Supporting Information

Monodisperse, sequence-defined macromolecules as tool to evaluate the limits of ring-closing metathesis

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1 Experimental section

1.1. Materials:

The following chemicals were used as received: 11-aminoundecanoic acid (97%, Sigma-Aldrich), benzyl alcohol (99%, Sigma-Aldrich), thionyl chloride (99%, Sigma-Aldrich), trimethyl orthoformate (99%, Sigma-Aldrich), diisopropylamine (> 99.5%, Sigma-Aldrich), phosphorous(V) oxychloride (99%, Sigma-Aldrich), palladium on activated charcoal (10% palladium basis, Sigma-Aldrich), hydrogen (99,999%, Air Liquide), propionaldehyde (97%, Sigma-Aldrich), cyclohexane carboxaldehyde (97%, Alfa Aesar), isobutyraldehyde (98%, Sigma-Aldrich), 10-undecenal (90%, SAFC), glutaric acid (99%, Sigma-Aldrich), sebacic acid (99%, Sigma-Aldrich), *p*-benzoquinone (> 98%, Sigma-Aldrich), Grubbs 1st generation catalyst (97%, Sigma-Aldrich), ethyl vinyl ether (99%, Sigma Aldrich), silica gel 60 (0.040 - 0.063, Sigma Aldrich), TLC silica gel F_{254} (Sigma Aldrich), cerium(IV)-sulfate (99%, Sigma Aldrich), phosphomolybdic acid hydrate (99%, Sigma Aldrich), chloroform-d (99.8 atom-% D, Euriso-Top), methanol-d_4 (99,8 atom-% D, Euriso-Top), sodium carbonate (98%, Sigma-Aldrich), sodium hydrogen carbonate (> 95%, Sigma Aldrich), sodium sulfate (> 99%, anhydrous, Sigma Aldrich). Ethyl acetate, cyclohexane and *n*-hexane were freshly distilled before use. Other solvents were used without further purification, unless otherwise noted.

1.2. Characterization:

NMR ^{1}H spectra were recorded on a Bruker AVANCE DRX at 300, 400 or 500 MHz spectrometers and ^{13}C-NMR Attached Proton Test (APT) spectra were recorded at 75, 101, and 125 MHz, respectively. $CDCl_3$ or CD_3OD were used as solvents. Chemical shifts are presented in parts per million (δ) relative to the resonance signal at 7.26 ppm (^{1}H, $CDCl_3$) and 77.16 ppm (^{13}C, $CDCl_3$) or 3.31 ppm (^{1}H, CD_3OD) and 49.00 ppm (^{13}C, CD_3OD), respectively.

Coupling constants (J) are reported in Hertz (Hz). All measurements were recorded in a standard fashion at 25 °C unless otherwise stated. Full assignment of structures was aided by 2D NMR analysis (COSY, HSQC and HMBC).

Oligomers were characterized on a Varian 390-LC **gel permeation chromatography (GPC)** system equipped with a LC-290 pump (Varian), refractive index detector (24 ° C), PL AS RT GPC-autosampler (Polymer laboratories) and a Varian Pro Star column oven Model 510, operating at 40 ° C. For separation, two SDV 5 µm linear S columns (8 × 300 mm) and a guard column (8 × 50 mm) supplied by PSS, Germany, were used. Tetrahydrofuran (THF) stabilized with butylated hydroxytoluene (BHT, HPLC-SEC grade) supplied by Sigma Aldrich was used at a flow rate 1.0 mL min^{-1}. Calibration was carried out with linear poly(methyl methacrylate) standards (Agilent) ranging from 875 to 1 677 000 Da. Detection was done by a refractive index detector operating in THF (flow rate 1.0 mL min^{-1}).

Infrared spectra (IR) were recorded on a Bruker Alpha-p instrument in a frequency range from 3998 to 374 cm^{-1} applying KBr and Attenuated Total Reflection (ATR) technology.

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

Orbitrap Electrospray-Ionization Mass Spectrometry (ESI-MS): mass spectra were recorded on a Q Excative (Orbitrap) mass spectrometer (Thermo Fisher Scientific, San Jose, 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.

SEC-ESI-MS spectra were recorded on a Q Exactive (Orbitrap) mass spectrometer (Thermo Fisher Scientific, San Jose, CA, USA) equipped with an 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 sheath gas 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, respectively. The Q Exactive was coupled to a UltiMate 3000 UHPLC System (Dionex, Sunnyvale, CA, USA) consisting of a pump (LPG 3400SD), autosampler (WPS 3000TSL), and a thermostated column department, operating at 30 °C (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 $mL{\cdot}min^{-1}$ was used as eluent. The mass spectrometer was coupled to the column in parallel to a RI-detector (RefractoMax520, ERC, Japan). 0.27 $mL{\cdot}min^{-1}$ of the eluent were directed through the RI-detector and 30 $\mu L{\cdot}min^{-1}$ 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 2 mg mL^{-1} was injected onto the HPLC system.

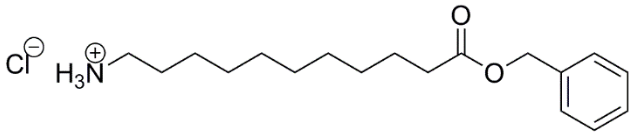
Electron ionization (EI): For the measurements that were performed with the electron ionization (EI) method, an instrument by Finnigan, model MAT 90 (70 eV), was used with 3-nitrobenzyl alcohol (3-NBA) as matrix. For the interpretation of the spectra, molecular peaks $[M]^+$, peaks of pseudo molecules $[M+H]^+$ 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%).

All **thin layer chromatography** experiments were performed on silica gel coated aluminum foil (silica gel 60 F_{254}, Sigma-Aldrich). Compounds were visualized by staining with Seebach-solution (mixture of phosphomolybdic acid hydrate, cerium(IV)-sulfate, sulfuric acid and water).

2 Monomer synthesis:

11-(Benzyloxy)-11-oxoundecan-1-aminium chloride

Synthesised according to previously reported procedure.[1]



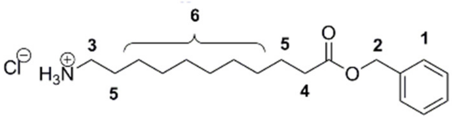
11-Aminoundecanoic acid (15.0 g, 74.8 mmol, 1.0 eq.) was suspended in 75 mL THF. Subsequently, benzyl alcohol (96.7 g, 0.89 mol, 12 eq.) was added and the suspension was cooled to 0 °C. Thionyl chloride (16.6 mL, 27.4 g, 0.23 mol, 3.1 eq.) was added dropwise. After addition of the thionyl chloride, the solution was warmed to room temperature and stirred overnight. The yellow solution was then poured into 500 mL diethyl ether and stored in the freezer for one hour. The product was filtered off and another 500 mL diethyl ether were added and the suspension was stored in the freezer for another hour. The product was filtered off and dried under high vacuum. 11-(Benzyloxy)-11-oxoundecan-1-aminium chloride was obtained in a yield of 87% (21.3 g, 65.0 mmol) as a white solid.

^{1}H-NMR: (300 MHz, CD_3OD) δ /ppm: 7,33 (s, 5H, 5 CH aromatic, ^{1}); 5,09 (s, 2H, CH_2, ^{2}); 2,90 (t, J = 7.5 Hz, 2H, CH_2, ^{3}); 2,34 (t, J = 7,3 Hz, 2H, CH_2, ^{4}); 1,61 (s, 4H, 2 CH_2, ^{5}); 1,31 (m, 12H, 6 CH_2, ^{6}).

^{13}C NMR (75 MHz, CD_3OD) δ /ppm: 175.2, 137.7, 129.5, 129.5, 129.2, 129.2, 67.1, 40.8, 35.0, 30.4, 30.3, 30.2, 30.1, 28.5, 27.4, 26.0.

HRMS-FAB-MS of $[C_{18}H_{30}NO_2]^+$: calculated: 292.2271, found: 292.2271.

IR (ATR platinum diamond): ν /cm^{-1} = 2916.5, 2847.7, 1737.2, 1601.6, 1527.7, 1495.8, 1462.9, 1385.9, 1359.8, 1332.2, 1307.4, 1278.9, 1246.1, 1208.4, 1152.0, 1043.3, 992.7, 959.9, 810.1, 742.7, 722.1, 695.3, 580.3, 509.3, 416.3.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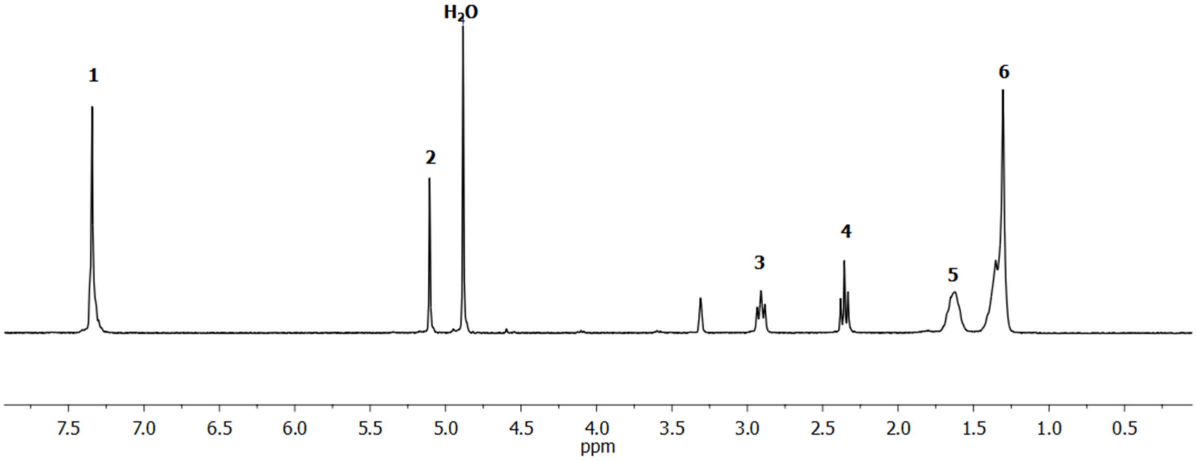
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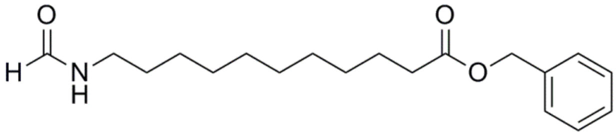
Benzyl-11-formamidoundecanoate

Synthesised according to previously reported procedure.[1]



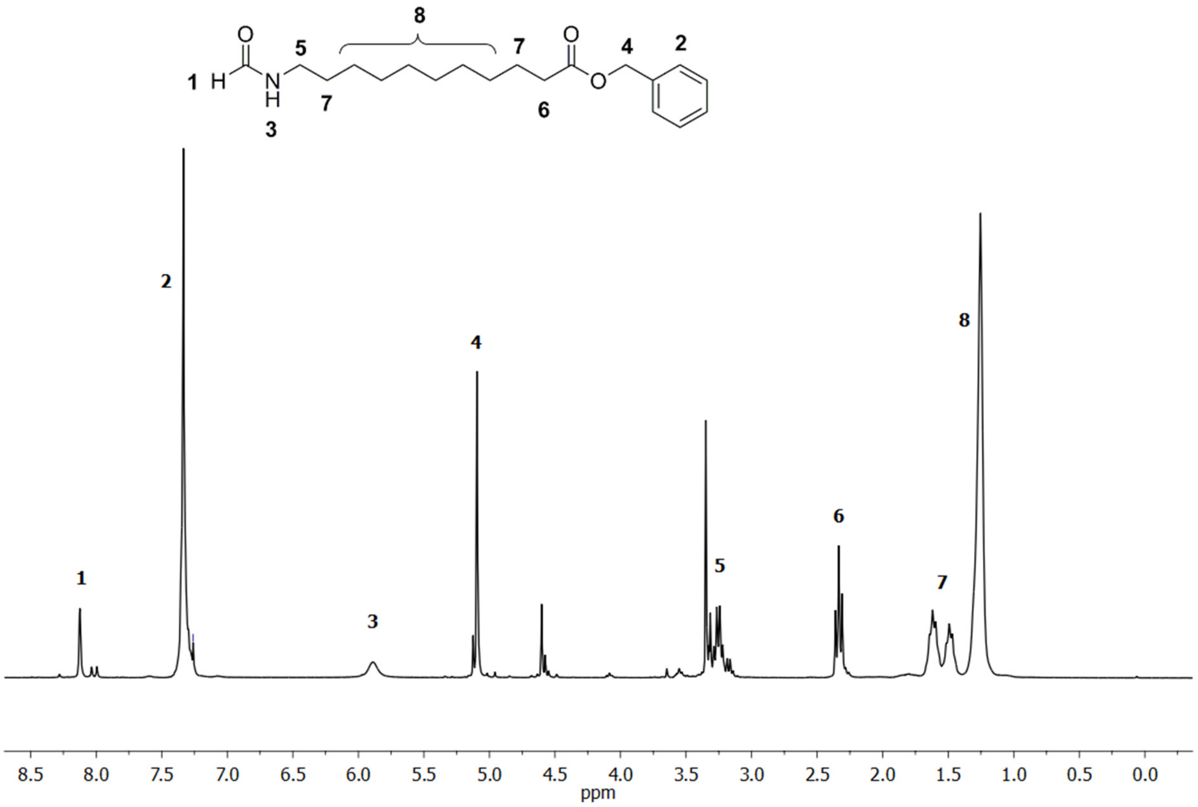
11-(Benzyloxy)-11-oxoundecan-1-aminium chloride (21.3 g, 64.7 mmol, 1.0 eq.) was dissolved in trimethyl orthoformate (71 mL, 68.9 g, 0.65 mol, 10 eq.) and heated to 100 °C. The reaction mixture was refluxed overnight at 100 °C. Trimethyl orthoformate was then removed under reduced pressure and the crude product (21.9 g) was used without further purification.

^{1}H NMR (300 MHz, $CDCl_3$) δ /ppm: 8.22 – 7.97 (m, 1H, CH, ^{1}), 7.37 (m, 5H aromatic, ^{2}), 5.61 (s, 1H, NH, ^{3}), 5.10 (s, 2H, CH_2, ^{4}), 3.42 – 3.11 (m, 2H, CH_2, ^{5}), 2.41 – 2.28 (t, J = 7.5 Hz, 2H, CH_2, ^{6}), 1.91 – 1.41 (m, 4H, 2CH_2, ^{7}), 1.26 (s, 12H, 6 CH_2, ^{8}).

^{13}C NMR (75 MHz, $CDCl_3$) δ /ppm: 173.8, 164.7, 161.3, 136.2, 128.6, 128.2, 66.1, 41.8, 38.2, 34.4, 31.3, 29.5, 29.4, 29.3, 29.2, 29.1, 26.9, 26.4, 25.0.

HRMS-FAB-MS of $[C_{19}H_{30}NO_3]^+$: calculated: 320.2220, found: 320.2222.

IR (ATR platinum diamond): ν / cm^{-1} = 3264.9, 3068.1, 2913.6, 2848.1, 1732.5, 1651.1, 1555.4, 1470.5, 1449.3, 1417.1, 1379.2, 1329.5, 1299.2, 1267.1, 1233.0, 1199.5, 1159.1, 1054.8, 996.7, 938.2, 866.1, 825.1, 806.2, 752.8, 718.3, 695.3, 608.9, 519.5, 487.1, 451.5.



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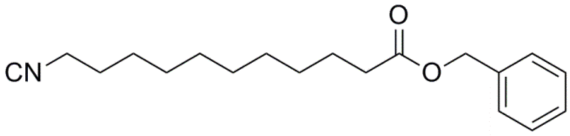
Benzyl-11-isocyanoundecanoate

Synthesised according to previously reported procedure.[1]



Benzyl-11-formamidoundecanoate (19.6 g, 61.2 mmol, 1.0 eq.) was dissolved in 185 mL dichloromethane (0.33 M). Diisopropylamine (26.7 mL, 19.2 g, 0.190 mol, 3 eq.) was added and the reaction mixture was cooled to 0 °C in an ice bath. Subsequently, phosphorous(V) oxychloride (6.7 mL, 11.3 g, 73.5 mmol, 1.2 eq.) was added dropwise and the reaction mixture was then stirred at room temperature for two hours. Subsequently, the mixture was cooled in an ice bath and the reaction was quenched by addition of sodium carbonate solution (20%, 75 mL) at 0 °C. After stirring for 30 minutes at room temperature, 50 mL dichloromethane and 50 mL water were added. After separation of the aqueous phase, the organic layer was washed with water (3 × 80 mL) and brine (80 mL). The organic layer was dried over sodium sulfate and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (hexane / ethyl acetate 19:1 → 8:1). The product **M1** was obtained as slightly yellow oil in a yield of 54% (9.95 g, 33.0 mmol).

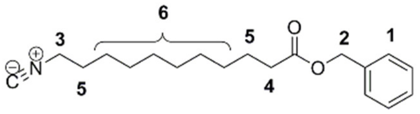
^{1}H NMR (300 MHz, $CDCl_3$) δ /ppm: 7.40 – 7.28 (m, 5CH aromatic, ^{1}), 5.11 (s, 2H, CH_2, ^{2}), 3.47 – 3.25 (m, 2H, CH_2, ^{3}), 2.35 (t, J = 7.5 Hz, 2H, CH_2, ^{4}), 1.65 (m, 4H, 2 CH_2, ^{5}), 1.51 – 0.99 (m, 12H, 6 CH_2, ^{6}).

^{13}C NMR (75 MHz, $CDCl_3$) δ /ppm: 173.8, 155.8, 155.7, 155.6, 136.2, 128.6, 128.3, 66.2, 41.7, 41.6, 41.6, 34.4, 29.4, 29.3, 29.2, 29.2, 28.8, 26.4, 25.0.

HRMS-FAB-MS of $[C_{19}H_{28}NO_2]^+$: calculated: 302.2115, found: 302.2113.

IR (ATR platinum diamond): ν / cm^{-1} = 3032.1, 2924.6, 2853.5, 2145.5 (isocyanide), 1732.4, 1496.9, 1454.3, 1380.2, 1350.0, 1211.7, 1160.2, 1100.4, 1001.0, 735.3, 696.7, 578.4, 494.9.

***R*$_f$**: (hexane / ethyl acetate 5:1) = 0.55.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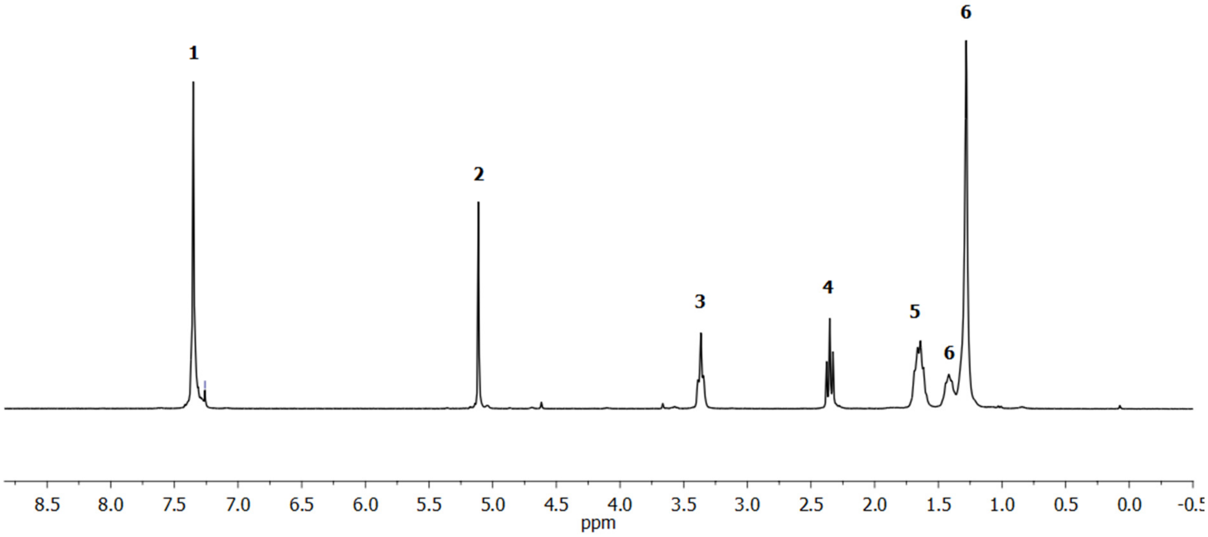
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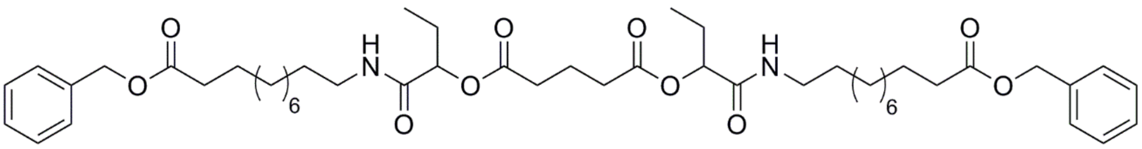
3 Oligomer synthesis:

3.1 Oligomer synthesis with propionaldehyde as side chain

1st Passerini reaction: Synthesis of Dimer 1



Glutaric acid (300 mg, 2.27 mmol, 1.0 eq.) was suspended in DCM (4.6 mL, 0.5 M). Subsequently, propionaldehyde (0.59 mL, 0.47 g, 8.18 mmol, 3.6 eq.) and monomer **M1** (2.05 g, 6.80 mmol, 3.0 eq.) were added and the reaction mixture was stirred at room temperature for 48 h. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (hexane / ethyl acetate 9:1 → 1:1) to obtain the desired product **1** in a yield of 69% (1.33 g, 1.57 mmol) as a yellowish oil.

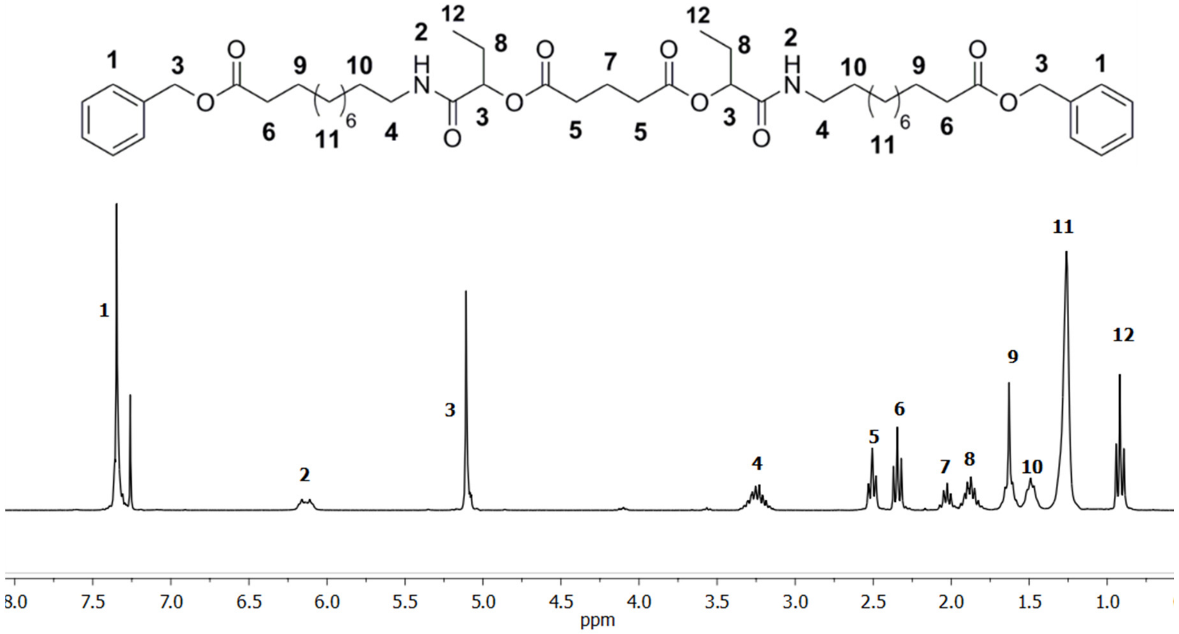
^{1}H NMR (300 MHz, $CDCl_3$) δ / ppm: 7.43 – 7.28 (m, 10CH aromatic, ^{1}), 6.28 – 6.01 (m, 2H, NH, ^{2}), 5.11 (s, 6H, 2 CH_2, 2 CH, ^{3}), 3.37 – 3.09 (m, 4H, 2 CH_2, ^{4}), 2.50 (t, J = 7.0 Hz, 4H, 2 CH_2, ^{5}), 2.34 (t, J = 7.5 Hz, 4H, 2 CH_2, ^{6}), 2.03 (m, 2H, CH_2, ^{7}), 1.88 (m, 4H, 2 CH_2, ^{8}), 1.68 – 1.56 (m, 4H, 2 CH_2, ^{9}), 1.48 (m, 4H, 2 CH_2, ^{10}), 1.26 (s, 24H, 12 CH_2, ^{11}), 0.92 (t, J = 7.4 Hz, 6H, 2 CH_3, ^{12}).

^{13}C NMR (75 MHz, $CDCl_3$) δ / ppm: 173.8, 172.0, 171.8, 169.5, 136.3, 128.7, 128.3, 75.3, 66.2, 39.4, 34.4, 33.1, 33.0, 29.7, 29.6, 29.5, 29.3, 29.2, 27.0, 25.2, 25.1, 20.2, 20.2, 9.2, 9.2.

HRMS-FAB-MS of $[C_{49}H_{75}N_2O_{10}]^+$: calculated: 851.5416 found: 851.5417.

IR (ATR platinum diamond): ν / cm^{-1} = 3303.7, 2924.4, 2852.5, 1733.9, 1654.6, 1533.9, 1454.6, 1379.5, 1229.1, 1148.7, 1100.4, 967.7, 734.7, 696.6.

***R*$_f$** : (hexane / ethyl acetate 2:3) = 0.79.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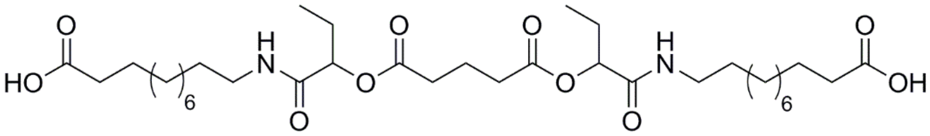
1st deprotection: Synthesis of Dimer 2



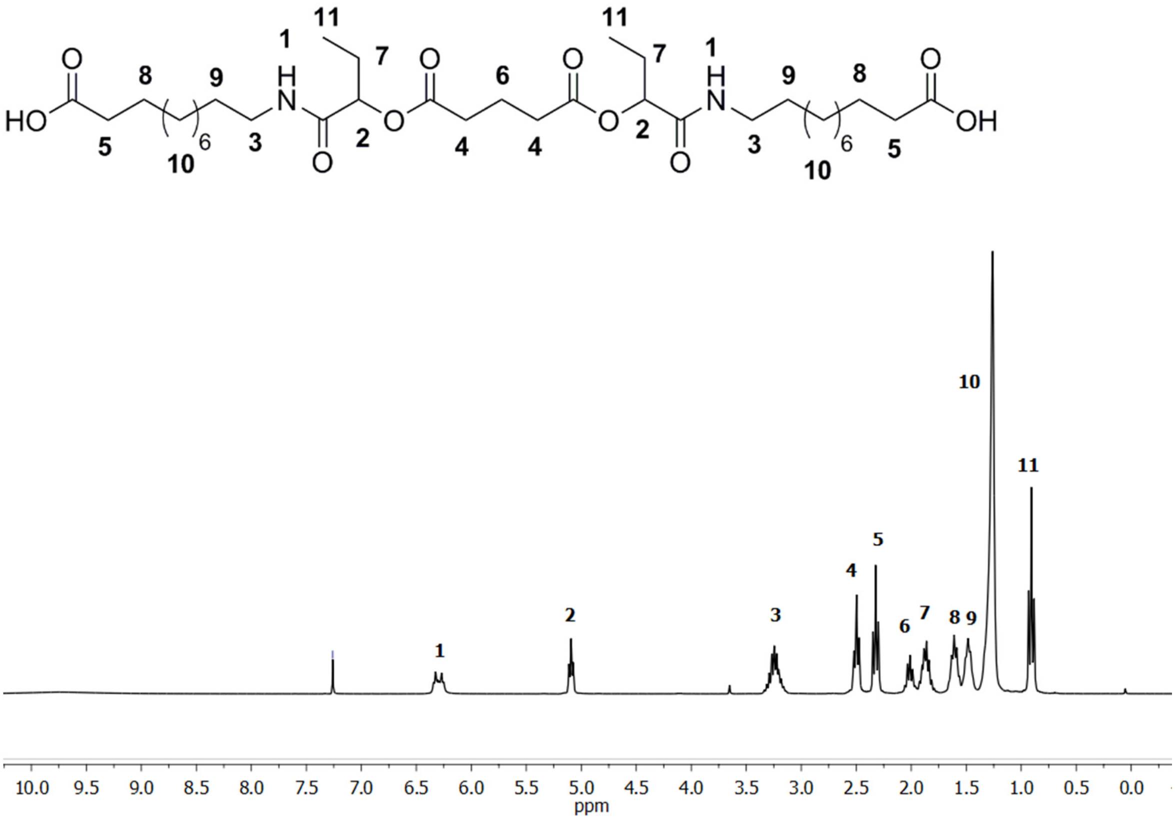
Substance **1** (1.09 g, 1.28 mmol, 1.0 eq) was dissolved in 2.2 mL ethyl acetate (0.5 M) and palladium on activated charcoal (0.11 g, 10 wt%) was added. The reaction mixture was purged with hydrogen (balloon) and then stirred overnight under hydrogen atmosphere. The heterogeneous catalyst was removed by filtration and the solvent was evaporated under reduced pressure to afford the product **2** without further purification in a yield of 96% (0.82 g, 1.22 mmol) as a highly viscous, colourless oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ / ppm: 6.30 (m, 2H, NH, ^{1}), 5.09 (t, J = 5.7 Hz, 2H, 2 CH, ^{2}), 3.35 – 3.11 (m, 4H, 2 CH_2, ^{3}), 2.50 (t, J = 7.0 Hz, 4H, 2 CH_2, ^{4}), 2.32 (t, J = 7.4 Hz, 4H, 2 CH_2, ^{5}), 2.07 – 1.94 (m, 2H, CH_2, ^{6}), 1.93 – 1.77 (m, 4H, 2 CH_2, ^{7}), 1.60 (m, 4H, 2 CH_2, ^{8}), 1.46 (m, 4H, 2 CH_2, ^{9}), 1.26 (s, 24H, 12 CH_2, ^{10}), 0.91 (t, J = 7.4 Hz, 6H, 2 CH_3, ^{11}).

^{13}C NMR (75 MHz, $CDCl_3$) δ / ppm: 179.2, 172.1, 171.9, 169.8, 75.3, 39.5, 34.2, 33.1, 32.9, 29.6, 29.4, 29.3, 29.2, 29.2, 29.1, 26.9, 25.2, 24.9, 20.2, 9.21, 9.2.

HRMS-FAB-MS of $[C_{35}H_{63}N_2O_{10}]^+$: calculated: 671.4477 found: 671.4479.

IR (ATR platinum diamond): ν [cm^{-1}] = 3291.4, 2921.3, 2850.7, 1734.8, 1698.0, 1653.6, 1544.4, 1435.7, 1376.5, 1234.7, 1145.4, 1104.3, 1047.3, 963.6, 909.1, 722.4, 679.6.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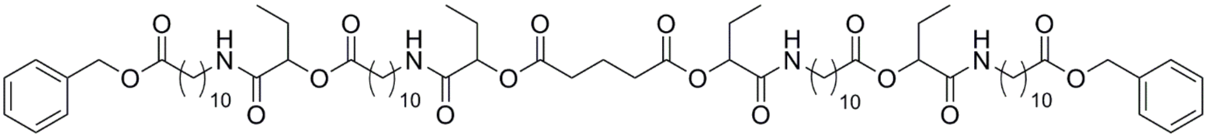
2^{nd} Passerini reaction: Synthesis of tetramer 3



Substance **2** (0.78 g, 1.17 mmol, 1.0 eq.) was dissolved in DCM (3.5 mL, 0.33 M). Subsequently, propionaldehyde (0.25 mL, 0.20 g, 3.51 mmol, 3.0 eq.) and monomer **M1** (1.07 g, 3.51 mmol, 3.0 eq.) were added. The reaction mixture was stirred at room temperature for 48 h. The solvent was evaporated under reduced pressure and the crude product was purified by column chromatography (hexane / ethyl acetate 4:1 → 1:6). The desired product **3** was obtained in a yield of 89% (1.45 g, 1.04 mmol) as a yellowish, viscous oil.

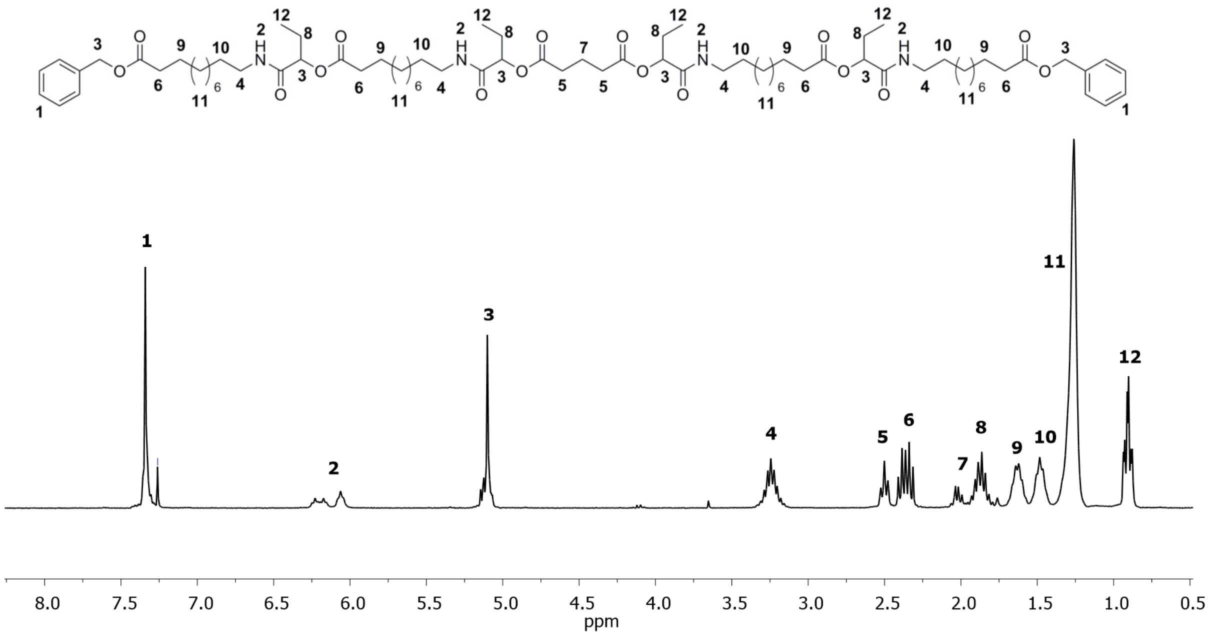
^{1}H NMR (400 MHz, $CDCl_3$) δ / ppm: 7.38 – 7.27 (m,10H, CH, aromatic,^{1}), 6.24 (t, J = 5.7 Hz, 1H, NH, ^{2}), 6.18 (t, J = 5.7 Hz, 1H, NH, ^{2}), 6.06 (t, J = 5.3 Hz, 2H, 2 NH, ^{2}), 5.16 – 5.02 (m, 8H, 4 CH, 2 CH_2, ^{3}), 3.32 – 3.15 (m, 8H, 4 CH_2, ^{4}), 2.54 – 2.44 (m, 4H, 2 CH_2, ^{5}), 2.41 – 2.29 (m, 8H, 4 CH_2, ^{6}), 2.01 (m, 2H, CH_2, ^{7}), 1.95 – 1.77 (m, 8H, 4 CH_2, ^{8}), 1.68 – 1.56 (m, 8H, 4 CH_2, ^{9}), 1.53 – 1.43 (m, 8H, 2 CH_2, ^{10}), 1.26 (s, 48H, 24 CH_2, ^{11}), 0.90 (m, 12H, 4 CH_3, ^{12}).

^{13}C NMR (101 MHz, $CDCl_3$) δ / ppm: 173.8, 172.5, 172.0, 171.8, 169.7, 169.5, 136.2, 128.6, 128.3, 128.2, 75.2, 74.9, 66.2, 39.4, 39.3, 34.4, 34.4, 33.0, 32.9, 29.7, 29.5, 29.4, 29.3, 29.2, 29.2, 26.9, 25.2, 25.2, 25.0, 20.2, 20.2, 9.2, 9.2, 9.1.

HRMS-FAB-MS of $[C_{79}H_{129}N_4O_{16}]^+$: calculated: 1389.9 found: 1388.9.

IR (ATR platinum diamond): ν [cm^{-1}] = 3305.3, 2923.8, 2852.3, 1735.6, 1653.9, 1533.6, 1455.2, 1377.5, 1230.1, 1150.3, 1100.3, 1047.9, 971.1, 732.0, 696.8.

***R*$_f$** (hexane / ethyl acetate 1:2) = 0.73.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1.5
1.0
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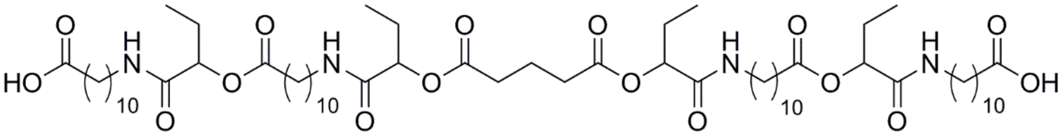
ppm

2nd deprotection: Synthesis of Tetramer 4



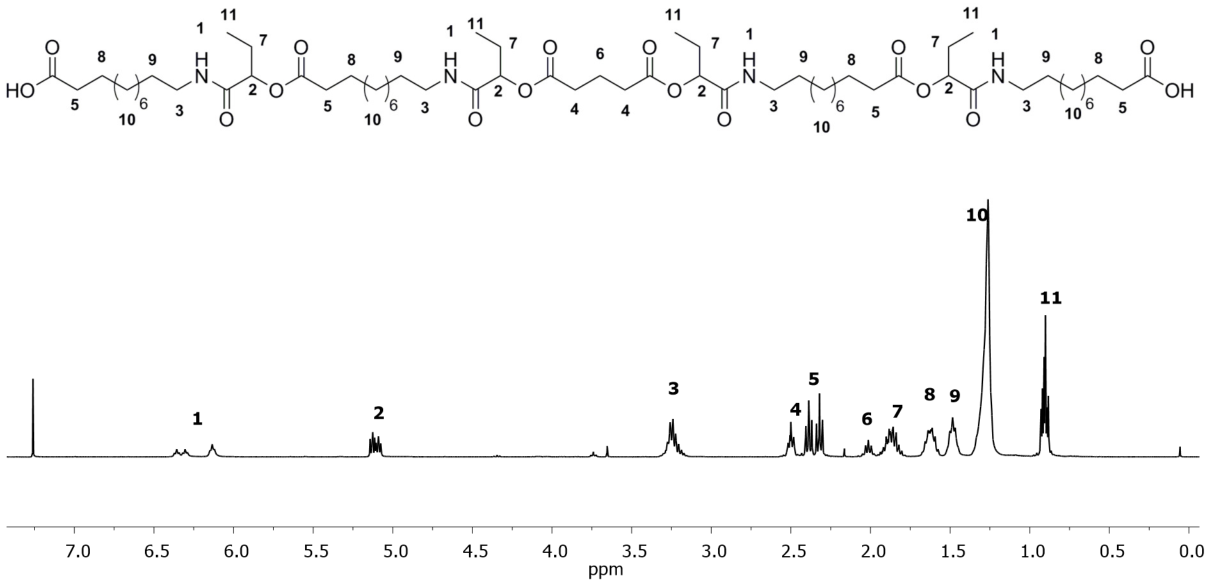
Substance **3** (1.35 g, 0.97 mmol, 1.0 eq.) was dissolved in ethyl acetate (2 mL, 0.5 M) and palladium on activated charcoal (0.14 g, 10 wt%) was added. The reaction mixture was purged with hydrogen (balloon) and stirred overnight under hydrogen atmosphere. The heterogeneous catalyst was removed by filtration and the solvent was evaporated under reduced pressure to afford the product **4** without further purification in a yield of 99% (1.16 g, 0.96 mmol) as highly viscous colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ / ppm: 6.33 (m, 2H, 2 NH, ^{1}), 6.13 (t, *J* = 5.4 Hz, 2H, 2 NH, ^{1}), 5.18 – 5.04 (m, 4H, CH, ^{2}), 3.33 – 3.15 (m, 8H, 4 CH_2, ^{3}), 2.54 – 2.46 (m, 4H, 2 CH_2, ^{4}), 2.42 – 2.27 (m, 8H, 4 CH_2, ^{5}), 2.06 – 1.95 (m, 2H, CH_2, ^{6}), 1.93 – 1.76 (m, 8H, 4 CH_2, ^{7}), 1.69 – 1.55 (m, 8H, 4 CH_2, ^{8}), 1.54 – 1.40 (m, 8H, 4 CH_2, ^{9}), 1.26 (s, 48H, 24 CH_2, ^{10}), 0.96 – 0.84 (m, 12H, 4 CH_3, ^{11}).

^{13}C NMR (101 MHz, $CDCl_3$) δ / ppm: 178.2, 172.6, 172.1, 172.0, 169.9, 169.9, 75.3, 74.9, 39.5, 39.3, 34.4, 34.1, 33.1, 32.9, 29.8, 29.6, 29.6, 29.5, 29.4, 29.3, 29.2, 29.2, 29.1, 26.9, 26.8, 25.2, 25.2, 25.1, 24.7, 20.2, 20.2, 9.22, 9.2, 9.2.

HRMS-FAB-MS of $[C_{65}H_{117}N_4O_{16}]^+$: calculated: 1209.8 found: 1209.1.

