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α-Helicomimetic foldamers as electron transfer mediators

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Contents:

1. Schemes of oligoureas synthesis

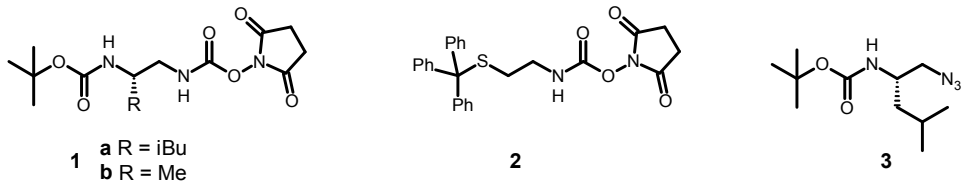
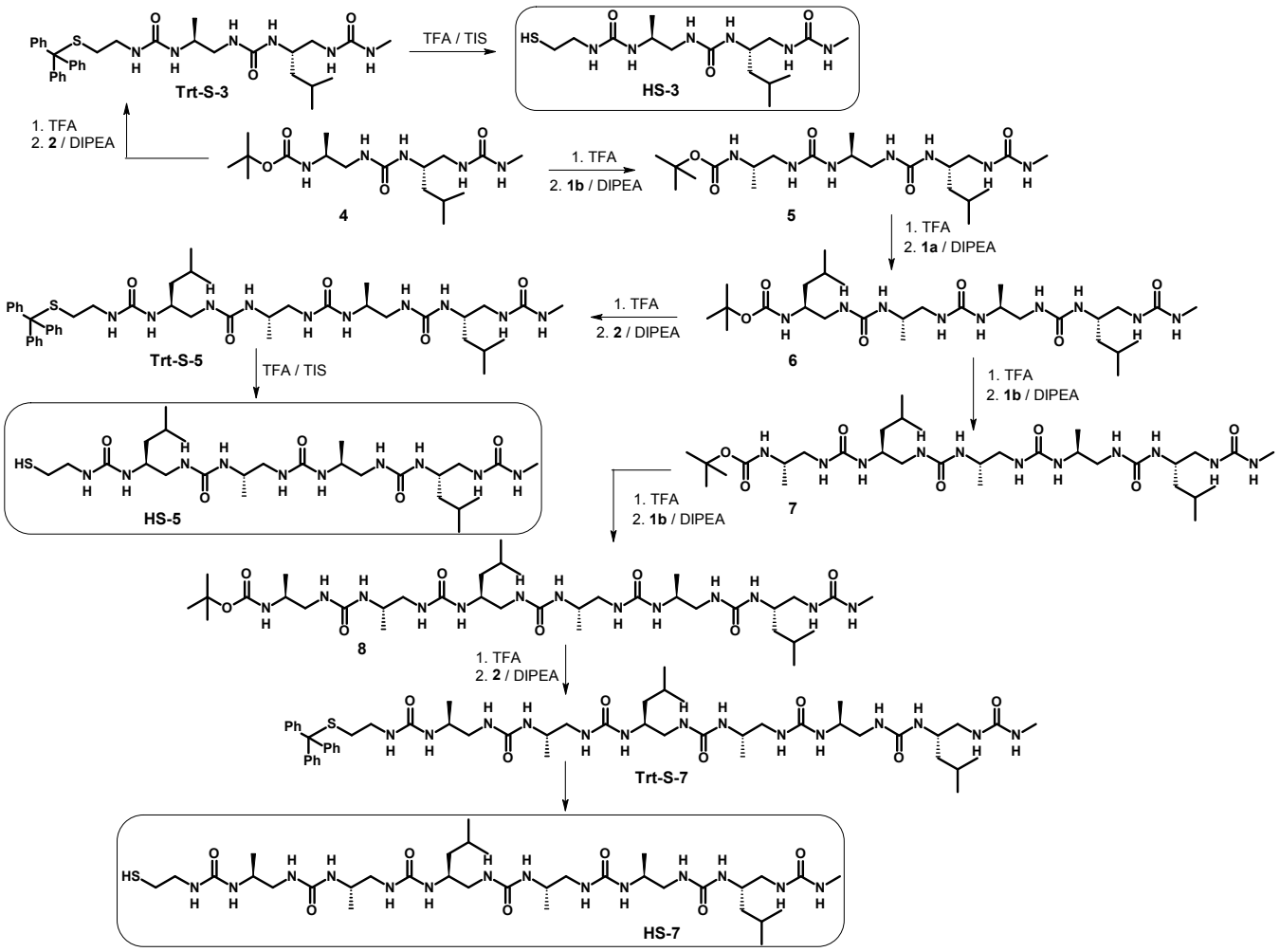
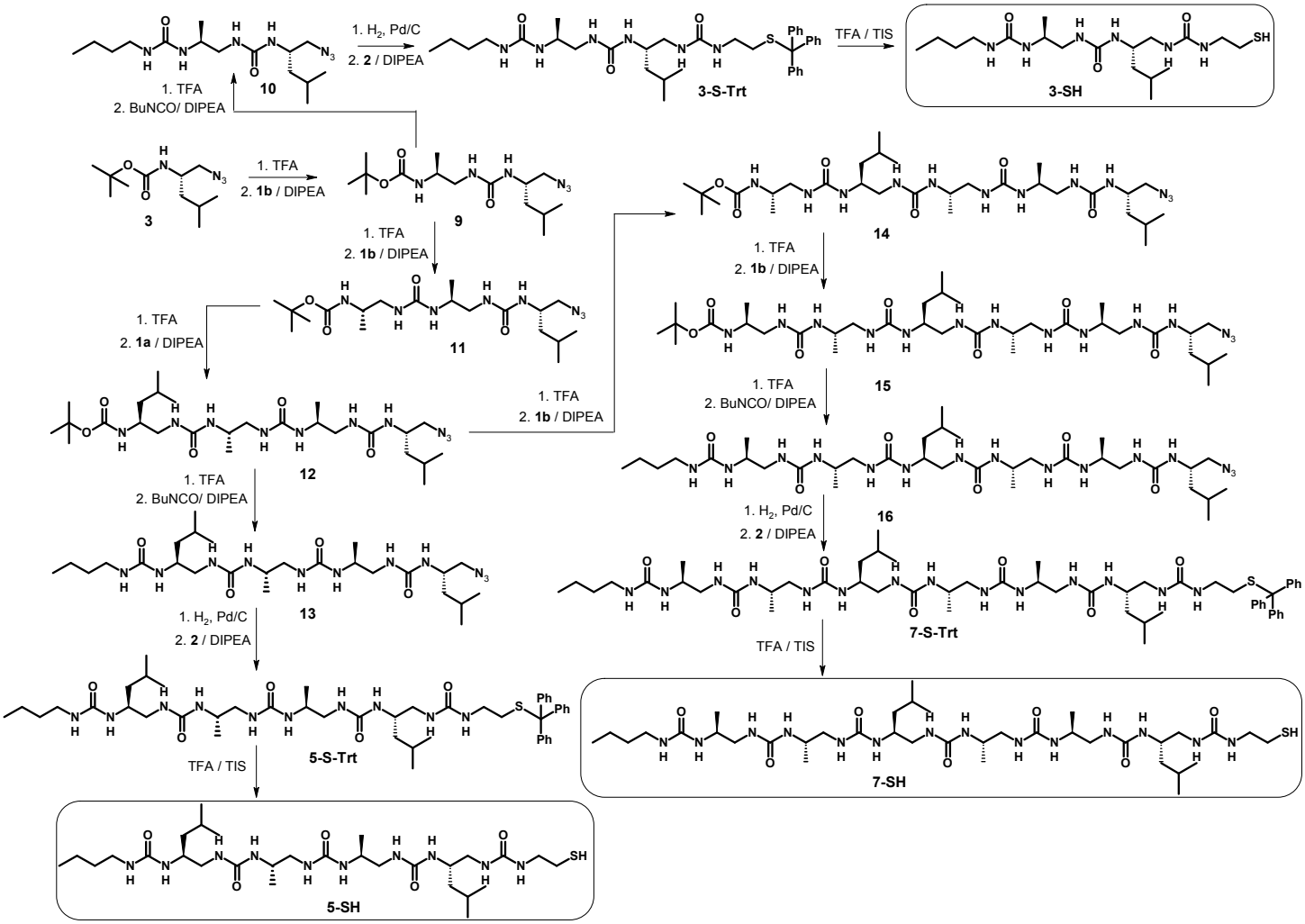


Figure S1. Building blocks used to the synthesis of oligoureas



Scheme S1. Synthesis of **HS-X** oligoureas



Scheme S2. Synthesis of **X-SH** oligoureas

2. General information - synthesis and characterisation

Thin layer chromatography (TLC) was performed on silica gel 60 F254 (Merck) with detection by UV light and charring with ninhydrin in ethanol (1g in 200mL EtOH) followed by heating. Flash column chromatography was carried out on silica gel (63-200μm).^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker AVANCE 300 MHz for ^{1}H and 75 MHz for ^{13}C. Chemical shifts are reported in parts per million (ppm). ^{1}H NMR splitting patterns with observed first-order coupling are designated as singlet (s), doublet (d), triplet (t), quartet (q), septet (sept) or multiplets (m). Coupling constants (*J*) are reported in hertz. Analytical RP-HPLC analyses were performed using a Jupiter 4u Proteo column 90Å (4.6 × 250 mm) at a flow rate of 1 mL.min^{-1}. The mobile phase was composed of 0.05% (v/v) TFA-H_2O (Solvent A) and 0.05% TFA-CH_3CN (Solvent B). The detection was performed at 200 nm and the column temperature in the oven was 25°C. Two gradients were used: gradient 1 (3-97% B in 20min and 97% B in 5 min) and gradient 2 (70-100% B in 20 min and 100% B in 5 min). Mass spectra were recorded on a LCT TOF spectrometer or LCMS-IT-TOF using electrospray ionization (positive ion mode)

Activated monomers **1** (**a** R = *i*Bu; **b** R = Me) and oligomer **4** were prepared using a previously described procedure.[1]

3. Building block synthesis and characterisation

Synthesis of building block 2

Trt protected cysteamine was prepared as previously described.[2] Trt-cysteamine (0.64 g, 2mmol) was dissolved in 20 ml of freshly distilled CH_2Cl_2 and was added dropwise to solid *N,N'*-disuccinimidyl carbonate (0.56 g, 2.2 mmol) under Ar. While adding amine solution, the mixture was cooled in ice/water bath and then left to reach RT. The reaction was finished after 1-2h. Organic phase was washed with 1M $KHSO_4$ (4x) and brine (1x), dried over Na_2SO_4. The product was obtained as creamy foam and was not further purified before the next step.

Yield: 0.9 g, 98%. %. ^{1}H NMR : (300MHz, CDCl3) δ = 7.47-7.43 (m, 6H), 7.35-7.22 (m, 9H), 5.54 (t, *J* = 5.9 Hz, 1H), 2.98 (q, *J* = 6.5 Hz, 2H), 2.77 (s, 4H), 2.48 (t, *J* = 6.7 Hz, 2H). ^{13}C (75MHz, CDCl3) δ =169.88, 151.15, 144.48, 129.53, 128.09, 126.92, 67.02, 40.74, 31.54, 25.46.

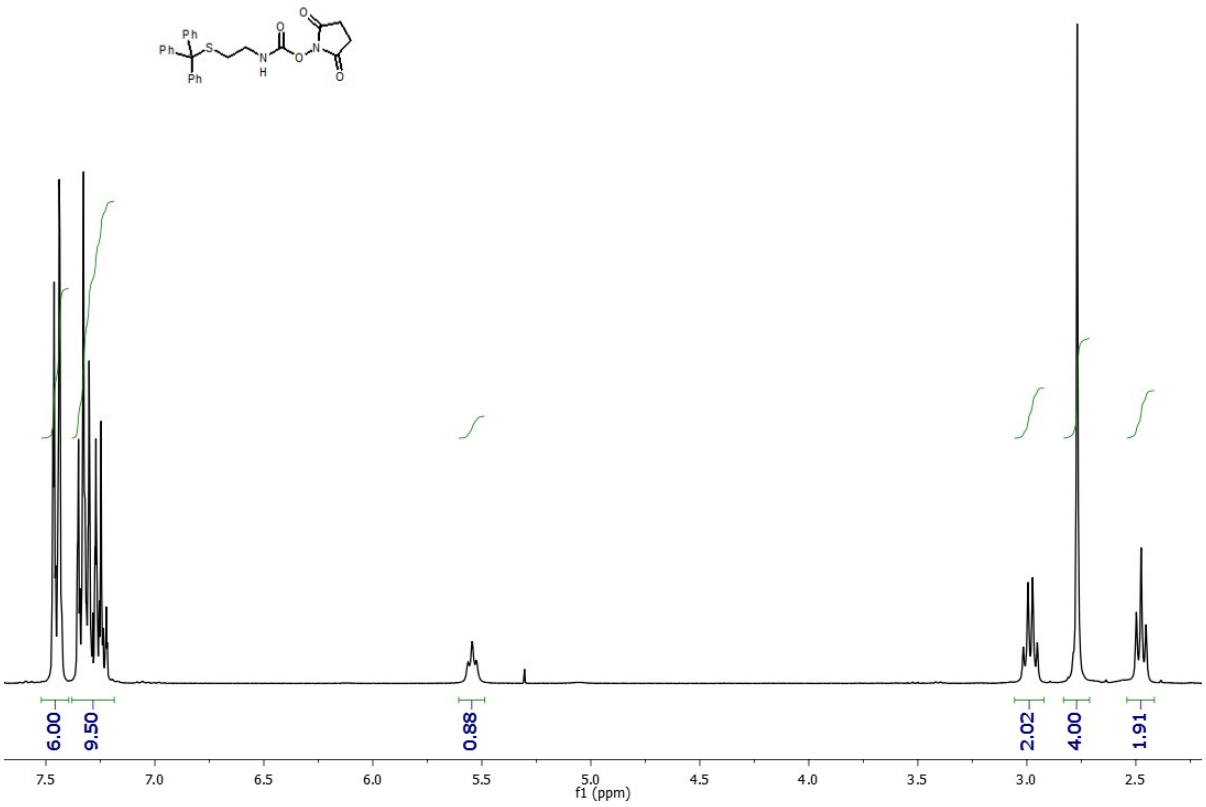


Figure S2. 1H NMR spectrum of building block 2

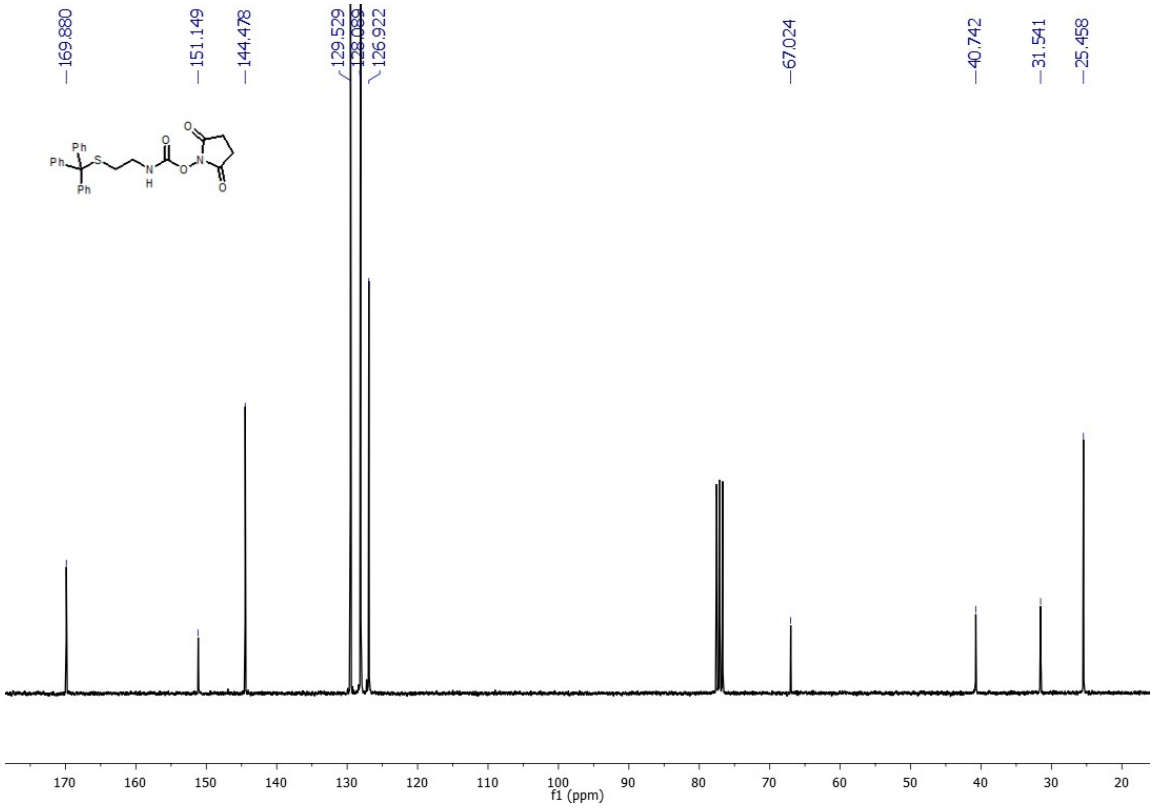


Figure S3. 13C NMR spectrum of building block **2**

Synthesis of building block 3

Building block **3** was prepared according to the previously described procedure for Boc-Pro.[3]

Yield after **3** steps: 2.56 g, 42%. ^{1}H NMR : (300MHz, CDCl3) δ = 4.49 (d, *J* = 7.6 Hz, 1H), 3.82 (bs, 1H), 3.40 (ddd, *J* = 40.9, 12.1, 3.8 Hz, 2H), 1.77 – 1.60 (m, 1H), 1.47 (s, 9H), 1.40-1.30 (m, 2H), 0.95 (d, *J* = 6.6 Hz, 6H).

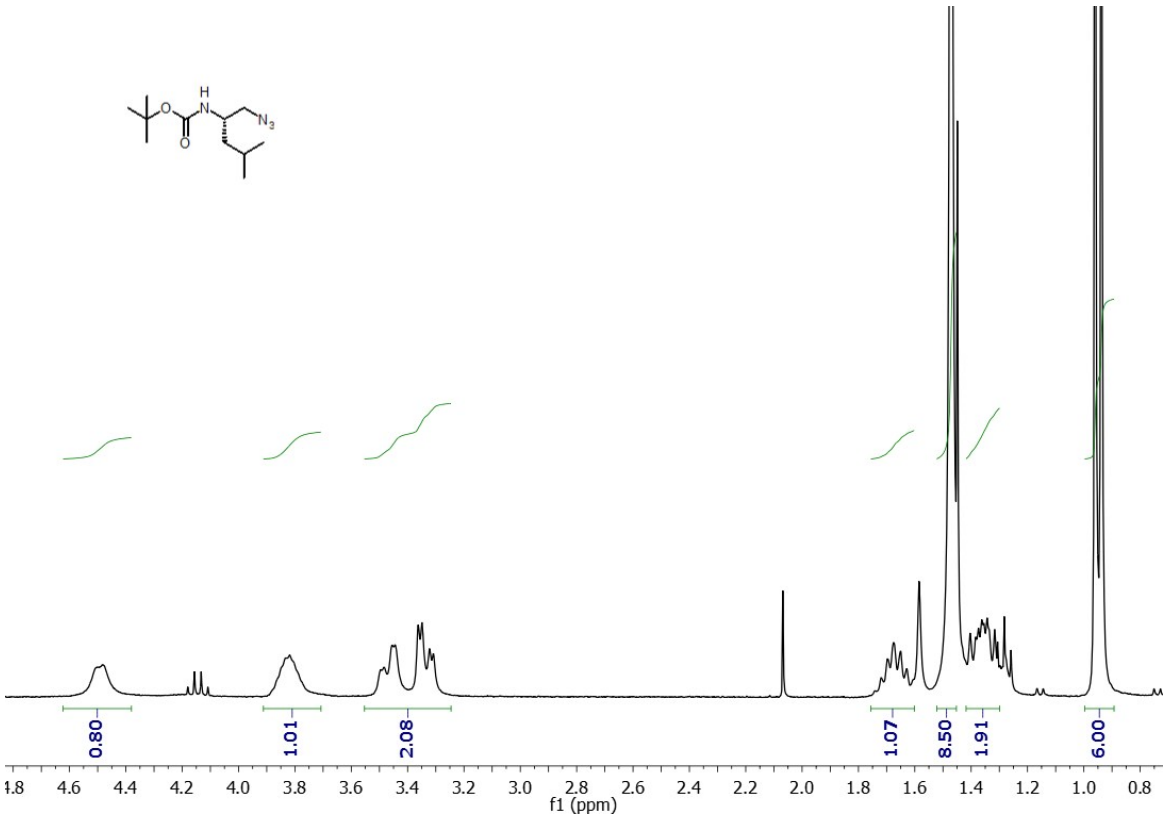


Figure S4. 1H NMR spectrum of building block **3**

4. Analytical characterisation of intermediates leading to oligoureas HS-3, HS-5, HS-7

Oligourea Trt-S-3

Purified by flash chromatography (95:5 to 92:8 DCM:MeOH), yield: 87%. ^{1}H NMR : (300MHz, DMSO d_6, integration problems due to the overlapping with solvent and residual water) δ = 7.37-7.22 (m, 15H), 5.95 (t, *J* = 5.7 Hz, 1H), 5.85-5.78 (m, 4H), 5.72 (d, *J* = 8.6 Hz, 1H), 3.54 (p, *J* = 6.6 Hz, 2H), 3.06 (dt, *J* = 12.9, 6.3 Hz, 1H), 2.97-2.78 (m, 5H), 2.18 (t, *J* = 6.9 Hz, 2H), 1.58 (sept, *J* = 6.7 Hz, 1H), 1.15 (t, *J* = 7.1 Hz, 2H), 0.94 (d, *J* = 6.6 Hz, 3H), 0.83 (dd, *J* = 9.6, 6.6 Hz, 6H); t_R = 20.6 min. (gradient 1).

