SUPPORTING INFORMATION

Precision polymers containing main-chain-amino acids: ADMET polymerization and crystallization

Jan Freudenberg[a], Silvio Poppe[b] and Wolfgang H. Binder*[a]

[a]Martin Luther University Halle-Wittenberg, Faculty of Natural Sciences II, Chair of Macromolecular Chemistry, D-06120 Halle
[b]Martin Luther University Halle-Wittenberg, Faculty of Natural Sciences II, Chair of Organic Chemistry, D-06120 Halle

content

S1. – S18. ^{1}H- and ^{13}C-NMR Spectra of monomers 2

S19. – S28. ESI-ToF-MS Spectra of monomers 11

S29. – S30. Synthesis and characterization of 10-Undeceneamine (**A2**) 15

S31. – S36. ^{1}H-NMR Spectra of polymers 17

S37. – S41. MALDI-ToF-MS Spectra of polymers 20

S42. – S51. IR Spectra of polymers 22

S52. Numbering of **3b** – **4b** 27

S53. Numbering of **3c** – **4c** 28

S1. – S18. ^{1}H- and ^{13}C-NMR Spectra of monomers

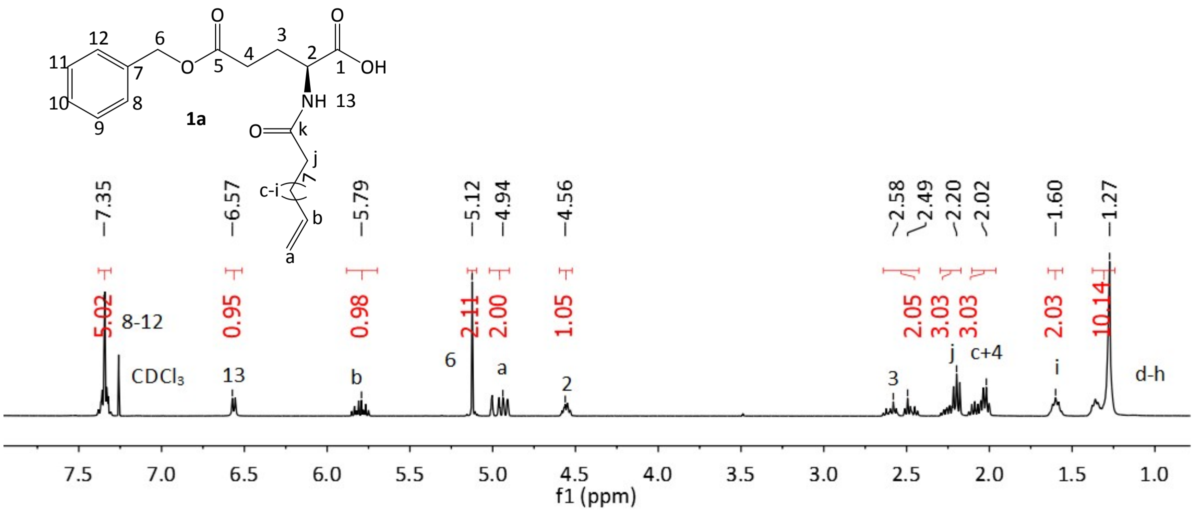

Figure S1. ^{1}H-NMR spectra of **1a**.

N-Glu (**1a**): ^{1}H-NMR (CDCl$_3$, 27 °C, 400 MHz): δ [ppm] 1.27 (m, 10H, H_d – H_h), 1.60 (m, 2H, H_i), 2.02 – 2.20 (m, 6H, $H_4 + H_c + H_j$), 2.49 (m, 1H, H_3), 2.58 (m, 1H, H_3), 4.56 (m, 1H, H_2), 4.94 (m, 2H, H_a), 5.12 (s, 2H, H_6), 5.79 (m, 1H, H_b), 6.57 (d, $^{3}J_{H,H}$ = 7.2 Hz, 1H, H_{13}), 7.31 – 7.45 (m, 5H, H_8 – H_{12}).

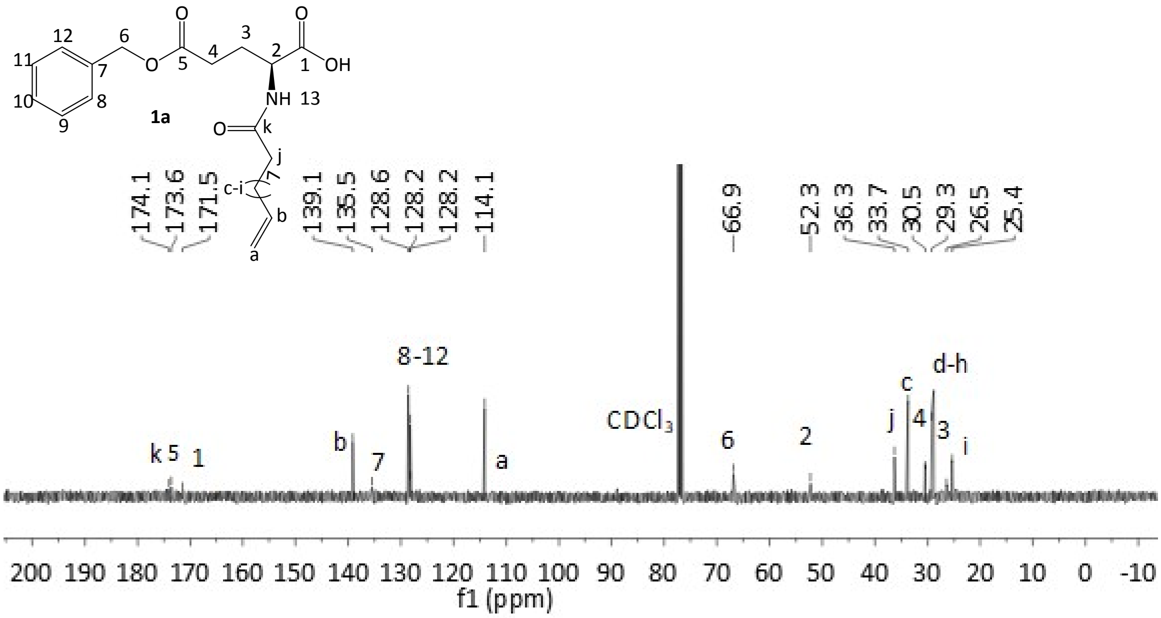

Figure S2. ^{13}C-NMR spectra of **1a**.

N-Glu (**1a**): ^{13}C-NMR (CDCl$_3$, 27 °C, 100 MHz): δ [ppm] 25.4 (C_i), 26.5 (C_3), 28.9 - 29.5 (C_d – C_h), 30.5 (C_4), 33.7 (C_c), 36.3 (C_j), 52.3 (C_2), 66.9 (C_6), 114.1 (C_a), 128.2 - 128.7 (C_8 - C_{12}), 135.5 (C_7), 139.1 (C_b), 171.5 (C_1), 173.6 (C_5), 174.1 (C_k).

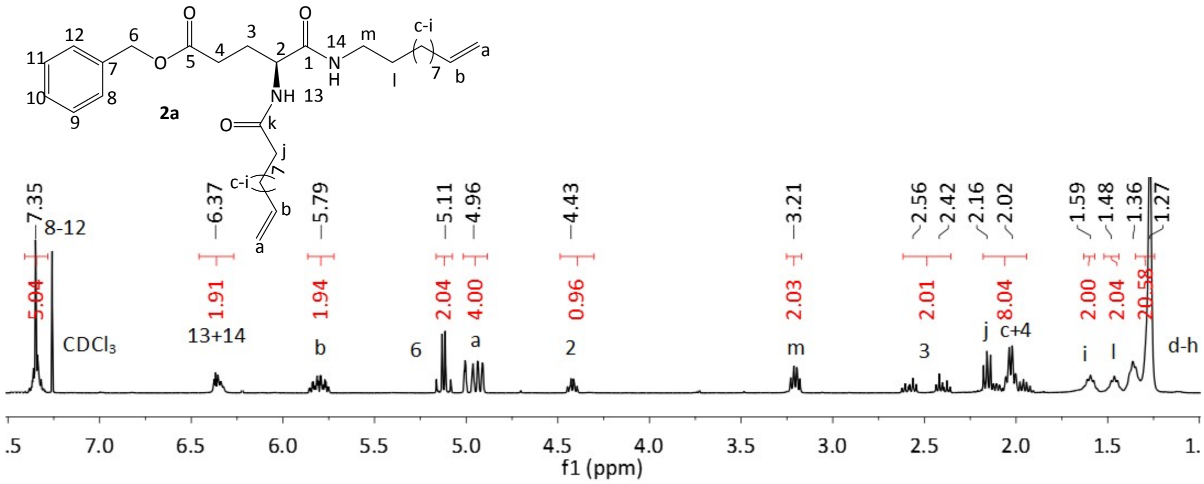

Figure S3. ^{1}H-NMR spectra of **2a**.

N- + *C*-Glu (**2a**): ^{1}H-NMR ($CDCl_3$, 27 °C, 400 MHz): δ [ppm] 1.27 – 1.36 (m, 20H, $H_d – H_h$), 1.48 – 1.59 (m, 4H, $H_l + H_i$), 2.02 – 2.16 (m, 8H, $H_4 + H_c + H_j$), 2.42 (m, 1H, H_3), 2.56 (m, 1H, H_3), 3.21 (m, 2H, H_m) 4.43 (m, 1H, H_2), 4.96 (m, 4H, H_a), 5.11 (s, 2H, H_6), 5.79 (m, 2H, H_b), 6.37 (m, 2H, $H_{13} + H_{14}$), 7.31 – 7.45 (m, 5H, $H_8 – H_{12}$).

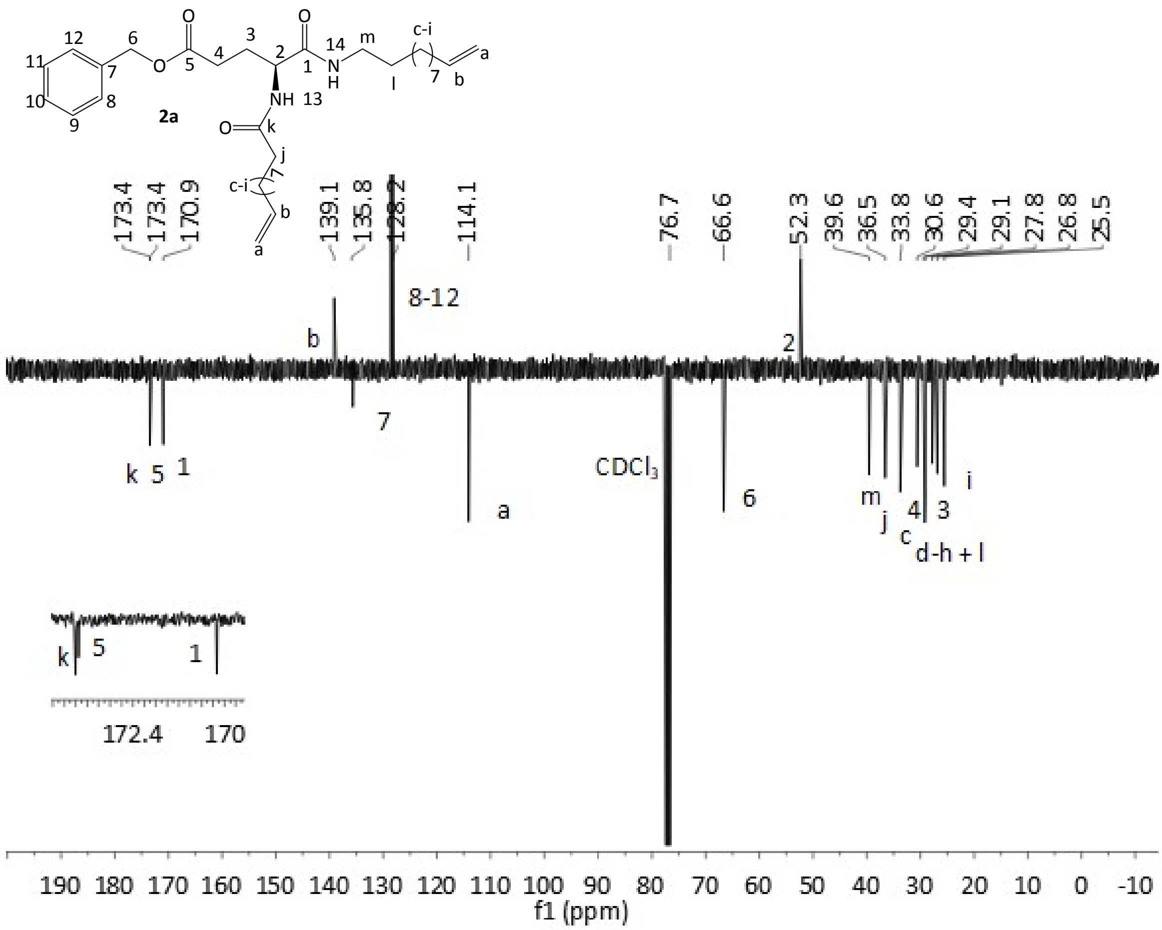

Figure S4. ^{13}C-APT spectra of **2a**.

N- + *C*-Glu (**2a**): ^{13}C-NMR ($CDCl_3$, 27 °C, 100 MHz): δ [ppm] 25.5 (C_i), 26.8 (C_i), 27.8 (C_3), 28.9 - 29.5 ($C_d – C_h + C_l$), 30.6 (C_4), 33.8 (C_c), 36.5 (C_j), 39.6 (C_m), 52.3 (C_2), 66.6 (C_6), 114.1 (C_a), 128.2 - 128.7 (C_8 - C_{12}), 135.8 (C_7), 139.1 (C_b), 170.9 (C_1), 173.4 (C_5), 173.4 (C_k).

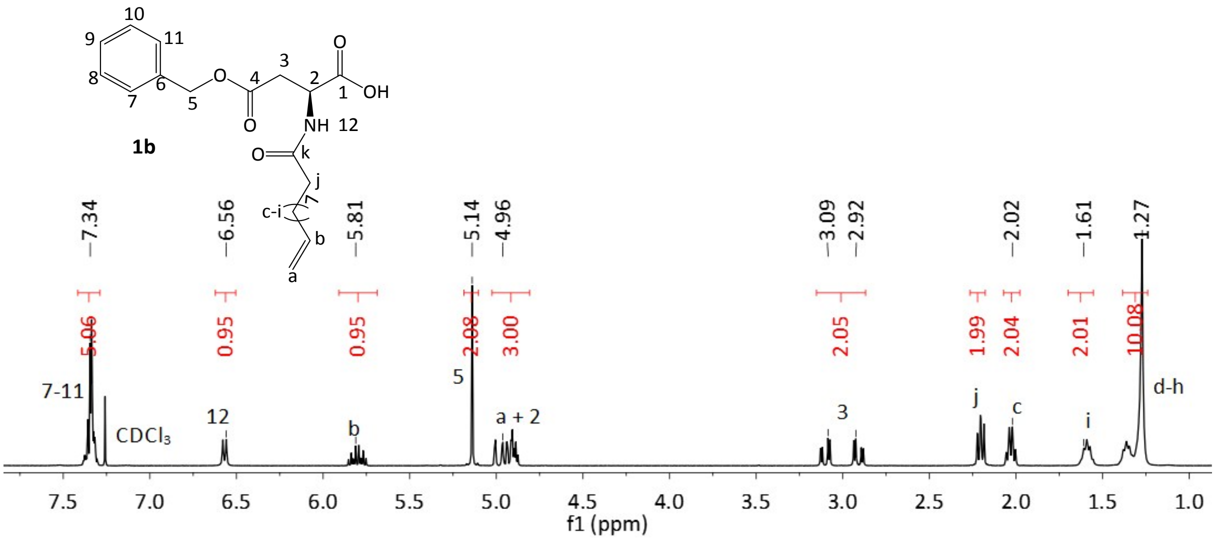

Figure S5. ^{1}H-NMR spectra of **1b**.

N-Asp (**1b**): ^{1}H-NMR (CDCl$_3$, 27 °C, 400 MHz): δ [ppm] 1.27 (m, 10H, $H_d - H_h$), 1.61 (m, 2H, H_i), 2.02 (m, 2H, H_c), 2.20 (m, 2H, H_j), 2.92 (m, 1H, H_3), 3.09 (m, 1H, H_3), 4.91 (m, 1H, H_2), 4.96 (m, 2H, H_a), 5.14 (s, 2H, H_5), 5.81 (m, 1H, H_b), 6.56 (d, $^3J_{H,H}$ = 7.2 Hz, 1H, H_{12}), 7.31 – 7.45 (m, 5H, $H_7 - H_{11}$).

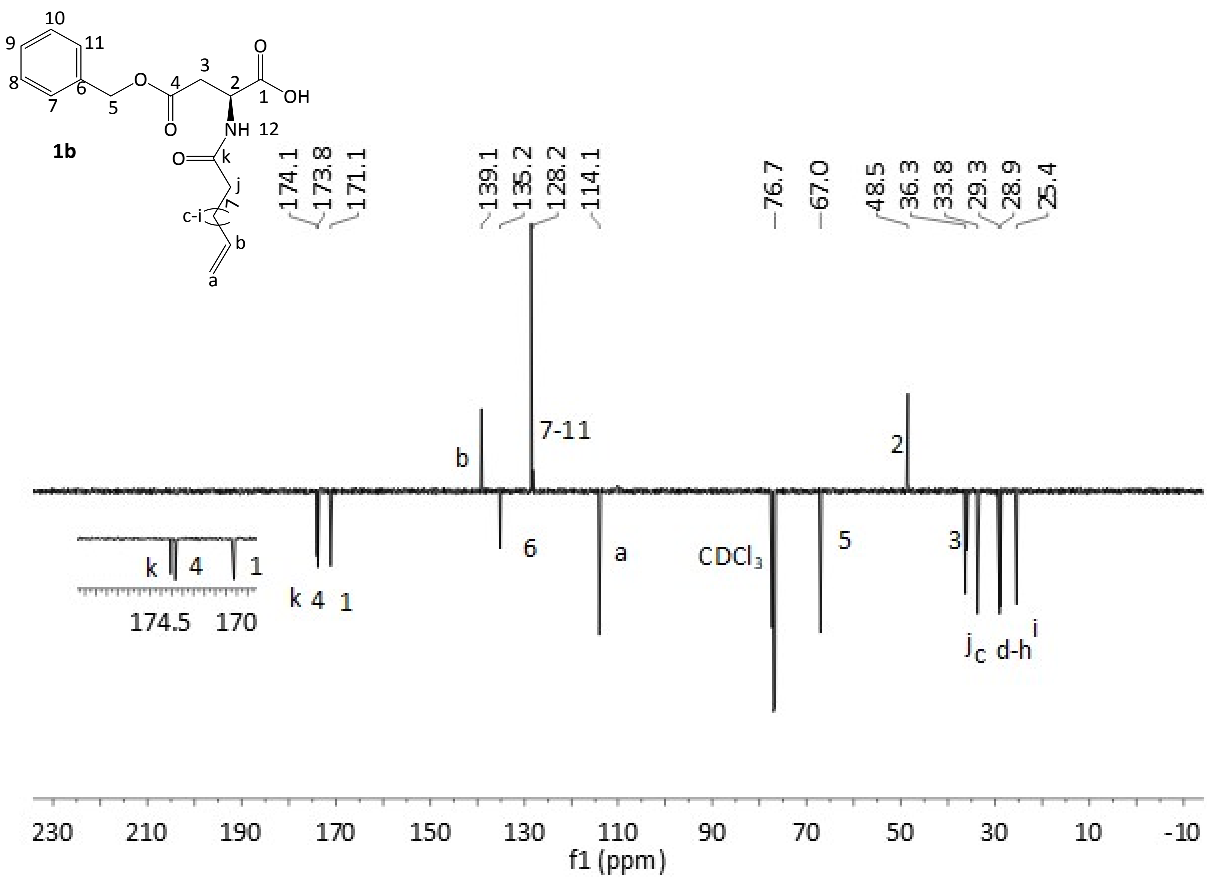

Figure S6. ^{13}C-APT spectra of **1b**.

