

## Supporting information

# Scalable design of uniform oligourethanes for impact study of chain length, sequence and end groups on thermal properties

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## Materials

All chemicals were used without further purification. 1,10-Decanediol (Sigma-Aldrich, 98%), 2-aminoethan-1-ol (Sigma-Aldrich, ≥99%), 2-(methylamino)ethan-1-ol (Sigma-Aldrich, ≥98%), acetonitrile (Chemlab, ≥99.9%), dichloromethane (DCM, Fisher Chemical, ≥99.8%), dimethyl sulfoxide (DMSO, Fisher Chemical, ≥99.8%), DMSO-d<sub>6</sub> (Eurisotop, 99,8%D), ethyl acetate (Fisher Chemical, ≥99,8%), hydrogen chloride (HCl, Chemlab, 36% aq. sol.), methanol (MeOH, Fisher Chemical, ≥99,8%), sodium chloride (NaCl, Chemlab, ≥99.8%), sodium hydroxide (NaOH, Chemlab, ≥98.5%), sodium sulfate (NaSO<sub>4</sub>, Roth, anhydrous, ≥99%), N-methylprop-2-en-1-amine (Apollo Scientific), N,N'-disuccinimidyl carbonate (DSuC, ABCR, 98%), prop-2-en-1-amine (Sigma-Aldrich, 98%), pyridine (Sigma-Aldrich, ≥99%), and tetrahydrofuran (THF, Fisher Chemical, ≥99.8%)

## Instrumentation

### Size-exclusion chromatography (SEC)

Oligomers were characterized on a Waters SEC system equipped with a Waters 1515 isocratic pump, Waters 2410 refractive index detector (24 °C), Waters 717plus autosampler and a Waters 2487 dual λ absorbance UV detector and column oven. For separation, a three-column setup was used with one SDV 3 μm, 8×50 mm precolumn and two SDV 3 μm, 1000 Å, 8×300 mm columns supplied by PSS, Germany. Tetrahydrofuran (THF) stabilized with butylated hydroxytoluene (BHT, HPLC-SEC grade) supplied by Biosolve was used at a flow rate 1.0 mL min<sup>-1</sup>. Calibration was carried out by three injections of a mixture of narrow polystyrene standards ranging from 162 to 38640 Da.

As the hydrogen bonding series (**H<sub>x</sub>-OH / H<sub>g</sub>-ene**) are not soluble in THF, size exclusion chromatography analyses were performed on a Waters instrument, with a RI detector (2414 Waters), equipped with 3 Polymer Standards Services SEC serial columns (1 GRAM Analytical 30 A, 10 ° mm and 2 GRAM Analytical 1000 A, 10 ° mm) at 35 °C. PMMA standards were used for calibration and DMA containing LiBr (5 g L<sup>-1</sup>) was used as a solvent at a flow rate of 1 mL min<sup>-1</sup>. This system utilizes a column calibrated for higher molecular weight ranges, resulting in the oligomers having a later retention time compared to the THF system.

### Nuclear magnetic resonance (NMR).

<sup>1</sup>H spectra were recorded on a Bruker Avance 300 (300 MHz) and a Bruker Avance 400 (400 MHz). DMSO-d<sub>6</sub> was used as solvent. Chemical shifts are presented in parts per million (δ) and calibrated to the characteristic residual solvent signals.

### **Differential scanning calorimetry (DSC)**

DSC analyses were performed with a Mettler Toledo instrument 1/700 under nitrogen atmosphere at a heating and cooling rate of 10 K.min<sup>-1</sup>. Measurements were performed from -100 to 200 °C.

### **Thermogravimetric analysis (TGA)**

TGA analyses were performed with a Mettler Toledo TGA/ SDTA851e instrument under nitrogen atmosphere at a heating rate of 10 K.min<sup>-1</sup> from 25 °C to 800 °C in dynamic mode.

### **Pyrolysis–gas chromatography–mass spectrometry**

Based on the TGA-profiles, the following pyrolysis temperatures were selected for a complete degradation of the oligo-urethanes: 300°C for H8-ene, 400°C for M8-ene, 300°C for B8-ene and 300°C for A8-ene. After pyrolysis, the compounds were separated using a HP-5MS column ((5%-phenyl)-methylpolysiloxane). The temperature program started at 50°C and was kept for 1 minute, after which the temperature rose at a rate of 15°C/min up to 325°C, which was held for 6 minutes. The compounds were analyzed using the MS in SCAN mode (m/z-ratios 25-675).

### **Electrospray Ionization – Orbitrap Mass Spectrometry**

An orbitrap mass analyzer was used to measure absolute mass values. Spectra were recorded on Q-Exactive Plus stand-alone benchtop Orbitrap mass spectrometer (Thermo Fisher Scientific), equipped with a heated electrospray ionization source (HESI). The instrument was calibrated in the m/z range 74-1822 using premixed calibration solutions (Thermo Scientific) and for the high mass mode in the m/z range of 600-8000 using ammonium hexafluorophosphate solution. A constant spray voltage of 3.5 kV, a dimensionless sheath gas and a dimensionless auxiliary gas flow rate of 10 and 0 were applied, respectively. The capillary temperature was set to 320 °C, the S-lens RF level was set to 150, and the aux gas heater temperature was set to 125 °C. The Q Exactive was coupled to an UltiMate 3000 UHPLC System (Dionex, Sunnyvale, CA, USA) consisting of a pump (LPG 3400SD), an autosampler (WPS 3000TSL), and a temperature-controlled column department (TCC 3000). The injection volume used for analysis was 10 µL of a 0.05 mg/mL solution.

## Synthesis procedures

### **General procedure for the synthesis of M<sub>x</sub>-OH, M<sub>8</sub>-ene, B<sub>x</sub>-OH, B<sub>8</sub>-ene, A<sub>x</sub>-OH and A<sub>8</sub>-ene**

An example of a synthesis protocol is given for H<sub>2</sub>-OH. Decanediol (15 g, 1eq.) was dissolved in 100mL ACN as the solvent and pyridine (14 mL, 2eq.) as catalyst while being stirred at 70°C. The disuccinimidyl carbonate (55 g, 2.5 eq) is added and the mixture is left to react for 15 min. The reaction is cooled down to room temperature before adding 4 equivalents (28 mL) of N-methylethanolamine. This reaction is left stirring for 30 min before transferring the whole medium to a separatory funnel. The product was washed three times with HCl, three times with NaOH, and once with brine, using DCM or ethyl acetate as the organic solvent. NaSO<sub>4</sub> was used to dry this organic phase before evaporating the solvent by means of rotary evaporation. This yielded a transparent to yellow viscous liquid in high yield (95%, 30.7 g). In order to obtain the M<sub>x</sub>-OH, B<sub>x</sub>-OH and A<sub>x</sub>-OH oligomers, the following procedure was repeated until the desired length is achieved. It is important to note that the aminoalcohol used for coupling should be adjusted based on the desired monomer addition. Ethanolamine is employed for a regular carbamate, and N-methylethanolamine for a substituted carbamate, while keeping the reaction parameters and work-up identical.

For the synthesis of M<sub>8</sub>-ene, B<sub>8</sub>-ene and A<sub>8</sub>-ene, the procedure was repeated three times, with the final coupling involving the addition of allylamine (B<sub>8</sub>-ene and A<sub>8</sub>-ene) or N-methylallylamine (M<sub>8</sub>-ene) while keeping the work-up unchanged. This yielded a transparent to yellow viscous with high yields (10 g, 80.6% M<sub>8</sub>-ene; 10 g, 82.8% B<sub>8</sub>-ene and 36 g, 75.2% A<sub>8</sub>-ene).

#### **General procedure for the synthesis of the oligomers H<sub>x</sub>-OH and H<sub>8</sub>-ene**

An example synthesis protocol is given for H<sub>2</sub>-OH. Decanediol (6 g, 1eq.) was dissolved in 50 mL equivalents of DMSO as the solvent and pyridine (5.5 mL, 2eq.) as catalyst while being stirred at 70 °C. The disuccinimidyl carbonate (22 g, 2.5 eq) is added and left to react for 15 min. The reaction is cooled down to room temperature before adding 8.3 mL (4eq.) of ethanolamine. This reaction is left stirring for 30 min before transferring the whole medium to a beaker. Water is added and the mixture is stirred vigorously to solubilize any side products present in the reaction mixture while leaving the product untouched as a white powder. After 1 h of washing, the product is filtered and left to dry in a vacuum oven at 40 °C overnight to remove any water traces. A white powder is obtained with high yields (11.6 g, 97%). To produce the H<sub>4</sub>-OH, H<sub>6</sub>-OH and H<sub>8</sub>-OH oligomer, the following procedure is repeated once, twice and three times, respectively.

For the synthesis of H<sub>8</sub>-ene the above procedure was repeated until the hexamer level. The final cycle followed the same procedure, with the only difference being the use of allylamine instead of aminoethanol, while maintaining the same work-up. This yielded a white powder with high yields (14 g, 85.7% after 4 cycles).

# NMR spectra

## M<sub>2</sub>-OH

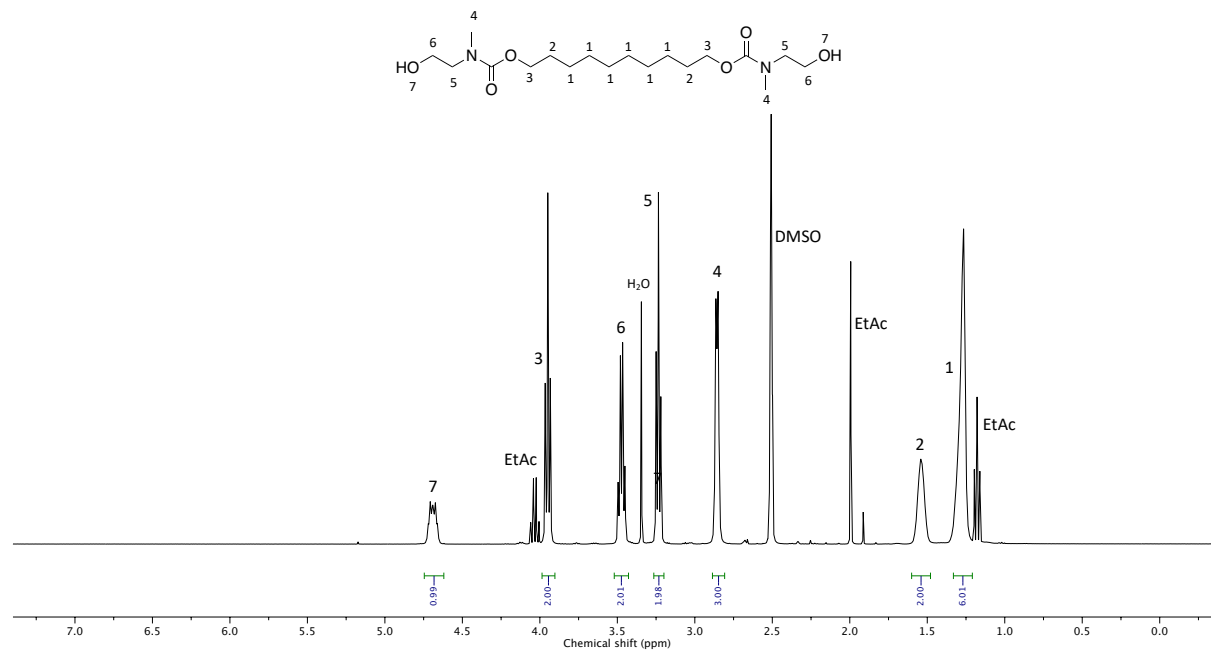


Figure S1: NMR spectrum of M<sub>2</sub>-OH.

