Electronic Supplementary Information:

Dual Side Chain Control in the Synthesis of Novel Sequence-Defined Oligomers through the Ugi Four-Component Reaction†

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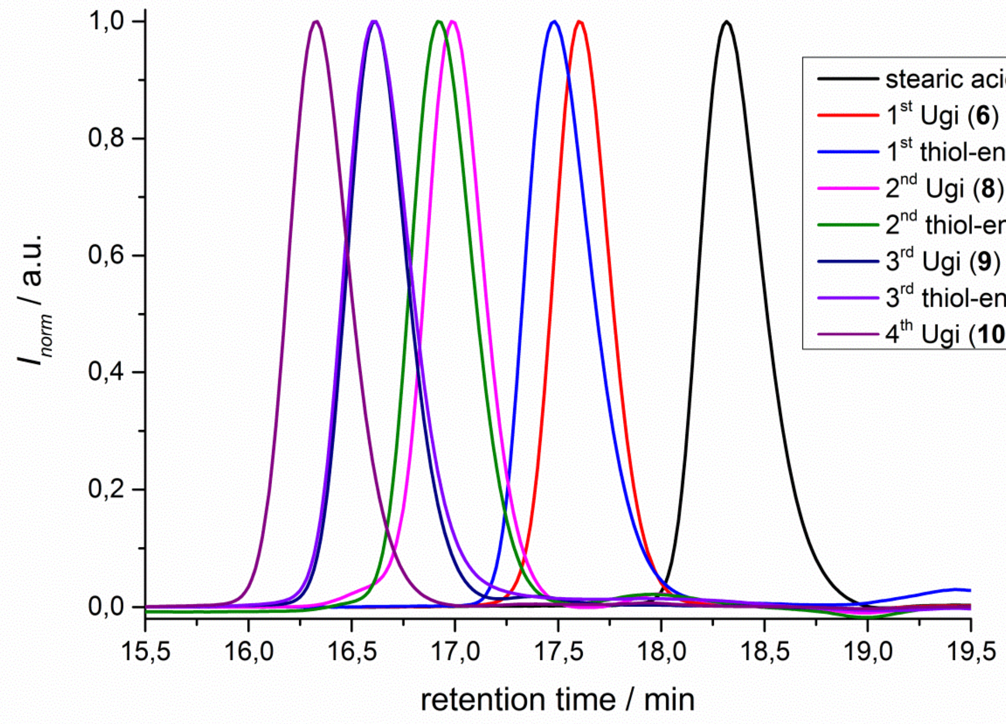
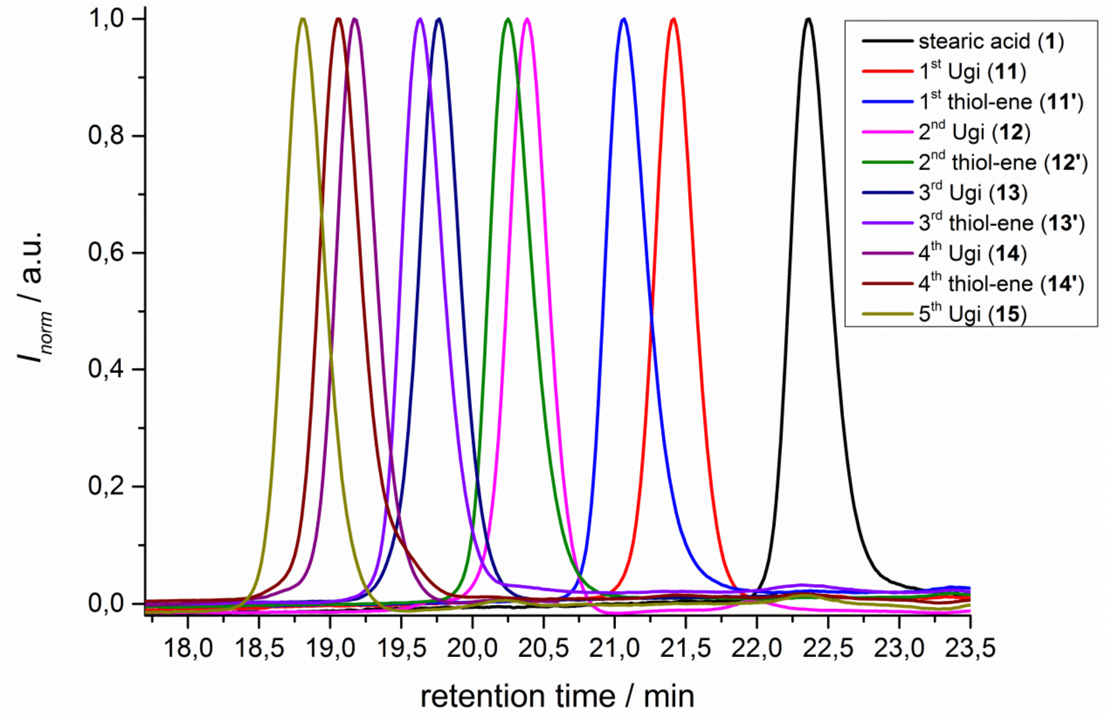
Content

1. GPC traces after the U-4CRs and thiol-ene additions:

1.1. Variation of the amine component:



1.1. Variation of the amine and the isocyanide component:



2. Experimental section:

2.1.Materials:

The following chemicals were used as received: 10-undecenal (>90 %, Sigma Aldrich), 3-mercaptopropionic acid (99 %, Sigma Aldrich), cyclohexyl isocyanide (98 %, Sigma Aldrich), *t*-butyl isocyanide (98 %, Sigma Aldrich), stearic acid (95 %, Sigma Aldrich), 2,2 dimethoxy-2-phenylacetophenone (DMPA, 99 %, Sigma Aldrich), 1-pentyl isocyanide (97 %, Sigma Aldrich), *n*-butyl isocyanide (98 %, Acros Organics), propylamine (> 99 %, Sigma Aldrich), benzylamine (> 99.5 %, Sigma Aldrich), cyclohexylamine (99 %, Sigma Aldrich), ethanolamine (> 98 %, Sigma Aldrich), 4-methoxybenzylamine (98 %, Sigma Aldrich), benzyl isocyanide (98 %, Sigma Aldrich), isopropylamine (> 98.5 %, 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), sodium hydrogen carbonate (> 95 %, Sigma Aldrich), sodium sulfate (> 99 %, anhydrous, Sigma Aldrich). Solvents were used without further purification, unless otherwise noted.

2.2.Characterization:

NMR spectra were recorded on a Bruker AVANCE DPX spectrometer operating at 300 MHz for ^{1}H- and at 75 MHz for ^{13}C-measurements. $CDCl_3$ was used as solvent and the resonance signal at 7.26 ppm (^{1}H) and 77.16 ppm (^{13}C) served as reference for the chemical shift δ.

Oligomers (**6-10**) 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 PLgel 5 µm Mixed-D columns (8 × 300 mm) and a guard column (8 × 50 mm) were used. Detection was done by a refractive index detector operating in THF (flow rate 1.0 mL min^{-1}). For calibration linear poly(methylmethacrylate) standards (Agilent) ranging from 875 to 1 677 000 Da were used.

Oligomers (**11-15**) 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) were used. Detection was done by a refractive index detector operating in THF (flow rate 1.0 mL min^{-1}). For calibration linear poly(methylmethacrylate) standards (Agilent) ranging from 875 to 1 677 000 Da were used.

Infrared spectra (IR) were recorded on a Bruker Alpha-p instrument in a frequency range from 3998 to 374 cm^{-1} applying KBr and 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: $[(M+H)]^+$.

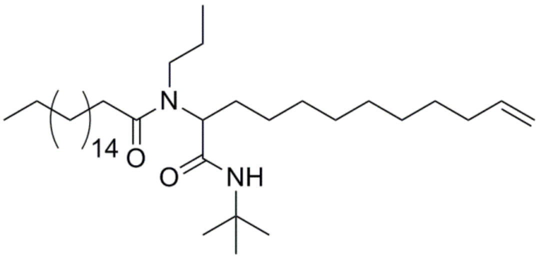
UV-Lamp: Thiol-ene additions were conducted using two handheld UV-lamps from Vetter Laborgeräte (Wiesloch) UVKL4U operating at 320 nm (4 W).

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

3. Syntheses:

3.1.Variation of the amine component:

1st Ugi reaction



1.34 g 10-Undecenal **2** (7.98 mmol, 1.70 eq.) were stirred for 15 minutes with 0.47 g propylamine **4** (7.88 mmol, 1.70 eq.) at room temperature. Subsequently, 1.30 g stearic acid **1** (4.59 mmol, 1.00 eq.), 0.70 g *t*-butyl isocyanide **5** (8.43 mmol, 1.80 eq.) and 5.25 mL (0.87 M) methanol were added and stirred for 24 hours at room temperature. The reaction was followed by GPC and after completion of the reaction, the solvent was removed under reduced pressure and the product was purified by column chromatography (hexane / ethylacetate 30:1 → 12:1). Product **6** was obtained as a colorless liquid in a yield of 91 % (2.42 g).

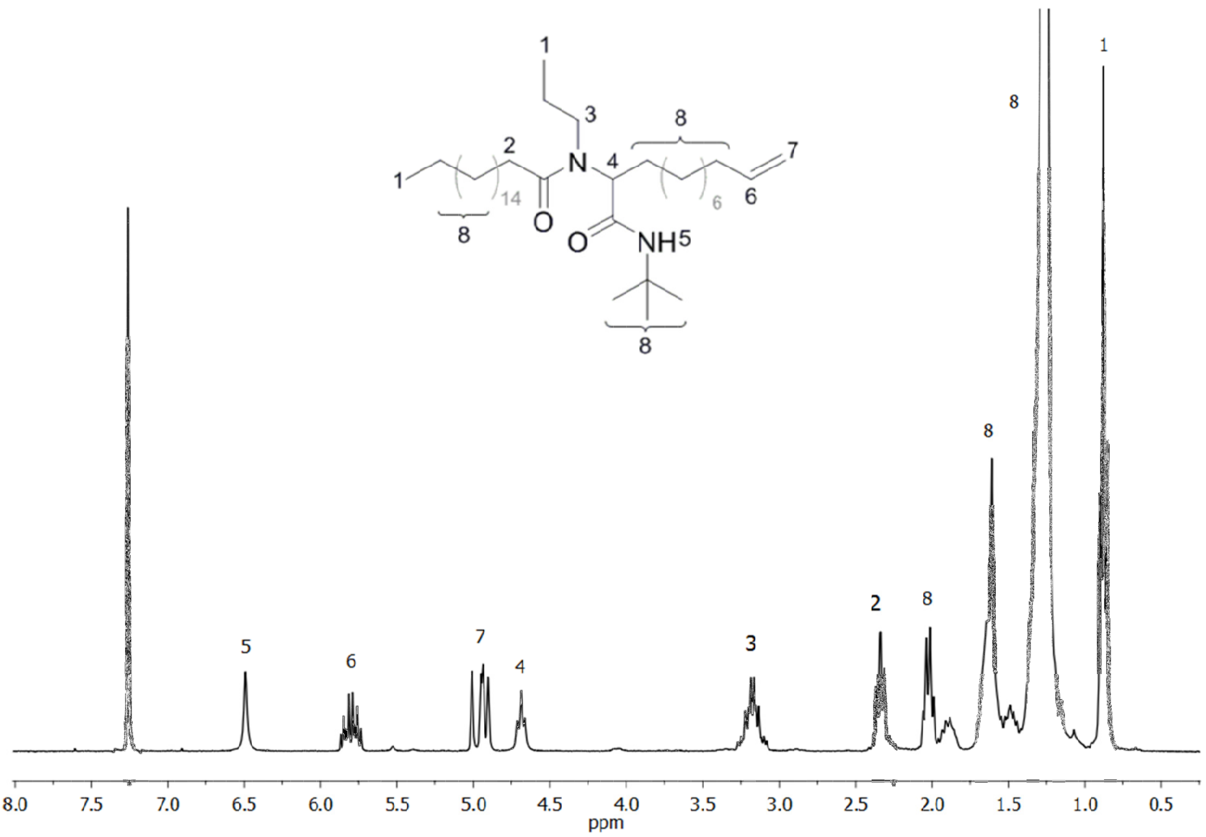
^{1}H NMR: (300 MHz, $CDCl_3$) δ /ppm: 6.49 (s, 1H, NH, ^{5}), 5.80 (ddt, J = 16.9, 10.2, 6.7 Hz, 1H, CH, ^{6}), 4.95 (dd, J = 17.3, 13.8 Hz, 2H, CH_2, ^{7}), 4.69 (t, J = 7.6 Hz, 1H, CH, ^{4}), 3.30 – 3.06 (m, 2H, CH_2, ^{3}), 2.34 (dd, J = 8.1, 6.3 Hz, 2H, CH_2, ^{2}), 2.08 – 1.00 (m, 57H, 24 CH_2, 3 CH_3, ^{8}), 0.88 (t, J = 7.1 Hz, 6H, CH_3, ^{1}).

^{13}C NMR: (75 MHz, $CDCl_3$) δ /ppm: 175.0, 171.0, 139.3, 114.2, 58.2, 50.9, 50,0, 33.9, 33.7, 32.1, 29.8, 29.8, 29.7, 29.6, 29.6, 29.6, 29.5, 29.5, 29.5, 29.2, 29.0, 28.8, 28.0, 26.3, 25.9, 23.5, 22.8, 14.2, 11.6.

FAB-MS: $[C_{37}H_{73}O_2N_2]^+$ calculated: 577.5669, found: 577.5667.

IR: (ATR): ν [cm^{-1}] = 3312.0, 2920.7, 2851.4, 1682.5, 1625.3, 1534.7, 1454.0, 1362.3, 1225.0, 1112.5, 991.3, 907.1, 720.5, 470.5.

