

Base catalyzed sustainable synthesis of phenyl esters from carboxylic acids using diphenyl carbonate

Oliver Kreye and Michael A. R. Meier*

Karlsruhe Institute of Technology (KIT), Institute of Organic Chemistry (IOC),
Laboratory of Applied Chemistry, Fritz-Haber-Weg 6, Building 30.42, D-76131
Karlsruhe, Germany; E-mail: m.a.r.meier@kit.edu; Internet: www.meier-michael.com.

Table of Contents

1. Materials and methods	2
1.1. Materials	2
1.2. Analysis methods	2
2. Synthesis procedures	4
2.1. Synthesis of ferulic acid derivative 2d	4
2.2. Synthesis of phenyl ester	8
2.3. Transesterification reactions of phenyl esters.....	33
2.4. Conversion of phenyl esters with amine compounds	42
3. References	48

1. Materials and methods

1.1. Materials

Diphenyl carbonate **1** (DPC, 99%, Aldrich), 10-undecenoic acid **2a** (98%, Aldrich), oleic acid **2b** (90%, Aldrich), stearic acid **2c** (97%, AppliChem), levulinic acid **2e** (98%, Aldrich), sebacic acid **2f** (99%, Aldrich), azelaic acid **2g** (98%, Aldrich), adipic acid **2h** (>99%, Aldrich), benzoic acid **2i** (>99.5%, Aldrich), 4-formylbenzoic acid **2j** (97%, Aldrich), 4-methoxybenzoic acid **2k** (99%, Aldrich), *m*-toluic acid **2l** (99%, Aldrich), benzyl alcohol **5a** (>99%, Aldrich), allyl alcohol **5b** (>99%, Aldrich), *n*-butanol **5c** (>99.4%, Aldrich), isopropanol **5d** (99.5%, Aldrich), ammonia **7a** (7N solution in methanol, Acros Organics), pyrrolidine **7c** (>99%, Acros Organics), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, >99%, Aldrich), 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD, 98%, Aldrich), 4-(dimethylamino)pyridine (DMAP, 99%, Aldrich), 1,4-diazabicyclo[2.2.2]octane (DABCO, 98%, Aldrich), potassium carbonate (>99%, Aldrich), pyridine (>99.8%, Fisher Scientific), dimethyl carbonate (DMC, 99%, Aldrich), lithium hydroxide (>98%, Aldrich), sodium sulfate (>99%, Acros Organics), sulfuric acid (96%, Acros Organics), hydrochloric acid (37%, Merck KGaA), sodium chloride (>99.5%, Aldrich), sodium bicarbonate (>99%, Fisher Scientific), silica gel 60 (0.035 – 0.070, Aldrich), cerium(IV)-sulfate (>99%, Aldrich), phosphomolybdic acid (>99%, Aldrich), chloroform-*d* (CDCl₃, 99.8 atom-% D, Euriso-top) were used as received. All solvents were used without any kind of purification.

Dec-9-en-1-amine **7b** was synthesized according to the procedure mentioned in the supporting information of the cited publication.¹

1.2. Analysis methods

TLC-identification of reactants and products was performed on silica gel coated aluminum foil (silica gel 60, F254 with fluorescence indicator) from Aldrich. Compounds were visualized by Seebach reagent (mixture of phosphomolybdic acid, cerium(IV)-sulfate, water and sulfuric acid) and/or UV light ($\lambda = 254$ nm).

NMR spectra were obtained in CDCl₃, DMSO-*d*₆ and methanol-*d*₄ and recorded with a Bruker AC 300 and AC 500. All ¹H NMR spectra are reported in ppm relative to the solvent signal for CDCl₃ at 7.26 ppm, methanol-*d*₄ at 3.30 ppm and DMSO-*d*₆ at 2.50 ppm. All ¹³C NMR spectra are reported in ppm relative to the central line of the triplet for CDCl₃ at 77.00 ppm, the septet for methanol-*d*₄ at 49.05 ppm and the septet for DMSO-*d*₆ at 39.43 ppm.