IR (ATR platinum diamond): ν [cm^{-1}] = 3303.8, 2923.8, 2852.8, 1737.9, 1650.3, 1540.3, 1458.9, 1376.9, 1231.7, 1151.8, 1101.2, 1048.7, 970.9, 721.9.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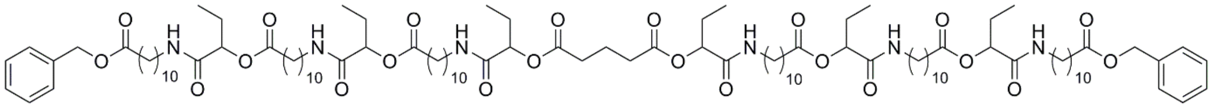
3rd Passerini reaction: Synthesis of Hexamer 5



Substance **4** (1.04 g, 0.86 mmol, 1.0 eq.) was dissolved in DCM (1.8 mL, 0.43 M) and propionaldehyde (0.19 mL, 0.15 g, 2.57 mmol, 3.0 eq.) and monomer **M1** (1.07 g, 3.51 mmol, 3.0 eq.) were added. The reaction mixture was stirred at room temperature for 24 h. Again, propionaldehyde (0.05 mL, 40 mg, 0.69 mmol, 0.80 eq.) was added and the reaction mixture was stirred at room temperature for another 24 h. The solvent was evaporated under reduced pressure and the crude product was purified by column chromatography (hexane / ethyl acetate 5:1 → 1:8). The desired product **5** was obtained in a yield of 75% (1.23 g, 0.64 mmol) as yellowish, highly viscous oil.

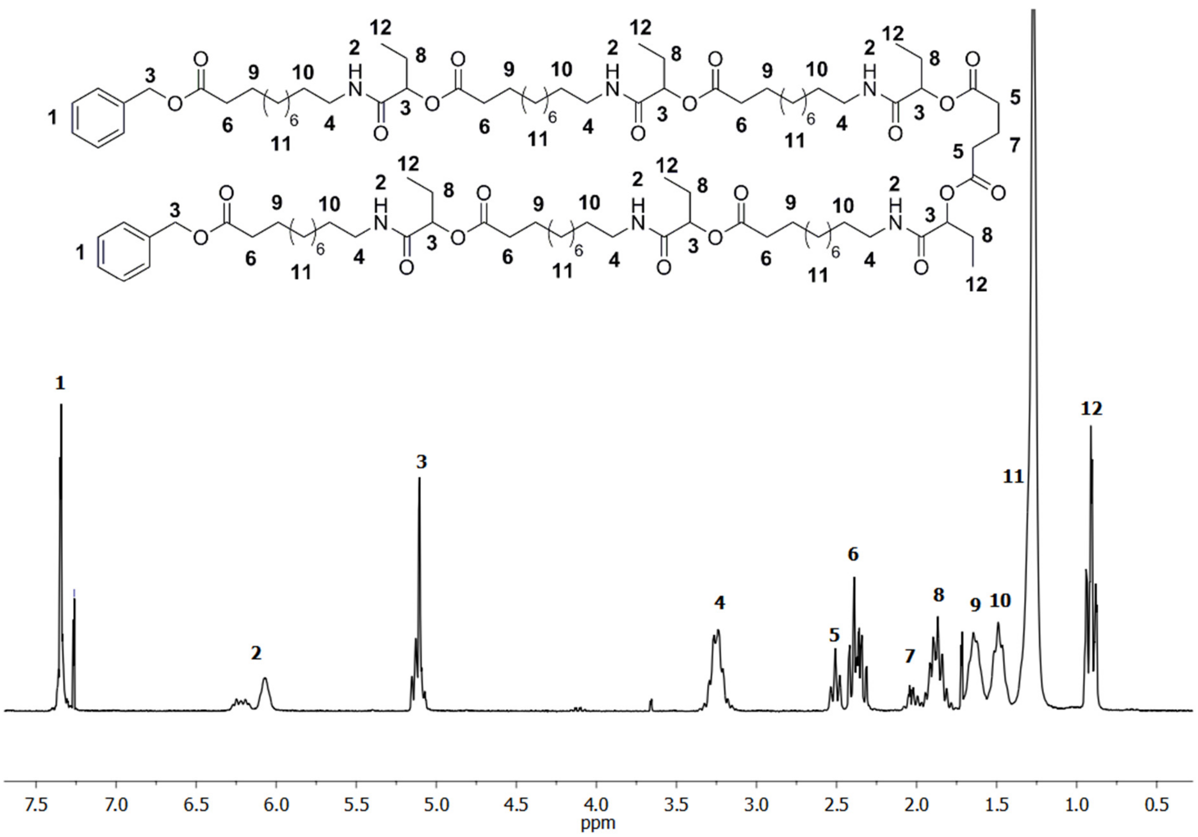
^{1}H NMR (600 MHz, $CDCl_3$) δ / ppm: 7.39 – 7.27 (m, 10H, CH, aromatic, ^{1}), 6.28 – 6.00 (m, 6H, 6 NH, ^{2}), 5.19 – 5.04 (m, 10H, 2 CH_2, 6 CH, ^{3}), 3.32 – 3.13 (m, 12H, 6 CH_2, ^{4}), 2.54 – 2.46 (m, 4H, 2 CH_2, ^{5}), 2.42 – 2.27 (m, 12H, 6 CH_2, ^{6}), 2.05 – 1.97 (m, 2H, CH_2, ^{7}), 1.94 – 1.78 (m, 12H, 6 CH_2, ^{8}), 1.63 (m, 12H, 6 CH_2, ^{9}), 1.52 – 1.43 (m, 12H, 6 CH_2, ^{10}), 1.27 (s, 72H, 36 CH_2, ^{11}), 0.91 (m, 18H, 6 CH_3, ^{12}).

^{13}C NMR (151 MHz, $CDCl_3$) δ / ppm: 173.8, 172.6, 172.6, 172.0, 171.9, 169.8, 169.7, 169.6, 136.2, 128.7, 128.3, 128.3, 75.3, 74.9, 66.2, 39.4, 39.4, 39.3, 39.3, 34.4, 34.4, 33.1, 33.0, 29.7, 29.6, 29.5, 29.3, 29.3, 29.2, 27.0, 25.3, 25.2, 25.1, 25.1, 20.2, 20.2, 9.2, 9.2, 9.2, 9.2.

HRMS-FAB-MS of $[C_{109}H_{183}N_6O_{22}]^+$: calculated: 1928.3380 found: 1928.33352.

IR (ATR platinum diamond): ν [cm^{-1}] = 3294.3, 2922.7, 2851.2, 1735.6, 1655.4, 1536.3, 1455.1, 1164.8, 696.8.

***R*f** (hexane / ethyl acetate 1:2) = 0.56.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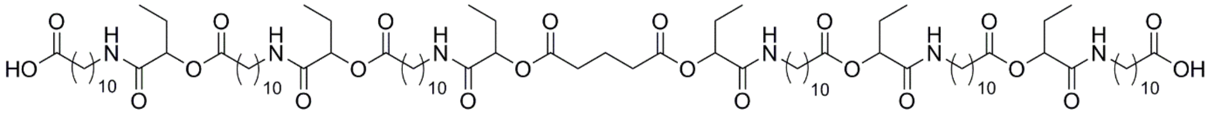
1.0
0.5
ppm

3rd deprotection: Synthesis of Hexamer 6



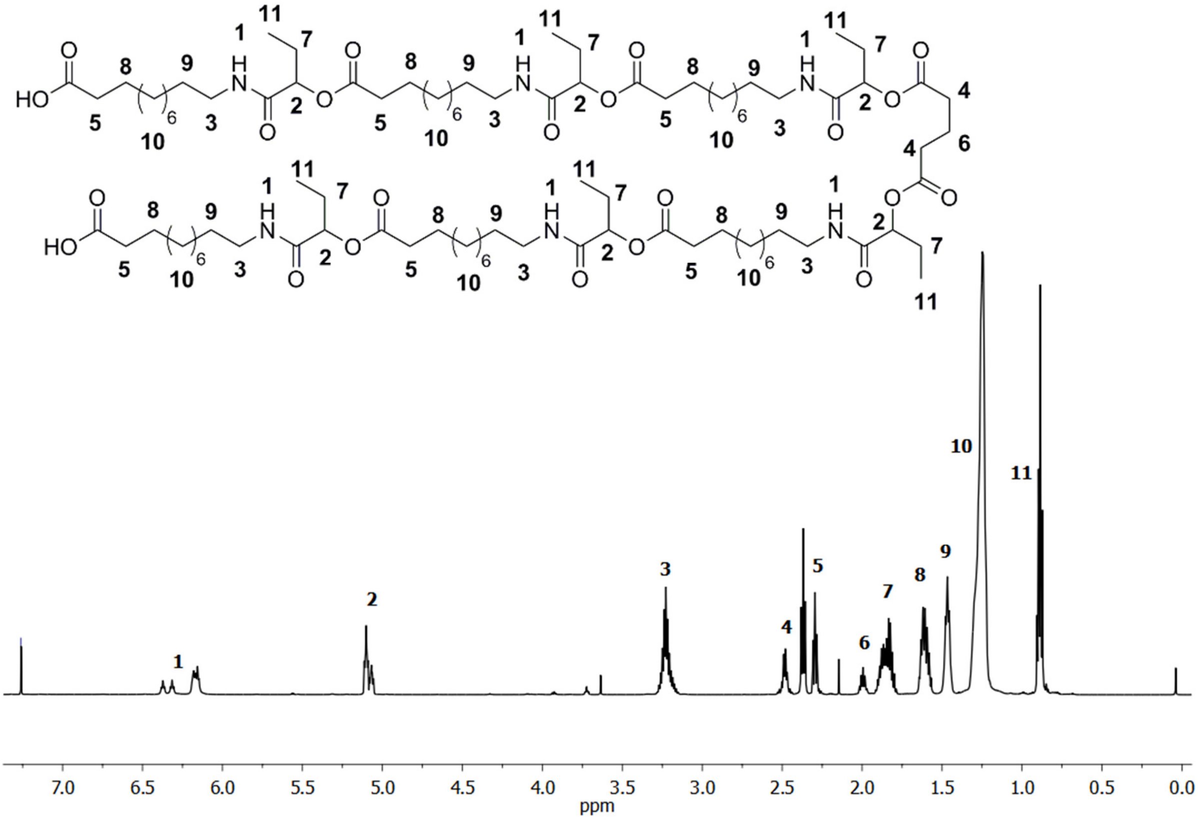
Substance **5** (1.12 g, 0.58 mmol, 1.0 eq.) was dissolved in ethyl acetate (5 mL, 0.22 M) and palladium on activated charcoal (0.11 g, 10 wt%) was added. The reaction mixture was purged with hydrogen (balloon) and stirred overnight under hydrogen atmosphere. The heterogeneous catalyst was removed by filtration and the solvent was evaporated under reduced pressure to afford the product **6** without further purification in quantitative yield (1.02 g, 0.58 mmol) as highly viscous, lightly yellowish oil.

^{1}H NMR (600 MHz, CDCl$_3$) δ / ppm: 6.44 – 6.08 (m, 6H, 6 NH, ^{1}), 5.14 – 5.01 (m, 6H, 6 CH, ^{2}), 3.29 – 3.16 (m, 12H, 6 CH$_2$, ^{3}), 2.50 – 2.43 (m, 4H, 2 CH$_2$, ^{4}), 2.37 (t, J = 7.5 Hz, 8H, 4 CH$_2$, ^{5}), 2.30 (t, J = 7.5 Hz, 4H, 2 CH$_2$, ^{5}), 2.04 – 1.95 (m, 2H, CH$_2$, ^{6}), 1.92 – 1.78 (m, 12H, 6 CH$_2$, ^{7}), 1.66 – 1.55 (m, 12H, 6 CH$_2$, ^{8}), 1.50 – 1.44 (m, 12H, 6 CH$_2$, ^{9}), 1.25 (m, 72H, 36 CH$_2$, ^{10}), 0.93 – 0.84 (m, 18H, 6 CH$_3$, ^{11}).

^{13}C NMR (151 MHz, CDCl$_3$) δ / ppm: 177.8, 172.6, 172.6, 172.0, 171.9, 167.0, 169.9, 169.8, 169.8, 75.2, 74.9, 39.4, 39.4, 39.3, 39.3, 34.4, 34.3, 34.1, 33.0, 32.9, 29.8, 29.6, 29.5, 29.5, 29.4, 29.4, 29.3, 29.3, 29.3, 29.2, 29.2, 29.1, 29.1, 26.9, 26.9, 26.9, 25.2, 25.2, 25.0, 25.0, 24.9, 20.2, 20.1, 9.2, 9.2, 9.1.

HRMS-FAB-MS of [$C_{95}H_{171}N_6O_{22}$]$^+$: calculated: 1748.2441 found: 1748.2413.

IR (ATR platinum diamond): ν [cm^{-1}] = 3304.9, 2923.3, 2852.5, 1737.7, 1650.5, 1537.1, 1460.0, 1375.0, 1160.3, 1100.5, 973.1, 721.0.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NH
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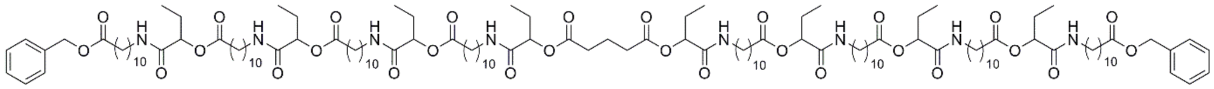
4th Passerini reaction: Synthesis of Octamer 7



Substance **6** (0.49 g, 0.28 mmol, 1.0 eq.) was dissolved in DCM (1 mL, 0.27 M) and propionaldehyde (84 µL, 68 mg, 1.17 mmol, 4.2 eq.) and monomer **M1** (0.27 g, 0.90 mmol, 3.2 eq.) were added. The reaction mixture was stirred at room temperature for 48 hours. The solvent was evaporated under reduced pressure and the crude product was purified by column chromatography (hexane / ethyl acetate 1:1 → 1:9). The desired product **7** was obtained in a yield of 85% (0.58 g, 0.24 mmol) as turbid, highly viscous oil.

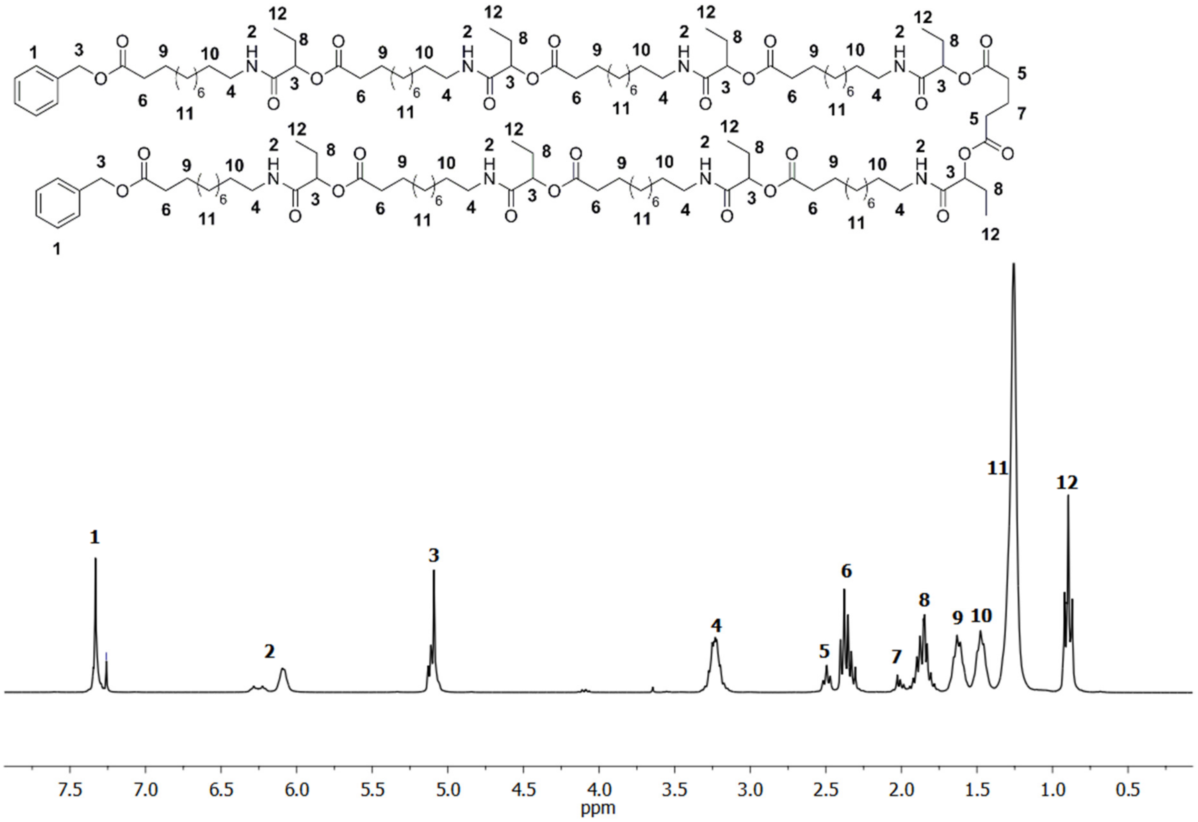
^{1}H NMR (400 MHz, $CDCl_3$) δ / ppm: 7.37 – 7.27 (m, 10H, CH, aromatic, ^{1}), 6.38 – 6.06 (m, 8H, 8 NH, ^{2}), 5.13 – 5.03 (m, 12H, 2 CH_2, 8 CH, ^{3}), 3.30 – 3.13 (m, 16H, 8 CH_2, ^{4}), 2.53 – 2.45 (m, 4H, 2 CH_2, ^{5}), 2.34 (m, 16H, 8 CH_2, ^{6}), 2.04 – 1.95 (m, 2H, CH_2, ^{7}), 1.93 – 1.75 (m, 16H, 8 CH_2, ^{8}), 1.68 – 1.55 (m, 16H, 8 CH_2, ^{9}), 1.45 (m, 16H, 8 CH_2, ^{10}), 1.23 (m, 96H, 48 CH_2, ^{11}), 0.93 – 0.81 (m, 24H, 8 CH_3, ^{12}).

^{13}C NMR (101 MHz, $CDCl_3$) δ / ppm: 173.7, 172.5, 172.5, 172.0, 171.8, 169.7, 169.7, 169.6, 169.6, 136.2, 128.6, 128.2, 128.2, 75.2, 74.8, 66.1, 39.3, 39.2, 34.4, 34.3, 33.0, 32.9, 29.7, 29.6, 29.5, 29.4, 29.3, 29.1, 26.9, 25.2, 25.2, 25.0, 20.2, 20.1, 9.2, 9.2, 9.1.

HRMS-FAB-MS of $[C_{139}H_{237}N_8O_{28}]^+$: calculated: 2466.7 found: 2466.4.

IR (ATR platinum diamond): ν [cm^{-1}] = 3294.3, 2923.6, 2852.3, 1737.2, 1654.3, 1535.2, 1455.9, 1375.3, 1231.4, 1161.9, 1101.0, 1048.4, 973.2, 721.9, 696.9, 412.8.

***R*$_f$** (hexane / ethyl acetate 1:4) = 0.70.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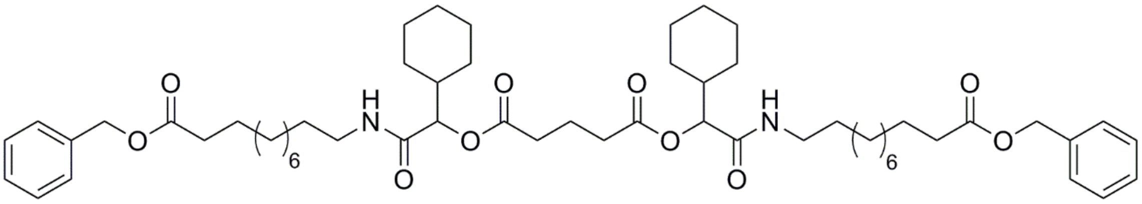
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
ppm

3.2 Oligomer synthesis with cyclohexane carboxaldehyde side chains

1st Passerini reaction: Synthesis of Dimer 8



Glutaric acid (400 mg, 3.03 mmol, 1.0 eq.) was suspended in DCM (6 mL, 0.5 M). Subsequently, cyclohexane carboxaldehyde (1.1 mL, 1.02 g, 9.08 mmol, 3.0 eq.) and monomer **M1** (2.75 g, 9.12 mmol, 3.0 eq.) were added and the reaction mixture was stirred at room temperature for 24 hours. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (hexane / ethyl acetate 8:1 → 1:3) to obtain the desired product **8** in a yield of 86% (2.48 g, 2.59 mmol) as a brown-orange oil.

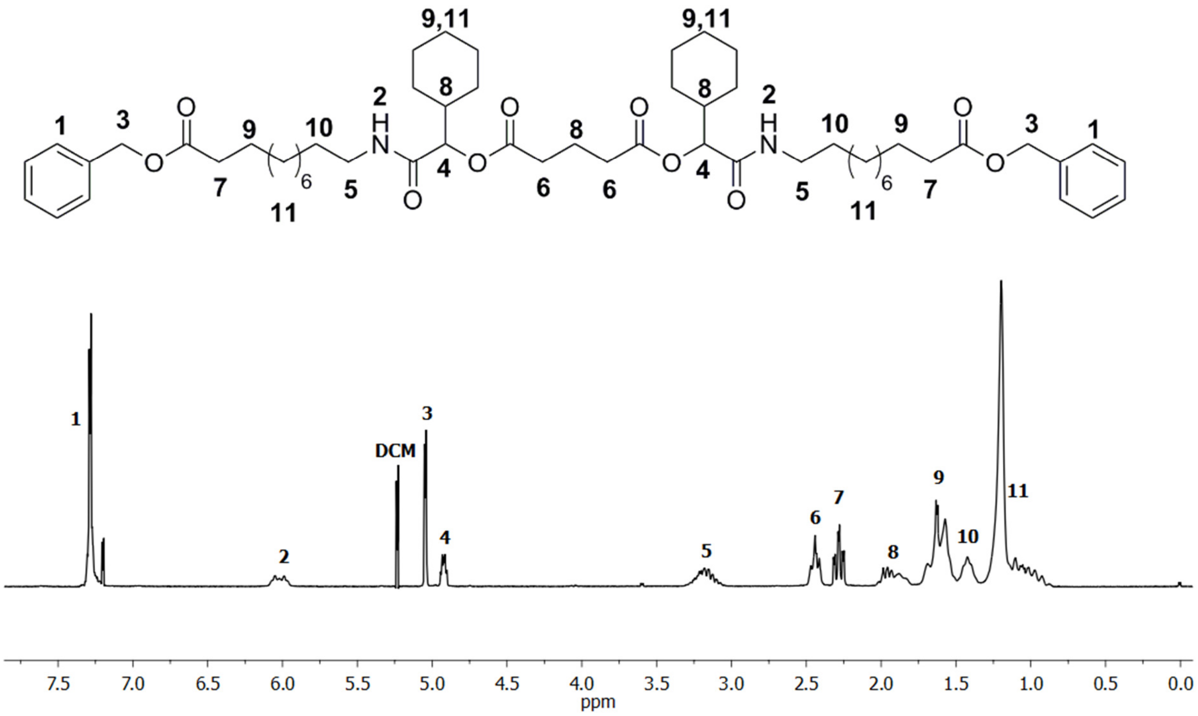
^{1}H NMR (400 MHz, $CDCl_3$) δ / ppm: 7.42 – 7.29 (m, 10H, CH aromatic, ^{1}), 6.12 (m, 2H, 2 NH, ^{2}), 5.10 (s, 4H, $2CH_2$, ^{3}), 4.98 (t, J = 4.7 Hz, 2H, 2 CH, ^{4}), 3.38 – 3.11 (m, 4H, 2 CH_2, ^{5}), 2.58 – 2.43 (m, 4H, 2 CH_2, ^{6}), 2.34 (t, J = 7.5 Hz, 4H, 2 CH_2, ^{7}), 2.09 – 1.99 (m, 2H, CH_2, ^{8}), 1.99 – 1.87 (m, 2H, 2 CH, ^{8}), 1.81 – 1.55 (m, 16H, $8CH_2$, ^{9}), 1.54 – 1.39 (m, 4H, $2CH_2$, ^{10}), 1.34 – 0.91 (m, 32H, 16 CH_2, ^{11}).

^{13}C NMR (101 MHz, $CDCl_3$) δ / ppm: 173.8, 172.1, 172.0, 169.1, 136.2, 128.7, 128.3, 78.2, 66.2, 40.1, 40.1, 39.4, 39.4, 34.4, 33.1, 31.0, 29.7, 29.6, 29.5, 29.3, 29.2, 27.5, 27.0, 26.2, 26.1, 26.0, 25.1.

HRMS-FAB-MS of $[C_{57}H_{87}N_2O_{10}]^+$: calculated: 959.6355, found: 959.6354.

IR (ATR platinum diamond): ν [cm^{-1}] = 2925.1, 2852.9, 1735.3, 1435.0, 1357.3, 1165.2, 697.7.

***R*$_f$** (hexane / ethyl acetate 1:1) = 0.73.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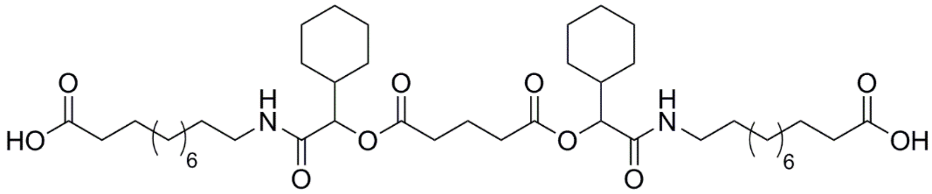
1st deprotection: Synthesis of Dimer 9



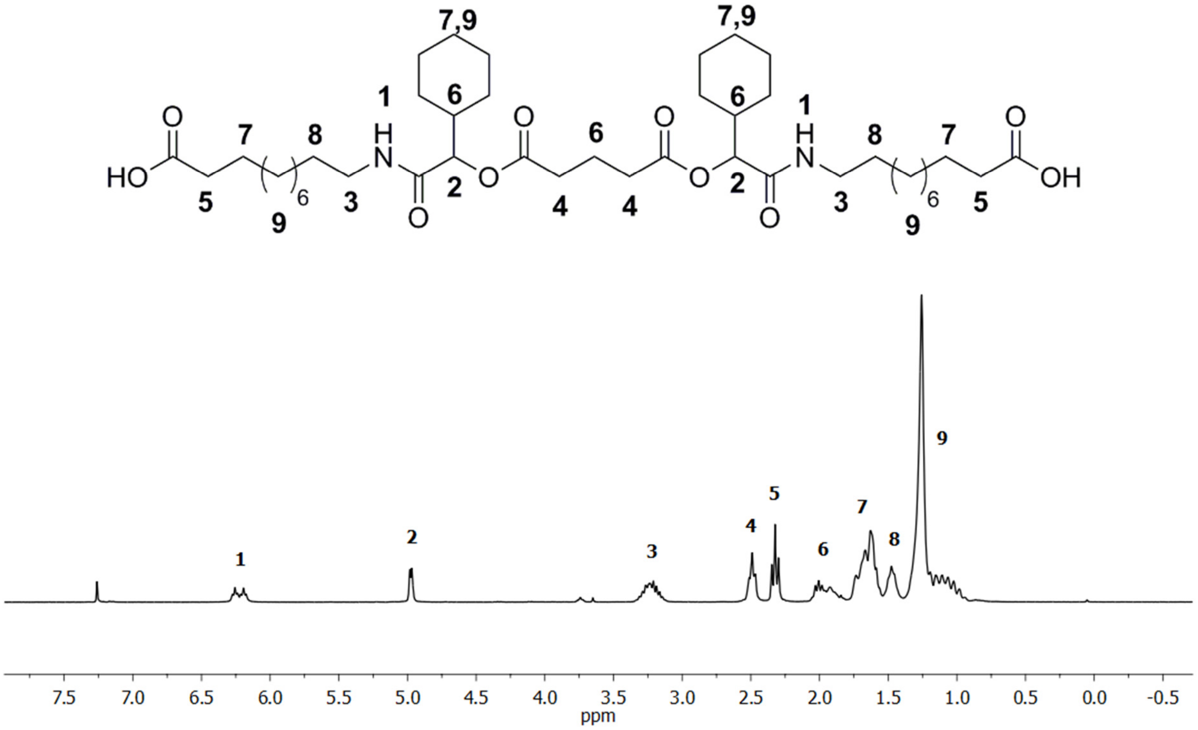
Substance **8** (2.31 g, 2.41 mmol, 1.0 eq.) was dissolved in ethyl acetate (4.9 mL, 0.5 M) and palladium on activated charcoal (0.24 g, 10 wt%) was added. The reaction mixture was purged with hydrogen (balloon) and then stirred overnight under hydrogen atmosphere. The reaction mixture became solid over night and was dissolved in THF. The heterogeneous catalyst was removed by filtration and the solvent was evaporated under reduced pressure to afford the product **9** without further purification in a yield of 94% (1.76 g, 2.26 mmol) as highly viscous, yellowish oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ / ppm: 6.33 – 6.15 (m, 2H, 2 NH, ^{1}), 4.96 (m, 2H, 2 CH, ^{2}), 3.35 – 3.09 (m, 4H, 2 CH_2, ^{3}), 2.57 – 2.40 (m, 4H, 2 CH_2, ^{4}), 2.35 – 2.25 (m, 4H, 2 CH_2, ^{5}), 2.04 – 1.82 (m, 4H, 2 CH, CH_2, ^{6}), 1.76 – 1.54 (m, 16H, 8 CH_2, ^{7}), 1.45 (m, 4H, 2 CH_2, ^{8}), 1.37 – 0.89 (m, 34H, 17 CH_2, ^{9}).

^{13}C NMR (101 MHz, $CDCl_3$) δ / ppm: 179.1, 172.2, 172.1, 169.4, 78.1, 40.0, 40.0, 39.4, 39.4, 34.2, 33.1, 32.9, 29.8, 29.5, 29.4, 29.3, 29.2, 29.21, 29.1, 27.5, 26.9, 26.1, 26.1, 25.9, 24.8, 20.3, 20.2.

HRMS-FAB-MS of $[C_{43}H_{75}N_2O_{10}]^+$: calculated: 779.5416, found: 779.5417.

IR (ATR platinum diamond): ν [cm^{-1}] = 2922.9, 2851.6, 1735.9, 1644.5, 1540.6, 1448.9, 1373.8, 1142.1, 1100.5, 983.9, 721.6, 430.1.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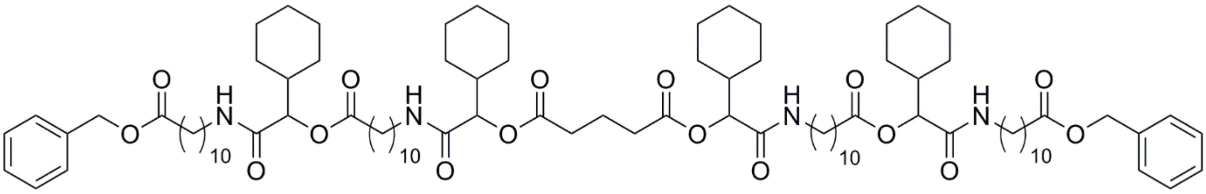
2nd Passerini reaction: Synthesis of Tetramer 10



Substance **9** (1.57 g, 2.02 mmol, 1.0 eq.) was dissolved in DCM (4.0 mL, 0.5 M). Subsequently, monomer **M1** (1.83 g, 6.09 mmol, 3.0 eq.) and cyclohexane carboxaldehyde (0.75 g, 6.69 mmol, 3.3 eq.) were added and the reaction mixture was stirred at room temperature for 24 hours. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (hexane / ethyl acetate 2:1 → 1:3) to obtain the desired product **10** in a yield of 91% (2.96 g, 1.84 mmol) as an orange, highly viscous oil.

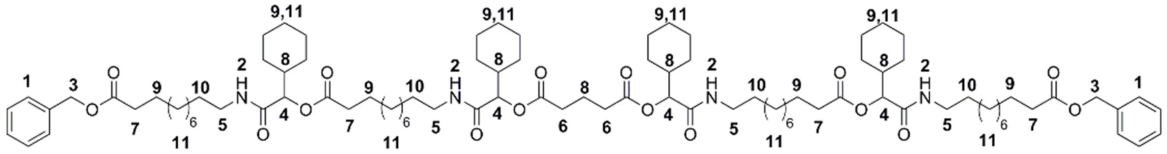
^{1}H NMR (600 MHz, $CDCl_3$) δ / ppm: 7.38 – 7.26 (m, 10H, CH, aromatic, ^{1}), 6.26 – 5.95 (m, 4H, 4 NH, ^{2}), 5.08 (s, 4H, 2 CH_2, ^{3}), 5.02 – 4.92 (m, 4H, 4 CH, ^{4}), 3.31 – 3.12 (m, 8H, 4 CH_2, ^{5}), 2.53 – 2.44 (m, 4H, 2 CH_2, ^{6}), 2.42 – 2.29 (m, 8H, 4 CH_2, ^{7}), 2.05 – 1.87 (m, 6H, 4 CH, CH_2, ^{8}), 1.77 – 1.54 (m, 24H, 12 CH_2, ^{9}), 1.46 (m, 8H, 4 CH_2, ^{10}), 1.38 – 0.89 (m, 72H, 36 CH_2, ^{11}).

^{13}C NMR (151 MHz, $CDCl_3$) δ / ppm: 173.7, 172.6, 172.1, 171.9, 169.3, 169.1, 136.2, 128.6, 128.2, 128.2, 78.1, 78.1, 66.1, 40.0, 40.0, 39.3, 39.3, 39.2, 34.4, 34.3, 33.0, 32.9, 29.6, 29.5, 29.5, 29.5, 29.4, 29.4, 29.3, 29.2, 29.2, 29.1, 27.4, 27.4, 26.9, 26.9, 26.1, 26.1, 26.0, 25.9, 25.0, 25.0, 20.3, 20.2.

HRMS-FAB-MS of $[C_{95}H_{153}N_4O_{16}]^+$: calculated: 1606.1 found: 1606.1.

IR (ATR platinum diamond): ν [cm^{-1}] = 3304.9, 2922.7, 2851.2, 1735.8, 1651.2, 1532.9, 1449.3, 1373.9, 1231.0, 1148.6, 1100.8, 984.3, 733.6, 696.4, 577.8, 453.9, 429.6.

***R*$_f$** (hexane / ethyl acetate (2:3)) = 0.68.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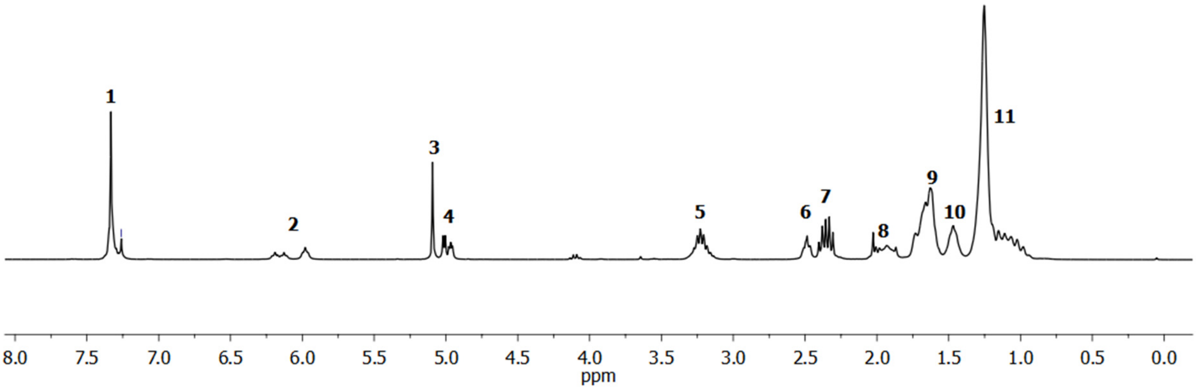
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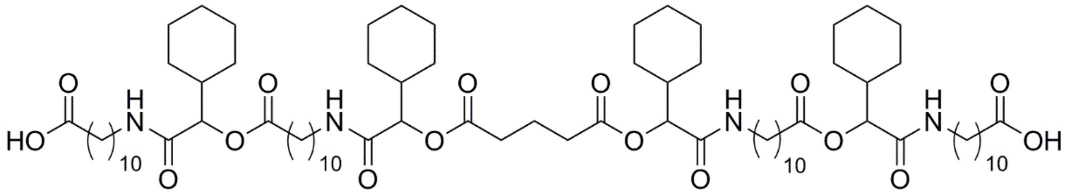
ppm

2^{nd} deprotection: Synthesis of Tetramer 11



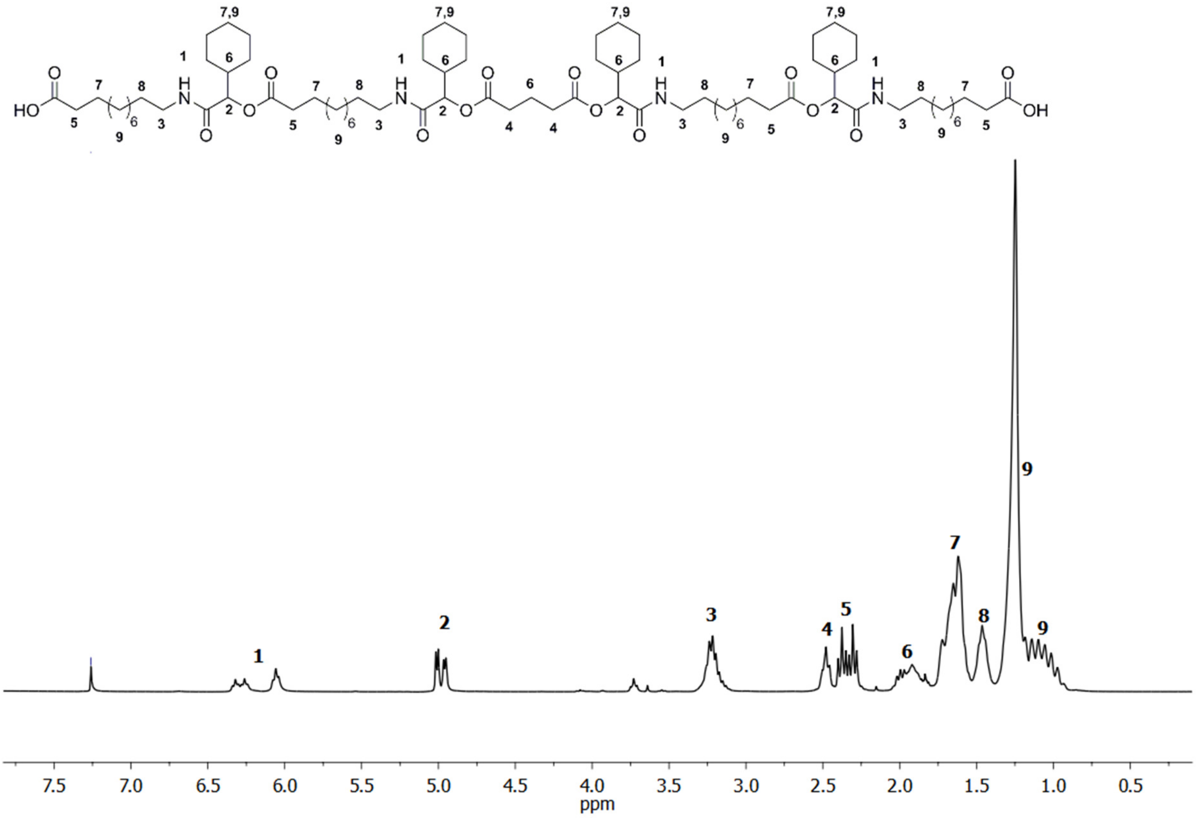
Substance **10** (2.73 g, 1.70 mmol, 1.0 eq.) was dissolved in ethyl acetate (5.5 mL, 0.3 M) and palladium on activated charcoal (0.27 g, 10 wt%) was added. The reaction mixture was purged with hydrogen (balloon) and then stirred overnight under hydrogen atmosphere. The heterogeneous catalyst was removed by filtration and the solvent was evaporated under reduced pressure to afford the desired product **11** without further purification in a yield of 94% (2.28 g, 1.60 mmol) as highly viscous, orange oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ / ppm: 6.36 – 6.00 (m, 4H, 4 NH, ^{1}), 5.06 – 4.89 (m, 4H, 4 CH, ^{2}), 3.30 – 3.09 (m, 8H, 4 CH_2, ^{3}), 2.53 – 2.42 (m, 4H, 2 CH_2, ^{4}), 2.40 – 2.24 (m, 8H, 4 CH_2, ^{5}), 2.03 – 1.76 (m, 6H, 4 CH, CH_2, ^{6}), 1.73 – 1.50 (m, 24H, 12 CH_2, ^{7}), 1.46 (s, 8H, 4 CH_2, ^{8}), 1.35 – 0.91 (m, 72H, 36 CH_2, ^{9}).

^{13}C NMR (151 MHz, $CDCl_3$) δ / ppm: 178.2, 172.7, 172.2, 172.1, 169.5, 169.4, 78.1, 68.0, 40.0, 39.4, 39.2, 34.3, 34.1, 33.1, 32.9, 29.6, 29.5, 29.4, 29.3, 29.2, 29.1, 27.5, 27.5, 27.4, 27.0, 26.9, 26.1, 26.0, 25.7, 25.1, 24.9, 20.3, 20.2.

HRMS-FAB-MS of $[C_{81}H_{141}N_4O_{16}]^+$: calculated: 1426.0337, found:1426.0304.

IR (ATR platinum diamond): ν [cm^{-1}] = 3305.2, 2922.5, 2851.4, 1737.0, 1649.3, 1537.0, 1449.0, 1372.1, 1146.4, 1100.8, 984.7, 893.0, 720.7, 430.4.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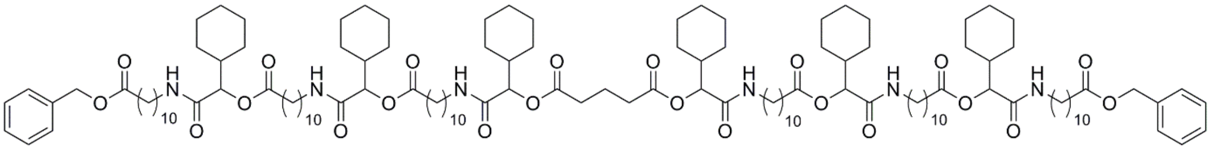
3rd Passerini reaction: Synthesis of Hexamer 12



Substance **11** (2.09 g, 1.47 mmol, 1.0 eq.) was dissolved in DCM (3.0 mL, 0.5 M). Subsequently, monomer **M1** (1.35 g 4.40 mmol, 3.0 eq.) and cyclohexane carboxaldehyde (0.50 g 4.40 mmol, 3.0 eq.) were added and the reaction mixture was stirred at room temperature for 24 hours. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (cyclohexane / ethyl acetate 2:1 → 1:2) to obtain the desired product **12** in a yield of 91% (3.00 g, 1.33 mmol) as an orange, highly viscous oil.

