

SUPPLEMENTARY INFORMATION

OLEFIN CROSS-METATHESIS AS A VALUABLE TOOL FOR THE PREPARATION OF RENEWABLE POLYESTERS AND POLYAMIDES FROM UNSATURATED FATTY ACID ESTERS AND CARBAMATES

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1. Materials

1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD, 99 %, Sigma Aldrich), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 98 %, Sigma Aldrich), benzyl alcohol (>99 %, Sigma Adrich), dimethylcarbonate (99 %, Acros), 2-mercaptoethanol (>99 %, Sigma Aldrich), methyl thioglycolate (95 %, Sigma Aldrich), methyl acrylate (99 %, containing ≤100 ppm monomethyl ether hydroquinone as inhibitor, Sigma Aldrich), Hoveyda-Grubbs 2nd generation catalyst (97 %, Sigma Aldrich), hexylamine (99 %, Acros), methyl oleate and methyl erucate (~92 %) was kindly provided by Croda, nylon 11 (Sigma Aldrich), nylon 12 (Sigma Aldrich). The hydroxamic acids necessary for Lossen rearrangements were prepared according to an already reported procedure of our group.¹ Dibenzyl carbonate was prepared by simple transesterification of dimethyl carbonate.² All solvents (technical grade) were used without purification.

2. Characterization

^1H -NMR measurements were performed on a Bruker Avance spectrometer operating at 300 MHz for ^1H and 75 MHz for ^{13}C . All samples were dissolved in CDCl_3 and the chemical shifts δ are reported in ppm relative to TMS. In case of the ^1H -NMR measurements of the prepared polyamides, drops of trifluoroacetic anhydride were added to dissolve the polymers in CHCl_3 .

For the characterization of the prepared polymers two different SEC systems were used. Determinations of molecular weights of the prepared polyamides were performed on a Tosoh EcoSEC HLC-8320 SEC system with HFIP containing 0.1 wt-% potassium trifluoroacetate as the solvent. The solvent flow was 0.40 mL/min at 30 °C. The analysis was performed on a three column system: PSS PFG Micro precolumn ($3.0 \times 0.46\text{cm}$, 10.000\AA), PSS PFG Micro ($25.0 \times 0.46\text{cm}$, 1000\AA) and PSS PFG Micro ($25.0 \times 0.46\text{cm}$, 100\AA). The system was calibrated with linear poly(methylmethacrylate) standards (Polymer Standard Service, Mp 102 – 981 000 Da). The molecular weights of the prepared polyesters were determined with a SEC System LC-20A from Shimadzu equipped with a SIL-20A autosampler, RID-10A refractive index detector operating on THF (flow rate 1 mL/min) at 50 °C. The analysis was performed on the following column system: main-column PSS SDV analytical ($5\mu\text{m}$, $300\text{ mm} \times 8.0\text{ mm}$, 10000\AA) with a PSS SDV analytical pre-column ($5\mu\text{m}$, $50\text{mm} \times 8.0\text{ mm}$). The calibration was created using narrow linear poly(methylmethacrylate) standards (Polymer Standards Service PPS, Germany) ranging from 1100 to 981 000 Da.

High resolution mass (HRMS) FAB or EI spectra were measured on a Finnigan MAT 95.

Differential scanning calorimetry (DSC) experiments were carried out on a DSC821e (Mettler Toledo) calorimeter, under nitrogen atmosphere, at a heating rate of $10\text{ }^\circ\text{C} \times \text{min}^{-1}$ up to a temperature of 300 °C, and using a sample mass of approximately 5 mg. Data (T_g and T_m) from second heating scans are reported. The melting temperature, T_m , is recorded as the minimum (endothermic transitions are represented downwards) of the endothermic melting peak.

Tensile-stress measurements were performed on a Gabo Eplexor 150N instrument using compression molten polymer samples and a 25 N force probe head. The compression molten polymer samples ($2\text{ cm} \times 1\text{ cm} \times 1\text{ mm}$) were prepared with a Weber press PW10 heating the polymer samples to 10°C above the corresponding melting point and pressing the samples with a pressure of 10 kN for 10 min, then slowly cooling down to room temperature. The polymer samples were precondition at ambient temperature and humidity. The measurements were performed with the following parameters: Target Load (force) = 23.00 N, strain rate = 1 %/min, max. elongation = 5 mm, initial load = 0.50 N. The E-modulus was determined by a linear fit (see Figure 34).

3. Experimental procedures / Results

a) General procedure for the Lossen rearrangement

To a mixture of the corresponding hydroxamic acid (10.0 mmol), dibenzyl carbonate (100 mmol) and benzyl alcohol (10 mmol) was added. After the reaction mixture was heated to 120 °C, TBD (2.00 mmol) was added and stirring was kept overnight. The crude reaction mixture was filtrated over a short silica pad while using ethyl acetate as eluent. After removal of ethyl acetate, the benzyl alcohol and dibenzyl carbonate were redistilled under reduced pressure (10^{-3} - 10^{-4} mbar) at a temperature of about 155 °C.

The mixture of dibenzyl carbonate and benzyl alcohol can be reused after analysis of the distillate by NMR and GC-MS.

Caution has to be taken for the distillation of benzyl alcohol and dibenzyl carbonate in case of the methyl undecenoate carbamate via Kugelrohr distillation, since here the vacuum and temperature has to be well adjusted to obtain a good separation of the methyl undecenoate carbamate and the reagents.

Benzyl dec-9-en-1-ylcarbamate (1)

Purification *via* column chromatography (hexane : ethyl acetate = 11 : 1 \rightarrow 7 : 1) led to a low melting colorless solid (yield 78 %).

$^1\text{H-NMR}$ (CDCl_3 , 300 MHz) δ / ppm: 7.40 – 7.29 (m, 5H, Ph), 5.89 - 5.73 (m, 1H, $-\text{CH}=\text{CH}_2$), 5.09 (s, 2H, $-\text{CH}_2\text{-Ph}$), 5.04 – 4.85 (m, 2H, $-\text{CH}=\text{CH}_2$), 4.74 (bs, 1H, NH), 3.27 – 3.09 (m, 2H, $-\text{CH}_2\text{-NH-}$), 2.10 – 1.94 (m, 2H, $-\text{CH}_2\text{-}$), 1.55 – 1.20 (m, 12H, $-\text{CH}_2\text{-}$).

$^{13}\text{C-NMR}$ (CDCl_3 , 75 MHz) δ / ppm: 156.5, 139.3, 136.8, 128.6, 128.2, 128.2, 114.3, 66.7, 41.2, 33.9, 30.1, 29.5, 29.3, 29.1, 29.0, 26.8.

HRMS (FAB):

$\text{C}_{18}\text{H}_{27}\text{NO}_2$ $[\text{M}+\text{H}]^+$ calc. 290.2115 found 290.2112.

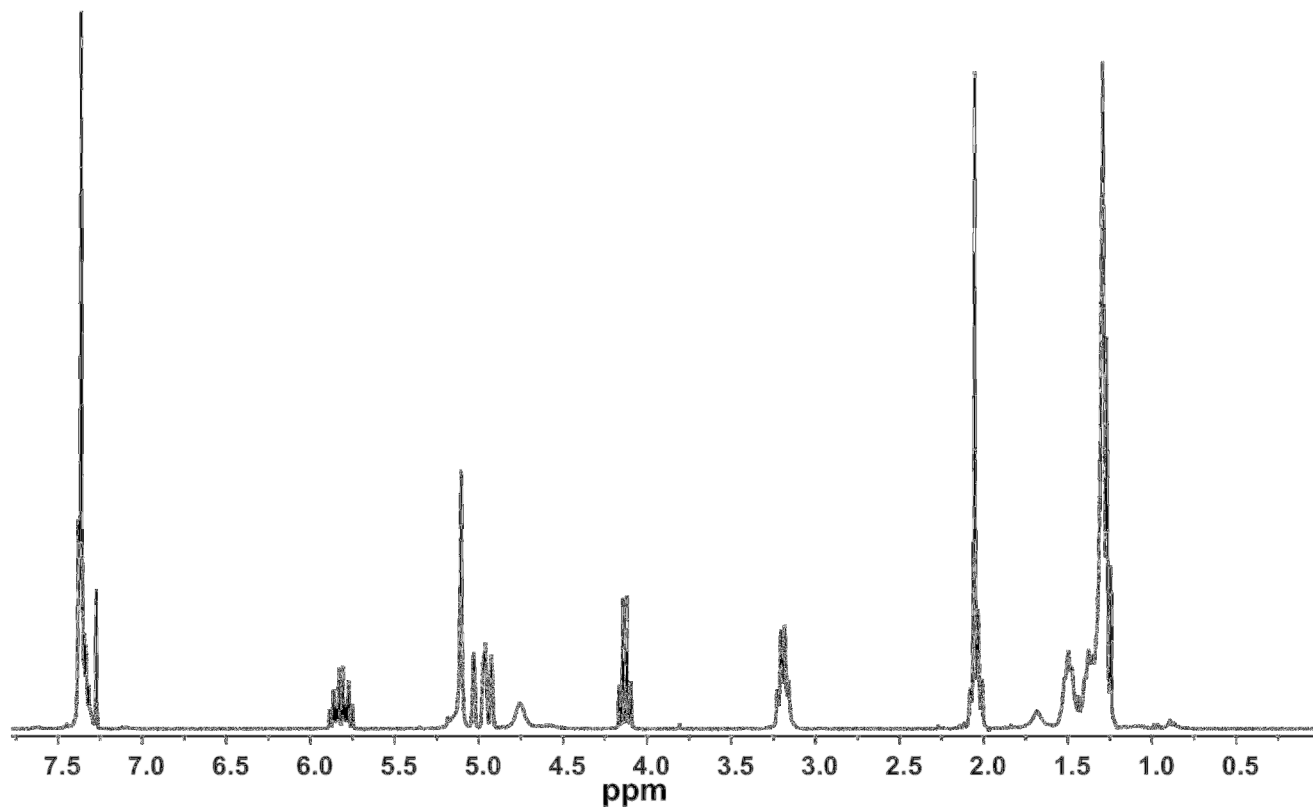


Figure 1: $^1\text{H-NMR}$ (300 MHz/ CDCl_3) of benzyl dec-9-en-1-ylcarbamate (1).

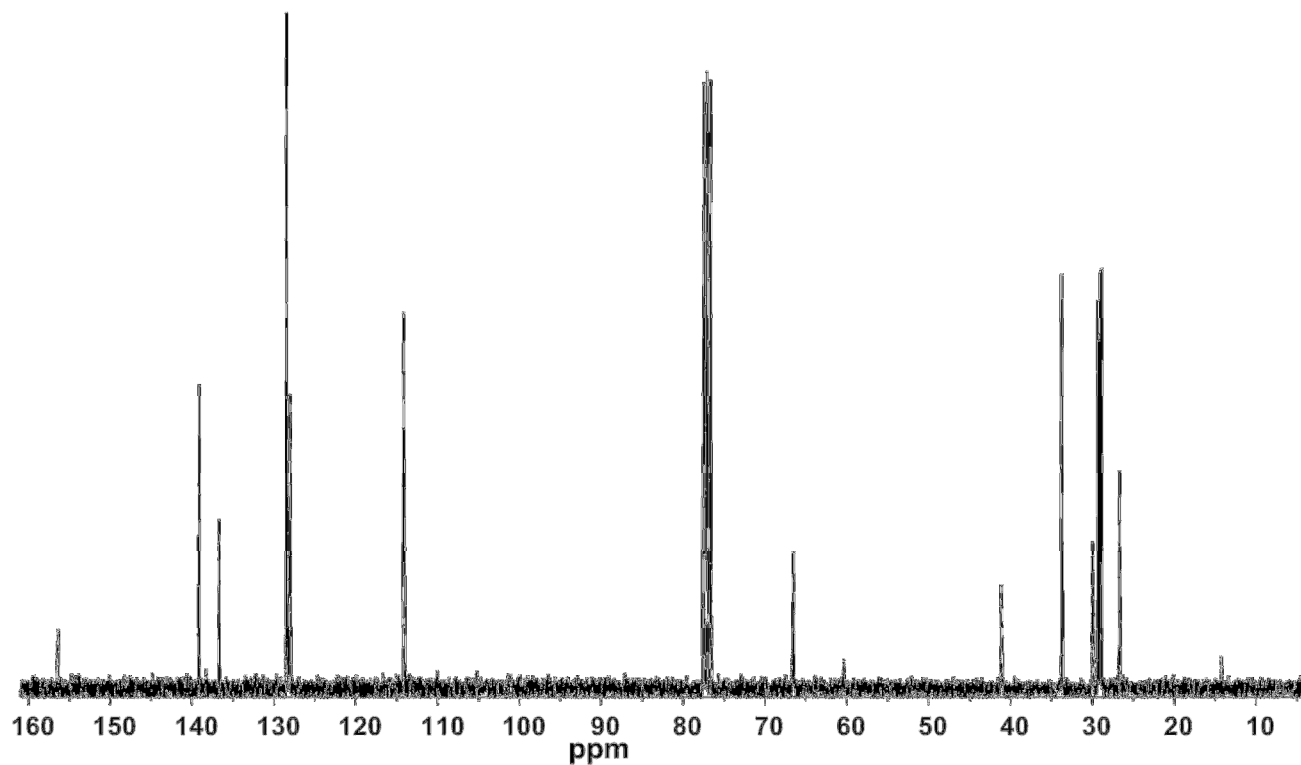


Figure 2: ^{13}C -NMR (75 MHz/ CDCl_3) of benzyl dec-9-en-1-ylcarbamate (**1**).

Benzyl heptadec-8-en-1-ylcarbamate (2**)**

Purification *via* column chromatography (hexane : diethyl ether = 12:1 \rightarrow 7 : 1) led to a colorless solid (yield 75 %).

^1H -NMR (CDCl_3 , 300 MHz) δ / ppm: 7.41 – 7.28 (m, 5H, Ph), 5.43 – 5.28 (m, 2H, $-\text{CH}=\text{CH}-$), 5.10 (s, 2H, $-\text{CH}_2\text{-Ph}$), 4.76 (bs, 1H, NH), 3.26 – 3.07 (m, 2H, $-\text{CH}_2\text{-NH}$), 2.10 – 1.90 (m, 4H, $-\text{CH}_2\text{-CH}=\text{CH-CH}_2-$), 1.60 – 1.12 (m, 22H, $-\text{CH}_2-$), 0.88 (t, J = 6.6 Hz, 3H, $-\text{CH}_3$).

^{13}C -NMR (CDCl_3 , 75 MHz) δ / ppm: 156.92, 156.5, 136.8, 130.1, 129.8, 128.6, 128.2, 66.7, 41.2, 32.0, 30.1, 29.9, 29.8, 29.7, 29.4, 29.3, 27.3, 26.8, 22.8, 14.2.

HRMS (FAB):

$\text{C}_{25}\text{H}_{41}\text{NO}_2$ $[\text{M}+\text{H}]^+$ calc. 388.3210 found 388.3212.

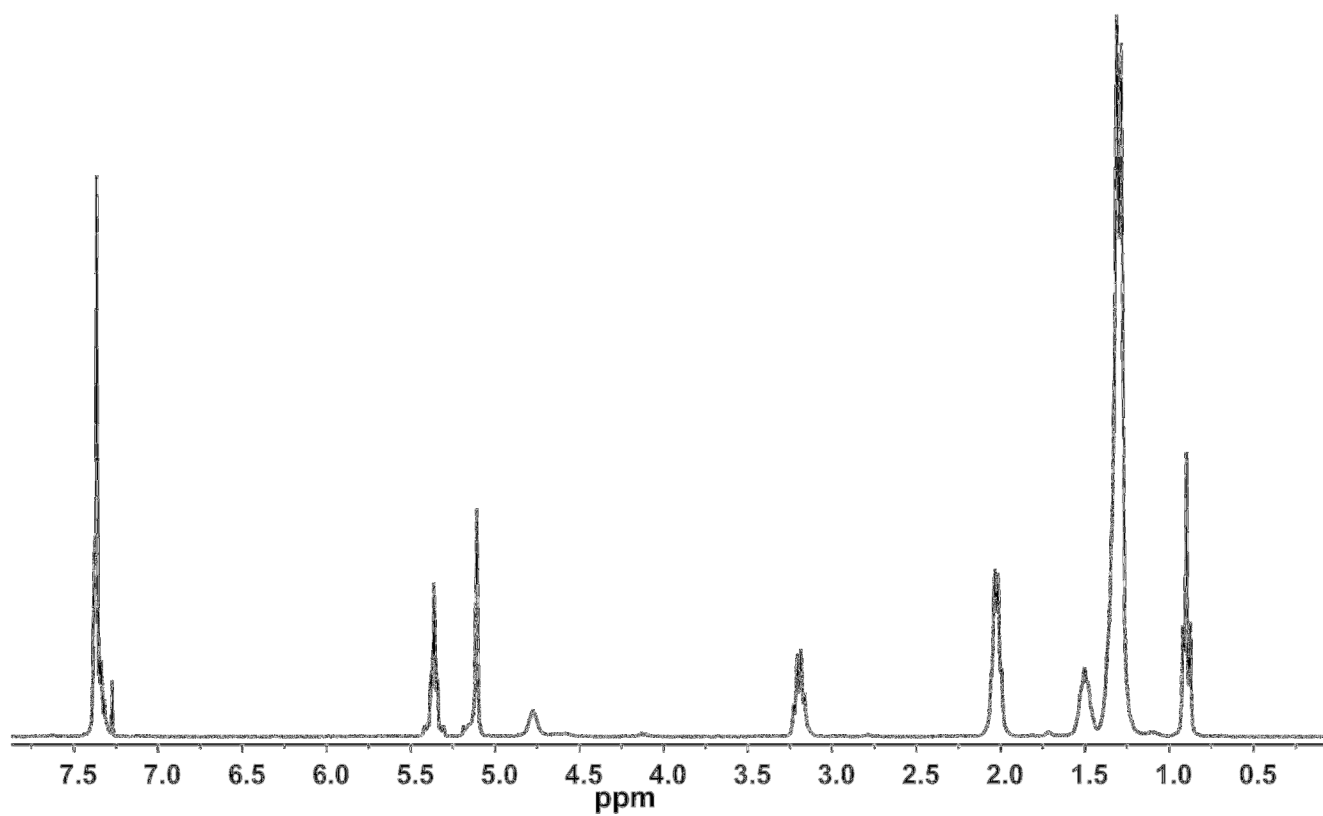


Figure 3: ^1H -NMR (300 MHz/ CDCl_3) of benzyl heptadec-8-en-1-ylcarbamate (2).

