2
F3	353	3900	3900	3900	1.00	92.8
F4	5590	3900	3900	3900	1.00	>99
F5	2400	3900	3900	3900	1.00	99.5
F6	3330	3900	3900	3900	1.00	>99
F7	1710	3900	3900	3900	1.00	>99
F8	762	3900	3900	3900	1.00	>99
F9	273	3900	3900	3900	1.00	>99
F10	87.1	3850	3850	3900	1.00	99.4
F11	39.4	3850	3900	3900	1.00	99.4
F12	44.0	3900	3900	3900	1.00	99.4
F13	18.0	3900	3900	3950	1.00	97.1

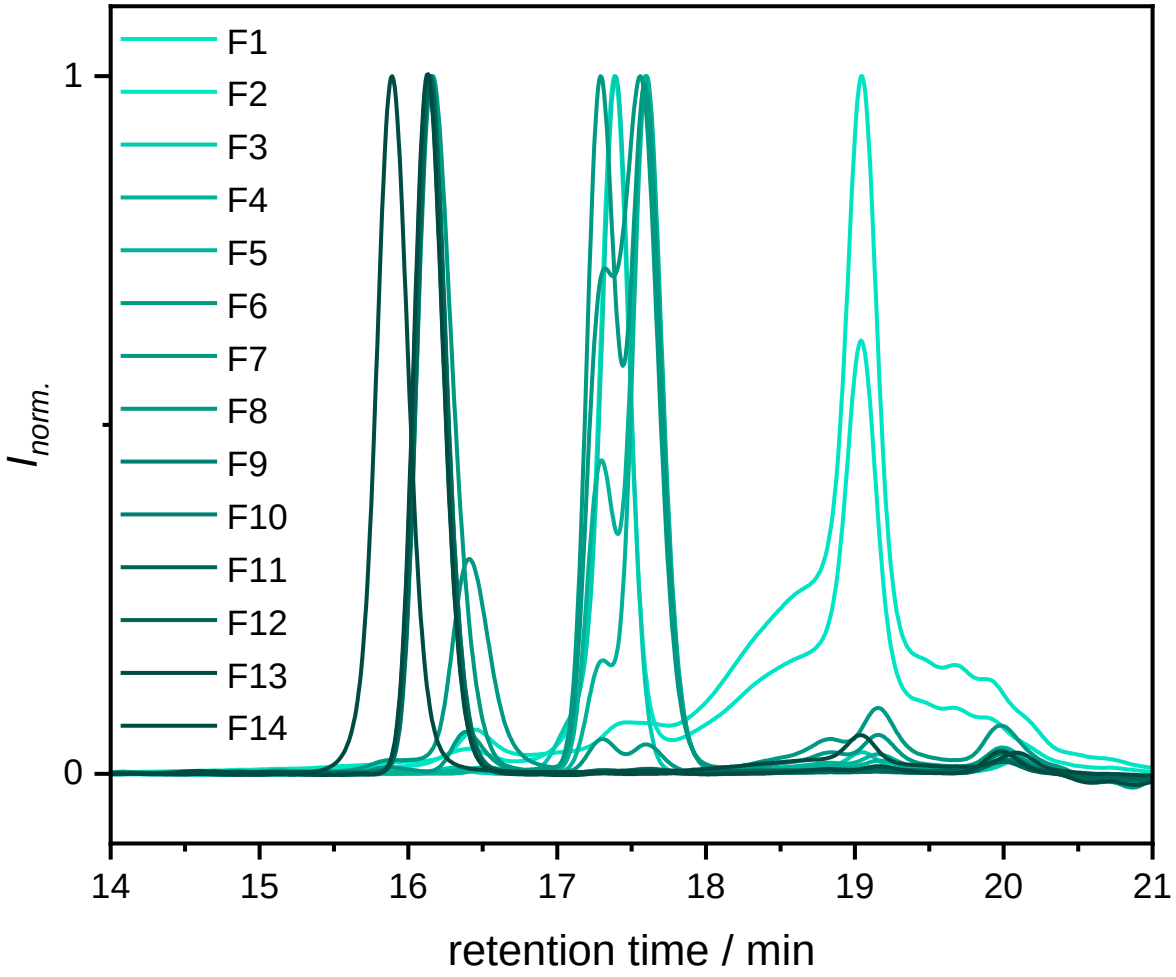
eluent: cyhex:EA = 3:1 → 2:1 → 1:1 → 0:1; [1]This fraction did not contain any product.



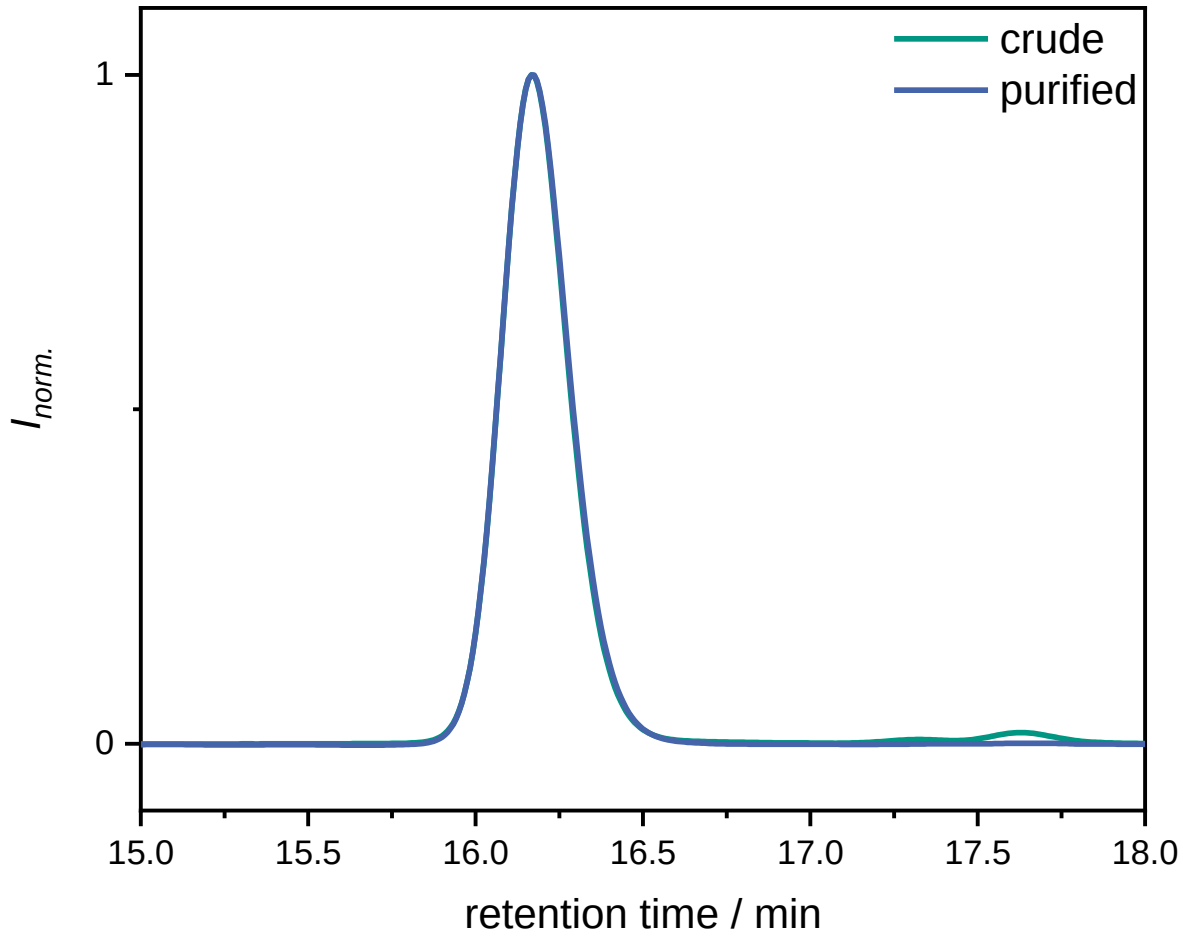
Supplementary Figure 61: SEC traces of the individual fractions obtained from the third purification *via* column chromatography of **TBDMS(CL)$_{16}$Bn**.

Supplementary Table 9: SEC results of the fourth purification of **TBDMS(CL)$_{16}$Bn**.						
cc 4	*m* / mg	M_n / Da	M_w / Da	M_z / Da	*Đ*	purity / %
F1	7.3	*n.a.*[1]	*n.a.*[1]	*n.a.*[1]	*n.a.*[1]	*n.a.*[1]
F2	7.8	*n.a.*[1]	*n.a.*[1]	*n.a.*[1]	*n.a.*[1]	*n.a.*[1]
F3	42.3	*n.a.*[1]	*n.a.*[1]	*n.a.*[1]	*n.a.*[1]	*n.a.*[1]
F4	99.5	*n.a.*[1]	*n.a.*[1]	*n.a.*[1]	*n.a.*[1]	*n.a.*[1]
F5	89.7	*n.a.*[1]	*n.a.*[1]	*n.a.*[1]	*n.a.*[1]	*n.a.*[1]
F6	55.6	*n.a.*[1]	*n.a.*[1]	*n.a.*[1]	*n.a.*[1]	*n.a.*[1]
F7	15.4	*n.a.*[1]	*n.a.*[1]	*n.a.*[1]	*n.a.*[1]	*n.a.*[1]
F8	248	3800	3800	3850	1.00	93.4
F9	1190	3850	3900	3900	1.00	>99
F10	1150	3850	3850	3900	1.00	>99
F11	711	3850	3900	3900	1.00	>99
F12	389	3900	3900	3900	1.00	99.4
F13	321	3900	3900	3950	1.00	97.1
F14	87.0	3850	3900	3900	1.00	96.8

eluent: cyhex:EA = 3:1 → 2:1 → 1:1 → 0:1; [1]This fraction did not contain any product.

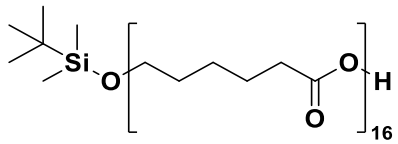


Supplementary Figure 62: SEC traces of the individual fractions obtained from the fourth purification *via* column chromatography of **TBDMS(CL)$_{16}$Bn**.



Supplementary Figure 63: SEC traces of product **TBDMS(CL)$_{16}$Bn** before and after four column chromatographic purification steps.

Carboxyl–terminated hexadecamer – TBDMS(CL)$_{16}$CO$_2$H



Chemical Formula: $C_{102}H_{176}O_{33}Si$
Exact Mass: 1957.1863 Da
Molecular Weight: 1958.5820 Da

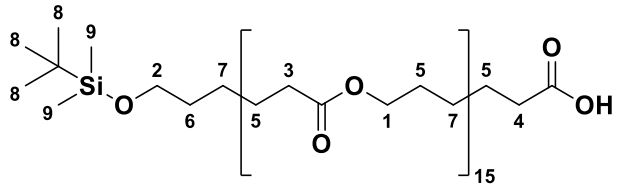
The carboxyl-terminated hexadecamer **TBDMS(CL)$_{16}$CO$_2$H** was prepared using the procedure described above for the synthesis of the carboxyl-terminated dimer **TBDMS(CL)$_2$CO$_2$H**.

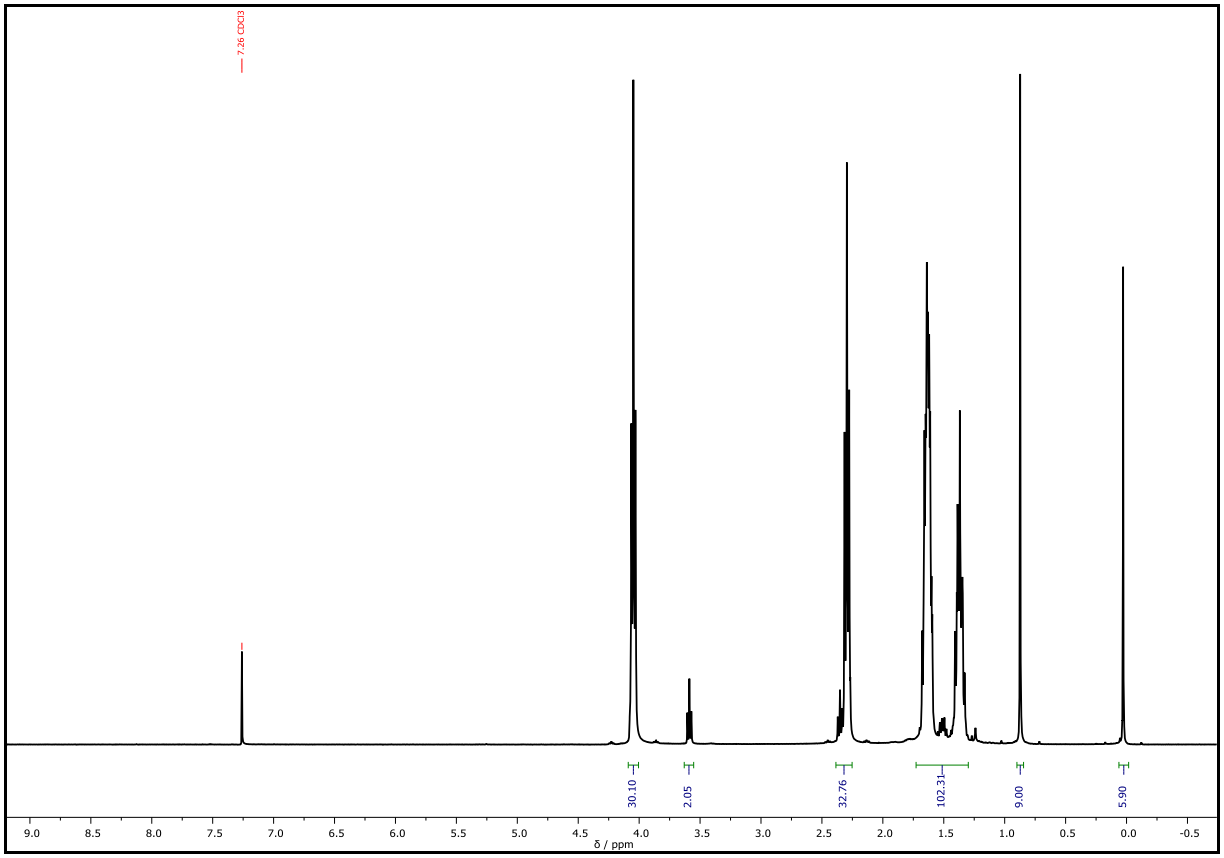
TBDMS(CL)$_{16}$Bn	14.9 g, 7.29 mmol, 1.00 equiv.
Pd/C	1.49 g, 10 wt%
EA	180 mL
yield	14.3 g, 7.29 mmol, quant. yield, white solid
Đ (system I)	1.00

HRMS (ESI) of $C_{102}H_{176}O_{33}Si$ $[M+H]^+$ calcd. 1958.1936, detected 1958.1937; $[M+NH_4]^+$ calcd. 1975.2201, detected 1975.2194.

IR (ATR platinum diamond) $\tilde{\nu}$ / cm^{-1} = 2944.0, 2864.0, 1720.5, 1470.8, 1418.6, 1396.9, 1365.0, 1292.8, 1238.6, 1176.0, 1106.2, 1065.2, 1044.0, 960.1, 933.5, 836.4, 775.5, 730.9, 584.5, 453.0.

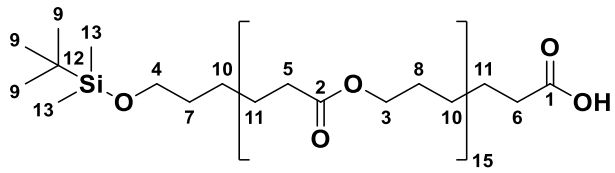
^{1}H NMR ($CDCl_3$, 400 MHz): δ / ppm = 4.05 (t, *J* = 6.7 Hz, 30H, CH_2^1), 3.59 (t, *J* = 6.5 Hz, 2H, CH_2^2), 2.50 – 2.19 (m, 32H. CH_2^3, CH_2^4), 1.84 – 1.27 (m, 96H, CH_2^5, CH_2^6 and CH_2^7), 0.87 (s, 9H, CH_3^8), 0.03 (s, 6H, CH_3^9).

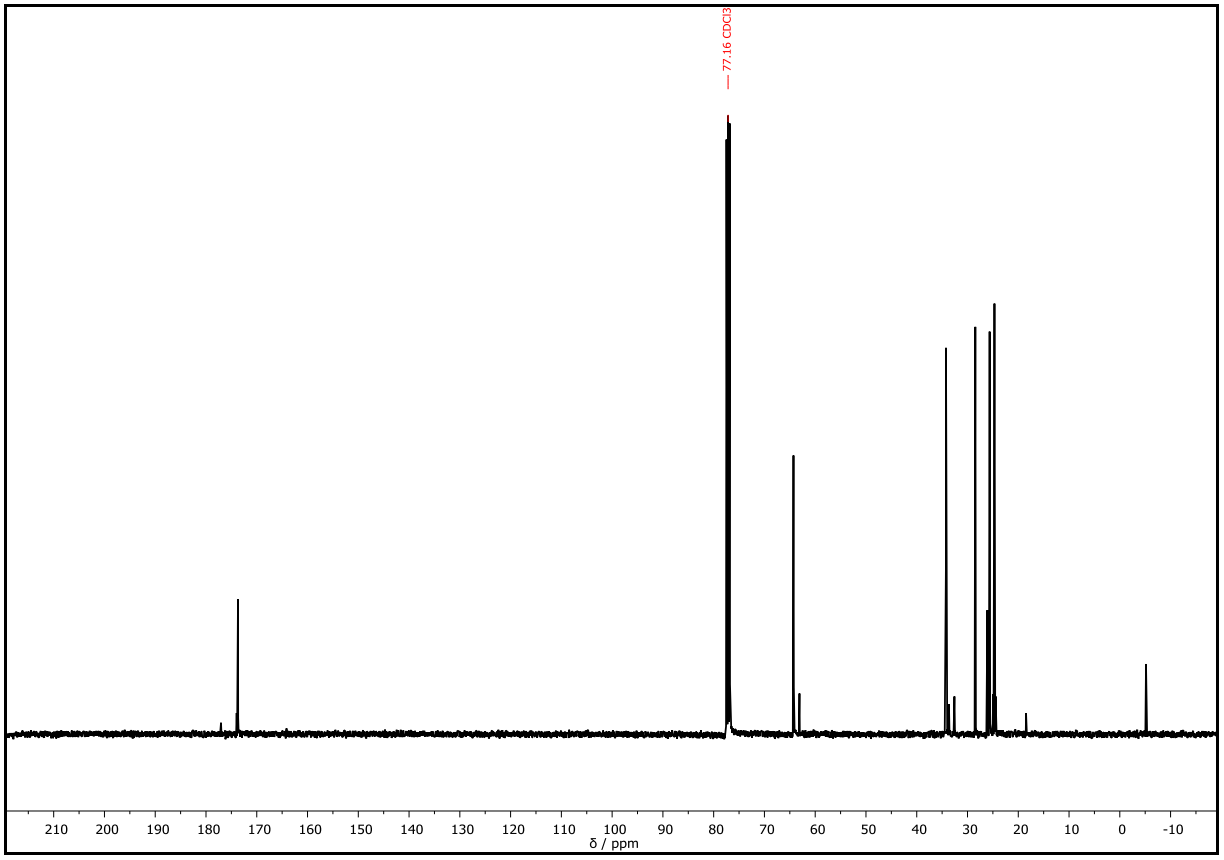




Supplementary Figure 64: ^{1}H NMR spectrum of **TBDMS(CL)$_{16}$CO$_2$H**, recorded at 400 MHz in $CDCl_3$.

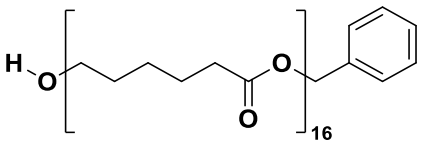
^{13}C NMR ($CDCl_3$, 101 MHz): δ / ppm = 173.96 (C_q^1), 173.84 (C_q^2), 173.70 (C_q^2), 64.32 (CH_2^3), 64.28 (CH_2^3), 64.21 (CH_2^3), 64.19 (CH_2^3), 63.10 (CH_2^4), 34.45 (CH_2^5), 34.29 (CH_2^5), 34.24 (CH_2^5), 33.65 (CH_2^6), 32.58 (CH_2^7), 28.46 (CH_2^8), 28.43 (CH_2^8), 26.08 (CH_3^9), 25.64 (CH_2^{10}), 25.56 (CH_2^{10}), 24.93 (CH_2^{11}), 24.69 (CH_2^{11}), 24.46 (CH_2^{11}), 18.47 (C_q^{12}), -5.16 (CH_3^{13}).





Supplementary Figure 65: ^{13}C NMR spectrum of **TBDMS(CL)$_{16}$CO$_2$H**, recorded at 101 MHz in $CDCl_3$.

Hydroxyl–terminated hexadecamer – HO(CL)$_{16}$Bn



Chemical Formula: $C_{103}H_{168}O_{33}$
Exact Mass: 1933.1468 Da
Molecular Weight: 1934.4440 Da

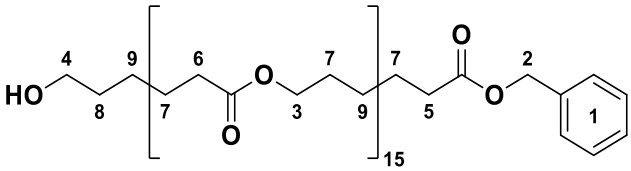
The hydroxyl-terminated tetramer **HO(CL)$_{16}$Bn** was prepared according to the procedure described above for the synthesis of the hydroxyl-terminated dimer **HO(CL)$_2$Bn**.

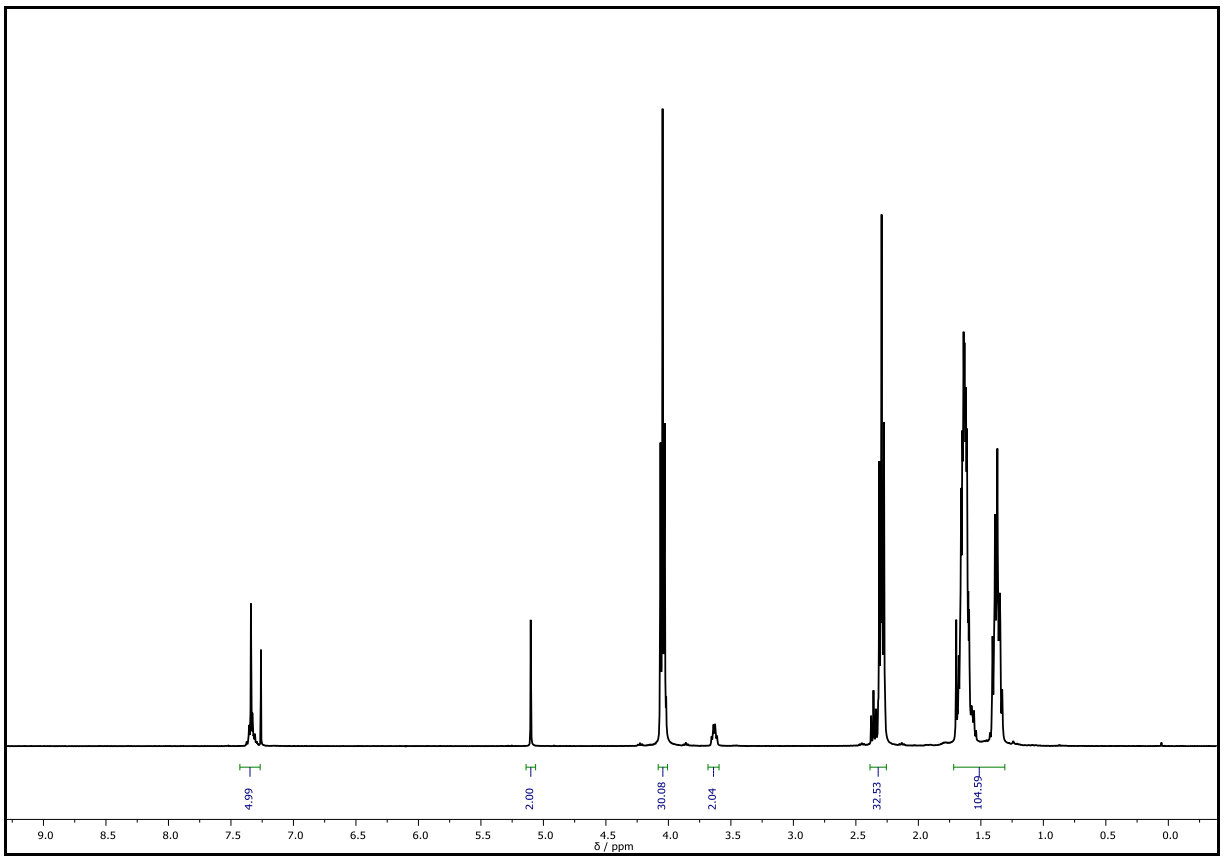
TBDMS(CL)$_{16}$Bn	15.0 g, 7.32 mmol, 1.00 equiv.
TBAF	4.62 g, 14.6 mmol, 2.00 equiv.
glacial acetic acid	838 µL, 879 mg, 14.6 mmol, 2.00 equiv.
total THF	35.0 mL
eluent	cyhex/EA = 1:2
yield	13.9 g, 7.16 mmol, 98.1%, white solid
R_f	0.42 (cyhex/EA = 1:1).
Đ (system I)	1.00

HRMS (ESI) of $C_{103}H_{168}O_{33}$ $[M+H]^+$ calcd. 1934.1541, detected 1934.43; $[M+NH_4]^+$ calcd. 1951.1806, detected 1951.1812; $[M+2H]^{2+}$ calcd. 967.5807, detected 967.5786; $[M+3H]^{3+}$ calcd. 645.3895, detected 645.3878.

IR (ATR platinum diamond) $\tilde{\nu}$ / cm^{-1} = 2943.6, 2864.8, 1720.2, 1470.6, 1364.9, 1292.6, 1238.0, 1171.9, 1107.2, 1043.6, 959.8, 731.1, 452.9.

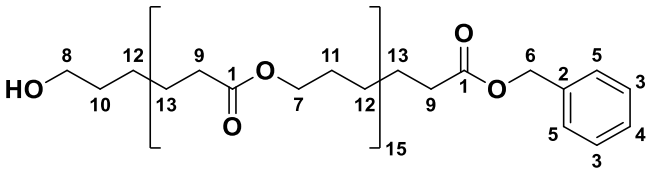
^{1}H NMR ($CDCl_3$, 400 MHz): δ / ppm = 7.39 – 7.29 (m, 5H, CH_{Ar}^{1}), 5.10 (s, 2H, CH_2^{2}), 4.05 (t, *J* = 6.7 Hz, 30H, CH_2^{3}), 3.63 (q, *J* = 6.0 Hz, 2H, CH_2^{4}), 2.36 (t, *J* = 7.5 Hz, 32H, CH_2^{5}, CH_2^{6}), 1.72 – 1.30 (m, 96H, CH_2^{7}, CH_2^{8} and CH_2^{9}).

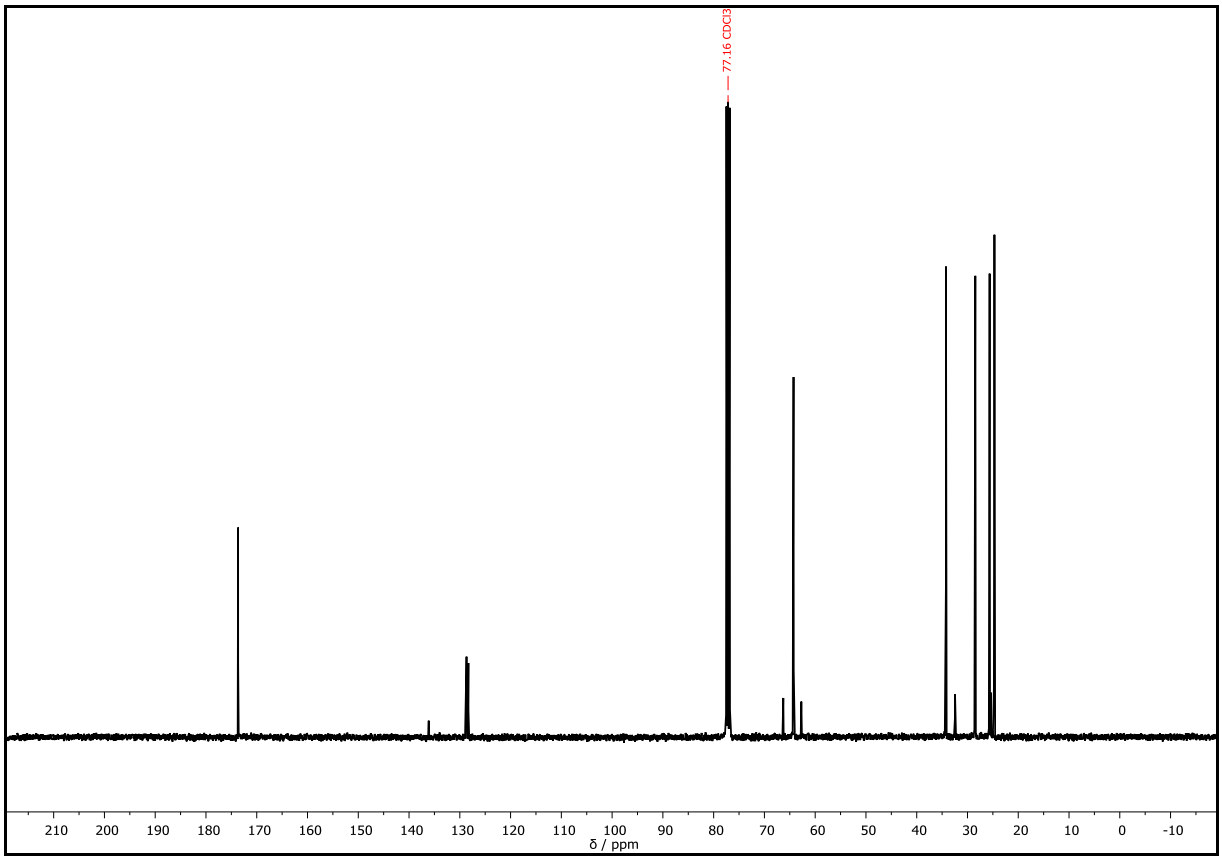




Supplementary Figure 66: ^{1}H NMR spectrum of **HO(CL)$_{16}$Bn**, recorded at 400 MHz in $CDCl_3$.

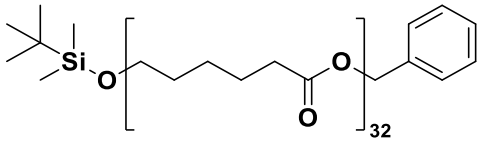
^{13}C NMR ($CDCl_3$, 101 MHz): δ / ppm = 173.86 (C_q^1), 173.73 (C_q^1), 173.67 (C_q^1), 173.43 (C_q^1), 136.13 ($C_{q,Ar}^2$), 128.68 ($CH_{Ar,meta}^3$), 128.34 ($CH_{Ar,para}^4$), 128.31 ($CH_{Ar,ortho}^5$), 66.28 (CH_2^6), 64.26 (CH_2^7), 64.23 (CH_2^7), 62.73 (CH_2^8), 34.34 (CH_2^9), 34.23 (CH_2^9), 32.45 (CH_2^{10}), 28.46 (CH_2^{11}), 25.64 (CH_2^{12}), 25.41 (CH_2^{12}), 24.80 (CH_2^{13}), 24.69 (CH_2^{13}).





Supplementary Figure 67: ^{13}C NMR spectrum of **HO(CL)$_{16}$Bn**, recorded at 101 MHz in $CDCl_3$.

Doubly protected 32-mer – TBDMS(CL)$_{32}$Bn



Chemical Formula: $C_{205}H_{342}O_{65}Si$
Exact Mass: 3872.3225 Da
Molecular Weight: 3875.0110 Da

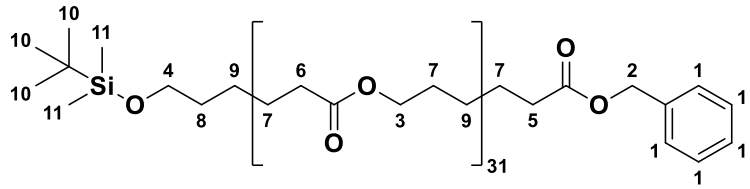
The doubly protected 32-mer **TBDMS(CL)$_{32}$Bn** was prepared using the procedure described above for the synthesis of the doubly protected dimer **TBDMS(CL)$_2$Bn**. 0.20 equiv. DPTS was used instead of 1.10 equiv. DMAP.

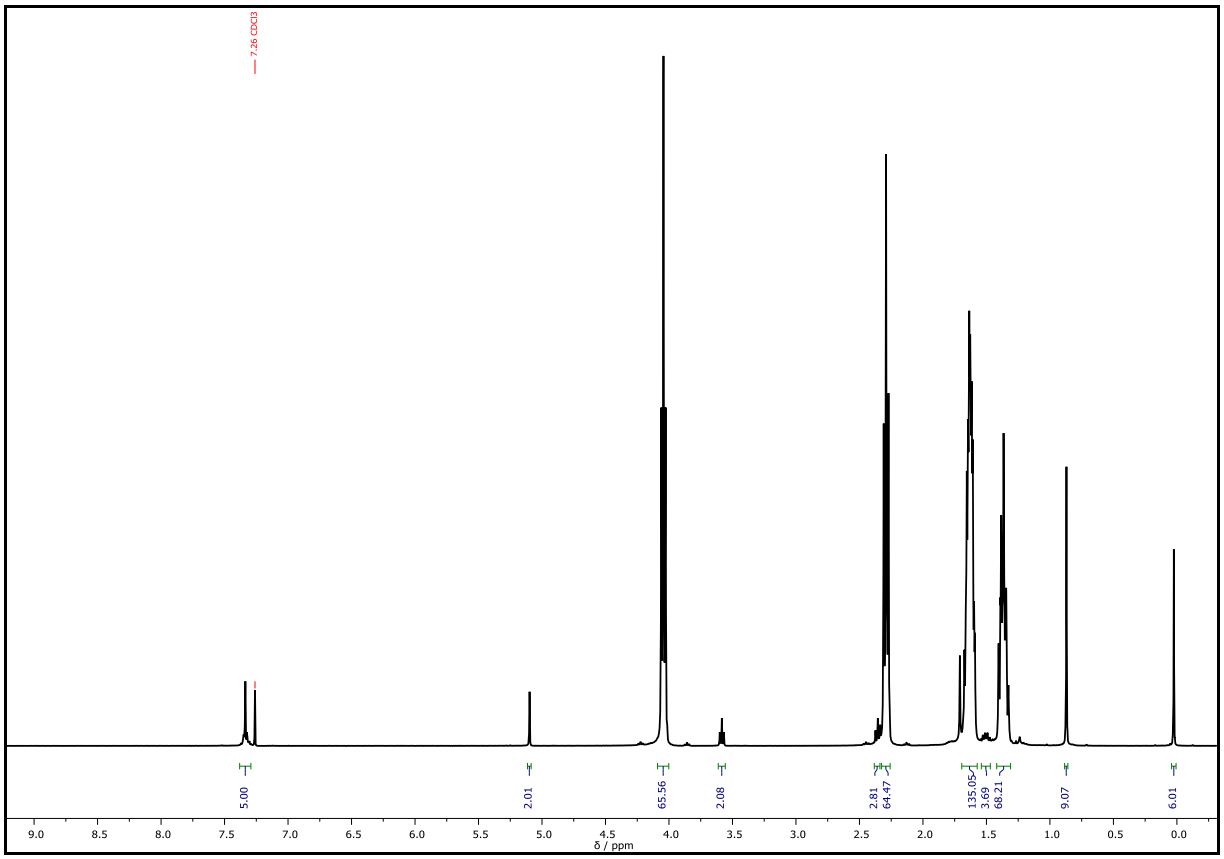
TBDMS(CL)$_{16}$CO$_2$H	10.5 g, 5.37 mmol, 1.00 equiv.
HO(CL)$_{16}$Bn	10.4 g, 5.37 mmol, 1.00 equiv.
DCC	1.22 g, 5.91 mmol, 1.10 equiv.
DPTS	316 mg, 1.07 mmol, 0.20 equiv.
DCM	100 mL
eluent	1st cc: cyhex/EA = 3:2 → 1:1,
	2nd cc: cyhex/EA = 3:2 → 5:4
yield	17.2 g, 4.44 mmol, 82.8%, white solid
R_f	0.88 (cyhex/EA = 1:2).
Đ (system I)	1.00

HRMS (ESI) of $C_{205}H_{342}O_{65}Si$ $[M+H]^+$ calcd. 3873.3298, detected 3873.3579; $[M+2H]^{2+}$ calcd. 1937.1685, detected 1937.16687.

IR (ATR platinum diamond) $\tilde{\nu}$ / cm^{-1} = 2943.7, 2864.3, 1720.9, 1470.6, 1364.4, 1292.6, 1237.9, 1161.6, 1106.0, 1043.0, 959.8, 837.6, 731.2, 452.9.

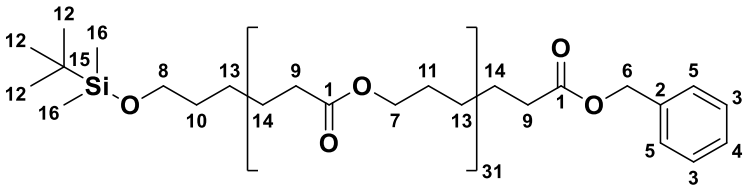
^{1}H NMR (400 MHz, $CDCl_3$) δ / ppm = 7.38 – 7.30 (m, 5H, CH_{Ar}^1), 5.10 (s, 2H, CH_2^2), 4.04 (t, *J* = 6.7 Hz, 62H, CH_2^3), 3.58 (t, *J* = 6.5 Hz, 2H, CH_2^4), 2.36 (t, *J* = 7.5 Hz, 2H, CH_2^5), 2.29 (t, *J* = 7.5 Hz, 62H, CH_2^6), 1.69 – 1.58 (m, 126H, CH_2^7), 1.55 – 1.47 (m, 2H, CH_2^8), 1.42 – 1.33 (m, 64H, CH_2^9), 0.87 (s, 9H, CH_3^{10}), 0.02 (s, 6H, CH_3^{11}).

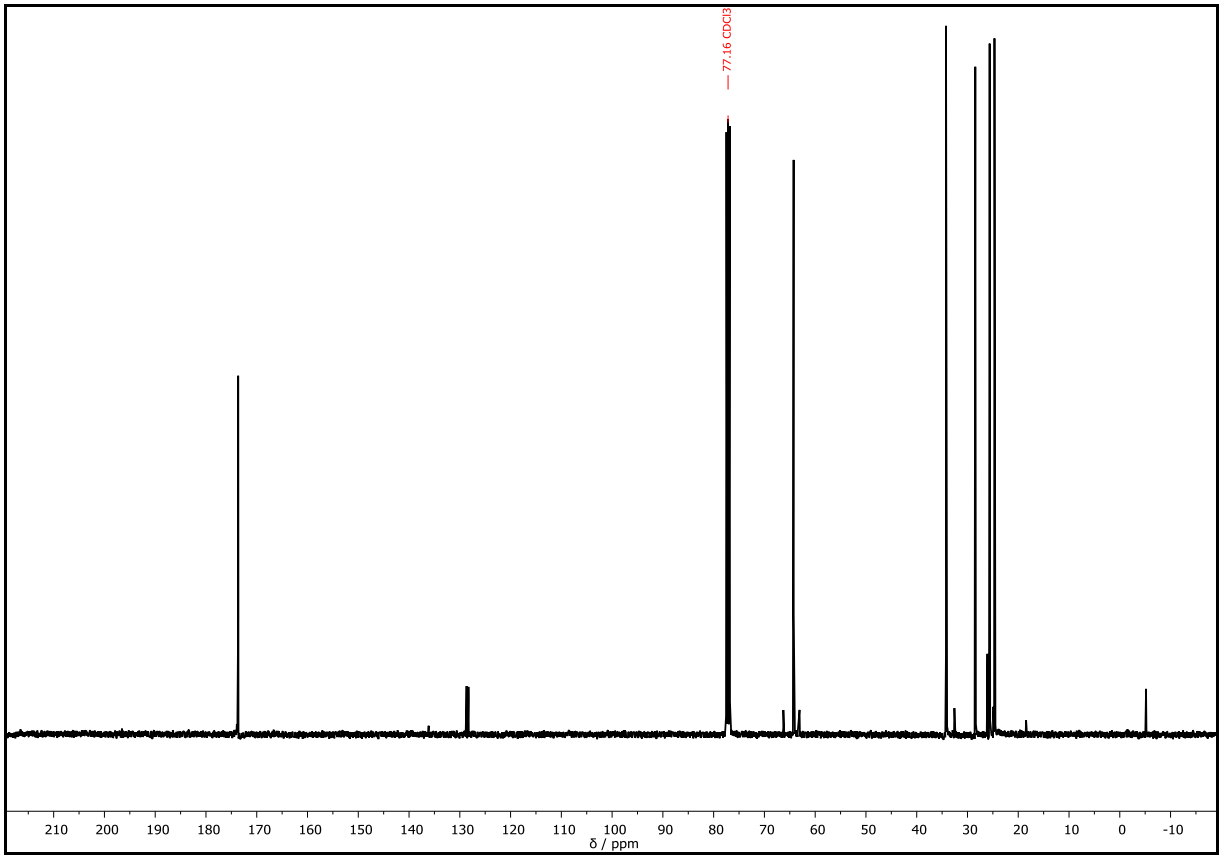




Supplementary Figure 68: ^{1}H NMR spectrum of **TBDMS(CL)$_{32}$Bn**, recorded at 400 MHz in $CDCl_3$.

