# Introducing multicomponent reactions to polymer science: Passerini reactions of renewable monomers

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# 1. Supporting Information

## 1.1 Materials

10-Undecenal (>=90%, Aldrich), 10-undecenoic acid (98%, Aldrich), cyclohexyl isonitrile (98%, Aldrich), *tert*-butyl isonitrile (97%, Aldrich), *tert*-butyl isocyanoacetate (>95%, Aldrich), silica gel 60 (0.035 – 0.070, Aldrich), heptanal (95%, Aldrich), trifluoroacetic acid (99%, Acros Organics), 1,4-benzoquinone (>99%, Aldrich), ethyl vinyl ether (99%, Aldrich), chloroform-d (99.8 atom-% D, Armar Chemicals), dimethylsulfoxide-d6 (99.5 atom-% D, Chemotrade), benzylidene-*bis*(tricyclohexylphosphine)dichlororuthenium (**C1**, Grubbs Catalyst 1$^{st}$ Generation, Aldrich), benzylidene [1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene] dichloro(tricyclohexylphosphine) ruthenium (**C2**, Grubbs Catalyst 2$^{nd}$ Generation, Aldrich), (1,3-bis-(2,4,6-trimethylphenyl)-2-imidazolidinylidene) dichloro(*o*-isopropoxyphenylmethylene) ruthenium (**C3**, Hoveyda–Grubbs Catalyst 2$^{nd}$ Generation, Aldrich), 1,3-*bis*-(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-yliden[2-(isopropoxy)-5-N,N-dimethylaminosulfonyl)phenyl]methylene ruthenium (II) dichloride (**C4**, Zhan catalyst, 96%, ABCR), 1,3-*bis*-(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-yliden[2-(isopropoxy)-5-nitro)phenyl]methylene ruthenium (II) dichloride (**C5**, nitro-Grela catalyst, Apeiron catalysts), [1,3-*bis*(2,4,6-trimethylphenyl)-2-imidazolidinylidene]dichloro-(3-phenyl-1H-inden-1-ylidene)(tricyclohexylphosphine)ruthenium(II) (**C6**, Umicore M2), [1,3-*bis*(2,4,6-trimethylphenyl)-2-imidazolidinylidene]dichloro-(3-phenyl-1H-inden-1-ylidene)(pyridyl)ruthenium(II) (**C7**, Umicore M3$_1$) and [1,3-*bis*(2,4,6-trimethylphenyl)-2-imidazolidinylidene]dichloro [2-(1-methylacetoxy)phenyl]methyleneruthenium(II) (**C8**, Umicore M5$_1$) were used as received. All solvents were used without any kind of purification.

## 1.2 Analysis of monomers and polymers

TLC-identifications of reactants and products were performed on silica gel coated aluminum foil (silica gel 60, F254 with fluorescence indicator) from Aldrich. Compounds were visualized by iodine or permanganate reagents.

NMR spectra were obtained in $CDCl_3$ and recorded with a Bruker Advance 300 NMR Instrument at 300.1 and 75.5 MHz. All $^{1}H$ NMR spectra are reported in ppm relative to TMS or to the solvent signal for $CDCl_3$ at 7.26 ppm. All $^{13}C$ NMR spectra are reported in ppm relative to the central line of the triplet for $CDCl_3$ at 77.00 ppm.

Polymer molecular weights were determined using a SEC system LC-20A from Shimadzu equipped with a SIL-20A autosampler, three PSS SDV columns (5 µm, 300mm x 7.5mm, 100Å, 1000 Å,10000Å), and a RID-10A refractive index detector in THF (flow rate 1mL/min) at 50°C. All determinations of molar mass were performed relative to PMMA standards (Polymer Standards Service, $M_p$ 102 – 981.000 Da).

Electronspray ionization mass spectra (ESI-MS) were recorded on a Micromass Q-$TOF_{micro}$ and high resolution mass spectra (HRMS) with electron impact ionization (EI) were recorded on a GC-TOF.

## 1.3 Monomer syntheses

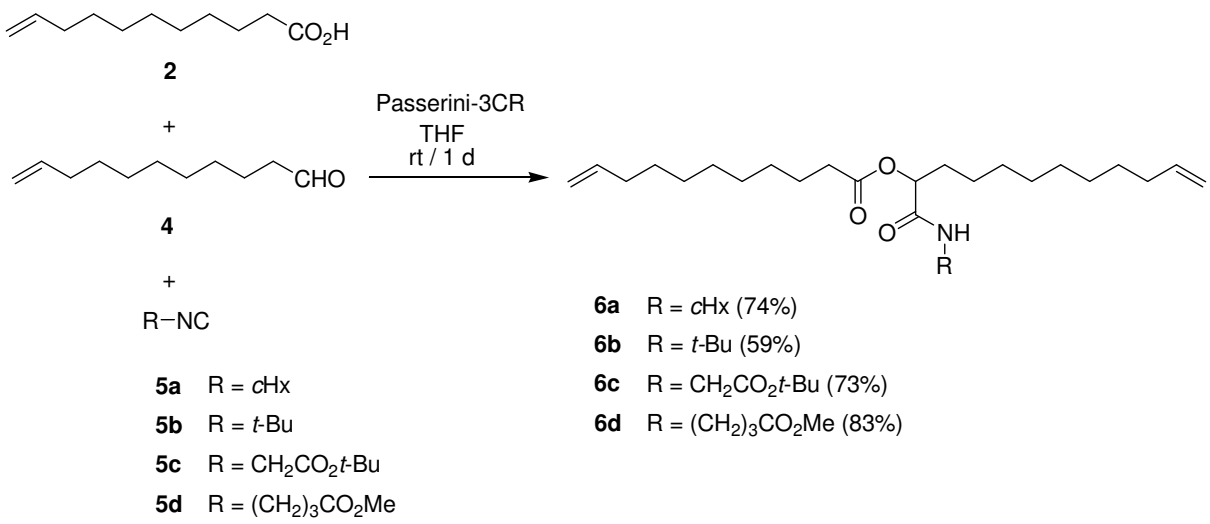
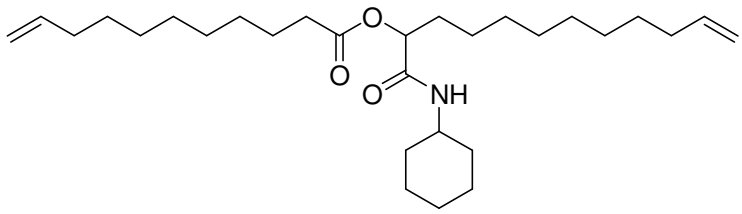



***Figure 1.*** *Passerini-3CR with 10-undecenoic acid* ***2****, 10-undecenal* ***4*** *and isonitriles* ***5a – 5d****.*

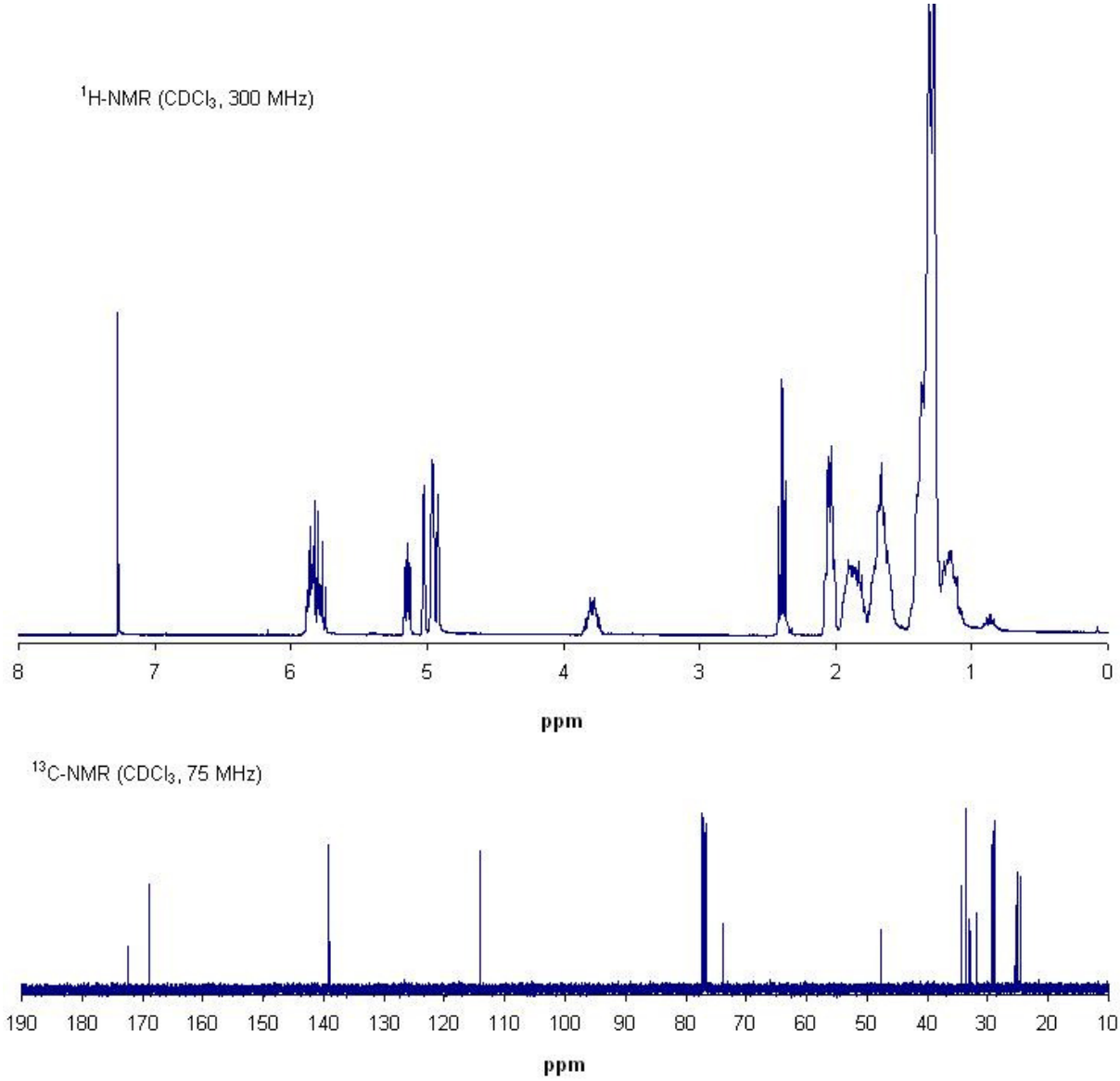
*Representative procedure for Passerini-3CR with 10-undecenoic acid and 10-undecenal:*
The isonitriles **5a - 5b** (16.5 mmol) and 10-undecenal **4** (2.78 g, 16.5 mmol) were dissolved in THF (30 mL) and subsequently 10-undecenoic acid **2** (3.04 g, 16.5 mmol) was added. The mixture was stirred over night at room temperature. When TLC-monitoring and ESI-MS indicated the formation of the Passerini-3CR product, the reaction mixture was evaporated under reduced pressure to give the crude substance. The residue is purified by column chromatography or recrystallization to obtain the pure product.

### 1.3.1 1-(Cyclohexylcarbamoyl)undec-10-enyl undec-10-enoate (6a)

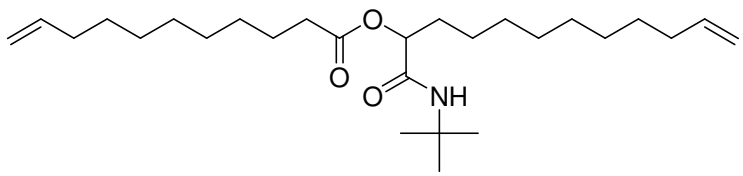



The Passerini-3CR of 10-undecenal **4** (2.78 g, 16.5 mmol), 10-undecenoic acid **2** (3.04 g, 16.5 mmol) and cyclohexyl isonitrile **5a** (1.80 g, 16.5 mmol) led to the formation of 1-(cyclohexylcarbamoyl)undec-10-enyl undec-10-enoate **6a**. After purification by

