SUPPLEMENTARY INFORMATION

HIGHLY EFFICIENT OXYFUNCTIONALIZATION OF UNSATURATED FATTY ACID ESTERS: AN ATTRACTIVE ROUTE FOR THE SYNTHESIS OF POLYAMIDES FROM RENEWABLE RESOURCES

Matthias Winkler[a] and Michael A. R. Meier[a,*]

[a]Laboratory of Applied Chemistry, Institute of Organic Chemistry, Karlsruhe Institute of Technology (KIT), Fritz-Haber-Weg 6, 76131 Karlsruhe, Germany E-mail: m.a.r.meier@kit.edu, Web: http://www.meier-michael.com

Keywords: Oxyfunctionalization, Keto Fatty Acid Esters, Renewable Polyamides, Wacker Oxidation, Biomaterials, Biopolymers

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

Table of content

1. Materials

1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD, 99 %, Sigma Aldrich), 1,8-Diazabicyclo[5.4.0]undec-7-en (DBU, 98 %, Sigma Aldrich), ammonium chloride (99.5 %, Sigma Aldrich), ammonium acetate (>98 %, Sigma Aldrich), dimethylacetamide (99 %, Acros), palladium(II)chloride (99,9 %, Strem Chemicals), triethylamine (99 %, Acros), CuCl (97 %, Sigma Aldrich), Oxygen (99,5 %, Air Liquide), synthetic air (20.5 % O_2 in N_2, Air Liquide) were used as received. Methyl oleate and methyl erucate (~92 %) was kindly provided by Croda. The Ra-Ni catalyst was prepared as a slurry solution in ethanol.[24] All solvents (technical grade) were used without purification.

2. Characterization

^{1}H-NMR measurements were performed on a Bruker Avance spectrometer operating at 300 MHz for ^{1}H 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. For the characterization of the prepared copolyamides, trifluoroacetic anhydride was added dropwise to the polymer in $CDCl_3$ with continuous shaking until a homogenous solution was obtained. Determinations of molecular weights 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 × 0.46cm, 10.000Å), PSS PFG Micro (25.0 × 0.46cm, 1000Å) and PSS PFG Micro (25.0 × 0.46cm, 100Å). The system was calibrated with linear poly(methylmethacrylate) standards (Polymer Standard Service, Mp 102 – 981000 Da)

FAB (Fast-Atom-Bombardement)-mass spectra and high resolution mass spectra (HRMS) FAB 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 °C × min^{-1} up to a temperature of 300 °C, and using a sample mass of approximately 5 mg. Data 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.

Infrared spectra (IR) spectra were recorded on a Bruker alpha-p instrument applying KBr- and ATR-technology.

Reductive aminations and Wacker oxidations were performed with a High-Pressure Laboratory Reactor (highpreactorTM) BR-100 of the company Berghof equipped with grease-free valves and connections.

3. Experimental procedures / Results

General procedure for the Wacker oxidation:

Preparation of Methyl 9(10)-oxostearate 1 (mixture of isomers) and Methyl 13(14)-oxodocosanoate 2 (mixture of isomers)

0.30 g methyl oleate (1.00 mmol) or 0.35 g methyl erucate (1.00 mmol) in 3 mL dimethylacetamide and 0.5 mL H_2O was placed in a Teflon reactor tube inset and palladium(II)chloride (2-5 mol%) was added. The reaction mixture was pressurized with oxygen (10 bar) and stirred for 48 h at 70 °C±5 °C. Afterwards, the reaction mixture was extracted with diethylether (2x 5 mL) and washed with H_2O (2x 5 mL). The product was recrystallized from hexane and dried under vacuum. The ketone functionalized fatty acid methyl ester was obtained as white solid (yield 85 %).

^{1}H-NMR ($CDCl_3$, 300 MHz): 3.65 (s, 3H, -OCH_3), 2.37 (t, J = 7.4 Hz, 4H, -CH_2-C(O)-CH_2), 2.29 (t, J = 7.5 Hz, 2H, CH_2-COOMe), 1.71 – 1.42 (m, 6H, 3x -CH_2-) 1.36 – 1.15 (m, 18H, 9x -CH_2- for oleate or 26H, 13x-CH_2- for erucate), 0.87 (t, J = 6.6 Hz, 3H).

^{13}C NMR (CDCl3, 75 MHz) δ / ppm: 211.88, 174.5, 51.5, 42.9, 34.2, 29.7, 29.5, 29.4, 29.2, 25.1, 24.0, 22.8, 14.2.

HRMS (FAB):

1: $C_{19}H_{36}O_3$ $[M+H]^+$ calc. 313.2737 found 313.2743

2: $C_{23}H_{44}O_3$ $[M+H]^+$ calc. 369.3363 found 369.3368

Please note: All Wacker oxidations were carried out in an appropriate high pressure reactor equipped with grease-free valves and connections to prevent any explosions!

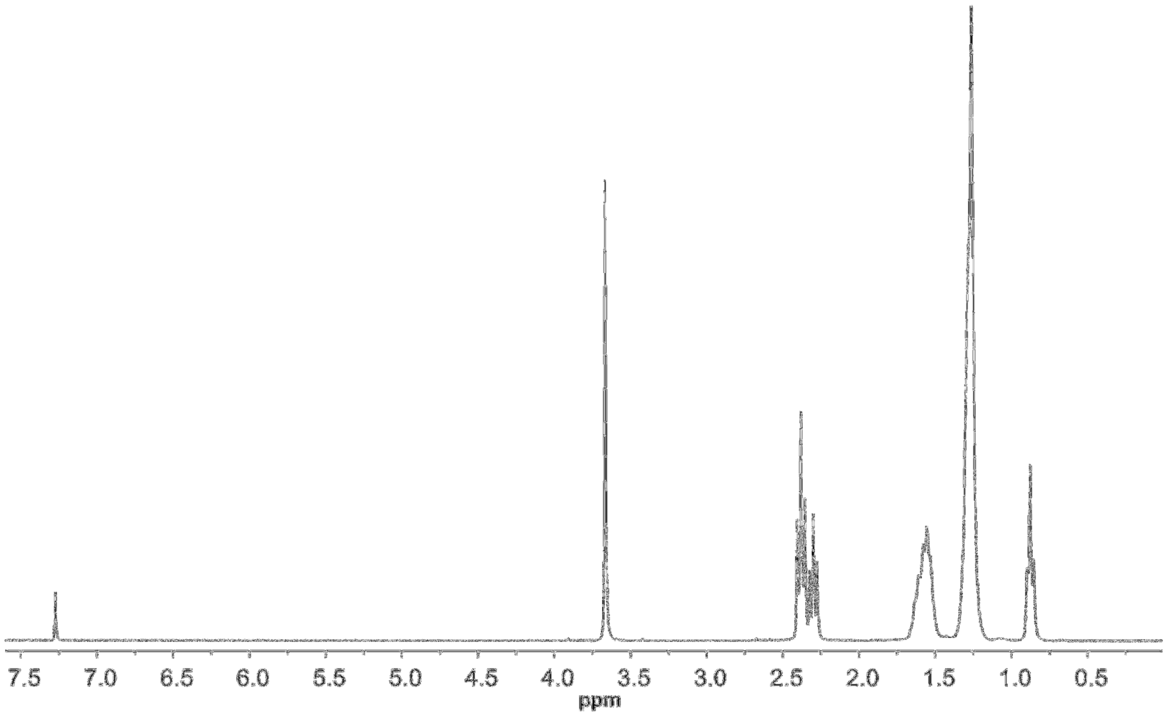


Figure S 1: ^{1}H-NMR (300 MHz/$CDCl_3$) of methyl 9(10)-oxostearate **1** (mixture of isomers).