^{13}C NMR ($CDCl_3$, 101 MHz): δ / ppm = 173.91 (C_q^1), 173.65 (C_q^1), 173.41 (C_q^1), 136.13 ($C_{q,Ar}^2$), 128.67 ($CH_{Ar,meta}^3$), 128.33 ($CH_{Ar,para}^4$), 128.30 ($CH_{Ar,ortho}^5$), 66.27 (CH_2^6), 64.25 (CH_2^7), 63.08 (CH_2^8), 34.44 (CH_2^9), 34.22 (CH_2^9), 32.57 (CH_2^{10}), 28.46 (CH_2^{11}), 26.07 (CH_3^{12}), 25.64 (CH_2^{13}), 24.92 (CH_2^{14}), 24.68 (CH_2^{14}), 18.45 (C_q^{15}), -5.17 (CH_3^{16}).





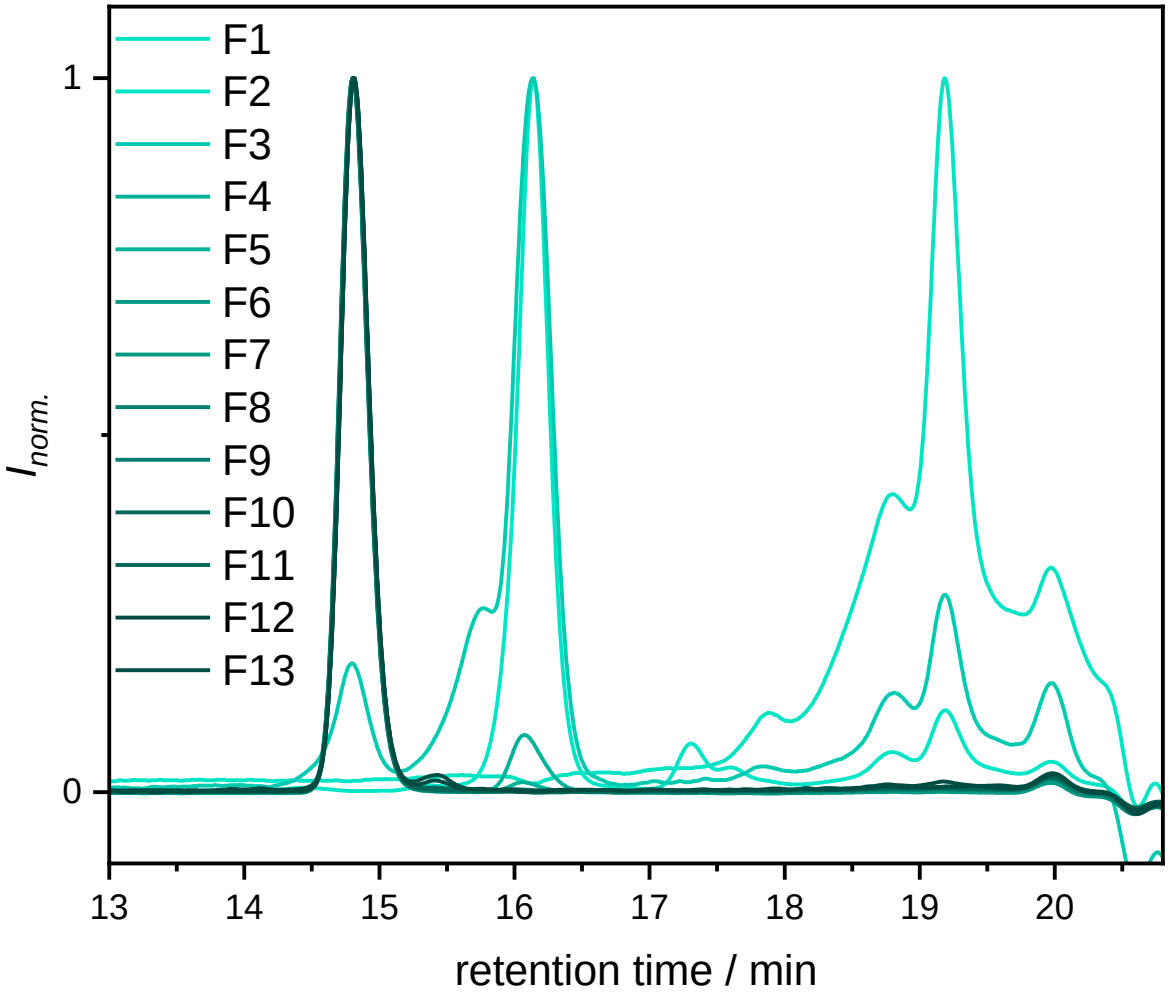
Supplementary Figure 69: ^{13}C NMR spectrum of **TBDMS(CL)$_{32}$Bn**, recorded at 101 MHz in $CDCl_3$.

The crude product of **TBDMS(CL)$_{32}$Bn** was purified *via* column chromatography twice. In total, 39 fractions were collected. The respective amounts, the analysis *via* GPC (system I) and the chromatograms are given in the following. The ones highlighted in green were used for further synthesis. The ones in yellow were purified once again *via* column chromatography and the fractions marked in red were discarded.

Supplementary Table 10 SEC results of the first purification of **TBDMS(CL)$_{32}$Bn**.

cc 1	*m* / g	M_n / Da	M_w / Da	M_z / Da	*Đ*	purity / %
F1	117E-3	*n.a.*[1]	*n.a.*[1]	*n.a.*[1]	*n.a.*[1]	*n.a.*[1]
F2	56.1E-3	*n.a.*[1]	*n.a.*[1]	*n.a.*[1]	*n.a.*[1]	*n.a.*[1]
F3	74.2E-3	8200	8250	8300	1.01	10.6
F4	2.20	8100	8100	8150	1.00	92.1
F5	2.68	8100	8100	8150	1.00	98.8
F6	2.09	8050	8100	8100	1.00	>99
F7	1.78	8100	8100	8150	1.00	>99
F8	1.62	8100	8150	8150	1.00	>99
F9	2.09	8050	8100	8100	1.00	>99
F10	2.81	8050	8100	8100	1.00	>99
F11	4.16	8050	8100	8100	1.00	>99
F12	1.48	8050	8100	8100	1.00	98.5
F13	271E-3	8050	8100	8100	1.00	981

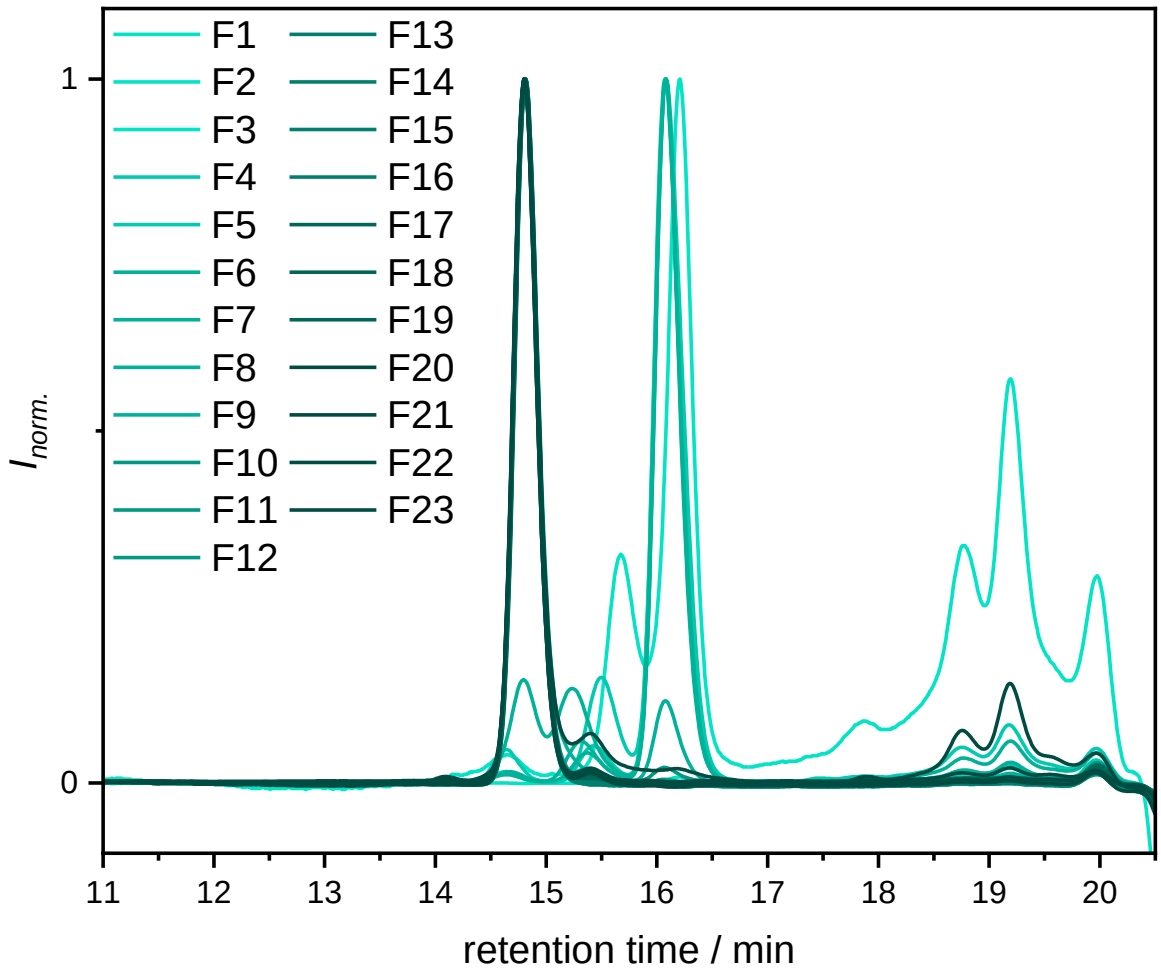
eluent: cyhex:EA = 3:2 → 1:1. [1]This fraction did not contain any product.



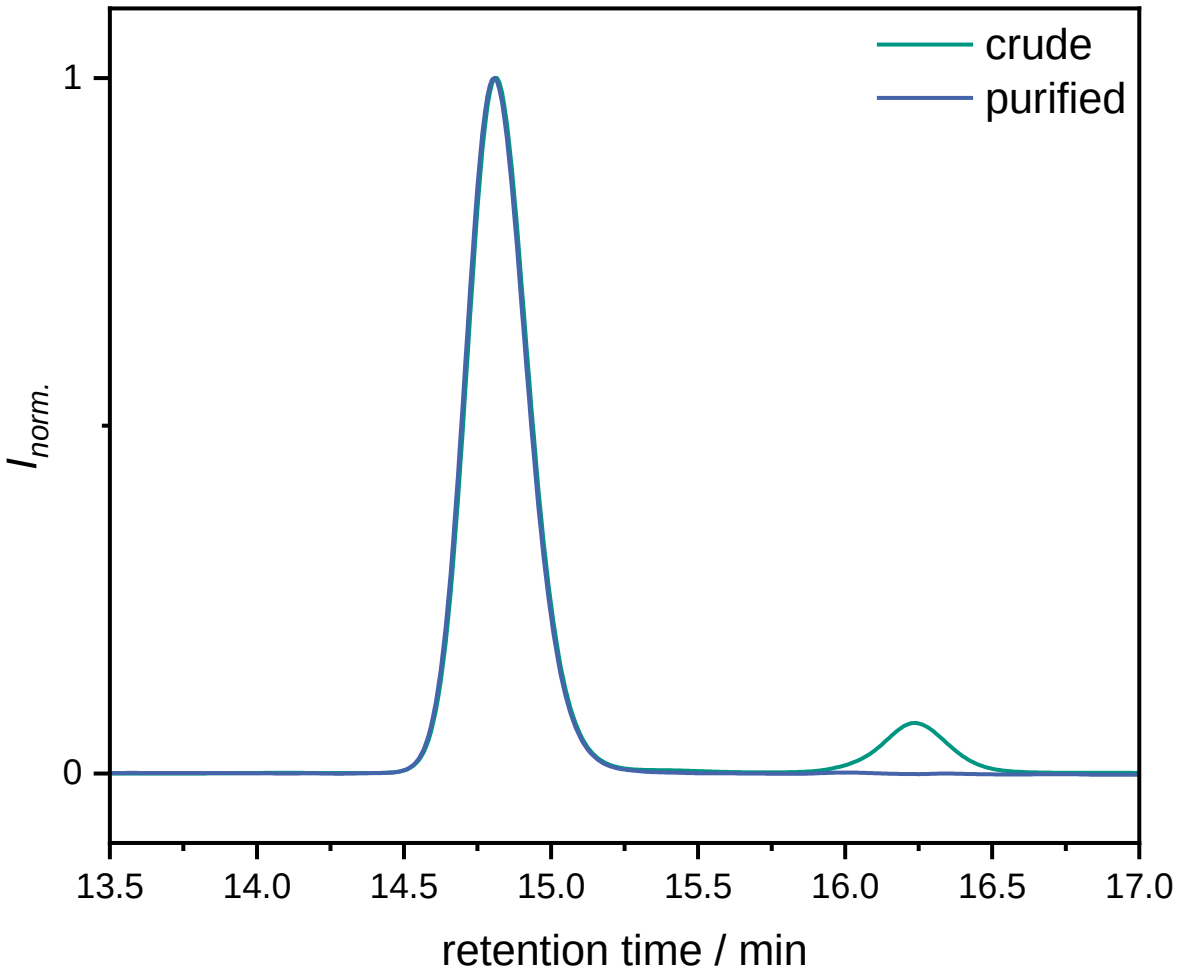
Supplementary Figure 70: SEC traces of the individual fractions obtained from the first purification *via* column chromatography of **TBDMS(CL)$_{32}$Bn**.

Supplementary Table 11: SEC results of the second purification of **TBDMS(CL)$_{32}$Bn**.						
cc 2	*m* / mg	M_n / Da	M_w/ Da	M_z/ Da	*Đ*	purity / %
F1	26.4	*n.a.*[1]	*n.a.*[1]	*n.a.*[1]	*n.a.*[1]	*n.a.*[1]
F2	33.6	*n.a.*[1]	*n.a.*[1]	*n.a.*[1]	*n.a.*[1]	*n.a.*[1]
F3	26.1	*n.a.*[1]	*n.a.*[1]	*n.a.*[1]	*n.a.*[1]	*n.a.*[1]
F4	33.7	*n.a.*[1]	*n.a.*[1]	*n.a.*[1]	*n.a.*[1]	*n.a.*[1]
F5	55.5	*n.a.*[1]	*n.a.*[1]	*n.a.*[1]	*n.a.*[1]	*n.a.*[1]
F6	62.1	*n.a.*[1]	*n.a.*[1]	*n.a.*[1]	*n.a.*[1]	*n.a.*[1]
F7	47.4	*n.a.*[1]	*n.a.*[1]	*n.a.*[1]	*n.a.*[1]	*n.a.*[1]
F8	31.1	8200	8300	8300	1.00	11.9
F9	96.1	7950	8000	8050	1.01	89.7
F10	272	8050	8050	8100	1.00	98.2
F11	426	8050	8100	8100	1.00	99.3
F12	566	8050	8100	8100	1.00	>99
F13	655	8100	8100	8150	1.00	>99
F14	659	8100	8150	8150	1.00	>99
F15	579	8050	8100	8100	1.00	>99
F16	812	8050	8050	8100	1.00	>99
F17	939	8050	8100	8100	1.00	99.6
F18	550	8050	8050	8100	1.00	99.1
F19	326	8050	8100	8100	1.00	98.6
F20	194	8100	8100	8150	1.00	98.3
F21	104	8100	8100	8150	1.00	98.2
F22	93.2	8100	8150	8150	1.00	98.3
F23		8050	8100	8100	1.00	76.6

eluent: cyhex:EA = 3:2 → 5:4. [1]This fraction did not contain any product.

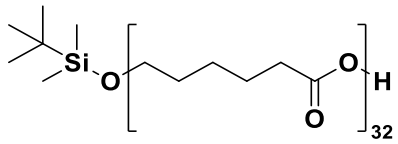


Supplementary Figure 71: SEC traces of the individual fractions obtained from the second purification *via* column chromatography of **TBDMS(CL)$_{32}$Bn**.



Supplementary Figure 72: SEC traces of product **TBDMS(CL)$_{32}$Bn** before and after two column chromatographic purification steps.

Carboxyl–terminated 32-mer – TBDMS(CL)$_{32}$CO$_2$H



Chemical Formula: $C_{198}H_{336}O_{65}Si$
Exact Mass: 3782.2756 Da
Molecular Weight: 3784.8860 Da

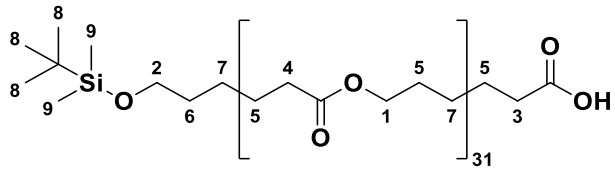
The carboxyl-terminated 32-mer **TBDMS(CL)$_{32}$CO$_2$H** was prepared using the procedure described above for the synthesis of the carboxyl-terminated dimer **TBDMS(CL)$_2$CO$_2$H**.

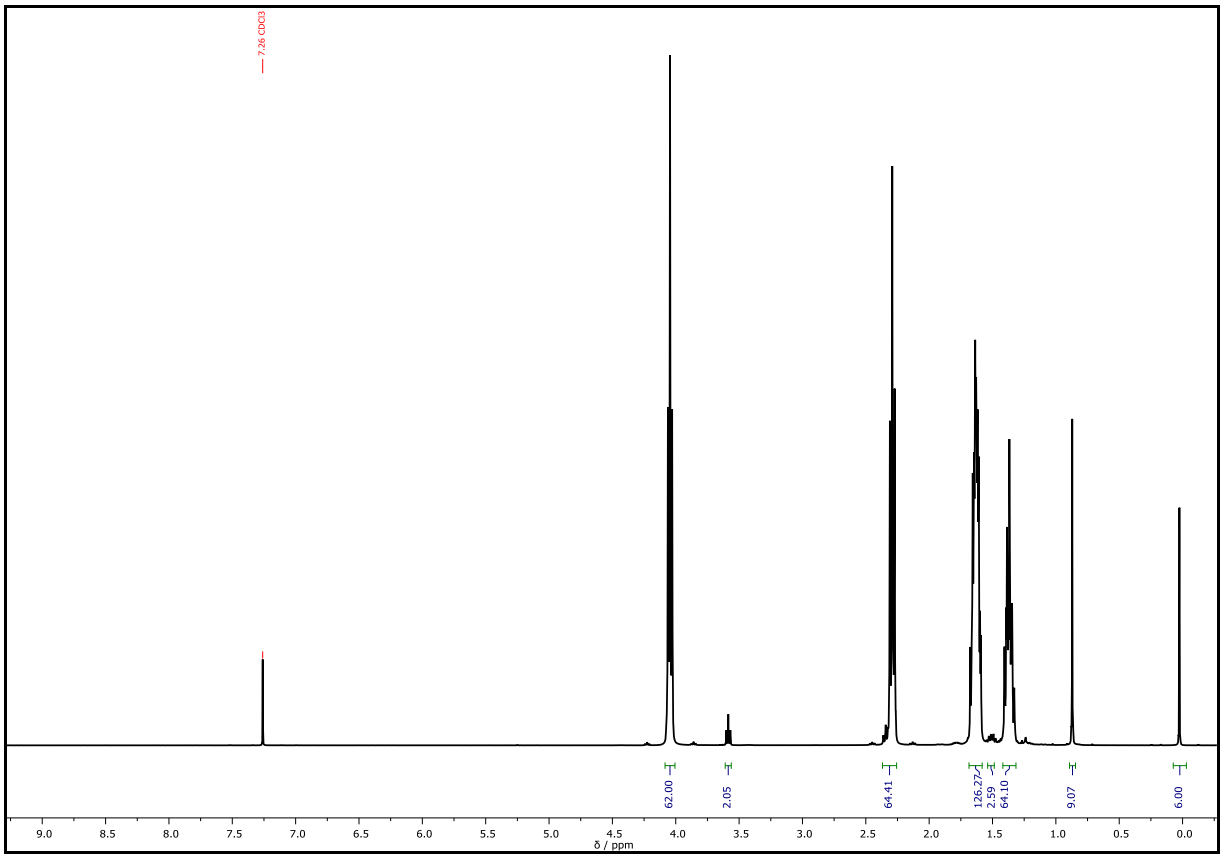
TBDMS(CL)$_{32}$Bn	7.00 g, 1.81 mmol, 1.00 equiv.
Pd/C	700 mg, 10 wt%
EA	45.0 mL
Yield	6.39 g, 1.69 mmol, 93.4%, white solid
R_f	0.47 (cyhex/EA = 1:2).
Đ (system I)	1.00

Note: The molecule was not detectable by ESI-MS analysis.

IR (ATR platinum diamond) $\tilde{\nu}$ / cm^{-1} = 2943.7, 2864.3, 1720.6, 1470.5, 1418.8, 1396.9, 1364.5, 1292.6, 1238.0, 1163.6, 1106.3, 1065.0, 1043.3, 959.8, 933.9, 837.9, 776.1, 731.1, 585.2, 524.1, 453.1.

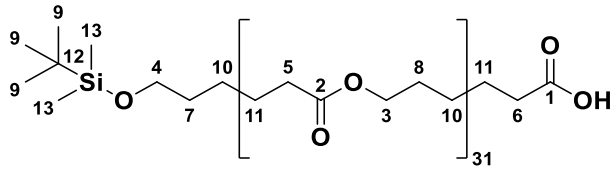
^{1}H NMR ($CDCl_3$, 400 MHz): δ / ppm = 4.05 (t, *J* = 6.7 Hz, 62H, CH_2^1), 3.59 (t, *J* = 6.5 Hz, 2H, CH_2^2), 2.35 (t, *J* = 7.3 Hz, 2H, CH_2^3), 2.29 (t, *J* = 7.5 Hz, 64H, CH_2^4), 1.71 – 1.57 (m, 126H, CH_2^5), 1.55 – 1.47 (m, 2H, CH_2^6), 1.42 – 1.32 (m, 64H, CH_2^7), 0.87 (s, 9H, CH_3^8), 0.03 (s, 6H, CH_3^9).

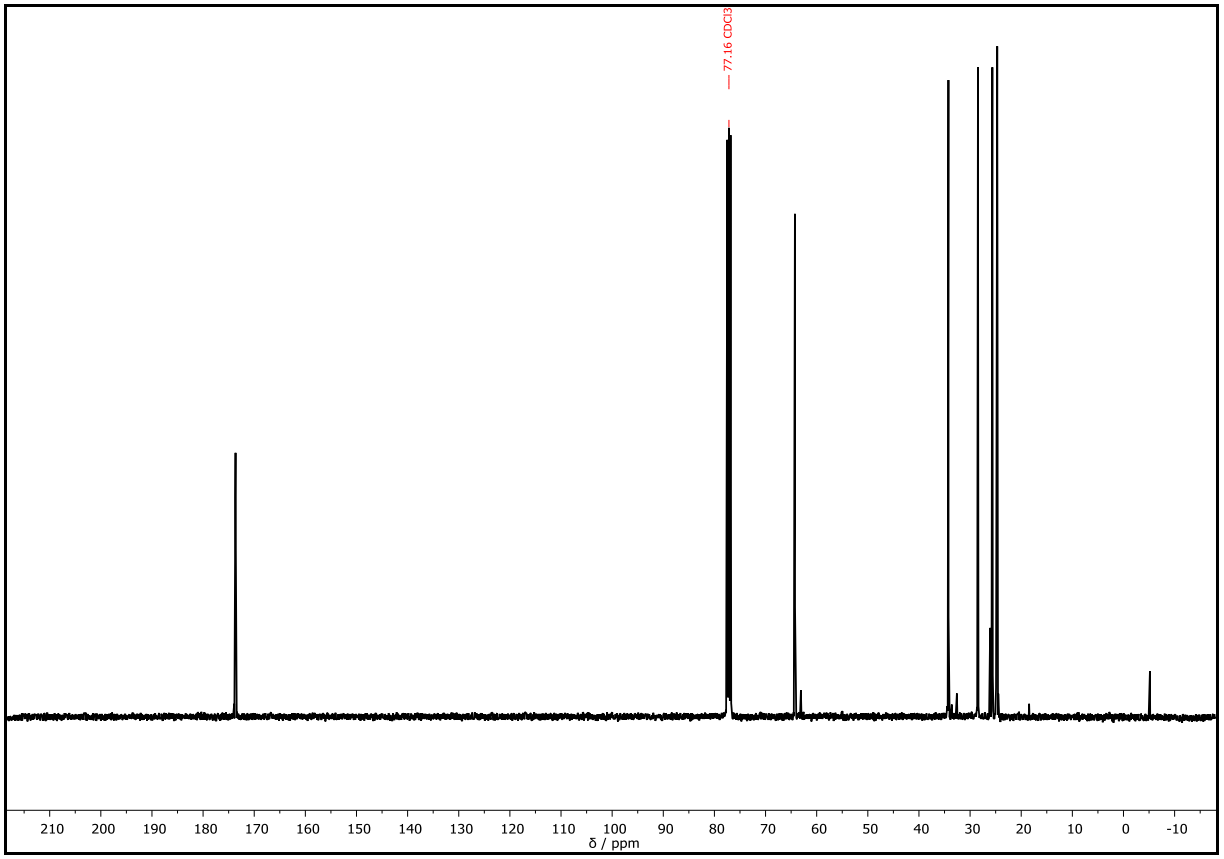




Supplementary Figure 73: ^{1}H NMR spectrum of **TBDMS(CL)$_{32}$CO$_2$H**, recorded at 400 MHz in $CDCl_3$.

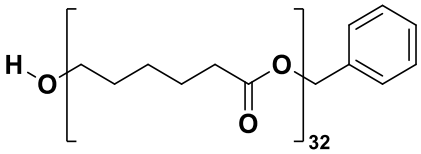
^{13}C NMR ($CDCl_3$, 101 MHz): δ / ppm = 173.92 (C_q^1), 173.82 (C_q^2), 173.65 (C_q^2), 64.31 (CH_2^3), 64.26 (CH_2^3), 64.17 (CH_2^3), 63.09 (CH_2^4), 34.45 (CH_2^5), 34.29 (CH_2^5), 34.23 (CH_2^5), 33.58 (CH_2^6), 32.58 (CH_2^7), 28.46 (CH_2^8), 28.42 (CH_2^8), 26.08 (CH_3^9), 25.64 (CH_2^{10}), 25.61 (CH_2^{10}), 25.56 (CH_2^{10}), 24.92 (CH_2^{11}), 24.69 (CH_2^{11}), 24.49 (CH_2^{11}), 18.45 (C_q^{12}), -5.17 (CH_3^{13}).





Supplementary Figure 74: ^{13}C NMR spectrum of **TBDMS(CL)$_{32}$CO$_2$H**, recorded at 101 MHz in $CDCl_3$.

Hydroxyl–terminated 32-mer – HO(CL)$_{32}$Bn



Chemical Formula: $C_{199}H_{328}O_{65}$
Exact Mass: 3758.2361 Da
Molecular Weight: 3760.7480 Da

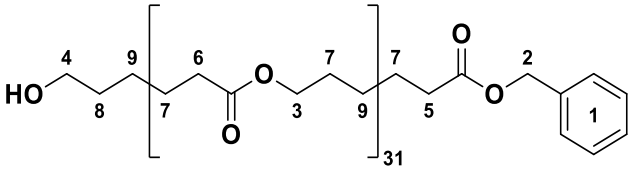
The hydroxyl-terminated tetramer **HO(CL)$_{32}$Bn** was prepared according to the procedure described above for the synthesis of the hydroxyl-terminated dimer **HO(CL)$_2$Bn**.

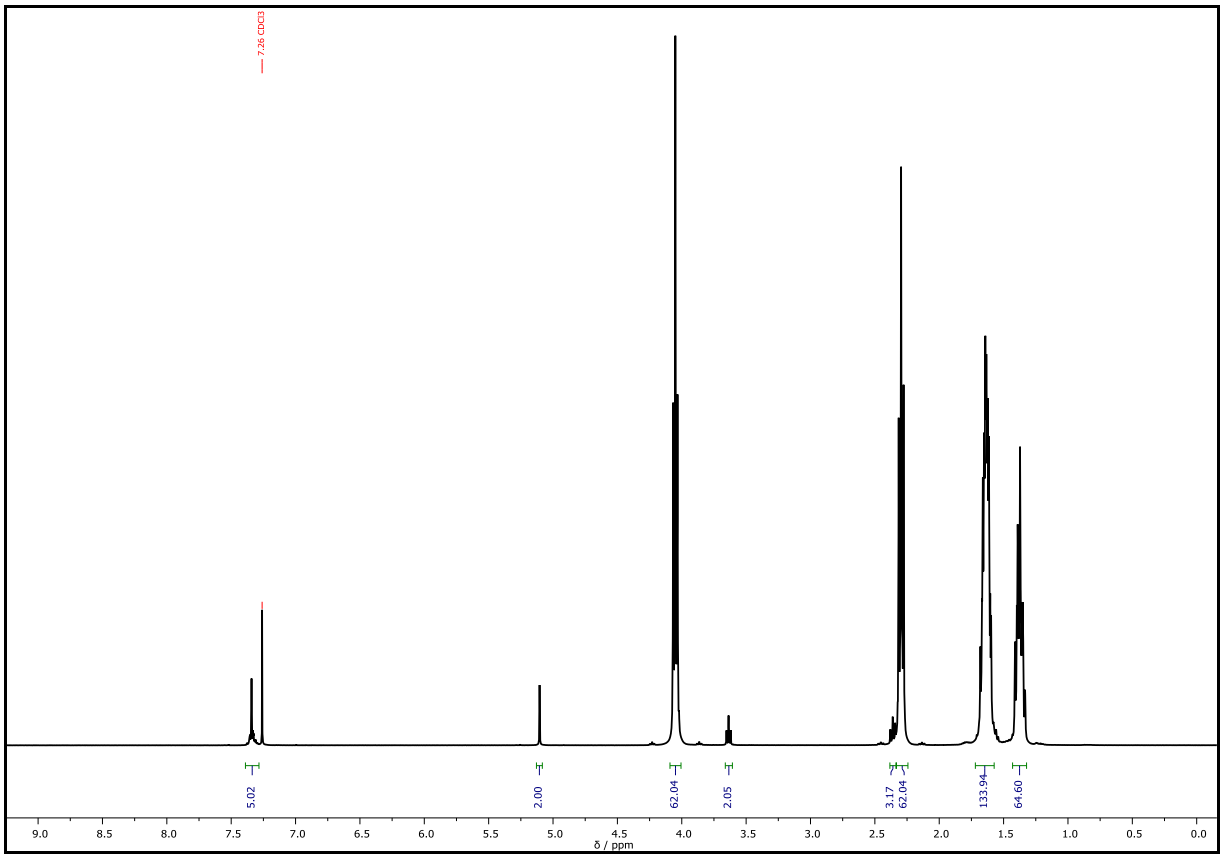
TBDMS(CL)$_{32}$Bn	7.00 g, 1.81 mmol, 1.00 equiv.
TBAF	1.14 g, 3.61 mmol, 2.00 equiv.
glacial acetic acid	207 µL, 217 mg, 3.61 mmol, 2.00 equiv.
total THF	7.20 mL
eluent	cyhex/EA = 1:1 → 1:2
yield	6.55 g, 1.74 mmol, 96.5%, white solid
R_f	0.63 (cyhex/EA = 1:2).
Đ (system I)	1.00

Note: The molecule was not detectable by ESI-MS analysis.

IR (ATR platinum diamond) $\tilde{\nu}$ / cm^{-1} = 2943.8, 2865.2, 1720.7, 1470.7, 1418.2, 1396.9, 1364.6, 1292.6, 1237.9, 1164.1, 1106.9, 1043.6, 959.7, 840.3, 731.5, 584.0, 452.6.

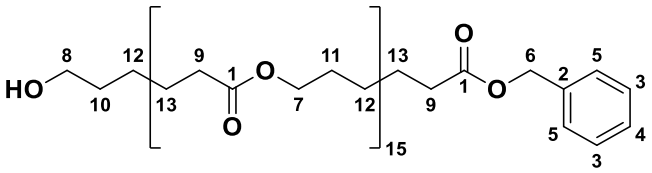
^{1}H NMR ($CDCl_3$, 400 MHz): δ / ppm = 7.39 – 7.29 (m, 5H, CH_{Ar}^1), 5.10 (s, 2H, CH_2^2), 4.05 (t, *J* = 6.7 Hz, 62H, CH_2^3), 3.64 (t, *J* = 6.5 Hz, 2H, CH_2^4), 2.36 (t, *J* = 7.5 Hz, 2H, CH_2^5), 2.30 (t, *J* = 7.5 Hz, 62H, CH_2^6), 1.72 – 1.55 (m, 128H, CH_2^7 and CH_2^8), 1.43 – 1.31 (m, 64H, CH_2^9).



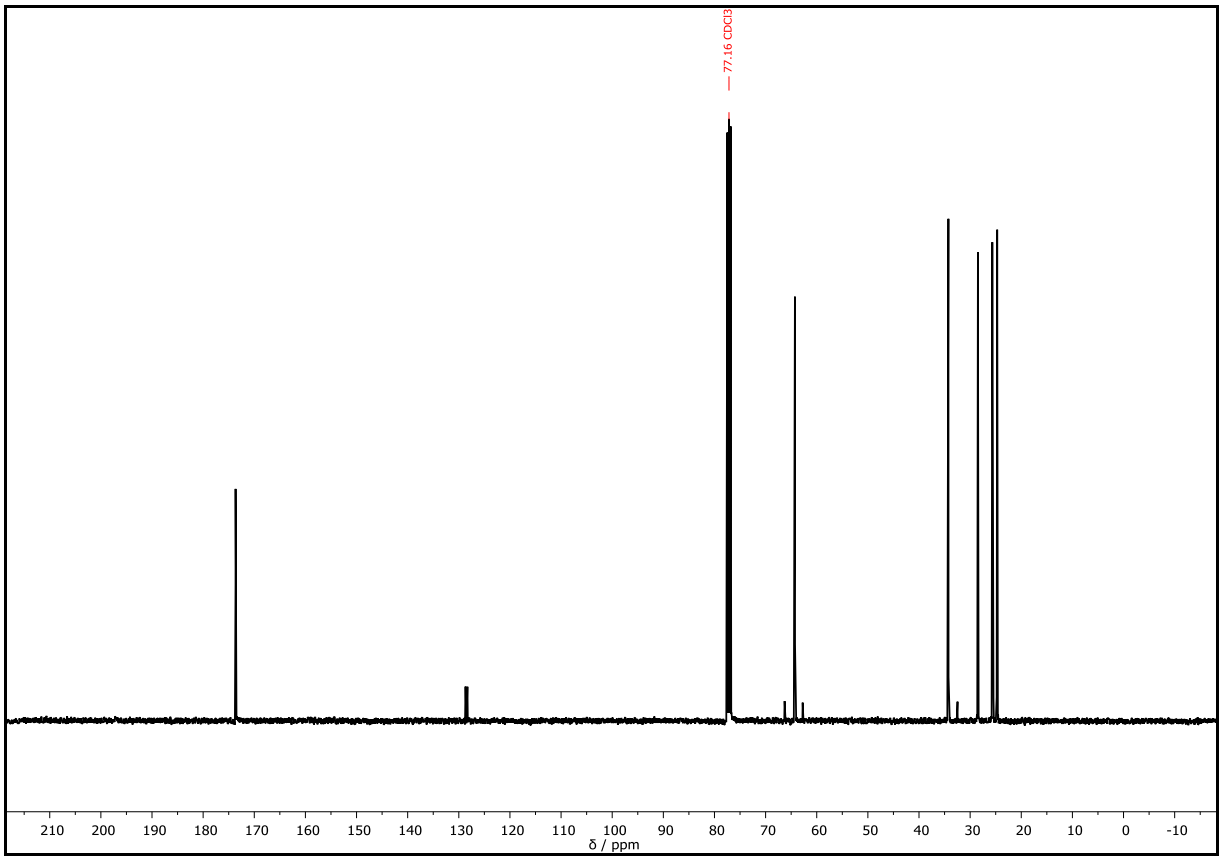


Supplementary Figure 75: ^{1}H NMR spectrum of **HO(CL)$_{32}$Bn**, recorded at 400 MHz in $CDCl_3$.

^{13}C NMR ($CDCl_3$, 101 MHz): δ / ppm = 173.85 (C_q^1), 173.66 (C_q^1), 173.42 (C_q^1), 128.69 ($CH_{Ar,meta}^3$), 128.34 ($CH_{Ar,para}^4$), 128.31 ($CH_{Ar,ortho}^5$), 66.28 (CH_2^6), 64.27 (CH_2^7), 62.75 (CH_2^8), 34.36 (CH_2^9), 34.25 (CH_2^9), 32.47 (CH_2^{10}), 28.48 (CH_2^{11}), 25.66 (CH_2^{12}), 25.43 (CH_2^{12}), 24.81 (CH_2^{13}), 24.71 (CH_2^{13}).

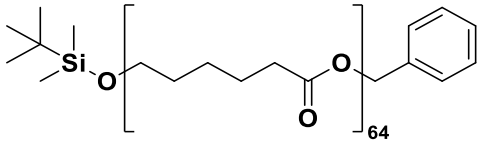


Note: $C_{q,Ar}^2$ at around 136 ppm was not visible in the ^{13}C spectrum.



Supplementary Figure 76: ^{13}C NMR spectrum of **HO(CL)$_{32}$Bn**, recorded at 101 MHz in $CDCl_3$.

Doubly protected 64-mer – TBDMS(CL)$_{64}$Bn



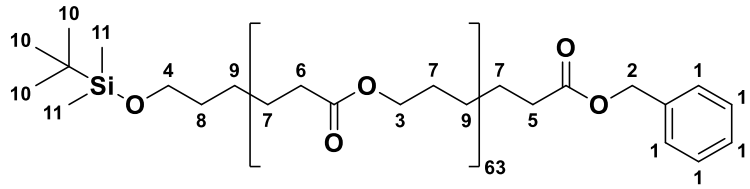
Chemical Formula: $C_{397}H_{662}O_{129}Si$
Exact Mass: 7522.5011 Da
Molecular Weight: 7527.6190 Da

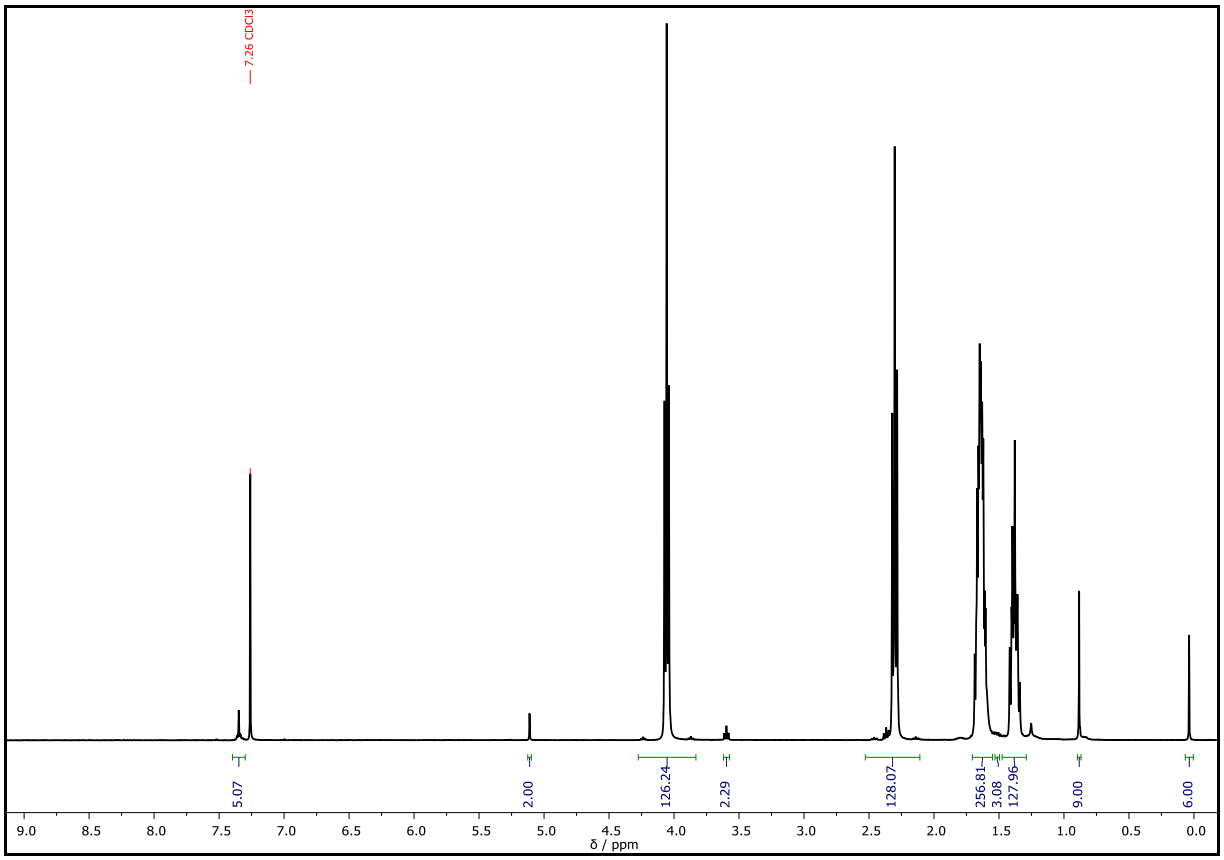
The doubly protected 64-mer **TBDMS(CL)$_{64}$Bn** was prepared using the procedure described above for the synthesis of the doubly protected dimer **TBDMS(CL)$_2$Bn**. 0.20 equiv. DPTS was used instead of 1.10 equiv. DMAP.