N-Asp (**1b**): ^{13}C-NMR (CDCl$_3$, 27 °C, 100 MHz): δ [ppm] 25.4 (C_i), 28.9 - 29.3 ($C_d - C_h$), 33.8 (C_c), 36.3 (C_j), 36.5 (C_3), 48.5 (C_2), 67.0 (C_5), 114.1 (C_a), 128.2 - 128.6 (C_7 - C_{11}), 135.23 (C_6), 139.1 (C_b), 171.1 (C_1), 173.8 (C_4), 174.1 (C_k).

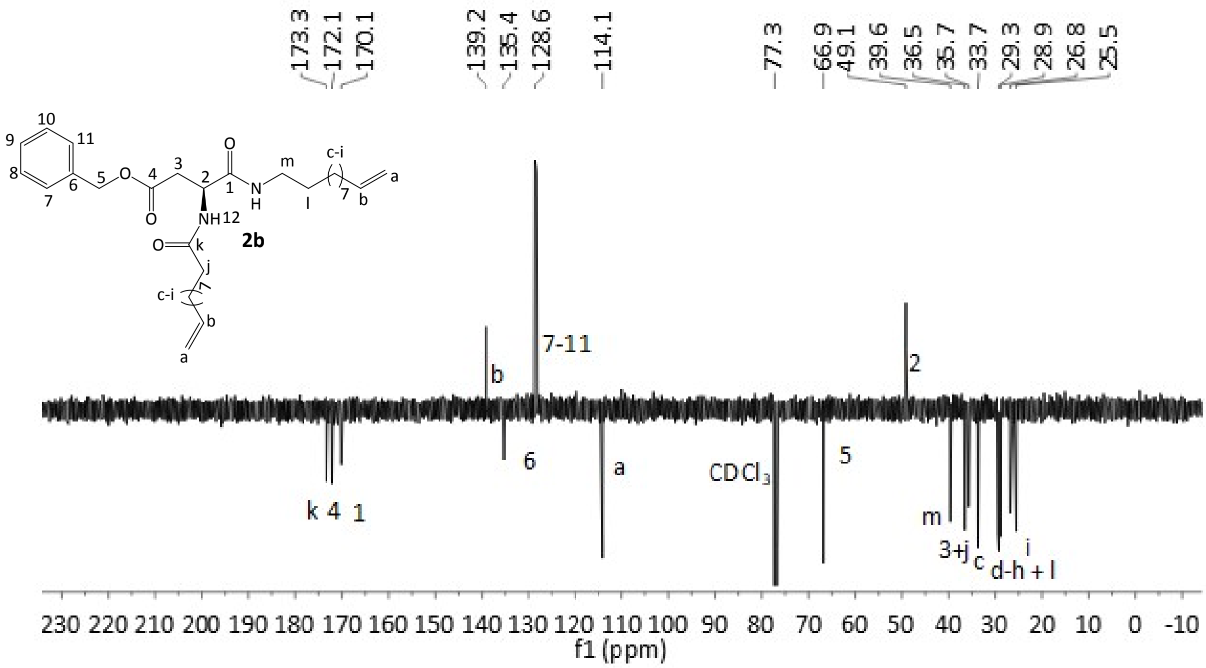

Figure S7. ^{13}C-APT spectra of **2b**.

N- + *C*-Asp (**2b**): ^{13}C-NMR ($CDCl_3$, 27 °C, 100 MHz): δ [ppm] 25.5 (C_i), 26.8 (C_i), 28.9 – 29.3 ($C_d - C_h + C_l$), 33.7 (C_c), 35.7 (C_j), 36.5 (C_3), 39.6 (C_m), 49.1 (C_2), 66.9 (C_5), 114.1 (C_a), 128.2 - 128.6 ($C_7 - C_{11}$), 135.4 (C_6), 139.2 (C_b), 170.1 (C_1), 172.1 (C_4), 173.3 (C_k).

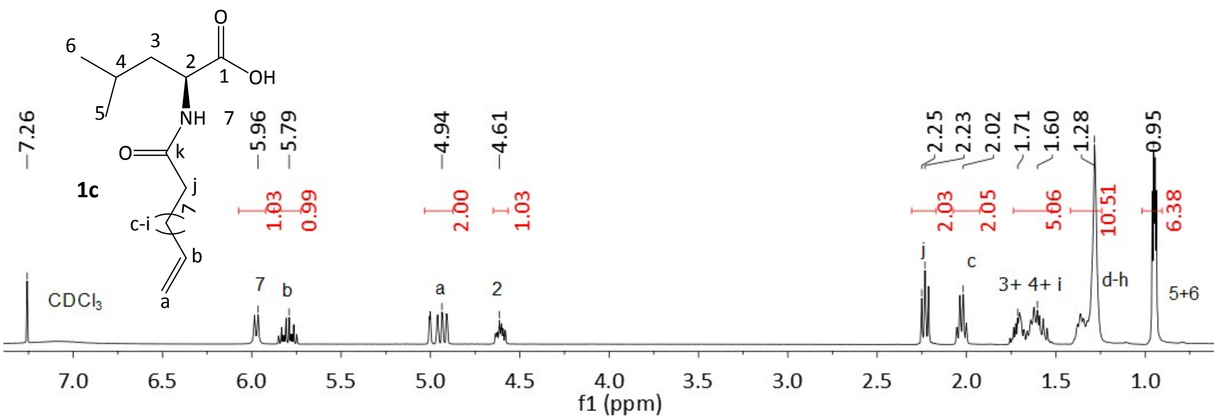

Figure S8. ^{1}H-NMR spectra of **1c**.

N-Leu (**1c**): ^{1}H-NMR ($CDCl_3$, 27 °C, 400 MHz): δ [ppm] 0.95 (m, 6H, $H_5 + H_6$), 1.28 (m, 10H, $H_d - H_h$), 1.60 – 1.71 (m, 5H, $H_i + H_3 + H_4$), 2.02 (m, 2H, H_c), 2.23 (m, 2H, H_j), 4.61 (m, 1H, H_2), 4.94 (m, 2H, H_a), 5.79 (m, 1H, H_b), 5. 96 (m, 1H, H_7).

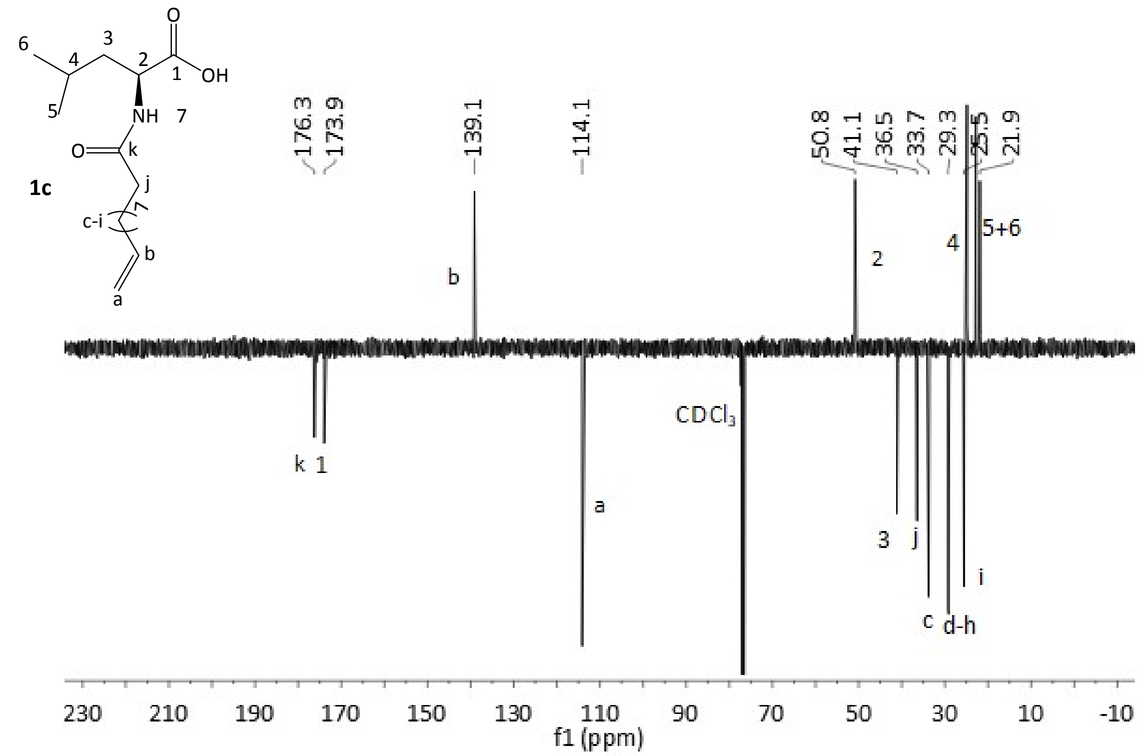

Figure S9. ^{13}C-APT spectra of **1c**.

N-Leu (**1c**): ^{13}C-NMR ($CDCl_3$, 27 °C, 100 MHz): δ [ppm] 21.9 – 22.8 ($C_5 + C_6$), 24.9 (C_4), 25.5 (C_i), 28.9 – 29.5 ($C_d - C_h$), 33.7 (C_c), 36.5 (C_j), 41.1 (C_3), 50.8 (C_2), 114.1 (C_a), 139.1 (C_b), 173.9 (C_1), 176.3 (C_k).

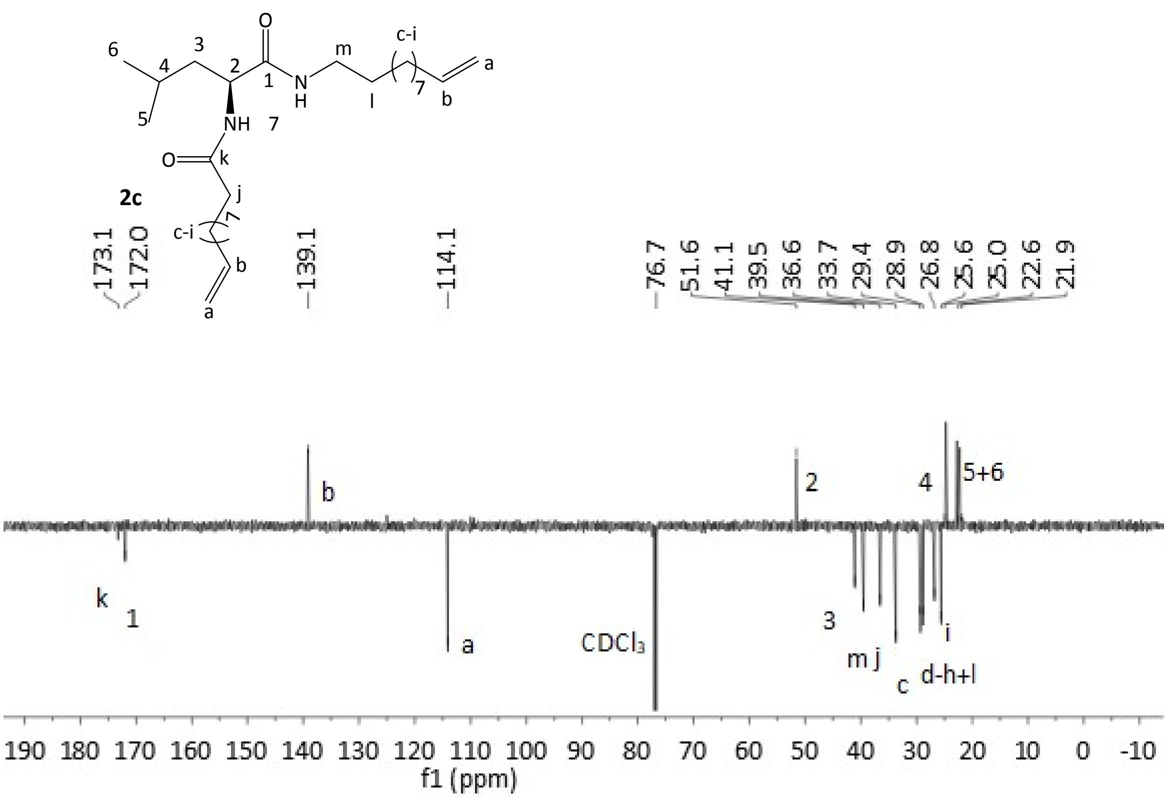

Figure S10. ^{13}C-APT spectra of **2c**.

N- + *C*-Leu (**2c**): ^{13}C-NMR ($CDCl_3$, 27 °C, 100 MHz): δ [ppm] 21.9 – 22.6 ($C_5 + C_6$), 25.0 (C_4), 25.6 (C_i), 26.8 (C_l), 28.9 – 29.5 ($C_d - C_h$), 33.7 (C_c), 36.6 (C_j), 39.5 (C_m), 41.1 (C_3), 51.6 (C_2), 114.1 (C_a), 139.1 (C_b), 172.0 (C_1), 173.1 (C_k).

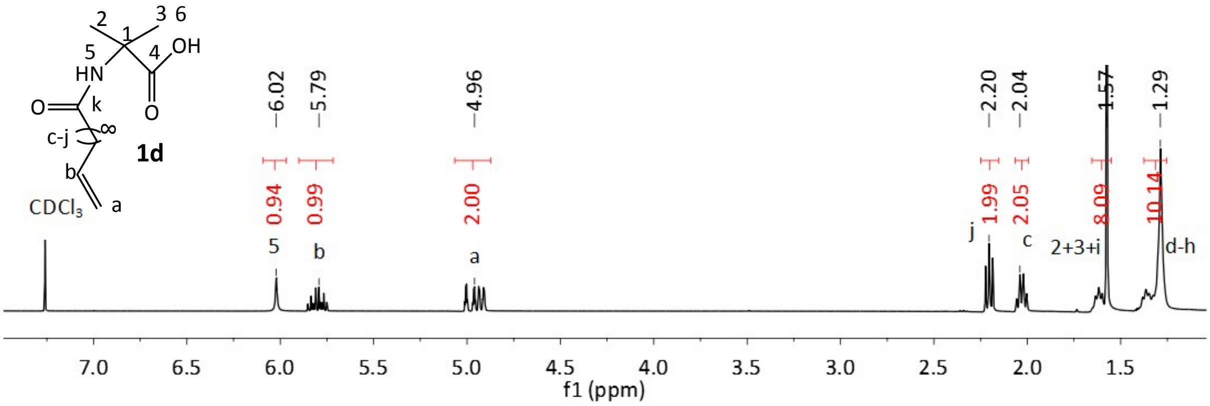

Figure S11. ^{1}H-NMR spectra of **1d**.

N-Aib (**1d**): ^{1}H-NMR ($CDCl_3$, 27 °C, 400 MHz): δ [ppm] 1.27 – 1.36 (m, 10H, H_d – H_h), 1.57-1.62 (m, 8H, $H_2 + H_3 + H_i$), 2.04 (m, 2H, H_c), 2.20 (m, 2H, H_j), 4.96 (m, 2H, H_a), 5.79 (m, 1H, H_b), 6.02 (m, 1H, H_5).

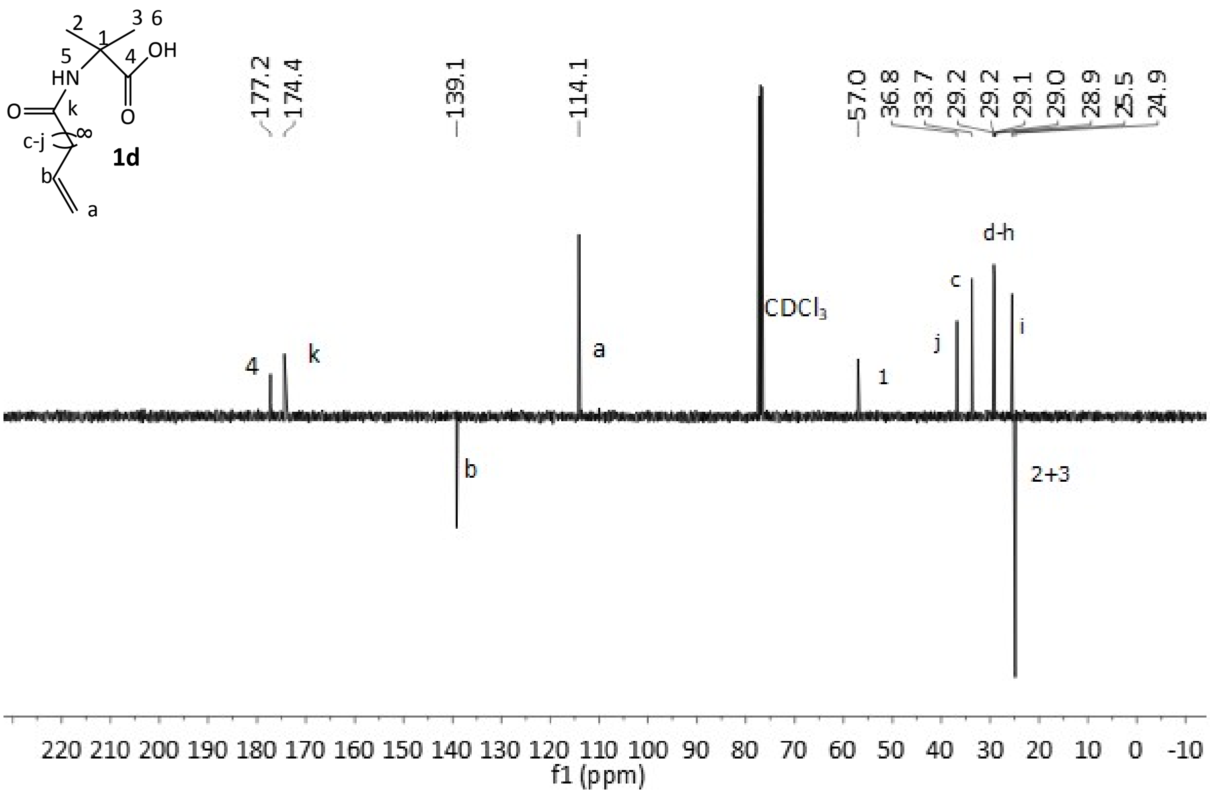

Figure S12. ^{13}C-APT spectra of **1d**.

N-Aib (**1d**): ^{13}C-NMR ($CDCl_3$, 27 °C, 100 MHz): δ [ppm] 24.9 ($C_2 + C_3$), 25.5 (C_i), 28.9 – 29.5 ($C_d – C_h$), 33.7 (C_c), 36.8 (C_j), 57.0 (C_1), 114.1 (C_a), 139.1 (C_b), 174.4 (C_k), 177.2 (C_4).