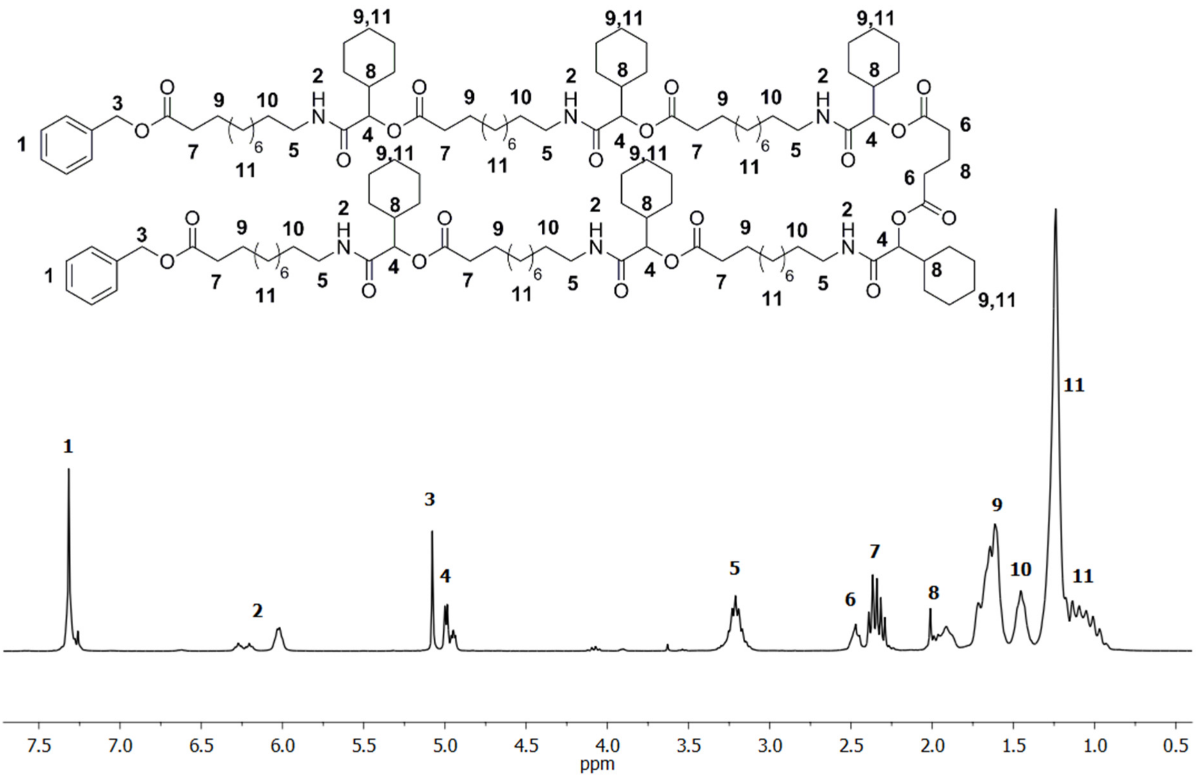
^{1}H NMR (400 MHz, $CDCl_3$) δ / ppm: 7.37 – 7.26 (m, 10H, CH, aromatic, ^{1}), 6.30 – 5.97 (m, 6H, 6 NH, ^{2}), 5.08 (s, 4H, 2 CH_2, ^{3}), 5.03 – 4.91 (m, 6H, 6 CH, ^{4}), 3.30 – 3.06 (m, 12H, 6 CH_2, ^{5}), 2.50 – 2.42 (m, 4H, 2 CH_2, ^{6}), 2.39 – 2.27 (m, 12H, 6 CH_2, ^{7}), 2.04 – 1.85 (m, 8H, 6 CH, CH_2, ^{8}), 1.79 – 1.52 (m, 36H, 18 CH_2, ^{9}), 1.44 (m, 12H, 6 CH_2, ^{10}), 1.33 – 0.89 (m, 108H, 54 CH_2, ^{11}).

^{13}C NMR (101 MHz, $CDCl_3$) δ / ppm: 173.7, 172.6, 172.1, 171.9, 169.3, 169.3, 169.1, 136.2, 128.6, 128.2, 128.2, 78.1, 78.0, 66.1, 40.0, 39.9, 39.3,39.2, 34.6, 34.3, 33.0, 32.9, 29.6, 29.5, 29.4, 29.3, 29.2, 29.1, 27.4, 26.9, 26.1, 26.1, 26.0, 25.9, 25.0.

HRMS-FAB-MS of $[C_{133}H_{219}N_6O_{22}]^+$: calculated: 2252.6, found: 2252.9.

IR (ATR platinum diamond): ν [cm^{-1}] = 3304.9, 2922.4, 2851.1, 1736.6, 1650.8, 1533.0, 1449.3, 1373.6, 1230.5, 1150.6, 1100.9, 985.1, 844.4, 731.1, 696.4, 577.3, 428.7.

***R*$_f$** (cyclohexane / ethyl acetate 2:3) = 0.68.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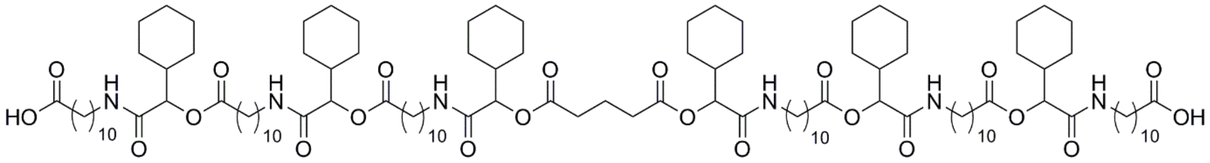
3rd deprotection: Synthesis of Hexamer 13



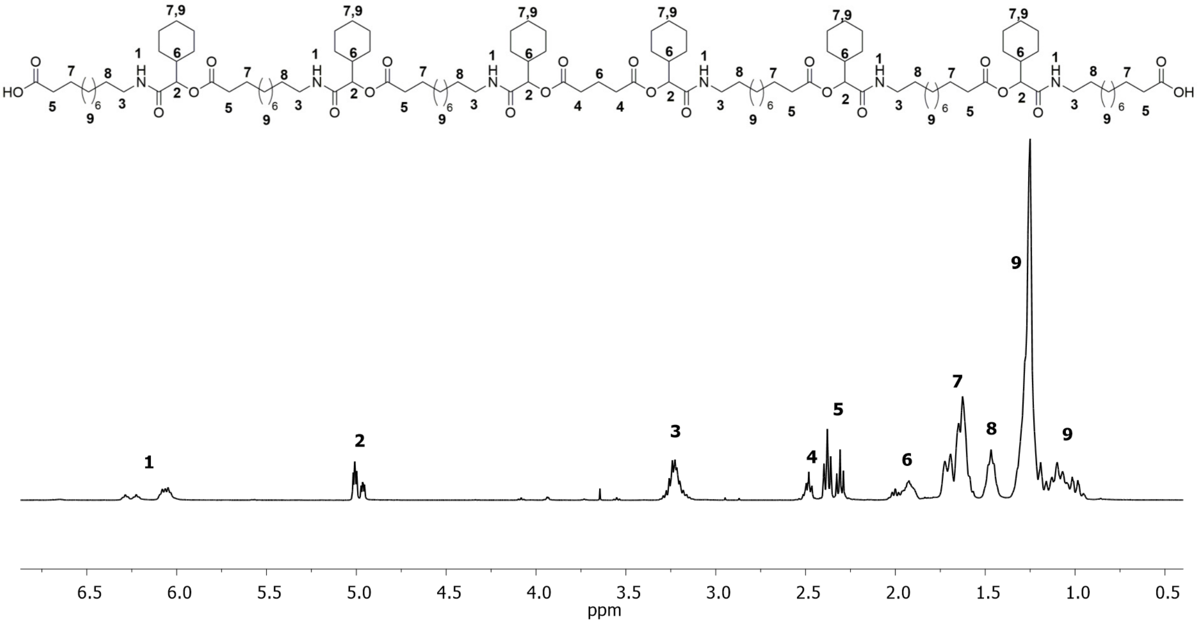
Substance **12** (2.83 g, 1.25 mmol, 1.0 eq.) was dissolved in ethyl acetate (4.2 mL, 0.15 M) and palladium on activated charcoal (0.22 g, 8 wt%) was added. The reaction mixture was purged with hydrogen (balloon) and then stirred overnight under hydrogen atmosphere. The heterogeneous catalyst was filtered off and the solvent was evaporated under reduced pressure to obtain the product **13** without further purification in a yield of 82% (2.12 g, 1.02 mmol) as highly viscous, yellowish oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ / ppm: 6.34 – 5.97 (m, 6H, 6 NH, ^{1}), 5.05 – 4.89 (m, 6H, 6 CH, ^{2}), 3.36 – 3.10 (m, 12H, 6 CH_2, ^{3}), 2.52 – 2.44 (m, 4H, 2 CH_2, ^{4}), 2.41 – 2.21 (m, 12H, 6 CH_2, ^{5}), 2.05 – 1.84 (m, 8H, 6 CH, CH_2, ^{6}), 1.78 – 1.54 (m, 36H, 21 CH_2, ^{7}), 1.53 – 1.38 (m, 12H, 6 CH_2, ^{8}), 1.37 – 0.89 (m, 108H, 53 CH_2, ^{9}).

^{13}C NMR (101 MHz, $CDCl_3$) δ / ppm: 177.9, 172.8, 172.7, 172.2, 172.1, 169.5, 169.3, 78.1, 40.1, 40.0, 39.4, 39.3, 34.4, 34.1, 33.1, 32.9, 29.6, 29.5, 29.4, 29.3, 29.2, 29.1, 27.5, 27.4, 27.0, 26.9, 26.2, 26.1, 26.0, 25.1, 24.9, 20.3, 20.2.

HRMS-FAB-MS of $[C_{119}H_{206}N_6O_{22}]^+$: calculated: 2072.5, found:2072.8.

IR (ATR platinum diamond): ν [cm^{-1}] = 3293.2, 2922.4, 2851.2, 1737.7, 1650.2, 1536.9, 1449.0, 1371.4, 1149.1, 1100.7, 985.4, 892.9, 720.8, 428.5.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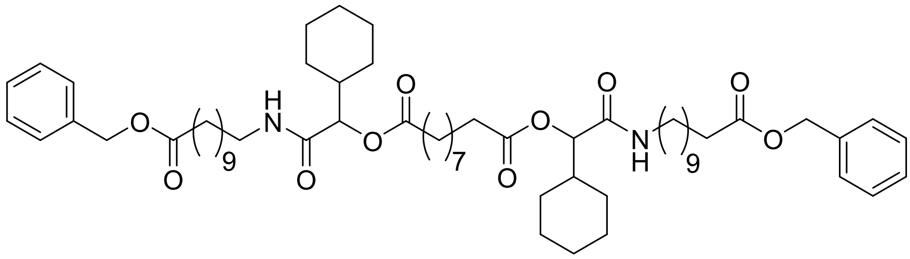
1st Passerini reaction: Synthesis of Dimer 14



Sebacic acid (776 mg, 3.85 mmol, 1.0 eq.) was suspended in DCM (7.6 mL, 0.5 M). Subsequently, cyclohexane carboxaldehyde (1.4 mL, 1.29 g, 11.5 mmol, 3.0 eq.) and monomer **M1** (3.48 g, 11.5 mmol, 3.0 eq.) were added and the reaction mixture was stirred at room temperature for 24 hours. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (cyclohexane / ethyl acetate 5:1 → 1:1) to obtain the desired product **14** in a yield of 97% (3.84 g, 3.73 mmol) as a yellowish oil.

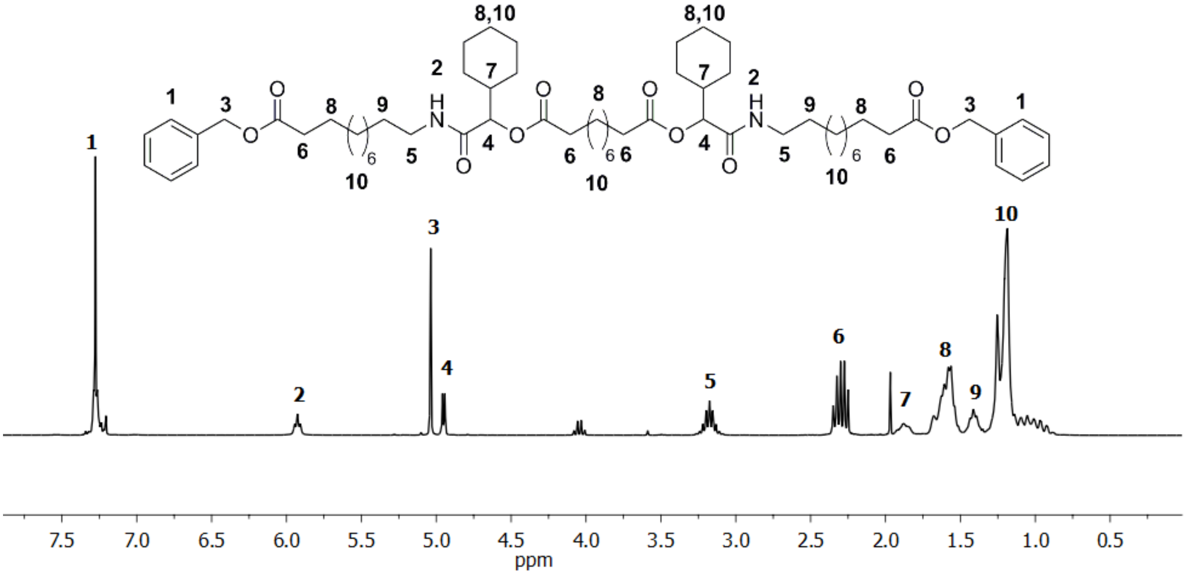
^{1}H NMR (300 MHz, $CDCl_3$) δ / ppm: 7.49 – 7.27 (m, 10H, CH, aromatic, ^{1}), 5.96 (t, J = 5.7 Hz, 2H, ^{2}), 5.10 (s, 4H, ^{3}), 5.01 (d, J = 4.7 Hz, 2H, ^{4}), 3.40 – 3.11 (m, 4H, ^{5}), 2.48 – 2.23 (m, 8H, ^{6}), 2.00 – 1.85 (m, 2H, ^{7}), 1.79 – 1.56 (m, 16H, ^{8}), 1.53 – 1.41 (m, 4H, ^{9}), 1.39 – 0.88 (m, 44H, ^{10}).

^{13}C NMR (75 MHz, $CDCl_3$) δ / ppm: 173.76, 172.58, 169.26, 136.21, 128.62, 128.24, 77.73, 66.15, 40.06, 39.24, 34.40, 34.33, 29.66, 29.53, 29.42, 29.29, 29.18, 29.14, 27.40, 26.93, 26.16, 26.08, 25.96, 25.02.

HRMS-FAB-MS of $[C_{62}H_{97}N_2O_{10}]^+$: calculated: 1029.7138, found: 1029.7136.

IR (ATR platinum diamond): ν [cm^{-1}] = 2925.1, 2852.9, 1735.3, 1435.0, 1357.3, 1165.2, 697.7.

***R*$_f$** (cyclohexane / ethyl acetate 2:1) = 0.54.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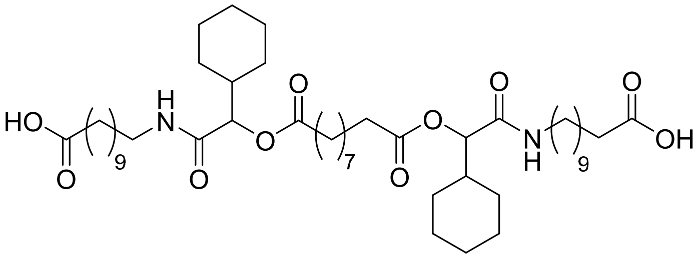
1st deprotection: Synthesis of Dimer 15



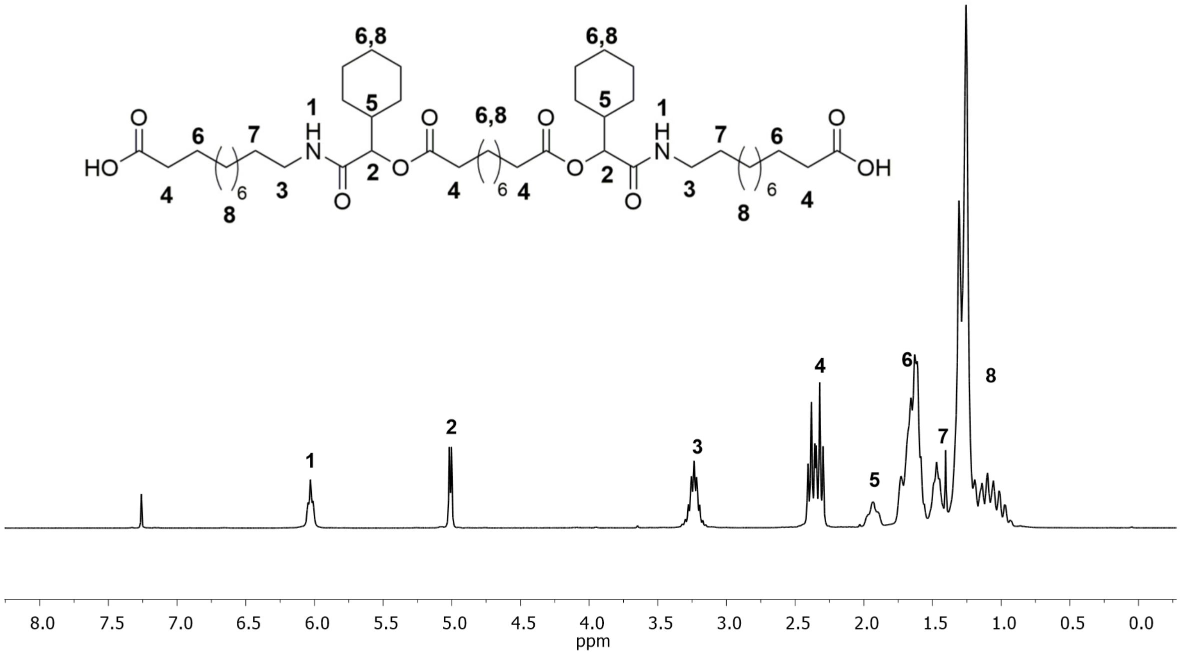
Substance **14** (3.61 g, 3.51 mmol, 1.0 eq.) was dissolved in ethyl acetate (7.0 mL, 0.5 M) and palladium on activated charcoal (0.36 g, 10 wt%) was added. The reaction mixture was purged with hydrogen (balloon) and then stirred overnight under hydrogen atmosphere. The reaction mixture became solid over night and was dissolved in THF. The heterogeneous catalyst was filtered off and the solvent was evaporated under reduced pressure to afford the product **15** without further purification in a quant. yield (2.98 g, 3.51 mmol) as highly viscous, yellowish oil.

^{1}H NMR (300 MHz, CDCl$_3$) δ / ppm: 6.03 (t, J = 5.4 Hz, 2H, ^{1}), 5.01 (d, J = 4.7 Hz, 2H, ^{2}), 3.36 – 3.09 (m, 4H, ^{3}), 2.52 – 2.18 (m, 8H, ^{4}), 2.03 – 1.84 (m, 2H, ^{5}), 1.78 – 1.53 (m, 16H, ^{6}), 1.43 (dd, J = 20.1, 6.3 Hz, 4H, ^{7}), 1.38 – 0.88 (m, 44H, ^{8}).

^{13}C NMR (75 MHz, CDCl$_3$) δ / ppm: 179.28, 172.69, 169.51, 157.13, 132.52, 101.48, 77.75, 40.02, 39.29, 34.33, 34.14, 29.57, 29.45, 29.33, 29.29, 29.22, 29.15, 29.07, 27.42, 27.21, 27.01, 26.88, 26.16, 26.07, 25.95, 25.00, 24.79.

HRMS-ESI-MS of [$C_{48}H_{84}N_2O_{10}Na$]$^+$: calculated: 871.6018, found: 871.6019.

IR (ATR platinum diamond): ν[cm^{-1}] = 2922.9, 2851.6, 1735.9, 1644.5, 1540.6, 1448.9, 1373.8, 1142.1, 1100.5, 983.9, 721.6, 430.1.



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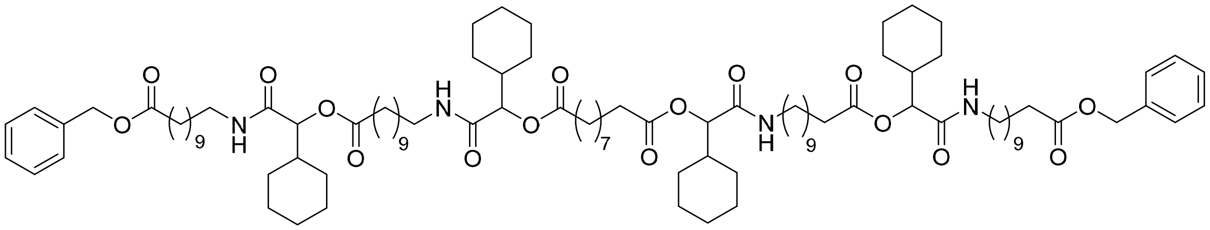
2nd Passerini reaction: Synthesis of Tetramer 16



Substance **15** (2.41 g 2.83 mmol, 1.0 eq.) was dissolved in DCM (5.6 mL, 0.5 M). Subsequently, monomer **M1** (2.56 g, 8.49 mmol, 3.0 eq.) and cyclohexane carboxaldehyde (0.95 g 8.49 mmol, 3.0 eq.) were added and the reaction mixture was stirred at room temperature for 24 hours. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (cyclohexane / ethyl acetate 3:1 → 1:2) to obtain the desired product **16** in a yield of 91% (4.29 g, 2.55 mmol) as a yellowish, highly viscous oil.

^{1}H NMR (300 MHz, CDCl$_3$) δ / ppm: 7.43 – 7.27 (m, 10H, ^{1}), 6.01 (t, J = 5.5 Hz, 4H, ^{2}), 5.08 (s, 4H, ^{3}), 4.99 (t, J = 4.3 Hz, 4H, ^{4}), 3.36 – 3.08 (m, 8H, ^{5}), 2.49 – 2.18 (m, 12H, ^{6}), 1.93 (m, 4H, ^{7}), 1.78 – 1.54 (m, 28H, ^{8}), 1.44 (m, 8H, ^{9}), 1.36 – 0.80 (m, 80H, ^{10}).

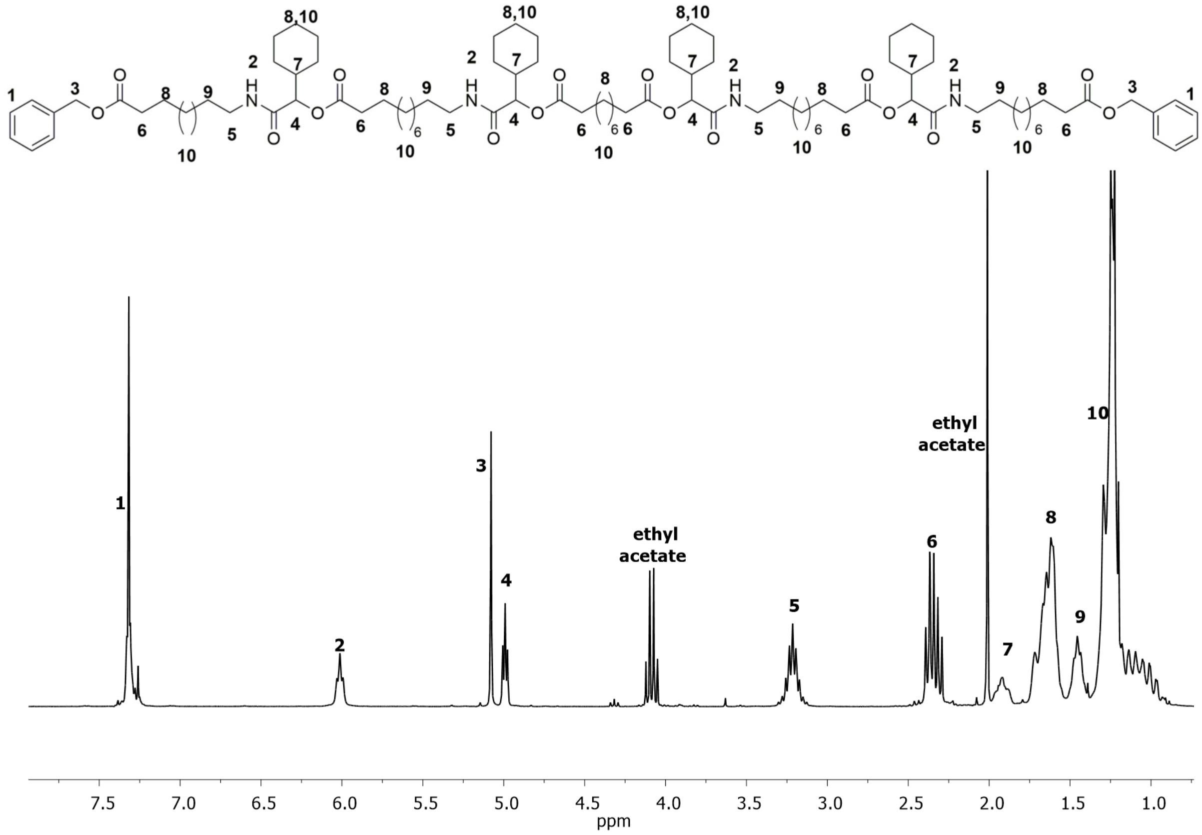
^{13}C NMR (75 MHz, CDCl$_3$) δ / ppm: 173.70, 172.59, 172.56, 171.17, 169.25, 136.16, 128.57, 128.18, 77.69, 77.65, 66.09, 60.42, 40.02, 39.18, 34.35, 34.31, 34.27, 29.61, 29.49, 29.38, 29.25, 29.14, 29.11, 27.38, 27.35, 26.89, 26.12, 26.04, 25.92, 25.02, 24.98, 21.08, 14.24.

HRMS-ESI-MS of $[C_{100}H_{162}N_4O_{16}Na]^+$: calculated: 1698.1878 found: 1698.1914.

$[C_{100}H_{162}N_4O_{16}Na_2]^{2+}$: calculated: 860.5885 found: 860.5882.

IR (ATR platinum diamond): ν [cm^{-1}] = 3304.9, 2922.7, 2851.2, 1735.8, 1651.2, 1532.9, 1449.3, 1373.9, 1231.0, 1148.6, 1100.8, 984.3, 733.6, 696.4, 577.8, 453.9, 429.6.

***R*$_f$** (cyclohexane / ethyl acetate 3:2) = 0.50.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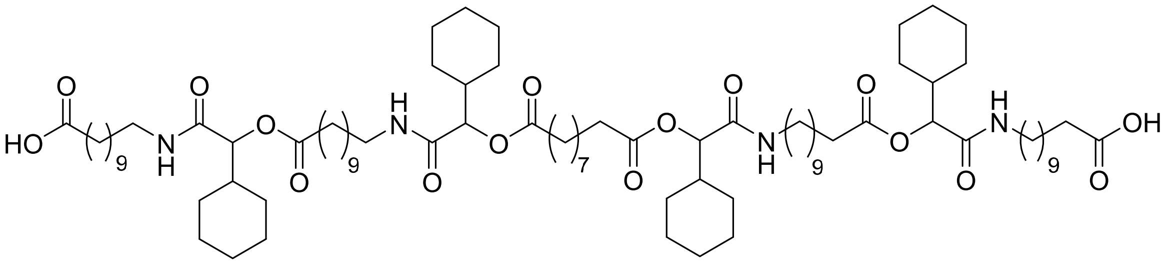
2nd deprotection: Synthesis of Tetramer 17



Substance **16** (3.89 g, 2.32 mmol, 1.0 eq.) was dissolved in ethyl acetate (5.0 mL, 0.5 M) and palladium on activated charcoal (0.39 g, 10 wt%) was added. The reaction mixture was purged with hydrogen (balloon) and then stirred overnight under hydrogen atmosphere. The heterogeneous catalyst was removed by filtration and the solvent was evaporated under reduced pressure to afford the desired product **17** without further purification in a yield of 98% (3.39 g, 2.26 mmol) as highly viscous, orange oil.

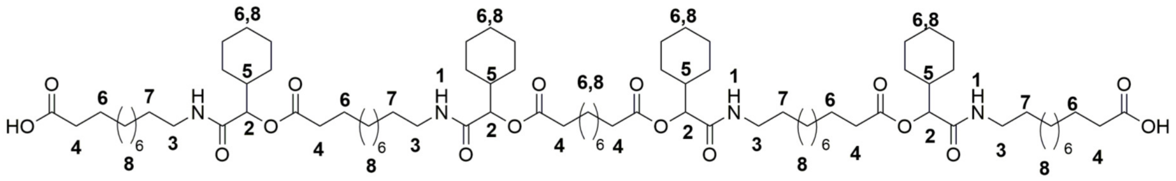
^{1}H NMR (300 MHz, $CDCl_3$) δ / ppm: 6.05 (d, J = 5.7 Hz, 4H, ^{1}), 5.11 – 4.89 (m, 4H, ^{2}), 3.35 – 3.08 (m, 8H, ^{3}), 2.56 – 2.15 (m, 12H, ^{4}), 1.97 (m, 4H, ^{5}), 1.81 – 1.52 (m, 28H, ^{6}), 1.43 (m, 8H, ^{7}), 1.37 – 0.79 (m, 80H, ^{8}).

^{13}C NMR (75 MHz, $CDCl_3$) δ / ppm: 178.35, 172.68, 169.46, 157.05, 133.81, 126.28, 113.98, 101.39, 77.76, 77.71, 40.03, 39.84, 39.30, 39.25, 34.36, 34.31, 34.10, 29.62, 29.54, 29.45, 29.34, 29.26, 29.22, 29.13, 29.10, 27.82, 27.45, 27.40, 26.92, 26.89, 26.16, 26.07, 25.96, 25.08, 24.99, 24.84.

HRMS-ESI-MS of $[C_{86}H_{150}N_4O_{16}Na]^+$: calculated: 1518.0939, found: 1518.0933.

$[C_{86}H_{150}N_4O_{16}Na_2]^{2+}$: calculated: 770.5416, found: 770.5398.

IR (ATR platinum diamond): $\nu\,[cm^{-1}]$ = 3305.2, 2922.5, 2851.4, 1737.0, 1649.3, 1537.0, 1449.0, 1372.1, 1146.4, 1100.8, 984.7, 893.0, 720.7, 430.4.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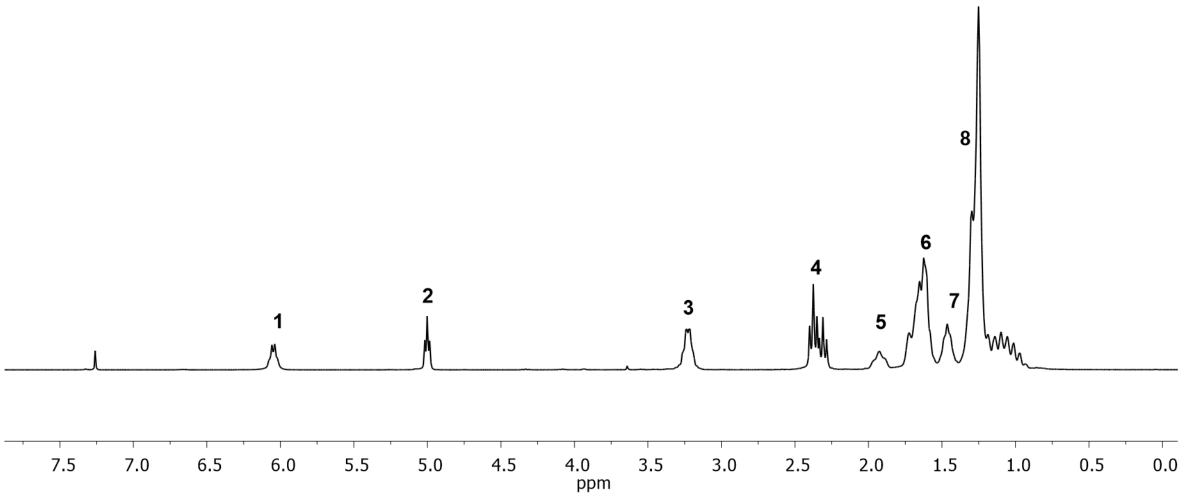
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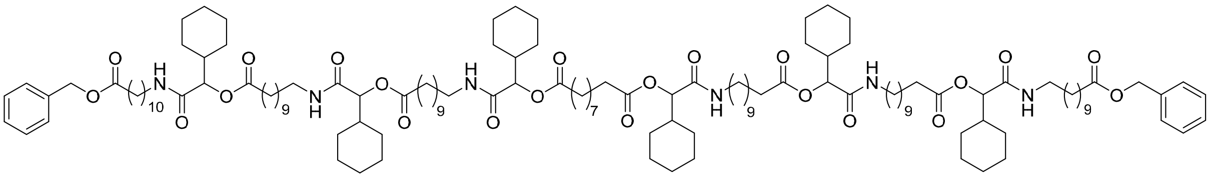
3rd Passerini reaction: Synthesis of Hexamer 18



Substance **17** (2.38 g, 1.58 mmol, 1.0 eq.) was dissolved in DCM (4.8 mL, 0.33 M). Subsequently, monomer **M1** (1.44 g 4.77 mmol, 3.0 eq.) and cyclohexane carboxaldehyde (0.53 g, 4.77 mmol, 3.0 eq.) were added and the reaction mixture was stirred at room temperature for 48 hours. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (cyclohexane / ethyl acetate 7:1 → 1:3) to obtain the desired product **18** in a yield of 97% (3.58 g, 1.54 mmol) as a yellowish, highly viscous oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ / ppm: 7.39 – 7.21 (m, 10H, ^{1}), 6.05 (s, 6H, ^{2}), 5.06 (s, 4H, ^{3}), 4.97 (t, J = 4.2 Hz, 6H, ^{4}), 3.32 – 3.04 (m, 12H, ^{5}), 2.44 – 2.24 (m, 16H, ^{6}), 1.88 (m, 6H, ^{7}), 1.65 (m, 40H, ^{8}), 1.51 – 1.36 (m, 12H, ^{9}), 1.35 – 0.83 (m, 116H, ^{10}).

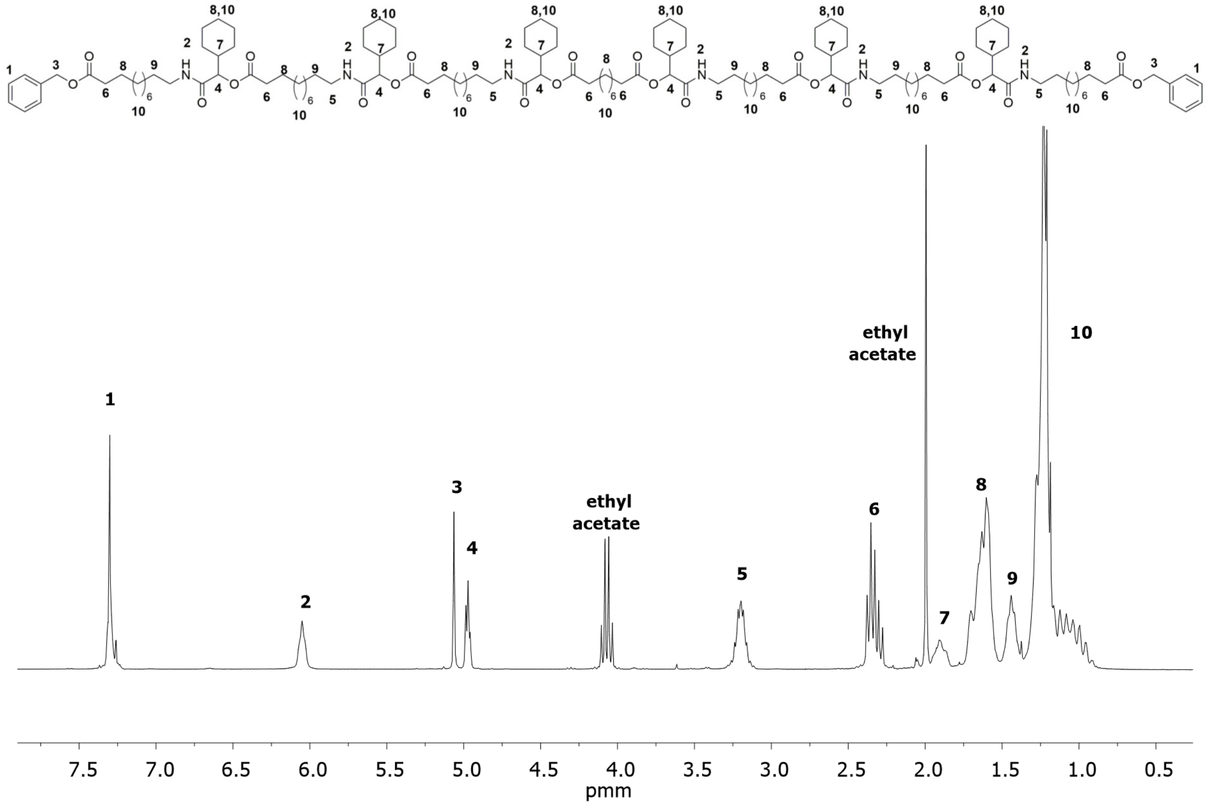
^{13}C NMR (75 MHz, $CDCl_3$) δ / ppm: 173.65, 172.57, 171.12, 169.22, 136.14, 128.54, 128.14, 77.65, 77.59, 66.05, 60.38, 39.99, 39.15, 34.31, 34.27, 34.23, 29.58, 29.46, 29.36, 29.23, 29.13, 29.10, 27.33, 27.15, 26.86, 26.09, 26.01, 25.90, 24.99, 24.94, 21.04, 14.21.

HRMS-ESI-MS of $[C_{138}H_{228}N_6O_{22}Na]^+$: calculated: 2344.6799, found: 2344.6778.

$[C_{138}H_{228}N_6O_{22}Na_2]^{2+}$: calculated: 1183.8346, found: 1183.8368.

IR (ATR platinum diamond): ν [cm^{-1}] = 3304.9, 2922.4, 2851.1, 1736.6, 1650.8, 1533.0, 1449.3, 1373.6, 1230.5, 1150.6, 1100.9, 985.1, 844.4, 731.1, 696.4, 577.3, 428.7.

***R*$_f$** (cyclohexane / ethyl acetate 2:1) = 0.51.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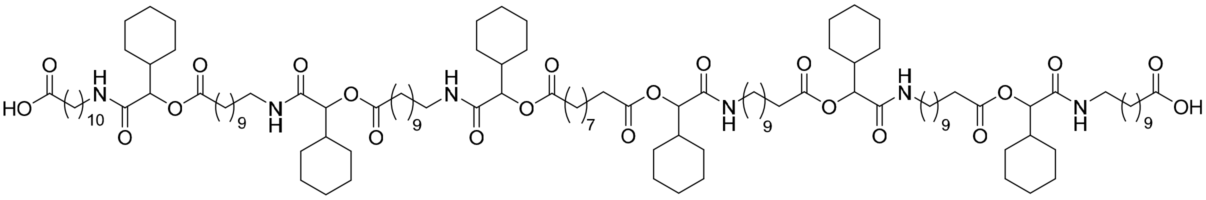
3rd deprotection: Synthesis of Hexamer 19



Substance **18** (3.24 g, 1.39 mmol, 1.0 eq.) was dissolved in ethyl acetate (4.5 mL, 0.3 M) and palladium on activated charcoal (0.32 g, 10 wt%) was added. The reaction mixture was purged with hydrogen (balloon) and then stirred overnight under hydrogen atmosphere. The heterogeneous catalyst was filtered off and the solvent was evaporated under reduced pressure to obtain the product **19** without further purification in a yield of 94% (2.80 g, 1.31 mmol) as highly viscous, yellowish oil.