TBDMS(CL)$_{32}$CO$_2$H	4.36 g, 1.16 mmol, 1.00 equiv.
HO(CL)$_{32}$Bn	4.39 g, 1.16 mmol, 1.00 equiv.
DCC	263 mg, 1.28 mmol, 1.10 equiv.
DPTS	68.3 mg, 232 µmol, 0.20 equiv.
DCM	30 mL
eluent	cyhex/EA = 1:1
yield	7.34 g, 975 µmol, 84.1%, white solid
R_f	0.14 (cyhex/EA = 1:1).
Đ (system I)	1.00

Note: The molecule was not detectable by ESI-MS analysis.

^{1}H NMR (400 MHz, $CDCl_3$) δ / ppm = 7.39 – 7.30 (m, 5H, CH_{Ar}^1), 5.11 (s, 2H, CH_2^2), 4.06 (t, *J* = 6.7 Hz, 126H, CH_2^3), 3.60 (t, *J* = 6.5 Hz, 2H, CH_2^4), 2.37 (t, *J* = 7.5 Hz, 2H, CH_2^5), 2.30 (t, *J* = 7.5 Hz, 126H, CH_2^6), 1.64 (m, 254H, CH_2^7), 1.54 – 1.49 (m, 2H, CH_2^8), 1.43 – 1.33 (m, 128H, CH_2^9), 0.88 (s, 9H, CH_3^{10}), 0.04 (s, 6H, CH_3^{11}).

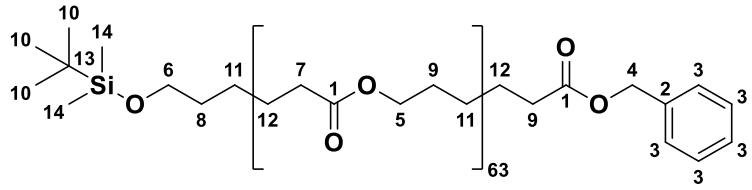


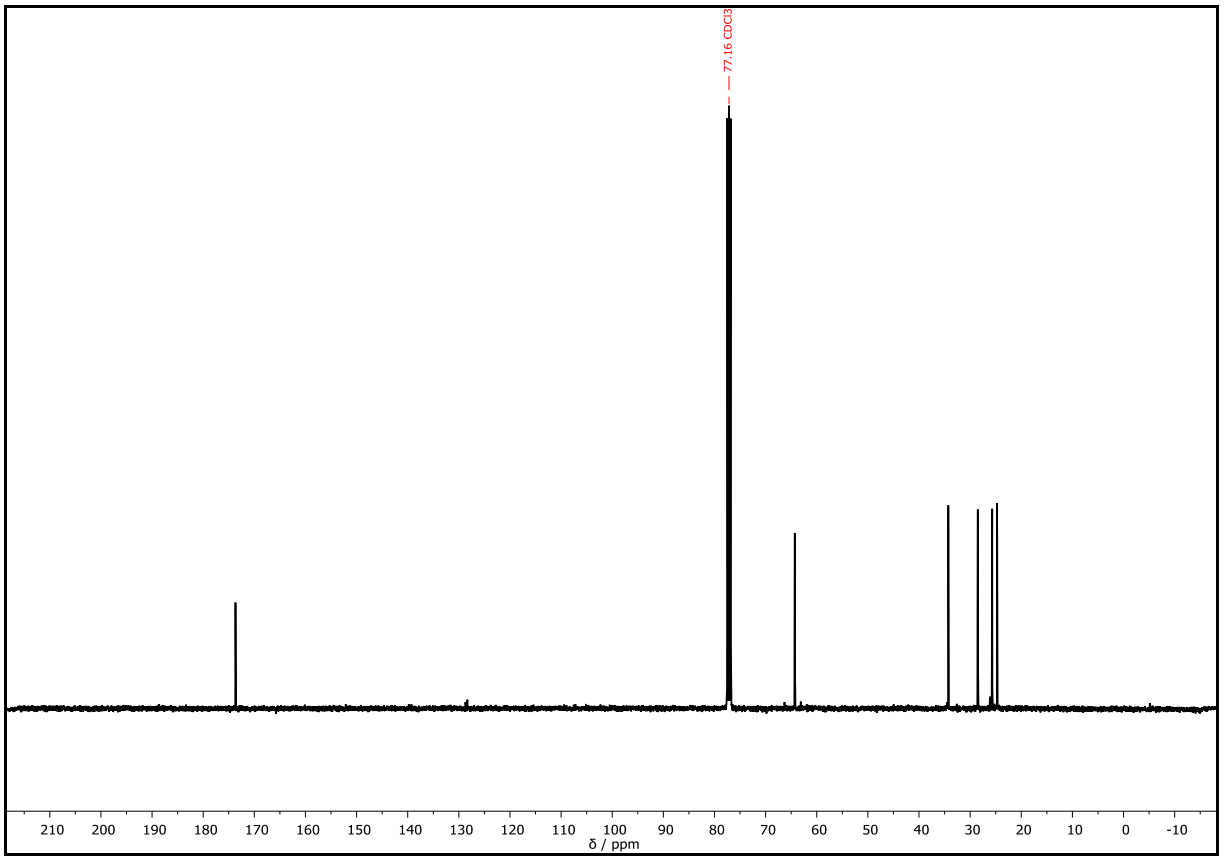


Supplementary Figure 77: ^{1}H NMR spectrum of **TBDMS(CL)$_{64}$Bn**, recorded at 400 MHz in $CDCl_3$.

^{13}C NMR ($CDCl_3$, 101 MHz): δ / ppm = 173.68 (C_q^1), 128.71 (CH_{Ar}^3), 128.33 (CH_{Ar}^3), 66.31 (CH_2^4), 64.29 (CH_2^5), 63.12 (CH_2^6), 34.49 (CH_2^7), 34.27 (CH_2^7), 32.61 (CH_2^8), 28.50 (CH_2^9), 26.11 (CH_2^{10}), 25.68 (CH_2^{11}), 24.73 (CH_2^{12}), -5.12 (CH_3^{14}).

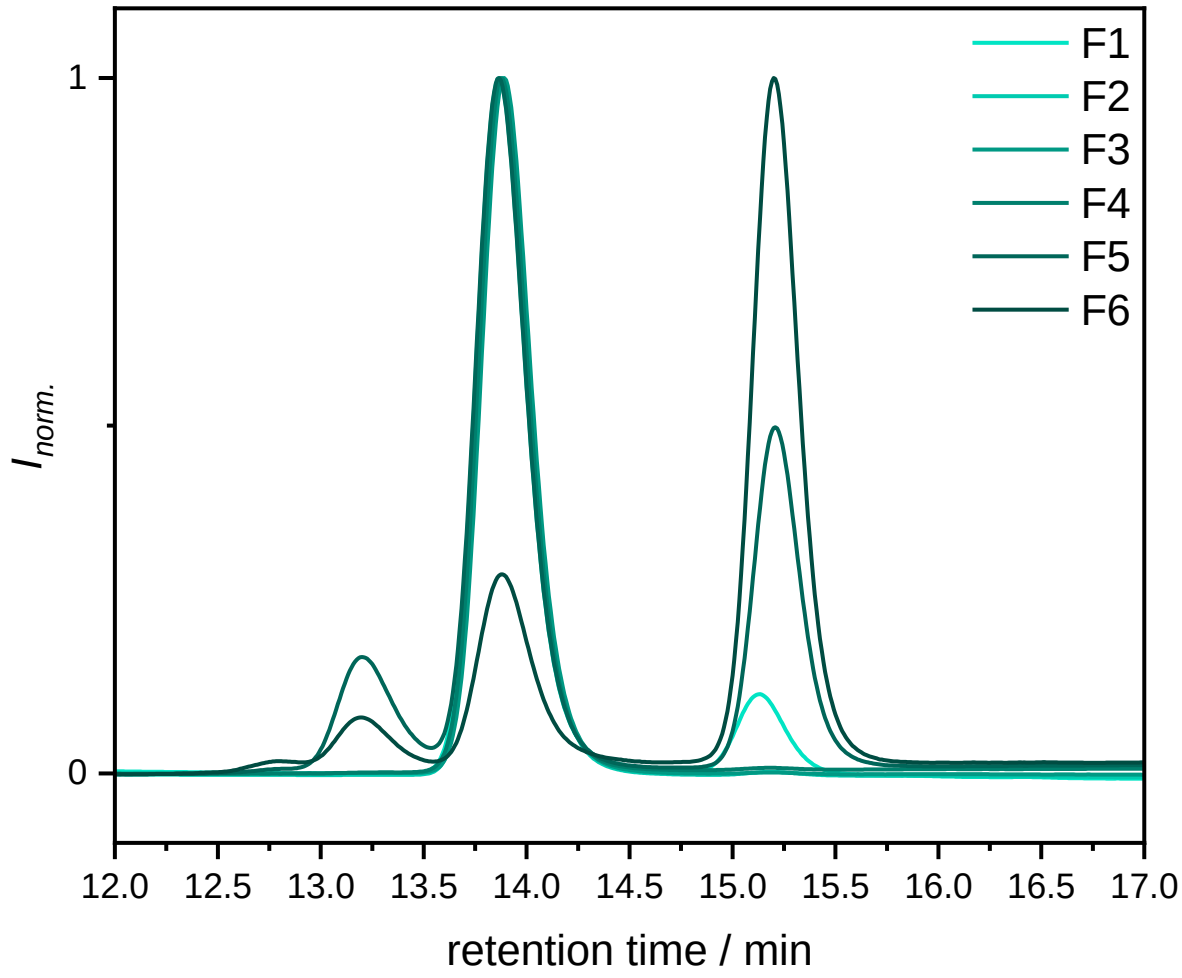
Note: C^2 and C^{13} are not visible in the ^{13}C NMR spectrum.





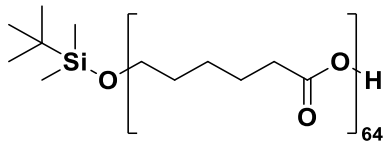
Supplementary Figure 78: ^{13}C NMR spectrum of **TBDMS(CL)$_{64}$Bn**, recorded at 101 MHz in $CDCl_3$.

Supplementary Table 12: SEC results of the purification of **TBDMS(CL)$_{64}$Bn**.						
cc 1	*m* / g	M_n / Da	M_w / Da	M_z / Da	*Đ*	purity / %
F1	3.28	16050	16150	16350	1.01	90.0
F2	2.44	16050	16100	16150	1.00	>99
F3	609 × 10^{-3}	15950	16050	16100	1.00	>99
F4	213 × 10^{-3}	16000	16100	16200	1.01	>99
F5	1.86	16150	16250	16350	1.01	61.7
F6	137 × 10^{-3}	15900	16000	16100	1.01	23.1



Supplementary Figure 79: SEC traces of the individual fractions obtained from the purification *via* column chromatography of **TBDMS(CL)$_{64}$Bn**.

Carboxyl–terminated 64-mer – TBDMS(CL)$_{64}$CO$_2$H



Chemical Formula: $C_{390}H_{656}O_{129}Si$
Exact Mass: 7432.4541 Da
Molecular Weight: 7437.4940 Da

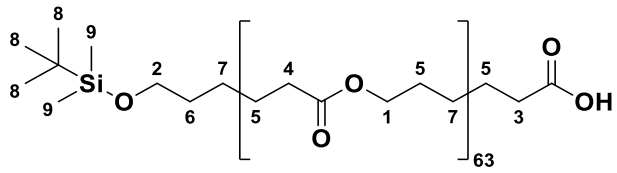
The carboxyl-terminated 64-mer **TBDMS(CL)$_{64}$CO$_2$H** was prepared according to the procedure described above for the synthesis of the carboxyl-terminated dimer **TBDMS(CL)$_2$CO$_2$H**.

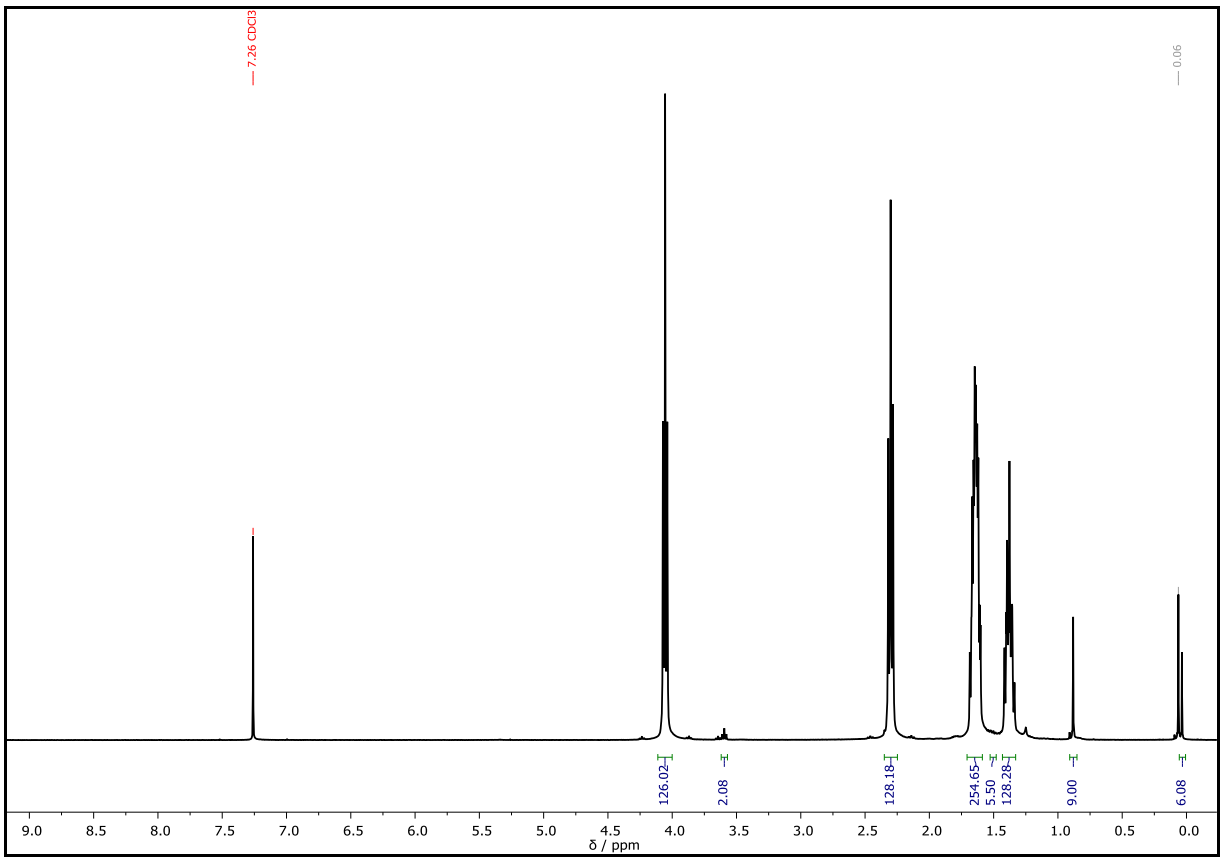
TBDMS(CL)$_{64}$Bn	3.00 g, 403 µmol, 1.00 equiv.
Pd/C	300 mg, 10 wt%
EA	35 mL
yield	2.85 g, 383 µmol, 95.0%
Đ (system I)	1.00

Note: The molecule was not detectable by ESI-MS analysis.

IR (ATR platinum diamond) $\tilde{\nu}$ / cm^{-1} = 2943, 2896, 2865, 1722, 1471, 1419, 1397, 1366, 1294, 1238, 1170, 1107, 1065, 1045, 991, 961, 934, 839, 775, 732, 710, 584, 453.

^{1}H NMR ($CDCl_3$, 500 MHz): δ / ppm = 4.06 (t, *J* = 6.7 Hz, 126H, CH_2^1), 3.60 (t, *J* = 6.5 Hz, 2H, CH_2^2), 2.30 (t, *J* = 7.5 Hz, 128H, CH_2^3 and CH_2^4), 1.63 (m, 254H, CH_2^5), 1.55 – 1.46 (m, 2H, CH_2^6), 1.42 (m, 128H, CH_2^7), 0.88 (s, 9H, CH_3^8), 0.04 (s, 6H, CH_3^9).

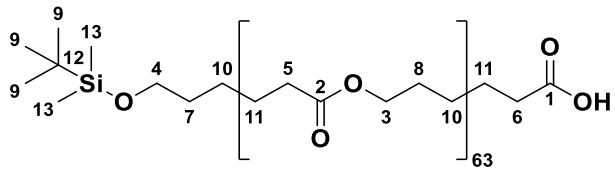


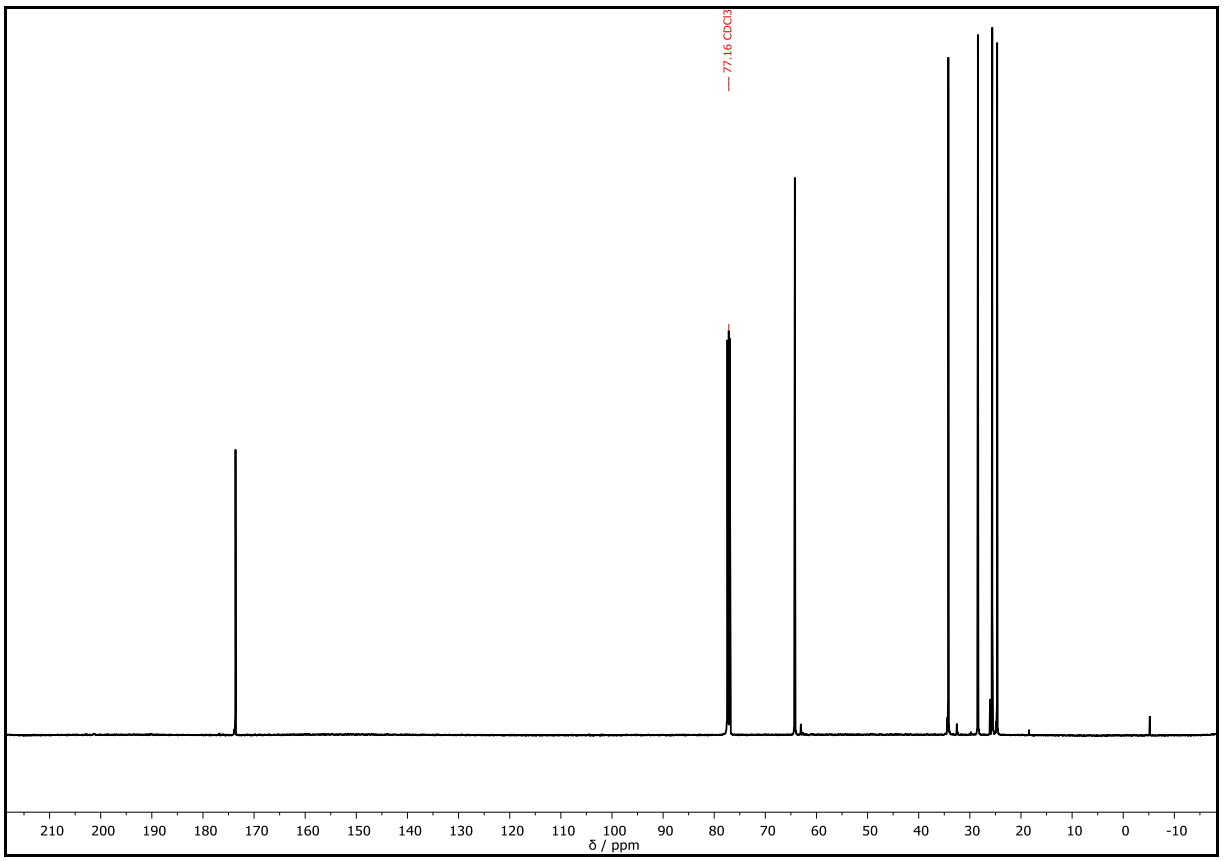


Supplementary Figure 80: ^{1}H NMR spectrum of **TBDMS(CL)$_{64}$CO$_2$H**, recorded at 500 MHz in $CDCl_3$.

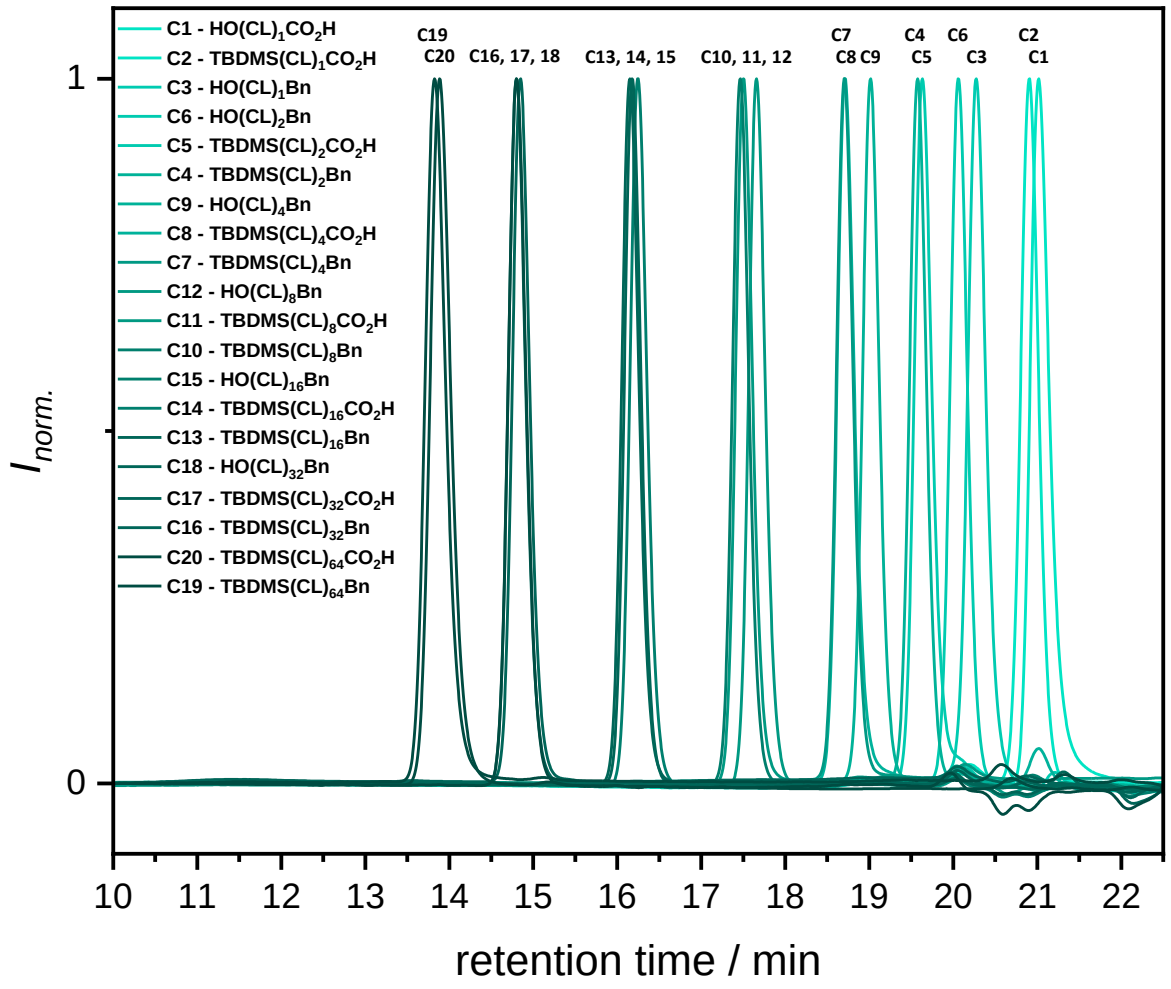
^{13}C NMR ($CDCl_3$, 126 MHz): δ / ppm = 173.63 (C_q^2), 64.38 (CH_2^3), 64.28 (CH_2^3), 64.23 (CH_2^3), 64.14 (CH_2^3), 63.06 (CH_2^4), 34.42 (CH_2^5), 34.32 (CH_2^5), 34.26 (CH_2^5), 34.20 (CH_2^5), 34.07 (CH_2^5), 33.96 (CH_2^5), 32.55 (CH_2^7), 28.57 (CH_2^8), 28.43 (CH_2^8), 28.29 (CH_2^8), 28.27 (CH_2^8), 26.05 (CH_3^9), 25.74 (CH_2^{10}), 25.61 (CH_2^{10}), 25.57 (CH_2^{10}), 25.53 (CH_2^{10}), 25.49 (CH_2^{10}), 25.39 (CH_2^{10}), 25.00 (CH_2^{11}), 24.89 (CH_2^{11}), 24.77 (CH_2^{11}), 24.66 (CH_2^{11}), 24.51 (CH_2^{11}), 18.43 (C_q^{12}), -5.20 (CH_3^{13}).

Note: C_q^1 and CH_2^6 are not visible in the ^{13}C spectrum





Supplementary Figure 81: ^{13}C NMR spectrum of **TBDMS(CL)$_{64}$CO$_2$H**, recorded at 126 MHz in $CDCl_3$.

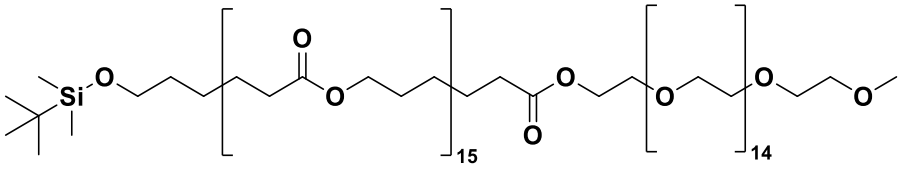


Supplementary Figure 82: SEC overview of the synthesized PCLs. The SEC traces range from the monomer, 6-hydroxyhexanoic acid **HO(CL)$_1$CO$_2$H** at a retention time of 21.0 min in light green to the doubly protected PCL$_{64}$ **TBDMS(CL)$_{64}$Bn** at 13.8 min in dark green.

Supplementary Table 13: Overview of scale, yield, dispersity, and purity of the synthesized PCLs.				
product	scale / mmol	yield / %	*Đ*[1]	purity[1] / %
HO(CL)$_1$CO$_2$H	263	94.3	1.00	>99
TBDMS(CL)$_1$CO$_2$H	125	85.3	1.00	>99
HO(CL)$_1$Bn	127	87.9	1.00	>99
TBDMS(CL)$_2$Bn	45.1	88.3	1.00	>99
TBDMS(CL)$_2$CO$_2$H	11.1	99.0	1.00	>99
HO(CL)$_2$Bn	27.7	98.9	1.00	>99
TBDMS(CL)$_4$Bn	86.3	87.9	1.00	>99
TBDMS(CL)$_4$CO$_2$H	14.7	99.1	1.00	>99
HO(CL)$_4$Bn	8.84	99.8	1.00	>99
TBDMS(CL)$_8$Bn	41.5	94.4	1.00	>99
TBDMS(CL)$_8$CO$_2$H	2.64	quant.	1.00	>99
HO(CL)$_8$Bn	2.64	97.3	1.00	>99
TBDMS(CL)$_{16}$Bn	1.92	97.1	1.00	>99
TBDMS(CL)$_{16}$CO$_2$H	7.29	quant.	1.00	>99
HO(CL)$_{16}$Bn	7.32	98.1	1.00	>99
TBDMS(CL)$_{32}$Bn	5.37	82.8	1.00	>99
TBDMS(CL)$_{32}$CO$_2$H	1.81	93.4	1.00	>99
HO(CL)$_{32}$Bn	1.81	96.5	1.00	>99
TBDMS(CL)$_{64}$Bn	1.16	84.1	1.00	>99
TBDMS(CL)$_{64}$CO$_2$H	0.40	95.0	1.00	99

[1] determined *via* SEC (system I)

***i*-TBDMS(CL)$_{16}$-(EG)$_{16}$OMe**



Chemical Formula: $C_{135}H_{242}O_{49}Si$
Exact Mass: 2675.6214 Da
Molecular Weight: 2677.4570 Da

The block copolymer ***i*-TBDMS(CL)$_{16}$-(EG)$_{16}$OMe** was prepared according to the procedure described above for the synthesis of the doubly protected dimer **TBDMS(CL)$_2$Bn**.

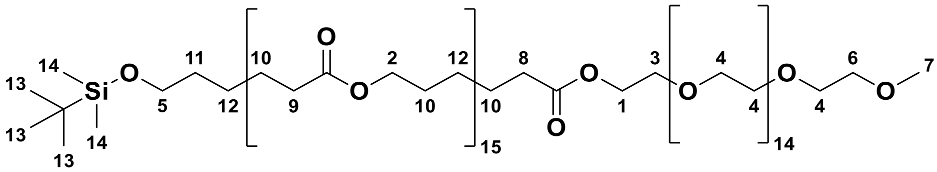
TBDMS(CL)$_{16}$CO$_2$H	319 mg, 163 µmol, 1.00 equiv.
HO(EG)$_{16}$OMe	120 mg, 163 µmol, 1.00 equiv.
DCC	202 mg, 977 µmol, 6.00 equiv.
DPTS	48.0 mg, 163 µmol, 1.00 equiv.
DCM	4.00 mL
eluent	1st column chromatography (cc): EA → EA:MeOH = 99:1 → 9:1 → acetone; 2nd cc: EA → acetone
yield	161 mg, 60.1 µmol, 36.9%, white solid
R_f	0.21 (EA:MeOH = 9:1)
Đ (system II)	1.01

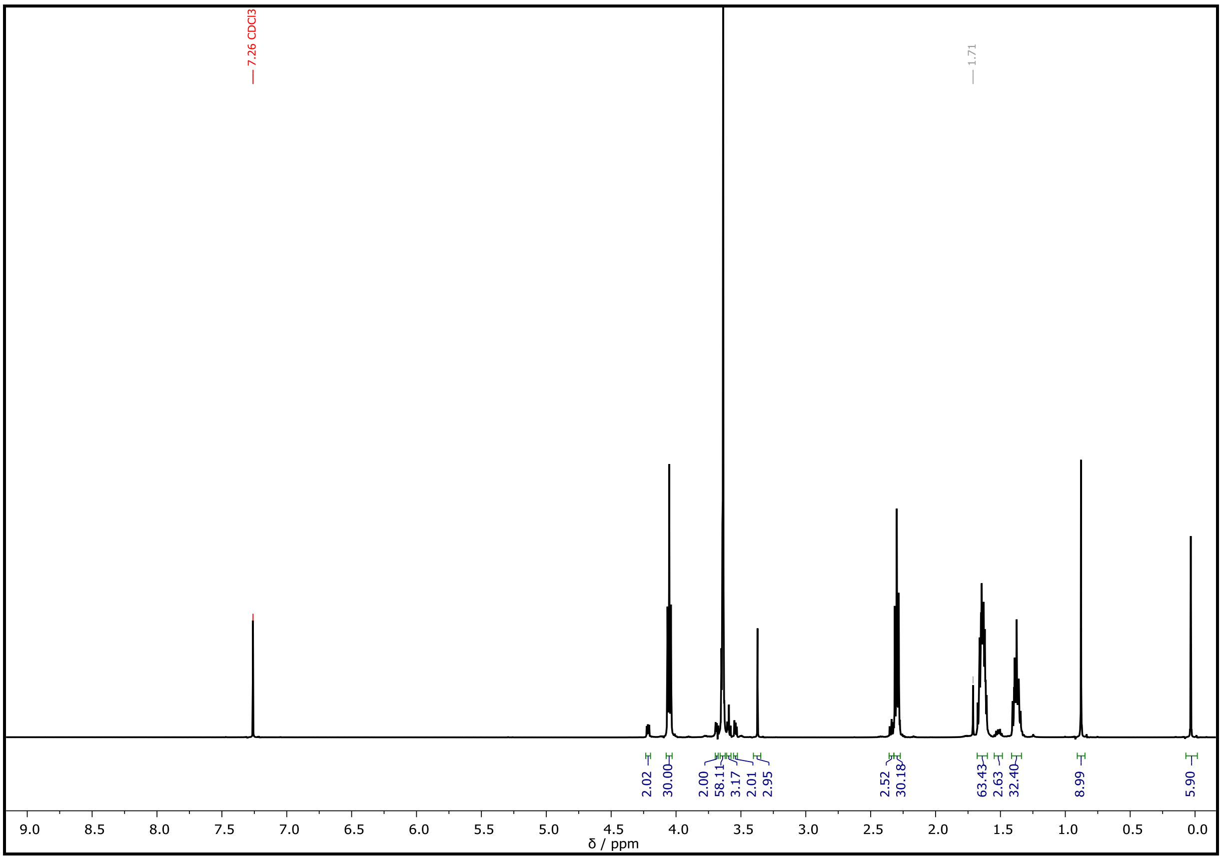
HRMS (ESI) of $C_{135}H_{242}O_{49}Si$ $[M+NH_4]^+$ *m/z* calc. 2693.6552, detected 2693.6589; $[M+Na]^+$ *m/z* calc. 2698.6106, detected 2698.6143; $[M+K]^+$ *m/z* calc. 2714.5846, detected 2714.5945. $[M+2Na]^{2+}$ *m/z* calc. 1360.7999, detected 1360.7990; $[M+Na+K]^{2+}$ *m/z* calc. 1368.7869, detected 1368.7859.

IR (ATR platinum diamond) $\tilde{\nu}$ / cm^{-1} = 2943, 2894, 2865, 1722, 1471, 1419, 1397, 1366, 1294, 1242, 1189, 1105, 1065, 1045, 961, 934, 837, 815, 775, 732, 710, 453.

***R*$_f$** = 0.21 (EA:methanol = 9:1).

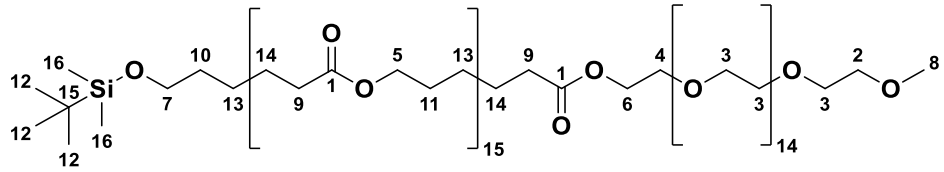
^{1}H NMR (500 MHz, $CDCl_3$): δ / ppm = 4.24 – 4.20 (m, 2H, CH_2[1]), 4.05 (t, *J* = 6.7 Hz, 30H, CH_2[2]), 3.70 – 3.68 (m, 2H, CH_2[3]), 3.66 – 3.63 (m, 58H, CH_2[4]), 3.61 – 3.58 (m, 2H, CH_2[5]), 3.56 – 3.53 (m, 2H, CH_2[6]), 3.37 (s, 3H, CH_3[7]), 2.34 (t, *J* = 7.6 Hz, 2H, CH_2[8]), 2.30 (t, *J* = 7.5 Hz, 30H, CH_2[9]), 1.69 – 1.60 (m, 62H, CH_2[10]), 1.54 – 1.49 (m, 2H, CH_2[11]), 1.42 – 1.33 (m, 32H, CH_2[12]), 0.88 (s, 9H, CH_3[13]), 0.03 (s, 6H, CH_3[14]).

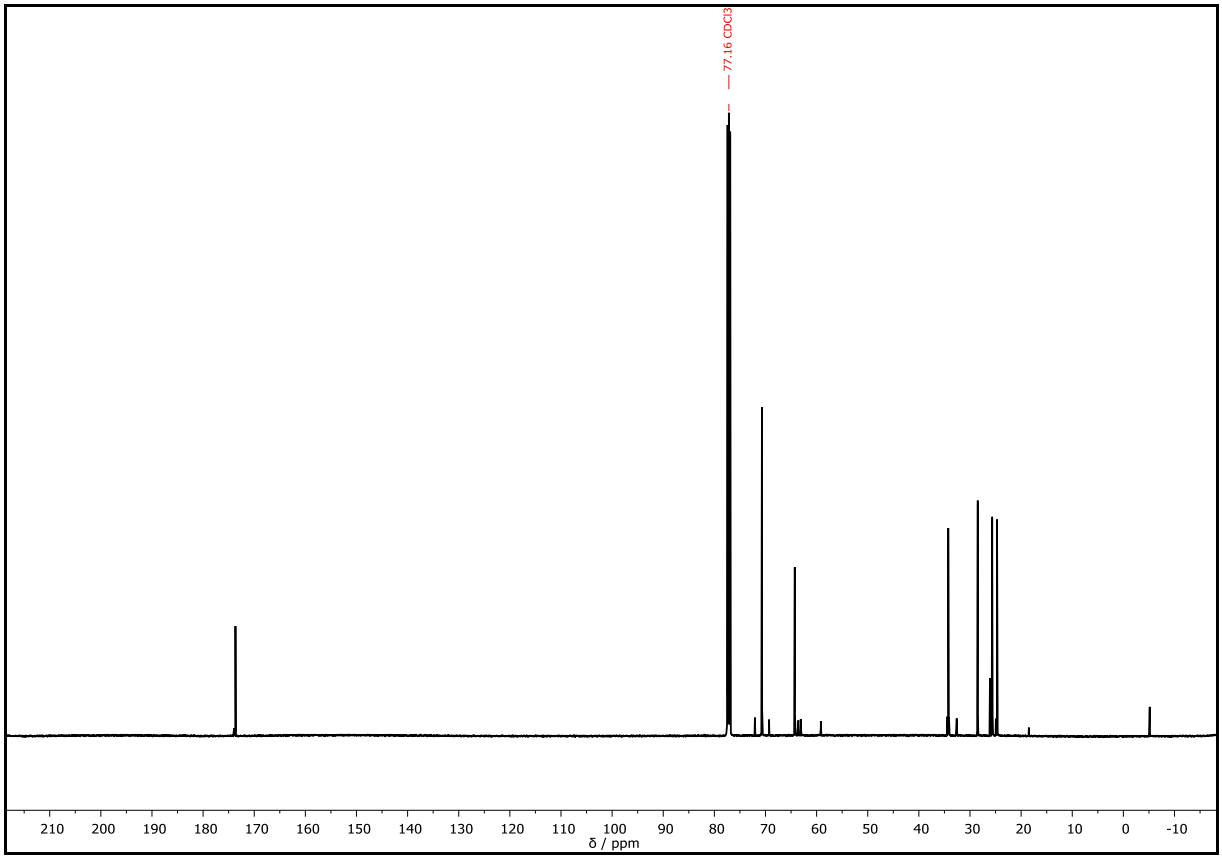




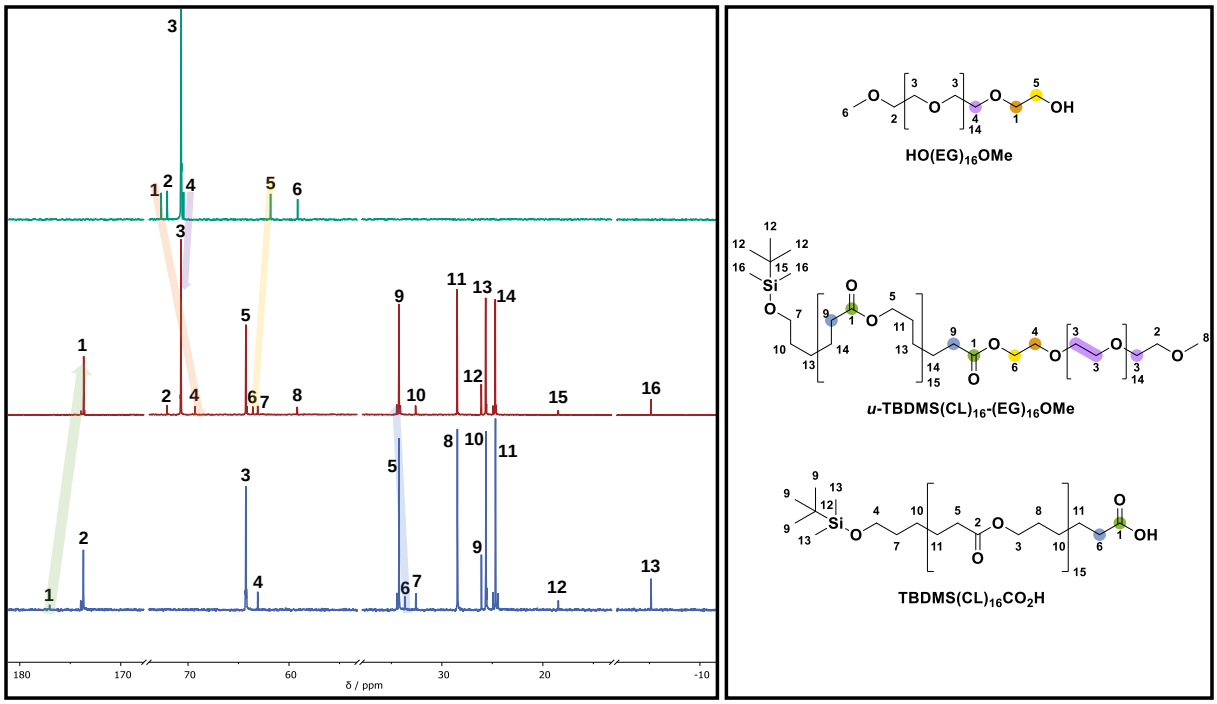
Supplementary Figure 83: ^{1}H NMR spectrum of ***i*-TBDMS(CL)$_{16}$-(EG)$_{16}$OMe** recorded at 500 MHz in $CDCl_3$.

^{13}C NMR (126 MHz, $CDCl_3$): δ / ppm = 173.94 (C_q^1), 173.67 (C_q^1), 173.59 (C_q^1), 72.07 (CH_2^2), 70.74 (CH_2^3), 70.70 (CH_2^3), 69.31 (CH_2^4), 64.27 (CH_2^5), 64.19 (CH_2^5), 63.58 (CH_2^6), 63.10 (CH_2^7), 59.18 (CH_3^8), 34.47 (CH_2^9), 34.25 (CH_2^9), 34.11 (CH_2^9), 32.60 (CH_2^{10}), 28.48 (CH_2^{11}), 26.10 (CH_3^{12}), 25.66 (CH_2^{13}), 25.58 (CH_2^{13}), 24.94 (CH_2^{14}), 24.71 (CH_2^{14}), 24.63 (CH_2^{14}), 18.48 (C_q^{15}), -5.15 (CH_3^{16}).