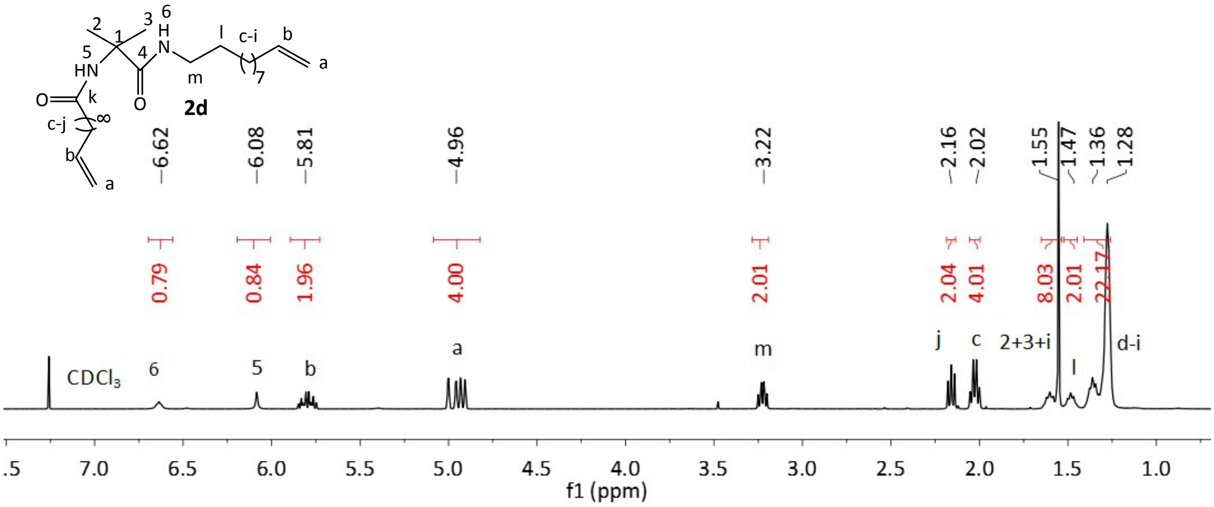

Figure S13. ^{1}H-NMR spectra of **2d**.

N- + *C*-Aib (**2d**): ^{1}H-NMR ($CDCl_3$, 27 °C, 400 MHz): δ [ppm] 1.27-1.36 (m, 20H, $H_d - H_h$), 1.47 (m, 2H, H_l), 1.55-1.62 (m, 8H, $H_2 + H_3 + H_i$), 2.02 (m, 4H, H_c), 2.16 (m, 2H, H_j), 3.22 (m, 2H, H_m), 4.96 (m, 4H, H_a), 5.81 (m, 2H, H_b), 6.08 (m, 1H, H_5), 6.62 (m, 1H, H_6).

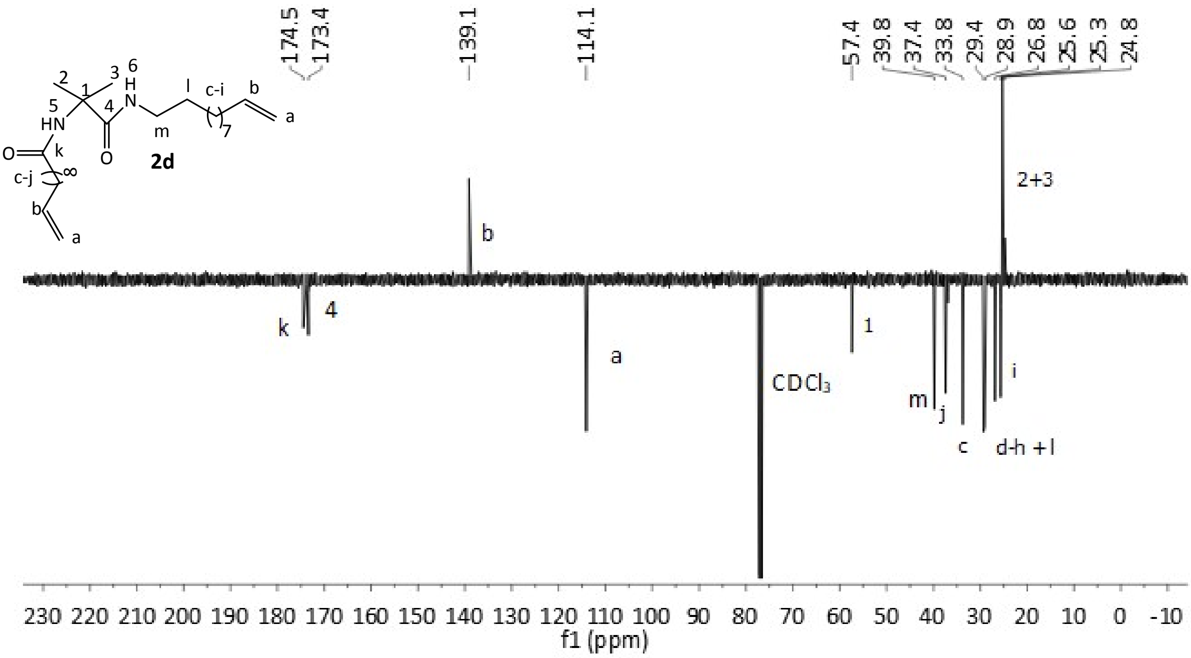

Figure S14. ^{13}C-APT spectra of **2d**.

N- + *C*-Aib (**2d**): ^{13}C-NMR ($CDCl_3$, 27 °C, 100 MHz): δ [ppm] 24.8 ($C_2 + C_3$), 25.5 (C_i), 26.8 (C_i), 28.9 – 29.5 ($C_d - C_h$), 33.8 (C_c), 37.4 (C_j), 39.8 (C_j), 57.4 (C_1), 114.1 (C_a), 139.1 (C_b), 173.4 (C_k), 174.5 (C_4).

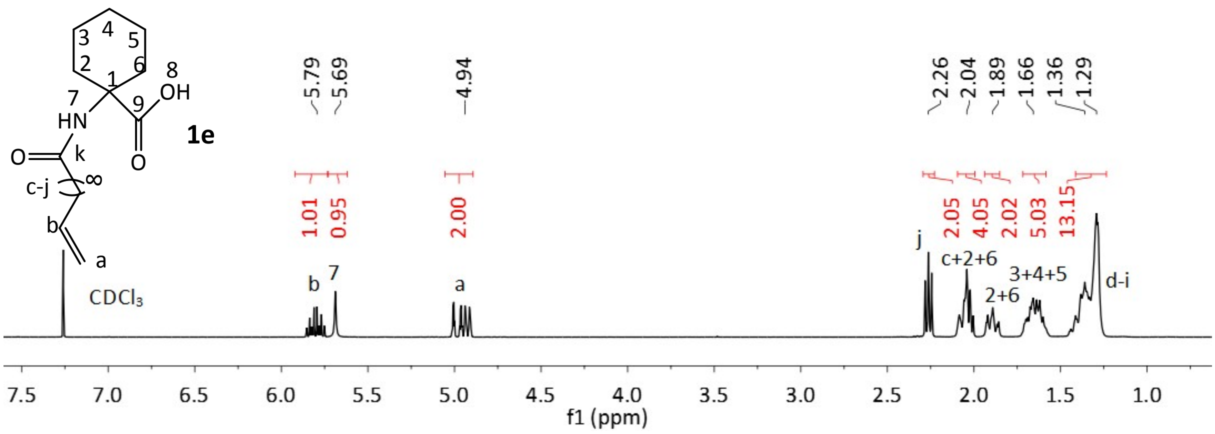

Figure S15. ^{1}H-NMR spectra of **1e**.

N-ACHC (**1e**): ^{1}H-NMR ($CDCl_3$, 27 °C, 400 MHz): δ [ppm] 1.29 – 1.45 (m, 12H, $H_d – H_i$), 1.66 (m, 6H, $H_3 + H_4 + H_5$), 1.89 (m, 2H, $H_2 + H_6$), 2.04 (m, 4H, $H_c + H_2 + H_6$), 2.26 (m, 2H, H_j), 4.94 (m, 2H, H_a), 5. 69 (m, 1H, H_7), 5.79 (m, 1H, H_b).

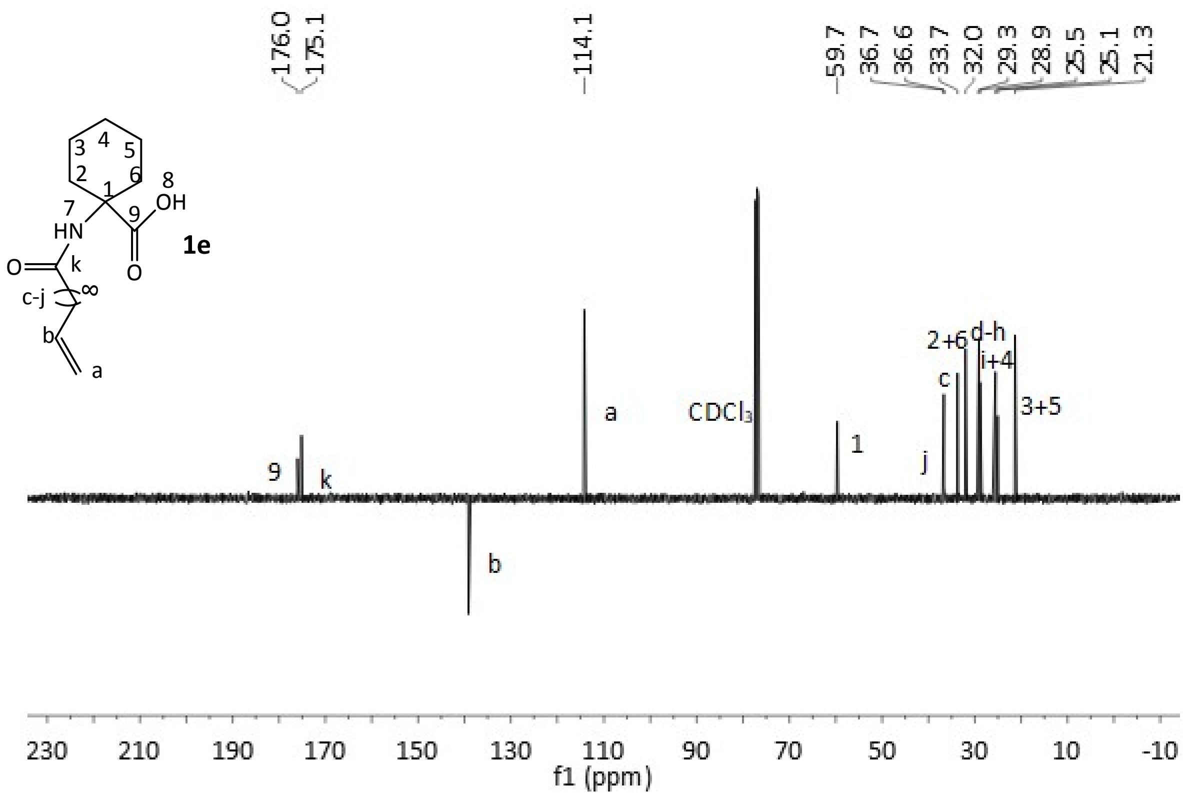

Figure S16. ^{13}C-APT spectra of **1e**.

N-ACHC (**1e**): ^{13}C-NMR ($CDCl_3$, 27 °C, 100 MHz): δ [ppm] 21.3 ($C_3 + C_5$), 25.1 - 25.5 ($C_i + C_4$), 28.9 – 29.5 ($C_d – C_h$), 32.0 - 33.7 ($C_2 + C_6 + C_c$), 36.6 (C_j), 59.7 (C_1), 114.1 (C_a), 139.1 (C_b), 175.1 (C_k), 176.0 (C_4).

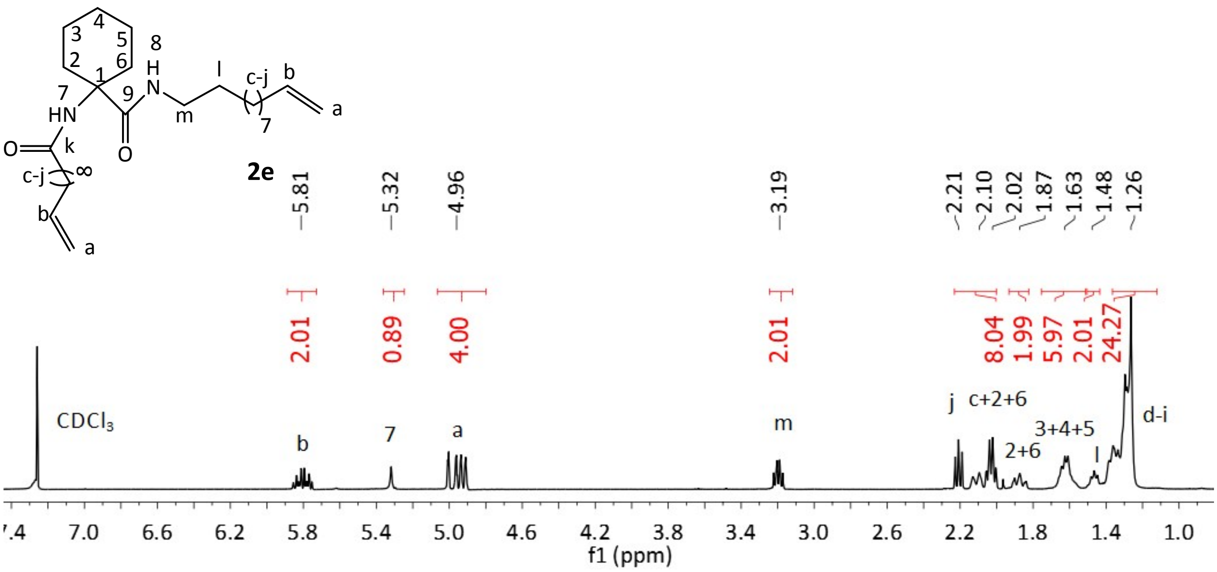

Figure S17. [1]H-NMR spectra of **2e**.

N- + *C*-ACHC (2**e**): [1]H-NMR ($CDCl_3$, 27 °C, 400 MHz): δ [ppm] 1.29-1.47 (m, 26H, $H_d - H_i + H_l$), 1.64 (m, 6H, $H_3 + H_4 + H_5$), 1.88 (m, 2H, $H_2 + H_6$), 2.04 (m, 6H, $H_c + H_2 + H_6$), 2.21 (m, 2H, H_j), 3.20 (m, 2H, H_m), 4.97 (m, 4H, H_a), 5.30 (m, 1H, H_7), 5.79 (m, 2H, H_b).

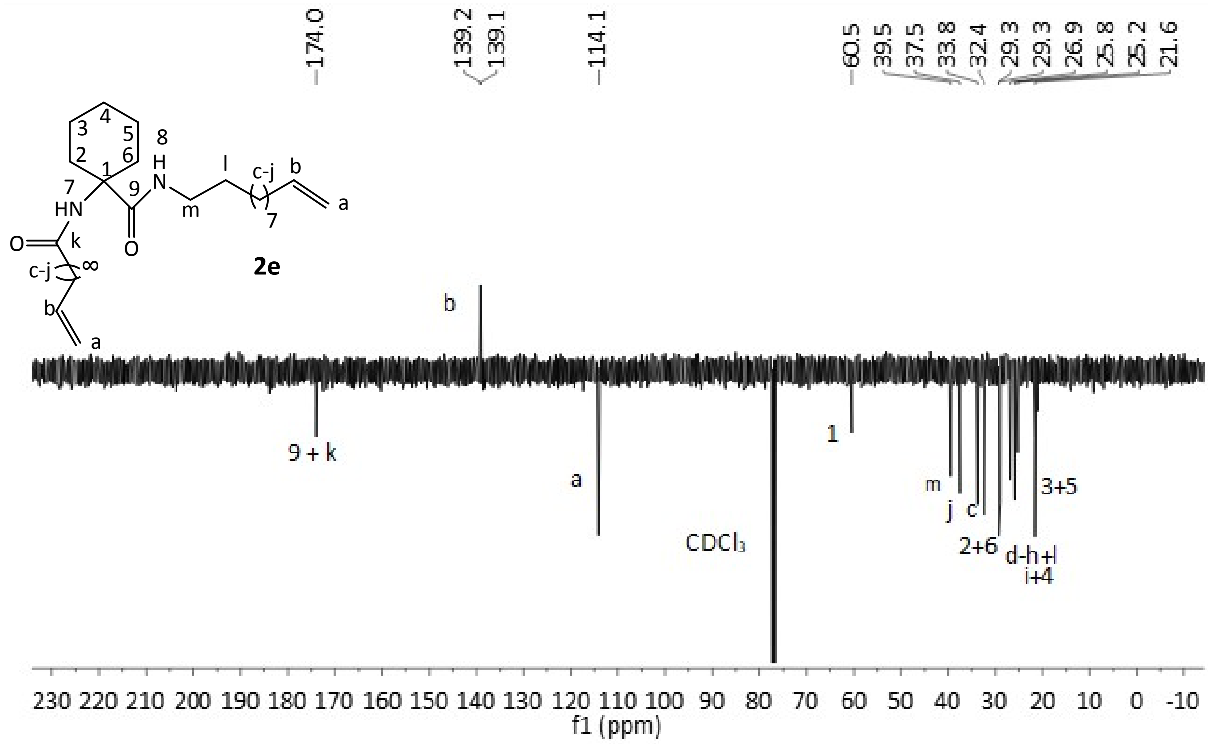

Figure S18. [13]C-APT spectra of **2e**.

N- + *C*-ACHC (**2e**): [13]C-NMR ($CDCl_3$, 27 °C, 100 MHz): δ [ppm] 21.6 ($C_3 + C_5$), 25.1 – 25.5 ($C_i + C_4$), 26.9 (C_i), 28.9 – 29.5 ($C_d - C_h + C_l$), 32.0 - 33.8 ($C_2 + C_6 + C_c$), 37.5 (C_j), 39.5 (C_m), 59.7 (C_1), 114.1 (C_a), 139.1 (C_b), 175.1 (C_k), 176.0 (C_4).

S19. – S28. ESI-ToF-MS Spectra of monomers

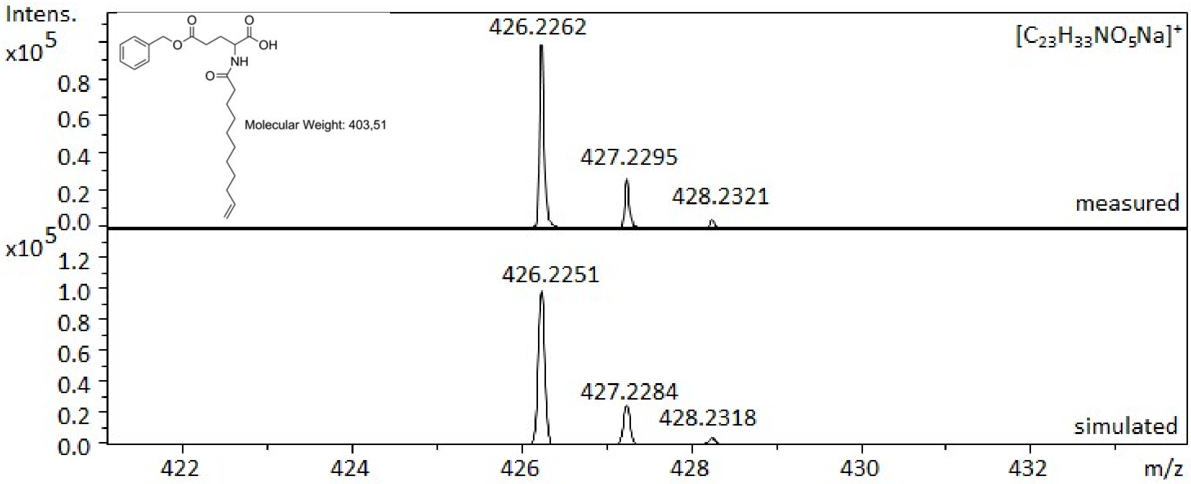

Figure S19. ESI-ToF-MS spectra of **1a**.

