Supporting information

Large aromatic amide helices via living polycondensation

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Materials and instrumentation

Materials

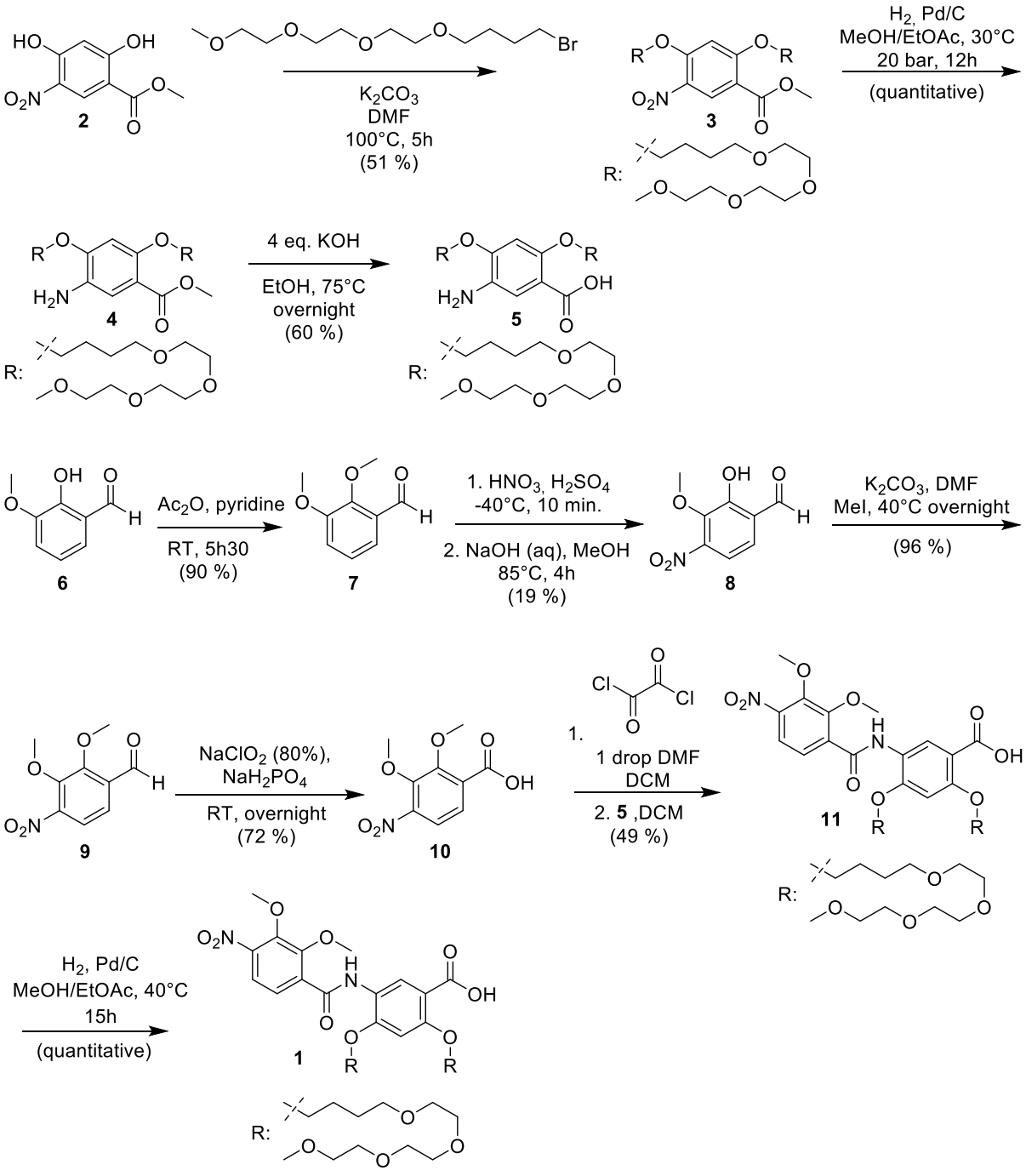
Aniline, anhydrous pyridine, anhydrous potassium carbonate, anhydrous tris(o-tolyl)phosphine and Pd on carbon (10 wt.% loading) were purchased from Sigma Aldrich and used without further purification. Dry dichloromethane, dry N,N-dimethylformamide (DMF), N, N-dimethylacetamide (DMAc) and 1M iodine monochloride solution in dichloromethane were purchased from Acros Organics and used without further purification. Rest of the reagents and solvents were purchased from Sigma-Aldrich or Acros Organics and used without further purification. Methyl 2,4-dihydroxy-5-nitrobenzoate and 15-bromo-2,5,8,11-tetraoxapentadecane were synthesized according to our previous report.[1] Deuterated solvents ($CDCl_3$ and CD_2Cl_2) were purchased from Cambridge Isotope Laboratories, Inc. Polymerization was performed in flame-dried glassware under argon atmosphere.

Instrumentation

All ^{1}H NMR, ^{13}C NMR, and ^{31}P NMR spectra were recorded on either a Bruker Avance III 300 MHz or a Bruker Avance III 400 MHz FT NMR spectrometer. Chemical shifts were given in ppm relative to the residual solvent peak ($CDCl_3$: 7.27 for ^{1}H NMR; $CDCl_3$: 77.16 for ^{13}C NMR). HR-MS (ESI+) mass spectra were measured on a Bruker FTMS 4.7T BioAPEX II and a Dionex Ultimate 3000 UHPLC system (ThermoFischer Scientifics, Germering, Germany) connected to a QExactive MS with a heated ESI source (ThermoFisher Scientific, Bremen, Germany); onflow injection of 1 μL sample (c = ca. 50 μg mL−1 in the indicated solvent) with an XRS auto-sampler (CTC, Zwingen, Switzerland); flow rate 120 μL min−1; ESI: spray voltage 3.0 kV, capillary temperature 280 °C, sheath gas 30 L min−1, aux gas 8 L min−1, s-lens RF level 55.0, aux gas temperature 250 °C (N2); full scan MS in the alternating (+)/(−)-ESI mode; mass ranges 80–1’200 m/z, 133–2’000 m/z, or 200–3’000 m/z at 70’000 resolution (full width half-maximum); automatic gain control (AGC) target of 3.00·106; maximum allowed ion transfer time (IT) 30 ms; mass calibration to <2 ppm accuracy with Pierce® ESI calibration solns. Relative molecular weights and molecular weight distributions were measured by gel permeation chromatography (SEC) with DMF as eluent. The DMF SEC system is an automated Agilent 1260 Infinity II HPLC system equipped with one Agilent PolarGel M guard column (particle size = 8 μm) and two Agilent PolarGel M columns (ID = 7.5 mm, L = 300 mm, particle size = 8 μm). Signals were recorded by an interferometric refractometer (Agilent 1260 series). Samples were measured using DMF + 0.05M LiBr as the eluent at 60 °C and a flow rate of 1.0 mL/min. The DMF SEC systems were calibrated with weight poly(styrene) standards in a range from $10^3$to 3×10^6 Da. All polymer samples were filtered through a PTFE syringe membrane filter (0.45 μm pore size, VWR) prior to SEC measurements. Slow additions of the monomers into the reaction mixtures were conducted using a syringe pump (World Precision Instruments, SP100iZ) equipped with a BD syringe and a needle measuring 0.8 mm in diameter. The polymers were purified by JAI LC-9130 recycling GPC with $CHCl_3$ as the eluent. The system consisted of two linear Jaigel-2H and Jaigel-1H columns. Signal detection was performed with a UV 600 Next detector. Preparative high-performance liquid chromatography (HPLC) of Jasco (pump -PU-2087 Plus, UV/VIS detector-UV-2075 Plus) was used to purify the macrocycles with methanol and DCM as eluent with a flow rate of 20 mL/min using preparative columns (250× 20 mm) Lichrosphere100 Si 10 μm.

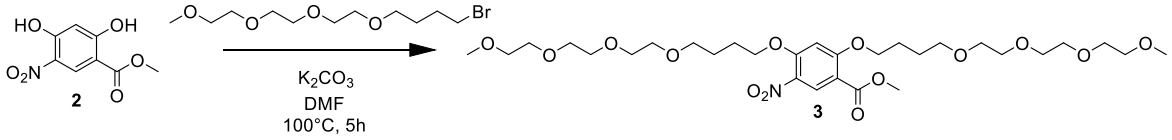
Supplemental experimental procedures

Synthesis of monomers



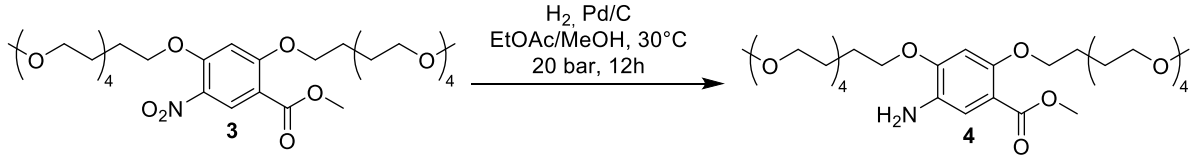
*Scheme S1. Synthesis plan of 2,4-bis((2,5,8,11-tetraoxapentadecan-15-yl)oxy)-5-(4-amino-2,3-dimethoxybenzamido)benzoic acid **1**.*

Synthesis of methyl 2,4-bis((2,5,8,11-tetraoxapentadecan-15-yl)oxy)-5-nitrobenzoate **3**



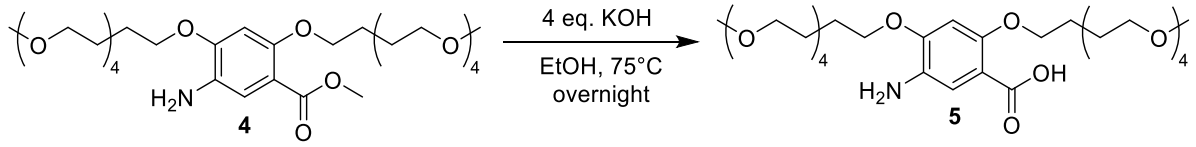
Methyl 2,4-dihydroxy-5-nitrobenzoate **2** (5.00 g, 1 Eq, 23.5 mmol), 15-bromo-2,5,8,11-tetraoxapentadecane (18.2 g, 2.6 Eq, 61.0 mmol) and potassium carbonate (19.5 g, 6 Eq, 141 mmol) were mixed in dry DMF (70 mL) and heated at 100 °C for 6 h. The excess potassium carbonate was filtrated and washed with DCM. The solvents were removed under reduced pressure. The crude residue was extracted 3x with DCM. The combined organic layers were washed with water and brine, dried over Mg_2SO_4 and concentrated. The crude product **3** was purified using reverse phase Isolera ($MeCN:H_2O$ gradient) and afforded a yellow oil (7.75 g, 51%). ^{1}H NMR (400 MHz, DICHLOROMETHANE-d_2) δ ppm 8.52 (s, 1 H), 6.53 (s, 1 H), 4.17 (dt, *J*=19.84, 6.28 Hz, 4 H), 3.84 (s, 3 H), 3.45 - 3.62 (m, 28 H), 3.27 - 3.41 (m, 6 H), 1.89 - 2.04 (m, 4 H), 1.74 - 1.89 (m, 4 H). ^{13}C NMR (101 MHz, DICHLOROMETHANE-d_2) δ ppm 164.69, 164.37, 158.15, 132.29, 131.50, 112.25, 98.73, 72.46, 71.13, 71.07, 70.94, 70.67, 70.45, 70.05, 59.15, 52.40, 26.61, 26.41, 26.36

Synthesis of methyl 2,4-bis((2,5,8,11-tetraoxapentadecan-15-yl)oxy)-5-aminobenzoate **4**



Methyl 2,4-bis((2,5,8,11-tetraoxapentadecan-15-yl)oxy)-5-nitrobenzoate **3** (1.00 g, 1 Eq, 1.54 mmol) was dissolved in a MeOH and ethyl acetate mixture (90:10). Pd/C (10 wt % loading) (0.1 g, 10 wt %) was added and the mixture was stirred and hydrogenated for 12h at 30°C under H_2 atmosphere (20 bar). The crude mixture was filtered through Celite®545 and the filtrate was concentrated under reduced pressure to afford the pure product **4** as a black oil (quantitative). ^{1}H NMR (400 MHz, DICHLOROMETHANE-d_2) δ ppm 7.16 (s, 1 H), 6.46 (s, 1 H), 4.05 (t, *J*=6.30 Hz, 2 H), 3.96 (t, *J*=6.17 Hz, 2 H), 3.75 - 3.81 (m, 3 H), 3.45 - 3.64 (m, 28 H), 3.33 (s, 6 H), 1.71 - 1.96 (m, 8 H). ^{13}C NMR (101 MHz, DICHLOROMETHANE-d_2) δ ppm 166.86, 153.63, 151.36, 130.72, 117.34, 112.88, 100.66, 72.47, 71.71, 71.42, 71.26, 71.11, 71.07, 71.01, 70.94, 70.75, 70.66, 68.90, 62.94, 59.15, 54.55, 54.27, 53.73, 53.46, 51.86, 30.66, 27.11, 26.90, 26.84, 26.58. ESI-HRMS m/z $(M+H)^+$: calculated 620.36, found 620.3622.

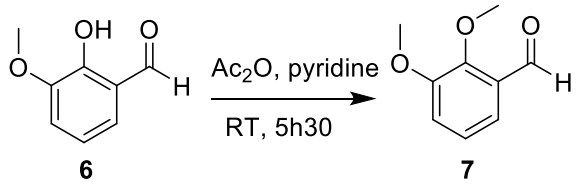
Synthesis of methyl 2,4-bis((2,5,8,11-tetraoxapentadecan-15-yl)oxy)-5-aminobenzoic acid **5**



Methyl 2,4-bis((2,5,8,11-tetraoxapentadecan-15-yl)oxy)-5-aminobenzoate **4** (3.7 g, 1 Eq, 6 mmol) and potassium hydroxide (1.3 g, 4 Eq, 23.84 mmol) were mixed in ethanol (60 mL), stirred and heated to reflux at 85°C overnight. The solvent was removed under reduced pressure and EtOAc was added. The product was extracted three times with water basified with KOH (pH = 9). The combined aqueous layers were acidified (pH = 5) with conc. HCl then extracted three times with DCM. The combined organic layers were dried over $MgSO_4$ and the solvent removed under reduced pressure. The crude product was purified by flash column chromatography using DCM:MeOH (97:3) as the eluent to afford the pure desired product **5** as a brown oil (2.16 g, 60%). ^{1}H NMR (400 MHz, CHLOROFORM-*d*) d ppm 7.48 (s, 1 H), 6.47 (s, 1 H), 4.20 (t, *J*=6.60 Hz, 2 H), 4.08 (t, *J*=6.30 Hz, 2 H), 3.50 - 3.74 (m, 30 H), 3.37 (d,

J=2.08 Hz, 6 H), 1.86 - 2.04 (m, 4 H), 1.70 - 1.86 (m, 4 H). ESI-HRMS m/z $(M+H)^+$: calculated 606.34, found 606.3473.

