

# Sequence-defined L-glutamamide oligomers with pendant supramolecular motifs via iterative synthesis and orthogonal post-functionalization

Marcin L. Ślęczkowski,<sup>1,2</sup> Ian Segers,<sup>2</sup> Yiliu Liu,<sup>1,2,3\*</sup> and Anja R. A. Palmans<sup>1,2\*</sup>

<sup>1</sup>Institute for Complex Molecular Systems, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands.

<sup>2</sup>Laboratory of Macromolecular and Organic Chemistry, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands.

<sup>3</sup>South China Advanced Institute for Soft Matter Science and Technology, South China University of Technology, Guangzhou, P. R. China, 510641

\*Corresponding authors: [liuyiliu@scut.edu.cn](mailto:liuyiliu@scut.edu.cn) and [a.palmans@tue.nl](mailto:a.palmans@tue.nl)

## Supplementary Information

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## 1. Materials and Methods

Reagents were purchased from Sigma Aldrich, TCI chemicals, Fisher Scientific, TCI Europe, and ABCR and used as received. BTA-olefin precursor **17** was synthesized according to previously reported method.<sup>[1]</sup> All solvents were purchased from Biosolve and dry solvents were obtained using MBraun solvent purification system (MB SPS-800). Deuterated solvents were provided by Cambridge Isotopes Laboratories. Reactions were monitored by the use of thin-layer chromatography (TLC) using 60-F254 silica gel plates (Merck) and compounds were visualized using an ultraviolet lamp (254 nm), potassium permanganate (KMnO<sub>4</sub>) stain, or iodide (I<sub>2</sub>) stain. Automated column chromatography was performed using a Biotage Isolera® One with Biotage Silica Cartridges and using a Grace Reveleris X2 using Reveleris Silica Flash Cartridges. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a Bruker ASCEND 400 MHz (400 MHz for <sup>1</sup>H NMR and 100 MHz for <sup>13</sup>C NMR). Proton chemical shifts are reported in ppm (δ) downfield from trimethylsilane (TMS) using the resonance frequency of the deuterated solvents (CDCl<sub>3</sub>; 7.26 ppm & DMSO-*d*<sub>6</sub>; 2.50 ppm containing TMS) as internal standards. Peak multiplicities are abbreviated as s: singlet; d: doublet; q: quartet; m: multiplet; br: broad; dd: doublet of doublets; dt: doublet of triplets and dq: doublet of quartet. Carbon chemical shifts are reported in ppm (δ) downfield from trimethylsilane (TMS) using the resonance frequency of the deuterated solvents (CDCl<sub>3</sub>; 77.16 ppm & DMSO-*d*<sub>6</sub>; 39.52 ppm containing TMS) as internal standards. Infrared spectra were recorded using a Perkin Elmer Spectrum Two FT-IR spectrometer equipped with a Perkin Elmer Universal ATR Two Accessory. Matrix assisted laser absorption/ionization mass time of flight (MALDI-TOF) spectra were obtained on a Bruker Autoflex Speed. α-cyano-4-hydroxycinnamic acid (CHCA) and *trans*-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCBT) were used as matrix. All samples were dissolved in CHCl<sub>3</sub> or CHCl<sub>3</sub>:DMSO (80:20). Circular dichroism spectra were recorded on a Jasco J-600 spectropolarimeter equipped with a PFD-425S/15 Peltier-type temperature controller. Experiments were performed in a 1 cm Hellma quartz cell. Polarized optical microscopy (POM) samples were placed on glass substrates and imaged using Nikon Xfinity1 Lumenera microscope with 10x magnification at room temperature. Differential scanning calorimetry (DSC) data were collected on a DSC Q2000 from TA instruments, calibrated with an indium standard. The samples were weighed directly into aluminum pans and hermetically sealed. The presented data are second heating/cooling cycle unless otherwise stated.

## 2. Synthetic Procedures

### *FmocHN-A-COOtBu* (**2**)

*FmocHN-A-COOtBu-COOH* (**1**) (8 g, 18.8 mmol) was dissolved in THF (200 mL). EDC·HCl (4.32 g, 22.5 mmol), HOBT·xH<sub>2</sub>O (2.54 g, 18.8 mmol) were added before the mixture was cooled to 0 °C. Finally, DIPEA (~6.5 mL, 37.1 mmol) and propargylamine (~1.35 mL, 20.7 mmol) were added, after which the reaction was left stirring at r.t. overnight. The reaction was quenched with EtOH (20 mL), and the solvents were evaporated *in vacuo*. The residue was dissolved in EtOAc (200 mL) and washed with aq. 10% citric acid-solution (pH 3-5) (4 x 150

mL), H<sub>2</sub>O (4 x 125 mL), dried (MgSO<sub>4</sub>), and evaporated under reduced pressure. The compound was purified by column chromatography (DCM-EtOAc, 8:2) to give FmocHN-A-COO*t*Bu (**2**) as a white solid (4.58 g, 53%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.77 (d, 2H, Fmoc), 7.59 (d, 2H, Fmoc), 7.41 (t, 2H, Fmoc), 7.32 (t, 2H, Fmoc), 6.52 (br s, 1H, NH), 5.71 (d, 1H, NH), 4.41 (t, 2H, Fmoc), 4.21 (m, 2H, Fmoc, Glu-H<sup>α</sup>), 4.06 (br s, 2H, CH<sub>2</sub>C≡CH), 2.44 (m, 1H, Glu-H<sup>γ</sup>), 2.33 (m, 1H, Glu-H<sup>γ</sup>), 2.23 (t, 1H, C≡CH), 2.08 (m, 1H, Glu-H<sup>β</sup>), 1.95 (m, 1H, Glu-H<sup>β</sup>), 1.46 (s, 9H, *t*-Bu). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 143.72, 141.31, 127.76, 127.10, 125.08, 120.02, 81.26, 79.07, 71.83, 67.13, 47.16, 31.71, 29.25, 28.09. MALDI-TOF (m/z) calculated for C<sub>27</sub>H<sub>30</sub>NaN<sub>2</sub>O<sub>5</sub>, [M+Na]<sup>+</sup> = 485.21, Obs. [M+Na]<sup>+</sup> = 485.23.

#### *FmocHN-T-COOtBu (3)*

FmocHN-T-COO*t*Bu-OH (5.14 g, 12.1 mmol) was dissolved in THF (200 mL). EDC·HCl (2.61 g, 13.6 mmol) and HOBT·xH<sub>2</sub>O (1.57 g, 11.6 mmol) were added before the mixture was cooled to 0 °C. Finally, DIPEA (~3.9 mL, 22.4 mmol) and tris[(allyloxy)methyl]aminomethane (3 g, 12.4 mmol) were added, after which the reaction was left stirring at r.t. overnight. The solvent was evaporated under reduced pressure. The residue was dissolved in EtOAc (200 mL) and washed with aq. 10% citric acid-solution (pH 3-5) (3 x 150 mL), brine (3 x 150 mL), dried (MgSO<sub>4</sub>), and evaporated under reduced pressure. The compound was purified by column chromatography (DCM-EtOAc, 95:5%) to give FmocHN-T-COO*t*Bu (**3**) (5.41 g, 67%) as a colorless oil.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.77 (d, 2H, Fmoc), 7.60 (d, 2H, Fmoc), 7.40 (t, 2H, Fmoc), 7.32 (t, 2H, Fmoc), 6.37 (br s, 1H, NH), 5.85 (m, 3H, CH<sub>3</sub>CH=CH<sub>2</sub>), 5.71 (d, 1H, NH), 5.31-5.10 (m, 6H, CH=CH<sub>2</sub>), 4.36 (t, 2H, Fmoc), 4.21 (m, 2H, Fmoc, Glu-H<sup>α</sup>), 3.96 (d, 6H, OCH<sub>2</sub>CH), 3.72 (s, 6H, CCH<sub>2</sub>CH), 2.38 (m, 2H, Glu-H<sup>γ</sup>), 1.93 (m, 2H, Glu-H<sup>β</sup>), 1.46 (s, 9H, *t*-Bu). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 172.82, 170.79, 143.80, 141.28 (d, *J* = 1.4 Hz), 134.61, 127.69, 127.06, 125.17, 119.96, 116.83, 80.77, 72.25, 68.56, 67.05, 60.39, 54.54, 47.17, 31.43, 28.82, 28.09. MALDI-TOF (m/z) calculated for C<sub>37</sub>H<sub>48</sub>NaN<sub>2</sub>O<sub>8</sub>, [M+Na]<sup>+</sup> = 671.33, Obs. [M+Na]<sup>+</sup> = 671.34.

#### *FmocHN-A-COOH (4a)*

FmocHN-A-(COO*t*Bu)propargylamide (**2**) (4.91 g, 10.6 mmol) was dissolved in DCM (50 mL) and the solution was cooled to 0 °C. TFA (50 mL, 653 mmol) was added and the reaction was stirred at room temperature for 3 hours. The solvents were evaporated under reduced pressure, where after the crude product was dissolved in DCM and dried under reduced pressure for two times to obtain FmocHN-T-COOH (**4a**) as a soft pink/yellow colored powder (4.55 g).

#### *FmocHN-A-COOPhF<sub>5</sub> (4b)*

FmocHN-A-COOH-propargylamide (4.55 g) (**4a**) was suspended in CHCl<sub>3</sub> (150 mL) and became dissolved after the addition of DIPEA (6 mL, 34.4 mmol). Pentafluorophenyl trifluoroacetate (2.4 mL, 14.0 mmol) was added and the reaction was stirred at room temperature for 3 hours. The mixture was washed with aq. 10% citric acid-solution (pH 3-5) (2

x 100 mL), H<sub>2</sub>O (2 x 100 mL), brine (2 x 100 mL), dried (MgSO<sub>4</sub>), and evaporated under reduced pressure to obtain FmocHN-T-COOPhF<sub>5</sub> (**4b**) as a solid (12.26 g).

#### *H<sub>2</sub>N-T-(COOtBu) (5)*

FmocHN-T-COObu (**3**) (7.88 g, 12.1 mmol) was dissolved in DCM (100 mL). Diethylamine (100 mL, 967 mmol) was added and the reaction was stirred at r.t. for 3 hours. On completion, volatiles were evaporated under reduced pressure and the residue was dissolved in DCM. The compound was purified by column chromatography (DCM-EtOAc, 95:5% up to DCM-EtOAc, 40:60%) to obtain H<sub>2</sub>N-A-COObu (**5**) (4.22 g, 81%) as a yellow oil.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.36 (d, *J* = 3.8 Hz, 1H), 5.96 – 5.81 (m, 3H), 5.34 – 5.10 (m, 6H), 3.99 (tq, *J* = 5.4, 1.5 Hz, 6H), 3.88 – 3.69 (m, 6H), 3.37 – 3.28 (m, 1H), 2.42 – 2.29 (m, 2H), 2.10 – 1.95 (m, 1H), 1.90 – 1.77 (m, 1H), 1.45 (d, *J* = 4.5 Hz, 11H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 174.38, 172.90, 134.79, 116.67, 80.34, 72.24, 68.71, 59.46, 55.10, 31.69, 30.43, 28.10.

#### *FmocHN-T-COOH (6a)*

FmocHN-T-COObu (**3**) (6.74 g, 10.4 mmol) was dissolved in DCM (50 mL) and the solution was cooled to 0 °C with an ice bath. Trifluoroacetic acid (50 mL, 653 mmol) was added and the reaction was stirred at room temperature for 3 hours. On completion, volatiles were evaporated under reduced pressure, where after the crude product was dissolved in DCM and dried under reduced pressure two times to obtain Fmoc-A-COOH (**6a**) (8.31 g) as a solid.

#### *FmocHN-T-COOPhF<sub>5</sub> (6b)*

Crude FmocHN-A-COOH (**6a**) (8.31 g) was dissolved in CHCl<sub>3</sub> (150 mL). DIPEA (7 mL, 40.2 mmol) and pentafluorophenyl trifluoroacetate (2.5 mL, 14.5 mmol) were added, and the reaction was stirred at room temperature for 1 hour. The reaction was washed with aq. 10% citric acid-solution (pH 3-5) (3 x 100 mL), H<sub>2</sub>O (3 x 100 mL), brine (3 x 100 mL), dried (MgSO<sub>4</sub>), and evaporated under reduced pressure to obtain crude FmocHN-A-COOPhF<sub>5</sub> (**6b**) (9.1 g).

#### *FmocHN-AT-COObu (7)*

Fmoc-A-COOPhF<sub>5</sub> (**4b**) (12.26 g) and H<sub>2</sub>N-T-COObu (**5**) (2.25 g, 5.27 mmol) were dissolved in DMF (100 mL) and the mixture was stirred at room temperature for 30 minutes. EtOAc (100 mL) was added and washed with H<sub>2</sub>O (100 mL), and brine (2 x 100 mL). The organic layer was dried (Na<sub>2</sub>SO<sub>4</sub>) and evaporated under reduced pressure. The title compound was purified by column chromatography (DCM-EtOAc, 50:50%) to obtain FmocHN-AT-COObu (**7**) (3.45 g, 80%) white solid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.76 (d, *J* = 7.5 Hz, 2H), 7.59 (d, *J* = 7.5 Hz, 2H), 7.44 – 7.27 (m, 4H), 6.72 (d, *J* = 7.5 Hz, 1H), 6.42 (s, 1H), 5.98 (d, *J* = 7.5 Hz, 2H), 5.85 (ddt, *J* = 17.3, 10.7, 5.5 Hz, 3H), 5.28 – 5.09 (m, 6H), 4.39 (dd, *J* = 18.2, 7.4 Hz, 2H), 4.26 – 4.14 (m, 3H), 4.03 – 3.90 (m, 8H), 3.83 – 3.65 (m, 6H), 2.49 – 2.26 (m, 4H), 2.24 (t, *J* = 2.5 Hz, 1H), 2.01 – 1.88 (m, 2H), 1.44 (s, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ = 172.97, 171.17, 143.84, 141.31, 134.63, 127.72, 127.10, 125.16, 119.98, 116.80, 81.04, 79.62, 72.25, 71.56, 68.56,

60.10, 53.11, 47.17, 32.45, 31.62, 28.99, 28.08. MALDI-TOF (m/z) calculated for  $C_{45}H_{58}NaN_4O_{10}$ ,  $[M+Na]^+ = 837.41$ , Obs.  $[M+Na]^+ = 837.41$ .

#### *FmocHN-TT-COObu (8)*

$H_2N-T-COObu$  (**5**) (4.02 g, 9.42 mmol) and crude FmocHN-T-COOPhF<sub>5</sub> (**6b**) (9.1 g) were dissolved in DMF (100 mL). The reaction was stirred at room temperature for 1.5 hours. EtOAc (150 mL) was added to the reaction mixture and the DMF was washed out with H<sub>2</sub>O (2 x 100 mL), and brine (2 x 100 mL) before the organic layer was dried (Na<sub>2</sub>SO<sub>4</sub>) and evaporated under reduced pressure. The compound was purified by column chromatography (DCM-EtOAc, 50:50%) to obtain FmocHN-TT-COObu (**8**) (6.94 g, 74%) as a white solid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 7.75$  (d,  $J = 7.5$  Hz, 2H), 7.59 (d,  $J = 7.5$  Hz, 2H), 7.35 (dt,  $J = 32.7, 7.5$  Hz, 4H), 7.12 (s, 1H), 6.79 (d,  $J = 7.8$  Hz, 1H), 6.39 (s, 1H), 5.86 (ddt,  $J = 16.9, 11.5, 5.9$  Hz, 6H), 5.34 – 5.08 (m, 12H), 4.38 (q,  $J = 7.2$  Hz, 2H), 4.32 (d,  $J = 7.6$  Hz, 2H), 4.20 (t,  $J = 7.2$  Hz, 1H), 3.97 (q,  $J = 5.0$  Hz, 12H), 3.87 – 3.60 (m, 12H), 2.48 – 2.18 (m, 4H), 2.11 – 1.79 (m, 4H), 1.44 (s, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta = 172.55, 171.37, 171.18, 143.88, 141.25, 134.71, 134.64, 127.65, 127.07, 125.22, 119.92, 117.02, 116.71, 80.76, 72.29, 72.22, 68.51, 68.22, 60.33, 60.14, 53.07, 47.19, 31.64, 28.09$ . MALDI-TOF (m/z) calculated for  $C_{55}H_{76}NaN_4O_{13}$ ,  $[M+Na]^+ = 1023.53$ , Obs.  $[M+Na]^+ = 1023.55$ .