## M<sub>4</sub>-OH

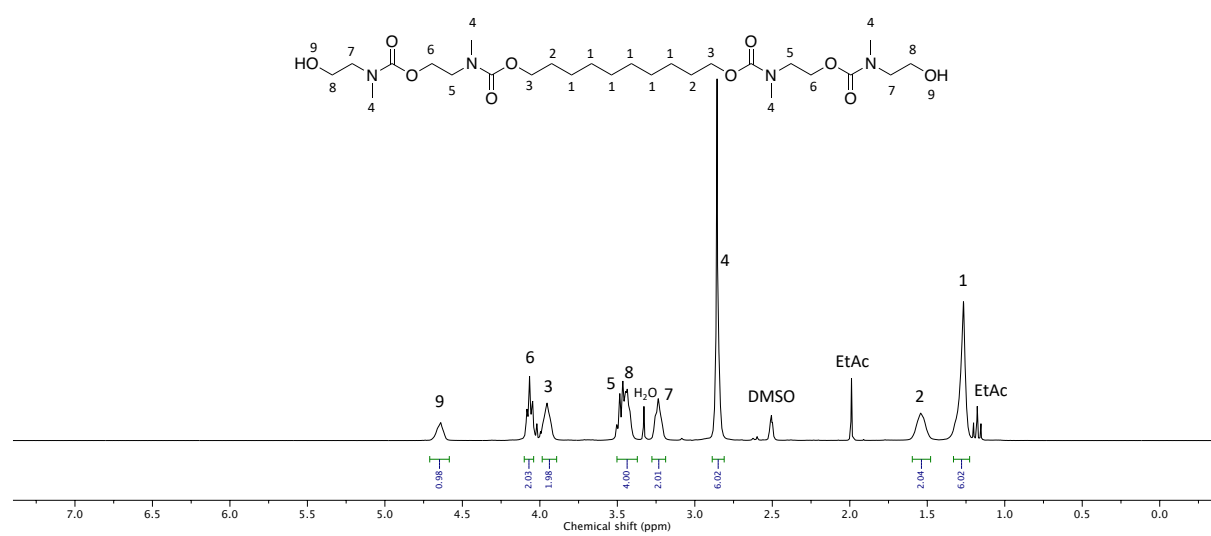


Figure S2: NMR spectrum of M<sub>4</sub>-OH.

## M<sub>6</sub>-OH

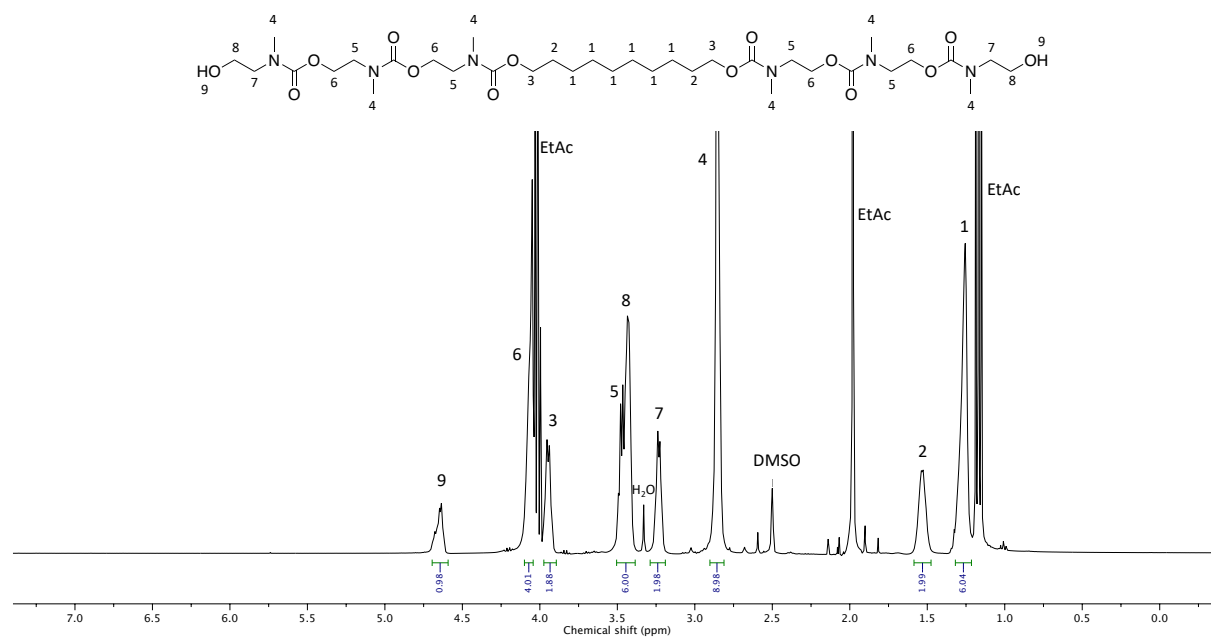


Figure S3: NMR spectrum of M<sub>6</sub>-OH.

## M<sub>8</sub>-OH

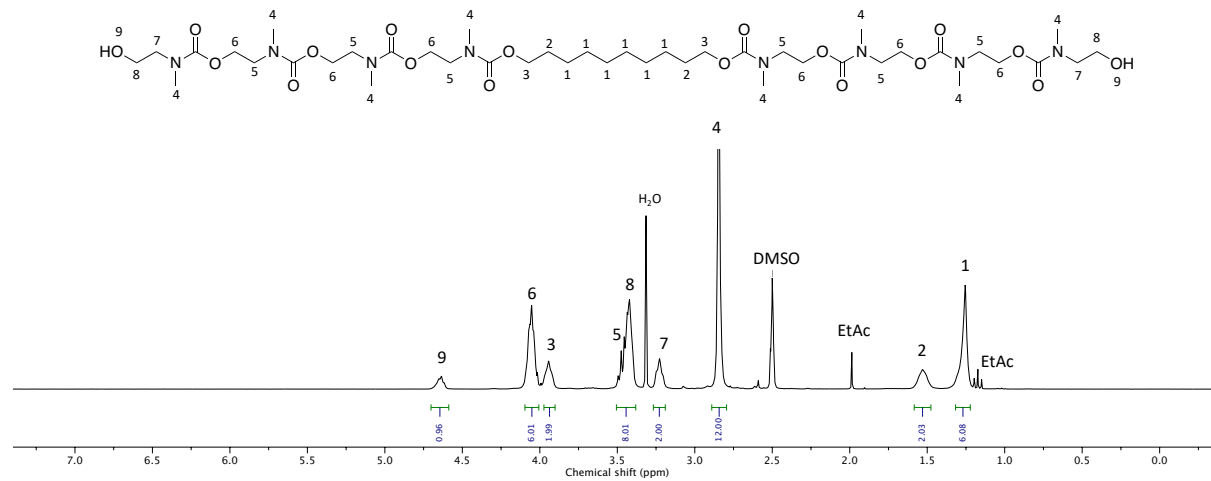


Figure S4: NMR spectrum of M<sub>8</sub>-OH.

## M<sub>8</sub>-ene

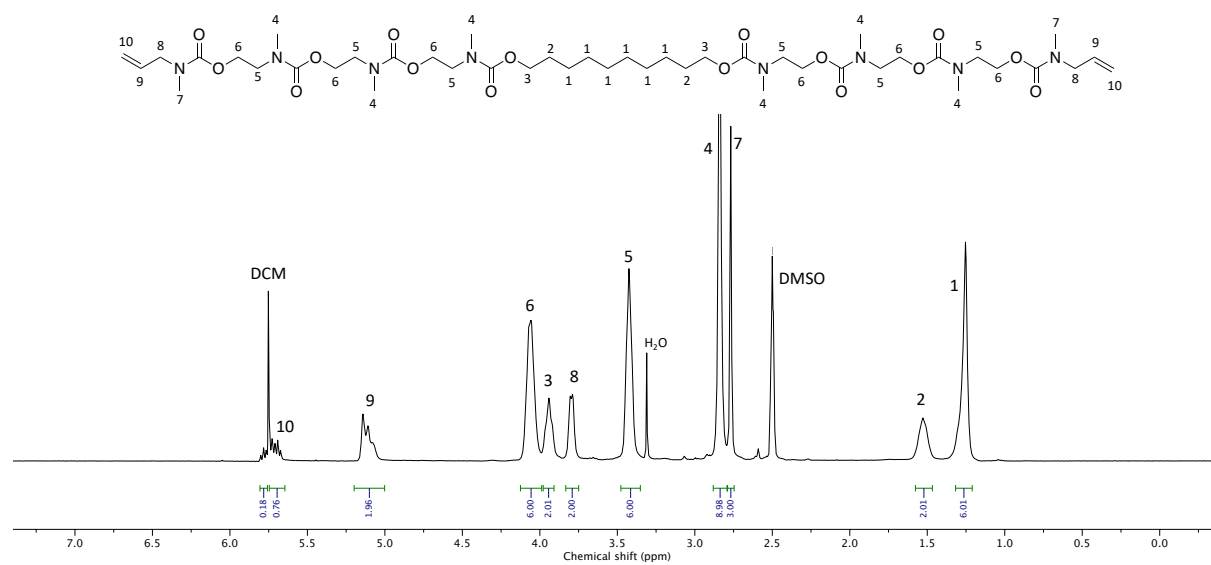


Figure S5: NMR spectrum of M<sub>8</sub>-ene.

## H<sub>2</sub>-OH

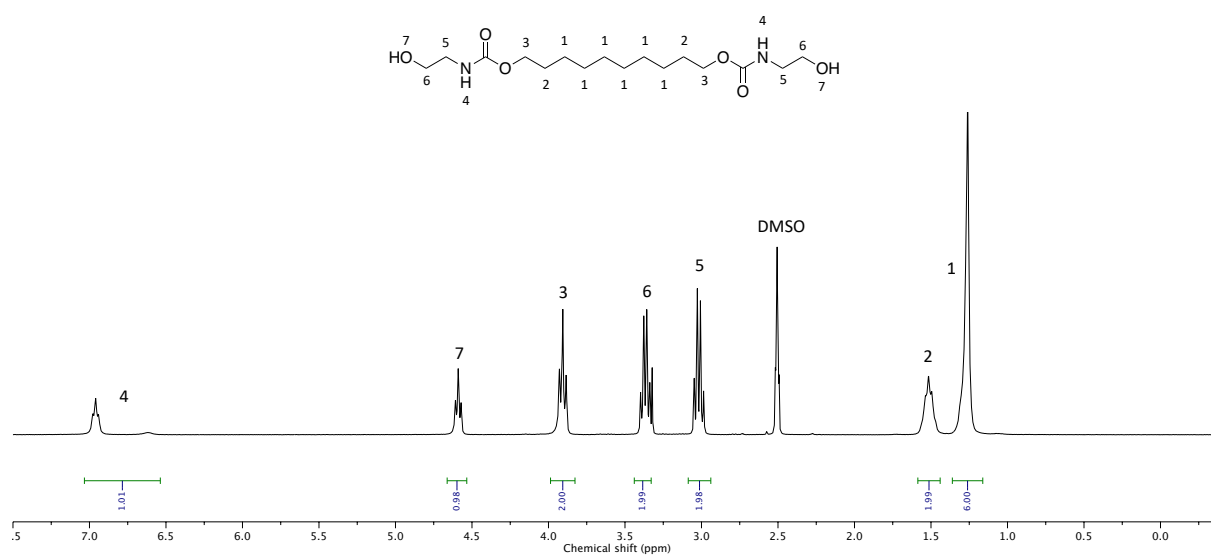


Figure S6: NMR spectrum of H<sub>2</sub>-OH.