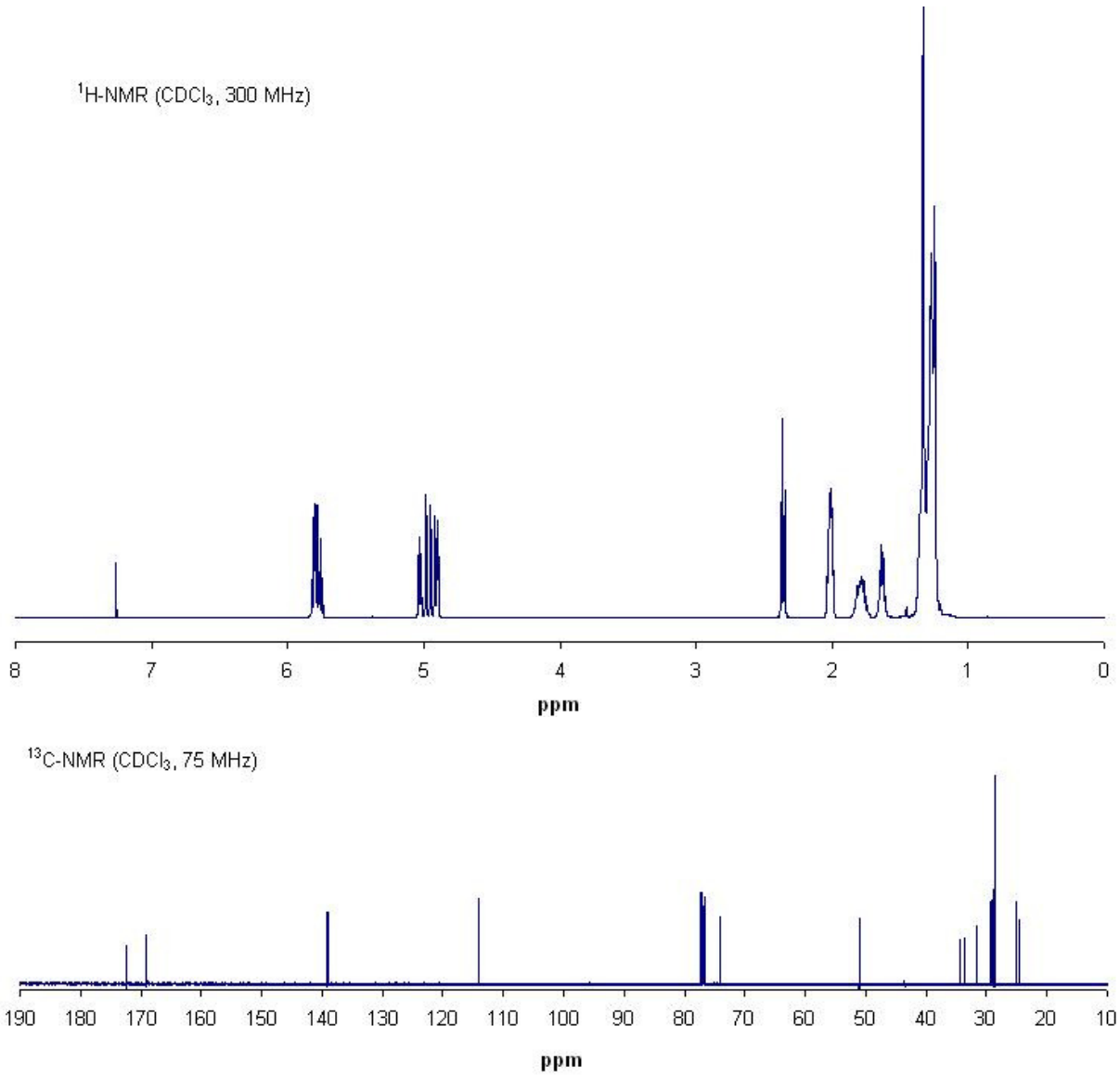
recrystallization from hexane, **6a** was obtained as a colorless solid (5.64 g, 74%). TLC (*n*-hexane / ethyl acetate 5 : 1) $R_f$ = 0.47; mp = 56.6 °C (ethyl acetate); $^1$H NMR ($CDCl_3$, 300 MHz) δ = 1.10 – 1.46 (m, 28 H, 14 $CH_2$), 1.56 – 1.96 (m, 8 H, 4 $CH_2$), 2.04 (q, *J* = 6.2 Hz, 4 H, 2 $CH_2$), 2.39 (t, *J* = 7.4 Hz, 2 H, $CH_2$), 3.71 – 3.86 (m, 1 H, CH), 4.90 – 5.03 (m, 4 H, 2 $CH_2$), 5.11 – 5.17 (m, 1 H, CH), 5.80 (tdd, *J* = 17.0 Hz, 10.4 Hz, 6.8 Hz, 2 H, 2 CH), 5.84 – 5.88 (m, 1 H, NH) ppm; $^{13}$C NMR ($CDCl_3$, 75 MHz) δ = 24.64, 24.66, 24.99, 25.44, 28.83, 28.85, 29.01, 29.06, 29.18, 29.25, 29.29, 31.83, 32.93, 33.01, 33.71, 33.73, 34.31, 47.75, 73.85, 114.08, 114.14, 139.02, 139.11, 168.87, 172.35 ppm; ESI-MS of $C_{29}H_{51}NO_3$ ($M+H^+$ = 462.41); HRMS of $C_{29}H_{51}NO_3$ $[M+H]^+$ calc. 462.3947 found 462.3932.



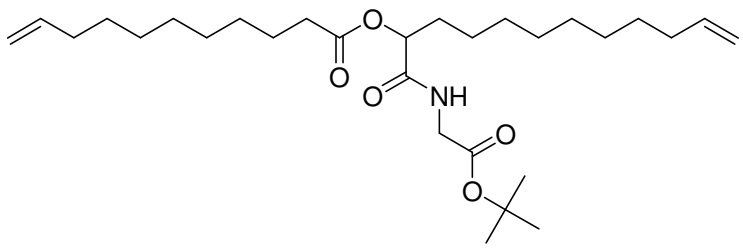
### 1.3.2 1-(*tert*-Butylcarbamoyl)undec-10-enyl undec-10-enoate (6b)




The Passerini-3CR of 10-undecenal **4** (2.02 g, 12.0 mmol), 10-undecenoic acid **2** (2.22 g, 12.0 mmol) and *tert*-butyl isonitrile **5b** (1.00 g, 12.0 mmol) led to the formation of 1-(*tert*-butylcarbamoyl)undec-10-enyl undec-10-enoate **6b**. After purification by column chromatography (*n*-hexane / ethyl acetate 9 : 1), **6b** was obtained as a colorless oil (3.09 g, 59%). TLC (*n*-hexane / ethyl acetate 5 : 1) $R_f$ = 0.41; $^1$H NMR ($CDCl_3$, 300 MHz) δ = 1.20 – 1.38 (m, 22 H, 11 $CH_2$), 1.33 (s, 9 H, 3 $CH_3$), 1.64 (quint., *J* = 7.2 Hz, 2 H, $CH_2$), 1.72 – 1.85 (m, 2 H, $CH_2$), 1.98 – 2.05 (m, 4 H, 2 $CH_2$), 2.36 (t, *J* = 7.4 Hz, 2 H, $CH_2$), 4.87 – 5.00 (m, 4 H, 2 $CH_2$), 5.02 – 5.05 (m, 1 H, CH), 5.80 (tdd, *J* = 17.0 Hz, 10.4 Hz, 6.6 Hz, 2 H, 2 CH), 5.80 (br, t, *J* = 3.3 Hz, 1 H, NH) ppm; $^{13}$C NMR ($CDCl_3$, 75 MHz) δ = 24.58, 24.98, 28.62, 28.81, 28.84, 28.98, 29.01, 29.05, 29.15, 29.16, 29.23, 29.29, 31.71, 33.71, 33.73, 34.34, 51.09, 74.03, 114.08, 114.14, 139.03, 139.11, 169.02, 172.35 ppm; ESI-MS of $C_{27}H_{49}NO_3$ ($M+H^+$ = 436.48; $M+Na^+$ = 458.45; $M+K^+$ = 474.45); HRMS of $C_{27}H_{49}NO_3$ $[M+H]^+$ calc. 436.3791 found 436.3773.

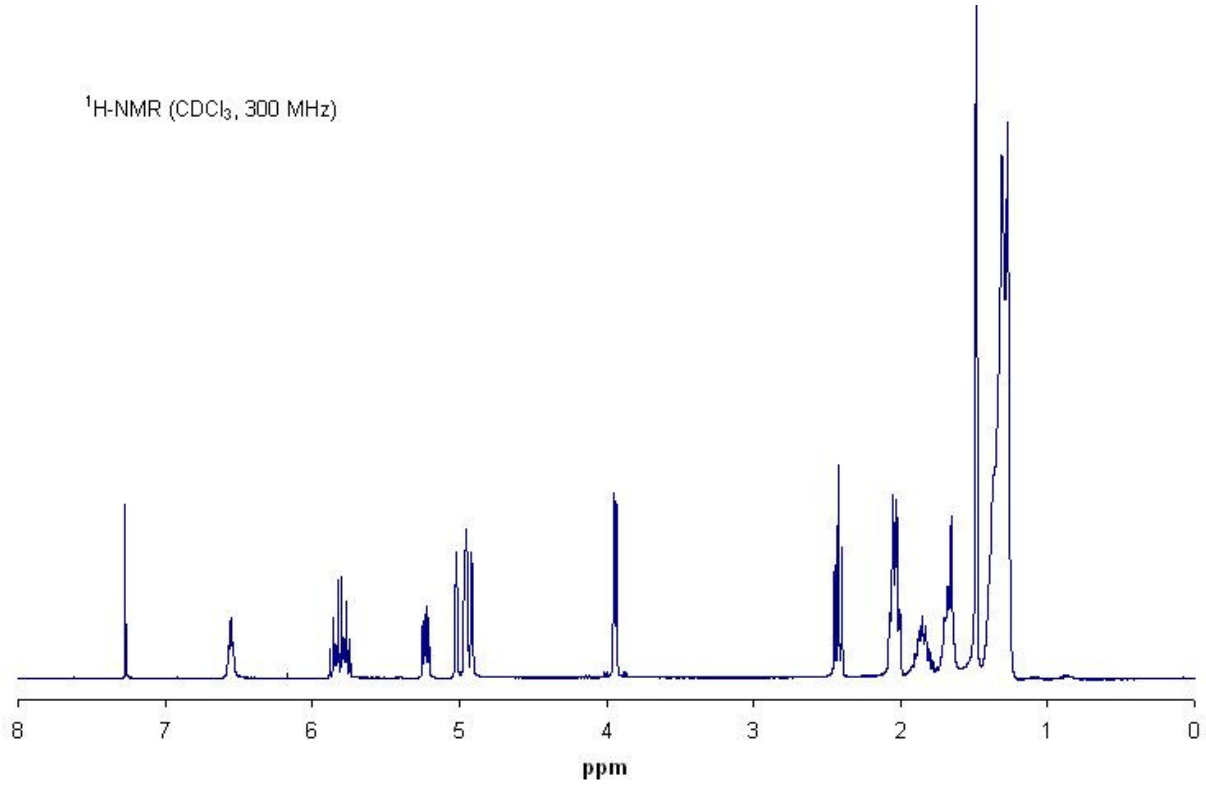


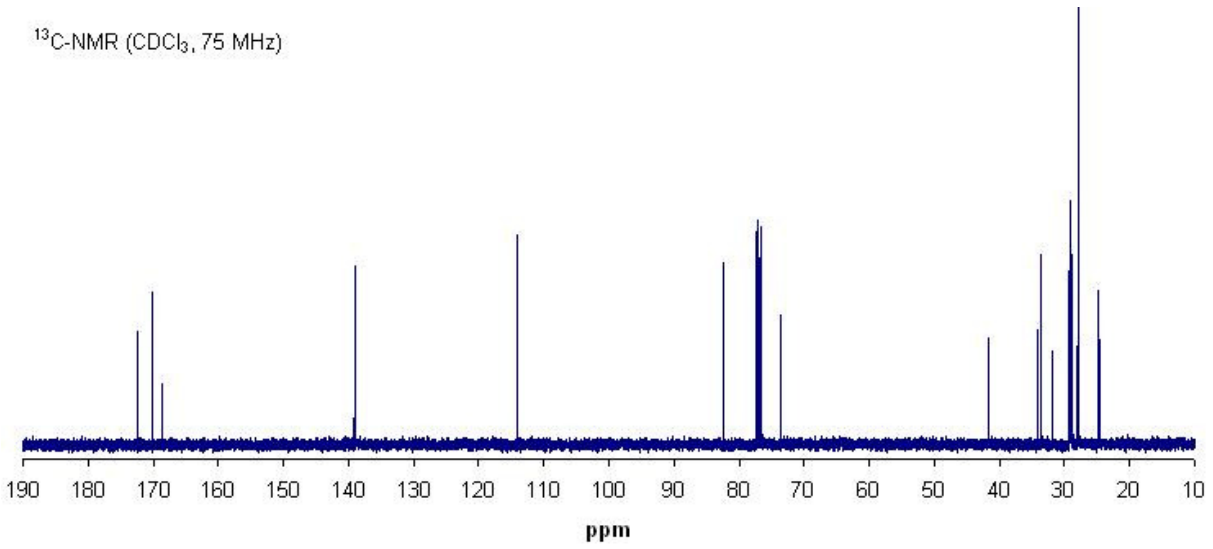

### 1.3.3 1-(*tert*-Butyloxycarbonylmethylcarbamoyl)undec-10-enyl undec-10-enoate (6c)



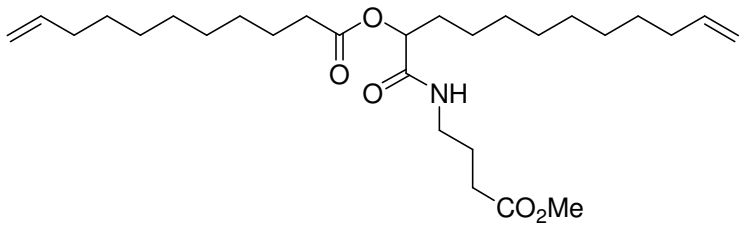

The Passerini-3CR of 10-undecenal **4** (1.19 g, 7.08 mmol), 10-undecenoic acid **2** (1.30 g, 7.08 mmol) and *tert*-butyl isocyanoacetate **5c** (1.00 g, 7.08 mmol) led to the formation of 1-(*tert*-

butyloxycarbonylmethylcarbamoyl)undec-10-enyl undec-10-enoate **6c**. After purification by column chromatography (*n*-hexane / ethyl acetate 9 : 1 to 5 : 1), **6c** was obtained as a slightly yellow oil (2.54 g, 73%). TLC (*n*-hexane / ethyl acetate 5 : 1) $R_f$ = 0.44; $^1$H NMR ($CDCl_3$, 300 MHz) δ = 1.23 – 1.44 (m, 22 H, 11 $CH_2$), 1.47 (s, 9 H, 3 $CH_3$), 1.63 – 1.72 (m, 2 H, $CH_2$), 1.74 – 1.93 (m, 2 H, $CH_2$), 2.02 (q, *J* = 6.5 Hz, 4 H, 2 $CH_2$), 2.41 (t, *J* = 7.5 Hz, 2 H, $CH_2$), 3.93 (d, *J* = 4.9 Hz, 2 H, $CH_2$), 4.89 – 5.02 (m, 4 H, 2 $CH_2$), 5.19 – 5.25 (m, 1 H, CH), 5.80 (tdd, *J* = 16.9 Hz, 10.2 Hz, 6.7 Hz, 2 H, 2 CH), 6.54 (br, t, *J* = 4.5 Hz, 1 H, NH) ppm; $^{13}$C NMR ($CDCl_3$, 75 MHz) δ = 24.68, 24.85, 27.96, 28.81, 28.98, 29.03, 29.11, 29.20, 29.25, 29.26, 31.85, 33.69, 34.23, 41.67, 73.57, 82.44, 114.06, 114.10, 139.03, 139.08, 168.62, 170.09, 172.43 ppm; ESI-MS of $C_{29}H_{51}NO_5$ ($M+Na^+$ = 516.48; $M+K^+$ = 532.45); HRMS of $C_{29}H_{51}NO_5$ $[M+H]^+$ calc. 494.3845 found 494.3866; $[M+Na]^+$ calc. 516.3665 found 516.3654.