#### *H<sub>2</sub>N-AT-COObu (9)*

FmocHN-AT-COObu (**7**) (3.45 g, 4.23 mmol) was dissolved in DCM (100 mL). Diethylamine (100 mL, 967 mmol) was added and the mixture was stirred at r.t. for 3 hours. Volatiles were evaporated under reduced pressure and the residue was dissolved in DCM (100 mL). The organic layer was washed with aq. 10% citric acid-solution (pH 3-5) (2 x 100 mL), Na<sub>2</sub>CO<sub>3</sub> (sat):H<sub>2</sub>O (20:80 vol%) solution (3 x 100 mL), brine (3 x 100 mL), dried (MgSO<sub>4</sub>) and the evaporated under reduced pressure. The residue was precipitated in pentane. H<sub>2</sub>N-AT-COObu (**9**) (2.25 g) was obtained as a yellow sticky solid.

#### *FmocHN-TT-COOH (10a)*

FmocHN-TT-COObu (**8**) (5.04 g, 5.03 mmol) was dissolved in DCM (50 mL) and the solution was cooled to 0 °C with an ice bath. Trifluoroacetic acid (50 mL, 653 mmol) was added and the reaction was stirred at room temperature overnight. On completion, volatiles were evaporated under reduced pressure, where after the crude product was dissolved in DCM and dried under reduced pressure for two times, to obtain FmocHN-TT-COOH (**10a**) as an orange viscous liquid.

#### *FmocHN-TT-COOPhF<sub>5</sub> (10b)*

FmocHN-TT-COOH (**10a**) (4.76 g, 5.03 mmol) was dissolved in CHCl<sub>3</sub> (150 mL). DIPEA (6 mL, 34.4 mmol), pentafluorophenyl trifluoroacetate (1.3 mL, 7.57 mmol) were added, and the reaction was stirred at room temperature for 1 hour. The reaction mixture was washed with aq. 10% citric acid-solution (pH 3-5) (3 x 100 mL), H<sub>2</sub>O (3 x 100 mL), brine (3 x 100 mL), dried (MgSO<sub>4</sub>), and evaporated under reduced pressure to obtain Fmoc-TT-OPhF<sub>5</sub> (**13b**) (5.44 g) as a yellow sticky solid.

### *FmocHN-TTAT-COObu (11)*

FmocHN-TT-COOPhF<sub>5</sub> (**10b**) (5.44 g) and H<sub>2</sub>N-AT-COObu (**9**) (2.25 g) were dissolved in DMF (100 mL) and the reaction was stirred at room temperature for 1 hour. EtOAc (200 mL) was added to the reaction mixture and the DMF was washed out with H<sub>2</sub>O (3 x 100 mL), and brine (3 x 100 mL) before the organic layer was dried (Na<sub>2</sub>SO<sub>4</sub>) and evaporated under reduced pressure. The filtrate and residue were dissolved in a mixture of CHCl<sub>3</sub> and MeOH, and separated from the Na<sub>2</sub>SO<sub>4</sub> by filtration. The residue solvents were evaporated under reduced pressure and the solid product was purified by column chromatography (CHCl<sub>3</sub>-EtOAc, 50:50%, up to 100% EtOAc) to obtain FmocHN-TTAT-COObu (**11**) (3.83 g, 60%) as a white solid.

<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ = 8.37 (t, *J* = 5.5 Hz, 1H), 7.97 – 7.68 (m, 7H), 7.53 – 7.21 (m, 8H), 5.82 (ddq, *J* = 20.6, 9.7, 5.0 Hz, 9H), 5.35 – 4.98 (m, 18H), 4.24 (dq, *J* = 22.2, 8.8, 8.0 Hz, 7H), 3.91 (d, *J* = 5.3 Hz, 18H), 3.84 (dt, *J* = 4.9, 2.4 Hz, 2H), 3.70 – 3.49 (m, 18H), 3.08 (t, *J* = 2.5 Hz, 1H), 2.28 – 2.05 (m, 8H), 1.93 – 1.59 (m, 8H), 1.37 (s, 9H). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>): δ = 172.09, 135.61, 135.59, 128.10, 127.54, 125.79, 120.56, 116.84, 116.77, 80.00, 79.43, 73.49, 71.96, 71.92, 68.23, 60.15, 28.19. IR ν (cm<sup>-1</sup>) 3277 (N-H stretching), 3075 (Ar C-H stretching), 2931, 2859 (aliphatic C-H stretching), 1730 (C=O ester stretching), 1690, 1660, 1634 (C=O amide stretching), 1525 (amide II), 1448, 1252, 1150, 1084, 988, 922, 737, 598, 426. MALDI-TOF (*m/z*) calculated for C<sub>81</sub>H<sub>114</sub>NaN<sub>8</sub>O<sub>20</sub>, [M+Na]<sup>+</sup> = 1541.80, Obs. [M+Na]<sup>+</sup> = 1541.80.

### *H<sub>2</sub>N-TTAT-COObu (12)*

Fmoc-TTAT-COObu (**11**) (1.395 g, 0.92 mmol) was dissolved in CHCl<sub>3</sub> (50 mL). Piperidine (50 mL, 506 mmol) was added and the mixture was stirred at room temperature for 1 hour. The CHCl<sub>3</sub> and piperidine were evaporated under reduced pressure and the residue was dissolved in CHCl<sub>3</sub> (150 mL). The organic layer was washed with aq. 10% citric acid-solution (pH 3-5) (3 x 100 mL), Na<sub>2</sub>CO<sub>3</sub> (sat):H<sub>2</sub>O (20:80 vol%) solution (2 x 100 mL), brine (2 x 100 mL), dried (MgSO<sub>4</sub>) and evaporated under reduced pressure. The residue was washed with pentane to partially remove the Fmoc-byproducts. H<sub>2</sub>N-TTAT-COObu (**12**) was obtained as a yellow solid.

### *FmocHN-TTAT-COOH (13a)*

FmocHN-TTAT-COObu (**11**) (1.395 g, 0.92 mmol) was dissolved in CHCl<sub>3</sub> (50 mL) and the solution was cooled to 0 °C with an ice bath. Trifluoroacetic acid (50 mL, 653 mmol) was added and the reaction was stirred at room temperature overnight. The volatiles were evaporated under reduced pressure, where after the crude product was dissolved in CHCl<sub>3</sub> and dried under reduced pressure for two times to obtain a product of FmocHN-TTAT-COOH (**13a**) as an orange solid.

### *FmocHN-TTAT-COOPhF<sub>5</sub> (13b)*

Fmoc-TTAT-COOH (**13a**) was dissolved in CHCl<sub>3</sub> (150 mL). DIPEA (6 mL, 34.4 mmol) and an excess of pentafluorophenyl trifluoroacetate (0.95 mL, 5.53 mmol) were added, and the reaction was stirred at r.t. for 2 hours. The reaction mixture was washed with aq. 10% citric

acid-solution (pH 3-5) (3 x 100 mL), H<sub>2</sub>O (3 x 100 mL), brine (3 x 100 mL), dried (MgSO<sub>4</sub>), and evaporated under reduced pressure to obtain Fmoc-TTAT-COOPhF<sub>5</sub> (**13b**) (5.44 g).

*FmocHN-TTATTTAT-COObu* (**14**)

FmocHN-TTAT-COOPhF<sub>5</sub> (**13b**) and H<sub>2</sub>N-TTAT-COObu (**12**) were dissolved in DMF (100 mL) and the reaction was stirred at room temperature for 1 hour. CHCl<sub>3</sub> (150 mL) was added to the reaction mixture and the DMF was washed out with H<sub>2</sub>O (1 x 100 mL & 2 x 150 mL), and brine (3 x 100 mL) before the organic layer was dried (Na<sub>2</sub>SO<sub>4</sub>) and evaporated under reduced pressure. The residue was washed with *n*-pentane and dried *in vacuo* (40 °C) overnight to remove the DMF. The solid product was purified by column chromatography (Acetone, 100%, CHCl<sub>3</sub>-MeOH, 95:5%, up to CHCl<sub>3</sub>-MeOH, 70:30%) to obtain FmocHN-TTATTTAT-COObu (**14**) (980 mg, 39 %) as yellow solid.

<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ = 8.42 – 7.22 (m, 24H), 5.83 (dddd, *J* = 15.6, 13.6, 6.8, 3.5 Hz, 18H), 5.16 (dd, *J* = 42.7, 13.8 Hz, 36H), 4.24 (dq, *J* = 17.6, 8.8, 8.1 Hz, 11H), 3.91 (d, *J* = 5.2 Hz, 36H), 3.84 (d, *J* = 5.5 Hz, 4H), 3.71 – 3.50 (m, 36H), 3.07 (q, *J* = 2.4 Hz, 2H), 2.16 (d, *J* = 18.7 Hz, 16H), 1.77 (dd, *J* = 74.9, 20.8 Hz, 16H), 1.37 (s, 9H). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>): δ = 135.59, 128.11, 116.85, 116.78, 81.38, 73.48, 71.95, 71.92, 68.22, 60.13, 28.19. IR ν (cm<sup>-1</sup>) 3273 (N-H stretching), 3075 (Ar C-H stretching), 2929, 2859 (aliphatic C-H stretching), 1729 (C=O ester stretching), 1690, 1660, 1634 (C=O amide stretching), 1533 (amide II), 1449, 1254, 1139, 1084, 989, 923, 738, 600. MALDI-TOF (*m/z*) calculated for C<sub>143</sub>H<sub>208</sub>NaN<sub>16</sub>O<sub>37</sub>, [M+Na]<sup>+</sup> = 2765.48, Obs. [M+Na]<sup>+</sup> = 2765.53.

*FmocHN-A-tBu-triazoleundecyl-bis((S)-3,7-dimethyloctyl)-BTA* (**21**).

Fmoc-Glu(*Obu*)-propargylamide (**5**) (18.3 mg, 0.04 mmol), **20** (28 mg, 0.04 mmol) and CuSO<sub>4</sub> (1.19 mg, 0.007 mmol) were dissolved in DMSO (0.5 mL) to obtain a green colored solution. (+)-Sodium L-ascorbate (2 mg, 0.010 mmol) was added and the yellow colored mixture was stirred at 50 °C overnight under an argon atmosphere. After conversion check by TLC (DCM:EtOAc 80:20%) additional CuSO<sub>4</sub> (1.2 mg, 0.008 mmol) and (+)-sodium L-ascorbate (1 mg, 0.005 mmol) in 5 drops of H<sub>2</sub>O was added to the reaction mixture. The clouded reaction mixture, which contained red particles, was further stirred at 50 °C overnight under an argon atmosphere. After IR analysis, no absorption band of azide group (ν -N<sub>3</sub> 2095 cm<sup>-1</sup>) was present. The reaction mixture was diluted in CHCl<sub>3</sub> (70 mL), washed with 0.1 M EDTA-solution (2 x 50 mL), H<sub>2</sub>O (1 x 50 mL), brine (1 x 50 mL), and dried (MgSO<sub>4</sub>). The solvents were evaporated under reduced pressure. The product was isolated by column chromatography (DCM, 100%, up to DCM-(10% isopropanol in EtOAc) (80:20%)) to obtain Fmoc-A-*t*Bu-triazoleundecyl-bis((*S*)-3,7-dimethyloctyl)-BTA (**30**) (15.6 mg, 34%) as a white solid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 8.44 – 8.29 (m, 3H), 7.80 – 7.70 (m, 2H), 7.62 – 7.53 (m, 2H), 7.50 (s, 1H), 7.39 (tt, *J* = 7.8, 1.7 Hz, 2H), 7.32 – 7.27 (m, 2H), 7.18 (s, 1H), 6.79 (s, 1H), 6.58 (s, 2H), 5.91 (d, *J* = 7.7 Hz, 1H), 4.53 (d, *J* = 5.7 Hz, 2H), 4.42 – 4.07 (m, 6H), 3.47 (tt, *J* = 13.8, 6.4 Hz, 6H), 2.31 (ddt, *J* = 23.5, 16.2, 7.3 Hz, 2H), 2.17 – 1.75 (m, 4H), 1.73 – 1.47 (m, 10H), 1.43 (s, 11H), 1.38 – 1.06 (m, 28H), 0.93 (d, *J* = 6.5 Hz, 6H), 0.86 (d, *J* = 6.6 Hz, 13H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 165.69, 144.46, 141.27, 135.33, 135.26, 128.02, 127.74, 127.08, 125.09, 122.03, 119.99, 81.03, 50.31, 47.13, 40.34, 39.24, 38.53, 37.13, 36.62, 35.16,

31.73, 30.75, 30.01, 29.38, 28.07, 28.00, 27.95, 26.71, 26.10, 24.63, 22.70, 22.60, 19.47. MALDI-TOF (m/z) calculated for C<sub>67</sub>H<sub>100</sub>NaN<sub>8</sub>O<sub>8</sub>, [M+Na]<sup>+</sup> = 1167.76, Obs. [M+Na]<sup>+</sup> = 1167.76.

*N*-(*tert*-butyloxycarbonyl)tris[(allyloxy)methyl]aminomethane-tridecylsulfane (**22**)

*N*-(*tert*-butyloxycarbonyl)tris[(allyloxy)methyl]aminomethane (110.3 mg, 0.32 mmol) was dissolved in THF (10 mL), and 1-decanethiol (0.6 mL, 4.18 mmol) and 2,2-dimethoxy-2-phenylacetophenone (114.7 mg, 0.45 mmol) were added before the mixture was purged with argon for 10 minutes. After purging, the reaction mixture was stirred for 4 hours at room temperature under UV light (315-400 nm). The solvent was evaporated under reduced pressure and the product was isolated by column chromatography (DCM-EtOAc, 90:10% up to EtOAc, 100 %) to give *N*-(*tert*-butyloxycarbonyl)tris[(allyloxy)methyl]aminomethane-tridecylsulfane (**22**) (129 mg, 51%) as a yellow oil.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 4.92 (s, 1H), 3.63 (s, 6H), 3.50 (t, *J* = 6.1 Hz, 6H), 2.53 (dt, *J* = 24.1, 7.4 Hz, 12H), 1.89 – 1.76 (m, 6H), 1.65 – 1.50 (m, 8H), 1.47 – 1.18 (m, 52H), 0.95 – 0.82 (m, 9H).