## H<sub>4</sub>-OH

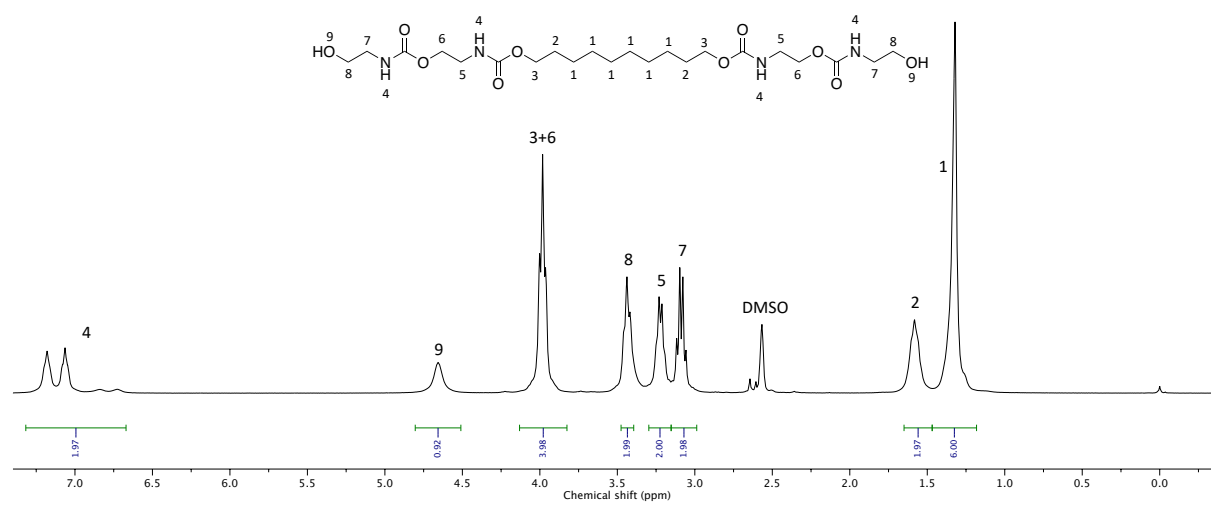


Figure S7: NMR spectrum of H<sub>4</sub>-OH.

## H<sub>6</sub>-OH

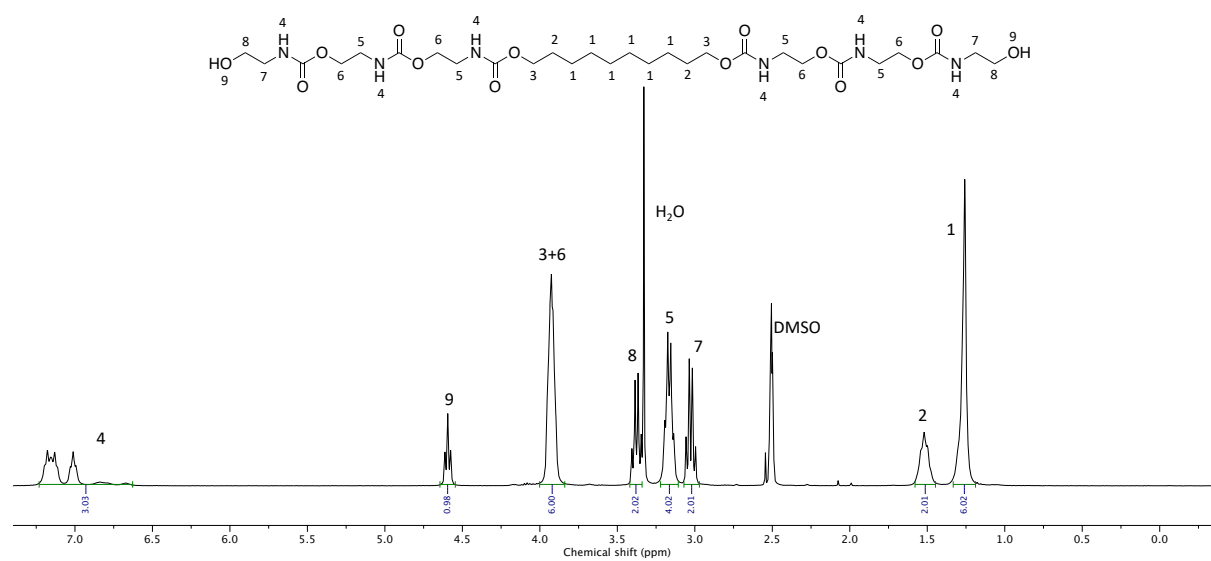


Figure S8: NMR spectrum of H<sub>6</sub>-OH.



## H<sub>8</sub>-OH

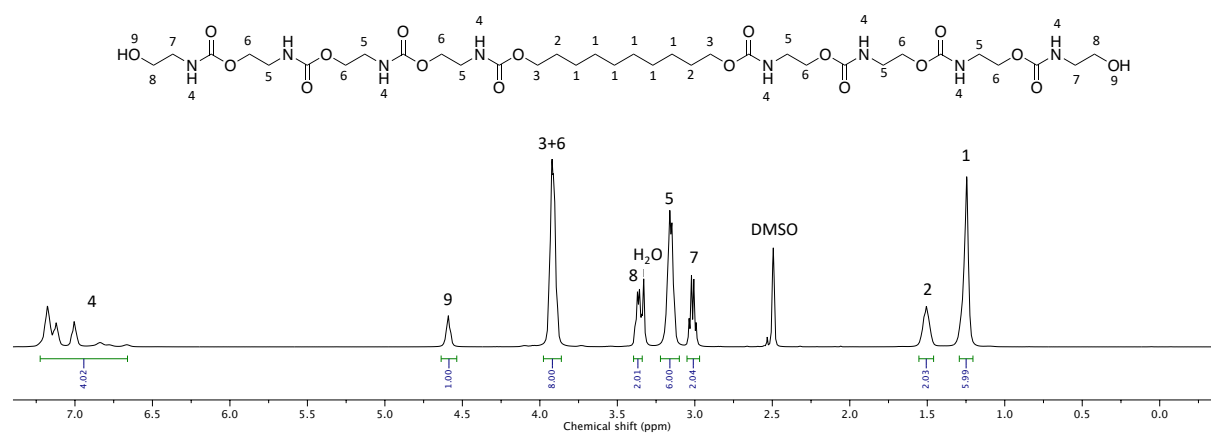


Figure S9: NMR spectrum of H<sub>8</sub>-OH.

## H<sub>8</sub>-ene

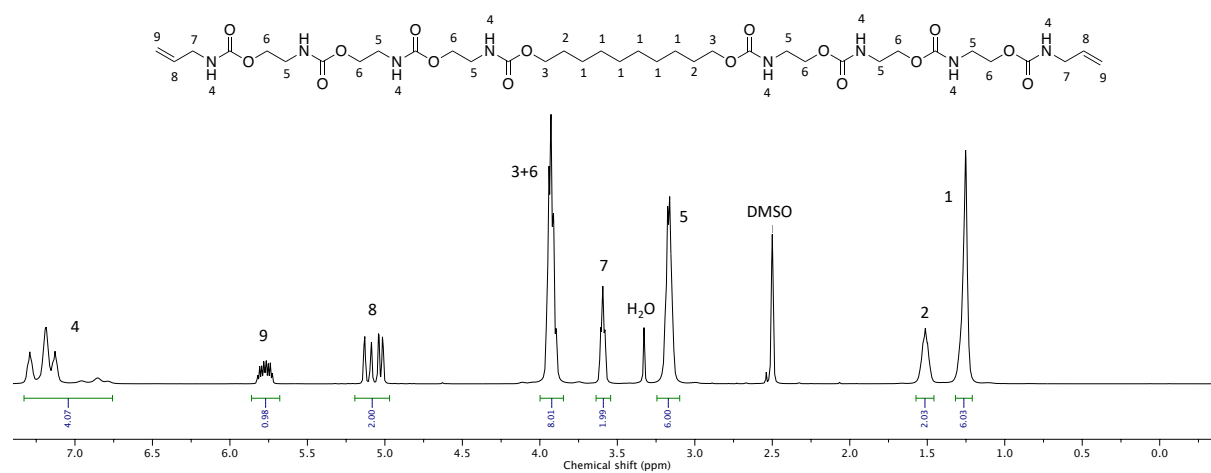


Figure S10: NMR spectrum of H<sub>8</sub>-ene.

## B<sub>8</sub>-OH

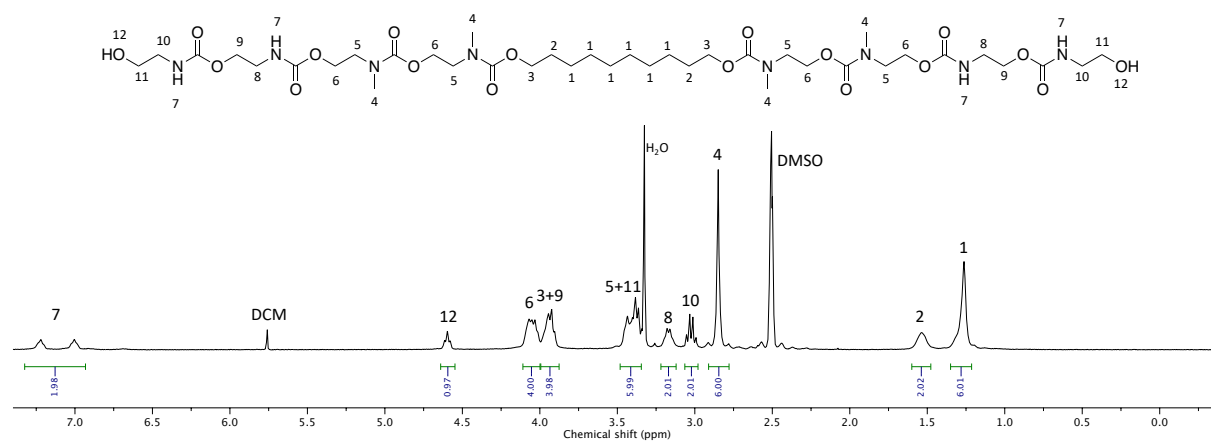


Figure S11: NMR spectrum of B<sub>8</sub>-OH.

## B<sub>8</sub>-ene

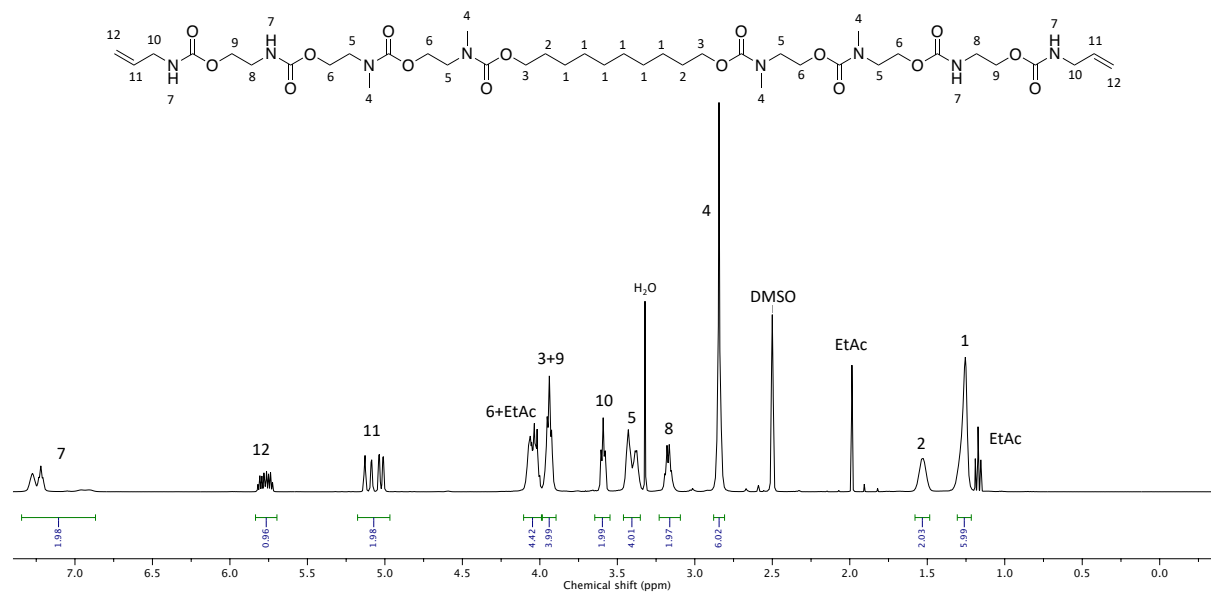


Figure S12: NMR spectrum of B<sub>8</sub>-ene.