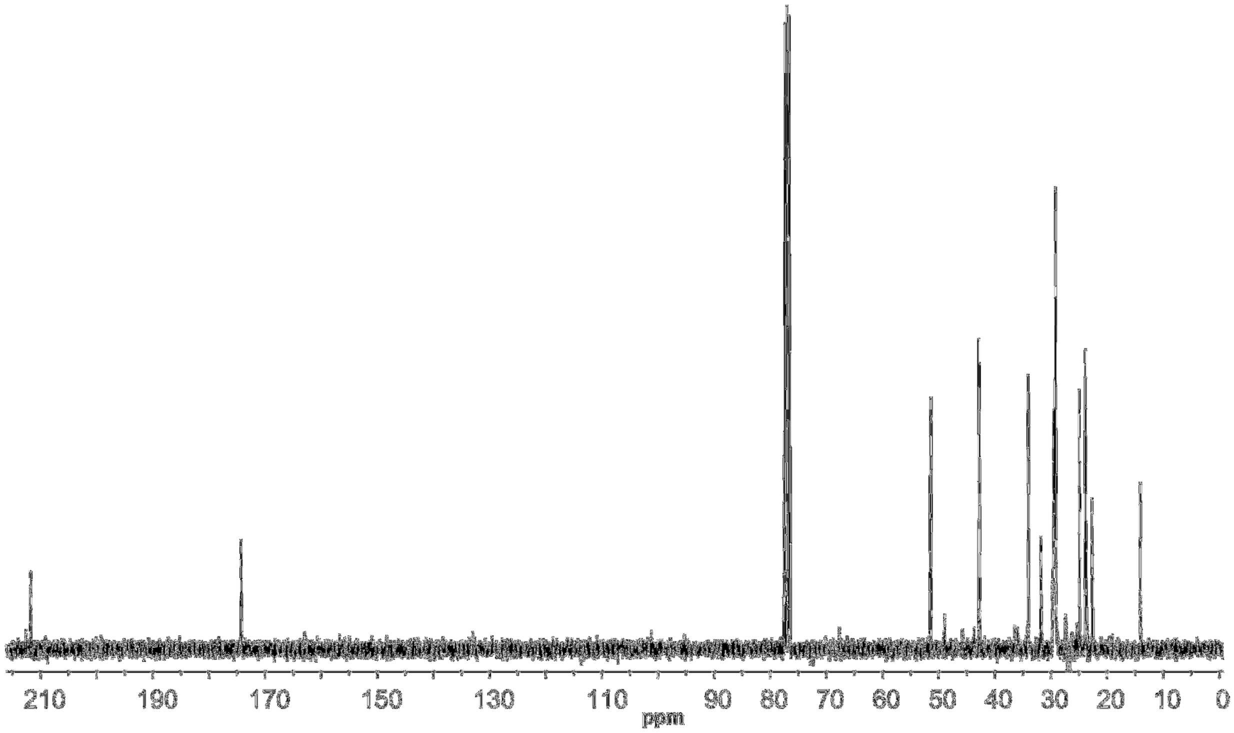


Figure S 2: ^{13}C-NMR (75 MHz/$CDCl_3$) of methyl 9(10)-oxostearate **1** (mixture of isomers).

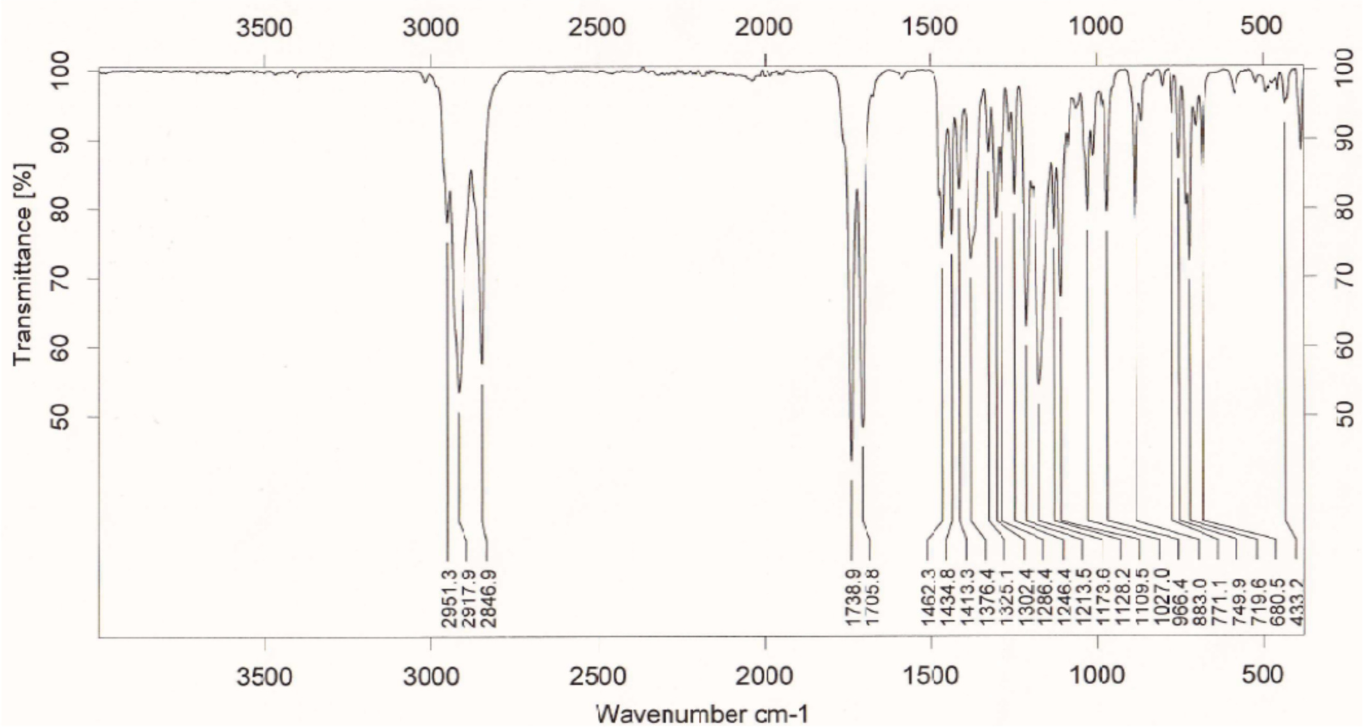


Figure S 3: IR spectrum of methyl 9(10)-oxostearate **1** (mixture of isomers).