*FmocHN*-(TTAT)<sub>2</sub>-*t*Bu-triazoleundecyl-bis((*S*)-3,7-dimethyloctyl)-BTA (**23**)

*FmocHN*-TTATTTAT-COO*t*Bu (**14**) (48.4 mg, 0.018 mmol) and (dimethyloctylamide)<sub>2</sub>-BTA-azide (**20**) (27.3 mg, 0.04 mmol) were separately dissolved in DMSO (0.5 mL). Both solutions were added to CuSO<sub>4</sub> (0.68 mg, 0.0043 mmol) and stirred at 50 °C under an argon atmosphere until CuSO<sub>4</sub> was completely dissolved. To the green colored solution, (+)-sodium L-ascorbate (1.9 mg, 0.0094 mmol) was added and the mixture was stirred at 50 °C until (+)-sodium L-ascorbate was dissolved. The reaction was consecutively stirred overnight at r.t. under an argon atmosphere. The reaction mixture was diluted in CHCl<sub>3</sub> (70 mL), washed with 0.1 M EDTA-solution (2 x 50 mL), H<sub>2</sub>O (2 x 50 mL), brine (2 x 50 mL), and dried (MgSO<sub>4</sub>). The solvents were evaporated under reduced pressure. The product was isolated by column chromatography (CHCl<sub>3</sub>, 100%, up to CHCl<sub>3</sub>-MeOH, 95:5%) to obtain *Fmoc*-(TTAT)<sub>2</sub>-*t*Bu-triazoleundecyl-bis((*S*)-3,7-dimethyloctyl)-BTA (**31**) (59.4 mg). According to integral calculations from the <sup>1</sup>H NMR-spectrum, the product consisted out of ~40% monofunctionalized octamer and ~60% bifunctionalized octamer. IR measurements of the BTA-azide fraction (7.3 mg), obtained from column chromatography, showed no azide band. MALDI-TOF spectra showed a mixture of substrate, monofunctionalized and bifunctionalized octamer. Indicated a loss of ~25-30% of functional BTA-azide, the functionalized octamer mixture and (dimethyloctylamide)<sub>2</sub>-BTA-azide (**23**) (13.1 mg, 0.02 mmol) were separately dissolved in DMSO (0.5 mL). Both solutions were added to CuSO<sub>4</sub> (1.11 mg, 0.007 mmol) and stirred at 50 °C under an argon atmosphere until CuSO<sub>4</sub> was dissolved. To the green colored solution, sodium ascorbate (4.38 mg, 0.022 mmol) was added and the mixture was stirred for 2 days at r.t. under an argon flow. The reaction mixture was purified with the same procedure as earlier described to obtain *Fmoc*-(TTAT)<sub>2</sub>-*t*Bu-triazoleundecyl-bis((*S*)-3,7-dimethyloctyl)-BTA (**23**) (26.9 mg, 37%) as a white solid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 8.61 (t, *J* = 5.7 Hz, 6H), 8.46 (s, 2H), 8.35 (s, 6H), 8.00 – 7.67 (m, 13H), 7.52 – 7.25 (m, 10H), 5.90 – 5.73 (m, 18H), 5.26 – 5.04 (m, 36H), 4.27 (dd, *J* = 12.0, 6.4 Hz, 18H), 3.90 (dq, *J* = 5.2, 1.7 Hz, 36H), 3.69 – 3.51 (m, 36H), 2.14 (s, 16H), 1.92

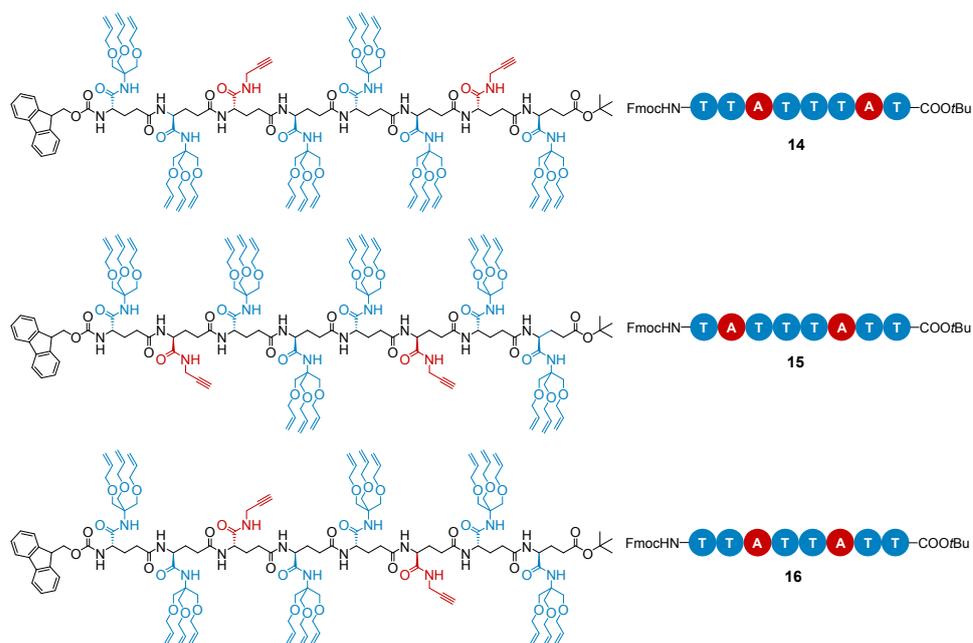
– 1.41 (m, 40H), 1.36 (s, 9H), 1.35 – 1.05 (m, 67H), 0.89 (d,  $J = 6.4$  Hz, 13H), 0.83 (d,  $J = 6.6$  Hz, 26H). IR  $\nu$  ( $\text{cm}^{-1}$ ) 3276 (N-H stretching), 3076 (Ar C-H stretching), 2926, 2854 (aliphatic C-H stretching), 1731 (C=O ester stretching), 1659, 1634 (C=O amide stretching), 1538 (amide II), 1449, 1366, 1256, 1138, 1087, 990, 923, 734, 691, 599. MALDI-TOF ( $m/z$ ) calculated for  $\text{C}_{222}\text{H}_{348}\text{NaN}_{28}\text{O}_{43}$ ,  $[\text{M}+\text{Na}]^+ = 4131.59$ , Obs.  $[\text{M}+\text{Na}]^+ = 4131.48$ .

*Fmoc-(TTAT)<sub>2</sub>-tBu-triazoleundecyl-bis((S)-3,7-dimethyloctyl)-BTA-decylsulfane (24)*

Fmoc-(TTAT)<sub>2</sub>-tBu-triazoleundecyl-bis((S)-3,7-dimethyloctyl)-BTA (**23**) (15 mg, 3.65  $\mu\text{mol}$ ), 1-decanethiol (0.05 mL, 0.24 mmol), and DMPA (8.8 mg, 0.034 mmol) were dissolved in dimethylacetamide (1 mL) and purged with argon for 10 minutes. After purging, the colorless reaction mixture was stirred for 4 hours at r.t. under UV light (315-400 nm). The yellow colored mixture was diluted with  $\text{CHCl}_3$  (70 mL), washed with  $\text{H}_2\text{O}$  (2 x 50 mL), brine (50 mL), dried ( $\text{MgSO}_4$ ), where after the organic layer was evaporated under reduces pressure. The residual liquid product was diluted in EtOAc (70 mL), washed with  $\text{H}_2\text{O}$  (3 x 50 mL), brine (50 mL), dried ( $\text{MgSO}_4$ ), where after the organic layer was evaporated under reduces pressure. The crude product was subjected to column chromatography ( $\text{CHCl}_3$ , 100%, up to  $\text{CHCl}_3$ -(10% isopropanol in EtOAc) (50:50%)) to obtain a colorless sticky solid (8.3 mg, 31%).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 8.97$  (d,  $J = 51.9$  Hz, 1H), 8.35 (d,  $J = 7.9$  Hz, 6H), 8.22 (s, 1H), 7.73 (d,  $J = 7.6$  Hz, 1H), 7.62 (dd,  $J = 15.6, 8.2$  Hz, 3H), 7.37 (t,  $J = 7.4$  Hz, 2H), 6.79 (qd,  $J = 76.3, 49.0, 43.3$  Hz, 17H), 4.75 (s, 2H), 4.27 (d,  $J = 27.4$  Hz, 14H), 3.89 – 3.56 (m, 36H), 3.46 (dq,  $J = 13.7, 6.0$  Hz, 49H), 3.32 (d,  $J = 5.1$  Hz, 3H), 2.88 (s, 1H), 2.59 – 2.42 (m, 72H), 2.33 (d,  $J = 52.1$  Hz, 18H), 1.80 (dt,  $J = 12.0, 5.7$  Hz, 37H), 1.72 (s, 25H), 1.53 (dq,  $J = 13.3, 7.3, 6.8$  Hz, 54H), 1.43 (s, 15H), 1.26 (s, 332H), 1.18 – 1.04 (m, 19H), 0.93 (dd,  $J = 6.6, 1.7$  Hz, 13H), 0.90 – 0.83 (m, 85H). IR  $\nu$  ( $\text{cm}^{-1}$ ) 3263 (N-H stretching), 3069 (Ar C-H stretching), 2922, 2853 (aliphatic C-H stretching), 1728 (C=O ester stretching), 1642 (C=O amide stretching), 1550 (amide II), 1464, 1366, 1295, 1107, 905, 721, 692. MALDI-TOF ( $m/z$ ) calculated for  $\text{C}_{403}\text{H}_{744}\text{NaN}_{28}\text{O}_{43}\text{S}_{18}$ ,  $[\text{M}+\text{Na}]^+ = 7268.19$ , Obs.  $[\text{M}+\text{Na}]^+ = 7269.65$ ,  $[\text{M}+\text{K}]^+ = 7285.39$ .

## *L*- $\gamma$ -Glutamamide octamers **15** and **16**



### **Scheme S1** Molecular structures and schematic representations of octamers **14**, **15** and **16**

Octamers **15** and **16** were synthesized according to protocol described for octamer **14**, using appropriate building blocks. The yield for octamer **16** was 39 % the yield of **15** was not calculated due to impurities present.

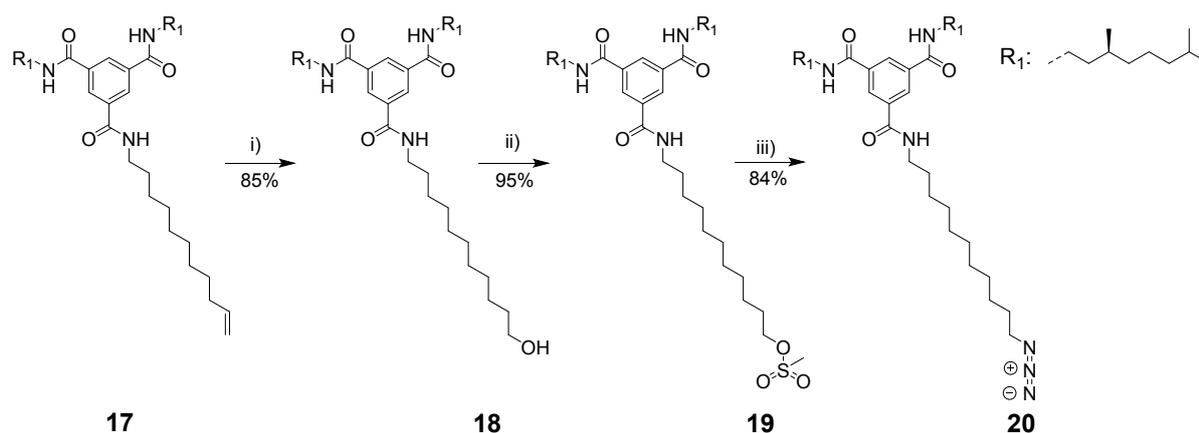
#### *FmocHN-TATTTATT-COObu (15)*

$^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ ):  $\delta$  = 8.42 – 7.22 (m, 24H), 5.83 (dddd,  $J$  = 15.6, 13.6, 6.8, 3.5 Hz, 18H), 5.16 (dd,  $J$  = 42.7, 13.8 Hz, 36H), 4.24 (dq,  $J$  = 17.6, 8.8, 8.1 Hz, 11H), 3.91 (d,  $J$  = 5.2 Hz, 36H), 3.84 (d,  $J$  = 5.5 Hz, 4H), 3.71 – 3.50 (m, 36H), 3.07 (q,  $J$  = 2.4 Hz, 2H), 2.16 (d,  $J$  = 18.7 Hz, 16H), 1.77 (dd,  $J$  = 74.9, 20.8 Hz, 16H), 1.37 (s, 9H).  $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ ):  $\delta$  = 135.59, 128.11, 116.85, 116.78, 81.38, 73.48, 71.95, 71.92, 68.22, 60.13, 28.19. IR  $\nu$  ( $\text{cm}^{-1}$ ) 3273 (N-H stretching), 3075 (Ar C-H stretching), 2929, 2859 (aliphatic C-H stretching), 1729 (C=O ester stretching), 1690, 1660, 1634 (C=O amide stretching), 1533 (amide II), 1449, 1254, 1139, 1084, 989, 923, 738, 600. MALDI-TOF ( $m/z$ ) calculated for  $\text{C}_{143}\text{H}_{208}\text{NaN}_{16}\text{O}_{37}$ ,  $[\text{M}+\text{Na}]^+ = 2765.48$ , Obs.  $[\text{M}+\text{Na}]^+ = 2765.53$ .

#### *FmocHN-TTATTATT-COObu (16)*

$^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ ):  $\delta$  = 8.42 – 7.22 (m, 24H), 5.83 (dddd,  $J$  = 15.6, 13.6, 6.8, 3.5 Hz, 18H), 5.16 (dd,  $J$  = 42.7, 13.8 Hz, 36H), 4.24 (dq,  $J$  = 17.6, 8.8, 8.1 Hz, 11H), 3.91 (d,  $J$  = 5.2 Hz, 36H), 3.84 (d,  $J$  = 5.5 Hz, 4H), 3.71 – 3.50 (m, 36H), 3.07 (q,  $J$  = 2.4 Hz, 2H), 2.16 (d,  $J$  = 18.7 Hz, 16H), 1.77 (dd,  $J$  = 74.9, 20.8 Hz, 16H), 1.37 (s, 9H).  $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ ):  $\delta$  = 135.59, 128.11, 116.85, 116.78, 81.38, 73.48, 71.95, 71.92, 68.22, 60.13, 28.19. IR  $\nu$  ( $\text{cm}^{-1}$ ) 3273 (N-H stretching), 3075 (Ar C-H stretching), 2929, 2859 (aliphatic C-H stretching), 1729 (C=O ester stretching), 1690, 1660, 1634 (C=O amide stretching), 1533 (amide II), 1449, 1254, 1139, 1084, 989, 923, 738, 600. MALDI-TOF ( $m/z$ ) calculated for  $\text{C}_{143}\text{H}_{208}\text{NaN}_{16}\text{O}_{37}$ ,  $[\text{M}+\text{Na}]^+ = 2765.48$ , Obs.  $[\text{M}+\text{Na}]^+ = 2765.53$ .

## Synthesis of BTA-azide (**20**)



**Scheme S2:** Synthetic route towards (*S*)-BTA-azide (**20**). Reaction conditions: i) 9-BBN, dry THF, argon, r.t., 2 h., then NaOH (6 M), H<sub>2</sub>O<sub>2</sub> (30 wt%); ii) methanesulfonyl chloride, pyridine, DCM, r.t., O/N. iii) NaN<sub>3</sub>, KI, dry DMF, 70 °C, O/N.

### *Bis*((*S*)-3,7-dimethyloctyl)-(11-hydroxyundecyl)-BTA (**18**)

Bis((*S*)-3,7-dimethyloctyl)-(undec-10-en-1-yl)-BTA (**17**) (516 mg, 0.81 mmol) was placed in a flame-dried round-bottomed flask, which was attached to the Schlenk line, evacuated and filled with dry argon. Under argon atmosphere, the substrate was dissolved in dry THF (15 mL) and the solution was placed in an ice bath and cooled to 0 °C. 9-Borabicyclo[3.3.1]nonane (5 mL, 0.5 M in THF) was added dropwise and the reaction was stirred under argon at r.t. for 2 hours. After a full conversion, the reaction was cooled back down to 0 °C and 6 M NaOH-solution (2.7 mL), and H<sub>2</sub>O<sub>2</sub>-solution (1.5 mL, 30 wt% in H<sub>2</sub>O) were added. After the reaction was completed, the mixture was diluted with EtOAc (100 mL), washed with H<sub>2</sub>O (2 x 100 mL), brine (2 x 100 mL), and dried (MgSO<sub>4</sub>). The crude product was purified by column chromatography (DCM, 100%, up to DCM-(10% isopropanol in EtOAc), 90:10%) to obtain bis((*S*)-3,7-dimethyloctyl)-(11-hydroxyundecyl)-BTA (**18**) (0.45 g, 85%).

### *Bis*((*S*)-3,7-dimethyloctyl)-(11-methylsulfonateundecyl)-BTA (**19**)

(Dimethyloctylamide)<sub>2</sub>-BTA-OH (**18**) (450 mg, 0.68 mmol) was dissolved in DCM (30 mL), and methanesulfonyl chloride (0.26 mL, 3.36 mmol) and pyridine (0.31 mL, 3.83 mmol) were added. The reaction was stirred at r.t. overnight. After the reaction was completed, the mixture was diluted with DCM (70 mL), washed with 1 M HCl-solution (2 x 80 mL), H<sub>2</sub>O (2 x 80 mL), brine (2 x 80 mL), and dried (MgSO<sub>4</sub>). The solvents were evaporated under reduced pressure to obtain bis((*S*)-3,7-dimethyloctyl)-(11-methylsulfonateundecyl)-BTA (**19**).