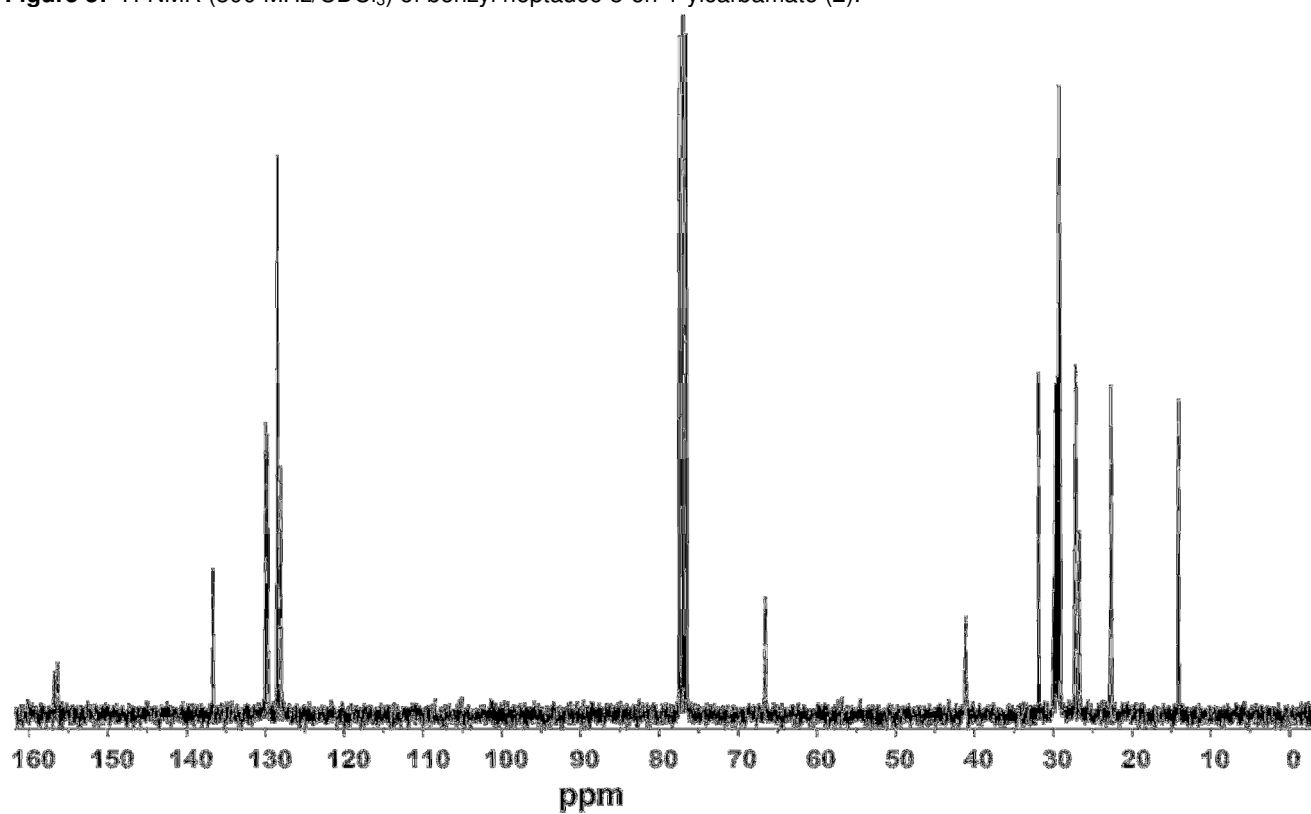


Figure 4: ^{13}C -NMR (75 MHz/ CDCl_3) of benzyl heptadec-8-en-1-ylcarbamate (2).

Benzyl henicos-12-en-1-ylcarbamate (3)

Purification *via* column chromatography (hexane : diethyl ether = 12 : 1 \rightarrow 7 : 1) led to a colorless solid (yield 80 %).

^1H -NMR (CDCl_3 , 300 MHz) δ / ppm: 7.45 – 7.29 (m, 5H, Ph), 5.43 – 5.29 (m, 2H, $-\text{CH}=\text{CH}-$), 5.10 (s, 2H, $-\text{CH}_2\text{-Ph}$), 4.76 (bs, 1H, NH), 3.24 – 3.07 (m, 2H, $-\text{CH}_2\text{-NH}$), 2.14 – 1.91 (m, 4H, $-\text{CH}_2\text{-CH}=\text{CH-CH}_2-$), 1.62 – 1.15 (m, 30H, $-\text{CH}_2-$), 0.89 (t, $J = 6.6$ Hz, 3H, $-\text{CH}_3$).

^{13}C -NMR (CDCl_3 , 75 MHz) δ / ppm: 156.9, 156.5, 136.8, 130.1, 129.8, 128.6, 128.2, 41.2, 32.0, 30.1, 29.9, 29.8, 29.7, 29.4, 29.3, 27.3, 26.8, 22.8, 14.2.

HRMS (FAB):

$\text{C}_{29}\text{H}_{49}\text{NO}_2$ $[\text{M}+\text{H}]^+$ calc. 444.3836 found 444.3835.

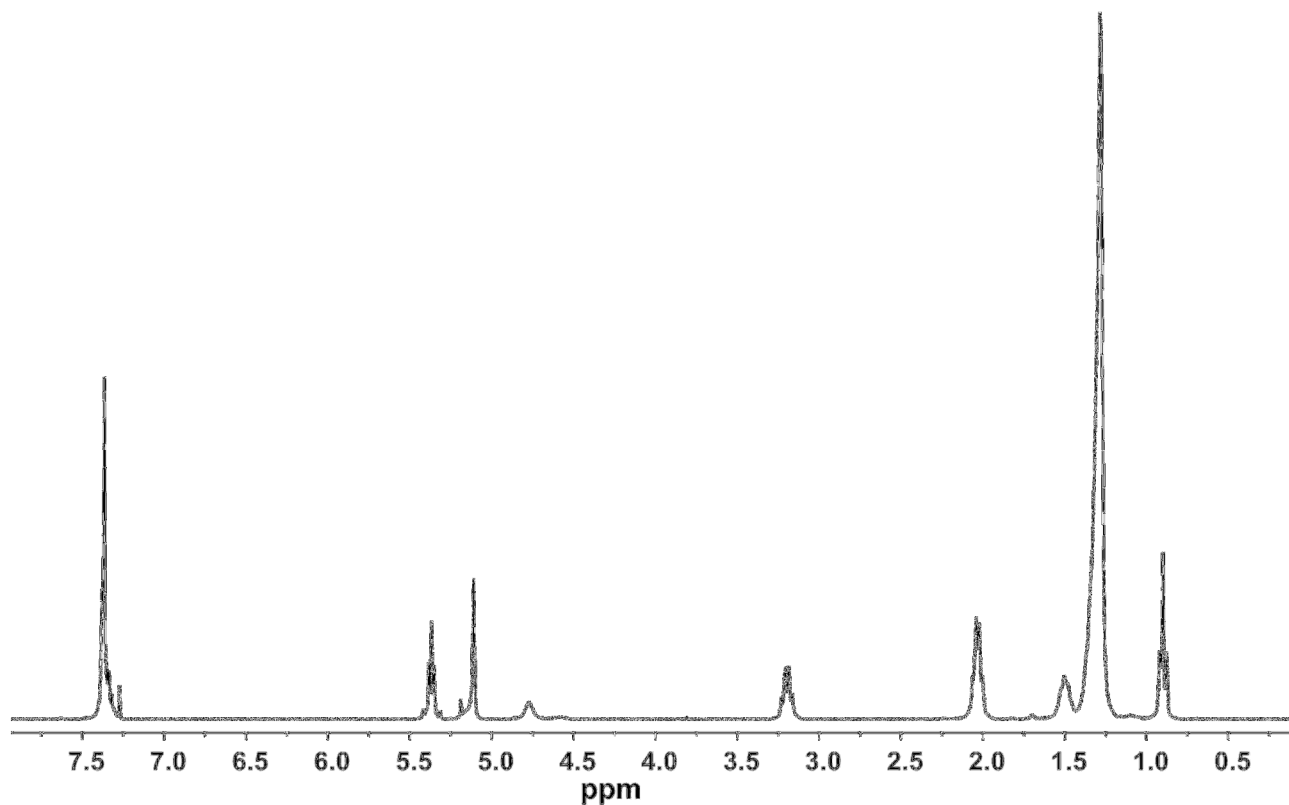


Figure 5: ^1H -NMR (300 MHz/ CDCl_3) of benzyl henicos-12-en-1-ylcarbamate (**3**).

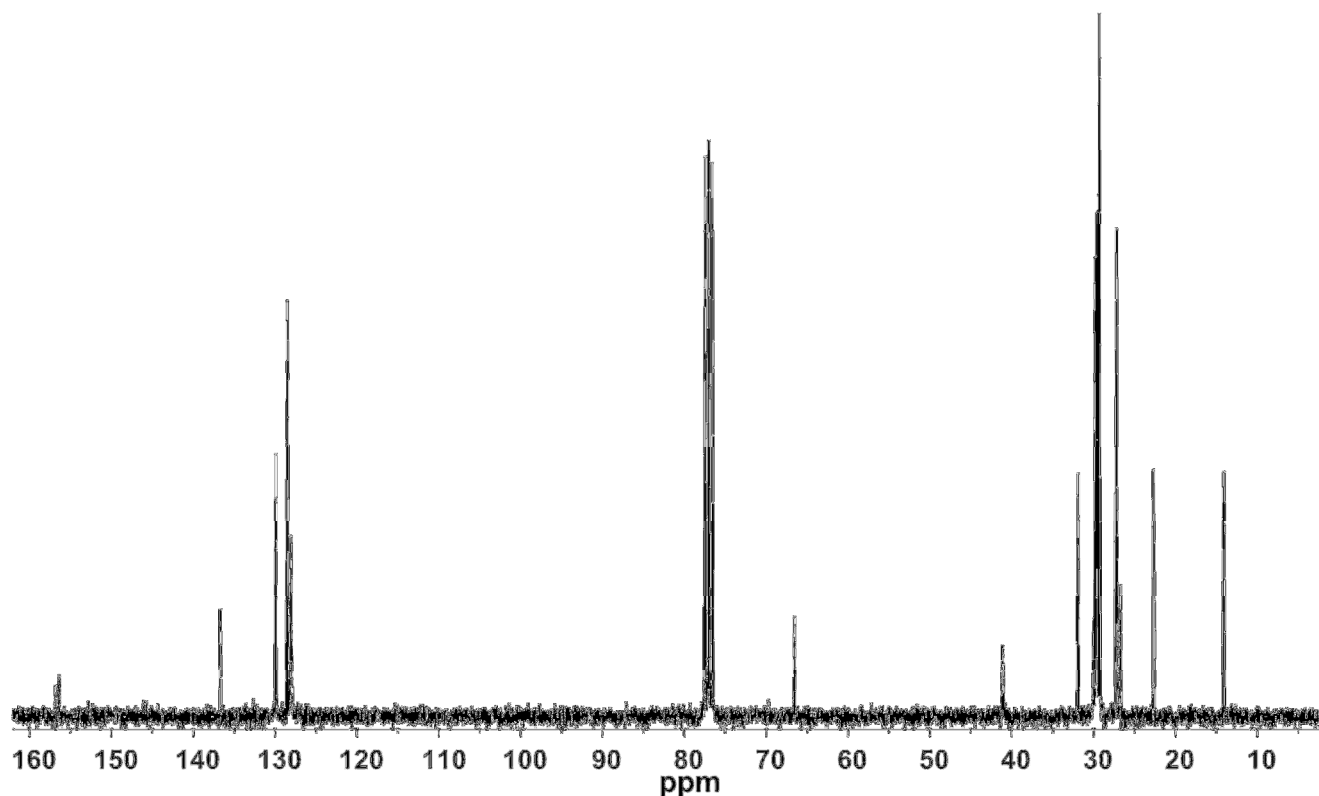


Figure 6: ^{13}C -NMR (75 MHz/ CDCl_3) of benzyl henicos-12-en-1-ylcarbamate (**3**).

b) Cross-metathesis of benzyl carbamates

Methyl 10-(((benzyloxy)carbonyl)amino)dec-2-enoate (**4**)

To a vigorously stirred mixture of 2.20 g carbamate **2** (5.68 mmol) and 4.89 g methyl acrylate (56.7 mmol) at 50 °C, 17.8 mg of the Hoveyda-Grubbs 2nd generation catalyst (0.5 mol%) was added. The reaction mixture was stirred under an argon atmosphere for 16 hours. Then, ethyl vinyl ether was added to quench the reaction. Methyl acrylate was evaporated and the crude reaction mixture was purified *via* column chromatography (hexane : ethyl acetate: 7 : 1 \rightarrow 4 : 1). Pure **4** was obtained as colorless solid (yield 91 %).

^1H -NMR (CDCl_3 , 300 MHz) δ / ppm: 7.40 – 7.27 (m, 5H, Ph), 7.03 – 6.87 (m, 1H, $-(\text{CO})-\text{CH}-$), 5.80 (d, $J = 15.7$ Hz, 1H, $-\text{CH}=\text{CH}-$), 5.08 (s, 2H, $-\text{CH}_2-\text{Ph}$), 4.84 (bs, 1H, NH), 3.71 (s, 3H, $-\text{OMe}$), 3.27 – 3.06 (m, 2H, $-\text{CH}_2-\text{NH}$), 2.28 – 2.08 (m, 2H, $-\text{CH}_2-$), 1.58 – 1.16 (m, 10H, $-\text{CH}_2-$).

^{13}C -NMR (CDCl_3 , 75 MHz) δ / ppm: 167.2, 156.5, 149.7, 136.8, 128.6, 128.1, 121.0, 66.6, 51.4, 41.1, 32.2, 30.0, 29.1, 28.0, 26.6.

HRMS (FAB):

$\text{C}_{19}\text{H}_{27}\text{NO}_4$ $[\text{M}+\text{H}]^+$ calc. 334.2013 found 334.2015.

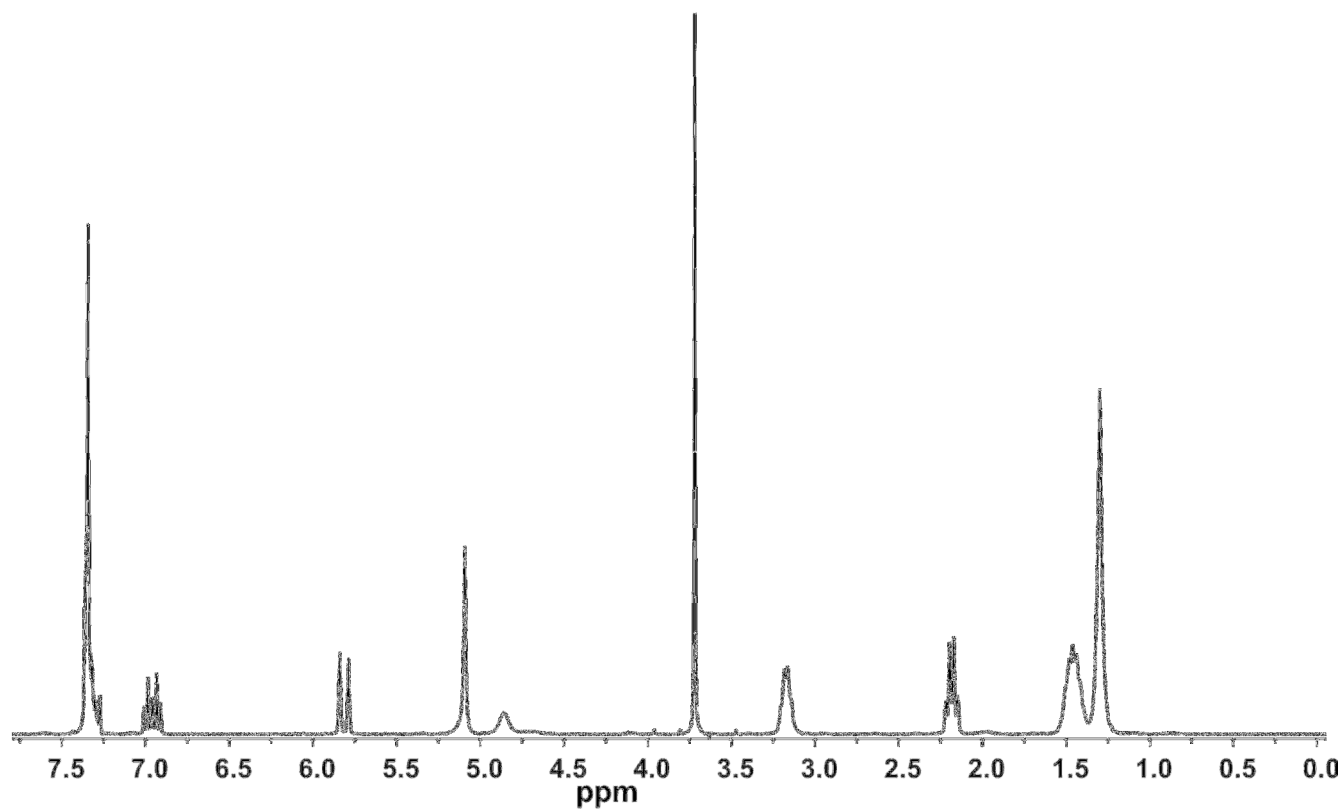


Figure 7: ^1H -NMR (300 MHz/ CDCl_3) of methyl 10-(((benzyloxy)carbonyl)amino)dec-2-enoate (**4**).