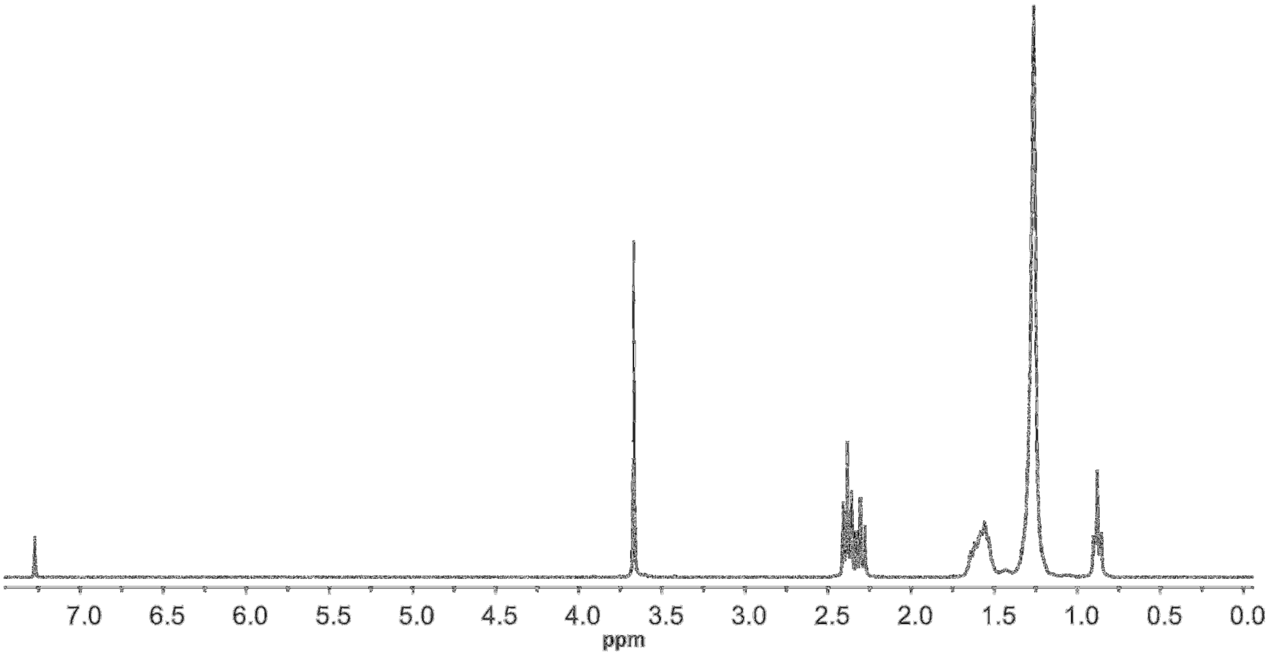


Figure S 4: ^{1}H-NMR (300 MHz/$CDCl_3$) of methyl 13(14)-oxodocosanoate **2** (mixture of isomers).

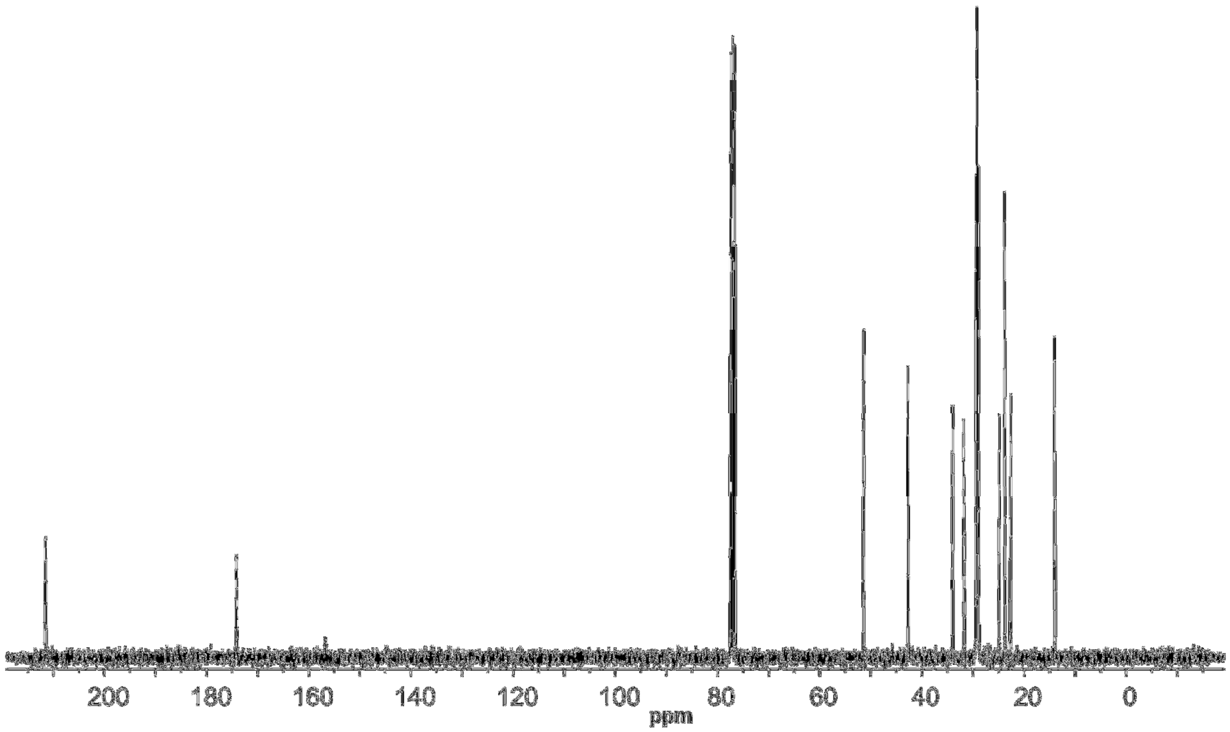


Figure S 5: ^{13}C-NMR (75 MHz/$CDCl_3$) of methyl 13(14)-oxodocosanoate **2** (mixture of isomers).

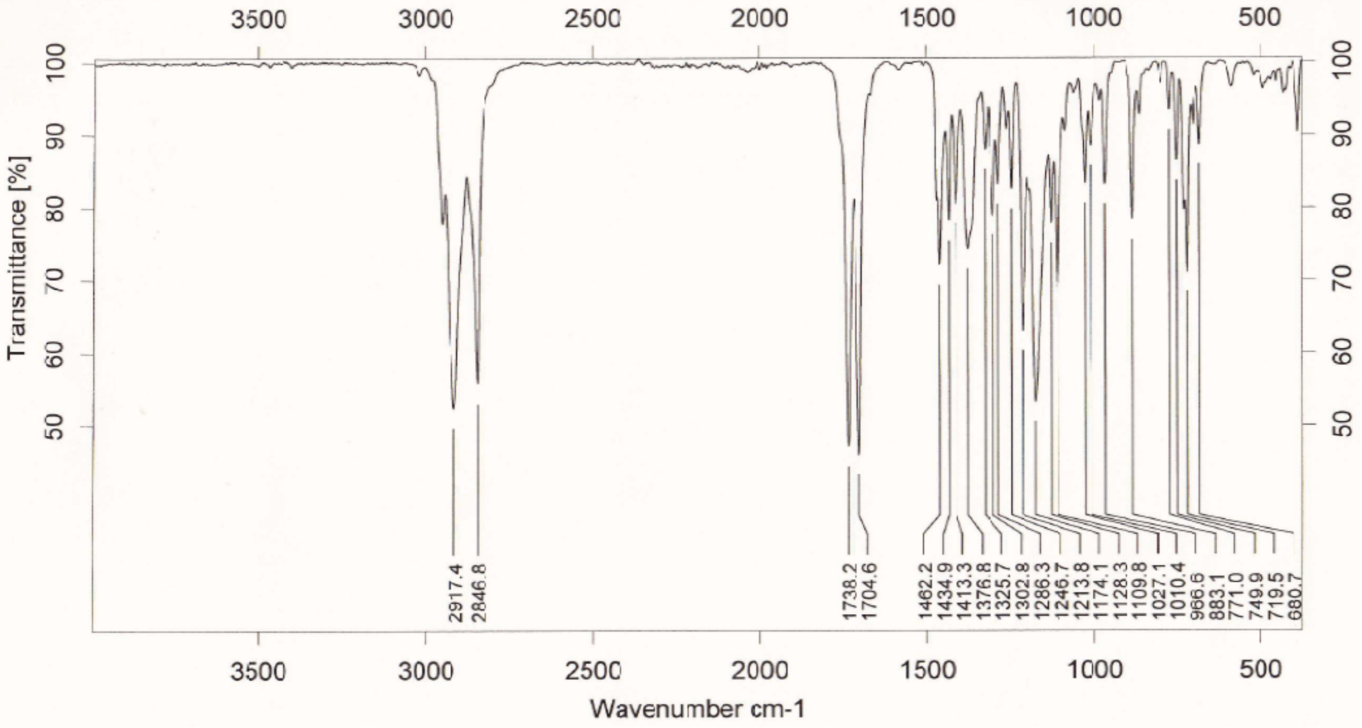


Figure S 6: IR spectrum of methyl 13(14)-oxodocosanoate **2** (mixture of isomers).