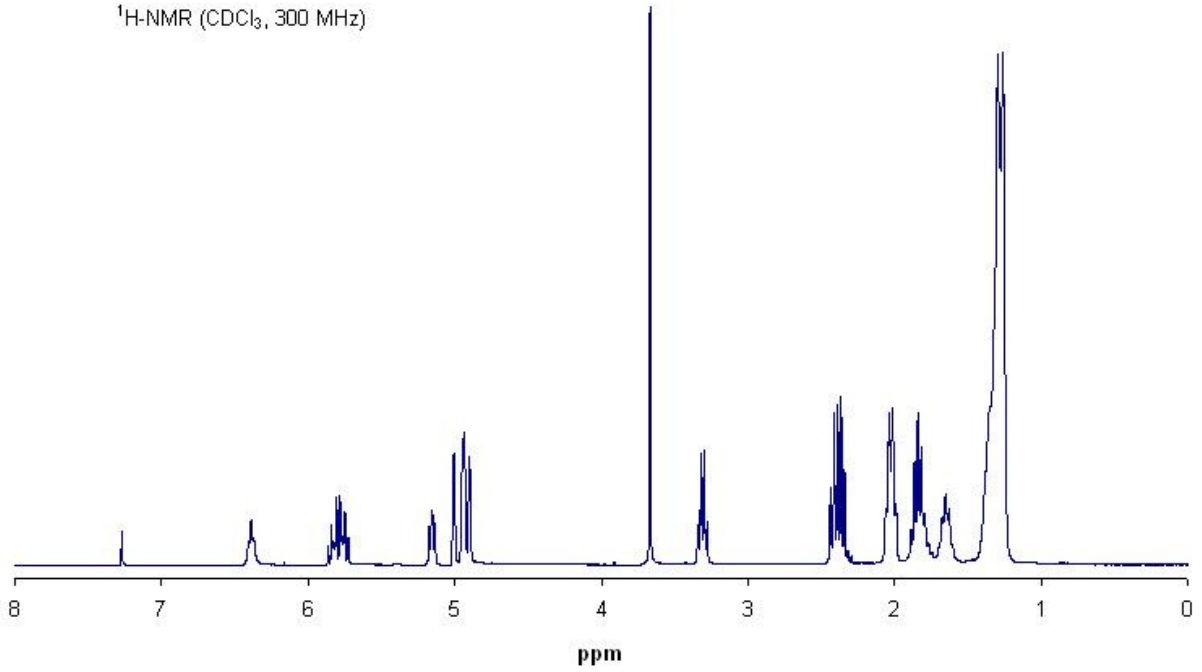


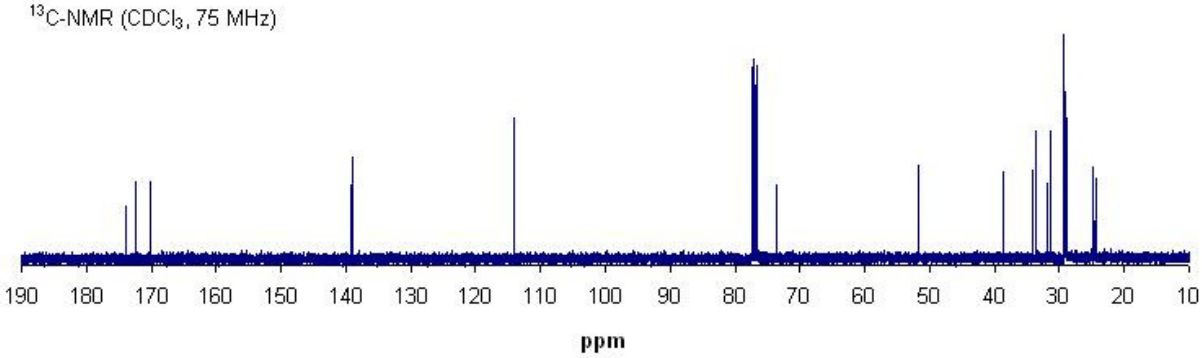



### 1.3.4 1-(Methyloxycarbonylpropylcarbamoyl)undec-10-enyl undec-10-enoate (6d)



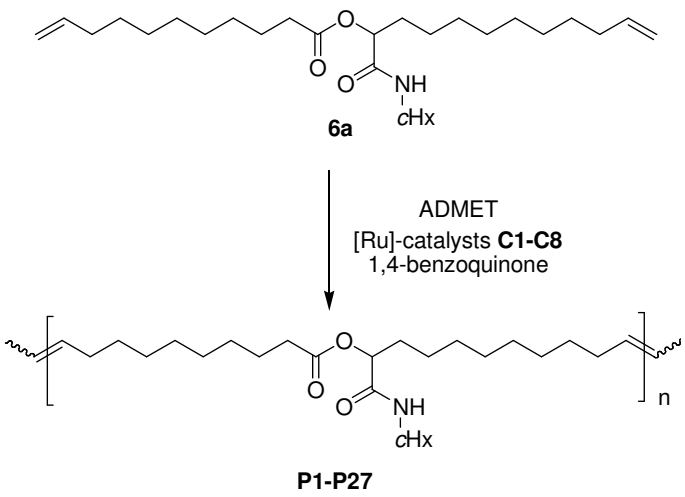

The Passerini-3CR of 10-undecenal **4** (1.32 g, 7.87 mmol), 10-undecenoic acid **2** (1.45 g, 7.87 mmol) and methyl 4-isocyanobutyrate **5d** (1.00 g, 7.87 mmol)[1] led to the formation of 1-(methyloxycarbonylpropylcarbamoyl)undec-10-enyl undec-10-enoate **6d**. After purification by column chromatography (*n*-hexane / ethyl acetate 9 : 1 to 5 : 1), **6d** was obtained as a slightly yellow oil (3.15 g, 83%). TLC (*n*-hexane / ethyl acetate 5 : 1) $R_f$ = 0.16; $^1$H NMR ($CDCl_3$, 300 MHz) δ = 1.22 – 1.44 (m, 22 H, 11 $CH_2$), 1.58 – 1.72 (m, 2 H, $CH_2$), 1.73 – 1.91 (m, 4 H, 2 $CH_2$), 2.01 (q, *J* = 6.5 Hz, 4 H, 2 $CH_2$), 2.28 – 2.44 (m, 4 H, 2 $CH_2$), 3.30 (q, *J* = 6.4 Hz, 2 H, $CH_2$), 3.66 (s, 3 H, $CH_3$), 4.87 – 5.02 (m, 4 H, 2 $CH_2$), 5.14 (t, *J* = 5.8 Hz, 1 H, CH), 5.79 (tdd, *J* = 16.8 Hz, 10.4 Hz, 6.7 Hz, 2 H, 2 CH), 6.38 (br, t, *J* = 5.3 Hz, 1 H, NH) ppm; $^{13}$C NMR ($CDCl_3$, 75 MHz) δ = 24.26, 24.72, 24.85, 28.82, 28.83, 28.99, 29.00, 29.05, 29.14, 29.23, 29.29, 31.42, 31.86, 33.70, 33.72, 34.22, 38.70, 51.67, 73.70, 114.07, 114.12, 139.03, 139.09, 170.15, 172.49, 173.88 ppm; ESI-MS of $C_{28}H_{49}NO_5$ ($M+H^+$ = 480.48; $M+Na^+$ = 502.46; $M+K^+$ = 518.45); HRMS of $C_{28}H_{49}NO_5$ $[M+H]^+$ calc. 480.3689 found 480.3652.


$^{1}$H-NMR ($CDCl_3$, 300 MHz)
8
7
6
5
4
3
2
1
0
ppm


$^{13}$C-NMR ($CDCl_3$, 75 MHz)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

## 1.4 Polymer syntheses

a) ADMET with Passerini-3CR product **6a**




b) Used catalysts **C1-C8**

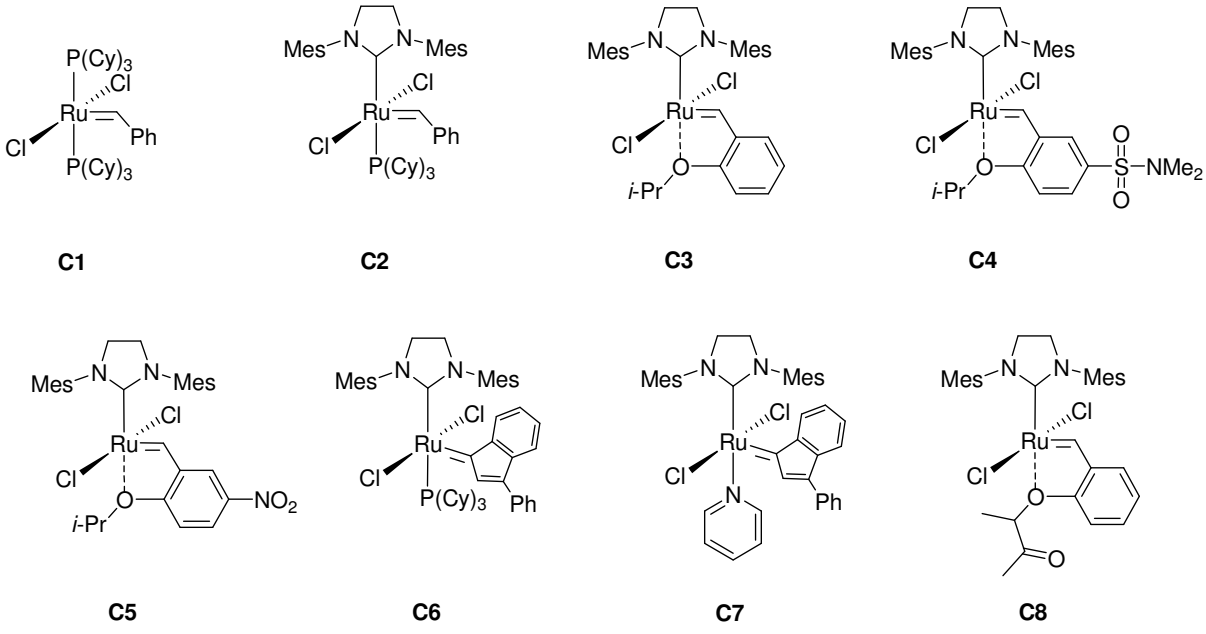
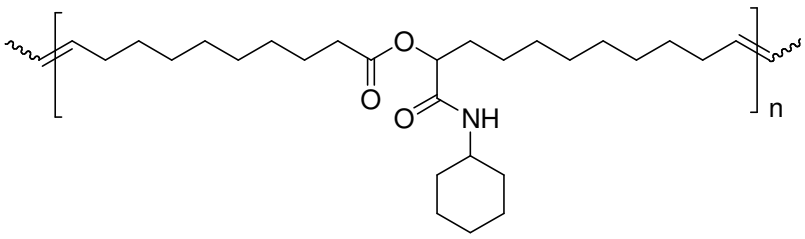



***Figure 2.*** *ADMET of Passerini-3CR product* ***6a*** *(a) and tested catalysts (b).*

### 1.4.1 Poly[1-(alkyl carbamoyl)alkyl alkanoates] derived from monomer 6a (P1 – P27)




*General procedure for acyclic diene metathesis (ADMET) of monomers **6a** – **6d**:*

Monomer **6a** (0.40 g, 0.87 mmol) and 1,4-benzoquinone (3 eq. per mol-% of catalyst **C1** – **C8**) were mixed and heated to 80 - 120°C with stirring under nitrogen atmosphere. The catalyst (**C1 - C8**, 0.2 - 2.0 mol-%) was then added and immediately an acute foaming was observed. The reaction mixture was stirred under a continuous nitrogen flow for four hours. Subsequently, THF (1 mL) and ethyl vinyl ether (0.4 mL) were added to quench the reaction. The obtained polymers **P1 - P27** were precipitated as high viscous substances by slow addition into cold methanol. Representative $^1$H NMR of **P10** ($CDCl_3$, 300 MHz) $\delta$ = 1.04 – 1.46 (m, $CH_2$), 1.55 – 2.06 (m, $CH_2$), 2.38 (t, $J$ = 7.4 Hz, $CH_2$), 3.70 – 3.84 (m, CH), 5.12 (t, $J$ = 5.8 Hz, CH), 5.28 – 5.46 (m, CH), 5.87 (br, d, $J$ = 7.5 Hz, NH) ppm.