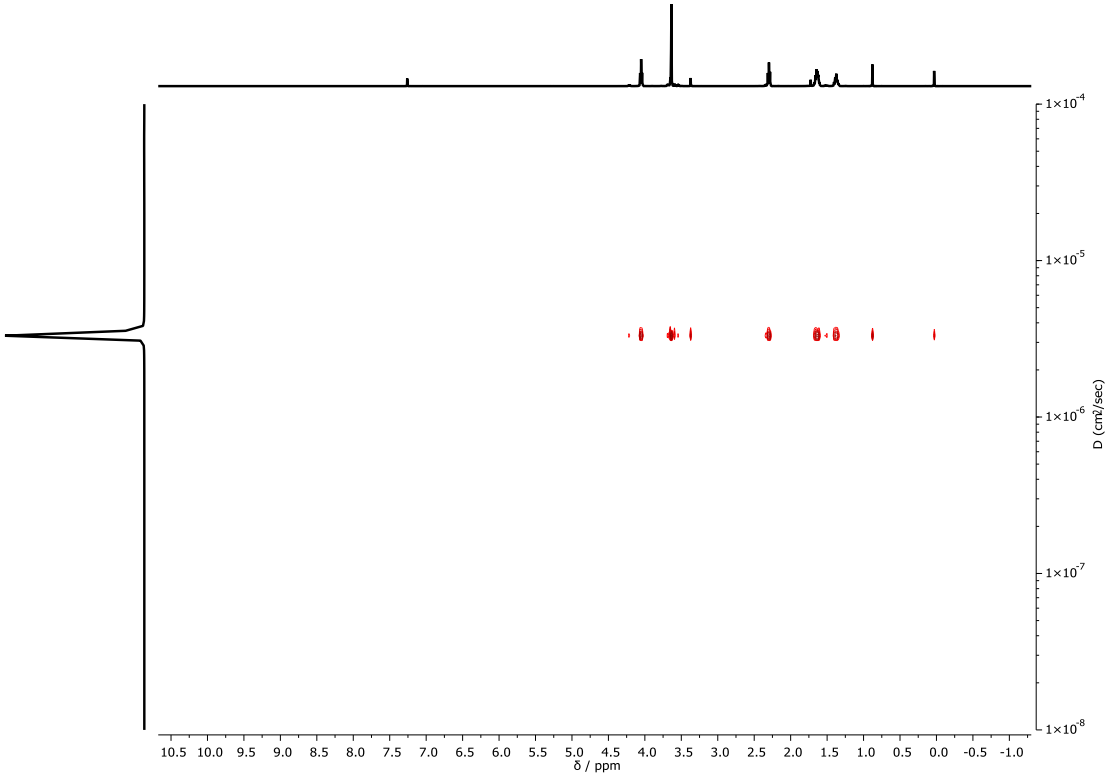




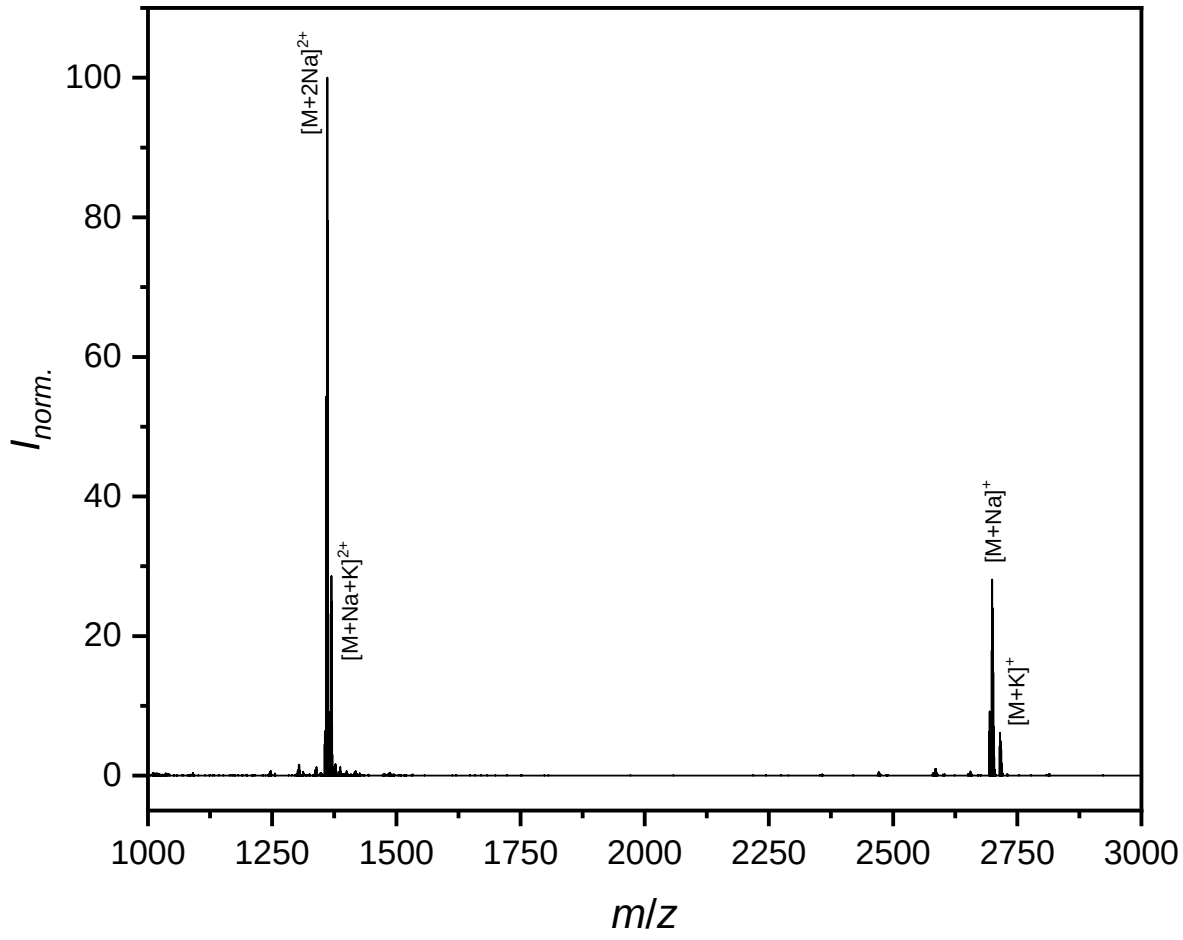
Supplementary Figure 84: ^{13}C NMR spectrum of ***i*-TBDMS(CL)$_{16}$-(EG)$_{16}$OMe** recorded at 126 MHz in $CDCl_3$.



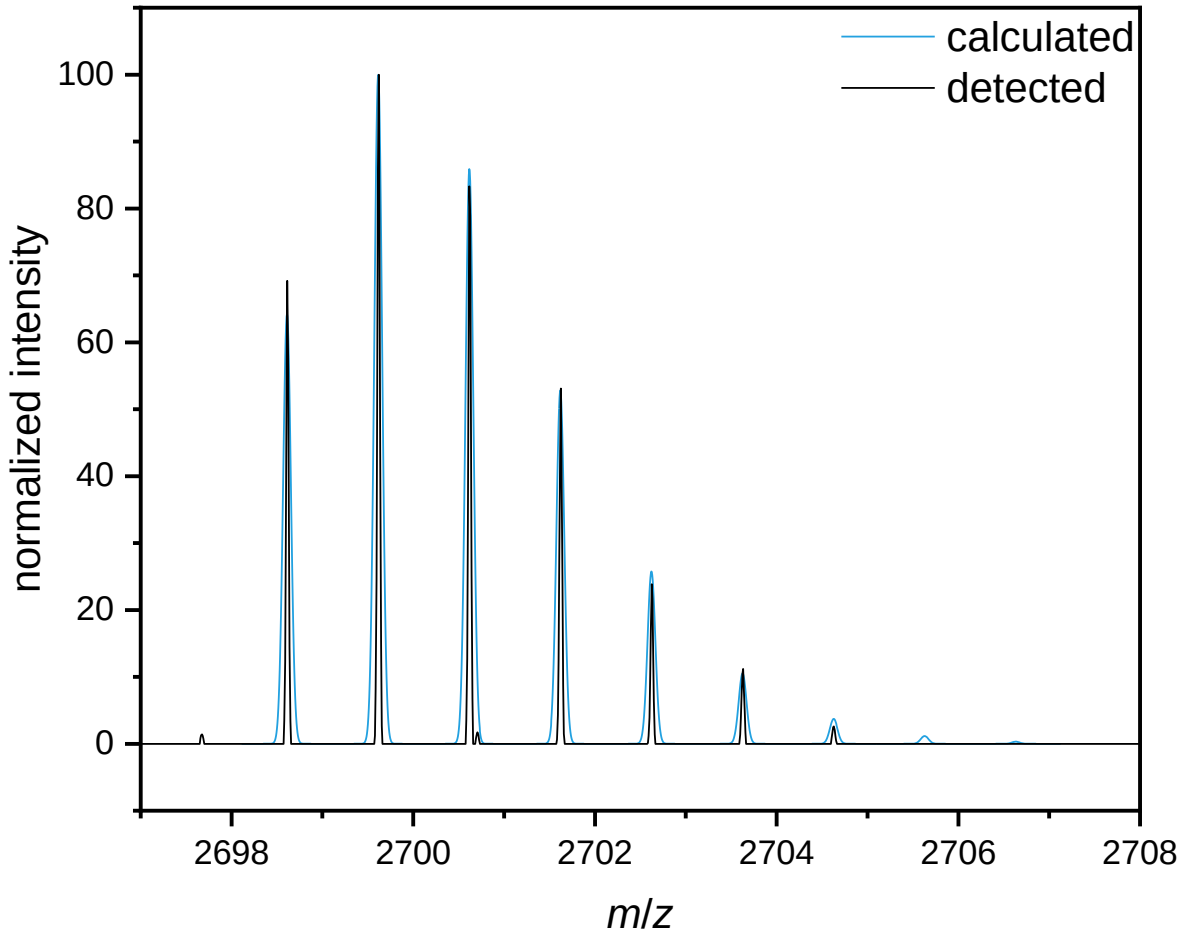
Supplementary Figure 85: Comparison of ^{13}C NMR spectra of ***i*-TBDMS(CL)$_{16}$-(EG)$_{16}$OMe**, **HO(EG)$_{16}$OMe**, and **TBDMS(CL)$_{16}$CO$_2$H** recorded at 126 MHz in $CDCl_3$.



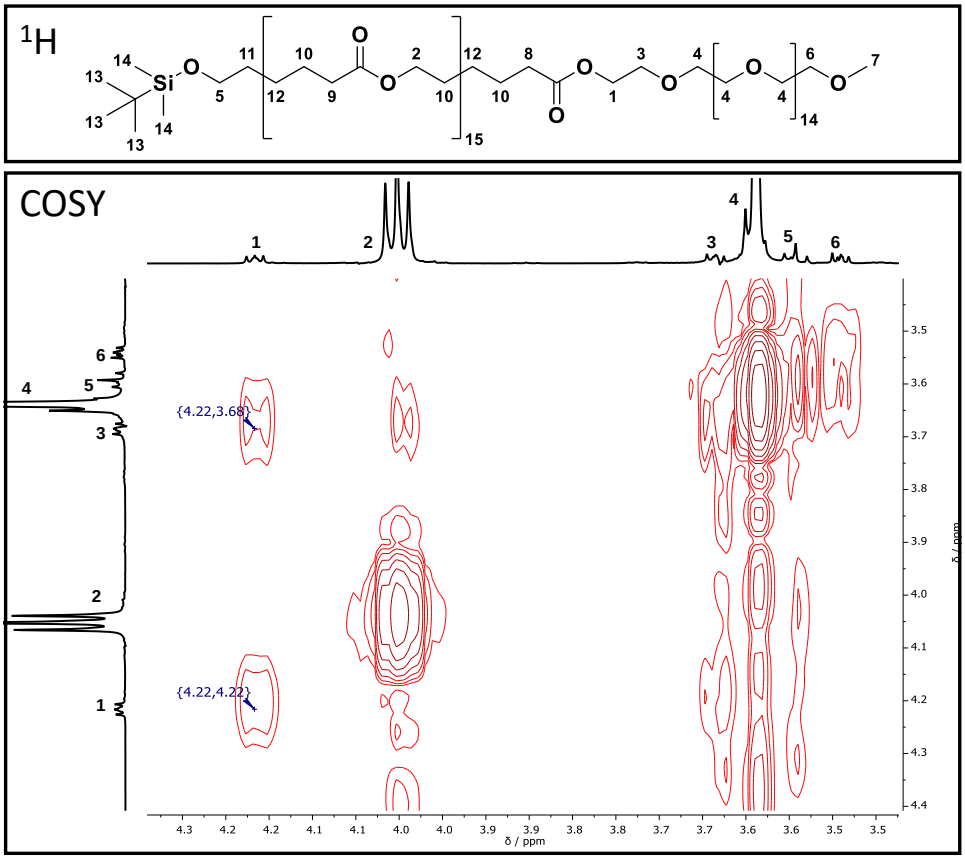
Supplementary Figure 86: DOSY NMR spectrum of ***i*-TBDMS(CL)$_{16}$-(EG)$_{16}$OMe** recorded at 500 MHz in $CDCl_3$.



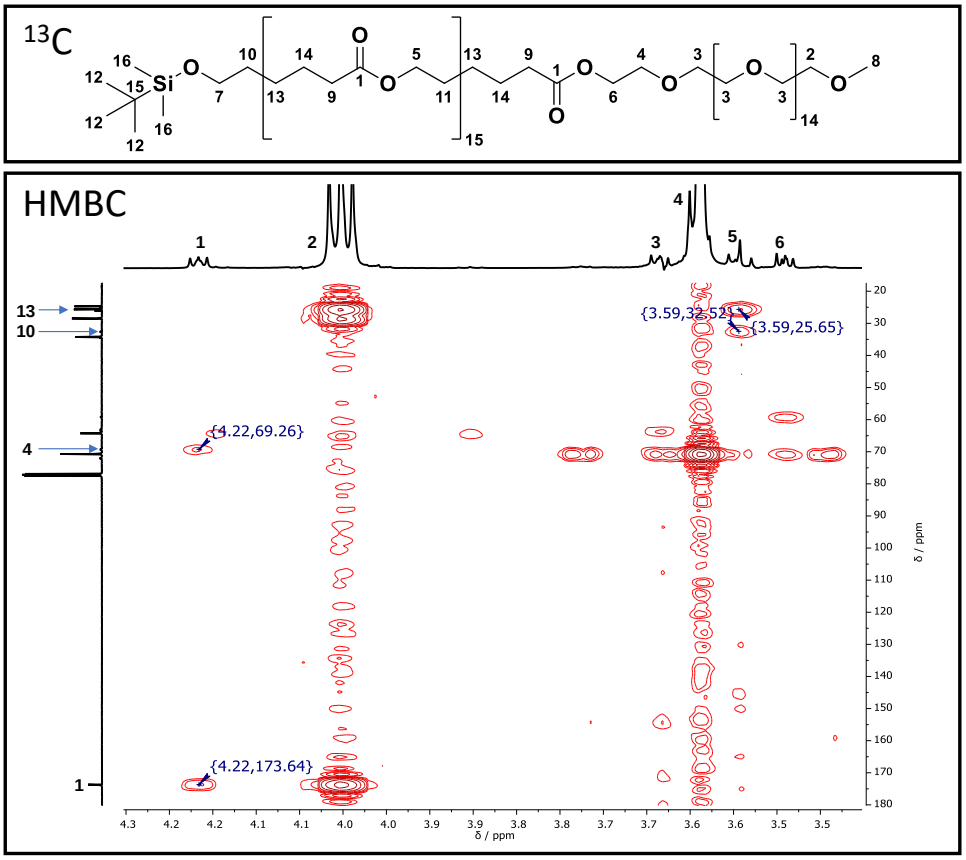
Supplementary Figure 87: ESI-MS spectrum of ***i*-TBDMS(CL)$_{16}$-(EG)$_{16}$OMe**.



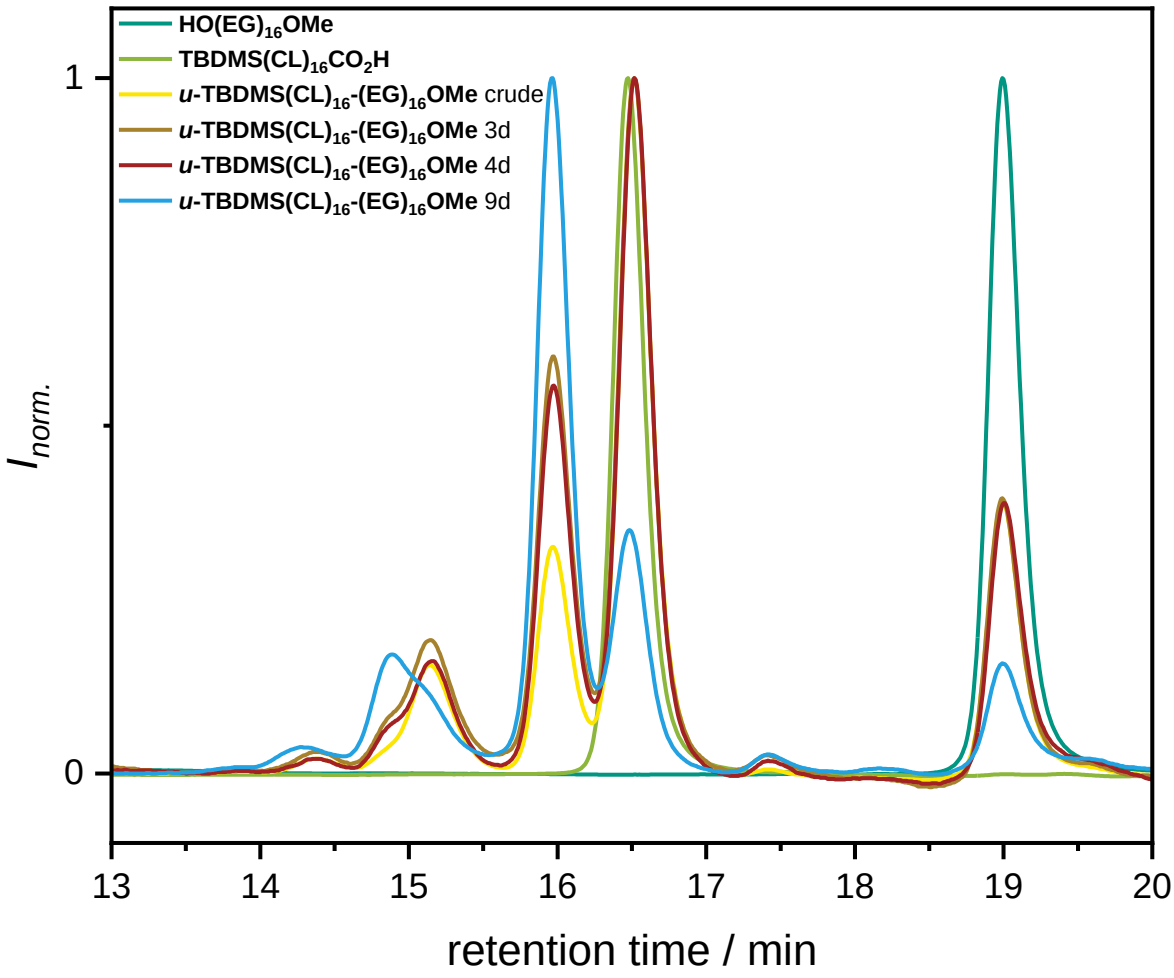
Supplementary Figure 88: Comparison of the calculated and experimental isotopic pattern (ESI-MS) of the sodium adduct of ***i*-TBDMS(CL)$_{16}$-(EG)$_{16}$OMe**.



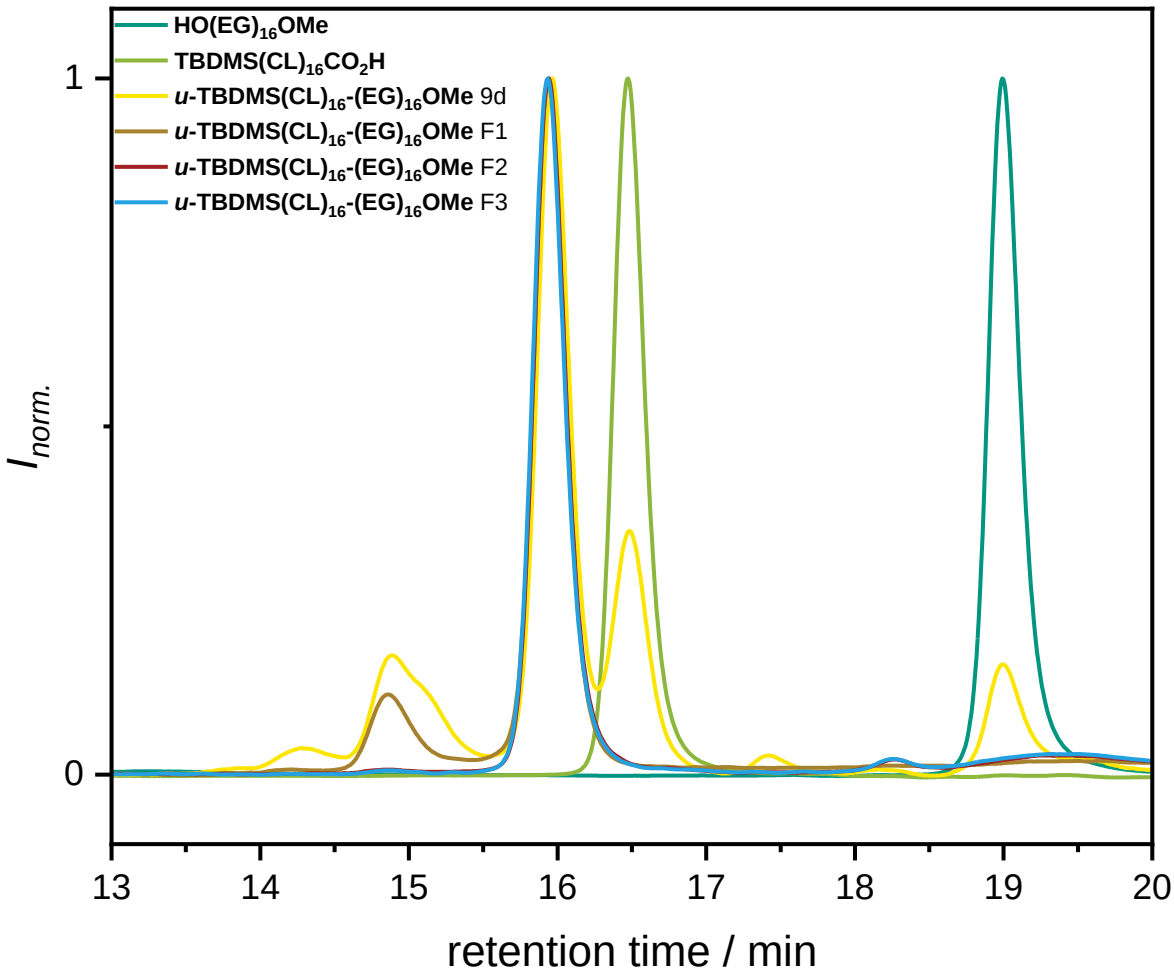
Supplementary Figure 89: COSY NMR spectrum of ***i*-TBDMS(CL)$_{16}$-(EG)$_{16}$OMe**.



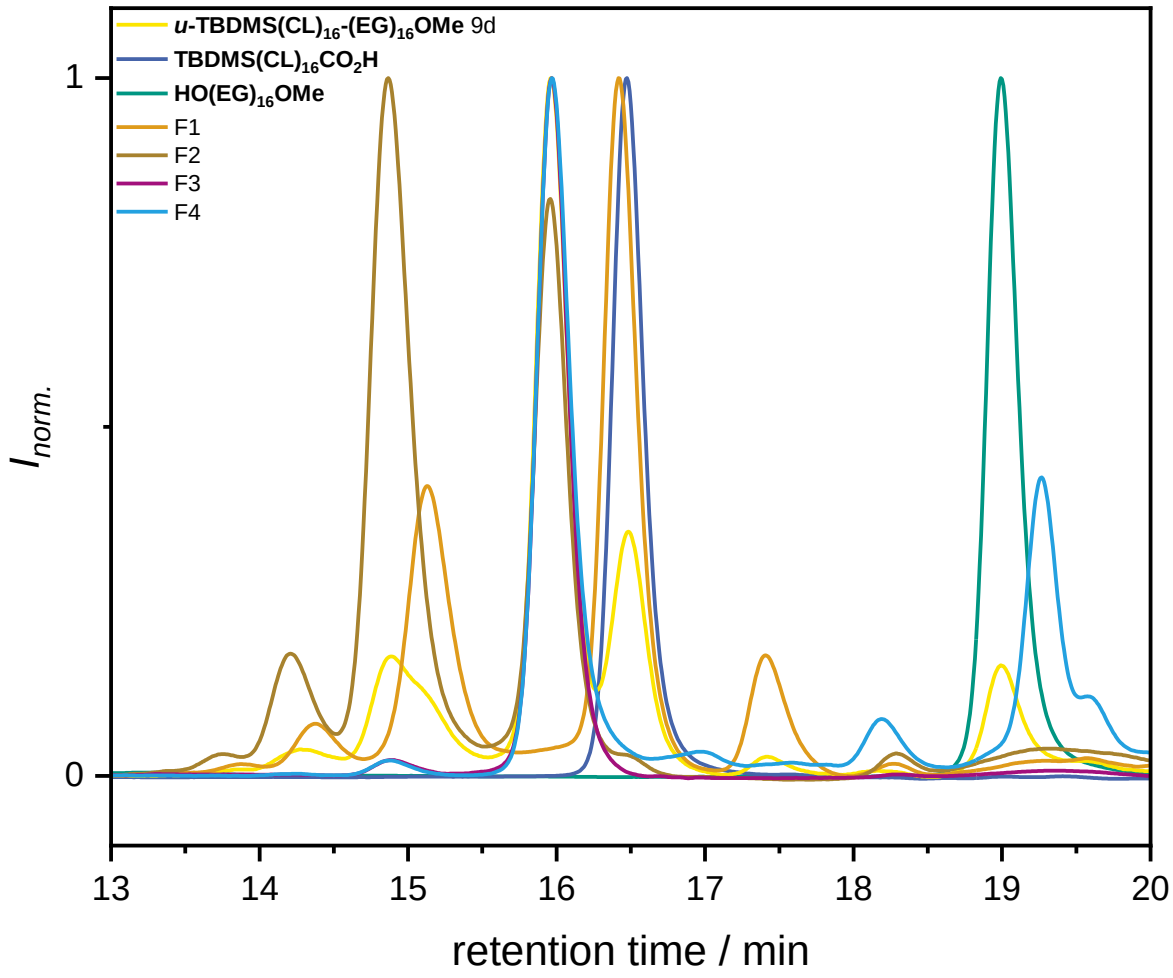
Supplementary Figure 90: HMBC NMR spectrum of ***i*-TBDMS(CL)$_{16}$-(EG)$_{16}$OMe**.



Supplementary Figure 91: Reaction monitoring for the synthesis of ***i*-TBDMS(CL)$_{16}$-(EG)$_{16}$OMe** *via* SEC and comparison to the starting materials **TBDMS(CL)$_{16}$CO$_2$H** and **HO(EG)$_{16}$OMe.**

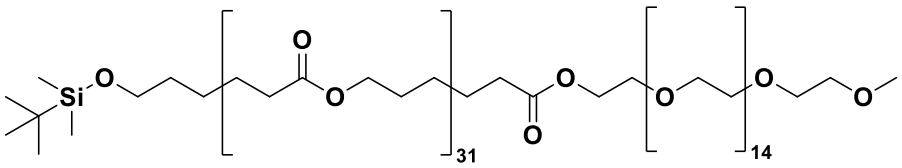


Supplementary Figure 92 SEC results of the first purification step of ***i*-TBDMS(CL)$_{16}$-(EG)$_{16}$OMe** *via* column chromatography compared to the starting materials **TBDMS(CL)$_{16}$CO$_2$H** and **HO(EG)$_{16}$OMe.**



Supplementary Figure 93: SEC results of the second purification step of ***i*-TBDMS(CL)$_{16}$-(EG)$_{16}$OMe** *via* column chromatography compared to the starting materials **TBDMS(CL)$_{16}$CO$_2$H** and **HO(EG)$_{16}$OMe.**

***i*-TBDMS(CL)$_{32}$-(EG)$_{16}$OMe**



Chemical Formula: $C_{231}H_{402}O_{81}Si$
Exact Mass: 4500.7107 Da
Molecular Weight: 4503.7610 Da

The block copolymer ***i*-TBDMS(CL)$_{32}$-(EG)$_{16}$OMe** was prepared according to the procedure described above for the synthesis of the doubly protected dimer **TBDMS(CL)$_2$Bn**.

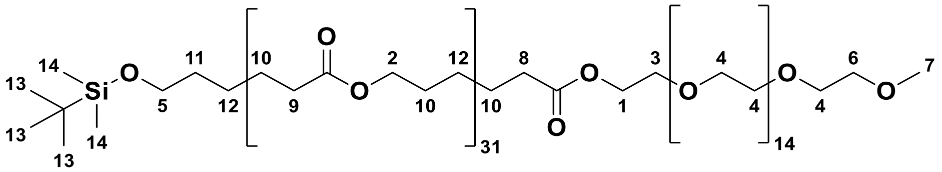
TBDMS(CL)$_{32}$CO$_2$H	257 mg, 67.9 µmol, 1.00 equiv.
HO(EG)$_{16}$OMe	50.0 mg, 67.9 µmol, 1.00 equiv.
DCC	84.0 mg, 407 µmol, 6.00 equiv.
DPTS	20.0 mg, 67.9 µmol, 1.00 equiv.
DCM	6.00 mL
eluent	1st cc: cyhex:EA = 1:2 → EA → EA:MeOH = 19:1 → 9:1 → acetone; 2nd cc: EA → EA:MeOH = 99:1 → 9:1 → acetone; 3rd cc: EA → EA:MeOH = 99:1 → 9:1 → acetone; 4th cc: EA → acetone
yield	132 mg, 29.3 µmol, 43.2%, white solid
R_f	0.18 (EA:MeOH = 9:1)
Đ (system II)	1.01

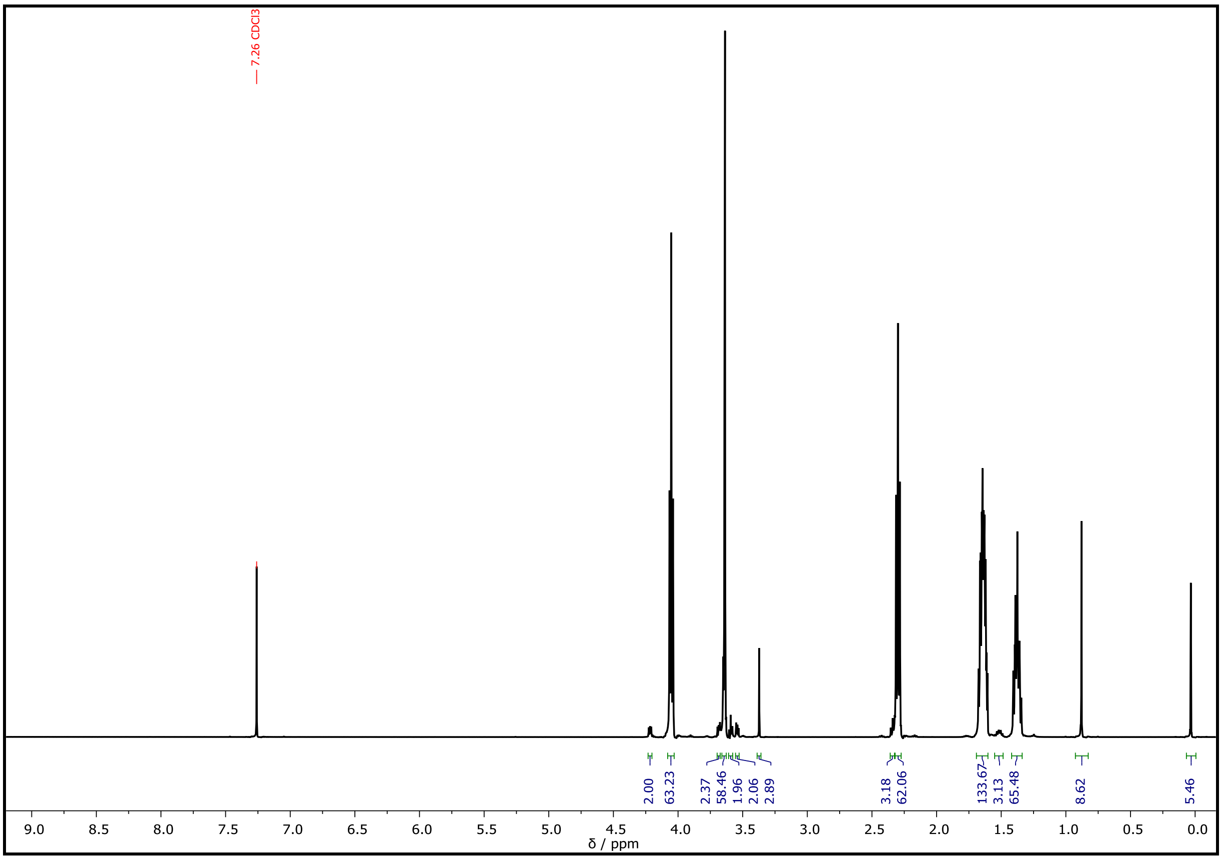
HRMS (ESI) of $C_{231}H_{402}O_{81}Si$ $[M+Na]^{1+}$ *m/z* calc. 4523.6999, detected 4523.6934; $[M+2Na]^{2+}$ *m/z* calc. 2273.3446, detected 2273.3415; $[M+Na+K]^{2+}$ *m/z* calc. 2281.3315, detected 2281.3361; $[M+2K]^{2+}$ *m/z* calc. 2289.3185, detected 2289.3427; $[M+3Na]^{3+}$ *m/z* calc. 1523.2261, detected 1523.2236; $[M+2Na+K]^{3+}$ *m/z* calc. 1528.5508, detected 1528.5493; $[M+Na+2K]^{3+}$ *m/z* calc. 1533.8754, detected 1533.8869; $[M+4Na]^{4+}$ *m/z* calc. 1148.1669, detected 1148.1660.

The mass of $mPEG_{16}$-*b*-PCL_{31}-TBDMS was detected as well. HRMS (ESI) of $C_{225}H_{392}O_{79}Si$ $[M+2Na]^{2+}$ *m/z* calc. 2216.3105, detected 2216.2996; $[M+Na+K]^{2+}$ *m/z* calc. 2224.2975, detected 2224.2905; $[M+2K]^{2+}$ *m/z* calc. 2232.2845, detected 2232.3013; $[M+3Na]^{3+}$ *m/z* calc. 1485.2034, detected 1485.2162; $[M+2Na+K]^{3+}$ *m/z* calc. 1490.5281, detected 1490.5225; $[M+Na+2K]^{3+}$ *m/z* calc. 1495.8527, detected 1495.8470.

IR (ATR platinum diamond) ν / cm^{-1} = 2943, 2894, 2865, 1722, 1471, 1438, 1419, 1397, 1366, 1323, 1294, 1238, 1174, 1105, 1065, 1043, 961, 934, 839, 775, 732, 710, 584, 537, 522, 502, 492, 483, 453, 424, 411.

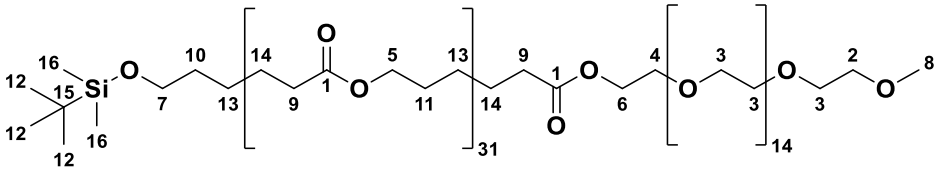
^{1}H NMR (500 MHz, $CDCl_3$): δ / ppm = 4.24 – 4.20 (m, 2H, $CH_2{}^1$), 4.05 (t, *J* = 6.7 Hz, 62H, $CH_2{}^2$), 3.71 – 3.67 (m, 2H, $CH_2{}^3$), 3.66 – 3.63 (m, 58H, $CH_2{}^4$), 3.61 – 3.58 (m, 2H, $CH_2{}^5$), 3.56 – 3.53 (m, 2H, $CH_2{}^6$), 3.37 (s, 3H, $CH_3{}^7$), 2.35 (t, *J* = 7.5 Hz, 2H, $CH_2{}^8$), 2.30 (t, *J* = 7.5 Hz, 62H, $CH_2{}^9$), 1.71 – 1.60 (m, 126H, $CH_2{}^{10}$), 1.55 – 1.49 (m, 2H, $CH_2{}^{11}$), 1.43 – 1.32 (m, 64H, $CH_2{}^{12}$), 0.88 (s, 9H, $CH_3{}^{13}$), 0.03 (s, 6H, $CH_3{}^{14}$).

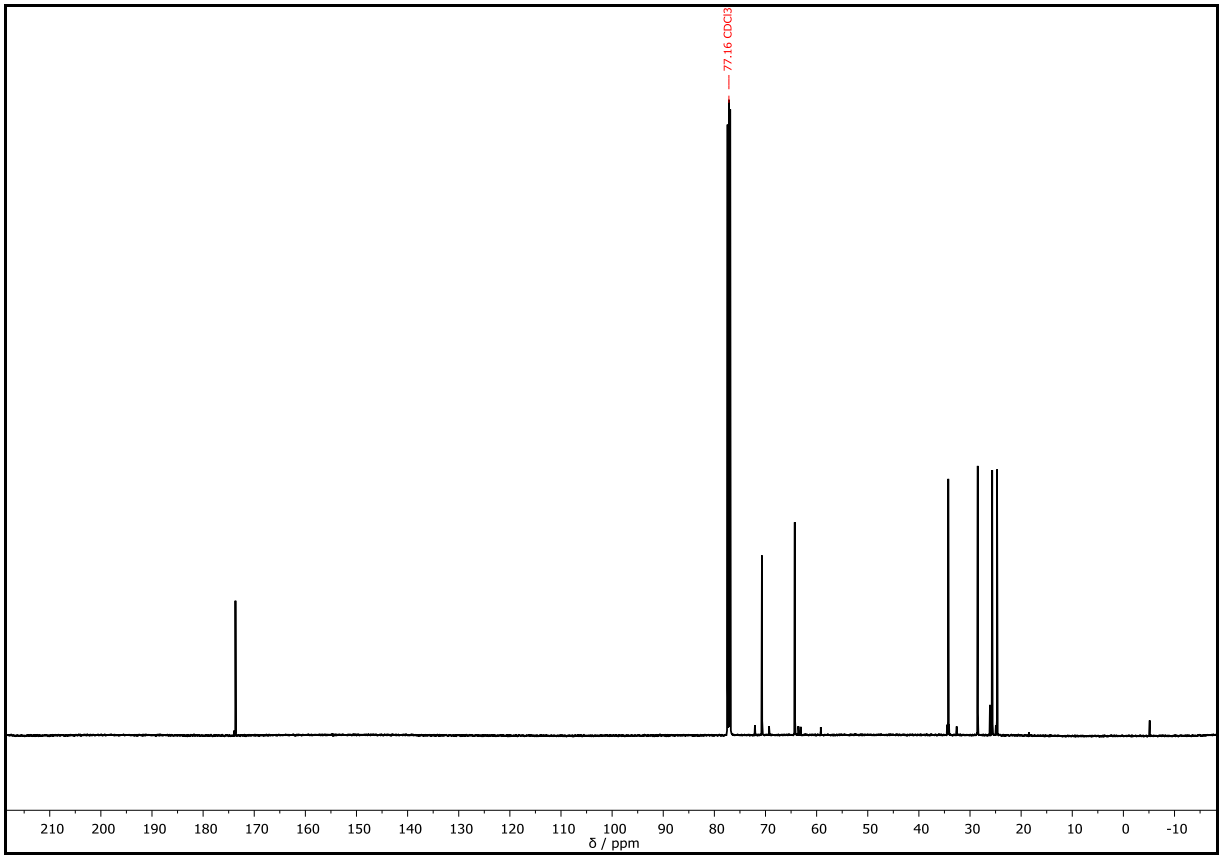




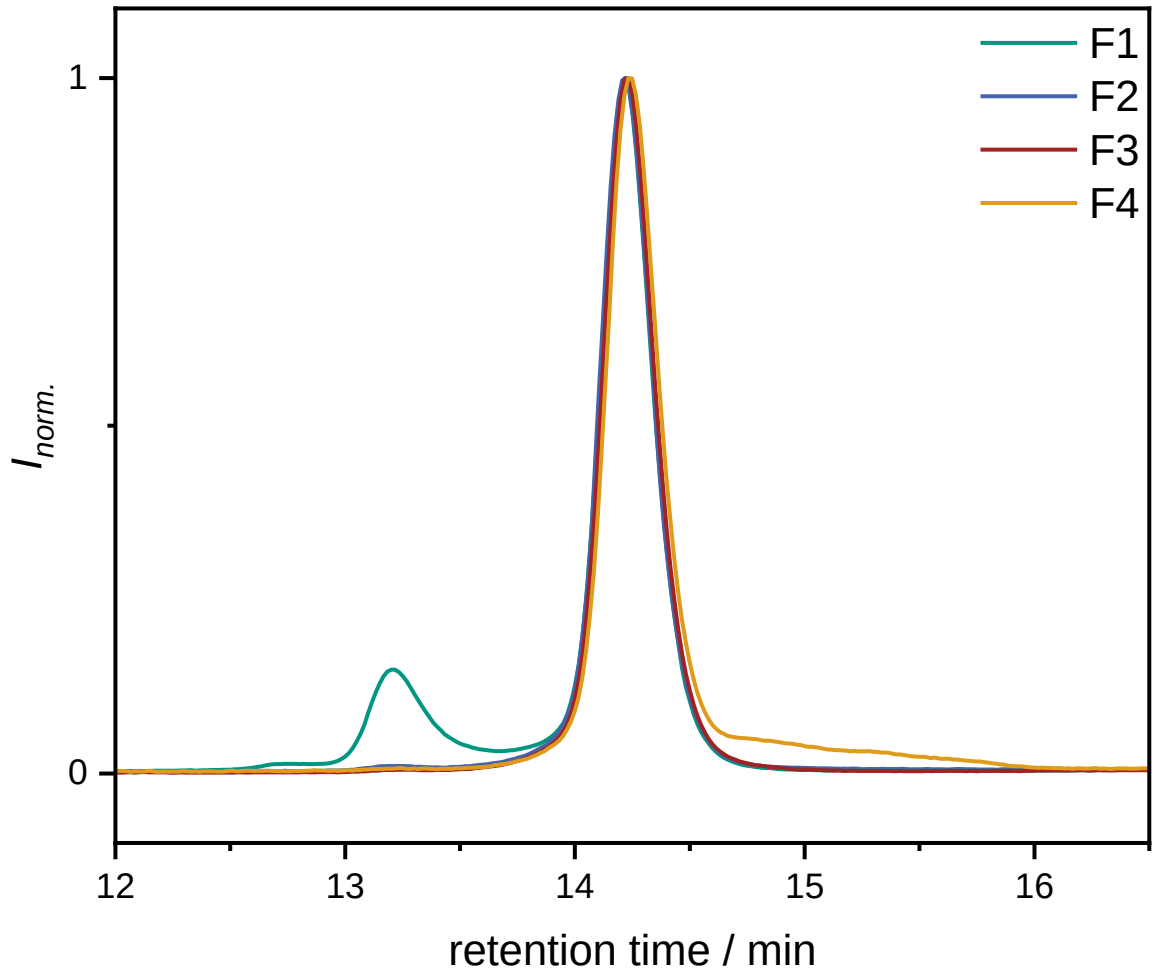
Supplementary Figure 94: ^{1}H NMR spectrum of ***i*-TBDMS(CL)$_{32}$-(EG)$_{16}$OMe** recorded at 500 MHz in $CDCl_3$.