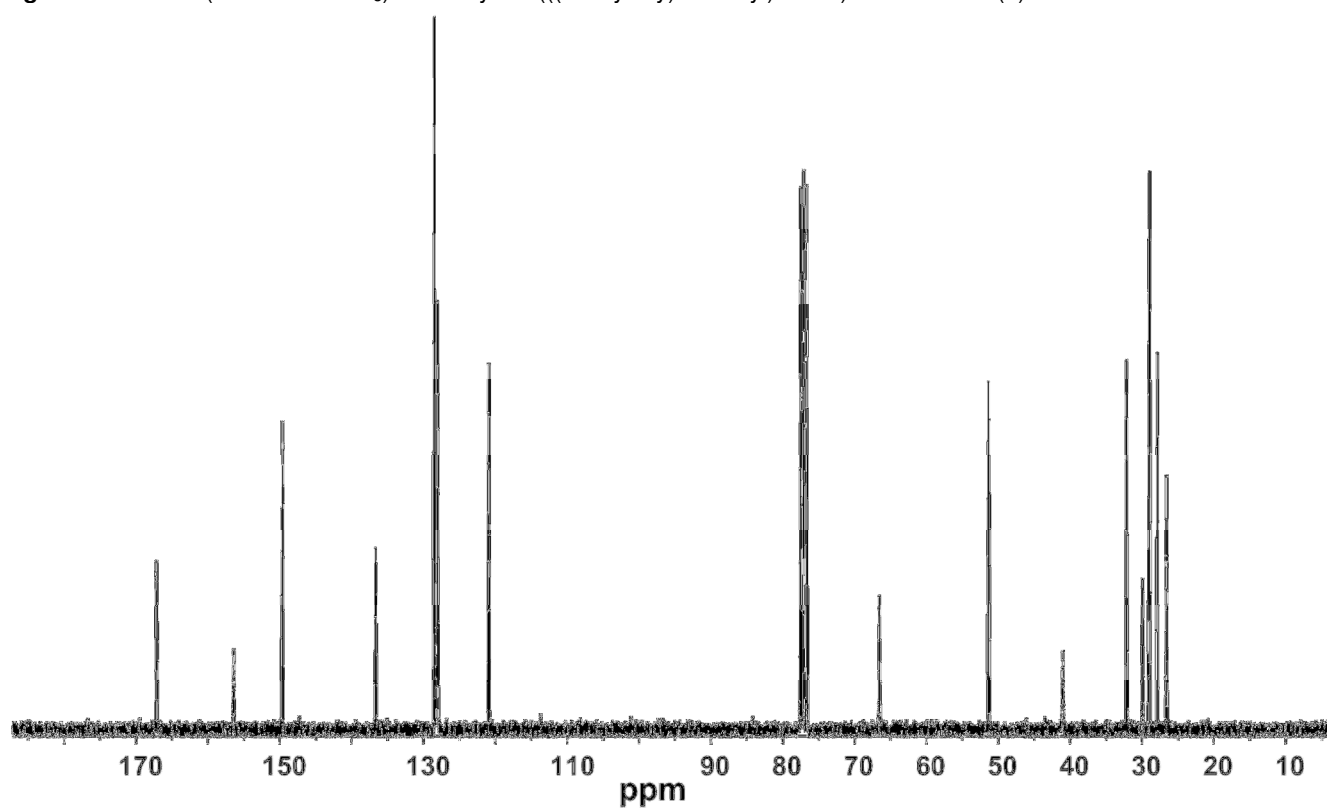


Figure 8: ^{13}C -NMR (75 MHz/ CDCl_3) of methyl 10-(((benzyloxy)carbonyl)amino)dec-2-enoate (**4**).

Methyl 11-(((benzyloxy)carbonyl)amino)undec-2-enoate (5)

To a vigorously stirred mixture of 2.00 g carbamate **1** (6.91 mmol) and 5.95 g methyl acrylate (69.1 mmol) at 25 °C, 21.7 mg of the Hoveyda-Grubbs 2nd generation catalyst (0.5 mol%) was added. Subsequently, the reaction temperature was raised to 50 °C within 20 min and stirred under an argon atmosphere for 16 hours at 50 °C. Then, ethyl vinyl ether was added to quench the reaction. Methyl acrylate was evaporated and the crude reaction mixture was purified *via* column chromatography (hexane : ethyl acetate: 7 : 1 → 4 : 1). Pure **5** was obtained as colorless solid (yield 90 %).

¹H-NMR (CDCl₃, 300 MHz) δ / ppm: 7.42 – 7.27 (m, 5H, Ph), 7.02 – 6.87 (m, 1H, -(CO)-CH-), 5.80 (d, J = 15.7 Hz, 1H, -CH=CH-), 5.08 (s, 2H, -CH₂-Ph), 4.84 (bs, 1H, NH), 3.71 (s, 3H, -OMe), 3.29 – 3.02 (m, 2H, -CH₂-NH), 2.28 – 2.05 (m, 2H, -CH₂-), 1.59 – 1.12 (m, 12H, -CH₂-).

¹³C-NMR (CDCl₃, 75 MHz) δ / ppm: 167.2, 156.5, 149.8, 136.8, 128.6, 128.1, 120.9, 66.6, 51.4, 41.2, 32.2, 30.0, 29.3, 29.2, 29.1, 28.0, 26.7.

HRMS (FAB):

C₂₀H₂₉NO₄ [M+H]⁺ calc. 348.2169 found 348.2167.

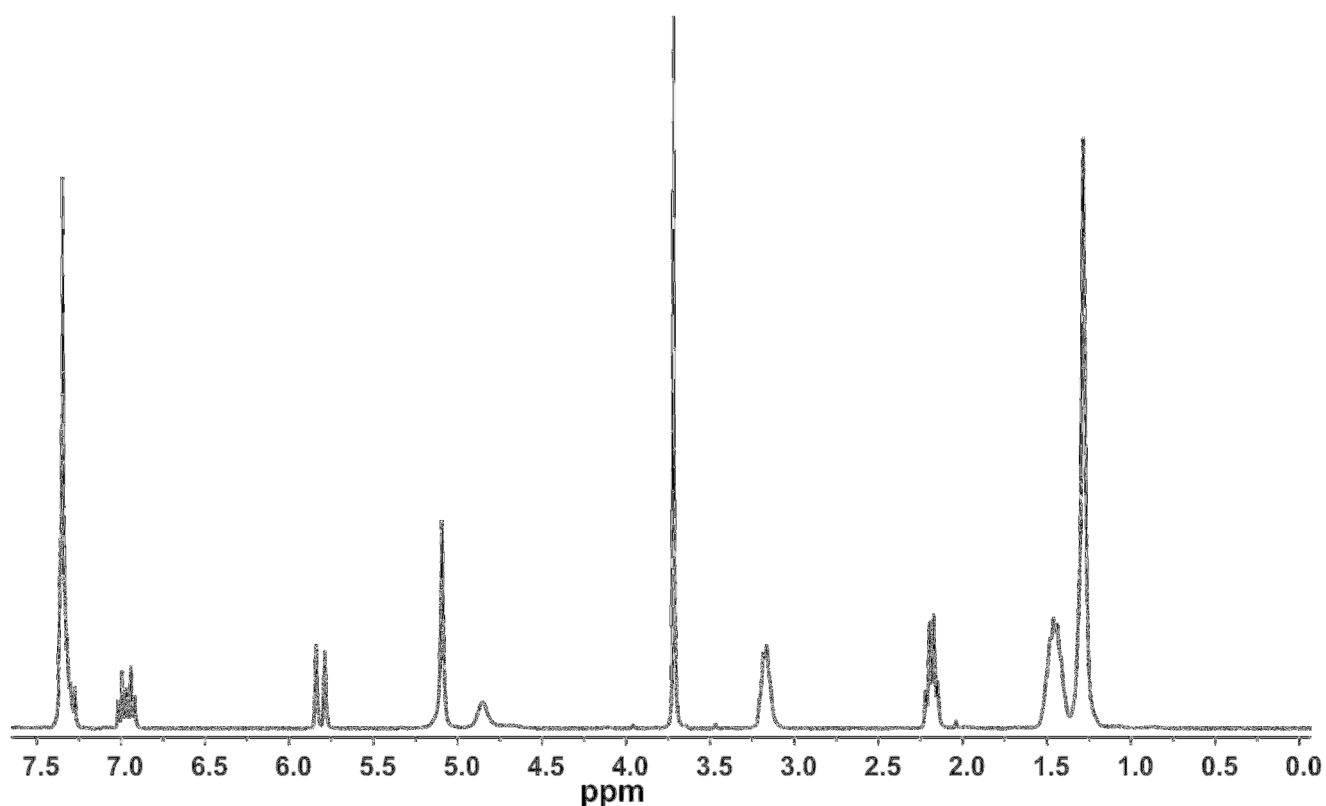


Figure 9: ¹H-NMR (300 MHz/CDCl₃) of methyl 11-(((benzyloxy)carbonyl)amino)undec-2-enoate (**5**).

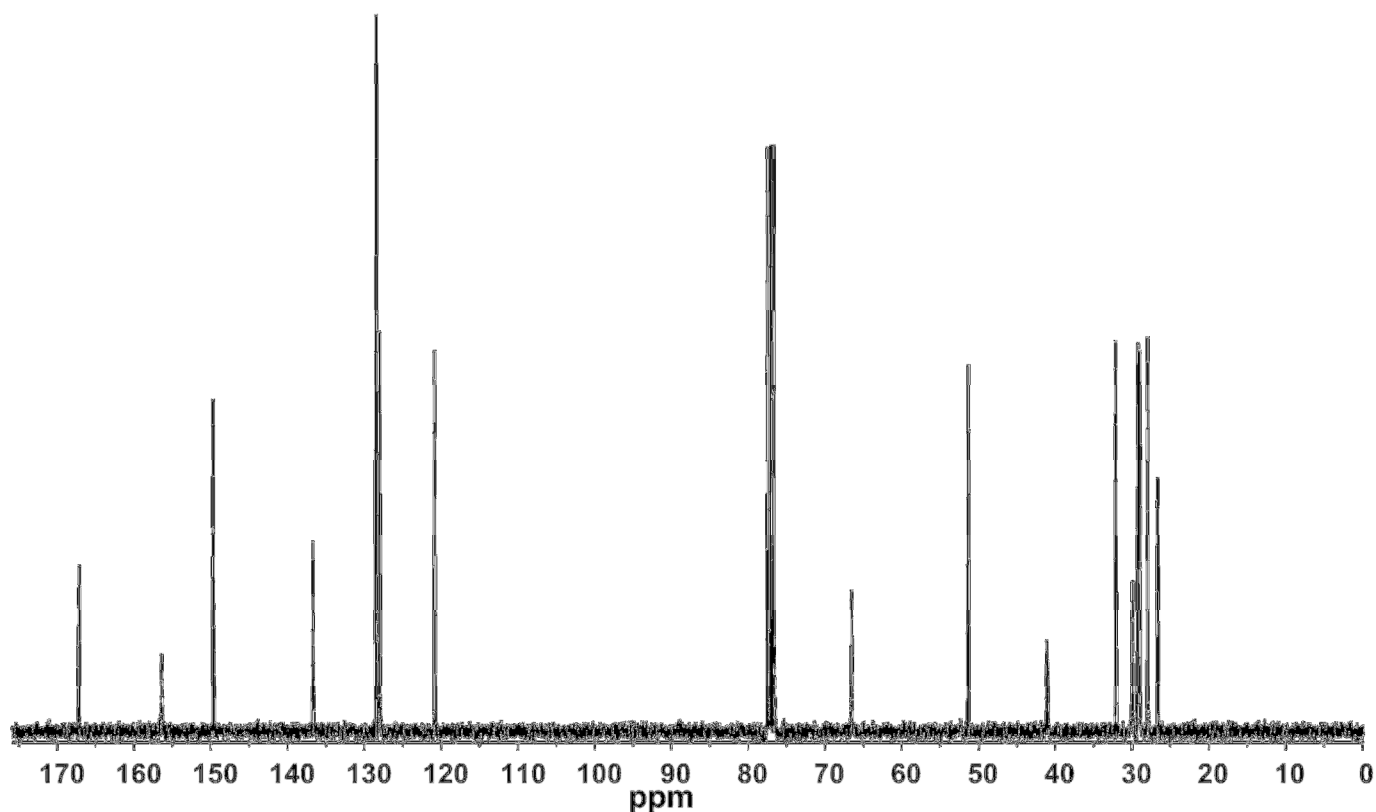


Figure 10: ^{13}C -NMR (75 MHz/ CDCl_3) of methyl 11-(((benzyloxy)carbonyl)amino)undec-2-enoate (**5**).

Methyl 14-(((benzyloxy)carbonyl)amino)tetradec-2-enoate (6**)**

To a vigorously stirred mixture of 1.50 g carbamate **3** (3.38 mmol) and 2.91 g methyl acrylate (33.4 mmol) at 50 °C, 10.6 mg of the Hoveyda-Grubbs 2nd generation catalyst (0.5 mol%) was added. The reaction mixture was stirred under an argon atmosphere for 16 hours. Then, ethyl vinyl ether was added to quench the reaction. Methyl acrylate was evaporated and the crude reaction mixture was purified *via* column chromatography (hexane : ethyl acetate: 7 : 1 \rightarrow 4 : 1). Pure **6** was obtained as colorless solid (yield 80 %).

^1H -NMR (CDCl_3 , 300 MHz) δ / ppm: 7.40 – 7.27 (m, 5H, Ph), 7.03 – 6.90 (m, 1H, -(CO)-CH-), 5.81 (d, J = 15.7 Hz, 1H, -CH=CH-), 5.08 (s, 2H, -CH₂-Ph), 4.83 (bs, 1H, NH), 3.71 (s, 3H, -OMe), 3.26 – 3.06 (m, 2H, -CH₂-NH), 2.26 – 2.10 (m, 2H, -CH₂-), 1.58 – 1.12 (m, 18H, -CH₂-).

^{13}C -NMR (CDCl_3 , 75 MHz) δ / ppm: 167.3, 156.5, 149.9, 136.8, 128.6, 128.1, 120.9, 66.6, 51.4, 41.2, 32.3, 30.0, 29.6, 29.5, 29.4, 29.3, 29.2, 28.1, 26.8.

HRMS (FAB):

$\text{C}_{23}\text{H}_{35}\text{NO}_4$ $[\text{M}+\text{H}]^+$ calc. 390.2639 found 390.2630.

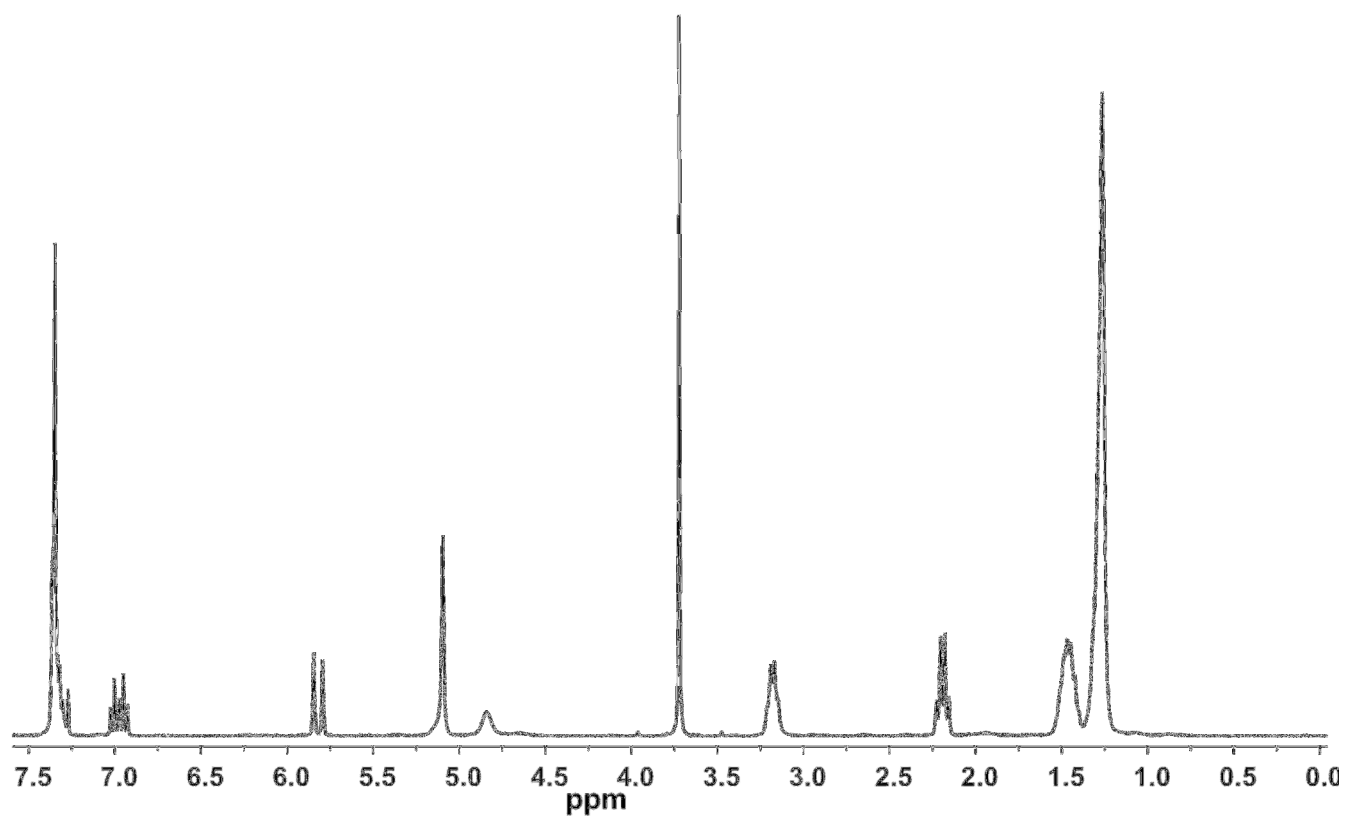


Figure 11: ¹H-NMR (300 MHz/CDCl₃) of methyl 14-(((benzyloxy)carbonyl)amino)tetradec-2-enoate (6).