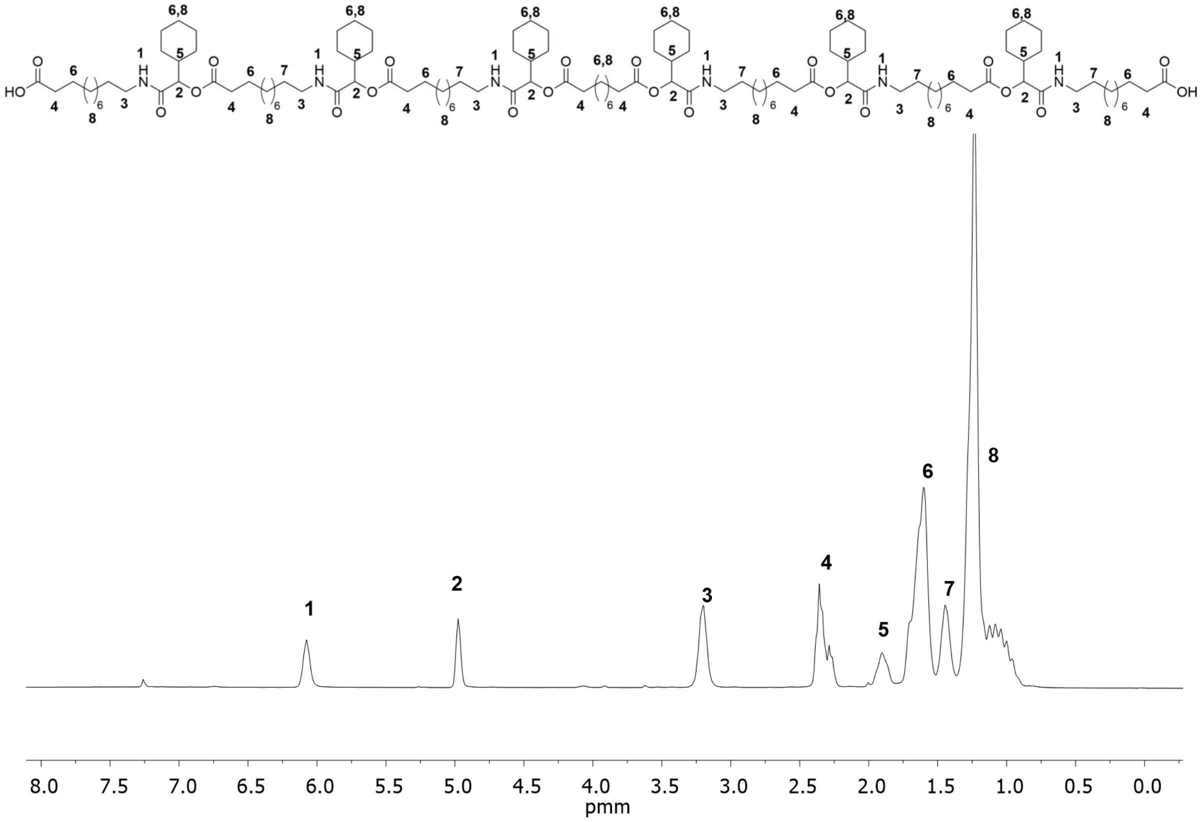
^{1}H NMR (300 MHz, CDCl$_3$) δ / ppm: 6.08 (m, 6H, ^{1}), 4.98 (m, 6H, ^{2}), 3.20 (m, 12H, ^{3}), 2.32 (m, 16H, ^{4}), 1.84 (m, 6H, ^{5}), 1.60 (m, 40H, ^{6}), 1.45 (m, 12H, ^{7}), 1.34 – 0.78 (m, 116H, ^{8}).

^{13}C NMR (75 MHz, CDCl$_3$) δ / ppm: 177.76, 172.64, 169.41, 156.85, 134.14, 133.85, 126.08, 113.51, 101.20, 77.67, 40.00, 39.65, 39.24, 34.30, 34.06, 29.57, 29.49, 29.39, 29.22, 29.09, 27.39, 26.88, 26.11, 26.03, 25.92, 25.02, 24.95, 24.84.

HRMS-ESI-MS of [$C_{124}H_{216}N_6O_{22}Na$]$^+$: calculated: 2164.5860, found: 2164.5895.

[$C_{124}H_{216}N_6O_{22}Na_2$]$^{2+}$: calculated: 1093.7876, found: 1093.7906.

IR (ATR platinum diamond): ν[cm^{-1}] = 3293.2, 2922.4, 2851.2, 1737.7, 1650.2, 1536.9, 1449.0, 1371.4, 1149.1, 1100.7, 985.4, 892.9, 720.8, 428.5.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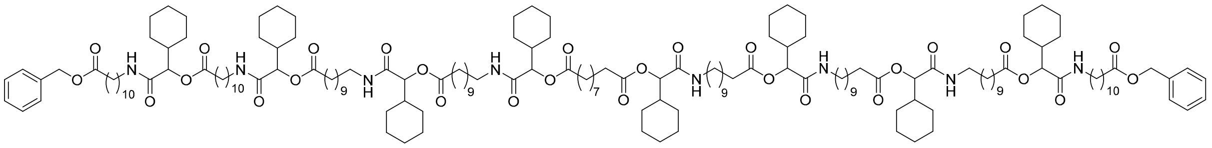
4th Passerini reaction: Synthesis of Octamer 20



Substance **19** (1.94 g, 0.90 mmol, 1.0 eq.) was dissolved in DCM (2.0 mL, 0.5 M). Subsequently, monomer **M1** (0.82 g, 2.71 mmol, 3.0 eq.) and cyclohexane carboxaldehyde (0.33 g, 2.71 mmol, 3.0 eq.) were added and the reaction mixture was stirred at room temperature for 48 hours. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (cyclohexane / ethyl acetate 5:1 → pure ethyl acetate) to obtain the desired product **20** in a yield of 99% (2.70 g, 0.90 mmol) as an orange, highly viscous oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ / ppm: 7.30 (s, 10H, ^{1}), 6.09 (m, 8H, ^{2}), 5.03 (s 4H, ^{3}), 4.98 (m, 8H, ^{4}), 3.19 (m, 16H, ^{5}), 2.47 – 2.21 (m, 20H, ^{6}), 1.90 (m, 8H, ^{7}), 1.75 – 1.52 (m, 52H, ^{8}), 1.40 (m, 16H, ^{9}), 1.34 – 0.68 (m, 152H, ^{10}).

^{13}C NMR (75 MHz, $CDCl_3$) δ / ppm: 173.65, 172.57, 169.23, 163.04, 156.88, 136.14, 128.53, 128.15, 128.13, 77.62, 66.05, 60.38, 39.99, 39.15, 34.32, 34.27, 34.23, 29.58, 29.46, 29.36, 29.22, 29.12, 29.10, 29.07, 27.34, 26.85, 26.09, 26.01, 25.90, 24.99, 24.94, 21.04, 14.21.

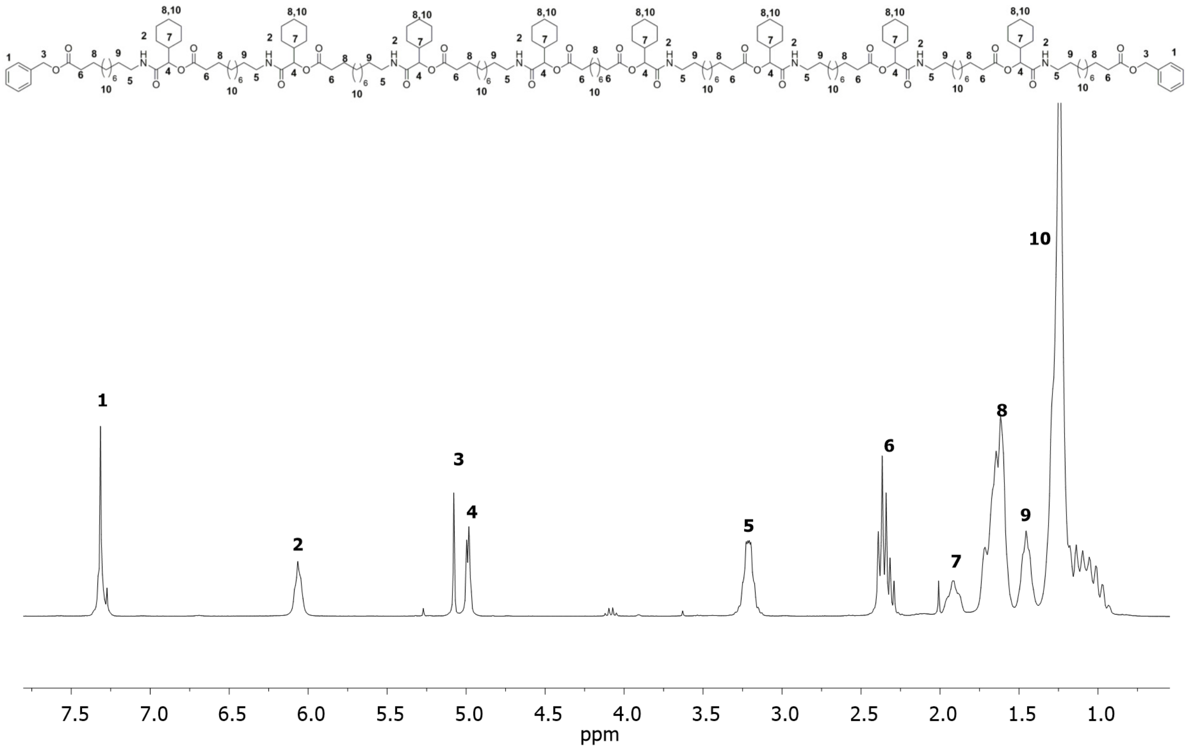
HRMS-ESI-MS of $[C_{176}H_{294}N_8O_{28}Na]^+$: calculated: 2991.1720, found:2991.1691.

$[C_{176}H_{294}N_8O_{28}Na_2]^{2+}$: calculated: 1507.0806, found: 1507.0835.

$[C_{176}H_{294}N_8O_{28}Na_3]^{3+}$: calculated: 1012.3835, found: 1012.3814.

IR (ATR platinum diamond): ν [cm^{-1}] = 3295.1, 2923.1, 2851.9, 1737.7, 1651.1, 1534.4, 1449.8, 1372.8, 1158.9, 1101.2, 986.3, 723.0, 697.0, 578.2, 430.6.

R_f (cyclohexane / ethyl acetate 1:1) = 0.57.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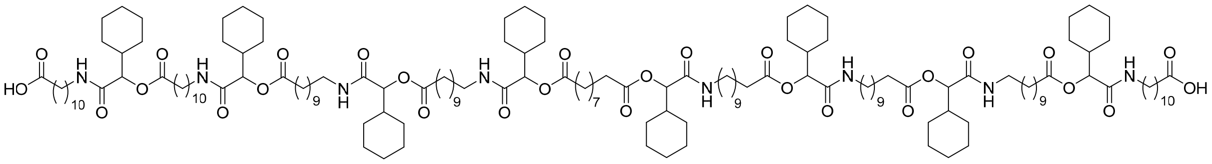
4th deprotection: Synthesis of Octamer 21



Substance **20** (2.51 g 0.85 mmol, 1.0 eq.) was dissolved in a mixture of 5.0 mL ethyl acetate and 0.5 mL methanol and palladium on activated charcoal (0.25 g, 10 wt%) was added. The reaction mixture was purged with hydrogen (balloon) and then stirred overnight under hydrogen atmosphere. The heterogeneous catalyst was filtered off and the solvent was evaporated under reduced pressure to obtain the product **21** without further purification in a yield of 78% (1.82 g, 0.65 mmol) as highly viscous, yellowish oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ / ppm: 6.10 (s, 8H, ^{1}), 4.96 (s, 8H, ^{2}), 3.19 (m, 16H, ^{3}), 2.31 (m, 20H, ^{4}), 1.83 (m, 8H, ^{5}), 1.75 – 1.52 (m, 52H, ^{6}), 1.39 (m, 16H, ^{7}), 1.32 – 0.81 (m, 152H, ^{8}).

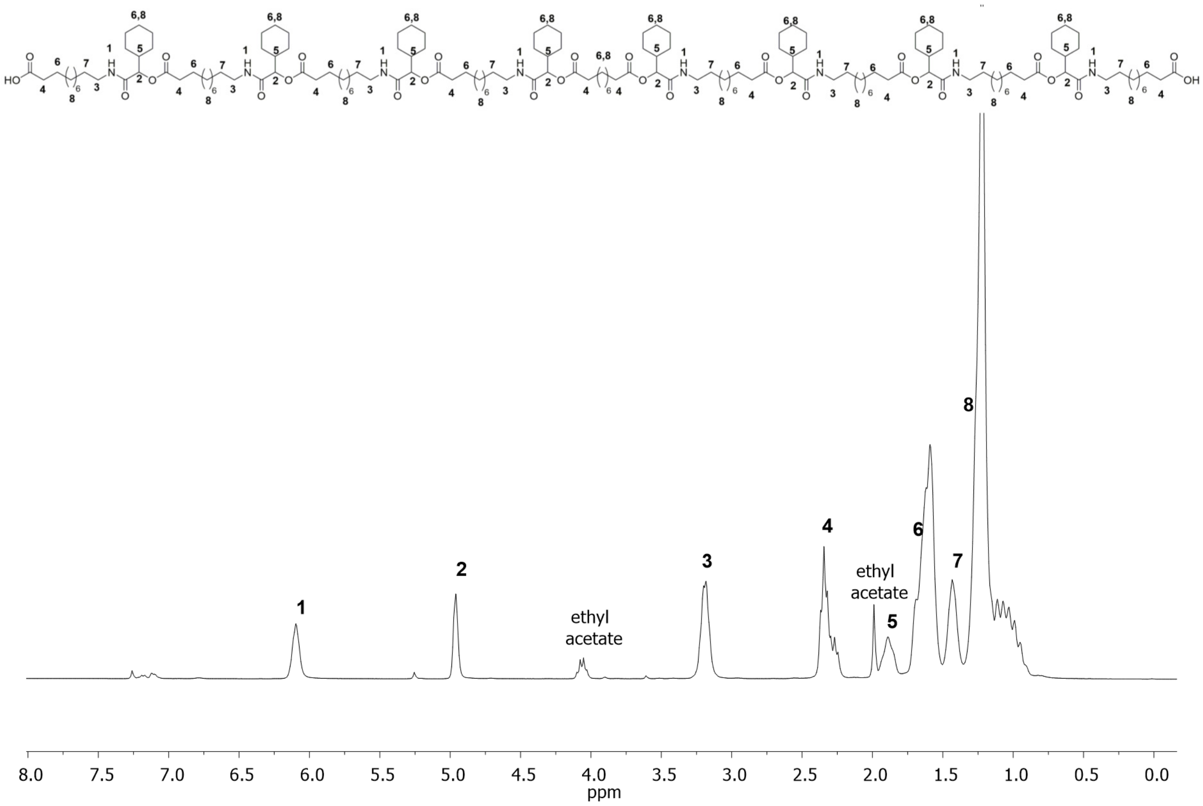
^{13}C NMR (75 MHz, $CDCl_3$) δ / ppm: 185.58, 182.89, 180.29, 177.43, 172.64, 169.39, 162.97, 156.81, 134.14, 133.28, 117.84, 78.21, 77.51, 77.03, 45.76, 39.96, 39.62, 39.20, 34.27, 34.05, 29.47, 29.37, 29.19, 27.39, 26.84, 26.06, 24.98, 15.00.

HRMS-ESI-MS of $[C_{162}H_{282}N_8O_{28}Na]^+$: calculated: 2811.0781, found: 2811.0787.

$[C_{162}H_{282}N_8O_{28}Na_2]^{2+}$: calculated: 1417.0337, found: 1417.0364.

$[C_{162}H_{282}N_8O_{28}Na_3]^{3+}$: calculated: 952.3522, found: 952.3505.

IR (ATR platinum diamond): ν [cm^{-1}] = 3292.9, 2922.5, 2851.7, 1738.4, 1649.2, 1535.2, 1449.4, 1371.8, 1159.6, 1100.9, 986.3, 722.1, 430.8.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ethyl acetate
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ethyl acetate
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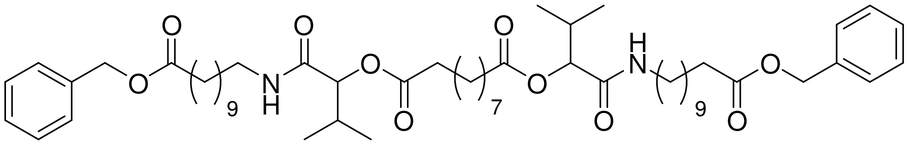
ppm

3.3 Oligomer with isopropyl side chains

1st Passerini reaction: Synthesis of Dimer 22



Sebacic acid (700 mg, 3.46 mmol, 1.0 eq.) was dissolved in DCM (7.0 mL, 0.5 M). Subsequently, monomer **M1** (3.13 g, 10.4 mmol, 3.0 eq.) and isobutyraldehyde (0.95 mL, 75.0 mg, 10.4 mmol, 3.0 eq.) were added and the reaction mixture was stirred at room temperature for 24 hours. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (cyclohexane / ethyl acetate 5:1 → 1:1) to obtain the desired product **22** in a yield of 99% (3.27 g, 3.45 mmol) as a yellowish, highly viscous oil.

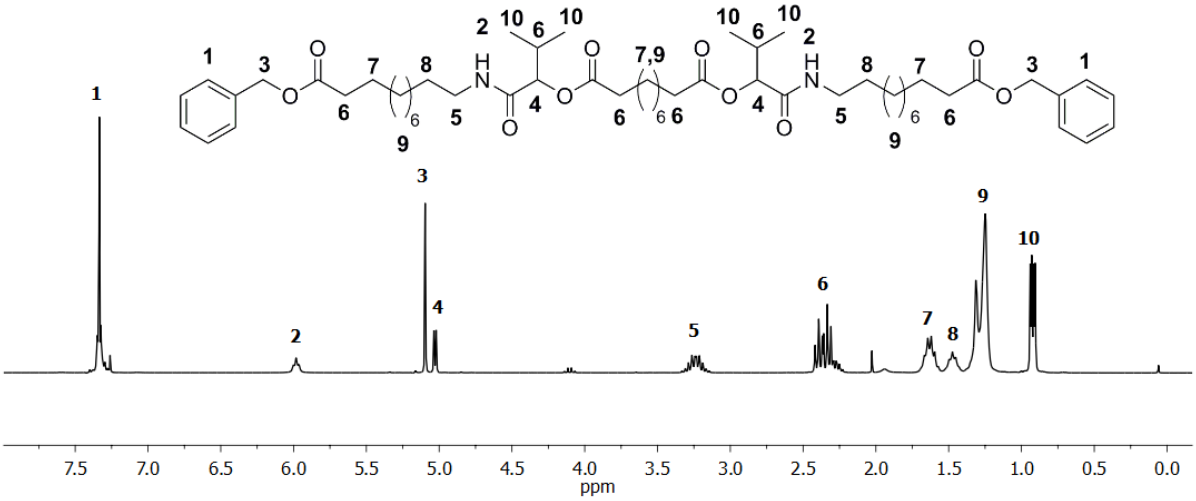
^{1}H NMR (300 MHz, $CDCl_3$) δ / ppm: 7.42 – 7.27 (m, 10H, ^{1}), 5.98 (t, *J* = 5.6 Hz, 2H, ^{2}), 5.10 (s, 4H, ^{3}), 5.03 (d, *J* = 4.5 Hz, 2H, ^{4}), 3.36 – 3.12 (m, 4H, ^{5}), 2.46 – 2.19 (m, 10H, ^{6}), 1.62 (m, 8H, ^{7}), 1.54 – 1.40 (m, 4H, ^{8}), 1.26 (m, 32H, ^{9}), 0.92 (dd, *J* = 6.9, 3.1 Hz, 12H, ^{10}).

^{13}C NMR (75 MHz, $CDCl_3$) δ / ppm: 173.75, 172.59, 169.33, 136.20, 128.61, 128.23, 78.04, 66.13, 39.24, 34.39, 34.31, 30.59, 29.65, 29.50, 29.40, 29.27, 29.17, 29.12, 26.91, 25.01, 18.86, 17.07.

HRMS-FAB-MS of $[C_{56}H_{89}O_{10}N_2]^+$: calculated: 949.6512, found: 949.6510.

IR (ATR platinum diamond): ν [cm^{-1}] = 3305.6, 2924.8, 2852.4, 1734.6, 1654.0, 1531.9, 1455.4, 1369.3, 1231.2, 1160.0, 1101.8, 734.6, 696.7.

***R*$_f$** (cyclohexane / ethyl acetate 2:1) = 0.60.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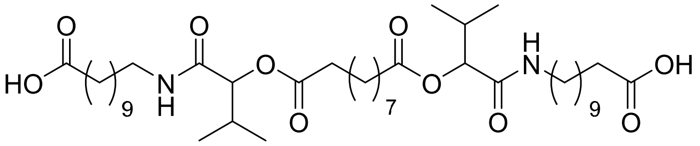
1st deprotection: Synthesis of Dimer 23



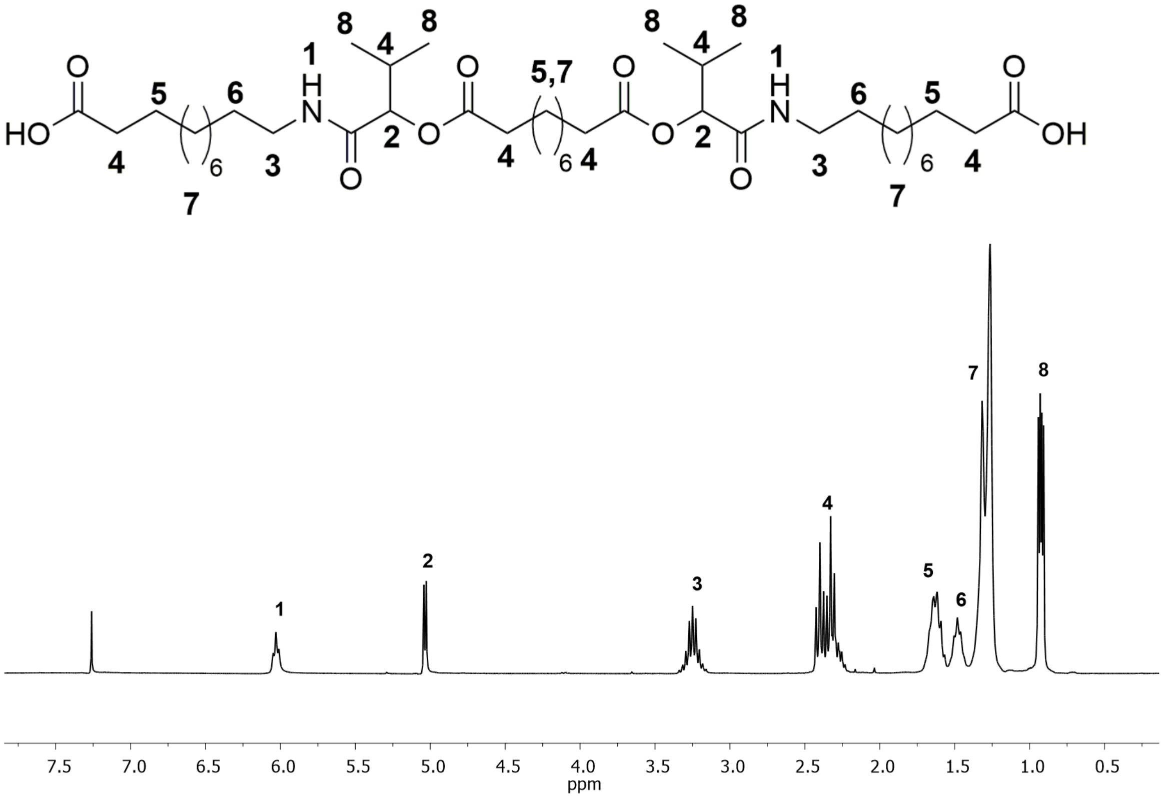
Substance **22** (3.08 g, 3.24 mmol, 1.0 eq) was dissolved in 8 mL ethyl acetate and palladium on activated charcoal (300 mg, 10 wt%) was added. The reaction mixture was purged with hydrogen (balloon) and then stirred overnight under hydrogen atmosphere. The heterogeneous catalyst was filtered off and the solvent was evaporated under reduced pressure to obtain product **23** without further purification in a yield of 97% (2.41 g, 3.13 mmol) as highly viscous, colourless oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ / ppm: 6.03 (t, J = 5.6 Hz, 2H, ^{1}), 5.03 (d, J = 4.5 Hz, 2H, ^{2}), 3.38 – 3.09 (m, 4H, ^{3}), 2.48 – 2.19 (m, 10H, ^{4}), 1.60 (m, 8H, ^{5}), 1.53 – 1.42 (m, 4H, ^{6}), 1.29 (m, 32H, ^{7}), 0.95 (ddd, J = 10.3, 6.9, 3.4 Hz, 12H, ^{8}).

^{13}C NMR (75 MHz, CDCl3) δ / ppm: 179.08, 172.72, 169.61, 78.10, 39.33, 34.33, 34.13, 30.60, 29.58, 29.43, 29.32, 29.21, 29.14, 29.06, 26.88, 25.03, 24.80, 18.86, 17.11.

HRMS-FAB-MS of $[C_{42}H_{77}N_2O_{10}]^+$: calculated: 769.5573, found: 769.5573.

IR (ATR platinum diamond): ν[cm^{-1}] = 3307.0, 2925.3, 2853.4, 1738.3, 1648.9, 1541.0, 1463.7, 1370.1, 1165.8, 1125.4, 1004.9, 929.0, 722.4.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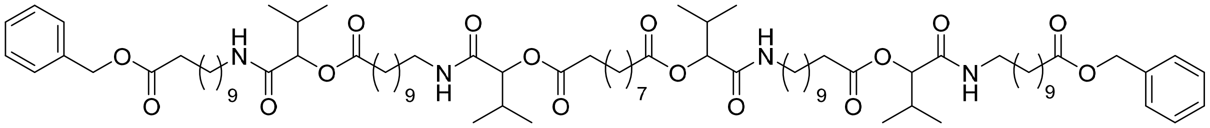
2nd Passerini reaction: Synthesis of Tetramer 24



Substance **23** (2.34 g, 3.05 mmol, 1.0 eq.) was dissolved in DCM (7.0 mL, 0.5 M). Subsequently, monomer **M1** (2.75 g 9.14 mmol, 3.0 eq.) and isobutyraldehyde (0.84 mL, 66.0 mg, 9.14 mmol, 3.0 eq.) were added and the reaction mixture was stirred at room temperature for 24 hours. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (cyclohexane / ethyl acetate 4:1 → 1:1) to obtain the desired product **24** in a yield of 99% (4.70 g, 3.04 mmol) as a yellowish, highly viscous oil.

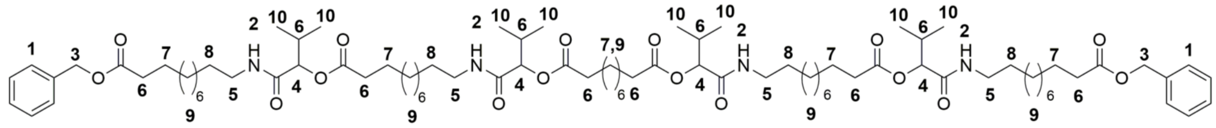
^{1}H NMR (300 MHz, $CDCl_3$) δ / ppm: 7.40 – 7.28 (m, 10H, ^{1}), 6.02 (dd, *J* = 13.8, 8.4 Hz, 4H, ^{2}), 5.08 (s, 4H, ^{3}), 5.03 – 4.97 (m, 4H, ^{4}), 3.37 – 3.10 (m, 8H, ^{5}), 2.48 – 2.11 (m, 16H, ^{6}), 1.72 – 1.53 (m, 12H, ^{7}), 1.50 – 1.39 (m, 8H, ^{8}), 1.27 (d, *J* = 16.4 Hz, 56H, ^{9}), 1.05 – 0.70 (m, 24H, ^{10}).

^{13}C NMR (75 MHz, $CDCl_3$) *δ* / ppm: 173.71, 172.60, 172.58, 169.31, 136.16, 128.57, 128.18, 77.99, 77.95, 66.09, 39.19, 34.35, 34.31, 34.26, 30.56, 29.62, 29.46, 29.37, 29.23, 29.13, 29.08, 26.87, 25.03, 24.97, 18.83, 17.04, 17.02.

HRMS-ESI-MS of $[C_{88}H_{146}O_{16}N_4Na]^+$: calculated: 1538.0626, found: 1538.0636.

IR (ATR platinum diamond): ν[cm^{-1}] = 3305.4, 2924.8, 2853.2, 1736.5, 1653.4, 1532.9, 1462.1, 1369.4, 1232.0, 1161.4, 1003.8, 734.4, 697.4.

***R*$_f$** (cyclohexane / ethyl acetate 1:1) = 0.75.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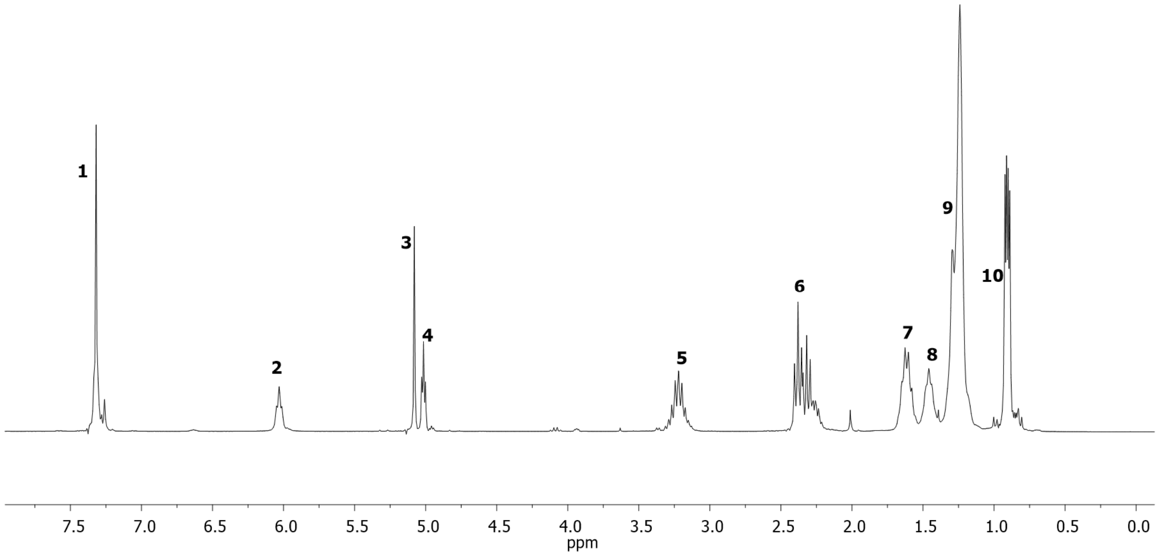
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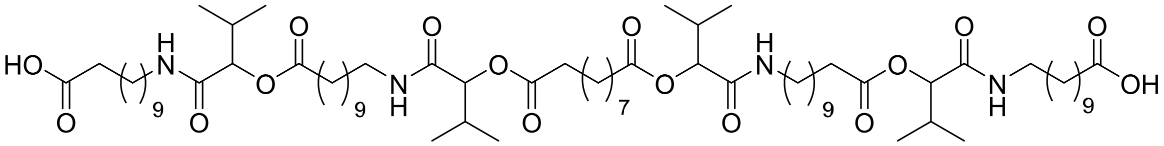
2nd deprotection: Synthesis of Tetramer 25



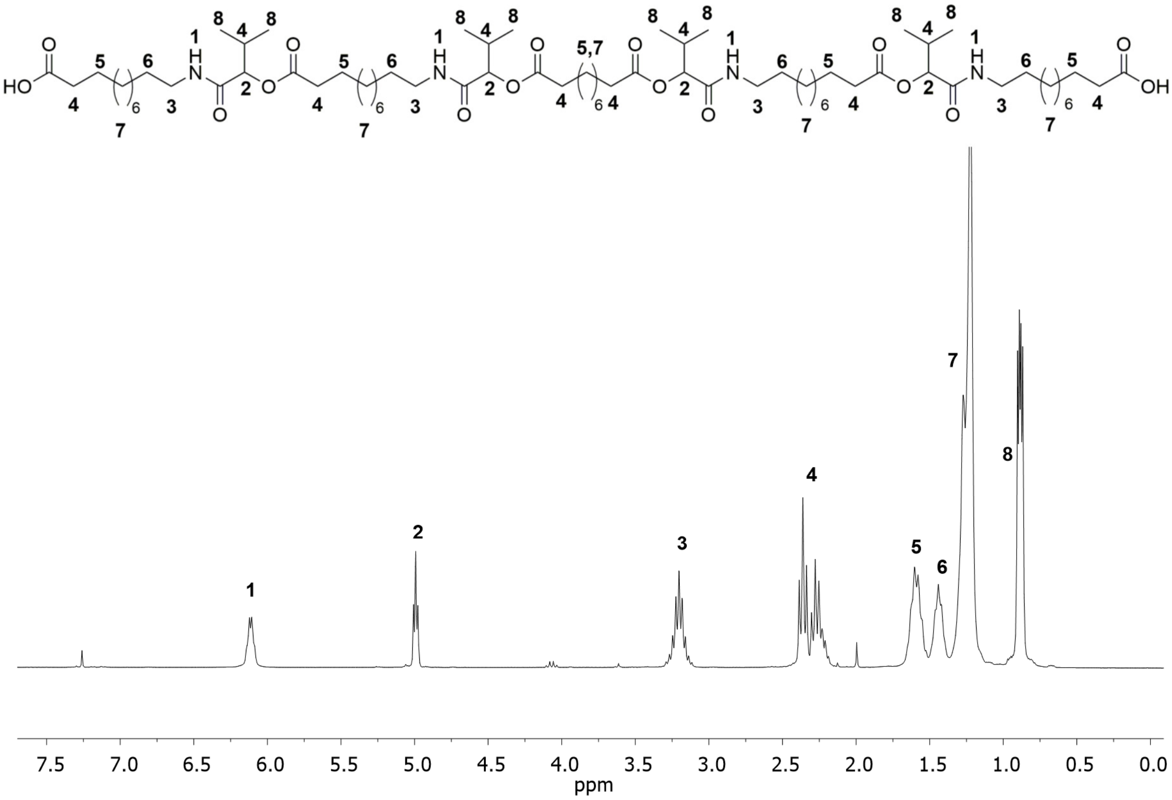
Substance **24** (1.78 g, 1.17 mmol, 1.0 eq) was dissolved in 3.5 mL ethyl acetate and palladium on activated charcoal (178 mg, 10 wt%) was added. The reaction mixture was purged with hydrogen (balloon) and then stirred overnight under hydrogen atmosphere. The heterogeneous catalyst was filtered off and the solvent was evaporated under reduced pressure to obtain product **25** without further purification in a yield of 97% (1.53 g, 1.14 mmol) as highly viscous, colourless oil.

^{1}H NMR (300 MHz, CDCl$_3$) δ / ppm: 6.24 – 5.95 (m, 4H, ^{1}), 4.99 (t, J = 4.3 Hz, 4H, ^{2}), 3.37 – 3.01 (m, 8H, ^{3}), 2.48 – 2.12 (m, 16H, ^{4}), 1.72 – 1.51 (m, 12H, ^{5}), 1.49 – 1.39 (m, 8H, ^{6}), 1.25 (m, 56H, ^{7}), 0.89 (dd, J = 6.8, 3.5 Hz, 24H, ^{8}).

^{13}C NMR (75 MHz, CDCl$_3$) δ / ppm: 178.21, 172.66, 169.53, 77.96, 77.92, 39.25, 39.22, 34.27, 34.22, 34.07, 30.52, 29.55, 29.50, 29.45, 29.40, 29.35, 29.30, 29.22, 29.18, 29.13, 29.05, 26.83, 25.01, 24.92, 24.78, 18.79, 17.03, 17.00.

HRMS-ESI-MS of [$C_{74}H_{134}N_4O_{16}Na$]$^+$: calculated: 1357.9687, found: 1357.9690.

IR (ATR platinum diamond): ν [cm^{-1}] = 3305.2, 2924.8, 2853.6, 1737.5, 1649.1, 1537.7, 1463.4, 1369.6, 1232.5, 1162.2, 1125.8, 1107.8, 923.7, 721.8, 646.3, 418.0.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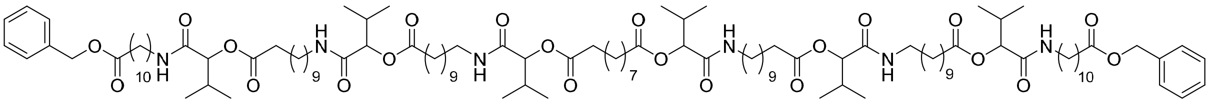
3rd Passerini reaction: Synthesis of Hexamer 26



Substance **25** (0.96 g, 0.72 mmol, 1.0 eq.) was dissolved in DCM (2.1 mL, 0.3 M). Subsequently, monomer **M1** (0.65 g, 2.15 mmol, 3.0 eq.) and isobutyraldehyde (0.20 mL, 15.0 mg, 2.15 mmol, 3.0 eq.) were added and the reaction mixture was stirred at room temperature for 48 hours. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (cyclohexane / ethyl acetate 5:1 → pure ethyl acetate) to obtain the desired product **26** in a yield of 95% (1.42 g, 0.68 mmol) as a yellowish, highly viscous oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ / ppm: 7.35 – 7.26 (m, 10H, ^{1}), 6.07 (s, 6H, ^{2}), 5.06 (s, 4H, ^{3}), 4.98 (t, *J* = 3.9 Hz, 6H, ^{4}), 3.30 – 3.08 (m, 12H, ^{5}), 2.48 – 2.11 (m, 22H, ^{6}), 1.59 (m, 16H, ^{7}), 1.50 – 1.35 (m, 12H, ^{8}), 1.35 – 1.09 (m, 80H, ^{9}), 0.91 (m, 36H, ^{10}).

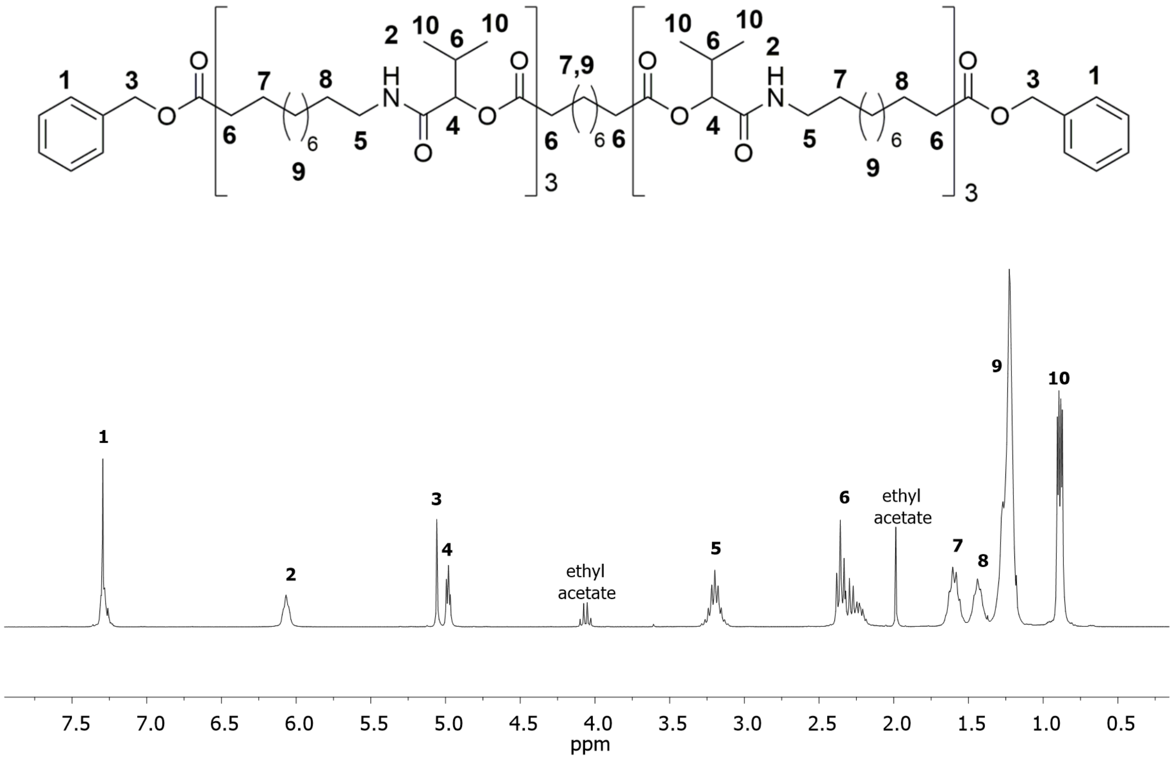
^{13}C NMR (75 MHz, $CDCl_3$) *δ* / ppm: 173.64, 172.57, 169.27, 162.93, 136.09, 132.16, 128.76, 128.34, 128.26, 127.87, 127.47, 127.18, 78.48, 77.81, 77.28, 66.01, 65.44, 40.01, 39.63, 39.13, 37.91, 34.28, 34.23, 34.19, 30.46, 29.54, 29.40, 29.31, 29.17, 29.08, 27.84, 27.25, 26.81, 24.96, 24.90, 19.33, 18.84, 18.69, 18.20, 17.55, 17.06, 16.89, 16.40, 16.24.

HRMS-ESI-MS of $[C_{120}H_{204}O_{22}N_6Na]^+$: calculated: 2104.4921, found: 2104.4951.

$[C_{120}H_{204}O_{22}N_6Na_2]^{2+}$: calculated: 1063.7407, found: 1063.7431.

IR (ATR platinum diamond): ν [cm^{-1}] = 3306.1, 2925.3, 2853.5, 1737.2, 1652.2, 1533.3, 1462.4, 1369.4, 1232.2, 1160.5, 1003.9, 724.3, 697.2, 411.7.

***R*f** (cyclohexane / ethyl acetate 1:1) = 0.30.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1.0
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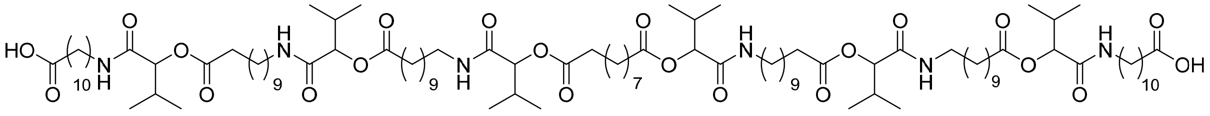
3rd deprotection: Synthesis of Hexamer 27



Substance **26** (1.17 g, 0.56 mmol, 1.0 eq) was dissolved in 5 mL ethyl acetate and palladium on activated charcoal (117 mg, 10 wt%) was added. The reaction mixture was purged with hydrogen (balloon) and then stirred overnight under hydrogen atmosphere. The heterogeneous catalyst was filtered off and the solvent was evaporated under reduced pressure to obtain product **27** without further purification in a yield of 99% (1.08 g, 0.56 mmol) as highly viscous, colourless oil.