General procedure for recycling experiments of the Wacker oxidation

0.30 g methyl oleate (1.00 mmol) or 0.35 g methyl erucate (1.00 mmol) in 3 mL dimethylacetamide and 0.5 mL H_2O was placed in a Teflon reactor tube inset and palladium(II)chloride (2.5 mol%) was added. The reaction mixture was pressurized with oxygen (10 bar) and stirred for 48 h at 70 °C±5 °C. Afterwards, the reaction mixture was extracted with heptane (2x 5 mL) and washed with H_2O (2x 5 mL). To the DMAC phase, containing the palladium catalyst, another portion of the unsaturated fatty acid methyl ester was added and the Wacker oxidation was repeated under the same conditions as already described.

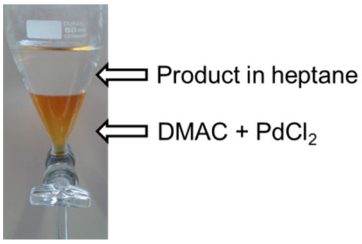


Figure S 7: Extraction of the reaction mixture with heptane and separation of the catalyst/solvent-mixture.

Table S 1: Results of the recycling experiments of the co-catalyst free-Wacker oxidation.

Reaction cycle	Conversion [%][a]
1	100
2	96
3	95

[a] conversion was determined via NMR spectroscopy based on the protons of the double bond of the FAME.

Typical procedure for reductive amination:

Preparation of Methyl 9(10)-aminostearate 3 (mixture of isomers) and Methyl 13(14)-aminodocosanoate 4 (mixture of isomers)

To the keto functional fatty acid methylester **1** or **2** (22.27 mmol), 7.22 g ammoniumacetate (133.6 mmol),1.72 g ammoniumchloride (22.27 mmol) and the freshly prepared Raney-Nickel catalyst (20 wt%) in 80 mL Ethanol was added. The reaction mixture was pressurized with hydrogen (40 bar) and stirred at 35 °C for 48 h to ensure full conversion. If necessary, for some reactions the crude product was further purified by a short silica column. First, the non-amine functional residues were separated by flushing the column with hexane / ethyl acetate = 4:1. Afterwards, the amine functionalized fatty acid methyl ester was collected with ethyl acetate/ MeOH/ Et_3N = 10:1:1. The product was obtained as light yellow oil (**3**) or light brown solid (**4**) in isolated yields >90%.

^{1}H-NMR ($CDCl_3$, 300 MHz): 3.67 (s, 3H, $-OCH_3$), 2.73 – 2.57 (m, 1H, C*H*-NH_2), 2.30 (t, J = 7.5 Hz, 2H, CH_2-COOMe), 1.70 – 1.10 (m, 30H, 15x -CH_2- for oleate or 38H, 19x-CH_2- erucate), 0.87 (t, J = 6.5 Hz, 3H).

^{13}C NMR (CDCl3, 75 MHz) δ / ppm: 174.4, 77.6, 77.2, 76.7, 51.5, 42.4, 34.2, 34.0, 29.7, 29.7, 29.6, 29.5, 29.3, 29.2, 27.0, 25.0.

HRMS (FAB):

3: $C_{19}H_{39}NO_2$ $[M+H]^+$ calc. 314.3054 found 314.3061

4: $C_{23}H_{47}NO_2$ $[M+H]^+$ calc. 370.3679 found 370.3689

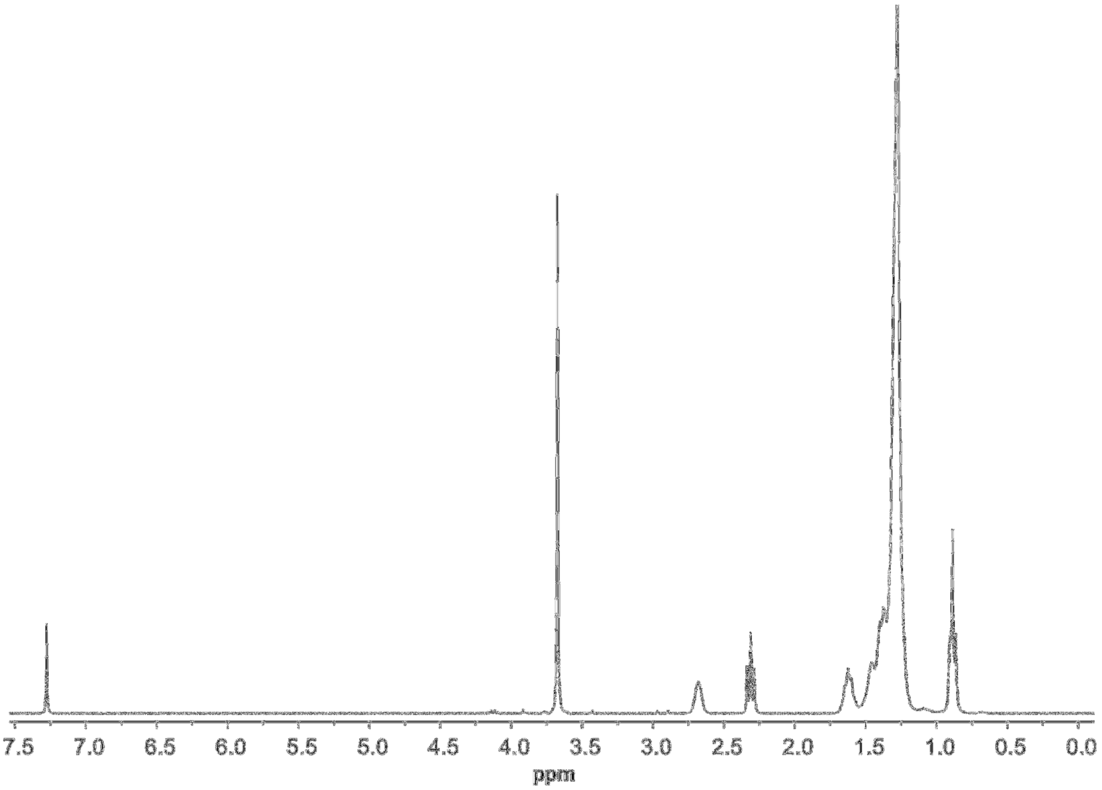


Figure S 8: ^{1}H-NMR (300 MHz/$CDCl_3$) of Methyl 9(10)-aminostearate **3** (mixture of isomers).