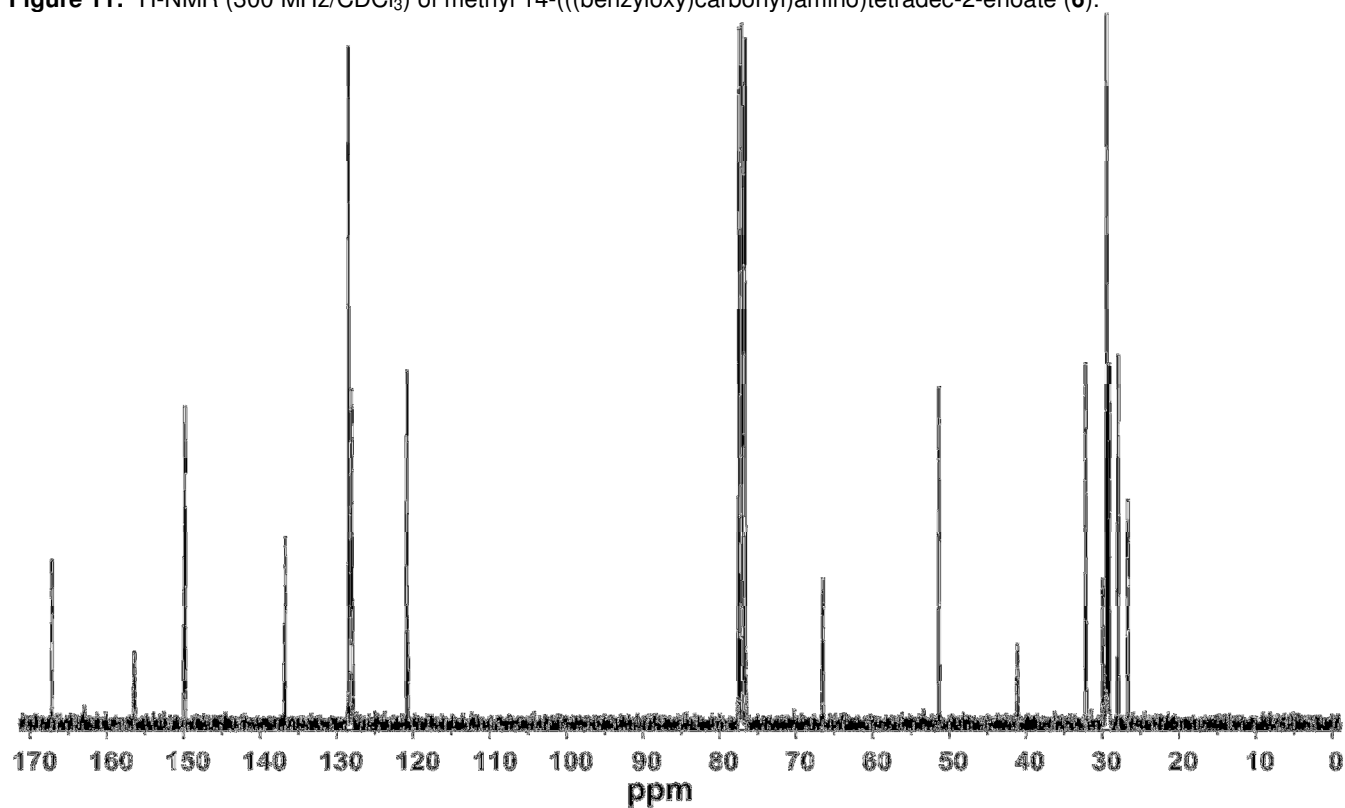


Figure 12: ¹³C-NMR (75 MHz/CDCl₃) of methyl 14-(((benzyloxy)carbonyl)amino)tetradec-2-enoate (6).

Methyl undec-2-enoate (7)

$^1\text{H-NMR}$ (CDCl_3 , 300 MHz) δ / ppm: 7.08 – 6.86 (m, 1H, $-\text{CH}=\text{CH}-$), 5.81 (d, $J = 15.6$ Hz, 1H, $\text{C}(\text{O})-\text{CH}=\text{CH}-$), 3.72 (s, 3H, $-\text{OMe}$), 2.28 – 2.08 (m, 2H, $-\text{CH}_2-$), 1.73 – 1.12 (m, 12H, $-\text{CH}_2-$), 0.87 (t, $J = 6.1$ Hz, 3H, $-\text{CH}_3$).

$^{13}\text{C-NMR}$ (CDCl_3 , 75 MHz) δ / ppm: 167.3, 149.9, 120.9, 51.5, 32.7, 32.5, 31.9, 29.6, 29.5, 29.2, 28.2, 22.8, 14.2.

HRMS (FAB):

$\text{C}_{12}\text{H}_{22}\text{O}_2$ $[\text{M}+\text{H}]^+$ calc. 199.1693 found 199.1698.

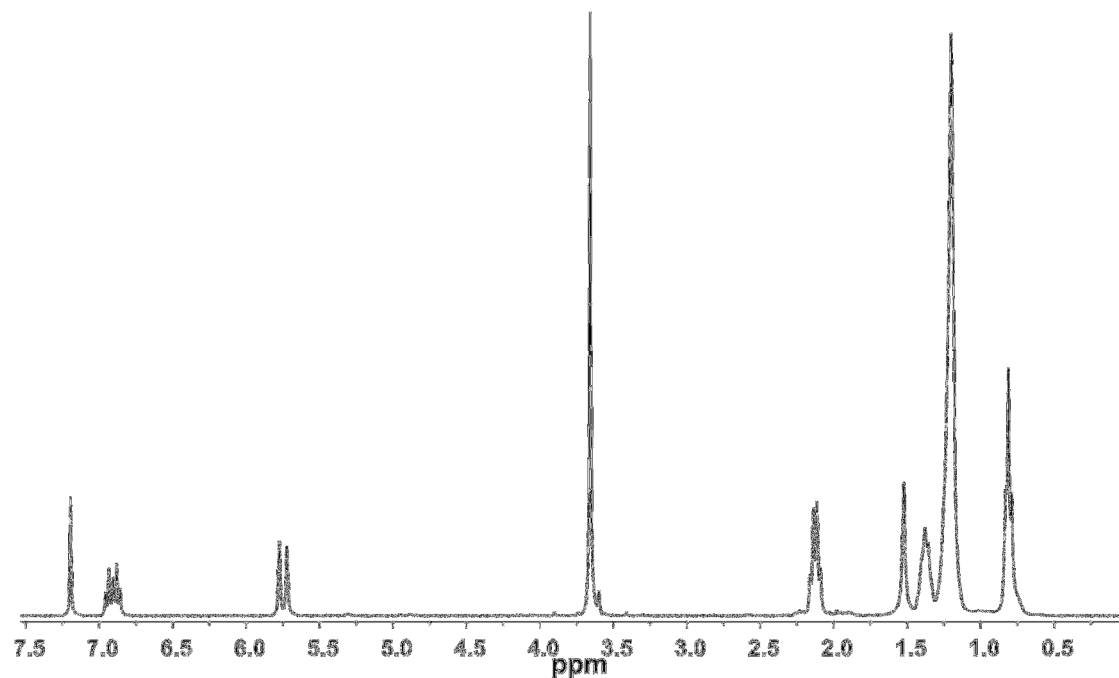


Figure 13: $^1\text{H-NMR}$ (300 MHz/ CDCl_3) of methyl undec-2-enoate (7).

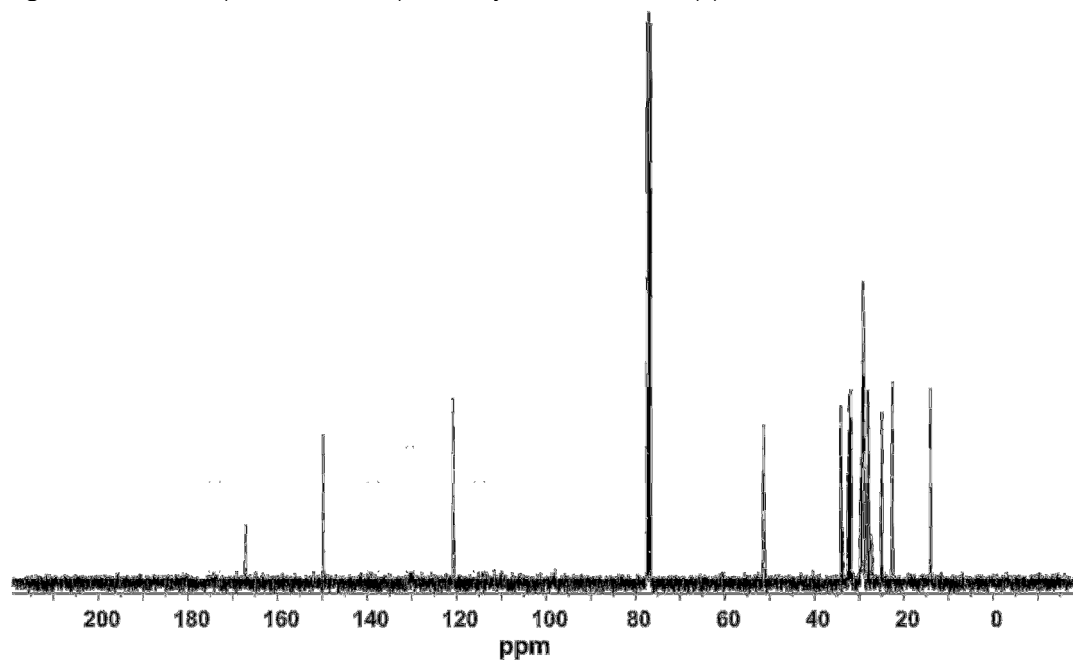


Figure 14: $^{13}\text{C-NMR}$ (75 MHz/ CDCl_3) of methyl undec-2-enoate (7).

c) General procedure for the carbamate cleavage

The benzyl carbamate (3.30 mmol) and $\text{Pd}(\text{OH})_2$ (10 wt%) were weighed into a round bottom flask capped with a septum. 25 mL methanol for carbamate **4** or 25 mL ethanol for carbamate **5-6** was added and hydrogen was gently bubbled through the reaction mixture for 15 min using a balloon. Subsequently, the reaction mixture was stirred at an atmospheric pressure of hydrogen at room temperature for 16 hours. The reaction mixture was filtrated over a pore size 4 filter and the solvent was removed under reduced pressure. The amino fatty acid methyl esters were obtained as colorless solids (yield 95-99 %).

Methyl 10-aminodecanoate (**8**)

^1H -NMR (CDCl_3 , 300 MHz) δ / ppm: 3.66 (s, 3H, -OMe), 2.69 (t, $J = 7.1$ Hz, 2H, $-\text{CH}_2\text{-NH}_2$), 2.59 (s, 2H, $-\text{NH}_2$), 2.29 (t, $J = 7.5$ Hz, 2H, $-\text{CH}_2\text{-COOMe}$), 1.68 – 1.53 (m, 2H, $-\text{CH}_2-$), 1.53 – 1.37 (m, 2H, $-\text{CH}_2-$), 1.38 – 1.21 (m, 10H, $-\text{CH}_2-$).

^{13}C -NMR (CDCl_3 , 75 MHz) δ / ppm: 174.4, 51.5, 41.5, 34.2, 32.3, 29.4, 29.4, 29.3, 29.2, 26.9, 25.0.

HRMS (EI):

$\text{C}_{11}\text{H}_{23}\text{NO}_2$: calc. 201.1723 found 201.1725.

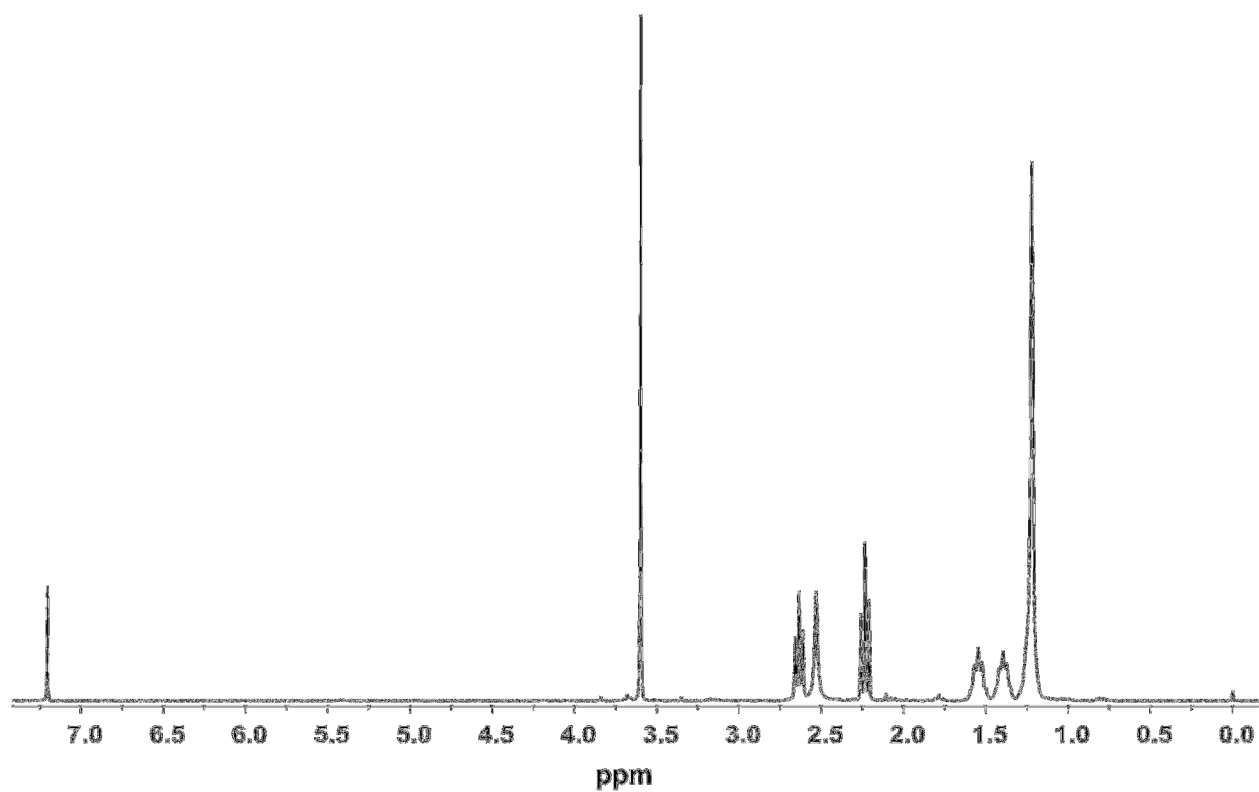


Figure 15: ^1H -NMR (300 MHz/ CDCl_3) of methyl 10-aminodecanoate (**8**).

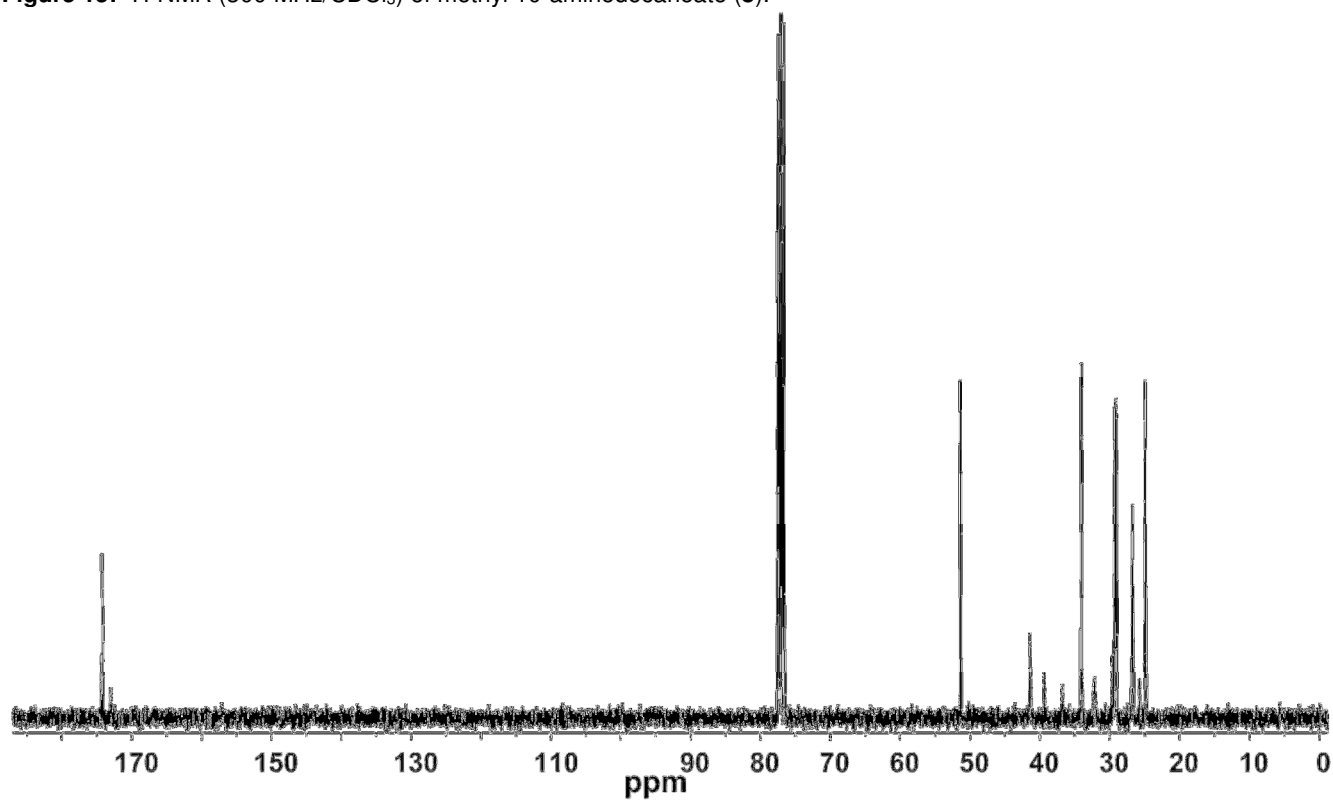


Figure 16: ^{13}C -NMR (75 MHz/ CDCl_3) of methyl 10-aminodecanoate (**8**).