***R*$_f$:** (hexane / ethyl acetate (9:1)) = 0.44.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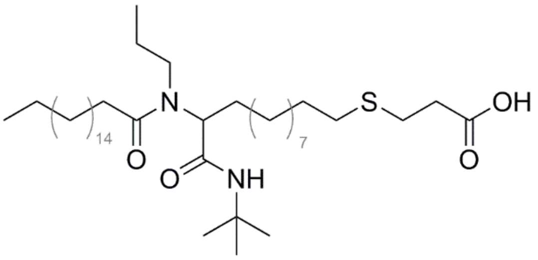
1st Thiol-ene addition



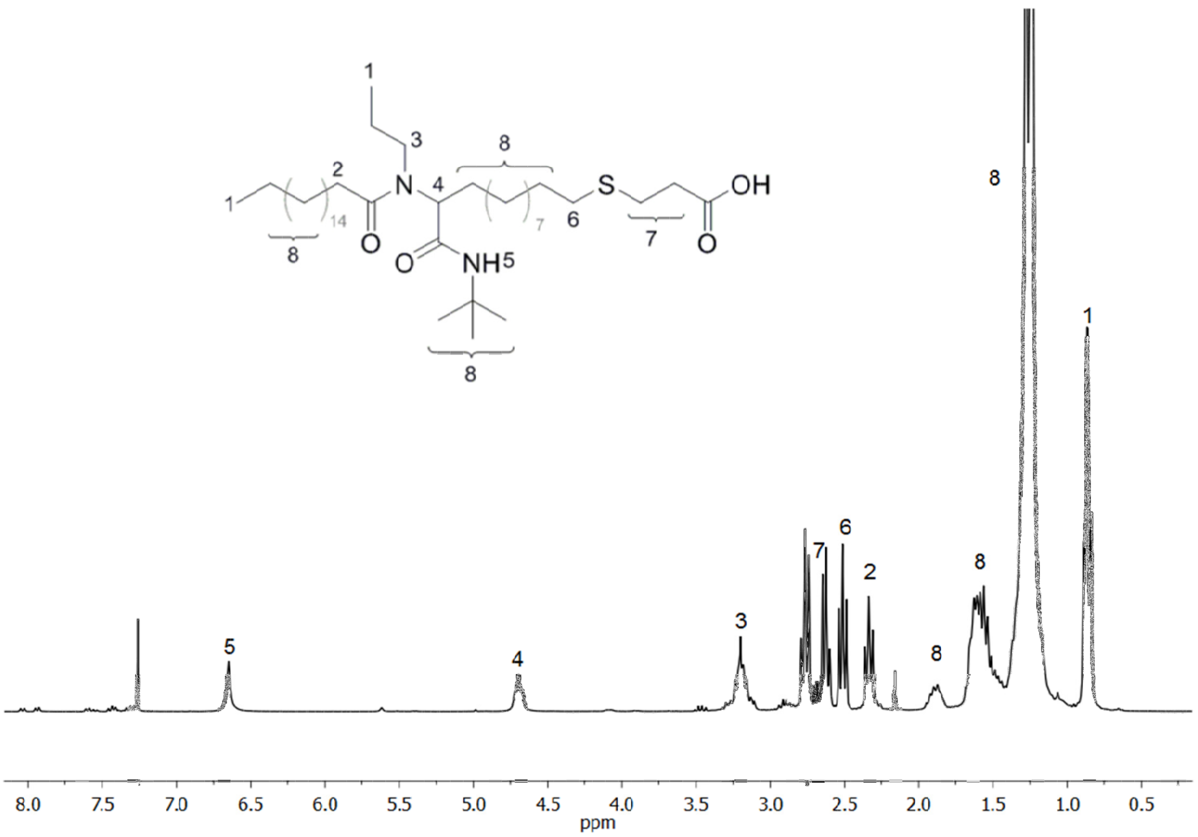
2.38 g of substance **6** (4.12 mmol, 1.00 eq.) were diluted with 2.20 g 3-mercaptopropionic acid **3** (20.7 mmol, 5.00 eq.) and 32 mg 2,2-dimethoxy-2-phenylacetophenone (DMPA) **7** (0.12 mmol, 3.00 mol%) were added. The reaction mixture was stirred under UV irradiation at room temperature for one hour. Full conversion of the double bonds was detected *via* ^{1}H NMR. The excess of 3-mercaptopropionic acid was removed by vacuum distillation and the residue was dissolved in diethyl ether. The organic layer was washed with water (3 × 100 mL) and brine (1 × 100 mL) and dried over sodium sulfate. After removing the solvent under reduced pressure, the desired product **6'** was obtained as yellowish oil in a yield of 91 % (2.56 g).

^{1}H NMR (300 MHz, $CDCl_3$) δ / ppm: 6.65 (s, 1H, NH, ^{5}), 4.69 (t, J = 7.1 Hz, 1H, CH, ^{4}), 3.34 – 3.07 (m, 2H, CH_2, ^{3}), 2.81 – 2.57 (m, 4H, 2 CH_2, ^{7}), 2.51 (t, J = 7.3 Hz, 2H, CH_2, ^{6}), 2.33 (t, J = 7.5 Hz, 2H, CH_2, ^{2}), 2.00 – 0.74 (m, 67H, 26 CH_2, 5 CH_3, ^{8,1}).

^{13}C NMR (75 MHz, $CDCl_3$) δ / ppm: 175.9, 175.2, 170.9, 58.3, 51.0, 47.0, 34.7, 33.5, 32.1, 31.9, 29.7, 29.6, 29.5, 29.4, 29.4, 29.3, 29.0, 28.7, 28.5, 28.1, 26.7, 26.1, 25.7, 23.4, 23.4, 22.7, 14.1, 11.4.

FAB-MS: $[C_{40}H_{79}O_2N_4S]^+$ calculated: 683.6, found: 683.6.

IR: (ATR): ν [cm^{-1}] = 2920.3, 2850.8, 1717.2, 1681.4, 1621.5, 1535.9, 1454.5, 1363.8, 1223.8, 8993.3, 720.4, 634.4.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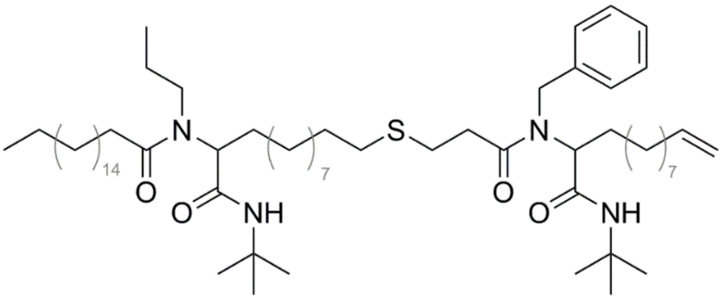
2^{nd} Ugi reaction



4.92 g of substance **6’** (7.20 mmol, 1.00 eq.) were stirred with 2.07 g 10-undecenal **2** (12.27 mmol, 1.70 eq.) and 1.34 g benzylamine (12.5 mmol, 1.70 eq.) in 7.2 mL methanol (1 M) at room temperature. Subsequently, 1.08 g *tert*-butyl isocyanide **5** (13.0 mmol, 1.80 eq.) were added and the mixture was stirred at room temperature for 24 hours. After completion of the reaction, the solvent was removed under reduced pressure and the crude product was purified by column chromatography. (hexane / ethyl acetate 12:1 → 3:1). Product **8** was obtained as yellowish oil in a yield of 76 % (5.62 g).

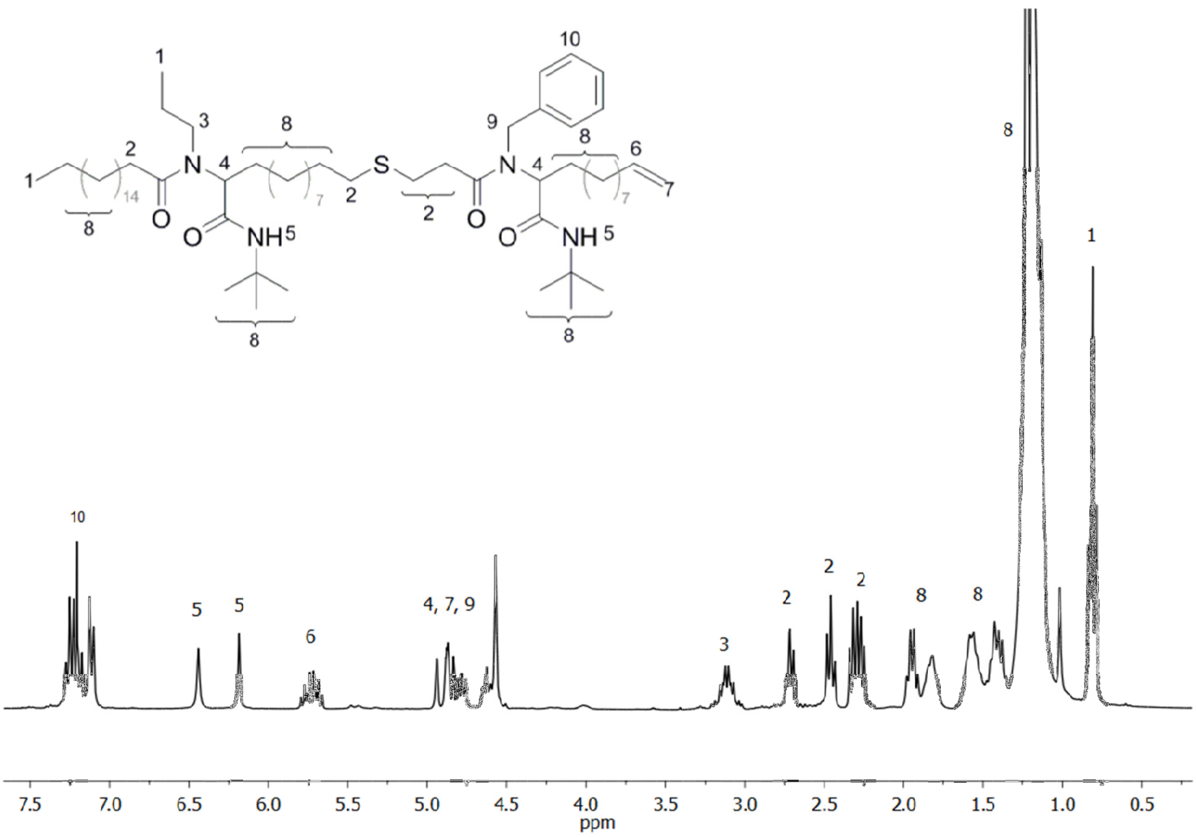
^{1}H NMR (300 MHz, $CDCl_3$) δ / ppm: 7.25 (ddd, J = 22.1, 14.5, 7.1 Hz, 5H, 5 CH aromatic, ^{10}), 6.50 (s, 1H, NH, ^{5}), 6.23 (s, 1H, NH, ^{5}), 5.89 – 5.68 (m, 1H, CH, ^{6}), 5.04 – 4.55 (m, 6H, 2 CH, 2 CH_2, ^{4,7,9}), 3.29 – 3.06 (m, 2H, CH_2, ^{3}), 2.85 – 2.69 (m, 2H, CH_2, ^{2}), 2.60 – 2.45 (m, 2H, CH_2, ^{2}), 2.42 – 2.27 (m, 4H, 2 CH_2, ^{2}), 2.08 – 0.99 (m, 84H, 33 CH_2, 6 CH_3, ^{8}), 0.87 (t, J = 7.1 Hz, 6H, 2 CH_3, ^{1}).

^{13}C NMR (75 MHz, $CDCl_3$) δ / ppm: 175.0, 173.9, 171.0, 169.9, 139.3, 137.8, 128.8, 127.4, 126.1, 114.22, 58.7, 51.3, 50.9, 48.2, 47.0, 34.4, 33.9, 33.7, 32.6, 32.0, 29.8, 29.8, 29.7, 29.7, 29.6, 29.6, 29.5, 29.5, 29.4, 29.3, 29.2, 29.0, 29.0, 28.8, 28.7, 28.5, 28.0, 28.0, 26.5, 26.3, 25.9, 23.5, 22.8, 14.2, 11.6.

FAB-MS: $[C_{63}H_{115}O_4N_4S]^+$ calculated: 1023.8632, found: 1023.8634.

IR: (ATR): ν [cm^{-1}] = 3322.0, 2920.9, 2851.2, 1680.2, 1625.9, 1536.9, 1452.3, 1419.2, 1390.2, 1361.7, 1224.6, 991.3, 907.5, 723.1, 695.7.

R_f: (hexane / ethyl acetate (3:1)) = 0.48.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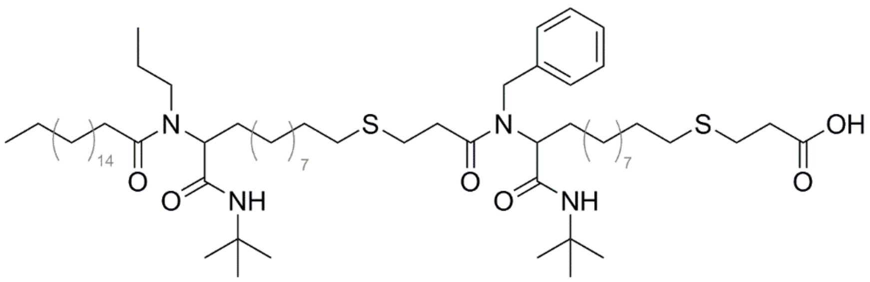
2nd Thiol-ene addition



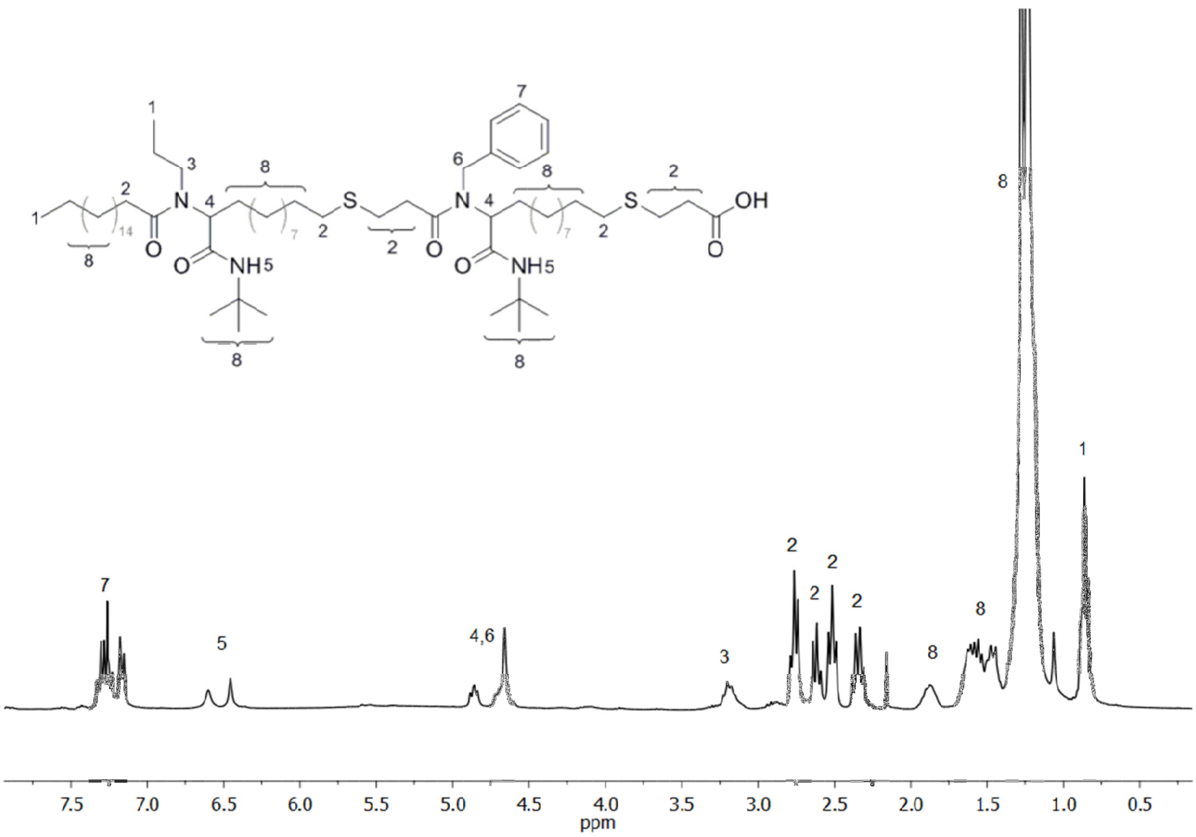
5.57 g of substance **8** (5.44 mmol, 1.00 eq.) were diluted with 2.89 g 3-mercaptopropionic acid **3** (27.3 mmol, 5.00 eq.) and 65 mg DMPA **7** (0.25 mmol, 5.00 mol%) were added. The reaction mixture was stirred under UV-irradiation at room temperature for one hour. Complete conversion of the double bonds was confirmed by proton NMR. Subsequently, the excess of 3-mertcaptopropionic acid **3** was removed applying vacuum distillation; the residue was diluted with diethyl ether (50 mL) and washed with water (3 × 50 mL). The organic layer was dried over sodium sulfate and concentrated *in vacuo*. The product **8'** was obtained as yellowish oil in a yield of 81 % (4.98 g).