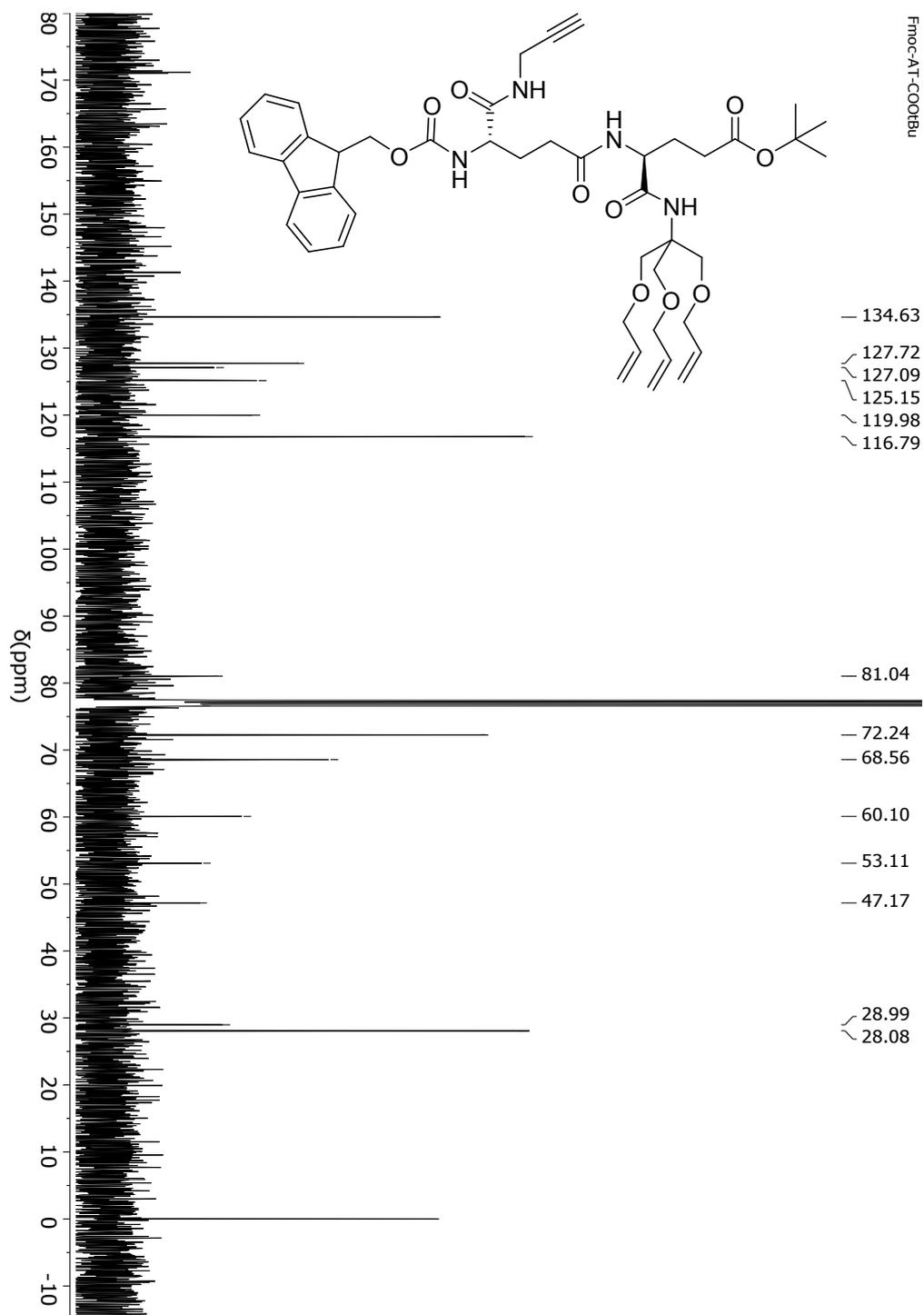
### *Bis*((*S*)-3,7-dimethyloctyl)-(11-azidoundecyl)-BTA (**20**)

Bis((*S*)-3,7-dimethyloctyl)-(11-methylsulfonateundecyl)-BTA (**19**) was dissolved in dry DMF (20 mL), where after sodium azide (113.3 mg, 1.74 mmol) and a potassium iodide (approximately 1 mg) were added. The reaction was stirred overnight at 50 °C. The temperature was increased to 70 °C to complete full conversion. The mixture was diluted with EtOAc (100 mL), washed with H<sub>2</sub>O (2 x 100 mL), brine (2 x 100 mL), and dried (MgSO<sub>4</sub>). The solvents were evaporated under reduced pressure. The crude product was purified by column

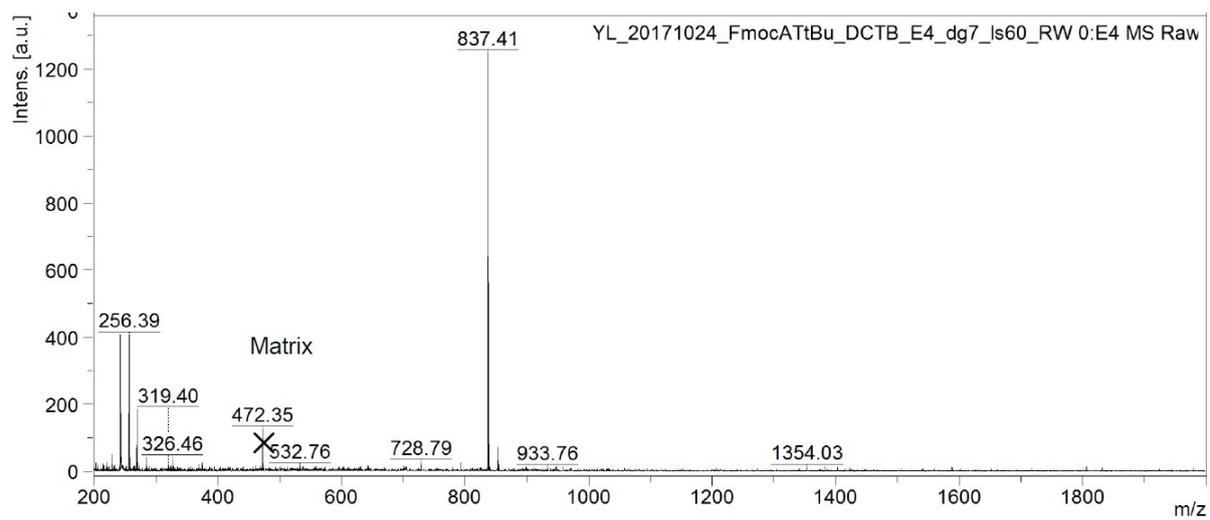
chromatography (CHCl<sub>3</sub>, 100%, up to DCM-(10% isopropanol in EtOAc), 90:10%) to obtain bis((S)-3,7-dimethyloctyl)-(11-azidoundecyl)-BTA (**23**) (391 mg, 84%) as a yellow sticky solid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 8.33 (s, 3H), 6.37 (dt, *J* = 16.1, 5.6 Hz, 3H), 3.61 – 3.39 (m, 6H), 3.25 (t, *J* = 6.9 Hz, 1H), 1.81 – 1.07 (m, 42H), 0.95 (d, *J* = 6.5 Hz, 6H), 0.87 (d, *J* = 6.6 Hz, 12H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 165.52, 135.28, 127.85, 51.49, 45.20, 40.39, 39.24, 38.53, 37.12, 36.63, 30.74, 29.55, 29.45, 29.27, 29.12, 28.84, 27.96, 26.97, 26.71, 24.63, 22.70, 22.60, 19.49. IR ν (cm<sup>-1</sup>) 3237 (N-H stretching), 3073 (Ar C-H stretching), 2925, 2855 (aliphatic C-H stretching), 2095 (azide stretching), 1637 (C=O stretching), 1557 (amide II), 1462, 1382, 1366, 1297, 1146, 1069, 906, 799, 729, 691, 558.