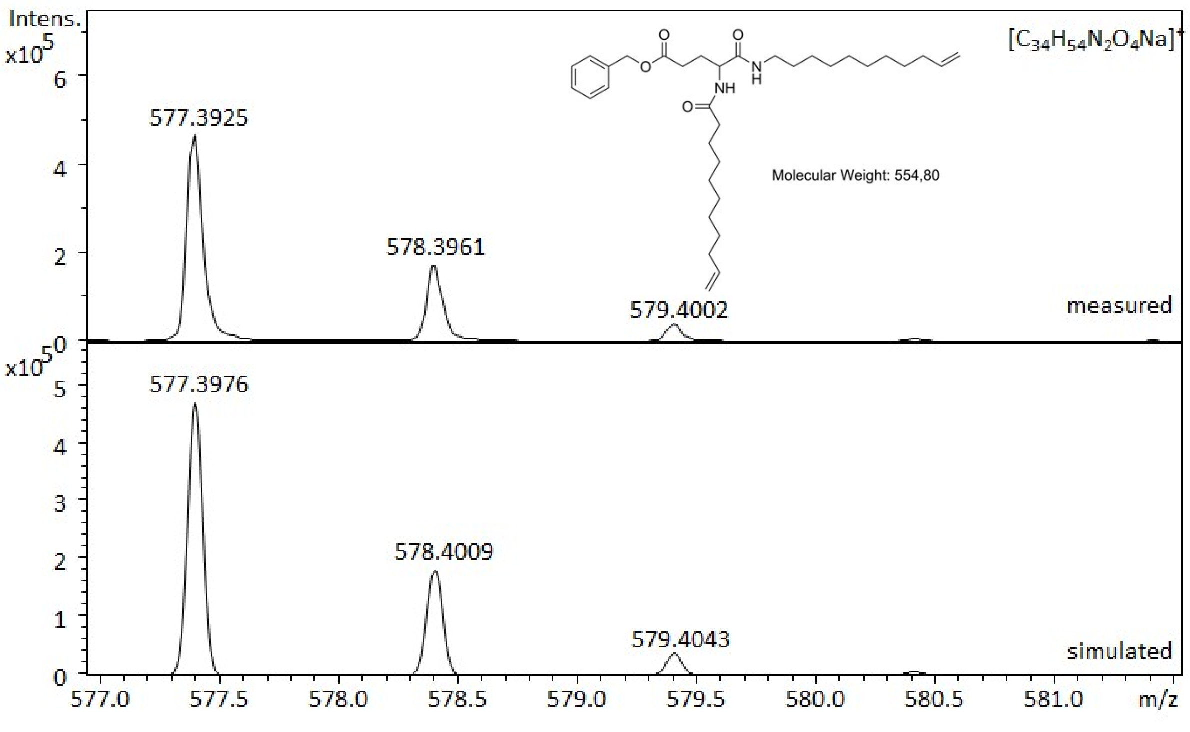

Figure S20. ESI-ToF-MS spectra of **2a**.

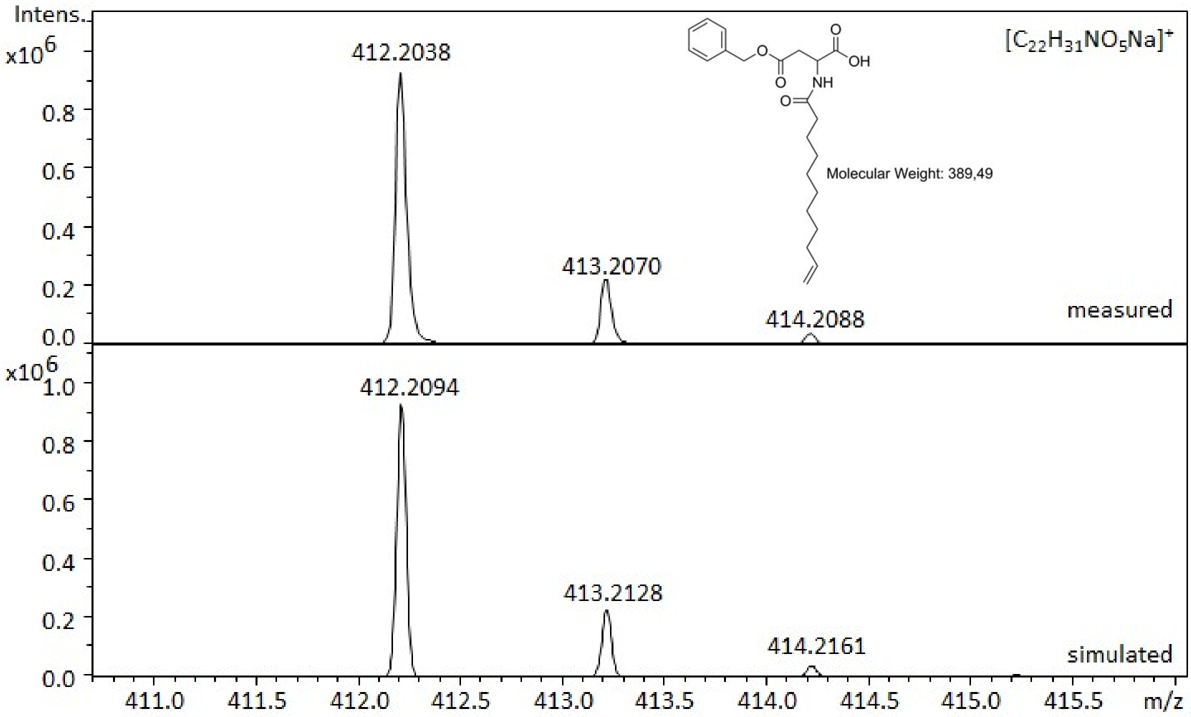

Figure S21. ESI-ToF-MS spectra of **1b**.

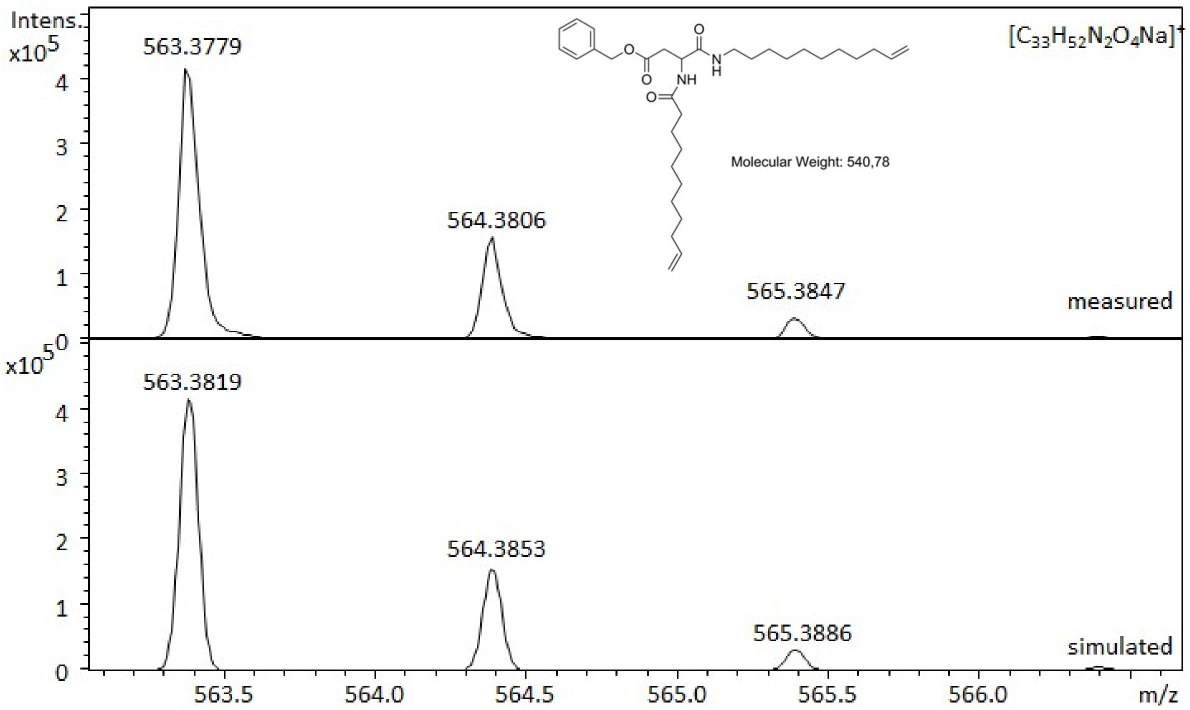

Figure S22. ESI-ToF-MS spectra of **2b**.

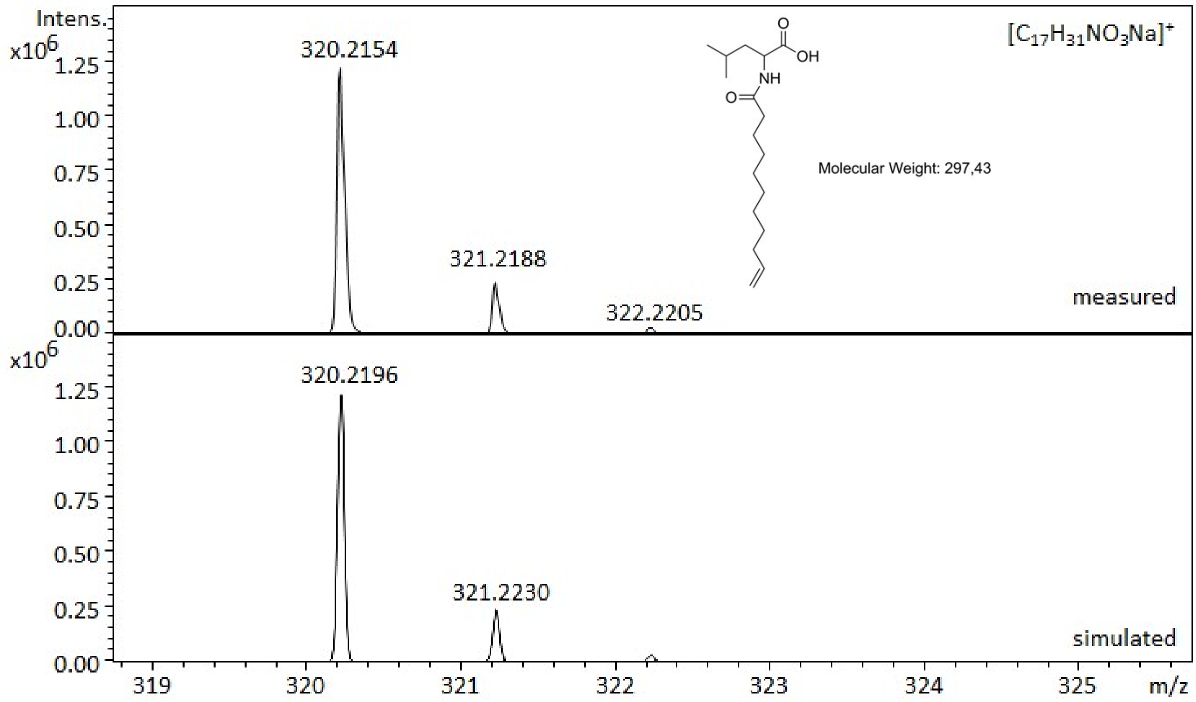

Figure S23. ESI-ToF-MS spectra of **1c**.

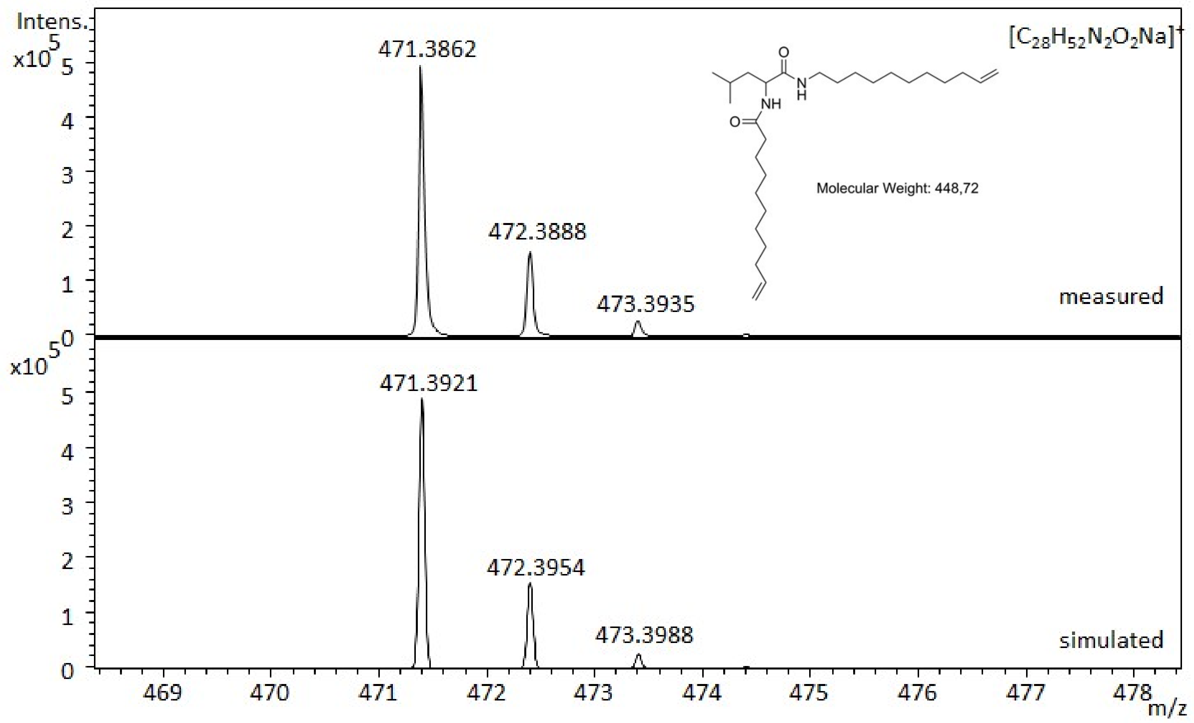

Figure S24. ESI-ToF-MS spectra of **2c**.

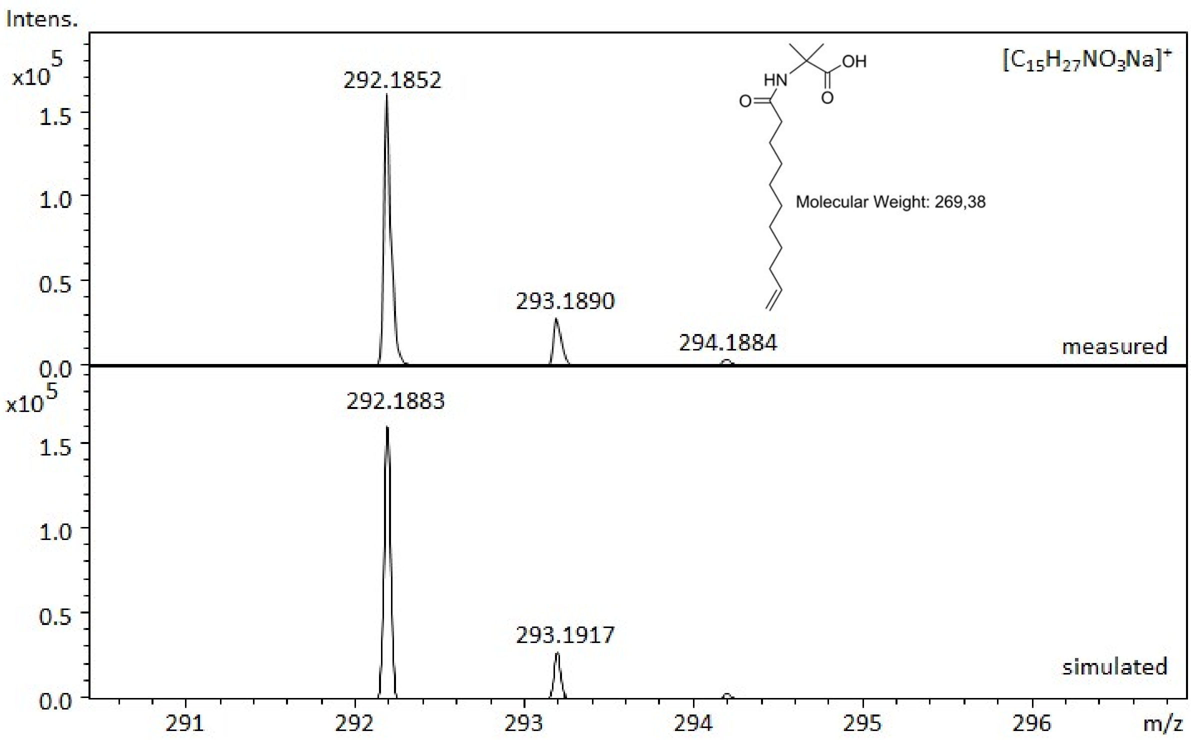

Figure S25. ESI-ToF-MS spectra of **1d**.

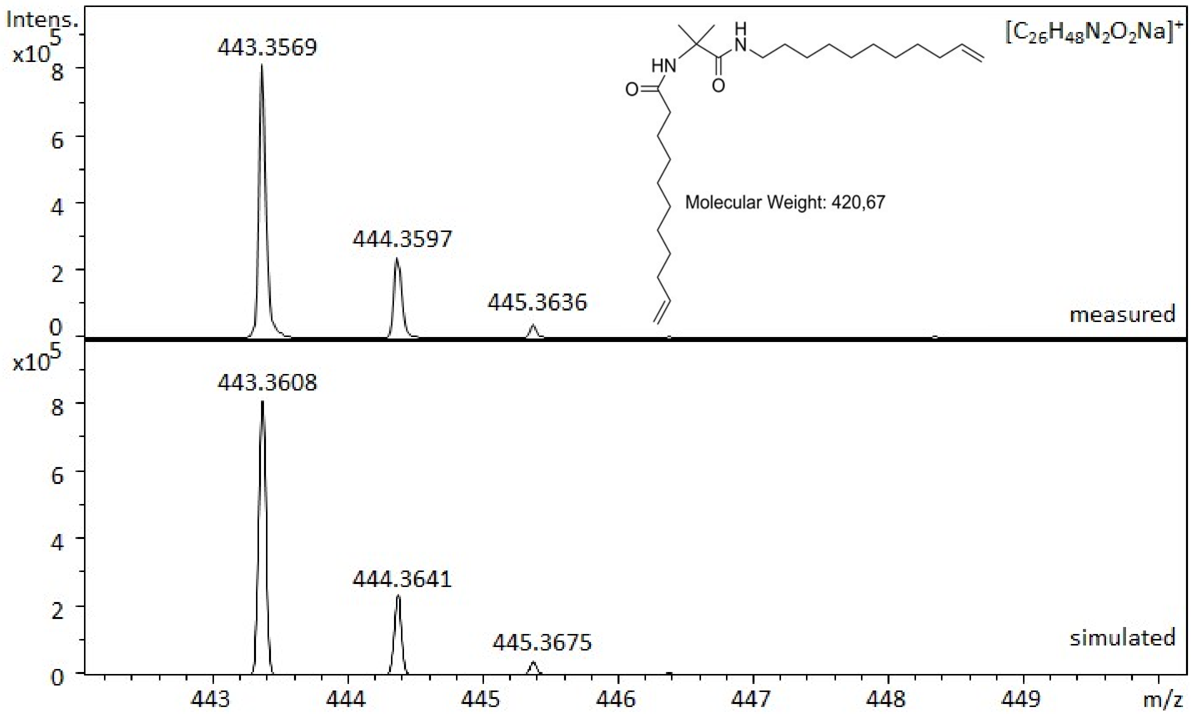

Figure S26. ESI-ToF-MS spectra of **2d**.