^{1}H NMR (300 MHz, $CDCl_3$) δ / ppm: 7.37 – 7.12 (m, 5H, 5 CH aromatic, ^{7}), 6.60 (s, 1H, NH, ^{5}), 6.46 (s, 1H, NH, ^{5}), 4.97 – 4.53 (m, 4H, 2 CH, 2 CH_2, ^{4,6}), 3.30 – 3.06 (m, 2H, CH_2, ^{3}), 2.82 – 2.26 (m, 14H, 7 CH_2, ^{2}), 1.99 – 0.74 (m, 92H, 34 CH_2, 8 CH_3, ^{8,1}).

^{13}C NMR (75 MHz, $CDCl_3$) δ / ppm: 175.3, 175.2, 174.1, 171.4, 171.0, 170.0, 164.3, 137.7, 132.3, 131.7, 128.8, 127.4, 126.1, 95.1, 51.4, 51.0, 48.3, 34.8, 34.4, 33.7, 32.6, 32.2, 32.0, 29.8, 29.8, 29.7, 29.6, 29.6, 29.5, 29.3, 29.3, 29.0, 28.7, 28.2, 28.0, 26.9, 26.4, 26.3, 25.9, 24.9, 23.5, 22.8, 22.6, 21.3, 14.6, 14.2, 11.53.

FAB-MS: $[C_{66}H_{122}O_4N_6S_2]^+$ calculated: 1129.9, found: 1129.4.

IR: (KBr): ν [cm^{-1}] = 3332.0, 2924.8, 2853.7, 1729.1, 1681.6, 1631.7, 1538.1, 1454.5, 1364.4, 1226.3, 725.6.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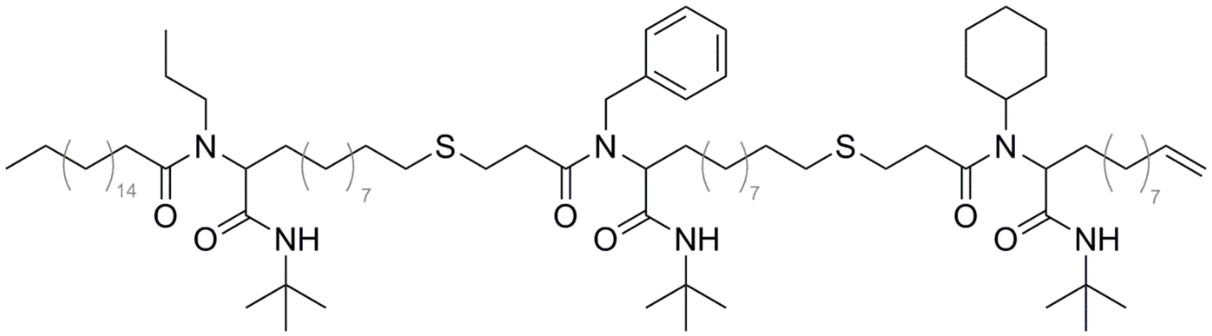
3rd Ugi reaction



4.94 g of subtance **8’** (4.37 mmol, 1.00 eq.), 1.26 g 10-undecenal **2** (7.46 mmol, 1.70 eq.) and 0.74 g cyclohexyl amine (7.44 mmol, 1.70 eq.) were dissolved in 4.4 mL methanol (1 M). Subsequently, 0.62 g *tert*-butyl isocyanide **5** (7.45 mmol, 1.70 eq.) were added and the mixture was stirred at room temperature for 48 hours. After completion of the reaction, the solvent was removed under reduced pressure and the crude product was purified by column chromatography (hexane / ethyl acetate 10:1 → 3:1). Product **9** was obtained as yellowish oil in a yield of 81 % (5.17 g).

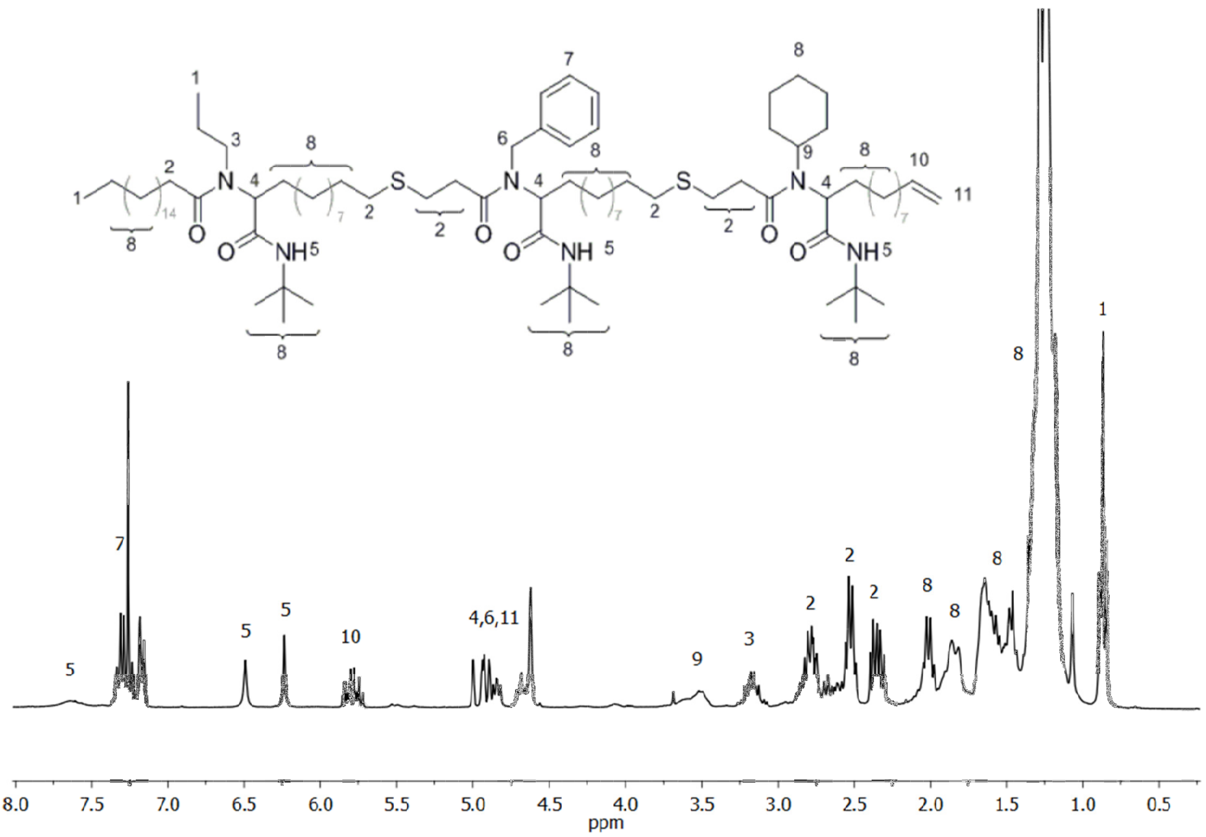
^{1}H NMR (300 MHz, $CDCl_3$) δ / ppm: 7.62 (s, J = 7.5 Hz, 1H, NH, ^{5}), 7.38 – 7.08 (m, 5H, 5 CH aromatic, ^{7}), 6.49 (s, 1H, NH, ^{5}), 6.23 (s, 1H, NH, ^{5}), 5.87 – 5.69 (m, 1H, CH, ^{10}), 5.04 – 4.49 (m, 7H, 3 CH, 2 CH_2, ^{4,6,11}), 3.53 (dd, J = 42.7, 35.2 Hz, 1H, CH, ^{9}), 3.29 – 3.01 (m, 2H, CH_2, ^{3}), 2.94 – 2.20 (m, 14H, 7 CH_2, ^{2}), 2.17 – 0.71 (m, 127H, 47 CH_2, 11 CH_3, ^{1,8}).

^{13}C NMR (75 MHz, $CDCl_3$) δ / ppm: 175.0, 173.9, 171.0, 169.9, 169.0, 168.6, 163.1, 157.0, 139.3, 128.9, 126.2, 126.1, 114.2, 99.7, 62.6, 58.7, 51.3, 50.9, 45.9, 33.9, 33.7, 32.9, 32.6, 32.0, 29.9, 29.8, 29.8, 29.8, 29.6, 29.6, 29.5, 29.5, 29.4, 29.2, 29.1, 29.0, 28.8, 28.8, 28.7, 28.5, 28.0, 27.3, 26.2, 25.9, 23.5, 23.5, 23.5, 22.8, 19.3, 14.3, 11.6.

FAB-MS: $[C_{88}H_{160}O_6N_6S_2]^+$ calculated: 1461.2, found: 1460.9.

IR: (ATR): ν [cm^{-1}] = 3317.6, 2921.0, 2851.2, 1673.2, 1625.5, 1540.8, 1452.1, 1389.7, 1361.5, 1224.8, 1121.3, 992.9, 907.1, 722.5, 695.3.

***R*$_f$:** (hexane / ethyl acetate (5:2)) = 0.48.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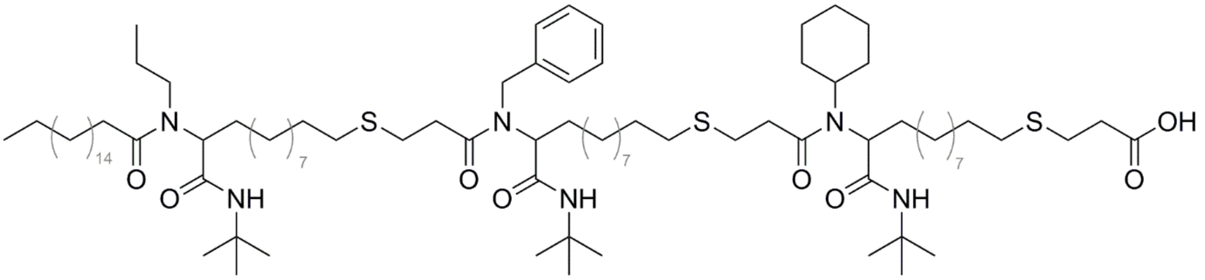
3rd Thiol-ene addition



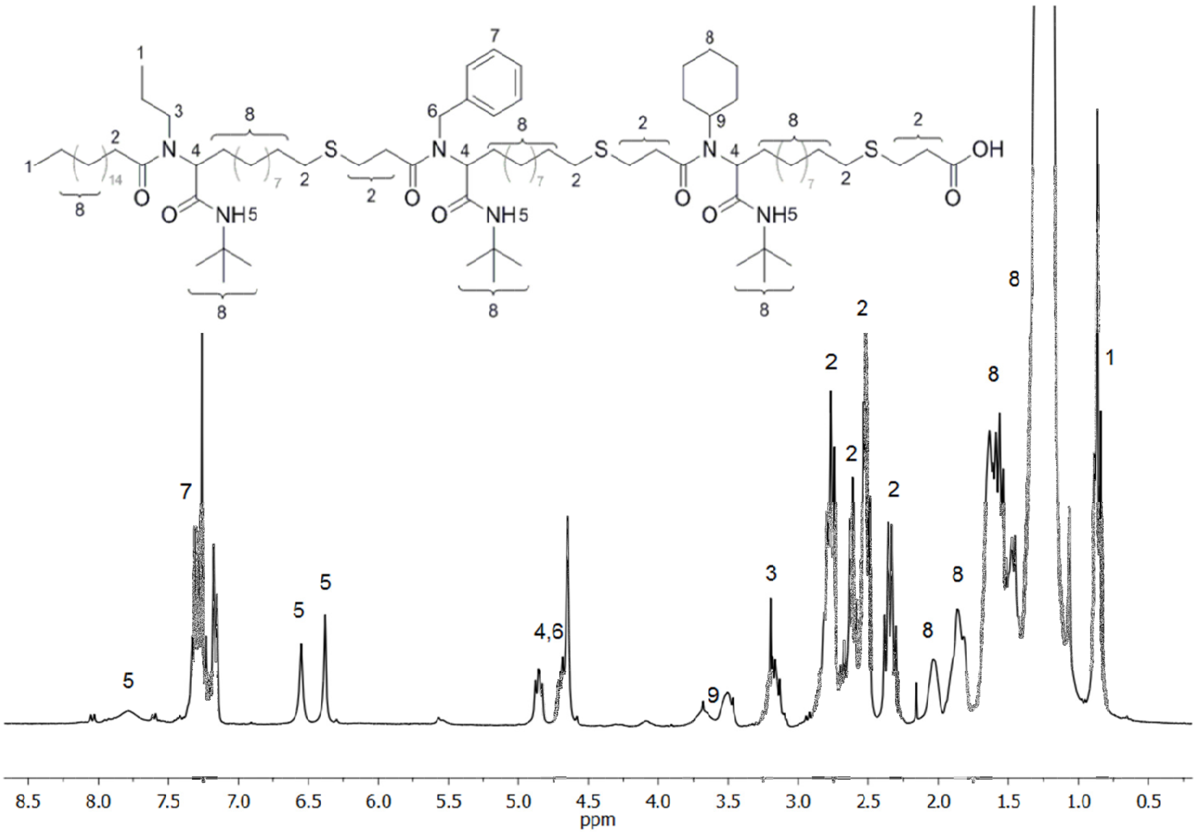
1.85 g 3-mercaptopropionic acid **3** (17.4 mmol, 5.00 eq.) were added to 5.06 g of substance **9** (3.46 mmol, 1.00 eq.) and 53,0 mg DMPA **7** (0.21 mmol, 6,00 mol%) and the mixture was stirred under UV-irradiation at room temperature for two hours. Complete consumption of the double bonds was confirmed by a ^{1}H NMR measurement. The excess of 3-mercaptopropionic acid **3** was removed by vacuum distillation and the residue was dissolved in diethyl ether (50 mL) and washed with water (3 × 50 mL). The organic layer was dried over sodium sulfate, filtered and the solvent was removed under reduced pressure to obtain product **9’** as highly viscous oil in a yield of 75 % (4.08 g).