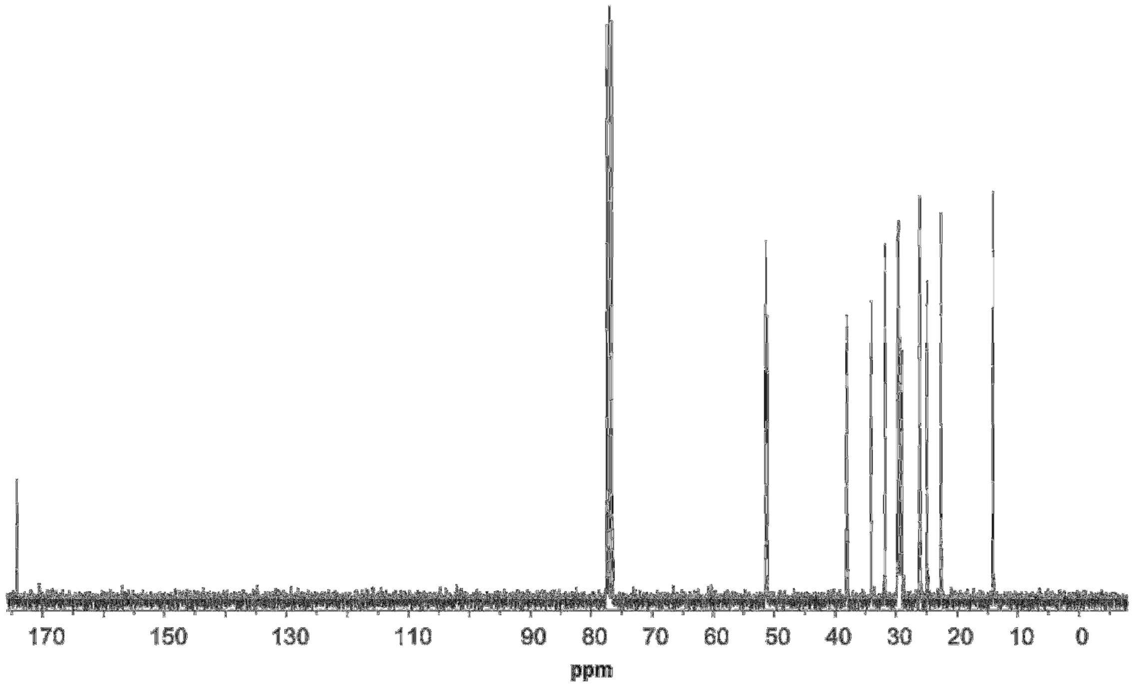


Figure S 9: ^{13}C-NMR (75 MHz/$CDCl_3$) of methyl 9(10)-aminostearate **3** (mixture of isomers).

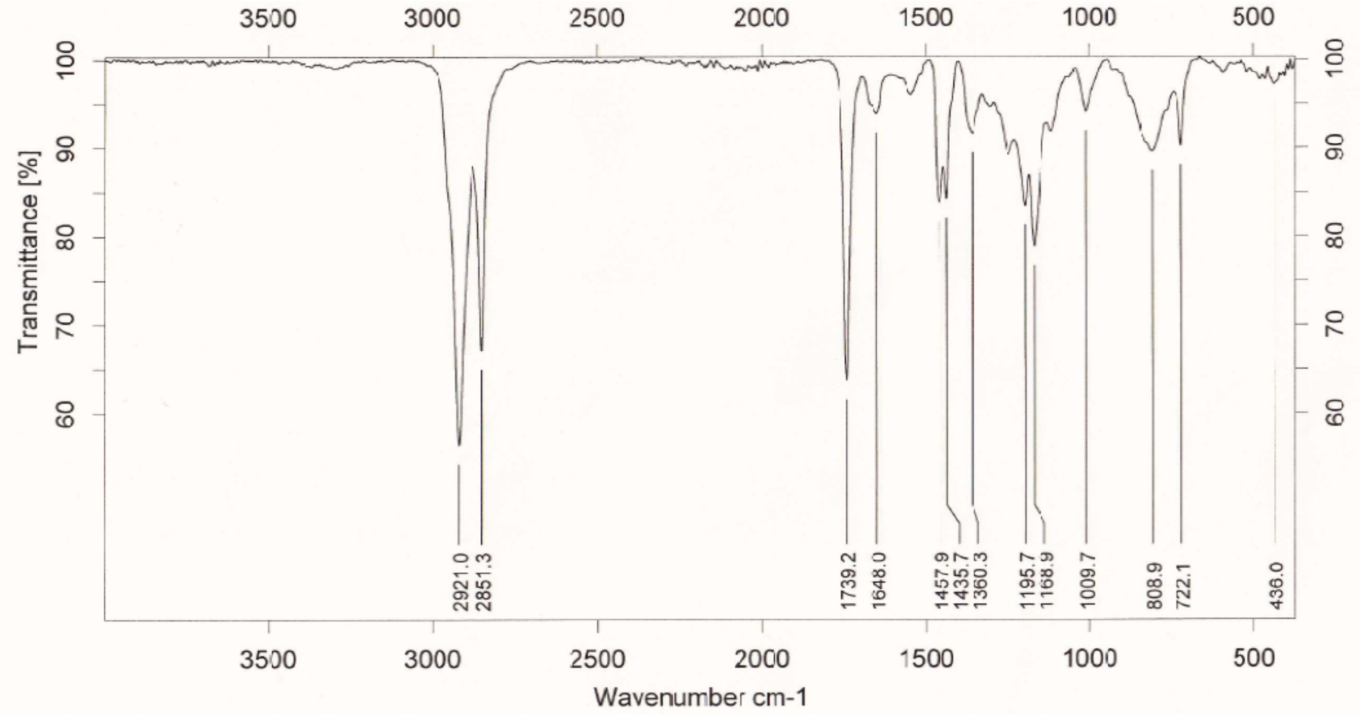


Figure S 10: IR spectrum of methyl 9(10)-aminostearate **3** (mixture of isomers).

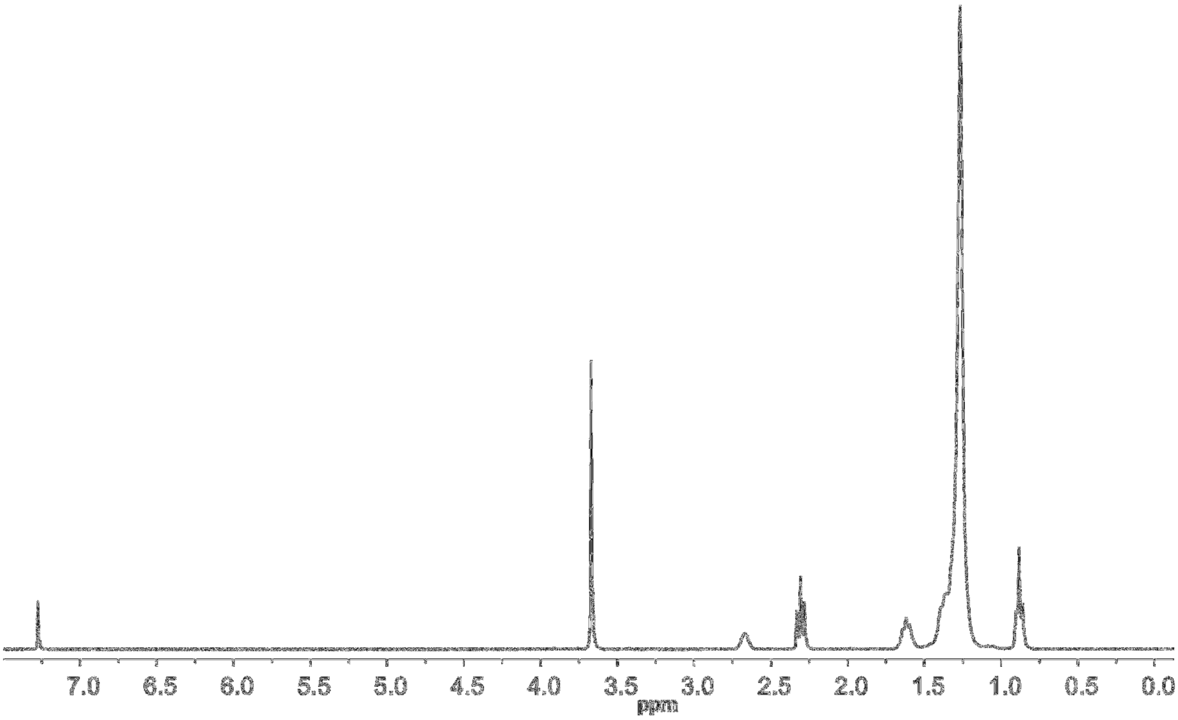


Figure S 11: ^{1}H-NMR (300 MHz/$CDCl_3$) of methyl 13(14)-aminodocosanoate **4** (mixture of isomers).