Oligourea 5

Purified by trituration with Et_2O, yield: 79%. ^{1}H NMR : (300MHz, DMSO d_6, integration problems due to the overlapping with solvent and residual water) δ =6.70 (d, *J* = 8.0 Hz, 1H), 5.92 (t, *J* = 5.8 Hz, 1H), 5.87-5.77 (m, 4H), 5.73 (d, *J* = 8.6 Hz, 1H), 3.64 – 3.53 (m, 3H), 3.14-2.77 (m, 8H), 1.60 (sept, *J* = 6.8 Hz, 1H), 1.38 (s, 9H), 1.16 (t, *J* = 7.0 Hz, 2H), 0.96 (d, *J* = 6.6 Hz, 6H), 0.84 (dd, *J* = 8.3, 6.6 Hz, 6H); t_R = 15.6 min. (gradient 1).

Oligourea 6

Purified by flash chromatography (92:8 DCM:MeOH), yield: 65%. ^{1}H NMR : (300MHz, DMSO d_6, integration problems due to the overlapping with solvent and residual water) δ = 6.65 (d, *J* = 9.0 Hz, 1H), 6.03-5.87 (m, 6H), 5.84 (d, *J* = 9.0 Hz, 1H), 5.79 (d, *J* = 8.8 Hz, 1H), 3.75-3.48 (m, 5H), 3.25-3.03 (m, 5H), 2.83-2.60 (m, 4H), 1.59 (sept, *J* = 6.9 Hz, 2H), 1.14 (p, *J* = 7.4 Hz, 4H),), 0.94 (d, *J* = 6.6 Hz, 3H),), 0.93(d, *J* = 6.5 Hz, 3H), 0.87-0.83 (m, 12H).; t_R = 19.1 min. (gradient 1).

Oligourea Trt-S-5

Purified by gel formation with Et_2O and petroleum ether, yield: 78%. (300MHz, DMSO d6, very broad peaks, integration problems due to the overlapping with solvent and residual water) δ = 7.36-7.22 (m, 15H), 6.06-5.79 (m, 10H), 3.79-3.58 (m, 5H), 3.27-3.09 (m, 4H), 3.02-2.84 (m, 3H), 2.65-2.2.59 (m, 2H), 2.55 (d, *J* = 4.6 Hz, 3H), 2.19 (sekst, *J* = 6.4 Hz, 2H), 1.65-1.52 (m, 2H), 1.17-1.10 (m, 4H), 0.90-0.79 (m, 18H); t_R = 10.1 min. (gradient 2).

Oligourea 7

Purified by gel formation with Et_2O and petroleum ether, yield: 72%. (300MHz, DMSO d_6, integration problems due to the overlapping with solvent and residual water) δ = 6.78 (d, *J* = 8.2 Hz, 1H), 6.13 (dd, *J* = 7.8, 2.8 Hz, 1H), 6.07-5.98 (m, 3H), 5.91-5.83 (m, 5H), 5.76 (d, *J* = 9.0 Hz, 1H), 3.83-3.58 (m, 4H), 3.54-3.45 (m, 1H), 3.29-3.18 (m, 7H), 3.10-3.00 (m, 2H), 2.91-2.82 (m, 1H), 2.64-2.59 (m, 1H), 2.56 (d, *J* = 4.6 Hz, 3H), 1.60 (sept, *J* = 6.6 Hz, 2H), 1.39 (s, 9H), 1.18-1.11 (m, 4H), 0.98 (d, *J* = 6.6 Hz, 3H), 0.94-0.2 (m, 18H); t_R = 20.1 min. (gradient 1).

Oligourea 8

Purified by trituration with Et_2O and petroleum ether, yield: 77%. ^{1}H NMR : (300MHz, DMSO d_6, integration problems due to the overlapping with solvent and residual water) δ = 6.80 (d, *J* = 8.4 Hz, 1H), 6.32 (bd, *J* = 8.6 Hz, 1H), 6.14-6.07 (m, 3H), 6.04-5.99 (m, 4H), 5.92-5.86 (m, 3H), 5.80 (d, *J* = 9.8 Hz, 1H), 5.75 (d, *J* = 9.2 Hz, 1H), 3.87-3.62 (m, 7H), 3.56-3.46 (m, 3H), 3.14-3.04 (m, 2H), 2.87-2.78 (m, 1H), 2.56 (d, *J* = 4.6 Hz, 3H), 2.37-2.29 (m, 4H), 1.60 (sept, *J* = 6.5 Hz, 2H), 1.39 (s, 9H), 1.13 (t, *J* = 7.0 Hz, 4H), 0.99 (d, *J* = 6.6 Hz, 3H), 0.98 (d, *J* = 6.7 Hz, 3H), 0.93-0.82 (m, 18H); t_R = 22.2 min. (gradient 1).

Oligourea Trt-S-7

Purified by trituration with Et_2O and petroleum ether, yield: 92%. ^{1}H NMR : (300MHz, DMSO d_6, integration problems due to the overlapping with solvent and residual water and peaks broadening) δ = 7.38-7.22 (m, 15H), 6.38 (bd, *J* = 8.6 Hz, 1H), 6.22 (bd, *J* = 7.4 Hz, 1H), 6.16-5.87 (m, 10H), 5.79 (d, *J* = 10.4 Hz, 1H), 5.75 (d, *J* = 9.0 Hz, 1H),3.90-3.61 (m, 9H), 3.19-2.77 (m, 5H), 2.56 (d, *J* = 4.7 Hz, 3H), 2.31-2.19 (m, 6H), 1.94 (t, *J* = 9.8 Hz, 2H), 1.59 (bsig, 1H), 1.15-1.05 (m, 4H), 0.99-0.80 (m, 24H); t_R = 17.4 min. (gradient 2).