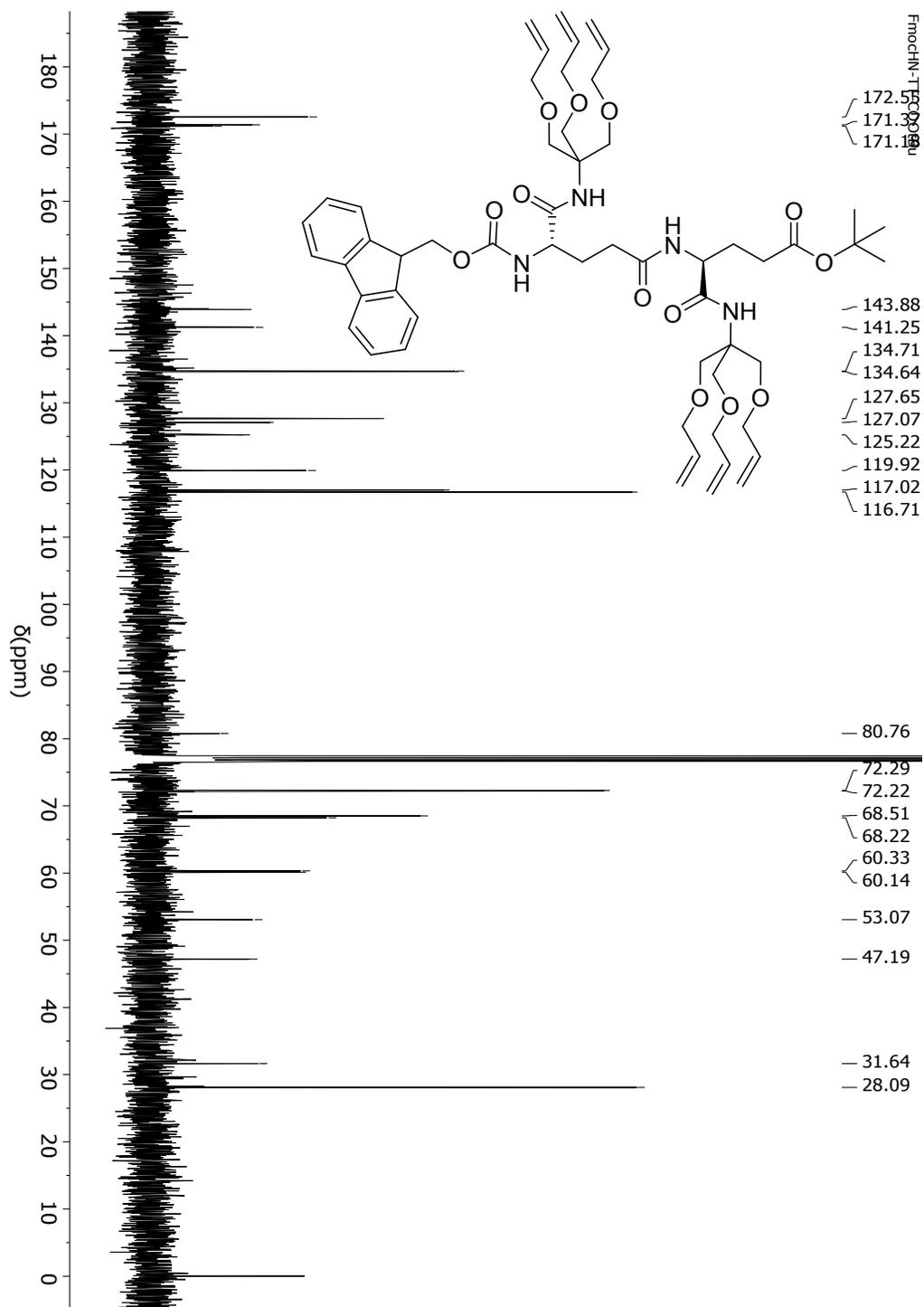


**Figure S2:**  $^{13}\text{C}$  NMR spectrum of FmocHN-AT-COOtBu (7) (CDCl<sub>3</sub>, 100 MHz)

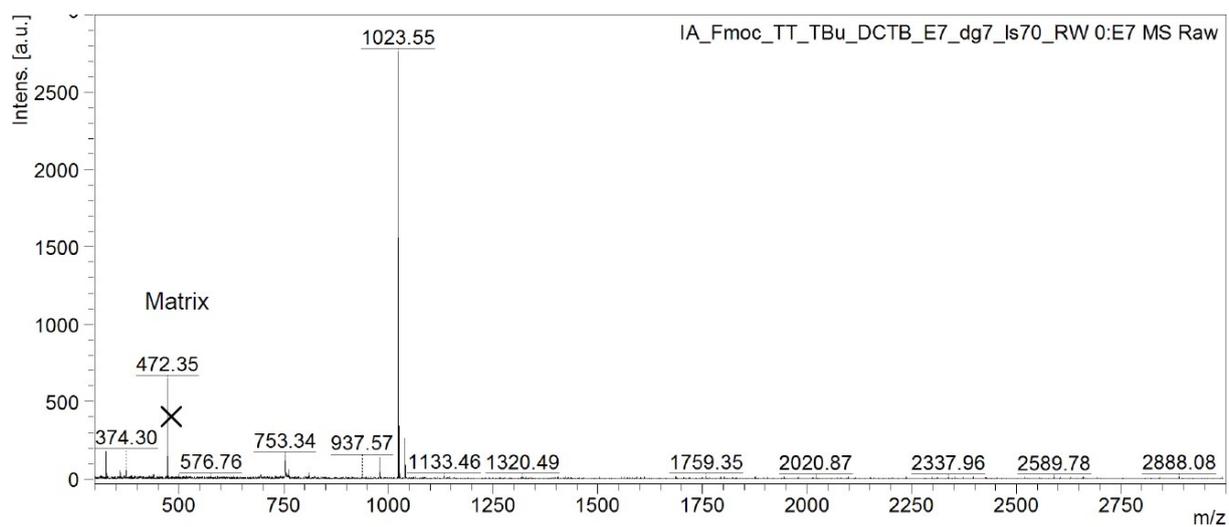


**Figure S3:** MALDI-TOF spectrum of *FmocHN-AT-COObu* (7)



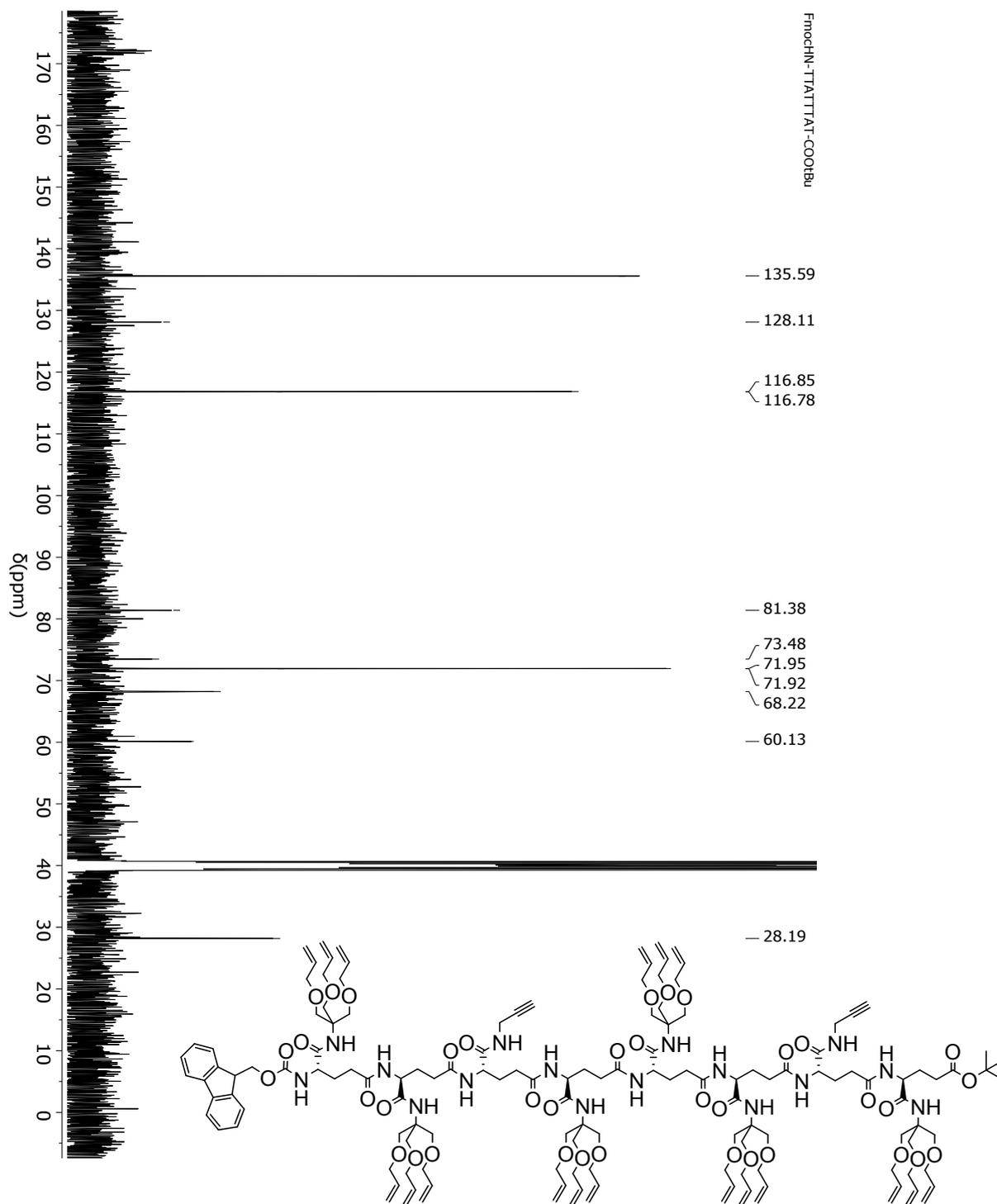


**Figure S5:**  $^{13}\text{C}$  NMR spectrum of FmocHN-TT-COOtBu (**8**) ( $\text{CDCl}_3$ , 100 MHz)



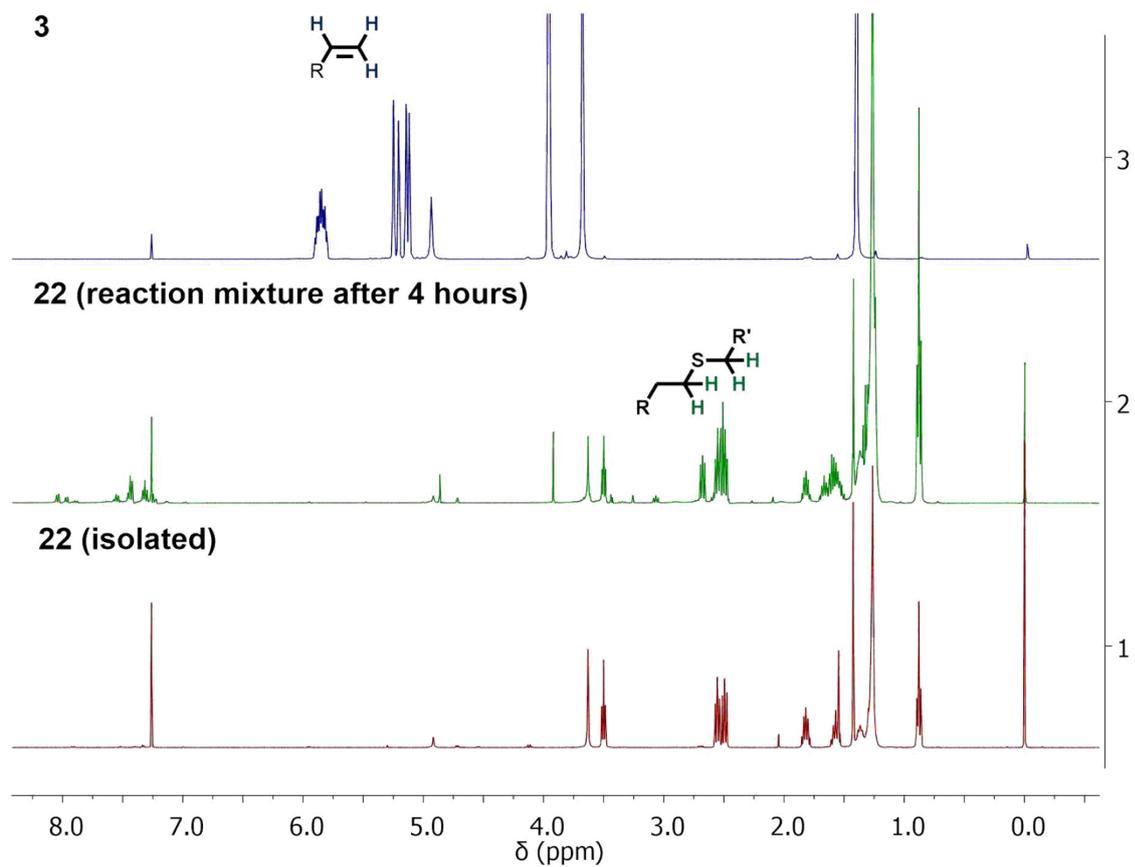
**Figure S6:** MALDI-TOF spectrum of *FmocHN-AT-COObu* (**8**)

*FmocHN-TTATTTAT-COObu (14)*



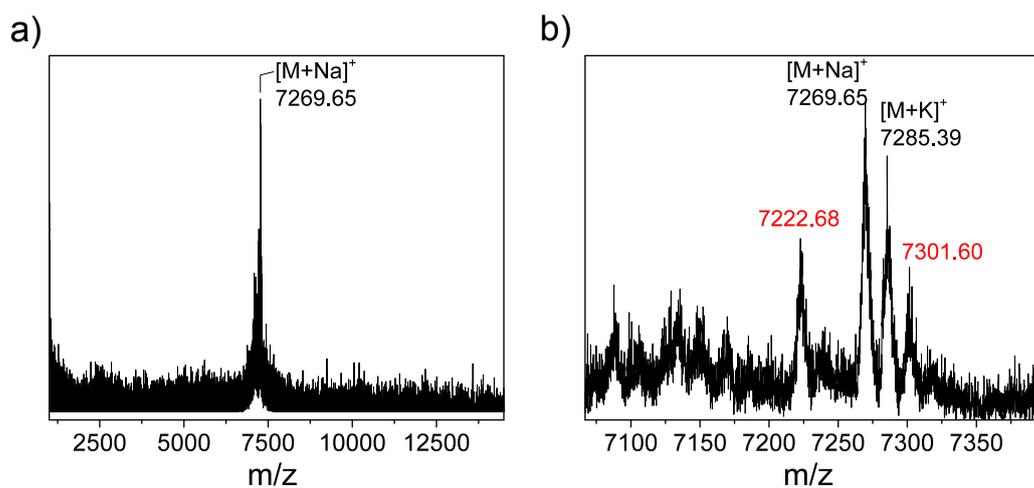
**Figure S7:** <sup>13</sup>C NMR spectrum of *FmocHN-TTATTTAT-COObu (14)* (DMSO-*d*<sub>6</sub>, 100 MHz)

Monitoring of the conversion of thiol-ene reaction of model compound (**3**).

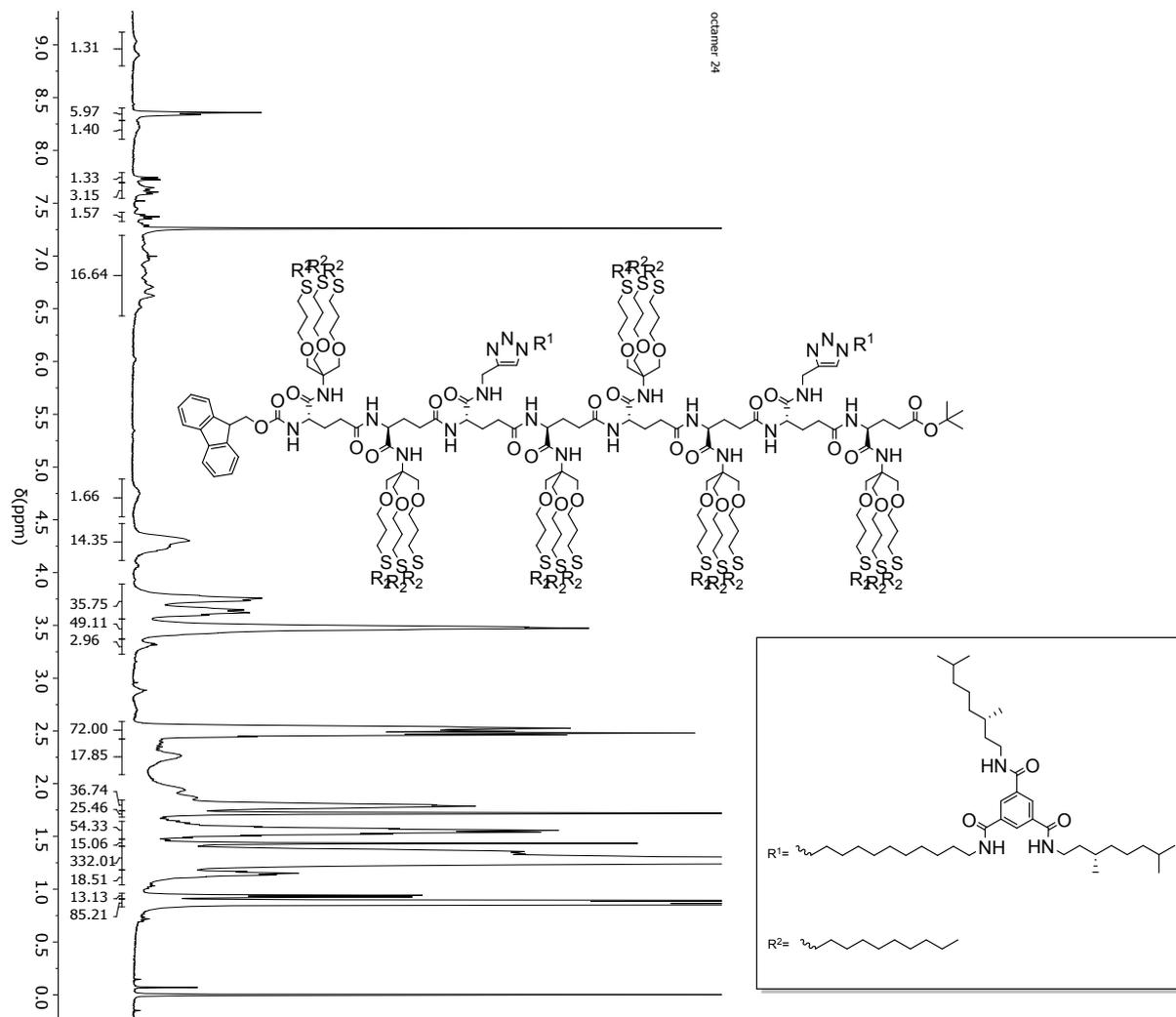


**Figure S8:** Stacked <sup>1</sup>H NMR spectra of **3**, **22** (in reaction mixture) and isolated **22** (CDCl<sub>3</sub>, 400 MHz).

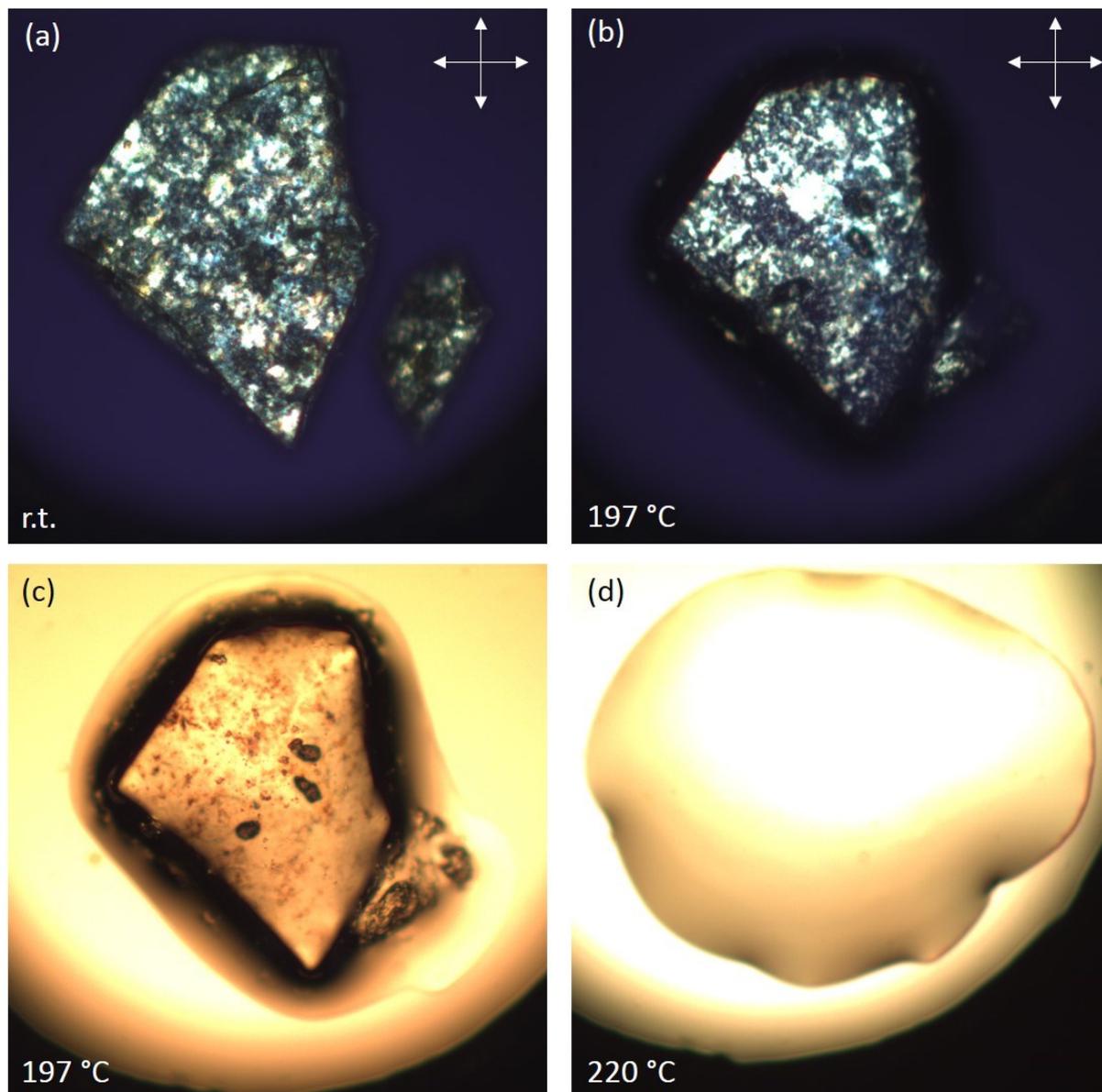
Fully functionalized octamer **24**



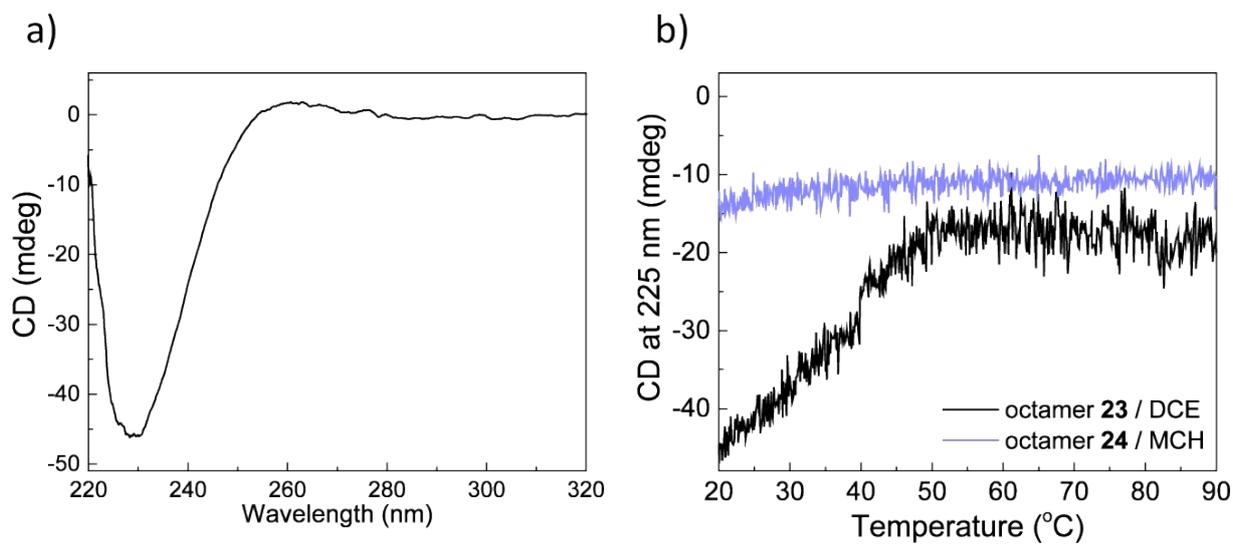
**Figure S9:** MALDI-TOF spectrum of fully functionalized octamer **24**, a) full spectrum; b) close-up showing extra peaks (in red)



**Figure S10:**  $^1\text{H}$  NMR spectrum of fully functionalized octamer 24 ( $\text{CDCl}_3$ , 400 MHz).



**Figure S11:** POM micrographs of *FmocHN-TTAT-COObu* (**11**) (a) at room temperature, crossed polarizers, (b) at 197 °C, crossed polarizers, (c) at 197 °C, and (d) at 220 °C.