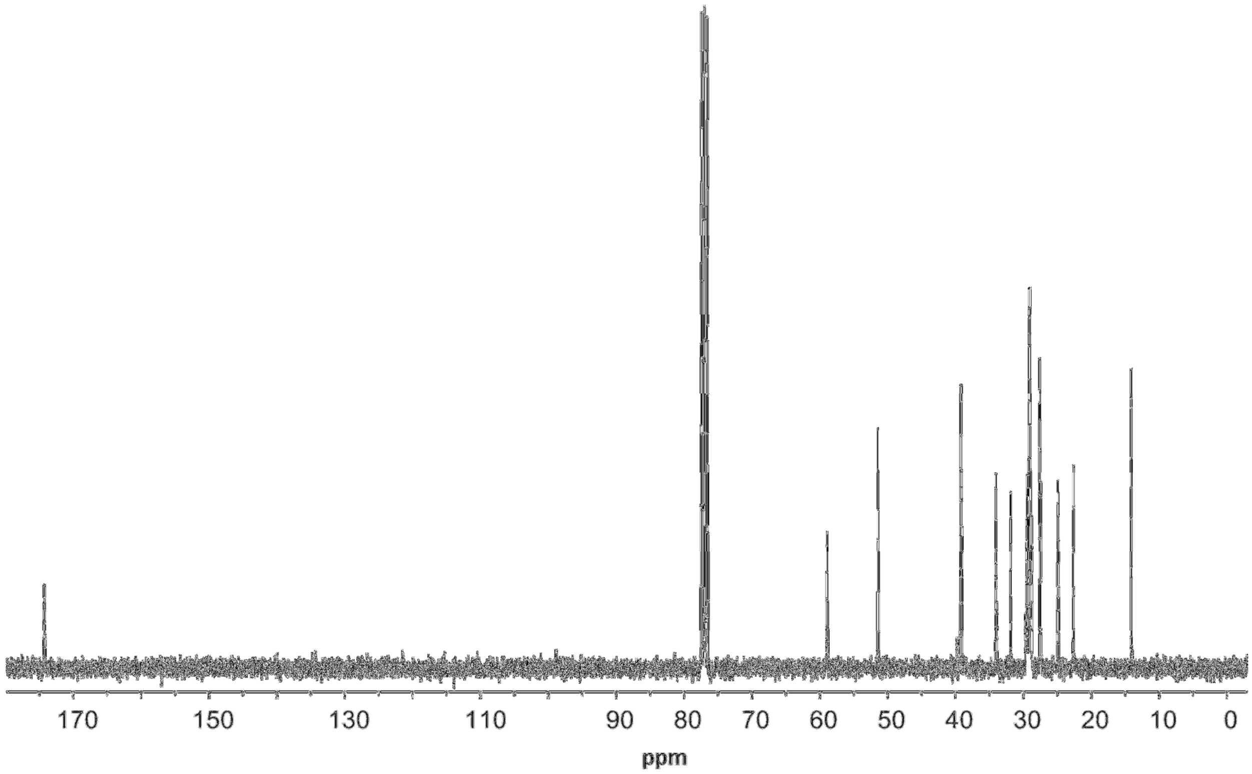


Figure S 12: ^{13}C-NMR (75 MHz/$CDCl_3$) of methyl 13(14)-aminodocosanoate **4** (mixture of isomers).

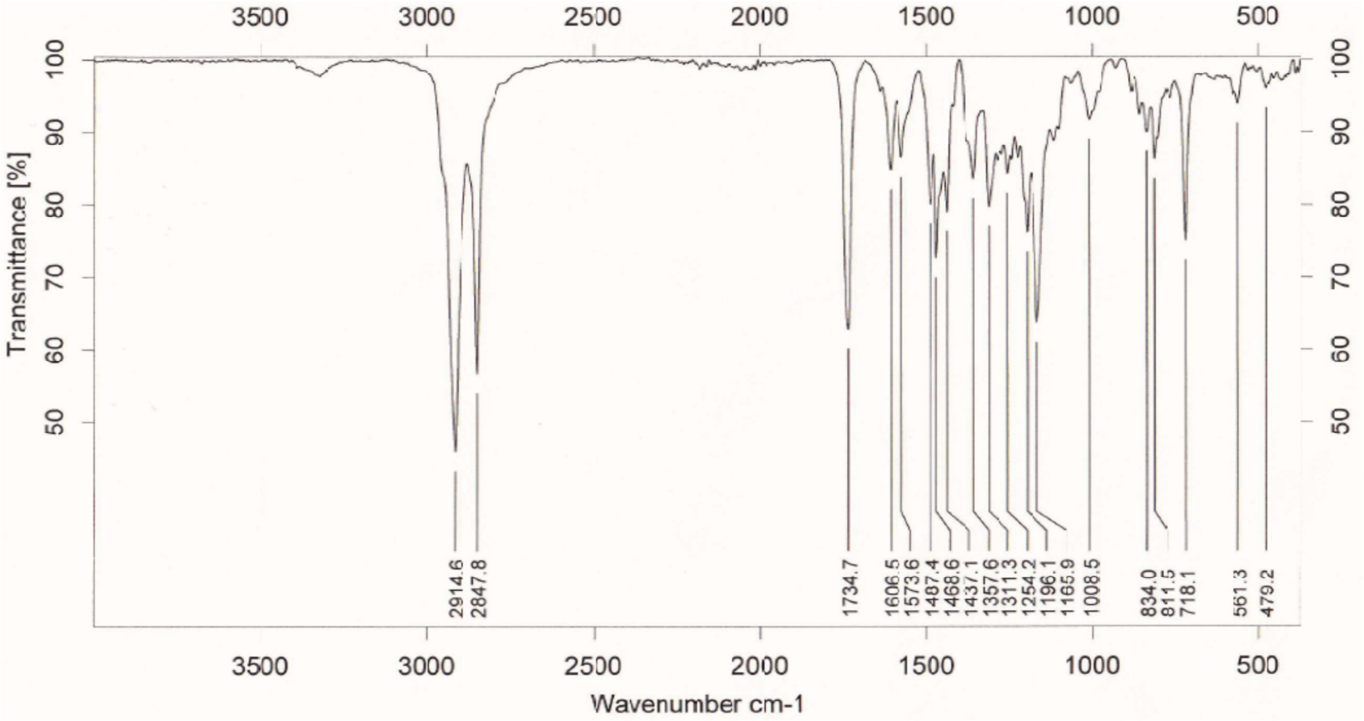


Figure S 13: IR spectrum of methyl 13(14)-aminodocosanoate **4** (mixture of isomers).