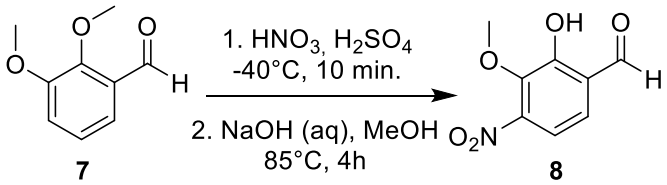
Synthesis of 2,3-dimethoxybenzaldehyde 7



6 **7**

In a flask of 100mL, 2-hydroxy-6-methoxybenzaldehyde **6** (19.6 g, 129.42 mmol) was dissolved in dry pyridine (20 mL). Acetic anhydride (15 mL, 158.96 mmol) was added to the mixture and the latter was stirred for 5h30. Then, a cold solution of 6M HCl was added to the mixture. The formed precipitate was filtered and washed with 1M HCl before being dried under reduced pressure. A white powder **7** (22 g, 115.82 mmol, 90%) was obtained. ^{1}H NMR (300 MHz, CHLOROFORM-*d*) δ ppm 10.14 (d, *J*=0.46 Hz, 1 H) 7.44 - 7.50 (m, 1 H) 7.31 -7.39 (m, 1 H) 7.20 - 7.25 (m, 1 H) 3.89 (s, 3 H) 2.41 (s, 3 H)

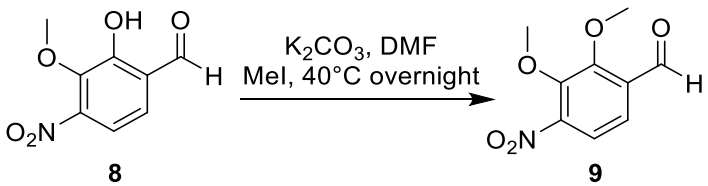
Synthesis of 2-hydroxy-3-methoxy-4-nitrobenzaldehyde 8



7 **8**

Aldehyde **7** (5.00 g, 23.08 mmol) was finely ground and added portion wise to a solution of fuming HNO_3 (15 mL) and concentrated H_2SO_4 (2 mL) at -40°C. Then, the solution was poured into ice cold water (240 mL) and extracted with DCM (4 x 100 mL). The combined organic layers were collected, washed with water (70 mL), saturated aqueous $NaHCO_3$ (70 mL), brine (70 mL) and finally dried over $MgSO_4$. After concentrating the solution, the residue was chromatographed with n-pentane:EtOAc (4:1). The residue was hydrolyzed with MeOH (50 mL) and NaOH 2M (20 mL, 1.75 g) under reflux for 4h and then concentrated. The residue was dissolved in DCM (12 mL) and HCl 1.5M (40 mL) and left stirring overnight. The organic layers were collected, washed with water (12 mL), dried over $MgSO_4$ and concentrated to afford compound **8** (843 mg, 4.27 mmol, 19%) as an orange solid. ^{1}H NMR (300 MHz, CHLOROFORM-*d*) δ ppm 12.60 (d, *J*=0.46 Hz, 1 H) 10.52 (s, 1 H) 7.77 (d, *J*=8.80 Hz, 1 H) 7.06 (d, *J*=8.90 Hz, 1 H) 4.03 (s, 3 H) 1.56 (s, 9 H)

Synthesis of 2,3-dimethoxy-4-nitrobenzaldehyde 9

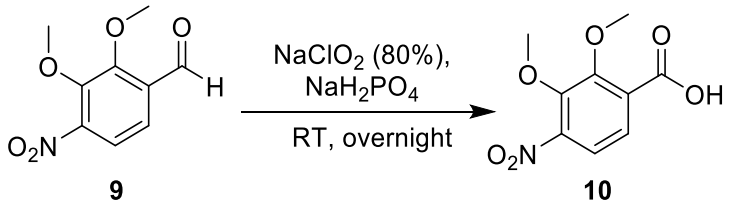


8 **9**

Aldehyde **8** (843 mg, 4.27 mmol, 1 eq) was mixed with DMF (20 mL), K_2CO_3 (1.1765 g, 2 eq) and MeI (0.8 mL, 12 eq), and stirred overnight at 40°C. Potassium carbonate was filtered, and the filtrate was concentrated under vacuum. The residue was extracted with 3 x 40 mL DCM and water. The combined organic layers were washed with water (30 mL) and then with brine (30 mL). **9** was obtained (0.863 g,

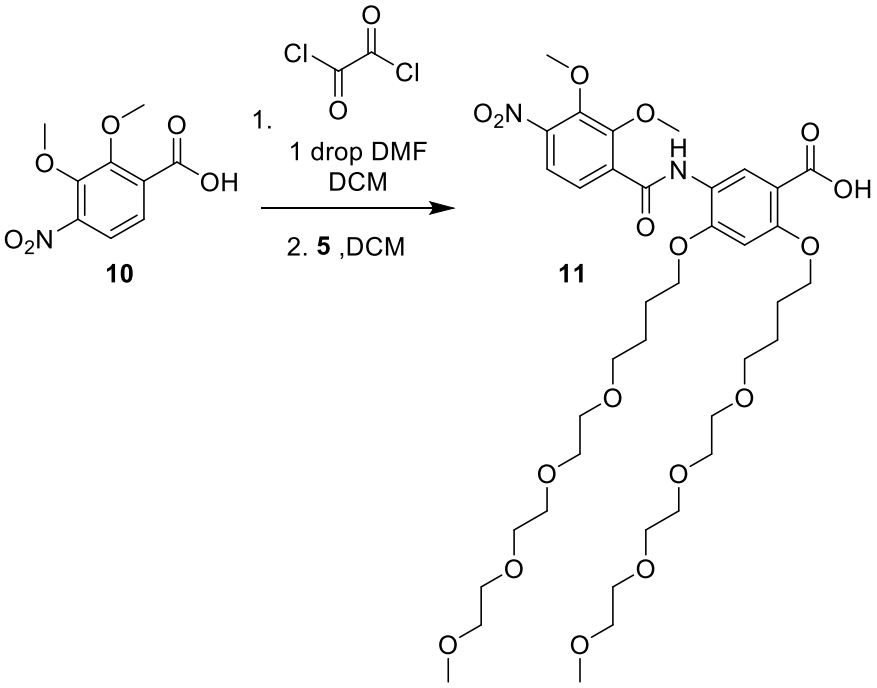
4.09 mmol, 96%) as a dark orange solid. ^{1}H NMR (300 MHz, CHLOROFORM-*d*) δ ppm 10.38 (s, 1 H) 7.99 (d, *J*=9.08 Hz, 1 H) 7.06 (d, *J*=9.08 Hz, 1 H) 4.01 (s, 3 H) 3.91 (s, 3 H)

Synthesis of 2,3-dimethoxy-4-nitrobenzoic acid **10**



To a stirred solution of **9** (0.863 g, 4.09 mmol) and 2-methyl-2-butene (1.2 mL) in ^{t}BuOH (6.2 mL), $NaClO_2$ 80% (0.229 g, 2.53 mmol) in 2.2 mL of 1M aq. NaH_2PO_4 (0.263 g, 2.19 mmol) was added dropwise. The mixture was stirred at room temperature overnight. Additional $NaClO_2$ (0.225 g, 2.48 mmol) in 2.2 mL 1M aq. NaH_2PO_4 (0.257 g, 2.14 mmol) were added to the mixture, which was stirred for 1h. The organic layer was washed with 1M HCl (20 mL), water (20 mL) and brine (20 mL). The organic layer was dried over $MgSO_4$ and concentrated in vacuo to afford compound **10** (0.666 g, 2.93 mmol, 72%) as a white powder. ^{1}H NMR (300 MHz, CHLOROFORM-*d*) δ ppm 8.06 (d, *J*=9.17 Hz, 1 H) 7.04 (d, *J*=9.17 Hz, 1 H) 4.02 (s, 3 H) 3.96 (s, 3 H)

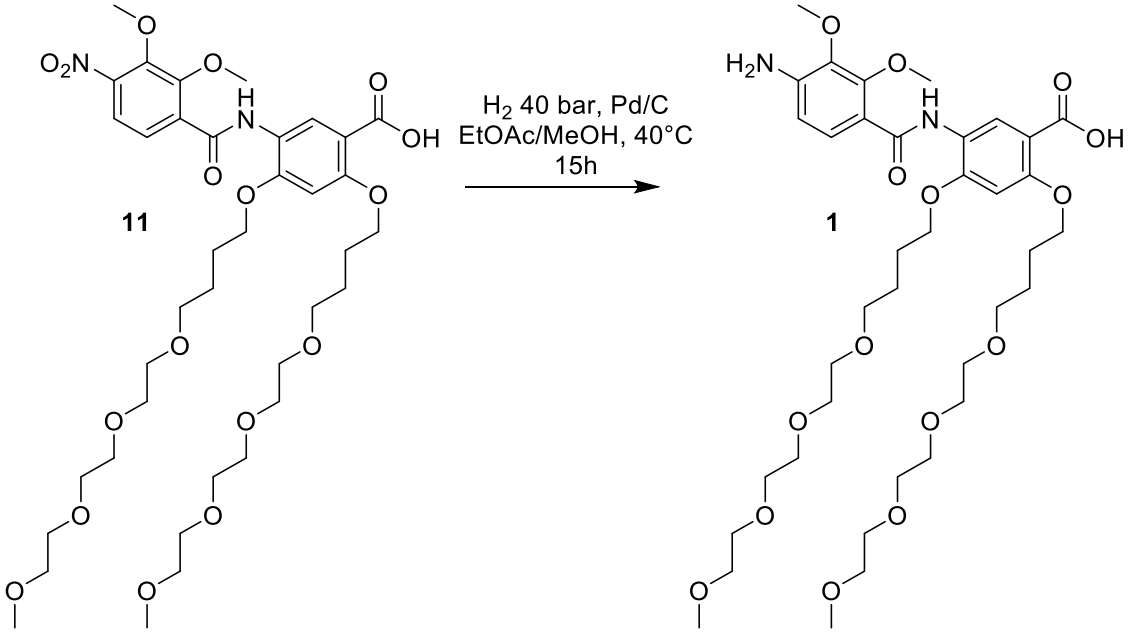
Synthesis of 2,4-bis((2,5,8,11-tetraoxapentadecan-15-yl)oxy)-5-(2,3-dimethoxy-4-nitrobenzamido)benzoic acid **11**



Oxalyl chloride (111.7 mg, 77.06 µL, 1 Eq, 880.4 µmol) and 2 drops of DMF are added to a solution of 2,3-dimethoxy-4-nitrobenzoic acid **10** (200.0 mg, 1 Eq, 880.4 µmol) in DCM (4 mL) under argon. The reaction mixture was stirred at room temperature for 3h. The solvent was removed in vacuo, then the crude product was redissolved in DCM (2 mL) and purged with argon. 2-((2,5,8,11-Tetraoxapentadecan-15-yl)oxy)-4-((2,5,8,11-tetraoxatetradecan-14-yl)oxy)-5-aminobenzoic acid **5** (494.9 mg, 0.95 Eq, 836.4 µmol) and triethylamine (89.09 mg, 123 µL, 1.0 Eq, 880.4 µmol) were dissolved in 2 mL of triethylamine and

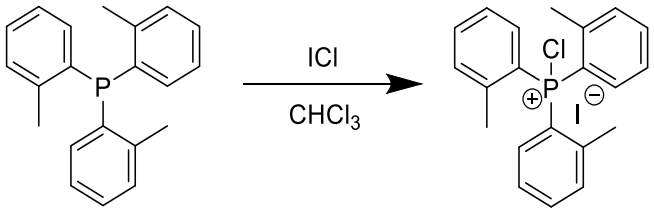
slowly added to the reaction mixture through a septum. After 15h, the reaction was quenched with $NaHCO_3$ (2 mL). The mixture was extracted with DCM (4 x 5 mL). The combined organic layers were concentrated, and the product was dissolved in EtOAc then added to the separation funnel. The organic mixture was extracted with a basic solution of KOH in water (pH = 12) (3 x 10 mL). The organic layer was removed, and the combined aqueous layers added back to the separation funnel. After acidifying the solution to pH = 1 with concentrated HCl, the aqueous phase was extracted with DCM (4 x 5 mL). The combined organic layers were dried over $MgSO_4$, and the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography using 4% MeOH in DCM as the eluent. The fractions containing the product were collected and concentrated. The nearly pure product was washed with hexane to remove grease impurities and then dried to obtain **11** as a yellow oil (0.345 g, 0.431 mmol, 49%). ^{1}H NMR (300 MHz, CHLOROFORM-*d*) d ppm 10.26 (s, 1 H), 9.21 (s, 1 H), 8.08 (d, *J*=8.80 Hz, 1 H), 7.61 (d, *J*=8.80 Hz, 1 H), 6.58 (s, 1 H), 4.24 (dt, *J*=17.79, 6.46 Hz, 4 H), 3.99 - 4.15 (m, 6 H), 3.47 - 3.70 (m, 28 H), 3.31 - 3.41 (m, 6 H), 1.93 - 2.11 (m, 4 H), 1.72 - 1.93 (m, 4 H). ^{13}C NMR (75 MHz, CHLOROFORM-*d*) d ppm 164.73, 160.23, 155.22, 153.13, 152.80, 146.89, 146.76, 130.90, 126.47, 125.18, 122.21, 119.64, 110.21, 96.60, 71.88, 70.57, 70.52, 70.47, 70.45, 70.35, 70.25, 70.12, 69.11, 62.37, 62.23 , 58.96, 26.15, 26.03, 25.93. ESI-HRMS m/z $(M-H)^-$: calculated 813.37, found 813.37.

Synthesis of 2,4-bis((2,5,8,11-tetraoxapentadecan-15-yl)oxy)-5-(4-amino-2,3-dimethoxybenzamido)benzoic acid **1**



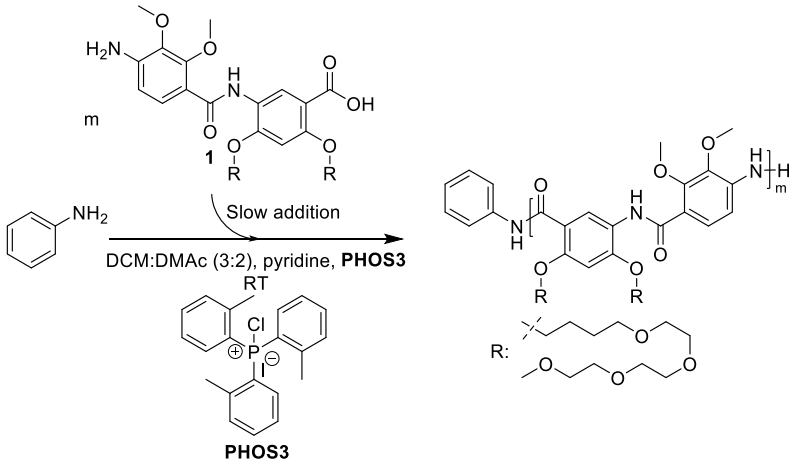
Nitroacid **11** (0.345 g, 1eq., 0.431 mmol) was dissolved in a mixture of EtOAc:MeOH (1:9) and Pd/C (10 wt % loading) (0.04 g, 10 wt %) was added. The mixture was stirred and hydrogenated for 15h at 40°C under H_2 atmosphere (40 bar). The crude mixture was filtered through Celite®545 and the filtrate was concentrated under reduced pressure to afford pure product **1** as a yellow oil (quantitative). ^{1}H NMR (300 MHz, CHLOROFORM-*d*) d ppm 10.24 (s, 1 H), 9.17 (s, 1 H), 7.77 (d, *J*=8.71 Hz, 1 H), 6.59 (d, *J*=8.71 Hz, 1 H), 6.48 (s, 1 H), 4.06 - 4.24 (m, 4 H), 3.96 (s, 3 H), 3.77 - 3.88 (m, 3 H), 3.43 - 3.70 (m, 28 H), 3.25 - 3.39 (m, 6 H), 1.86 - 2.04 (m, 4 H), 1.63 - 1.86 (m, 4 H). ^{13}C NMR (75 MHz, CHLOROFORM-*d*) d ppm 164.95 (s), 162.68 (s), 154.23 (s), 152.76 (s), 152.05 (s), 145.09 (s), 138.47 (s), 127.32 (s), 124.18 (s), 123.17 (s), 115.20 (s), 110.66 (s), 109.53 (s), 96.34 (s), 71.70 (s), 70.48 (s), 70.38 (s), 70.35 (s), 70.28 (s), 70.27 (s), 70.21 (s), 69.98 (s), 69.92 (s), 68.78 (s), 61.29 (s), 59.67 (s), 58.79 (s), 25.91 (s), 25.83 (s), 25.79 (s), 25.74 (s). ESI-HRMS m/z $(M-H)^-$: calculated 783.40, found 783.39.

Synthesis of reagent chlorotri-o-tolylphosphonium iodide PHOS3



A 50 mL Schlenk flask containing a magnetic stirrer is backfilled with argon 3x. A solution of iodine chloride (1.6 g, 9.9 mL, 1 molar, 1 Eq, 9.9 mmol) in chloroform and 10 mL of dry chloroform are added to the flask. Tri-o-tolylphosphane (3.0 g, 1 Eq, 9.9 mmol) is dissolved in 10 mL of dry chloroform and added slowly (4 mL/h) to the flask with a syringe pump. The solvent is evaporated through the Schlenk line into trappers cooled with liquid nitrogen. Dry pentane (20 mL) is added to the flask to wash the reagent then removed through the Schlenk line. The content of the flask is kept under inert atmosphere. ^{31}P NMR (400 MHz, CHLOROFORM-d) δ ppm 63.73.