FAB (*Fast-Atom-Bombardment*)-mass spectra and high resolution mass spectra HRMS (FAB) were measured with MAT95 of the company Finnigan.

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

Melting points were determined by differential scanning calorimetry (DSC). The experiments were carried out under nitrogen atmosphere at a heating rate of 10 or 20°C×min⁻¹ with a DSC star^e (Mettler Toledo) calorimeter starting from -20°C to a temperature of 300°C using 40 µl aluminum crucibles and a sample mass of 4-8 mg. The melting temperature was reported as the minimum of the endothermic peak of the second heating scan.

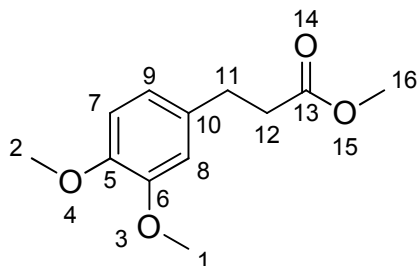
High pressure reactions were performed in a Berghof High-Pressure Laboratory Reactor (highpreactorTM) BR-100.

For microwave reactions, the model Discover[®] of the company CEM was used equipped with an explorer Hybrid 12 auto sampler.

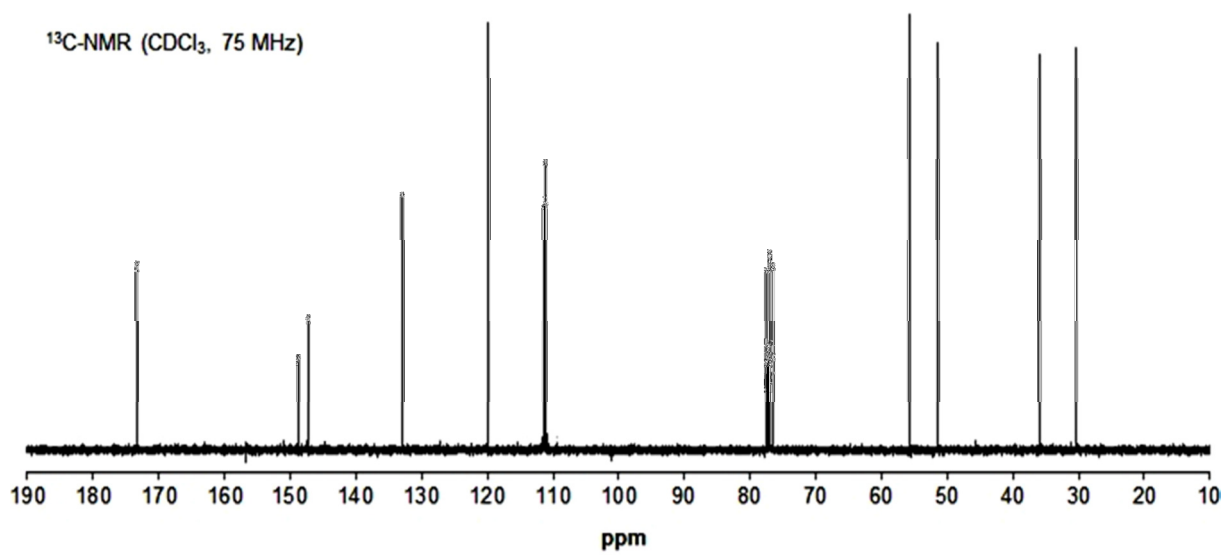
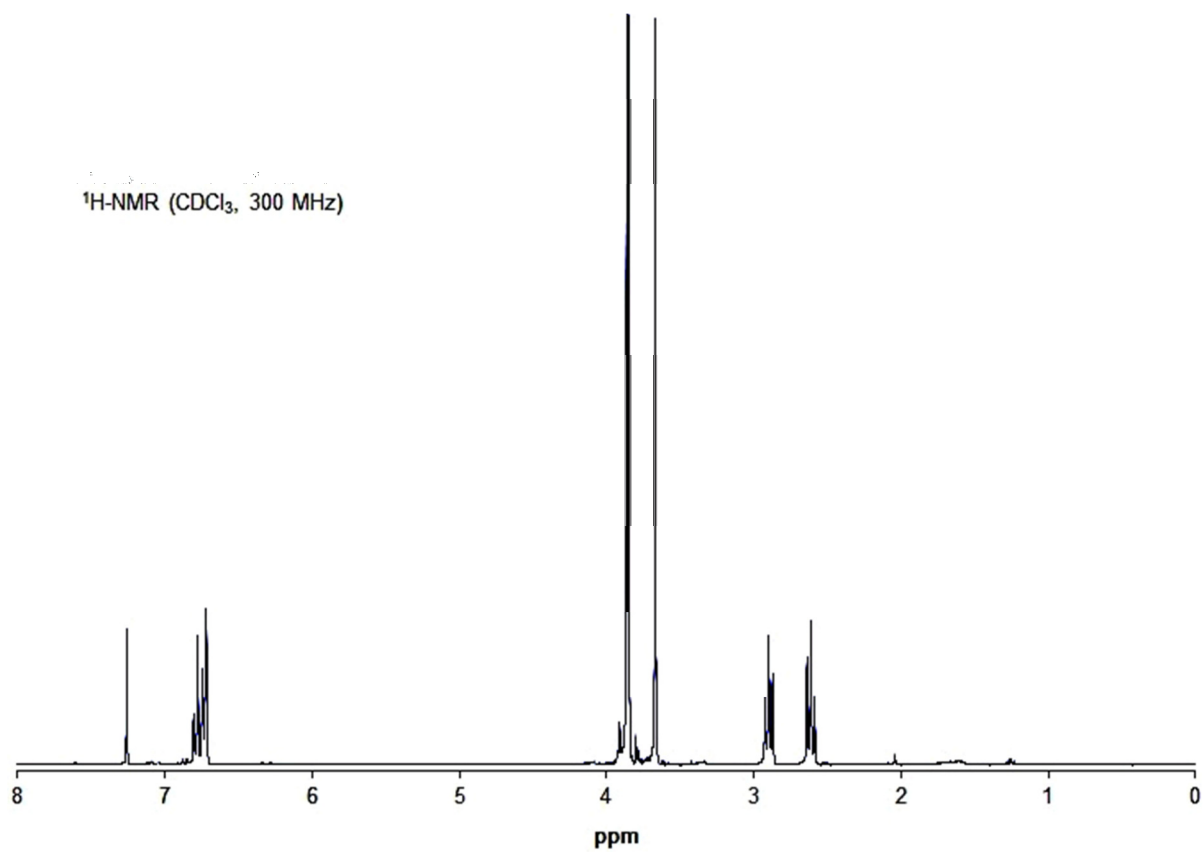
2. Synthesis procedures