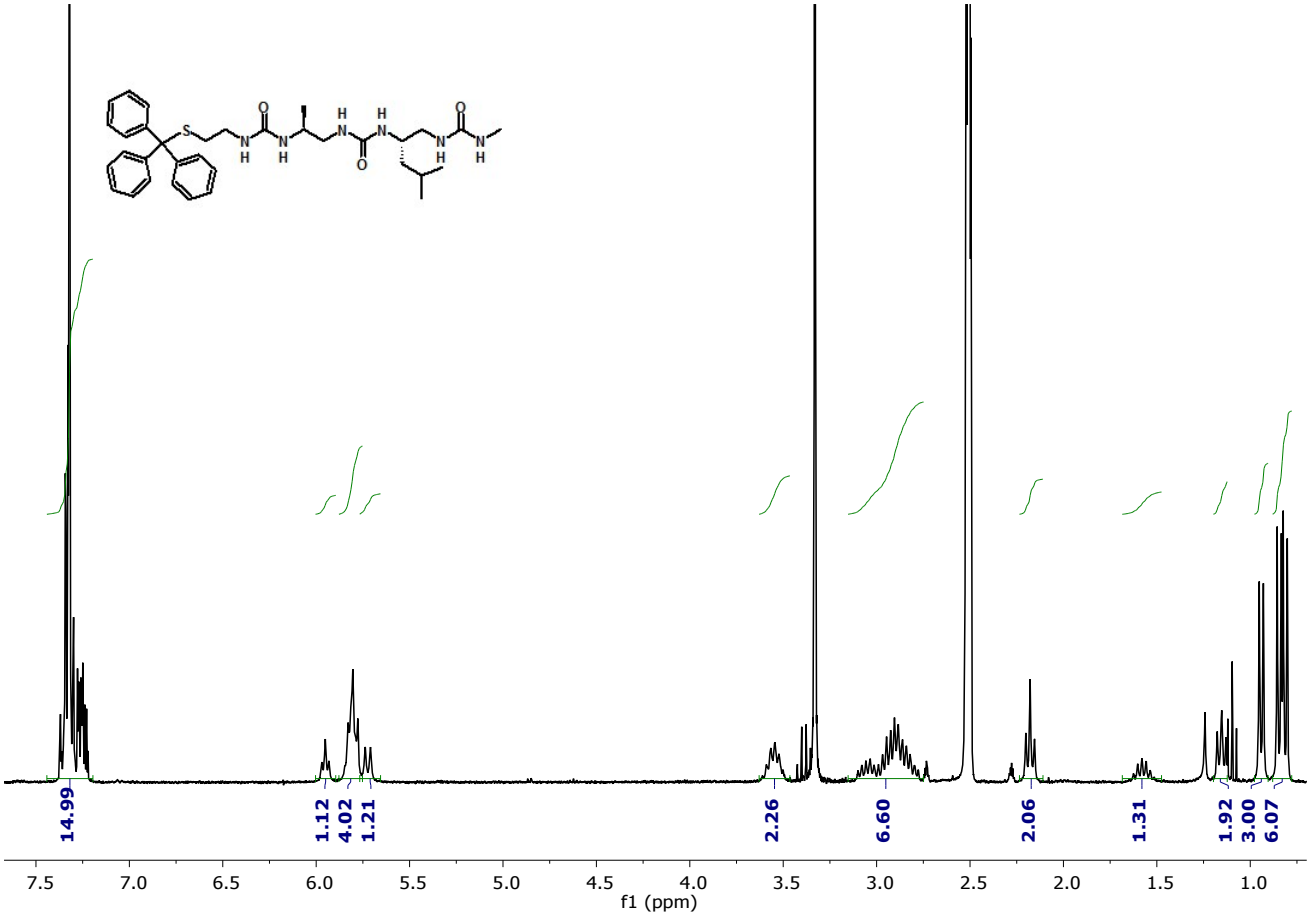


Figure S5. 1H NMR spectrum of compound **Trt-S-3**

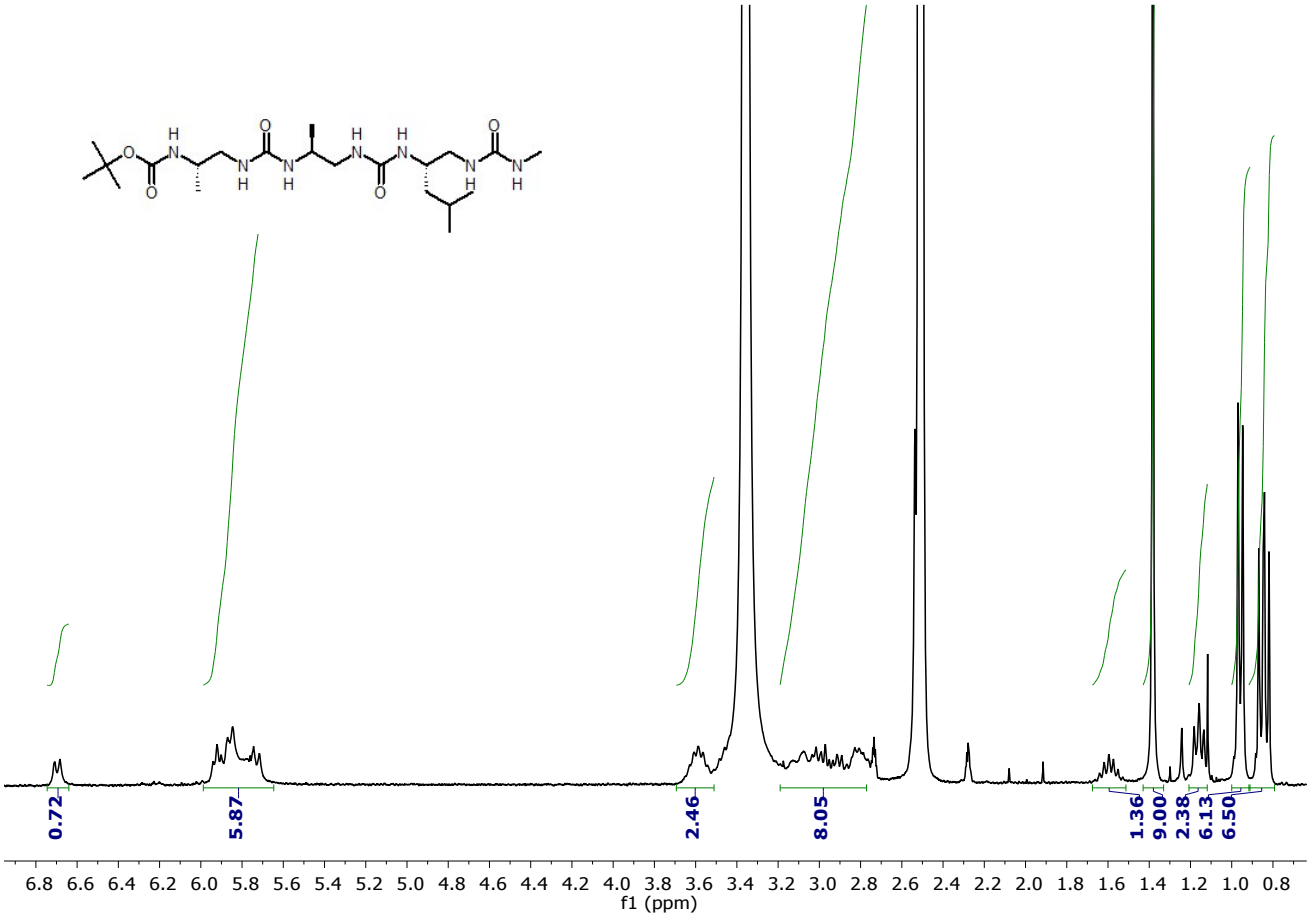


Figure S6. 1H NMR spectrum of compound **5**

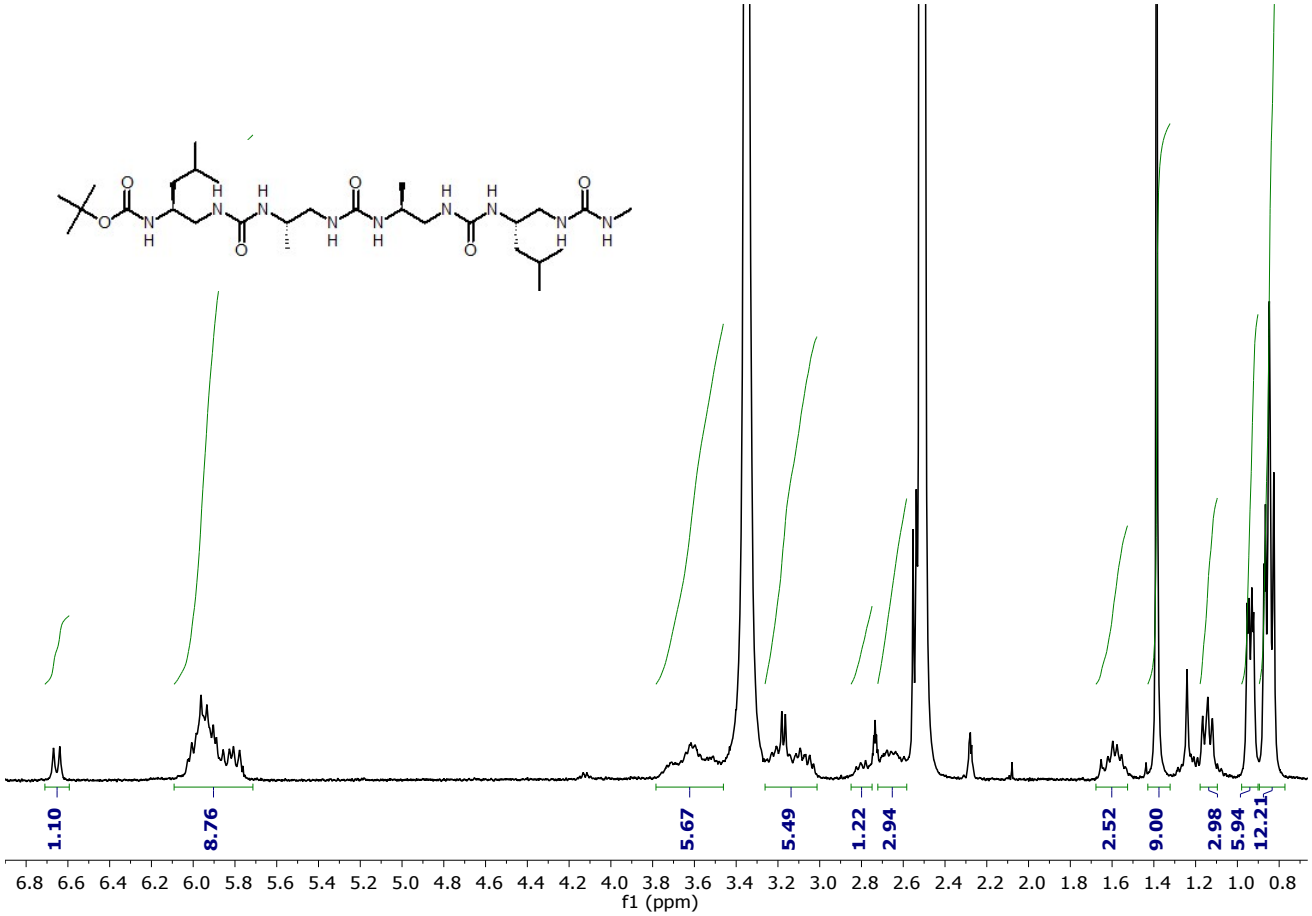


Figure S7. 1H NMR spectrum of compound **6**

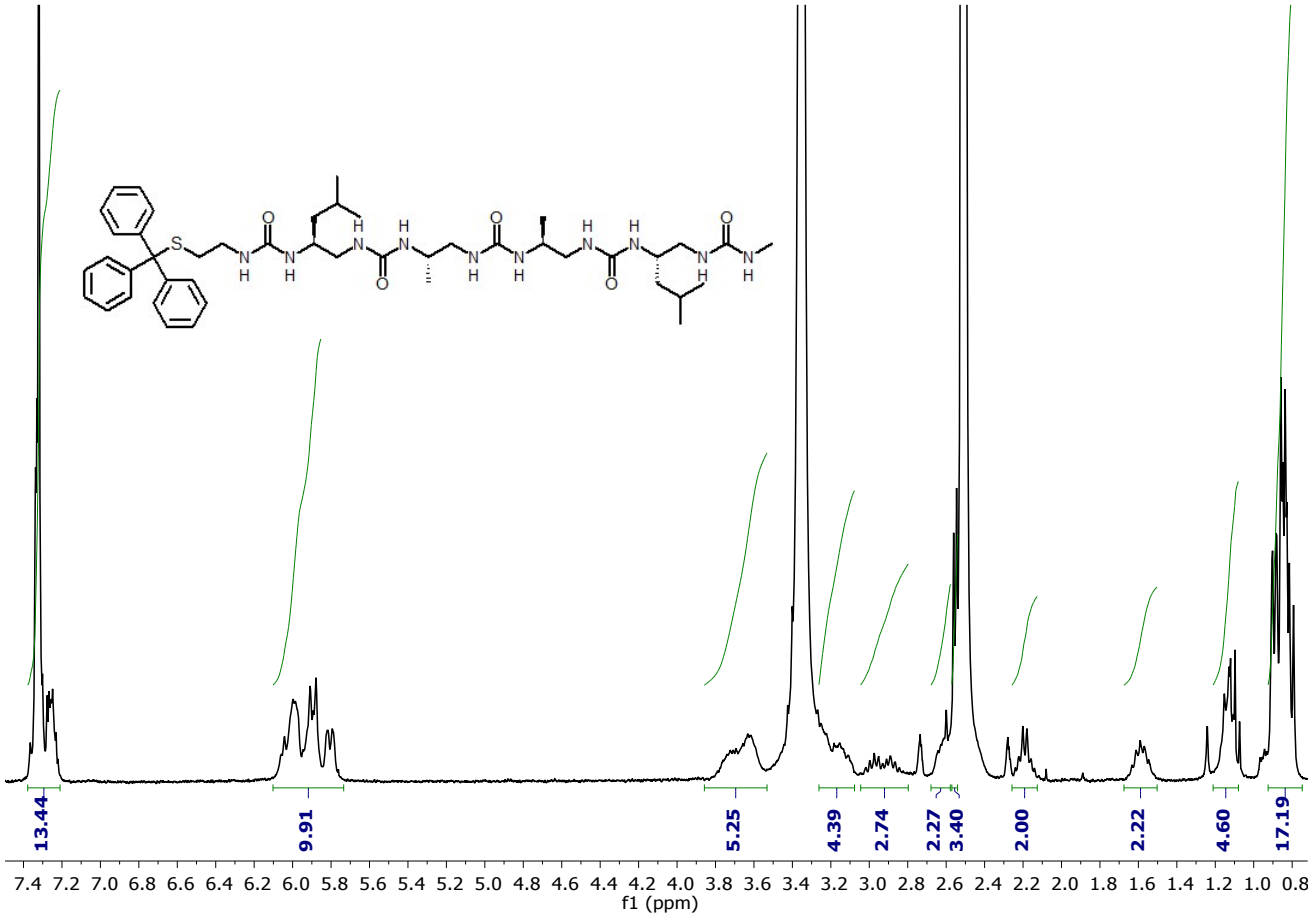


Figure S8. 1H NMR spectrum of compound **Trt-S-5**

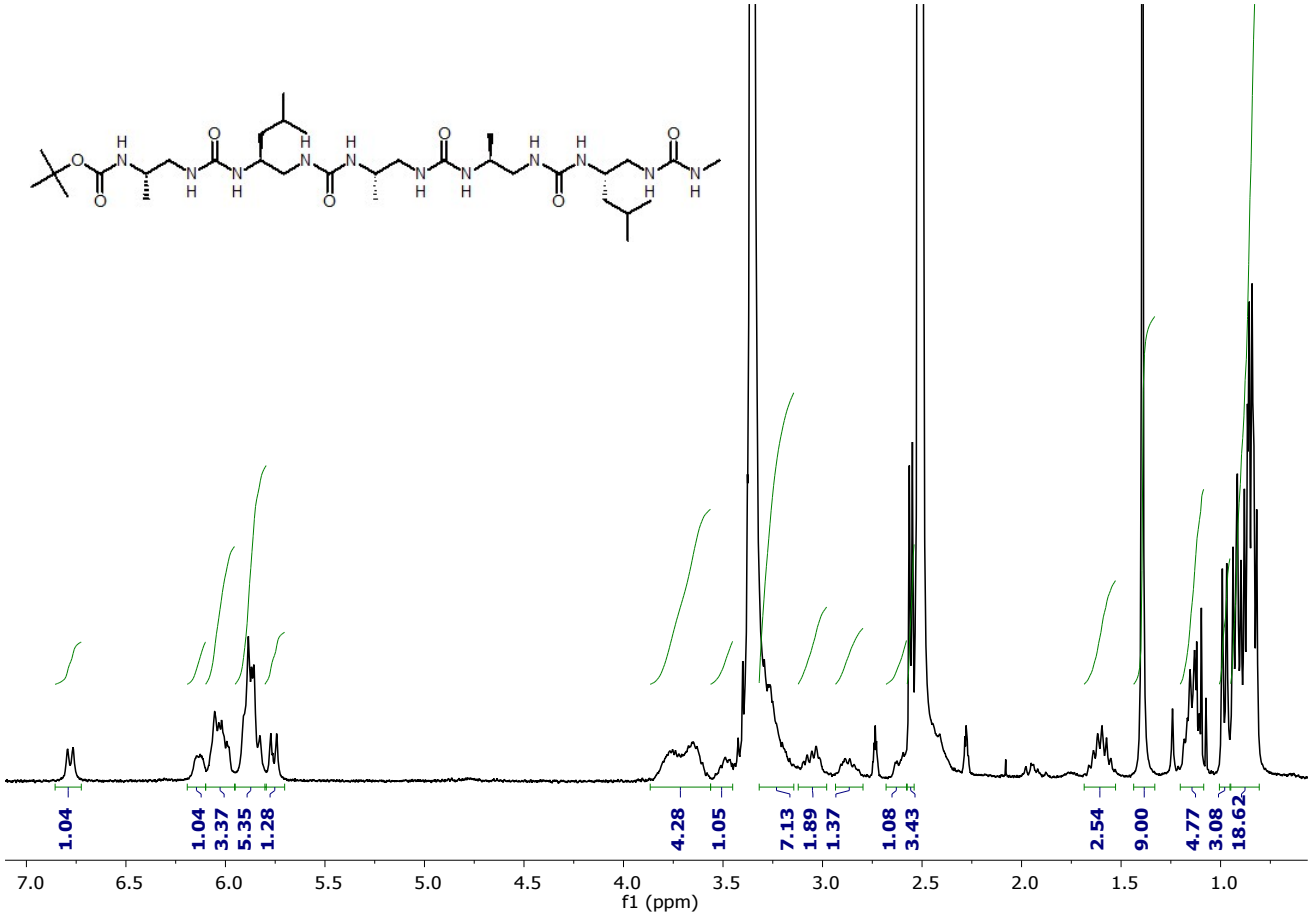


Figure S9. 1H NMR spectrum of compound **7**

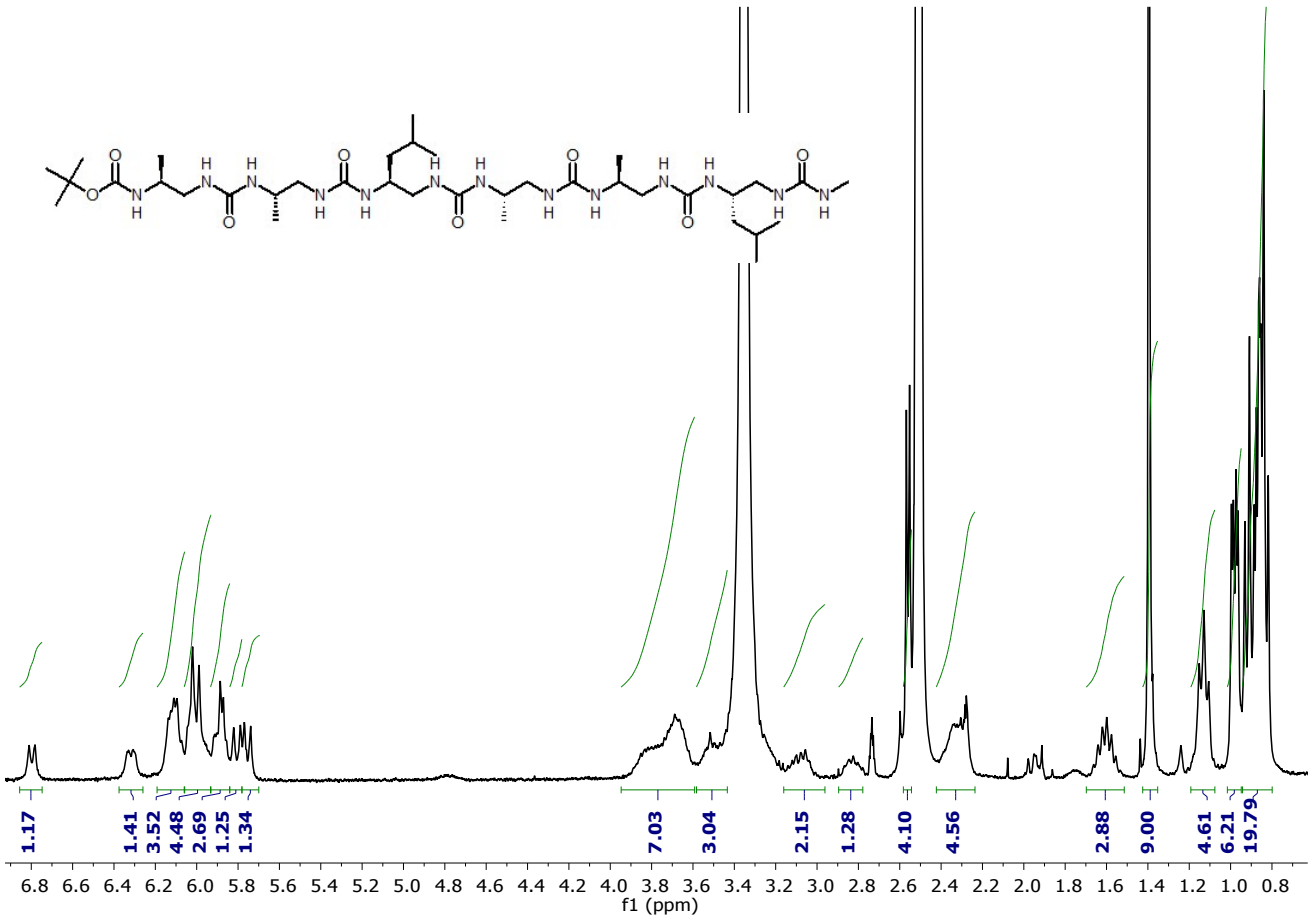


Figure S10. 1H NMR spectrum of compound **8**

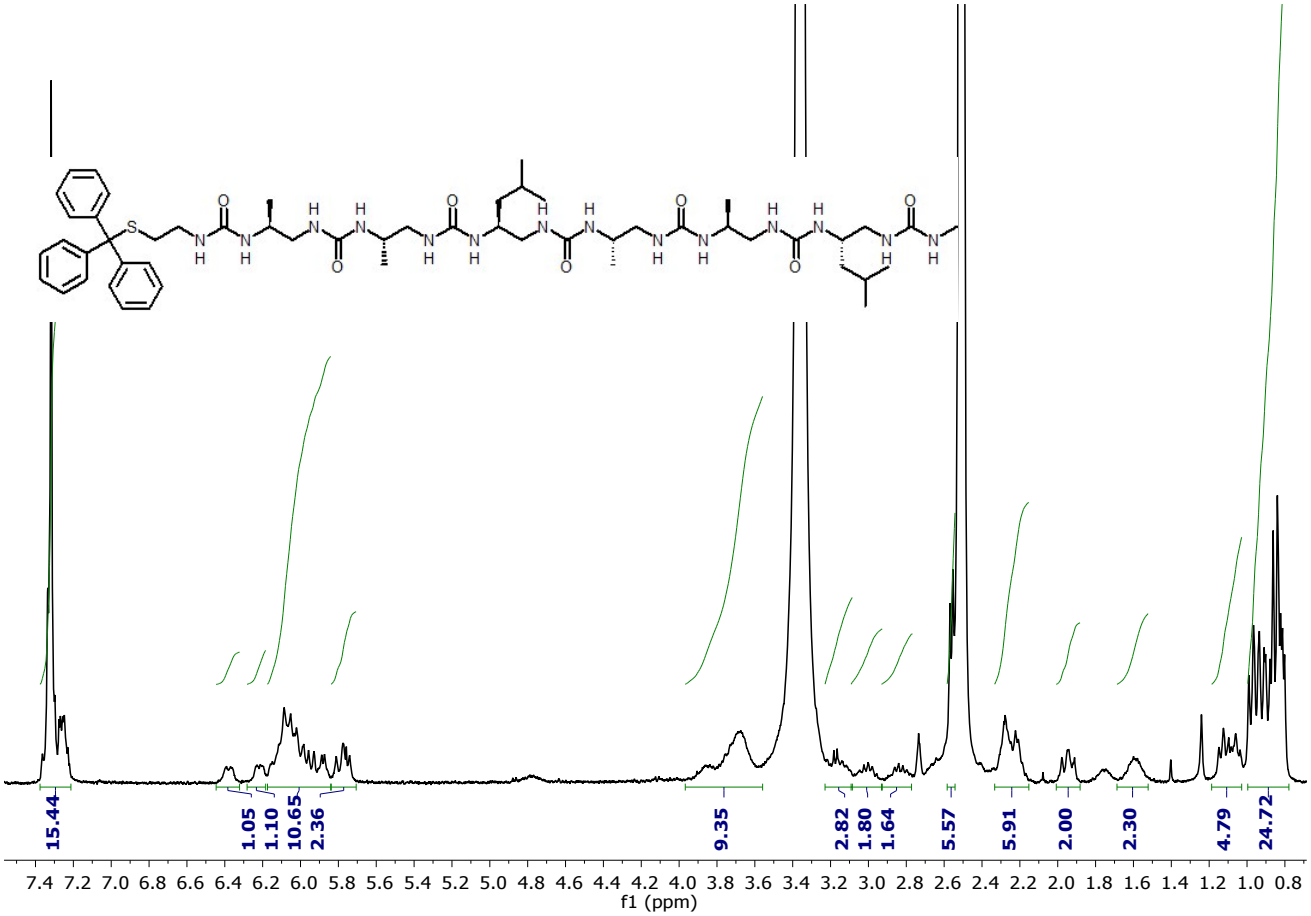


Figure S11. 1H NMR spectrum of compound **Trt-S-7**

5. Analytical characterisation of intermediates leading to oligoureas 3-SH, 5-SH, 7-SH

Oligourea 9

Purified by flash chromatography (97:3 DCM:MeOH), yield: 76%. ^{1}H NMR : (300MHz, DMSO d_6) δ = 6.63 (d, *J* = 7.7 Hz, 1H), 5.96 (d, *J* = 8.5 Hz, 1H), 5.86 (t, *J* = 5.9 Hz, 1H), 3.83-3.72 (m, 1H), 3.43 (p, *J* = 6.5 Hz, 1H), 3.26 (d, *J* = 5.4 Hz, 2H), 2.97 (t, *J* = 6.2 Hz, 2H), 1.67-1.53 (m, 1H), 1.38 (s, 9H), 1.34-1.14 (m, 2H), 0.96 (d, *J* = 6.6 Hz, 3H), 0.86 (dd, *J* = 8.3, 6.6 Hz, 7H); t_R = 18.9 min. (gradient 1).

Oligourea 10

Purified by flash chromatography (98:2 DCM:MeOH), yield: 76%. ^{1}H NMR : (300MHz, DMSO d_6) δ = 6.00 (d, *J* = 8.4 Hz, 1H), 5.87 (t, *J* = 5.7 Hz, 1H), 5.80 (t, *J* = 5.7 Hz, 1H), 5.66 (d, *J* = 7.7 Hz, 1H), 3.83-3.72 (m, 1H), 3.54 (p, *J* = 6.7 Hz, 1H), 3.27 (d, *J* = 5.3 Hz, 2H), 3.03-2.90 (m, 4H), 1.67-1.53 (m, 1H), 1.39-1.14(m, 6H), 0.96 (d, *J* = 6.6 Hz, 3H), 0.89-0.83 (m, 9H); t_R = 17.4 min. (gradient 1).

Oligourea 3-S-Trt

Purified by gel formation with Et_2O and petroleum ether, yield: 75%. ^{1}H NMR : (300MHz, DMSO d_6) δ =7.37-7.21 (m, 15H), 6.10 (bt, *J* = 5.5 Hz, 1H), 5.89-5.81 (m, 3H), 5.76 (d, *J* = 8.7 Hz, 1H), 5.69 (d, *J* = 7.9 Hz, 1H), 3.64-3.52 (m, 2H), 3.1-2.73 (m, 8H), 2.17 (t, *J* = 6.8 Hz, 2H), 1.67 – 1.49 (m, 1H), 3.38-3.21 (m, 4H), 1.14 (t, *J* = 6.7 Hz, 2H), 0.94 (d, *J* = 6.6 Hz, 3H), 0.88-0.80 (m, 9H); t_R = 22.0 min. (gradient 1).

Oligourea 11

Purified by flash chromatography (97:3 to 95:5 DCM:MeOH), yield: 80%. ^{1}H NMR : (300MHz, ACN d_3) δ = 5.62 (bs, 1H), 5.32-5.20 (m, 3H), 5.10 (d, *J* = 7.8 Hz, 1H), 3.96-3.85 (m, 1H), 3.74-3.61 (m, 2H), 3.31 (d, *J* = 5.3 Hz, 2H), 3.19-3.11 (m, 2H), 3.02-2.92 (m, 2H), 1.72-1.60 (m, 1H), 1.43 (s, 9H), 1.40-1.22 (m, 2H), 1.06 (d, *J* = 6.7 Hz, 6H), 0.92 (dd, *J* = 6.6, 5.4 Hz, 6H); t_R = 17.8 min. (gradient 1).

Oligourea 12

Purified by flash chromatography (97:3 to 95:5 DCM:MeOH), yield: 71%. ^{1}H NMR : (300MHz, ACN d_3, integration problems due to the peaks broadening) δ = 6.04 (bd, *J* = 8.6 Hz, 1H), 5.81 (d, *J* = 8.7 Hz, 1H), 5.49 b(d, *J* = 11.4 Hz, 1H), 5.36-5.29 (m, 3H), 4.90 (d, *J* = 9.8 Hz, 1H), 3.98-3.82 (m, 5H), 3.63-3.49 (m, 2H), 3.42-3.28 (m, 3H), 2.57-2.44 (m, 2H), 2.28 (bt, *J* = 10.7 Hz, 1H), 1.74-1.62 (m, 2H), 1.46 (s, 9H), 1.34-1.10 (m, 5H), 1.01 (t, *J* = 6.6 Hz, 6H), 0.93 (d, *J* = 6.7 Hz, 3H), 0.92 (d, *J* = 6.6 Hz, 7H), 0.87 (d, *J* = 6.6 Hz, 3H); t_R = 19.7 min. (gradient 1).

Oligourea 13

Crude product (taken to the next step without purification), ^{1}H NMR : (300MHz, DMSO d_6, integration problems due to the peaks broadening) δ = 6.02 (d, *J* = 8.5 Hz, 1H), 5.96-5.82 (m, 6H), 5.62 (d, *J* = 8.8 Hz, 1H), 3.81-3.56 (m, 6H), 3.28 (t, *J* = 5.3 Hz, 2H), 3.19-3.09 (m, 5H), 2.99 (q, *J* = 6.5 Hz, 2H), 2.84-2.64 (m, 4H), 1.66-1.54 (m, 2H), 1.38-1.30 (m, 2H), 1.98-1.18 (m, 2H), 0.95 (d, *J* = 6.6 Hz, 6H), 0.89-0.81 (m, 15H); t_R = 18.8 min. (gradient 1).

Oligourea 5-S-Trt

Purified by trituration with Et_2O and petroleum ether, yield: 70%.^{1}H NMR : (300MHz, DMSO d_6, integration problems due to the peaks broadening) δ = 7.33-7.21 (m, 15H), 6.11-6.00 (m, 4H), 5.96-5.90 (m, 4H), 5.77 (d, *J* = 9.0 Hz, 1H), 5.70 (d, *J* = 9.1 Hz, 1H), 3.82-3.74 (m, 2H), 3.67-3.59 (m, 2H), 3.28-3.13 (m, 4H), 3.04-2.86 (m, 5H), 2.38 (broad peak, 2H), 2.17 (t, *J* = 6.9 Hz, 2H), 1.65-1.51 (m, 2H), 1.42-1.28 (m, 4H), 1.19-1.08 (m, 4H), 0.90-0.81 (m, 21H); t_R = 24.2 min. (gradient 1).

Oligourea 14

Purified by flash chromatography (97:3 to 92:8 DCM:MeOH), yield: 75%. ^{1}H NMR : (300MHz, DMSO d_6, integration problems due to the peaks broadening and overlapping with solvent and residual water) δ = 6.73 (d, *J* = 8.1 Hz, 1H), 6.01-5.90 (m, 4H), 5.82 (bd, *J* = 8.6 Hz, 4H), 3.82-3.57 (m, 5H), 3.52-3.41 (m, 1H), 3.28 (t, *J* = 5.5 Hz, 2H), 3.18-3.01 (m, 3H), 3.06-2.98 (m, 1H), 2.94-2.87 (m, 1H), 1.67-1.55 (m, 2H), 1.22-1.14 (m, 2H), 0.96 (*pseudo* t, *J* = 6.6 Hz, 9H), 0.88-0.81 (m, 12H); t_R = 20.3 min. (gradient 1).

Oligourea 15

Purified by flash chromatography (95:5 to 92:8 DCM:MeOH), yield: 74%. ^{1}H NMR : (300MHz, DMSO d_6, integration problems due to the peaks broadening and overlapping with solvent and residual water) δ = 6.77 (d, *J* = 8.3 Hz, 1H), 6.04-5.87 (m, 8H), 5.88– 5.77 (m, 2H), 3.82-3.64 (m, 6H), 3.56-3.47 (m, 1H), 3.30-3.18 (m, 5H), 3.11-3.03 (m, 1H), 2.88-2.79 (m, 1H), 2.70-2.60 (m, 2H), 1.67-1.56 (m, 2H), 1.39 (s, 9H), 1.33-1.18 (m, 3H), 1.16-1.09 (m, 2H), 0.99-0.93 (m, 12H), 0.88-0.80 (m, 12H); t_R = 21.7 min. (gradient 1).

Oligourea 16

Purified by gel formation with Et_2O and petroleum ether, yield: 90%. ^{1}H NMR : (300MHz, DMSO d_6, integration problems due to the peaks broadening and overlapping with solvent and residual water) δ = 6.14-5.95 (m, 10H), 5.79 (*pseudo* t, *J* = 8.8 Hz, 2H), 3.84-3.64 (m, 7H), 3.29-3.11 (m, 5H), 3.07-2.93 (m, 3H), 2.71-2.61 (m, 2H), 2.44-2.31 (m, 2H), 1.71-1.54 (m, 2H), 1.41-1.21 (m, 7H), 1.09 (*pseudo* t, *J* = 7.0 Hz, 2H), 0.99-0.93 (m, 12H), 0.89-0.81 (m, 15H); t_R = 20.7 min. (gradient 1).

Oligourea 7-S-Trt

Purified by flash chromatography (92:8 DCM:MeOH), yield: 92%. ^{1}H NMR : (300MHz, DMSO d_6, integration problems due to the peaks broadening and overlapping with solvent and residual water) δ =7.36-7.20 (m, 15H), 6.41 (*pseudo* d, *J* = 9.2 Hz, 1H), 6.27 (*pseudo* d, *J* = 8.0 Hz, 1H), 6.16-6.05 (m, 7H), 6.00 (*pseudo* t, *J* = 5.7 Hz, 2H), 5.84 (d, *J* = 8.7 Hz, 1H), 5.77 (d, *J* = 10.1 Hz, 1H), 5.72 (d, *J* = 9.3 Hz, 1H), 3.94-3.61 (m, 7H), 3.46-3.37 (m, 4H), 3.22-3.13 (m, 2H), 3.08-2.83 (m, 5H), 2.17 (t, *J* = 7.2 Hz, 3H), 1.66-1.51 (m, 2H), 1.42-1.29 (m, 4H), 1.11 (t, *J* = 7.1 Hz, 4H), 0.97 (t, *J* = 6.4 Hz, 6H), 0.90-0.81 (m, 21H); t_R = 15.5 min. (gradient 2).