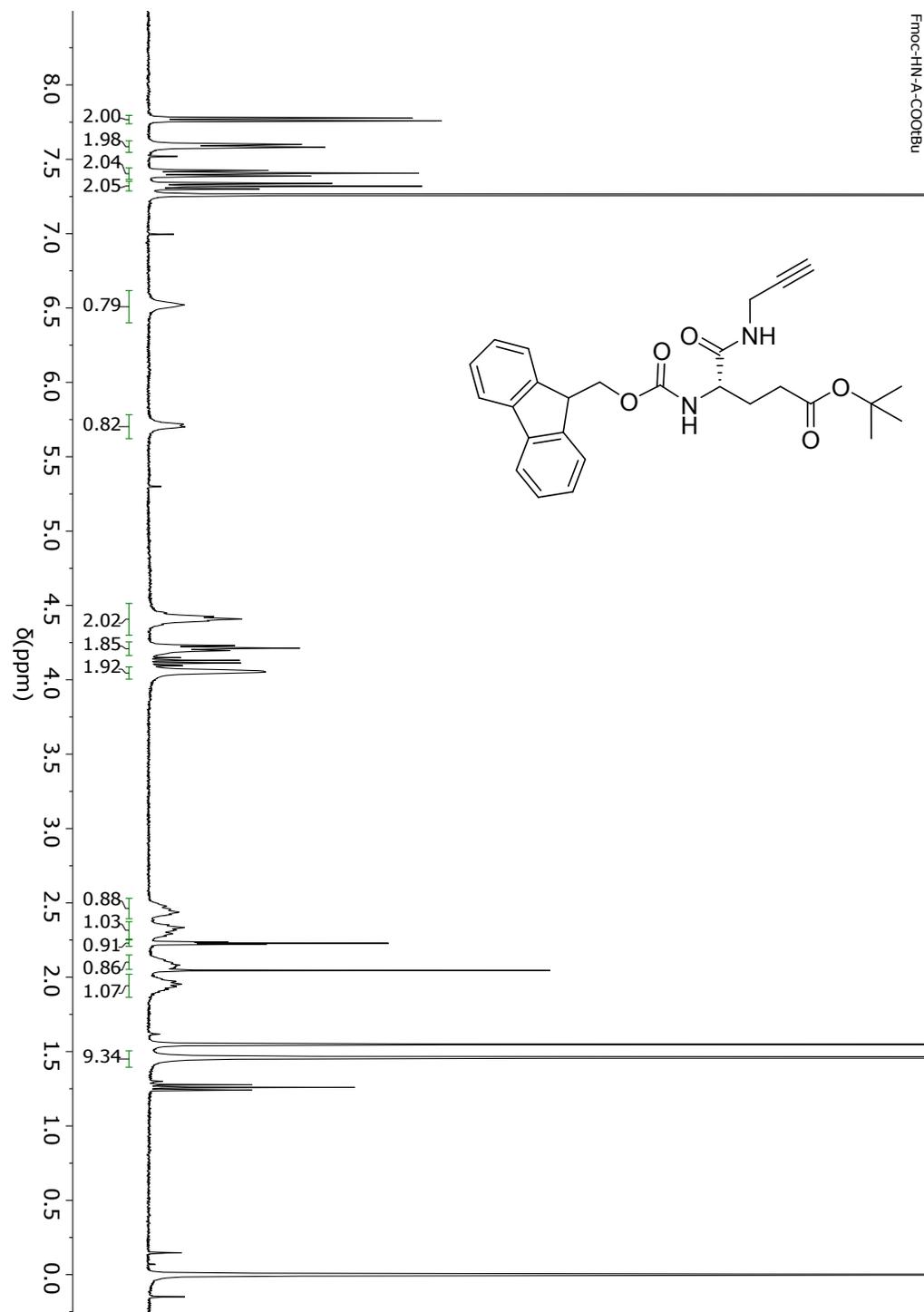


**Figure S12:** a) CD spectrum of *FmocHN-TTATTTAT-COObu* (**14**) in DCE at 20 °C; VT-CD of octamers 23 and 24 in DCE and MCH, respectively, at cooling rate of 1 °C min<sup>-1</sup>. In all samples:  $c = 25 \mu\text{M}$ ,  $l = 1 \text{ cm}$ .

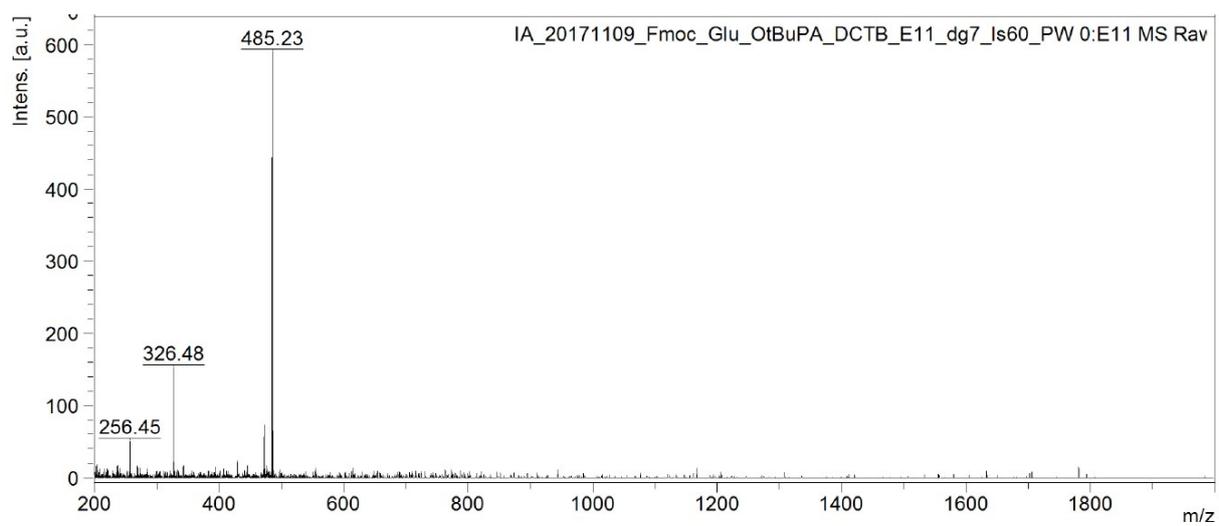
#### 4. Characterization Figures of Intermediate Structures.