^{1}H NMR (300 MHz, $CDCl_3$) δ / ppm: 7.78 (s, 1H, NH, ^{5}), 7.24 (m, 5H, 5 CH aromatic, ^{7}), 6.55 (s, 1H, NH, ^{5}), 6.38 (s, 1H, NH, ^{5}), 4.92 – 4.55 (m, 5H, 3 CH, CH_2, ^{4,6}), 3.83 – 3.04 (m, 3H, CH, CH_2, ^{3,9}), 2.99 – 2.18 (m, 20H, 10 CH_2, ^{2}), 2.16 – 0.48 (m, 129H, 48 CH_2, 11 CH_3, ^{1,8}).

^{13}C NMR (75 MHz, $CDCl_3$) δ / ppm:175.1, 174.7, 172.8, 171.0, 169.9, 163.1, 137.8, 128.8, 127.4, 126.1, 58.7, 51.4, 51.0, 50.8, 48.3, 47.0, 47.0, 35.4, 34.8, 34.4, 33.7, 32.9, 32.6, 32.1, 32.0, 29.8, 29.7, 29.7, 29.6, 29.5, 29.5, 29.4, 29.3, 29.1, 29.0, 29.0, 28.7, 28.7, 28.6, 28.2, 28.1, 28.0, 27.1, 27.0, 26.5, 26.3, 26.2, 26.0, 25.9, 25.1, 23.5, 22.8, 14.3, 11.6.

FAB-MS: $[C_{91}H_{167}O_6N_8S_3]^+$ calculated: 1567.2, found:1567.3.

IR: (ATR): ν [cm^{-1}] = 3306.9, 2921.2, 2851.0, 1720.6, 1675.4, 1626.7, 1541.0, 1452.4, 1390.5, 1362.3, 1223.8, 894.8, 723.9, 695.8.



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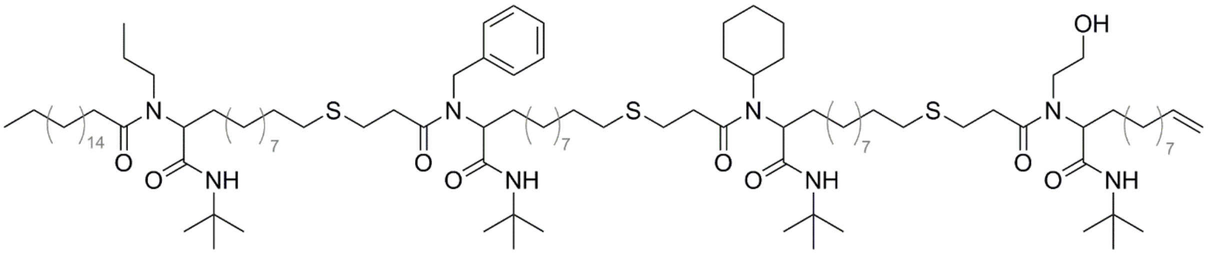
4th Ugi reaction



4.01 g of substance **9’** (2.55 mmol, 1.00 eq.), 0.73 g of 10-undecenal **2** (4.35 mmol, 1.70 eq.) and 0.27 g ethanolamine (4.50 mmol, 1.70 eq.) were stirred with 2.5 mL methanol (1 M). Subsequently, 0.37 g *tert*-butyl isocyanide **5** (4.43 mmol, 1.70 eq.) were added and the reaction mixture was stirred at room temperature for 48 hours. Afterwards, the solvent was evaporated under reduced pressure and the crude reaction mixture was purified by column chromatography (hexane / ethyl acetate 9:1 → 1:2). The desired product **10** was obtained as highly viscous oil in a yield of 48 % (2.30 g).

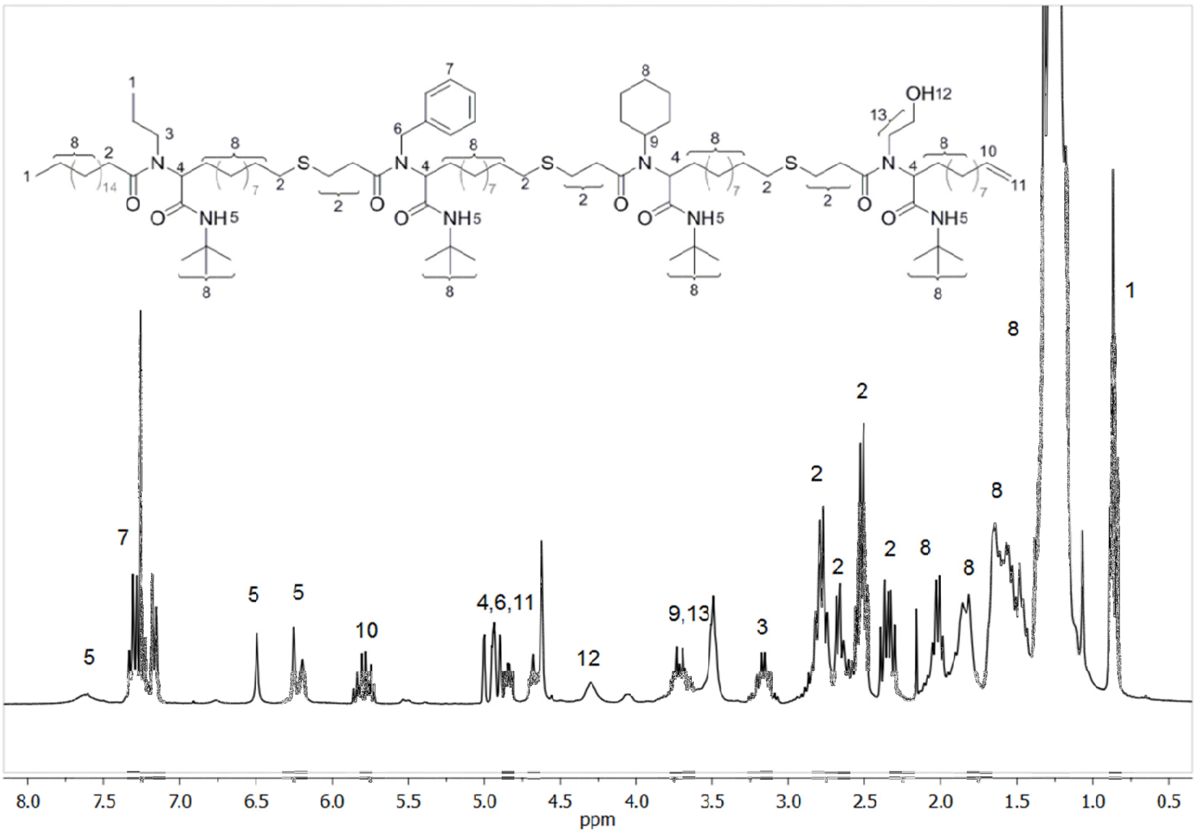
^{1}H NMR (300 MHz, $CDCl_3$) δ / ppm: 7.61 (bs, 1H, NH, ^{5}), 7.40 – 7.09 (m, 5H, 5 CH aromatic, ^{7}), 6.49 (s, 1H, NH, ^{5}), 6.22 (m, 2H, 2 NH, ^{5}), 5.79 (m, 1H, CH, ^{10}), 5.07 – 4.45 (m, 8H, 4 CH, 2 CH_2, ^{4,6,11}), 4.30 (bs, 1H, OH, ^{12}), 3.91 – 3.31 (m, 5H, 1 CH, 2 CH_2, ^{9,13}), 3.17 (m, 2H, CH_2, ^{3}), 3.00 – 2.21 (m, 20H, 10 CH_2, ^{2}), 2.18 – 0.76 (m, 154H, 56 CH_2, 14 CH_3, ^{1,8}).

^{13}C NMR (75 MHz, $CDCl_3$) δ / ppm: 175.0, 173.9, 173.0, 172.5, 171.0, 169.9, 162.9, 139.3, 128.8, 127.4, 126.2, 126.1, 114.3, 101.3, 61.8, 58.7, 51.7, 51.3, 50.9, 50.7, 34.5, 34.4, 33.9, 33.7, 32.9, 32.7, 32.6, 32.0, 29.8, 29.8, 29.8, 29.6, 29.5, 29.5, 29.4, 29.2, 29.1, 29.0, 29.0, 28.8, 28.7, 28.7, 28.6, 28.0, 26.6, 26.4, 25.9, 25.1, 23.5, 22.8, 14.2, 11.6.

FAB-MS: $[C_{109}H_{201}O_8N_9S_3]^+$ calculated: 1861.5, found: 1861.1.

IR: (ATR): ν[cm^{-1}] = 3306.1, 2921.3, 2851.4, 2625.5, 1541.5, 1452.5, 1390.5, 1361.9, 1224.7, 1077.1, 994.4, 907.4, 723.3, 696.0, 503.3.

***R*f:** (hexane / ethyl acetate (3:2)) = 0.5.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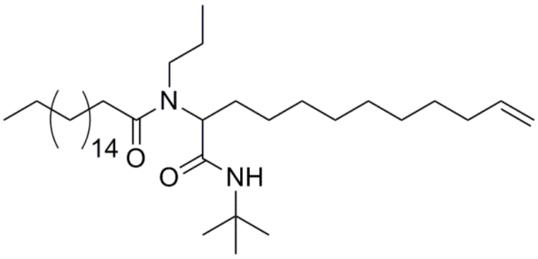
3.2. Variation of the amine and the isocyanide component:

1st Ugi reaction:



1.34 g 10-undecenal **2** (7.98 mmol, 1.70 eq.) and 0.47 g propylamine **4** (7.88 mmol, 1.70 eq.) were stirred for 15 minutes at room temperature. Subsequently, 1.30 g stearic acid **1** (4.59 mmol, 1.00 eq.), 0.70 g *tert*-butyl isocyanide **5** (8.43 mmol, 1.80 eq.) and 5.25 mL (0.87 M) methanol were added and stirred for 24 hours at room temperature. The reaction was followed by GPC and after completion of the reaction, the solvent was removed under reduced pressure and the product was purified by column chromatography (hexane / ethyl acetate 30:1 → 12:1). Product **11** was obtained as a colorless liquid in a yield of 91 % (2.42 g).

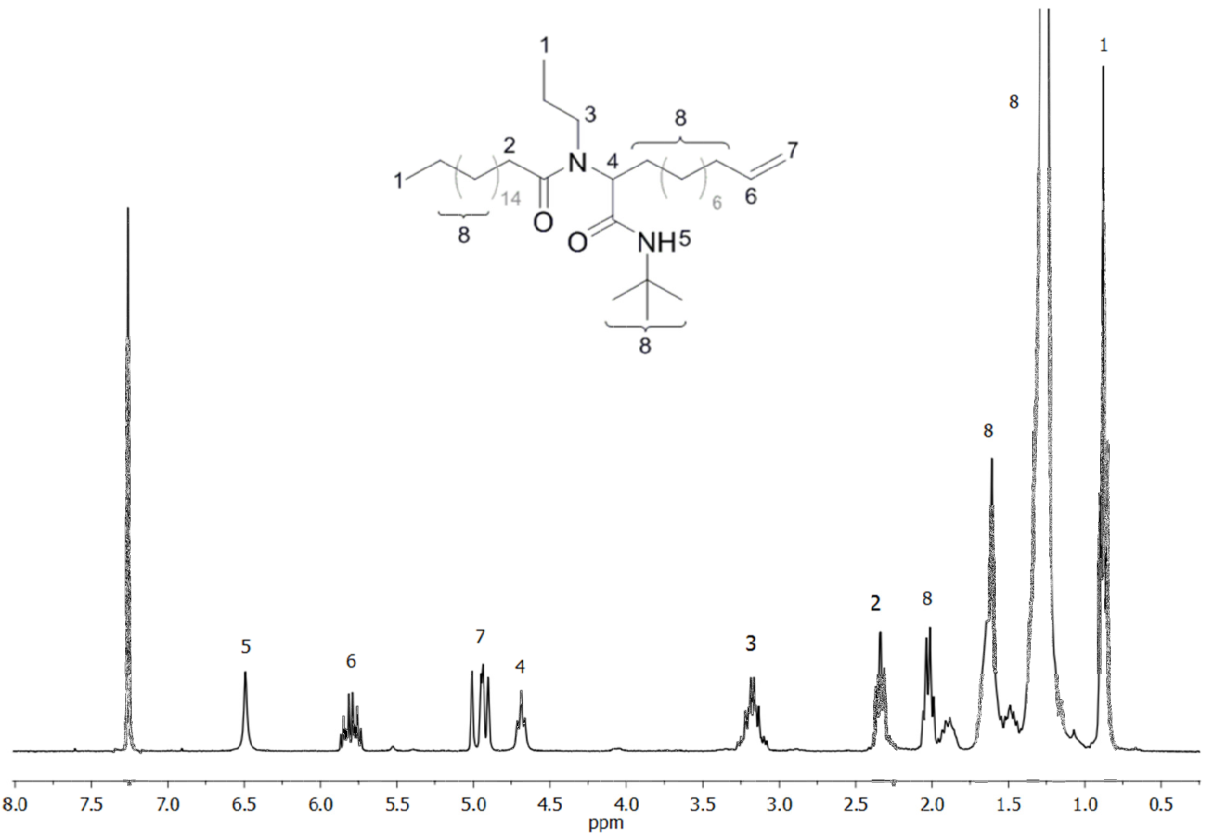
^{1}H NMR: (300 MHz, CDCl$_3$) δ /ppm: 6.49 (s, 1H, NH, ^{5}), 5.80 (m, 1H, CH, ^{6}), 4.95 (dd, J = 17.3, 13.8 Hz, 2H, CH$_2$, ^{7}), 4.69 (t, J = 7.6 Hz, 1H, CH, ^{4}), 3.30 – 3.06 (m, 2H, CH$_2$, ^{3}), 2.34 (dd, J = 8.1, 6.3 Hz, 2H, CH$_2$, ^{2}), 2.08 – 1.00 (m, 57H, 24 CH$_2$,3 CH$_3$, ^{8}), 0.88 (t, J = 7.1 Hz, 6H, 2 CH$_3$, ^{1}).