Synthesis of polymers and macrocycles



Scheme S2. General polymerization strategy.

Synthesis of 10-mer giant helix (P1)

Chlorotri-o-tolylphosphonium iodide **PHOS3** (176 mg, 25 Eq, 376 µmol) was introduced into a Schlenk flask under inert atmosphere and dissolved in 1.15 mL of dry DCM and dry DMAc (3:2) mixture. Dry pyridine (182 µL, 150 Eq, 2.25 mmol) and aniline (1.40 mg, 1 Eq, 15 µmol) in 0.1 mL of dry DCM were added to the solution under stirring. In another Schlenk flask, **1** (118 mg, 10 Eq, 150 µmol) was evacuated and backfilled with argon three times. A solution (0.28 M) of **1** in dry DCM and dry DMAc (3:2) mixture was added dropwise to the reaction mixture at RT using a syringe pump (0.08 mL/h). The reaction was quenched with a 1 N HCl solution and extracted with DCM three times. The combined organic layers were dried over $MgSO_4$ and concentrated under reduced pressure. The crude polymer was purified by recycling gel permeation chromatography (chloroform) to afford purified polymer **P1**.

Synthesis of 20-mer giant helix (P2)

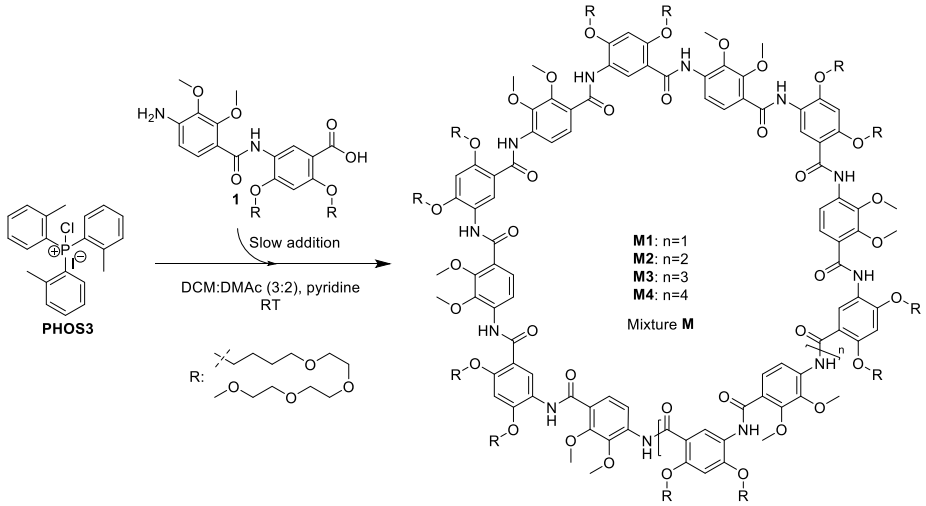
Chlorotri-o-tolylphosphonium iodide **PHOS3** (250 mg, 50 Eq, 537 µmol) was introduced into a Schlenk flask under inert atmosphere and dissolved in 1.63 mL of dry DCM and dry DMAc (3:2) mixture. Dry pyridine (259 µL, 300 Eq, 3.22 mmol) and aniline (1.00 mg, 1 Eq, 10.7 µmol) in 0.1 mL of dry DCM were added to the solution under stirring. In another Schlenk flask, **1** (169 mg, 20 Eq, 215 µmol) was

evacuated and backfilled with argon three times. A solution (0.28 M) of **1** in dry DCM and dry DMAc (3:2) mixture was added dropwise to the reaction mixture at RT using a syringe pump (0.08 mL/h). The reaction was quenched with a 1 N HCl solution and extracted with DCM three times. The combined organic layers were dried over $MgSO_4$ and concentrated under reduced pressure. The crude polymer was purified by recycling gel permeation chromatography (chloroform) to afford purified polymer **P2**.

Attempt at the synthesis of 40-mer giant helix (P3)/Synthesis of 7-mer macrocycle

Chlorotri-o-tolylphosphonium iodide **PHOS3** (276 mg, 100 Eq, 591 µmol) was introduced into a Schlenk flask under inert atmosphere and dissolved in 1.63 mL of dry DCM and dry DMAc (3:2) mixture. Dry pyridine (285 µL, 600 Eq, 3.54 mmol) and aniline (0.55 mg, 1 Eq, 5.91 µmol) in 0.1 mL of dry DCM were added to the solution under stirring. In another Schlenk flask, **1** (185 mg, 40 Eq, 236 µmol) was evacuated and backfilled with argon three times. A solution (0.28 M) of **1** in dry DCM and dry DMAc (3:2) mixture was added dropwise to the reaction mixture at RT using a syringe pump (0.08 mL/h). The reaction was quenched with a 1 N HCl solution and extracted with DCM three times. The combined organic layers were dried over $MgSO_4$ and concentrated under reduced pressure. The crude polymer mixture was purified by recycling gel permeation chromatography (chloroform) to separate purified polymer **P3** and a mixture of macrocycles. The mixture of macrocycles was purified by semi-preparative HPLC (MeOH:DCM gradient) to afford 16 mg of purified 7-mer macrocycle **M2**. ^{1}H NMR (500 MHz, CHLOROFORM-*d*) d ppm 10.26 (br. s., 7 H), 10.09 (br. s., 7 H), 9.40 (s, 7 H), 8.64 (d, *J*=8.85 Hz, 7 H), 8.12 (d, *J*=8.70 Hz, 7 H), 6.58 (br. s., 7 H), 4.30 (br. s., 14 H), 4.20 (br. s., 14 H), 4.06 (s, 18 H), 3.96 (s, 18 H), 3.48 - 3.72 (m, 196 H), 3.37 (d, *J*=2.75 Hz, 42 H), 1.97 - 2.16 (m, 28 H), 1.80 - 1.97 (m, 28 H). ^{13}C NMR (126 MHz, CHLOROFORM-*d*) d ppm 163.21 (s), 162.32 (s), 153.54 (s), 152.25 (s), 150.73 (s), 141.23 (s), 137.11 (s), 127.98 (s), 125.77 (s), 122.54 (s), 120.93 (s), 114.59 (s), 96.64 (s), 71.89 (s), 70.64 (s), 70.59 (s), 70.56 (s), 70.51 (s), 70.49 (s), 70.18 (s), 70.10 (s), 69.90 (s), 68.65 (s), 61.59 (s), 60.75 (s), 59.00 (s), 26.14 (s), 26.00 (s), 25.97 (s). MALDI-ToF MS m/z [M+Na$^+$]: calculated 5387.71, found 5386.97.

Synthesis of macrocycles M1-M4



Chlorotri-o-tolylphosphonium iodide **PHOS3** (89 mg, 3 Eq, 0.19 mmol) was introduced into a Schlenk flask under inert atmosphere and dissolved in 0.59 mL of dry DCM and dry DMAc (3:2) mixture. Dry pyridine (41 µL, 8 Eq, 3.22 mmol) was added to the solution under stirring. In another Schlenk flask, dimer **1** (50 mg, 1 Eq, 64 µmol) was evacuated and backfilled with argon three times. A solution (0.15 M) of **1** in dry DCM and dry DMAc (3:2) mixture was added dropwise to the reaction mixture at RT using a syringe pump (0.08 mL/h). Isotopically resolved MALDI-ToF mass spectrum of the crude solution revealed the presence of macrocycles **M1**, **M2**, **M3**, and **M4**.

Synthesis of reagent PHOS3

Chlorotri-o-tolylphosphonium iodide **PHOS3** (89 mg, 3 Eq, 0.19 mmol) was introduced into a Schlenk flask under inert atmosphere and dissolved in 5.45 mL of dry DCM and dry DMAc (3:2) mixture. Dry pyridine (41 µL, 8 Eq, 0.51 mmol) was added to the solution under stirring. In another Schlenk flask, **1** (50 mg, 1 Eq, 64 µmol) was evacuated and backfilled with argon three times. A solution (0.15 M) of **1** in dry DCM and dry DMAc (3:2) mixture was added dropwise to the reaction mixture at RT using a syringe pump (0.08 mL/h). The reaction was quenched with a 1 N HCl solution and extracted with DCM three times.

SEC (DMF) elugram

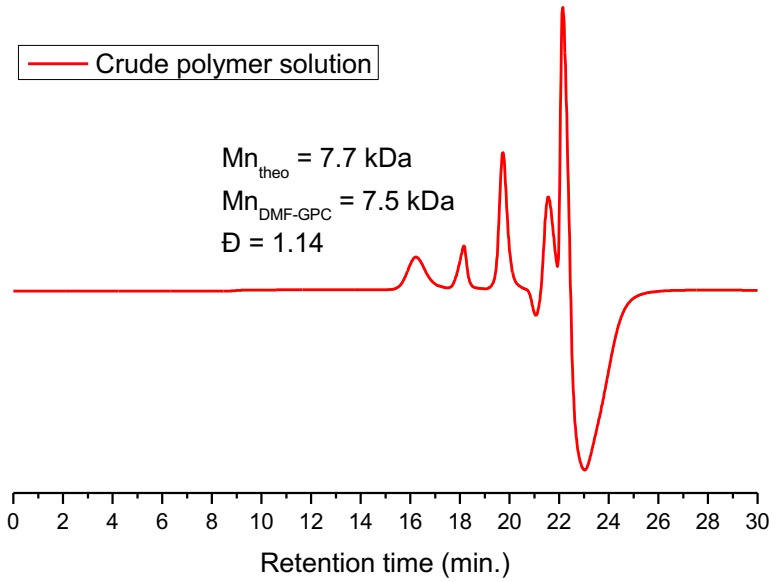


***Figure S1**. GPC (DMF) trace of crude polymer **P1**.*

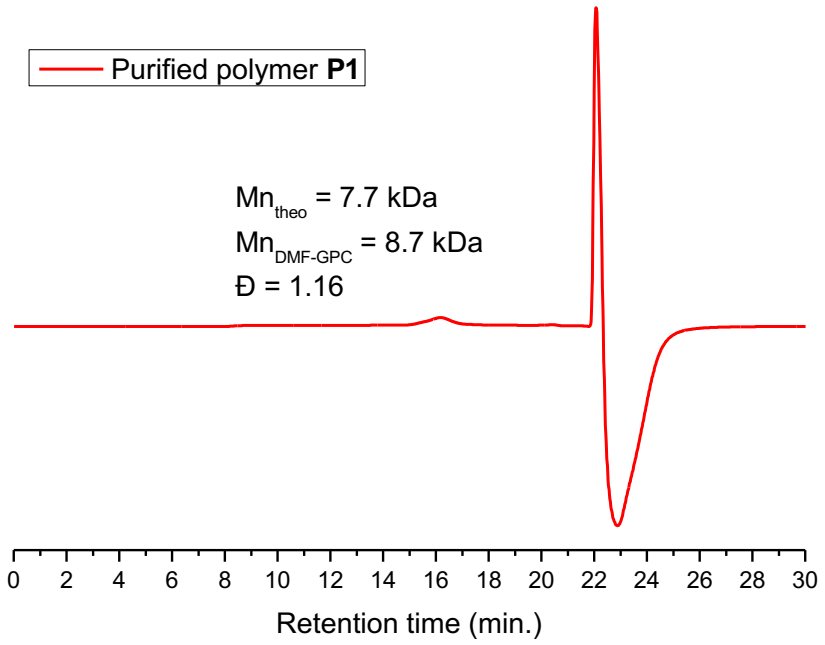


***Figure S2**. GPC (DMF) trace of purified polymer **P1**.*

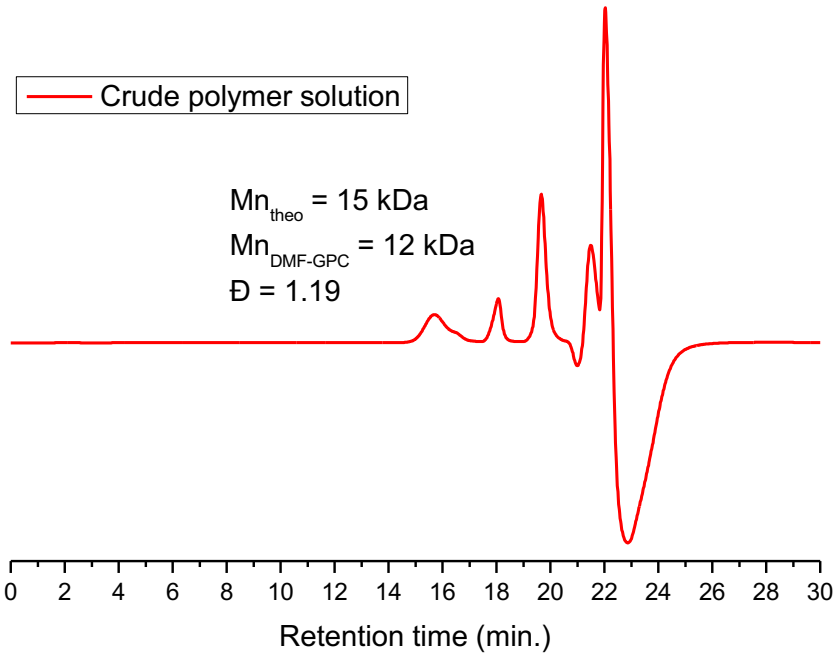


***Figure S3**. GPC (DMF) trace of crude polymer **P2**.*

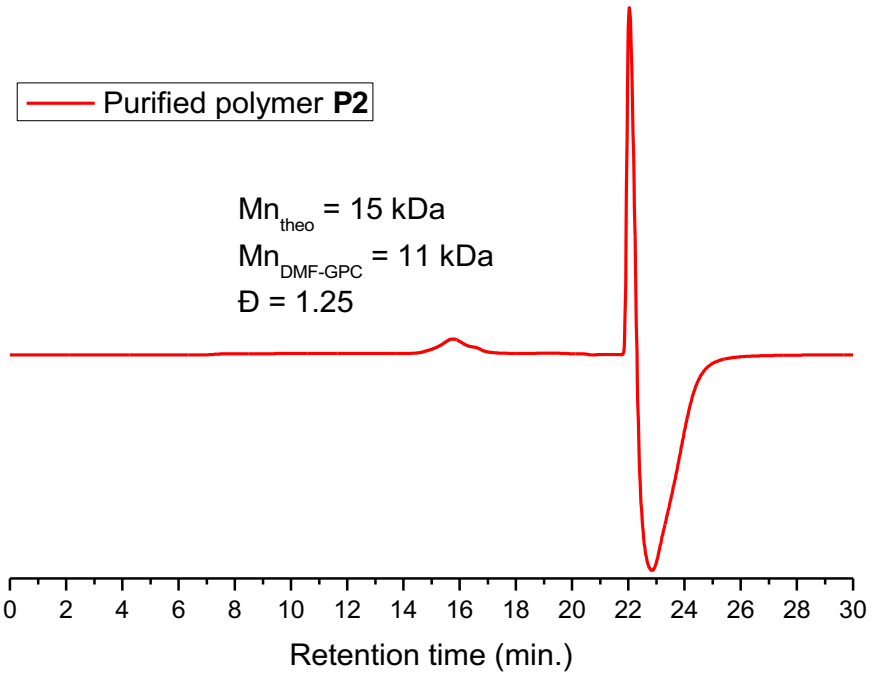


***Figure S4**. GPC (DMF) trace of purified polymer **P2**.*

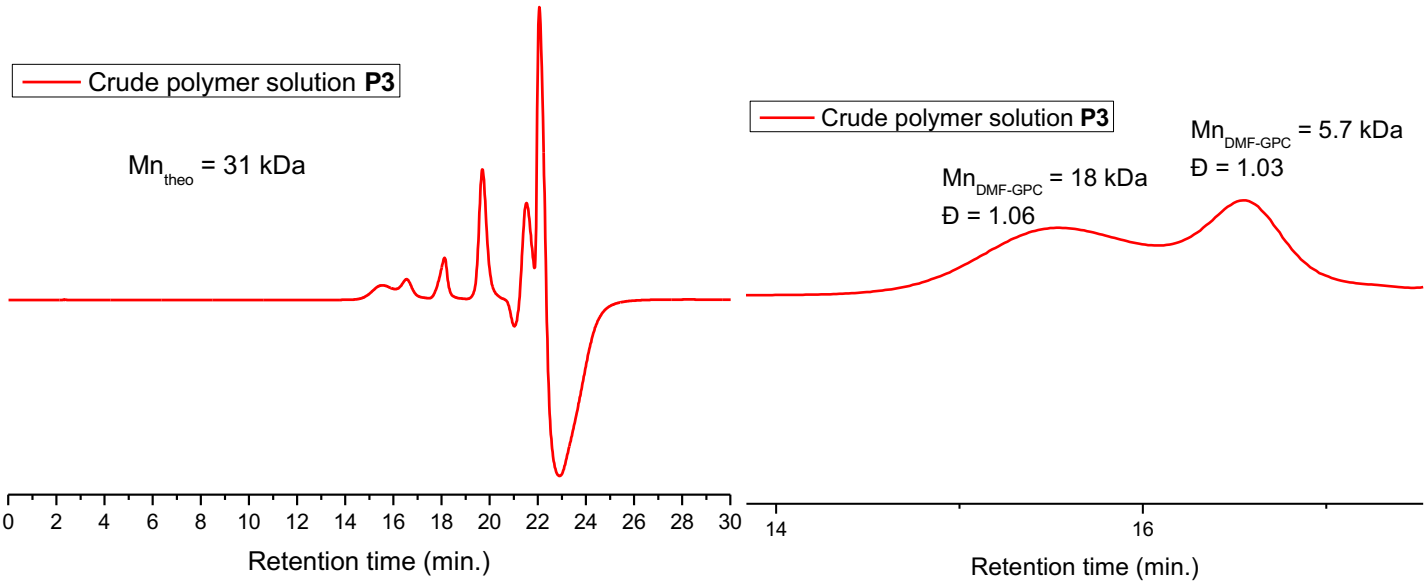


***Figure S5**. GPC (DMF) trace of crude polymer **P3** (left) and zoom on the GPC (DMF) trace of crude polymer **P3** (right).*