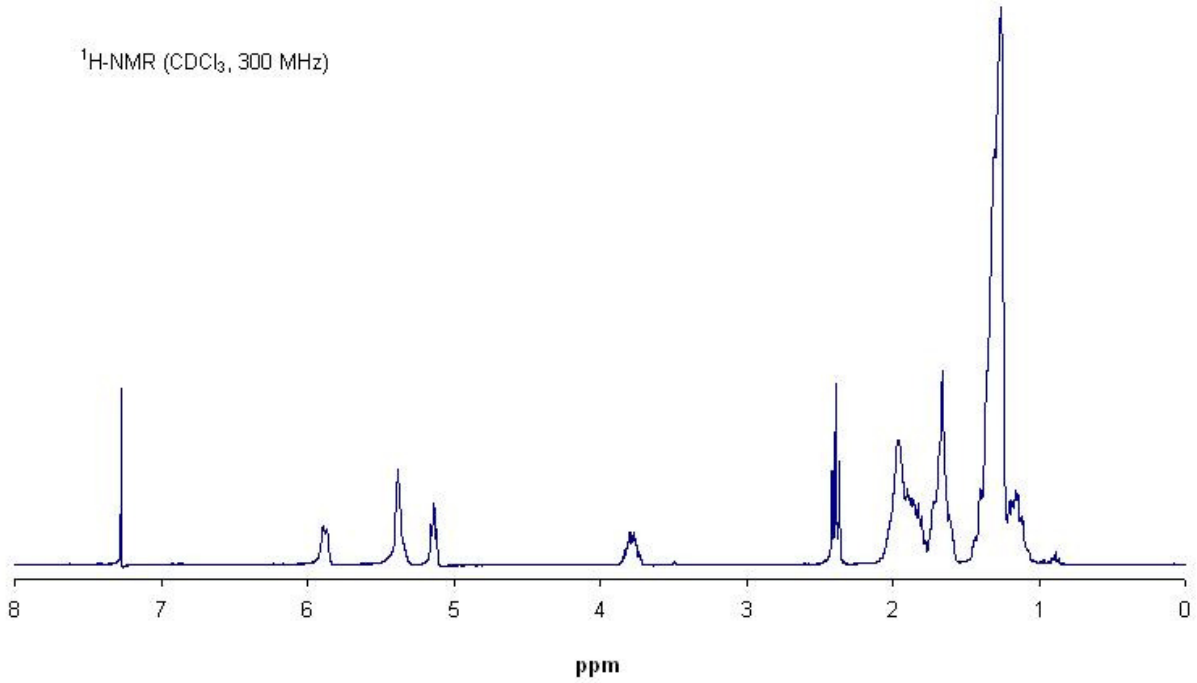


**Table 1:** Results of catalyst screening of the ADMET with Passerini-3CR product **6a**.

| entry | catalyst type | catalyst amount [mol-%] | temperature [°C] | $M_n$ [g / mol] precipitated | PDI $M_w$ / $M_n$ precipitated |
|---|---|---|---|---|---|
| **P1** | **C1** | 2.0 | 80 | 10000 | 1.51 |
| **P2** | **C1** | 1.0 | 80 | 7400 | 1.42 |
| **P3** | **C1** | 0.5 | 80 | 10650 | 1.68 |
| **P4** | **C1** | 1.0 | 100 | 7650 | 1.44 |
| **P5** | **C1** | 0.5 | 100 | 7050 | 1.40 |
| **P6** | **C2** | 1.0 | 80 | 12750 | 1.48 |
| **P7** | **C2** | 0.5 | 80 | 13750 | 1.44 |
| **P8** | **C2** | 1.0 | 100 | 19150 | 1.48 |
| **P9** | **C3** | 2.0 | 80 | 18650 | 1.38 |
| **P10** | **C3** | 1.0 | 80 | 21650 | 1.35 |
| **P11** | **C3** | 0.5 | 80 | 24700 | 1.34 |
| **P12** | **C3** | 2.0 | 100 | 14850 | 1.57 |
| **P13** | **C3** | 1.0 | 100 | 16800 | 1.47 |
| **P14** | **C3** | 0.5 | 100 | 17800 | 1.49 |
| **P15** | **C3** | 2.0 | 120 | 13950 | 1.60 |
| **P16** | **C4** | 1.0 | 80 | 10700 | 1.51 |
| **P17** | **C4** | 0.5 | 80 | 10250 | 1.45 |
| **P18** | **C5** | 1.0 | 80 | 12050 | 1.43 |
| **P19** | **C5** | 0.5 | 80 | 11350 | 1.46 |
| **P20** | **C5** | 1.0 | 100 | 13600 | 1.53 |
| **P21** | **C5** | 0.5 | 100 | 13750 | 1.45 |
| **P22** | **C6** | 2.0 | 80 | 12150 | 1.58 |
| **P23** | **C6** | 1.0 | 80 | 9000 | 1.50 |
| **P24** | **C7** | 2.0 | 80 | 15350 | 1.55 |
| **P25** | **C7** | 1.0 | 80 | 12750 | 1.48 |
| **P26** | **C8** | 2.0 | 80 | 14600 | 1.54 |
| **P27** | **C8** | 1.0 | 80 | 11750 | 1.60 |

Conditions: neat / 1,4-benzoquinone (3 eq. according to catalyst) / $N_2$-purged.

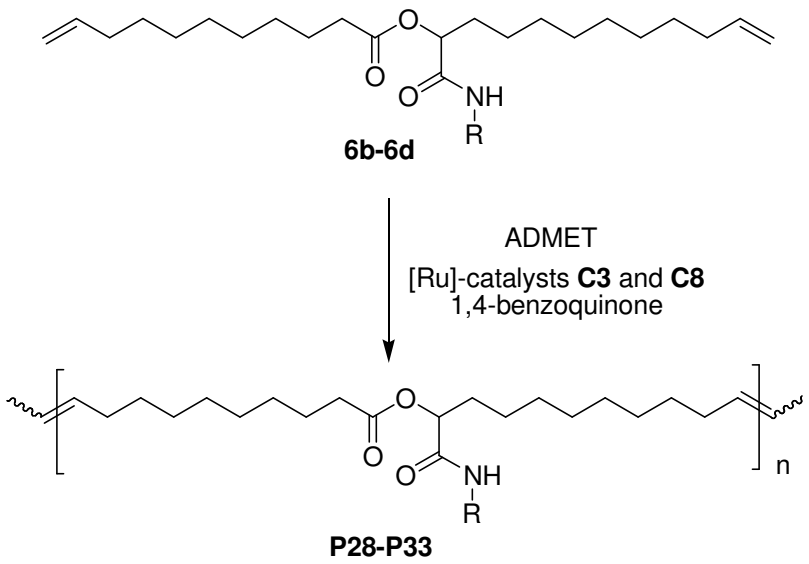
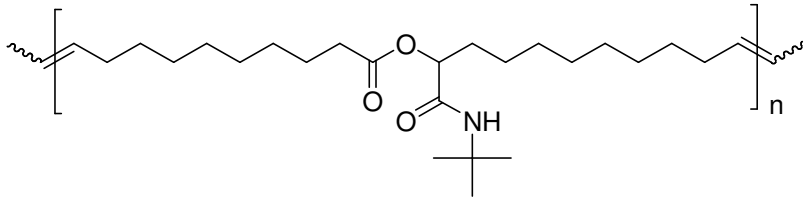
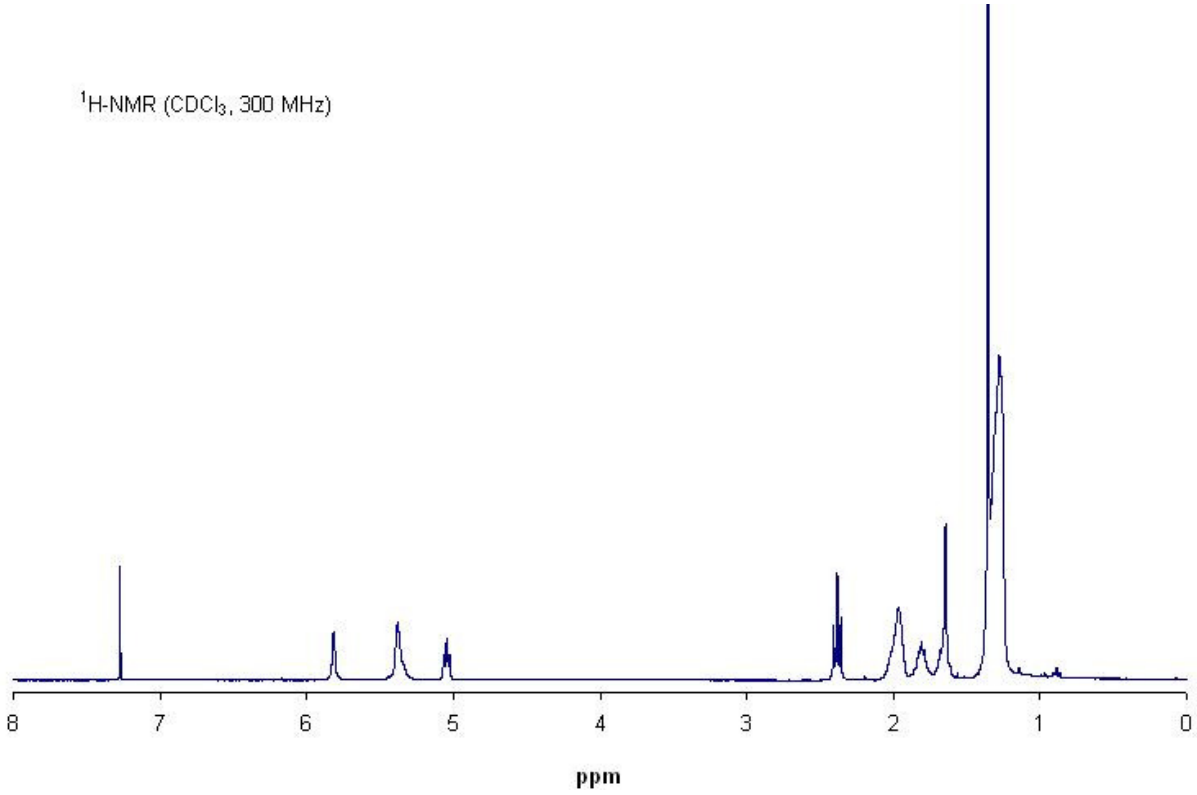



***Figure 3.*** *ADMET of Passerini-3CR products* ***6b – d****.*

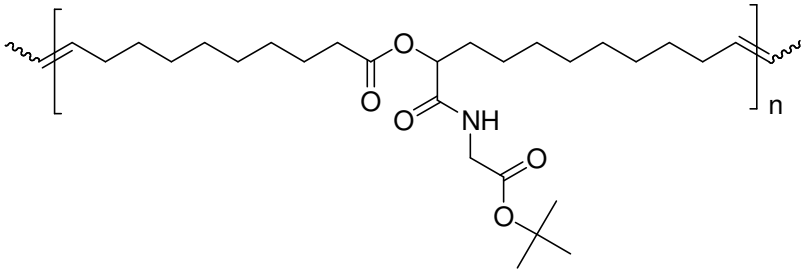
### 1.4.2 Poly[1-(alkyl carbamoyl)alkyl alkanoates] derived from monomer 6b (P28, P29)



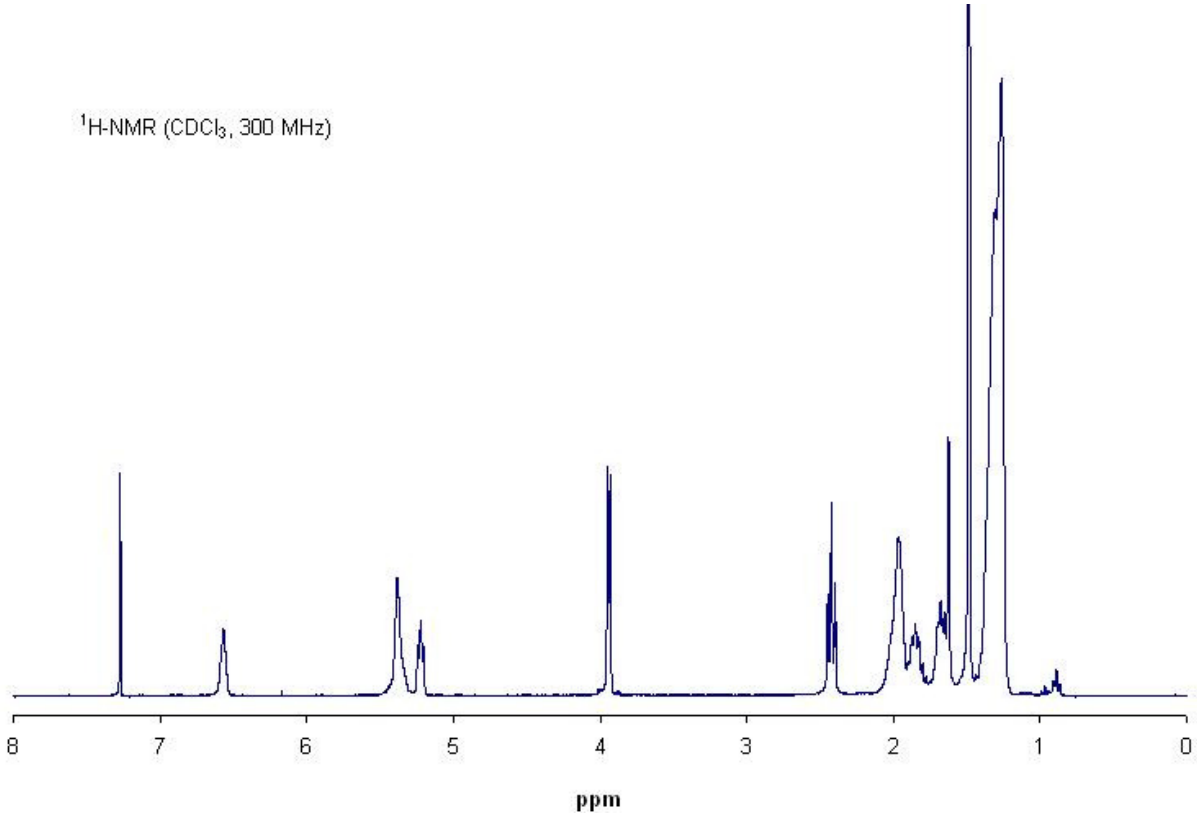

Monomer **6b** (0.40 g, 0.92 mmol) was polymerized with **C3** and **C8** (1.0 mol-%) at 80°C using the general procedure as described above to obtain the polymers **P28** and **P29**. Representative $^1$H NMR of **P28** ($CDCl_3$, 300 MHz) $\delta$ = 1.22 – 1.40 (m, $CH_2$), 1.34 (s, $CH_3$), 1.60 – 1.69 (m, $CH_2$), 1.74 – 1.85 (m, $CH_2$), 1.90 – 2.05 (m, $CH_2$), 2.37 (t, $J$ = 7.4 Hz, $CH_2$), 5.03 (t, $J$ = 5.8 Hz, CH), 5.29 – 5.44 (m, CH), 5.80 (br, s, NH) ppm.



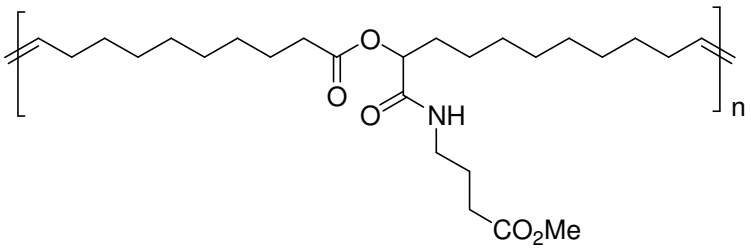

### 1.4.3 Poly[1-(alkyl carbamoyl)alkyl alkanoates] derived from monomer 6c (P30, P31)




Monomer **6c** (0.40 g, 0.81 mmol) was polymerized with **C3** and **C8** (1.0 mol-%) at 80°C using the general procedure as described above to obtain the polymers **P30** and **P31**. Representative $^1$H NMR of **P31** ($CDCl_3$, 300 MHz) $\delta$ = 1.22 – 1.41 (m, $CH_2$), 1.47 (s, $CH_3$), 1.59 – 1.72 (m, $CH_2$), 1.76 – 2.06 (m, $CH_2$), 2.41 (t, $J$ = 7.5 Hz, $CH_2$), 3.93 (d, $J$ = 4.9 Hz, $CH_2$), 5.21 (t, $J$ = 5.9 Hz, CH), 5.30 – 5.44 (m, CH), 6.52 – 6.61 (m, NH) ppm.




### 1.4.4 Poly[1-(alkyl carbamoyl)alkyl alkanoates] derived from monomer 6d (P32, P33)




Monomer **6d** (0.40 g, 0.83 mmol) was polymerized with **C3** and **C8** (1.0 mol-%) at 80°C using the general procedure as described above to obtain the polymers **P32** and **P33**. Representative $^1$H NMR of **P32** ($CDCl_3$, 300 MHz) $\delta$ = 1.21 – 1.39 (m, $CH_2$), 1.58 – 1.72 (m, $CH_2$), 1.73 – 1.89 (m, $CH_2$), 1.90 – 2.05 (m, $CH_2$), 2.29 – 2.44 (m, $CH_2$), 3.31 (q, $J$ = 6.4 Hz, $CH_2$), 3.67 (s, $CH_3$), 5.11 – 5.17 (m, CH), 5.29 – 5.40 (m, CH), 6.38 (br, s, NH) ppm.