^{13}C NMR: (75 MHz, CDCl$_3$) δ /ppm: 175.0, 171.0, 139.3, 114.2, 58.2, 50.9, 50,0, 33.9, 33.7, 32.1, 29.8, 29.8, 29.7, 29.6, 29.6, 29.6, 29.5, 29.5, 29.5, 29.2, 29.0, 28.8, 28.0, 26.3, 25.9, 23.5, 22.8, 14.2, 11.6.

FAB-MS: [$C_{37}H_{73}O_2N_2$]$^+$ calculated: 577.5669, found: 577.5667.

IR: (ATR): ν [cm^{-1}] = 3312.0, 2920.7, 2851.4, 1682.5, 1625.3, 1534.7, 1454.0, 1362.3, 1225.0, 1112.5, 991.3, 907.1, 720.5, 470.5.

***R*$_f$:** (hexane / ethyl acetate (9:1)) = 0.44.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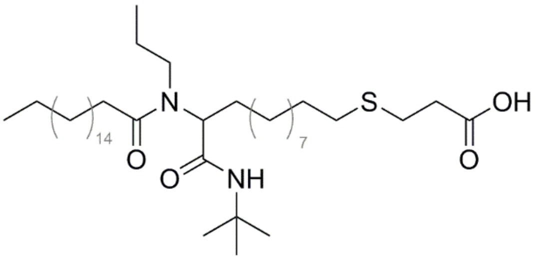
1^{st} Thiol-ene addition:



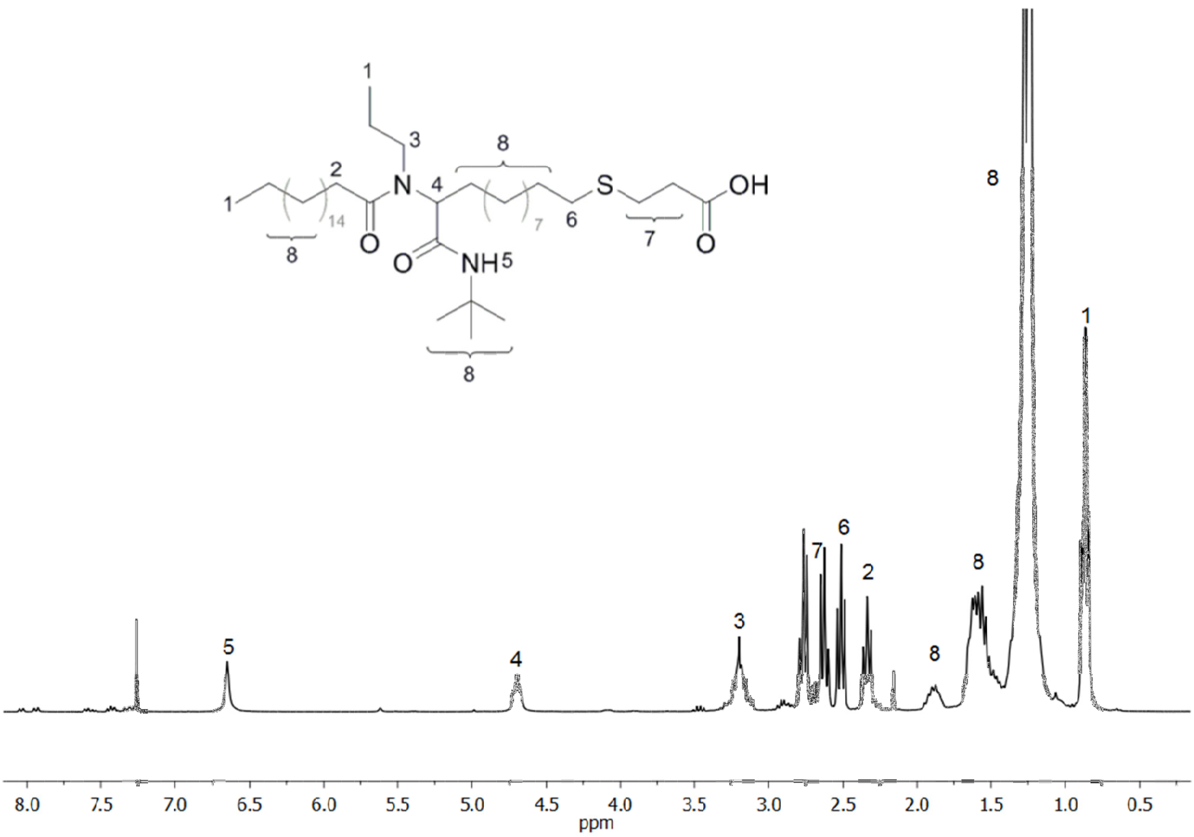
3.02 g of substance **11** (5.23 mmol, 1.00 eq.) were diluted with 2.82 g 3-mercaptopropionic acid **3** (27.0 mmol, 5.20 eq.) and 72.3 mg DMPA **7** (0.28 mmol, 5.40 mol%) were added. The reaction mixture was stirred under UV irradiation at room temperature for one hour. Full conversion of the double bonds was detected by ^{1}H NMR. The excess of 3-mercaptopropionic acid was removed by vacuum distillation and the residue was dissolved in diethyl ether. The organic layer was washed with water (3 × 100 mL) and brine (100 mL) and dried over sodium sulfate. After removing the solvent under reduced pressure, the desired product **11'** was obtained as yellowish oil in a yield of 99 % (3.54 g).

^{1}H NMR (300 MHz, $CDCl_3$) δ /ppm: 6.65 (s, 1H, NH, ^{5}), 4.69 (t, J = 7.1 Hz, 1H, CH, ^{4}), 3.34 – 3.07 (m, 2H, CH_2, ^{3}), 2.81 – 2.57 (m, 4H, 2 CH_2, ^{7}), 2.51 (t, J = 7.3 Hz, 2H, CH_2, ^{6}), 2.33 (t, J = 7.5 Hz, 2H, CH_2, ^{2}), 2.00 – 0.74 (m, 67H, 26 CH_2, 5 CH_3, ^{8,1}).

^{13}C NMR (75 MHz, $CDCl_3$) δ /ppm: 175.9, 175.2, 170.9, 58.3, 51.0, 47.0, 34.7, 33.5, 32.1, 31.9, 29.7, 29.6, 29.5, 29.4, 29.4, 29.3, 29.0, 28.7, 28.5, 28.1, 26.7, 26.1, 25.7, 23.4, 23.4, 22.7, 14.1, 11.4.

FAB-MS: $[C_{40}H_{79}O_2N_4S]^+$ calculated: 683.6, found: 683.6.

IR: (ATR): ν [cm^{-1}] = 2920.3, 2850.8, 1717.2, 1681.4, 1621.5, 1535.9, 1454.5, 1363.8, 1223.8, 8993.3, 720.4, 634.4.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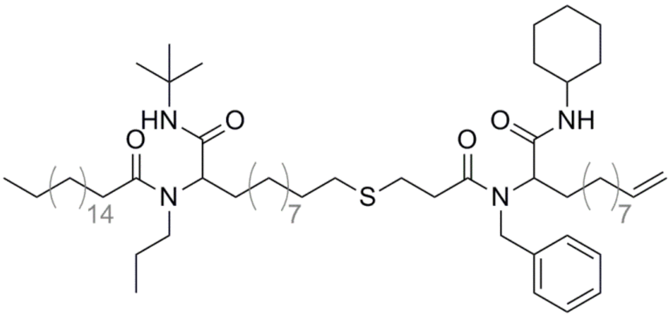
2nd Ugi reaction:



1.44 g of 10-undecenal **2** (8.56 mmol, 1.70 eq.) were mixed with 0.93 g benzylamine (8.69 mmol, 1.70 eq.) and 5.0 mL (1M relative to the acid) methanol and stirred for 30 minutes. Subsequently, 3.43 g of substance **11'** (5.02 mmol, 1.00 eq.) and 0.86 g of cyclohexyl isocyanide (7.92 mmol, 1.60 eq.) were added and the reaction mixture was stirred at room temperature for 48 hours. The solvent was removed under reduced pressure and the product was separated by column chromatography (hexane / ethyl acetate 10:1 → 3:1) to afford 53 % of substance **12** (2.79 g).

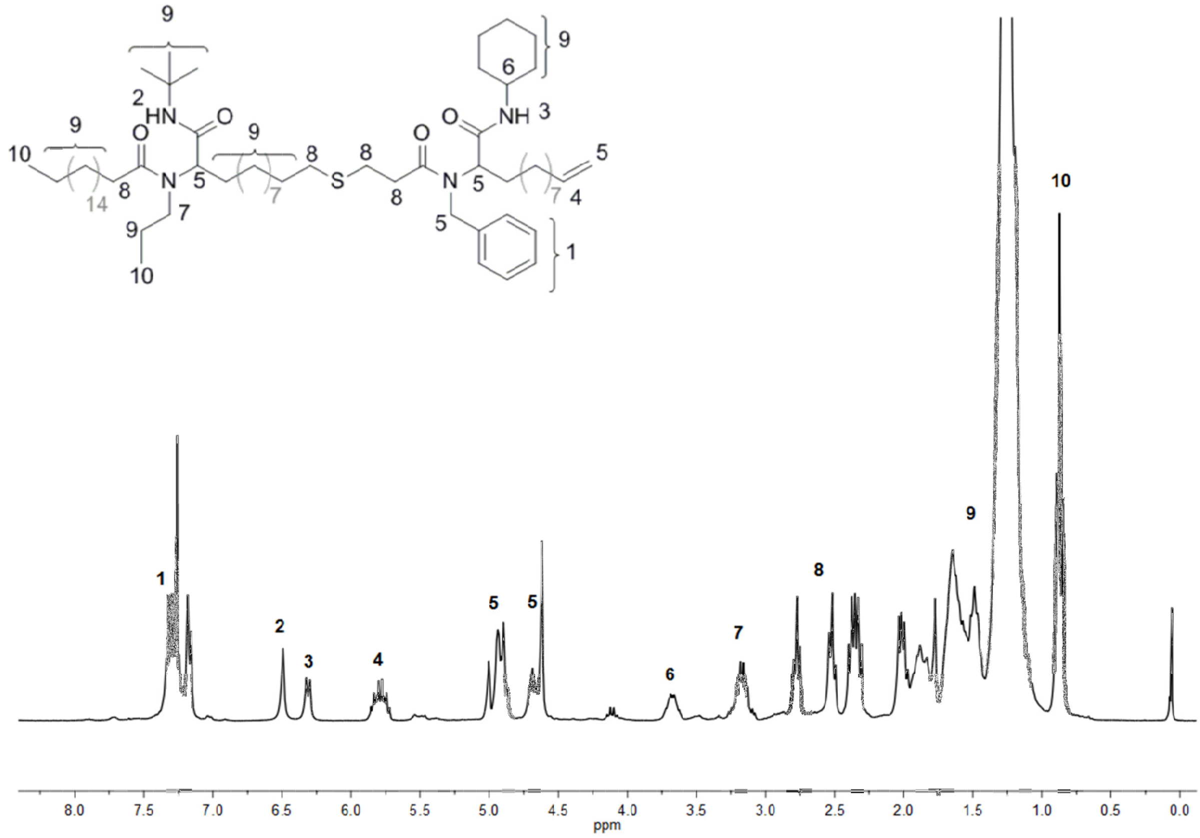
^{1}H NMR (300 MHz, $CDCl_3$) δ /ppm: 7.44 – 7.08 (m, 5H, 5 CH aromatic, ^{1}), 6.49 (s, 1H, NH, ^{2}), 6.31 (d, J = 8.1 Hz, 1H, NH, ^{3}), 5.92- 5.69 (m, 1H, CH, ^{4}), 5.06 – 4.81 (m, 3H, CH_2, CH, ^{5}), 4.75 – 4.52 (m, 3H, CH_2, CH, ^{5}), 3.80 – 3.55 (m, 1H, CH, ^{6}), 3.30-3,04 (m, 2H, CH_2, ^{7}), 2.86 – 2.21 (m, 8 H, 4 CH_2, ^{8}), 2.14 – 0.97 (m, 85 H, 38 CH_2, 3 CH_3, ^{9}), 0.87 (m, 6H, 2 CH_3, ^{10}).

^{13}C NMR (75 MHz, $CDCl_3$) δ /ppm 175.0, 173.9, 171.0, 169.7, 139.3; 137.7, 128.9, 127.4, 126.0, 114.2, 58.3, 50.9, 48.5, 48.2, 34.4, 33.9, 33.7, 33.1, 32.9, 32.6, 32.0, 29.8, 29.8, 29.7, 29.6, 29.4, 29.3, 29.1, 29.0, 28.9, 28.7, 28.5, 28.0, 26.5, 26.3, 25.8, 25.6, 24.8, 23.5, 22.8, 14.2, 11.6.

FAB-MS of $[C_{65}H_{117}O_4N_4S]^+$: calculated: 1049.9, found: 1049.7.

IR (KBr): ν [cm^{-1}] = 3320.0, 2925.0, 2853.7, 1680.6, 1631.3, 1537.8, 1453.5, 1363.4, 1227.4, 992.6, 908.7, 725.4, 696.9.