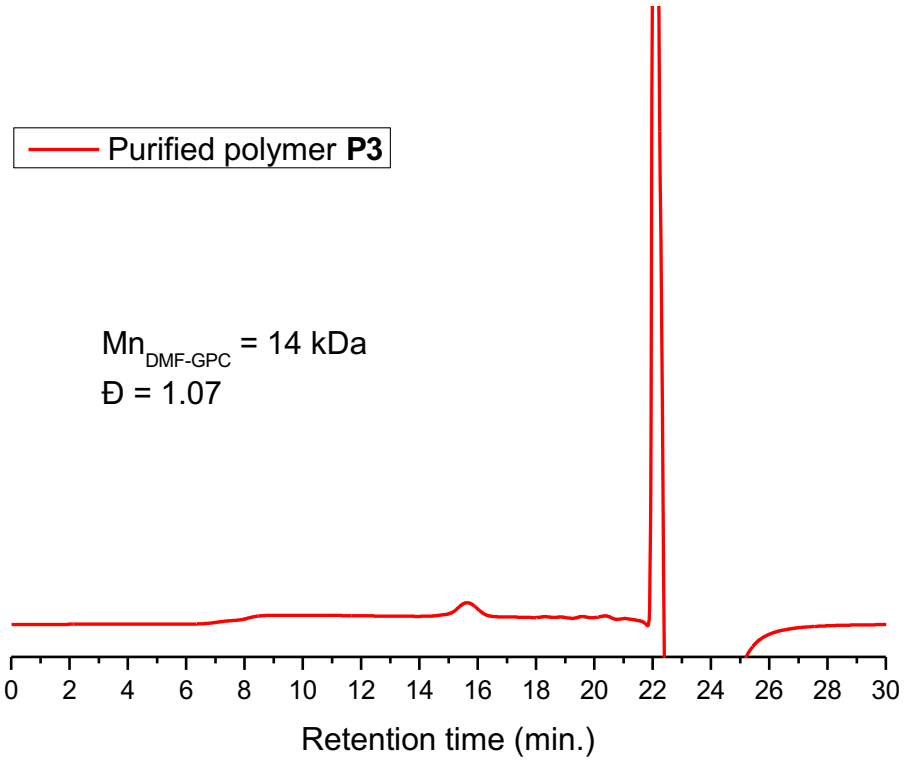


***Figure S6**. GPC (DMF) trace of purified polymer **P3**.*

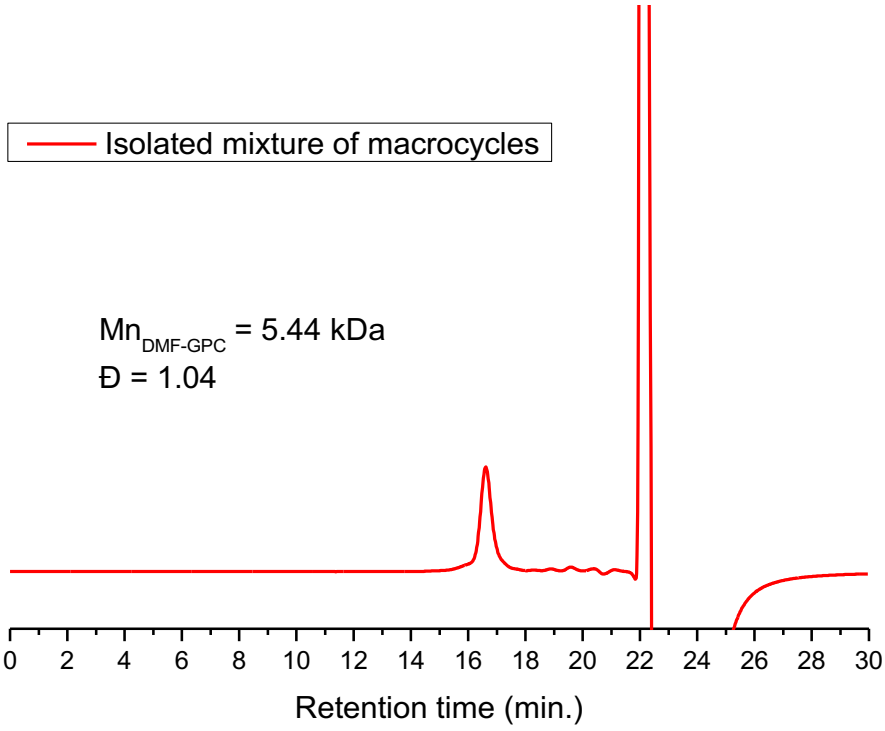


***Figure S7**. GPC (DMF) trace of isolated mixture of macrocycles.*

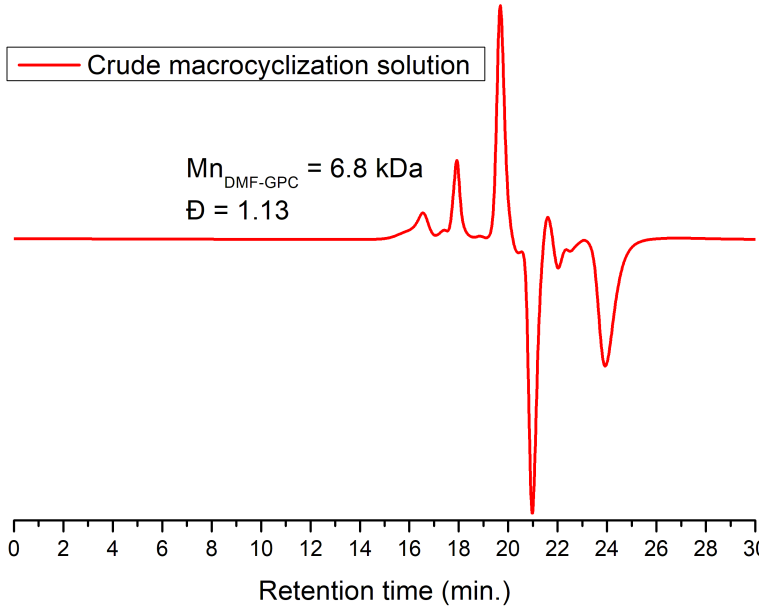


***Figure S8**. GPC (DMF) trace of crude macrocycles mixture of **M1**, **M2**, **M3**, and **M4**.*

NMR spectra

NMR spectra of monomers

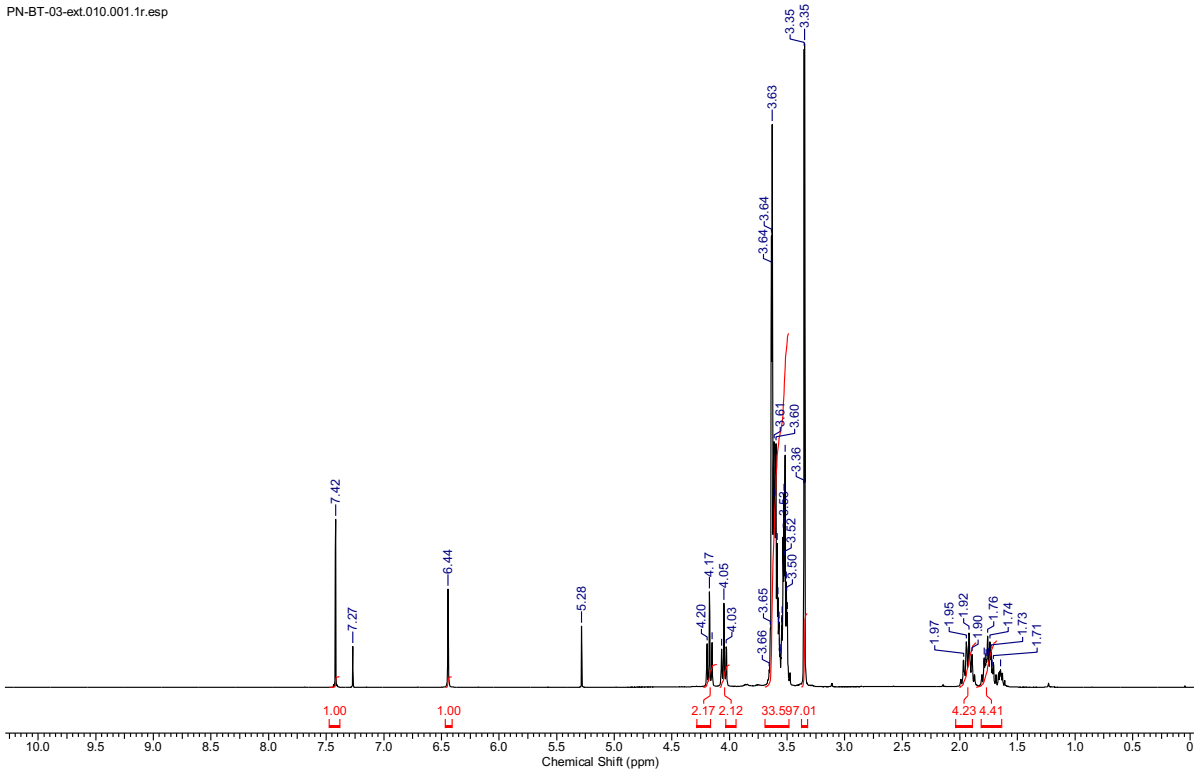


***Figure S9**. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of monomer **5**.*

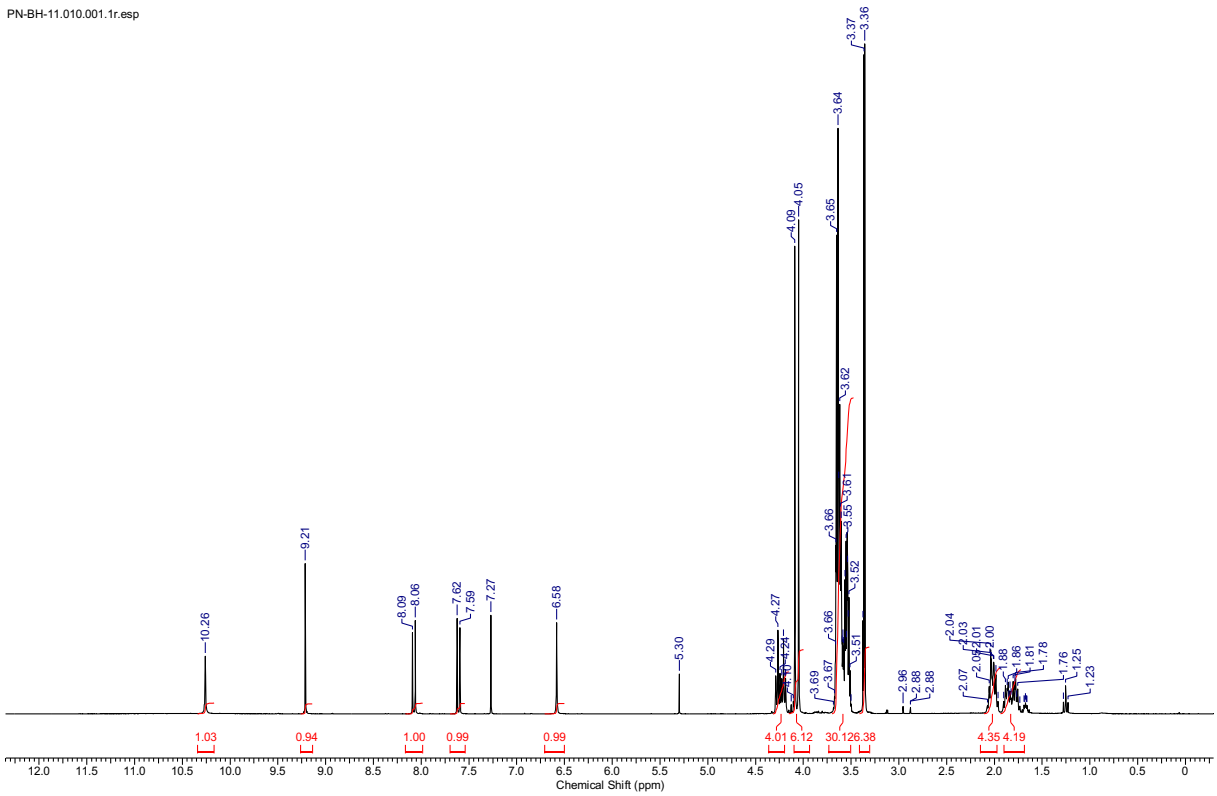