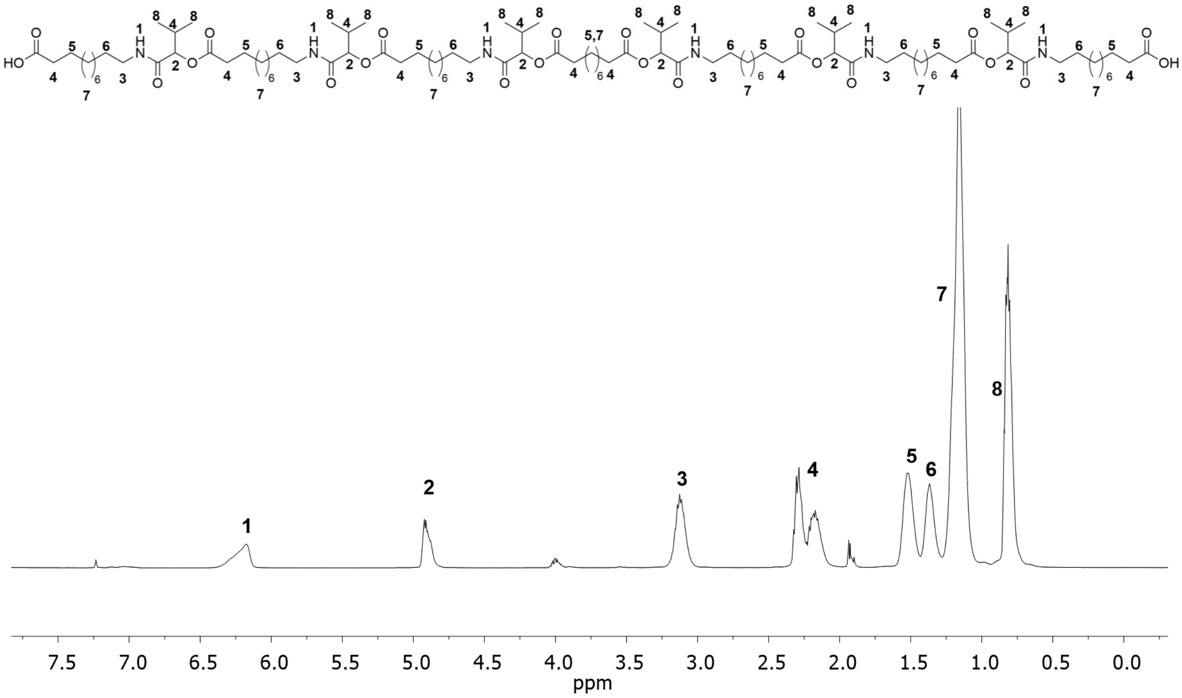
^{1}H NMR (400 MHz, CDCl$_3$) δ / ppm: 6.17 (s, 6H, ^{1}), 4.90 (m, 6H, ^{2}), 3.13 (m, 12H, ^{3}), 2.40 – 1.98 (m, 22H, ^{4}), 1.52 (m, 16H, ^{5}), 1.32 (m, 12H, ^{6}), 1.16 (s, 80H, ^{7}), 0.87 – 0.73 (m, 36H, ^{8}).

^{13}C NMR (101 MHz, CDCl$_3$) δ / ppm: 177.46, 172.63, 172.61, 172.58, 171.20, 169.51, 77.80, 60.36, 39.14, 34.12, 34.01, 30.43, 29.40, 29.36, 29.33, 29.26, 29.23, 29.10, 29.03, 28.98, 26.74, 24.89, 24.83, 24.75, 20.98, 19.17, 18.70, 16.92, 15.47, 14.12.

HRMS-ESI-MS of $[C_{106}H_{192}N_6O_{22}Na]^+$: calculated:1924.3982, found: 1924.4089.

$[C_{106}H_{192}N_6O_{22}Na_2]^{2+}$: calculated: 973.6937, found: 973.6936.

IR (ATR platinum diamond): ν[cm^{-1}] = 3306.4, 2924.9, 2853.6, 1738.1, 1650.2, 1536.9, 1463.5, 1369.7, 1233.0, 1162.7, 1162.7, 1126.2, 1007.6, 924.2, 721.8, 646.9, 411.6.



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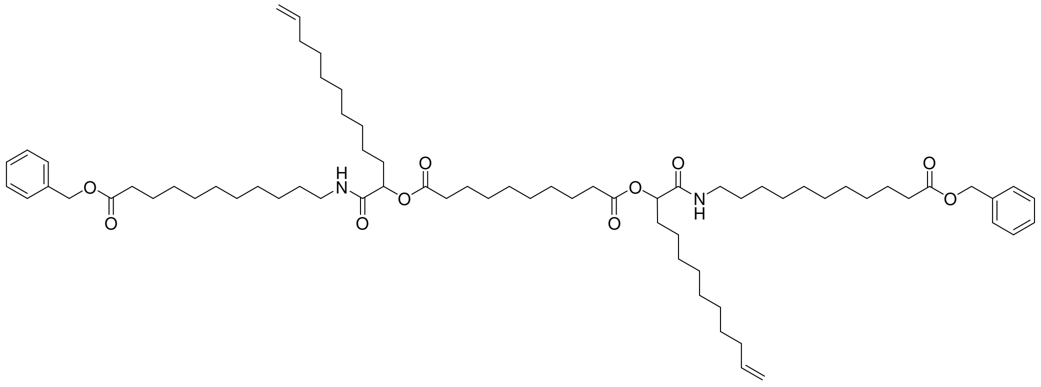
3.4 Introduction of the double bond to the oligomeric backbone

Dimer with terminal double bonds: Synthesis of Dimer 28



Stearic acid (500 mg, 2.47 mmol, 1.0 eq.) was dissolved in 2.5 mL DCM. Subsequently, monomer **M1** (2.24 g, 7.42 mmol, 3.0 eq.) and 10-undecenal (1.50 mL, 1.25 g, 7.42 mmol, 3.0 eq.) were added and the reaction mixture was stirred at room temperature for 24 hours. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (cyclohexane / ethyl acetate 8:1 → 2:1) to obtain the desired product **28** in a yield of 89% (2.52 g, 2.20 mmol) as a yellowish, highly viscous oil.

^{1}H NMR (300 MHz, CDCl$_3$) δ / ppm: 7.43 – 7.27 (m, 10H, ^{1}), 6.01 (t, J = 5.5 Hz, 2H, ^{2}), 5.79 (ddt, J = 16.9, 10.2, 6.7 Hz, 2H, ^{3}), 5.21 – 5.06 (m, 6H, ^{4}), 4.94 (m, 4H, ^{5}), 3.35 – 3.12 (m, 4H, ^{6}), 2.47 – 2.20 (m, 8H, ^{7}), 2.02 (q, J = 6.8 Hz, 4H, ^{8}), 1.91 – 1.71 (m, 4H, ^{9}), 1.63 (m, 8H, ^{10}), 1.54 – 1.40 (m, 4H, ^{11}), 1.29 (m, 56H, ^{12}).

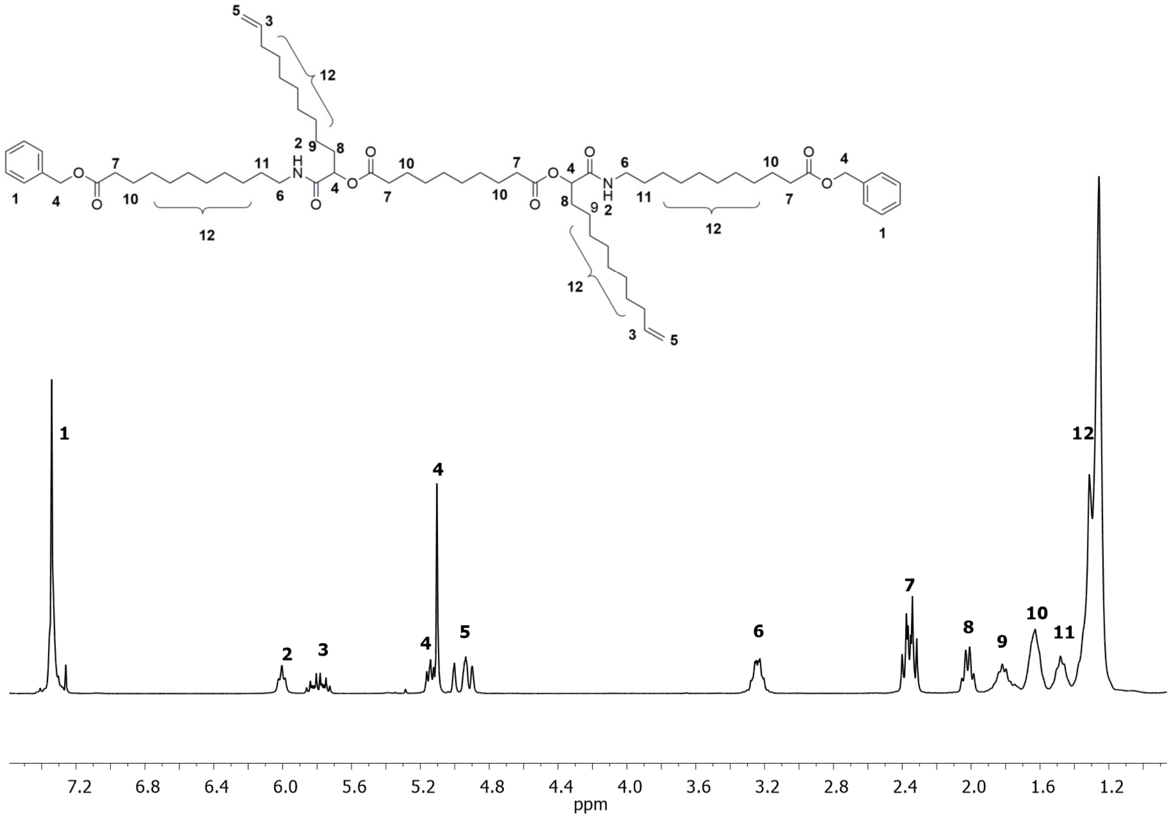
^{13}C NMR (75 MHz, CDCl$_3$) δ / ppm: 173.74, 172.48, 169.89, 163.24, 139.23, 136.20, 128.62, 128.23, 114.24, 74.03, 66.14, 39.28, 34.39, 34.34, 33.87, 31.99, 29.64, 29.53, 29.43, 29.30, 29.18, 29.15, 28.97, 26.91, 25.01, 24.96, 24.84.

HRMS-ESI-MS of $[C_{70}H_{112}O_{10}N_2Na]^+$: calculated: 1163.8209, found:1163.8230.

$[C_{70}H_{112}O_{10}N_2Na_2]^{2+}$: calculated: 593.4051, found: 593.3827.

IR (ATR platinum diamond): ν [cm^{-1}] = 3327.7, 2920.5, 2850.4, 1738.2, 1660.7, 1537.0, 1468.8, 1437.8, 1417.1, 1388.6, 1363.6, 1289.1, 1262.7, 1236.7, 1211.7, 1166.3, 1047.0, 985.3, 908.5, 908.5, 803.6, 720.7, 696.0, 658.9, 577.7, 456.6, 412.1.

***R*$_f$** (cyclohexane / ethyl acetate 2:1) = 0.48.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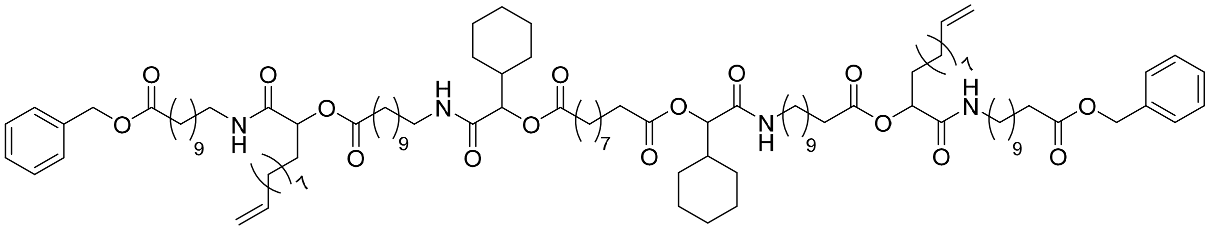
Tetramer with terminal double bonds and cyclohexyl side chains: Synthesis of Tetramer 29



Substance **15** (492 mg, 0.58 mmol, 1.0 eq.) was dissolved in 1.2 mL DCM. Subsequently, monomer **M1** (0.52 g 1.74 mmol, 3.0 eq.) and 10-undecenal (0.35 mL, 29.0 mg, 1.74 mmol, 3.0 eq.) were added and the reaction mixture was stirred at room temperature for 24 hours. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (cyclohexane / ethyl acetate 10:1 → 1:1) to obtain the desired product **29** in a yield of 92% (0.95 g, 0.53 mmol) as a yellowish, highly viscous oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ / ppm: 7.32 (s, 10H, ^{1}), 6.03 (m, 4H, ^{2}), 5.77 (ddt, *J* = 13.3, 10.1, 6.6 Hz, 4H, ^{3}), 5.06 (m, 8H, ^{4}), 4.90 (m, 4H, ^{5}), 3.22 (m, 8H, ^{6}), 2.33 (m, 12H, ^{7}), 2.10 – 1.87 (m, 6H, ^{8}), 1.84 – 1.53 (m, 22H, ^{9}), 1.42 (m, 8H, ^{10}), 1.37 – 0.70 (m, 92H, ^{11}).

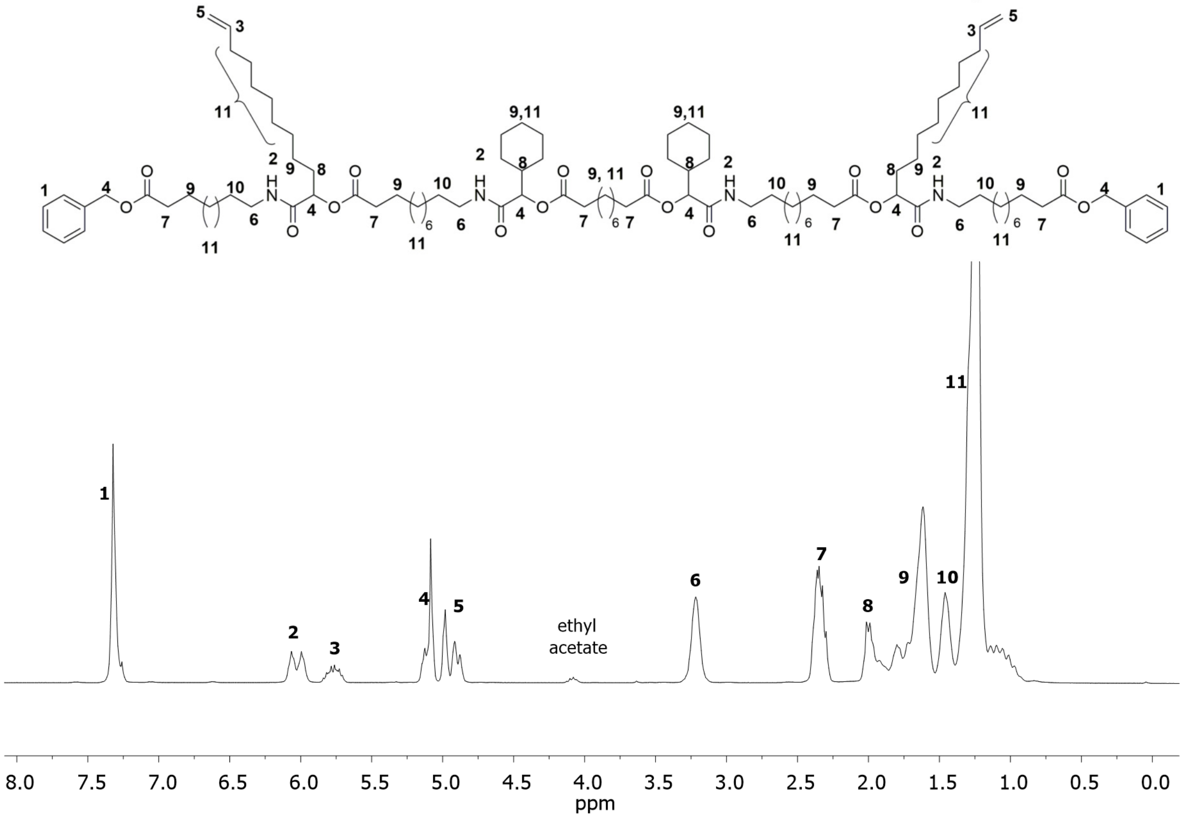
^{13}C NMR (75 MHz, $CDCl_3$) *δ* / ppm: 173.68, 172.54, 172.50, 169.89, 169.23, 139.16, 136.16, 128.56, 128.16, 114.18, 77.69, 73.94, 66.08, 40.00, 39.22, 39.18, 34.33, 34.25, 33.81, 31.95, 29.58, 29.47, 29.38, 29.24, 29.12, 29.09, 28.92, 27.40, 26.86, 26.11, 26.02, 25.91, 24.97, 24.79.

HRMS-ESI-MS of $[C_{108}H_{178}O_{16}N_4Na]^+$: calculated: 1810.3130, found: 1810.3153.

$[C_{108}H_{178}O_{16}N_4Na_2]^{2+}$: calculated: 916.6511, found: 916.6506.

IR (ATR platinum diamond): ν [cm^{-1}] = 3294.9, 2919.6, 2850.4, 1733.2, 1655.2, 1554.0, 1465.5, 1379.4, 1213.8, 1173.1, 1102.5, 988.2, 908.6, 722.5, 695.9.

***R*$_f$** (cyclohexane / ethyl acetate 2:1) = 0.48.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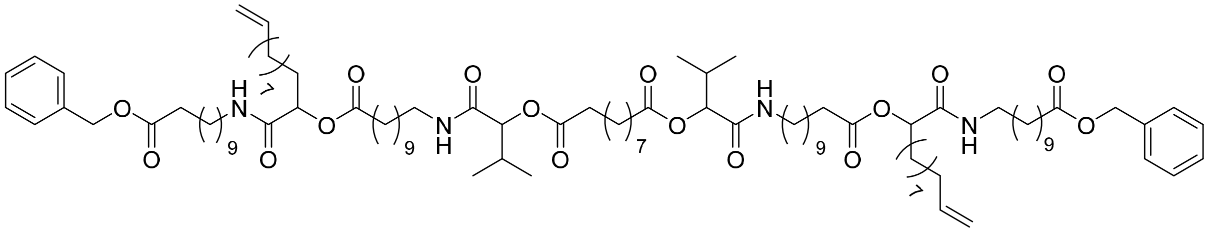
Tetramer with terminal double bonds and isopropyl side chains: Synthesis of Tetramer 30



Substance **23** (380 mg, 0.49 mmol, 1.0 eq.) was dissolved in 1.0 mL DCM. Subsequently, monomer **M1** (0.45 g 1.48 mmol, 3.0 eq.) and 10-undecenal (300 µL, 250 mg, 1.48 mmol, 3.0 eq.) were added and the reaction mixture was stirred at room temperature for 24 hours. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (cyclohexane / ethyl acetate 5:1 → 1:1) to obtain the desired product **30** in a yield of 98% (0.83 g, 0.48 mmol) as a yellowish, highly viscous oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ / ppm: 7.44 – 7.28 (m, 10H, ^{1}), 6.05 (m, 4H, ^{2}), 5.77 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 4H, ^{3}), 5.19 – 5.05 (m, 8H, ^{4}), 5.05 – 4.82 (m, 4H, ^{5}), 3.36 – 3.08 (m, 8H, ^{6}), 2.49 – 2.16 (m, 12H, ^{7}), 2.00 (q, *J* = 6.7 Hz, 4H, ^{8}), 1.88 – 1.72 (m, 4H, ^{9}), 1.62 (m, 12H, ^{10}), 1.51 – 1.39 (m, 8H, ^{11}), 1.27 (m, 80H, ^{12}), 0.96 – 0.82 (m, 12H, ^{13}).

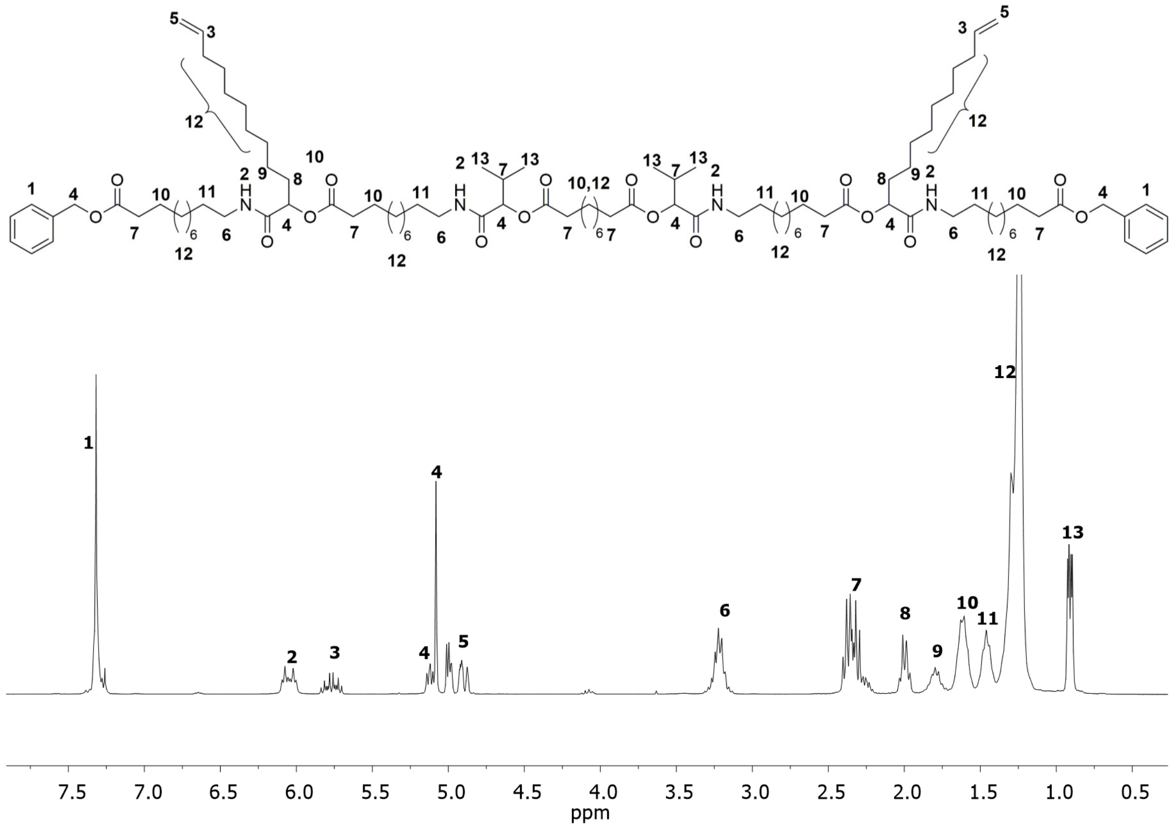
^{13}C NMR (75 MHz, $CDCl_3$) *δ* / ppm: 173.69, 172.56, 172.50, 169.90, 169.30, 139.17, 136.17, 128.57, 128.17, 114.19, 78.01, 73.95, 66.08, 39.21, 34.34, 34.26, 33.82, 31.96, 30.56, 29.63, 29.58, 29.48, 29.39, 29.25, 29.13, 29.09, 28.93, 26.87, 24.97, 24.80, 18.82, 17.06.

HRMS-ESI-MS of $[C_{102}H_{170}O_{16}N_4Na]^+$: calculated: 1730.2504, found: 1730.2545.

$[C_{102}H_{170}O_{16}N_4Na_2]^{2+}$: calculated: 876.6198, found: 876.6189.

IR (ATR platinum diamond): ν [cm^{-1}] = 3295.6, 2920.9, 2851.0, 1735.3, 1653.6, 1542.2, 1465.4, 1368.9, 1238.8, 1215.1, 1166.6, 992.6, 909.6, 722.6, 696.7, 417.4.

***R*$_f$** (cyclohexane / ethyl acetate 2:1) = 0.31.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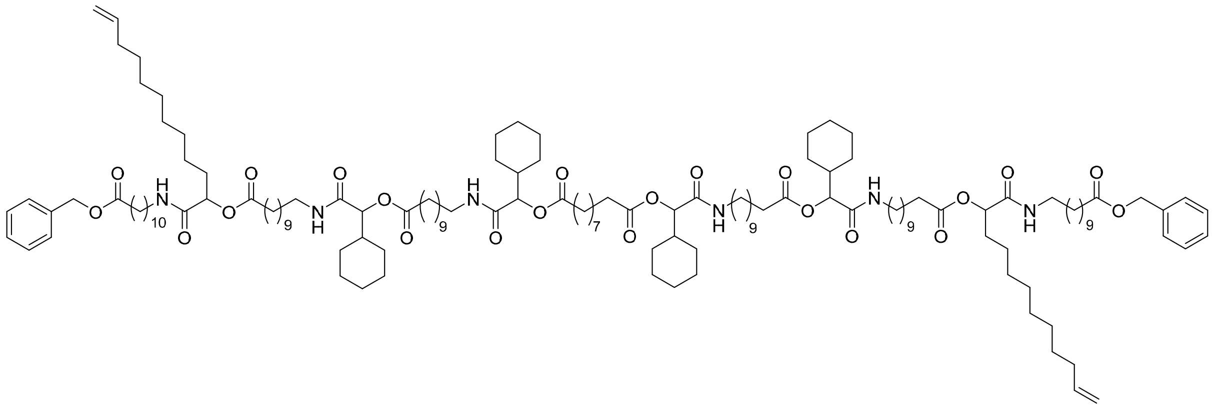
Hexamer with terminal double bonds and cyclohexyl side chains: Synthesis of Hexamer 31



Substance **17** (907 mg, 0.61 mmol, 1.0 eq.) was dissolved in 1.8 mL DCM. Subsequently, monomer **M1** (2.24 g 7.42 mmol, 3.0 eq.) and 10-undecenal (1.50 mL 1.25 g, 7.42 mmol, 3.0 eq.) were added and the reaction mixture was stirred at room temperature for 48 hours. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (cyclohexane / ethyl acetate 8:1 → 2:1) to obtain the desired product **31** in a yield of 89% (2.52 g, 2.20 mmol) as a yellowish, highly viscous oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ / ppm: 7.42 – 7.27 (m, 10H, ^{1}), 6.06 (m, 6H, ^{2}), 5.78 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 4H, ^{3}), 5.20 – 5.06 (m, 8H, ^{4}), 5.02 – 4.86 (m, 4H, ^{5}), 3.36 – 3.09 (m, 12H, ^{6}), 2.46 – 2.28 (m, 16H, ^{7}), 2.08 – 1.87 (m, 8H, ^{8}), 1.83 – 1.55 (m, 36H, ^{9}), 1.52 – 1.40 (m, 12H, ^{10}), 1.37 – 0.89 (m, 128H, ^{11}).

^{13}C NMR (75 MHz, $CDCl_3$) *δ* / ppm: 173.70, 172.59, 172.56, 172.51, 169.89, 169.26, 169.24, 139.18, 136.16, 128.57, 128.18, 114.19, 77.69, 77.65, 73.95, 70.64, 66.09, 46.02, 40.02, 39.23, 39.18, 34.35, 34.27, 33.83, 31.96, 29.62, 29.50, 29.40, 29.26, 29.22, 29.14, 29.11, 28.93, 27.78, 27.36, 26.89, 26.12, 26.04, 25.92, 24.98, 24.80.

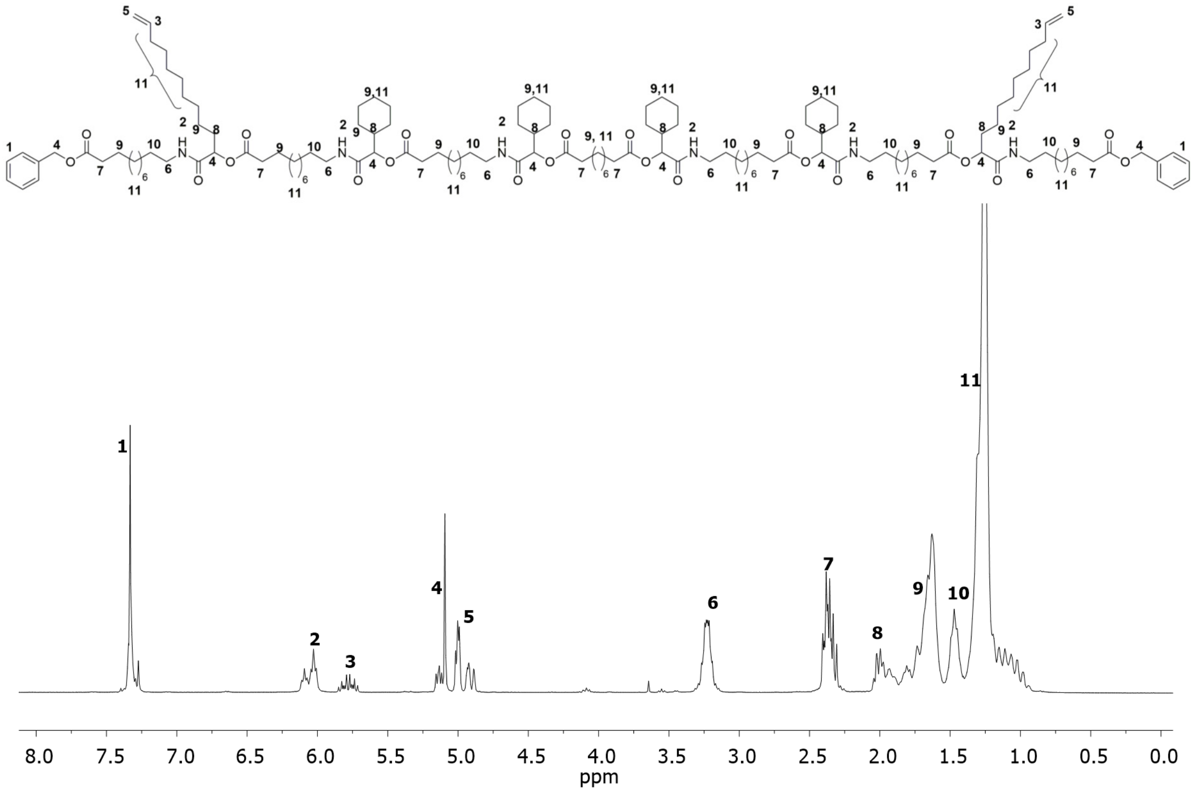
HRMS-ESI-MS of $[C_{146}H_{244}O_{22}N_6Na]^+$: calculated:2456.8051, found: 2456.8034.

$[C_{146}H_{244}O_{22}N_6Na_2]^{2+}$: calculated: 1239.8972, found: 1239.8995.

$[C_{146}H_{244}O_{22}N_6Na_3]^{3+}$: calculated: 834.2612, found: 834.2596.

IR (ATR platinum diamond): ν [cm^{-1}] = 3293.4, 2922.3, 2851.7, 1736.8, 1654.6, 1535.7, 1450.5, 1375.3, 1161.8, 1101.7, 989.3, 908.7, 722.9, 696.8.

***R*$_f$** (cyclohexane / ethyl acetate 2:1) = 0.48.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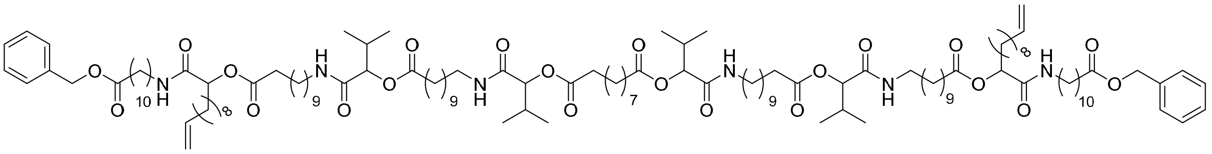
Hexamer with terminal double bonds and isopropyl side chains: Synthesis of Hexamer 32



Substance **25** (294 mg, 0.22 mmol, 1.0 eq.) was dissolved in 2.0 mL DCM. Subsequently, monomer **M1** (199 mg 0.66 mmol, 3.0 eq.) and 10-undecenal (0.13 mL, 0.11 g, 0.66 mmol, 3.0 eq.) were added and the reaction mixture was stirred at room temperature for 48 hours. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (cyclohexane / ethyl acetate 5:1 → pure ethyl acetate) to obtain the desired product **32** in a yield of 88% (0.44 g, 0.19 mmol) as a yellowish, highly viscous oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ / ppm: 7.43 – 7.23 (m, 10H), 6.16 – 5.91 (m, 6H), 5.76 (ddt, J = 16.9, 10.2, 6.7 Hz, 2H), 5.19 – 5.05 (m, 10H), 5.01 – 4.80 (m, 4H), 3.36 – 3.11 (m, 12H), 2.47 – 2.16 (m, 20H), 2.06 – 1.94 (m, 4H), 1.88 – 1.70 (m, 4H), 1.61 (m, 16H), 1.50 – 1.39 (m, 12H), 1.35 – 1.07 (m, 104H), 0.93 (m, 24H).

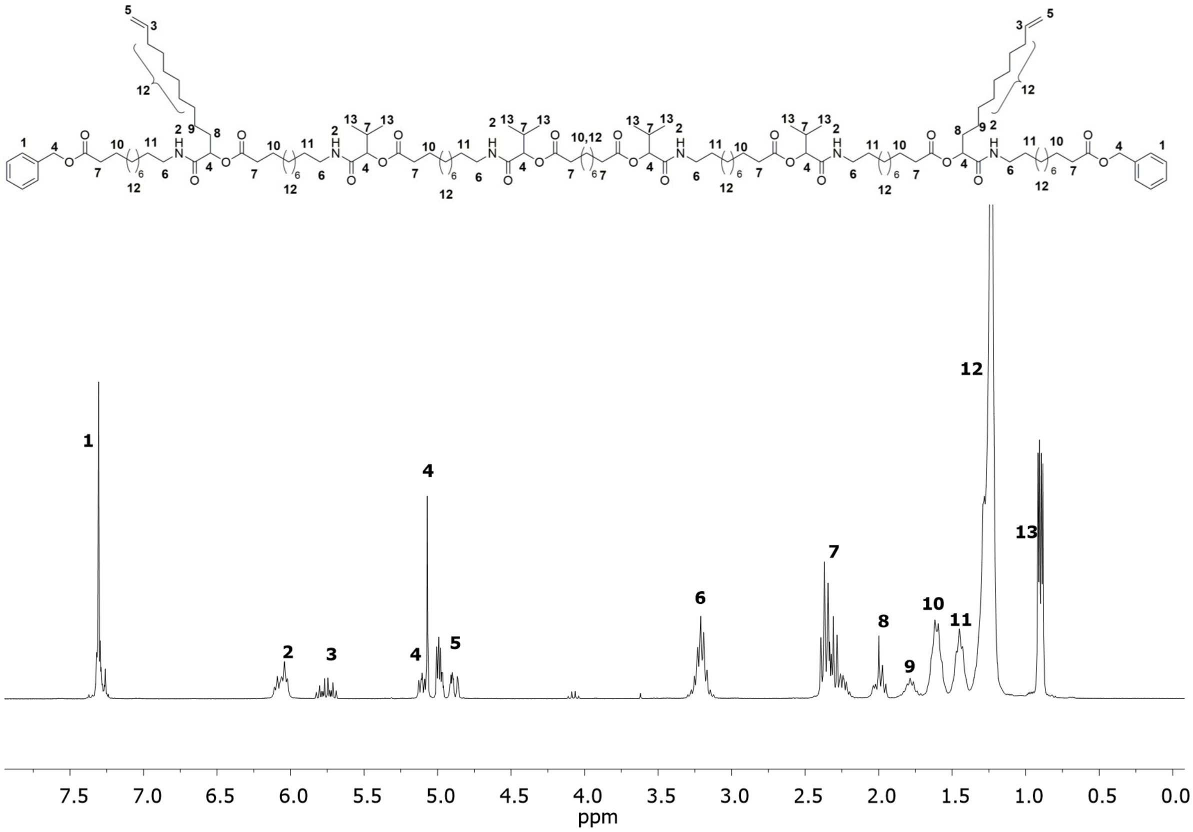
^{13}C NMR (75 MHz, $CDCl_3$) δ / ppm: 173.69, 172.62, 172.58, 172.52, 169.90, 169.33, 156.85, 139.18, 136.19, 128.58, 128.18, 114.20, 101.45, 78.03, 77.99, 73.97, 66.09, 39.21, 34.36, 34.32, 34.28, 33.82, 31.97, 30.57, 29.64, 29.60, 29.49, 29.39, 29.25, 29.15, 29.10, 28.94, 26.88, 25.04, 24.99, 24.81, 18.83, 17.05.

HRMS-ESI-MS of $[C_{134}H_{228}O_{22}N_6H]^+$: calculated: 2274.6979, found: 2274.6714

$[C_{134}H_{228}O_{22}N_6Na_2]^{2+}$: calculated: 1137.8526, found: 1137.7821.

IR (ATR platinum diamond): ν [cm^{-1}] = 3292.7, 2922.8, 2851.9, 1736.2, 1655.5, 1536.8, 1464.9, 1370.4, 1239.6, 1166.3, 994.6, 909.4, 722.6, 696.7, 417.8.

***R*$_f$** (cyclohexane / ethyl acetate 3:2) = 0.40.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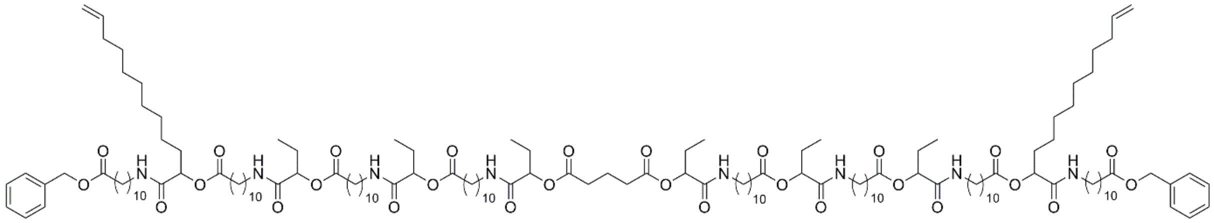
Octamer with terminal double bonds and ethyl side chains: Synthesis of Octamer 33



Substance **6** (0.43 g, 0.25 mmol, 1.0 eq.) was dissolved in DCM (1 mL, 0.25 M). Subsequently, 10-undecenal (0.17 mL, 0.14 g, 0.83 mmol, 3.3 eq.) and the monomer **M1** (0.25 g, 0.81 mmol, 3.2 eq.) were added. The reaction mixture was stirred at room temperature for 48 hours and the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography (hexane / ethyl acetate 1:1 → 1:6) to obtain substance **33** as colourless, highly viscous oil in a yield of 91% (0.60 g, 0.23 mmol).

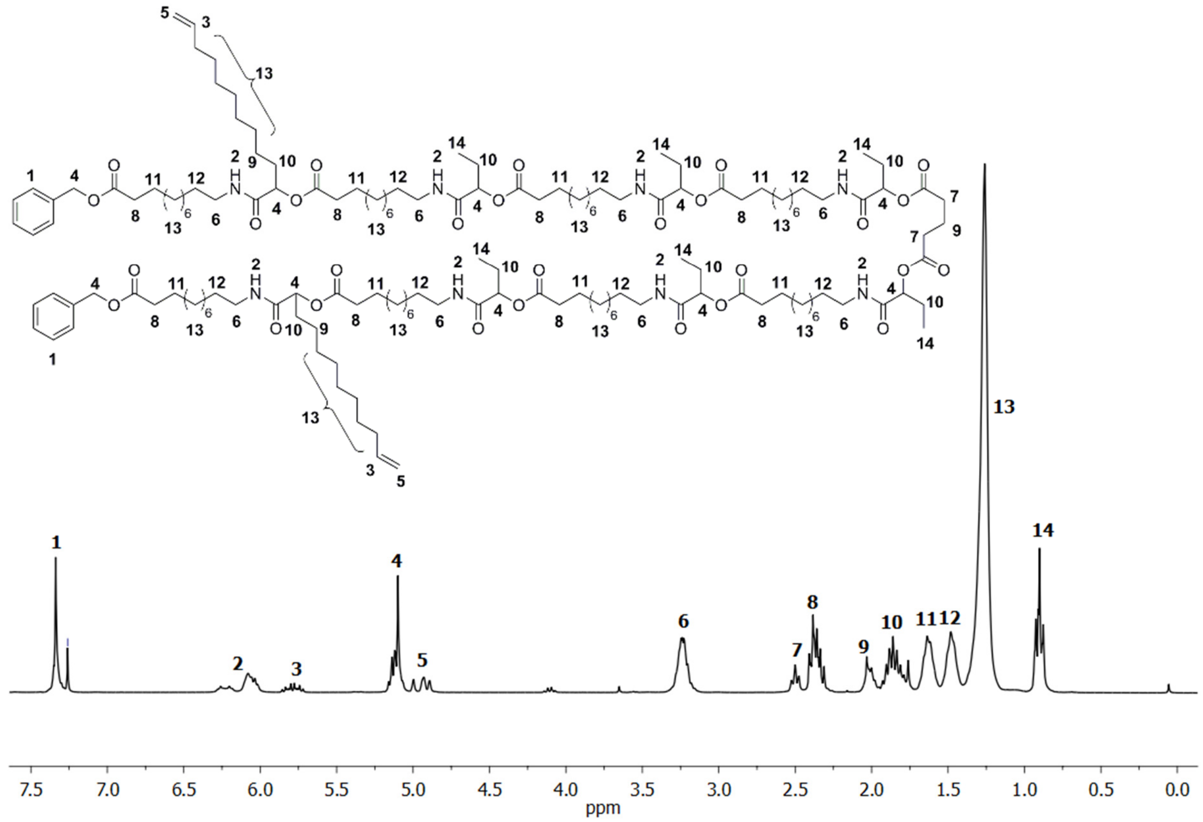
^{1}H NMR (600 MHz, $CDCl_3$) δ / ppm: 7.38 – 7.27 (m, 10H, CH, aromatic, ^{1}), 6.33 – 6.02 (m, 8H, 8 NH, ^{2}), 5.77 (ddt, J = 16.9, 10.2, 6.7 Hz, 2H, 2 CH=, ^{3}), 5.15 – 5.03 (m, 12H, 2 CH_2, 8 CH, ^{4}), 4.98 – 4.87 (m, 4H, 2 =CH_2, ^{5}), 3.31 – 3.13 (m, 16H, 8 CH_2, ^{6}), 2.53 – 2.45 (m, 4H, 2 CH_2, ^{7}), 2.40 – 2.29 (m, 16H, 8 CH_2, ^{8}), 2.03 – 1.96 (m, 6H, 3 CH_2, ^{9}), 1.93 – 1.72 (m, 16H, 8 CH_2, ^{10}), 1.68 – 1.56 (m, 16H, 8 CH_2, ^{11}), 1.47 (m, 16H, 8 CH_2, ^{12}), 1.29 (m, 120H, 60 CH_2, ^{13}), 0.93 – 0.83 (m, 18H, 6 CH_3, ^{14}).