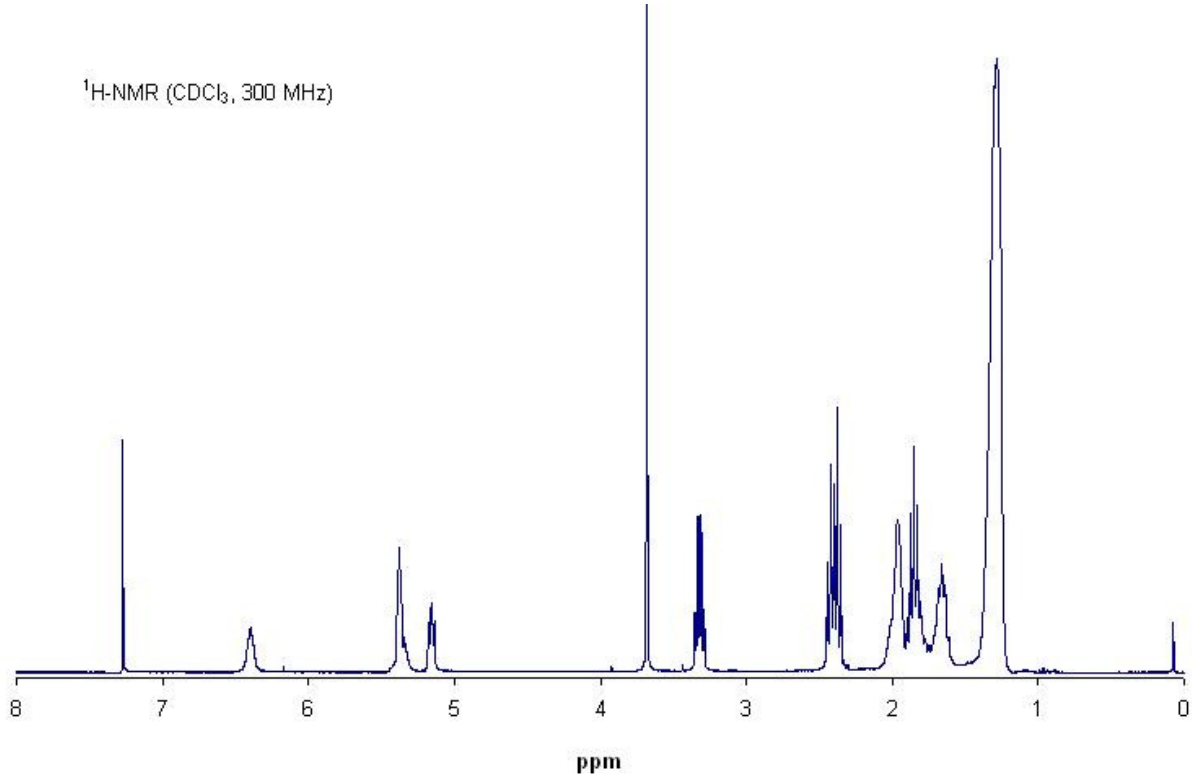



***Table 2:*** *Results of ADMET with Passerini-3CR products* ***6b – d****.*

| entry | monomer | catalyst type | $M_n$ [g / mol] | PDI $M_w$ / $M_n$ |
|---|---|---|---|---|
| **P28** | **6b** | **C3** | 16500 | 1.45 |
| **P29** | **6b** | **C8** | 14100 | 1.50 |
| **P30** | **6c** | **C3** | 11450 | 1.40 |
| **P31** | **6c** | **C8** | 15500 | 1.41 |
| **P32** | **6d** | **C3** | 17800 | 1.43 |
| **P33** | **6d** | **C8** | 13900 | 1.44 |

Conditions: neat / 1.0 mol-% of Ru-catalyst / 1,4-benzoquinone (3 eq. per Ru-catalyst) / 80°C / 4 hours reaction time / $N_2$-purged.

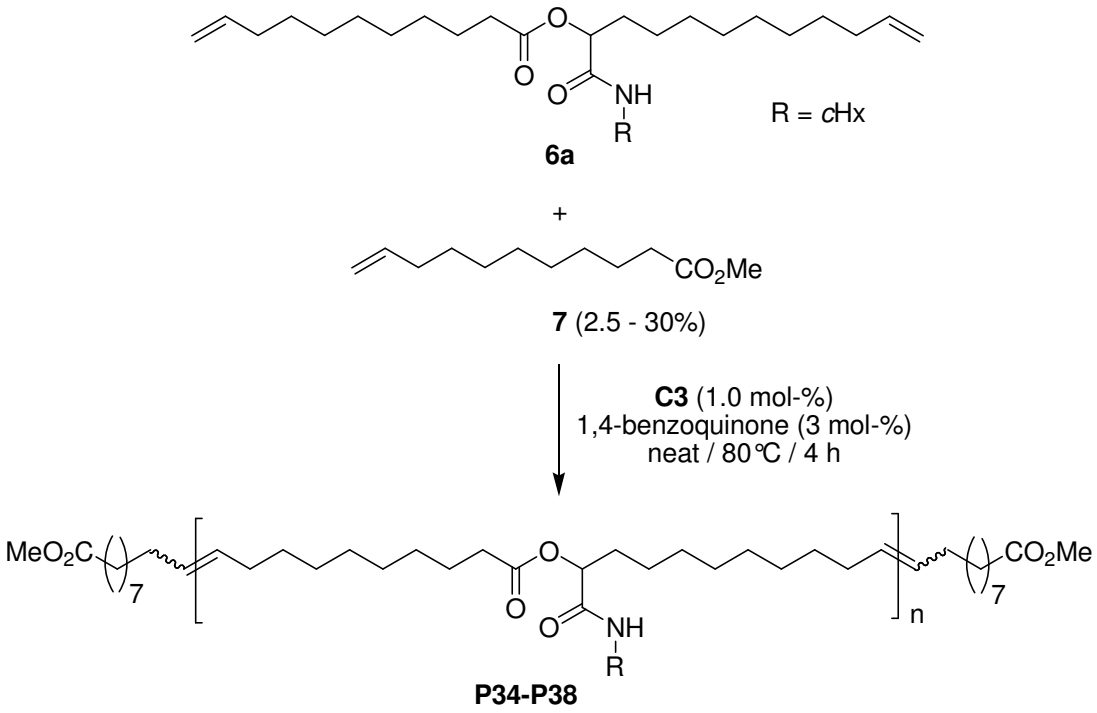
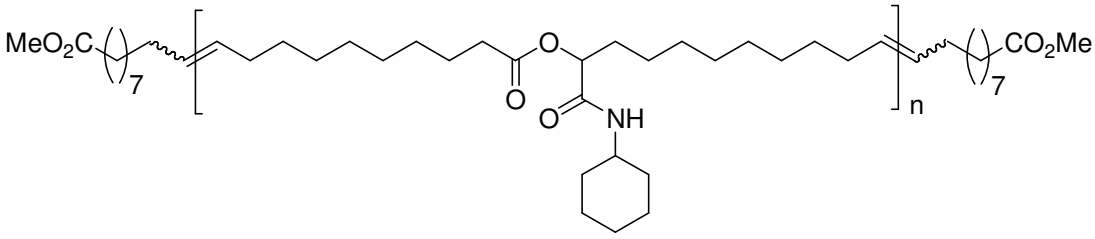



***Figure 4.*** *ADMET with monomer* ***6a*** *and methyl 10-undecenoate* ***7*** *as chain stopper.*

### 1.4.5 Poly[1-(alkyl carbamoyl)alkyl alkanoates] derived from monomer 6a with methyl 10-undecenoate 7 as chain stopper (P34 – P38)




*General procedure for acyclic diene metathesis (ADMET) with monomer* ***6a*** *and methyl 10-undecenoate* ***7*** *as chain stopper:*

Monomer **6a** (0.40 g, 0.87 mmol), methyl 10-undecenoate **7** (2.5 – 30 mol-%) and 1,4-benzoquinone (3.00 mg, 0.03 mmol, 3 mol-%) were mixed and heated to 80°C with stirring under nitrogen atmosphere. The catalyst **C3** (6.00 mg, 0.01 mol, 1.0 mol-%) was then added and immediately an acute foaming was observed. The reaction mixture was stirred under a continuous nitrogen flow for four hours. Subsequently, THF (1.0 mL) and ethyl vinyl ether

(0.4 mL) was added to quench the reaction. The obtained polymers **P34 – P38** were precipitated as highly viscous substances by slow addition into cold methanol. Representative $^1$H NMR of **P36** ($CDCl_3$, 300 MHz) δ = 1.07 – 1.42 (m, $CH_2$), 1.57 – 2.04 (m, $CH_2$), 2.38 (t, *J* = 7.5 Hz, $CH_2$), 3.66 (s, $CH_3$), 3.73 – 3.81 (m, CH), 5.11 – 5.15 (m, CH), 5.31 – 5.42 (m, CH), 5.88 (br, d, *J* = 5.4 Hz, NH) ppm.

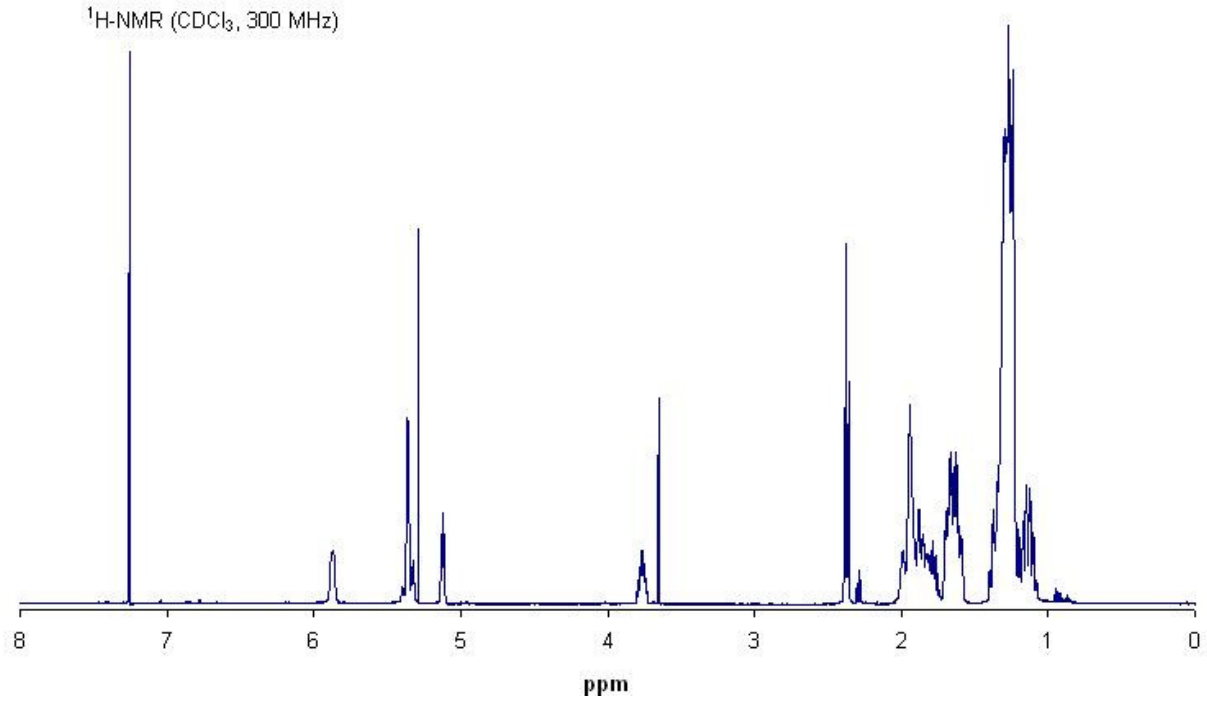



***Table 3:*** *Results of ADMET with Passerini-3CR products* ***6a*** *and different amounts of chain stopper* ***7****.*

| entry | amount of chain stopper (mol-%) | polymerisation degree *n* | $M_n$ (calc.) [g / mol] | $M_n$ [g / mol] precipitated | PDI $M_w$ / $M_n$ precipitated |
|---|---|---|---|---|---|
| **P34** | 30 | ~14 | 6450 | 5300 | 1,48 |
| **P35** | 20 | ~17 | 7750 | 8300 | 1.43 |
| **P36** | 10 | ~31 | 13600 | 9100 | 1.54 |
| **P37** | 5.0 | ~42 | 18600 | 10550 | 1.59 |
| **P38** | 2.5 | ~117 | 51150 | 12850 | 1,66 |