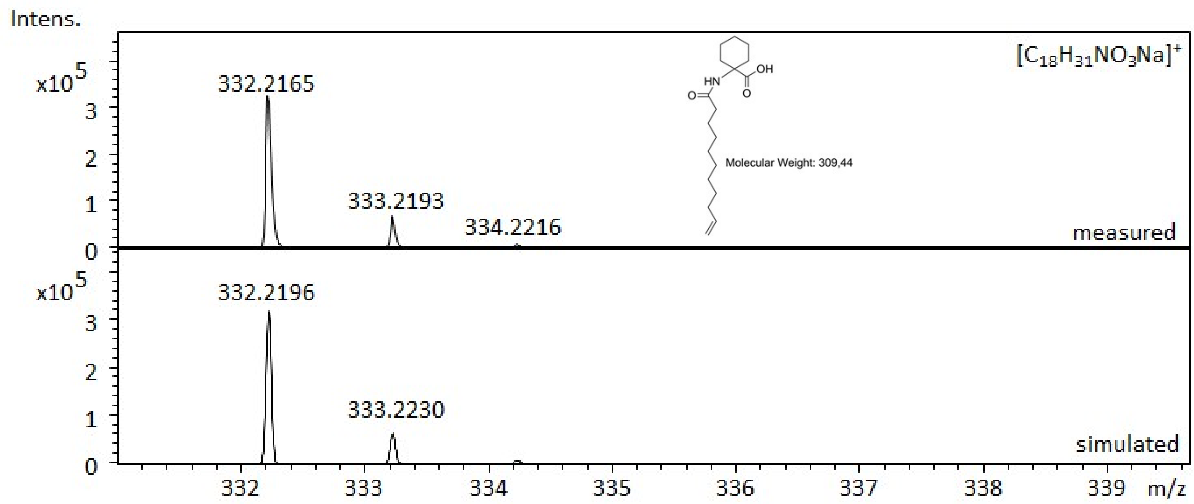

Figure S27. ESI-ToF-MS spectra of **1e**.

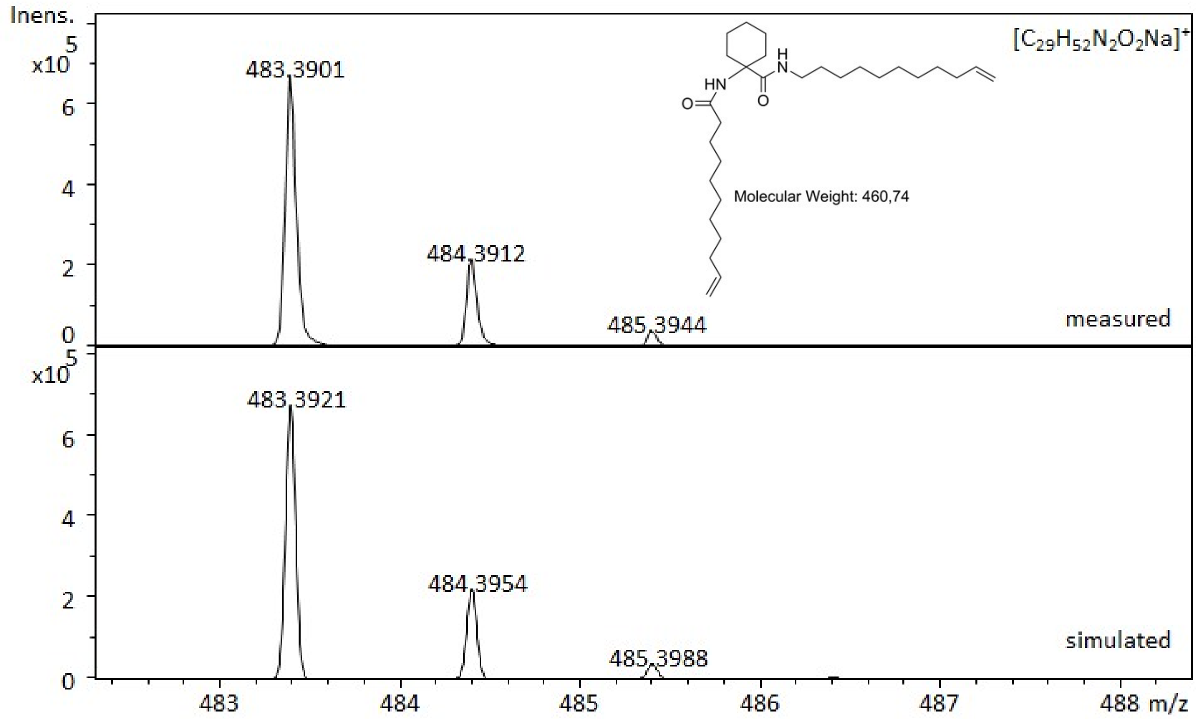

Figure S28. ESI-ToF-MS spectra of **2e**.

S29. – S30. Synthesis and characterization of 10-Undeceneamine (A2)

*Synthesis of 10-Undecenecarboxamide (***A1***)* [43]

In a two necked round bottom flask equipped with a magnetic stirrer the a solution of aqueous ammonium hydroxide (250 mL) were added and cooled to 0°C. 10-Undecenoyl chloride (12.69 g; 0.06 mol; 1 eq) was dissolved in THF (50 mL) and added dropwise to the solution which was allowed to stir at room temperature for 3h. The solid product was filtered of, washed with destilled water (3x100 mL) and dried under vacuum to yield 10.85 g (95 %) of 10-Undecencarboxamide (**A1**).

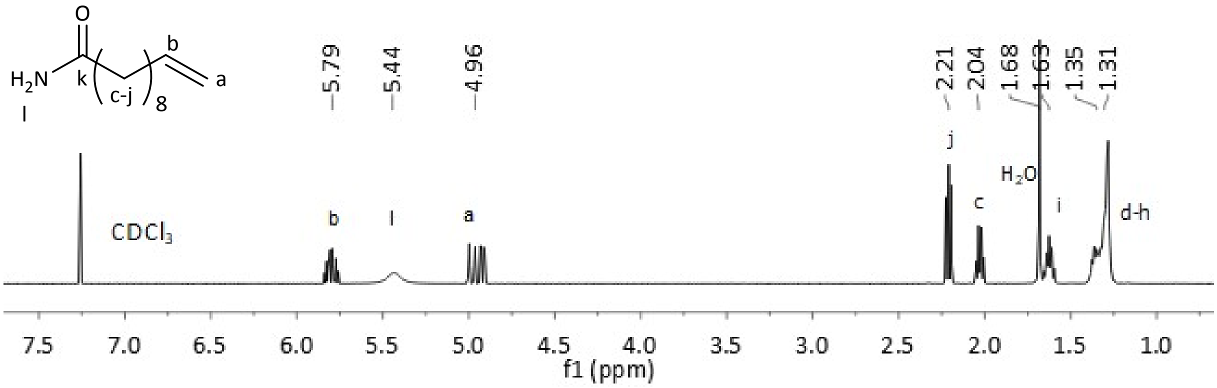

Figure S29. ^{1}H-NMR spectra of **A1**.

10-Undecenecarboxamide (**A1**): ^{1}H-NMR ($CDCl_3$, 27 °C, 400 MHz): δ [ppm] 1.29 – 1.38 (m, 10H, H_d – H_h), 1.63 (m, 2H, H_i), 2.05 (m, 2H, H_c), 3.25 (t, $^3J_{H,H}$ = 7,0 Hz, 2H, H_j), 4.96 (m, 2H, H_a), 5.83 (m, 1H, H_b).

*Synthesis of 10-Undecene-1-amine (***A2***)* [43]

Reaction was performed under a N_2-atmosphere. $LiAlH_4$ (6,50 g; 171,3 mmol; 2.9 eq) was suspended in dried THF (150 mL) and cooled to 0 °C. **A1** (10.85 g; 59.2 mmol; 1.0 eq) was dissolved in dried THF (150 mL) and added dropwise to the solution. The mixture was allowed to stir at room temperature for 24h, then cooled to 0 °C and the reaction was quenched carefully by adding water (20 mL), 1M NaOH-solution (40 mL) and water (20 mL). The mixture was filtered and the filtrate was concentrated in vacuum. The crude product was dissolved in diethyl ether (50 mL) and washed with brine (2x100 mL). The organic layer was dried over Na_2SO_4, filtrated and concentrated in vacuum. Purification of the crude product was realized by high vacuum distillation (30 – 38 °C at 0,032 mbar) to yield 5.52 g (55%) of 10-Undeceneamine (**A2**).

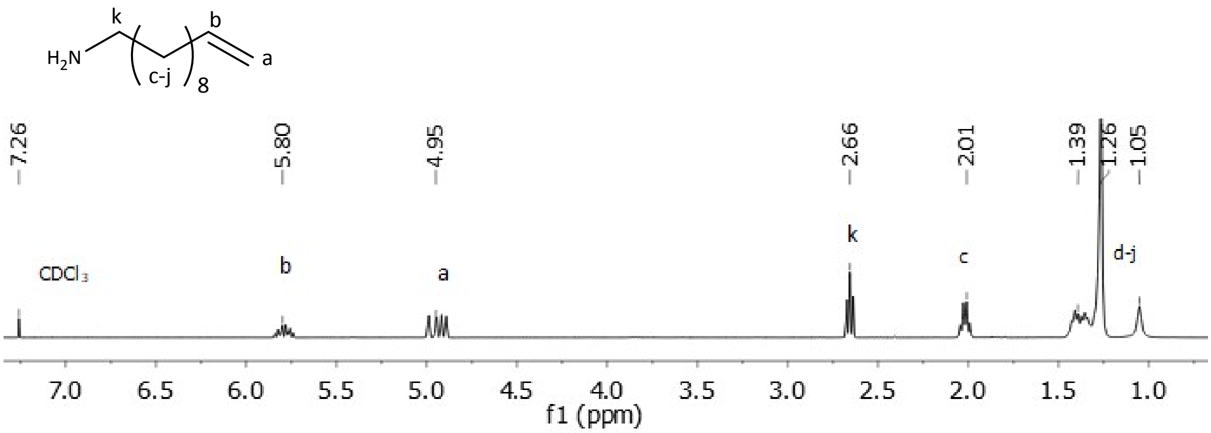

Figure S30. ^{1}H-NMR spectra of **A2**.

10-Undeceneamine (**A2**): ^{1}H-NMR ($CDCl_3$, 27 °C, 400 MHz): δ [ppm] 1.05 – 1.39 (m, 14H, H_d – H_j), 2.01 (m, 1H, H_c), 2.65 (t, $^3J_{H,H}$ = 7.0 Hz, 1H, H_k), 4.95 (m, 1H, H_a), 5,80 (m, 2H, H_b).

S31. – S36. ^{1}H-NMR Spectra of polymers

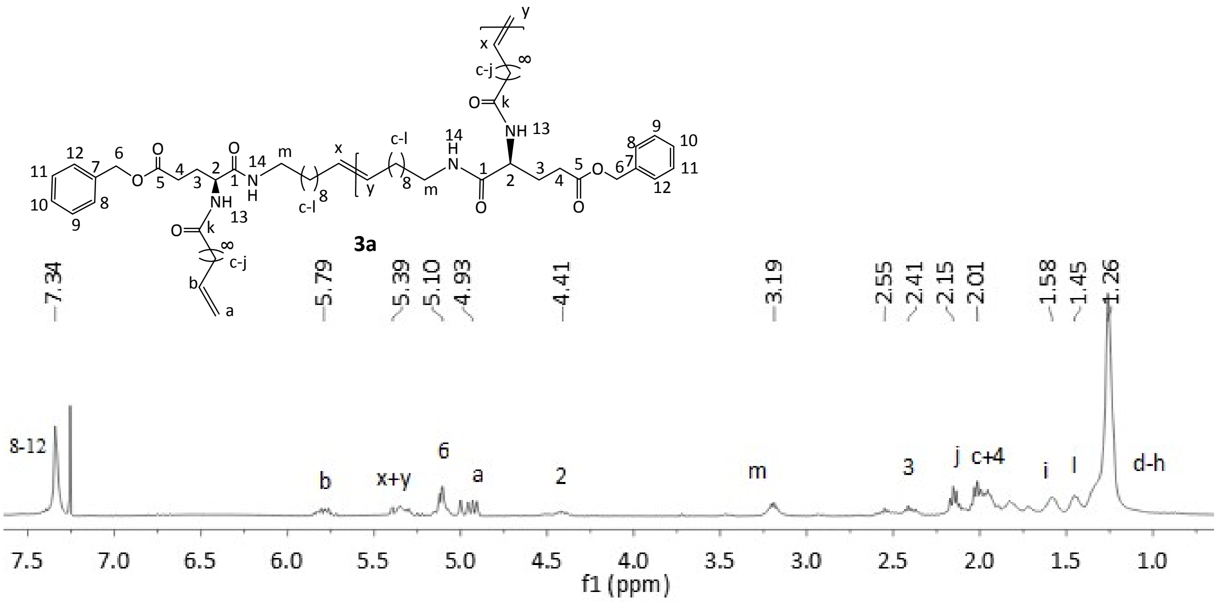

Figure S31. ^{1}H-NMR spectra of **3a**.

ADMET-Glu (**3a**): ^{1}H-NMR ($CDCl_3$, 27 °C, 400 MHz): δ [ppm] 1.26 – 1.34 (m, $H_{rep.unit}$, $H_d - H_h$), 1.44 – 1.59 (m, $H_{rep.unit}$, $H_i + H_l$), 1.95 – 2.01 (m, $H_{rep.unit}$, $H_4 + H_c$), 2.16 (m, $H_{rep.unit}$, H_j) 2.41 (m, $H_{rep.unit}$, H_3), 2.55 (m, $H_{rep.unit}$, H_3), 3.20 (m, $H_{rep.unit}$, H_m) 4.41 (m, $H_{rep.unit}$, H_2), 4.96 (m, 4H, H_a), 5.10 (s, $H_{rep.unit}$, H_6), 5.36 (m, $H_{rep.unit}$, $H_x + H_y$), 5.79 (m, 2H, H_b), 7.34 (m, $H_{rep.unit}$, $H_8 - H_{12}$).

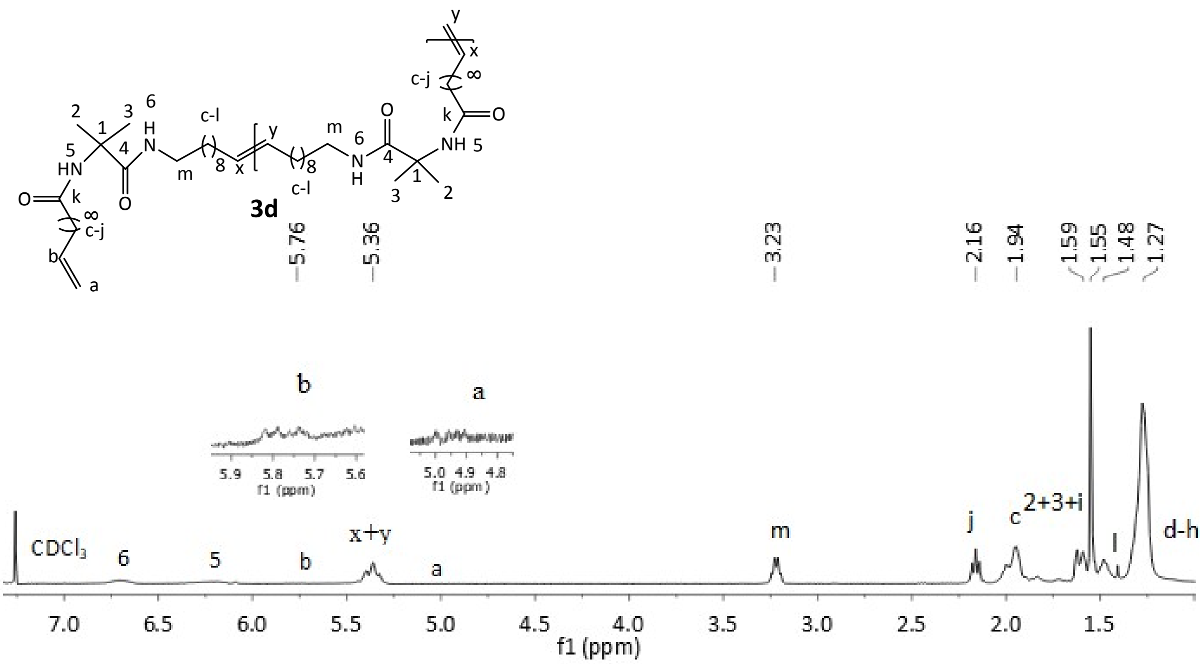

Figure S32. ^{1}H-NMR spectra of **3d**.

ADMET-Aib (**3d**): ^{1}H-NMR ($CDCl_3$, 27 °C, 400 MHz): δ [ppm] 1.27 – 1.36 (m, $H_{rep.unit}$, $H_d - H_h$), 1.48 (m, $H_{rep.unit}$, H_l), 1.55-1.59 (m, $H_{rep.unit}$, $H_2 + H_3 + H_i$), 1.94 (m, $H_{rep.unit}$, H_c), 2.16 (m, $H_{rep.unit}$, H_j), 3.23 (m, $H_{rep.unit}$, H_m), 4.96 (m, 2H, H_a), 5.36 (m, $H_{rep.unit}$, $H_x + H_y$), 5.76 (m, 1H, H_b), 6.08 (m, $H_{rep.unit}$, H_5), 6.65 (m, $H_{rep.unit}$, H_6).