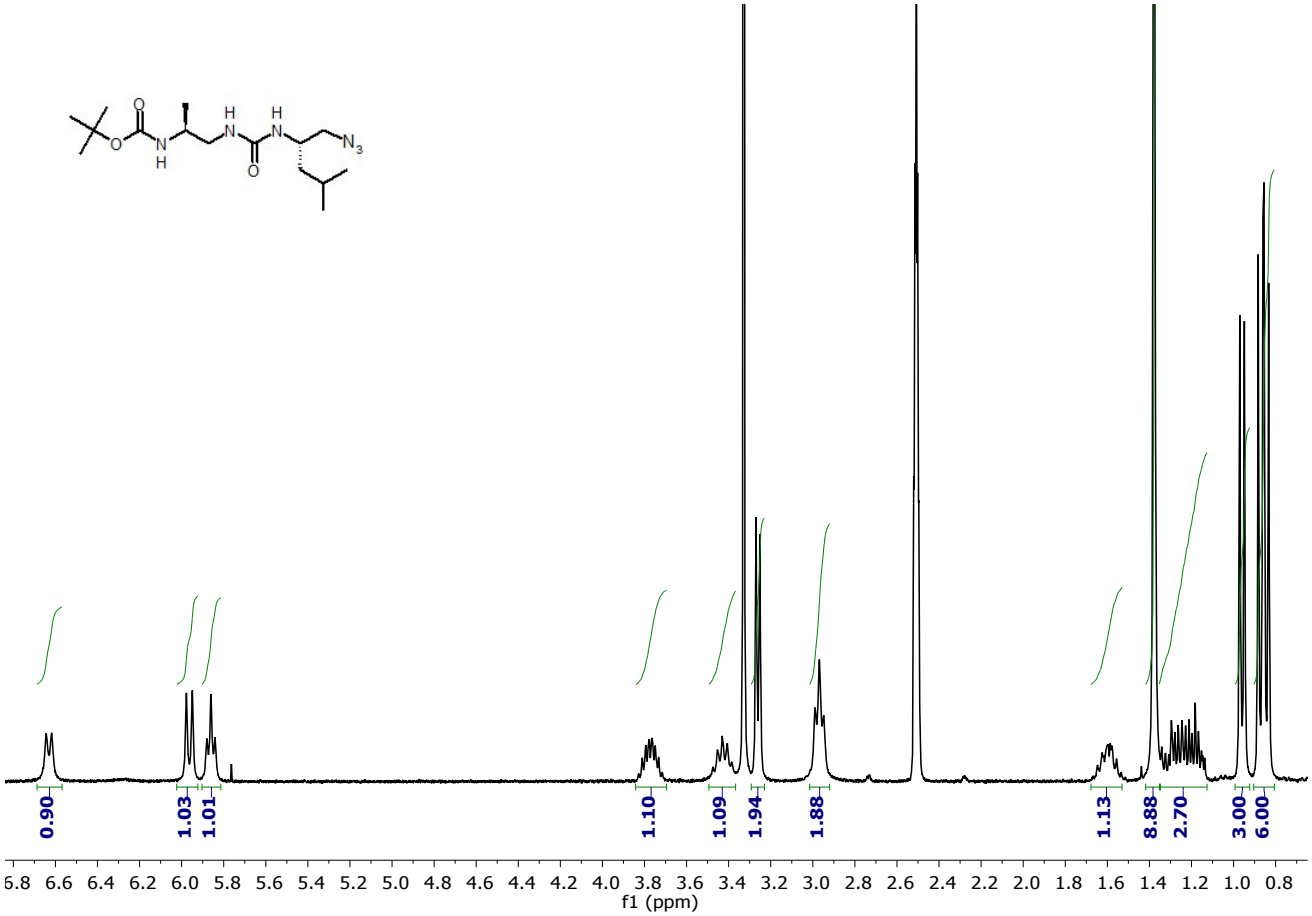


Figure S12. 1H NMR spectrum of compound **9**

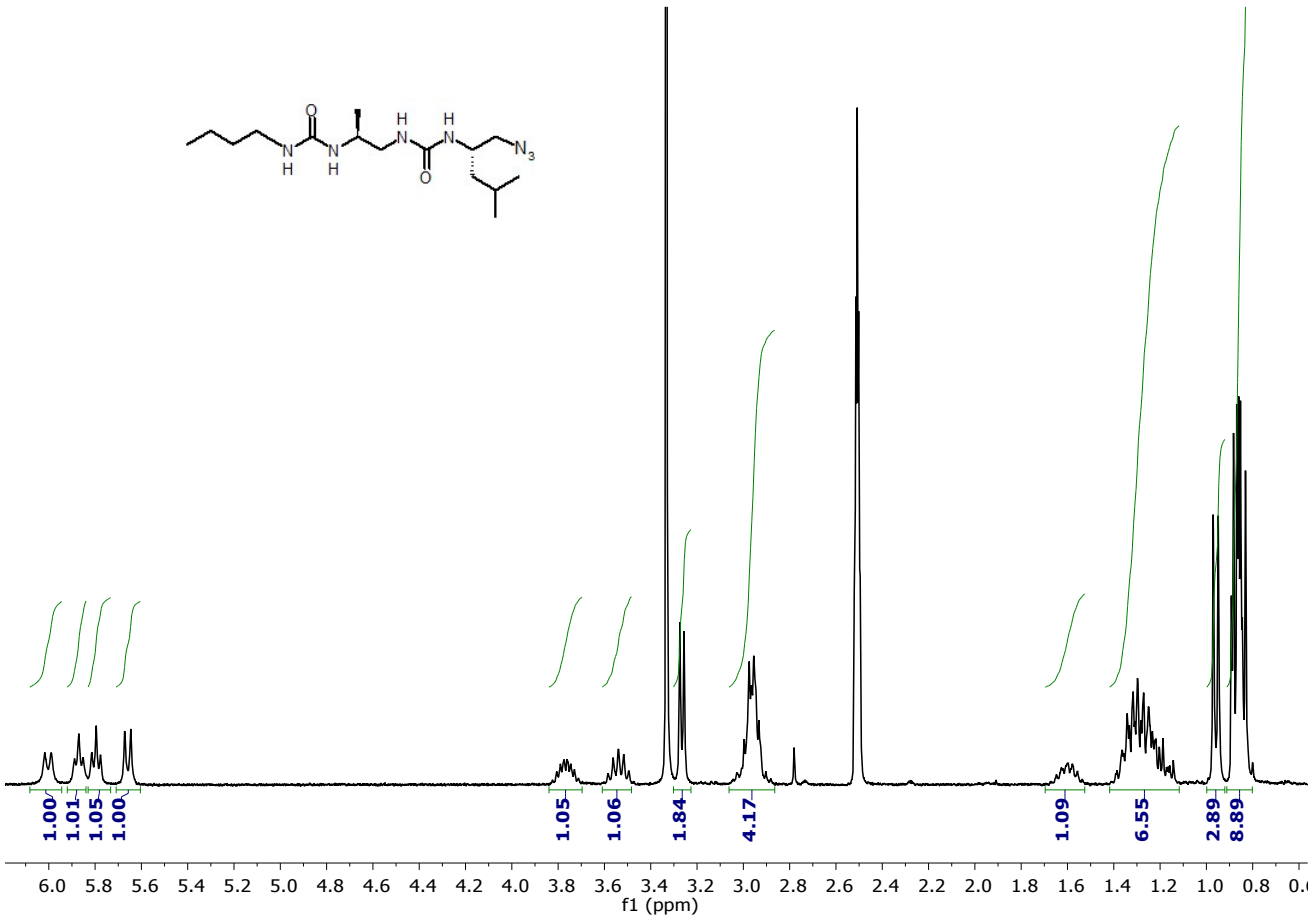


Figure S13. 1H NMR spectrum of compound **10**

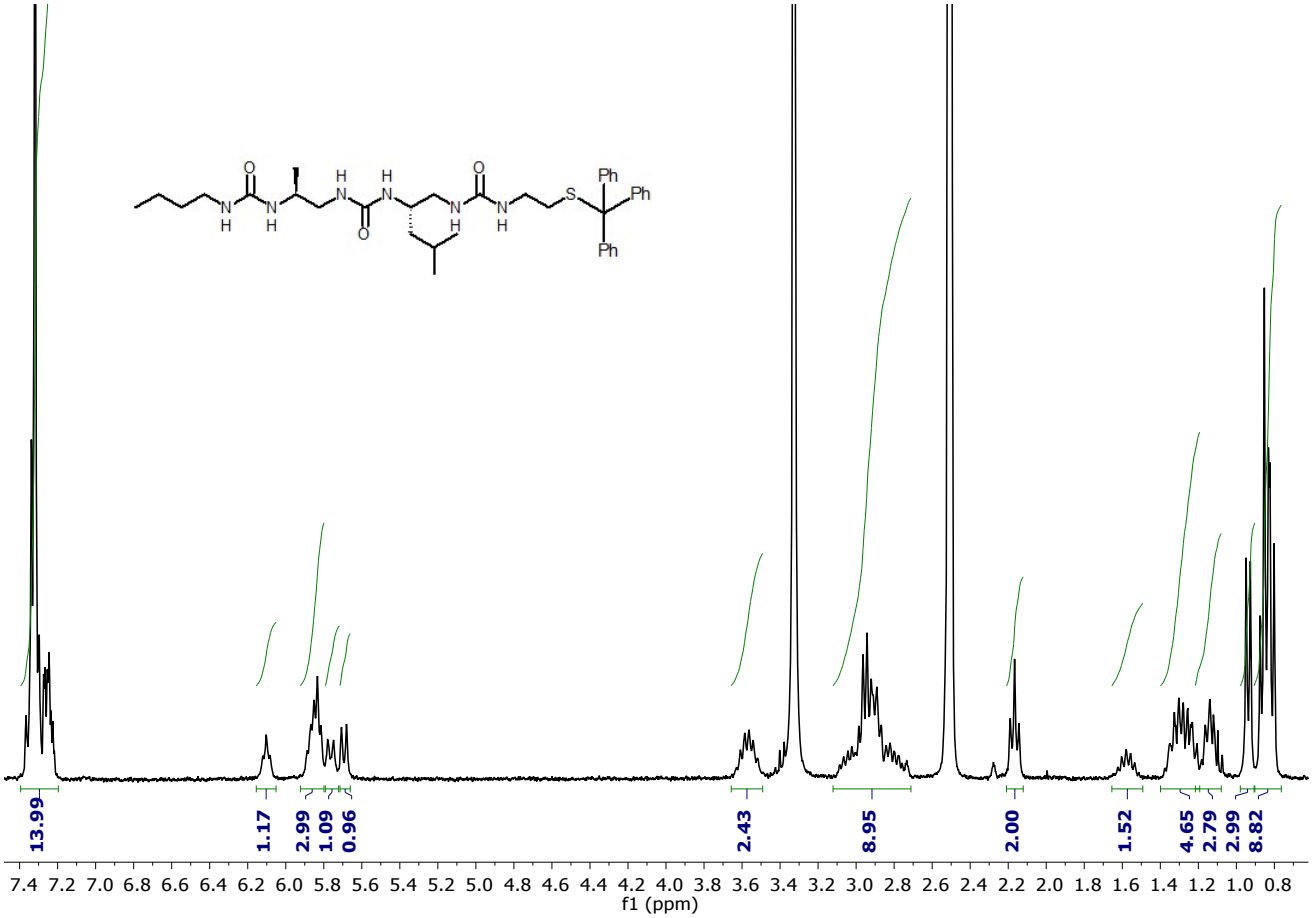


Figure S14. 1H NMR spectrum of compound **3-S-Trt**

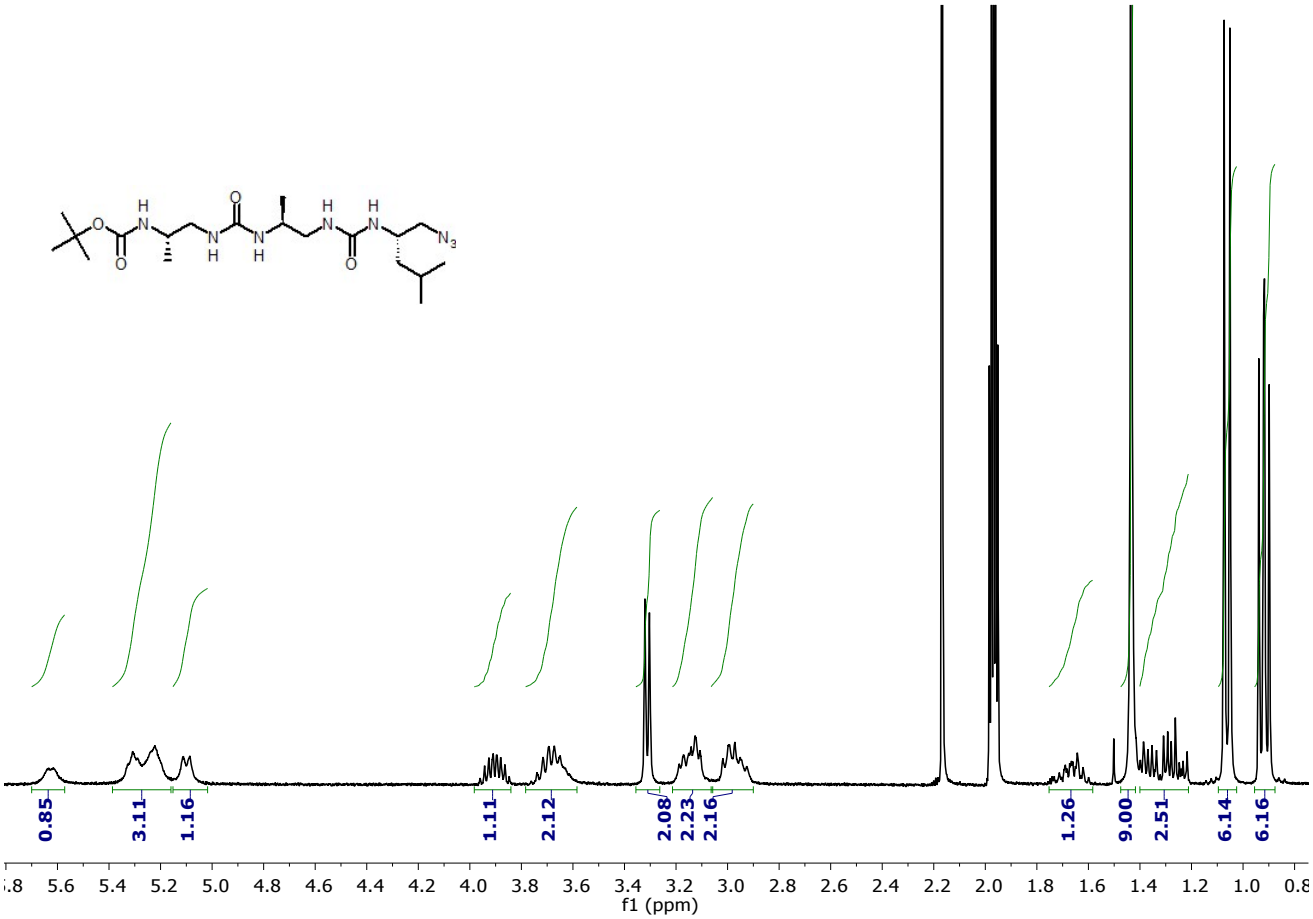


Figure S15. 1H NMR spectrum of compound **11**

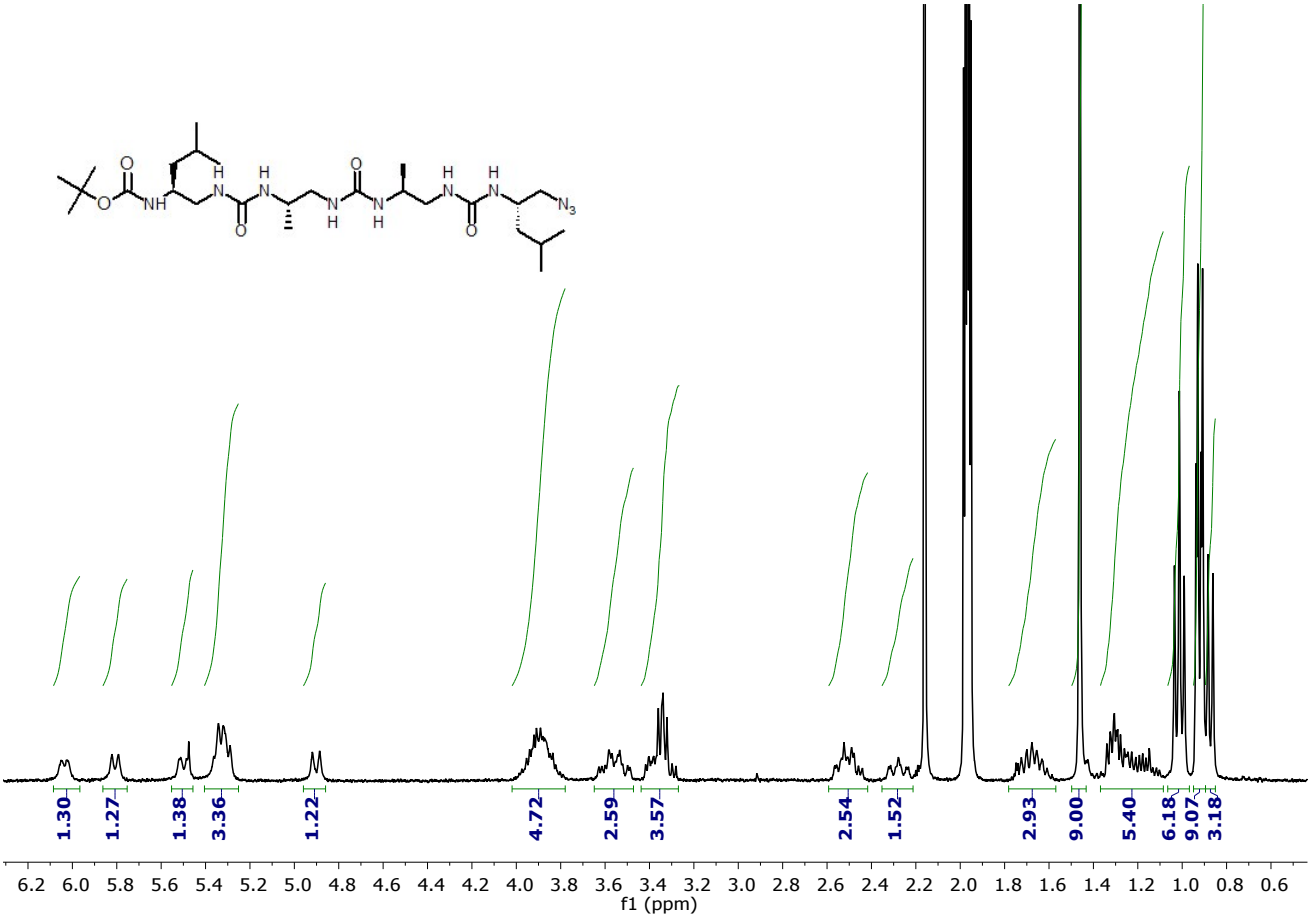


Figure S16. 1H NMR spectrum of compound **12**

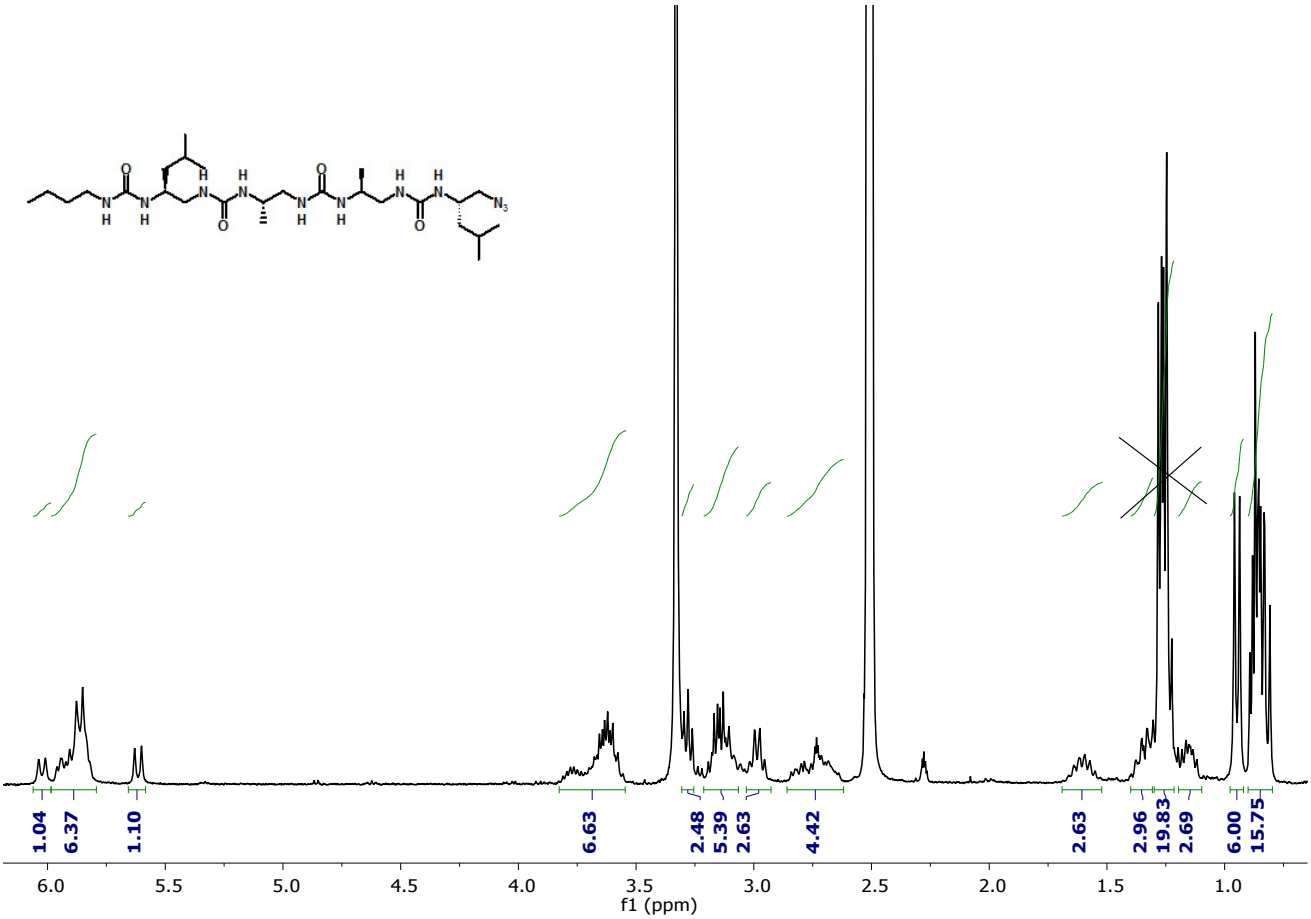


Figure S17. 1H NMR spectrum of compound **13**

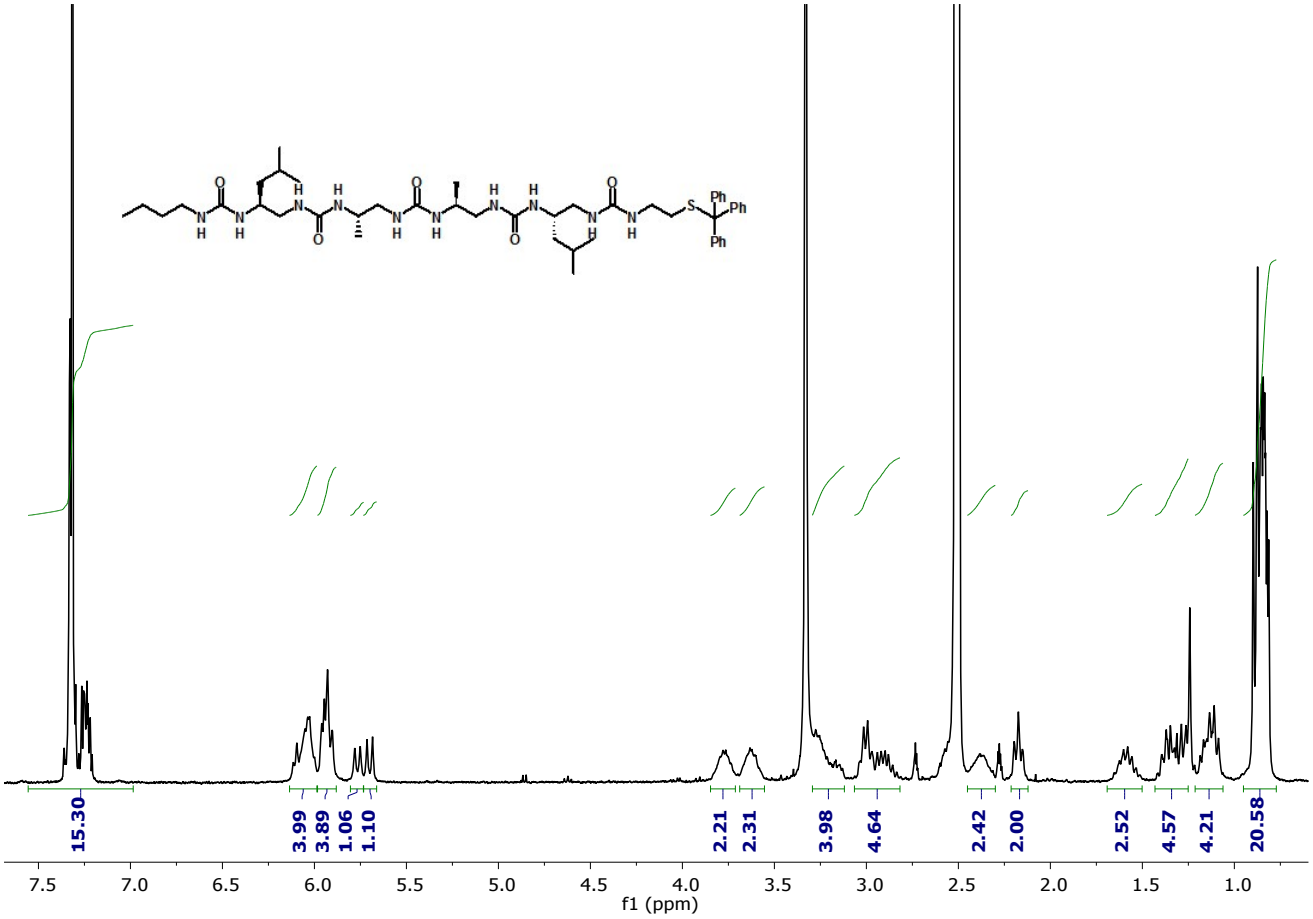


Figure S18. 1H NMR spectrum of compound **5-S-Trt**

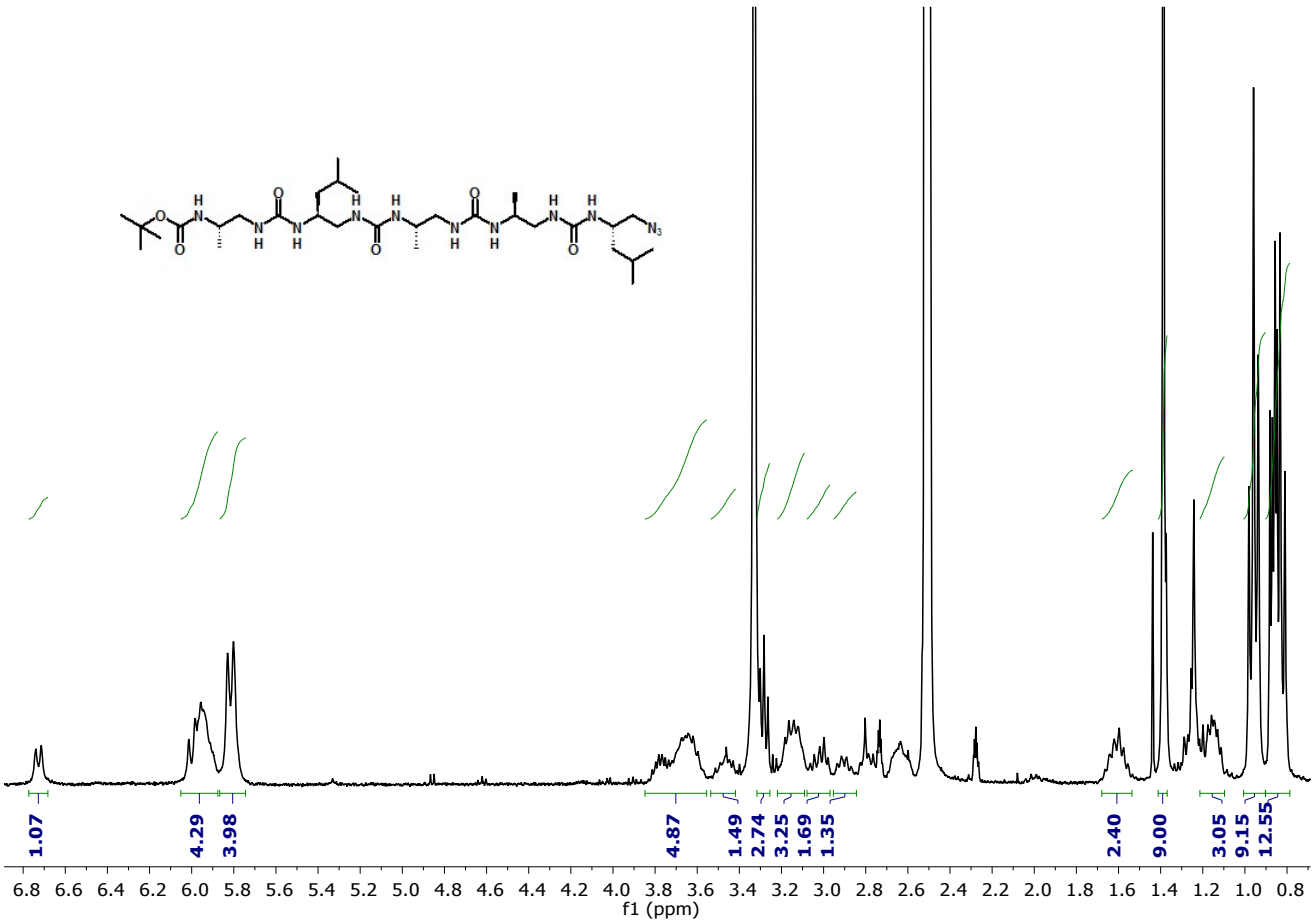


Figure S19. 1H NMR spectrum of compound **14**