Figure S10. *^{1}H NMR spectrum (300 MHz, $CDCl_3$) of* ***11****.*

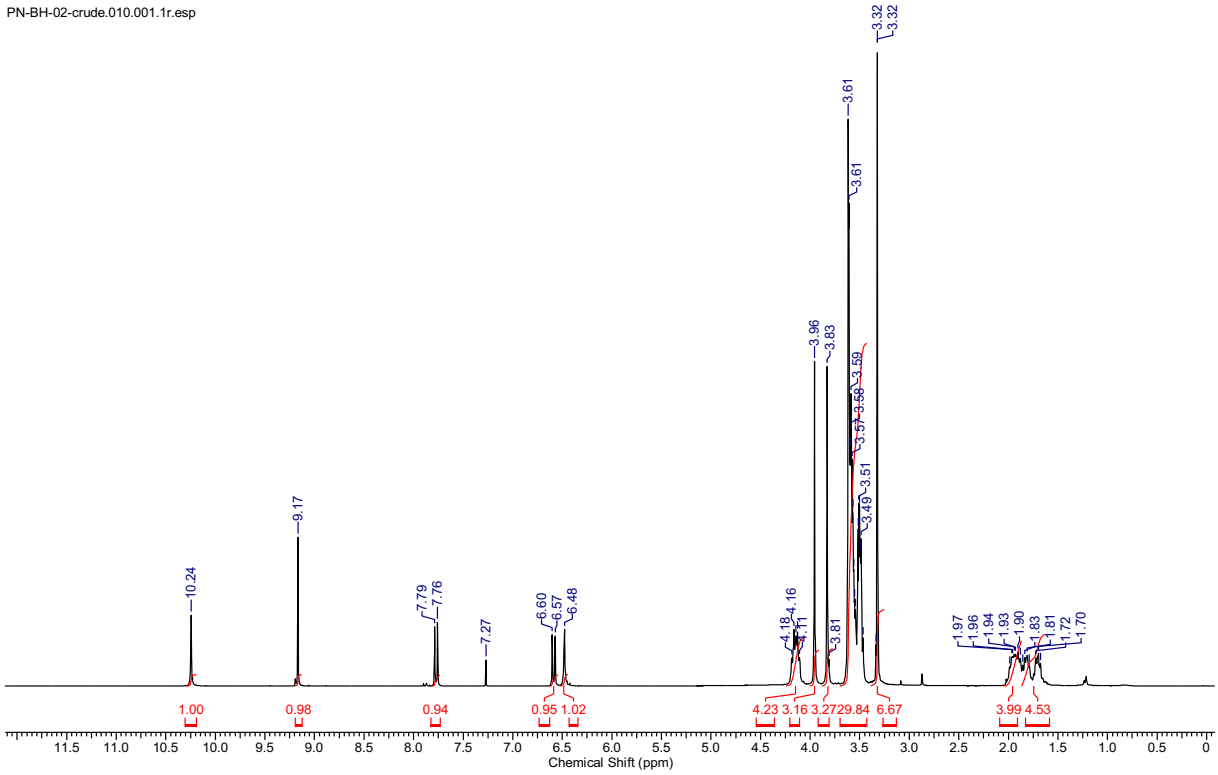


Figure S11. *^{1}H NMR spectrum (300 MHz, $CDCl_3$) of* ***1****.*

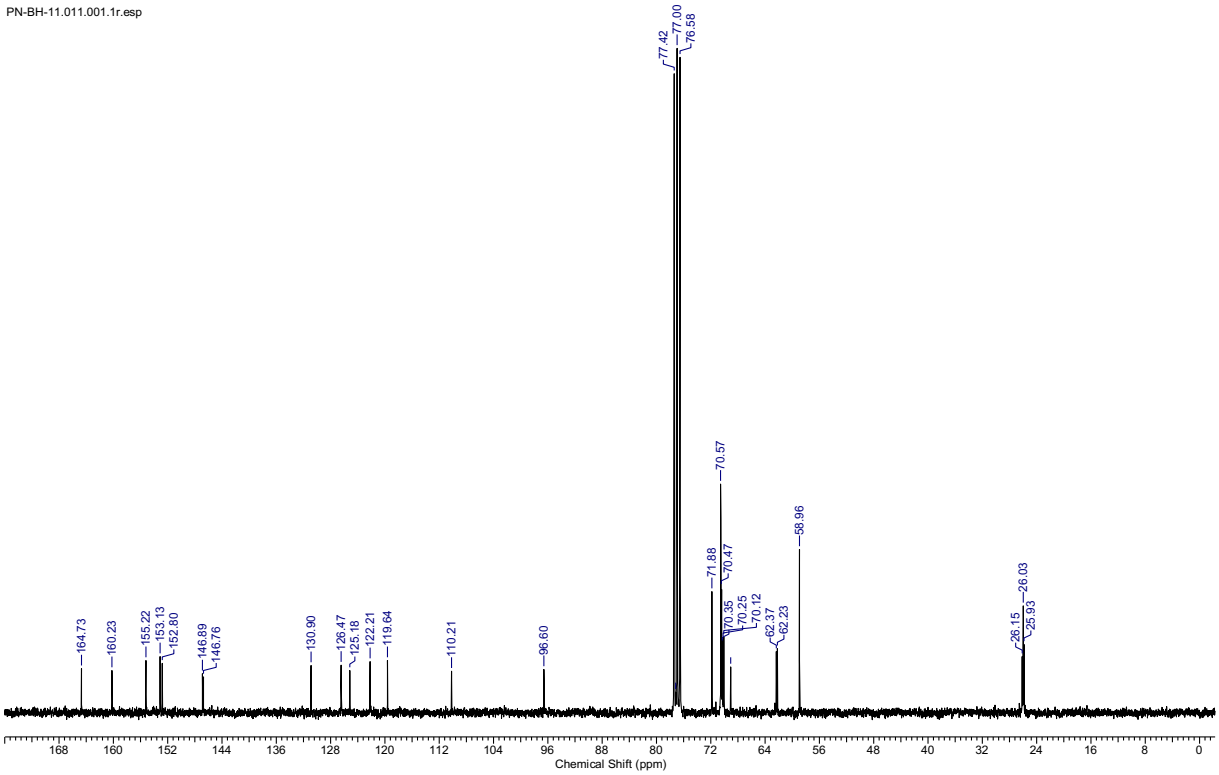


Figure S12. *^{13}C NMR spectrum (300 MHz, $CDCl_3$) of* ***11****.*

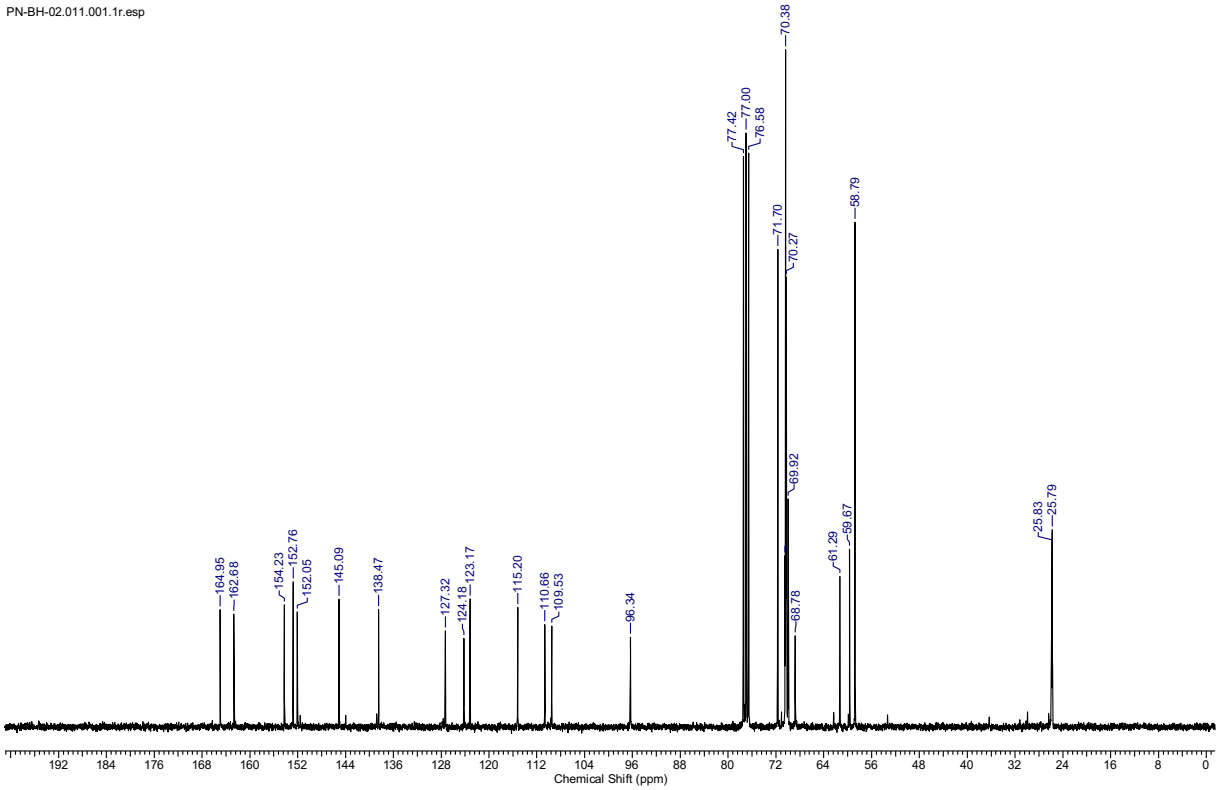


Figure S13*. ^{13}C NMR spectrum (300 MHz, $CDCl_3$) of* ***1****.*

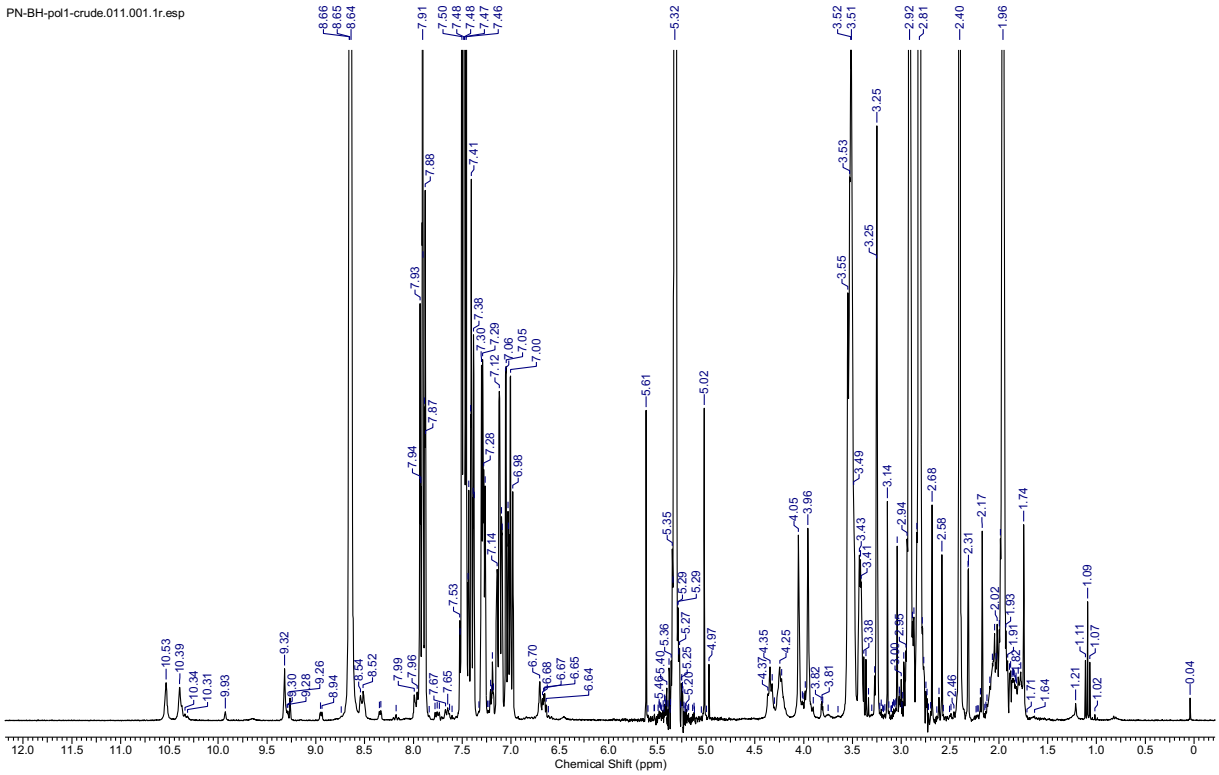


Figure S14. *^{1}H NMR spectrum (300 MHz, CD_2Cl_2) of crude solution of polymer **P1**.*