Methyl 11-aminoundecanoate (9)

^1H -NMR (CDCl_3 , 300 MHz) δ / ppm: 3.64 (s, 3H, OMe), 2.66 (t, $J = 7.0$ Hz, 2H, $-\text{CH}_2\text{-NH}_2$), 2.28 (t, $J = 7.5$ Hz, 2H, $-\text{CH}_2\text{-COOMe}$), 1.99 (bs, 2H, $-\text{NH}_2$), 1.68 – 1.52 (m, 2H, $-\text{CH}_2-$), 1.48 – 1.14 (m, 14H, $-\text{CH}_2-$).

^{13}C -NMR (CDCl_3 , 75 MHz) δ / ppm: 174.4, 51.5, 42.1, 34.2, 33.4, 29.6, 29.5, 29.4, 29.3, 29.2, 26.9, 25.0.

HRMS (EI):

$\text{C}_{12}\text{H}_{25}\text{NO}_2$: calc. 215.1880 found 215.1881.

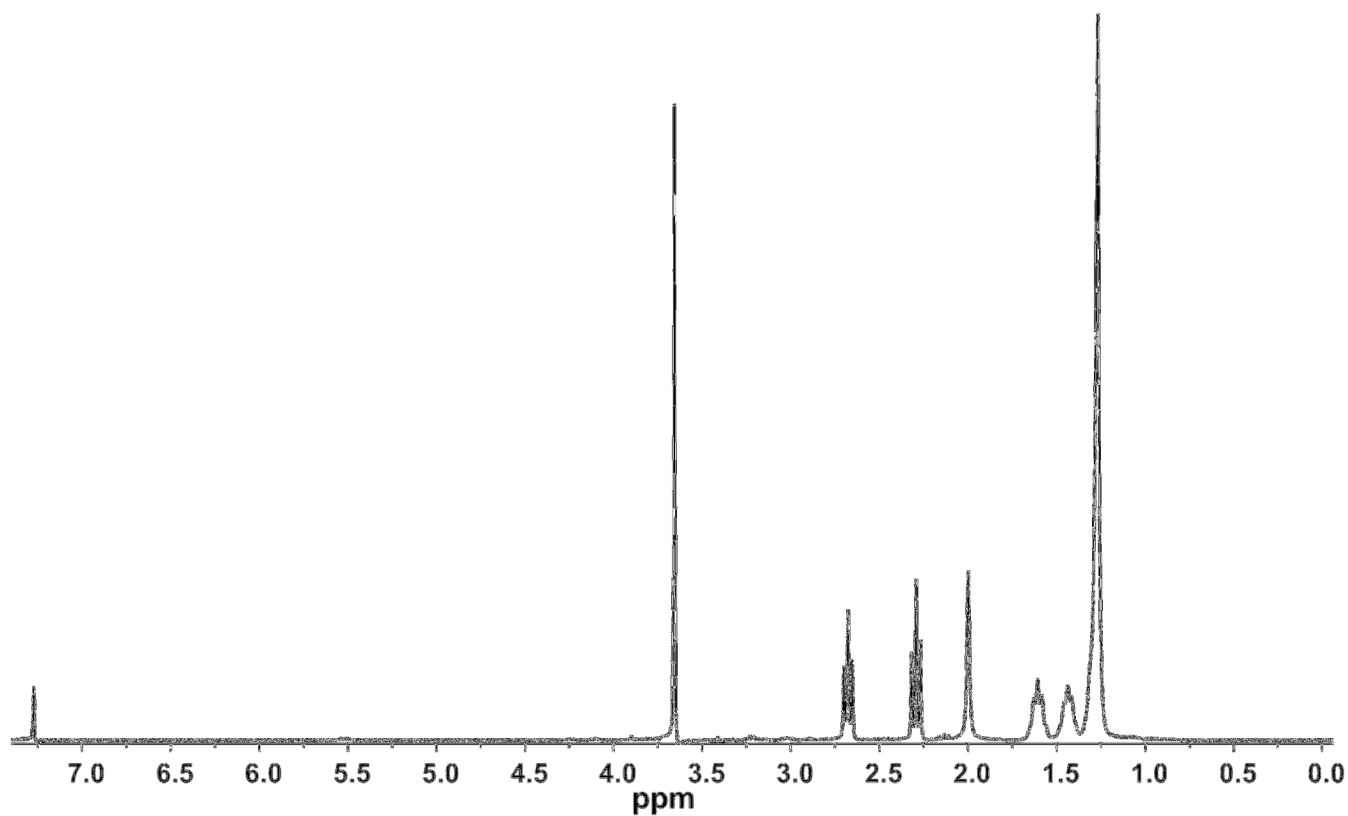


Figure 17: ^1H -NMR (300 MHz/ CDCl_3) of methyl 11-aminoundecanoate (9).

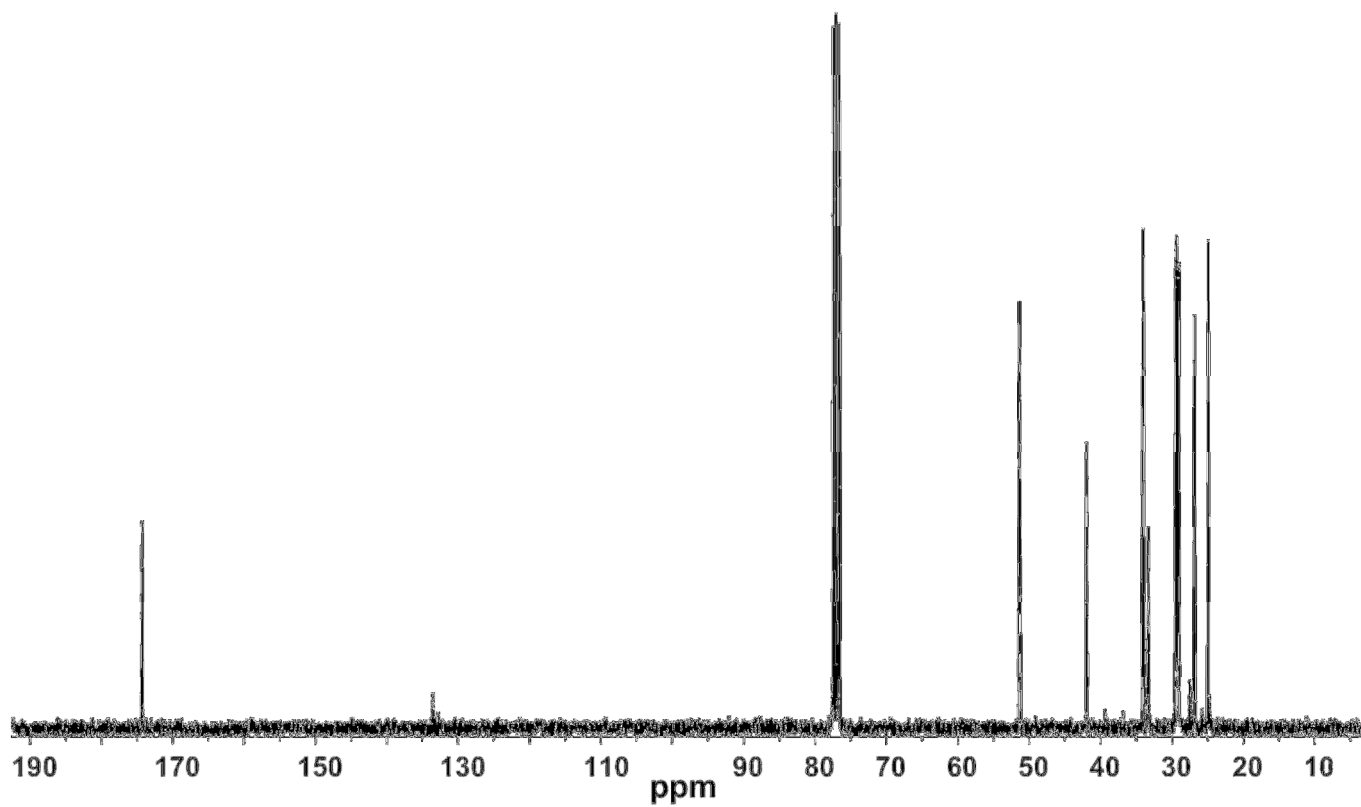


Figure 18: ^{13}C -NMR (75 MHz/ CDCl_3) of methyl 11-aminoundecanoate (9).

Methyl 14-aminotetradecanoate (10)

^1H -NMR (CDCl_3 , 300 MHz) δ / ppm: 3.63 (s, 3H, OMe), 2.66 (t, $J = 7.0$ Hz, 2H, $-\text{CH}_2-\text{NH}_2$), 2.27 (t, $J = 7.5$ Hz, 2H, $-\text{CH}_2-\text{COOMe}$), 2.19 (bs, 2H, $-\text{NH}_2$), 1.65 – 1.50 (m, 2H, $-\text{CH}_2-$), 1.49 – 1.35 (m, 2H, $-\text{CH}_2-$), 1.34 – 1.13 (m, 18H, $-\text{CH}_2-$).

^{13}C -NMR (CDCl_3 , 75 MHz) δ / ppm: 174.4, 51.5, 42.1, 34.2, 33.4, 29.7, 29.6, 29.5, 29.3, 29.2, 27.0, 25.0.

HRMS (FAB):

$\text{C}_{15}\text{H}_{31}\text{NO}_2$ $[\text{M}+\text{H}]^+$ calc. 258.2428 found 258.2425.

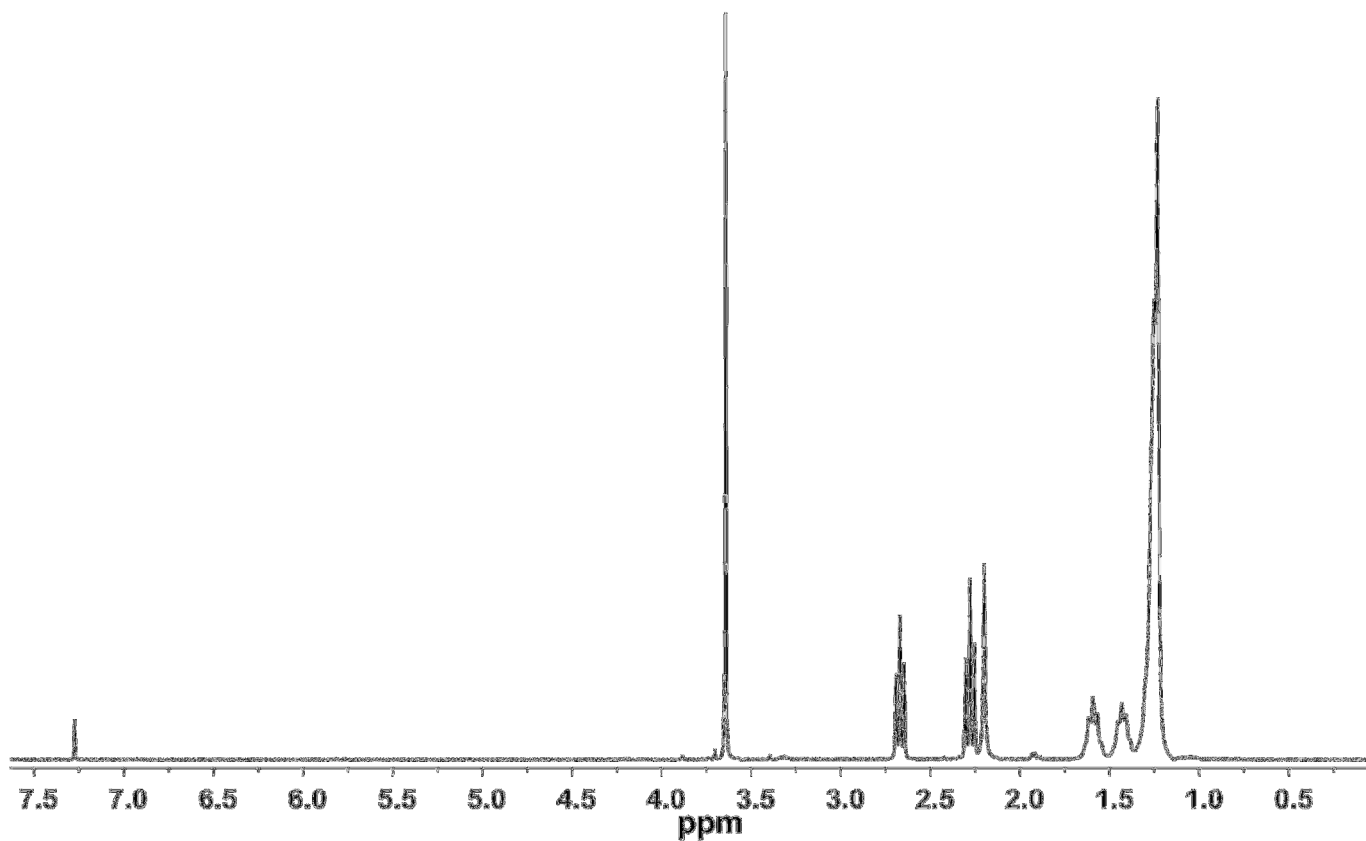


Figure 19: ^1H -NMR (300 MHz/ CDCl_3) of methyl 14-aminotetradecanoate (**10**).

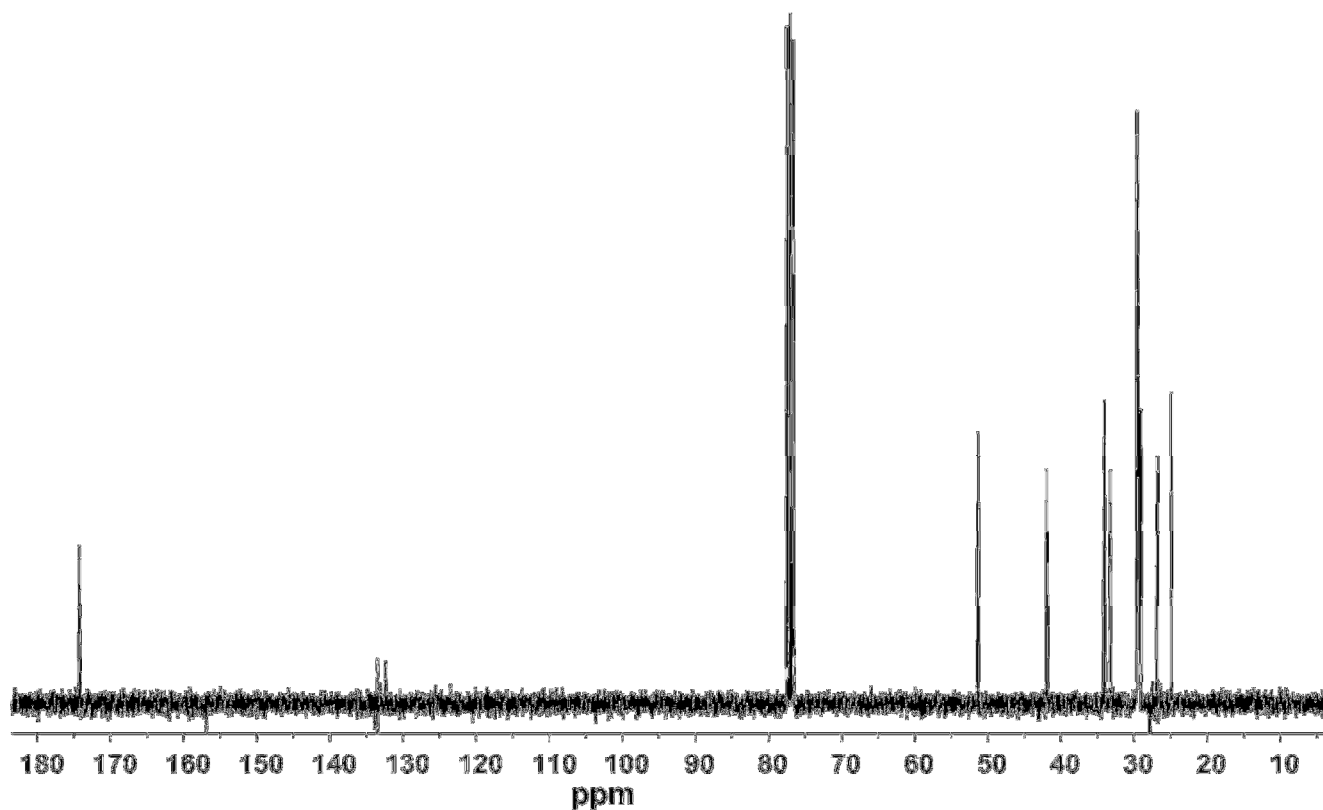


Figure 20: ^{13}C -NMR (75 MHz/ CDCl_3) of methyl 14-aminotetradecanoate (**10**).

d) General procedure for the synthesis of polyamides

All polymerizations were performed in a RR98072 carousel reactor (from RadleysTM Discovery Technologies, UK). The respective monomers were weighed into a reaction tube and the catalyst was added. The reaction mixture was stirred at evaluated temperatures for a specific time, first at 120 °C for 2 h under a gentle argon flow. Subsequently, the reaction mixture was set under vacuum (10-2 mbar) and stirred for further 3 h at 135 °C. Finally, the temperature was raised to 180-195 ° depending on the employed monomer.

Polymerization of monomer **15** was performed at a final temperature of 180 ° using TBD as catalyst. Polymerization of monomer **14** was performed at a temperature of 195 °C. Herein, DBU was used as catalyst.

P1 was obtained by polymerization of monomer **8**.

^1H -NMR (CDCl_3 / TFAA, 300 MHz) δ / ppm: 3.78 – 3.59 (m, 2H, $-\text{CH}_2-\text{N}(\text{CO})\text{CF}_3$), 2.78 (t, $J = 7.3$ Hz, 2H, $-\text{CH}_2-(\text{CO})\text{N}(\text{CO})\text{CF}_3$), 1.77 – 1.46 (m, 4H, $-\text{CH}_2-$), 1.42 – 1.10 (m, 11H, $-\text{CH}_2-$, $-\text{NH}$).

SEC: $M_n = 1.49$ kDa, $\text{Đ} = 2.20$, DSC: $T_m = 186$ °C.