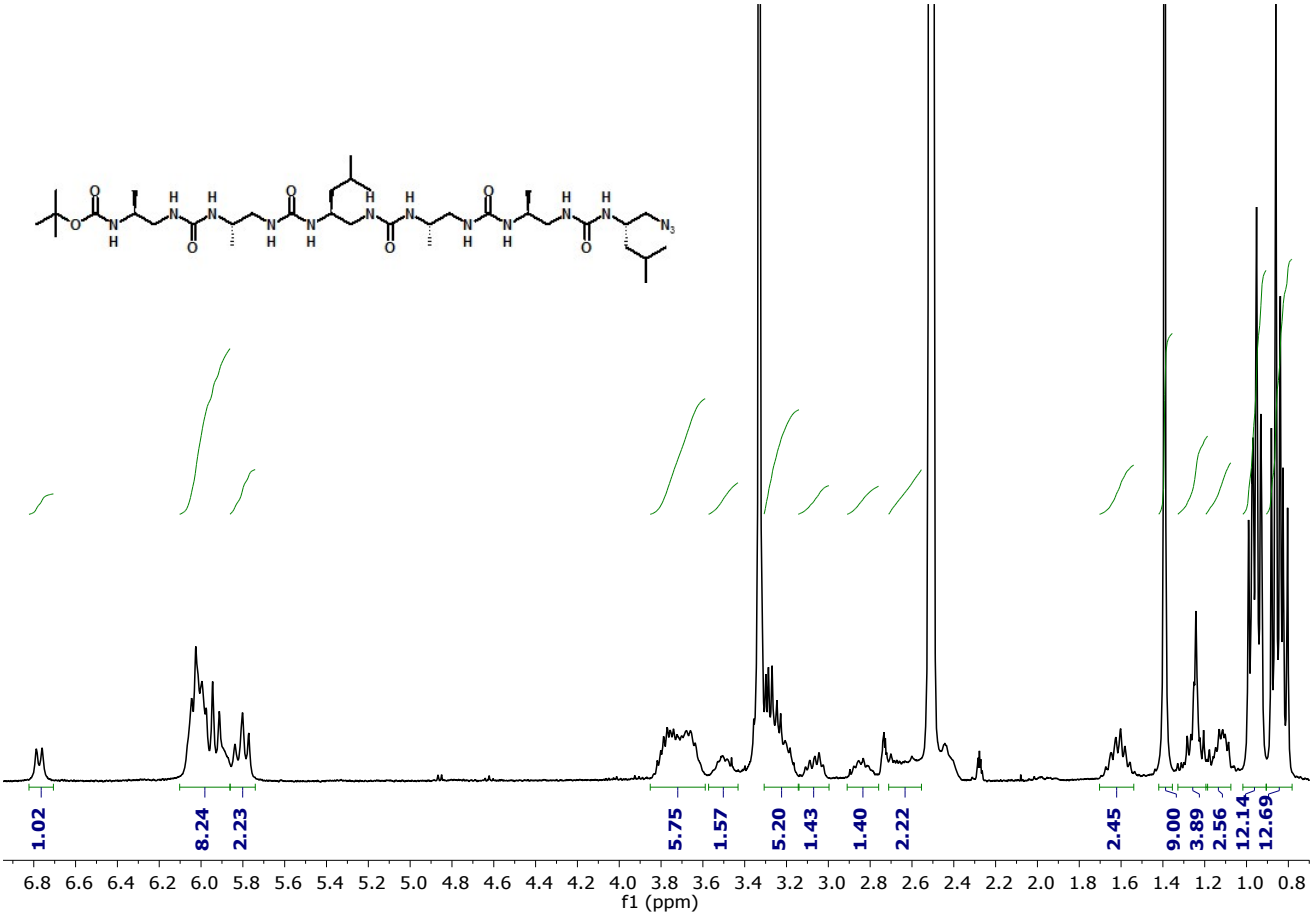


Figure S20. 1H NMR spectrum of compound **15**

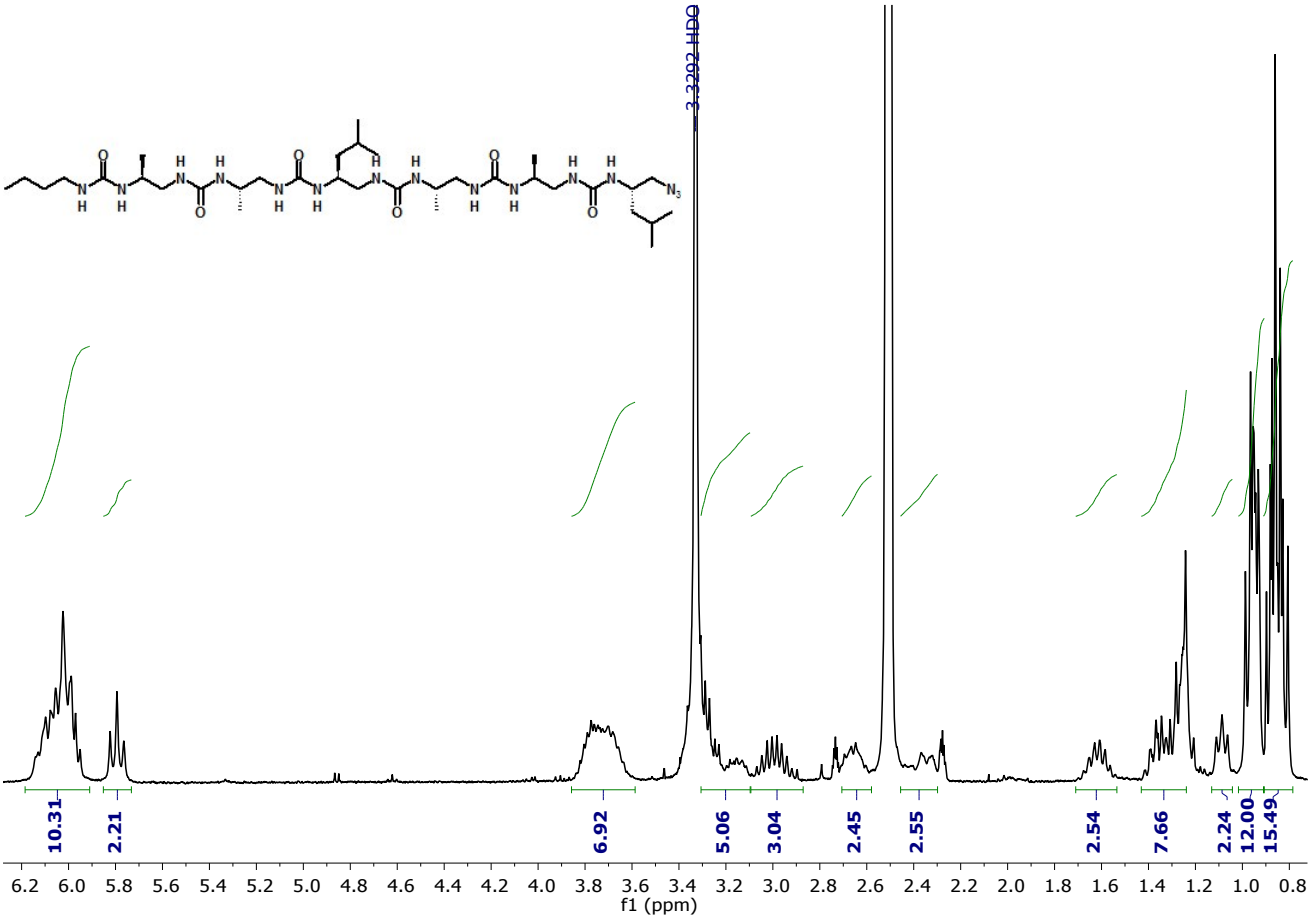


Figure S21. 1H NMR spectrum of compound **16**

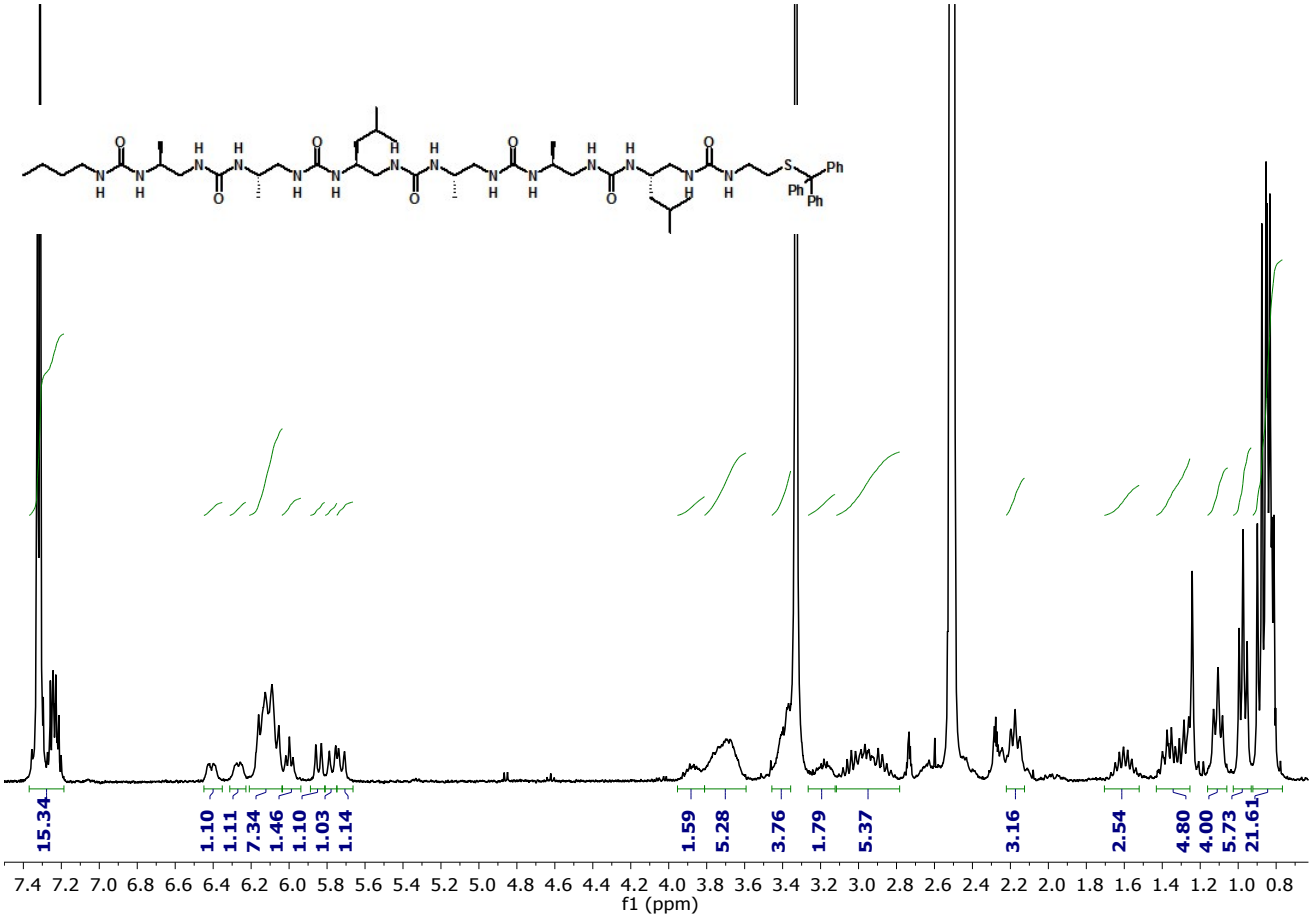


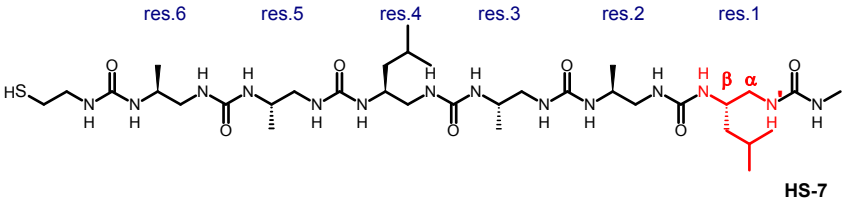
Figure S22. 1H NMR spectrum of compound **7-S-Trt**

6. 2D NMR and CD characterization of oligoureas with thiol group

Experiments were recorded on a Bruker AVANCE 500 (500MHz) spectrometer at 298K. Spin systems were assigned using COSY and TOCSY spectra. Sequential assignment was performed on the basis of N'H(*i*+1) / NH(*i*) ROESY correlations. Oligomers were dissolved in 500 µl of 30% DMSO d_6 in CD_3CN at 2mM concentration.