^{13}C NMR (126 MHz, $CDCl_3$): δ / ppm = 173.94 (C_q^1), 173.67 (C_q^1), 173.60 (C_q^1), 72.07 (CH_2^2), 70.70 (CH_2^3), 69.31 (CH_2^4), 64.28 (CH_2^5), 64.19 (CH_2^5), 63.58 (CH_2^6), 63.11 (CH_2^7), 59.18 (CH_3^8), 34.47 (CH_2^9), 34.25 (CH_2^9), 34.11 (CH_2^9), 32.60 (CH_2^{10}), 28.48 (CH_2^{11}), 26.10 (CH_3^{12}), 25.66 (CH_2^{13}), 24.95 (CH_2^{14}), 24.71 (CH_2^{14}), 18.48 (C_q^{15}), -5.15 (CH_3^{16}).

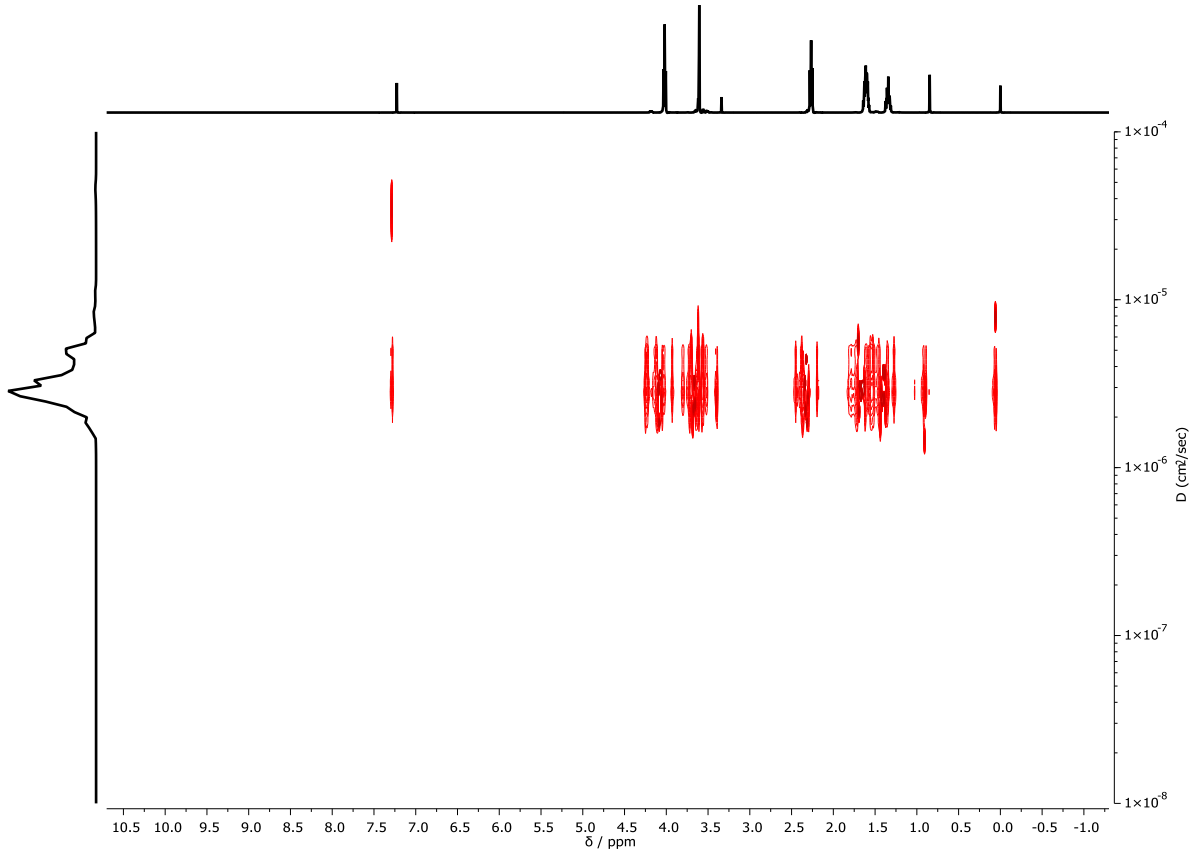




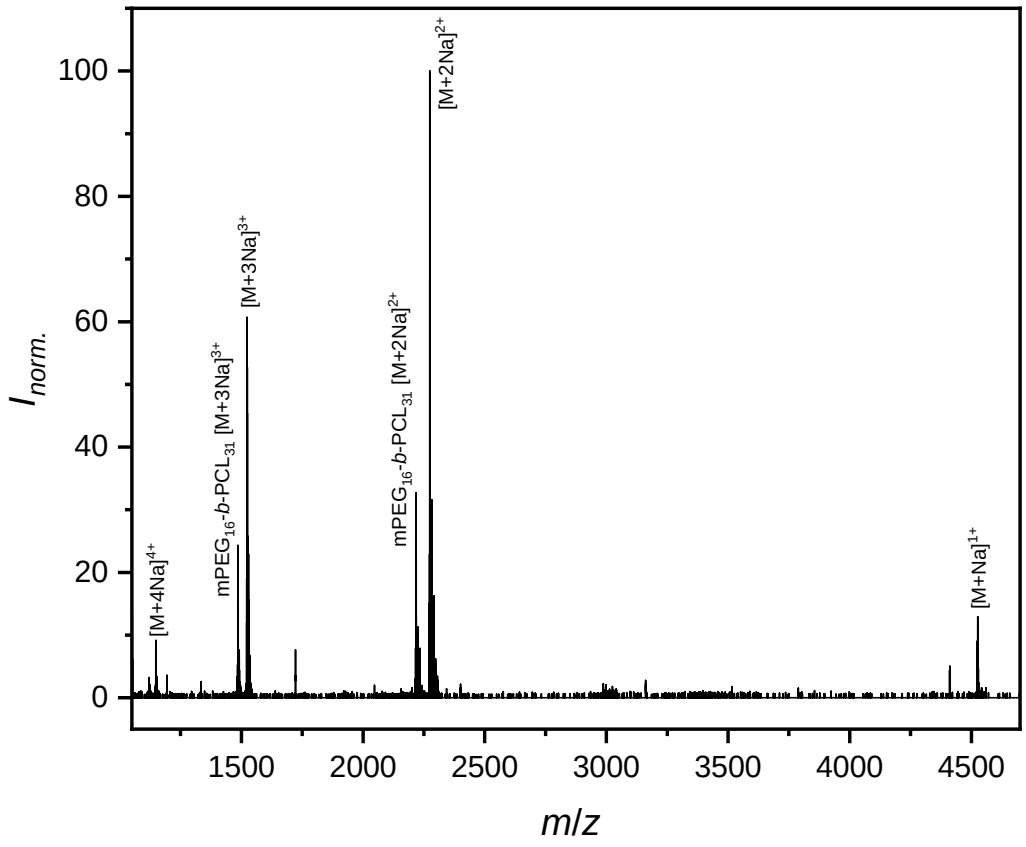
Supplementary Figure 95: ^{13}C NMR spectrum of ***i*-TBDMS(CL)$_{32}$-(EG)$_{16}$OMe** recorded at 126 MHz in $CDCl_3$.



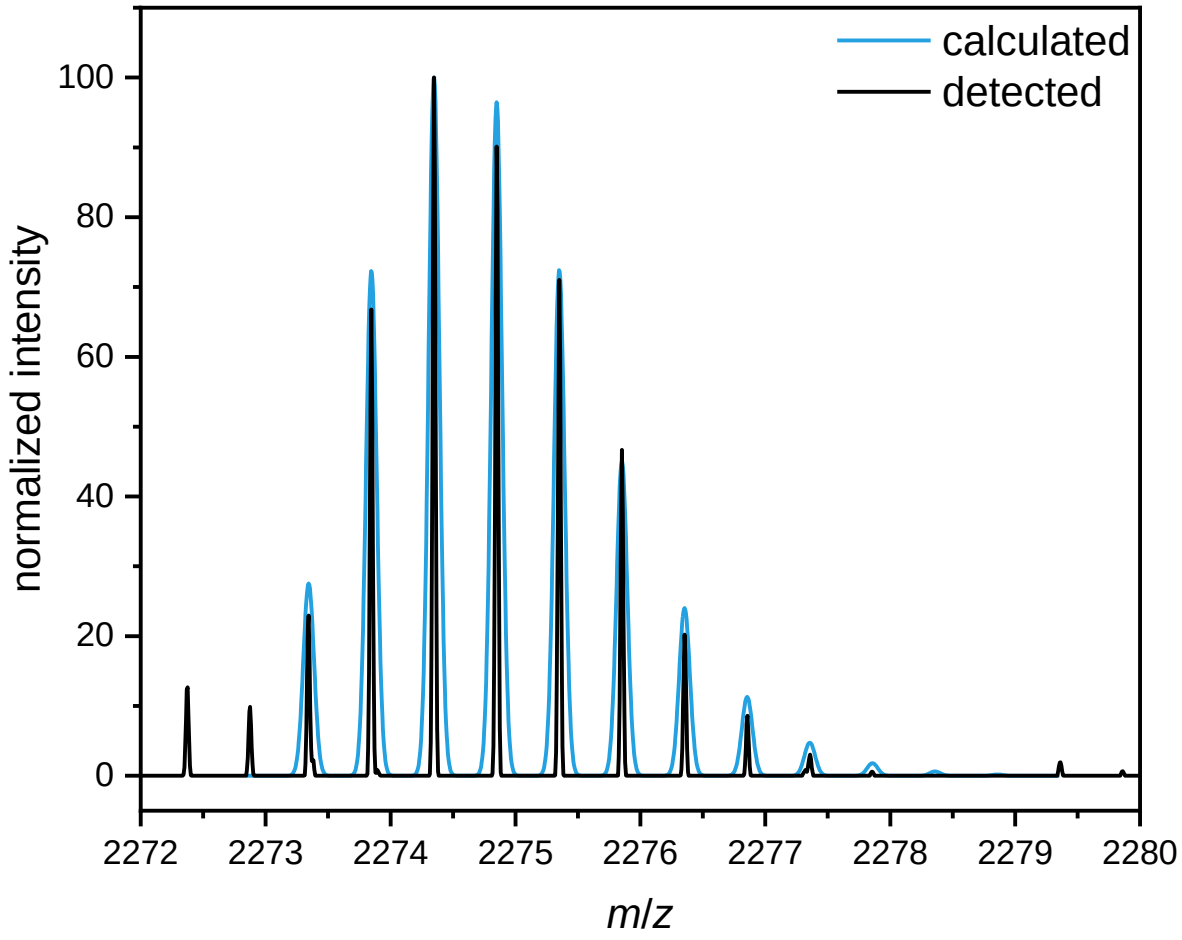
Supplementary Figure 96: SEC results of the 4th purification step of ***i*-TBDMS(CL)$_{32}$-(EG)$_{16}$OMe** *via* column chromatography.



Supplementary Figure 97: DOSY NMR spectrum of ***i*-TBDMS(CL)$_{32}$-(EG)$_{16}$OMe** recorded at 500 MHz in $CDCl_3$.

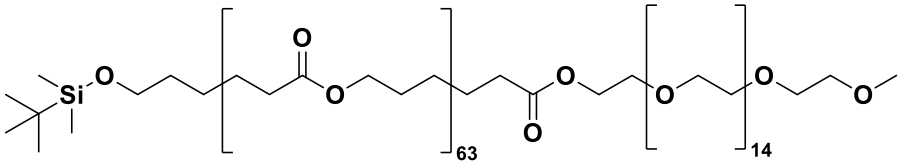


Supplementary Figure 98: ESI-MS spectrum of ***i*-TBDMS(CL)$_{32}$-(EG)$_{16}$OMe**.



Supplementary Figure 99: Comparison of the calculated and experimental isotopic pattern (ESI-MS) of the sodium adduct of ***i*-TBDMS(CL)$_{32}$-(EG)$_{16}$OMe**.

***i*-TBDMS(CL)$_{64}$-(EG)$_{16}$OMe**



Chemical Formula: $C_{423}H_{722}O_{145}Si$
Exact Mass: 8150.8892 Da
Molecular Weight: 8156.3690 Da

The block copolymer ***i*-TBDMS(CL)$_{64}$-(EG)$_{16}$OMe** was prepared according to the procedure described above for the synthesis of the doubly protected dimer **TBDMS(CL)$_2$Bn**.

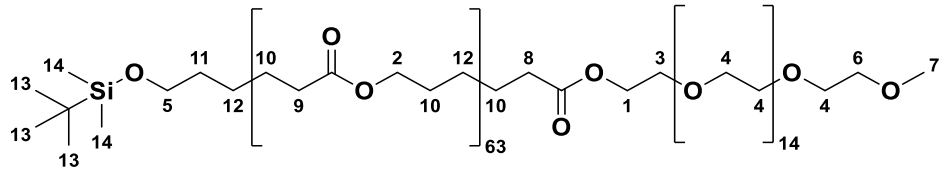
TBDMS(CL)$_{64}$CO$_2$H	505 mg, 67.9 µmol, 1.00 equiv.
HO(EG)$_{16}$OMe	50.0 mg, 67.9 µmol, 1.00 equiv.
DCC	84.0 mg, 407 µmol, 6.00 equiv.
DPTS	20.0 mg, 67.9 µmol, 1.00 equiv.
DCM	6.00 mL
eluent	1st cc: cyhex:EA = 1:2 → EA → EA:MeOH = 99:1 → 4:1 → acetone 2nd cc: EA → EA:MeOH = 99:1 → 9:1 → acetone; acetone; 3rd cc: EA → acetone
yield	102 mg, 12.5 µmol, 18.4%, white solid
R_f	0.68 (EA:MeOH = 4:1)
Đ (system II)	1.01

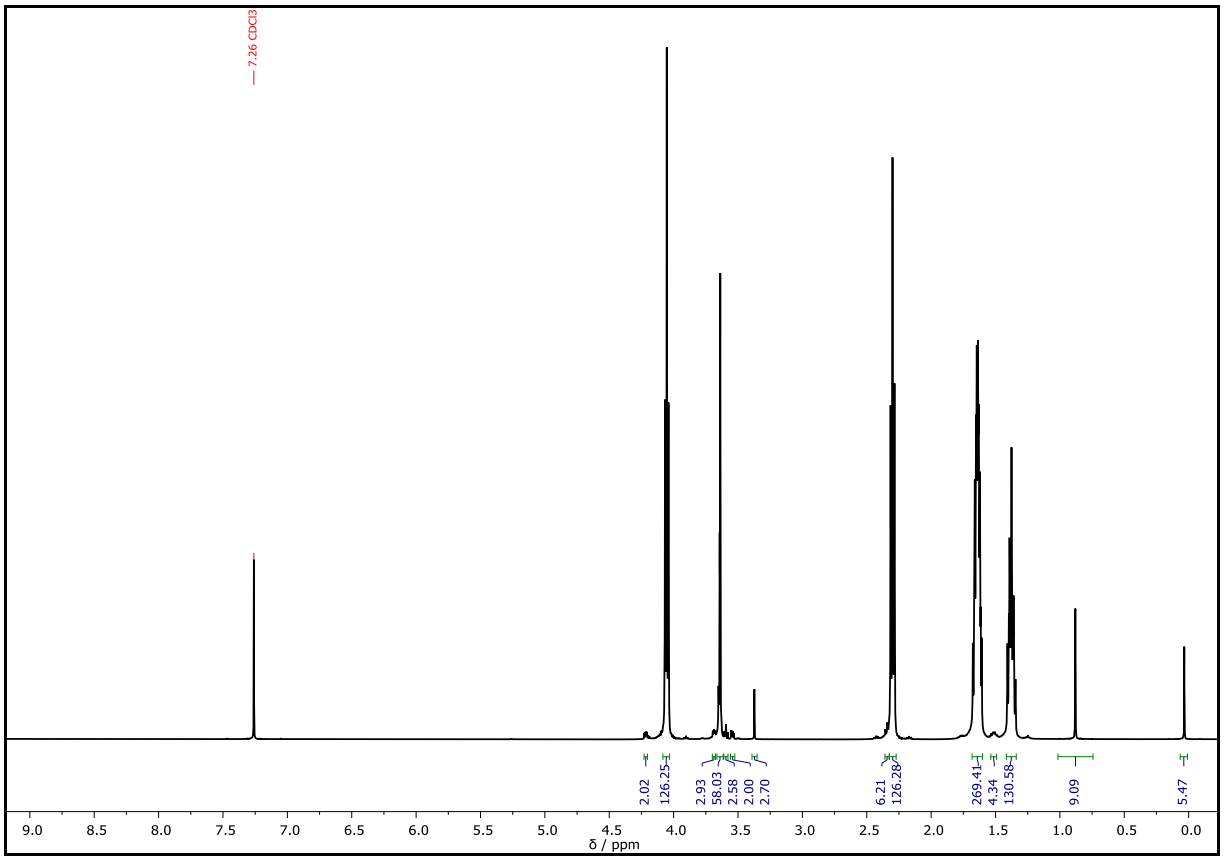
HRMS (ESI) of $C_{423}H_{722}O_{145}Si$ $[M+2Na]^{2+}$ *m/z* calc. 4100.9427, detected 4100.9558 (most intense peak of isotopic pattern); $[M+3Na]^{3+}$ *m/z* calc. 2739.9523, detected 2739.9696; $[M+2Na+K]^{3+}$ *m/z* calc. 2746.9478, detected 2746.9524 (most intense peak of isotopic pattern); $[M+Na+2K]^{3+}$ *m/z* calc. 2752.2725, detected 2752.2813 (most intense peak of isotopic pattern); $[M+4Na]^{4+}$ *m/z* calc. 2060.7225, detected 2060.7280; $[M+3Na+K]^{4+}$ *m/z* calc. 2064.7050, detected 2064.7099; $[M+2Na+2K]^{4+}$ *m/z* calc. 2068.6985, detected 2068.7167; $[M+Na+3K]^{4+}$ *m/z* calc. 2072.6920, detected 2072.6946; $[M+5Na]^{5+}$ *m/z* calc. 1653.1671, detected 1653.1743; $[M+4Na+K]^{5+}$ *m/z* calc. 1656.3619, detected 1656.3705; $[M+3Na+2K]^{5+}$ *m/z* calc. 1659.5566, detected 1659.5607; $[M+6Na]^{6+}$ *m/z* calc. 1381.4708, detected 1381.4686; $[M+5Na+K]^{6+}$ *m/z* calc. 1384.1331, detected 1384.1423; $[M+4Na+2K]^{6+}$ *m/z* calc. 1386.7954, detected 1386.7979.

The mass of $mPEG_{16}$-*b*-PCL_{63}-TBDMS was detected as well. HRMS (ESI) of $C_{417}H_{712}O_{143}Si$ $[M+3Na]^{3+}$ *m/z* calc. 2701.9296, detected 2701.9394; $[M+4Na]^{4+}$ *m/z* calc. 2032.1945, detected 2032.2086; $[M+3Na+K]^{4+}$ *m/z* calc. 2036.1880, detected 2036.2043; $[M+5Na]^{5+}$ *m/z* calc. 1630.3534, detected 1630.3623; $[M+4Na+K]^{5+}$ *m/z* calc. 1633.5482, detected 1633.5529.

IR (ATR platinum diamond) $\tilde{\nu}$ / cm^{-1} = 2943, 2894, 2865, 1722, 1471, 1419, 1397, 1366, 1294, 1238, 1172, 1107, 1065, 1045, 961, 934, 868, 839, 775, 732, 710, 586, 453.

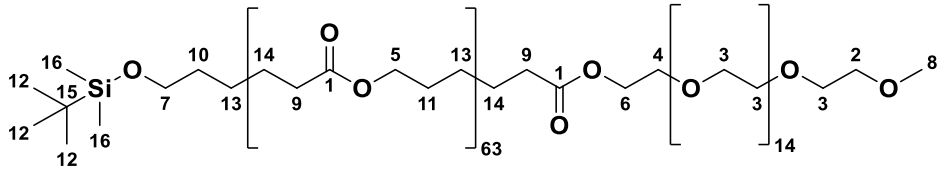
^{1}H NMR (500 MHz, $CDCl_3$): δ / ppm = 4.24 – 4.20 (m, 2H, CH_2^{1}), 4.05 (t, *J* = 6.7 Hz, 126H, CH_2^{2}), 3.70 – 3.67 (m, 2H, CH_2^{3}), 3.66 – 3.62 (m, 58H, CH_2^{4}), 3.59 (t, *J* = 6.5 Hz, 2H, CH_2^{5}), 3.56 – 3.53 (m, 2H, CH_3^{6}), 3.37 (s, 3H, CH_2^{7}), 2.35 (t, *J* = 7.4 Hz, 2H, CH_2^{8}), 2.30 (t, *J* = 7.5 Hz, 126H, CH_2^{9}), 1.69 – 1.60 (m, 254H, CH_2^{10}), 1.55 – 1.48 (m, 2H, CH_2^{11}), 1.42 – 1.34 (m, 128H, CH_2^{12}), 0.88 (s, 9H, CH_3^{13}), 0.03 (s, 6H, CH_3^{14}).

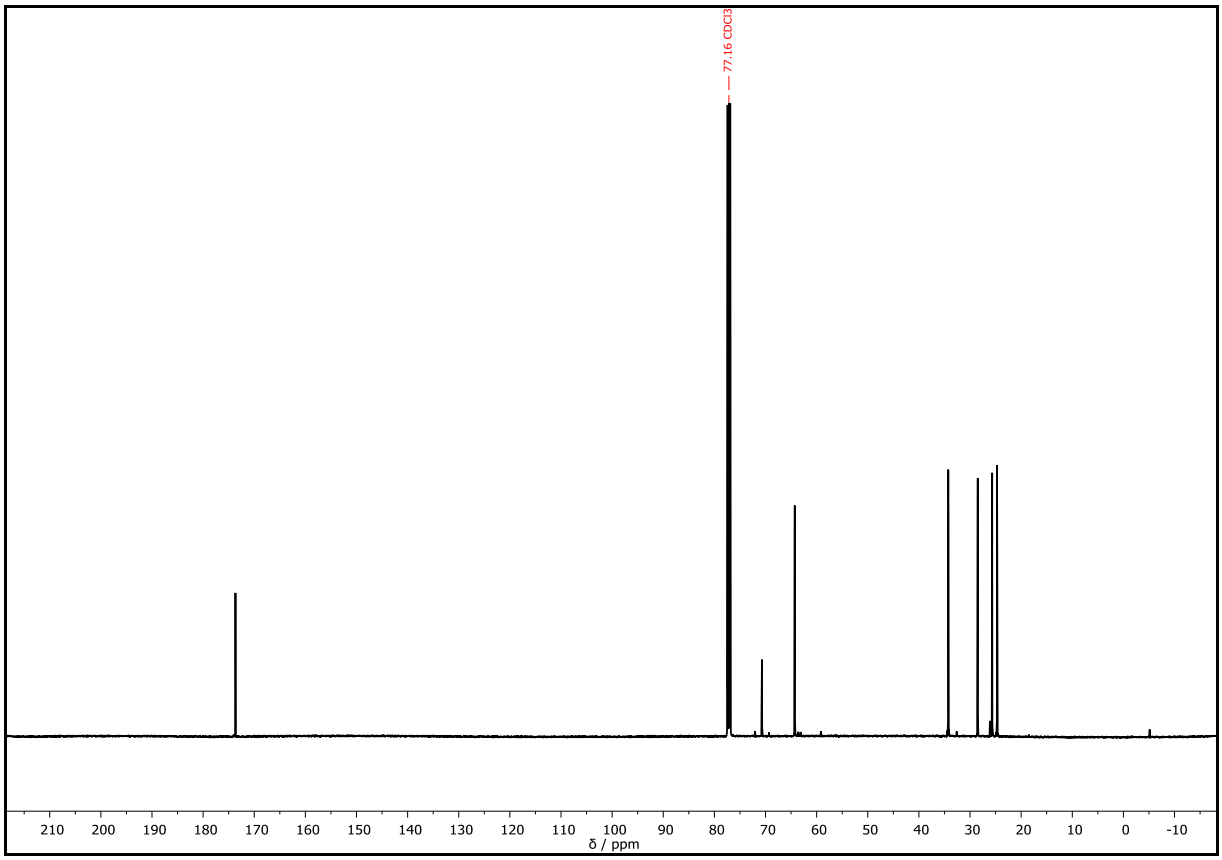




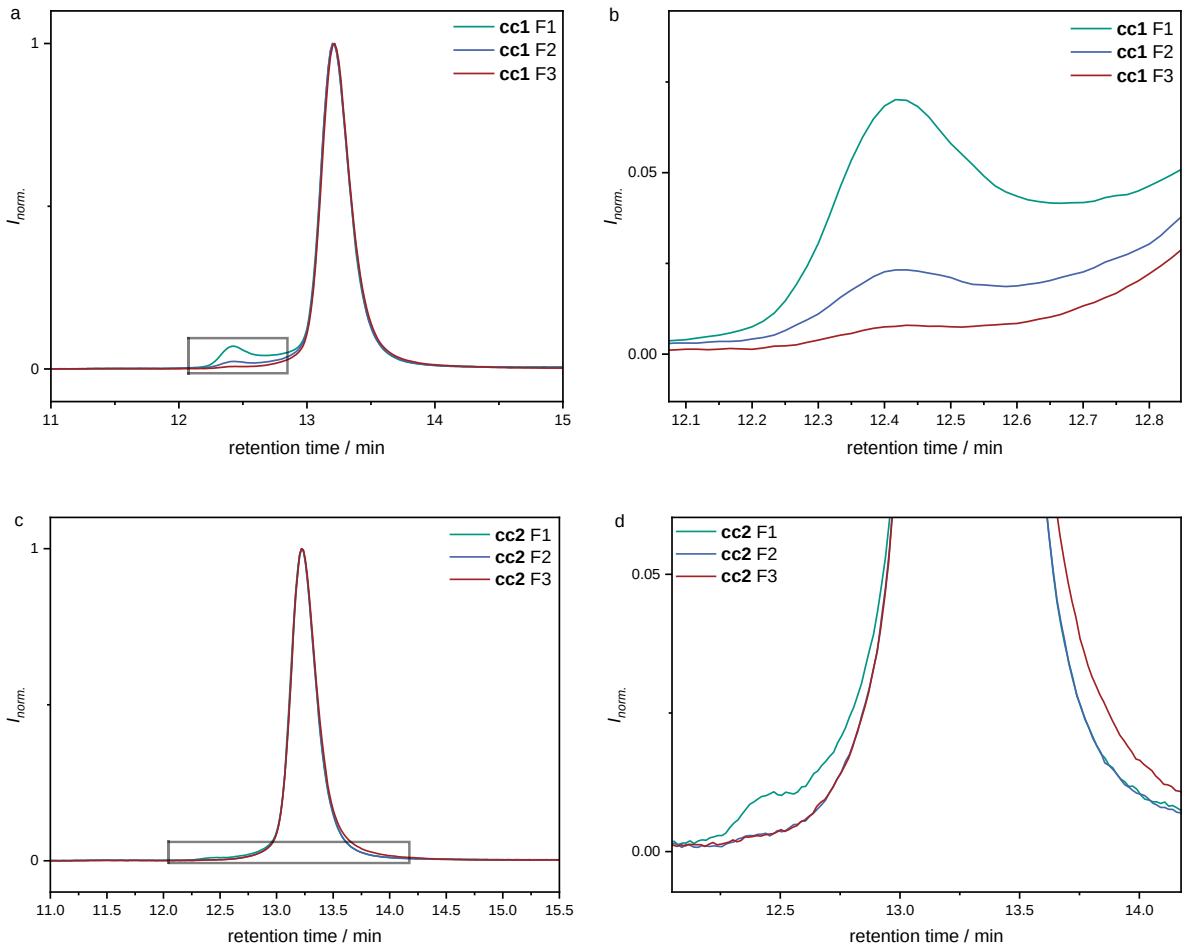
Supplementary Figure 100: ^{1}H NMR spectrum of ***i*-TBDMS(CL)$_{64}$-(EG)$_{16}$OMe** recorded at 500 MHz in $CDCl_3$.

^{13}C NMR (126 MHz, $CDCl_3$): δ / ppm = 173.68 (C_q^1), 72.07 (CH_2^2), 70.70 (CH_2^3), 69.31 (CH_2^4), 64.28 (CH_2^5), 63.58 (CH_2^6), 63.11 (CH_2^7), 59.18 (CH_3^8), 34.47 (CH_2^9), 34.25 (CH_2^9), 32.61 (CH_2^{10}), 28.49 (CH_2^{11}), 26.10 (CH_3^{12}), 25.67 (CH_2^{13}), 24.71 (CH_2^{14}), 18.48 (C_q^{15}), -5.14 (CH_3^{16}).

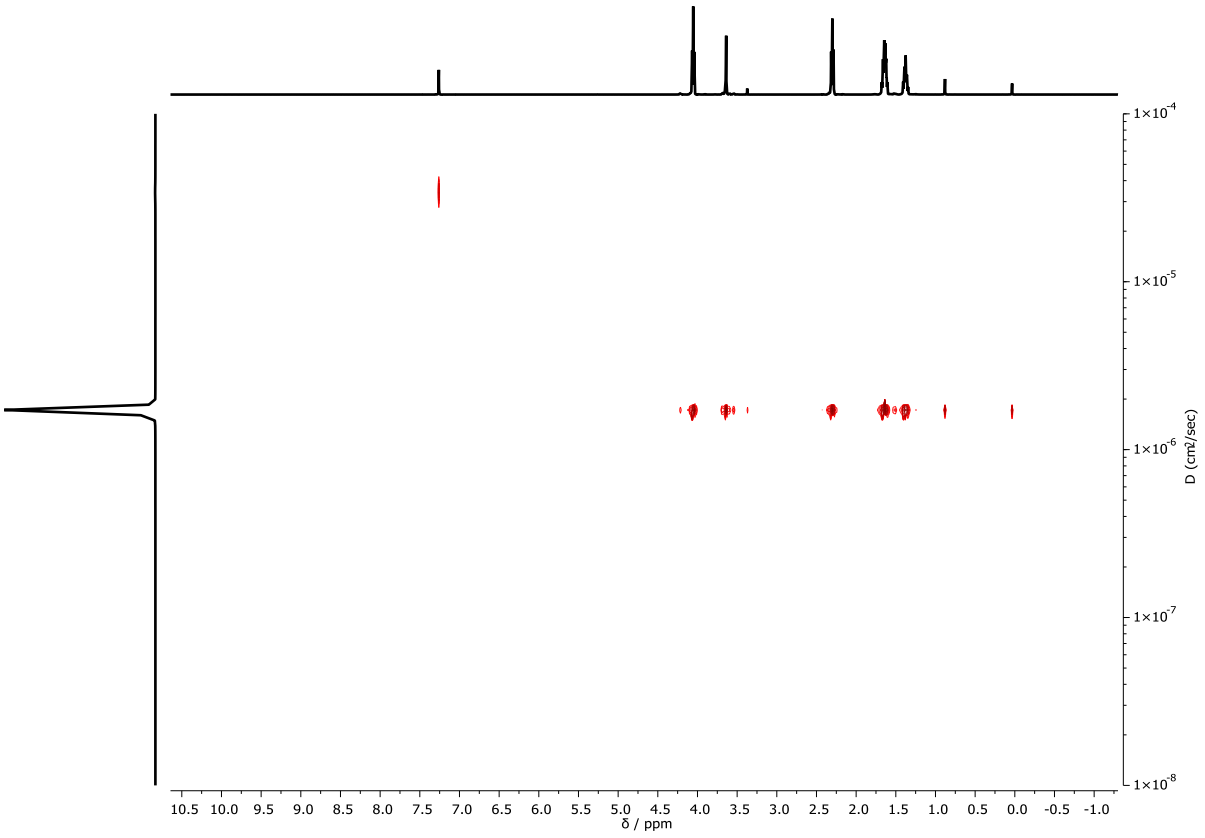




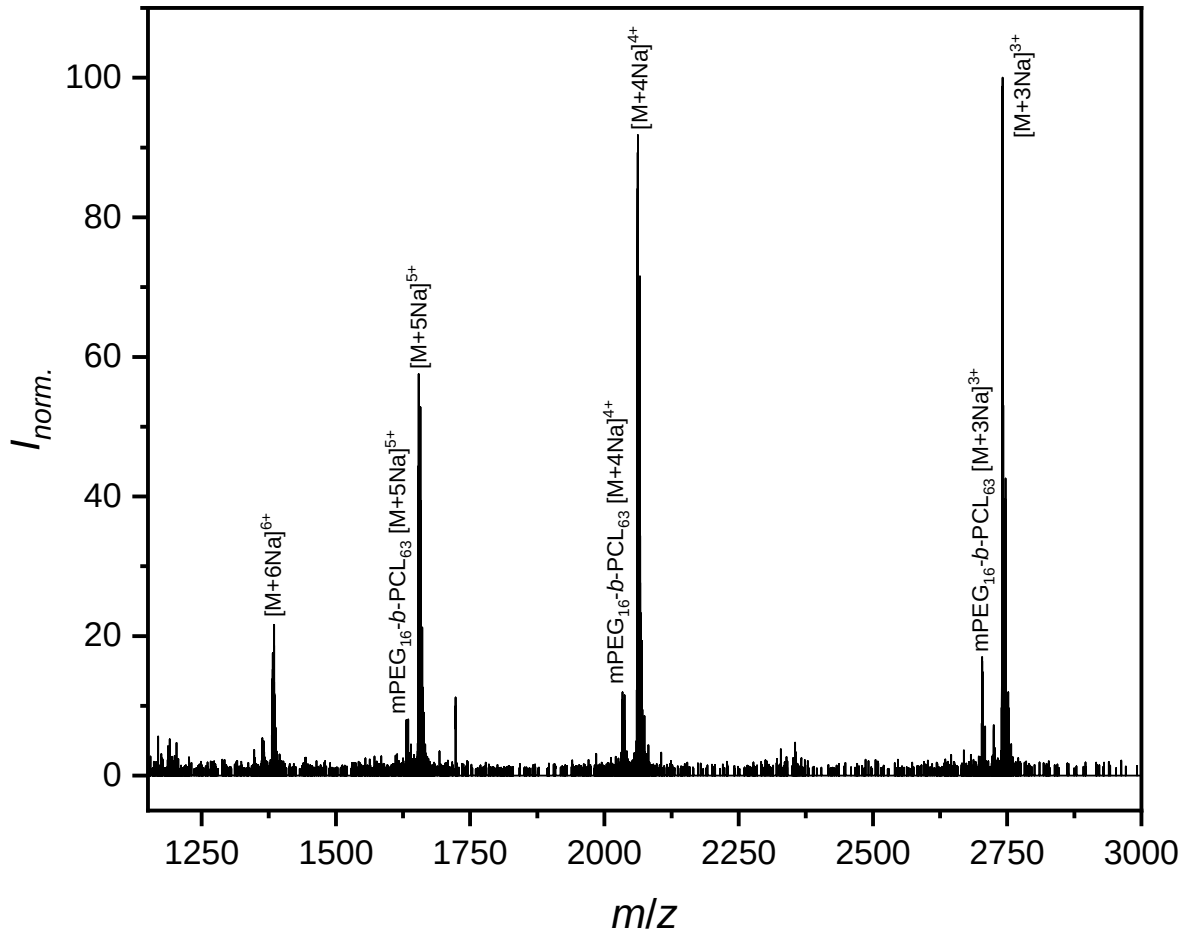
Supplementary Figure 101: ^{13}C NMR spectrum of ***i*-TBDMS(CL)$_{64}$-(EG)$_{16}$OMe** recorded at 126 MHz in $CDCl_3$.



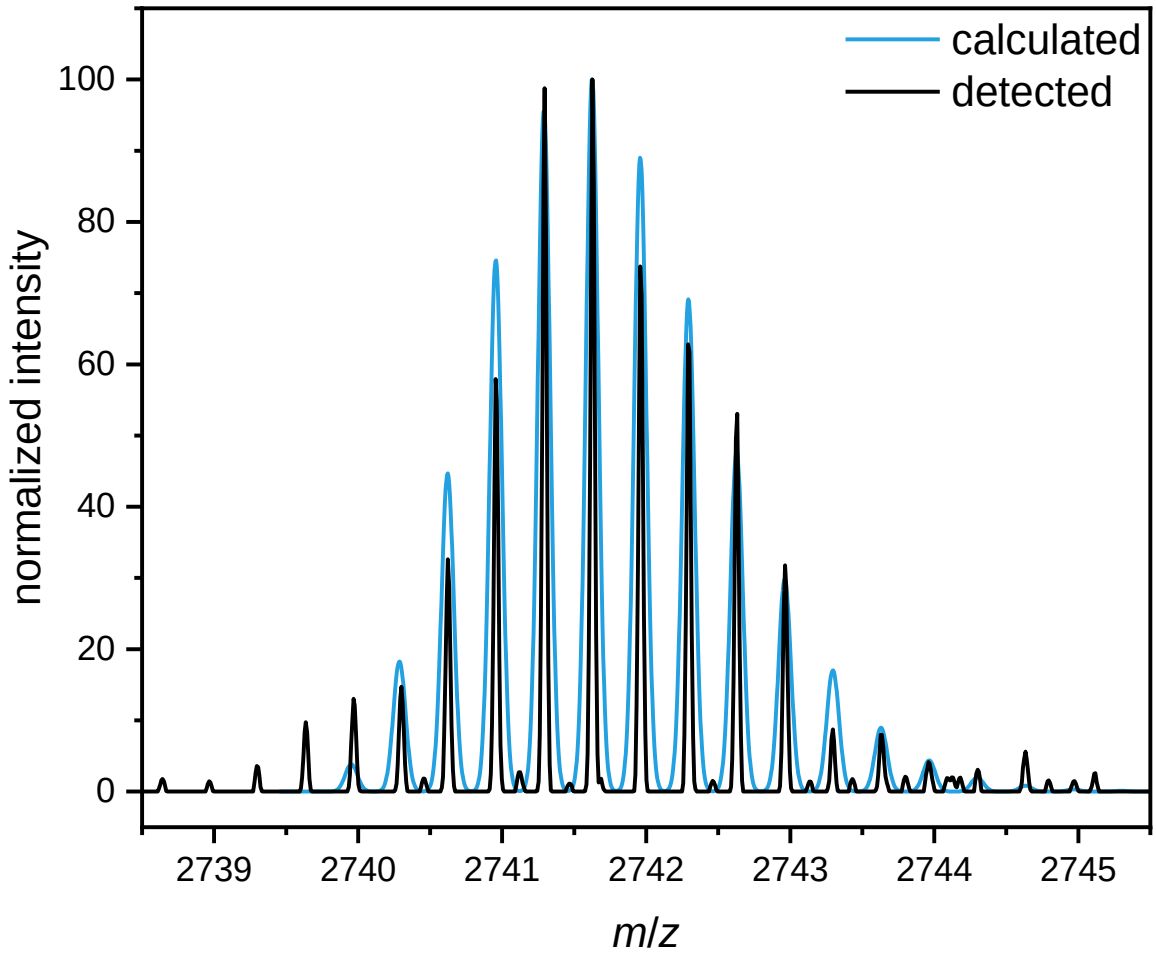
Supplementary Figure 102: **a** SEC traces of the individual fractions obtained after the first column chromatographic purification of the crude product ***i*-TBDMS(CL)$_{64}$-(EG)$_{16}$OMe**; **b** Zoom to the high molecular weight shoulder; **c** SEC traces of the individual fractions obtained after the second column chromatographic purification of ***i*-TBDMS(CL)$_{64}$-(EG)$_{16}$OMe** F3; **d** Zoom to the high molecular weight shoulder and tailing towards higher retention times.