## A<sub>8</sub>-OH

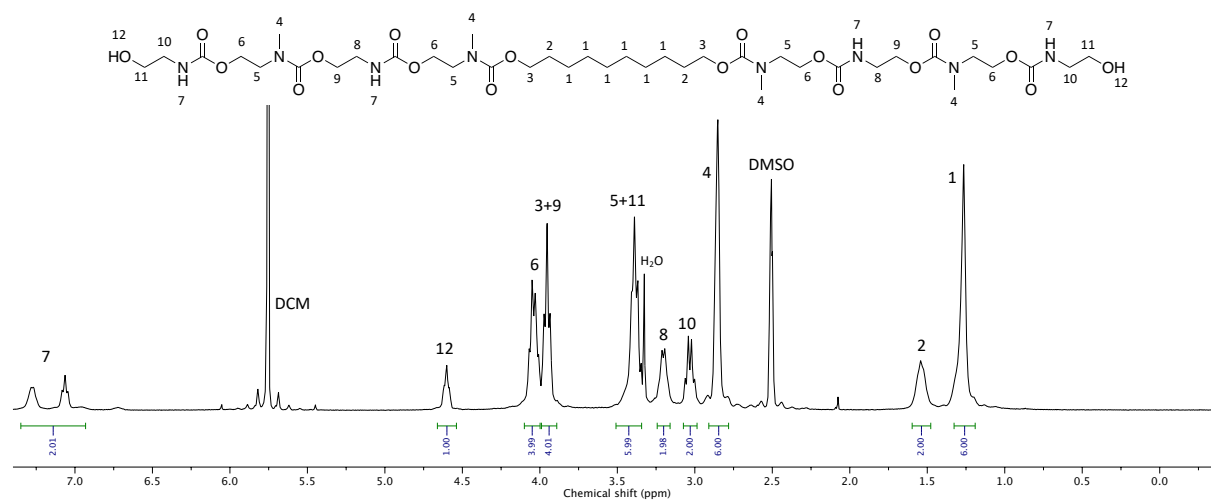


Figure S13: NMR spectrum of A<sub>8</sub>-OH.

## A<sub>8</sub>-ene

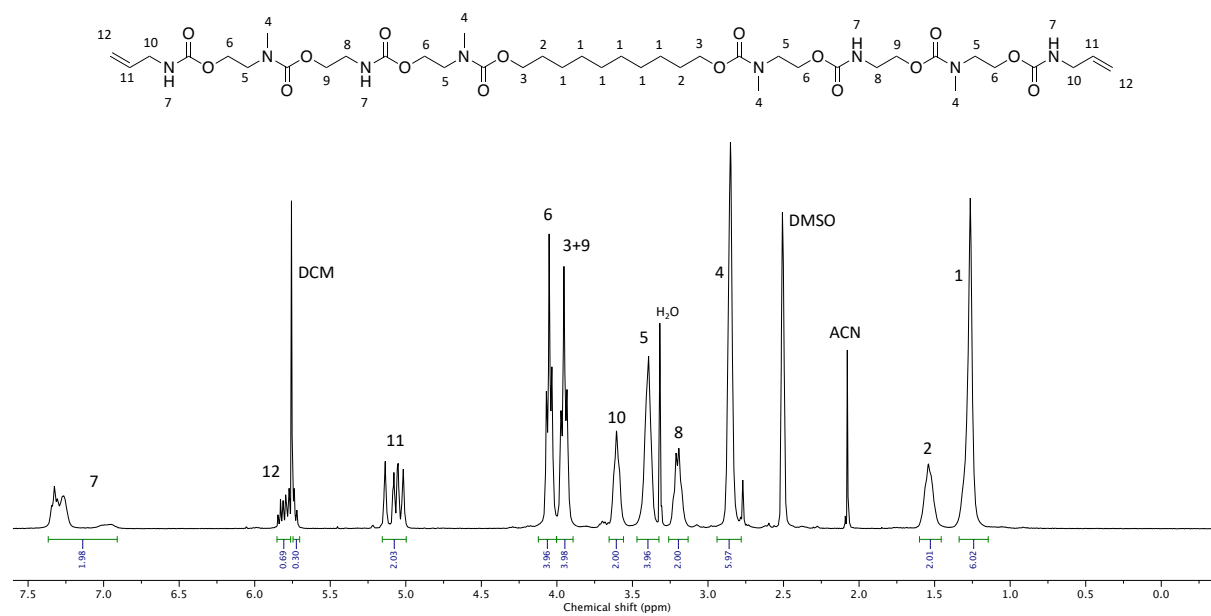


Figure S14: NMR spectrum of A<sub>8</sub>-ene.

# Electrospray Ionization – Mass Spectrometry (ESI-MS)

## **M<sub>8</sub>-OH**

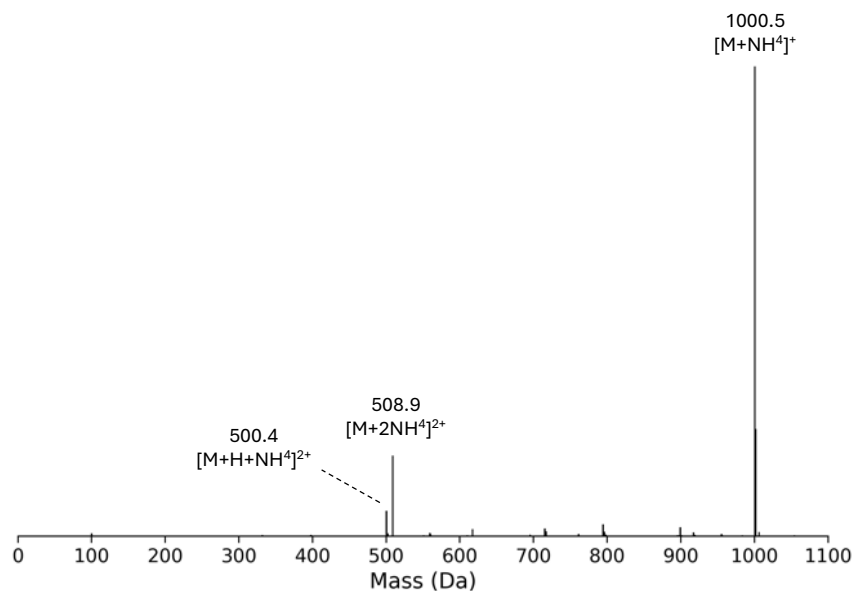
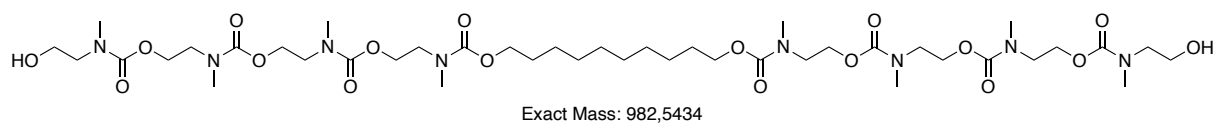


Figure S15: ESI-MS spectrum of M<sub>8</sub>-OH.

## **M<sub>8</sub>-ene**

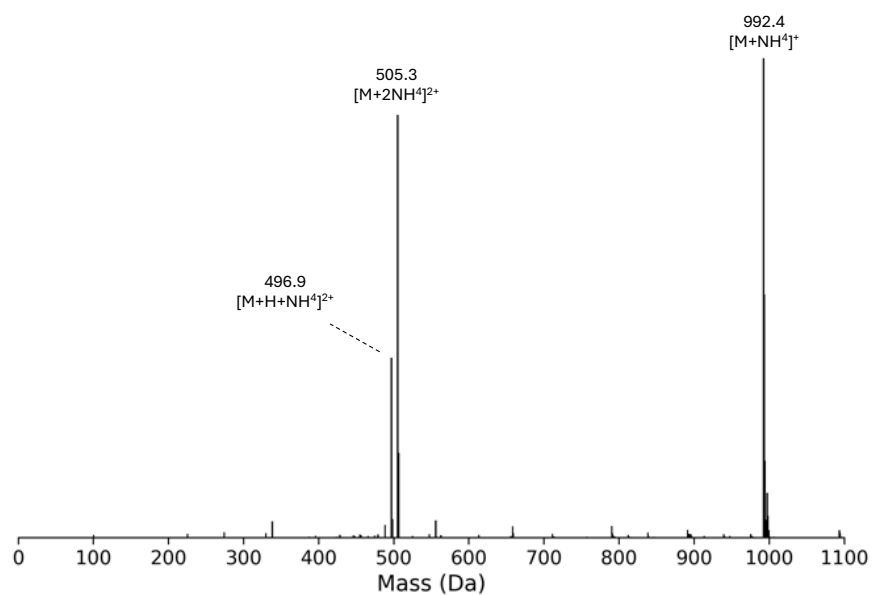
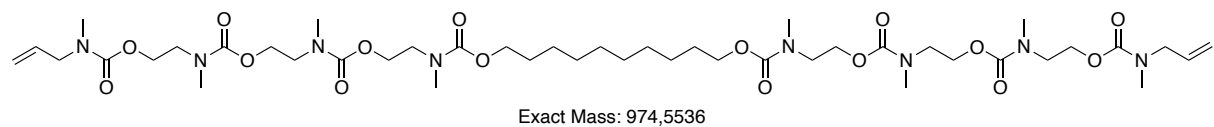


Figure S16: ESI-MS spectrum of M<sub>8</sub>-ene.

### H<sub>8</sub>-OH

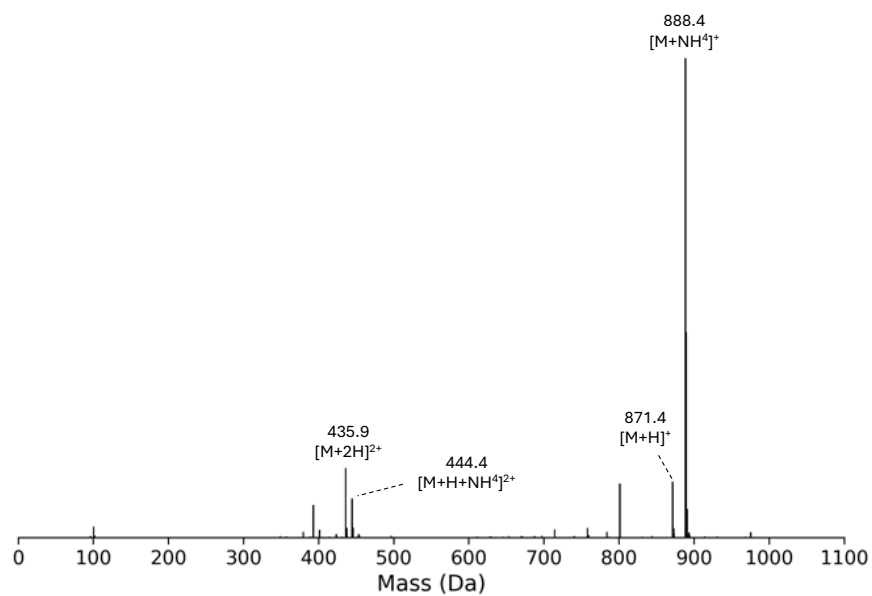
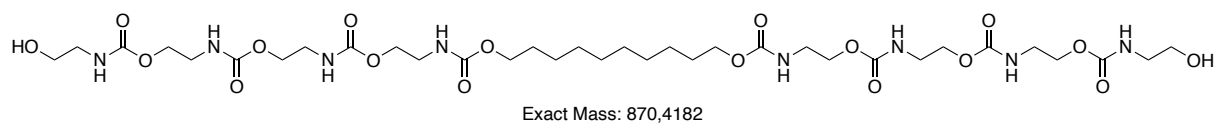


Figure S17: ESI-MS spectrum of H<sub>8</sub>-OH.