^{13}C NMR (151 MHz, $CDCl_3$) δ / ppm: 173.7, 172.5, 172.0, 171.8, 169.9, 169.7, 169.5, 169.5, 139.2, 136.2, 128.6, 128.2, 128.2, 114.2, 75.2, 74.9, 74.0, 66.1, 39.4, 39.3, 39.3, 34.4, 34.4, 33.9, 33.0, 32.9, 32.0, 29.6, 29.6, 29.5, 29.4, 29.4, 29.3, 29.3, 29.2, 29.2, 29.1, 29.0, 26.9, 25.2, 25.2, 25.0, 24.8, 20.2, 20.1, 9.2, 9.2, 9.1.

HRMS-FAB-MS of $[C_{155}H_{265}N_8O_{28}]^+$: calculated: 2686.9, found: 2685.6.

IR (ATR platinum diamond): ν[cm^{-1}] = 3304.1, 3077.9, 2922.6, 2851.9, 1737.2, 1653.6, 1534.1, 1456.1, 1374.5, 1230.7, 1156.7, 1100.8, 990.4, 907.7, 722.5, 696.9, 404.7.

***R*$_f$** (hexane / ethyl acetate 5:11) = 0.58.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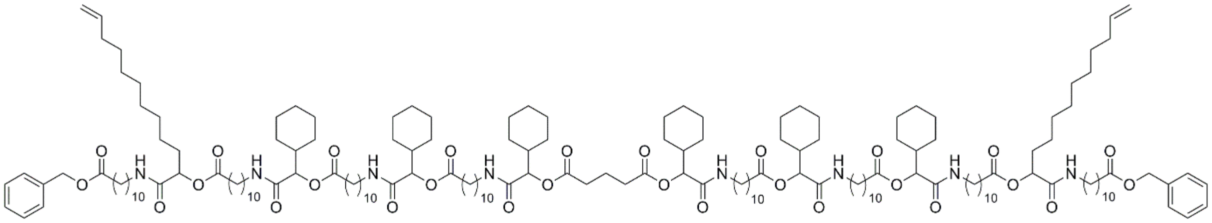
Octamer with terminal double bonds and cyclohexyl side chains: Synthesis of Octamer 34



Substance **13** (0.31 g, 0.15 mmol, 1.0 eq.) was dissolved in DCM (0.3 mL, 0.5 M). Subsequently, monomer **M1** (0.13 g, 0.44 mmol, 3.0 eq.) and 10-undecenal (73.0 mg 0.44 mmol, 3.0 eq.) were added and the reaction mixture was stirred at room temperature for 48 hours. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (cyclohexane / ethyl acetate 5:1 → 1:3) to obtain the product **34** in a yield of 93% (1.25 g, 0.42 mmol) as lightly yellow, highly viscous oil.

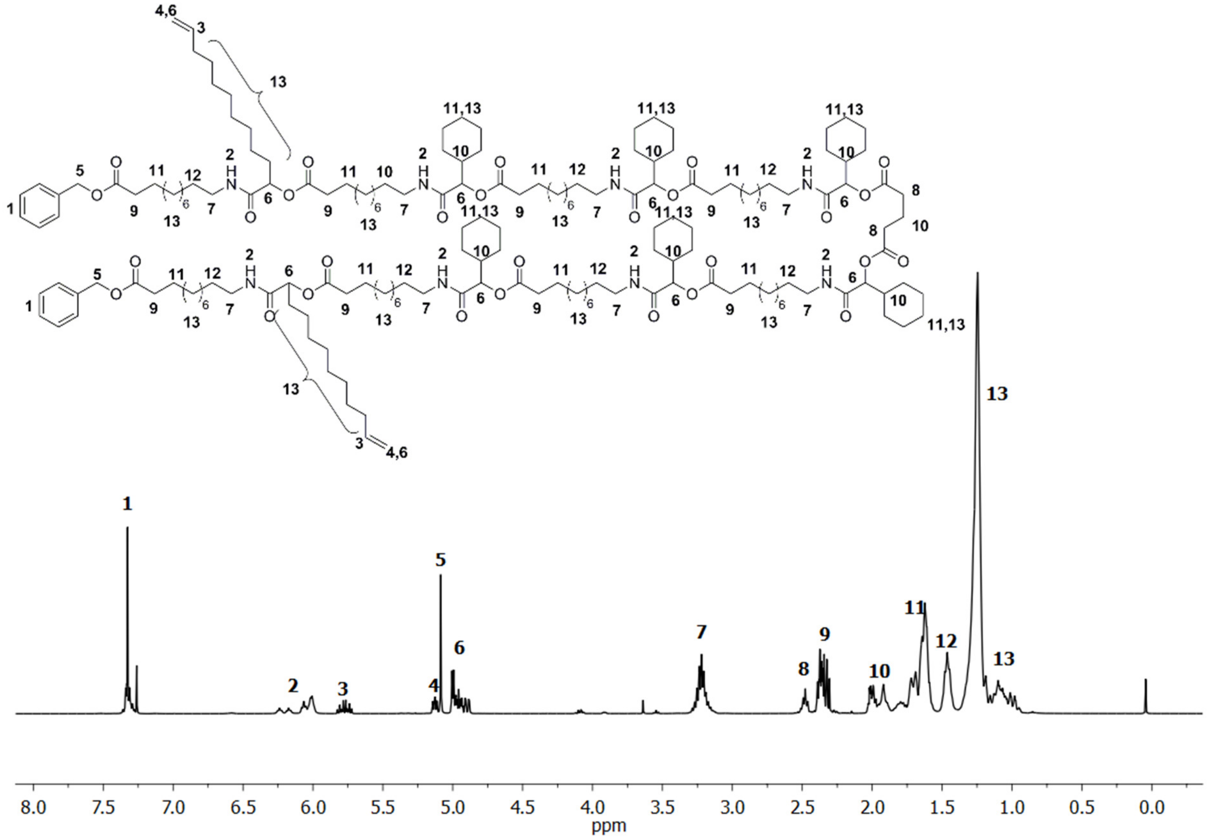
^{1}H NMR (400 MHz, $CDCl_3$) δ / ppm: 7.36 – 7.28 (m, 10H, CH, aromatic, ^{1}), 6.27 – 5.95 (m, 8H, 8 NH, ^{2}), 5.77 (ddt, J = 16.9, 10.2, 6.7 Hz, 2H, 2 CH=, ^{3}), 5.13 (dd, J = 7.1, 4.8 Hz, 2H, =CH_2, ^{4}), 5.09 (s, 4H, 2 CH_2, ^{5}), 5.02 – 4.92 (m, 8H, 8 CH, ^{6}), 4.90 (ddt, J = 10.2, 2.2, 1.1 Hz, 2H, =CH_2, ^{6}), 3.33 – 3.11 (m, 16H, 8 CH_2, ^{7}), 2.53 – 2.44 (m, 4H, 2 CH_2, ^{8}), 2.42 – 2.25 (m, 16H, 8 CH_2, ^{9}), 2.07 – 1.85 (m, 8H, 6 CH, CH_2, ^{10}), 1.85 – 1.54 (m, 50H, 25 CH_2, ^{11}), 1.53 – 1.39 (m, 16H, 8 CH_2, ^{12}), 1.38 – 0.87 (m, 154H, 77 CH_2, ^{13}).

^{13}C NMR (101 MHz, $CDCl_3$) δ / ppm: 173.8, 172.6, 172.5, 172.1, 172.0, 169.9, 169.3, 169.1, 139.2, 136.2, 128.6, 128.2, 128.2, 114.2, 78.1, 78.1, 76.8, 74.0, 66.1, 40.0, 40.0, 39.3, 39.3, 39.2, 34.4, 34.3, 33.9, 33.1, 32.9, 32.0, 29.7, 29.6, 29.5, 29.4, 29.3, 29.3, 29.2, 29.2, 29.1, 29.0, 27.4, 27.4, 26.9, 26.1, 26.1, 26.1, 26.0, 25.1, 25.0, 25.0, 24.8.

HRMS-FAB-MS of $[C_{179}H_{301}N_8O_{28}]^+$: calculated: 3011.2 found: 3011.1.

IR (ATR platinum diamond): ν [cm^{-1}] = 3303.0, 2922.1, 2851.2, 1737.5, 1651.8, 1533.2, 1449.5, 1371.7, 1232.9, 1232.9, 1150.3, 1100.8, 987.8, 907.9, 722.2, 696.3, 580.6, 428.2.

***R*$_f$** (cyclohexane / ethyl acetate 1:1) = 0.67.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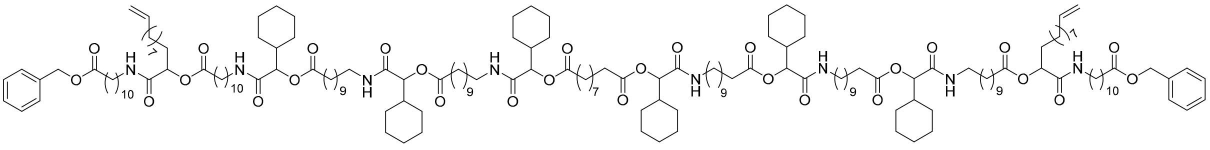
Octamer with terminal double bonds and cyclohexyl side chains: Synthesis of Octamer 35



Substance **19** (311 mg, 0.145 mmol, 1.0 eq.) was dissolved in DCM (0.3 mL, 0.5 M). Subsequently, monomer **M1** (131 mg, 0.44 mmol, 3.0 eq.) and 10-undecenal (73.0 mg, 0.44 mmol, 3.0 eq.) were added and the reaction mixture was stirred at room temperature for 48 hours. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (cyclohexane / ethyl acetate 5:1 → pure ethyl acetate) to obtain the product **35** in a yield of 93% (415 g, 0.14 mmol) as lightly yellow, highly viscous oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ / ppm: 7.38-7.17 (m, 10H, ^{1}), 6.18-5.95 (m, 8H, ^{2}), 5.88-5.63 (m, 2H, ^{3}), 5.17-5.02 (m, 12H, ^{4}), 5.00 – 4.79 (m, 4H, ^{5}), 3.33-3.06 (m, 16H, ^{6}), 2.43-2.23 (m, 20H, ^{7}), 2.17 – 1.84 (m, 10H, ^{8}), 1.80 – 1.51 (m, 48H, ^{9}), 1.52-1.35 (m, 16H, ^{10}), 1.37 – 0.72 (m, 164H, ^{11}).

^{13}C NMR (75 MHz, $CDCl_3$) δ / ppm: 173.64, 172.56, 172.48, 169.87, 169.23, 139.12, 136.13, 128.53, 128.13, 114.15, 101.21, 73.91, 66.04, 39.98, 39.14, 34.27, 33.78, 31.93, 29.58, 29.45, 29.35, 29.22, 29.11, 29.06, 28.89, 27.34, 26.85, 26.08, 26.00, 25.89, 24.98, 24.94, 24.77.

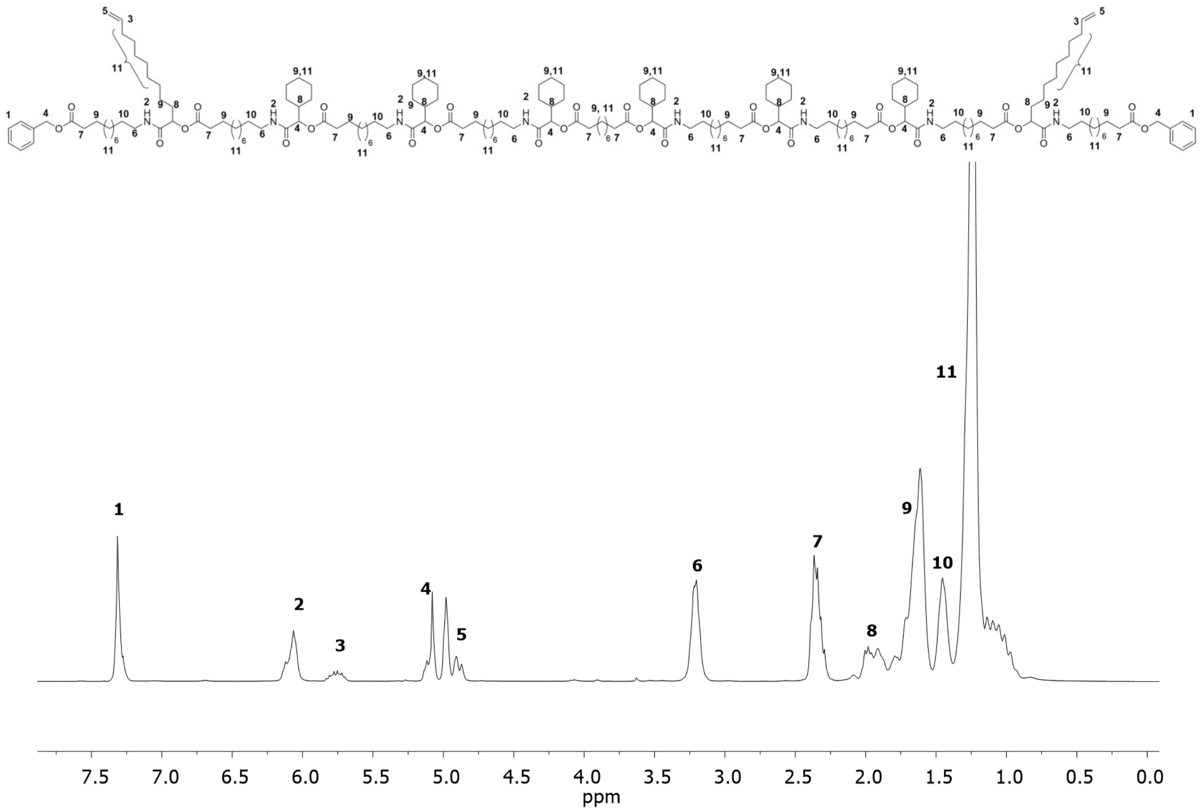
HRMS-ESI-MS of $[C_{184}H_{310}N_8O_{28}Na]^+$: calculated: 3103.2972, found: 3103.2957.

$[C_{184}H_{310}N_8O_{28}Na_2]^{2+}$: calculated: 1563.1432, found: 1563.1469.

$[C_{184}H_{310}N_8O_{28}Na_3]^{3+}$: calculated: 1049.7585, found: 1049.7561.

IR (ATR platinum diamond): ν [cm^{-1}] = 3305.5, 2922.9, 2852.2, 1738.0, 1651.8, 1534.8, 1450.3, 1373.1, 1159.6, 1101.5, 989.5, 908.6, 722.7, 696.9, 429.9.

***R*$_f$** (cyclohexane / ethyl acetate 1:1) = 0.67.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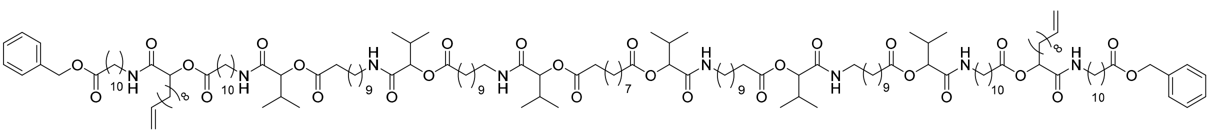
Octamer with terminal double bonds and isopropyl side chains: Synthesis of Octamer 36



Substance **27** (0.17 g, 89 µmol, 1.0 eq.) was dissolved in DCM (0.2 mL, 0.25 M) and 10-undecenal (54 µL, 45 mg, 0.27 mmol, 3.0 eq.) and monomer **M1** (81 mg, 0.27 mmol, 3.0 eq.) were added. The reaction mixture was stirred at room temperature for 48 hours and the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography (cyclohexane / ethyl acetate 4:1 → pure ethyl acetate) to obtain substance **36** as colourless, highly viscous oil in a yield of 91% (0.23 g, 0.23 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ / ppm: 7.38 – 7.27 (m, 10H, ^{1}), 6.14 – 5.97 (m, 8H, ^{2}), 5.76 (ddt, J = 16.9, 10.2, 6.7 Hz, 2H, ^{3}), 5.17 – 5.05 (m, 12H, ^{4}), 5.03 – 4.84 (m, 4H, ^{5}), 3.34 – 3.06 (m, 16H, ^{6}), 2.46 – 2.16 (m, 26H, ^{7}), 2.03 – 1.93 (m, 4H, ^{8}), 1.86 – 1.69 (m, 4H, ^{9}), 1.69 – 1.54 (m, 20H, ^{10}), 1.51 – 1.37 (m, 16H, ^{11}), 1.36 – 1.11 (m, 128H, ^{12}), 1.01 – 0.75 (m, 36H, ^{13}).

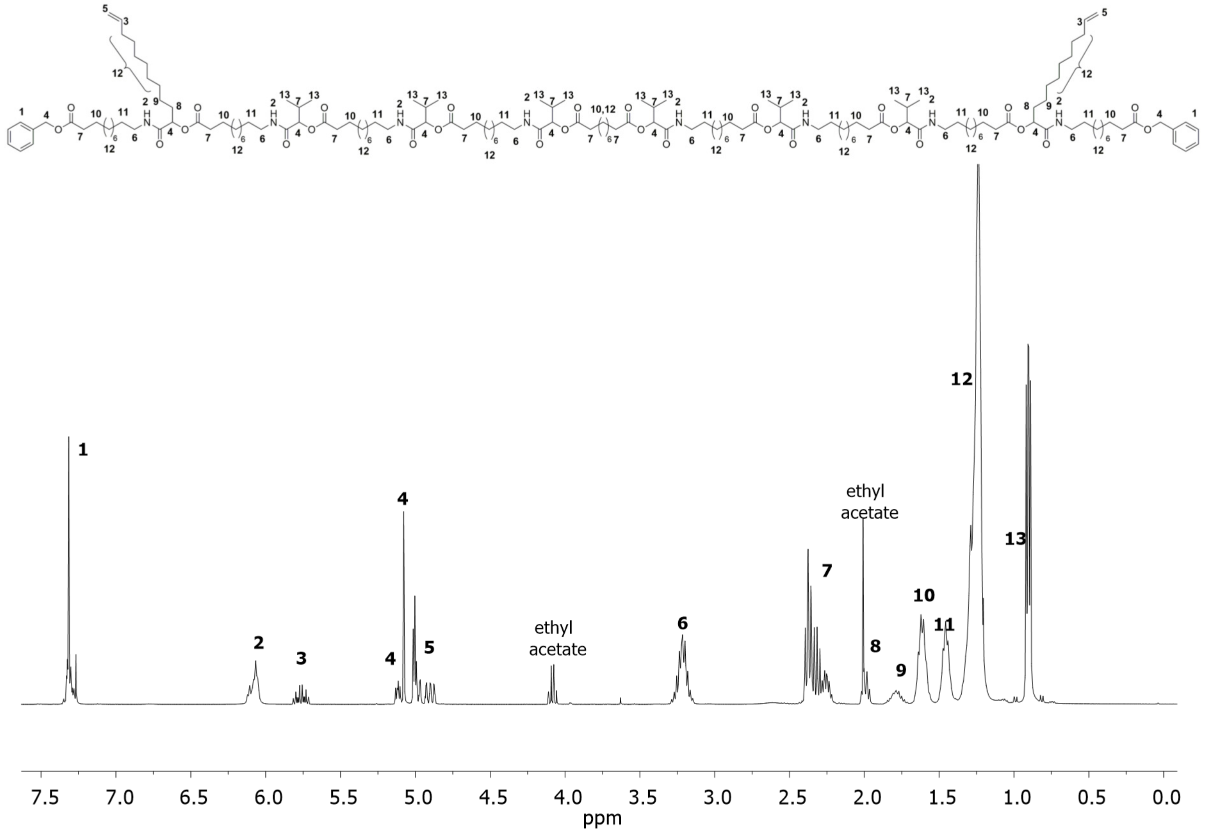
^{13}C NMR (101 MHz, $CDCl_3$) δ / ppm: 173.69, 172.62, 172.58, 172.51, 171.16, 169.90, 169.34, 169.31, 139.16, 136.13, 128.55, 128.40, 128.18, 128.16, 114.18, 77.97, 77.93, 77.36, 73.92, 66.07, 60.41, 51.46, 39.21, 39.18, 34.33, 34.32, 34.28, 34.24, 33.80, 31.94, 30.54, 29.60, 29.56, 29.46, 29.37, 29.23, 29.20, 29.13, 29.12, 29.08, 28.91, 26.86, 25.01, 24.96, 24.78, 21.07, 19.26, 18.81, 17.01, 15.48, 14.23.

HRMS-ESI-MS of $[C_{166}H_{286}N_8O_{28}Na_2]^{2+}$: calculated: 1443.0493, found: 1443.0526.

$[C_{166}H_{286}N_8O_{28}Na_3]^{3+}$: calculated: 969.6959, found: 969.6964

IR (ATR platinum diamond): ν [cm^{-1}] = 3292.0, 2923.0, 2852.1, 1736.3, 1655.4, 1536.7, 1464.8, 1370.5, 1239.4, 1166.0, 1107.9, 995.2, 909.9, 722.8, 696.8, 419.0.

***R*$_f$** (cyclohexane / ethyl acetate 2:3) = 0.42.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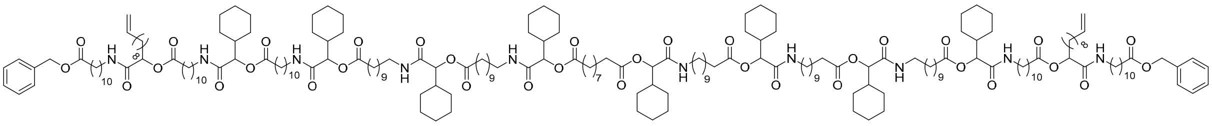
Decamer with terminal double bonds and cyclohexyl side chains: Synthesis of Decamer 37



Substance **21** (278 mg, 99 µmol, 1.0 eq.) was dissolved in DCM (0.3 mL, 0.3 M). Subsequently, monomer **M1** (90 mg, 0.30 mmol, 3.0 eq.) and 10-undecenal (50 mg, 0.30 mmol, 3.0 eq.) were added and the reaction mixture was stirred at room temperature for 48 hours. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (cyclohexane / ethyl acetate 4:1 → pure ethyl acetate) to obtain the product **37** in a yield of 99% (400 g, 99 µmol) as lightly yellow, highly viscous oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ / ppm: 7.39 – 7.27 (m, 10H, ^{1}), 6.16 – 5.97 (m, 10H, ^{2}), 5.77 (m, 2H, ^{3}), 5.16 – 5.06 (m, 14H, ^{4}), 5.03 – 4.84 (m, 4H, ^{5}), 3.32 – 3.11 (m, 20H, ^{6}), 2.47 – 2.24 (m, 24H, ^{7}), 2.09 – 1.76 (m, 12H, ^{8}), 1.75 – 1.53 (m, 60H, ^{9}), 1.52 – 1.39 (m, 20H, ^{10}), 1.37 – 0.69 (m, 200H, ^{11}).

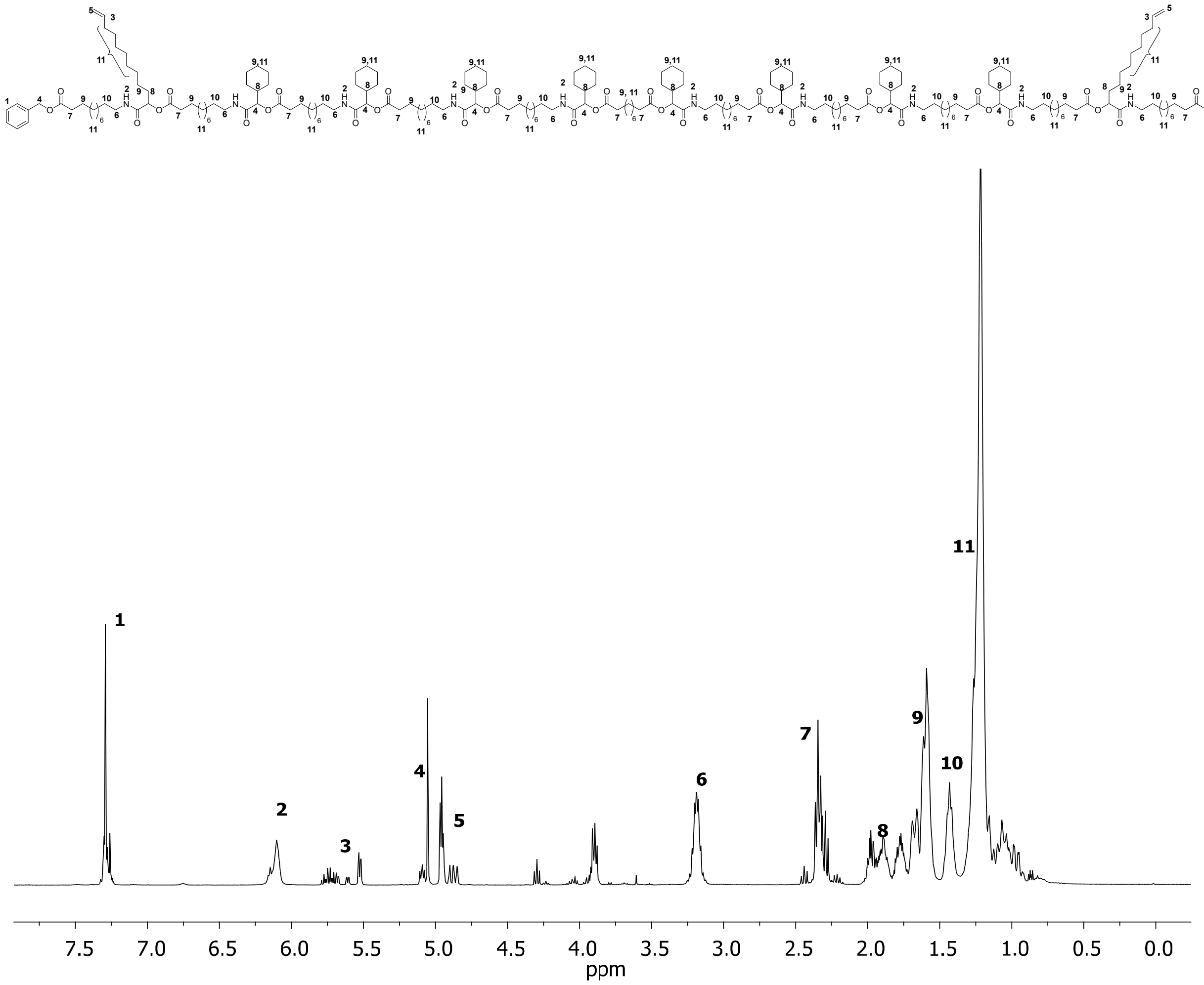
^{13}C NMR (101 MHz, $CDCl_3$) δ / ppm: 177.84, 174.24, 173.69, 172.61, 172.58, 172.51, 169.97, 169.33, 169.31, 161.06, 139.10, 136.06, 128.50, 128.34, 128.13, 128.10, 114.13, 107.80, 107.58, 106.33, 77.60, 77.56, 77.36, 76.00, 73.85, 72.78, 72.01, 68.55, 67.62, 67.54, 67.40, 66.04, 61.01, 60.39, 51.43, 41.63, 39.92, 39.19, 39.14, 37.25, 34.89, 34.28, 34.24, 34.22, 34.18, 33.75, 31.89, 29.65, 29.51, 29.43, 29.33, 29.19, 29.15, 29.08, 29.03, 28.85, 27.79, 27.30, 27.06, 26.81, 26.04, 25.96, 25.84, 24.94, 24.90, 24.87, 24.72, 23.89, 23.81, 23.79, 22.66, 22.42, 22.16, 21.02, 19.05, 14.17, 14.10.

HRMS-ESI-MS of $[C_{222}H_{376}N_{10}O_{34}Na_2]^{2+}$: calculated: 1886.3892, found: 1886.4028.

$[C_{222}H_{376}N_{10}O_{34}Na_3]^{3+}$: calculated: 1265.2559, found: 1265.2576.

IR (ATR platinum diamond): ν [cm^{-1}] = 3294.7, 2923.3, 2853.1, 1737.8, 1651.5, 1536.1, 1450.2, 1369.1, 1160.5, 1101.1, 1071.8, 989.0, 925.7, 722.6, 697.4.

R_f (cyclohexane / ethyl acetate 1:1) = 0.58.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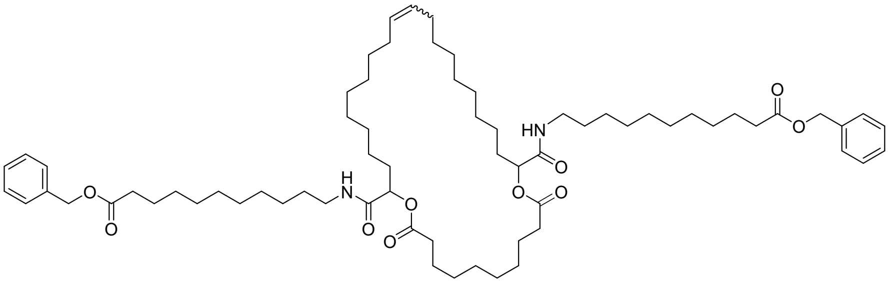
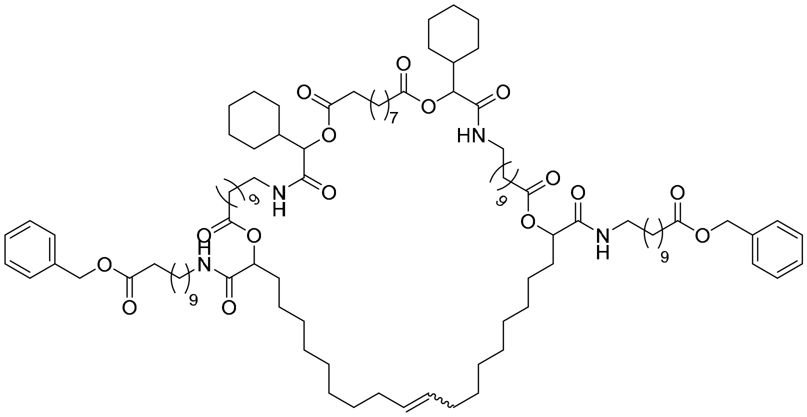
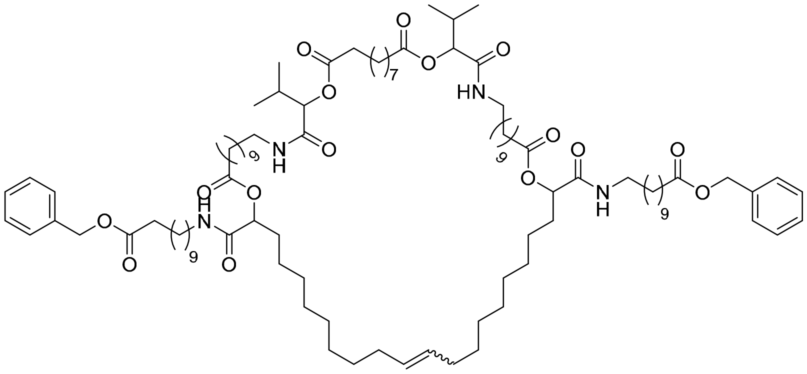
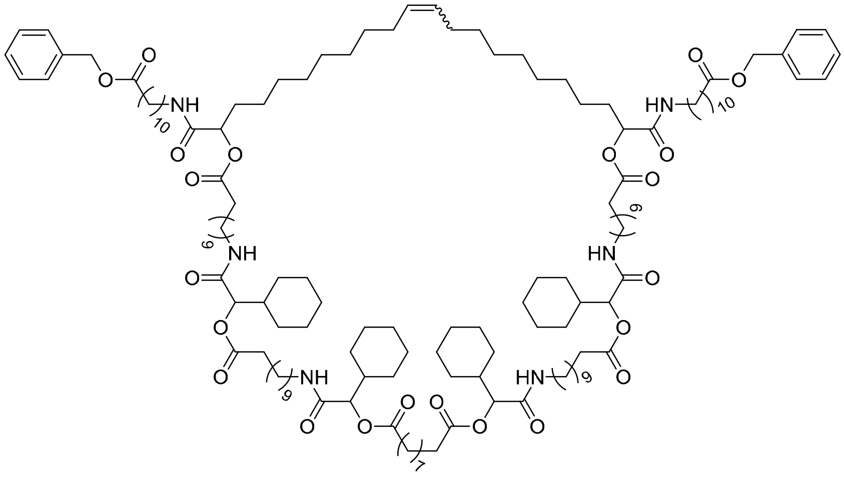
4 Formation of the macrocycles

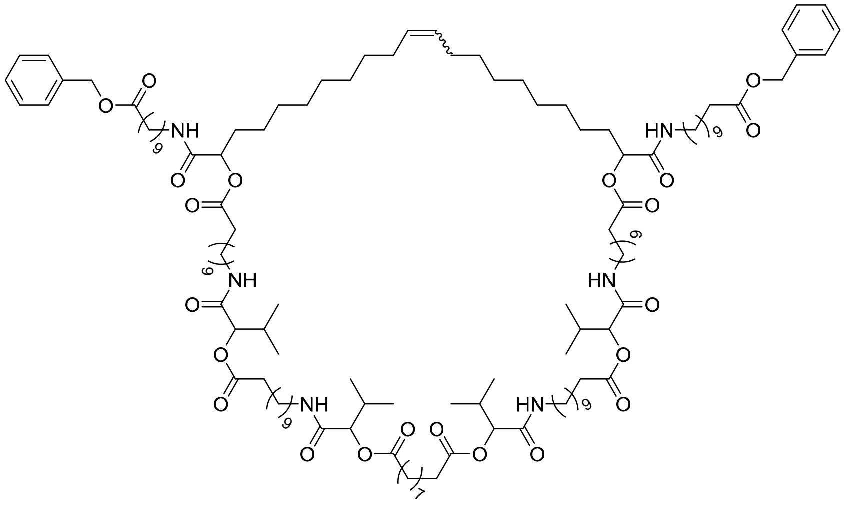
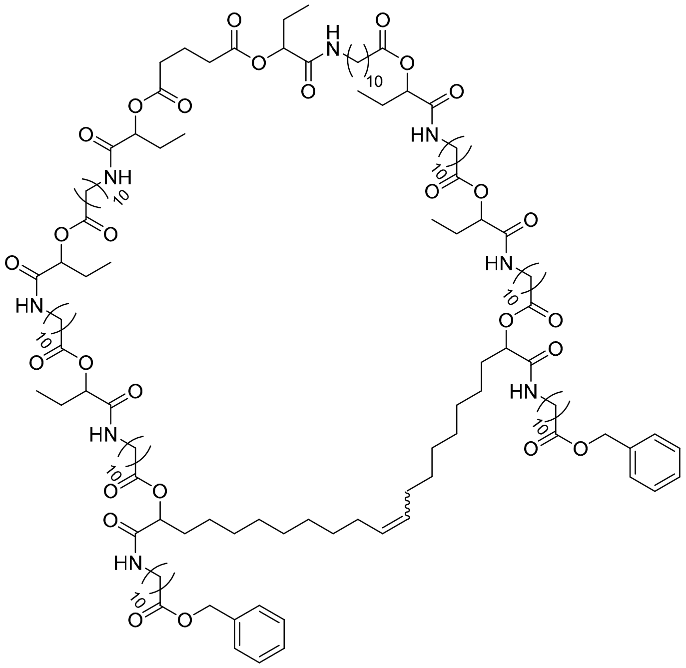
The different macrocycles were formed *via* ring-closing metathesis of the substances **28** - **37**.

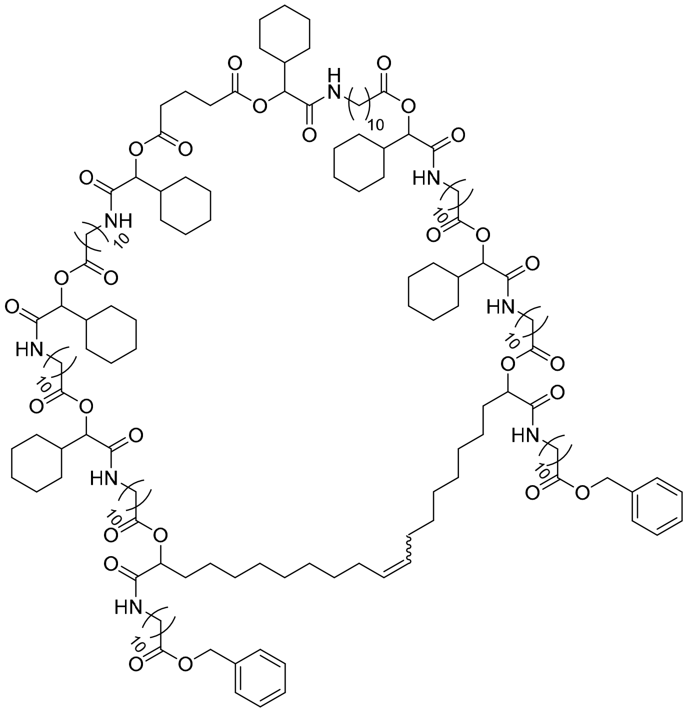
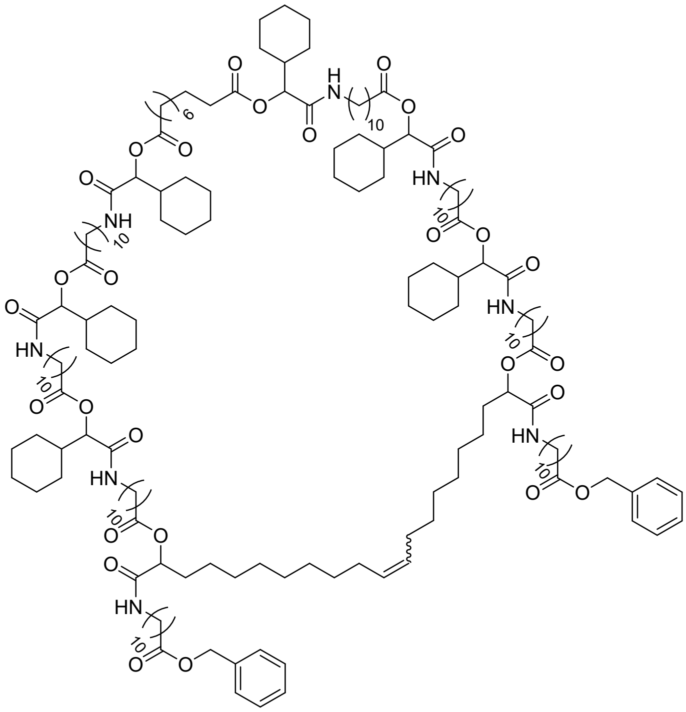
For this purpose, the following optimized synthesis protocol was applied:

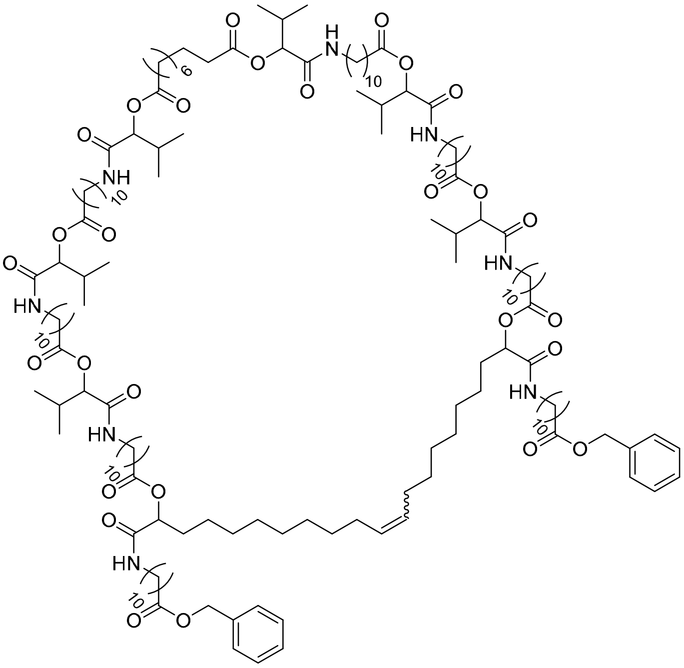
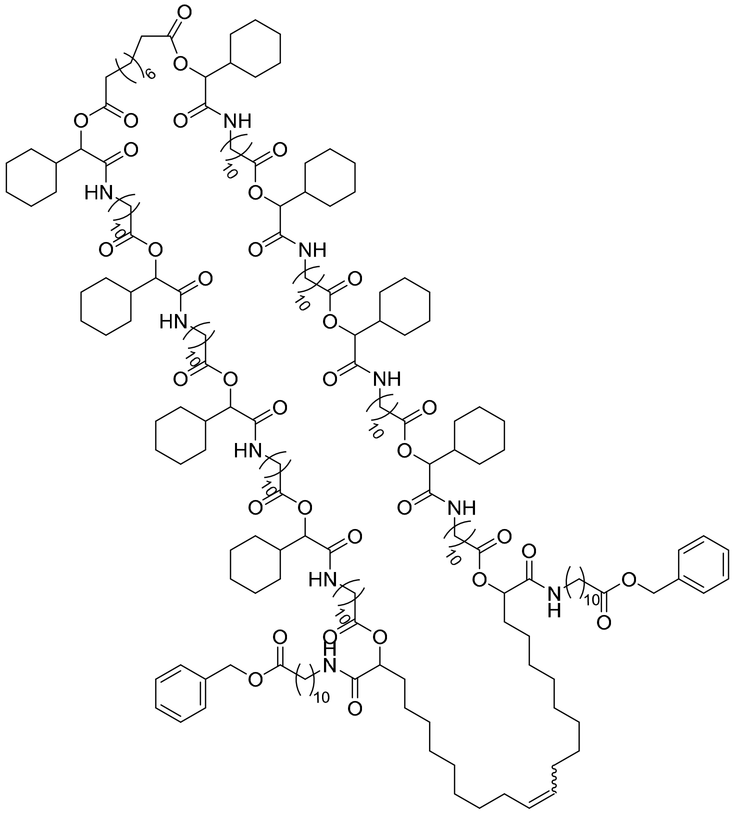
The linear oligomer (substances **28** – **37**) (0.03 mmol, 1.0 eq.) was dissolved in chloroform (5×10^{-4} M). Subsequently, *p*-benzoquinone (0.3 eq.) and Grubbs 1st generation catalyst (10 mol%), both dissolved in of chloroform (2 mL), were added under argon atmosphere. The reaction mixture was heated to 45 °C and stirred under argon atmosphere. After two, three and four hours of reaction time, another 10 mol% of Grubbs 1st generation catalyst, dissolved in 2 mL of chloroform, were added to the solution. After a reaction time of five hours, the reaction was quenched by addition of ethyl vinyl ether. The solvent was removed under reduced pressure and the crude product (substances **38** – **47**, see below) was analyzed by SEC-ESI-MS.