Supplementary Figure 103: DOSY NMR spectrum of ***i*-TBDMS(CL)$_{64}$-(EG)$_{16}$OMe** recorded at 500 MHz in $CDCl_3$.



Supplementary Figure 104: ESI-MS spectrum of ***i*-TBDMS(CL)$_{64}$-(EG)$_{16}$OMe**.

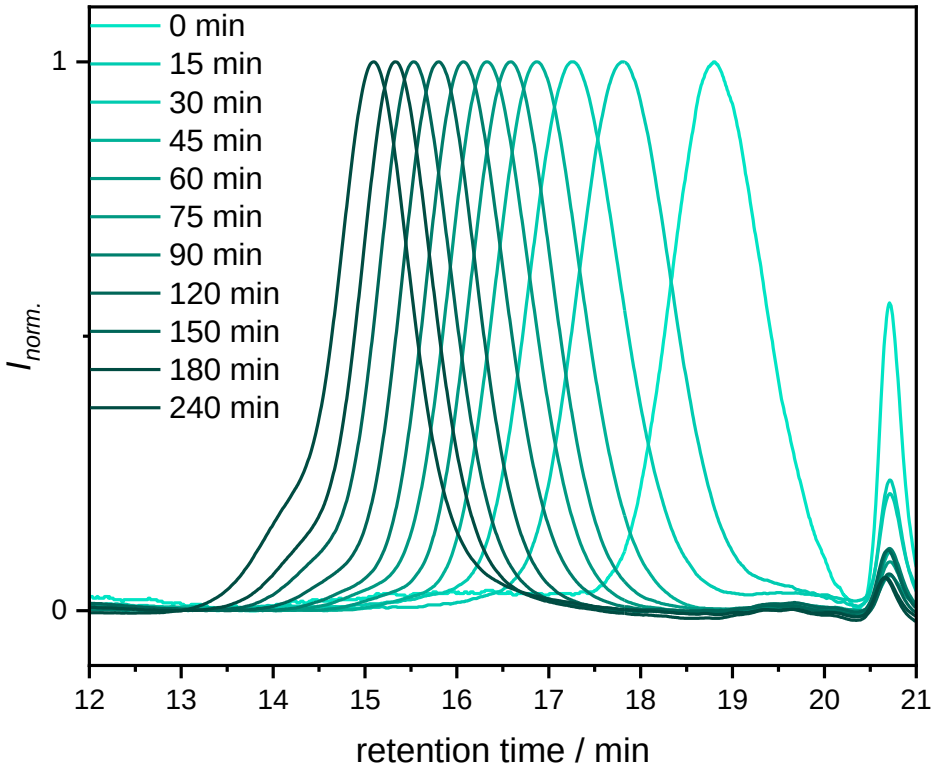


Supplementary Figure 105: Comparison of the calculated and experimental isotopic pattern (ESI-MS) of the sodium adduct of ***i*-TBDMS(CL)$_{64}$-(EG)$_{16}$OMe**.

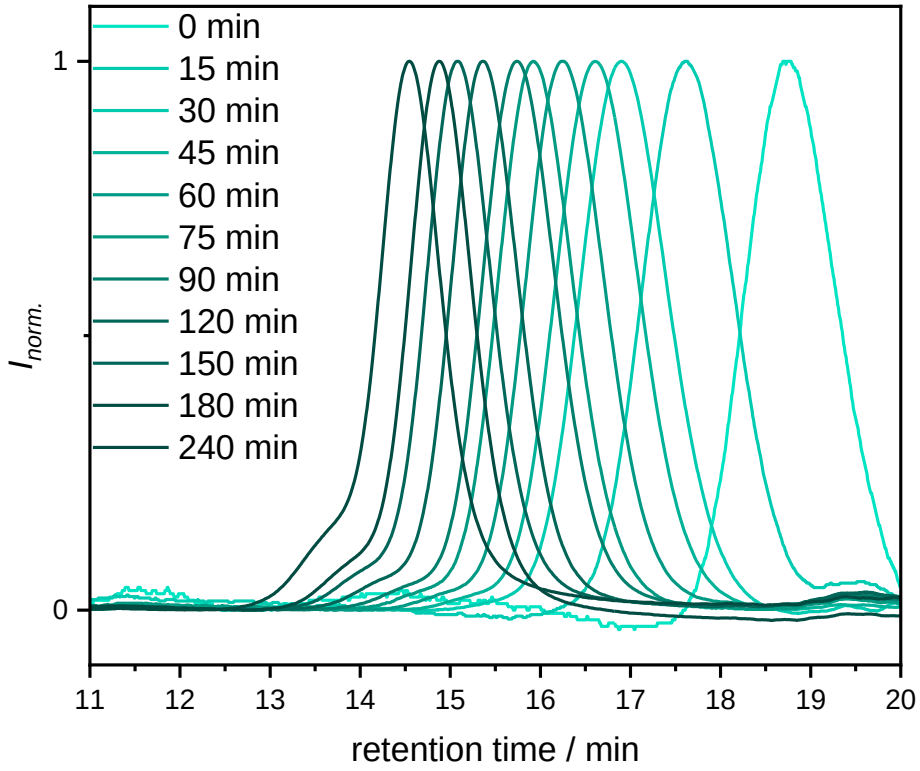
General procedure for the ring opening polymerization of ε-caprolactone with mPEG (M_n = 750 Da)

The reaction procedure was adopted from Waymouth and Hedrick *et. al*.[3] A stock solution of $mPEG_{750}$ (M_n = 750 Da) and TBD in extra dry toluene was prepared in a flame dried young flask. Hereby, the concentration of the mPEG (M_n = 750 Da) varied according to the targeted DP values. Subsequently, the catalyst and initiator solution were added to another in flame dried young flasks filled with extra dry toluene. ε-Caprolactone was added to the reaction fast with a syringe, while stirring vigorously under argon atmosphere. After the respective reaction time for the three different polymers, the reaction process was quenched by the fast addition of benzoic acid. Afterwards, the solvent was removed under reduced pressure and the residue was precipitated twice out of cold *n*-hexane. Further individual purification steps for the obtained block copolymers by column chromatography as well as the quantities of the starting materials are described below.

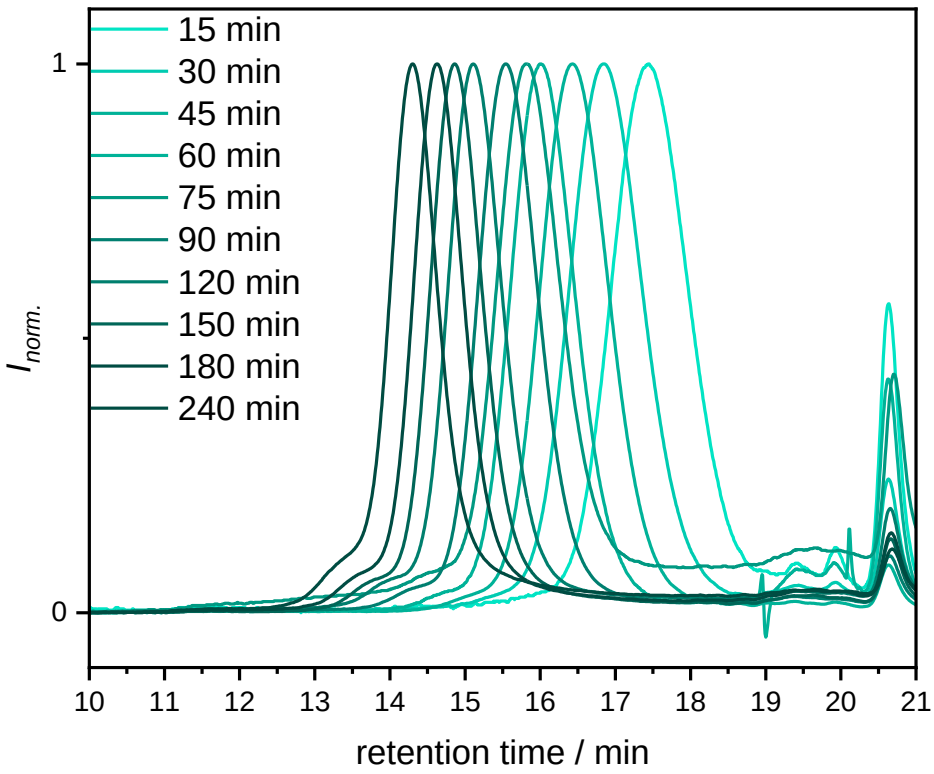
SEC reaction monitoring of the ROP of ε-caprolactone



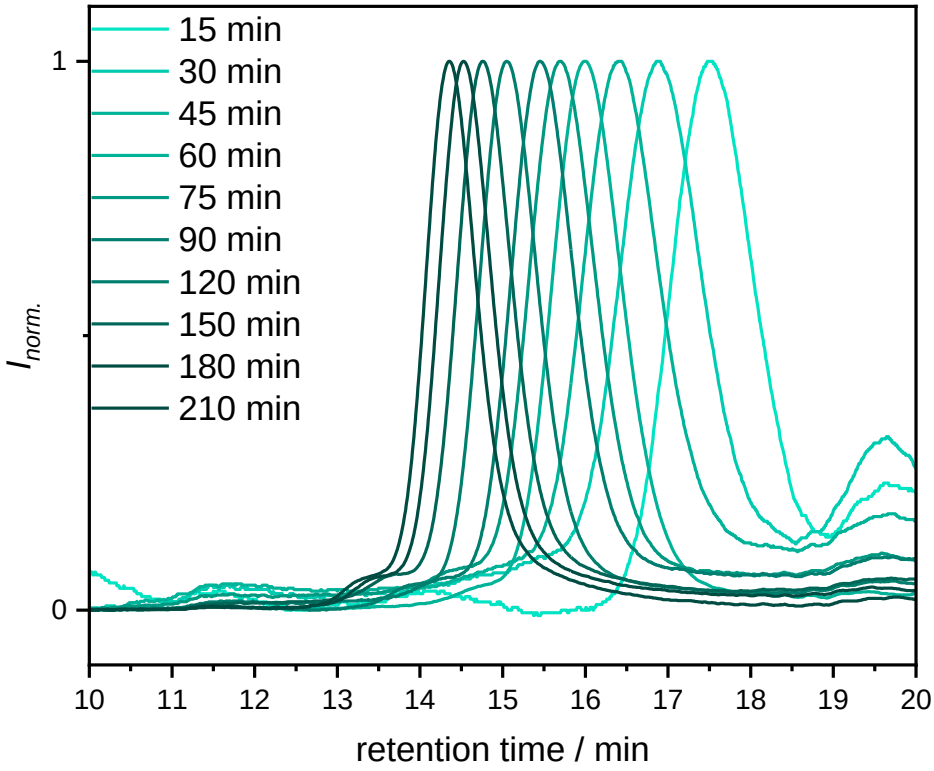
Supplementary Figure 106: SEC reaction monitoring of the ROP of ε-caprolactone with mPEG (M_n = 750 Da). Ratio of the monomer ε-caprolactone (M) to macroinitiator mPEG (I, M_n = 750 Da); M/I = 40.



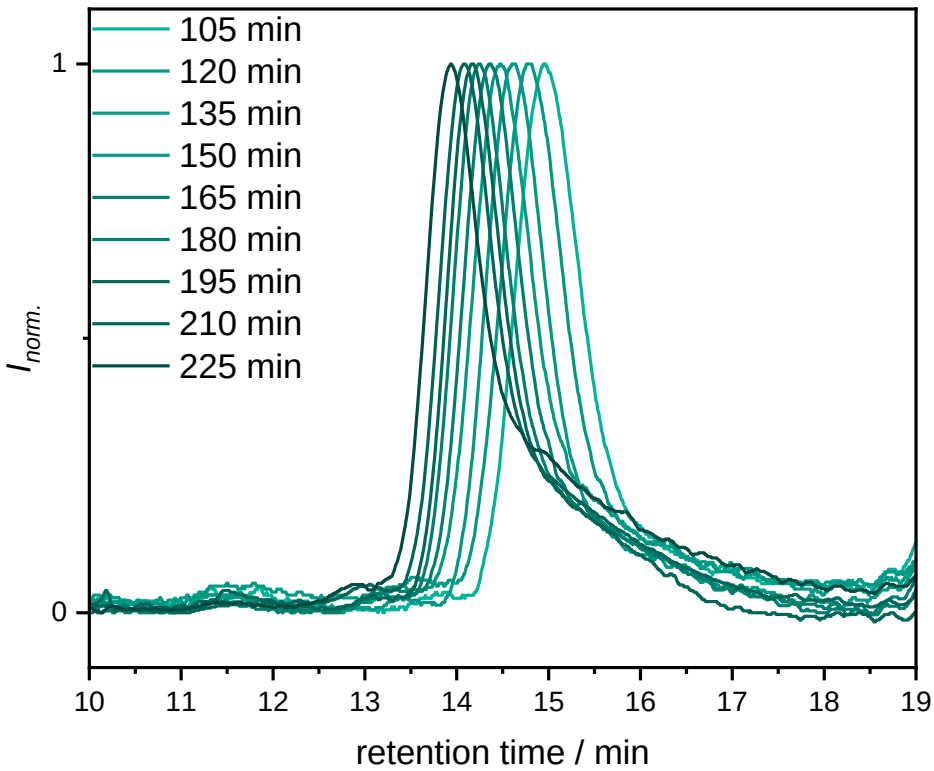
Supplementary Figure 107: SEC reaction monitoring of the ROP of ε-caprolactone with mPEG (M_n = 750 Da). Ratio of the monomer ε-caprolactone (M) to macroinitiator mPEG (I, M_n = 750 Da); M/I = 80.



Supplementary Figure 108: SEC reaction monitoring of the ROP of ε-caprolactone with mPEG (M_n = 750 Da). Ratio of the monomer ε-caprolactone (M) to macroinitiator mPEG (I, M_n = 750); M/I = 167.

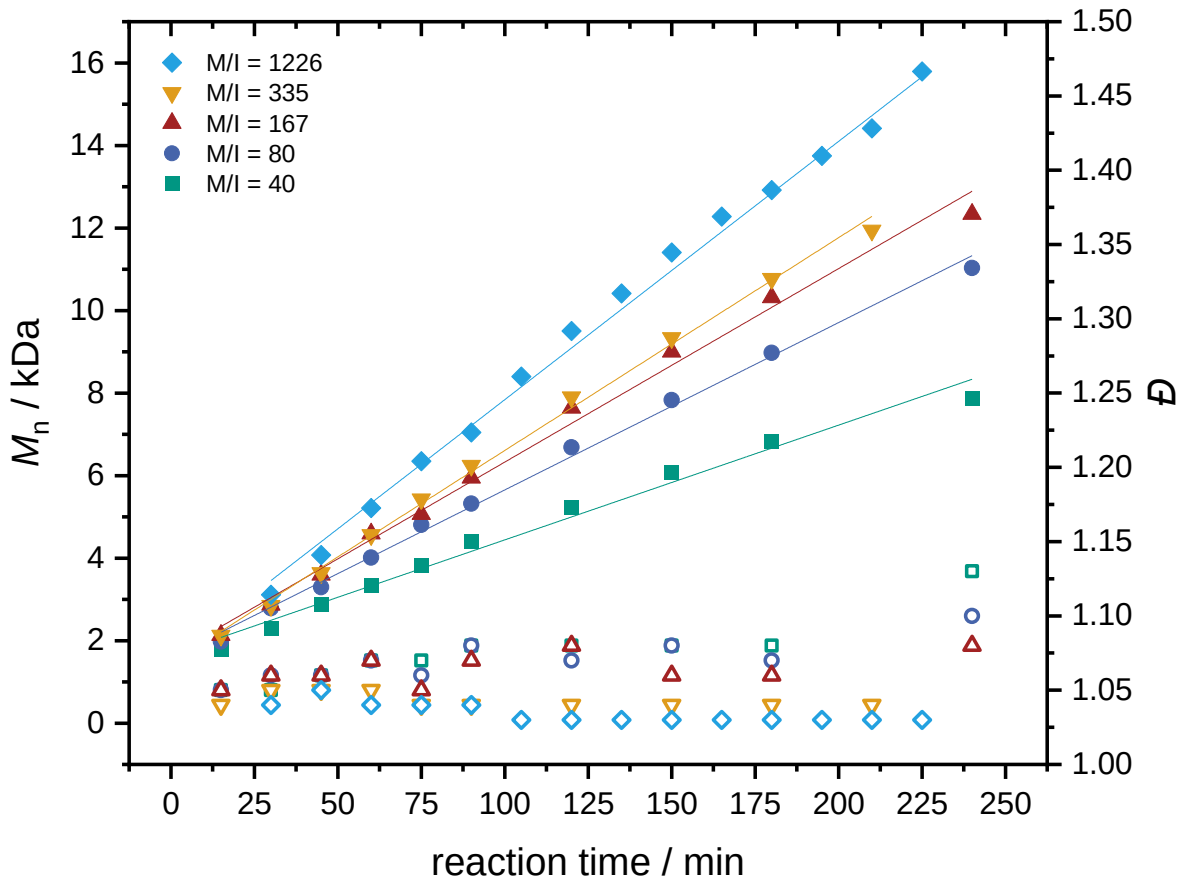


Supplementary Figure 109: SEC reaction monitoring of ROP of ε-caprolactone with mPEG (M_n = 750 Da). Ratio of the monomer ε-caprolactone (M) to macroinitiator mPEG (I, M_n = 750 Da); M/I = 335.



Supplementary Figure 110: SEC reaction monitoring of the ROP of ε-caprolactone with mPEG (M_n = 750 Da). Ratio of the monomer ε-caprolactone (M) to macroinitiator mPEG (I, M_n = 750 Da); M/I = 1226.

Supplementary Table 14: SEC data of the monitoring of the ROP of ε-caprolactone using mPEG as initiator.										
	M/I = 40		M/I = 80		M/I = 167		M/I = 335		M/I = 1226	
t / min	M_n / Da	*Đ*	M_n / Da	*Đ*	M_n / Da	*Đ*	M_n / Da	*Đ*	M_n / Da	*Đ*
15	1800	1.05	2000	1.05	2150	1.05	2100	1.04	-	-
30	2300	1.05	2800	1.06	2850	1.06	2850	1.05	3100	1.04
45	3850	1.06	3300	1.06	3600	1.06	3650	1.05	4100	1.05
60	3350	1.07	4000	1.07	4600	1.07	4550	1.05	5200	1.04
75	3850	1.07	4800	1.06	5050	1.05	5450	1.04	6350	1.04
90	4400	1.08	5300	1.08	5950	1.07	6250	1.04	7050	1.04
105	-	-	-	-	-	-	-	-	8400	1.03
120	5250	1.08	6700	1.07	7650	1.08	7900	1.04	9500	1.03
135	-	-	-	-	-	-	-	-	10400	1.03
150	6100	1.08	7850	1.08	9000	1.06	9350	1.04	11400	1.03
165	-	-	-	-	-	-	-	-	12300	1.03
180	6850	1.08	8950	1.07	10300	1.06	10750	1.04	12900	1.03
195	-	-	-	-	-	-	-	-	13750	1.03
210	-	-	-	-	-	-	11950	1.04	14400	1.03
225	-	-	-	-	-	-	-	-	15800	1.03
240	7850	1.13	1100	1.10	12350	1.08	-	-	-	-



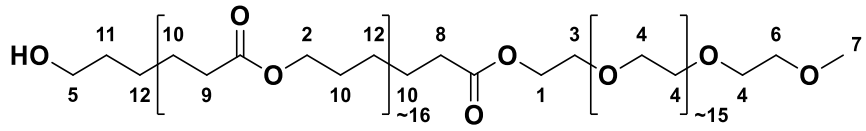
Supplementary Figure 111: ROP of ε-caprolactone (M) with the macroinitiator mPEG (I, M_n = 750 Da) and TBD as organocatalyst. The molecular weight M_n in kDa of the resulting dBCP is plotted against the reaction time in minutes, depended on the different M/I ratios. The open symbols represent the corresponding dispersity *Đ*.

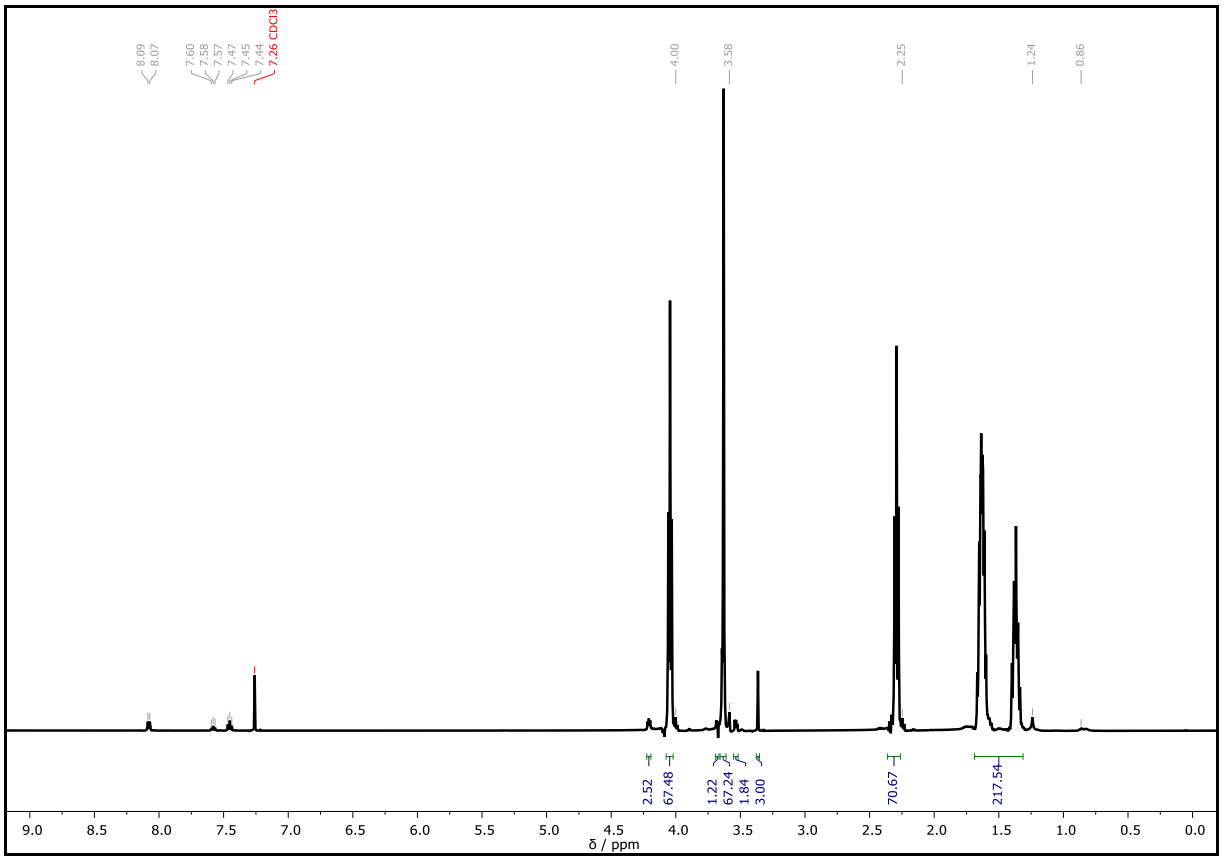
***p*-HO(CL)$_{17}$-(EG)$_{17}$OMe**

ε-Caprolactone	20.0 mL, 21.6 g, 189 mmol (167 equiv.)
mPEG (M_n = 750 Da)	848 mg, 1.13 mmol, (1.00 equiv.)
TBD	127 mg, 912 µmol (0.81 equiv.)
toluene (total amount)	90 mL
reaction time	52 min
yield	5.15 g

IR (ATR platinum diamond) $\tilde{\nu}$ / cm^{-1} = 3493, 2943, 2894, 2865, 1722, 1652, 1471, 1440, 1419, 1397, 1366, 1323, 1294, 1240, 1187, 1177, 1105, 1065, 1043, 961, 934, 860, 841, 815, 796, 788, 730, 716, 675, 654, 617, 584, 574, 562, 520, 514, 490, 479, 469, 453, 422, 411, 401.

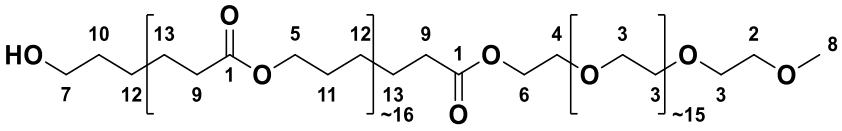
^{1}H NMR (500 MHz, $CDCl_3$): δ / ppm = 4.23 – 4.19 (m, CH_2^{1}), 4.04 (t, *J* = 6.6 Hz, CH_2^{2}), 3.69 – 3.67 (m, CH_2^{3}), 3.66 – 3.61 (m, CH_2^{4} and CH_2^{5}), 3.55 – 3.52 (m, CH_2^{6}), 3.36 (s, CH_3^{7}), 2.29 (t, *J* = 7.6 Hz, CH_2^{8} and CH_2^{9}), 1.69 – 1.31 (m, CH_2^{10}, CH_2^{11} and CH_2^{12}).

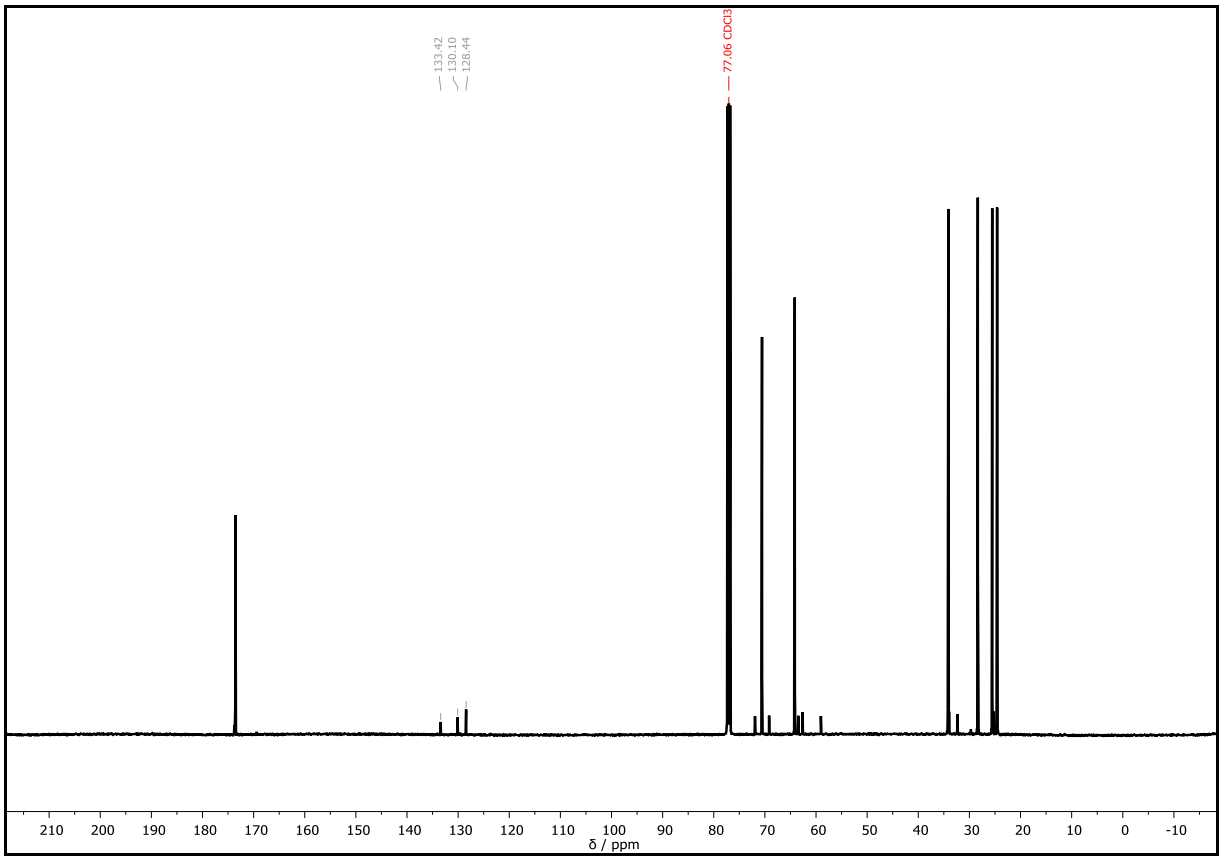




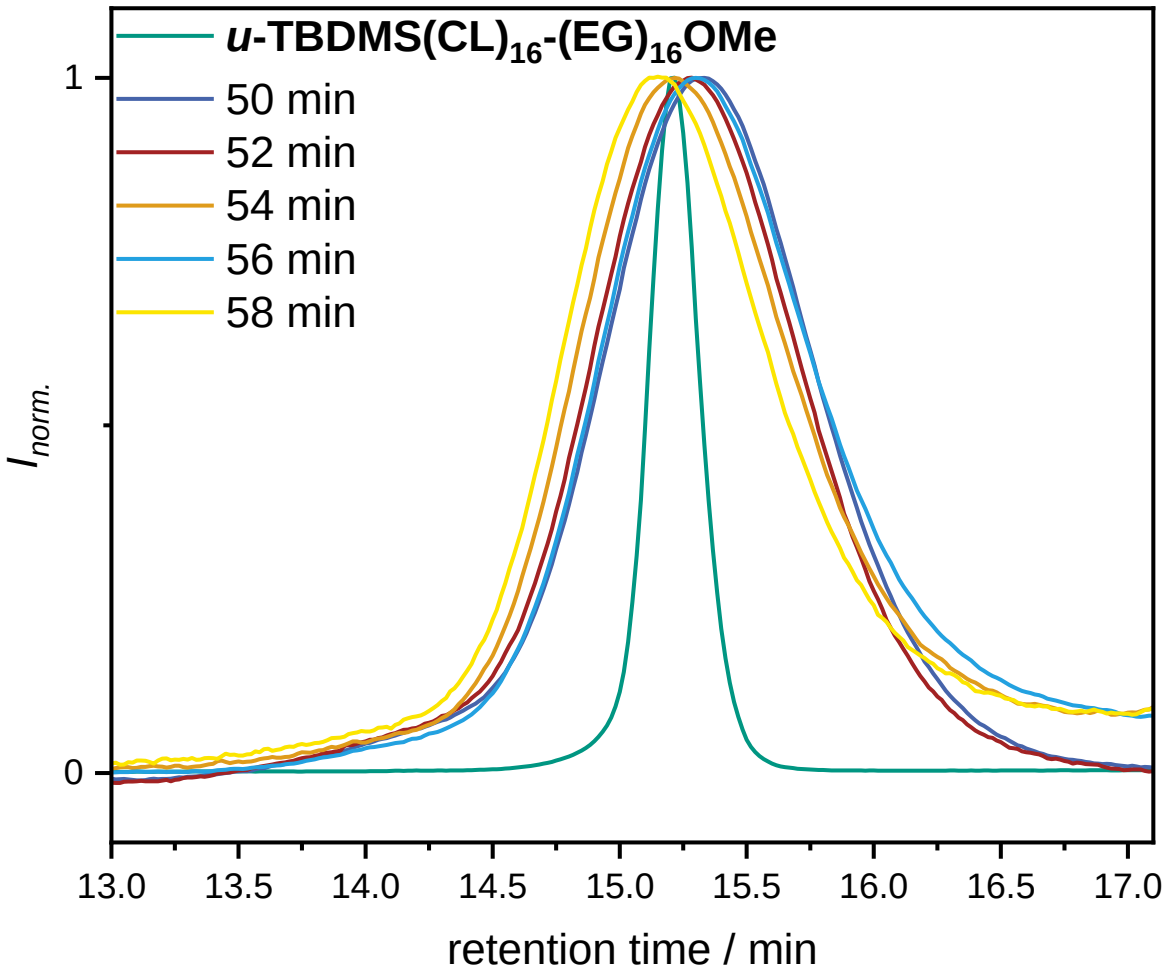
Supplementary Figure 112: ^{1}H NMR spectrum of ***p*-HO(CL)$_{17}$-(EG)$_{17}$OMe** recorded at 500 MHz in $CDCl_3$. Impurities are marked in grey.

^{13}C NMR (126 MHz, $CDCl_3$): δ / ppm = 173.76 (C_q^1), 173.62 (C_q^1), 173.59 (C_q^1), 173.57 (C_q^1), 173.48 (C_q^1), 71.94 (CH_2^2), 70.61 (CH_2^3), 70.57 (CH_2^3), 70.51 (CH_2^3), 69.18 (CH_2^4), 64.16 (CH_2^5), 64.12 (CH_2^5), 63.45 (CH_2^6), 62.62 (CH_2^7), 59.05 (CH_3^8), 34.24 (CH_2^9), 34.19 (CH_2^9), 34.15 (CH_2^9), 34.12 (CH_2^9), 33.98 (CH_2^9), 32.33 (CH_2^{10}), 28.35 (CH_2^{11}), 25.57 (CH_2^{12}), 25.54 (CH_2^{12}), 25.50 (CH_2^{12}), 24.69 (CH_2^{13}), 24.58 (CH_2^{13}), 24.50 (CH_2^{13}).





Supplementary Figure 113 ^{13}C NMR spectrum of ***p*-HO(CL)$_{17}$-(EG)$_{17}$OMe** recorded at 126 MHz in $CDCl_3$. Impurities are marked in grey.



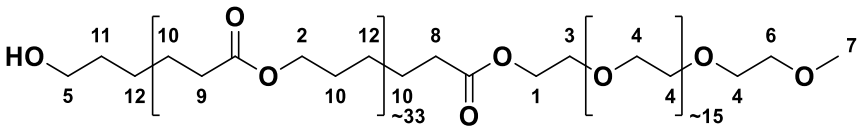
Supplementary Figure 114. SEC traces of the ring-opening polymerization of ε-caprolactone (M/I = 167) after the respective reaction time in comparison to ***i*-TBDMS(CL)$_{16}$-(EG)$_{16}$OMe**.

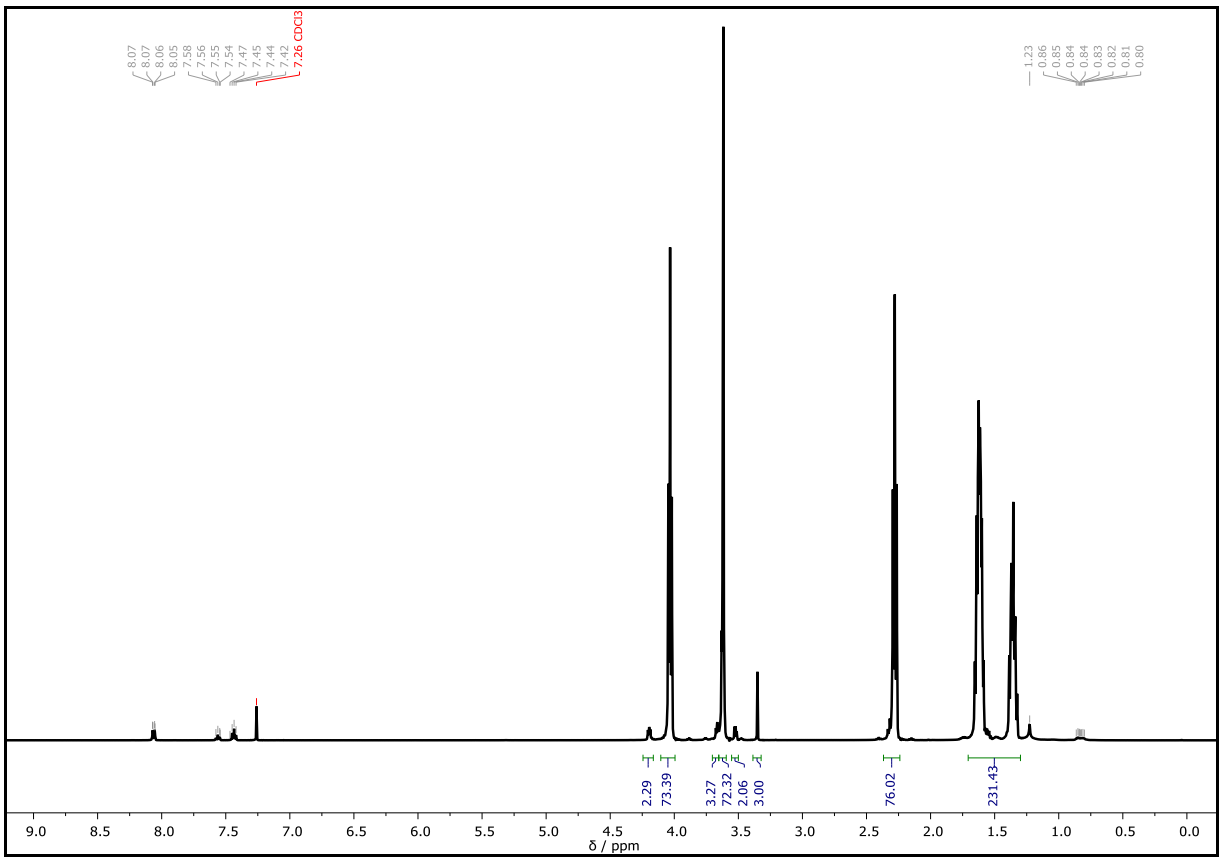
***p*-HO(CL)$_{34}$-(EG)$_{17}$OMe**

ε-Caprolactone	20.0 mL, 21.6 g, 189 mmol (335 equiv.)
mPEG (M_n = 750 Da)	424 mg, 565 µmol, (1.00 equiv.)
TBD	127 mg, 912 µmol (1.61 equiv.)
toluene (total amount)	90 mL
reaction time	109 min
yield	6.35 g
eluent	EA → EA:MeOH = 9:1 → acetone
R_f	0.41 (EA:MeOH = 9:1)

IR (ATR platinum diamond) $\tilde{\nu}$ / cm^{-1} = 3507, 2943, 2894, 2865, 1722, 1471, 1438, 1419, 1397, 1366, 1294, 1238, 1174, 1105, 1065, 1043, 961, 934, 841, 810, 775, 732, 714, 648, 584, 555, 525, 512, 502, 485, 453, 436, 428, 413.

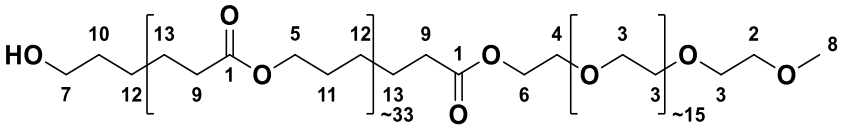
^{1}H NMR (500 MHz, $CDCl_3$): δ / ppm = 4.23 – 4.17 (m, CH_2^1), 4.03 (t, *J* = 6.7 Hz, CH_2^2), 3.66 (dd, *J* = 5.7, 4.1 Hz, CH_2^3), 3.65 (s, CH_2^4 and CH_2^5), 3.52 (dd, *J* = 5.8, 3.6 Hz, CH_2^6), 3.35 (s, CH_3^7), 2.28 (t, *J* = 7.5 Hz, CH_2^8 and CH_2^9), 1.69 – 1.30 (m, CH_2^{10}, CH_2^{11} and CH_2^{12}).