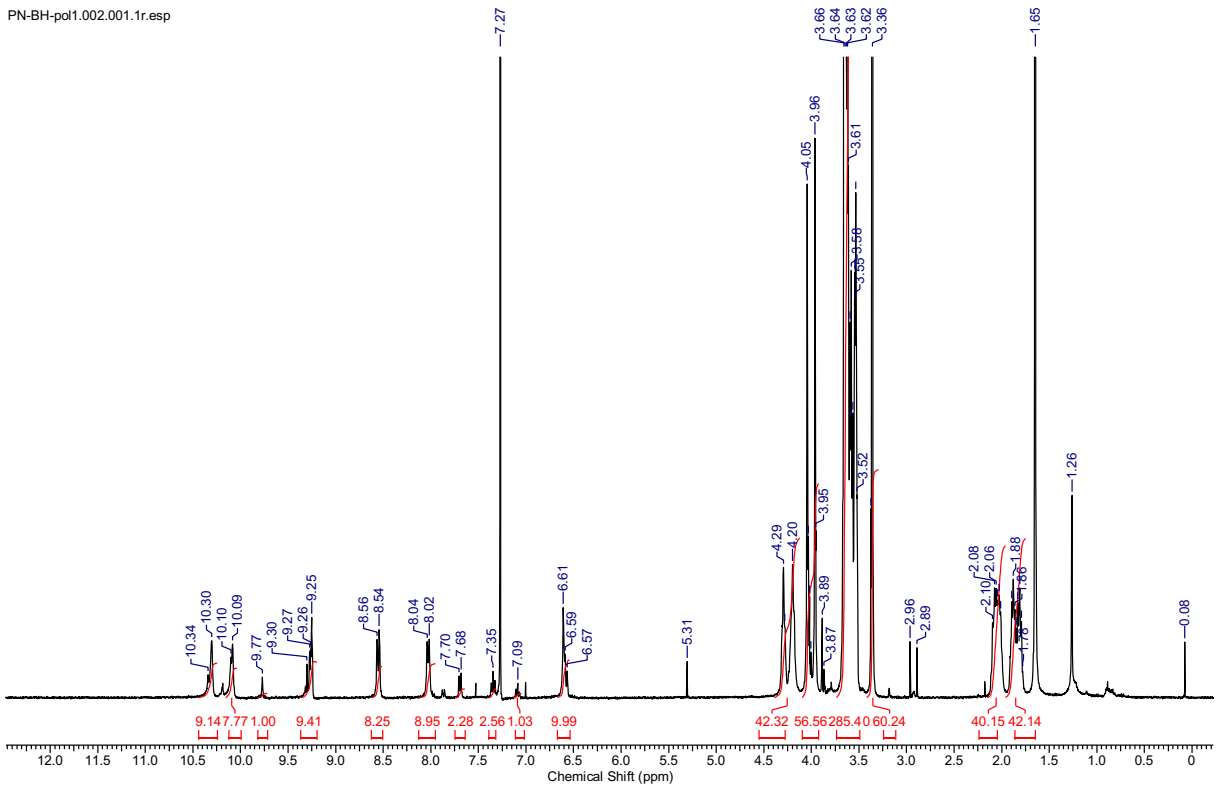


Figure S15. *^{1}H NMR spectrum (400 MHz, $CDCl_3$) of purified polymer **P1**.*

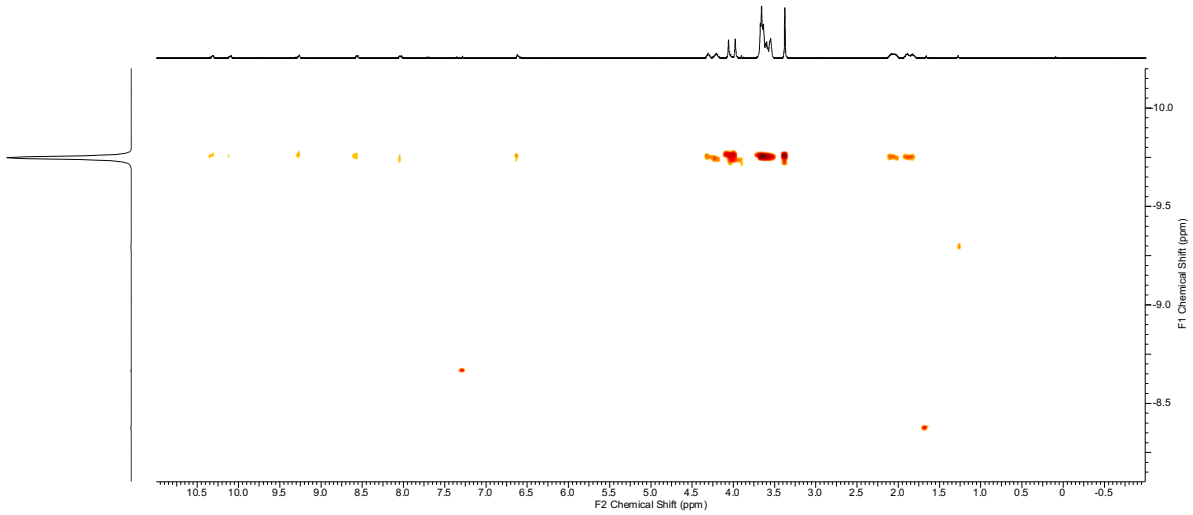


***Figure S16**. DOSY experiment (400 MHz, $CDCl_3$) of purified polymer **P1**.*

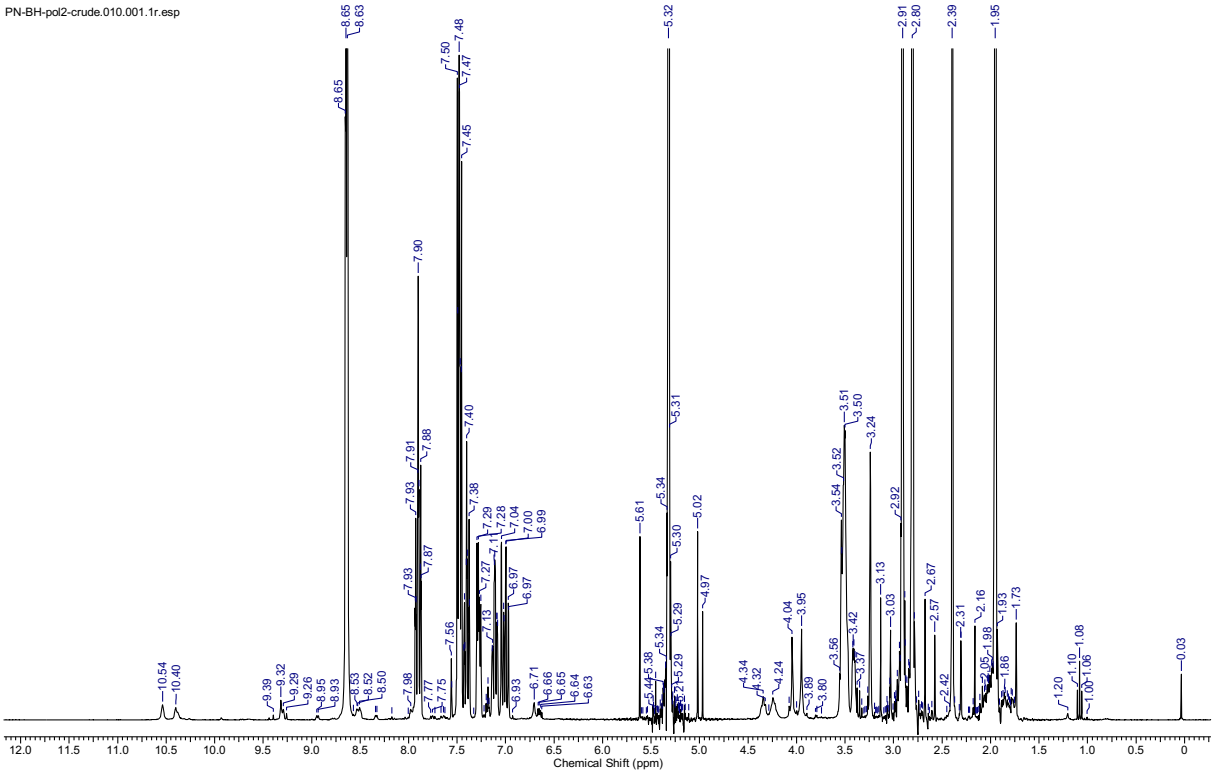


***Figure S17.** ^{1}H NMR spectrum (300 MHz, CD_2Cl_2) of crude solution of polymer **P2**.*

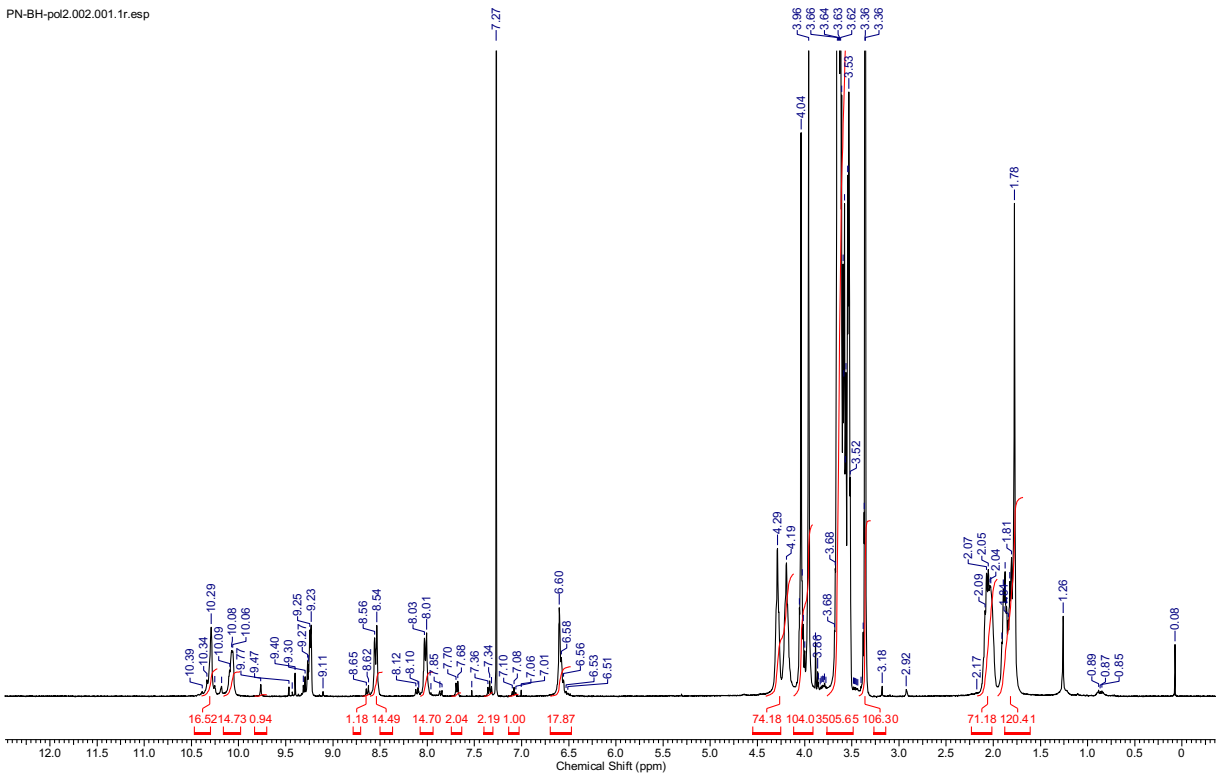


Figure S18. *^{1}H NMR spectrum (400 MHz, $CDCl_3$) of purified polymer* ***P2****.*

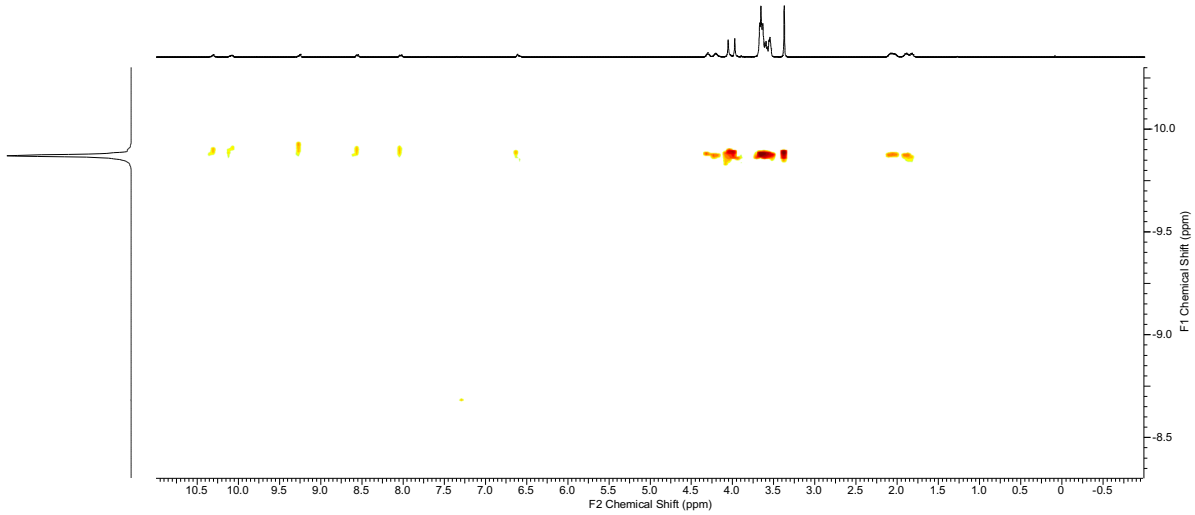


Figure S19*. DOSY experiment (400 MHz, $CDCl_3$) of purified polymer* ***P2****.*

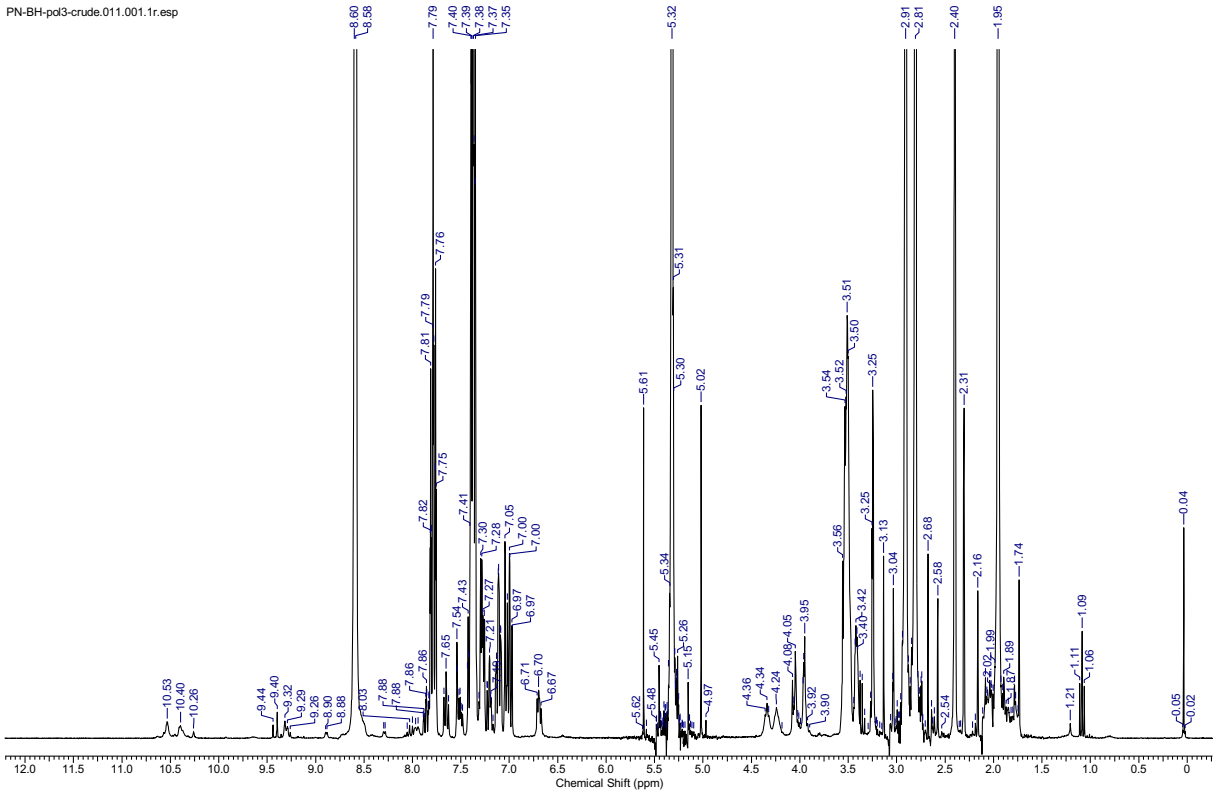


Figure S20. *^{1}H NMR spectrum (300 MHz, CD_2Cl_2) of crude solution of polymer **P3**.*

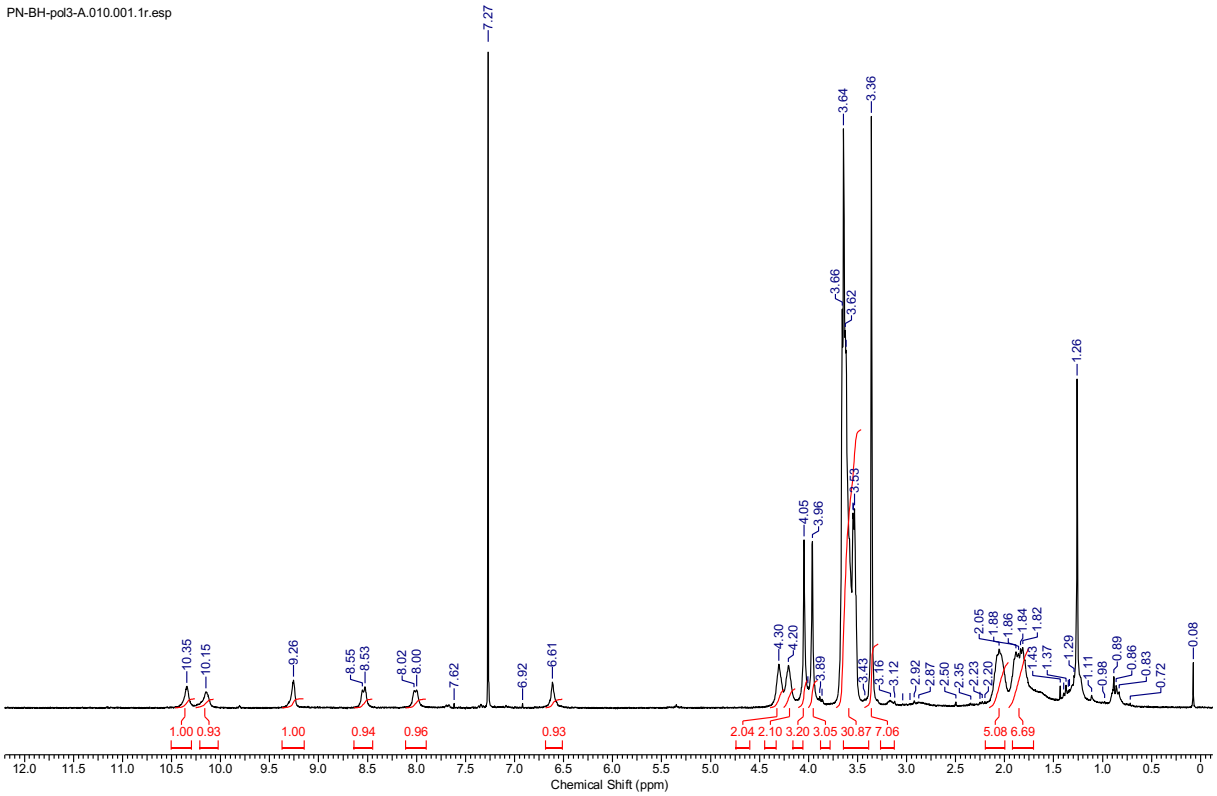


Figure S21*. ^{1}H NMR spectrum (300 MHz, CD_2Cl_2) of purified polymer **P3**.*

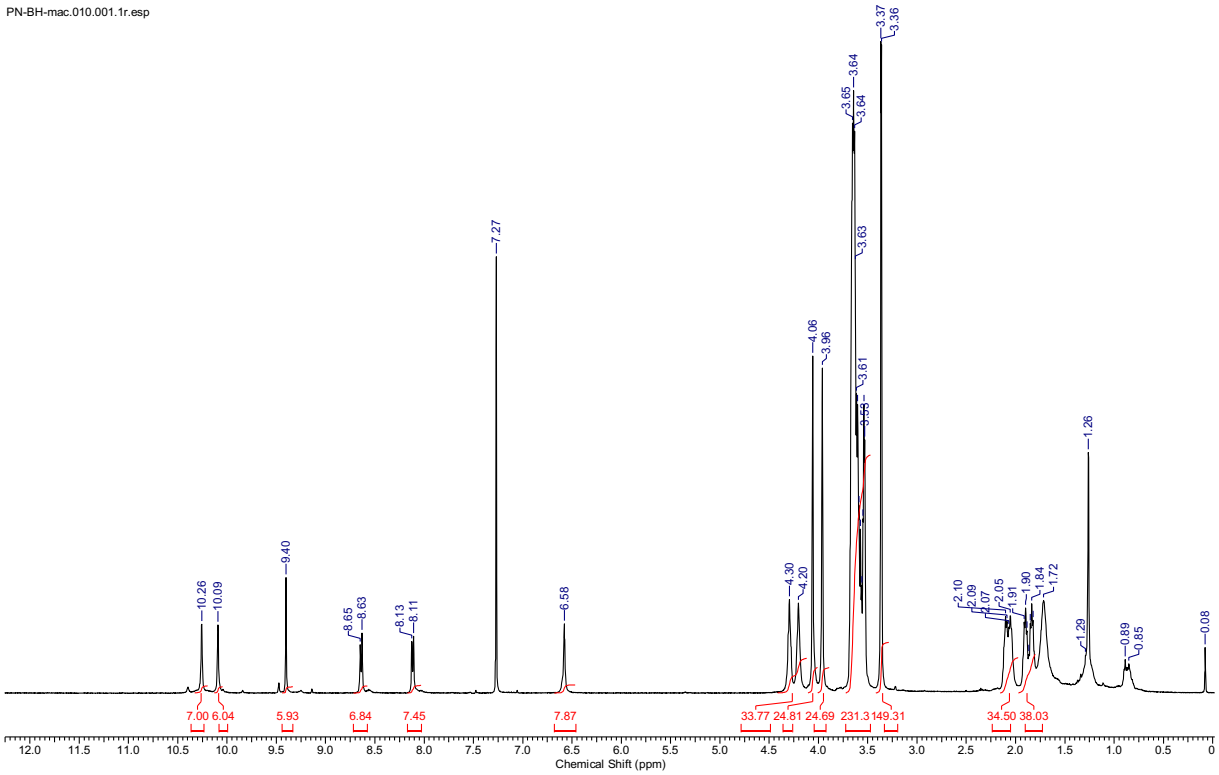


Figure S22. *^{1}H NMR spectrum (500 MHz, $CDCl_3$) of purified 7mer macrocycle* ***M2***.