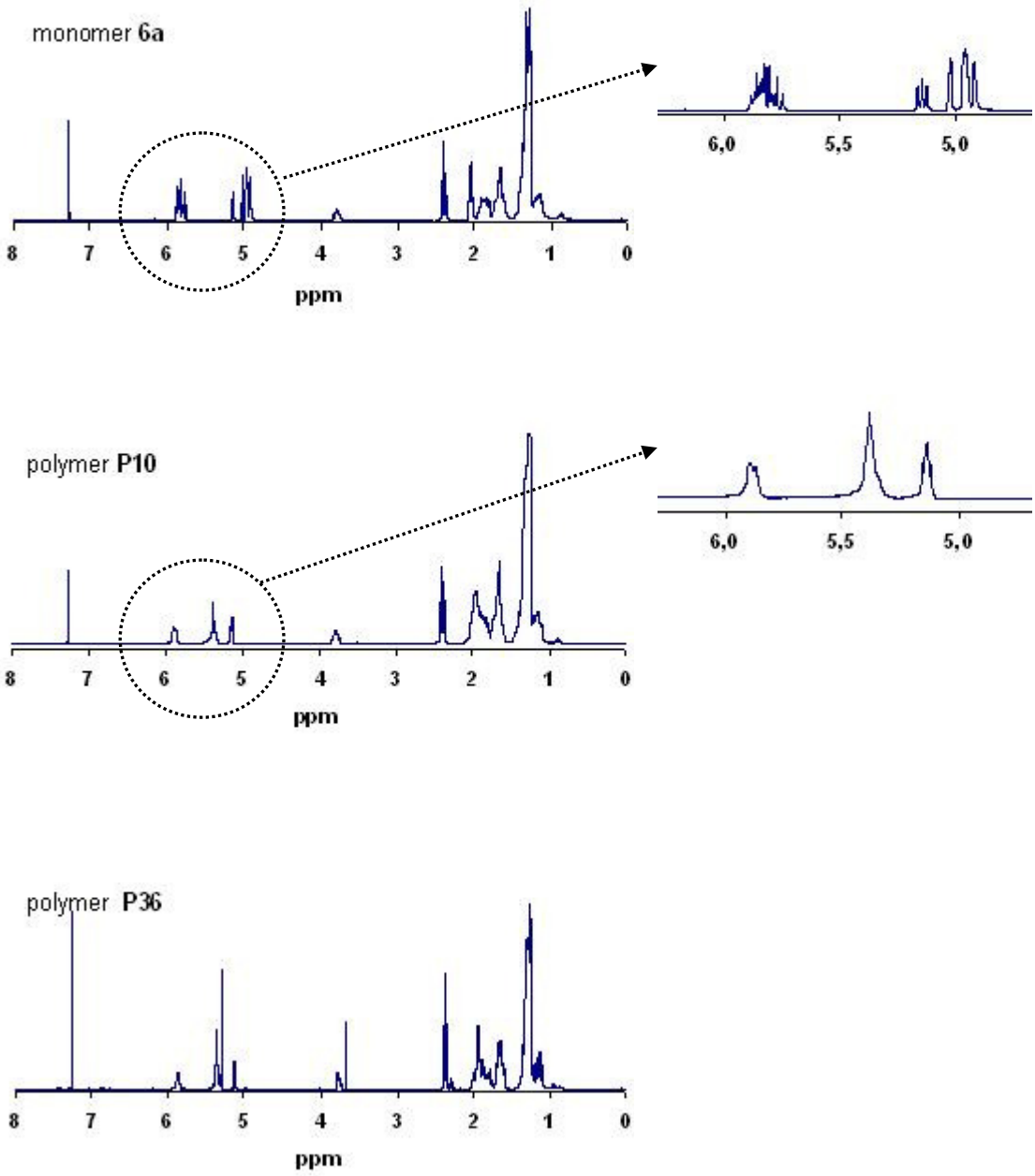
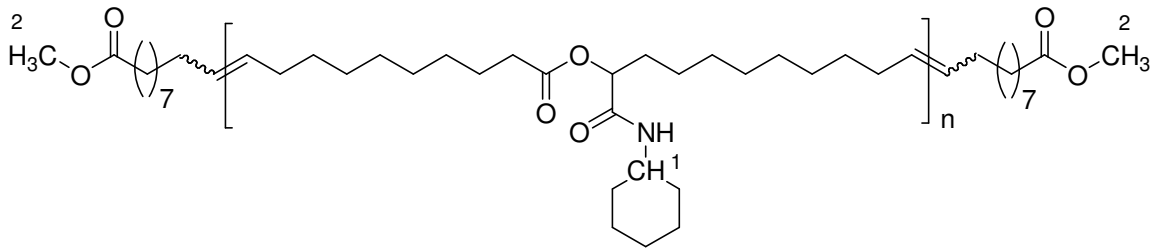


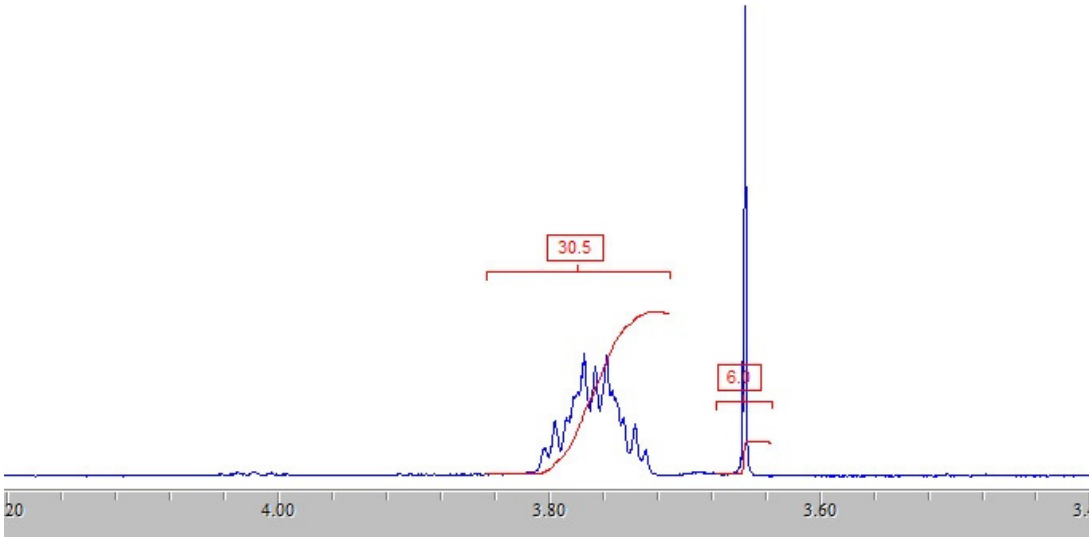

***Figure 5.*** *$^1$H NMR spectra ($CDCl_3$, 300 MHz) of monomer **6a**, polymer **P10** and polymer with chain stopper **P36**.*

Calculation of the degree of polymerization via integral correlation of $^{1}$H NMR signals:

Generally, the integrals of the methyl ester end-groups present in polymers **P34**-**P38** were correlated to repeat unit signals, such as the integral of the of the CH group of the cyclohexyl-ring resulting from monomer **6a** (see structure of polymer below).




An example of such a correlation is shown below for the $^{1}$H NMR spectrum of **P36**:




It is important that no terminal double bonds are observed. Thus, it can be assumed that each side of the polymer is terminated with methyl ester groups of methyl 10-undecenoate **7**. The integral value of the cyclohexyl-CH (1) is determined with a value of about 30.5 (see above) and represents the degree of polymerization *n* of **P36**.

The calculation of the molecular weight (MW) is carried out using following general formula:

$$Mn_{polymer} \approx n \cdot MW_{monomer\,6a} + 2 \cdot MW_{methylundecenoate} - (n+1) \cdot MW_{ethylene}$$

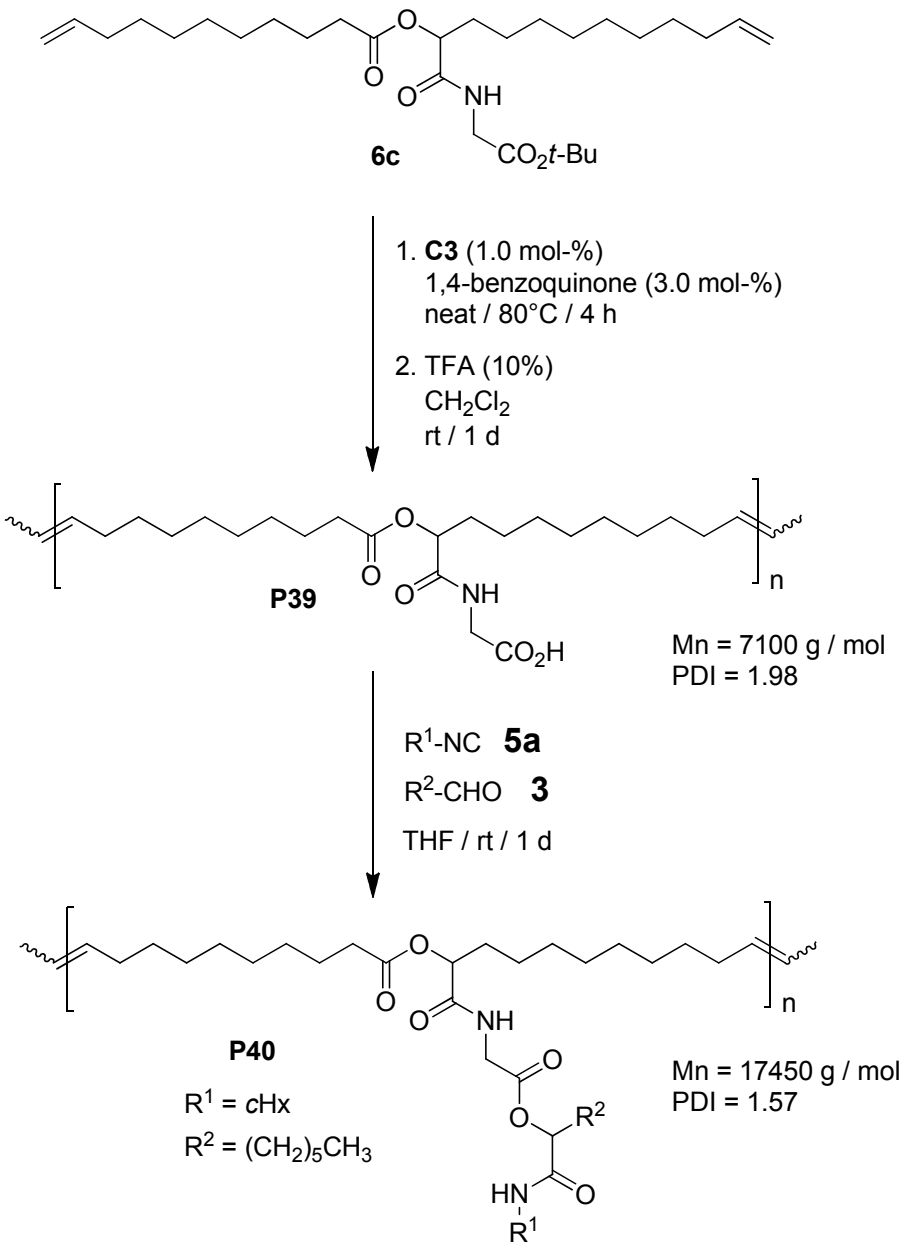
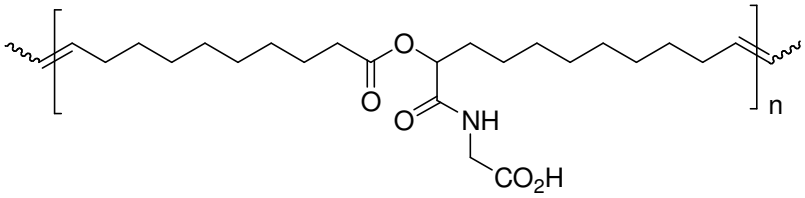
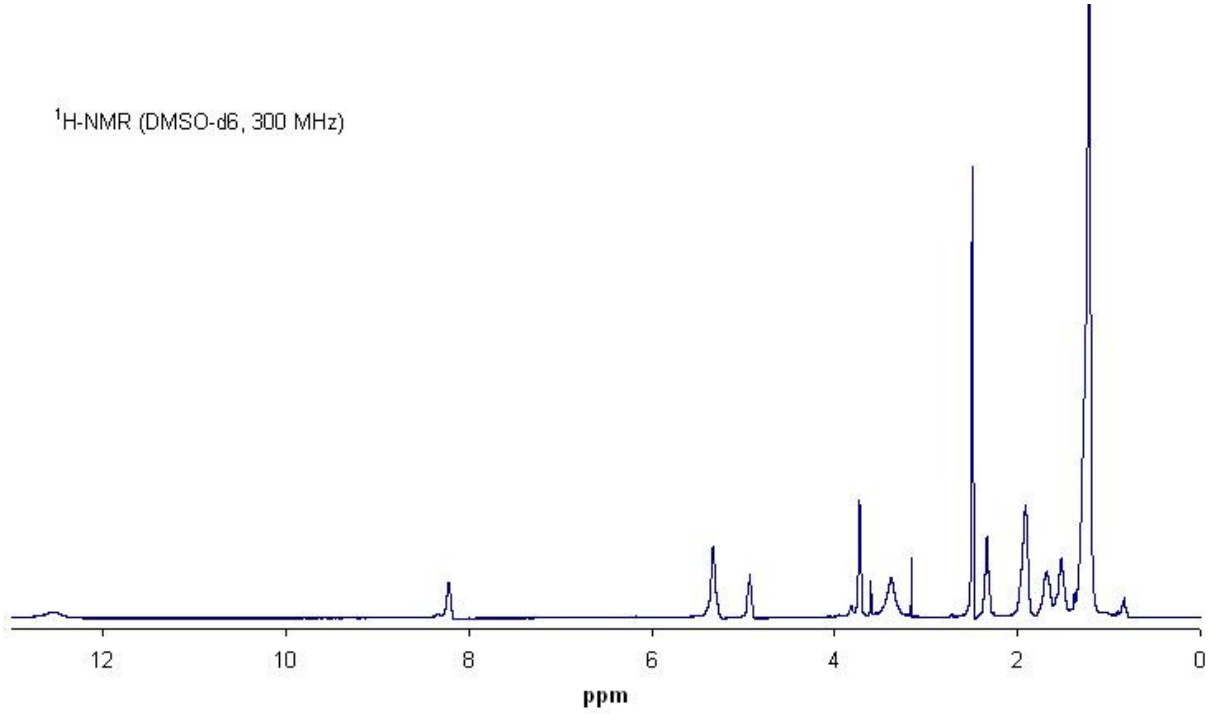



***Figure 6.*** *One-pot reaction sequence of ADMET and saponification.*

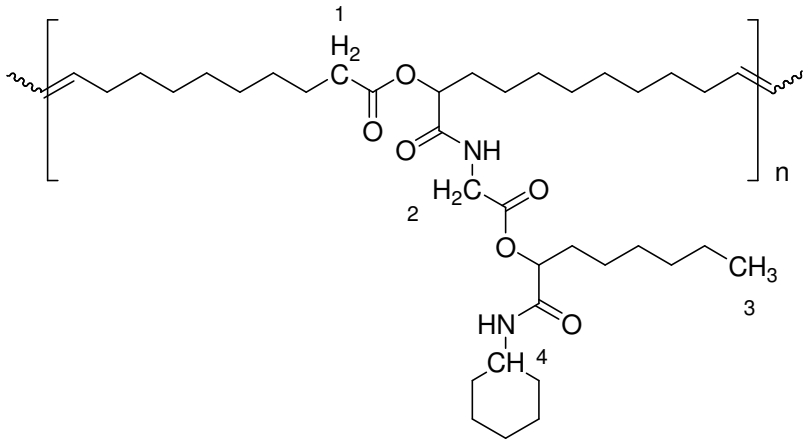
### 1.4.6 Poly[1-(alkyl carbamoyl)alkyl alkanoates] derived from monomer 6c and subsequent saponification of the *tert*-butyl ester (P39)