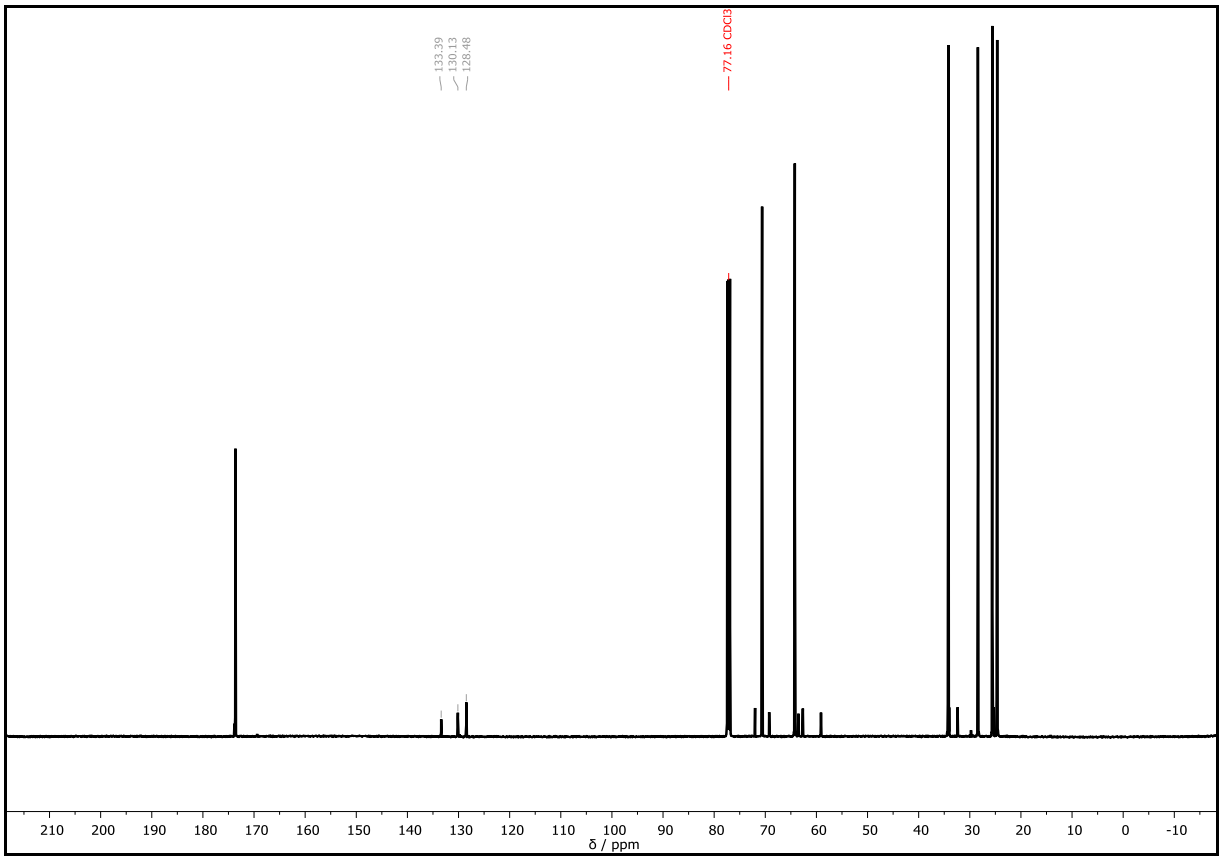




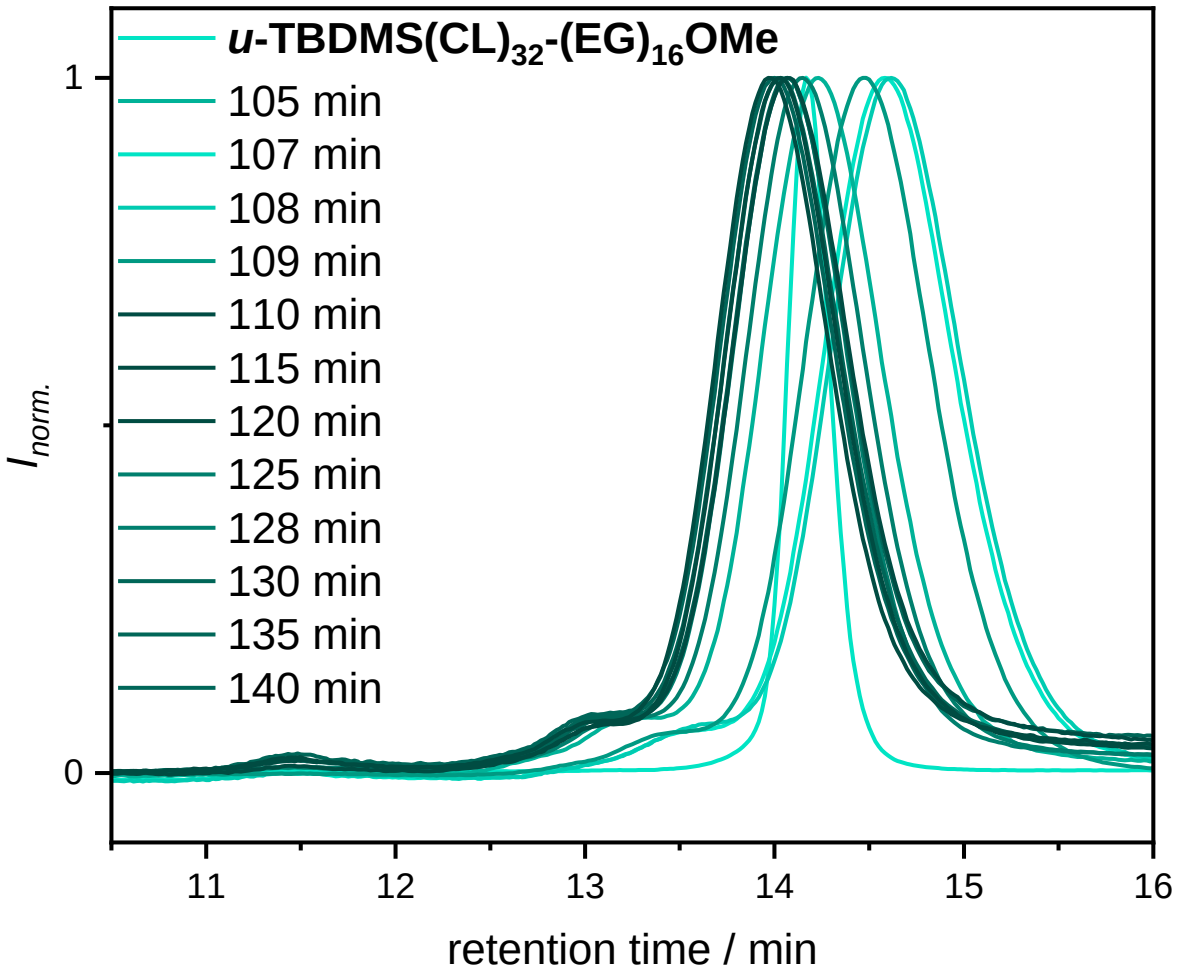
Supplementary Figure 115: ^{1}H NMR spectrum of ***p*-HO(CL)$_{34}$-(EG)$_{17}$OMe** recorded at 500 MHz in $CDCl_3$. Impurities are marked in grey.

^{13}C NMR (126 MHz, $CDCl_3$): δ / ppm = 173.83 (C_q^1), 173.69 (C_q^1), 173.66 (C_q^1), 173.63 (C_q^1), 173.55 (C_q^1), 72.00 (CH_2^2), 70.68 (CH_2^3), 70.67 (CH_2^3), 70.63 (CH_2^3), 70.57 (CH_2^3), 69.24 (CH_2^4), 64.22 (CH_2^5), 64.18 (CH_2^5), 63.52 (CH_2^6), 62.65 (CH_2^7), 59.11 (CH_3^8), 34.30 (CH_2^9), 34.23 (CH_2^9), 34.19 (CH_2^9), 34.05 (CH_2^9), 32.39 (CH_2^{10}), 28.42 (CH_2^{11}), 25.63 (CH_2^{12}), 25.60 (CH_2^{12}), 25.57 (CH_2^{12}), 24.76 (CH_2^{13}), 24.65 (CH_2^{13}), 24.57 (CH_2^{13}).

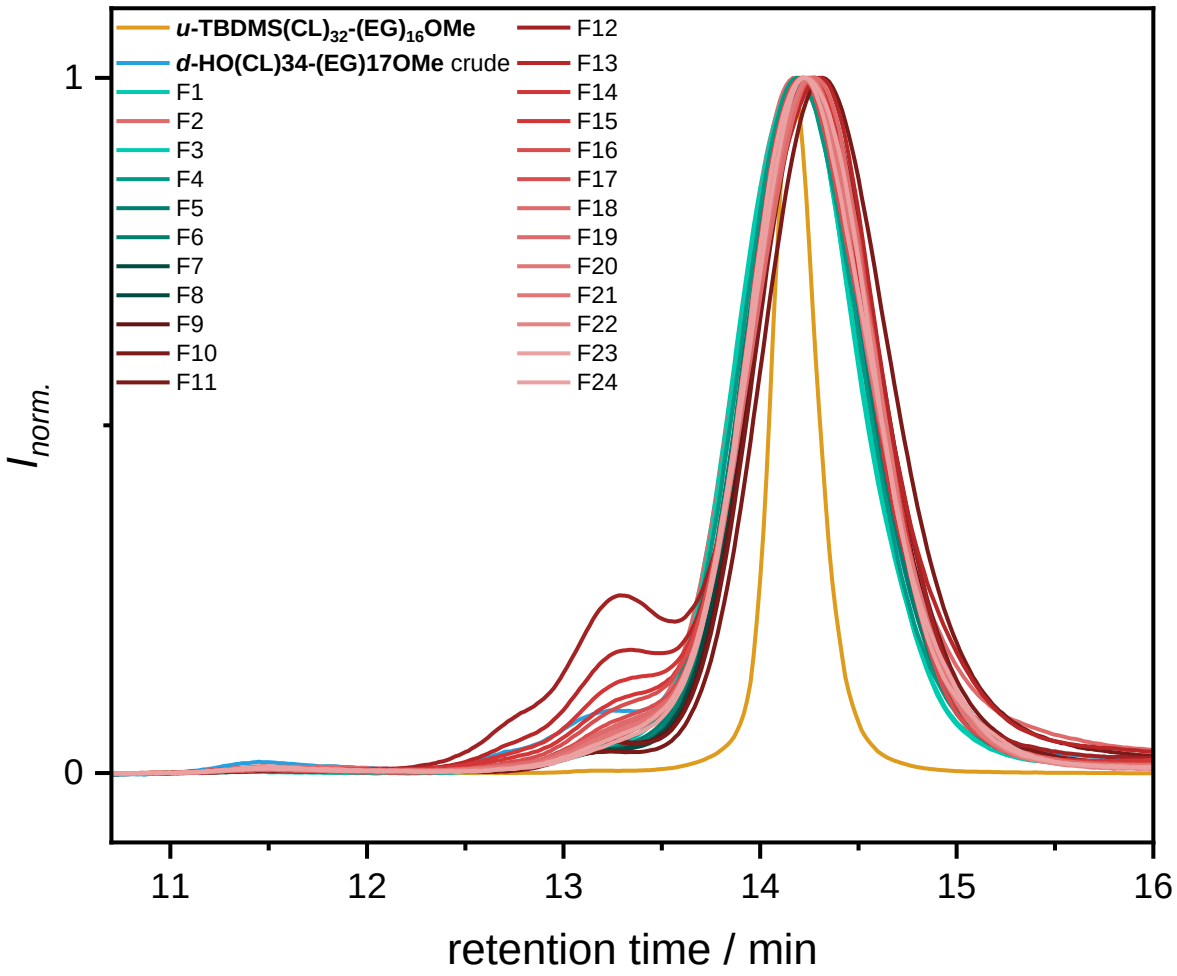




Supplementary Figure 116 ^{13}C NMR spectrum of ***p*-HO(CL)$_{34}$-(EG)$_{17}$OMe** recorded at 126 MHz in $CDCl_3$. Impurities are marked in grey.



Supplementary Figure 117: SEC traces of the ROP of ε-caprolactone (M/I = 335) after the respective reaction time in comparison to ***i*-TBDMS(CL)$_{32}$-(EG)$_{16}$OMe**.



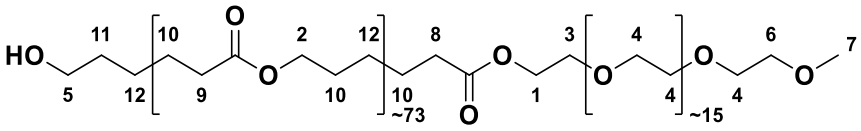
Supplementary Figure 118: SEC traces of the individual fractions of the column chromatographic purification of ***p*-HO(CL)$_{34}$-(EG)$_{17}$OMe** (109 min.) in comparison to the crude product (blue trace) and ***i*-TBDMS(CL)$_{32}$-(EG)$_{16}$OMe** (yellow trace). The fractions in green were combined and employed in the subsequent protection step. The fractions in red were discarded.

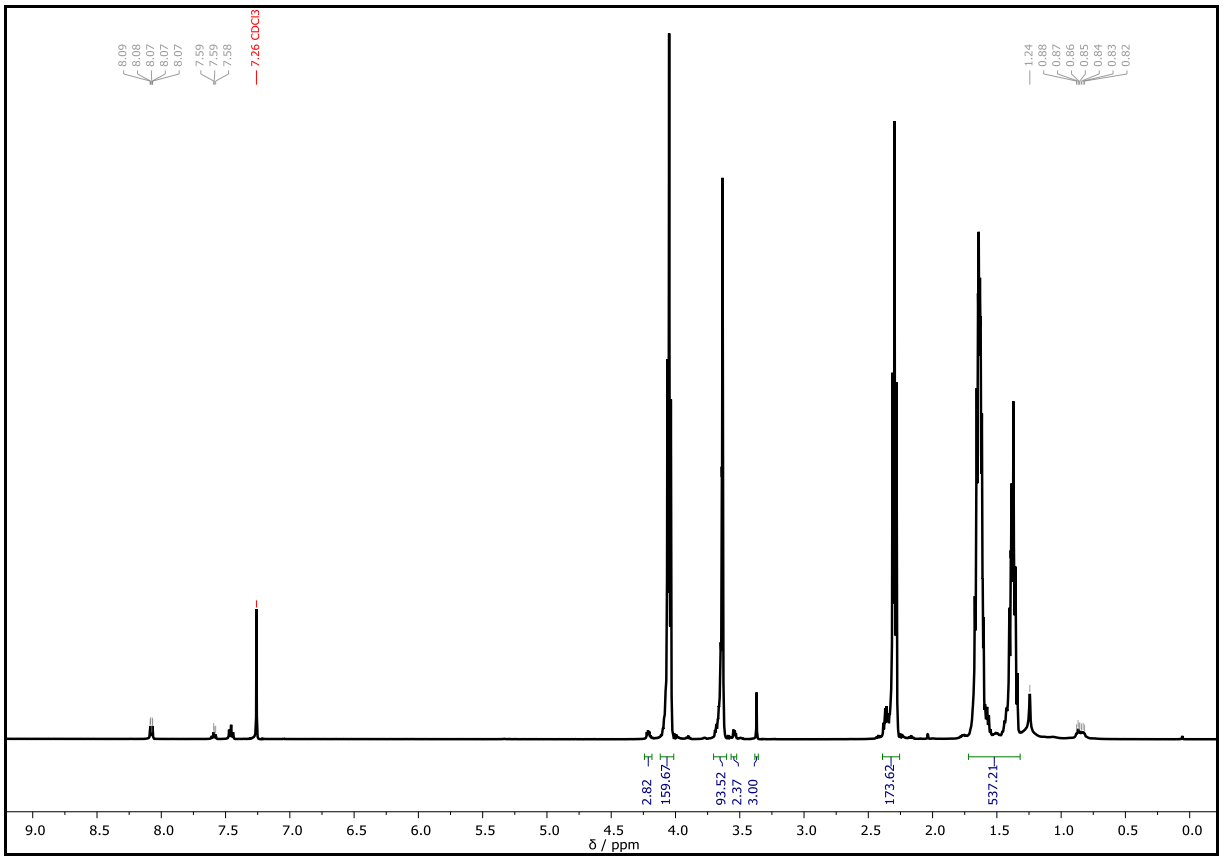
***p*-HO(CL)$_{74}$-(EG)$_{17}$OMe**

ε-Caprolactone	10.0 mL, 10.3 g, 90.2 mmol (1226 equiv.)
mPEG (M_n = 750 Da)	55.2 mg, 73.6 µmol (1.00 equiv.)
TBD	67.0 mg, 481 µmol (6.54 equiv.)
toluene (total amount)	45 mL
reaction time	225 min
yield	350 mg
eluent	EE → EE:MeOH = 9:1 → acetone
R_f	0.61 (EE:MeOH = 9:1)
Đ (system II)	1.05 (1.18 before purification)

IR (ATR platinum diamond) $\tilde{\nu}$ / cm^{-1} = 3449, 2941, 2896, 2865, 1722, 1471, 1419, 1397, 1366, 1294, 1240, 1185, 1177, 1107, 1065, 1045, 961, 934, 887, 866, 841, 732, 714, 582, 453.

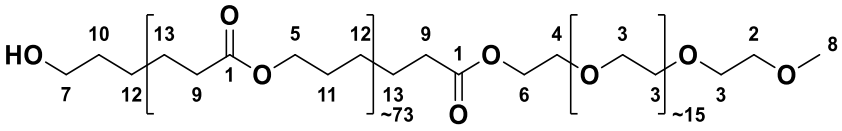
^{1}H NMR (500 MHz, $CDCl_3$): δ / ppm = 4.24 – 4.18 (m, CH_2^{1}), 4.05 (t, *J* = 6.7 Hz, CH_2^{3}), 3.70 – 3.61 (m, CH_2^{3}, CH_2^{4} and CH_2^{5}), 3.54 (dd, *J* = 5.8, 3.6 Hz, CH_2^{6}), 3.37 (s, CH_3^{7}), 2.39 – 2.27 (m, CH_2^{8} and CH_2^{9}), 1.72 – 1.33 (m, CH_2^{10}, CH_2^{11} and CH_2^{12}).

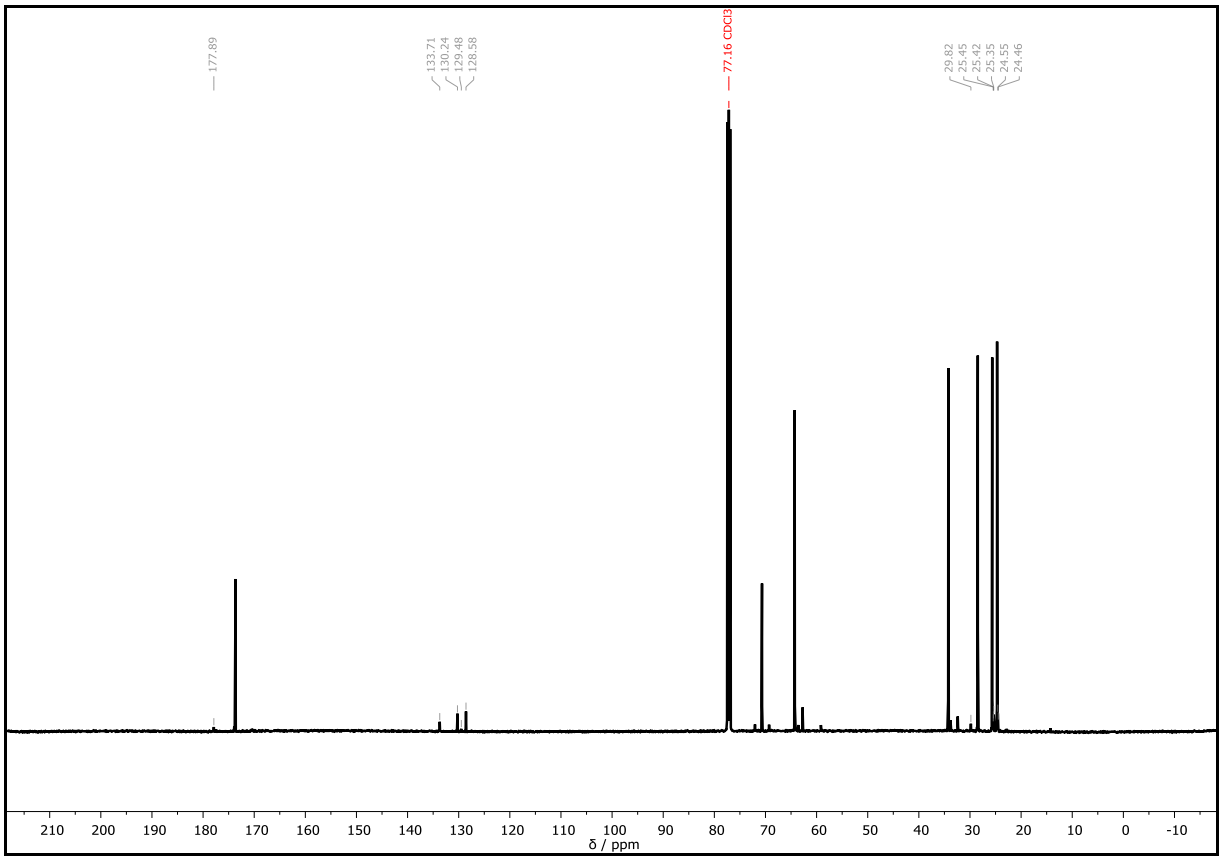




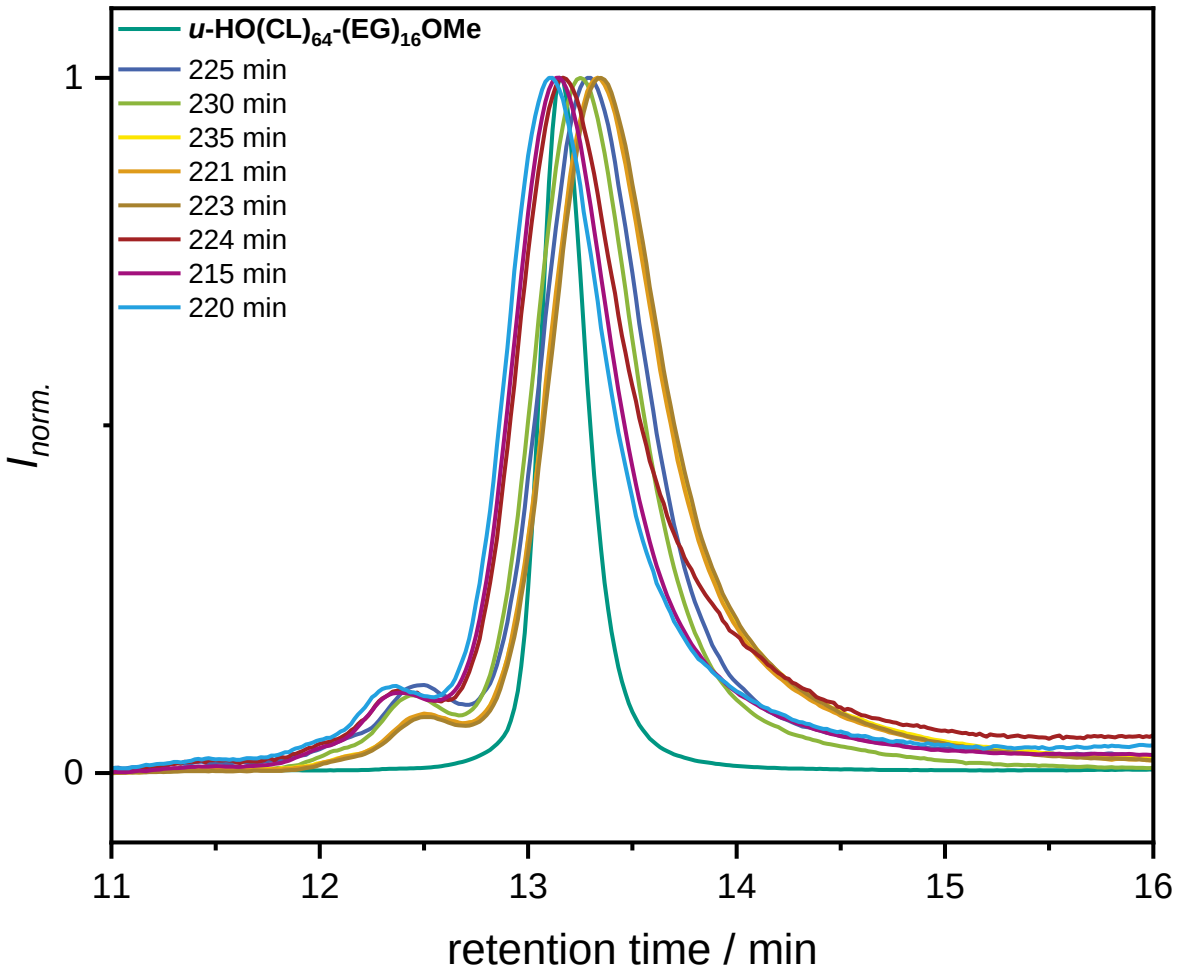
Supplementary Figure 119: ^{1}H NMR spectrum of ***p*-HO(CL)$_{74}$-(EG)$_{17}$OMe** recorded at 500 MHz in $CDCl_3$. Impurities are marked in grey.

^{13}C NMR (126 MHz, $CDCl_3$): δ / ppm = 173.91 (C_q^1), 173.70 (C_q^1), 173.61 (C_q^1), 72.05 (CH_2^2), 70.72 (CH_2^3), 70.68 (CH_2^3), 70.63 (CH_2^3), 69.29 (CH_2^4), 64.28 (CH_2^5), 64.13 (CH_2^5), 63.58 (CH_2^6), 62.81 (CH_2^7), 59.16 (CH_3^8), 34.40 (CH_2^9), 34.35 (CH_2^9), 34.29 (CH_2^9), 34.24 (CH_2^9), 34.10 (CH_2^9), 32.43 (CH_2^{10}), 32.39 (CH_2^{10}), 32.34 (CH_2^{10}), 28.47 (CH_2^{11}), 25.65 (CH_2^{12}), 25.60 (CH_2^{12}), 25.54 (CH_2^{12}), 24.80 (CH_2^{13}), 24.70 (CH_2^{13}), 24.62 (CH_2^{13}).

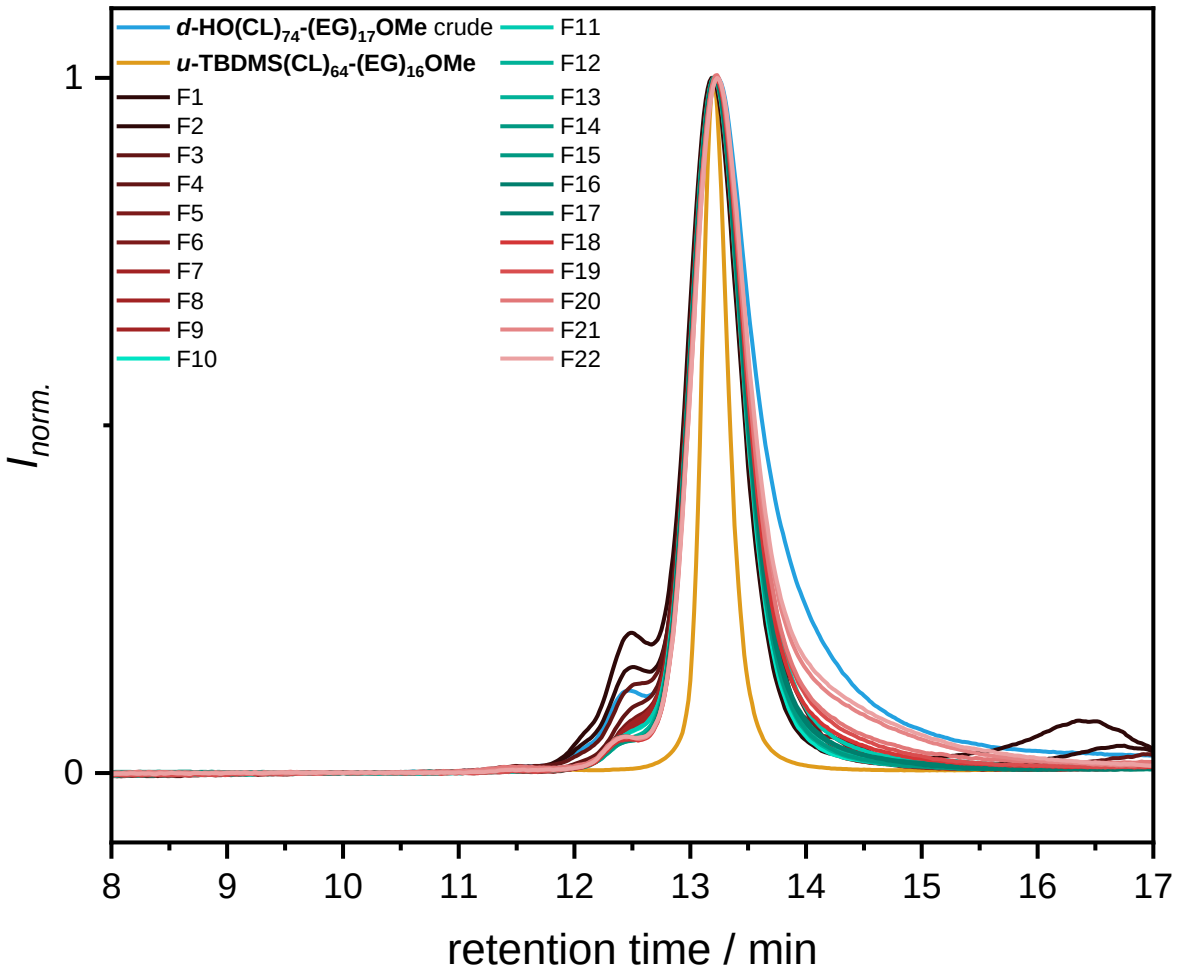




Supplementary Figure 120: ^{1}H NMR spectrum of ***p*-HO(CL)$_{74}$-(EG)$_{17}$OMe** recorded at 126 MHz in $CDCl_3$. Impurities are marked in grey.



Supplementary Figure 121: SEC traces of the ROP of ε-caprolactone (M/I = 1226) after the respective reaction time in comparison to ***i*-TBDMS(CL)$_{64}$-(EG)$_{16}$OMe**.



Supplementary Figure 122: SEC traces of the individual fractions of the column chromatographic purification of ***p*-HO(CL)$_{74}$-(EG)$_{17}$OMe** (225 min.) in comparison to the crude product (blue trace) and ***i*-TBDMS(CL)$_{64}$-(EG)$_{16}$OMe** (yellow trace). The fractions in green were combined and employed in the subsequent protection step. The fractions in red were discarded.

General procedure for the protection of the BCP alcohol with TBDMS-Cl

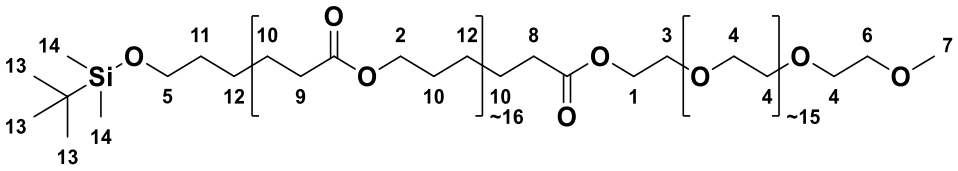
1*H*-Imidazole (30.0 equiv.) was added to a solution of the BCP alcohol (1.00 equiv.) in dry DMF. The reaction was stirred for 10 min at room temperature and TBDMS-Cl (30.0 equiv.) was added. The mixture was stirred at 50 °C under argon atmosphere overnight. The product was precipitated in cold *n*-hexane. The precipitate was dissolved in DCM, washed with water (2 ×) and brine (2 ×), filtered and the solvent was removed under reduced pressure. The crude product was purified *via* column chromatography (1st column chromatography: EA → EA:MeOH = 99:1 → 9:1 → acetone; 2nd column chromatography: EA → acetone). The quantities of the starting materials are mentioned in the corresponding sections.

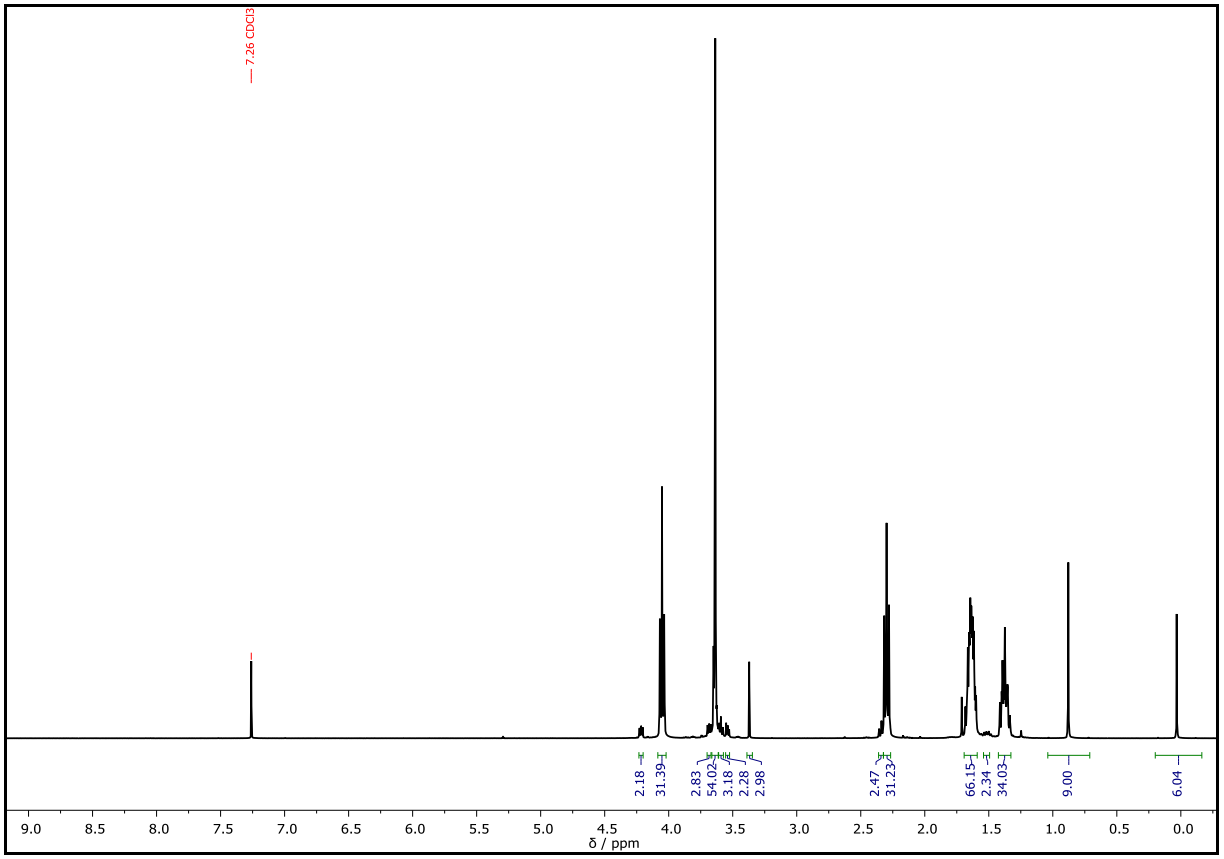
***p*-TBDMS(CL)$_{17}$-(EG)$_{17}$OMe**

1*H*-imidazole	573 mg, 8.41 mmol, 30.0 equiv.
***p*-HO(CL)$_{17}$-(EG)$_{17}$OMe**	750 mg, 280 µmol, 1.00 equiv.
TBDMS-Cl	1.27 g, 8.41 mmol, 30.0 equiv.
dry DMF	7.50 mL
yield	122 mg
R_f(product)	0.18 (EA:MeOH = 9:1)
Đ (system II)	1.06

IR (ATR platinum diamond) $\tilde{\nu}$ / cm^{-1} = 2943, 2894, 2865, 1722, 1471, 1438, 1419, 1397, 1366, 1323, 1294, 1240, 1187, 1105, 1065, 1045, 961, 934, 837, 775, 732, 710, 582, 578, 557, 533, 522, 502, 485, 467, 453, 418, 409.

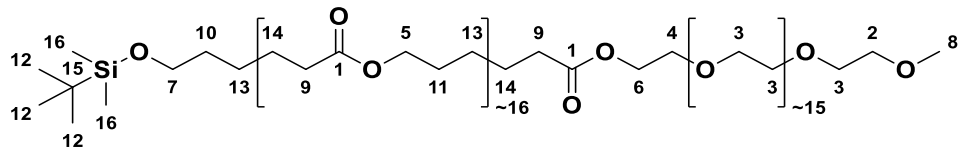
^{1}H NMR (400 MHz, $CDCl_3$): δ / ppm = 4.25 – 4.18 (m, 2H, CH_2^{1}), 4.05 (t, *J* = 6.7 Hz, 32H, CH_2^{2}), 3.70 – 3.67 (m, 2H, CH_2^{3}), 3.65 – 3.62 (m, 54H, CH_2^{4}), 3.59 (t, *J* = 6.5 Hz, 2H, CH_2^{5}), 3.56 – 3.52 (m, 2H, CH_2^{6}), 3.37 (s, 3H, CH_3^{7}), 2.35 (t, *J* = 7.5 Hz, 2H, CH_2^{8}), 2.30 (t, *J* = 7.5 Hz, 32H, CH_2^{9}), 1.69 – 1.59 (m, 66H, CH_2^{10}), 1.54 – 1.49 (m, 2H, CH_2^{11}), 1.42 – 1.33 (m, 34H, CH_2^{12}), 0.88 (s, 9H, CH_3^{13}), 0.03 (s, 6H, CH_3^{14}).

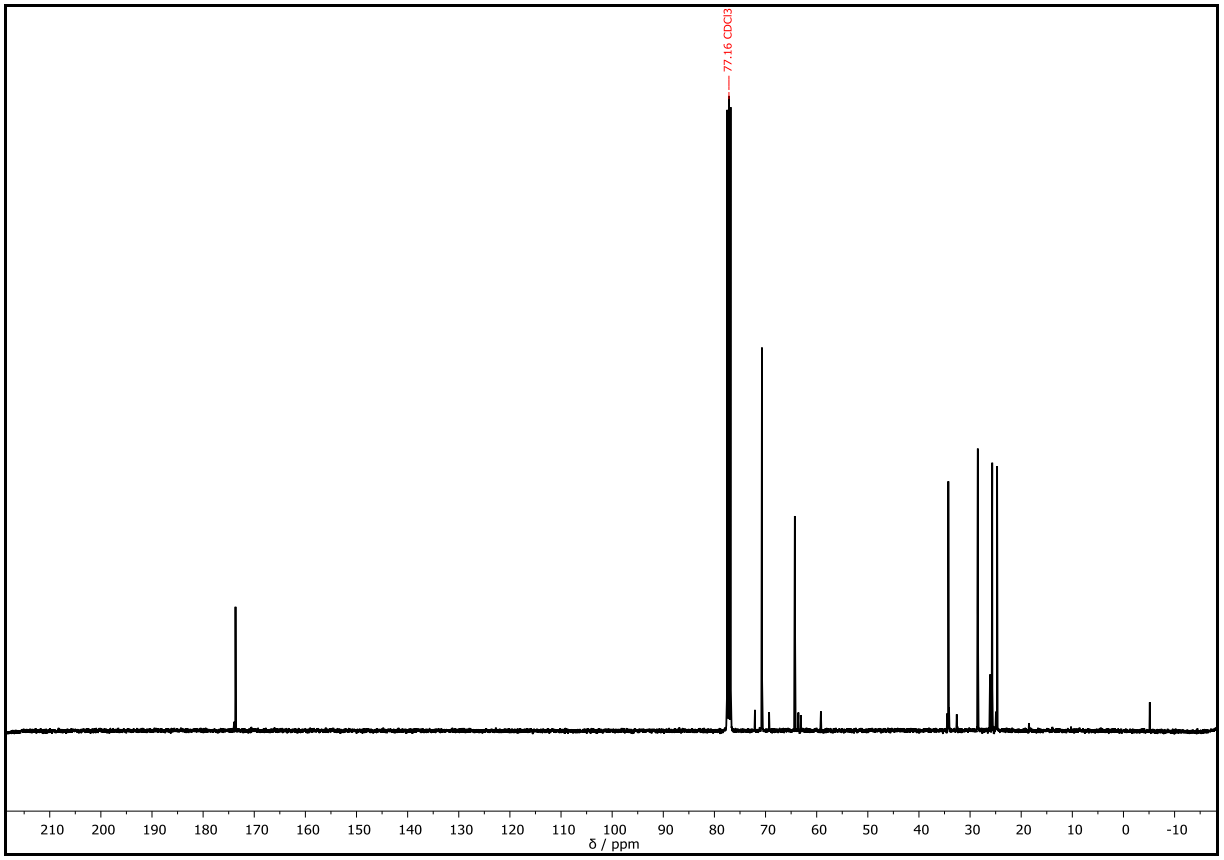




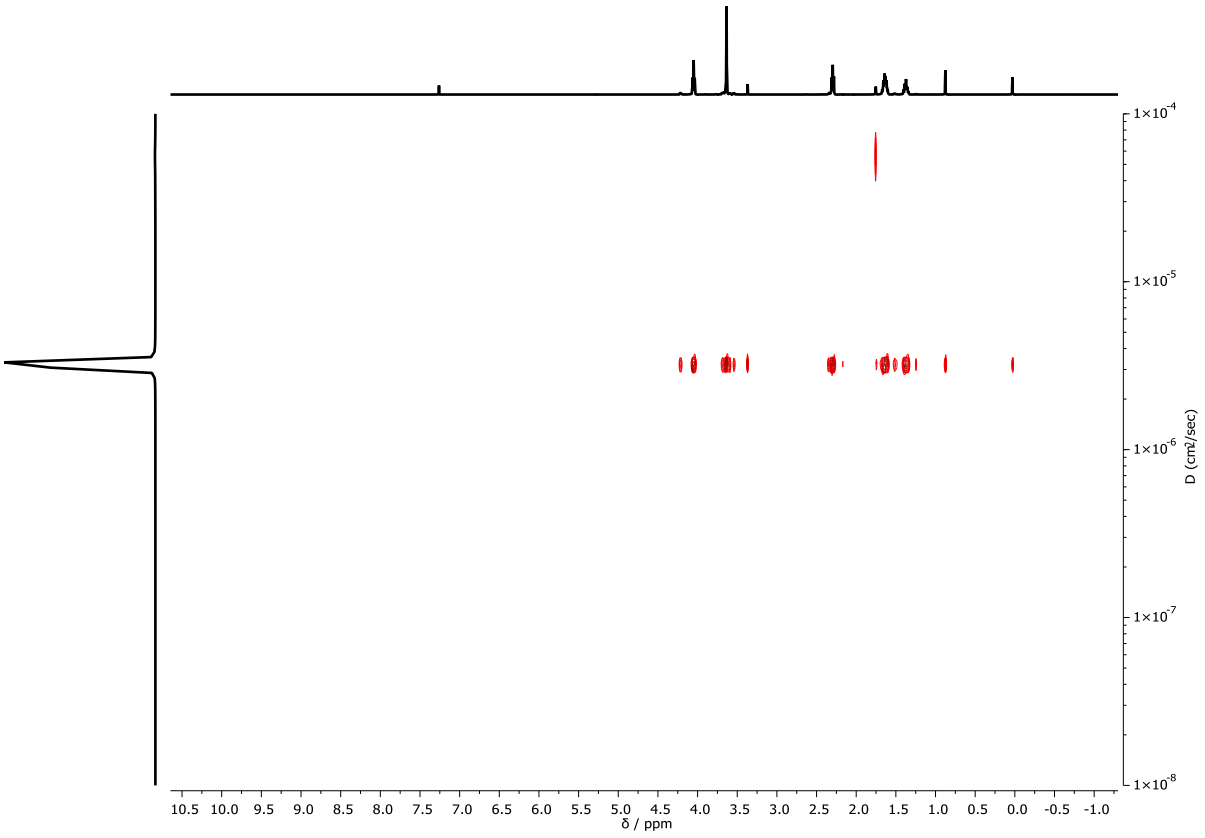
Supplementary Figure 123: ^{1}H NMR spectrum of ***p*-TBDMS(CL)$_{17}$-(EG)$_{17}$OMe** recorded at 500 MHz in $CDCl_3$.