### H<sub>8</sub>-ene

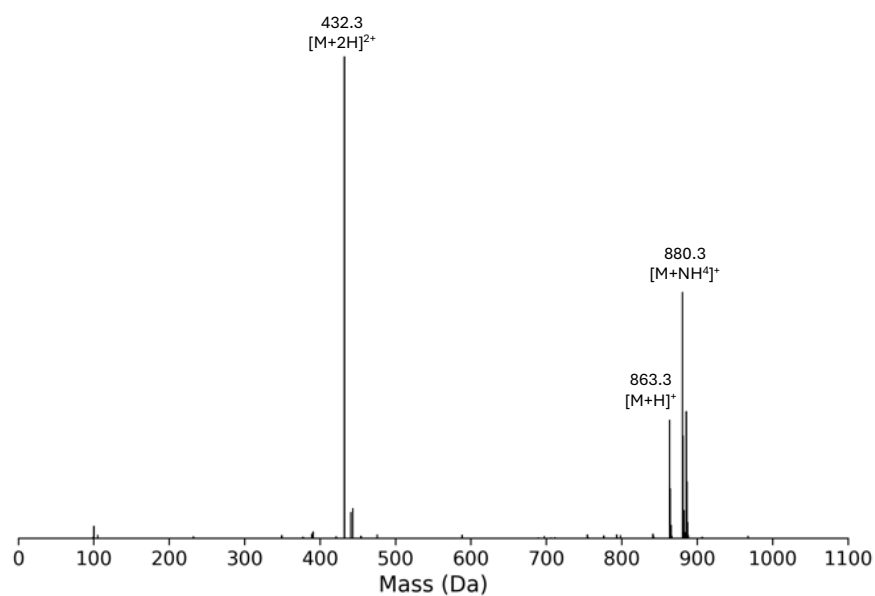
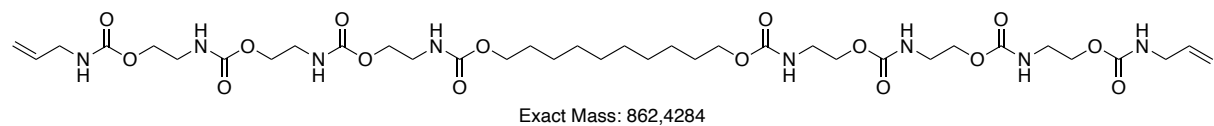


Figure S18: ESI-MS spectrum of H<sub>8</sub>-ene.

### B<sub>8</sub>-OH

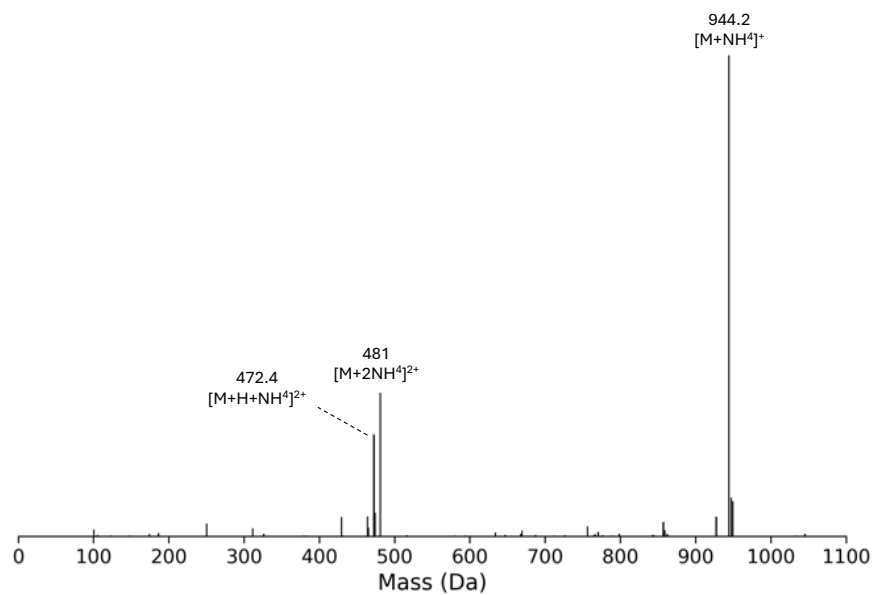
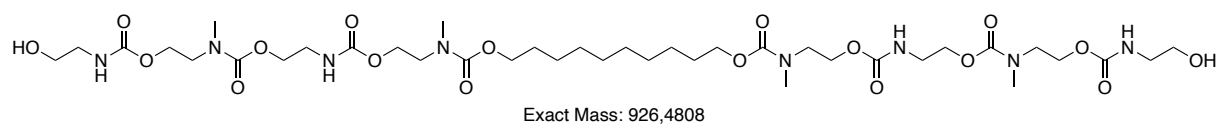


Figure S19: ESI-MS spectrum of B<sub>8</sub>-OH.

### B<sub>8</sub>-ene

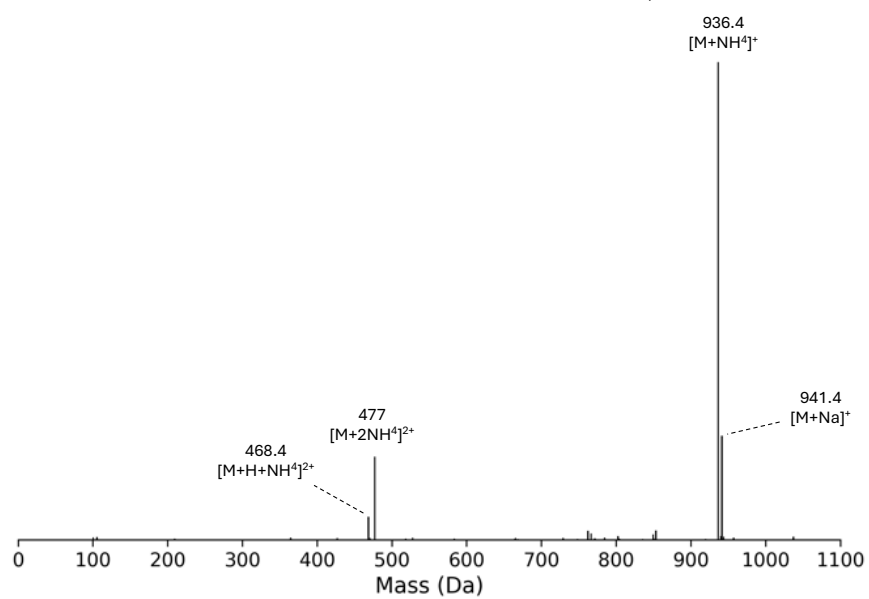
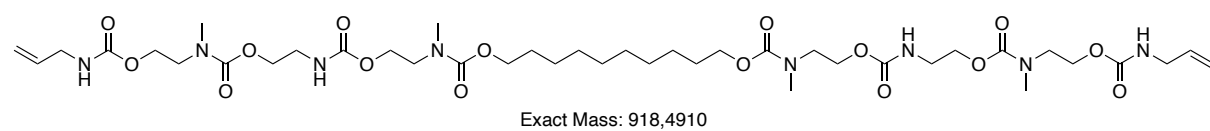


Figure S20: ESI-MS spectrum of B<sub>8</sub>-ene.



# SEC

## $M_x$ series:

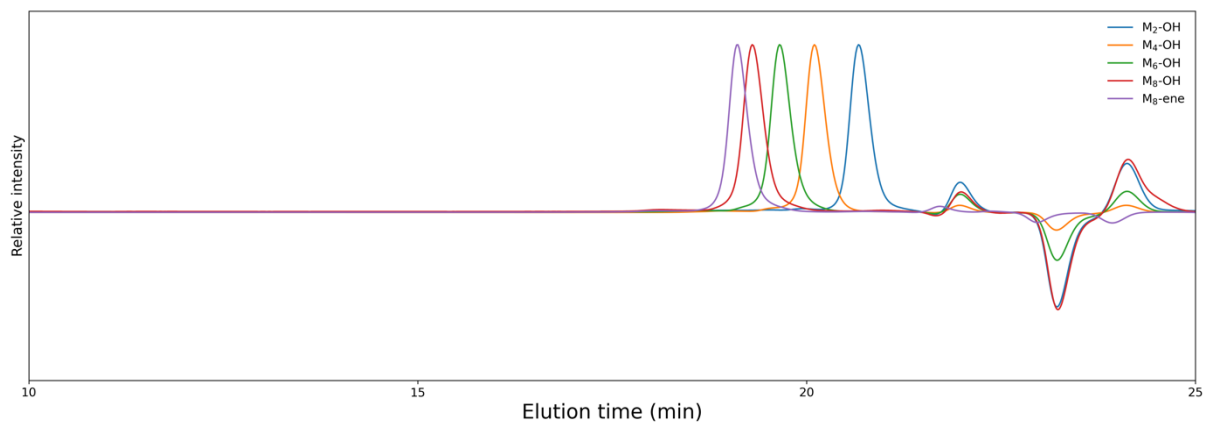


Figure S23: SEC traces of the methyl-substituted series.

## $H_x$ series:

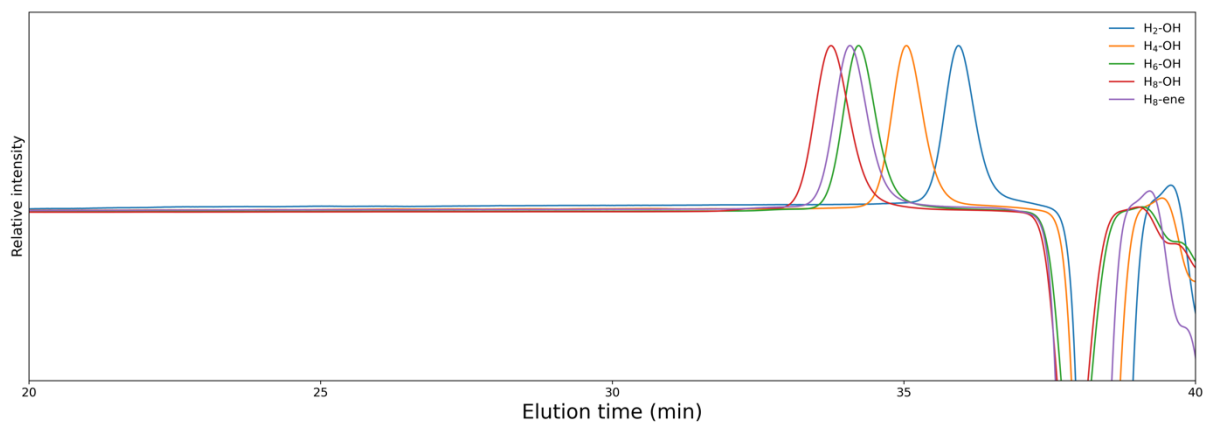


Figure S24: SEC traces of the non-substituted series.



**B<sub>x</sub> series:**

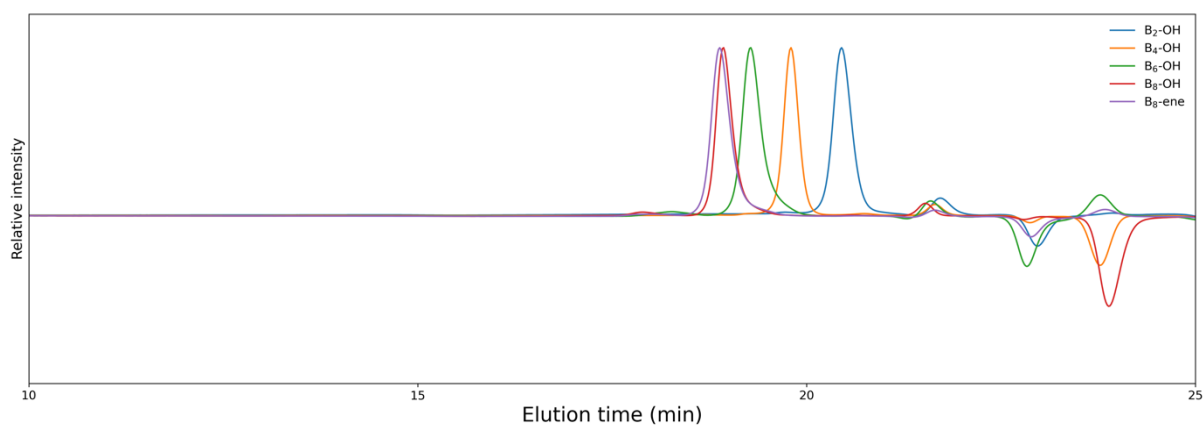


Figure S25: SEC traces of the blocky copolymer series.