5 List of the obtained macrocycles

Substance	Structure
38 Dimer	
39 Tetramer with cyclohexyl side chains	
40 Tetramer with isopropyl side chains	
41 Hexamer with cyclohexyl side chains	

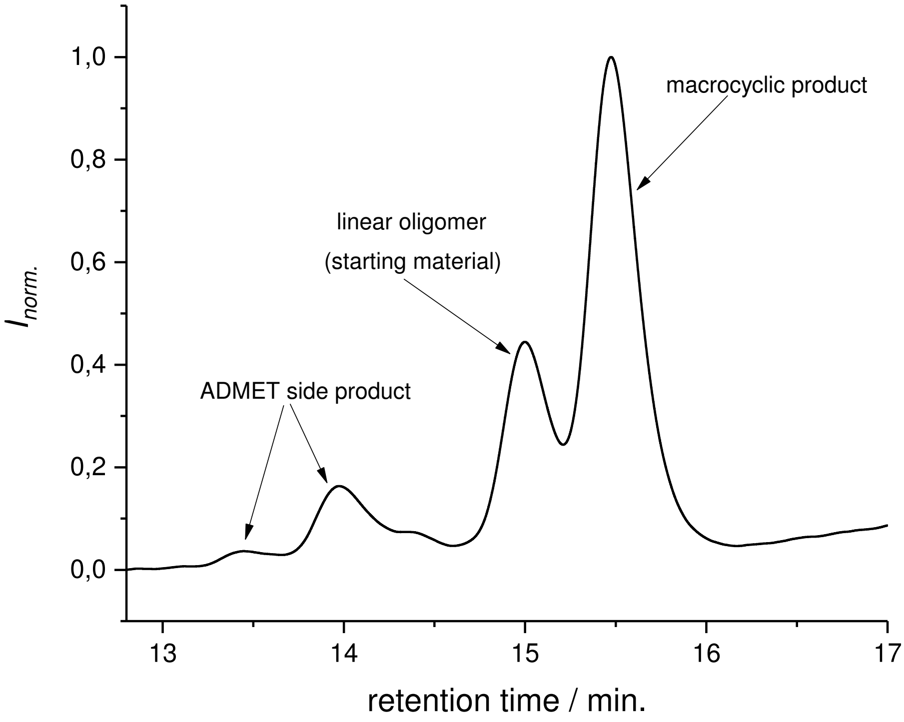
42 Hexamer with isopropyl side chains	
43 Octamer with ethyl side chains (C5 core unit)	

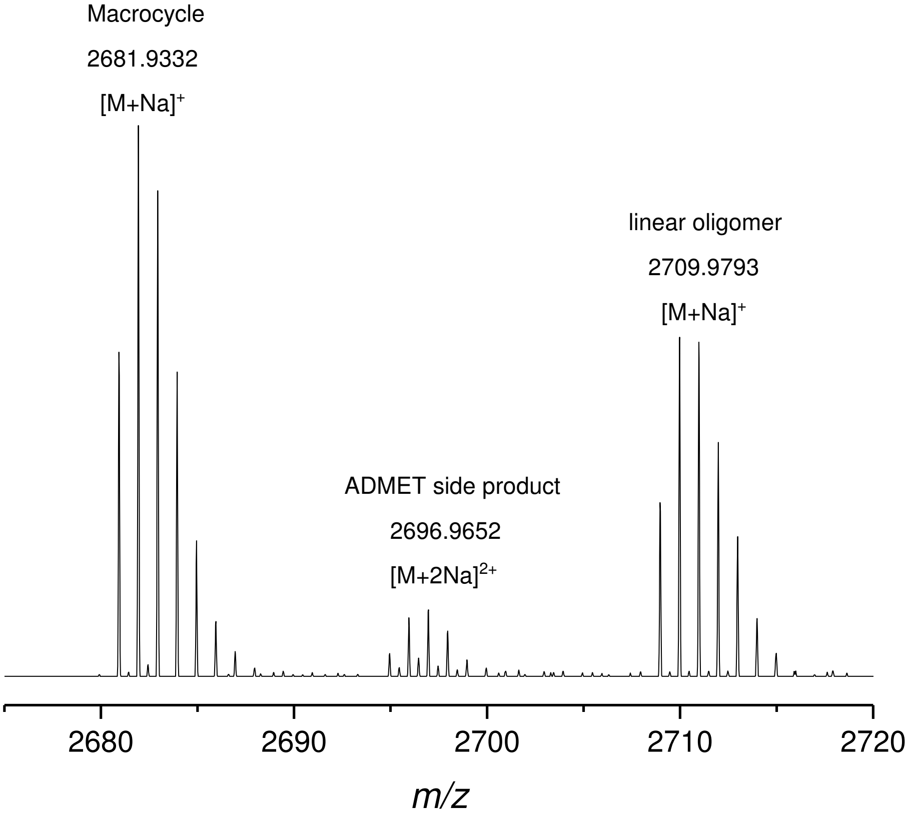
44 Octamer with cyclohexyl side chains (C5 core unit)	
45 Octamer with cyclohexyl side chains (C10 core unit)	

46 Octamer with isopropyl side chains	
47 Decamer with cyclohexyl side chains	

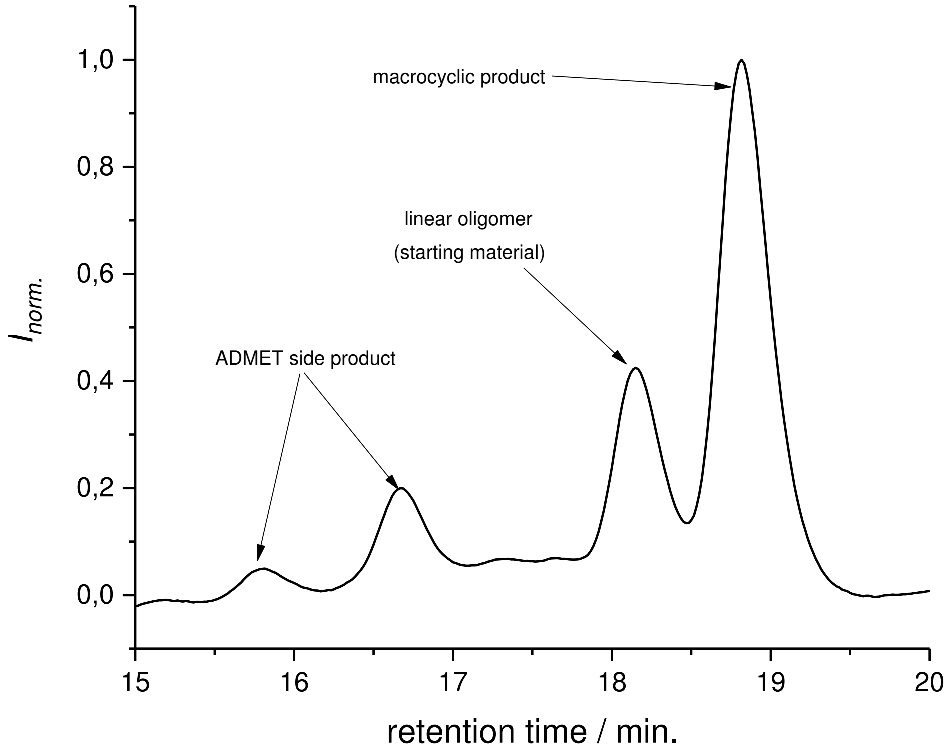
6 Examples of SEC-ESI-MS analysis of crude macrocycles to identify side products

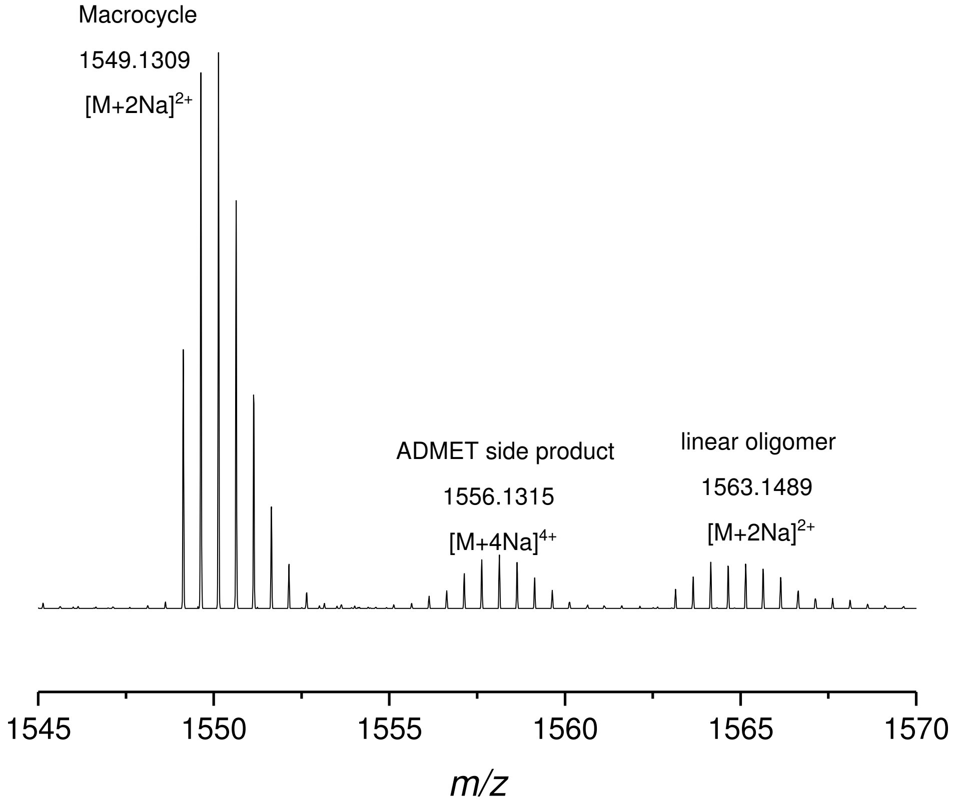
6.1 Cyclic octamer with ethyl side chains (Substance 43)





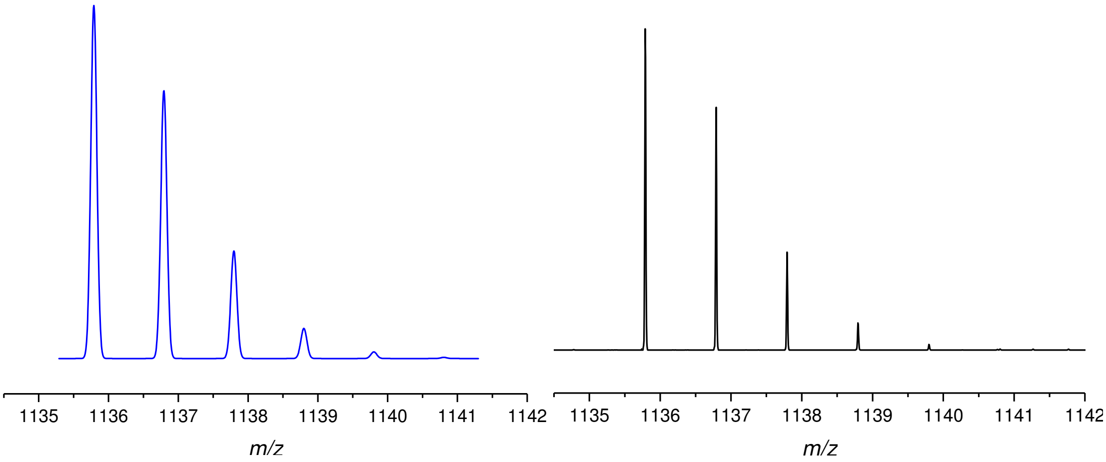
6.2 Cyclic octamer with cyclohexyl side chains (Substance 45)



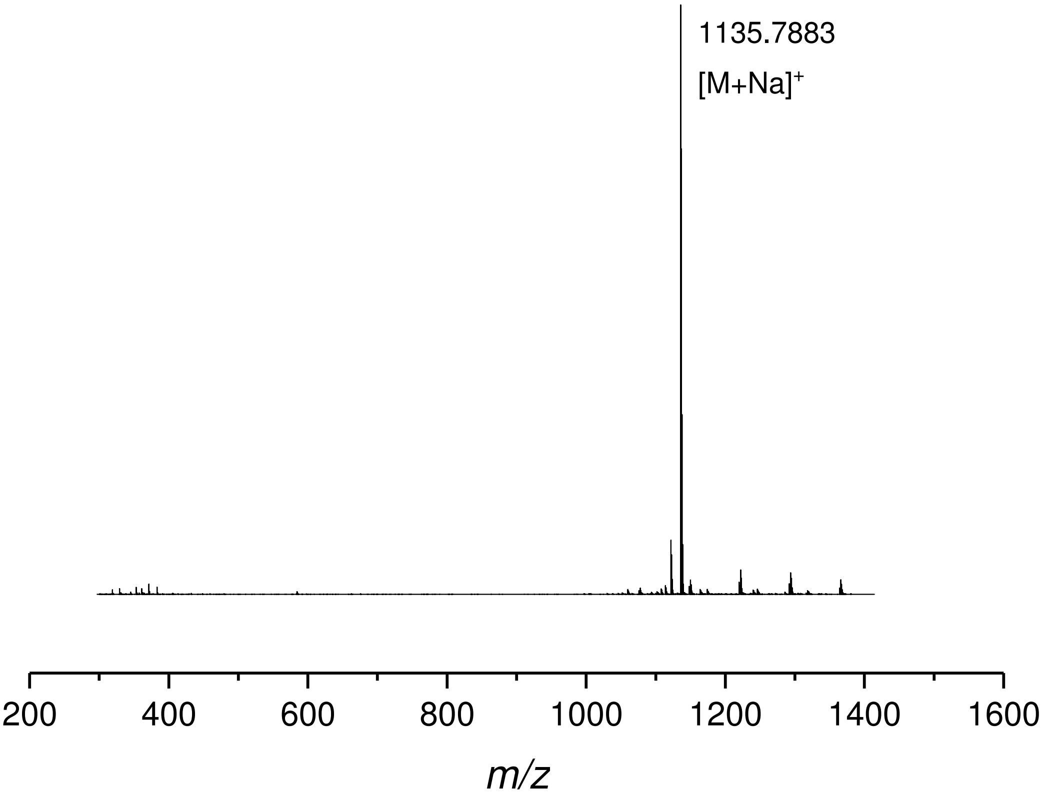


7 Characterization of the macrocycles via ESI-MS

7.1 Characterization of the cyclic dimer 39

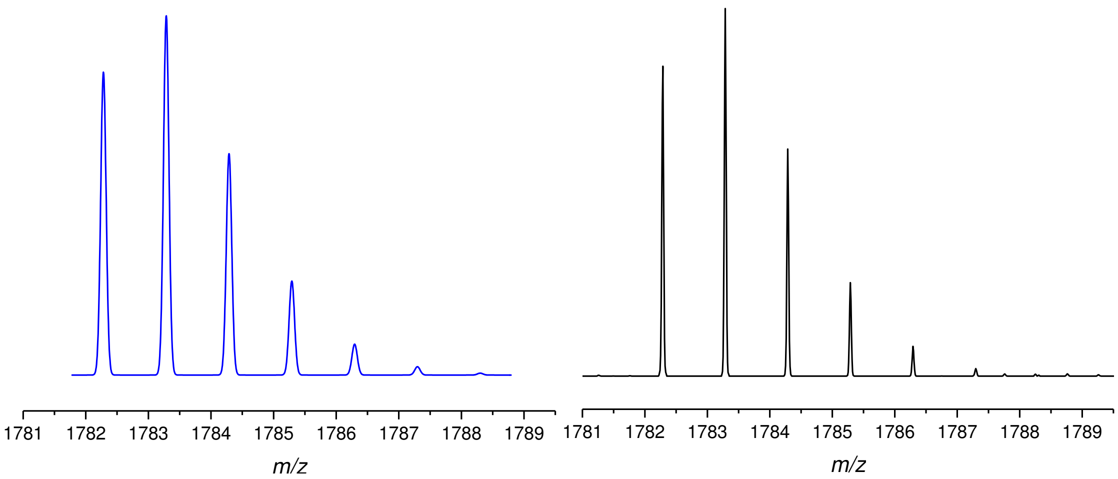


Comparison of the calculated isotopic pattern (blue) with the measured one (black).

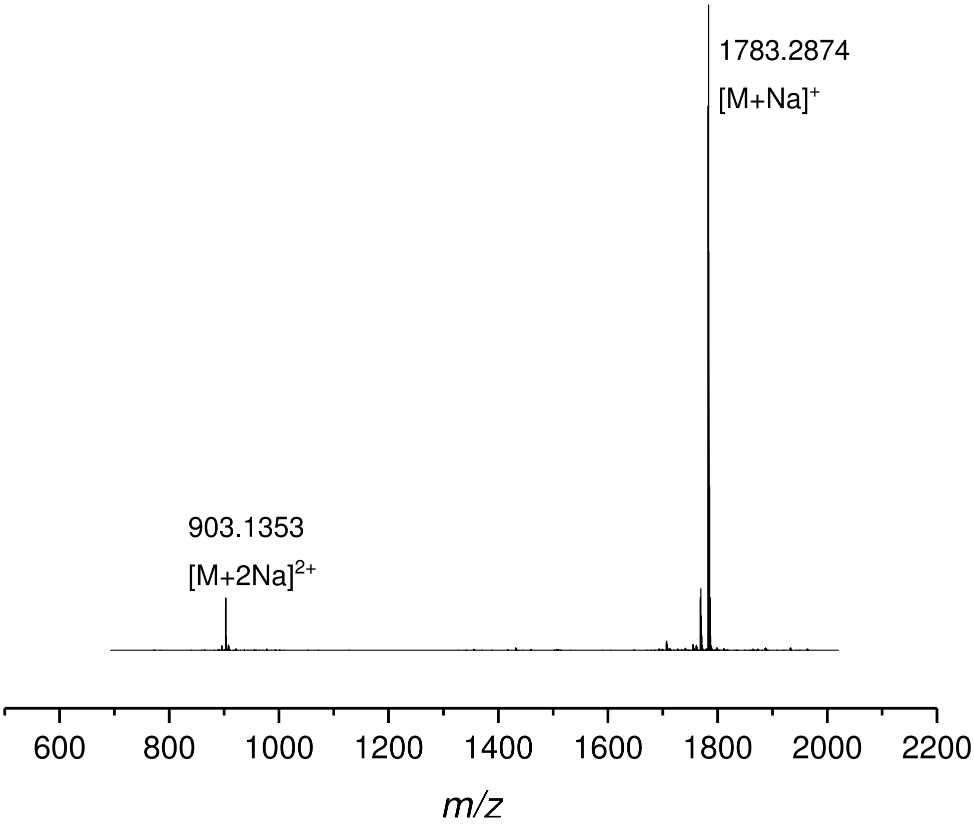


ESI-MS spectrum of the crude reaction mixture after cyclization. The singly charged sodium cation of the macrocycle was observed.

7.2 Characterization of the cyclic tetramer with cyclohexyl side chains 40

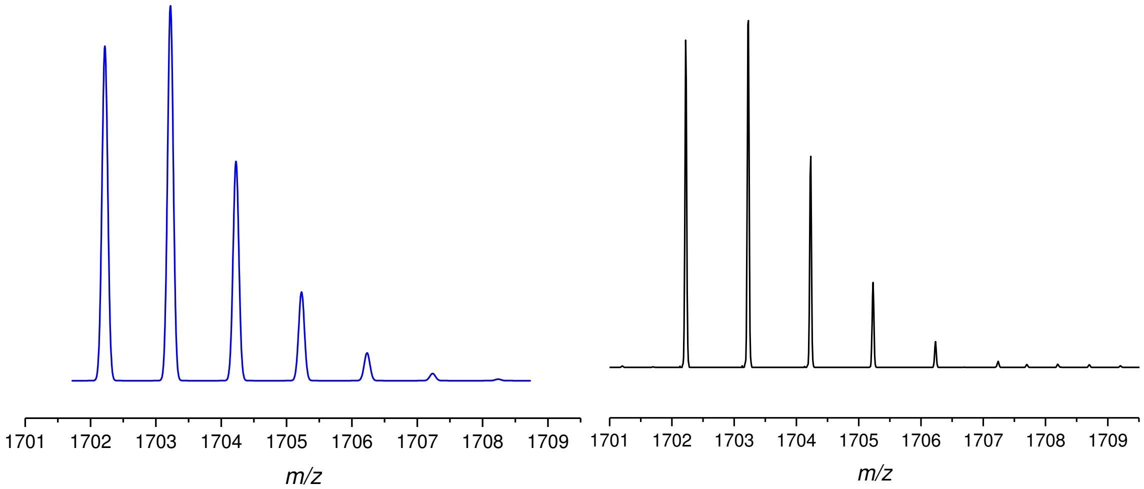


Comparison of the calculated isotopic pattern (blue) with the measured one (black).

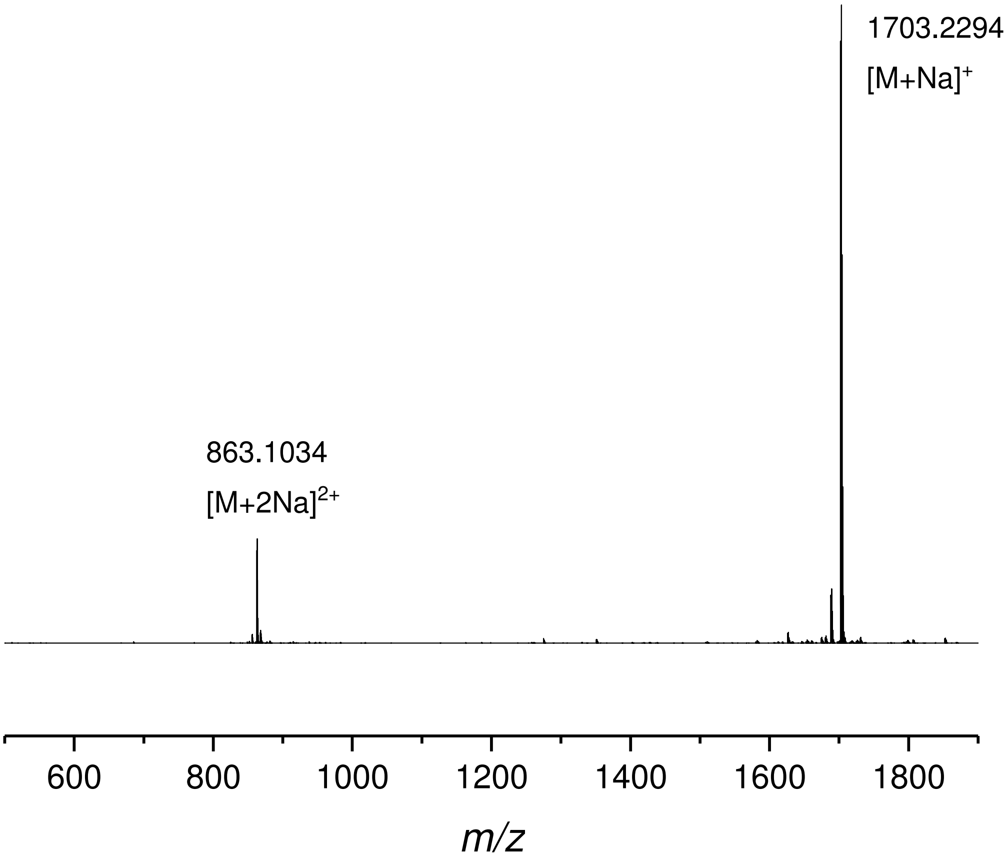


ESI-MS spectrum of the crude reaction mixture after cyclization. The singly and doubly charged sodium cations of the macrocycle were observed.

7.3 Characterization of the cyclic tetramer with isopropyl side chains 41

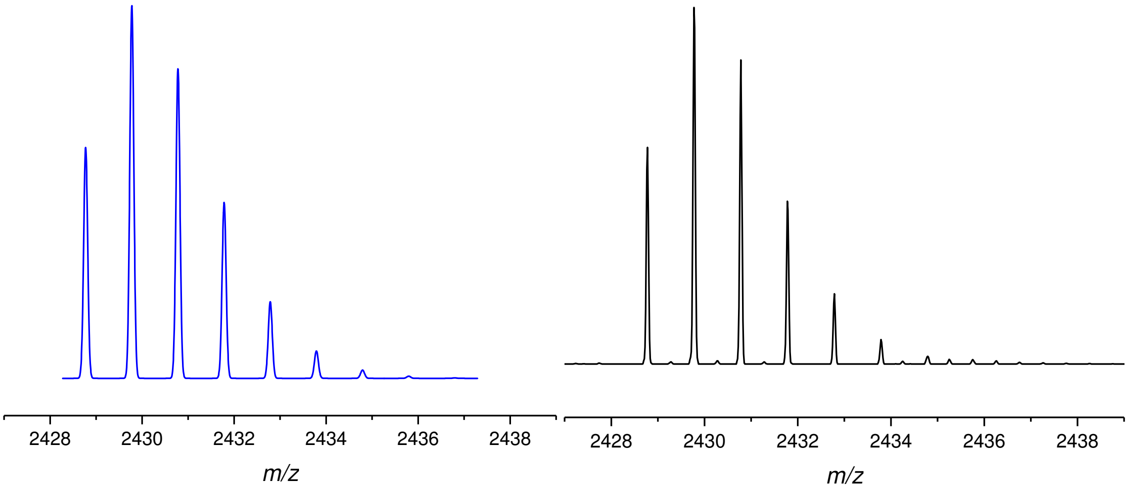


Comparison of the calculated isotopic pattern (blue) with the measured one (black).

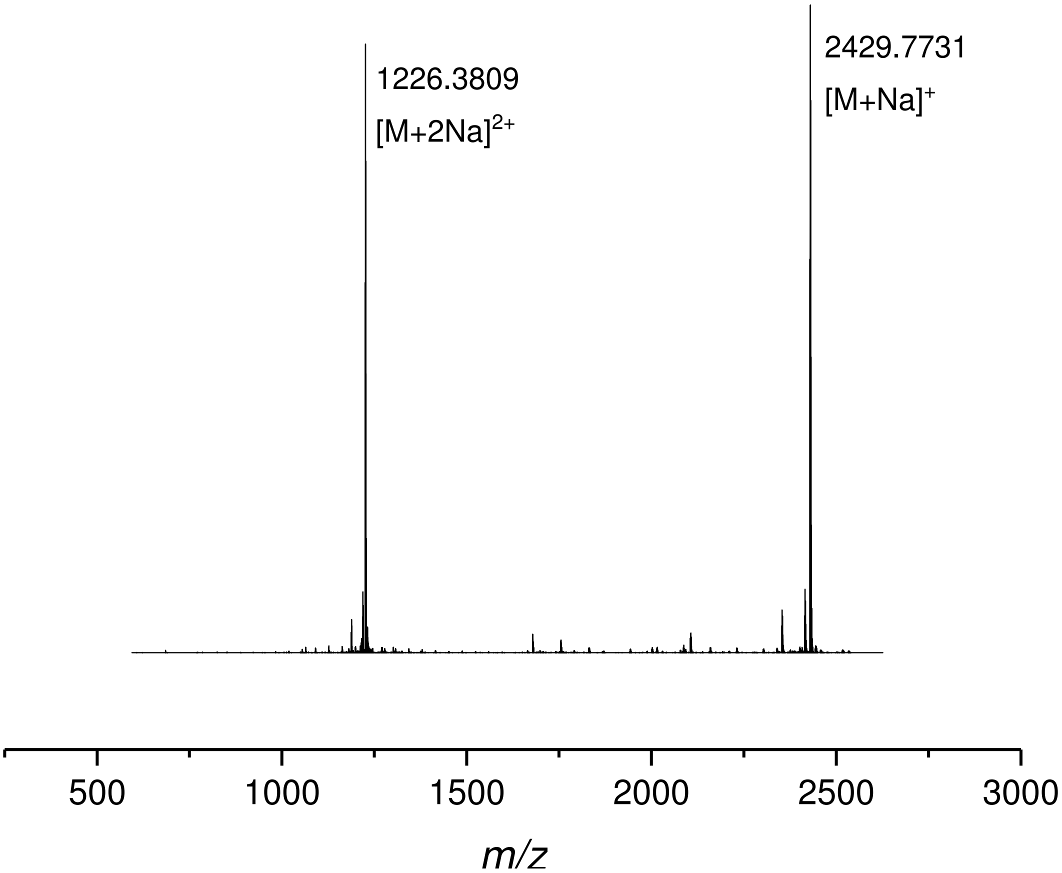


ESI-MS spectrum of the crude reaction mixture after cyclization. The singly and doubly charged sodium cations of the macrocycle were observed.

7.4 Characterization of the cyclic hexamer with cyclohexyl side chains 42

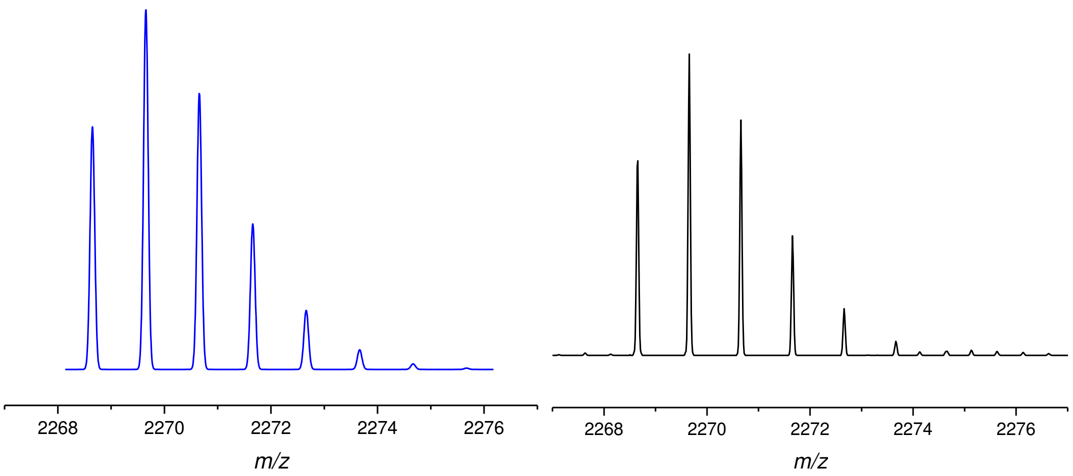


Comparison of the calculated isotopic pattern (blue) with the measured one (black).

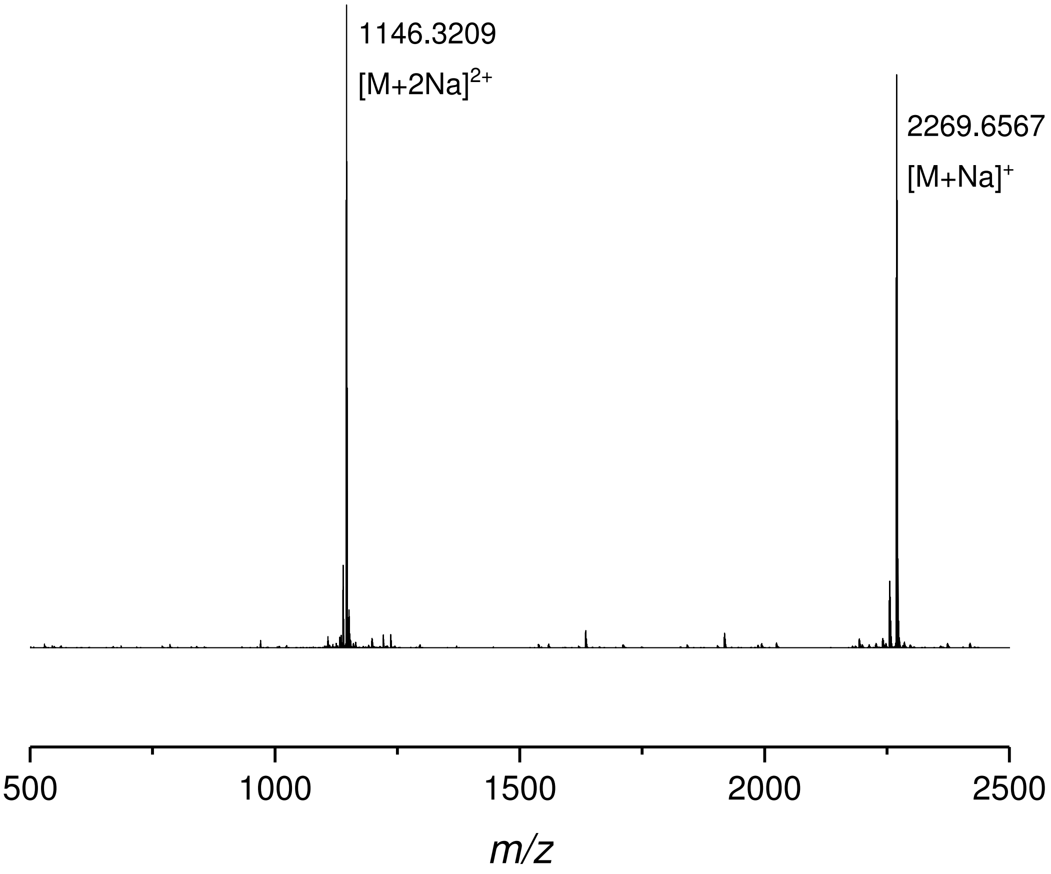


ESI-MS spectrum of the crude reaction mixture after cyclization. The singly and doubly charged sodium cations of the macrocycle were observed.

7.5 Characterization of the cyclic hexamer with isopropyl side chains 43

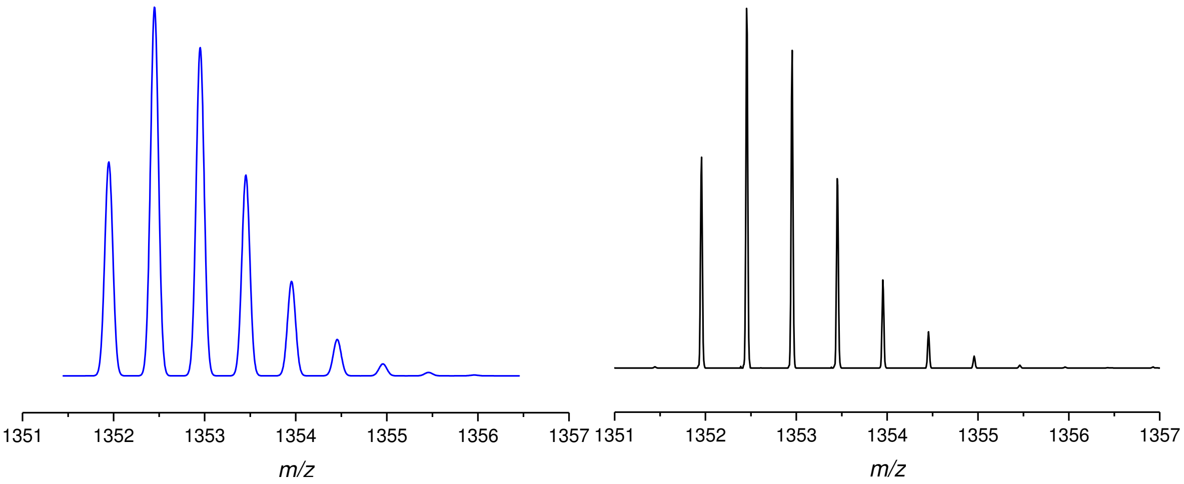


Comparison of the calculated isotopic pattern (blue) with the measured one (black).

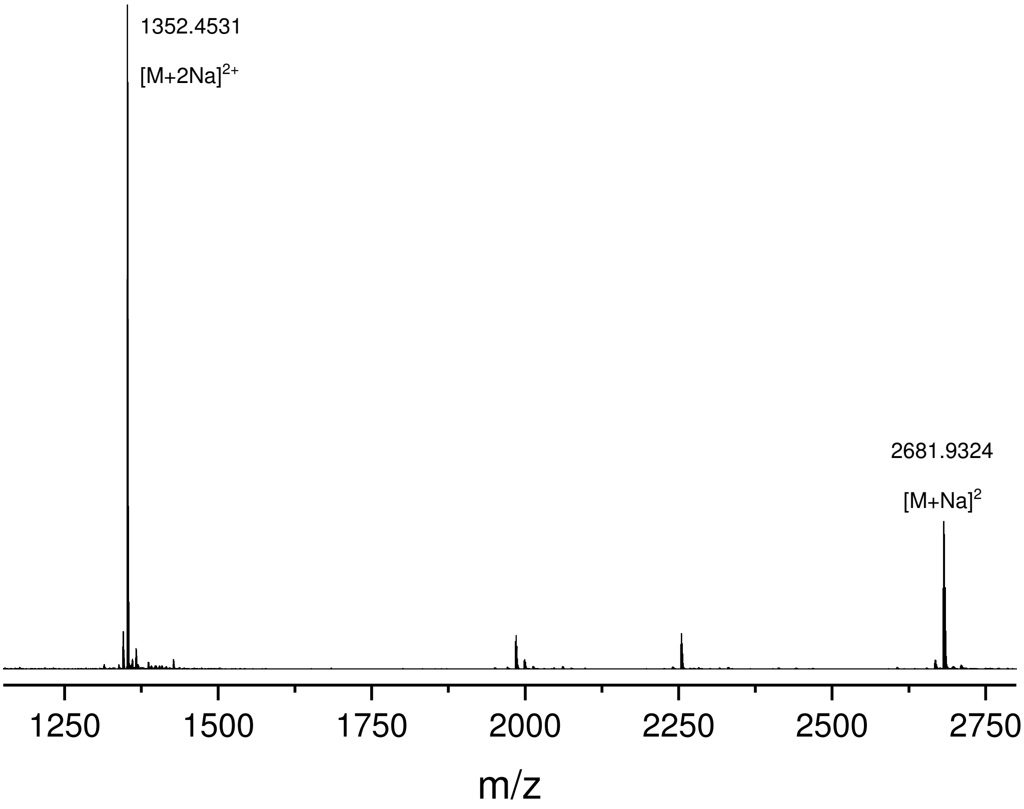


ESI-MS spectrum of the crude reaction mixture after cyclization. The singly and doubly charged sodium cations of the macrocycle were observed.

7.6 Characterization of the cyclic octamer with ethyl side chains (C5 core unit) 44

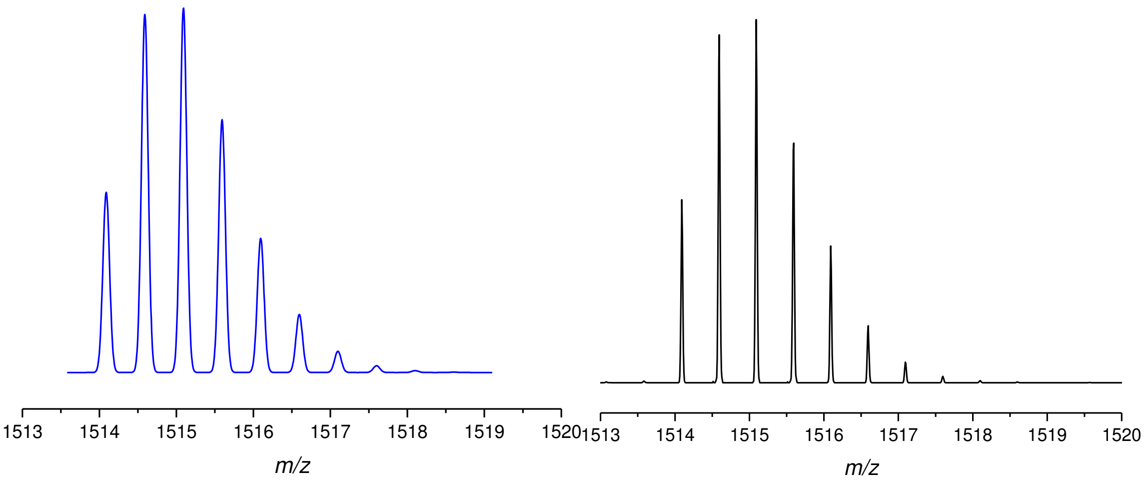


Comparison of the calculated isotopic pattern (blue) with the measured one (black).

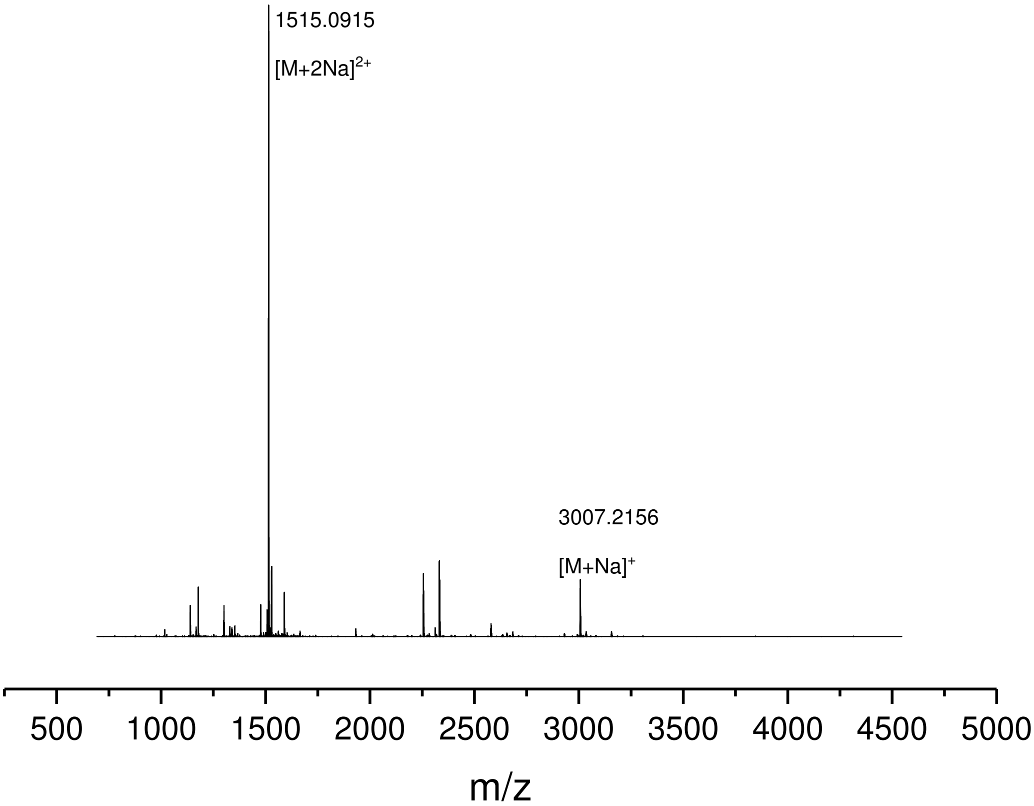


ESI-MS spectrum of the crude reaction mixture after cyclization. The singly and doubly charged sodium cations of the macrocycle were observed.