2.1. Synthesis of ferulic acid derivative 2d

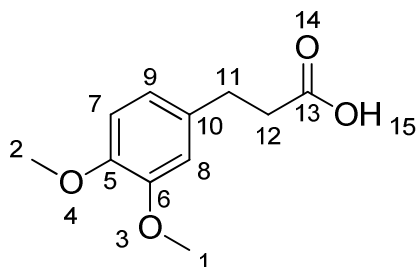
2.1.1. Methyl 3-(3,4-dimethoxyphenyl)propanoate (9)



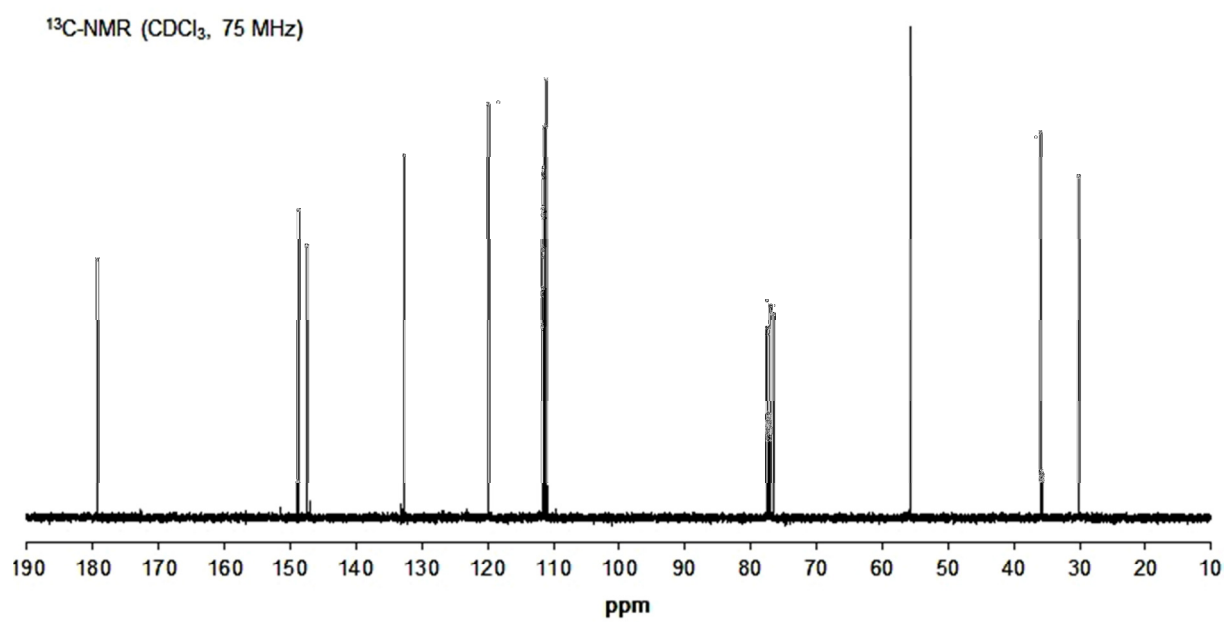
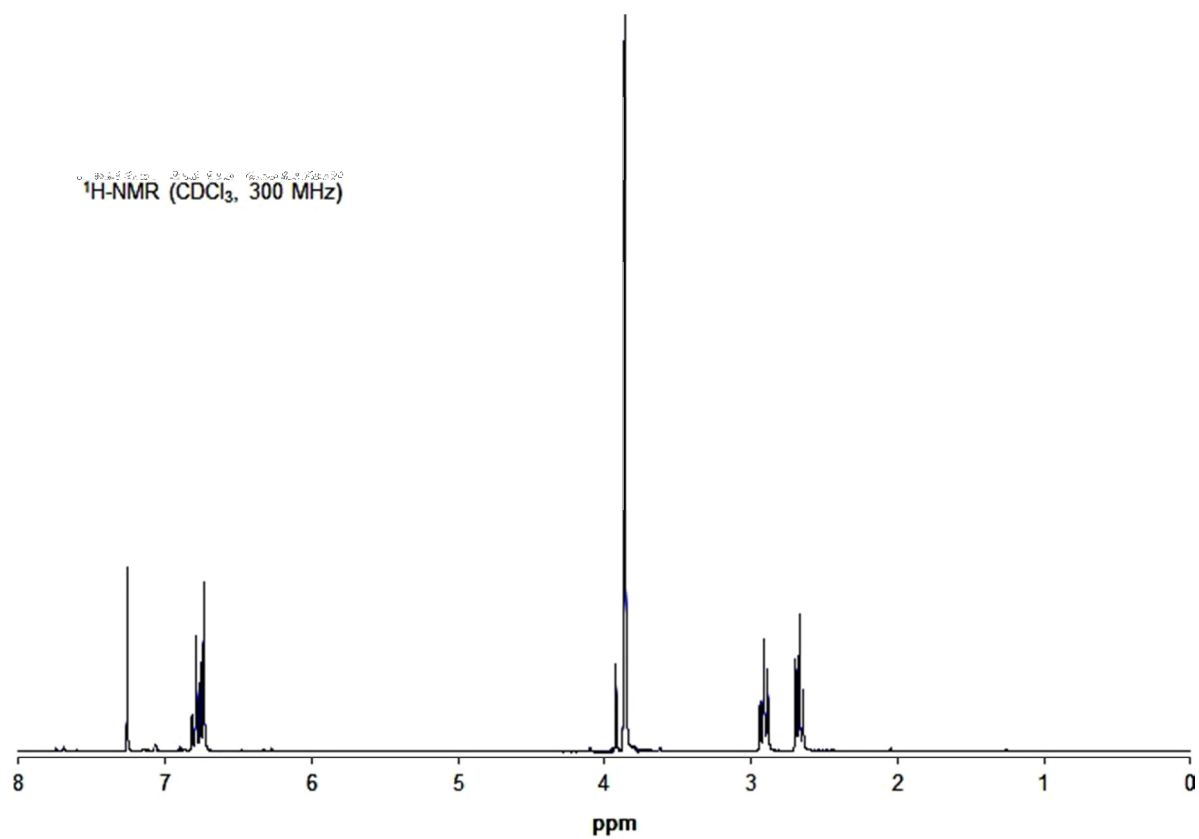
Methyl 3-(4-hydroxy-3-methoxyphenyl)propanoate (3.00 g, 14.3 mmol)² was dissolved in dimethyl carbonate (12.9 g, 143 mmol, 10 eq.) and subsequently, DBU (1.09 g, 7.14 mmol, 0.5 eq.) was added. The mixture was heated to reflux for one day until TLC (*n*-hexane / ethyl acetate 2 : 1) indicated a full conversion. The reaction mixture was evaporated under reduced pressure. The residue was dissolved in ethyl acetate (50 mL) and washed with 1N HCl (3 × 20 mL) and saturated sodium chloride solution (20 mL). After drying over sodium sulfate, the solution was evaporated to dryness on a rotary evaporator to obtain the crude product as yellowish oil. The oil crystallized completely after a few minutes and pure methyl 3-(3,4-dimethoxyphenyl)propanoate **9** was obtained as