**A<sub>x</sub> series:**

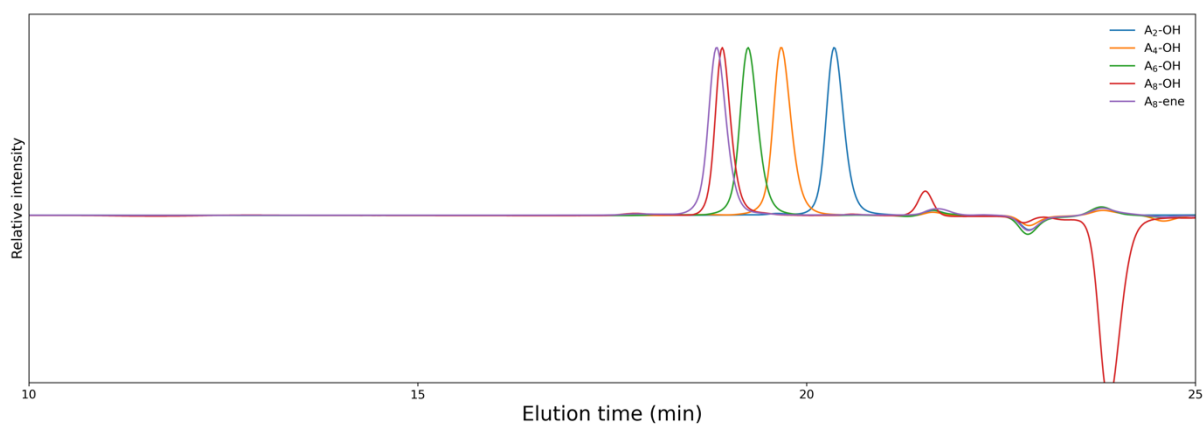


Figure S26: SEC traces of the alternating copolymer series.

DSC

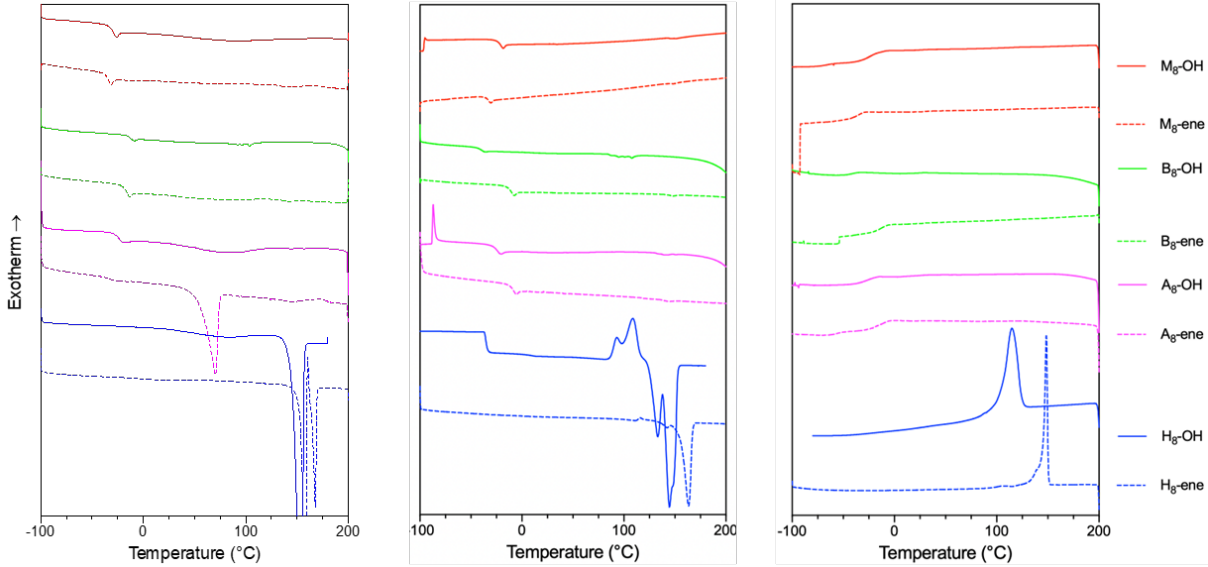


Figure S27: From left to right: DSC-curves of the first heating run, second heating run, and cooling performed at a rate of 10K/min.

## TGA

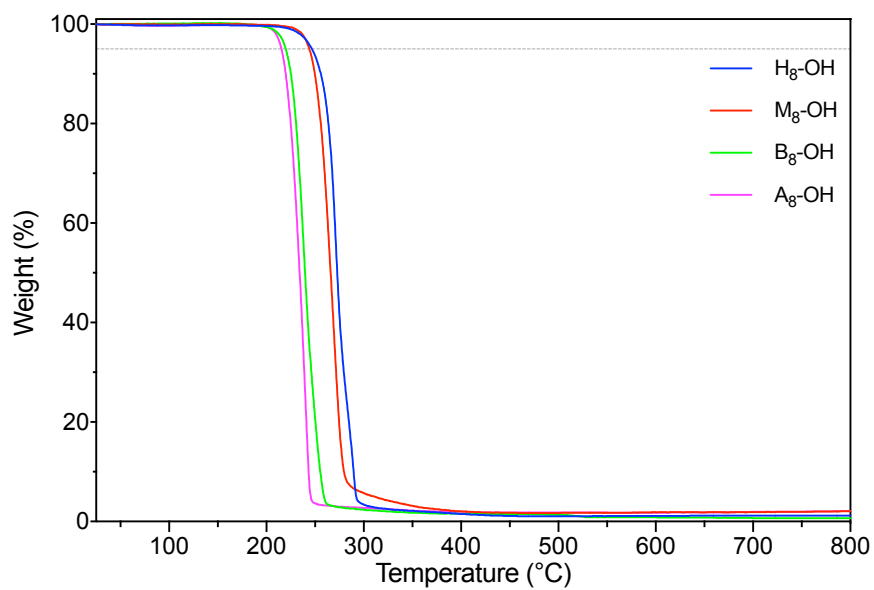


Figure S28: TGA measurements of the OH-terminated octamers.

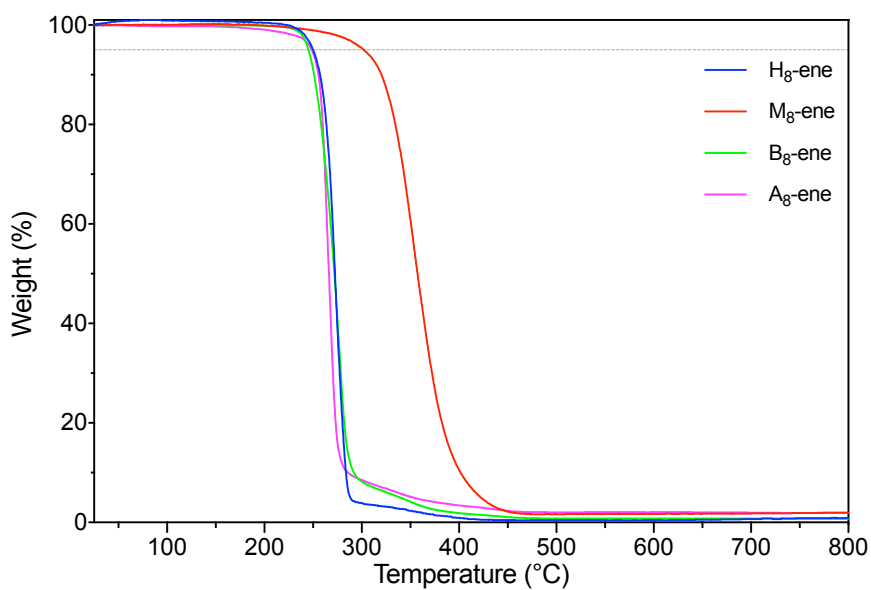


Figure S29: TGA measurements of the alkene-terminated octamers.

# Electrospray Ionization – Orbitrap Mass Spectrometry (ESI-Orbitrap)

## M<sub>2</sub>-OH

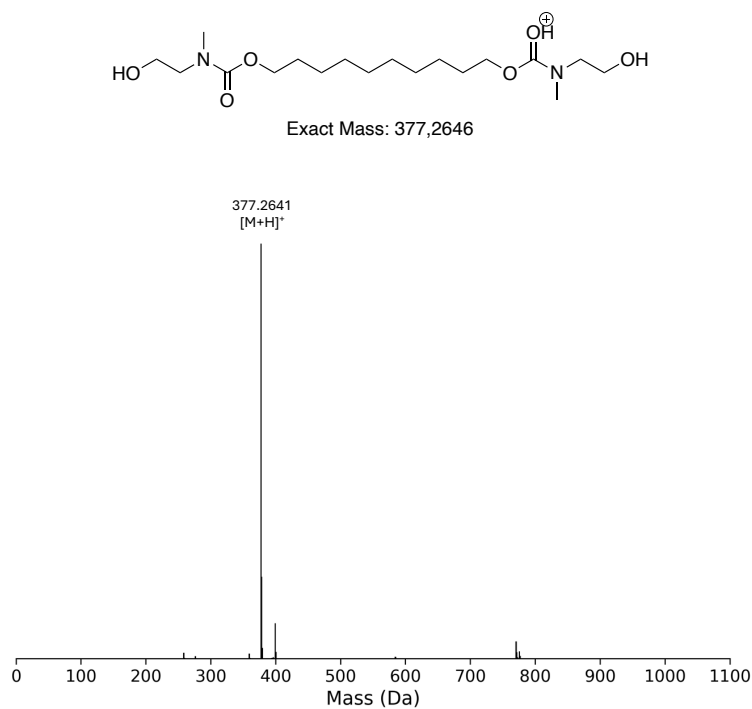


Figure S30: ESI-Orbitrap MS spectrum of M<sub>2</sub>-OH.

## M<sub>4</sub>-OH

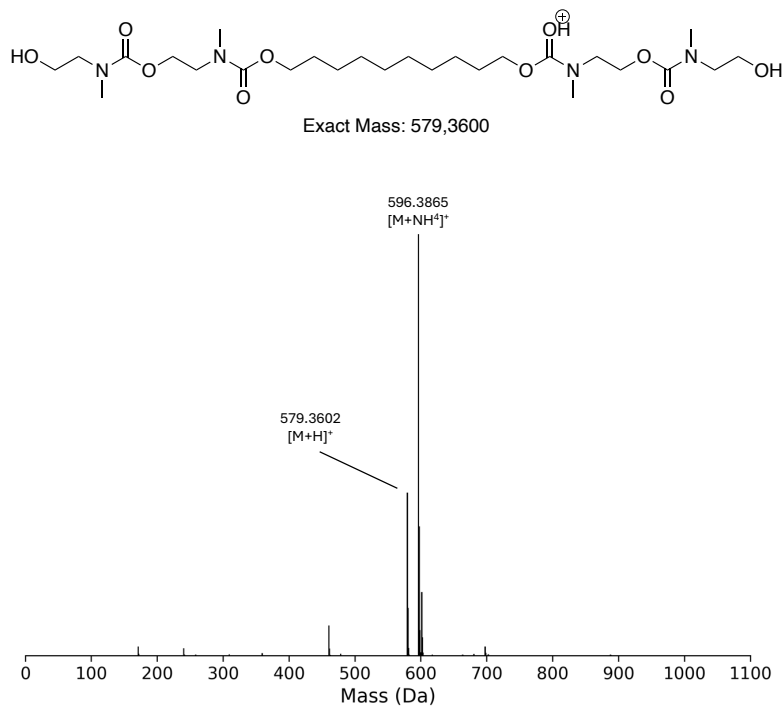


Figure S31: ESI-Orbitrap MS spectrum of M<sub>4</sub>-OH.