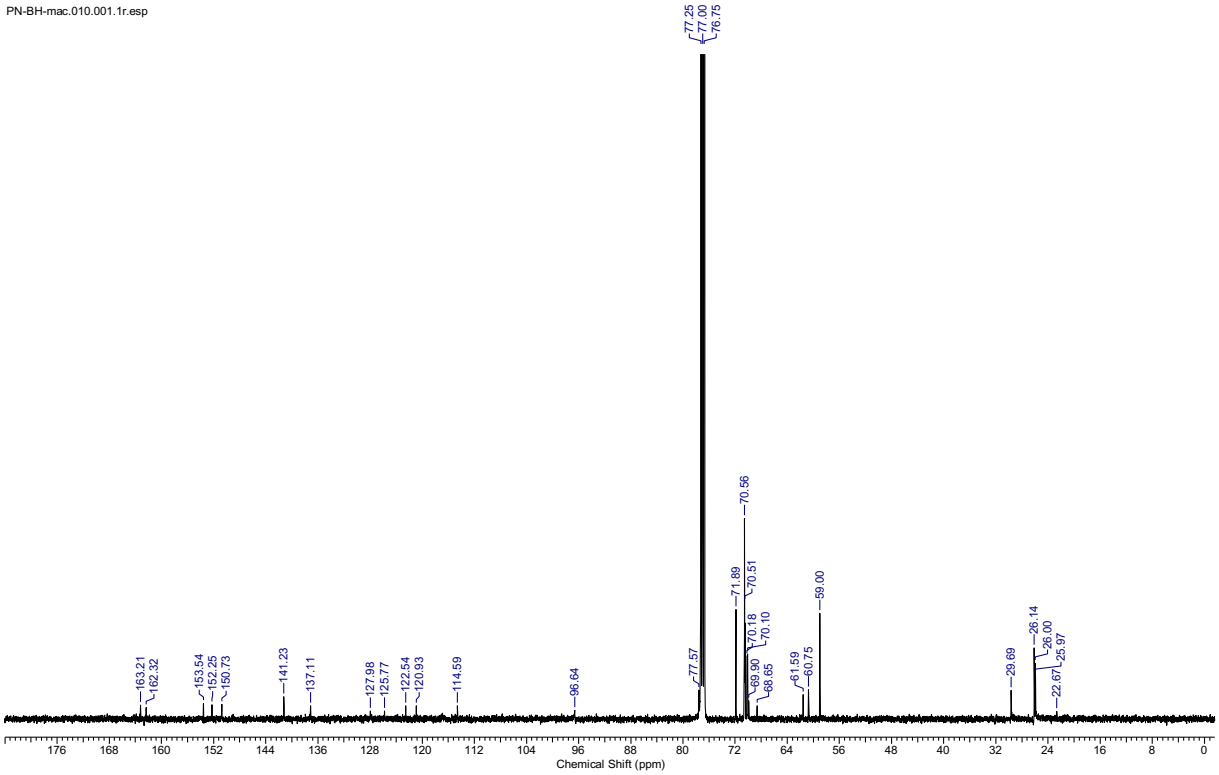


Figure S23. *^{13}C NMR spectrum (500 MHz, $CDCl_3$) of purified 7mer macrocycle* ***M2***.

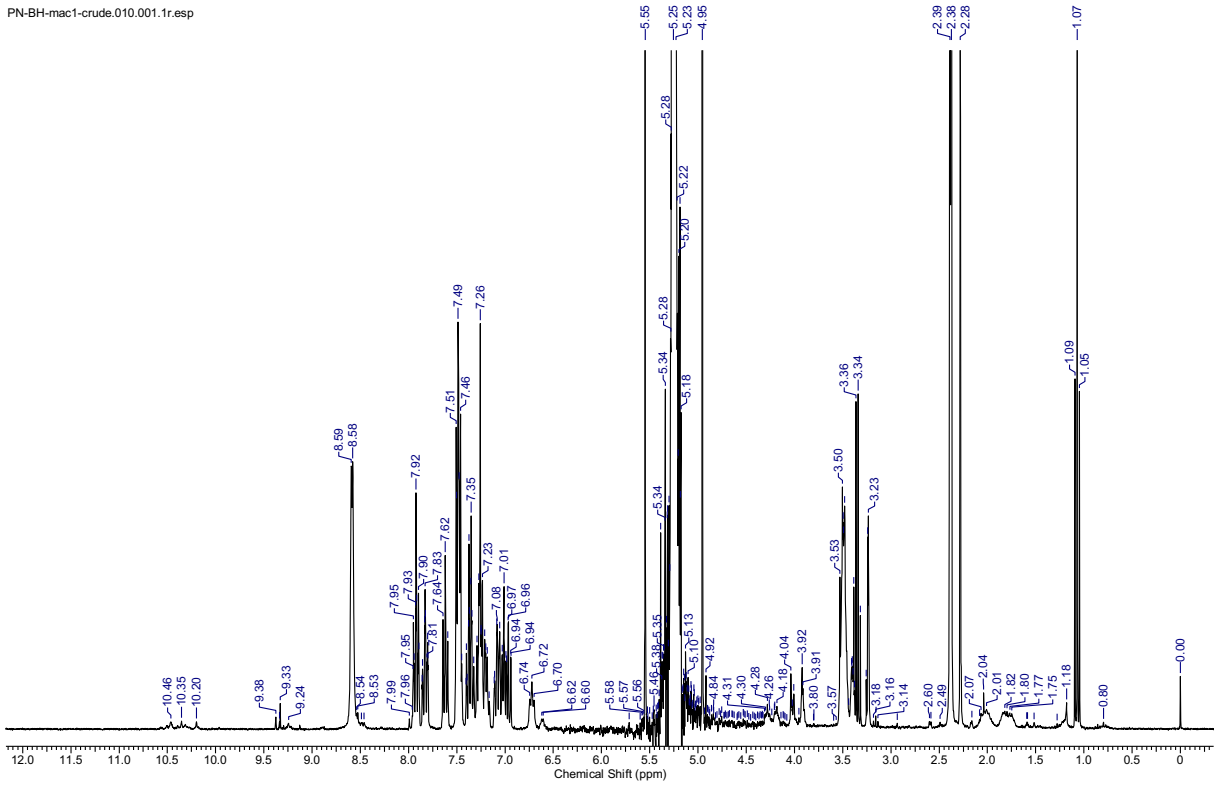


Figure S24. *^{1}H NMR spectrum (300 MHz, CD_2Cl_2) of crude solution of macrocycles mixture* ***M***.

High-resolution mass spectra (HR-MS)

Solvent: MeOH

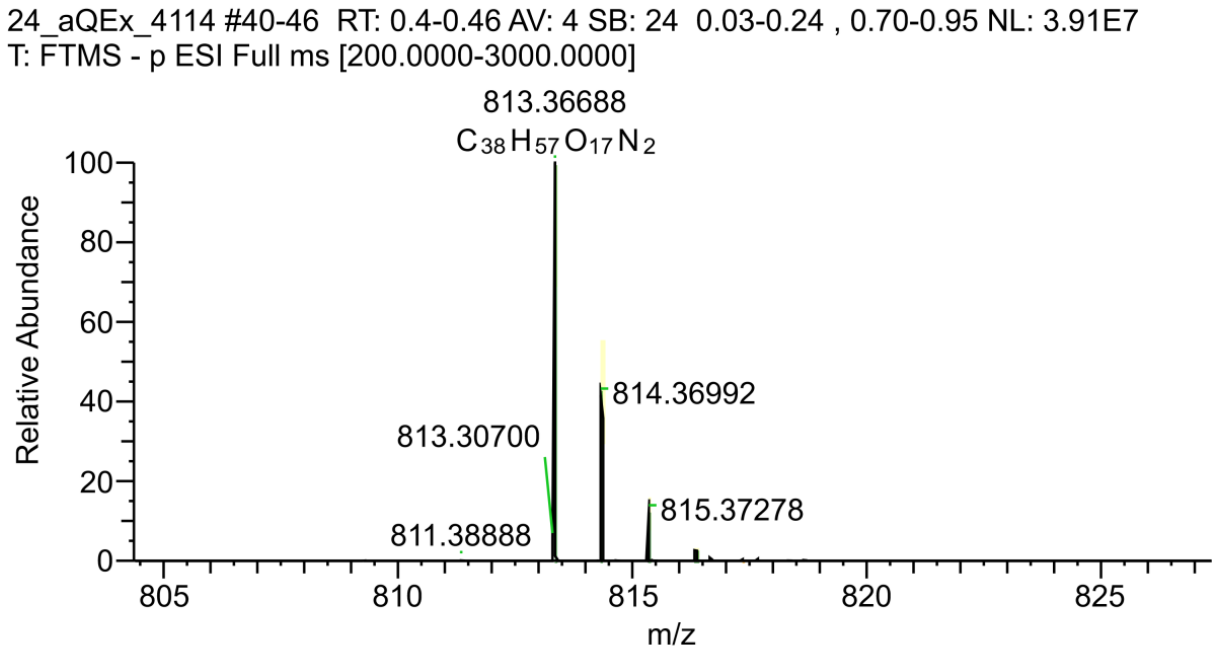


Figure S25. *ESI-HRMS spectrum of* ***11*** *in MeOH, negative mode.*

Solvent: MeOH

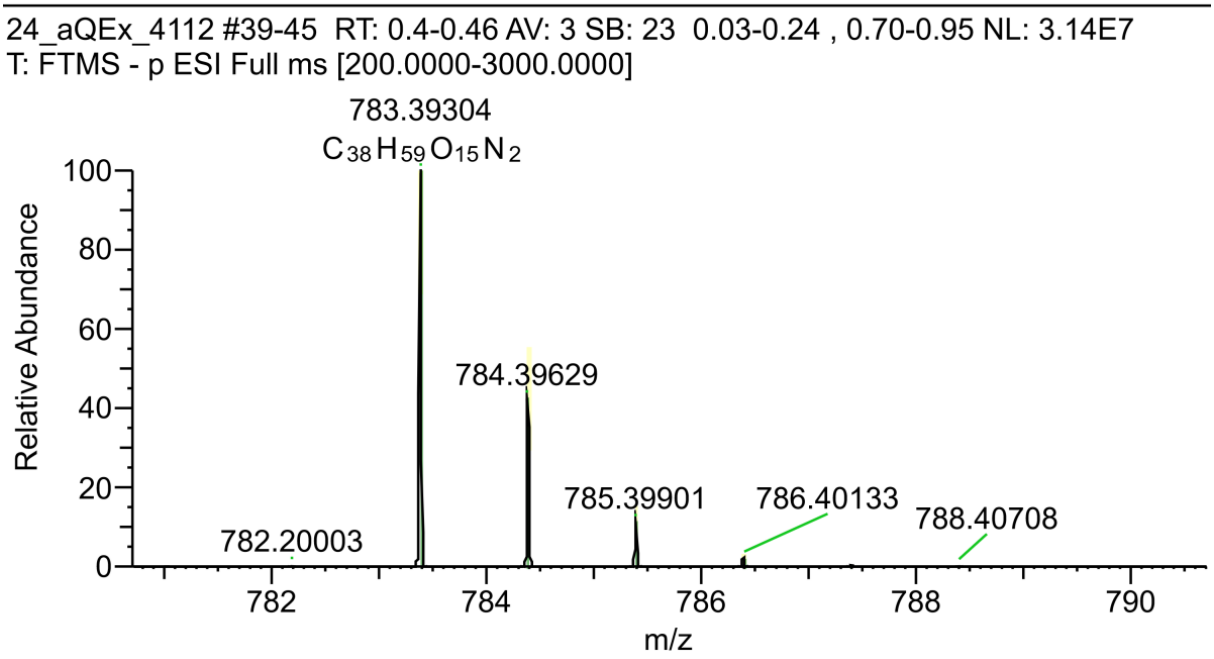


Figure S26. *ESI-HRMS spectrum of* ***1*** *in MeOH, negative mode.*

MALDI-ToF mass spectra

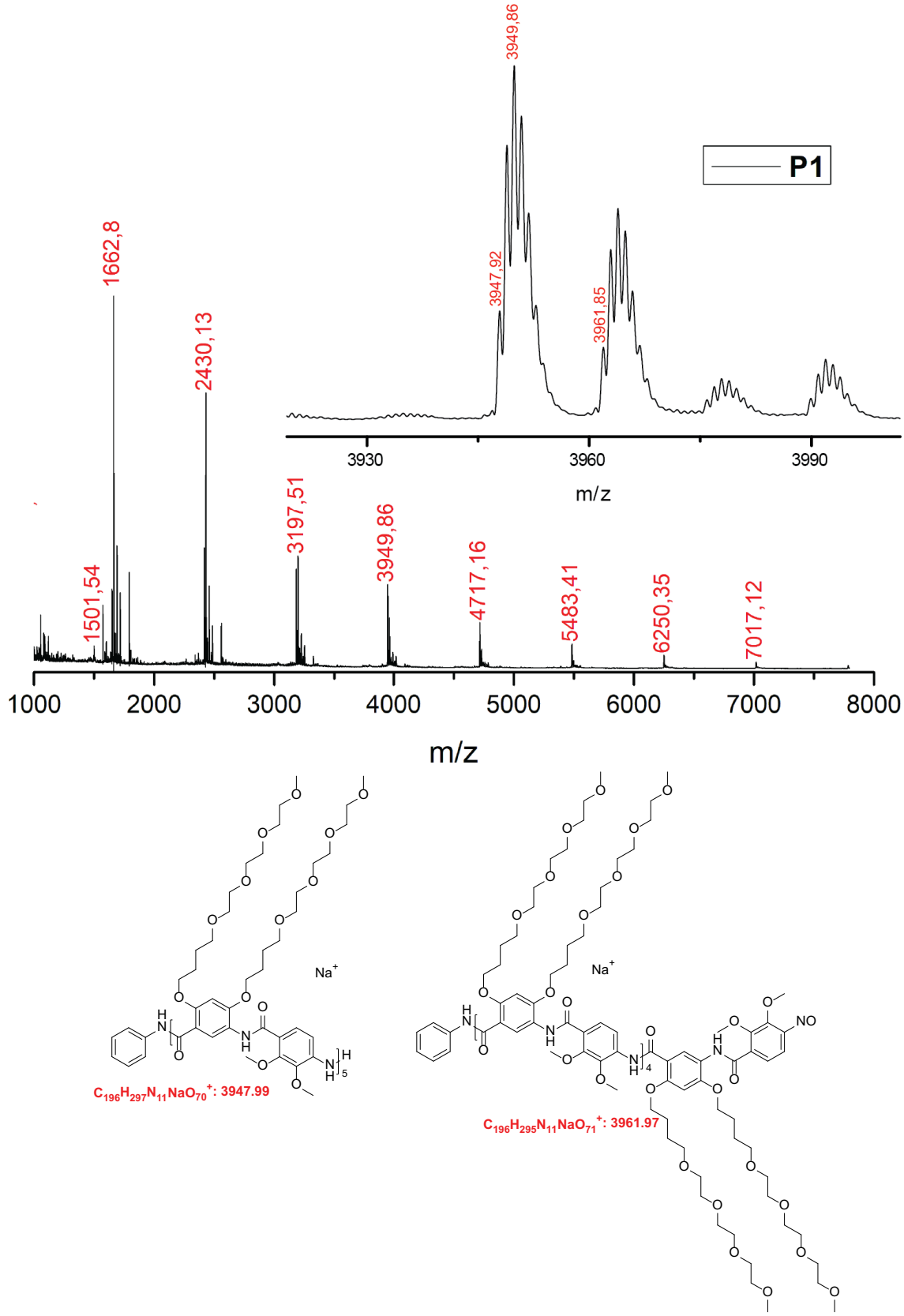


***Figure S27**. Top: MALDI-ToF mass spectrum with the main size distribution of polymer **P1**. Zoom into the 3949.86 peak. DCTB was used as the matrix and NaTFA as the ionizing salt. Bottom: monoisotopic masses of corresponding oligomeric species.*