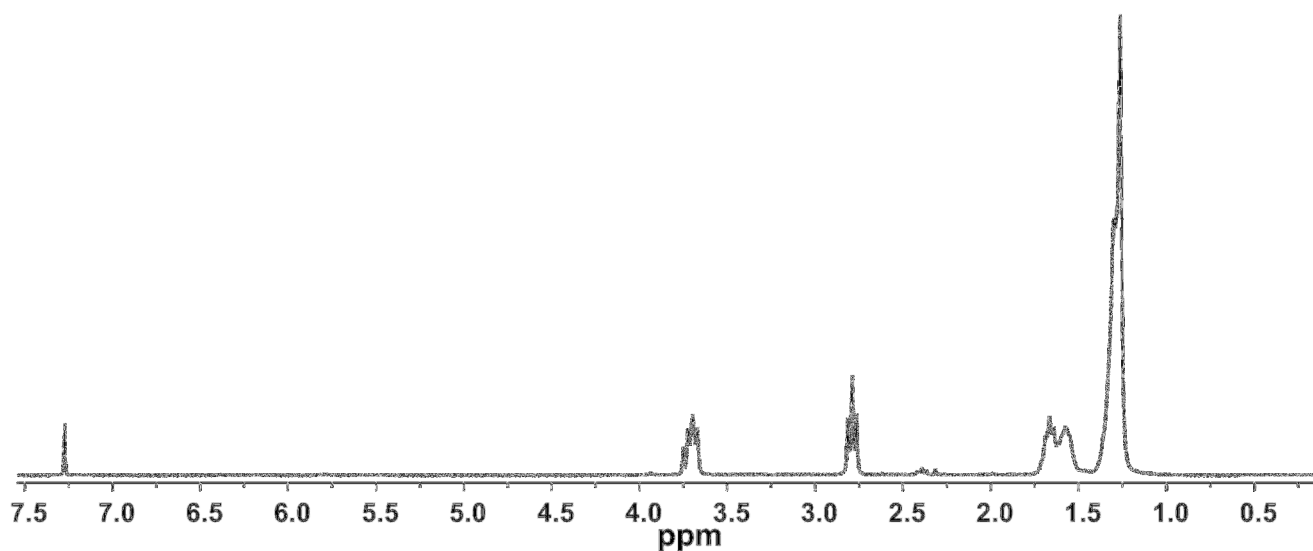


Figure 21: ^1H -NMR (300 MHz/ CDCl_3 + TFAA) of **P1**.

P2 was obtained by polymerization of monomer **9**.

^1H -NMR (CDCl_3 / TFAA, 300 MHz) δ / ppm: 3.79 – 3.57 (m, 2H, $-\text{CH}_2-\text{N}(\text{CO})\text{CF}_3$), 2.78 (t, $J = 7.4$ Hz, 2H, $-\text{CH}_2-(\text{CO})\text{N}(\text{CO})\text{CF}_3$), 1.77 – 1.44 (m, 4H, $-\text{CH}_2-$), 1.44 – 1.07 (m, 13H, $-\text{CH}_2-$, $-\text{NH}$).

SEC: $M_n = 1.52$ kDa, $\text{Đ} = 1.73$, DSC: $T_m = 182$ °C.

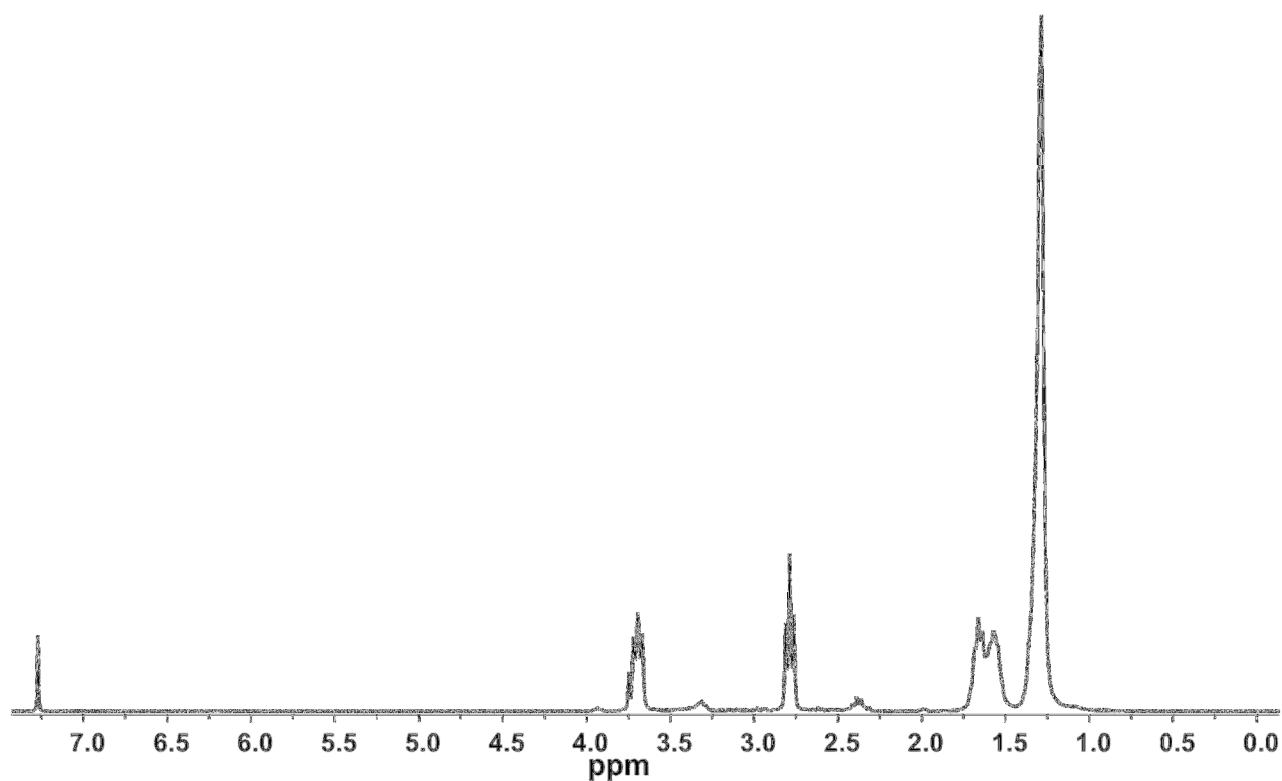


Figure 22: ^1H -NMR (300 MHz/ CDCl_3 + TFAA) of **P2**.

P3 was obtained by polymerization of monomer **10**.

$^1\text{H-NMR}$ (CDCl_3 / TFAA, 300 MHz): 3.81 – 3.56 (m, 2H, $-\text{CH}_2-\text{N}(\text{CO})\text{CF}_3$), 2.78 (t, $J = 7.4$ Hz, 2H, $-\text{CH}_2-(\text{CO})\text{N}(\text{CO})\text{CF}_3$), 1.78 – 1.46 (m, 4H, $-\text{CH}_2-$), 1.43 – 0.99 (m, 19H, $-\text{CH}_2-$, $-\text{NH}$).

SEC: $M_n = 2.26$ kDa, $\text{Đ} = 2.13$, DSC: $T_m = 169$ °C.

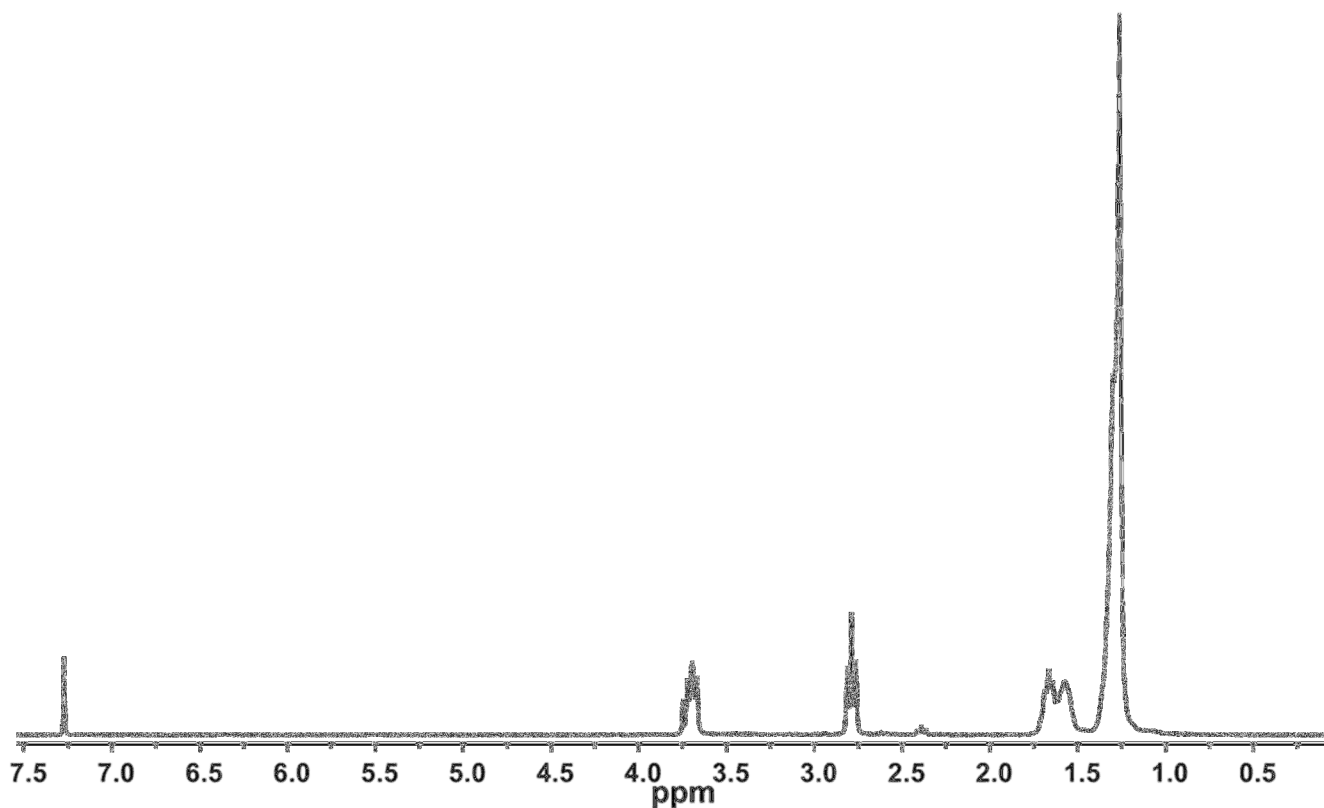


Figure 23: $^1\text{H-NMR}$ (300 MHz/ CDCl_3 + TFAA) of **P3**.

a) General procedure for Thia-Michael additions

Thia-Michael additions were performed in bulk and with a small excess of the thiol (1.2 equivalents). Thus, methyl undec-2-enoate (5.05 mmol) and the respective thiol (6.06 mmol) were weighed into a round bottom flask. Hexylamine (10 mol%) was added and the reaction mixture was stirred at 50 °C for 8 hours. The crude reaction mixture was purified by column chromatography (hexane : ethyl acetate = 4 : 1).

Methyl 3-((2-hydroxyethyl)thio)undecanoate (11)

Pure **6** was obtained as light yellow oil (yield 86%).

$^1\text{H-NMR}$ (CDCl_3 , 300 MHz) δ / ppm: 3.83 – 3.64 (m, 5H, -OMe, $-\text{CH}_2\text{-OH}$), 3.15 – 3.00 (m, 1H, $-\text{S-CH-}$), 2.73 (t, $J = 5.8$ Hz, 2H, $-\text{CH}_2\text{-S-}$), 2.67 – 2.46 (m, 2H, $-\text{CH}_2\text{-COOMe}$), 2.36 (bs, 1H, $-\text{OH}$), 1.66 – 1.51 (m, 2H, $-\text{CH}_2\text{-}$), 1.50 – 1.17 (m, 12H, $-\text{CH}_2\text{-}$), 0.87 (t, $J = 6.6$ Hz, 3H, $-\text{CH}_3$).

$^{13}\text{C-NMR}$ (CDCl_3 , 75 MHz) δ / ppm: 172.6, 61.2, 51.9, 41.7, 40.8, 35.8, 34.4, 31.9, 29.5, 29.5, 29.3, 28.8, 26.9, 22.7, 14.2.

HRMS (FAB):

$\text{C}_{14}\text{H}_{28}\text{O}_3\text{S}$ $[\text{M}+\text{H}]^+$ calc. 277.1832 found 277.1830.

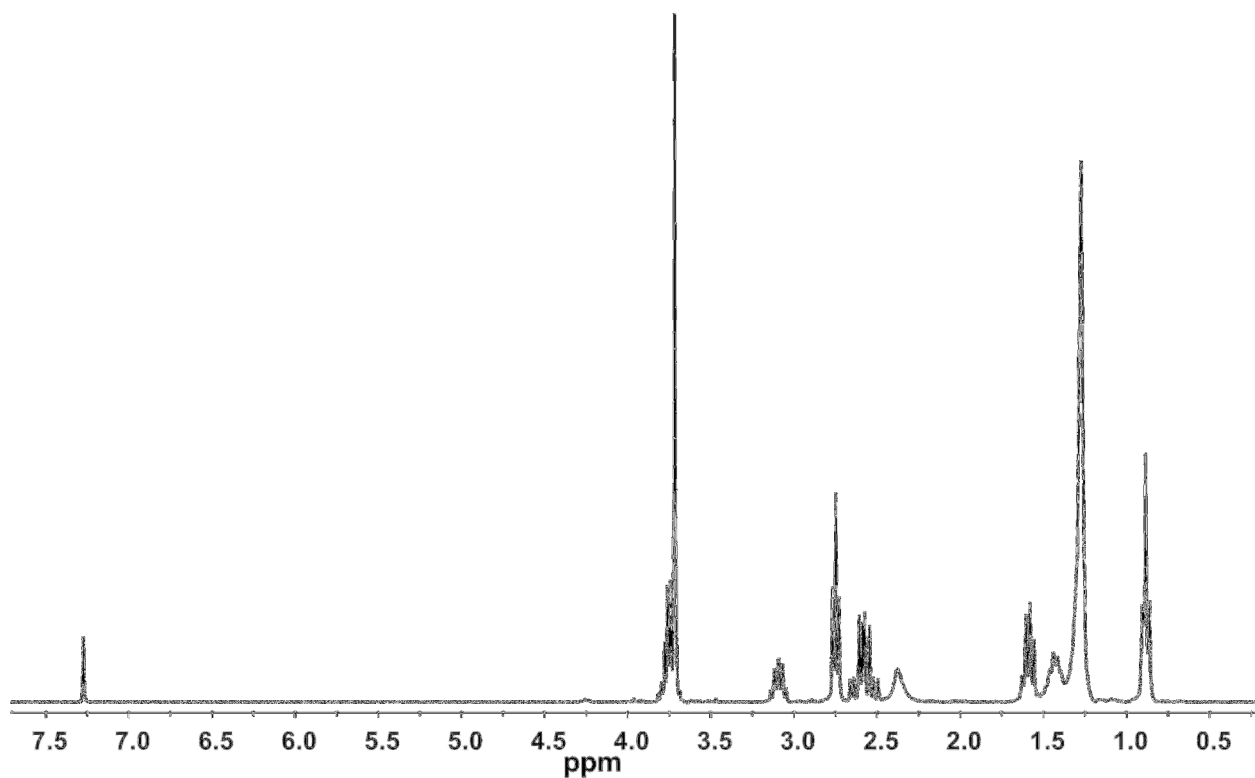


Figure 24: $^1\text{H-NMR}$ (300 MHz/ CDCl_3) of methyl 3-((2-hydroxyethyl)thio)undecanoate (**11**).

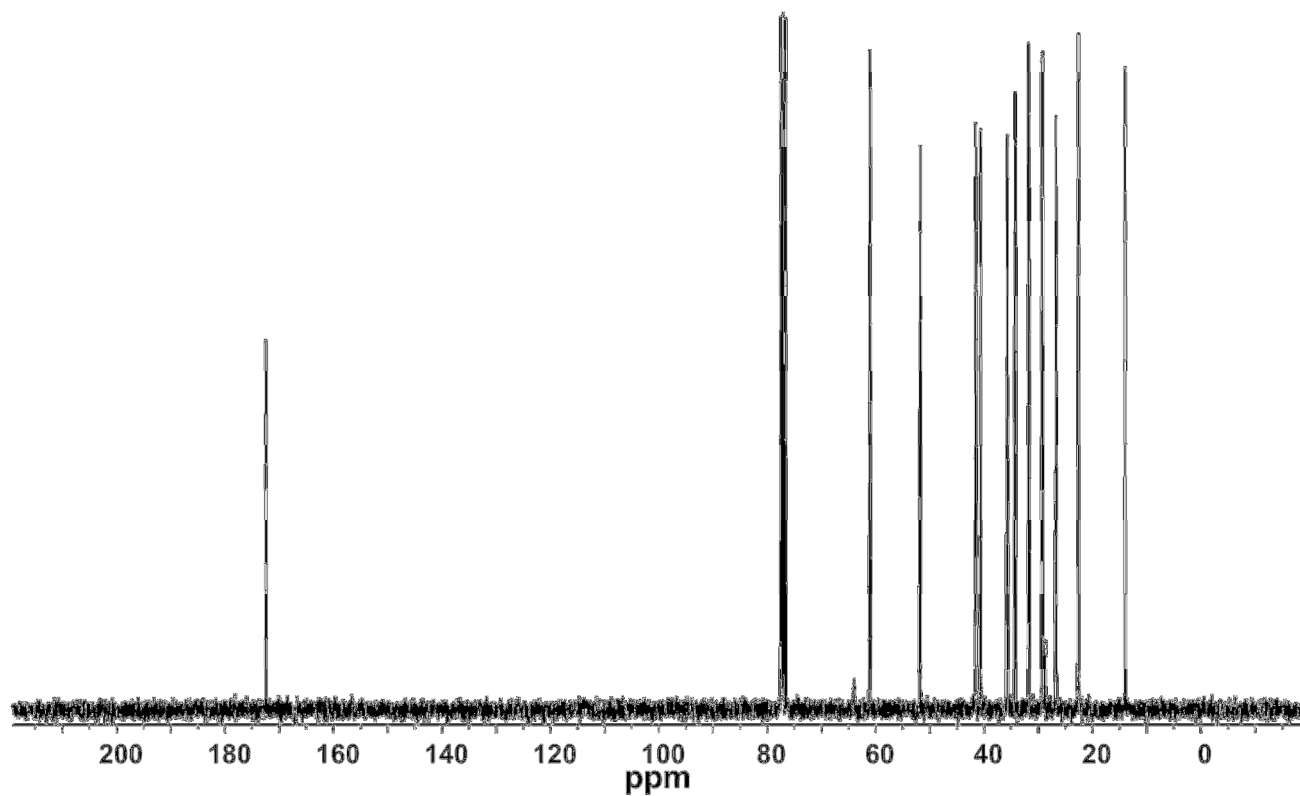


Figure 25: ^{13}C -NMR (75 MHz/ CDCl_3) of methyl 3-((2-hydroxyethyl)thio)undecanoate (**11**).