HS-X oligoureas

6-residues, 7-ureas moieties



HS-7

Residue	**HN**	**HN'**	**$^{\alpha}CH^{1}$**	**$^{\alpha}CH^{2}$**	**$^{\beta}CH$**	**$^{\gamma}CH$**	**$^{\delta}CH$**	**$^{\varepsilon}CH$**	**Term CH**
NHMe	5.85 (overlaid with other signal)	-	-	-	-	-	-	-	2.59
1	5.72 (d, *J* = 9.5 Hz)	6.10 (overlaid with other signal)	3.49	2.42	3.74	1.11	1.58	0.85/0.91	
2	5.71 (d, *J* = 10.6 Hz)	6.26 (dd, *J* = 10.0, 3.2 Hz)	3.49	2.17	3.97	0.92	-	-	
3	6.02 (overlaid with other signal)	6.61 (dd, *J*=10.2, 2.4 Hz)	3.47	2.17	3.76	0.88	-	-	
4	6.07 (overlaid with other signal)	6.47 (dd, *J*=9.5, 2.5 Hz)	3.49	2.18	3.82	1.11	1.64	0.84/0.98	
5	5.86 (overlaid with other signal)	6.17 (dd, *J*=9.6, 3.4 Hz)	3.48	2.29	3.74	0.97	-	-	
6	5.87 (overlaid with other signal)	6.05 (overlaid with other signal)	3.32	2.44	3.84	0.99	-	-	
$HSCH_2CH_2NH$	-	6.10 (overlaid with other signal)							3.21 (CH_2), 2.55 (CH_2SH), 1.84 (SH)

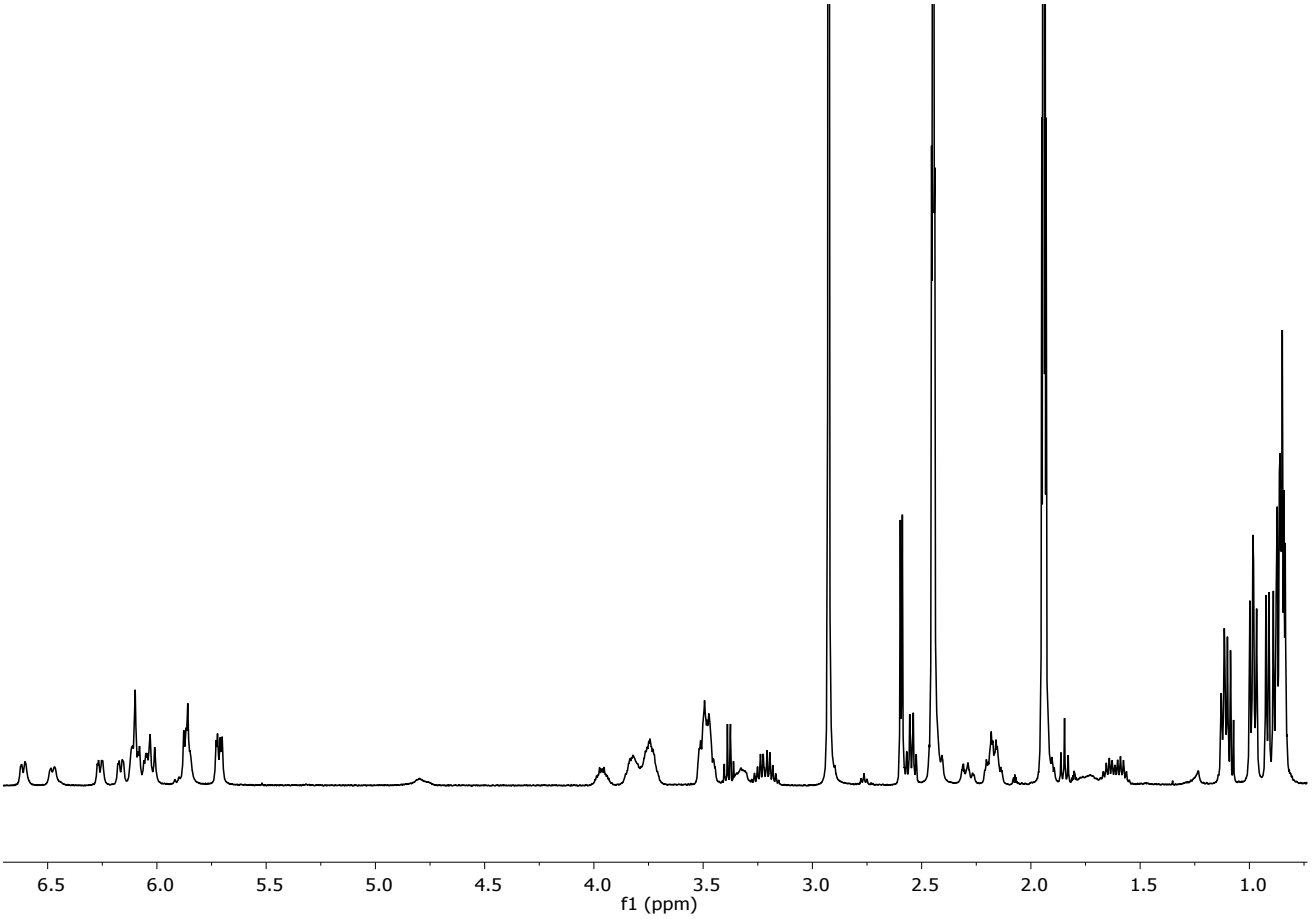


Figure S23. 1H NMR spectrum of compound **HS-7**

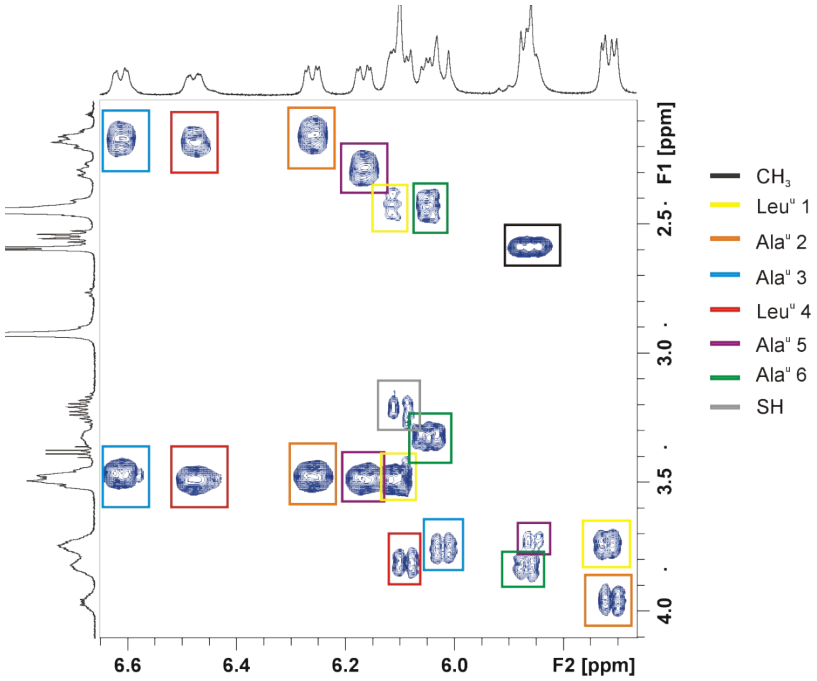


Figure S24. Fingerprint NH/β-CH and N'H/α-CH region of the COSY experiment of compound **HS-7**.

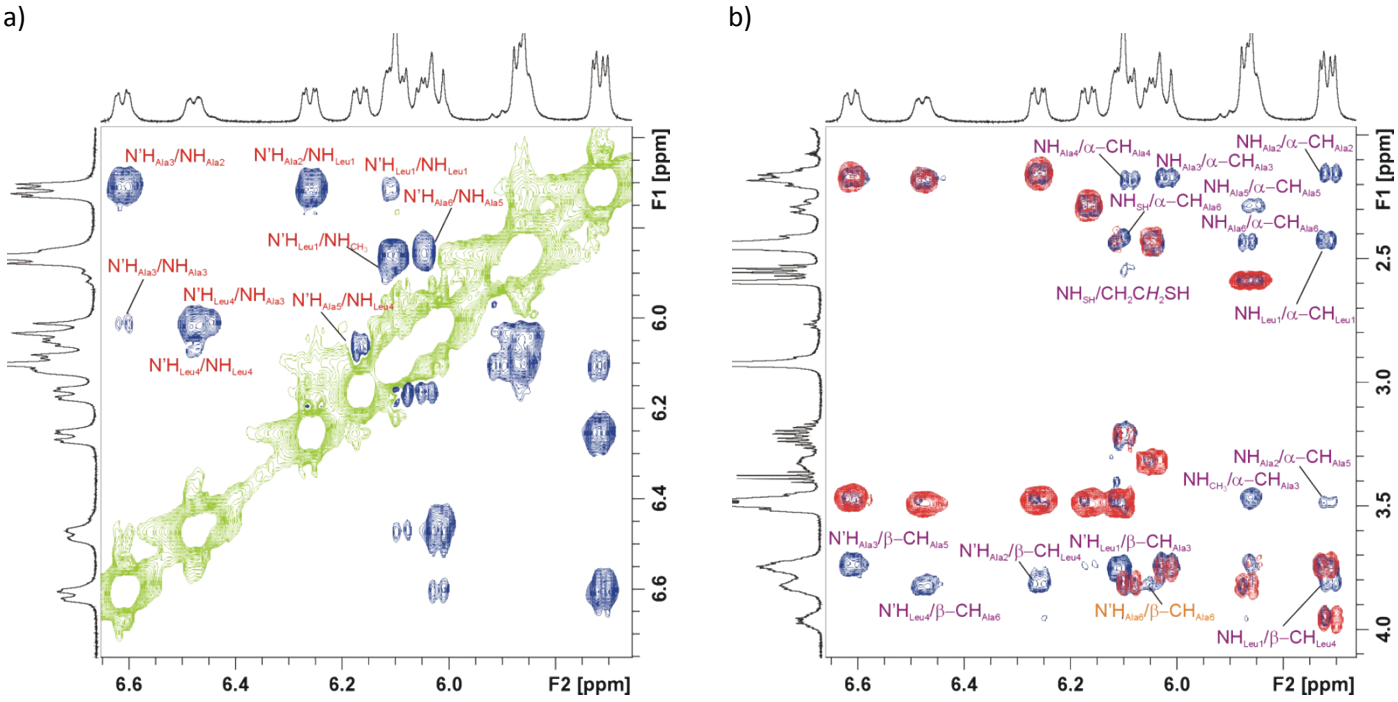
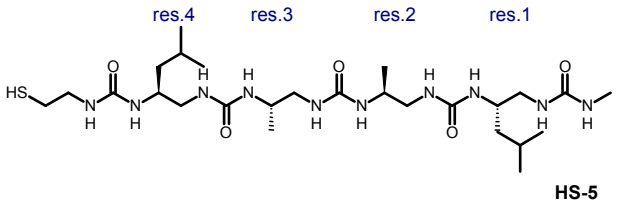


Figure S25. a) ROESY spectrum with ROE cross peaks showing the transfer of nuclear spin polarisation within urea group (NH/N'H) for **HS-7** b) Overlapping of COSY and ROESY spectra. NH and N'H with α-CH and β-CH cross peaks, characteristic for 2.5-helix.

4-residues, 5-ureas moieties



HS-5

Residue	**HN**	**HN'**	**$^{\alpha}$CH^{1}**	**$^{\alpha}$CH^{2}**	**$^{\beta}$CH**	**$^{\gamma}$CH**	**$^{\delta}$CH**	**$^{\varepsilon}$CH**	**Term CH**
NHMe	5.85 (overlaid with other signal)	-	-	-	-	-	-	-	2.59
1	5.72 (d, *J* = 10.2 Hz)	6.05 (dd, *J*=10.9, 2.2 Hz)	3.47	2.43	3.71	1.11	1.58	0.84	
2	5.84 (overlaid with other signal)	6.14 (dd, *J* = 9.5, 2.5 Hz)	3.45	2.18	3.90	0.91	-	-	
3	5.73 (d, *J* = 6.3 Hz)	6.12 (dd, *J*=10.5, 2.5 Hz)	3.42	2.24	3.71	0.89	-	-	
4	5.75 (d, *J* = 6.4 Hz)	5.89 (dd, J = 8.0, 4.5)	3.33	2.37	3.87	1.16	1.60	0.84/0.93	
$HSCH_2CH_2NH$	-	6.08 (d, *J* = 6.0 Hz)							3.21 (CH_2), 2.53 (CH_2SH), 1.88 (SH)

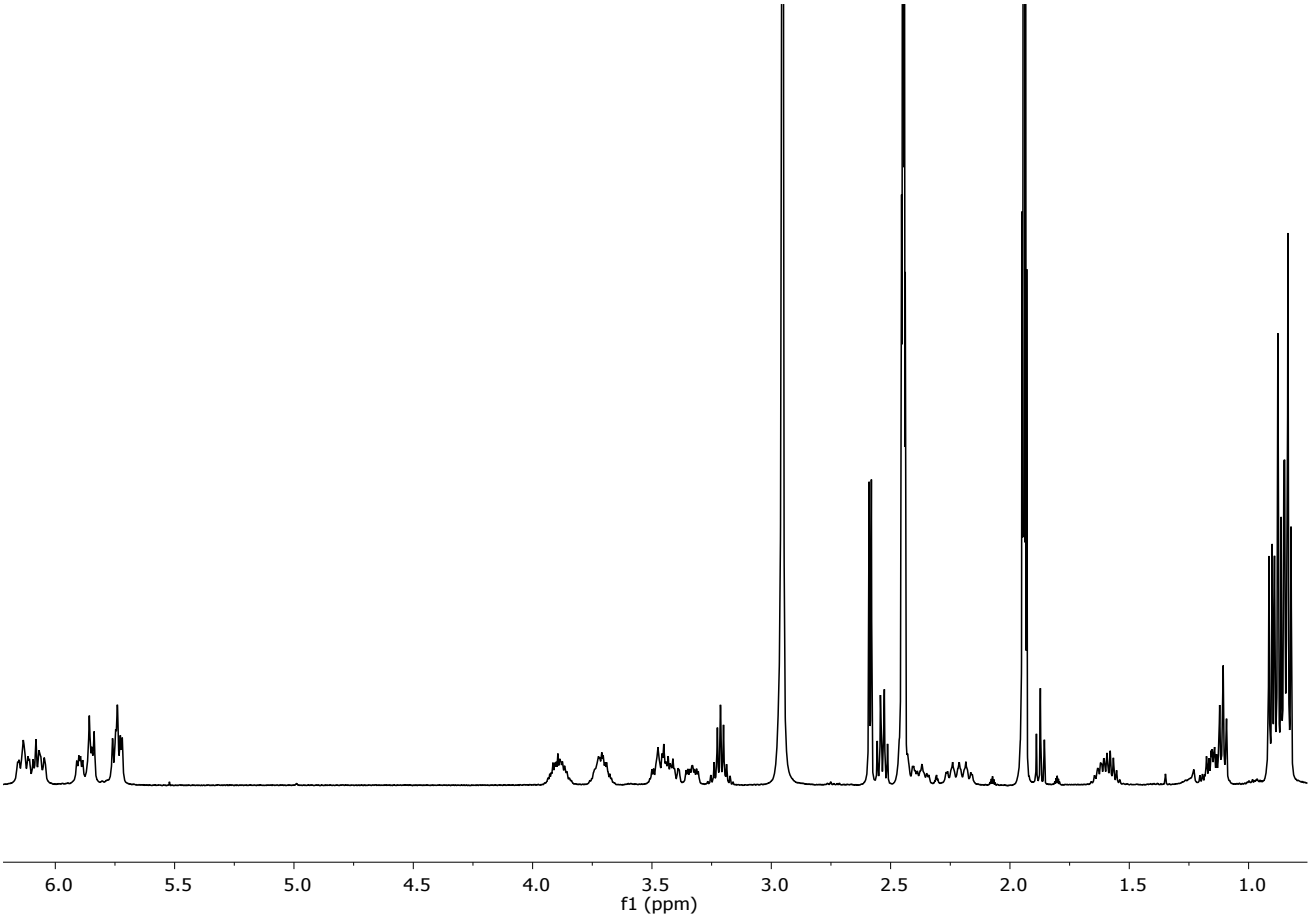


Figure S26. 1H NMR spectrum of compound **HS-5**

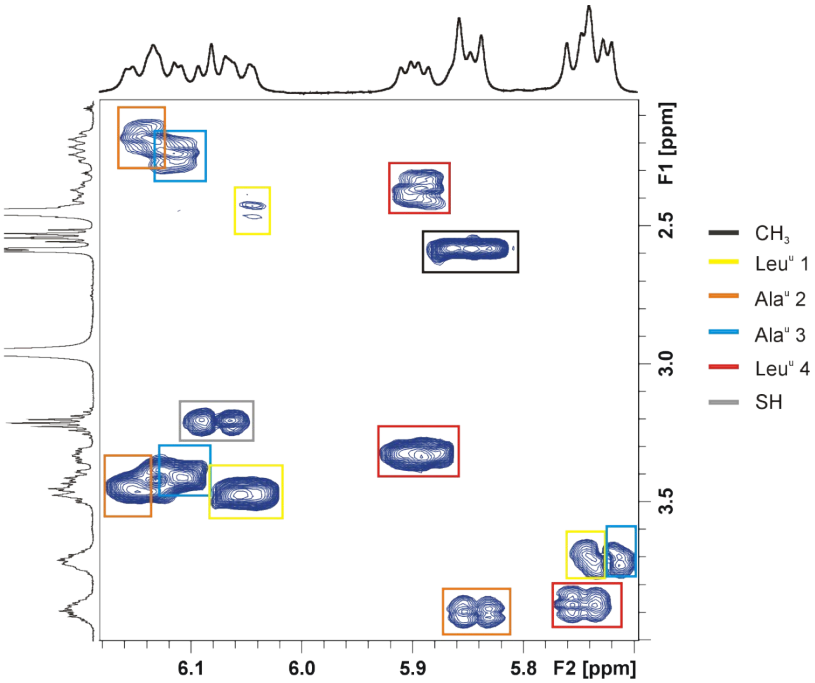


Figure S27. Fingerprint NH/β-CH and N'H/α-CH region of the COSY experiment of compound **HS-5**

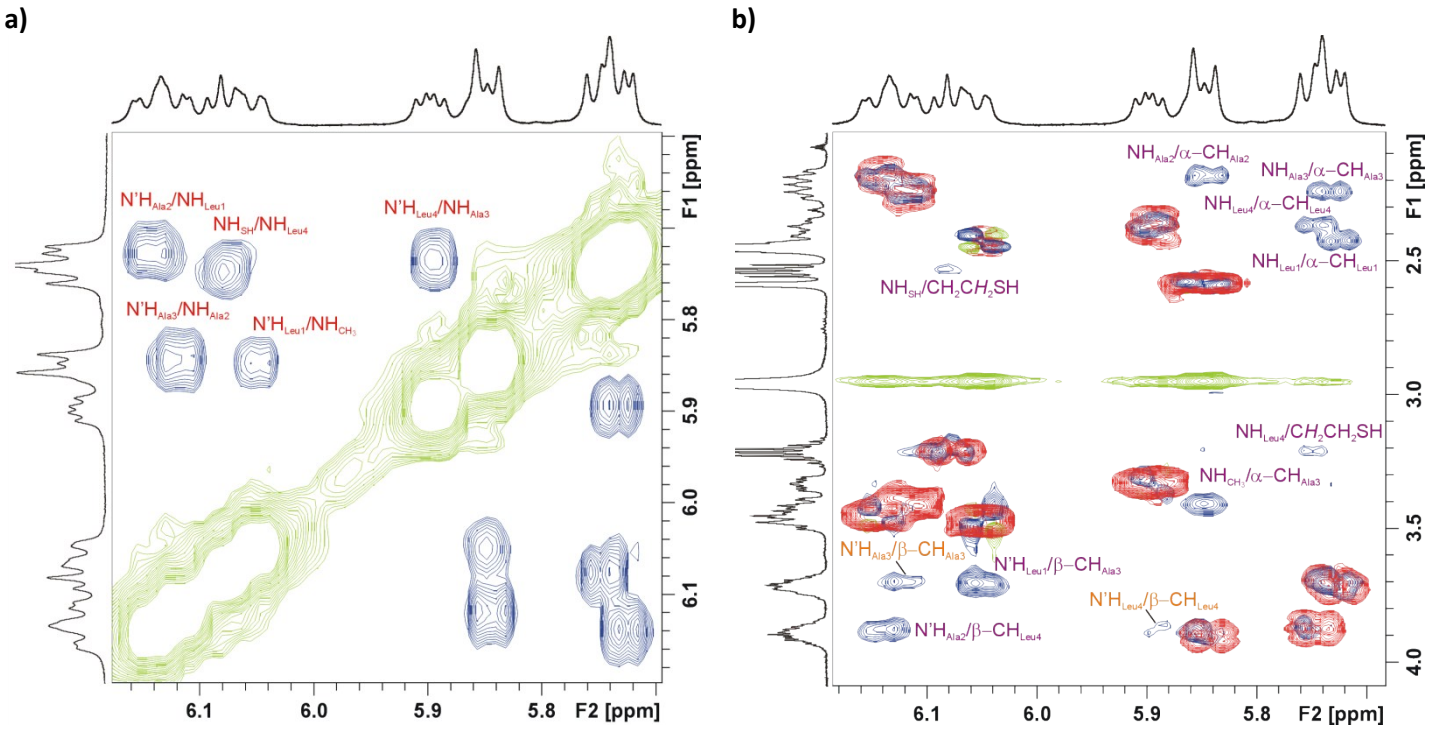
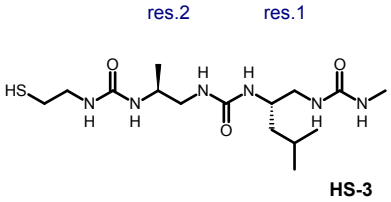


Figure S 28. a) ROESY spectrum with ROE cross peaks showing the transfer of nuclear spin polarisation within urea group (NH/N'H) for **HS-5**; b) Overlapping of COSY and ROESY spectra. NH and N'H with α-CH and β-CH cross peaks, characteristic for 2.5-helix.