##### *Fmoc-HN-A-CO<sub>2</sub>tBu* (**2**)

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) of **2**

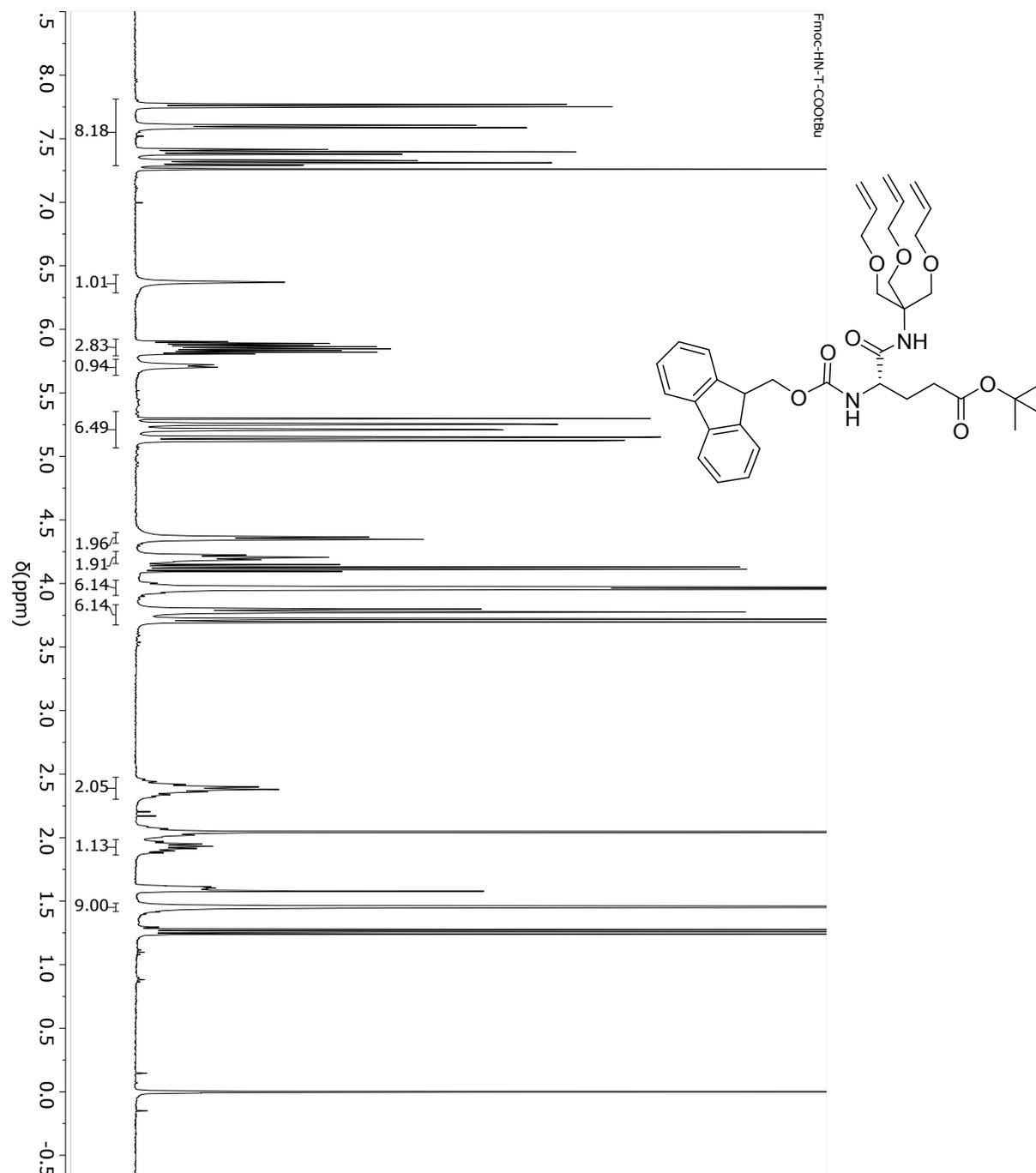


## MALDI-TOF (CHCA) of **2**

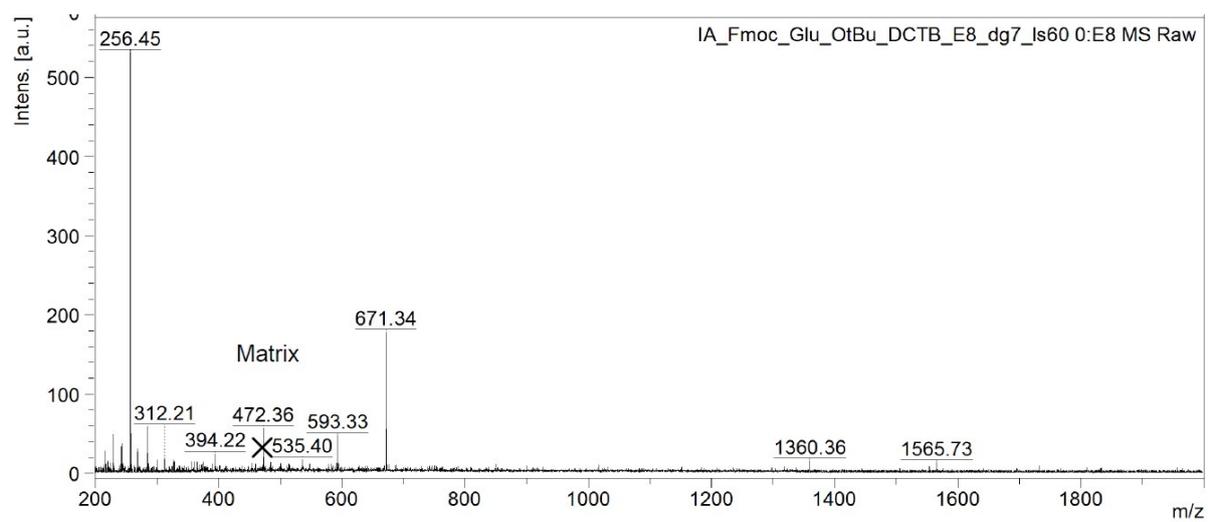


***Fmoc-HN-T-COObu (3)***

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) of **3**

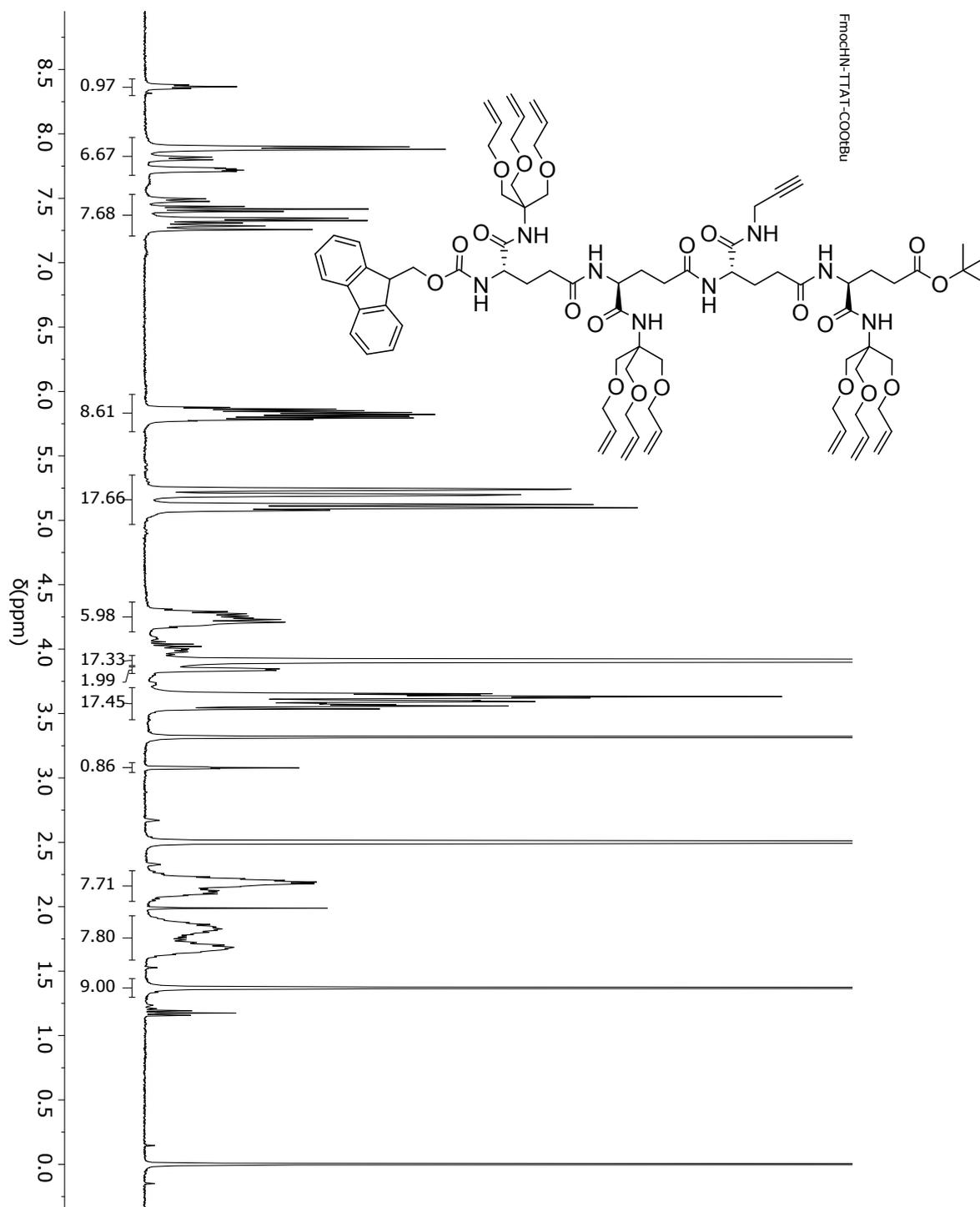


# MALDI-TOF (DCTB) of **3**

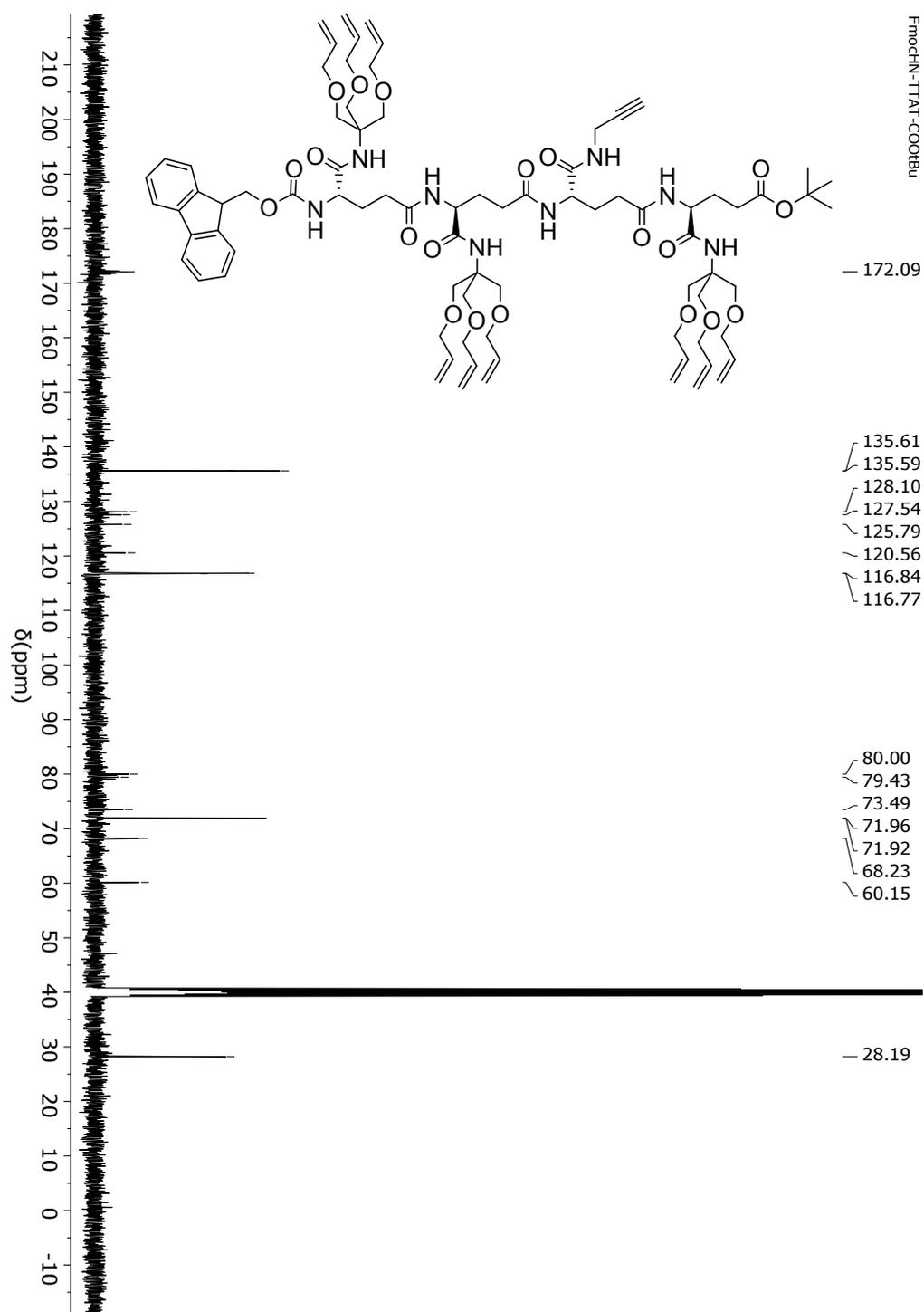


***FmocHN-TTAT-CO<sub>2</sub>tBu (11)***

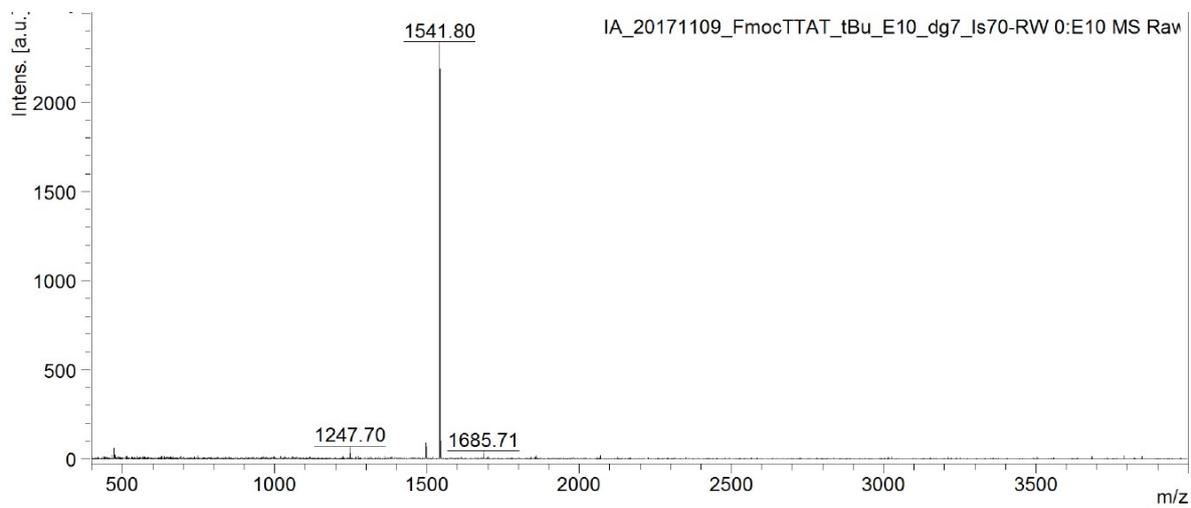
<sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz) of **11**