Methyl 3-((2-methoxy-2-oxoethyl)thio)undecanoate (12)

Pure **7** was obtained as light yellow oil (yield 81%).

$^1\text{H-NMR}$ (CDCl_3 , 300 MHz) δ / ppm: 3.74 (s, 3H, -OMe), 3.70 (s, 3H, -OMe), 3.38 – 3.12 (m, 3H, -CH-S-CH₂-COOMe), 2.71 – 2.53 (m, 2H, -CH₂-COOMe), 1.69 – 1.18 (m, 14H, -CH₂-), 0.88 (t, J = 6.7 Hz, 3H, -CH₃).

$^{13}\text{C-NMR}$ (CDCl_3 , 75 MHz) δ / ppm: 172.0, 171.1, 52.5, 51.8, 42.74, 40.5, 34.8, 32.8, 32.0, 29.6, 29.5, 29.3, 26.8, 22.8, 14.2.

HRMS (FAB):

$\text{C}_{15}\text{H}_{28}\text{O}_4\text{S}$ $[\text{M}+\text{H}]^+$ calc. 305.1781 found 305.1781.

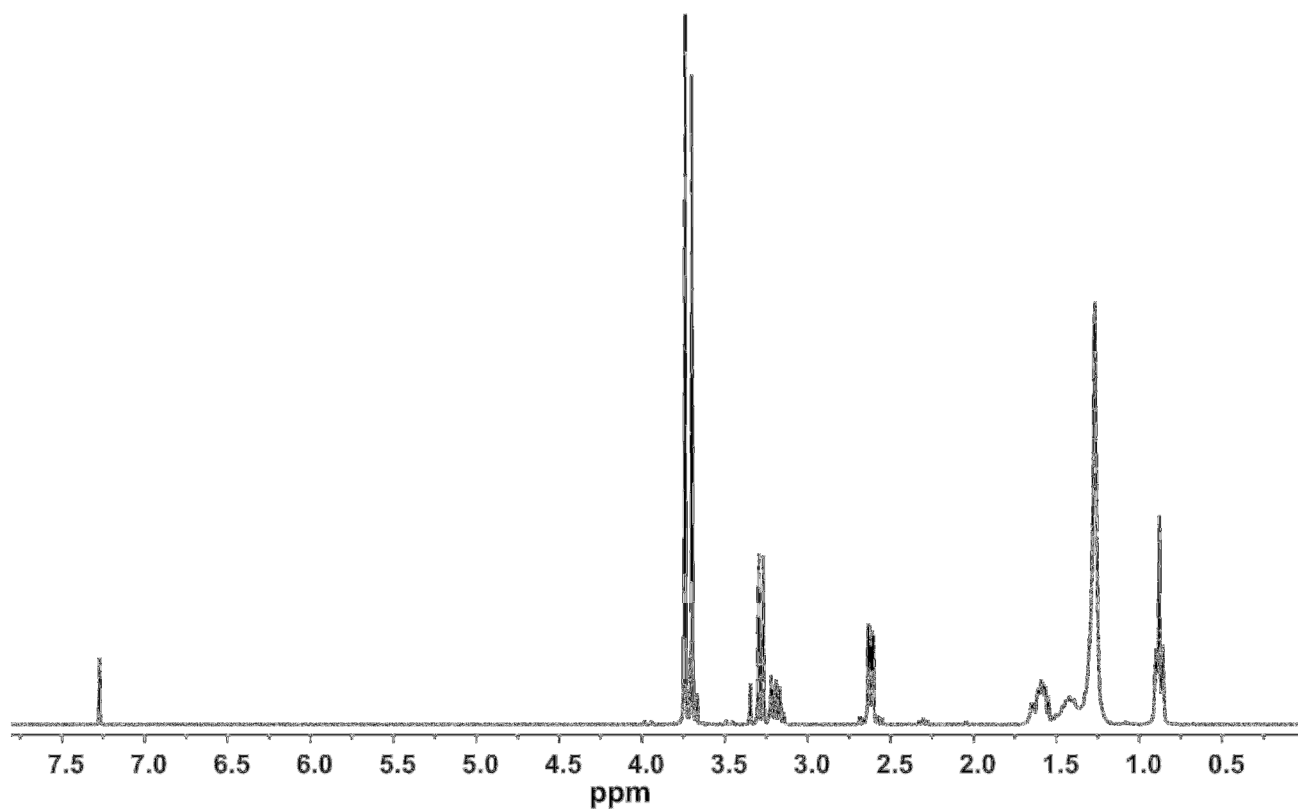


Figure 26: ^1H -NMR (300 MHz/ CDCl_3) of methyl 3-((2-methoxy-2-oxoethyl)thio)undecanoate (**12**).

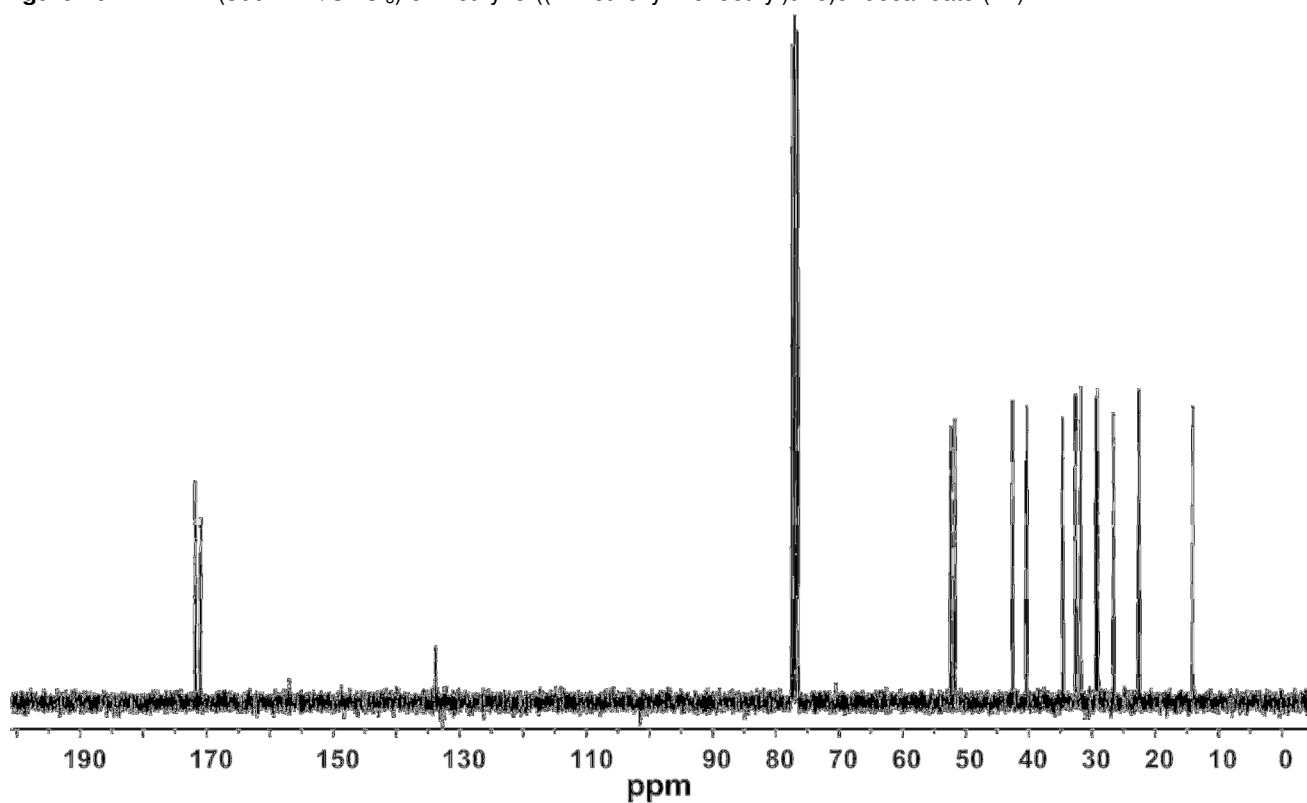


Figure 27: ^{13}C -NMR (75 MHz/ CDCl_3) of methyl 3-((2-methoxy-2-oxoethyl)thio)undecanoate (**12**).

b) General procedure for the synthesis of polyesters

All polymerizations were performed in a RR98072 carousel reactor (from RadleysTM Discovery Technologies, UK). The respective monomers were weighed into a reaction tube and tin(II) octanoate (5 mol%) was added. The reaction mixture was stirred at evaluated temperatures for a specific time. 120 °C for 2 h under a gentle argon flow. Subsequently, the reaction mixture was set under vacuum (10-2 mbar) and stirred for further 12 h at 135 °C. It should be noted that the use of $\text{Ti}(\text{O}^i\text{Pr})_4$ as catalyst led to similar results.

P4 was obtained by polymerization of monomer **11**.

^1H -NMR (CDCl_3 , 300 MHz) δ / ppm: 4.34 – 4.11 (m, 2H, $-\text{CH}_2\text{-O}-$), 3.17 – 2.98 (m, 1H, $-\text{S-CH-}$), 2.85 – 2.67 (m, 2H, $-\text{S-CH}_2-$), 2.65 – 2.46 (m, 2H, $-\text{CH}_2\text{-COO}-$), 1.75 – 1.14 (m, 14H, $-\text{CH}_2-$), 0.88 (t, $J = 6.6$ Hz, 3H, $-\text{CH}_3$).

SEC: $M_n = 17100$ Da, $\text{Đ} = 1.52$, DSC: $T_g = 8$ °C.

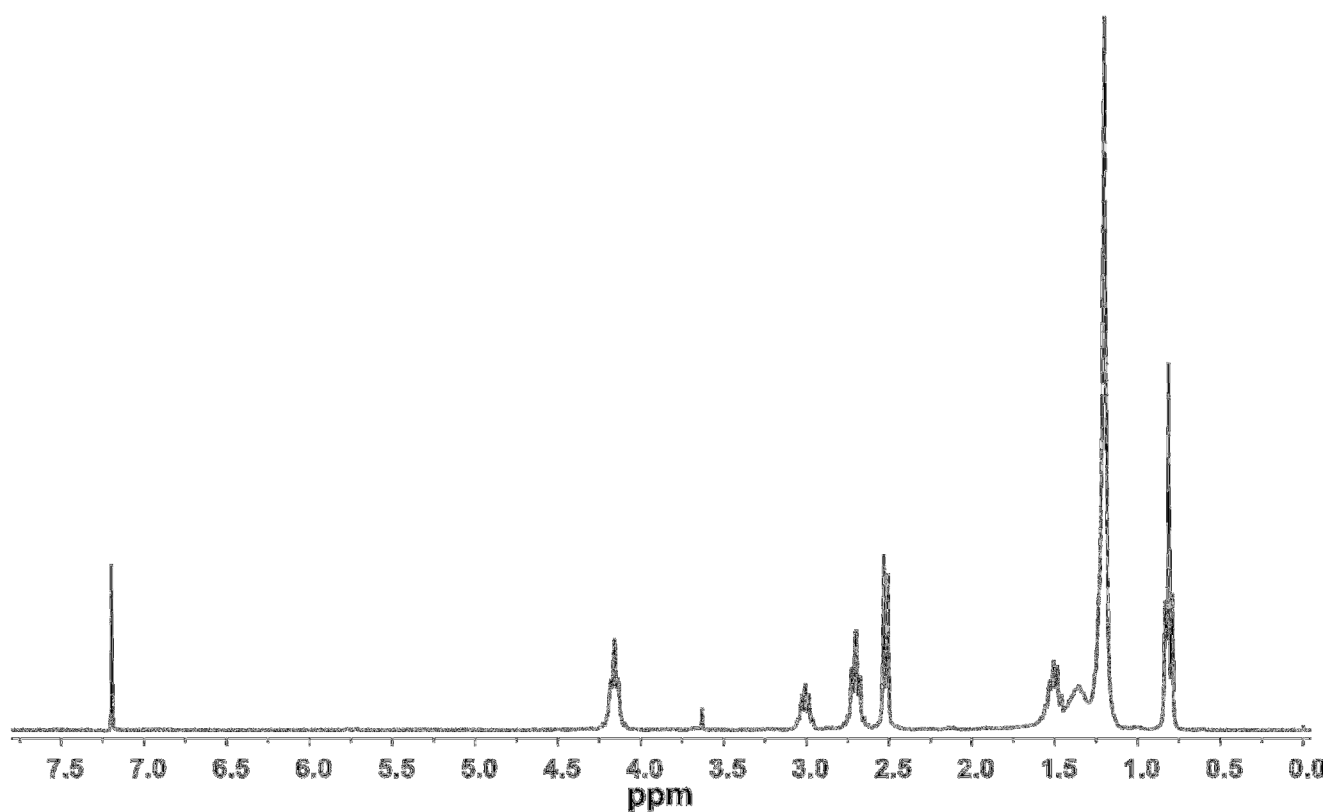


Figure 28: ^1H -NMR (300 MHz/ CDCl_3) of **P4**.

P5 was obtained by polymerization of monomer **12** and **17**.

$^1\text{H-NMR}$ (CDCl_3 , 300 MHz) δ / ppm: 4.19 – 4.00 (m, 4H, $-\text{CH}_2\text{-O-}$), 3.35 – 3.10 (m, 3H, $-\text{S-CH}_2-$, $-\text{S-CH-}$), 2.70 – 2.49 (m, 2H, $-\text{CH}_2\text{-COO-}$), 1.75 – 1.16 (m, 34H, $-\text{CH}_2-$), 0.87 (t, $J = 6.7$ Hz, 3H, $-\text{CH}_3$).

SEC: $M_n = 18930$ Da, $\text{Đ} = 1.74$, DSC: $T_m = -18.6$ °C.

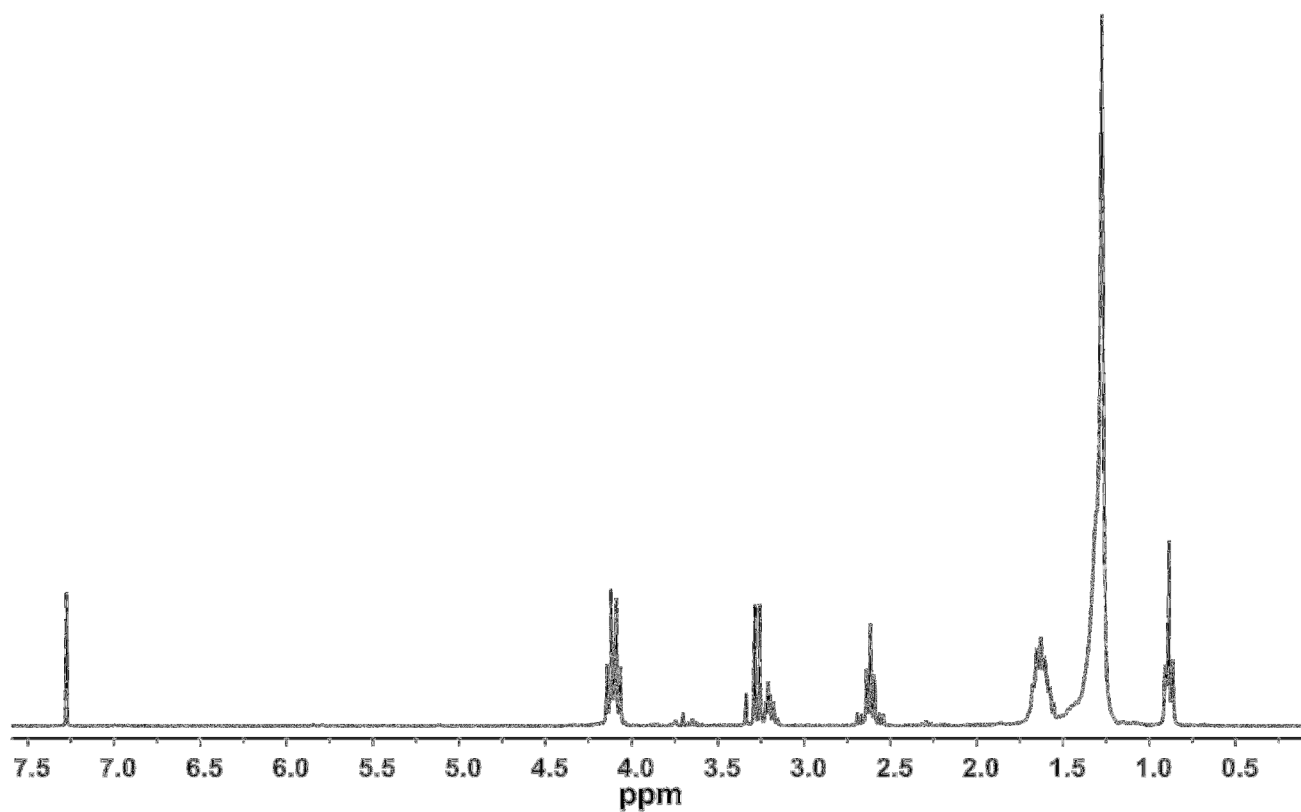


Figure 29: $^1\text{H-NMR}$ (300 MHz/ CDCl_3) of **P5**.