### M<sub>8</sub>-ene

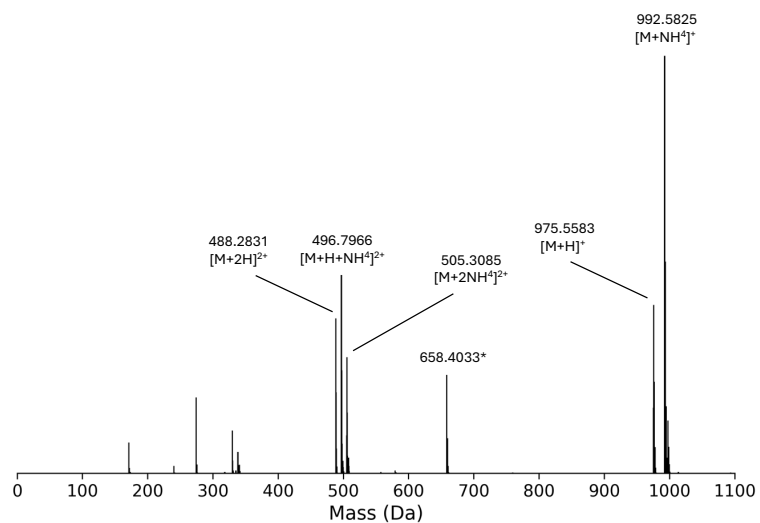
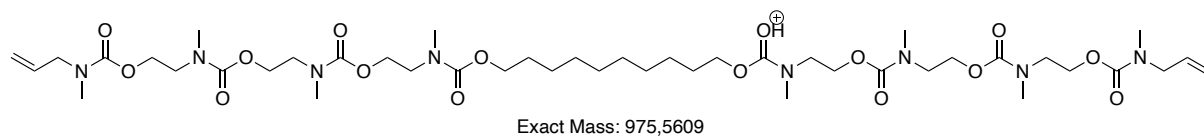


Figure S34: ESI-Orbitrap MS spectrum of M<sub>8</sub>-ene.

### H<sub>2</sub>-OH

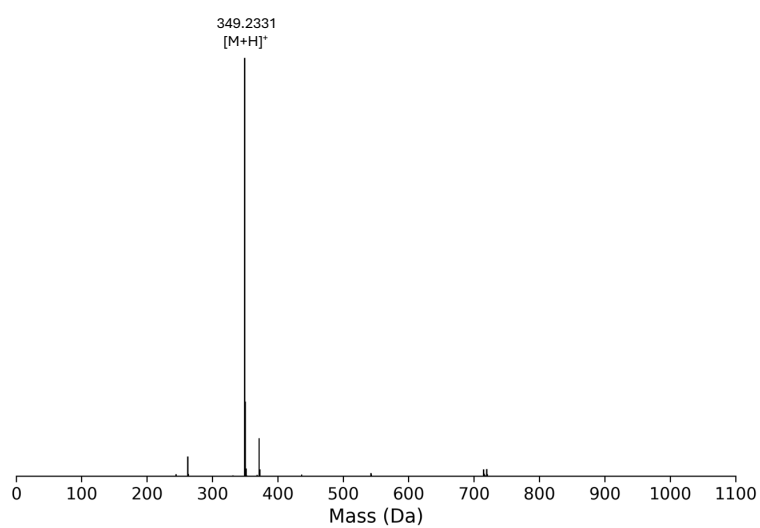
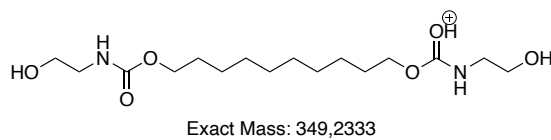


Figure S35: ESI-Orbitrap MS spectrum of H<sub>2</sub>-OH.

## H<sub>4</sub>-OH

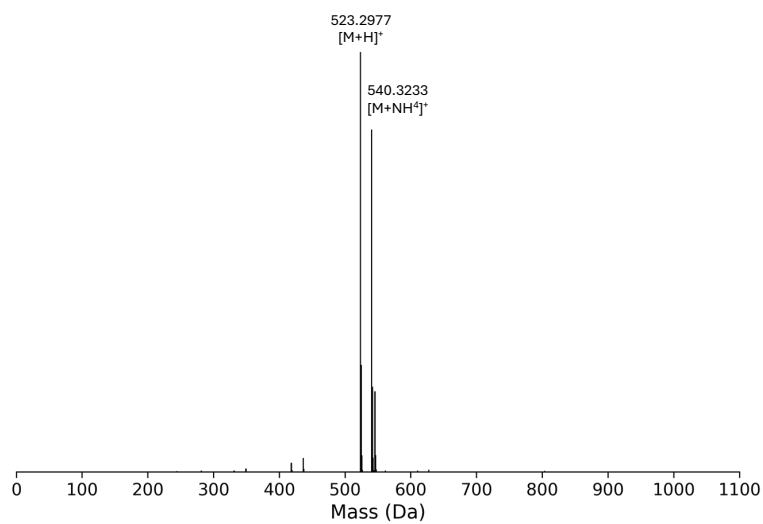
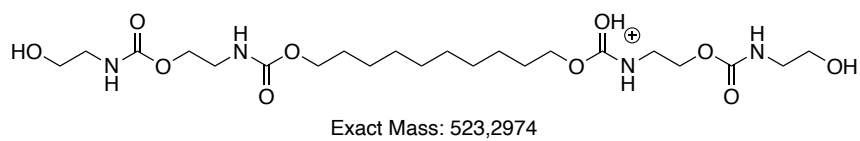


Figure S36: ESI-Orbitrap MS spectrum of H<sub>4</sub>-OH.

## H<sub>6</sub>-OH

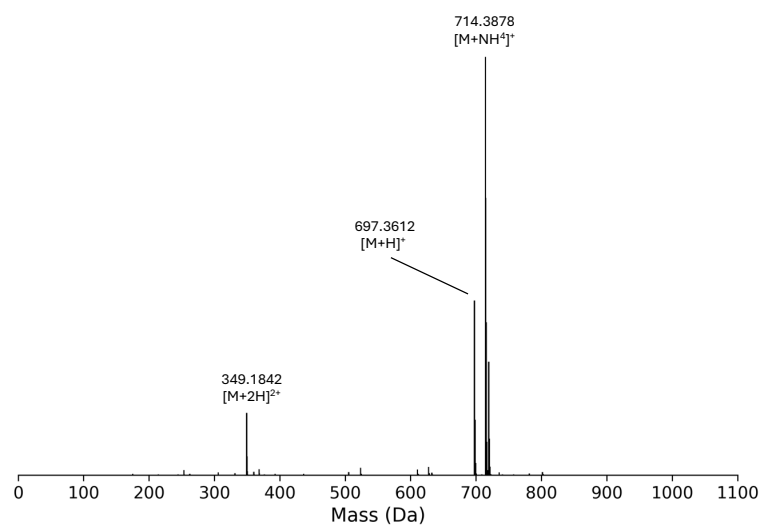
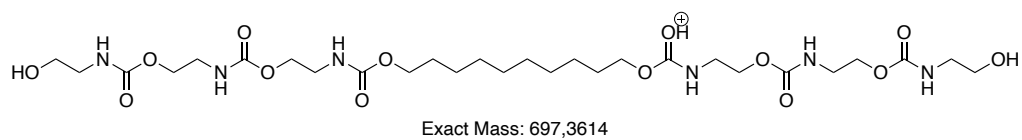


Figure S37: ESI-Orbitrap MS spectrum of H<sub>6</sub>-OH.

## H<sub>8</sub>-OH

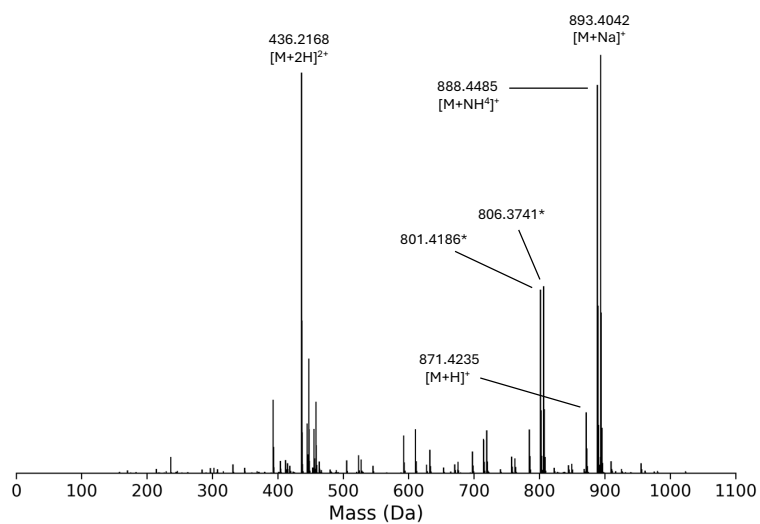
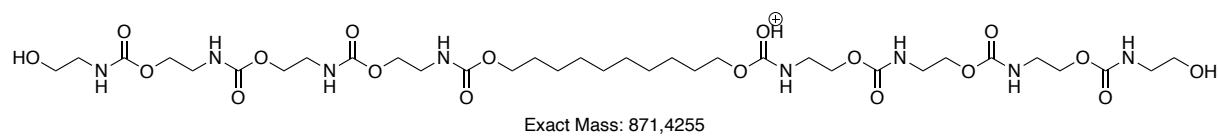


Figure S38: ESI-Orbitrap MS spectrum of H<sub>8</sub>-OH.

## H<sub>8</sub>-ene

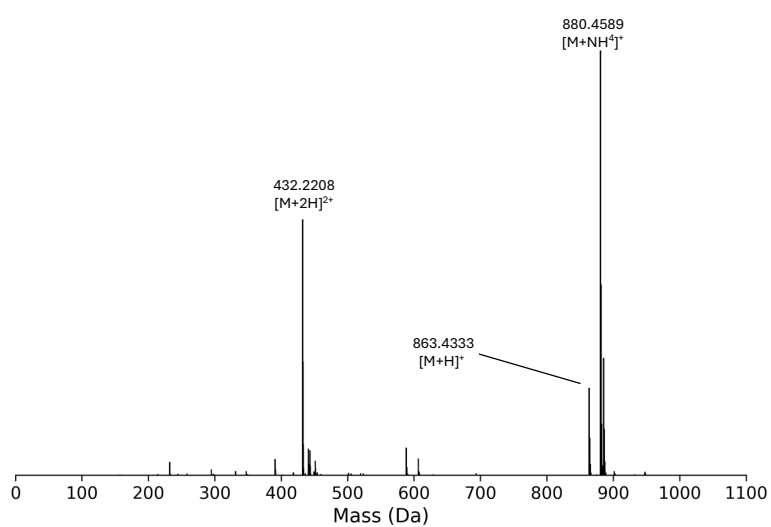
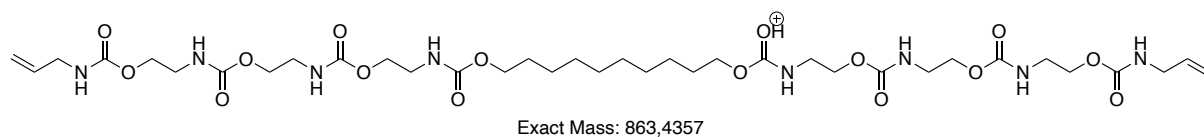


Figure S39: ESI-Orbitrap MS spectrum of H<sub>8</sub>-ene.