General procedure for TBD catalyzed polycondensations

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. 120 °C for 12 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.

For the preparation of polymer P1 and P2, TBD (5 mol%, relative to ester groups) was used. First the reaction mixture was stirred for 6 hours under a gentle stream of argon at 120 °C. For additional 18 hours the reaction mixture was stirred at 130 °C under vacuum (10^{-2} mbar). The polymers were dissolved in hexafluoroisopropanol and precipitated in cold methanol.

^{1}H NMR (300 MHz, $CDCl_3$) δ 3.88 (bs, 1H, -N*H*-CO-), 3.33-3.17 (m, 1H, -C*H*-NHCO-), 2.14 (t, J = 7.5 Hz, 2H, -CH_2-CONH-), 1.65 – 1.15 (m, 30H for P1/ 38 H for P2), 0.87 (t, J = 6.5 Hz, 3H, -CH_3).

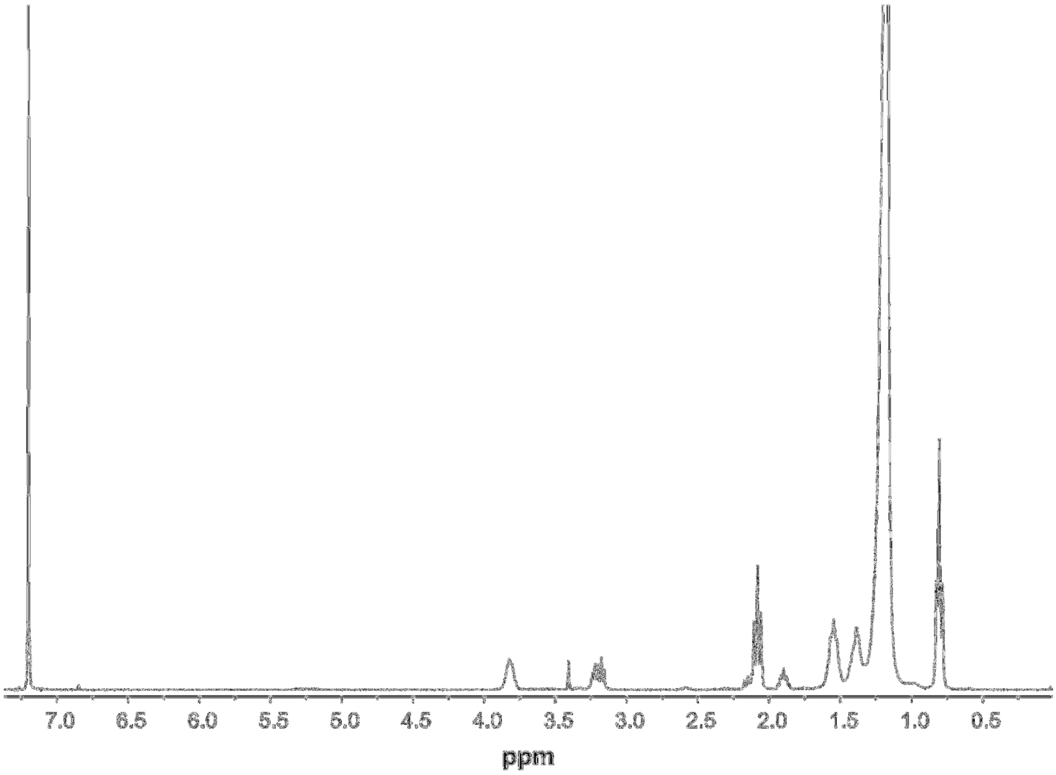


Figure S 14: ^{1}H-NMR (300 MHz/$CDCl_3$) of **P1**.

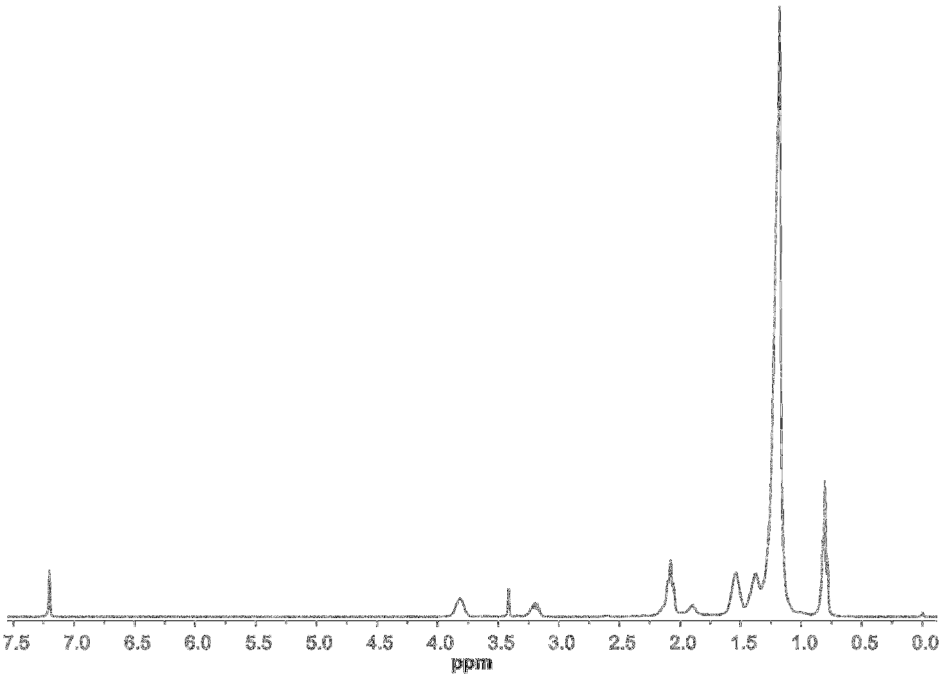


Figure S 15: ^{1}H-NMR (300 MHz/CDCl$_3$) of **P2**.

For the preparation of P0 and P3-P8, DBU (10 mol%, relative to ester groups) was used. First, the reaction mixture was stirred for 6 hours under a gentle stream of argon at 120 °C. Afterwards the reaction mixture was heated to 180 °C and stirred for 1 hour maintaining the gentle argon stream. For 12 additional hours the reaction mixture was stirred at 220 °C under high vacuum (10^{-2} mbar). Then, the reaction mixture was heated to 275 °C and stirred for an additional 4 hours at high vacuum. The final polymers were dissolved in hexafluoroisopropanol and precipitated in cold methanol.

^{1}H NMR (300 MHz, CDCl$_3$/TFAA) δ 3.73-3.61 (m,-C*H*-NH-, -N*H*), 3.35-3.20 (m, -CH_2-NH-), 2.88-2.72 (m, -CH_2-COONH-), 2.68-2.55 (m, -CH_2-COONH-), 2.50-2.30 (m, -CH$_2$-), 1.80 – 1.05 (m, -C$H_{2\ \mathrm{aliphatic}}$-), 0.87 (t, J = 6.5 Hz, -CH_3).