P6 was obtained by polymerization of monomer **12** and **18**.

$^1\text{H-NMR}$ (CDCl_3 , 300 MHz) δ / ppm: 4.20 – 3.97 (m, 4H, $-\text{CH}_2\text{-O-}$), 3.36 – 3.11 (m, 3H, $-\text{S-CH}_2-$, $-\text{S-CH-}$), 2.71 – 2.49 (m, 2H, $-\text{CH}_2\text{-COO-}$), 1.79 – 1.10 (m, 42H, $-\text{CH}_2-$), 0.87 (t, $J = 6.7$ Hz, 3H, $-\text{CH}_3$).

SEC: $M_n = 18030$ Da, $\text{Đ} = 1.90$, DSC: $T_m = 15.5$ °C.

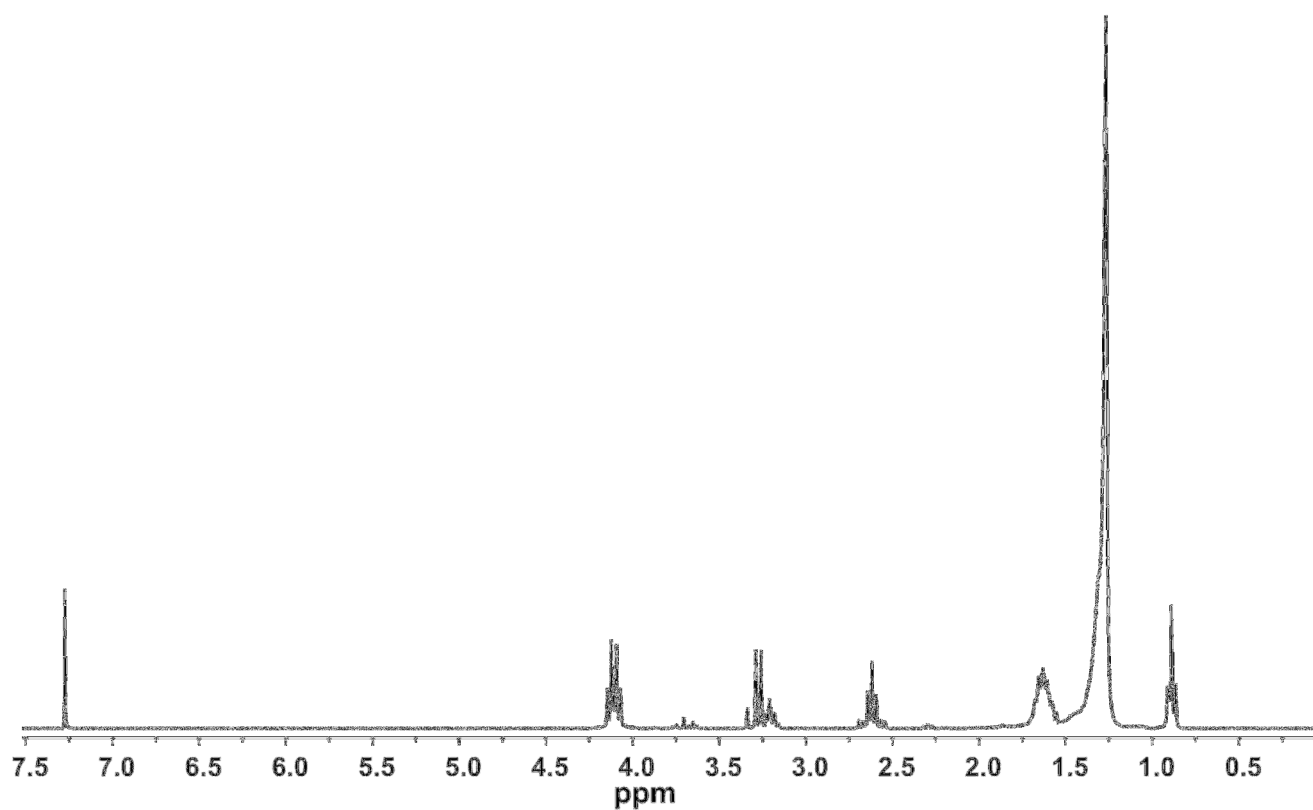


Figure 30: $^1\text{H-NMR}$ (300 MHz/ CDCl_3) of **P6**.

c) General procedure for the oxidation of the sulfur containing polyesters

To the polyester (**P4-P6**) (0.15 g) dissolved in 15 mL CHCl_3 , mCPBA (3 equivalents per sulfur) was added. The reaction mixture was stirred at room temperature for 24 hours. To the reaction mixture a saturated solution of $\text{Na}_2\text{S}_2\text{O}_3$ was added to quench the oxidizing agent and the phases were separated. The turbid polymer solution was evaporated to dryness under high vacuum.

P7

^1H -NMR (CDCl_3 , 300 MHz) δ /ppm: 4.75 – 4.40 (m, 2H, $-\text{CH}_2\text{-O-}$), 3.69 – 3.48 (m, 1H, $-\text{CH-SO}_2\text{-}$), 3.46 – 3.23 (m, 2H, $-\text{CH}_2\text{-SO}_2\text{-}$), 3.10 – 2.83 (m, 1H, $-\text{CH}_2\text{-CO-}$), 2.66 (m, 1H, $-\text{CH}_2\text{-CO-}$), 2.09 – 1.85 (m, 1H, $-\text{CH}_2\text{-}$), 1.78 – 1.14 (m, 13H, $-\text{CH}_2\text{-}$), 0.88 (t, $J = 6.6$ Hz, 3H, $-\text{CH}_3$).

DSC: $T_m = 21$ °C.

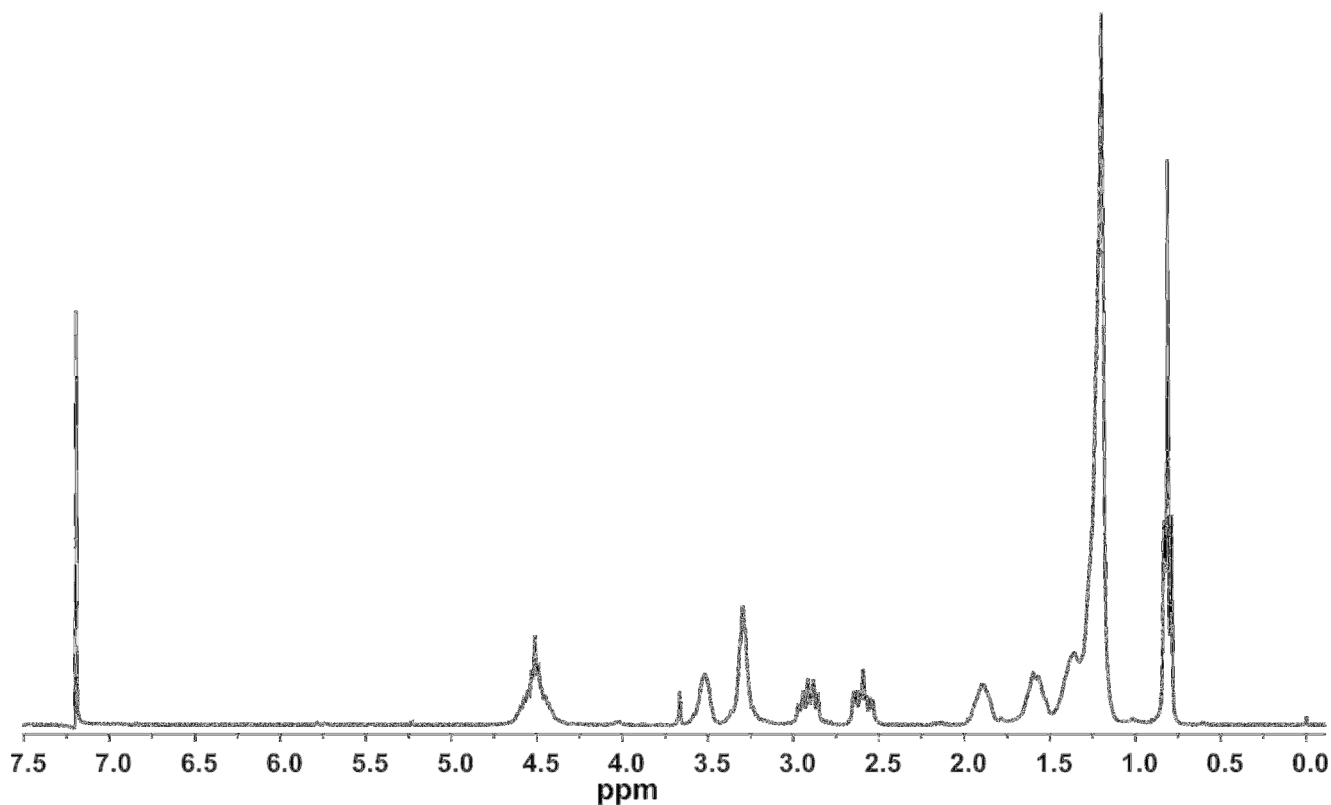


Figure 31: ^1H -NMR (300 MHz/ CDCl_3) of **P7**.

P8

^1H -NMR (CDCl_3 , 300 MHz) δ / ppm: 4.19 (t, $J = 6.7$ Hz, 2H, $-\text{CH}_2\text{-O}(\text{CO})-$), 4.14 – 4.03 (m, 3H, $-\text{CH}_2\text{-O}(\text{CO})-$, $-\text{SO}_2\text{-CH}-$), 4.03 – 3.83 (m, 2H, $-\text{SO}_2\text{-CH}_2\text{-COO}-$), 3.01 (dd, $J = 17.1, 6.2$ Hz, 1H, $-\text{CH}_2\text{-COO}-$), 2.61 (dd, $J = 17.1, 6.2$ Hz, 1H, $-\text{CH}_2\text{-COO}-$), 2.09 – 1.90 (m, 1H, $-\text{CH}_2-$), 1.79 – 1.11 (m, 33H, $-\text{CH}_2-$), 0.86 (t, $J = 6.6$ Hz, 3H, $-\text{CH}_3$).

DSC: $T_m = -5$ °C.

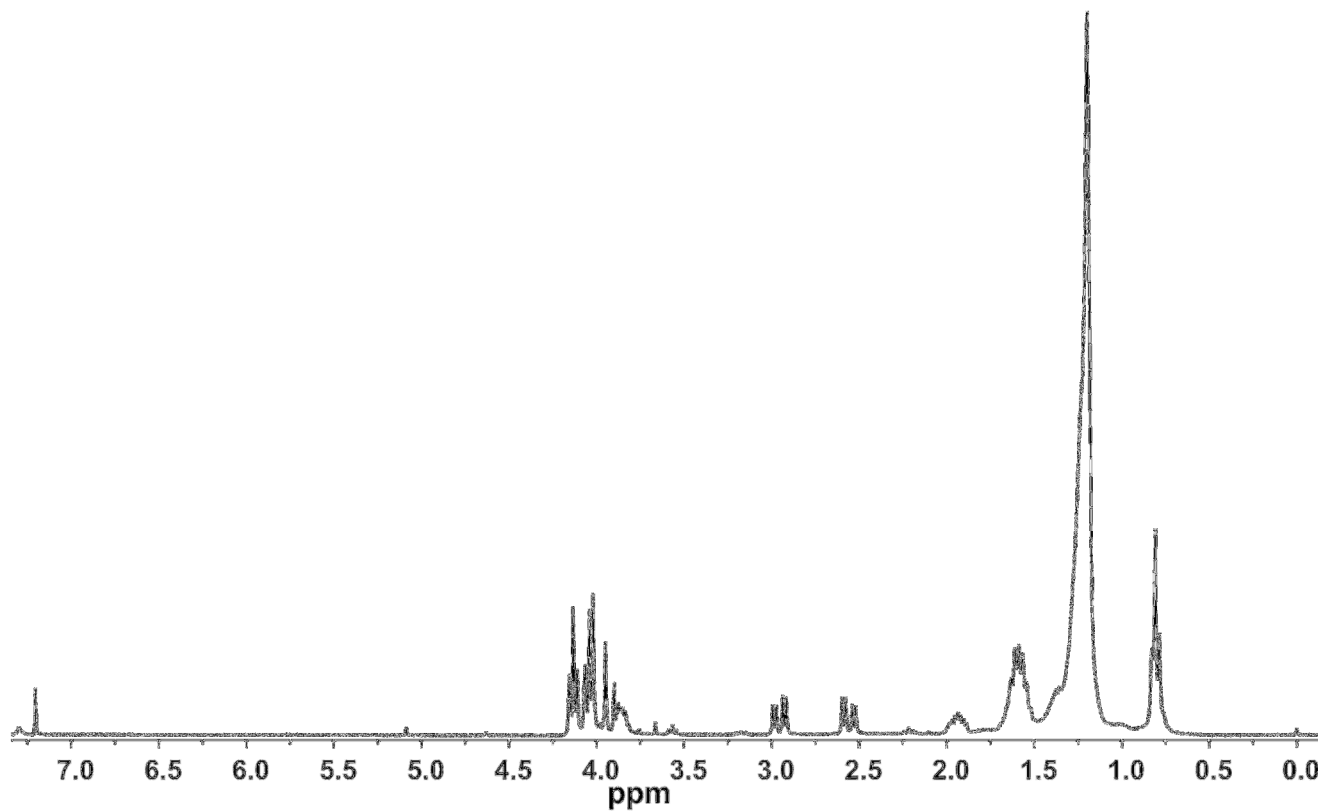


Figure 32: ^1H -NMR (300 MHz/ CDCl_3) of **P8**.

P9

^1H -NMR (CDCl_3 , 300 MHz) δ / ppm: 4.20 (t, $J = 6.8$ Hz, 2H, $-\text{CH}_2\text{-O}(\text{CO})-$), 4.15 – 4.03 (m, 3H, $-\text{CH}_2\text{-O}(\text{CO})-$, $-\text{SO}_2\text{-CH}-$), 4.03 – 3.85 (m, 2H, $-\text{SO}_2\text{-CH}_2\text{-COO}-$), 3.02 (dd, $J = 17.1, 6.2$ Hz, 1H, $-\text{CH}_2\text{-COO}-$), 2.62 (dd, $J = 17.1, 6.2$ Hz, 1H, $-\text{CH}_2\text{-COO}-$), 2.09 – 1.92 (m, 1H, $-\text{CH}_2-$), 1.78 – 1.15 (m, 41H, $-\text{CH}_2-$), 0.87 (t, $J = 6.6$ Hz, 3H, $-\text{CH}_3$).

DSC: $T_m = 25$ °C.

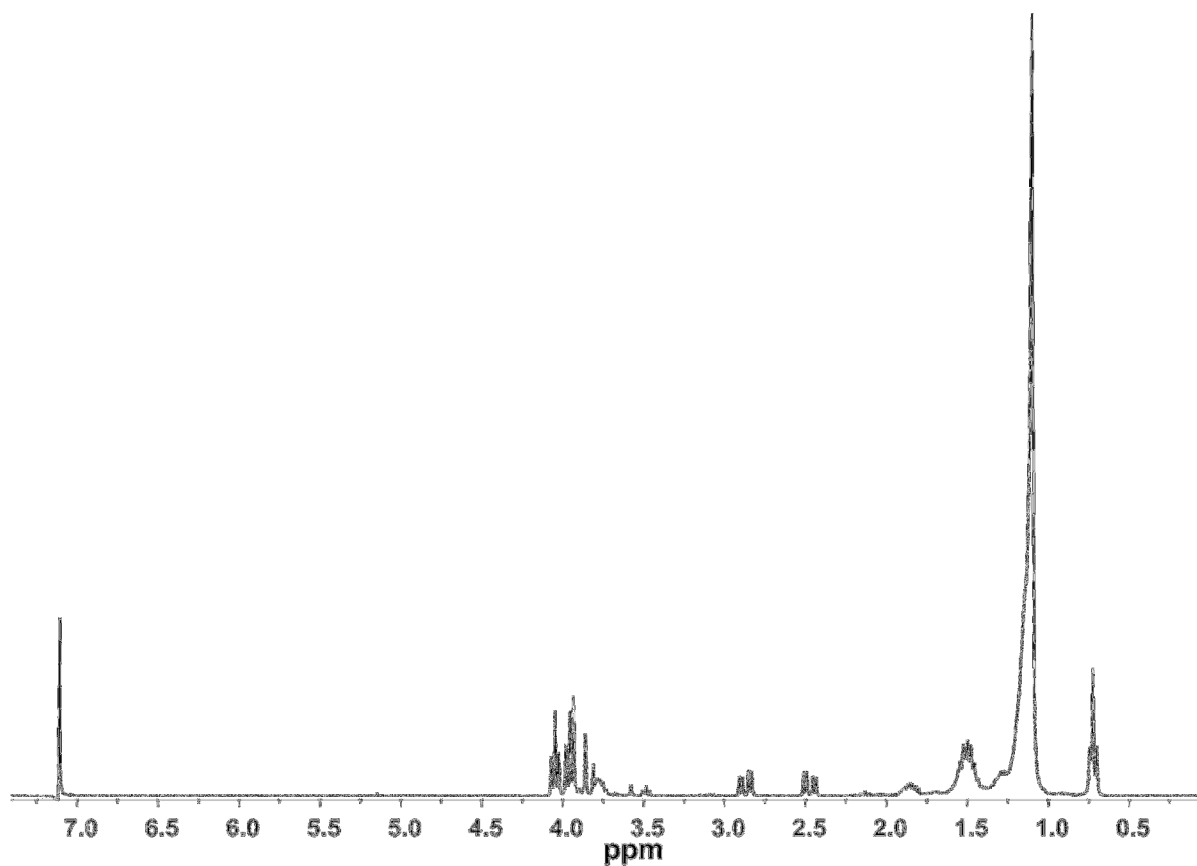


Figure 33: ^1H -NMR (300 MHz/ CDCl_3) of **P9**.

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3. M. Abbas and C. Slugovc, *Monatsh Chem*, 2012, **143**, 669-673.
4. A. Rybak and M. A. R. Meier, *Green Chem.*, 2007, **9**, 1356-1361.