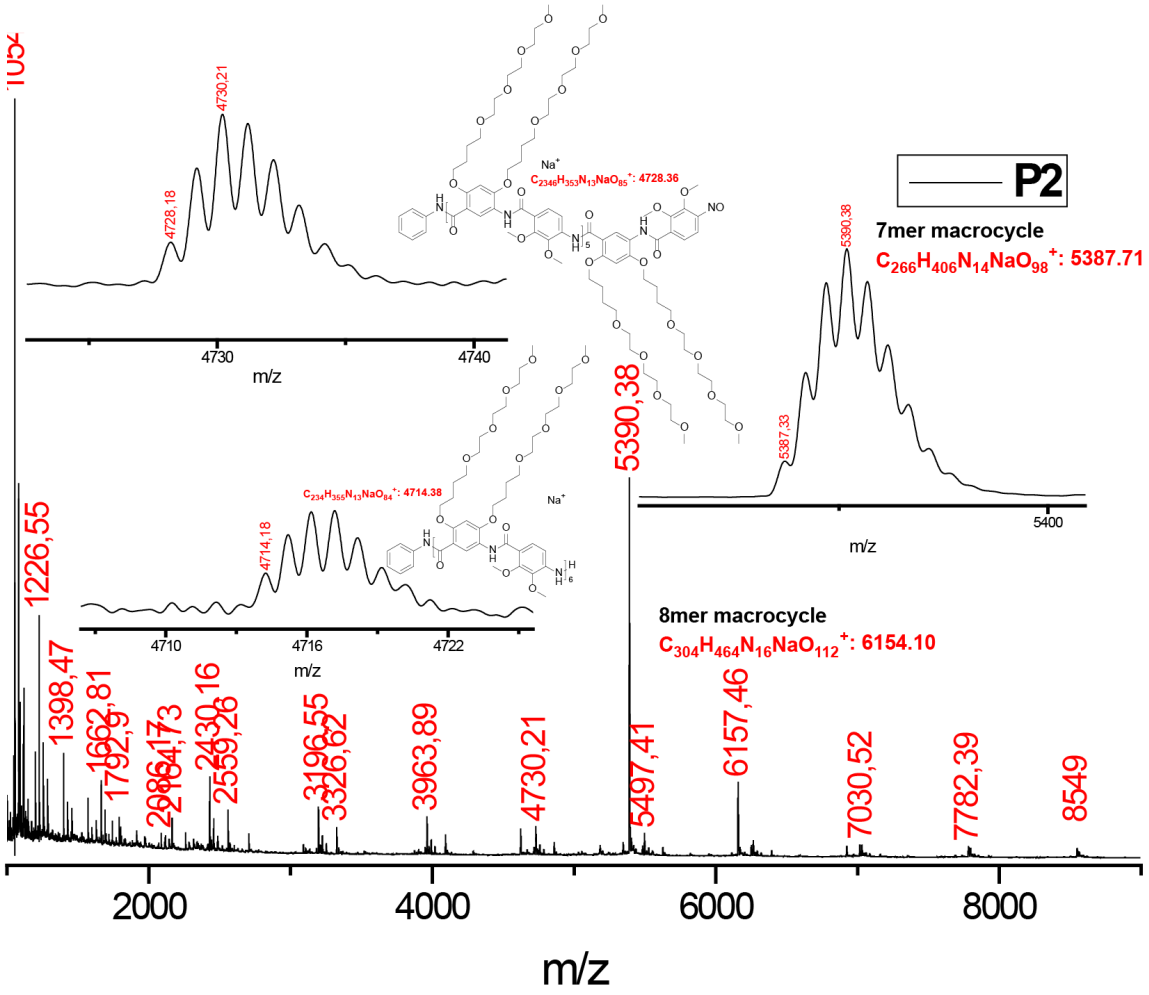


***Figure S28**. MALDI-ToF mass spectrum with the main size distribution of polymer **P2**. Zoom into relevant peaks and corresponding monoisotopic mass for each oligomer/macrocycle is written down. DCTB was used as the matrix and NaTFA as the ionizing salt.*

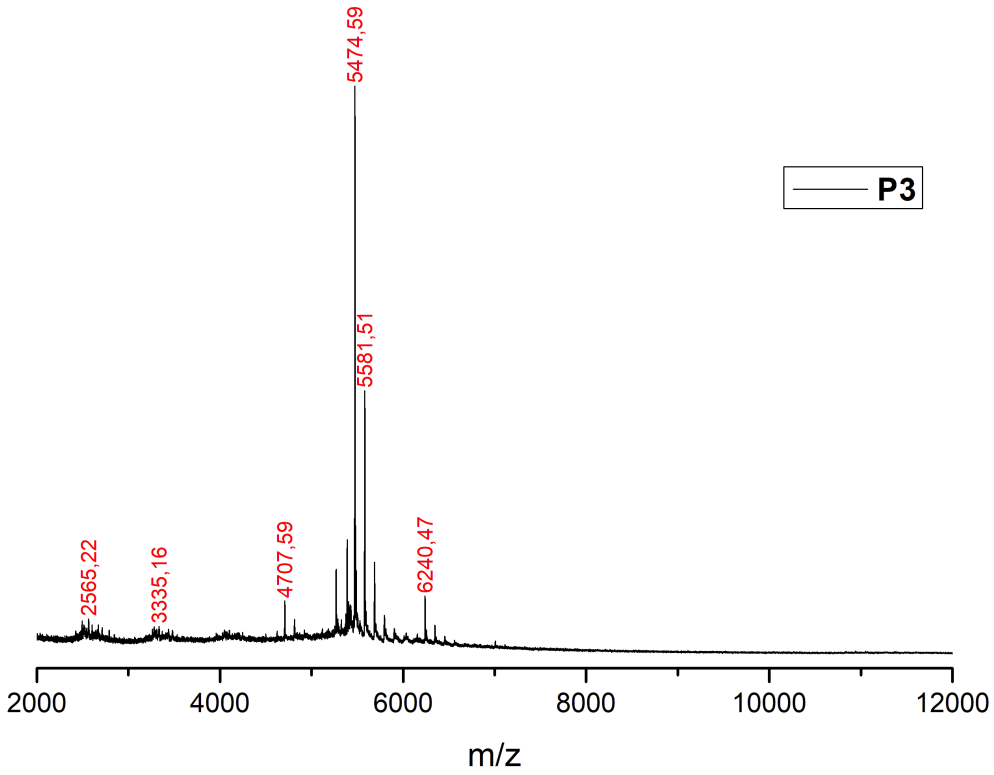


***Figure S29**. MALDI-ToF mass spectrum of isolated polymer **P3**. DCTB was used as the matrix and NaTFA as the ionizing salt.*

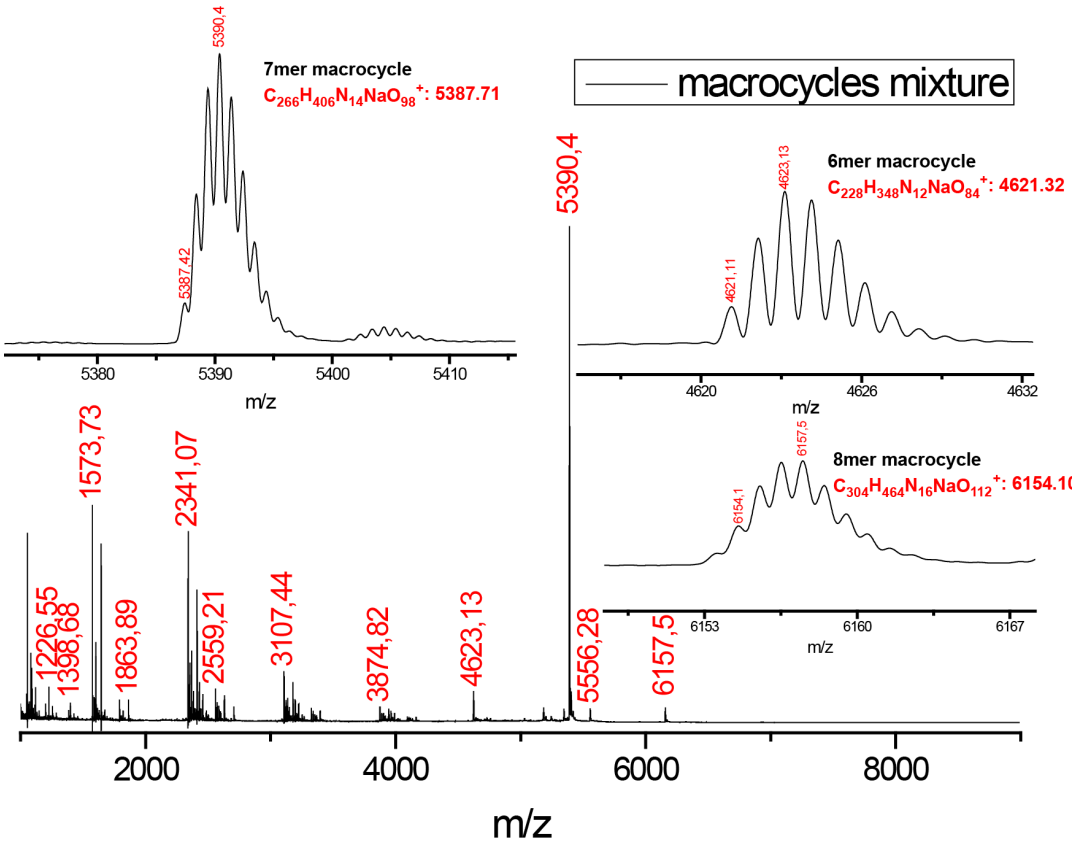


***Figure S30**. MALDI-ToF mass spectrum with the main size distribution of macrocycles mixture **M1**, **M2**, and **M3** after recycling GPC. Zoom into relevant peaks and corresponding monoisotopic mass for each macrocycle is written down. DCTB was used as the matrix and NaTFA as the ionizing salt.*

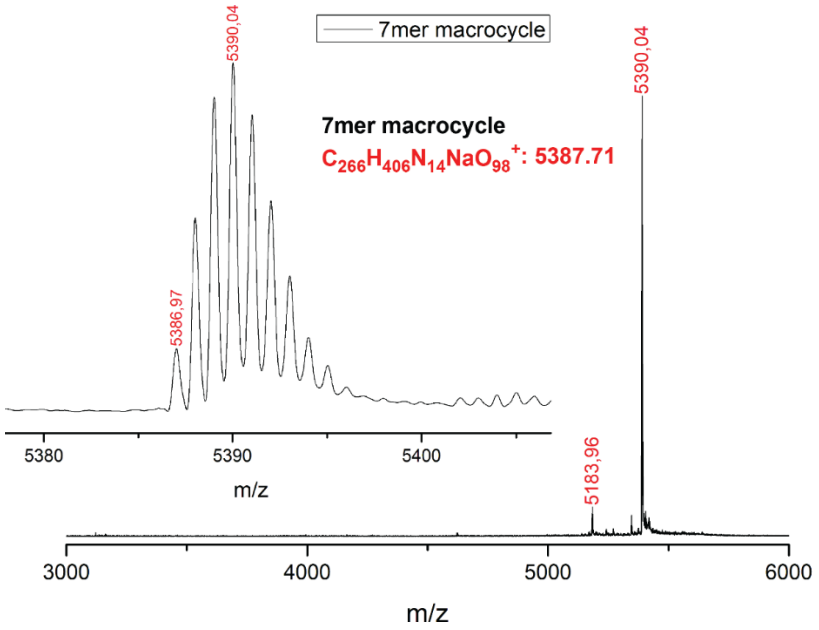


***Figure S31**. MALDI-ToF mass spectrum of macrocycle **M2** after purification by semi-preparative HPLC. DCTB was used as the matrix and NaTFA as the ionizing salt.*

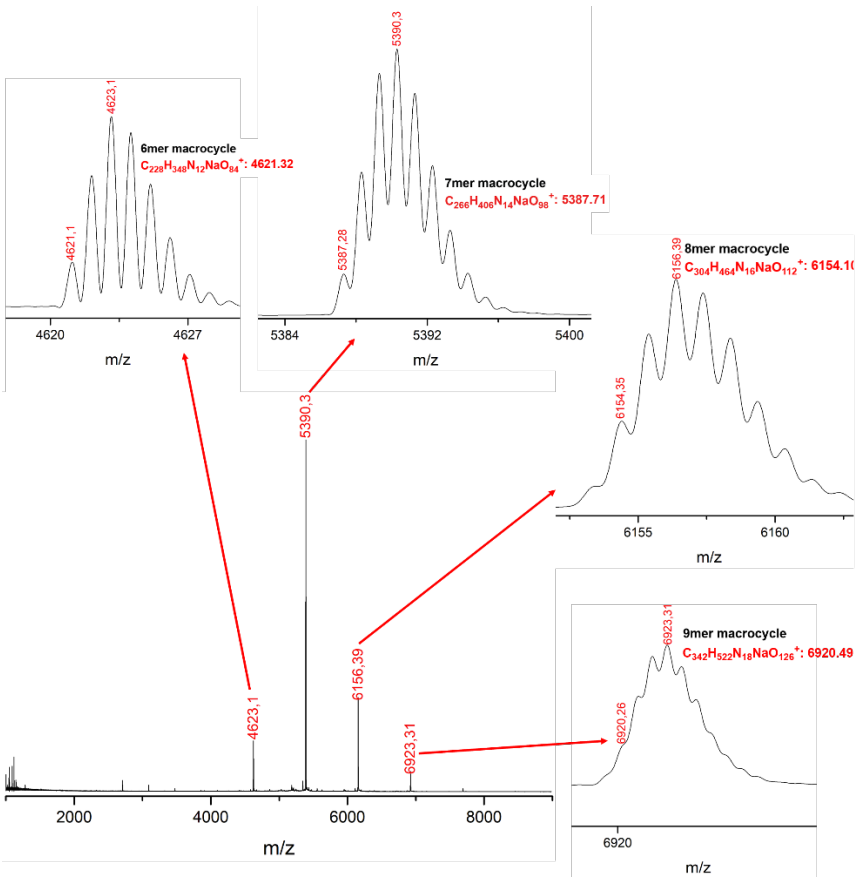


***Figure S32**. MALDI-ToF mass spectrum with the main size distribution of crude solution of macrocycles mixture of **M1**, **M2**, **M3** and **M4**. Corresponding monoisotopic masses are shown. DCTB was used as the matrix and NaTFA as the ionizing salt.*

References

[1] A. F. M. Kilbinger, S. Pal, D. P. T. Nguyen, A. Molliet, M. Alizadeh, A. Crochet, R. D. Ortuso, A. Petri-Fink, *Nat. Chem.* **2021**, *13*, 705–713.