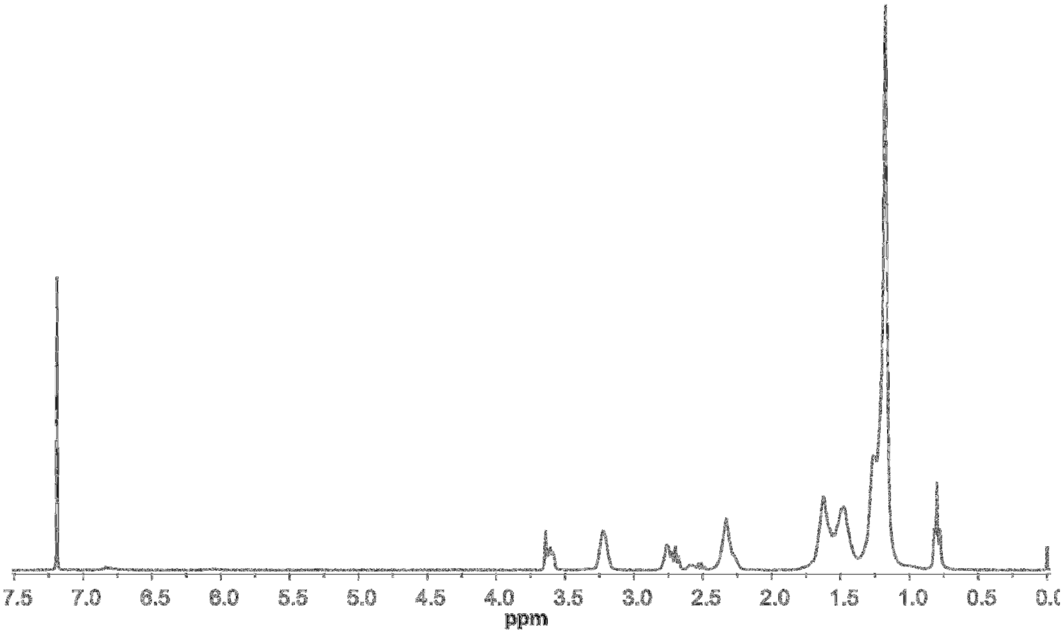


Figure S 16: ^{1}H-NMR (300 MHz/CDCl$_3$) of **P8**.

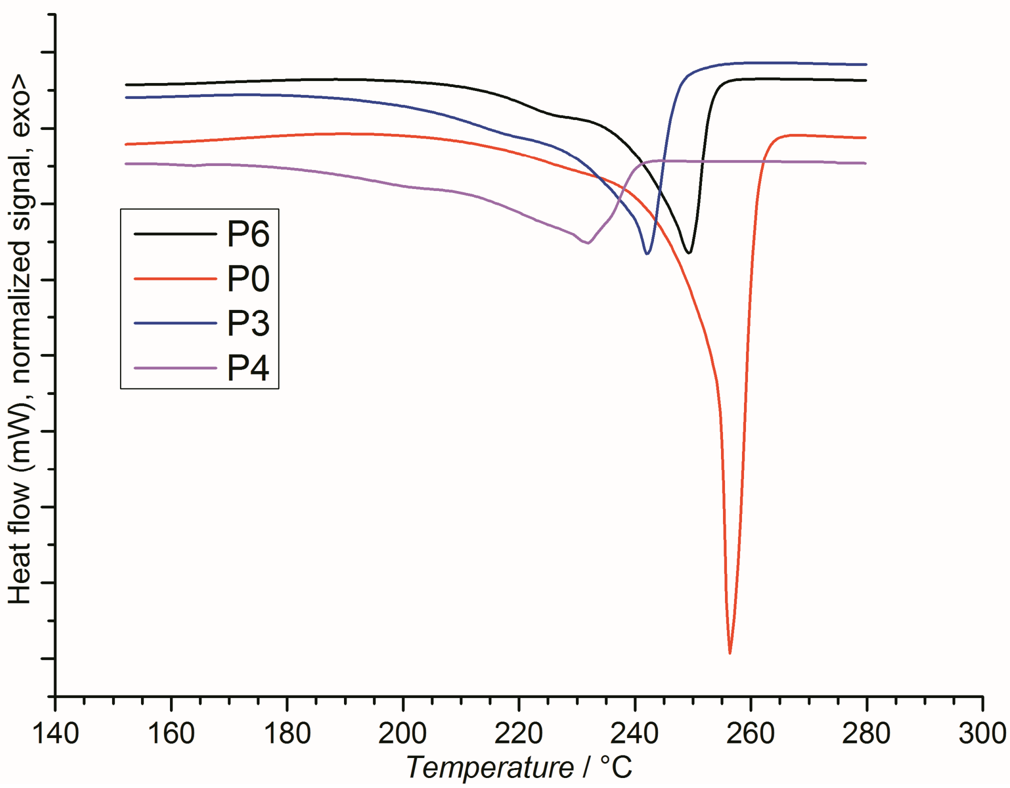
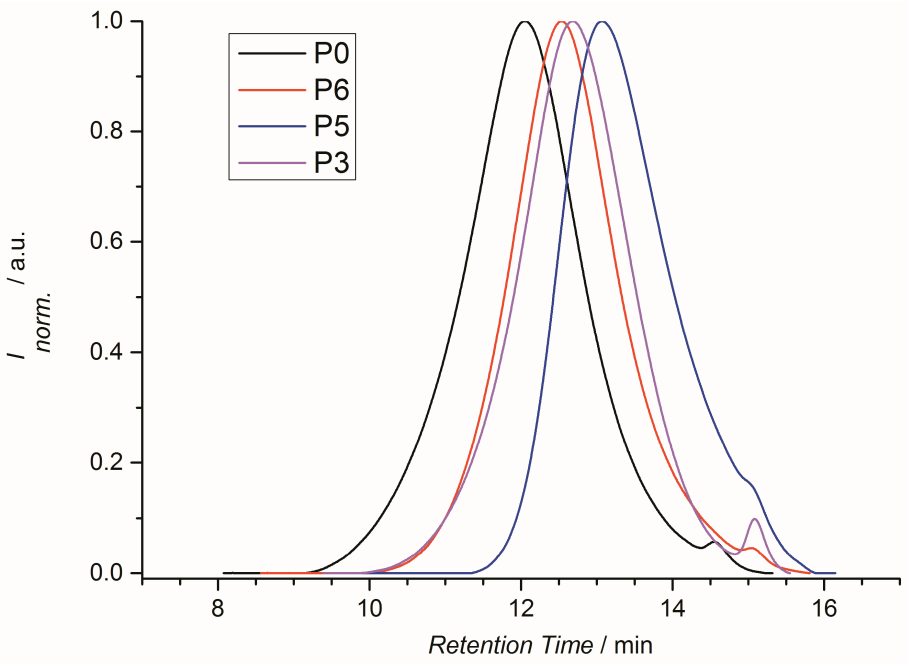


Figure S 17: DSC analysis of selected polyamides synthesized via TBD catalyzed polycondensation. Second heating scans recorded at a heating rate of 10 ºC/min are reported.



Water-uptake tests:

The polymers were compression molded into a unified rectangle-shape (l × w × h=2 cm × 1 cm × 1mm), kept in the desiccator overnight and immersed into 10 mL water for 16 hours at 25 °C, similar to already known described procedures.[20-21] Afterwards, the polymer samples were carefully blotted on a tissue to remove the water on the surface and weighed. After 1 hour on the lab bench for further drying, the polymer sticks were again blotted and weighed. To obtain accurate results and to avoid weighing errors, the measurements were repeated 3 times using different polymer specimen. The average increase in weight was calculated according to the convenient equation.[22, 23]

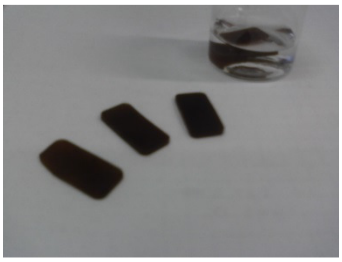


Figure S1: Water-uptake test with the compression molded polymer samples.