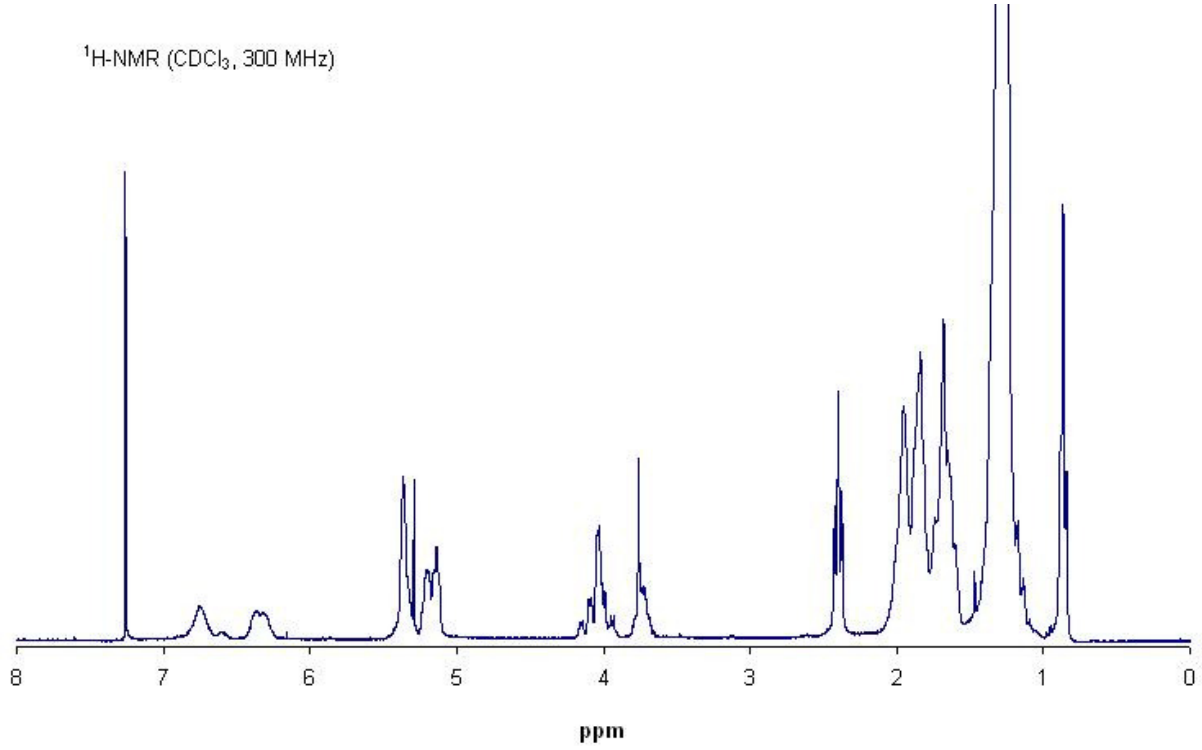
Monomer **6c** (0.40 g, 0.81 mmol) was polymerized with **C3** (5.00 mg, 0.09 mmol, 1.0 mol-%) at 80°C using the general procedure as described above. After precipitation, the obtained polymer was dissolved in dichloromethane (3.0 mL) and trifluoroacetic acid (1.0 mL) was added. The reaction was stirred for three hours and then precipitated to obtain polymer **P39** as a rubbery substance by slow addition into methanol. Representative $^{1}$H NMR (DMSO-d6, 300 MHz) $\delta$ = 1.18 – 1.39 (m, $CH_2$), 1.46 – 1.78 (m, $CH_2$), 1.86 – 2.03 (m, $CH_2$), 2.34 (t, $J$ = 6.5 Hz, $CH_2$), 3.73 (d, $J$ = 5.7 Hz, $CH_2$), 4.93 (t, $J$ = 5.4 Hz, CH), 5.27 – 5.42 (m, CH), 8.18 – 8.38 (m, NH), 12.56 (br, s, OH) ppm.



### 1.4.7 Postmodified poly[1-(alkylcarbamoyl)undecenyl undecenoate] derived from the poly-Passerini3CR of poly-carboxylic acid derivative P39, heptanal 3 and cyclohexyl isonitrile 5a (P40)

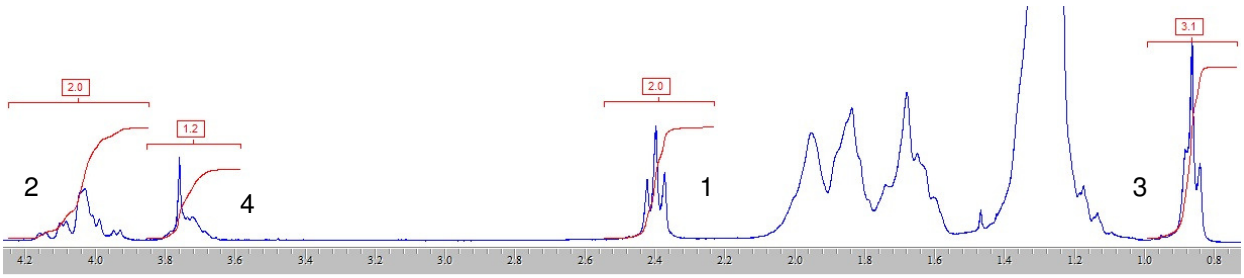



The precipitated and dried polymer **P39** was dissolved in THF (0.3 mL). Cyclohexyl isonitrile **5a** (88.0 mg, 0.81 mmol) and heptanal **3** (92.0 mg, 0.81 mmol) were then added and the reaction mixture was stirred for one day at room temperature. The polymer **P40** was precipitated as a high viscous substance by slow addition in methanol. $^1$H NMR ($CDCl_3$, 300 MHz) $\delta$ = 0.87 (t, $J$ = 6.4 Hz, $CH_3$), 1.13 – 1.47 (m, $CH_2$), 1.57 – 2.06 (m, $CH_2$), 2.40 (t, $J$ = 7.5 Hz, $CH_2$), 3.66 – 3.82 (m, CH), 3.93 – 4.17 (m, $CH_2$), 5.10 – 5.25 (m, CH), 5.28 – 5.43 (m, CH), 6.24 – 6.44 (m, NH), 6.55 – 6.88 (m, NH) ppm.




Detailed $^1$H NMR characterization of **P40** to access the functional group conversion of **P39**:

The correlation of integrals indicates that the carboxyl groups converted completely during the grafting onto reaction *via* Passerini-3CR. A zoom into the $^1$H NMR of **P40** (see below) reveals the expected integral ratios for protons 1-4 (see structure above). Moreover, no protons of free carboxylic acids or –NH-C$H_2$-COOH groups were observed. Both findings indicate complete conversion of **P39** to **P40**.



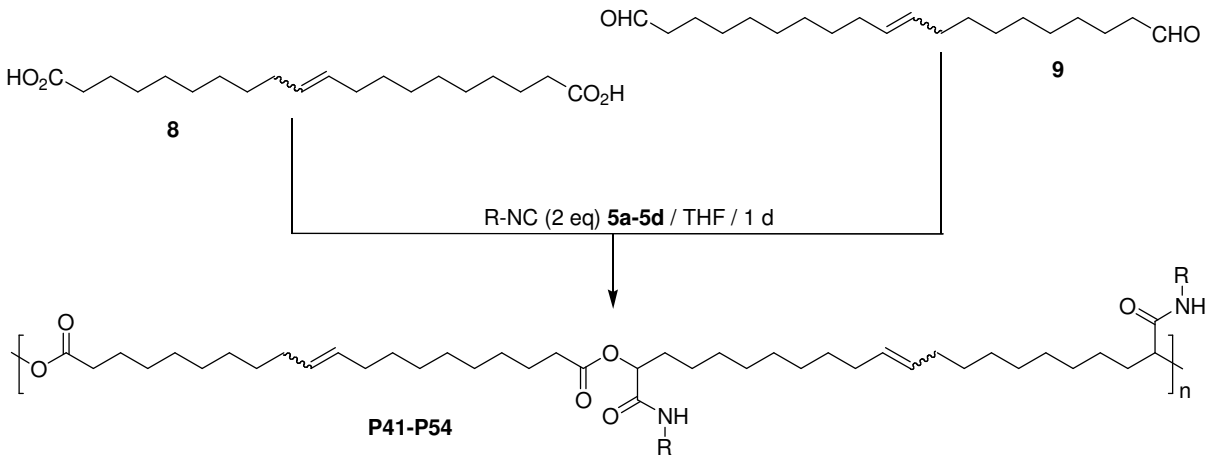
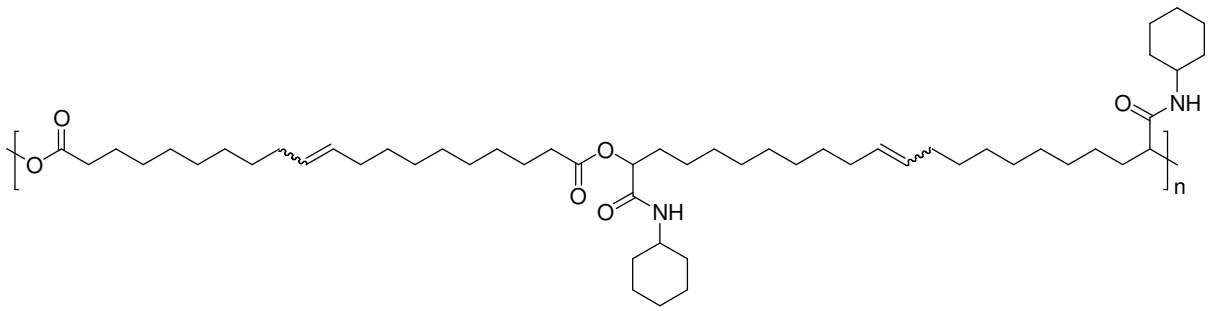



***Figure 7.*** *Passerini-3CR polymerization with dialdehyde* ***8****, dicarboxylic acid* ***9*** *and isonitriles* ***5a, b*** *and* ***d****.*

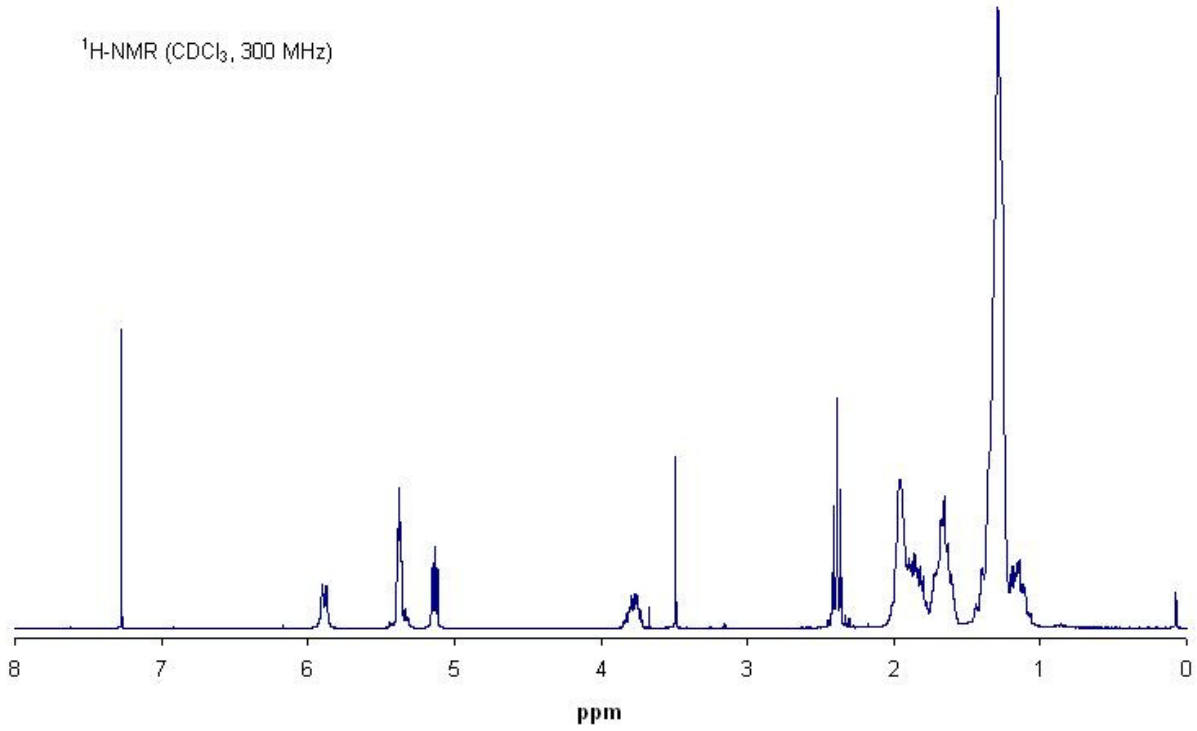
### 1.4.8 Poly[1-(alkylcarbamoyl)undecenyl undecenoate]derived from the Passerini-3CR polymerization of *trans*-icos10-enedioic acid 10, *trans*-icos-10-enedial 9 and cyclohexyl isonitrile 5a (P41-P50)



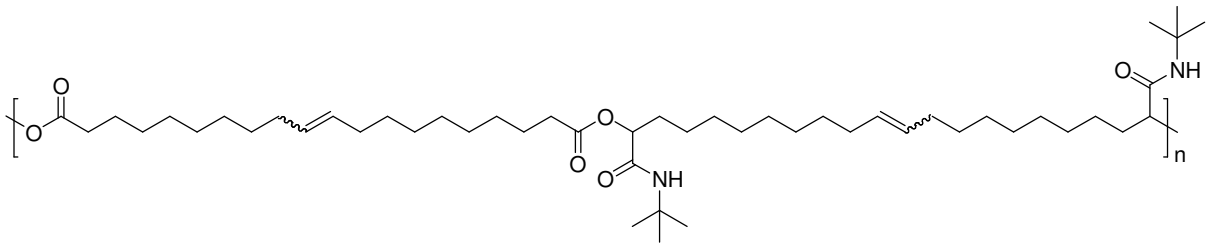
*General procedure for a Passerini-3CR polymerization with trans-icos-10-enedioic acid* ***8*** *and trans-icos-10-enedial* ***9****:*

*trans*-Icos-10-enedioic acid **8** (0.20 g, 0.59 mmol)[2,3] and *trans*-icos-10-enedial **9** (0.18 g, 0.59 mmol)[4] were dissolved in THF (0.3 – 4.0 mL) or dichloromethane (4.0 mL) and heated up to 40 or 50°C. In the case using $CH_2Cl_2$ as solvent, the reaction was performed at room temperature. Subsequently, cyclohexyl isonitrile **5a** (0.13 g, 1.18 mmol) was added and the reaction mixture stirred for one day. The obtained polymers **P41 – P50** were precipitated as highly viscous substances by slow addition into cold methanol. Representative $^1$H NMR of **P47** ($CDCl_3$, 300 MHz) $\delta$ = 1.05 – 1.44 (m, $CH_2$), 1.56 – 2.03 (m, $CH_2$), 2.38 (t, $J$ = 7.4 Hz,