$^{13}\text{C}$  NMR (DMSO- $d_6$ , 100 MHz) of **11**

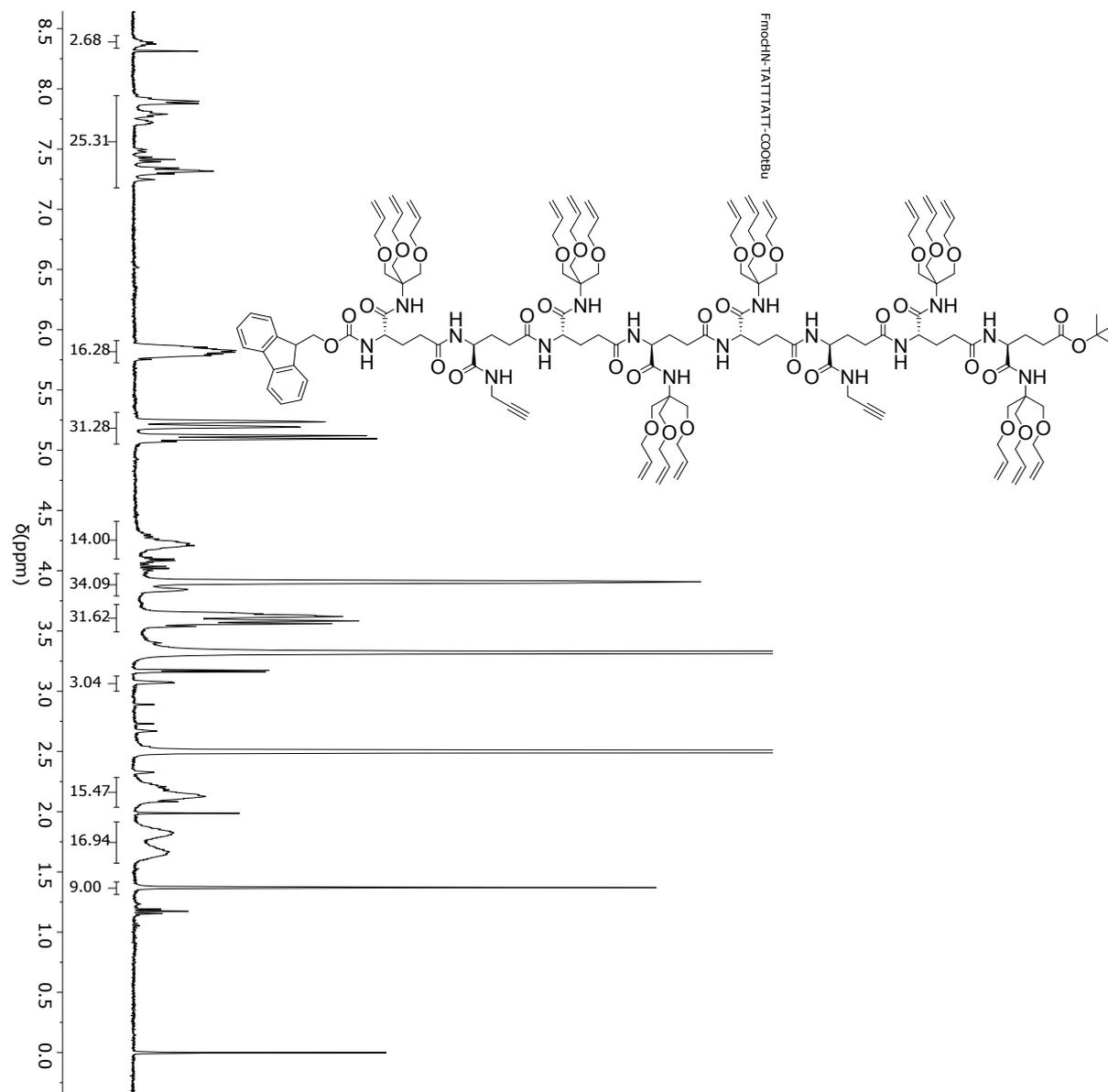


# MALDI-TOF (CHCA) of 11

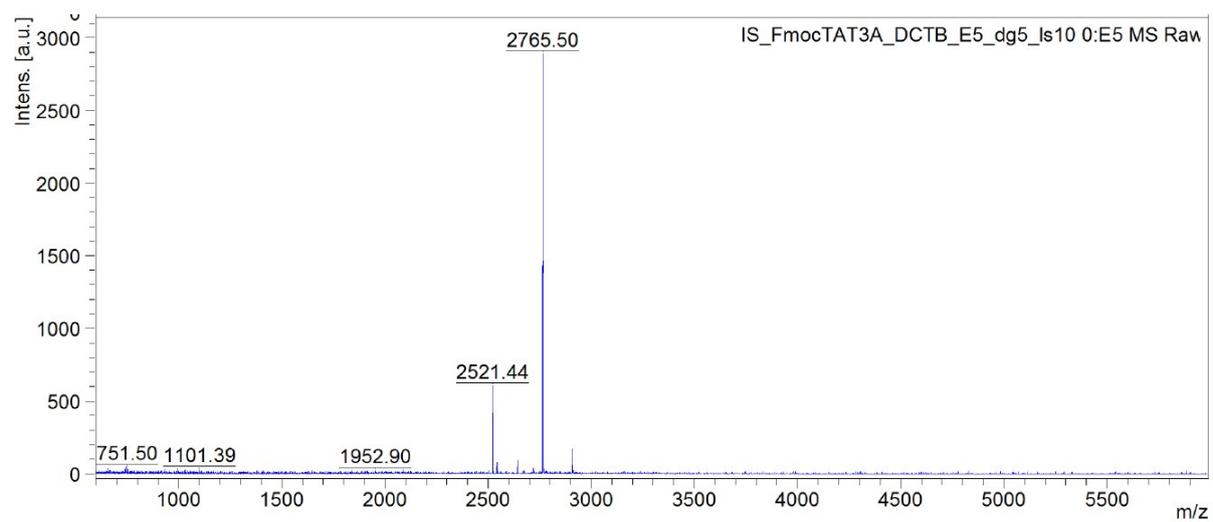


***FmocHN-TATTTATT-COObu (15)***

<sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz) of **15**

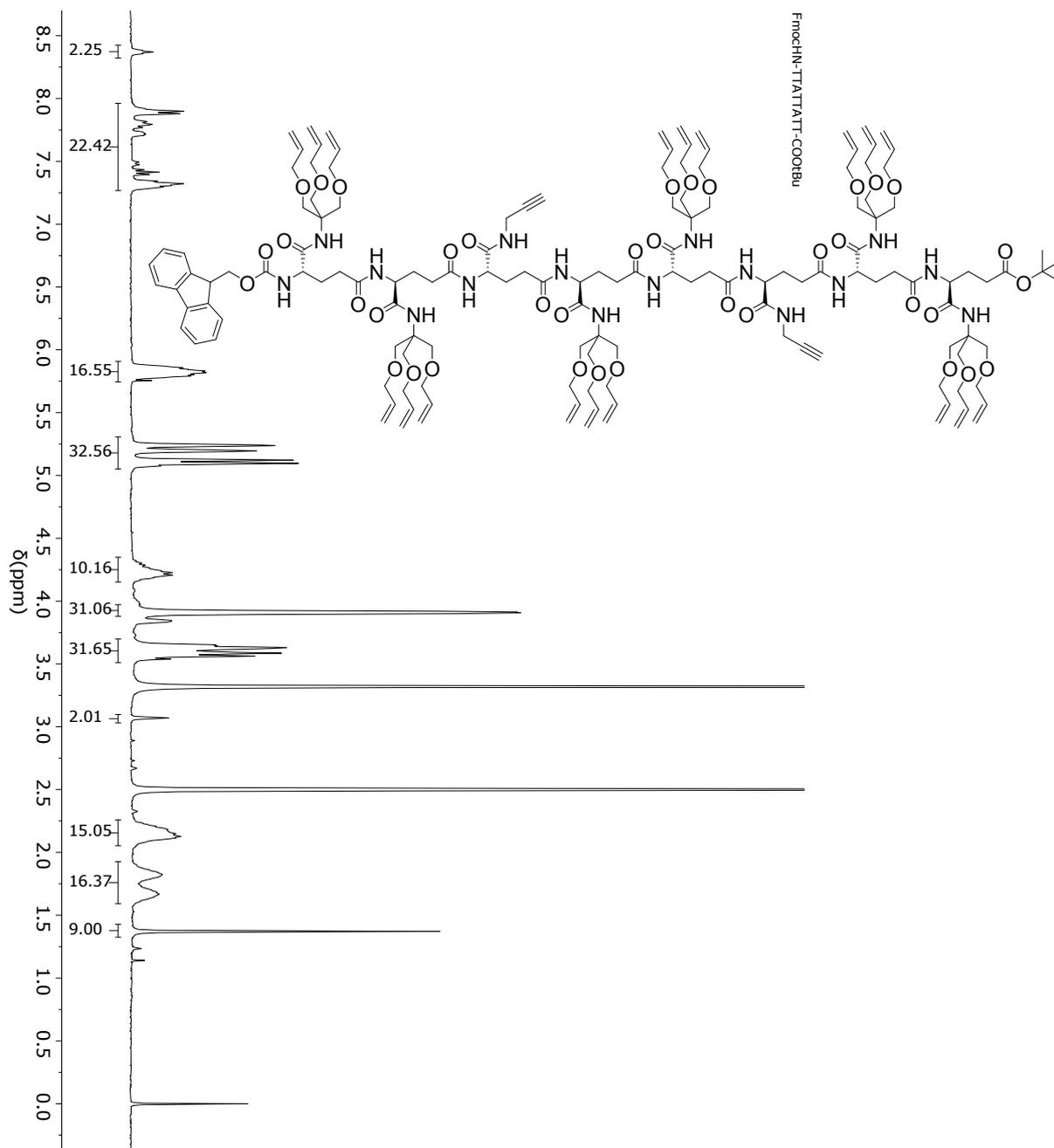


# MALDI-TOF (DCTB) of **15**

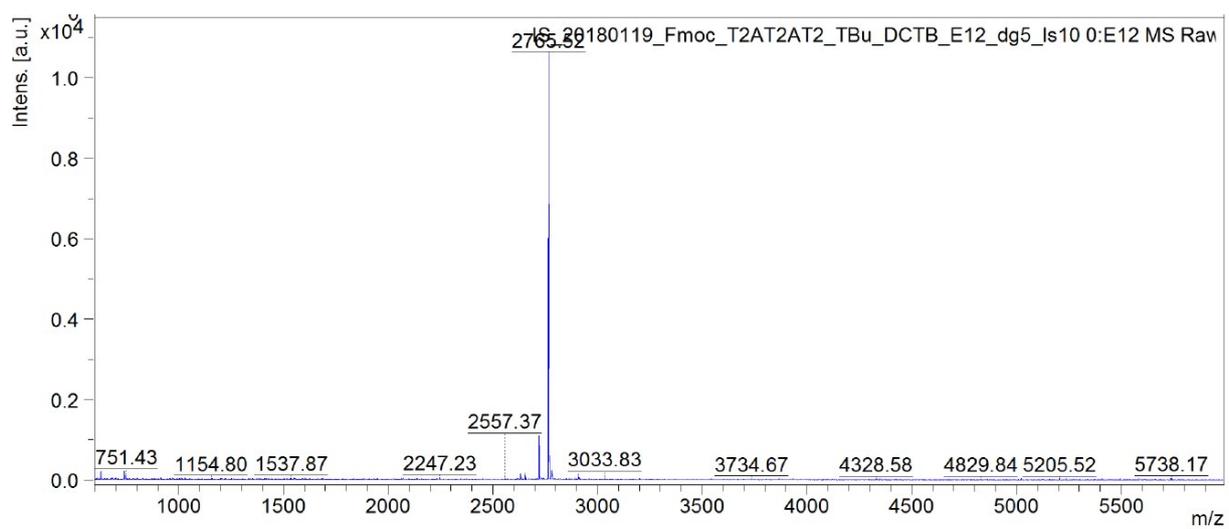


***FmocHN-TTATTATT-COObu (16)***

<sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz) of **16**

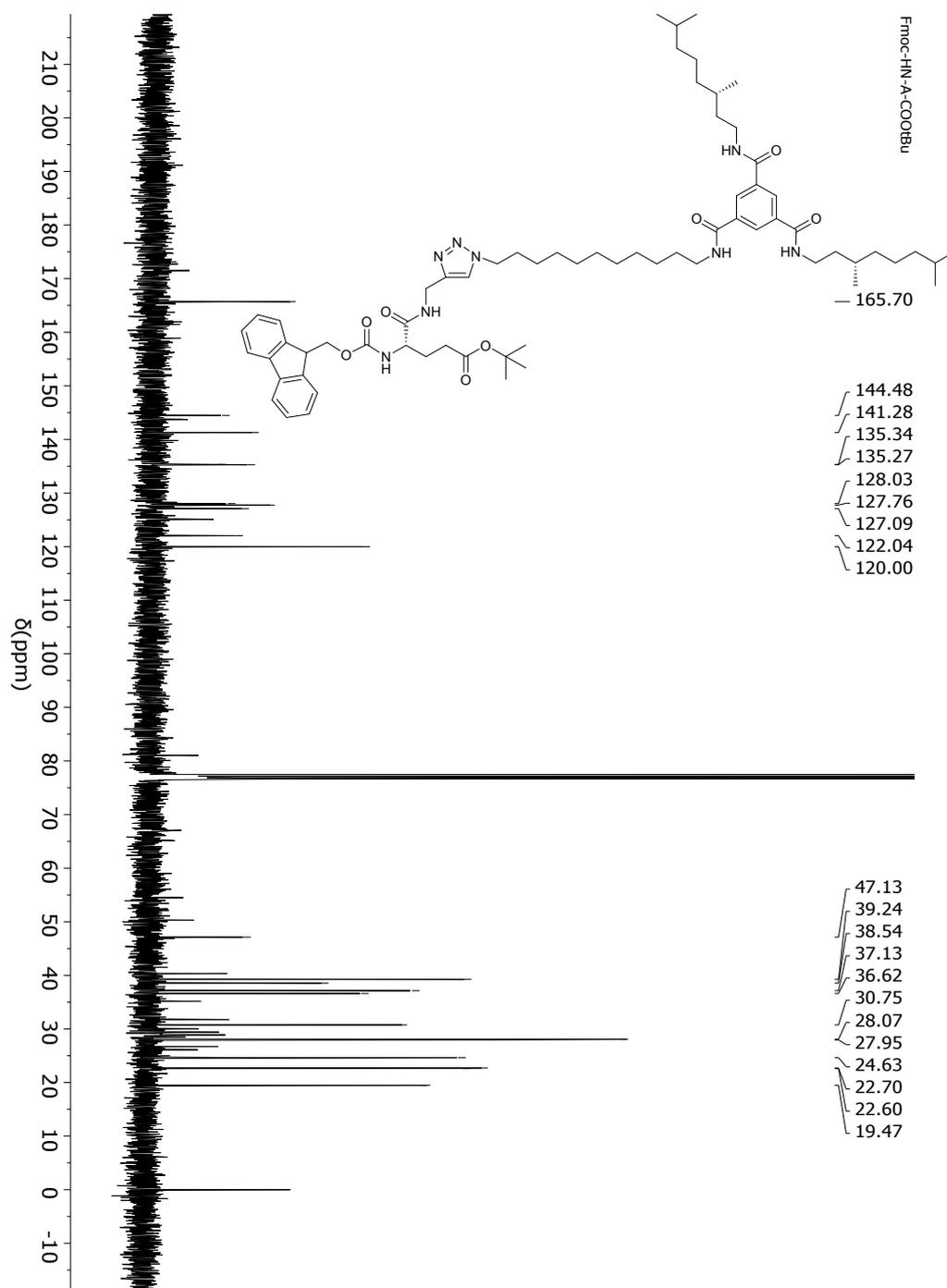


# MALDI-TOF (DCTB) of **16**

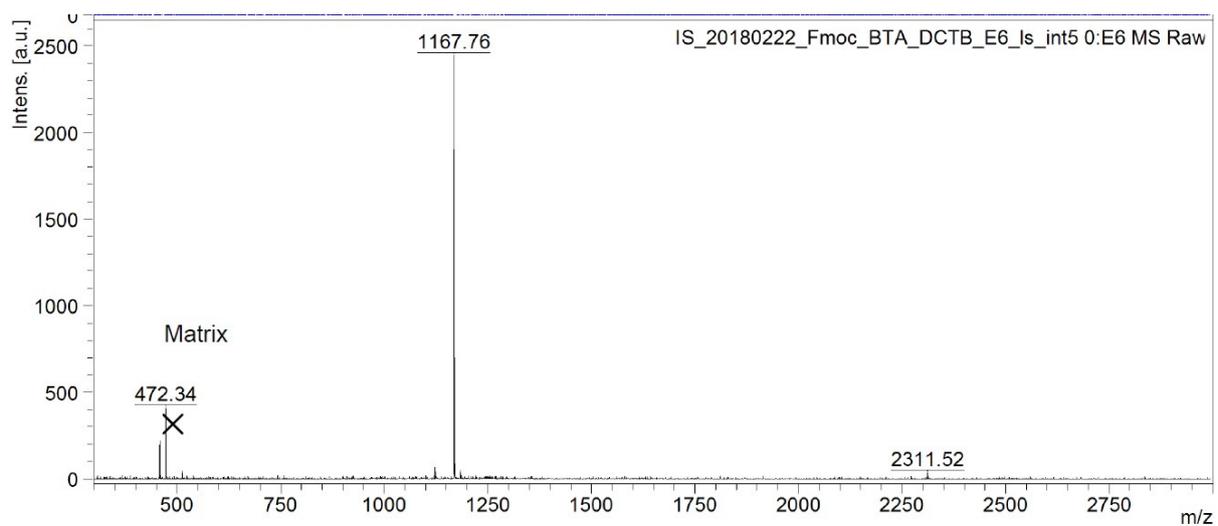




$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz) of **21**

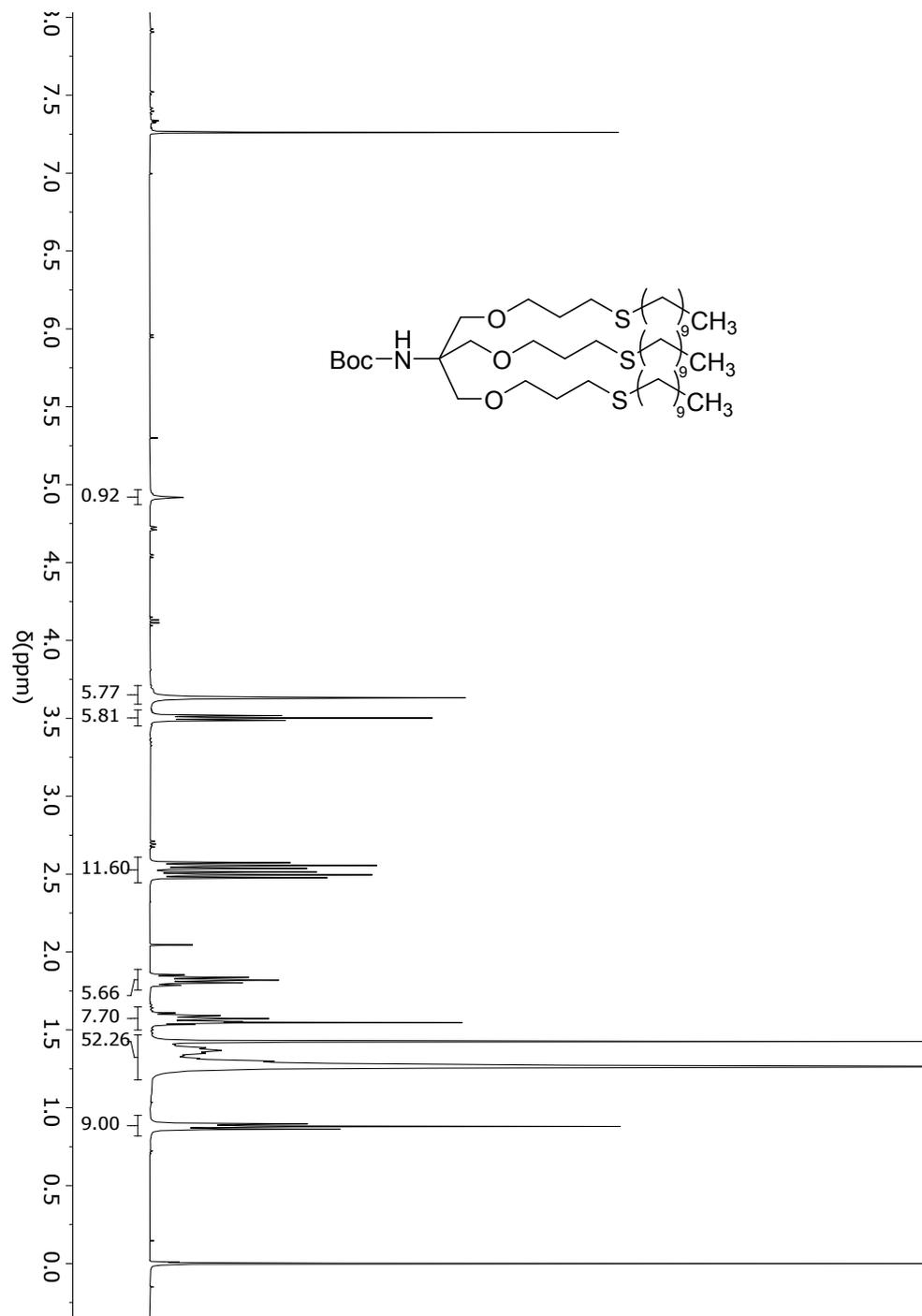


# MALDI-TOF (DCTB) of **21**



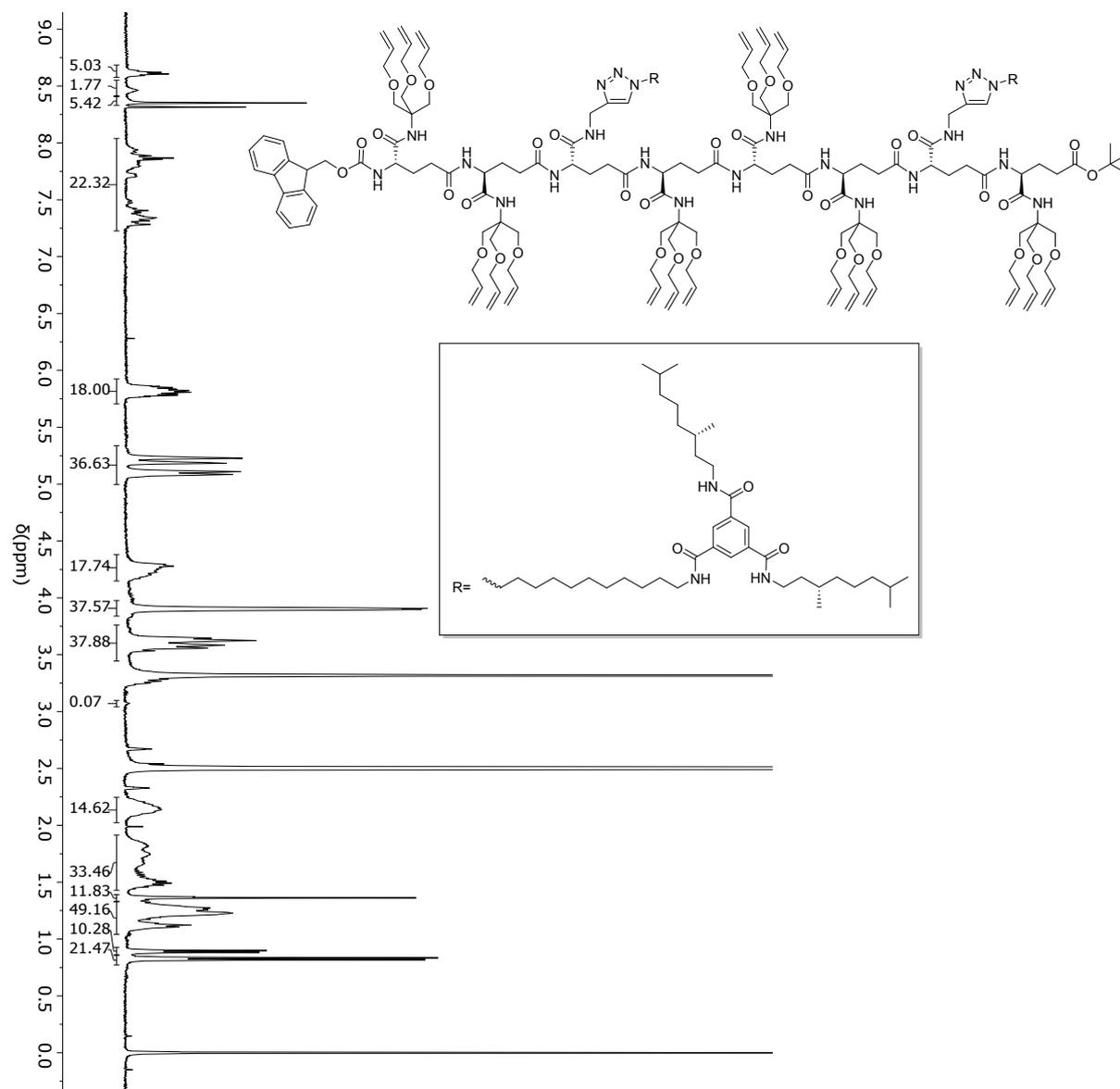
*N*-(*Tert*-butyloxycarbonyl)tris[(allyloxy)methyl]aminomethane-tridecylsulfane **22**

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz) of **22**

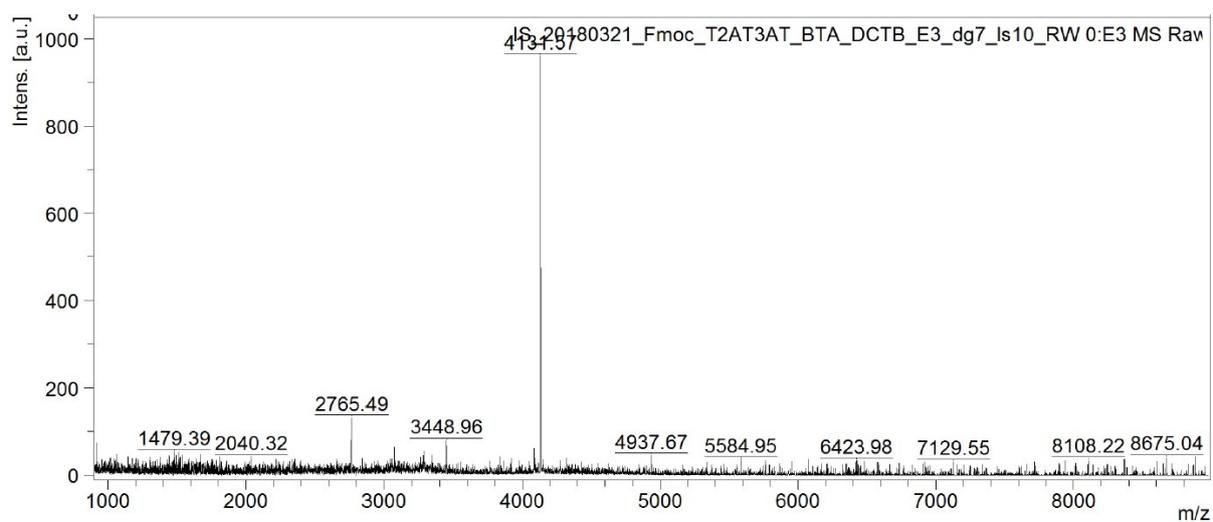


**BTA functionalized octamer 23**

<sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz) of **23**



## MALDI-TOF (DCTB) of **23**



## 5. References

- [1] M. L. Ślęczkowski, E. W. Meijer, A. R. A. Palmans, *Macromol. Rapid Commun.* 2017, **38**, 1700566.