7.7 Characterization of the cyclic octamer with cyclohexyl side chains (C5 core unit) 45

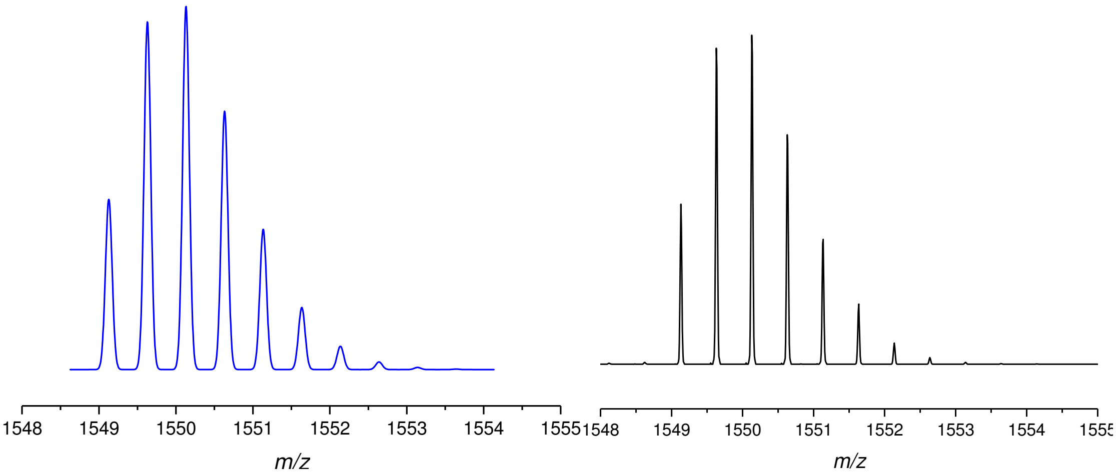


Comparison of the calculated isotopic pattern (blue) with the measured one (black).

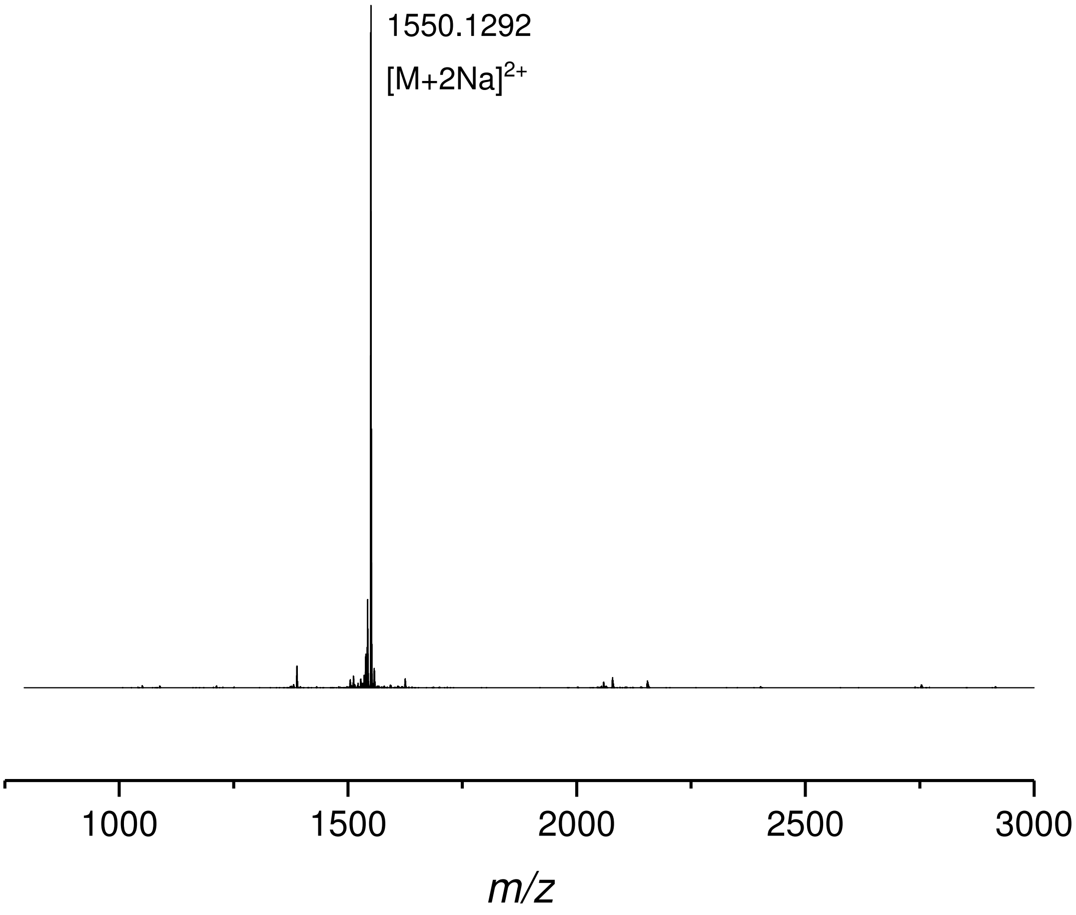


ESI-MS spectrum of the crude reaction mixture after cyclization. The singly and doubly charged sodium cations of the macrocycle were observed.

7.8 Characterization of the cyclic octamer with cyclohexyl side chains (C10 core unit) 46

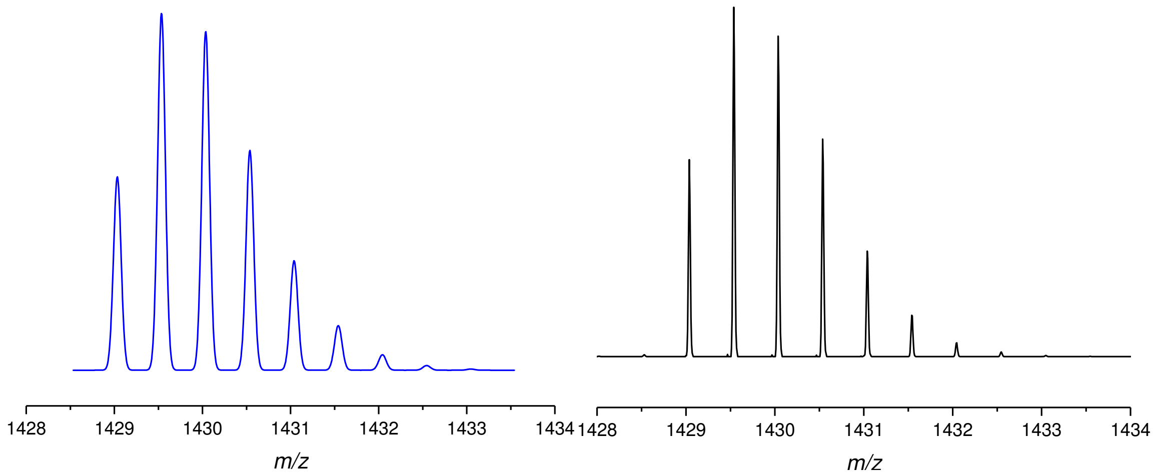


Comparison of the calculated isotopic pattern (blue) with the measured one (black).

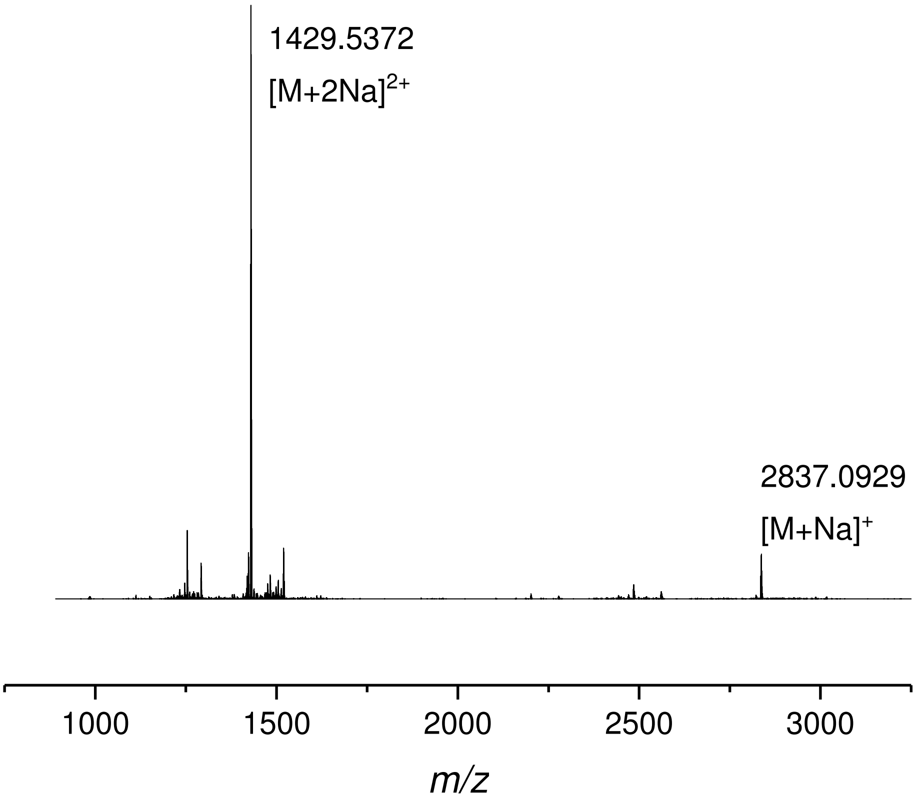


ESI-MS spectrum of the crude reaction mixture after cyclization. The doubly charged sodium cation of the macrocycle was observed.

7.9 Characterization of the cyclic octamer with isopropyl side chains 47

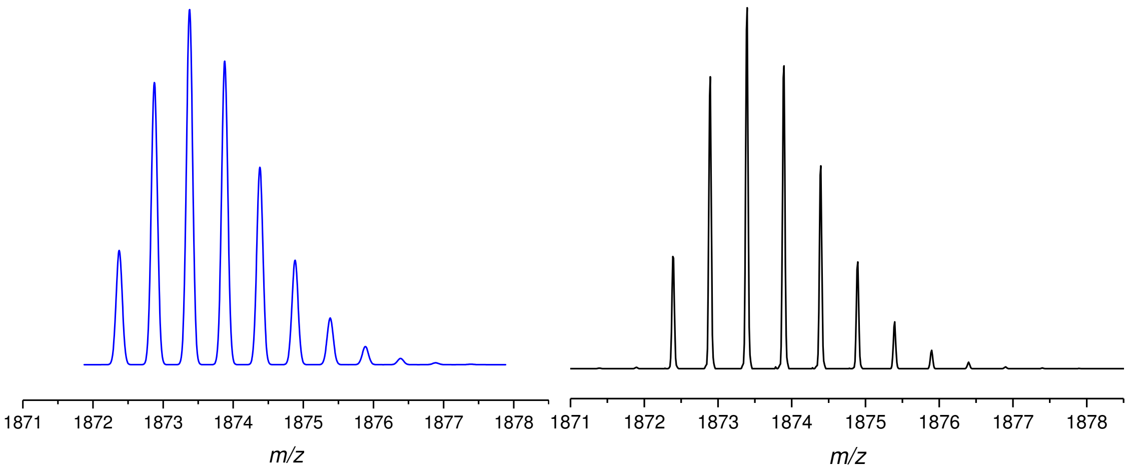


Comparison of the calculated isotopic pattern (blue) with the measured one (black).

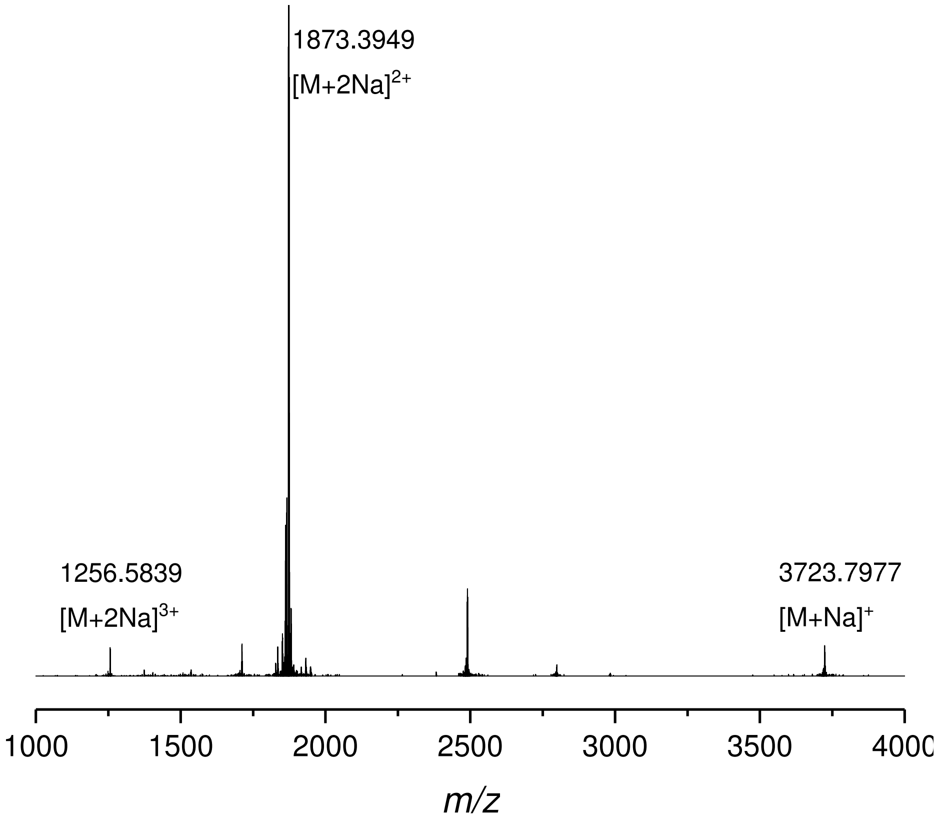


ESI-MS spectrum of the crude reaction mixture after cyclization. The singly and doubly charged sodium cations of the macrocycle were observed.

7.10 Characterization of the cyclic decamer with cyclohexyl side chains 48



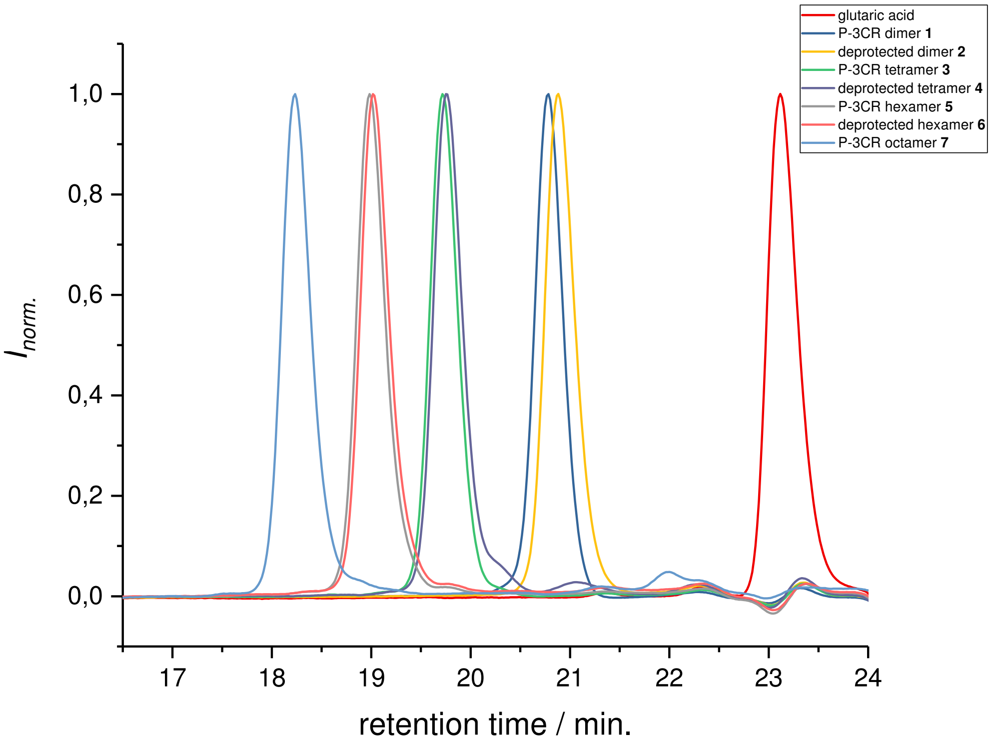
Comparison of the calculated isotopic pattern (blue) with the measured one (black).



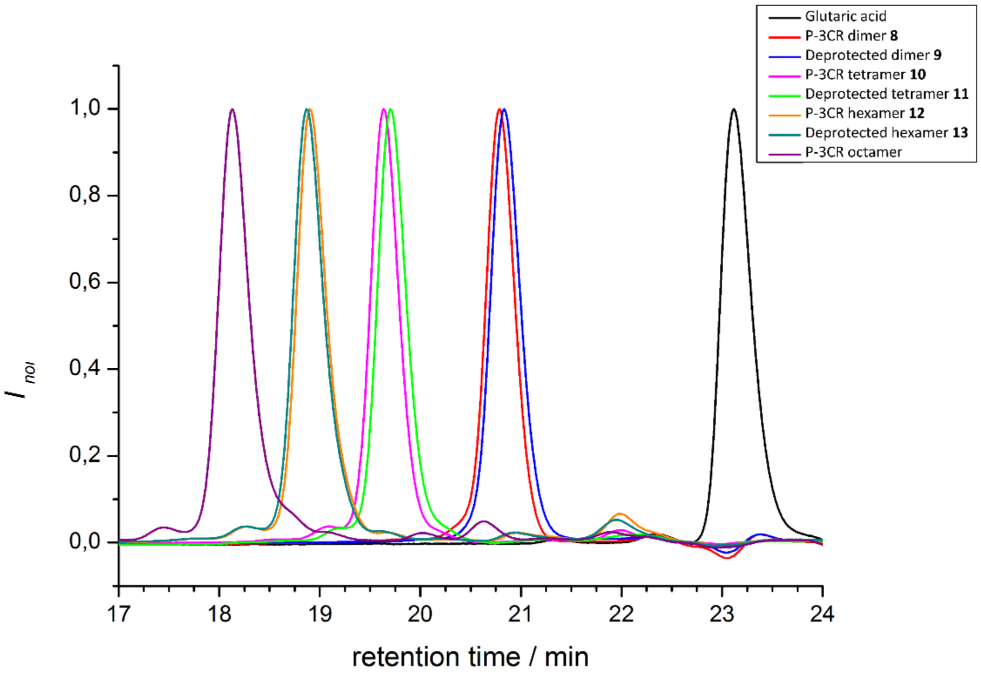
ESI-MS spectrum of the crude reaction mixture after cyclization. The singly doubly and triply charged sodium cations of the macrocycle were observed.

8 SEC Characterization

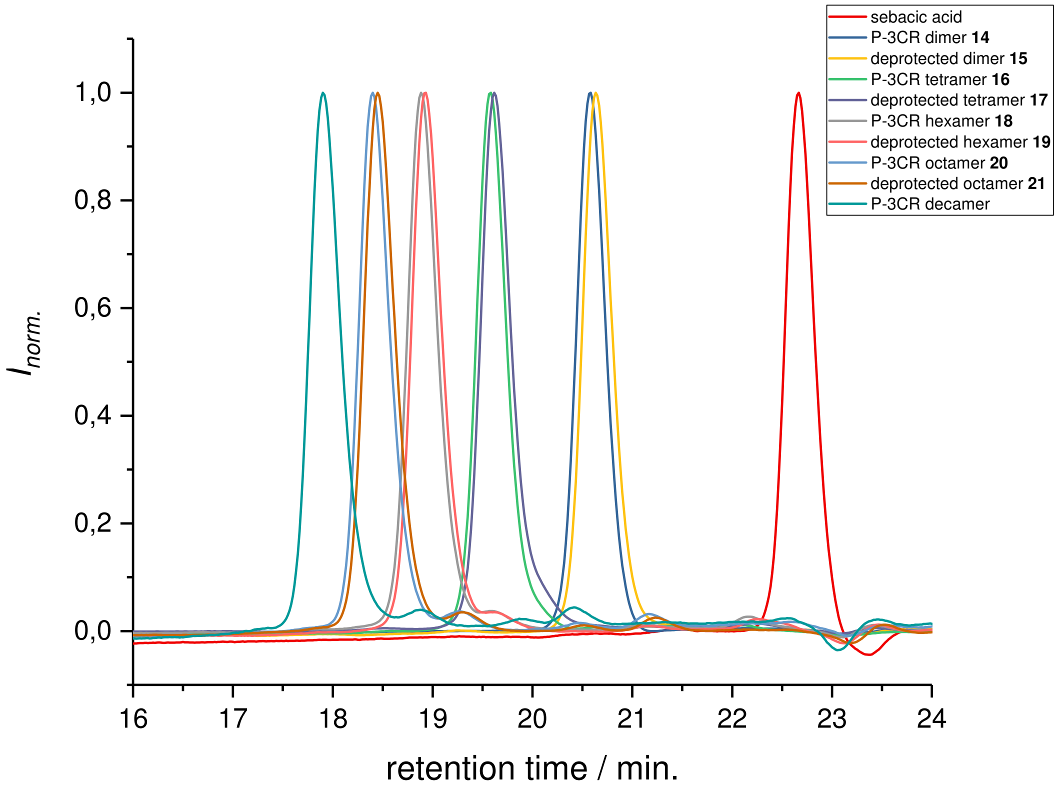
8.1 Linear oligomers with ethyl side chains and C5 core unit



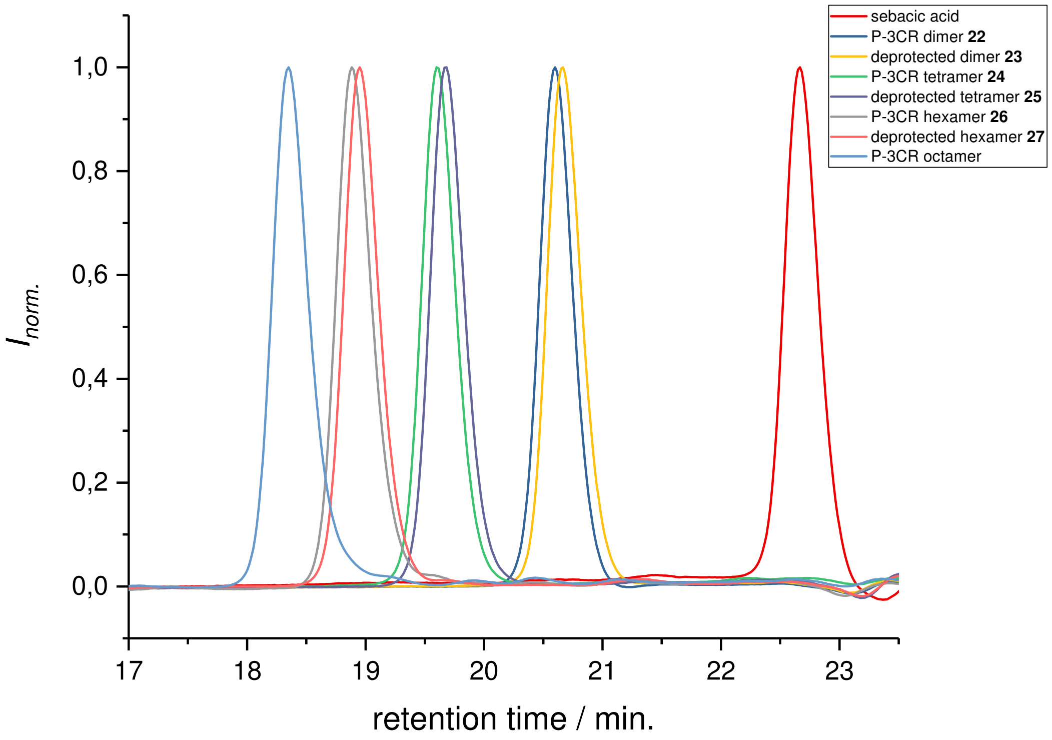
8.2 Linear oligomers with cyclohexyl side chains and C5 core unit



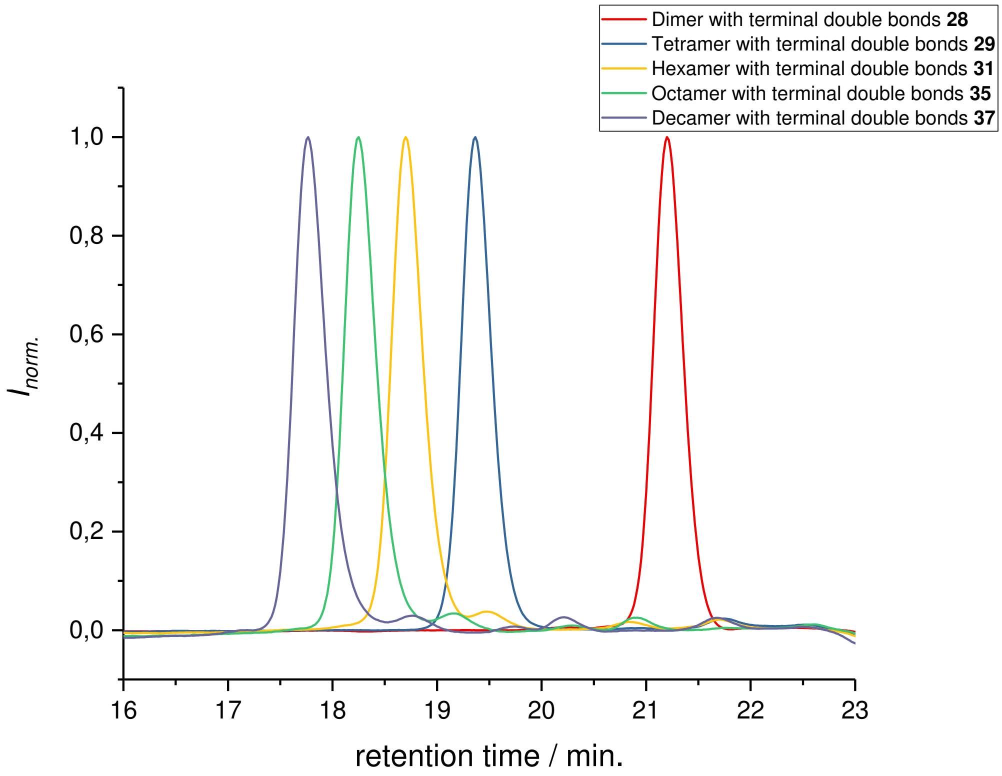
8.3 Linear oligomers with cyclohexyl side chains and C10 core unit



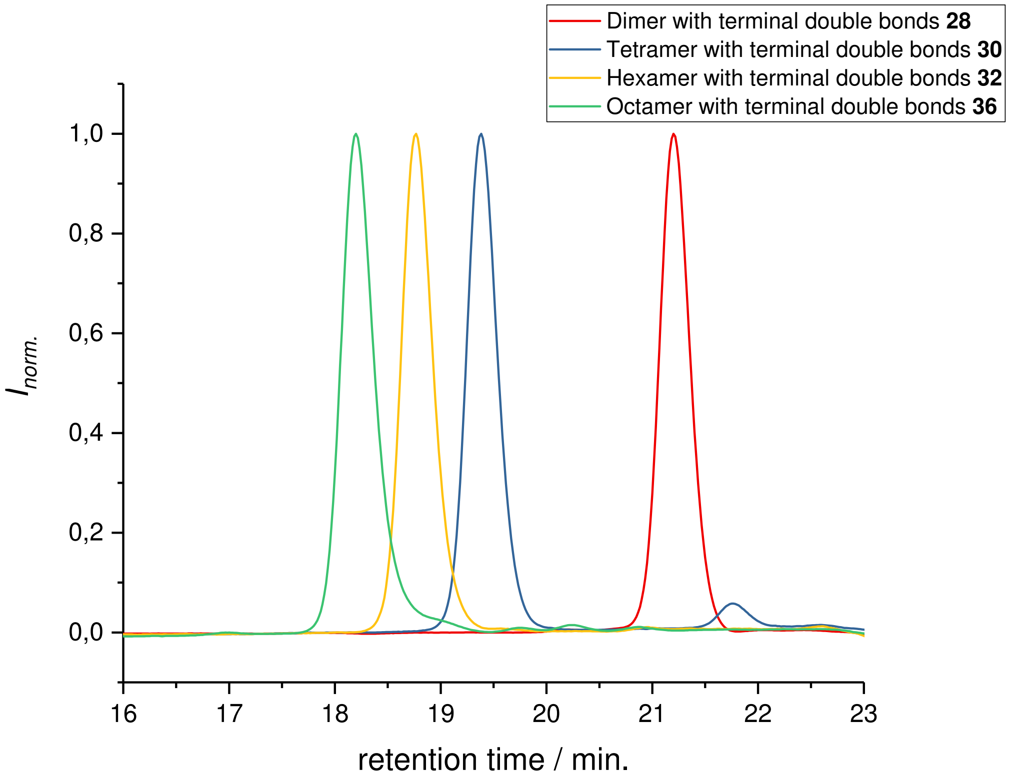
8.4 Linear oligomers with isopropyl side chains and C10 core unit



8.5 Linear oligomers with cyclohexyl side chains and terminal double bonds

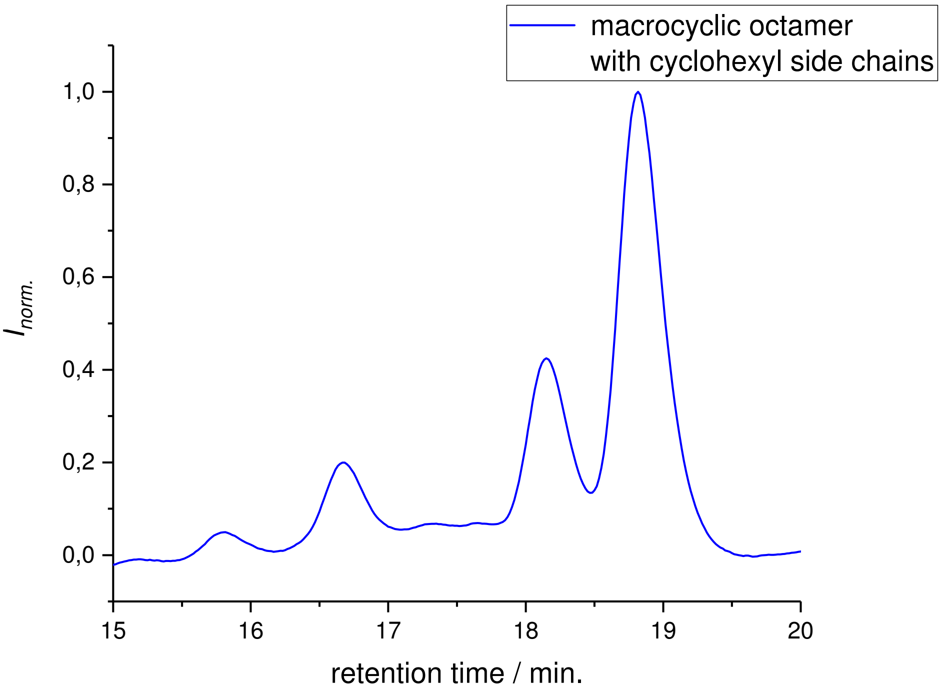


8.6 Linear oligomers with isopropyl side chains and terminal double bonds

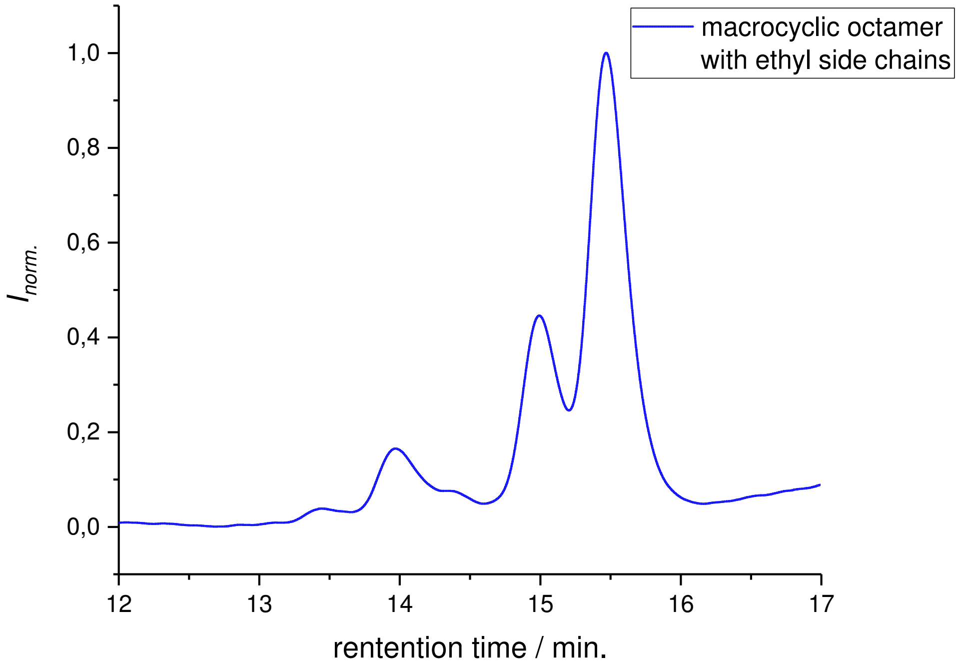


8.7 Comparison of the conversion of three macrocyclic octamers with different side chains

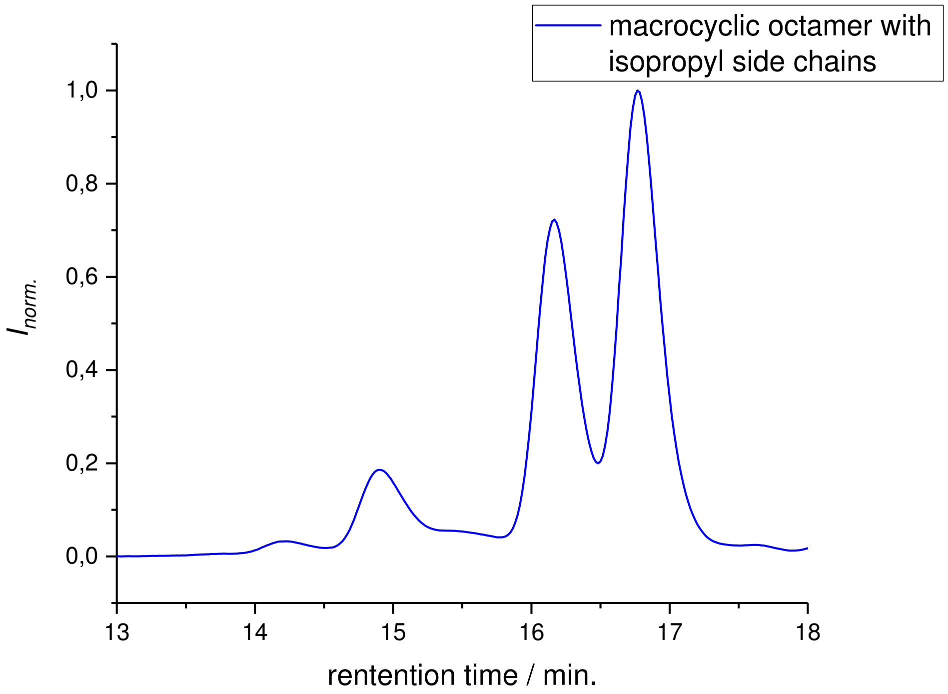
8.7.1 Cyclohexyl side chains (Substance 45)



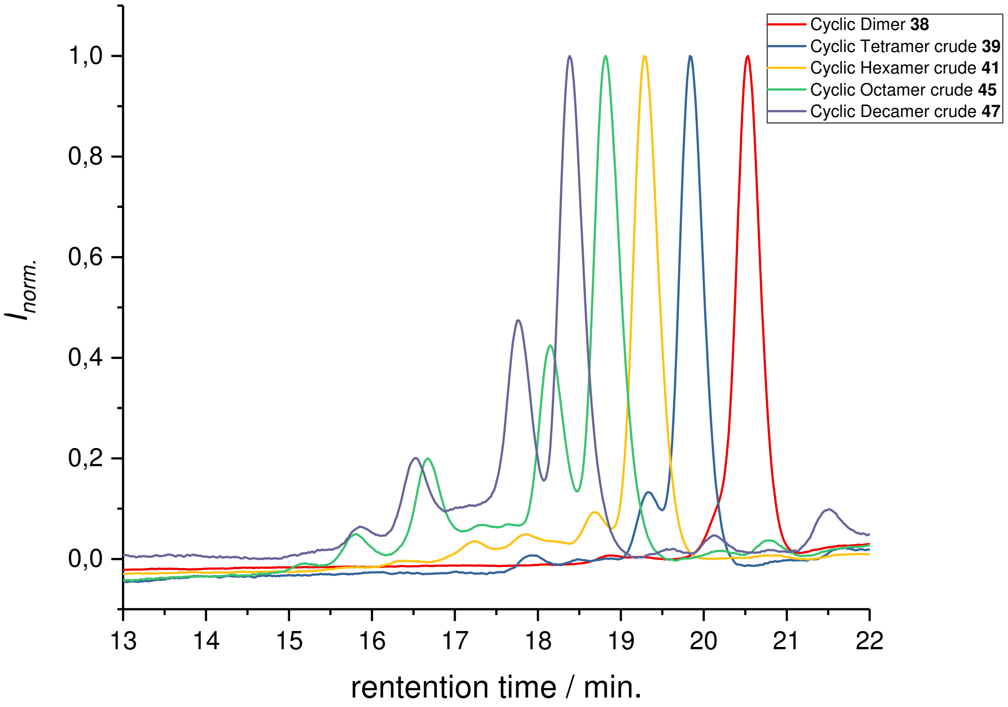
8.7.2 Ethyl side chains (Substance 43)



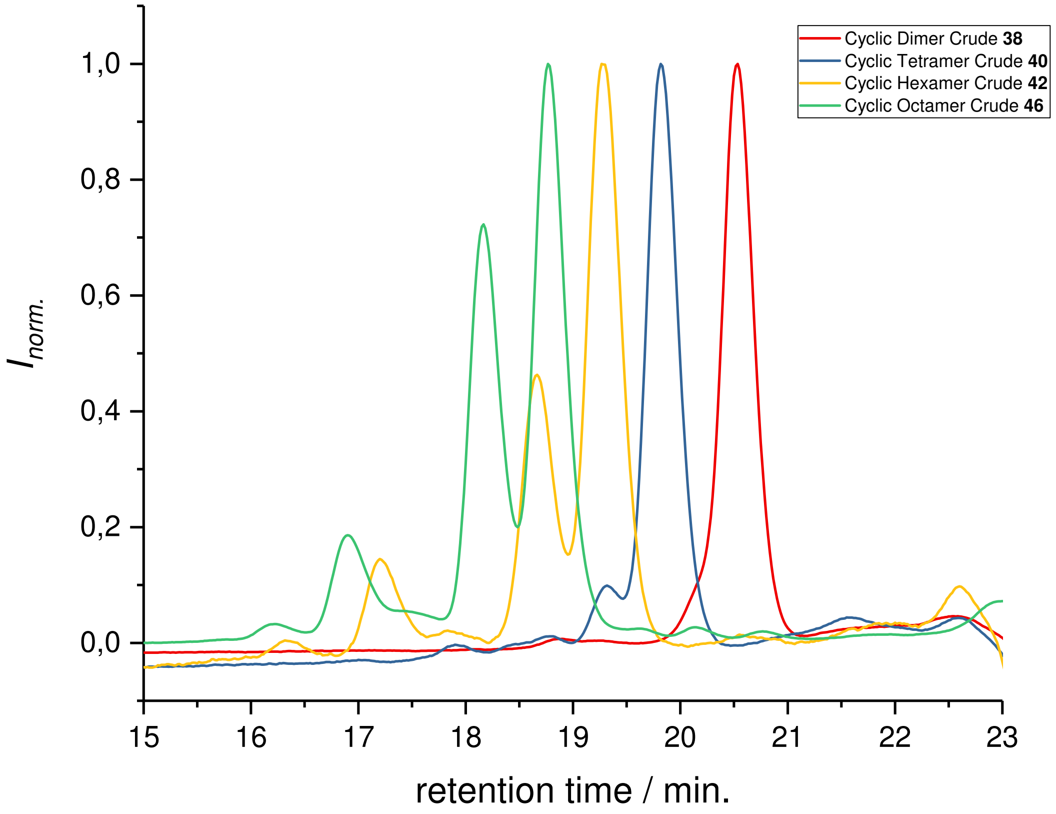
8.7.3 Isopropyl side chains (Substance 46)



8.8 Crude macrocycles of different size with cyclohexyl side chains



8.9 Crude macrocycles of different size with isopropyl side chains



9 References:

[1] S. C. Solleder, D. Zengel, K. S. Wetzel, M. A. R. Meier, *Angew. Chem. Int. Ed.* **2016**, *55*, 1204-1207.