^{13}C NMR (101 MHz, $CDCl_3$): δ / ppm = 173.93 (C_q^1), 173.66 (C_q^1), 173.59 (C_q^1), 72.07 (CH_2^2), 70.70 (CH_2^3), 69.31 (CH_2^4), 64.27 (CH_2^5), 64.18 (CH_2^5), 63.58 (CH_2^6), 63.10 (CH_2^7), 59.17 (CH_3^8), 34.47 (CH_2^9), 34.25 (CH_2^9), 34.11 (CH_2^9), 32.60 (CH_2^{10}), 28.49 (CH_2^{11}), 26.10 (CH_3^{12}), 25.67 (CH_2^{13}), 25.58 (CH_2^{13}), 24.94 (CH_2^{14}), 24.71 (CH_2^{14}), 24.63 (CH_2^{14}), 18.48 (C_q^{15}), -5.15 (CH_3^{16}).

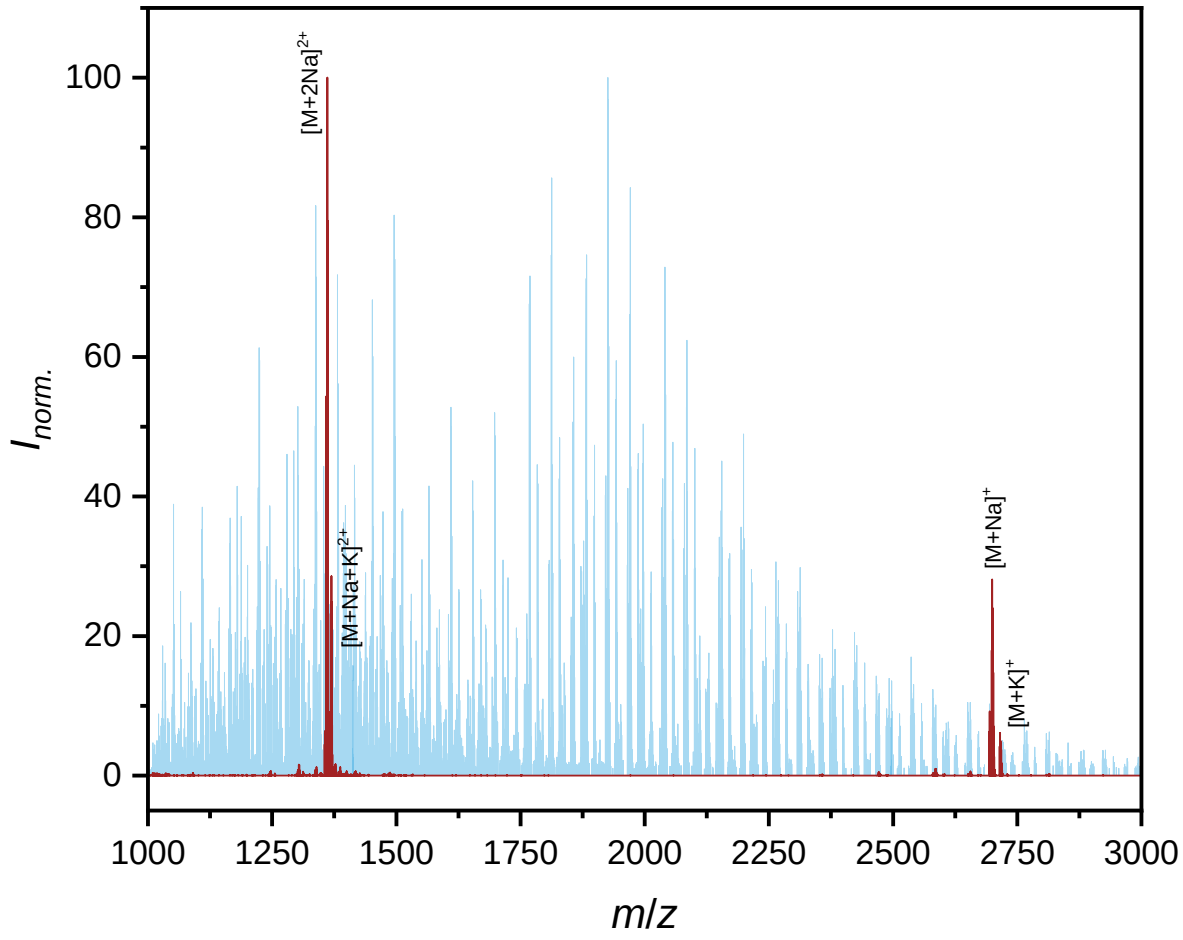




Supplementary Figure 124: ^{13}C NMR spectrum of ***p*-TBDMS(CL)$_{17}$-(EG)$_{17}$OMe** recorded at 126 MHz in $CDCl_3$.



Supplementary Figure 125: DOSY NMR spectrum of ***p*-TBDMS(CL)$_{17}$-(EG)$_{17}$OMe** recorded at 500 MHz in $CDCl_3$.



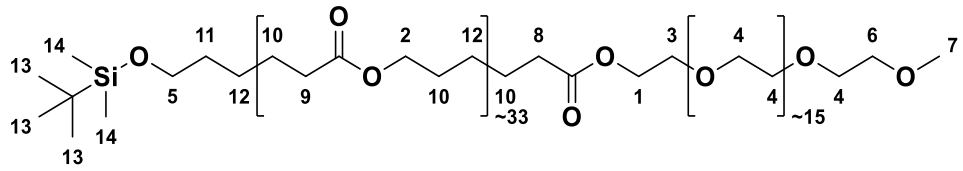
Supplementary Figure 126: ESI-MS spectrum of ***p*-TBDMS(CL)$_{17}$-(EG)$_{17}$OMe** (blue) in comparison to ***i*-TBDMS(CL)$_{16}$-(EG)$_{16}$OMe** (red).

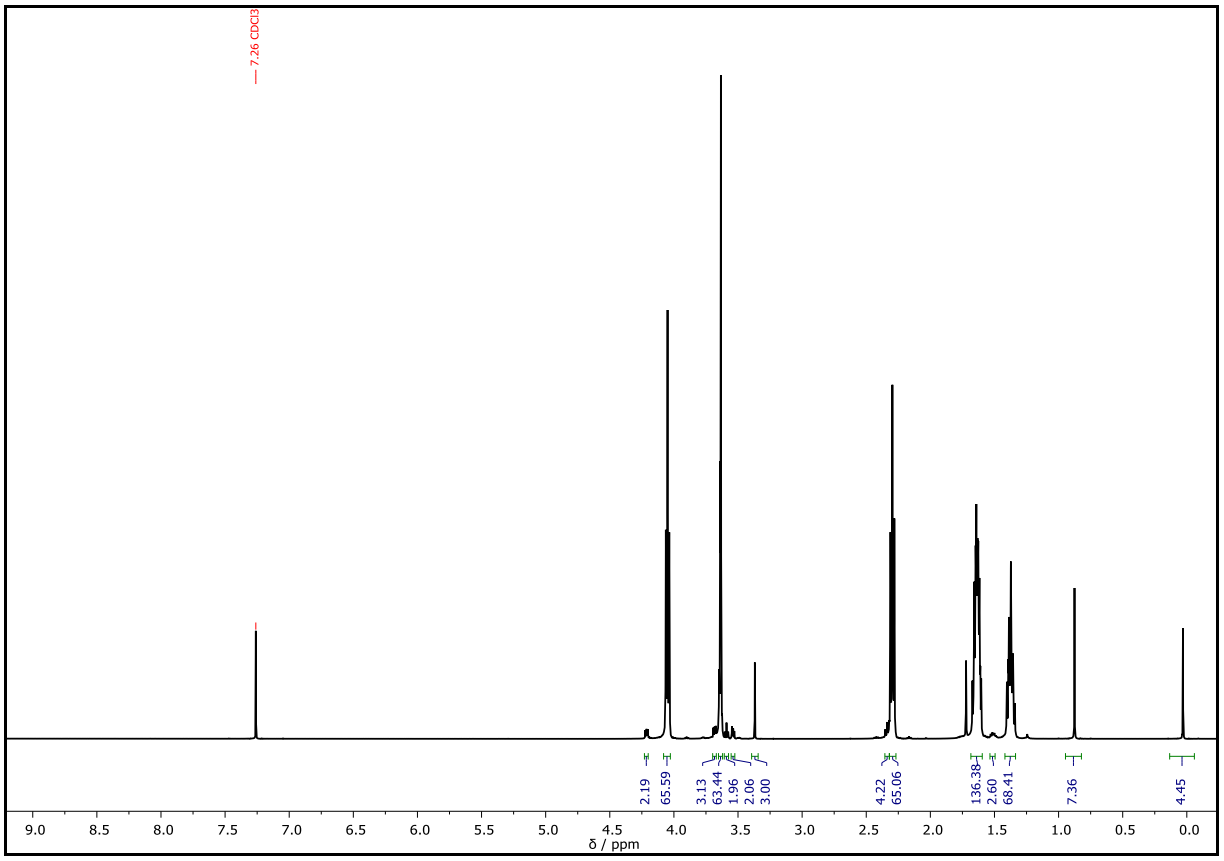
***p*-TBDMS(CL)$_{34}$-(EG)$_{17}$OMe**

1*H*-imidazole	227 mg, 3.33 mmol, 30.0 equiv.
***p*-HO(CL)$_{34}$-(EG)$_{17}$OMe**	500 mg, 111 µmol, 1.00 equiv.
TBDMS-Cl	502 mg, 3.33 mmol, 30.0 equiv.
dry DMF	5.00 mL
yield	160 mg
R_f(product)	0.19 (EA:MeOH = 9:1)
Đ (system II)	1.06

IR (ATR platinum diamond) $\tilde{\nu}$ / cm^{-1} = 2943, 2894, 2865, 1722, 1471, 1438, 1419, 1397, 1366, 1323, 1294, 1238, 1177, 1105, 1065, 1043, 961, 934, 839, 817, 775, 732, 710, 584, 541, 522, 453, 436, 424, 401.

^{1}H NMR (500 MHz, $CDCl_3$): δ / ppm = 4.23 – 4.20 (m, 2H, CH_2^1), 4.05 (t, *J* = 6.7 Hz, 66H, CH_2^2), 3.70 – 3.67 (m, 2H, CH_2^3), 3.65 – 3.62 (m, 64H, CH_2^4), 3.59 (t, *J* = 6.5 Hz, 2H, CH_2^5), 3.55 – 3.53 (m, 2H, CH_2^6), 3.37 (s, 3H, CH_3^7), 2.34 (t, *J* = 7.8 Hz, 2H, CH_2^8), 2.30 (t, *J* = 7.5 Hz, 66H, CH_2^9), 1.69 – 1.59 (m, 134H, CH_2^{10}), 1.53 – 1.49 (m, 2H, CH_2^{11}), 1.42 – 1.34 (m, 68H, CH_2^{12}), 0.88 (s, 9H, CH_3^{13}), 0.03 (s, 6H, CH_3^{14}).

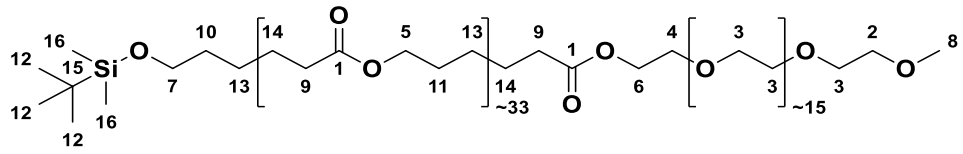


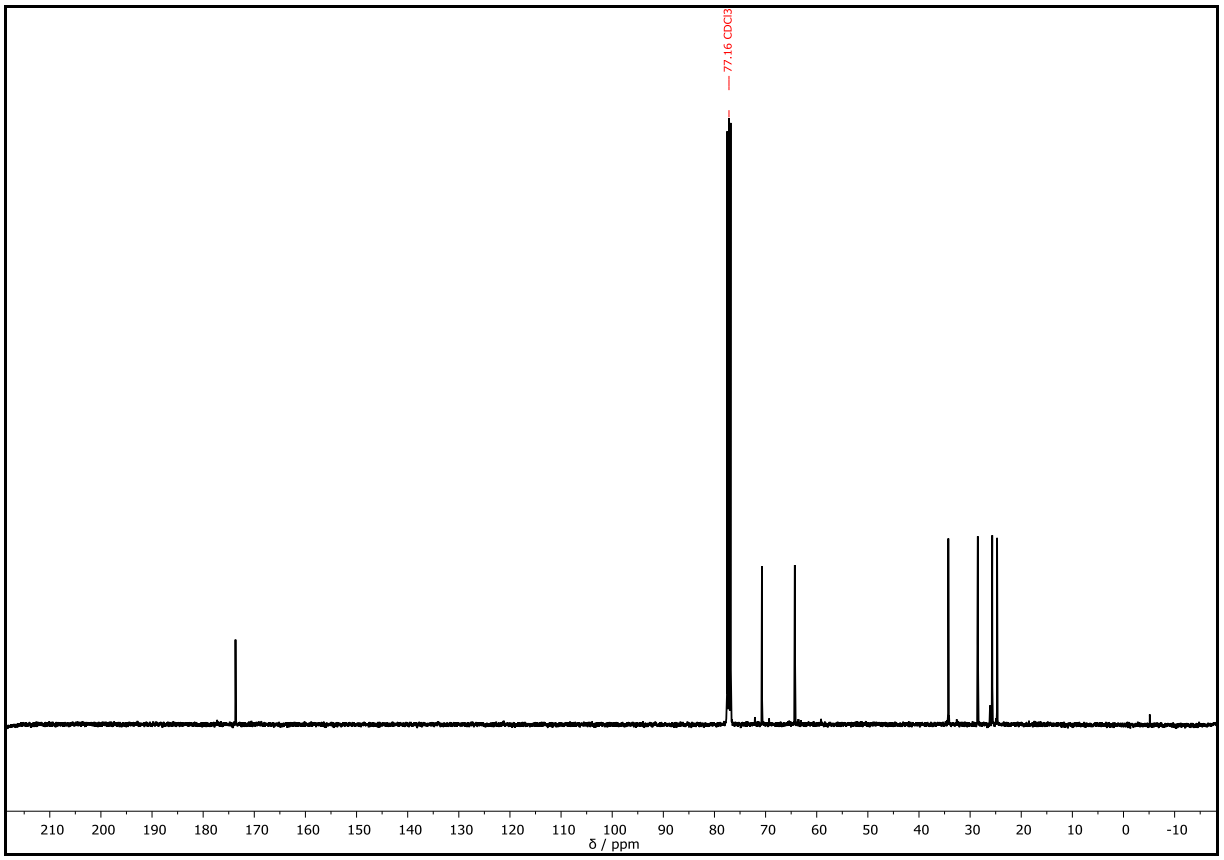


Supplementary Figure 127: ^{1}H NMR spectrum of ***p*-TBDMS(CL)$_{34}$-(EG)$_{17}$OMe** recorded at 500 MHz in $CDCl_3$.

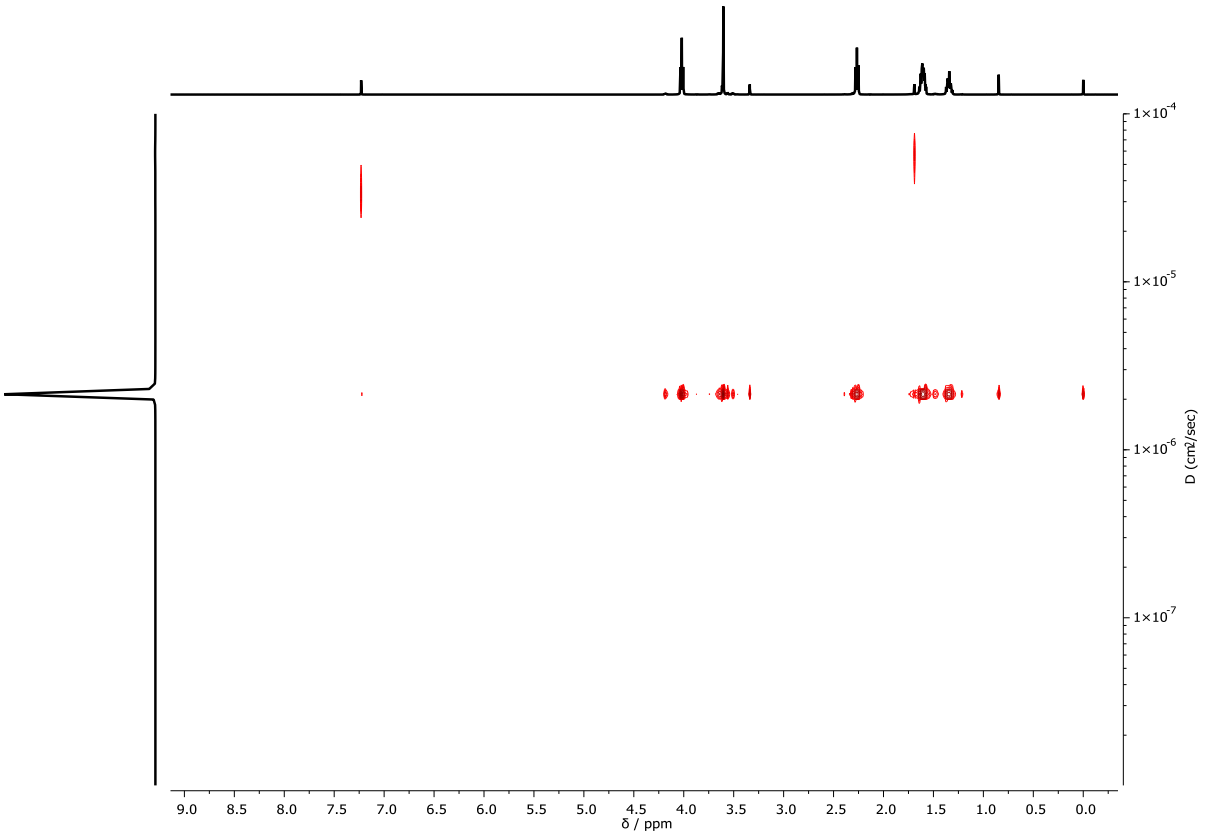
^{13}C NMR (126 MHz, $CDCl_3$): δ / ppm = 173.67 (C_q^1), 72.09 (CH_2^2), 70.72 (CH_2^3), 69.32 (CH_2^4), 64.28 (CH_2^5), 64.19 (CH_2^5), 63.59 (CH_2^6), 63.11 (CH_2^7), 59.19 (CH_3^8), 34.26 (CH_2^9), 32.61 (CH_2^{10}), 34.12 (CH_2^9), 28.50 (CH_2^{11}), 26.10 (CH_3^{12}), 25.67 (CH_2^{13}), 25.59 (CH_2^{13}), 24.95 (CH_2^{14}), 24.72 (CH_2^{14}), -5.14 (CH_3^{16}).

Note: C_q^{15} is not visible in the ^{13}C NMR spectrum.

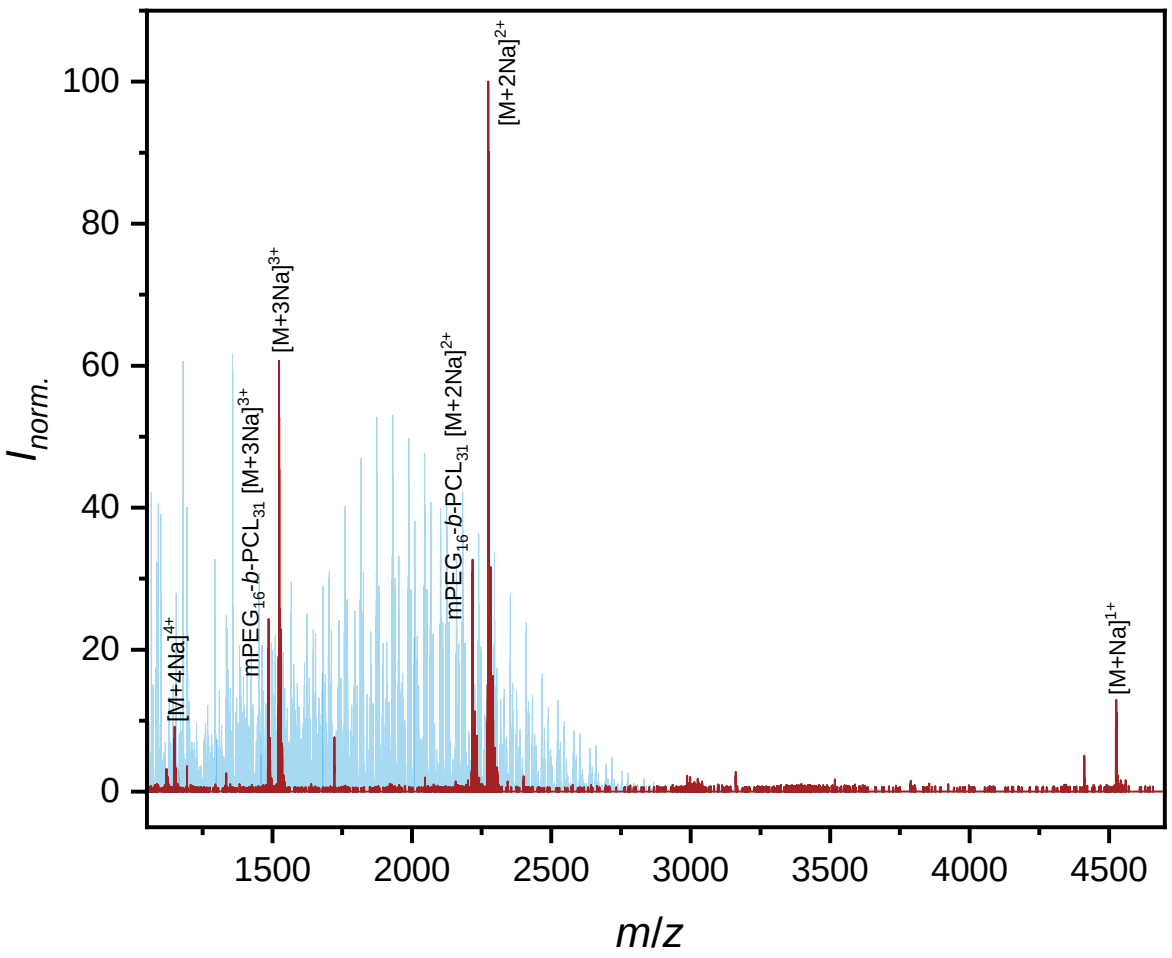




Supplementary Figure 128: ^{13}C NMR spectrum of ***p*-TBDMS(CL)$_{34}$-(EG)$_{17}$OMe** recorded at 126 MHz in $CDCl_3$.



Supplementary Figure 129: DOSY NMR spectrum of ***p*-TBDMS(CL)$_{34}$-(EG)$_{17}$OMe** recorded at 500 MHz in $CDCl_3$.



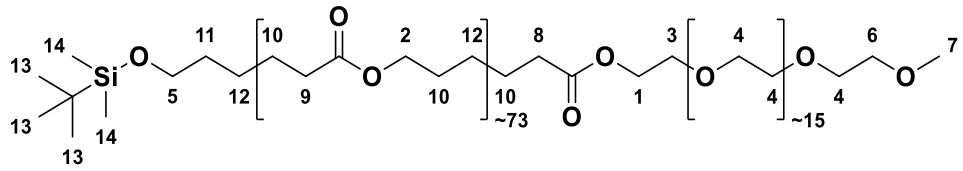
Supplementary Figure 130: ESI-MS spectrum of ***p*-TBDMS(CL)$_{34}$-(EG)$_{17}$OMe** (blue) in comparison to ***i*-TBDMS(CL)$_{32}$-(EG)$_{16}$OMe** (red).

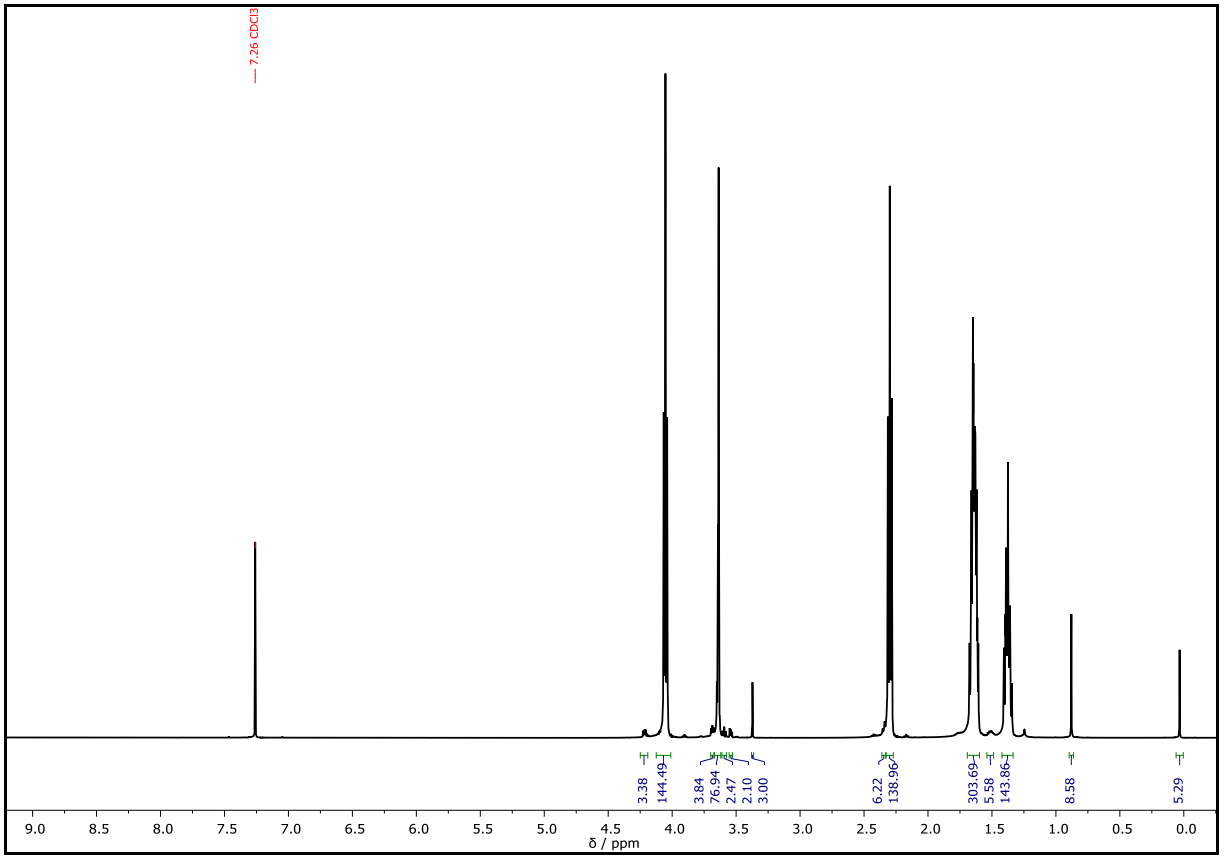
***p*-TBDMS(CL)$_{74}$-(EG)$_{17}$OMe**

1*H*-imidazole	70.9 mg, 1.04 mmol, 30.0 equiv.
***p*-HO(CL)$_{74}$-(EG)$_{17}$OMe**	283 mg, 34.7 µmol, 1.00 equiv.
TBDMS-Cl	157 mg, 1.04 mmol, 30.0 equiv.
dry DMF	5.00 mL
yield	91.5 mg
R_f(product)	0.26 (EA:MeOH = 9:1)
Đ (system II)	1.06

IR (ATR platinum diamond) $\tilde{\nu}$ / cm^{-1} = 2943, 2896, 2865, 1722, 1471, 1438, 1419, 1397, 1366, 1323, 1294, 1240, 1174, 1107, 1065, 1045, 961, 934, 839, 817, 775, 732, 710, 584, 453.

^{1}H NMR (500, MHz, $CDCl_3$): δ / ppm = 4.24 – 4.21 (m, 1H, CH_2^{1}), 4.05 (t, *J* = 6.7 Hz, CH_2^{2}), 3.70 – 3.67 (m, CH_2^{3}), 3.67 – 3.62 (m, CH_2^{4}), 3.61 – 3.58 (m, CH_2^{5}), 3.56 – 3.53 (m, CH_2^{6}), 3.37 (s, CH_3^{7}), 2.36 – 2.32 (m, CH_2^{8}), 2.30 (t, *J* = 7.5 Hz, CH_2^{9}), 1.69 – 1.59 (m, CH_2^{10}), 1.54 – 1.48 (m, CH_2^{11}), 1.44 – 1.33 (m, CH_2^{12}), 0.88 (s, CH_3^{13}), 0.03 (s, CH_3^{14}).

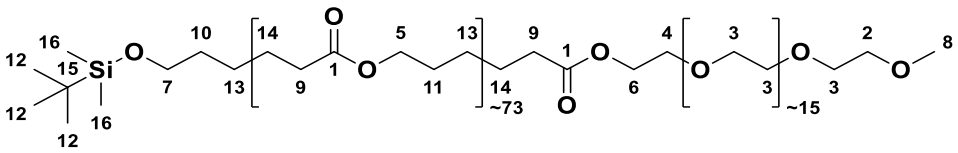


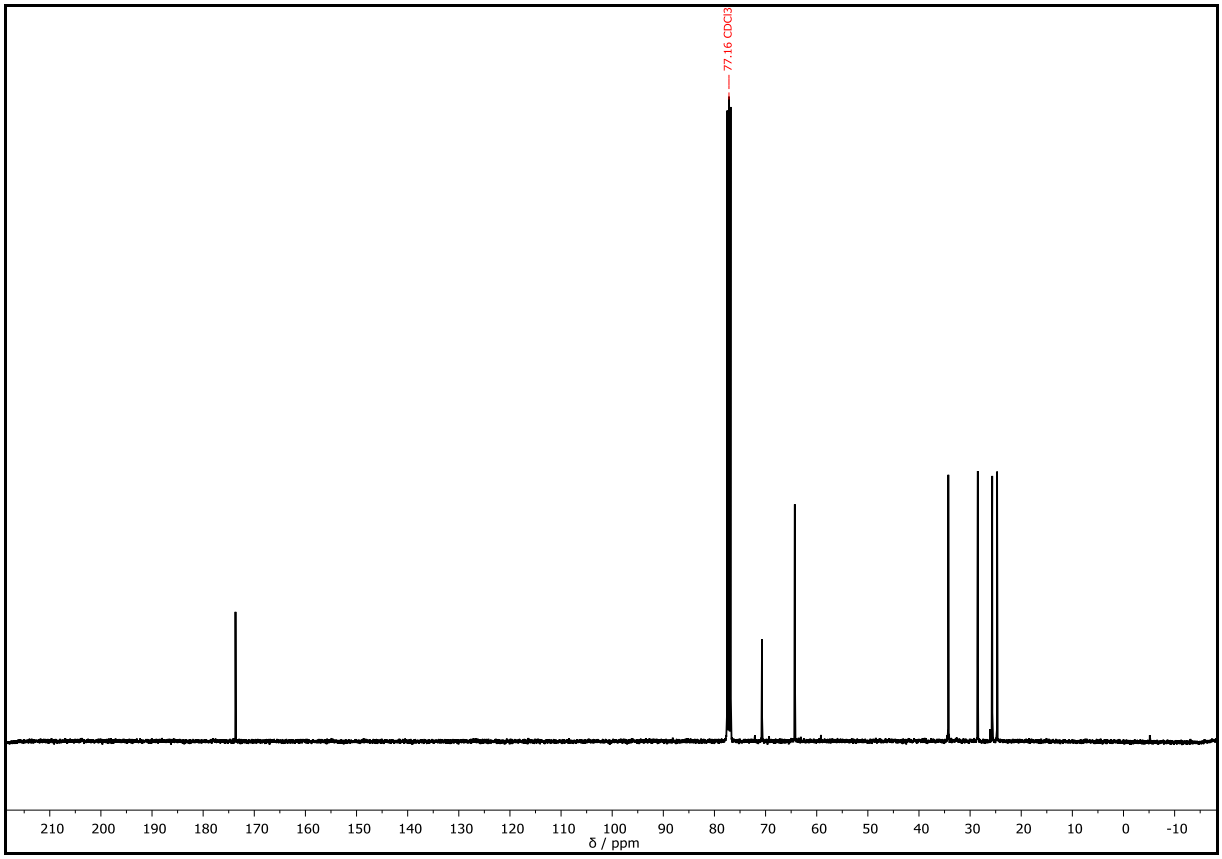


Supplementary Figure 131 ^{1}H NMR spectrum of ***p*-TBDMS(CL)$_{74}$-(EG)$_{17}$OMe** recorded at 500 MHz in $CDCl_3$.

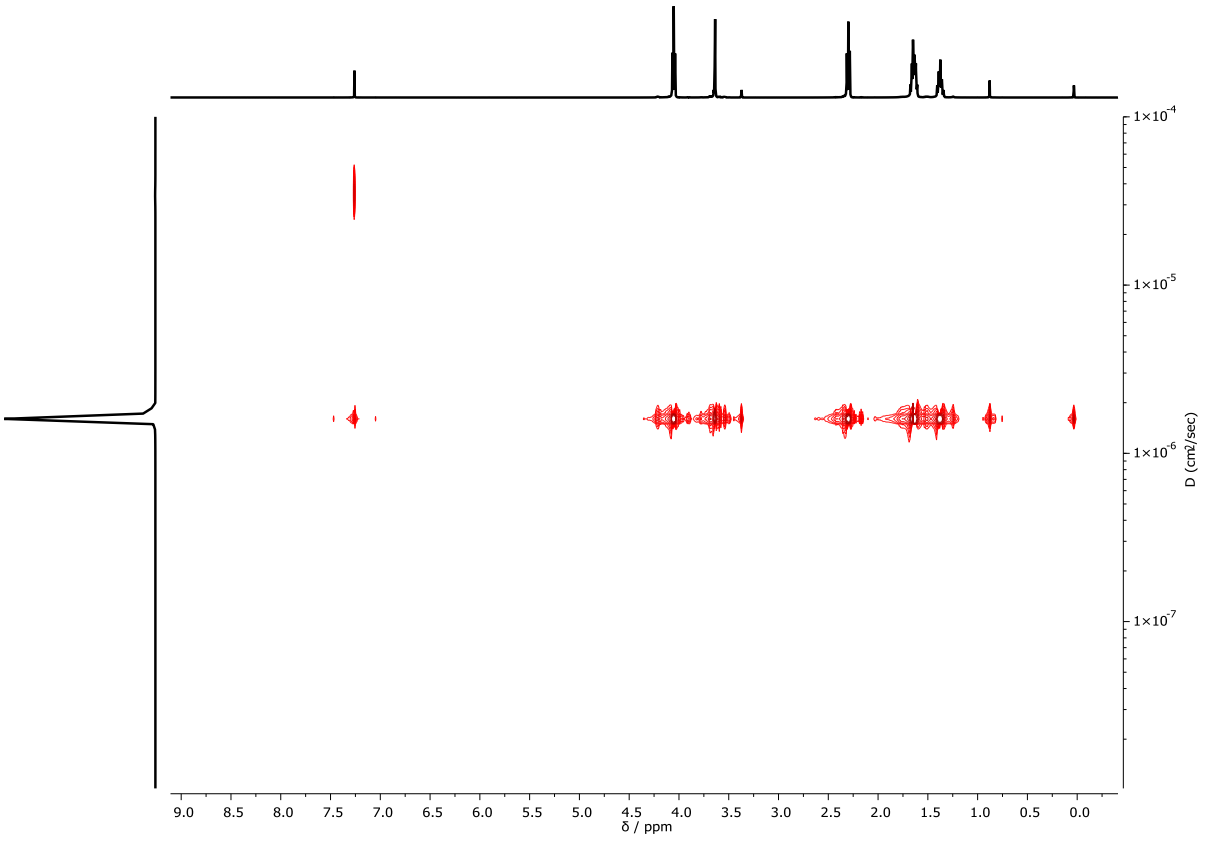
^{13}C NMR (126, MHz, $CDCl_3$): δ / ppm = 173.67 (C_q^1), 72.08 (CH_2^2), 70.70 (CH_2^3), 69.32 (CH_2^4), 64.28 (CH_2^5), 63.59 (CH_2^6), 63.11 (CH_2^7), 59.18 (CH_3^8), 34.26 (CH_2^9), 28.49 (CH_2^{11}), 26.10 (CH_3^{12}), 25.67 (CH_2^{13}), 24.72 (CH_2^{14}), -5.14 (CH_3^{13}).

Note: CH_2^{10} and C_q^{15} are not visible in the ^{13}C NMR spectrum.

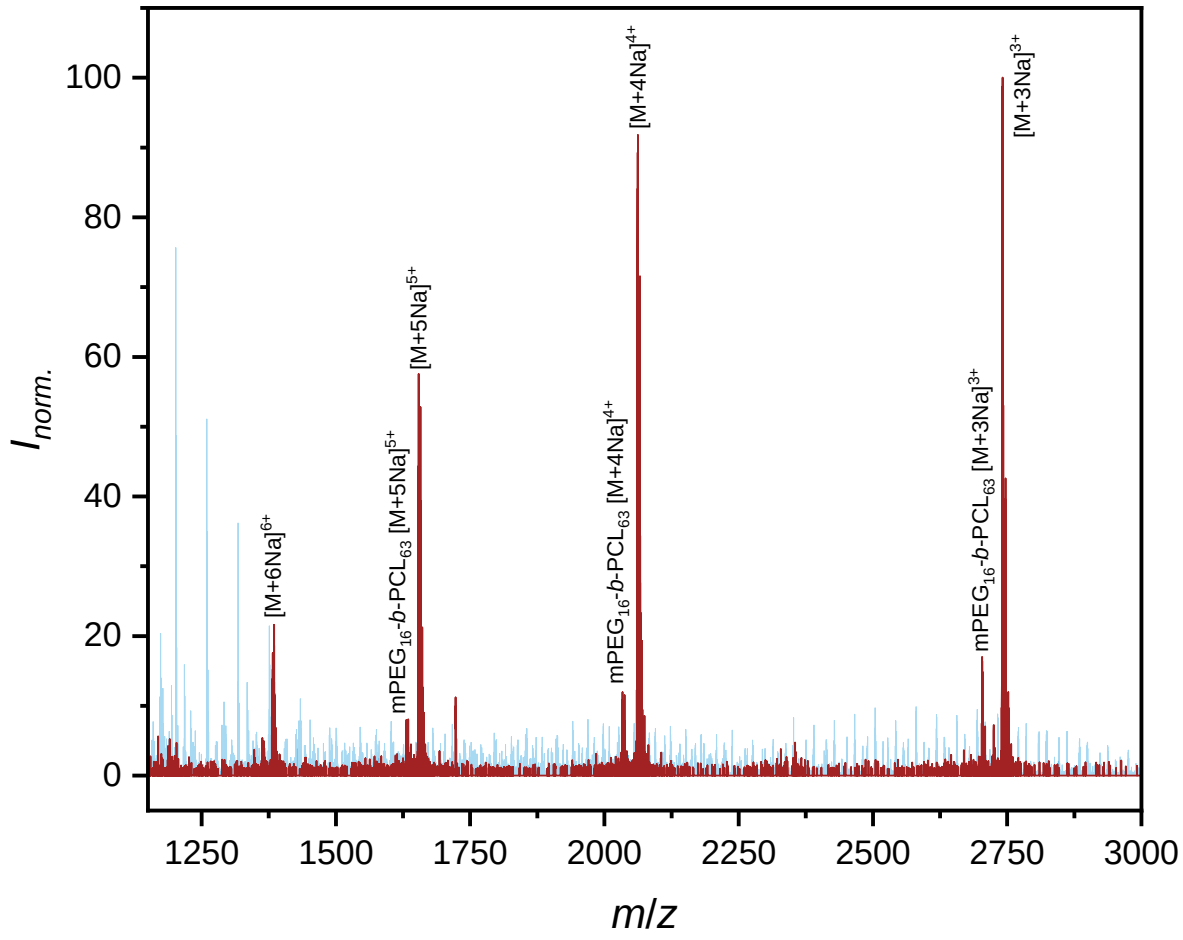




Supplementary Figure 132 ^{13}C NMR spectrum of ***p*-TBDMS(CL)$_{74}$-(EG)$_{17}$OMe** recorded at 126 MHz in $CDCl_3$.



Supplementary Figure 133: DOSY NMR spectrum of ***p*-TBDMS(CL)$_{74}$-(EG)$_{17}$OMe** recorded at 500 MHz in $CDCl_3$.



Supplementary Figure 134: ESI-MS spectrum of ***p*-TBDMS(CL)$_{74}$-(EG)$_{17}$OMe** (blue) in comparison to ***i*-TBDMS(CL)$_{64}$-(EG)$_{16}$OMe** (red).

[1] Q. Zhang, H. Ren, G. L. Baker, *Tetrahedron Lett.* **2014**, *55*.
[2] K. Maranski, Y. G. Andreev, P. G. Bruce, *Angew. Chem. Int. Ed.* **2014**, *53*.
[3] B. G. G. Lohmeijer, R. C. Pratt, F. Leibfarth, J. W. Logan, D. A. Long, A. P. Dove, F. Nederberg, J. Choi, C. Wade, R. M. Waymouth et al., *Macromolecules* **2006**, *39*, 8574.