2 residues, 3-ureas moieties



HS-3

Residue	**HN**	**HN'**	**$^{\alpha}$CH^{1}**	**$^{\alpha}$CH^{2}**	**$^{\beta}$CH**	**$^{\gamma}$CH**	**$^{\delta}$CH**	**$^{\varepsilon}$CH**	**Term CH**
NHMe	5.70 (overlaid with other signal, broad peak)	-	-	-	-	-	-	-	2.56
1	5.52 (d, *J* = 8.8 Hz)	5.68 (overlaid with other signal, broad peak)	3.20	2.75	3.63	1.16	1.59	0.83/0.85	
2	5.70 (overlaid with other signal, broad peak)	5.66 (overlaid with other signal, broad peak)	3.12	2.75	3.69	0.97	-	-	
$HSCH_2CH_2NH$	-	5.95 (t, *J*=5.9 Hz)							3.15 (CH_2), 2.50 (CH_2SH), 1.82 (SH)

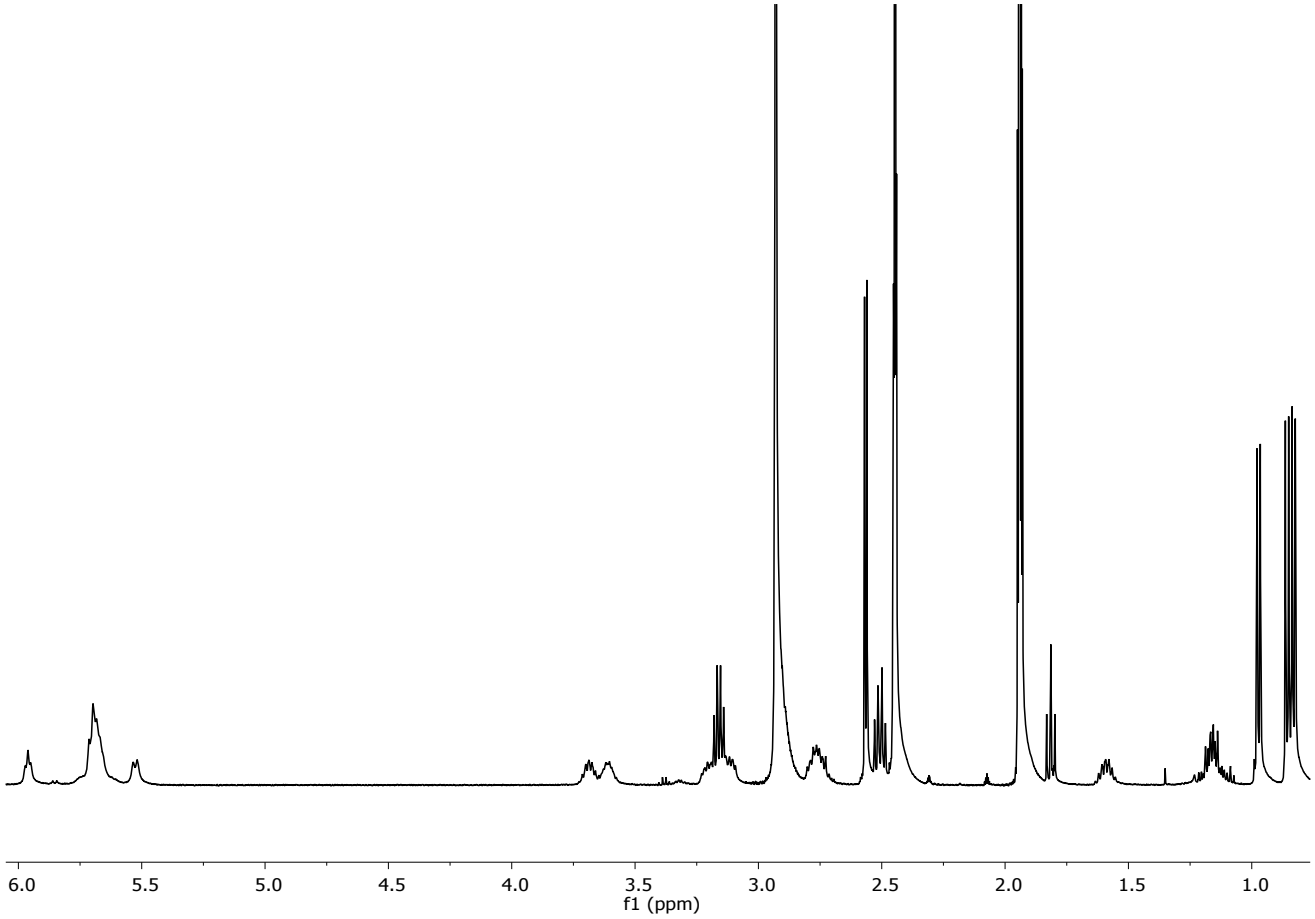


Figure S29. 1H NMR spectrum of compound **HS-3**

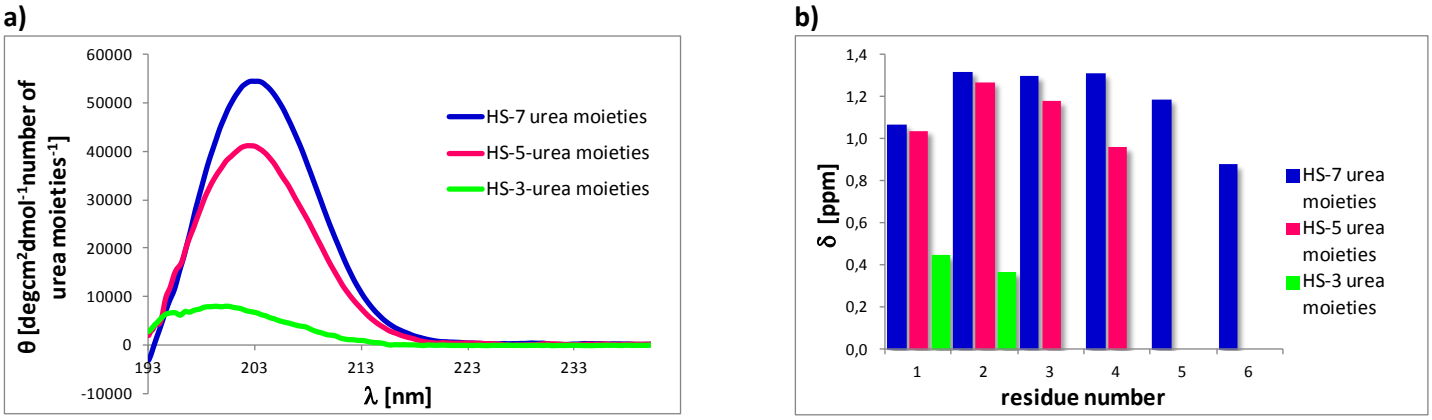
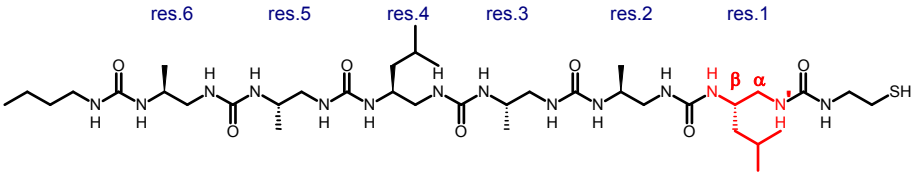


Figure S30. a) A comparison of CD spectra of oligoureas with thiol group at *N*-terminus; b) Chemical shift differences ($\Delta\delta$) between geminal α-CH_2 protons in oligoureas with thiol group at *N*-terminus

X-SH oligoureas

6-residues, 7-ureas moieties



7-SH

Residue	**HN**	**HN'**	**$^{\alpha}$CH^{1}**	**$^{\alpha}$CH^{2}**	**$^{\beta}$CH**	**$^{\gamma}$CH**	**$^{\delta}$CH**	**$^{\varepsilon}$CH**	**Term CH**
HNCH$_2$CH$_2$SH	6.26 (overlaid with other signal)	-	-	-	-	-	-	-	3.25 and 3.11 (CH_2), 2.52(CH_2SH), 2.0 (SH)
1	5.71 (d, *J* = 10.0 Hz)	6.23 (overlaid with other signal)	3.46	2.35	3.76	1.09	1.59	0.84/0.90	
2	5.72 (d, *J* = 10.9 Hz)	6.27 (overlaid with other signal)	3.48	2.16	4.00	0.90	-	-	
3	6.06 (overlaid with other signal)	6.63 (dd, *J*=9.8, 2.8 Hz)	3.52	2.18	3.76	0.89	-	-	
4	6.17 (overlaid with other signal)	6.48 (dd, *J*=8.4, 2.8 Hz)	3.49	2.17	3.81	1.10	1.63	0.97/0.85	
5	5.88 (d, *J*=9.7 Hz)	6.18 (overlaid with other signal)	3.49	2.27	3.73	0.97	-	-	
6	5.70 (d, *J*=9.6 Hz)	6.04 (overlaid with other signal)	3.31	2.42	3.83	0.98	-	-	
BuNH	5.85 (t, *J*=5.7 Hz)								3.08 and 2.96 (CH_2NH), 1.39 and 1.28 (CH_2x2), 0.89 (CH_3)

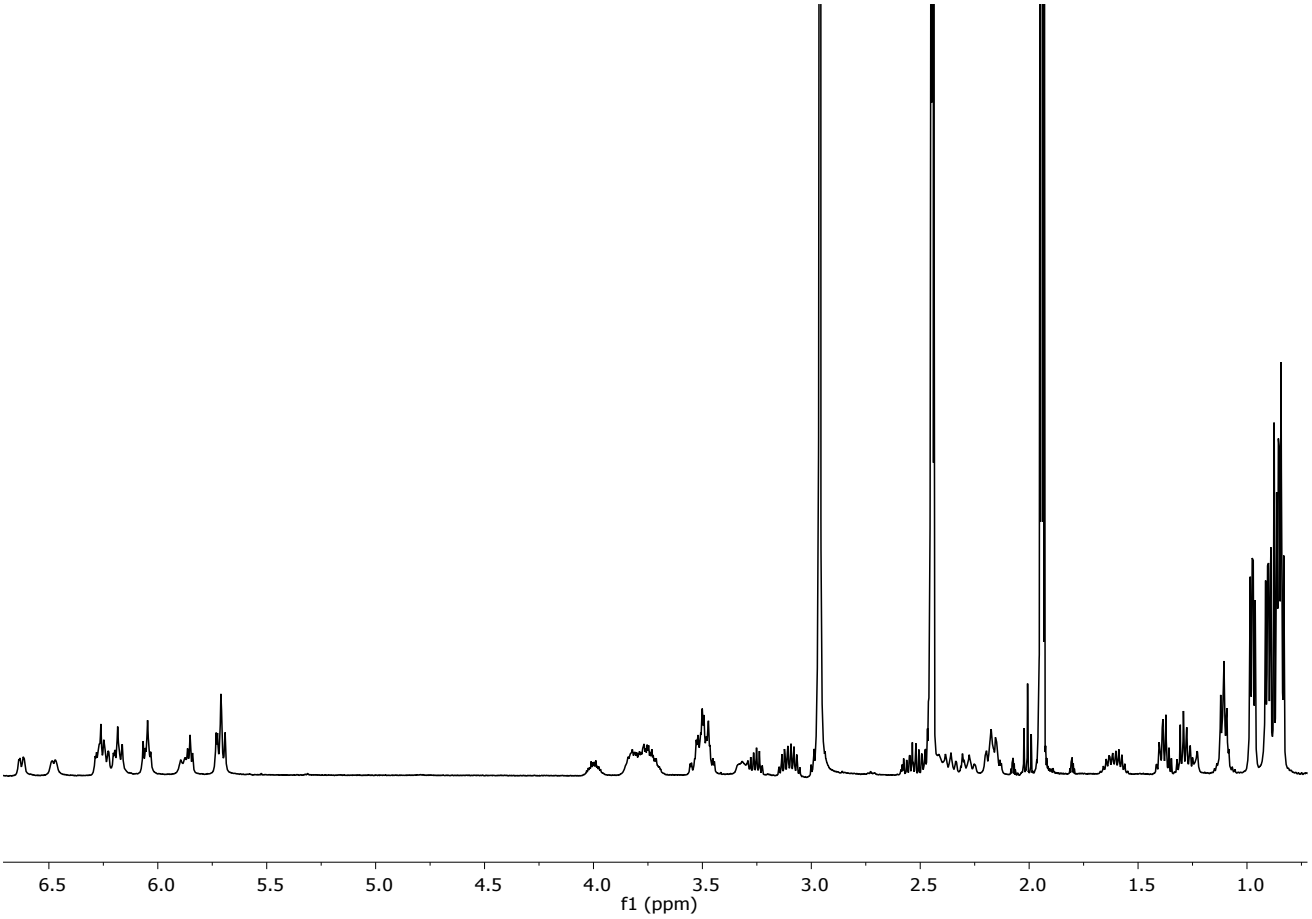


Figure S31. 1H NMR spectrum of compound **7-SH.**

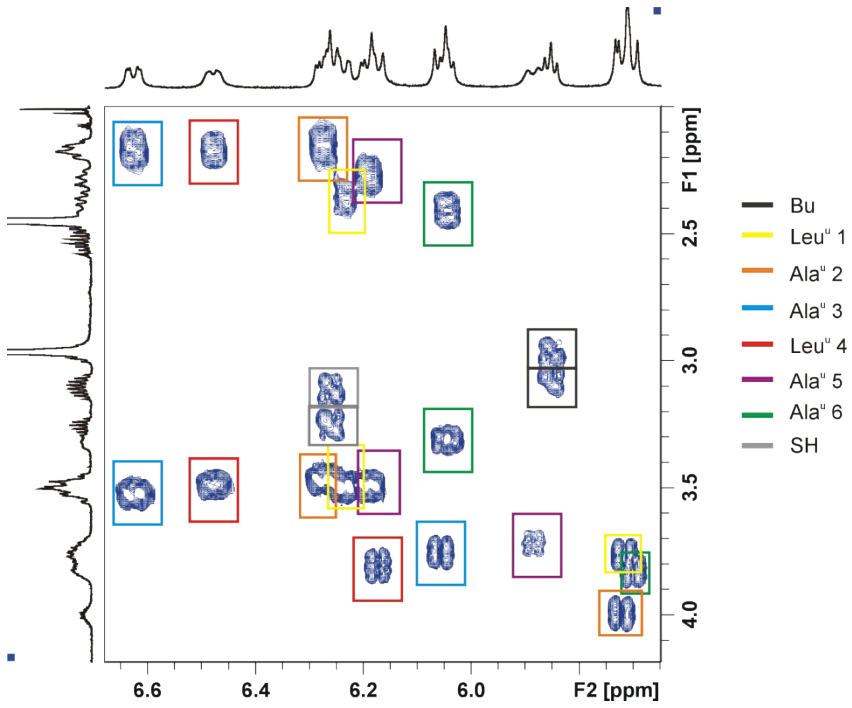


Figure S32. Fingerprint NH/β-CH and N'H/α-CH region of the COSY experiment of compound **7-SH**.

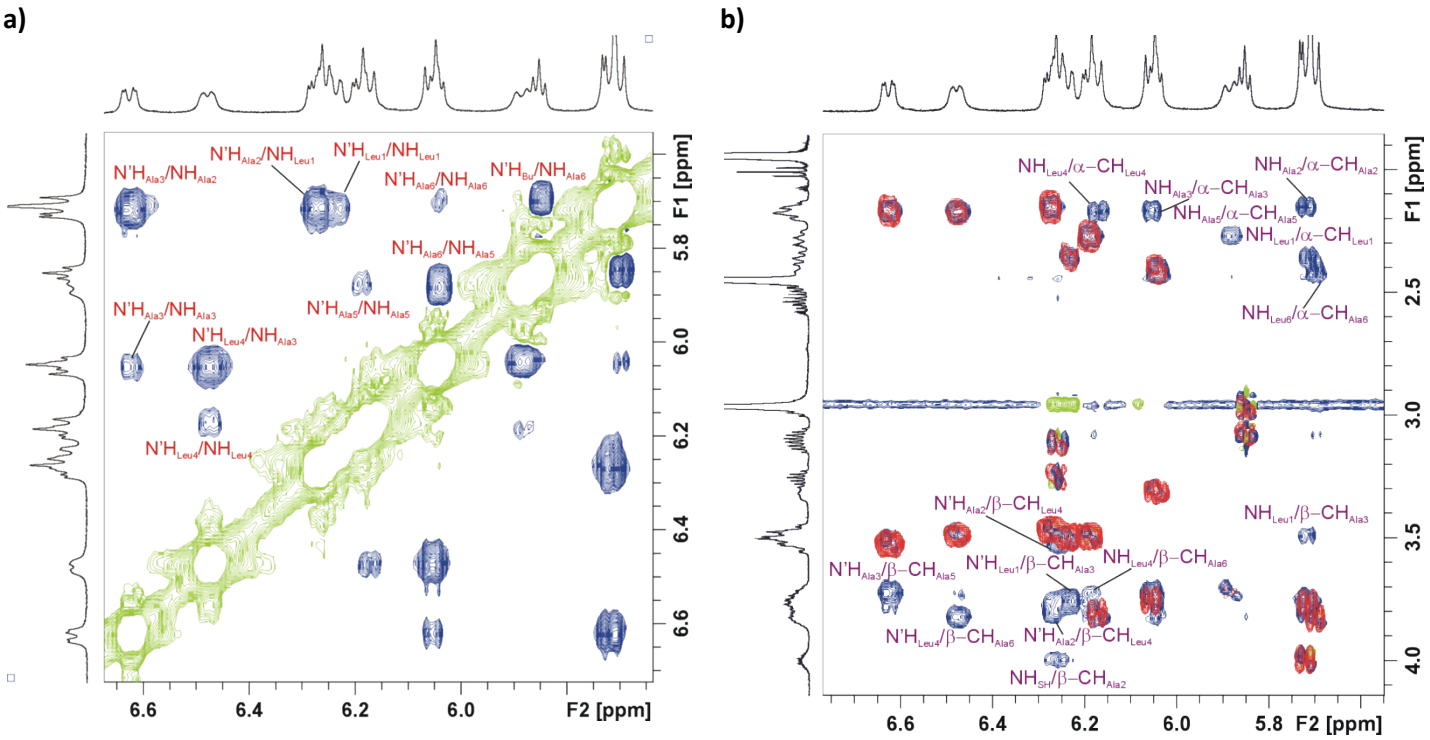
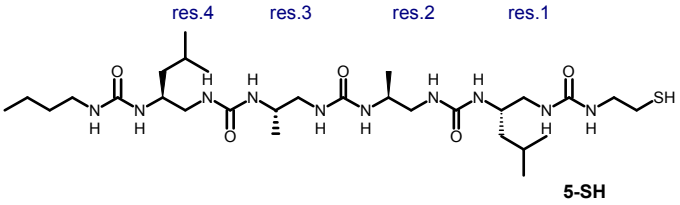


Figure S33. a) ROESY spectrum with ROE cross peaks showing the transfer of nuclear spin polarisation within urea group (NH/N'H) for **7-SH**; b) Overlapping of COSY and ROESY spectra. NH and N'H with α-CH and β-CH cross peaks, characteristic for 2.5-helix.