### B<sub>8</sub>-OH

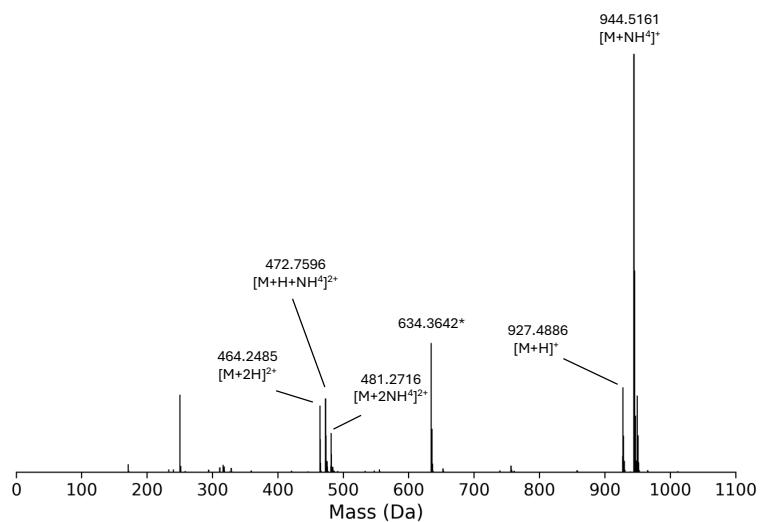
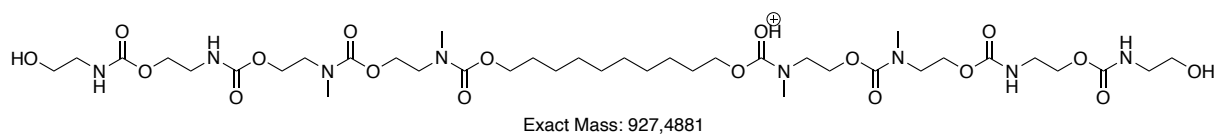


Figure S40: ESI-Orbitrap MS spectrum of B<sub>8</sub>-OH.

### B<sub>8</sub>-ene

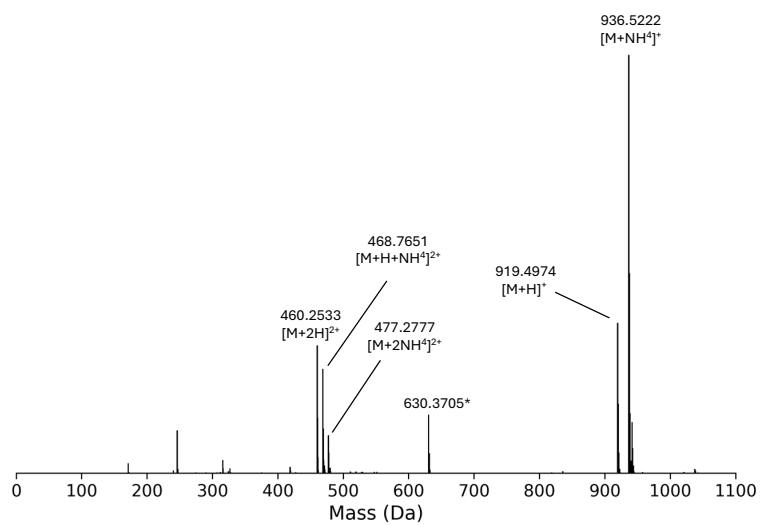
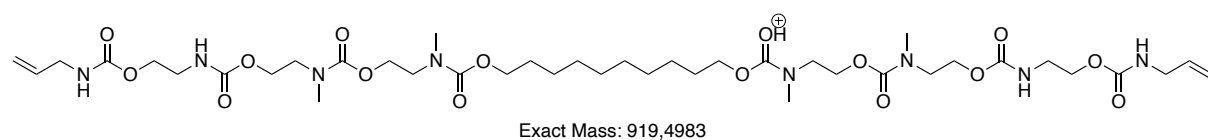


Figure S41: ESI-Orbitrap MS spectrum of B<sub>8</sub>-ene.



# Pyrolysis-GC-MS spectra

## M<sub>8</sub>-ene

Table S1: Degradation products of M<sub>8</sub>-ene detected in GC-MS.

| #  | RT(min) | Compound   | Area     | Area% |
|----|---------|--|----------|-------|
| 1  | 3.10    | N-Methylallylamine   | 8.69E+07 | 6.87  |
| 2  | 4.45    | Piperazine, 1,4-dimethyl-  | 1.44E+06 | 0.11  |
| 3  | 5.66    | 1,9-Decadiene  | 1.70E+07 | 1.35  |
| 4  | 7.03    | 2-Oxazolidinone, 3-methyl-   | 8.47E+08 | 67.0  |
| 5  | 7.88    | 1-Methylimidazolidin-2-one   | 1.86E+06 | 0.15  |
| 6  | 8.51    | 5-Dodecene, (E)-   | 6.04E+06 | 0.48  |
| 7  | 8.56    | 10-Undecen-1-ol  | 4.55E+07 | 3.60  |
| 8  | 8.62    | 1-Decanol  | 3.88E+06 | 0.31  |
| 9  | 8.86    | Carbamic acid, (2-amino-1-methyl-2-oxoethyl)-, 1,1-dimethylethyl ester | 6.42E+07 | 5.08  |
| 10 | 9.43    | 3-Amino-1-propanol, N,O-diacetyl-                                      | 4.81E+06 | 0.38  |
| 11 | 10.27   | N-Allyl-2,2,N-trimethylpropionamide                                    | 5.13E+05 | 0.04  |
| 12 | 10.35   | 1-Butanamine, N-methyl-N-2-propenyl-                                   | 5.68E+05 | 0.04  |
| 13 | 10.57   | 2-Nonene, (E)-   | 1.57E+06 | 0.12  |
| 14 | 11.02   | 11-Tetradecen-1-ol, (E)-   | 1.61E+06 | 0.13  |
| 15 | 11.30   | 1,10-Decanediol  | 2.15E+07 | 1.70  |
| 16 | 12.33   | 1-Propanoylpyrrolidine-2-carboxylic acid                               | 1.66E+06 | 0.13  |
| 17 | 12.78   | Carbamic acid, N-methyl-N-ethyl-, decyl ester                          | 3.02E+06 | 0.24  |
| 18 | 12.89   | 10-Undecen-1-al, 2-methyl-   | 5.01E+07 | 3.96  |
| 19 | 12.93   | Carbonic acid, allyl heptyl ester                                      | 5.59E+06 | 0.44  |
| 20 | 13.19   | Dodecanal  | 8.26E+05 | 0.07  |
| 21 | 13.34   | Glycine, N-allyloxycarbonyl-, undec-10-enyl ester                      | 1.67E+07 | 1.32  |
| 22 | 13.53   | Carbonic acid, but-3-yn-1-yl undecyl ester                             | 9.48E+06 | 0.75  |
| 23 | 13.69   | Pent-4-enoyl amide, 2-methyl-N-butyl-                                  | 7.22E+06 | 0.57  |
| 24 | 13.87   | Glycine, N-allyloxycarbonyl-, tetradecyl ester                         | 1.06E+07 | 0.84  |
| 25 | 14.47   | Carbamic acid, N-methyl-N-dodecyl-, (1R)-(-)-menthyl ester             | 7.87E+05 | 0.06  |
| 26 | 14.58   | Succinic acid, dec-4-enyl pentyl ester                                 | 3.66E+05 | 0.03  |
| 27 | 14.65   | Propanamide, N-(1,1-dimethylethyl)-2,2-dimethyl-                       | 1.73E+07 | 1.37  |
| 28 | 15.12   | Carbonic acid, allyl octyl ester                                       | 1.58E+07 | 1.25  |
| 29 | 15.16   | Glycine, N-allyloxycarbonyl-, nonyl ester                              | 1.19E+07 | 0.94  |
| 30 | 15.53   | Cyclopentanecarboxylic acid, octyl ester                               | 9.12E+06 | 0.72  |

## H<sub>8</sub>-ene

Table S2: Degradation products of H<sub>8</sub>-ene detected in GC-MS.

| # | RT (min) | Compound   | Area     | Area% |
|---|----------|--|----------|-------|
| 1 | 3.54     | Allyl isocyanate                                 | 2.63E+08 | 40.5  |
| 2 | 8.27     | Oxazolidin-2-one                                 | 2.27E+08 | 35.0  |
| 3 | 8.57     | 10-Undecen-1-ol                                  | 4223362  | 0.65  |
| 4 | 9.41     | Urea, N,N'-di-2-propenyl-                        | 3184949  | 0.49  |
| 5 | 10.26    | Carbamic acid, 2-propenyl-, 2-hydroxyethyl ester | 13092420 | 2.02  |
| 6 | 11.03    | 2,3-Dimethylsuccinic acid                        | 12742857 | 1.96  |
| 7 | 11.33    | 1,10-Decanediol                                  | 1.26E+08 | 19.4  |

## B<sub>8</sub>-ene

Table S3: Degradation products of B<sub>8</sub>-ene detected in GC-MS.

| # | RT (min) | Compound   | Area     | Area% |
|---|----------|--|----------|-------|
| 1 | 2.96     | Acetic acid, 2-(methylaminoethyl) ester          | 8.84E+06 | 0.96  |
| 2 | 3.20     | Allyl isocyanate                                 | 2.42E+08 | 26.2  |
| 3 | 6.99     | 2-Oxazolidinone, 3-methyl-                       | 5.38E+08 | 58.4  |
| 4 | 7.89     | 3-Methylpiperidin-2-one                          | 2.00E+07 | 2.17  |
| 5 | 8.12     | Oxazolidin-2-one                                 | 4.63E+07 | 5.03  |
| 6 | 10.51    | Carbamic acid, 2-propenyl-, 2-hydroxyethyl ester | 1.55E+06 | 0.17  |
| 7 | 11.01    | 2,3-Dimethylsuccinic acid                        | 1.18E+07 | 1.29  |
| 8 | 11.32    | 1,10-Decanediol                                  | 5.28E+07 | 5.74  |

## A<sub>8</sub>-ene

Table S4: Degradation products of H<sub>8</sub>-ene detected in GC-MS.

| #  | RT(min) | Compound                                  | Area     | Area% |
|----|---------|---|----------|-------|
| 1  | 2.77    | Methylene chloride                        | 9.31E+07 | 6.12  |
| 2  | 3.35    | Allyl isocyanate                          | 5.04E+08 | 33.1  |
| 3  | 7.03    | 2-Oxazolidinone, 3-methyl-                | 7.39E+08 | 48.5  |
| 4  | 7.76    | 2-Propanol, 1-(dibutylamino)-             | 1.91E+07 | 1.25  |
| 5  | 7.91    | 3-Methylpiperidin-2-one                   | 8.00E+07 | 5.26  |
| 6  | 8.11    | Oxazolidin-2-one                          | 8.55E+06 | 0.56  |
| 7  | 8.58    | 1,11-Undecanediol                         | 3.51E+06 | 0.23  |
| 8  | 9.48    | Urea, N,N'-di-2-propenyl-                 | 1.51E+06 | 0.10  |
| 9  | 10.39   | 1,1':3',1''-Tercyclopentane               | 1.37E+06 | 0.09  |
| 10 | 10.50   | Carbonic acid, ethyl hexyl ester          | 2.49E+06 | 0.16  |
| 11 | 10.79   | dl-Alanyl-dl-.alpha.-amino-n-butyric acid | 6.47E+06 | 0.43  |
| 12 | 11.01   | 2,3-Dimethylsuccinic acid                 | 9.26E+06 | 0.61  |
| 13 | 11.32   | 1,10-Decanediol                           | 5.43E+07 | 3.57  |