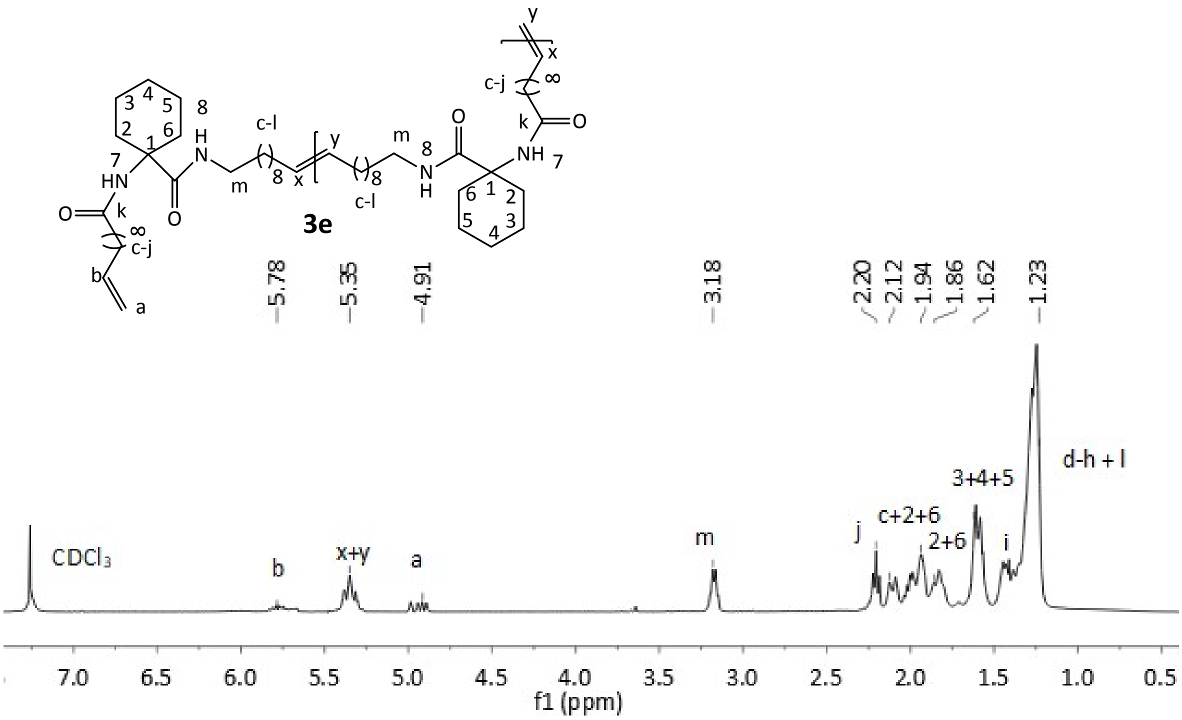

Figure S33. ^{1}H-NMR spectra of 3**e**.

ADMET-ACHC (**3e**): ^{1}H-NMR (CDCl$_3$, 27 °C, 400 MHz): δ [ppm] 1.23 – 1.47 (m, $H_{rep.unit}$, $H_d - H_h + H_l + H_i$), 1.62 (m, $H_{rep.unit}$, $H_3 + H_4 + H_5$), 1.86 (m, $H_{rep.unit}$, $H_2 + H_6$), 1.94-2.12 (m, $H_{rep.unit}$,, $H_c + H_2 + H_6$), 2.21 (m, $H_{rep.unit}$, H_j), 3.20 (m, $H_{rep.unit}$, H_m), 4.91 (m, 4H, H_a), 5. 35 (m, $H_{rep.unit}$, $H_x + H_y$), 5.78 (m, 2H, H_b).

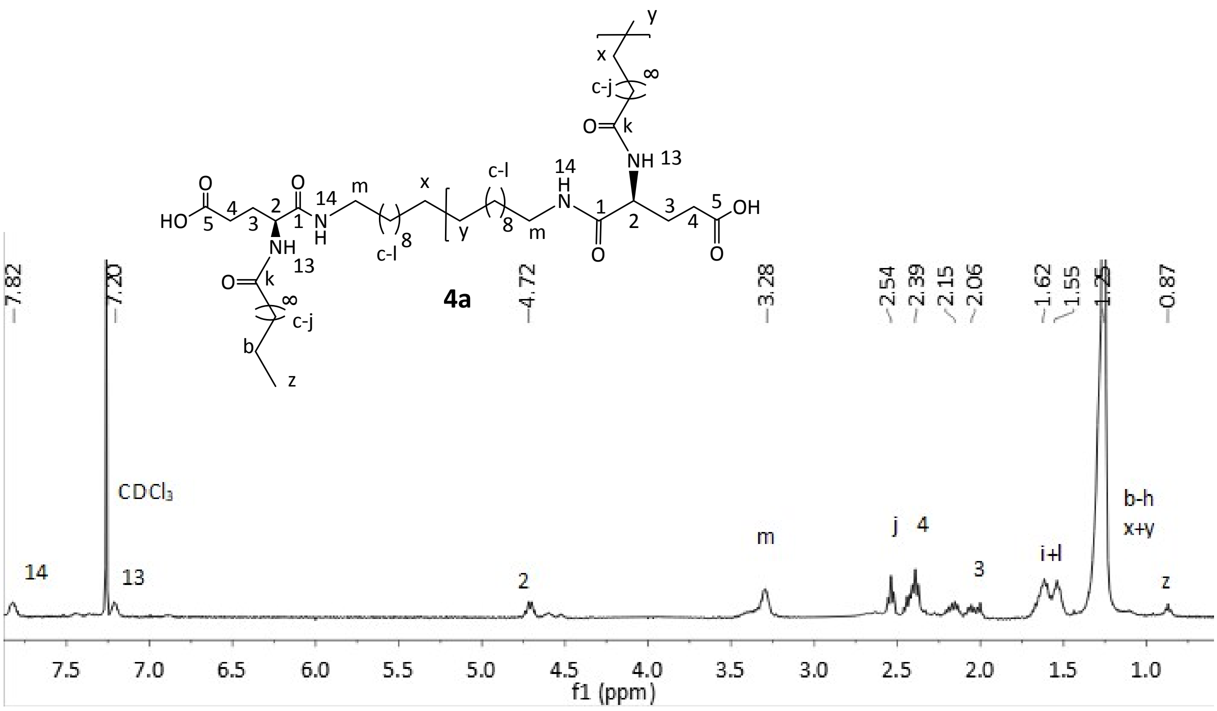

Figure S34. ^{1}H-NMR spectra of **4a**.

ADMET-Glu H (**4a**): ^{1}H-NMR (CDCl$_3$, 27 °C, 400 MHz): δ [ppm] 0.87 (m, 6H, H_z), 1.25-1.34 (m, $H_{rep.unit}$, $H_b - H_h + H_x + H_y$), 1.54-1.60 (m, $H_{rep.unit}$, $H_i + H_l$), 2.00 – 2.16 (m, $H_{rep.unit}$, H_3), 2.39 (m, $H_{rep.unit}$, H_4), 2.54 (m, $H_{rep.unit}$, H_j), 3.29(m, $H_{rep.unit}$, H_m) 4.73 (m, $H_{rep.unit}$, H_2), 7.21 (m, $H_{rep.unit}$, H_{13}), 7.81 (m, $H_{rep.unit}$, H_{14}).

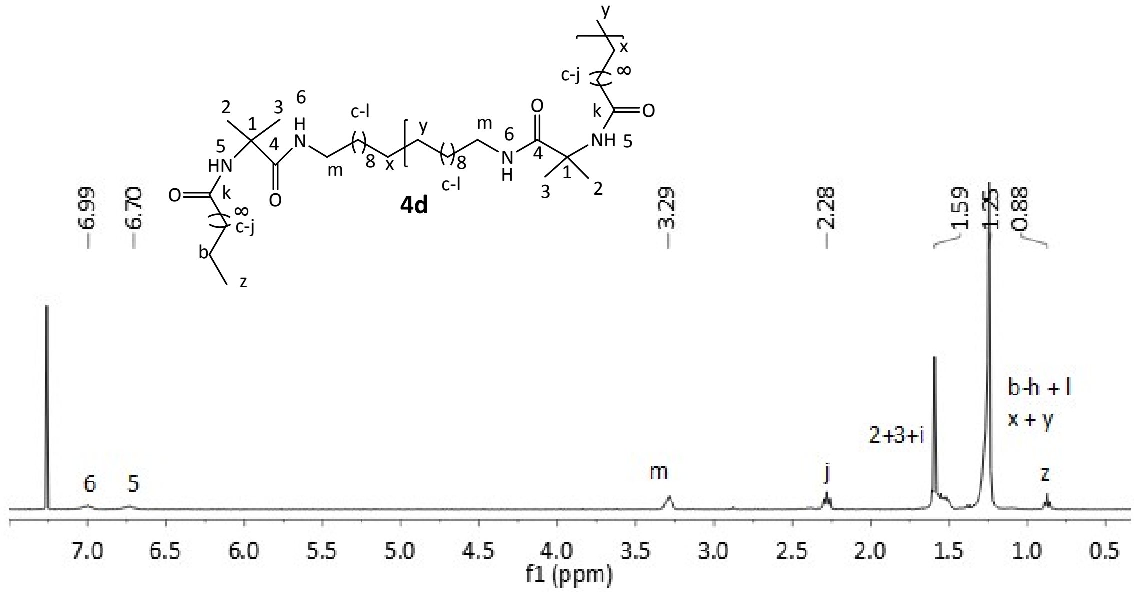

Figure S35. ^{1}H-NMR spectra of **4d**.

ADMET-Aib H (**4d**): ^{1}H-NMR ($CDCl_3$, 27 °C, 400 MHz): δ [ppm] 0.88 (m, 6H, H_z), 1.25 (m, $H_{rep.unit}$, $H_b - H_h + H_l + H_x + H_y$), 1.55-1.59 (m, $H_{rep.unit}$, $H_2 + H_3 + H_i$), 2.28 (m, $H_{rep.unit}$, H_j), 3.29 (m, $H_{rep.unit}$, H_m), 6.70 (m, $H_{rep.unit}$, H_5), 6.99 (m, $H_{rep.unit}$, H_6).

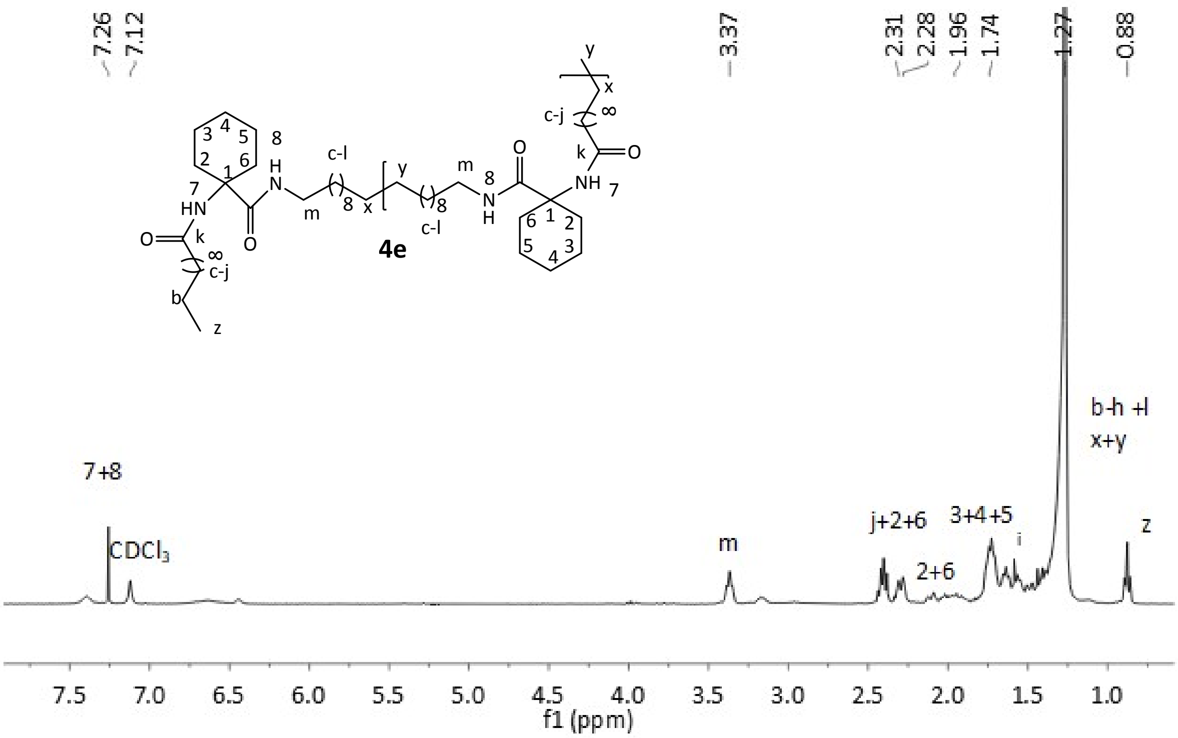

Figure S36. ^{1}H-NMR spectra of **4e**.

ADMET-ACHC H (**4e**): ^{1}H-NMR ($CDCl_3$, 27 °C, 400 MHz): δ [ppm] 0.88 (m, 6H, H_z), 1.27 – 1.46 (m, $H_{rep.unit}$, $H_b - H_h + H_l + H_x + H_y + H_i$), 1.74 (m, $H_{rep.unit}$, $H_3 + H_4 + H_5$), 1.96 – 2.31 (m, $H_{rep.unit}$,, $H_j + H_2 + H_6$), 3.37 (m, $H_{rep.unit}$, H_m), 7.12 – 7.26 (m, $H_{rep.unit}$, $H_7 + H_8$).

S37. – S41. MALDI-ToF-MS Spectra of polymers

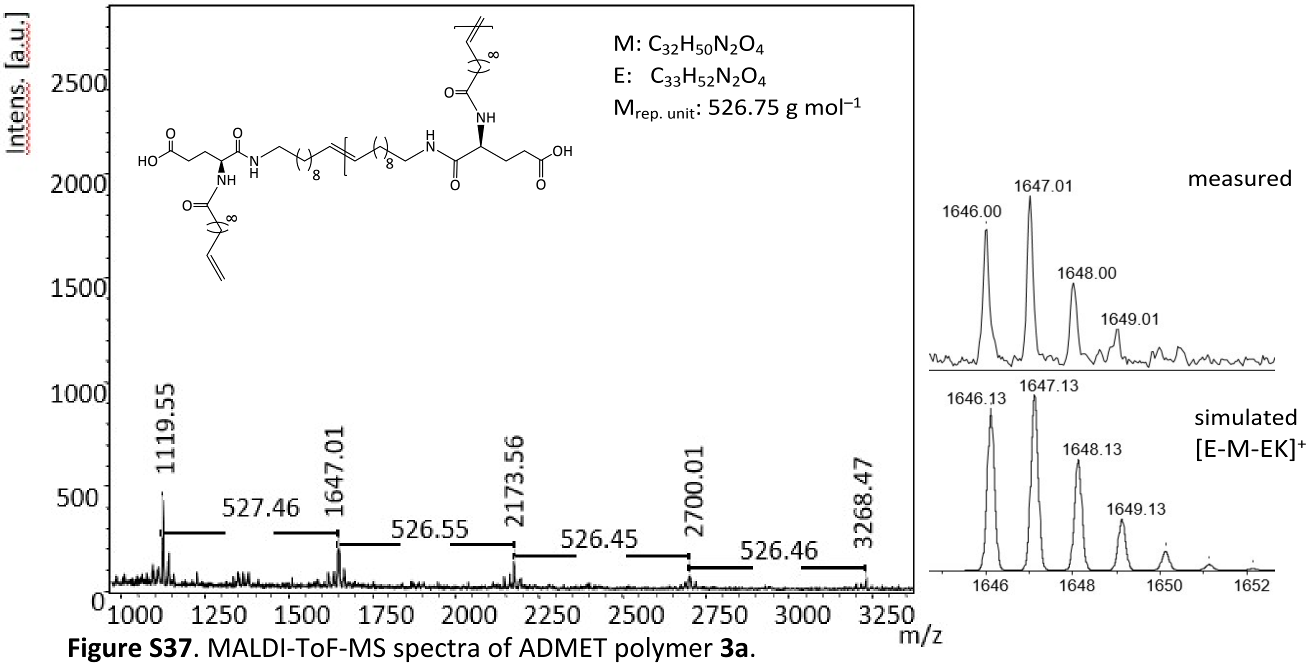

Figure S37. MALDI-ToF-MS spectra of ADMET polymer **3a**.

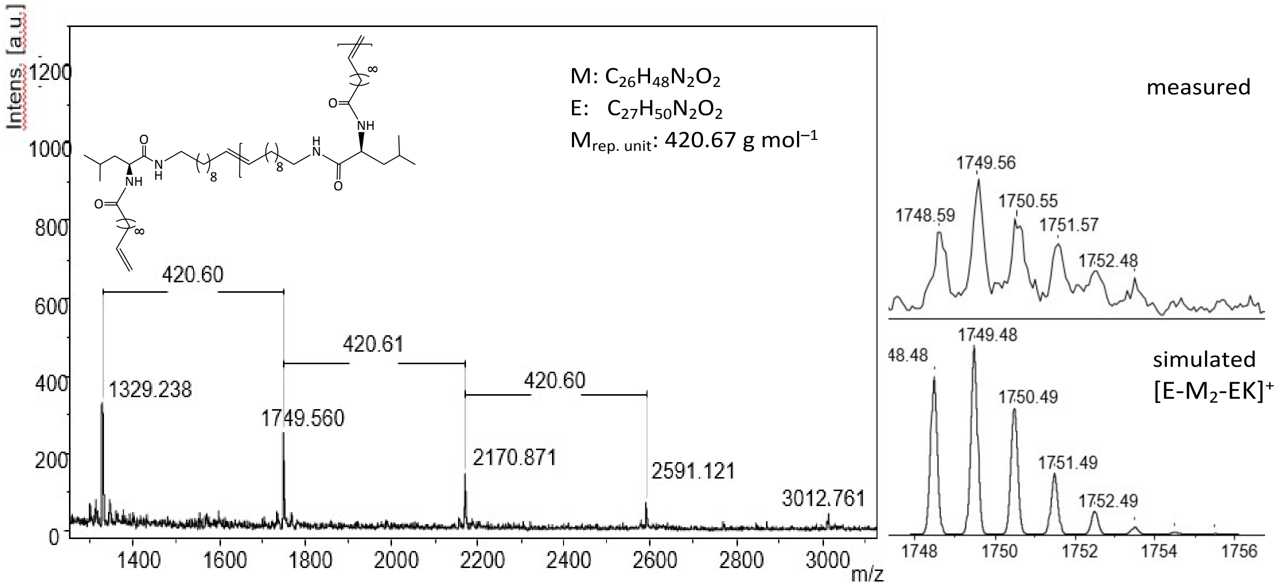

Figure S38. MALDI-ToF-MS spectra of ADMET polymer **3c**.

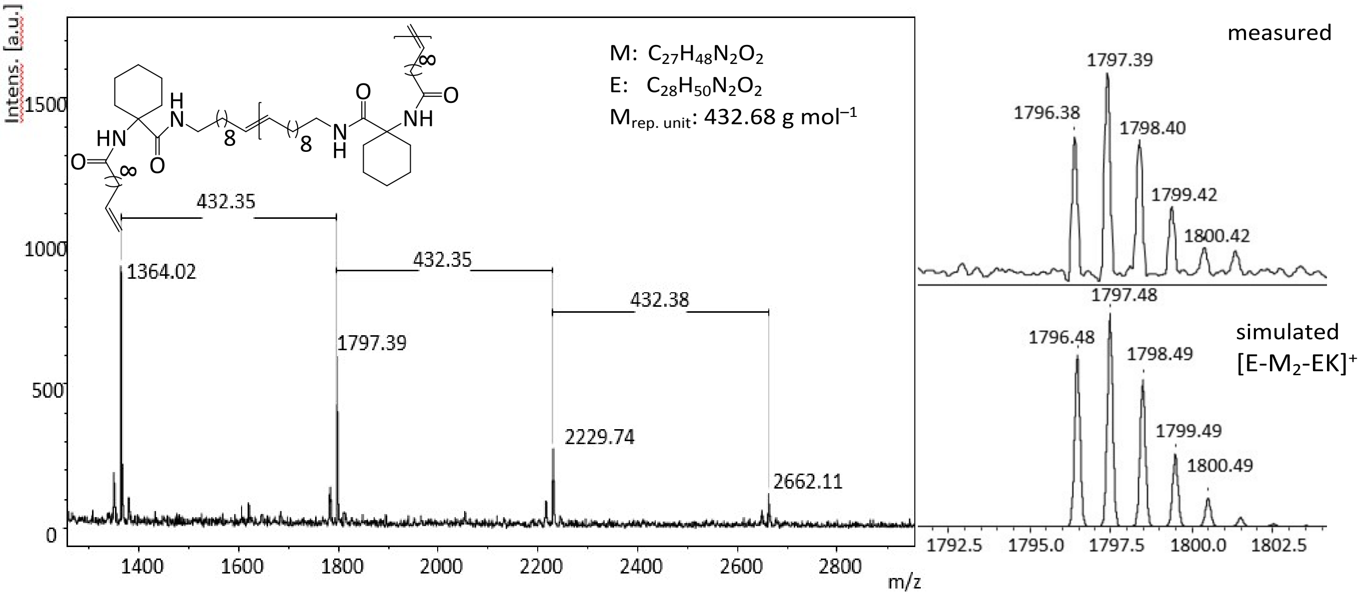

Figure S39. MALDI-ToF-MS spectra of ADMET polymer **3e**.