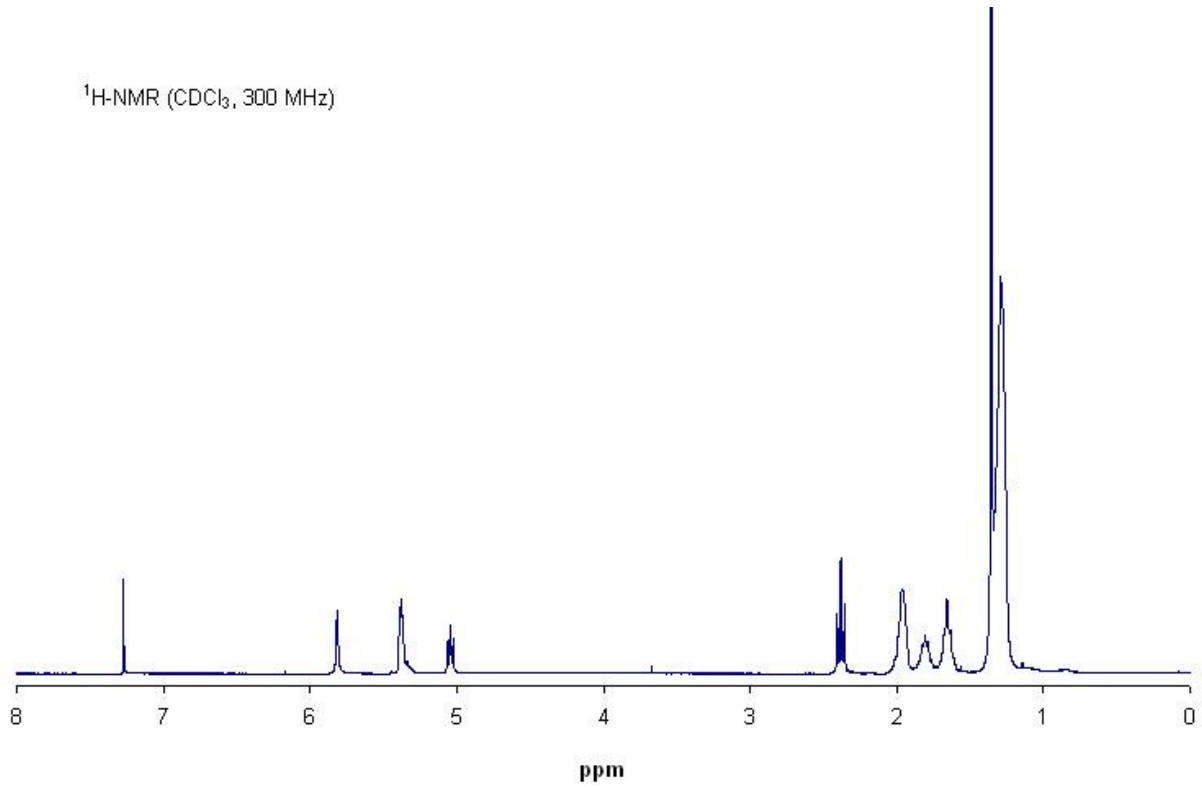
$CH_2$), 3.70 – 3.83 (m, CH), 5.12 (t, *J* = 5.8 Hz, CH), 5.29 – 5.43 (m, CH), 5.87 (br, d, *J* = 7.5 Hz, NH) ppm.



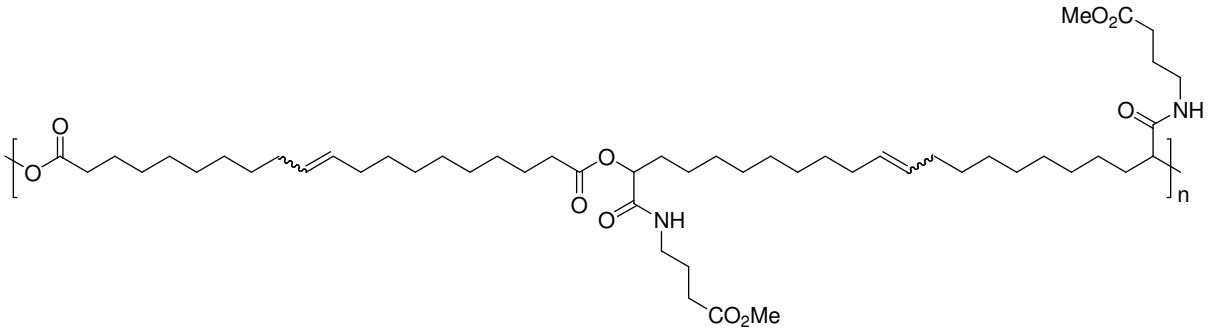

### 1.4.9 Poly[1-(alkylcarbamoyl)undecenyl undecenoate]derived from the Passerini-3CR polymerization of *trans*-icos 10-enedioic acid 10, *trans*-icos-10-enedial 9 and *tert*-butyl isonitrile 5b (P51, P52)




The Passerini-3CR with *trans*-icos-10-enedioic acid **8** (0.20 g, 0.59 mmol), *trans*-icos-10-enedial **9** (0.18 g, 0.59 mmol) and *tert*-butyl isonitrile **5b** (98.0 mg, 1.18 mmol) was performed using the general procedure as described above to obtain the polymers **P51** and **P52.** Representative $^1$H NMR of **P51** ($CDCl_3$, 300 MHz) δ = 1.19 – 1.40 (m, $CH_2$), 1.34 (s, $CH_3$), 1.58 – 1.70 (m, $CH_2$), 1.74 – 1.85 (m, $CH_2$), 1.90 – 2.03 (m, $CH_2$), 2.37 (t, *J* = 7.4 Hz, $CH_2$), 5.03 (t, *J* = 5.8 Hz, CH), 5.29 – 5.46 (m, CH), 5.80 (br, s, NH) ppm.




### 1.4.10 Poly[1-(alkylcarbamoyl)undecenyl undecenoate]derived from the Passerini-3CR polymerization of *trans*-icos-10-enedioic acid 10, *trans*-icos-10-enedial 9 and methyl 4-isocyanobutyrate 5d (P53, P54)




The Passerini-3CR with *trans*-icos-10-enedioic acid **8** (0.20 g, 0.59 mmol), *trans*-icos-10-enedial **9** (0.18 g, 0.59 mmol) and methyl 4-isocyanobutyrate **5d** (150 mg, 1.18 mmol) was performed using the general procedure as described above to obtain the polymers **P53** and **P54.** Representative $^1$H NMR of **P53** ($CDCl_3$, 300 MHz) $\delta$ = 1.21 – 1.40 (m, $CH_2$), 1.58 – 1.71 (m, $CH_2$), 1.73 – 1.89 (m, $CH_2$), 1.90 – 2.04 (m, $CH_2$), 2.29 – 2.46 (m, $CH_2$), 3.30 (q, $J$ = 6.4 Hz, $CH_2$), 3.67 (s, $CH_3$), 5.11 – 5.19 (m, CH), 5.31 – 5.43 (m, CH), 6.39 (br, s, NH) ppm.

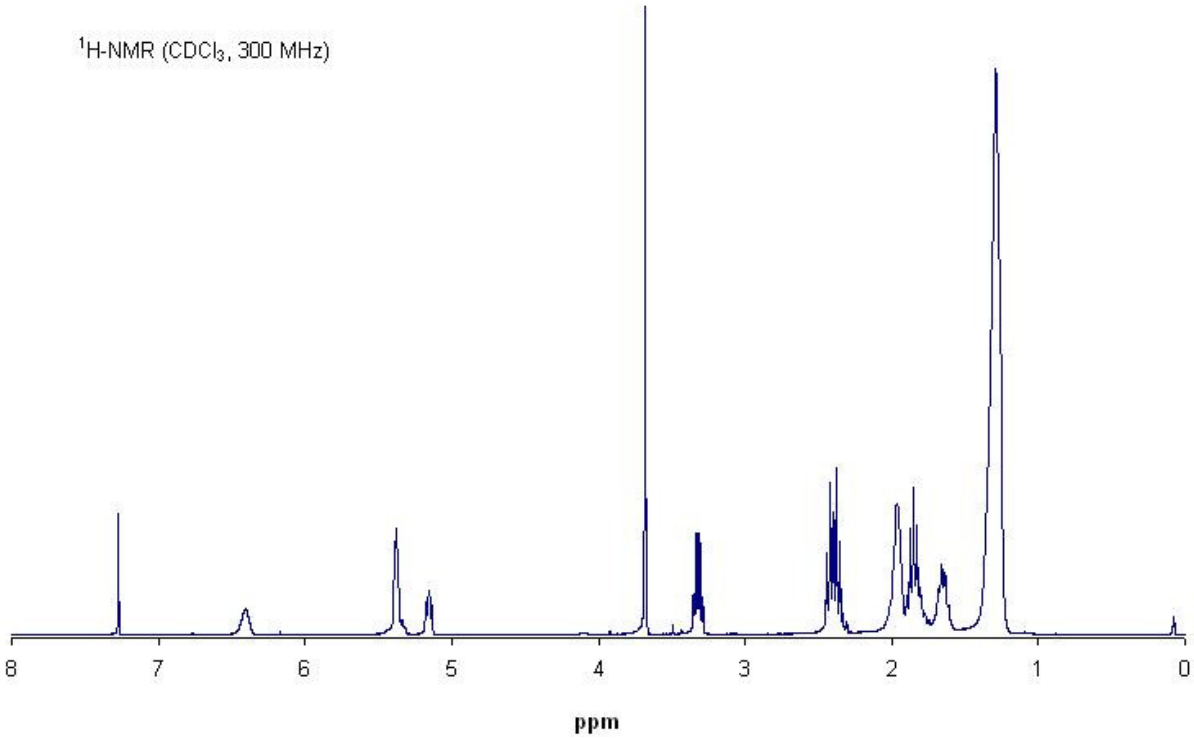

$^1$H-NMR ($CDCl_3$, 300 MHz)
8
7
6
5
4
3
2
1
0
ppm

***Table 4:*** *GPC-results of Passerini 3CR polymerizations.*

| entry | isonitrile | solvent (volume) | temperature [°C] | $M_n$ [g / mol] precipitated | PDI $M_w$ / $M_n$ precipitated |
|---|---|---|---|---|---|
| **P41** | **5a** | THF (4.0 mL) | 40 | 10500 | 1.49 |
| **P42** | **5a** | $CH_2Cl_2$ (4.0 mL) | rt | 25100 | 1.62 |
| **P43** | **5a** | THF (3.0 mL) | 40 | 9050 | 1.47 |
| **P44** | **5a** | THF (2.0 mL) | 40 | 8000 | 1,40 |
| **P45** | **5a** | THF (1.0 mL) | 40 | 29900 | 1.53 |
| **P46** | **5a** | THF (0.5 mL) | 40 | 50500 | 1.46 |
| **P47** | **5a** | THF (0.4 mL) | 40 | 41600 | 1.40 |
| **P48** | **5a** | THF (0.4 mL) | 50 | 18000 | 1.48 |
| **P49** | **5a** | THF (0.3 mL) | 40 | 55550 | 1.62 |
| **P50** | **5a** | THF (0.2 mL) | 40 | 56450 | 1.42 |
| **P51** | **5b** | THF (0.5 mL) | 40 | 42250 | 1.60 |
| **P52** | **5b** | THF (0.4 mL) | 40 | 34050 | 1.66 |
| **P53** | **5d** | THF (0.5 mL) | 40 | 7600 | 1.43 |
| **P54** | **5d** | THF (0.4 mL) | 40 | 7850 | 1.40 |

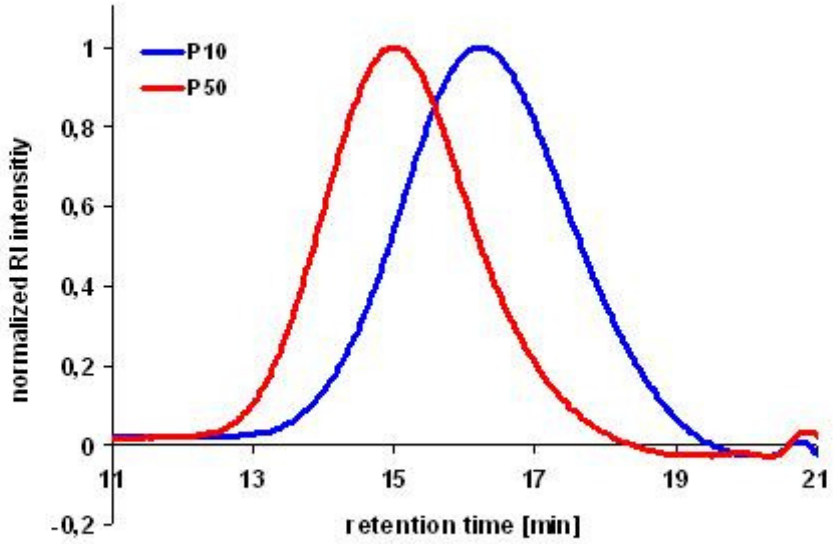



***Figure 8.*** *Selected GPC results of polymer* ***P10*** *(obtained by ADMET) and* ***P50*** *(obtained via poly-Passerini 3CR).*

***Table 5:*** *DSC-results of some elected poly[1-(alkylcarbamoyl)undecenyl undecenoate].*

| entry | DSC results glass transition [°C] | | melting point [°C] |
|---|---|---|---|
| | onset | midpoint | |
| **P10** | -0.91 | 2.00 | - |
| **P11** | -0.59 | 2.41 | - |
| **P12** | -3.69 | 0.31 | - |
| **P48** | -4.55 | -0.25 | - |
| **P28** | -8.38 | -6.25 | - |
| **P30** | -8.96 | -8.16 | - |
| **P33** | -34.50 | -34.70 | 6.75 |
| **P54** | - | - | 28.79 |

## 2. References


[1] Kreye, O.; Martin Luther University, Halle-Wittenberg (MLU), Germany, *Dissertation* **2009**, 122-123.

[2] Rybak, A.; Meier, M. A. R. *Green Chem.* **2007**, *9*, 1356-1361.

[3] Mutlu, H.; Meier, M. A. R. *Chem. Phys.* **2009**, *210*, 1019-1025.

[4] Miao, X.; Fischmeister, C.; Bruneau, C.; Dixneuf, P. H. *Chem. Sus. Chem.* **2009**, *2*, 542-545.