R



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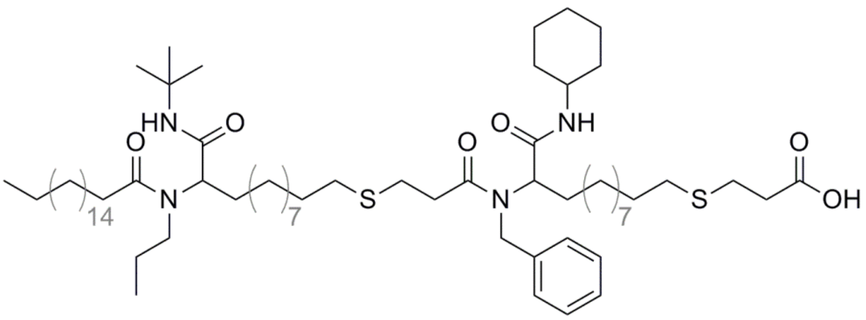
2^{nd} thiol-ene addition:



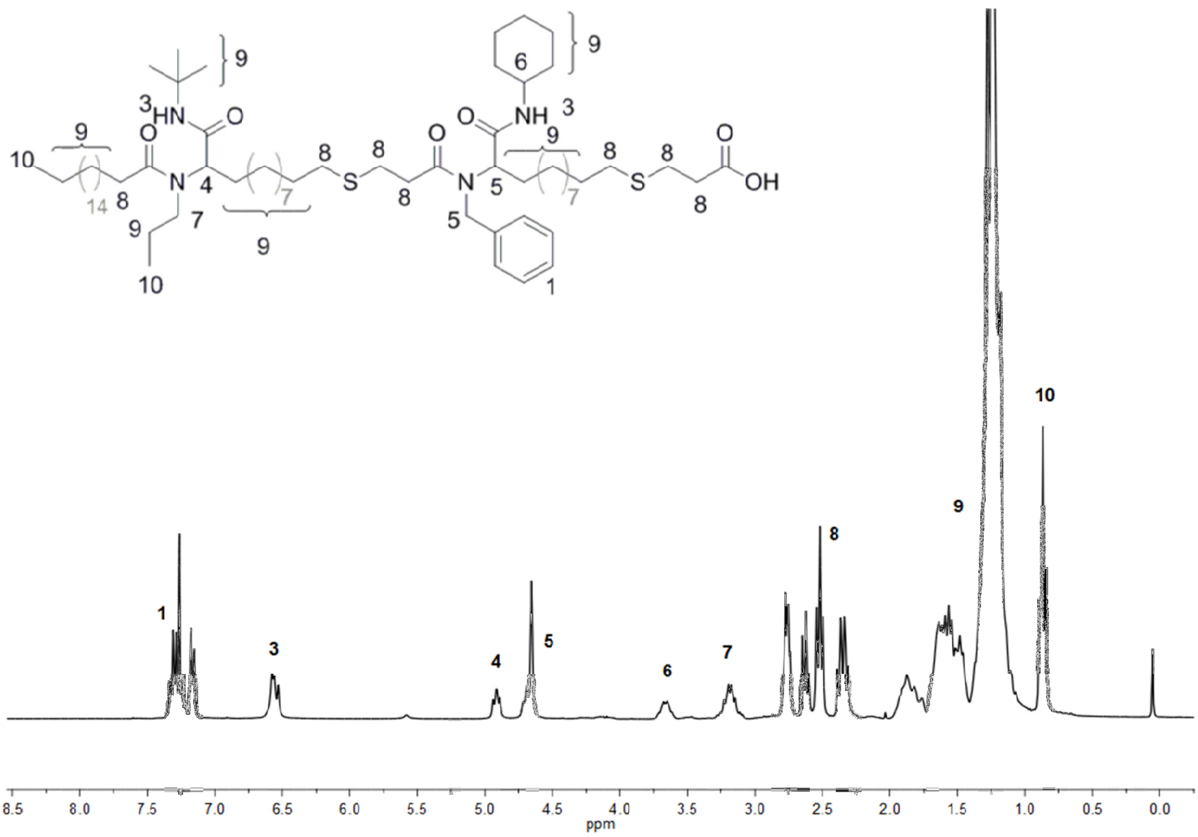
2.36 g of substance **12** (2.25 mmol, 1.00 eq.) were diluted with 1.21 g 3-mercaptopropionic acid **3** (11.4 mmol, 5.10 eq.) and 29.3 mg DMPA **7** (0.12 mmol, 5.10 mol%) were added. The mixture was stirred under UV-irradiation at room temperature for three hours and the full conversion of the double bond was confirmed by ^{1}H NMR. Subsequently, the excess of 3-mercaptopropionic acid was removed by vacuum distillation. The residue was diluted with diethyl ether (25 mL) and washed with water (3 × 50 mL) and brine (50 mL). The organic layer was dried over sodium sulfate and the solvent was removed under reduced pressure to afford the desired product **12'** as slightly yellow oil in a yield of 92 % (2.38 g).

^{1}H NMR (300 MHz, CDCl$_3$) δ/ ppm: 7.38 – 7.12 (m, 5H, 5 CH aromatic, ^{1}), 6.66 – 6.47 (m, 2H, 2 NH, ^{2}), 4.99 – 4.83 (m, 1H, CH, ^{3}), 4.77 – 4.55 (m, 3H, CH$_2$, CH, ^{3}), 3.77 – 3.57 (m, 1H, CH, ^{4}), 3.31 – 3.05 (m, 2H, CH$_2$, ^{5}), 2.90 – 2,21 (m, 14H, 7 CH$_2$, ^{6}), 2.01 – 1.00 (m, 87H, 3 CH$_3$, 39 CH$_2$, ^{7}), 0.94 – 0.77 (m, 6H, 2 CH$_3$, ^{8}).

^{13}C NMR (75 MHz, CDCl3) δ/ 175.2, 174.1, 171.0, 171.0, 169.8, 137.6, 128.9, 127.4, 126.0, 114.0, 51.0, 48.5, 48.3, 34.8, 33.7, 33.0, 32.8, 32.6, 32.2, 32.0, 29.8, 29.8, 29.7, 29.6, 29.6, 29.5, 29.4, 29.3, 29.0, 28.7, 28.1, 28.0, 26.9, 26.4, 26.3, 25.9, 25.6, 25.6, 24.8, 23.5, 22.8, 14.2, 11.5.

FAB-MS of $[C_{68}H_{123}O_6N_4S_2]^+$: calculated: 1155.9, found: 1155.6.

IR (KBr): ν [cm^{-1}] = 3317.5, 2920.7, 2850.8, 1723.9, 1677.4, 1623.7, 1534.7, 1451.2, 1418.8, 1362.9, 1224.4, 891.2, 724.0, 695.8, 458.5.



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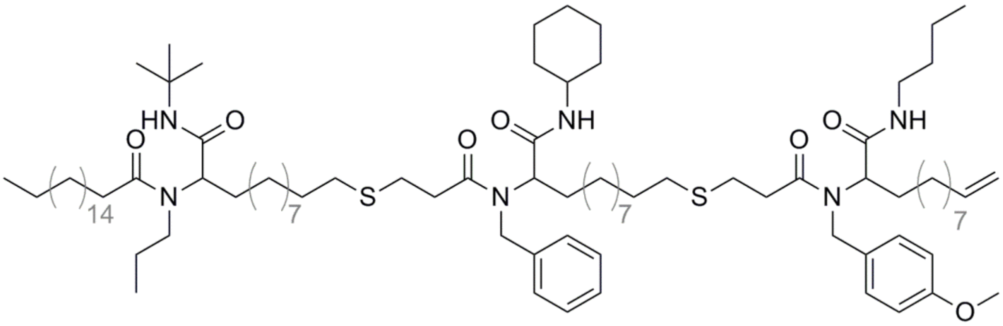
3rd Ugi reaction:



0.05 g of 10-undecenal **2** (0.30 mmol, 1.70 eq.) were mixed with 0.05 g 4-methoxy benzylamine (0.34 mmol, 1.90 eq.) and 0.25 mL (0.72M relative to the acid) methanol and stirred for 30 minutes. Subsequently, 0.21 g of substance **12'** (0.18 mmol, 1.00 eq.) and 0.03 g of *n*-butyl isocyanide (0.30 mmol, 1.70 eq.) were added and the reaction mixture was stirred at room temperature for 40 hours. The solvent was removed under reduced pressure and the product was separated by column chromatography (hexane / ethyl acetate 6:1 → 1:1) to afford 80 % of substance **13** (0.23 g).

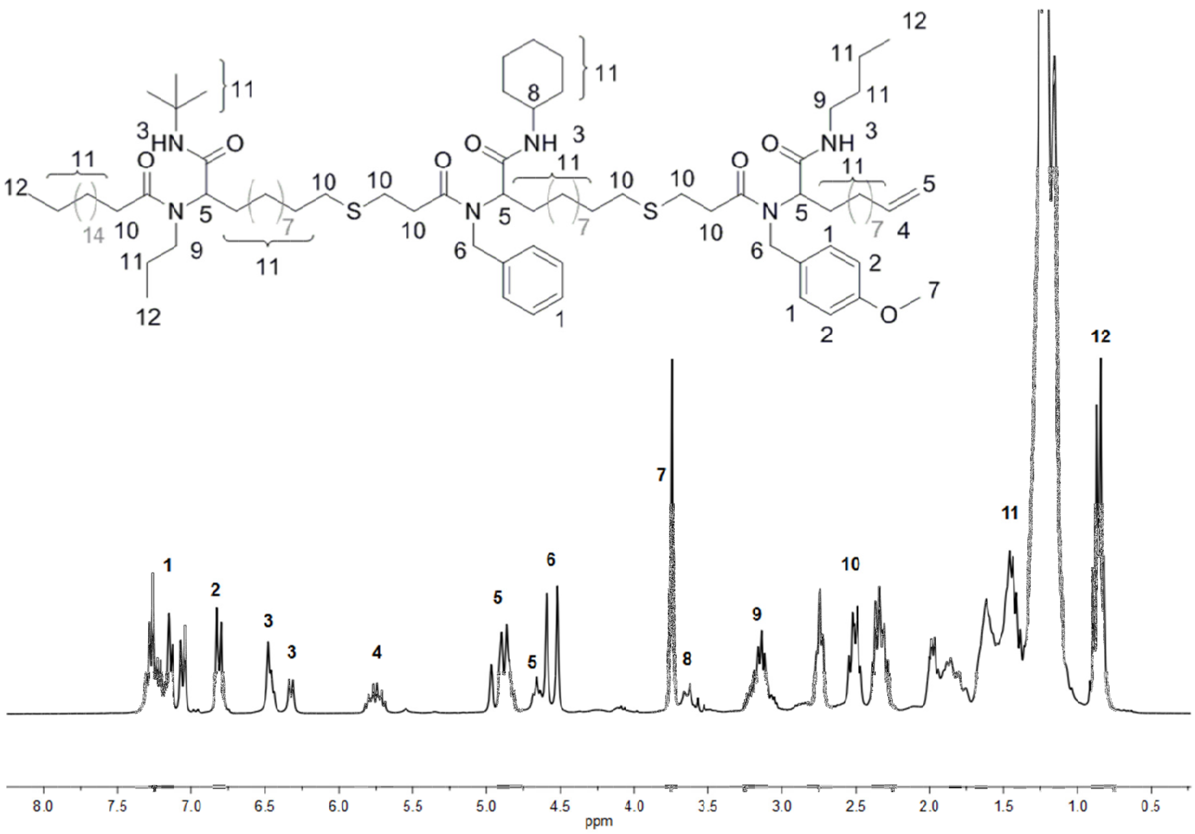
^{1}H NMR (300 MHz, CDCl$_3$) δ/ ppm: 7.39 – 7.00 (m, 7H, 7 CH aromatic, ^{1}), 6.88 – 6.73 (m, 2H, 2 CH aromatic, ^{2}), 6.53 – 6.40 (m, 2H, 2 NH, ^{3}), 6.32 (d, J = 8.1 Hz, 1H, NH, ^{3}), 5.86 – 5.64 (m, 1H, CH, ^{4}), 5.02 – 4.78 (m, 4H, 2 CH, CH$_2$, ^{5}), 4.74 – 4.45 (m, 5H, CH, 2 CH$_2$, ^{5,6}), 3.84 – 3.55 (m, 4H, CH, OCH$_3$, ^{7,8}), 3.28 – 3.01 (m, 4H, 2 CH$_2$, ^{9}), 2.92 – 2.21 (m, 14 H, 7 CH$_2$, ^{10}), 2.18 – 0.95 (m, 107 H, 3 CH$_3$, 49 CH$_2$, ^{11}), 0.97 – 0.72 (m, 9H, 3 CH$_3$, ^{12}).

^{13}C NMR (75 MHz, CDCl$_3$) δ/ ppm: 174.9, 173.8, 173.8, 170.9, 170.6, 169.6, 158.9, 139.2, 137.7, 129.4, 129.3, 128.8, 127.3, 127.2, 126.0, 114.2, 58.3, 58.2, 55.3, 52.4, 50.8, 48.4, 48.1, 48.0, 46.9, 39.1, 38.6, 34.3, 33.8, 33.6, 33.0, 32.8, 32.6, 32.5, 32.0, 31.9, 31.6, 29.7, 29.7, 29.7, 29.6, 29.5, 29.5, 29.4, 29.3, 29.2, 29.1, 28.9, 28.7, 28.4, 28.4, 27.9, 27.9, 26.5, 26.3, 25.8, 25.6, 24.8, 23.4, 22.7, 20.1, 14.2, 13.8, 11.5.

FAB-MS of [$C_{92}H_{161}O_7N_6S_2$]$^+$: calculated: 1526.2, found: 1526.3.

IR (film KBr): ν [cm^{-1}] = 3321.4, 2925.3, 2853.7, 1631.3, 1513.7, 1454.5, 1363.1, 1247.9, 1037.9, 909.0, 820.0, 725.3.