colorless crystals (2.99 g, 94%). TLC (*n*-hexane / ethyl acetate 2 : 1) $R_f = 0.64$; $T_m = 40.9$ °C (ethyl acetate); $^1\text{H NMR}$ (CDCl_3 , 300 MHz) $\delta = 2.61$ (t, $J = 7.7$ Hz, 2 H, CH_2^{12}), 2.90 (t, $J = 7.7$ Hz, 2 H, CH_2^{11}), 3.67 (s, 3 H, CH_3^{16}), 3.85, 3.86 (2s, 6 H, 2 $\text{CH}_3^{1,2}$), 6.70 – 6.82 (m, 3 H, 3 $\text{CH}^{7,9}$) ppm; $^{13}\text{C NMR}$ (CDCl_3 , 75 MHz) $\delta = 30.5$ (CH_2^{11}), 35.9 (CH_2^{12}), 51.5 (CH_3^{16}), 55.7 ($\text{CH}_3^{1,2}$), 55.8 ($\text{CH}_3^{1,2}$), 111.2 ($\text{CH}^{7,8}$), 111.5 ($\text{CH}^{7,8}$), 120.0 (CH^9), 133.0 (C^{10}), 147.4 (C^5), 148.7 (C^6), 173.2 (CO^{13}) ppm; FAB of $\text{C}_{12}\text{H}_{16}\text{O}_4$ ($M^+ = 224.1$, $[\text{M}+\text{H}]^+ = 225.1$); HRMS(FAB) of $\text{C}_{12}\text{H}_{16}\text{O}_4$ M^+ calc. 224.1043 found 224.1042; IR (ATR) $\nu = 2955.6, 2837.7, 1729.0$ (ester), 1588.5, 1512.4, 1432.5, 1365.8, 1292.4, 1234.1, 1189.1, 1151.5, 1025.5, 976.4, 887.1, 856.6, 808.9, 765.2 cm^{-1} .