4-residues, 5-ureas moieties



5-SH

Residue	**HN**	**HN'**	**$^{\alpha}$CH^{1}**	**$^{\alpha}$CH^{2}**	**$^{\beta}$CH**	**$^{\gamma}$CH**	**$^{\delta}$CH**	**$^{\varepsilon}$CH**	**Term CH**
HNCH$_2$CH$_2$SH	6.26	-	-	-	-	-	-	-	3.23 and 3.13 (CH_2), 2.51 and 2.49(CH_2SH), 2.0 (SH)
1	5.76 (d, *J* = 9.8 Hz)	6.19	3.49	2.35	3.76	1.10	1.58	0.84	
2	5.94 (d, *J* = 10.3 Hz)	6.17	3.45	2.17	3.96	0.89	-	-	
3	5.76 (d, *J* = 10.4 Hz)	6.20	3.48	2.21	3.67	0.93	-	-	
4	5.58 (d, *J*=9.5 Hz)	5.89 (dd, *J*=7.8, 4.4 Hz)	3.31	2.32	3.89	1.13	1.62	0.87/0.82	
BuNH	5.83 (t, *J*=5.7 Hz)								3.04 and 3.00 (CH_2NH), 1.39 and 1.29(CH_2x2), 0.87 (CH_3)

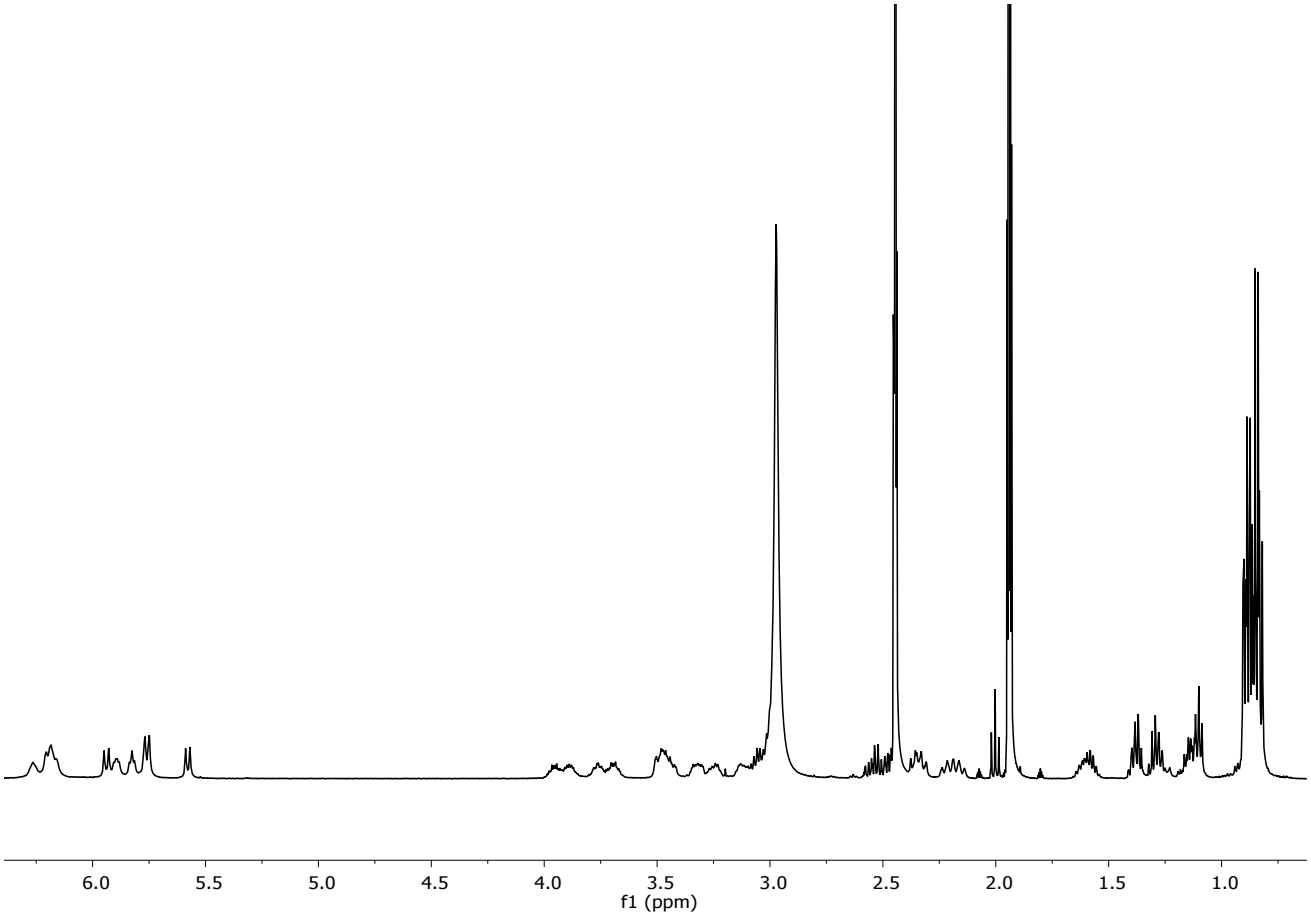


Figure S34. 1H NMR spectrum of compound **5-SH.**

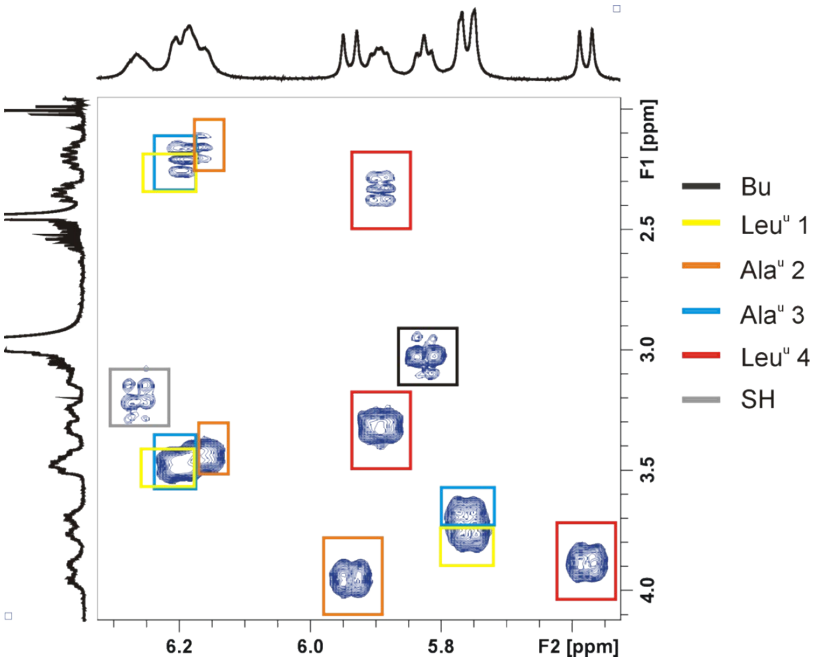


Figure S35. Fingerprint NH/β-CH and N'H/α-CH region of the COSY experiment of compound **5-SH**.

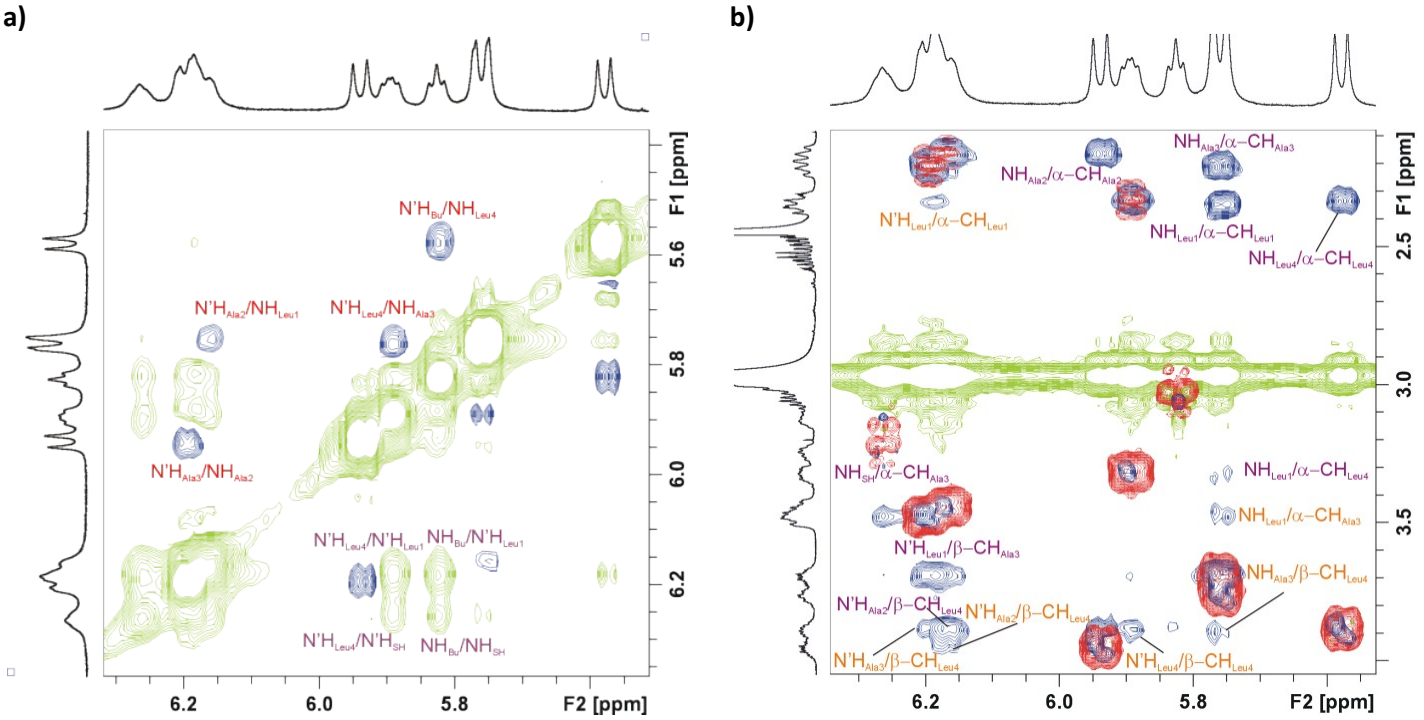
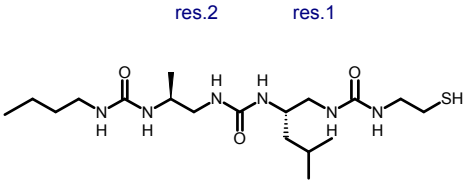


Figure S36. a) ROESY spectrum with ROE cross peaks showing the transfer of nuclear spin polarisation within urea group (NH/N'H) for **5-SH** (in violet – so called "exchange peaks"); b) Overlapping of COSY and ROESY spectra. NH and N'H with α-CH and β-CH cross peaks, characteristic for 2.5-helix. In orange ROE peaks showing unstability of 2.5-helix in solution

2 residues, 3-ureas moieties



3-SH

Residue	**HN**	**HN'**	**$^{\alpha}$CH^{1}**	**$^{\alpha}$CH^{2}**	**$^{\beta}$CH**	**$^{\gamma}$CH**	**$^{\delta}$CH**	**$^{\varepsilon}$CH**	**Term CH**
HNCH$_2$CH$_2$SH	6.15	-	-	-	-	-	-	-	3.16 (CH_2), 2.49(CH_2SH), 1.86 (SH)
1	5.53 broad peak	5.62 broad peak	3.20	2.71	3.63	1.15	1.59	0.83	
2	Because of the peaks broadening, it is difficult to find this signal	5.81	3.1	2.74	3.71	0.96	-	-	
BuNH	5.65 broad peak								2.98 (CH_2NH), 1.35 and 1.27(CH_2x2), 0.83 (CH_3)

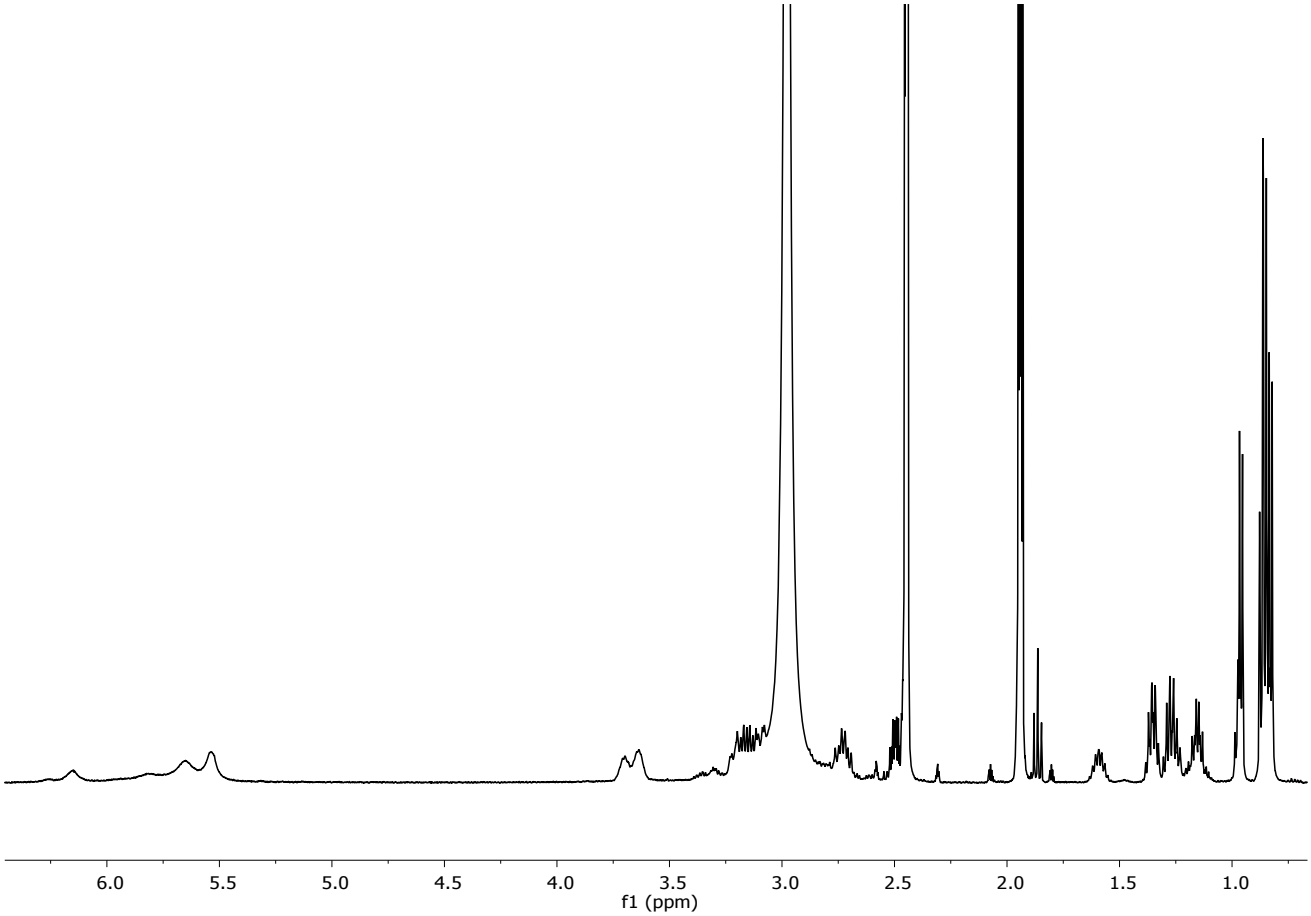


Figure S37. 1H NMR spectrum of compound **3-SH**

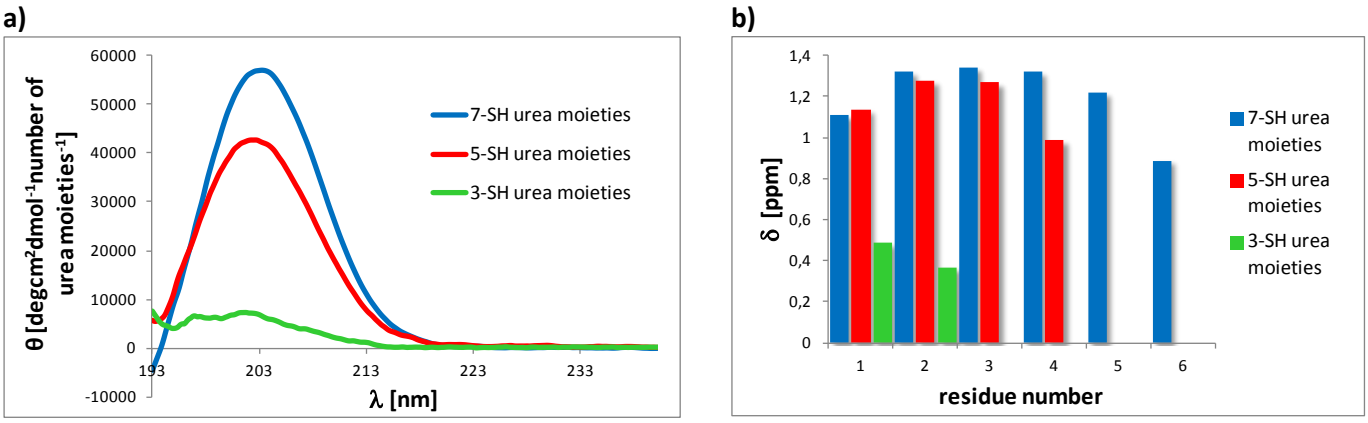


Figure S38. a) A comparison of CD spectra of oligoureas with thiol group at *C*-terminus; b) Chemical shift differences ($\Delta\delta$) between geminal α-CH_2 protons in oligoureas with thiol group at *C*-terminus

7. The X-Ray diffraction studies

The X-ray measurement of **Trt-S-5** was performed at 100(2) K on a Bruker D8 Venture Photon100 CMOS diffractometer equipped with a mirror monochromator and a CuKα INCOATEC IμS micro-focus source (λ=1.54178 Å). A total of 1241 frames were collected with Bruker APEX2 program.[4] The frames were integrated with the Bruker SAINT software package[5] using a narrow-frame algorithm. The integration of the data using an orthorhombic unit cell yielded a total of 24071 reflections to a maximum θ angle of 59.11° (0.90 Å resolution), of which 6515 were independent (average redundancy 3.695, completeness = 98.0%, R_{int}=4.70%, R_{sig}=4.12%) and 6253 (95.98%) were

greater than $2\sigma(F^2)$. The final cell constants of a= 13.8373(6) Å, b=35.4652(15) Å, c=9.5082(4) Å, V=4666.1(3) Å^3, are based upon the refinement of the XYZ-centroids of 9894 reflections above 20 σ(I) with 6.857°<2ϑ<118.2°. Data were corrected for absorption effects using the multi-scan method (SADABS).[6] The ratio of minimum to maximum apparent transmission was 0.827. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.6820 and 0.9060.

The structure was solved and refined using SHELXTL Software Package[7] using the space group $P2_12_12$, with Z=4 for the formula unit, $C_{45}H_{68}N_{10}O_5S_{65}$ and the Flack parameter equal to 0.088(14).[8] The final anisotropic full-matrix least-squares refinement on F^2 with 618 variables converged at $R1$=7.68%, for the observed data and $wR2$=17.56% for all data. The goodness-of-fit was 1.246. The largest peak in the final difference electron density synthesis was 0.351 e$^-$/Å^3 and the largest hole was -0.321 e$^-$/Å^3 with an RMS deviation of 0.073 e$^-$/Å^3. On the basis of the final model, the calculated density was 1.226 g/cm^3 and F(000), 1856 e$^-$.

Due to small size and weak diffracting power of the investigated crystal it was not possible to collect reflections to satisfactory 2ϑ limit. The data were integrated to maximum 2ϑ less than 120º. This is responsible for two Alerts B presence in the Checkcif report. In the crystal lattice the molecules exhibit positional disorder in isopropyl side chains. To correctly model the disorder a number of geometrical and ADP constraints were used. Both isopropyl groups were refined in two positions with occupancy ratios equal to 0.5:0.5.

All non-hydrogen atoms were refined anisotropically. Most of hydrogen atoms were placed in calculated positions and refined within the riding model. Coordinates of hydrogen atoms engaged in hydrogen bonds were refined. The temperature factors of the hydrogen atoms were not refined and were set to be equal to either 1.2 or 1.5 times larger than U_{eq} of the corresponding heavy atom. The atomic scattering factors were taken from the International Tables.[9] [6].

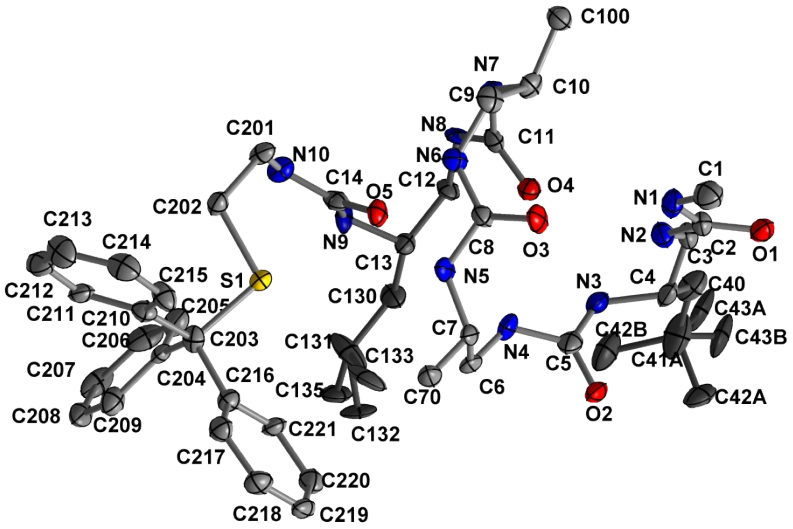


Figure S39. ORTEP representation

8. AFM images of the SAM

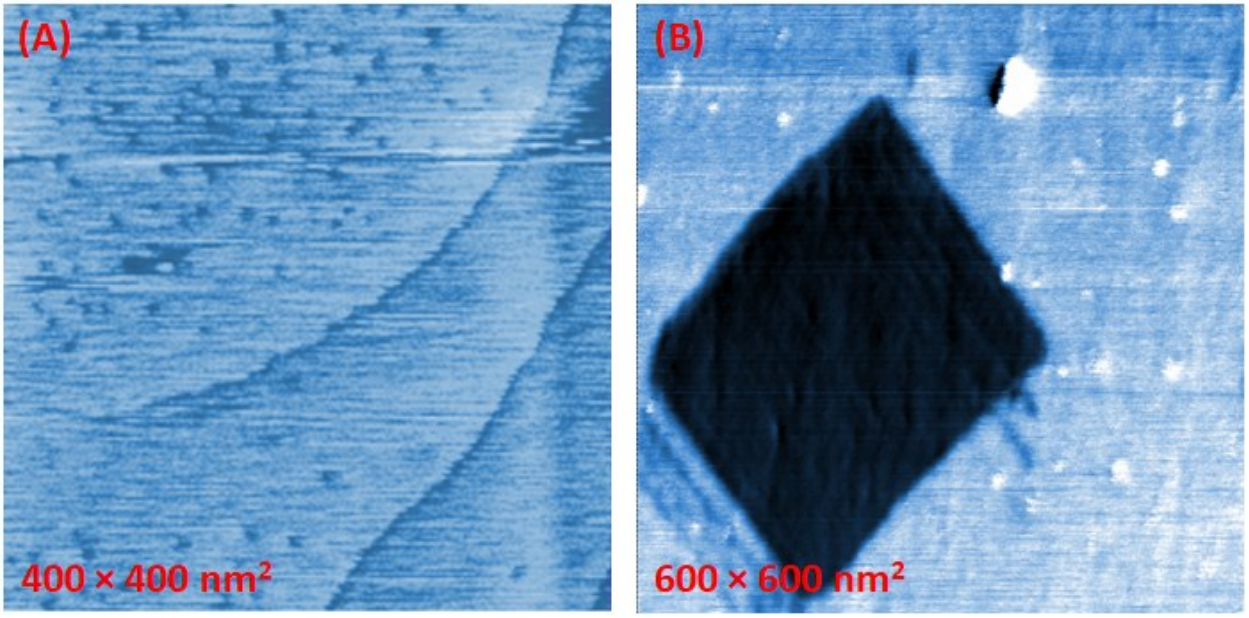


Figure S40. Exemplary AFM images recorded for **HS-7** oligomer. (a) Intact monolayer adsorbed on Au(111) with visible etching pits (dark spots) and the edges of gold terraces. (b) Monolayer subjected to nanolithography (see Experimental section). Nanoshaved region is visible as dark rectangle.

9. Dipol moments of oligoureas

Preliminary molecular dynamics simulations indicate that the dipole moment for oligoureas is aligned with molecular axis and its value varies between 3.4 to 4.7 D per residue depending on location of the terminal thiol group. These values are comparable to the value of 3.5 D per residue for α-helical peptides.

10. References

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