***R*$_f$:** (hexane / ethyl acetate (3:2)) = 0.47.



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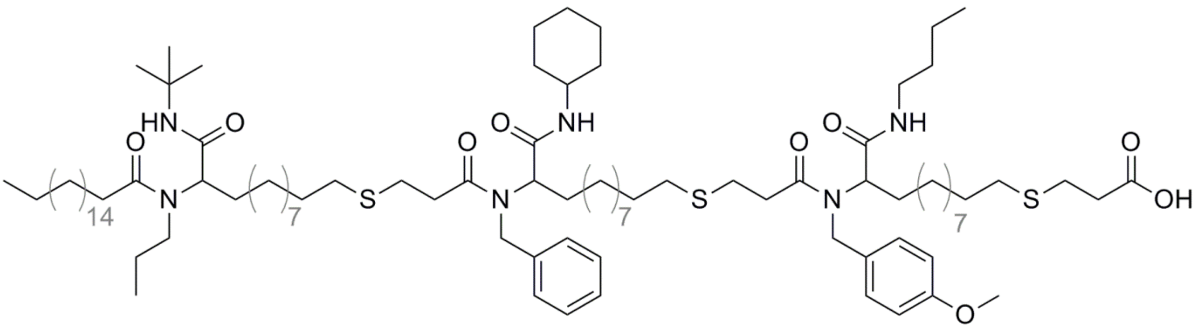
3rd thiol-ene addition:



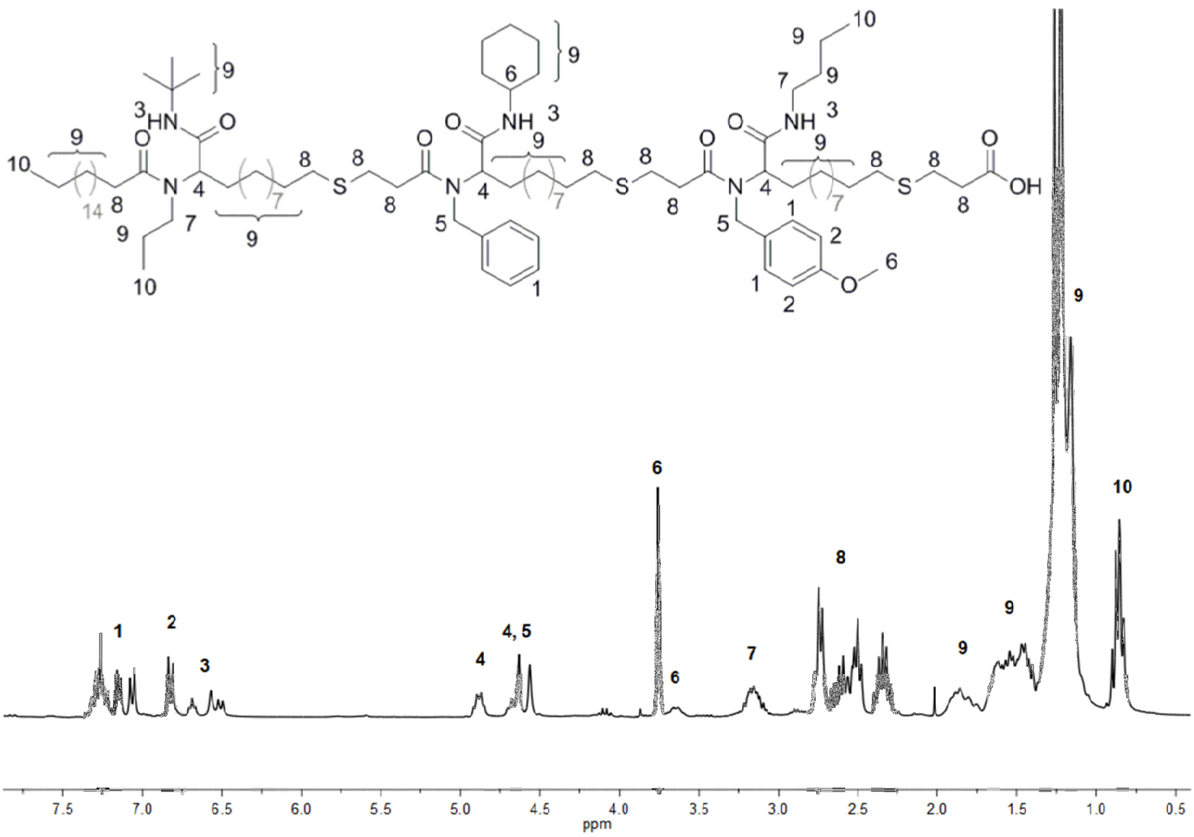
1.57 g of substance **13** (1.03 mmol, 1.00 eq.) were diluted with 0.58 g 3-mercaptopropionic acid **3** (5.50 mmol, 5.50 eq.) and 13.5 mg DMPA **7** (0.05 mmol, 5.10 mol%) were added. The mixture was stirred under UV-irradiation at room temperature for three hours and the full conversion of the double bond was confirmed by ^{1}H NMR. Subsequently, the excess of 3-mercaptopropionic acid was removed by vacuum distillation. The residue was diluted with diethyl ether (25 mL) and washed with water (3 × 50 mL) and brine (50 mL). The organic layer was dried over sodium sulfate and the solvent was removed under reduced pressure to afford the desired product **13'** as slightly yellow oil in a yield of 99 % (1.66 g).

^{1}H NMR (300 MHz, $CDCl_3$) δ /ppm: 7.39 – 7.00 (m, 7H, 7 CH aromatic, ^{1}), 6.82 (d, J = 8.6 Hz, 2H, 2 CH aromatic, ^{2}), 6.69 (t, J = 5.6 Hz, 1H, NH, ^{3}), 6.61 – 6.43 (m, 2H, 2 NH, ^{3}), 4.97 – 4.76 (m, 2H, 2 CH, ^{4}), 4.73 – 4.37 (m, 5H, 2 CH_2, 1 CH, ^{4,5}), 3.80 – 3.56 (m, 4H, CH_3, CH, ^{6}), 3.31 – 3.00 (m, 4H, 2 CH_2, ^{7}), 2.80 – 2.24 (m, 20H, 10 CH_2, ^{8}), 1.98 – 0.95 (m, 109 H, 3 CH_3, 50 CH_2, ^{9}), 0.94 – 0.72 (m, 9H, 3 CH_3, ^{10}).

^{13}C NMR (75 MHz, $CDCl_3$) δ /ppm: 175.2, 175.1, 174.9, 174.0, 171.0, 170.8, 169.7, 158.9, 137.6, 129.3, 128.8, 127.4, 127.3, 126.0, 114.2, 58.3, 55.3, 50.9, 48.4, 48.2, 48.1, 47.0, 39.2, 38.4, 34.8, 34.4, 33.6, 32.9, 32.8, 32.6, 32.5, 32.1, 32.0, 31.5, 29.8, 29.7, 29.7, 29.6, 29.5, 29.4, 29.4, 29.3, 29.1, 29.0, 28.7, 28.6, 28.5, 28.1, 27.9, 26.9, 26.5, 26.4, 26.3, 25.8, 25.6, 24.8, 23.5, 22.8, 20.1, 19.8, 14.2, 13.8, 11.5.

FAB-MS of $[C_{95}H_{167}O_9N_6S_3]^+$: calculated: 1632.2, found: 1632.1.

IR (ATR): ν [cm^{-1}] = 3322.6, 2920.8, 2850.8, 1726.4, 1624.7, 1535.3, 1512.4, 1452.1, 1362.2, 1245.5, 1175.4, 1033.5, 890.9, 805.0, 722.7, 696.0, 460.1.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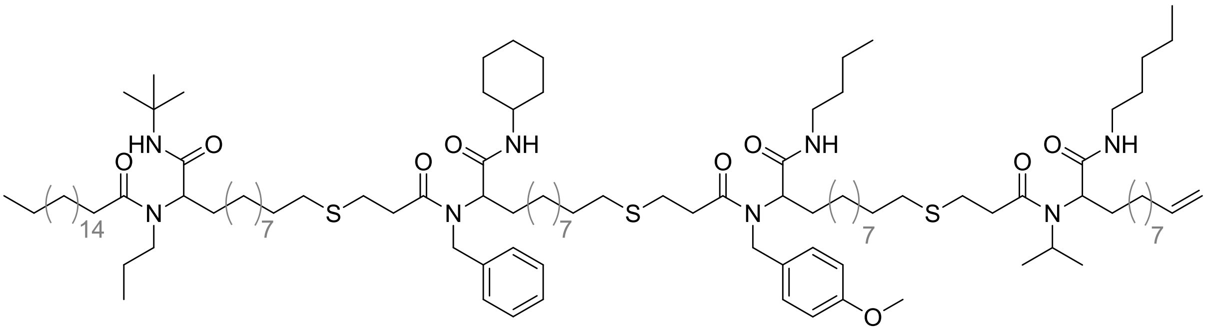
4th Ugi reaction:



0.05 g of 10-undecenal **2** (0.32 mmol, 2.50 eq.) were mixed with 0.02 g *iso*-propylamine (0.34 mmol, 1.90 eq.) and 0.20 mL (0.65 M relative to the acid) methanol and stirred for 30 minutes. Subsequently, 0.21 g of substance **13'** (0.13 mmol, 1.00 eq.) and 0.03 g of *n*-pentyl isocyanide (0.28 mmol, 2.20 eq.) were added and the reaction mixture was stirred at room temperature for 48 hours. The solvent was removed under reduced pressure and the product was separated by column chromatography (hexane / ethyl acetate 5:1 → 1:3) to afford 77 % of substance **14** (0.19 g).

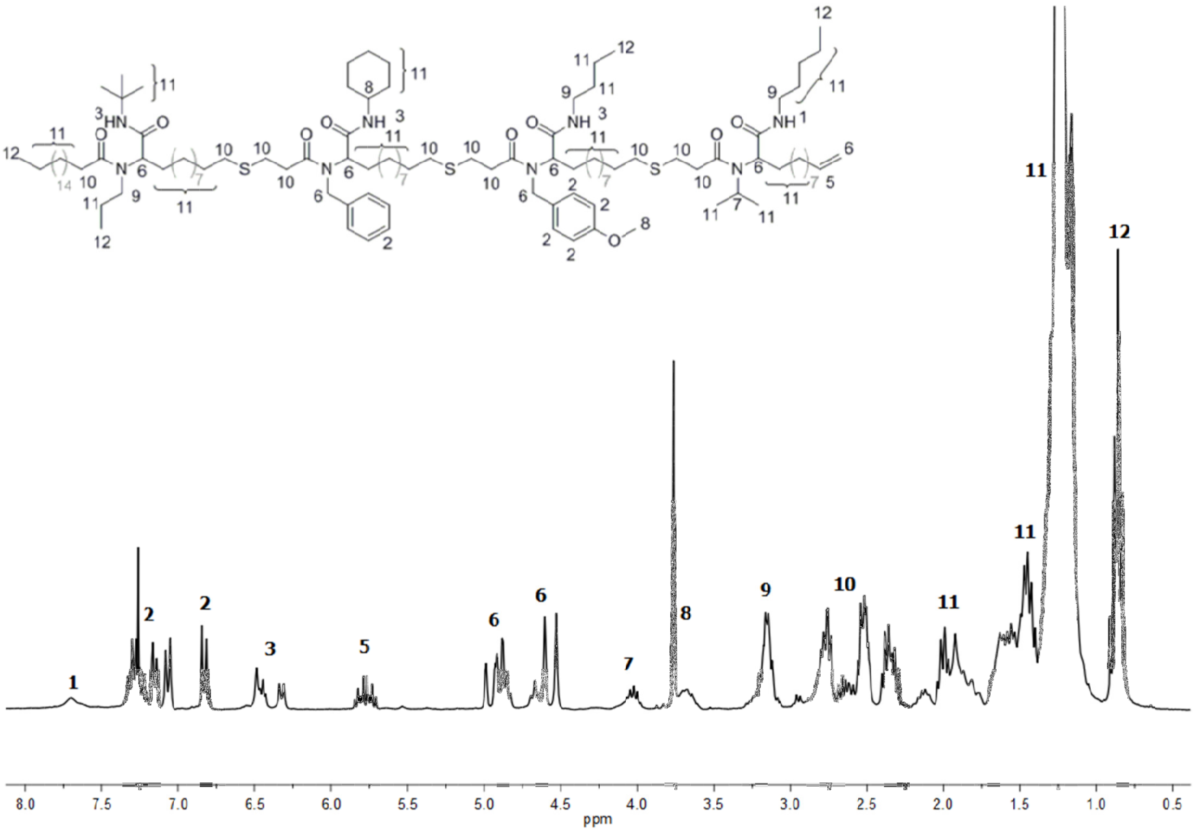
^{1}H NMR (300 MHz, $CDCl_3$) δ /ppm: 7.66 (s, 1H, NH ^{1}), 7.36 – 6.95 (m, 7H, 7 CH aromatic, ^{2}), 6.78 (d, J = 8.6 Hz, 2H, 2 CH aromatic, ^{2}), 6.58 – 6.34 (m, 2H, 2 NH, ^{3}), 6.28 (d, J = 8.1 Hz, 1H, NH, ^{3}), 5.73 (m, 1H, CH, ^{5}), 4.99 – 4.72 (m, 5H, CH_2, 3 CH, ^{6}), 4.69 – 4.37 (m, 5H, 2 CH_2, CH, ^{6}), 3.97 (m, 1H, CH, ^{7}), 3.79 – 3.50 (m, 4H, CH_3, CH, ^{8}), 3.31 – 2.96 (m, 6H, 3 CH_2 ^{9}), 2.95 – 2.17 (m, 20H, 10 CH_2, ^{10}), 2.17 – 0.91 (m, 137H, 5 CH_3, 61 CH_2, ^{11}), 0.91 – 0.57 (m, 12H, 4 CH_3 ^{12}).

^{13}C NMR (75 MHz, $CDCl_3$) δ /ppm: 175.0, 173.9, 173.9, 173.2, 172.6, 171.0, 170.7, 169.6, 158.9, 139.3, 137.7, 129.4, 128.8, 127.4, 127.3, 126.0, 114.2, 58.3, 58.3, 55.4, 50.9, 49.8, 48.2, 39.3, 39.1, 35.4, 34.4, 33.9, 33.6, 33.0, 32.9, 32.8, 32.6, 32.6, 32.0, 31.6, 30.2, 29.8, 29.7, 29.7, 29.6, 29.6, 29.5, 29.5, 29.3, 29.2, 29.0, 28.7, 28.5, 28.4, 28.0, 27.2, 26.6, 26.6, 26.3, 25.8, 25.6, 24.8, 23.5, 22.8, 22.4, 21.2, 21.0, 20.1, 14.2, 14.1, 13.9, 11.5.

FAB-MS of $[C_{115}H_{204}N_8O_9S_3]^+$: calculated: 1937.5, found: 1937.9

IR (ATR platinum diamond): ν [cm^{-1}] = 3306.6, 2921.3, 2851.3, 1626.4, 1536.5, 1512.8, 1451.2, 1362.1, 1293.0, 1246.4, 1036.4, 907.9, 819.2, 723.6, 696.1.