2.1.2. 3-(3,4-Dimethoxyphenyl)propanoic acid (**2d**)



Methyl 3-(3,4-dimethoxyphenyl)propanoate **9** (2.75 g, 12.3 mmol) was dissolved in THF (30 mL) and water (15 mL). Subsequently, lithium hydroxide (0.88 g, 36.8 mmol, 3.0 eq.) was added. The mixture was stirred at room temperature for one day until TLC (ethyl acetate) indicated a full conversion. The mixture was acidified with 1N HCl (25 mL) and extracted with ethyl acetate (50 mL). Then, the organic layer was washed with 1N HCl (20 mL), water (20 mL) and saturated sodium chloride solution (20 mL). After drying over sodium sulfate, the solution was evaporated to dryness on a rotary evaporator. The crude product was recrystallized in ethyl acetate to obtain pure 3-(3,4-dimethoxyphenyl)propanoic acid **2d** as colorless crystals (2.42 g, 94%). TLC (ethyl acetate) $R_f = 0.68$; $T_m = 103.0$ °C (ethyl acetate); $^1\text{H NMR}$ (CDCl_3 , 300 MHz) $\delta = 2.67$ (t, $J = 7.7$ Hz, 2 H, CH_2^{12}), 2.91 (t, $J = 7.7$ Hz, 2 H, CH_2^{11}), 3.86, 3.87 (2s, 6 H, 2 $\text{CH}_3^{1,2}$), 6.72 – 6.83 (m, 3 H, 3 CH^{7-9}), 11.07 (br, s, 1 H, COOH^{15}) ppm; $^{13}\text{C NMR}$ (CDCl_3 , 75 MHz) $\delta = 30.1$ (CH_2^{11}), 35.8 (CH_2^{12}), 55.7 ($\text{CH}_3^{1,2}$), 55.8 ($\text{CH}_3^{1,2}$), 111.2 ($\text{CH}^{7,8}$), 111.5 ($\text{CH}^{7,8}$), 120.0 (CH^9), 132.6 (C^{10}), 147.4 (C^5), 148.7 (C^6), 179.2 (CO^{13}) ppm; FAB of $\text{C}_{11}\text{H}_{14}\text{O}_4$ ($M^+ = 210.1$, $[\text{M}+\text{H}]^+ = 211.2$); HRMS(FAB) of $\text{C}_{11}\text{H}_{14}\text{O}_4$ M^+ calc. 210.0887 found 210.0889; IR (ATR) $\nu = 2914.9$, 2836.5, 1695.7 (CO_2H), 1590.4, 1514.1, 1462.0, 1427.3, 1341.2, 1305.8, 1235.9, 1144.5, 1025.1, 930.3, 838.9, 808.1, 767.1 cm^{-1} .