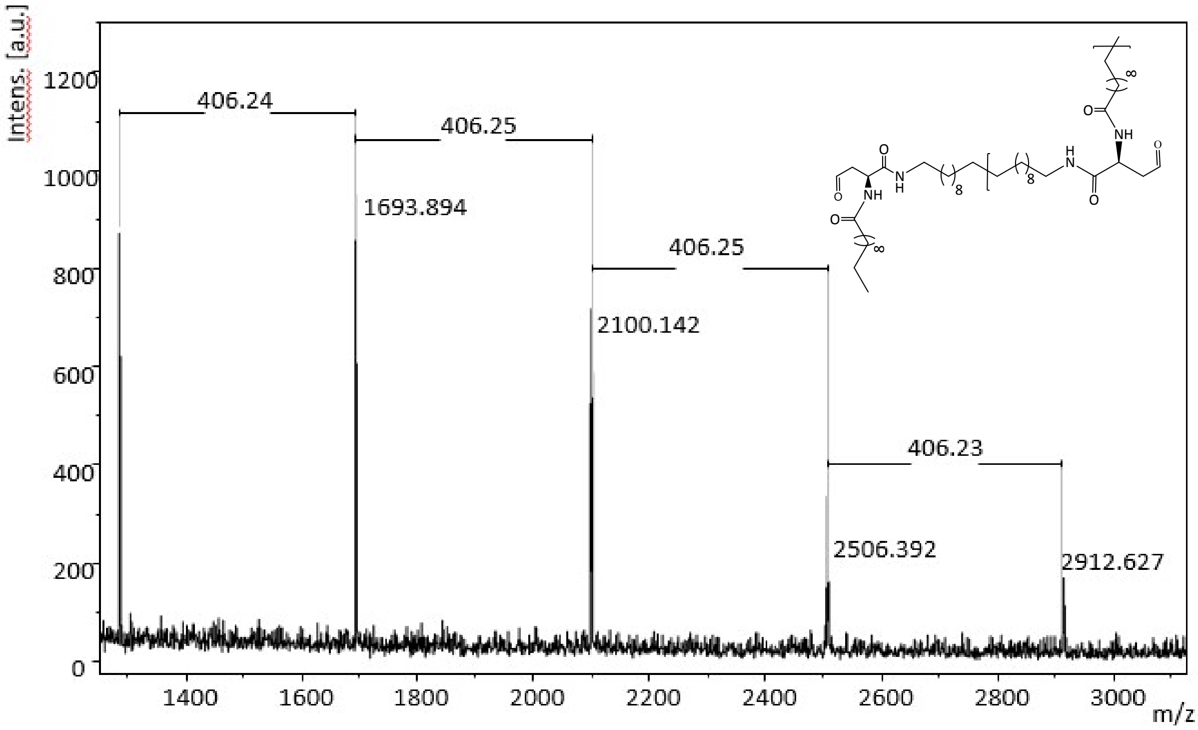

Figure S40. MALDI-ToF-MS spectra of ADMET polymer **4b**. High Laser energy leads to loss of H_2O in the molecule during measurements.

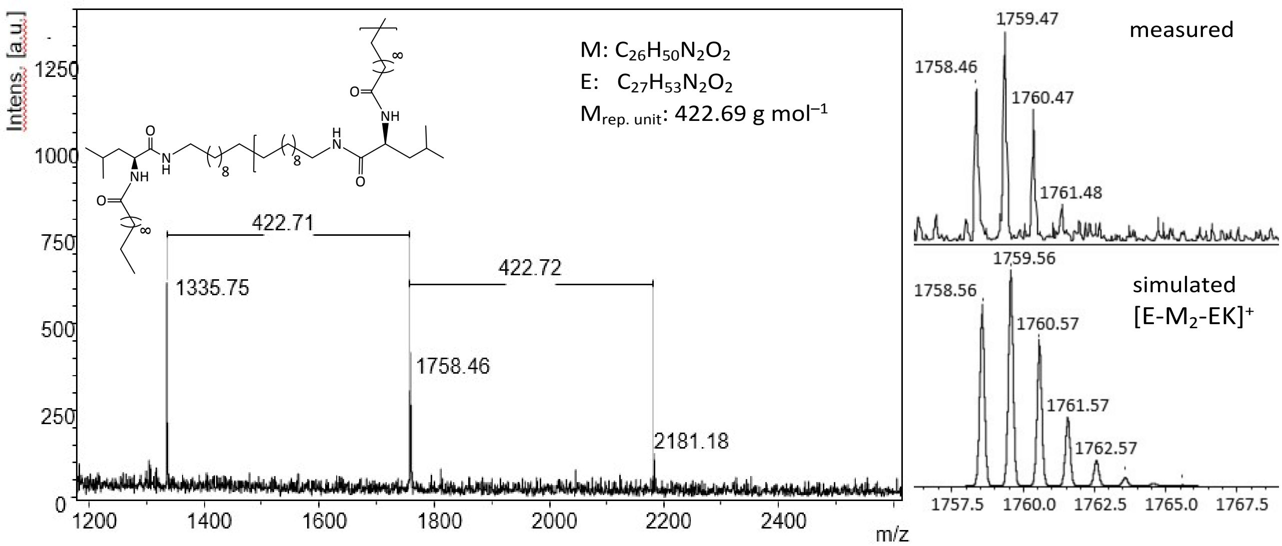

Figure S41. MALDI-ToF-MS spectra of ADMET polymer **4c**.

S42. – S51. IR Spectra of polymers

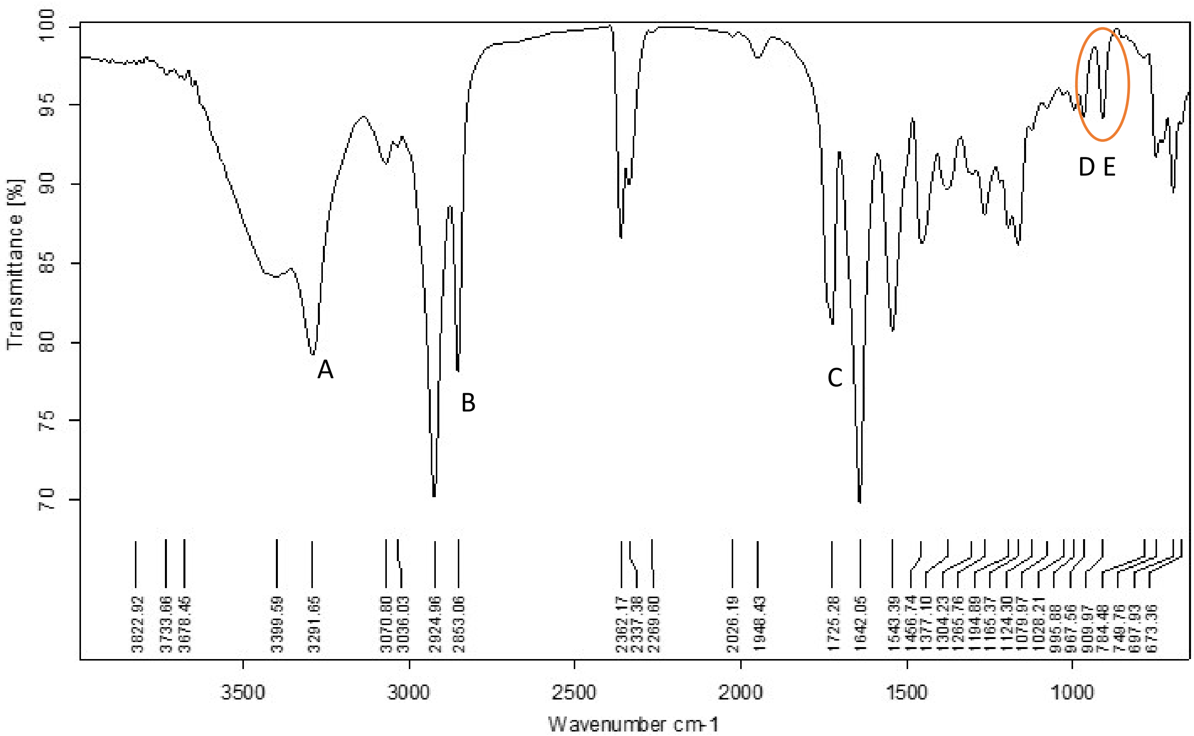

Figure S42. IR spectra of **3a**: A. 3291 cm^{-1} $\nu_{asymm.}$ CONH; B. 2924 – 2853 ν CH_2; C. 1642 cm^{-1} δ CONH; D. 967 δ RCH=CHR; E. 909 δ RCH=CH_2.

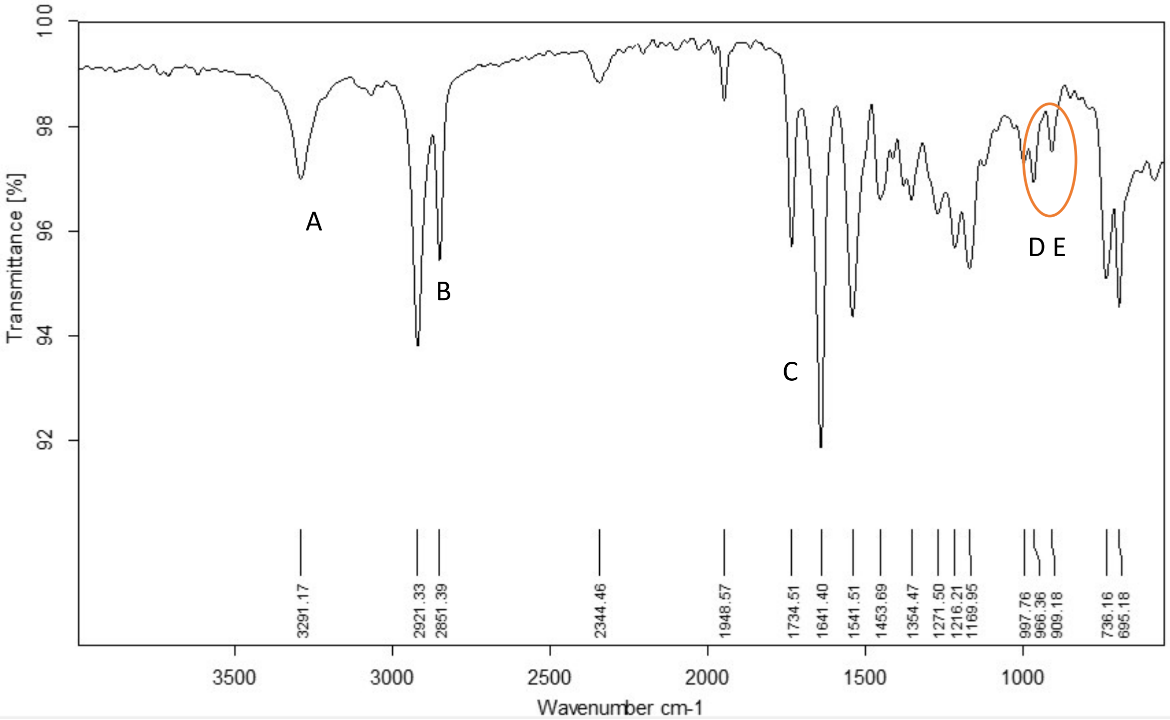

Figure S43. IR spectra of **3b**: A. 3291 cm^{-1} $\nu_{asymm.}$ CONH; B. 2921 – 2851 ν CH_2; C. 1641 cm^{-1} δ CONH; D. 966 δ RCH=CHR; E. 909 δ $RCH=CH_2$.

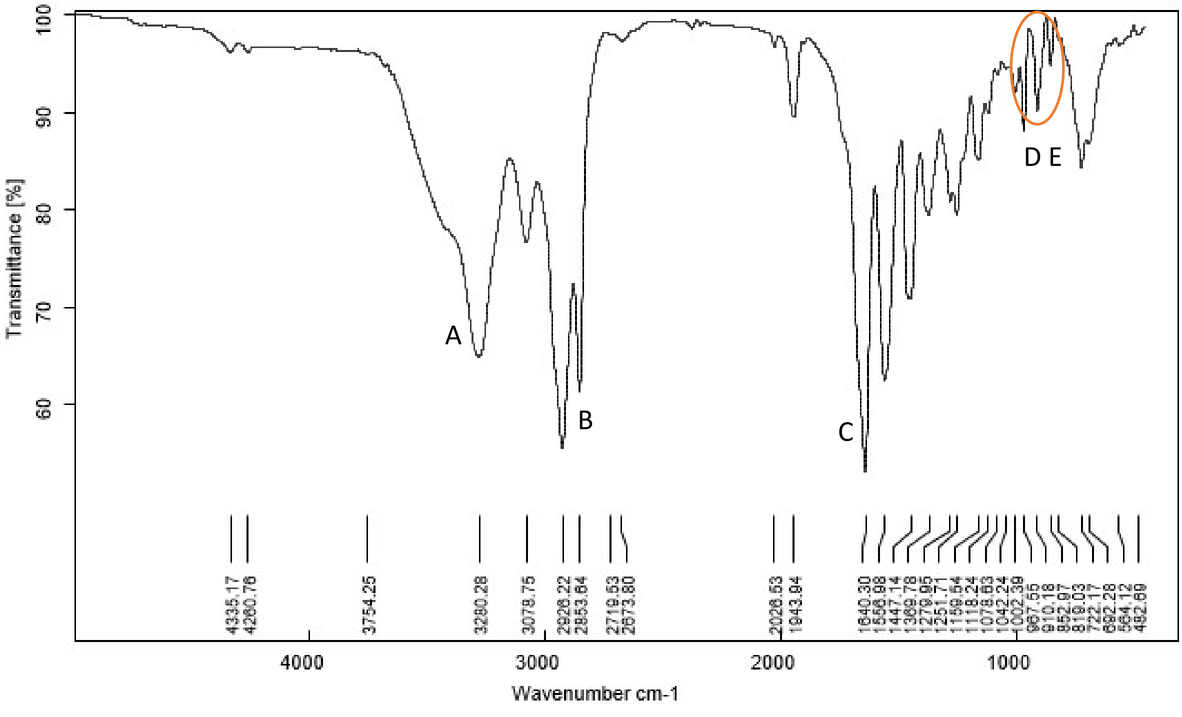

Figure S44. IR spectra of **3c**: A. 3280 cm^{-1} $\nu_{asymm.}$ CONH; B. 2926 – 2853 ν CH_2; C. 1640 cm^{-1} δ CONH; D. 967 δ RCH=CHR; E. 910 δ $RCH=CH_2$.

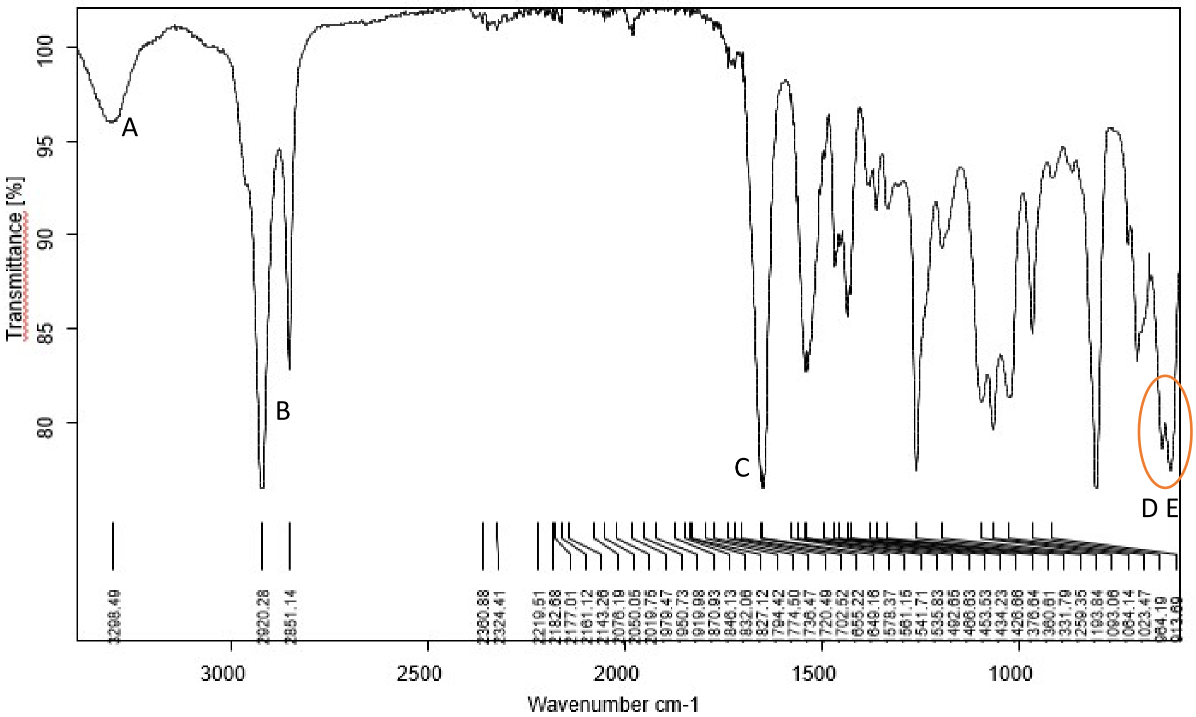

Figure S45. IR spectra of **3d**: A. 3298 cm^{-1} $\nu_{asymm.}$ CONH; B. 2920 – 2851 ν CH_2; C. 1658 cm^{-1} δ CONH; D. 964 δ RCH=CHR; E. 913 δ $RCH=CH_2$.