***R*$_f$:** (hexane / ethyl acetate (3:2)) = 0.48.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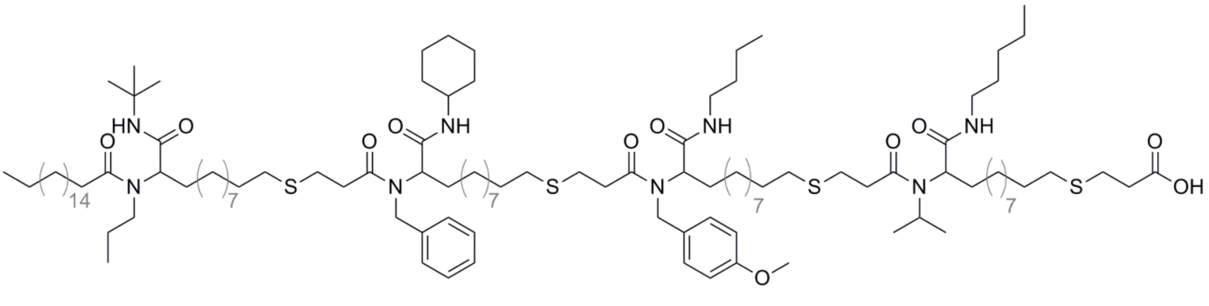
4th thiol-ene addition:



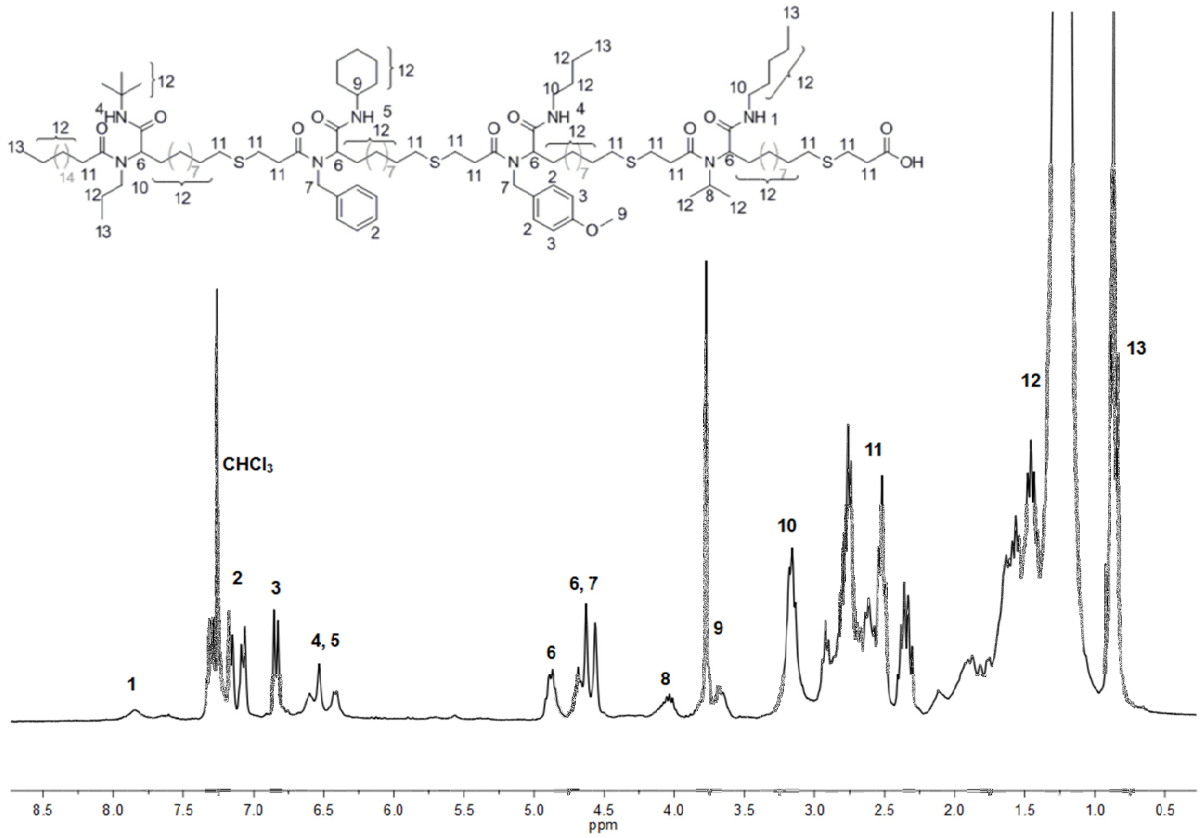
0.57 g of substance **14** (0.29 mmol, 1.00 eq.) were diluted with 0.18 g 3-mercaptopropionic acid **3** (1.65 mmol, 5.60 eq.) and 4.1 mg DMPA **7** (0.02 mmol, 5.50 mol%) were added. The mixture was stirred under UV-irradiation at room temperature for four hours and the full conversion of the double bond was confirmed by ^{1}H NMR. Subsequently, the excess of 3-mercaptopropionic acid was removed by vacuum distillation. The residue was diluted with diethyl ether (25 mL) and washed with water (3 × 50 mL) and brine (50 mL). The organic layer was dried over sodium sulfate and the solvent was removed under reduced pressure to afford the desired product **14'** as slightly yellow oil in a yield of 99 % (0.60 g).

^{1}H NMR (300 MHz, $CDCl_3$) δ /ppm: 7.84 (s, 1H, NH, ^{1}), 7.41 – 6.98 (m, 7H, 7 CH aromatic, ^{2}), 6.84 (d, J = 8.6 Hz, 2H, 2 CH aromatic, ^{3}), 6.68 – 6.28 (m, 3H, 3 NH, $^{4, 5}$), 4.88 (m, 3H, 3 CH, ^{6}), 4.64 (m, 5H, 2 CH_2, 1CH, $^{6, 7}$), 4.05 (m, 1H, CH, ^{8}), 3.89 – 3.58 (m, 4H, CH_3, CH, ^{9}), 3.40 – 3.00 (m, 6H, 3 CH_2, ^{10}), 3.00 – 2.22 (m, 26H, 13 CH_2, ^{11}), 2.00 – 0.98 (m, 139H, 5 CH_3, 62 CH_2, ^{12}), 0.98 – 0.60 (m, 12H, 4 CH_3, ^{13}).

^{13}C NMR (75 MHz, $CDCl_3$) δ /ppm: 175.1, 174.6, 174.0, 173.0, 172.8, 171.0, 169.7, 159.0, 139.2, 137.7, 129.4, 128.9, 127.4, 127.3, 126.0, 114.3, 58.4, 58.2, 55.4, 51.0, 48.3, 47.0, 39.5, 39.2, 35.4, 34.4, 33.7, 33.0, 32.9, 32.6, 32.0, 31.6, 29.8, 29.8, 29.7, 29.6, 29.5, 29.4, 29.2, 29.0, 28.7, 28.6, 28.1, 28.0, 27.3, 27.2, 27.0, 26.6, 26.3, 25.9, 25.6, 24.9, 23.5, 22.8, 22.4, 20.2, 14.3, 14.2, 13.9, 11.6.

FAB-MS of $[C_{118}H_{210}O_{11}N_8S_4]^+$: calculated: 2043.5, found: 2044.1.

IR (ATR): ν [cm^{-1}] = 3315.6, 2920.9, 2850.8, 1725.7, 1625.5, 1535.3, 1512.4, 1451.1, 1361.7, 1245.2, 1033.7, 891.2, 816.5, 722.8, 695.7, 616.9.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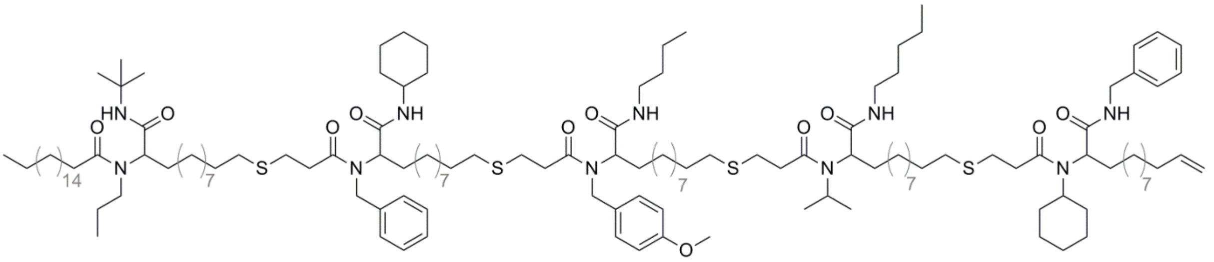
5th Ugi reaction:



0.04 g of 10-undecenal **2** (0.22 mmol, 3.20 eq.) were mixed with 0.02 g cyclohexylamine (0.19 mmol, 2.80 eq.) and 0.30 mL (0.23 M relative to the acid) methanol and stirred for 30 minutes. Subsequently, 0.14 g of substance **14’** (0.07 mmol, 1.00 eq.) and 0.02 g of benzyl isocyanide (0.21 mmol, 3.00 eq.) were added and the reaction mixture was stirred at room temperature for 24 hours. The solvent was removed under reduced pressure and the product was separated by column chromatography (hexane / ethyl acetate 7:1 → 1:1) to afford 56 % of substance **15** (0.09 g).

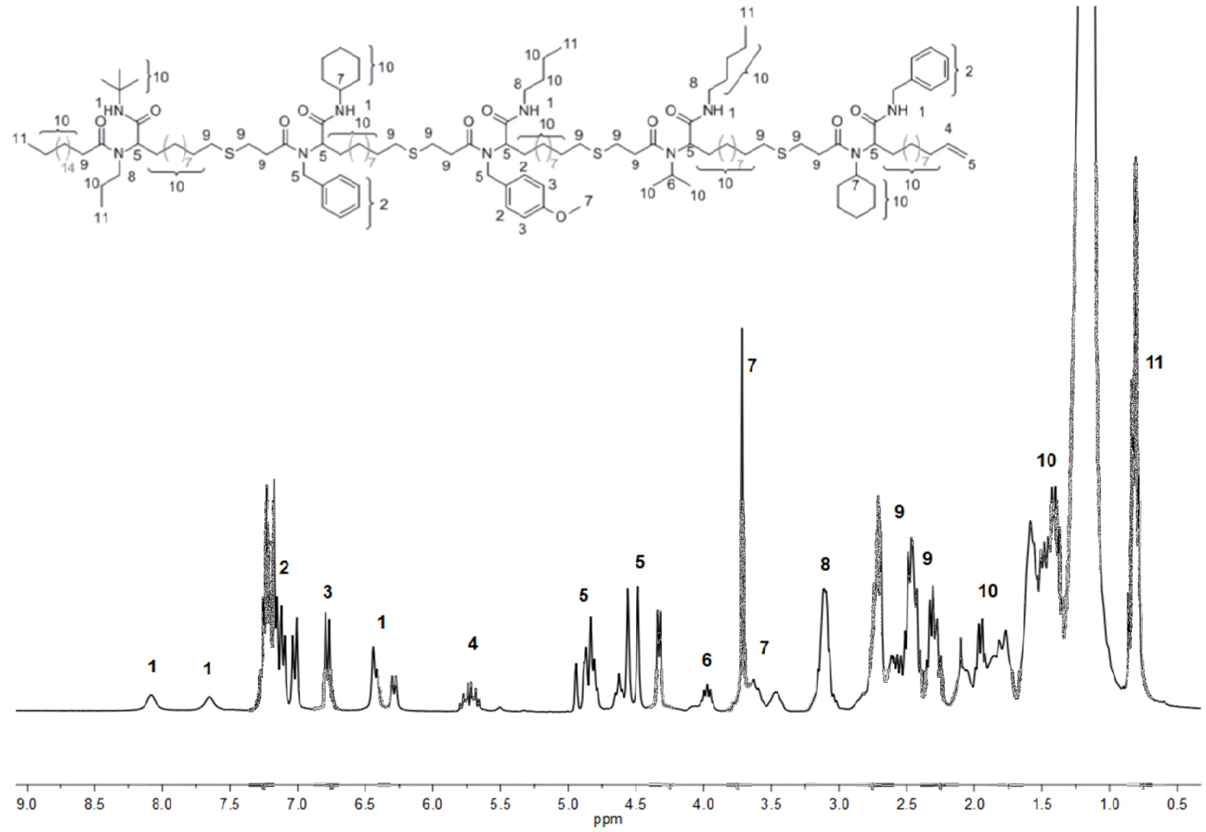
^{1}H NMR (300 MHz, $CDCl_3$) δ /ppm: 8.14 (bs, 1H, NH, [1]), 7.71 (bs, 1H, NH, [1]), 7.40 – 7.00 (m, 12H, 12 CH aromatic, [2]), 6.84 (d, J = 8.5 Hz, 2H, 2 CH aromatic, [3]), 6.60 – 6.23 (m, 3H, 3 NH, [1]), 5.79 (m, 1H, CH, [4]), 5.07 – 4.19 (m, 13H, 5 CH, 4 CH_2, [5]), 4.17 – 3.93 (m, 1H, CH, [6]), 3.87 – 3.42 (m, 5H, CH_3, 2 CH, [7]), 3.29 – 3.01 (m, 6H, 3 CH_2, [8]), 2.98 – 2.26 (m, 26H, 13 CH_2, [9]), 2.23 – 0.95 (m, 165H, 5 CH_3, 75 CH_2, [10]), 0.88 (m, 12H, 4 CH_3, [11]).

^{13}C NMR (75 MHz, $CDCl_3$) δ /ppm: 174.9, 173.8, 173.8, 173.2, 173.1, 172.7, 172.5, 170.9, 170.6, 169.6, 158.8, 139.2, 138.7, 137.6, 129.4, 128.8, 128.5, 127.4, 127.2, 127.1, 125.9, 114.2, 58.8, 58.2, 55.3, 50.8, 48.4, 48.1, 48.0, 43.2, 39.3, 39.1, 35.3, 35.2, 34.3, 33.8, 33.6, 33.0, 32.8, 32.8, 32.6, 32.5, 32.0, 31.6, 31.5, 31.3, 30.3, 30.2, 29.7, 29.7, 29.7, 29.6, 29.5, 29.5, 29.4, 29.4, 29.3, 29.1, 28.9, 28.9, 28.7, 28.4, 27.9, 27.3, 27.2, 26.5, 26.5, 26.3, 26.0, 25.8, 25.8, 25.6, 25.0, 24.8, 23.4, 22.7, 22.4, 21.2, 21.0, 20.1, 14.2, 14.1, 13.8, 11.5.

FAB-MS of $[C_{143}H_{248}N_{10}O_{11}S_4]^+$: calculated: 2409.8, found: 2410.3.

IR (KBr): ν [cm^{-1}] = 3314.8, 2923.0, 2851.6, 1629.6, 1536.3, 1513.1, 1452.6, 1361.8, 1245.8, 1030.7, 906.7, 817.4, 723.1, 697.2.

***R*$_f$:** (hexane / ethyl acetate (3:2)) = 0.33.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