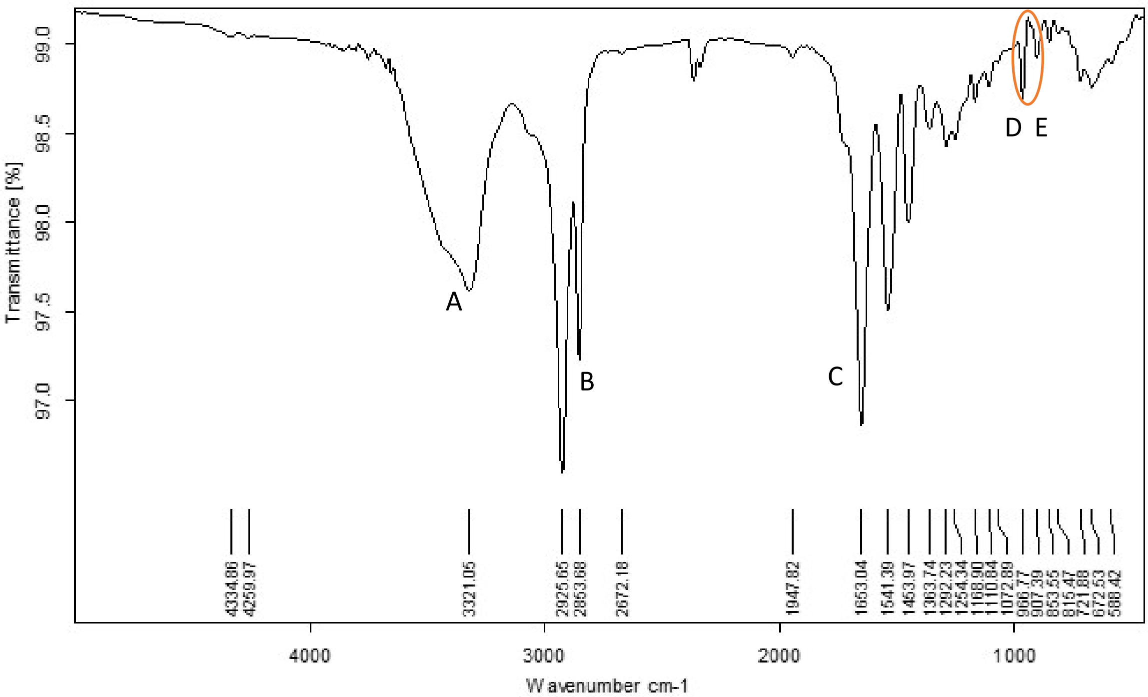

Figure S46. IR spectra of **3e**: A. 3221 cm^{-1} $\nu_{asymm.}$ CONH; B. 2925 – 2853 ν CH_2; C. 1653 cm^{-1} δ CONH; D. 966 δ RCH=CHR; E. 907 δ $RCH=CH_2$.

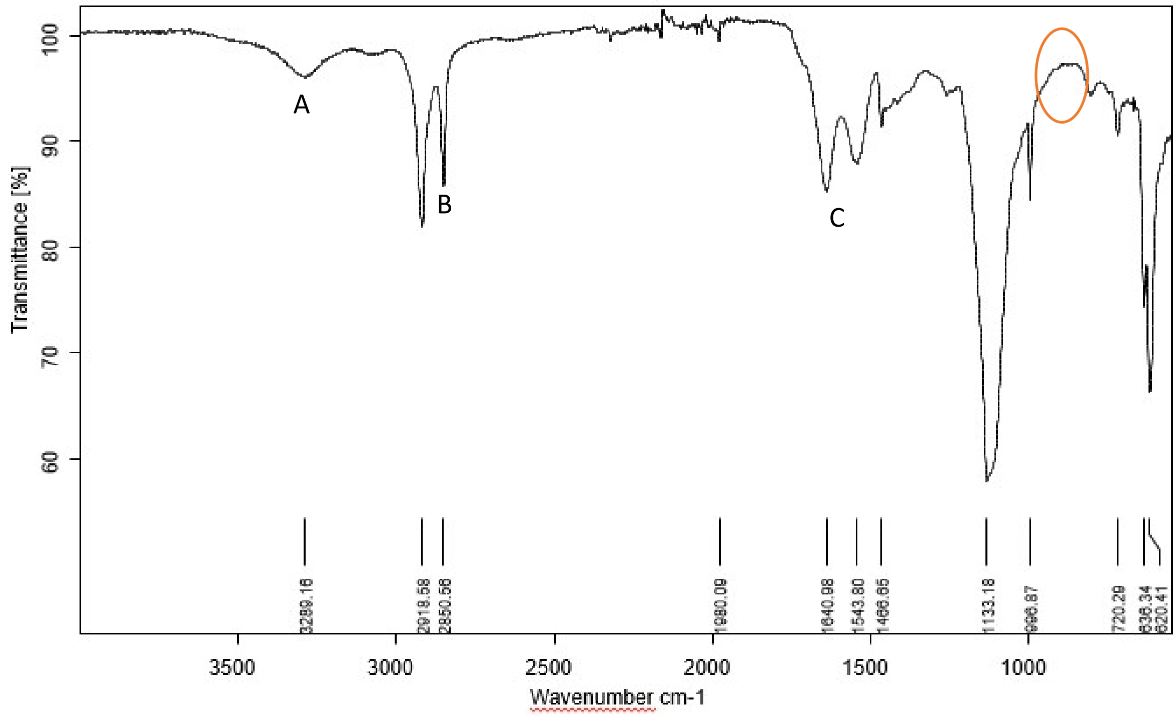

Figure S47. IR spectra of **4a**: A. 3289 cm^{-1} $\nu_{asymm.}$ CONH; B. 2918 – 2850 ν CH_2; C. 1640 cm^{-1} δ CONH.

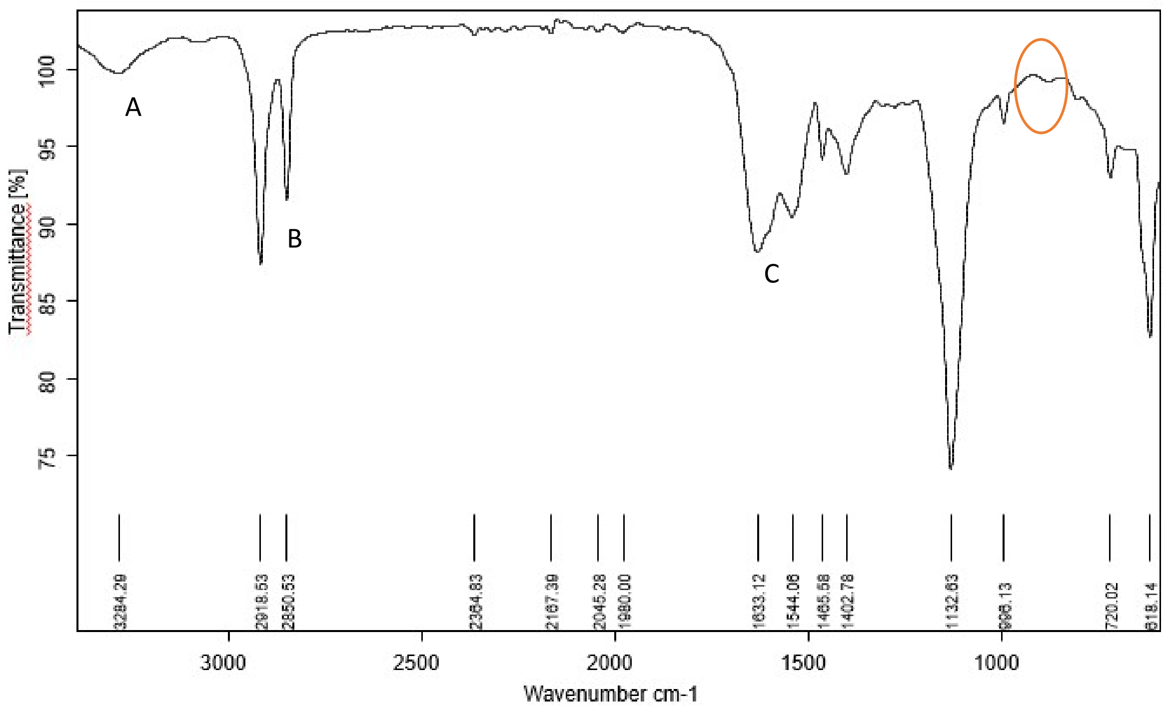

Figure S48. IR spectra of **4b**: A. 3284 cm^{-1} $\nu_{asymm.}$ CONH; B. 2918 – 2850 ν CH_2; C. 1633 cm^{-1} δ CONH.

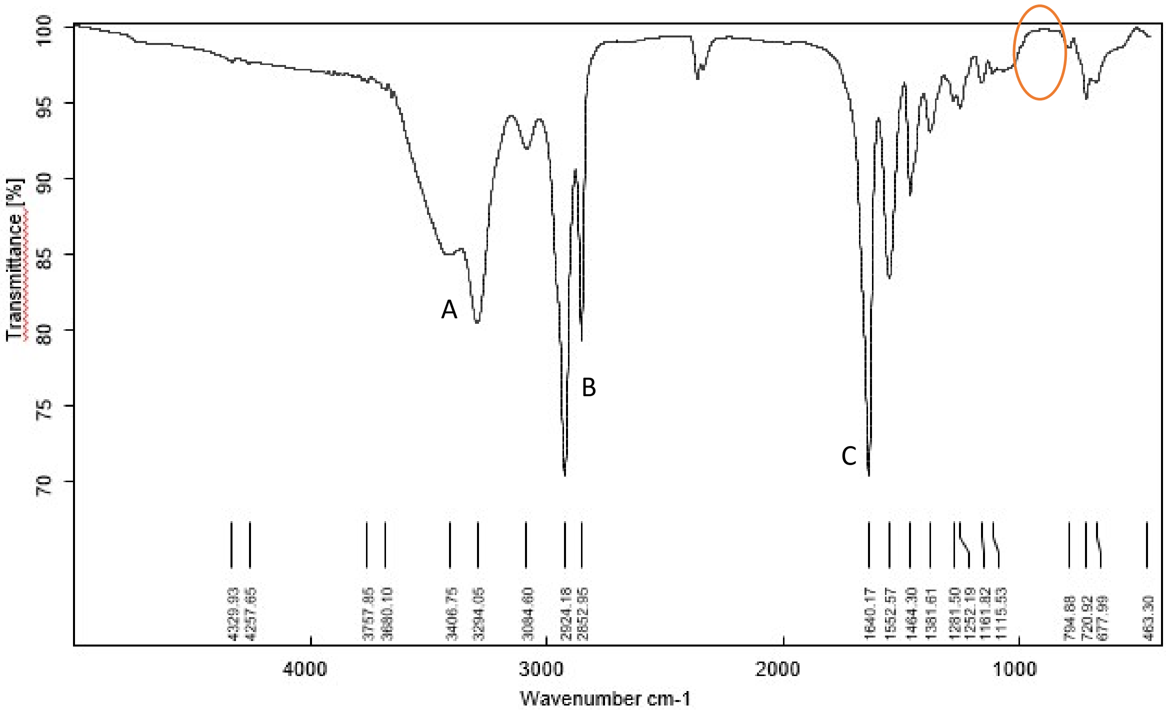

Figure S49. IR spectra of **4c**: A. 3406 - 3294 cm^{-1} $\nu_{asymm.}$ CONH; B. 2924 – 2852 ν CH_2; C. 1640 cm^{-1} δ CONH.

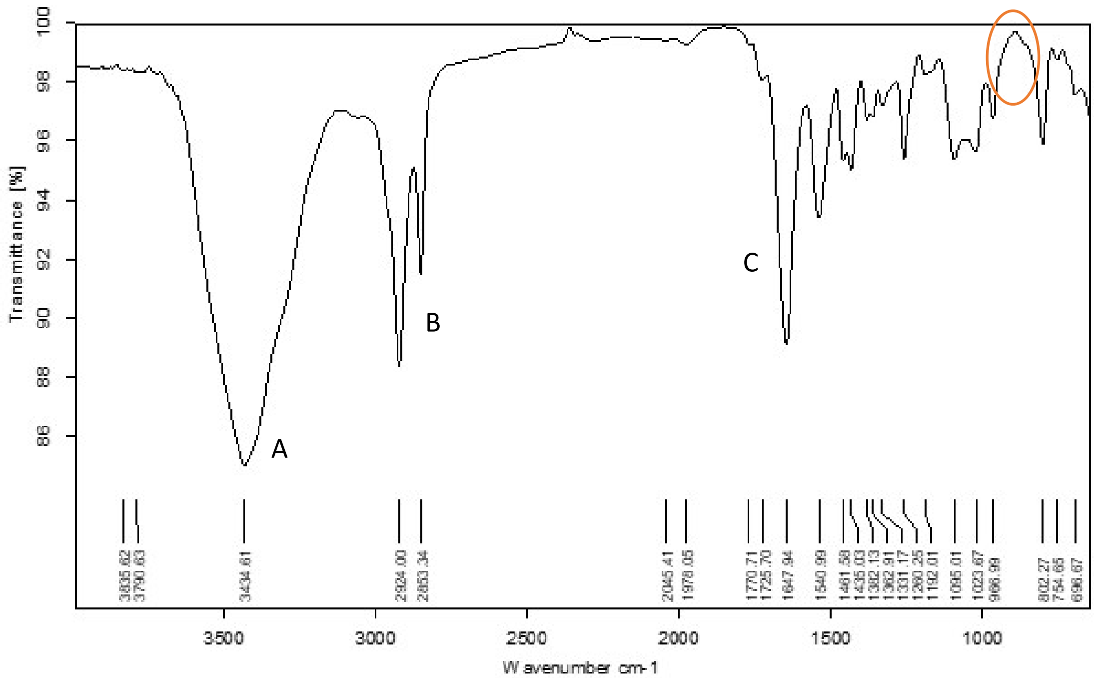

Figure S50. IR spectra of **4d**: A. 3434 cm^{-1} $\nu_{asymm.}$ CONH; B. 2924 – 2853 ν CH_2; C. 1647 cm^{-1} δ CONH.

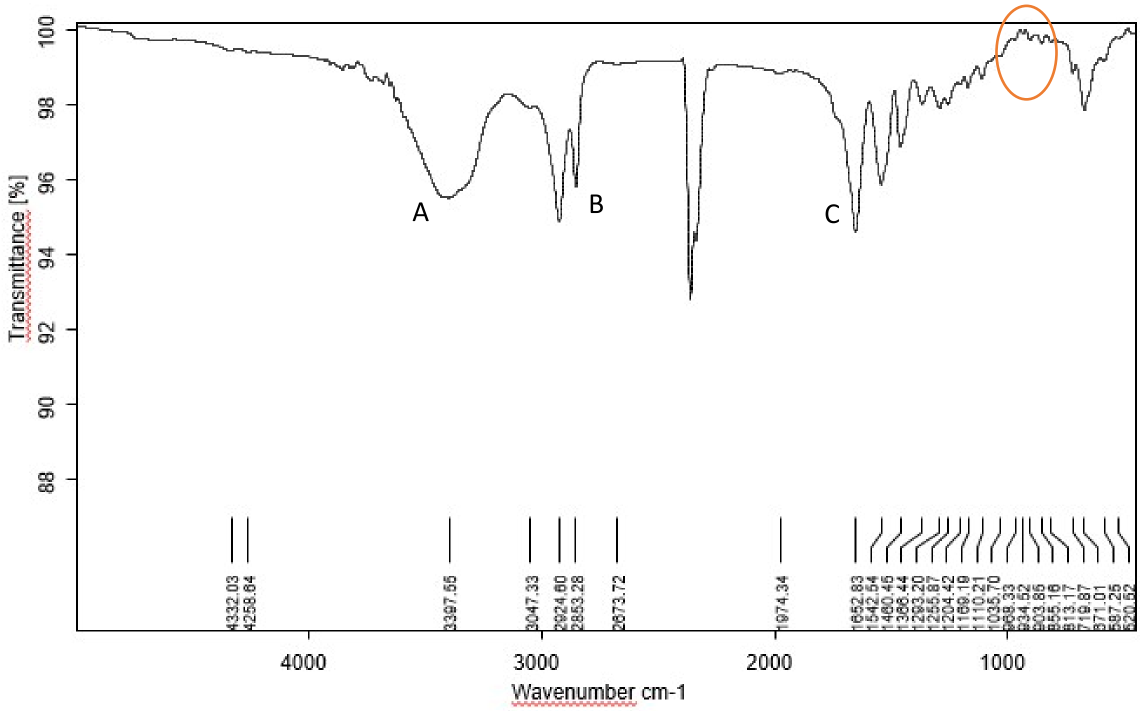

Figure S51. IR spectra of **4e**: A. 3397 cm^{-1} $\nu_{asymm.}$ CONH; B. 2924 – 2853 ν CH_2; C. 1652 cm^{-1} δ CONH.

S52. Numbering of 3b – 4b

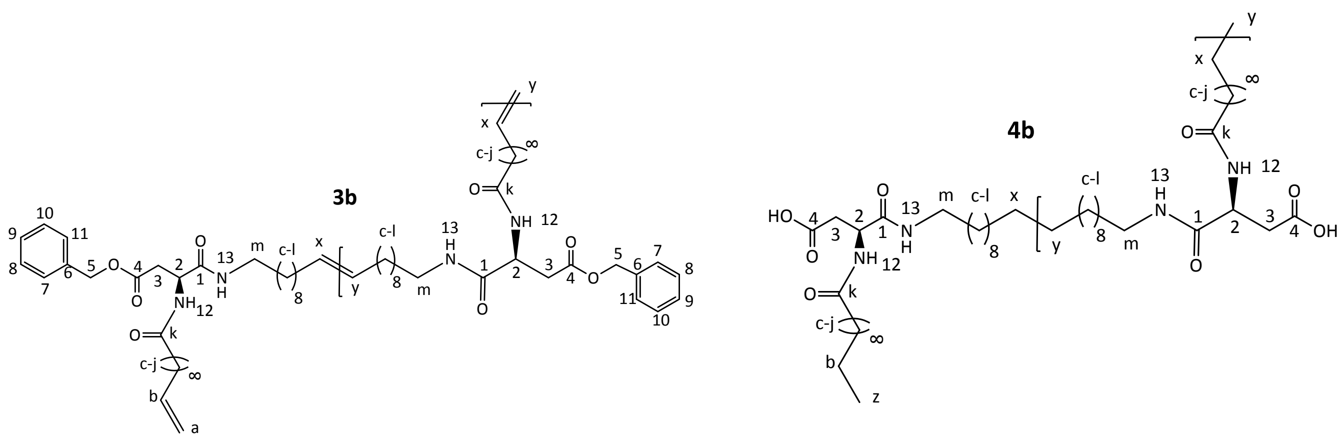

Figure S52. Numbering of 3b – 4b

S53. Numbering of 3c – 4c

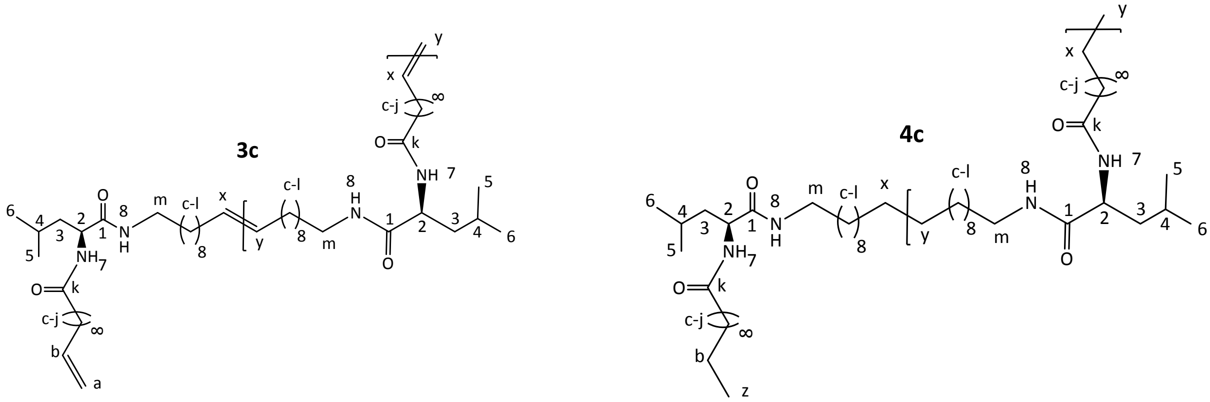

Figure S53. Numbering of 3c – 4c