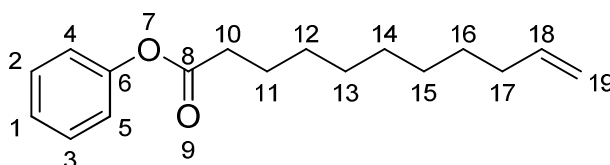


2.2.Synthesis of phenyl ester

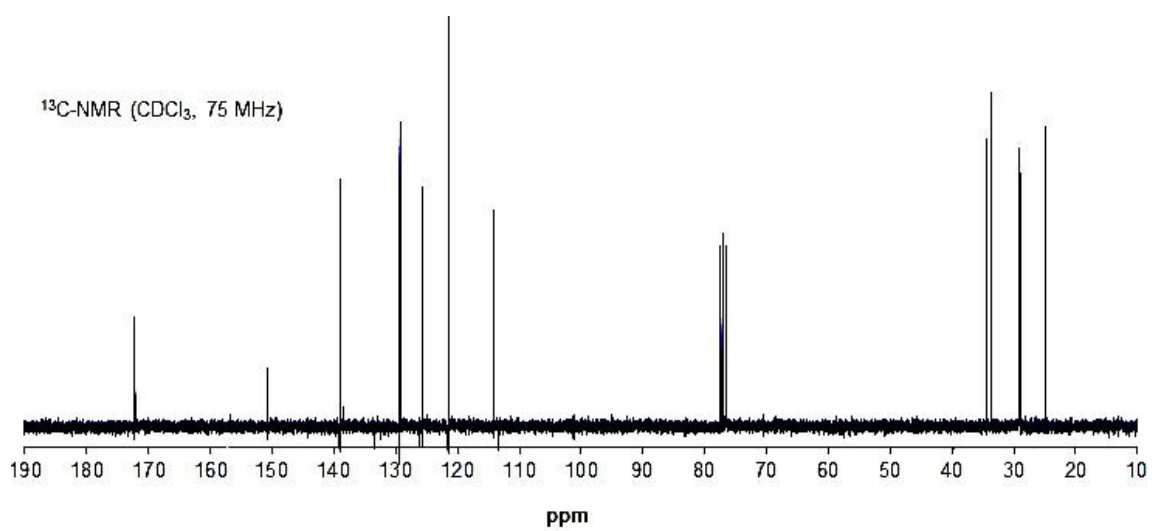
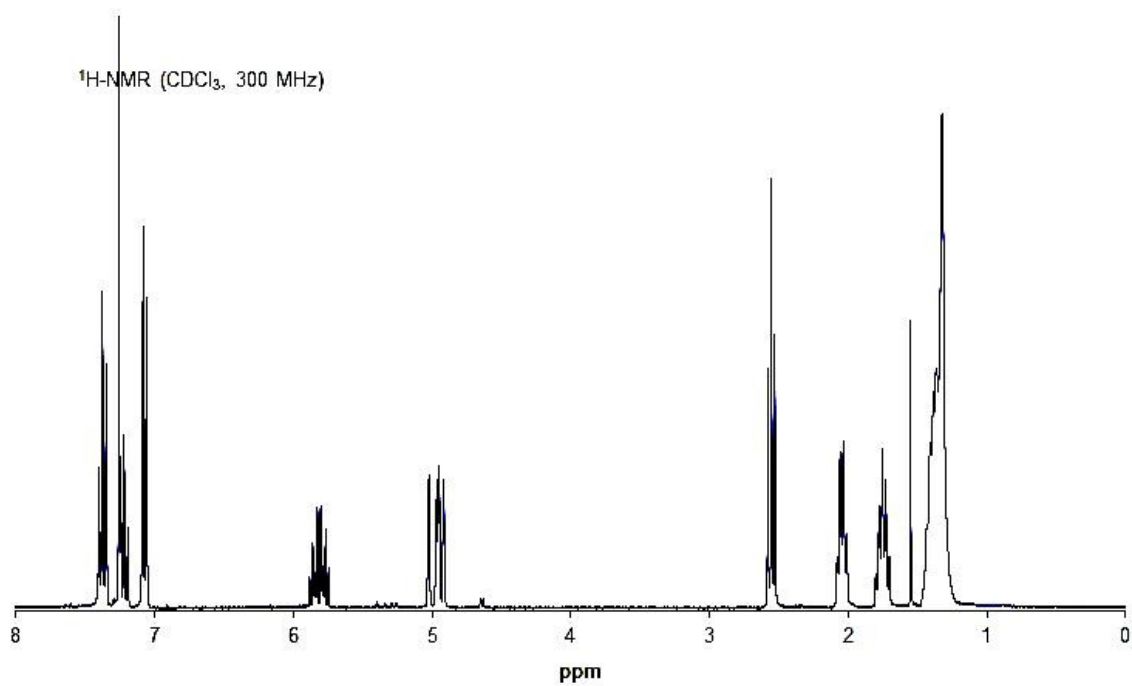
Representative procedure for the synthesis of phenyl ester 3a–j from carboxylic acids 2a–j and diphenyl carbonate (DPC) 1 in the presence of catalytic amounts of DBU:

10-Undecenoic acid **2a** (50.0 g, 271 mmol), DPC **1** (58.1 g, 271 mmol) and DBU (1.24 g, 8.14 mmol, 3.0 mol%) were mixed and heated to 160 °C while stirring. After eight hours, TLC (*n*-hexane / ethyl acetate 19 : 1) and ¹H NMR spectroscopy indicated a full conversion. Then, the by-product phenol was removed *via* vacuum distillation (80 °C, 7.0 mbar) to recover it in a yield of 92% (23.6 g). The crude product was purified by column chromatography (increasing gradient of polarity, *n*-hexane / ethyl acetate 49 : 1 to 9 : 1) to obtain pure phenyl undec-10-enoate **3a** as colorless oil (63.2 g, 89%).

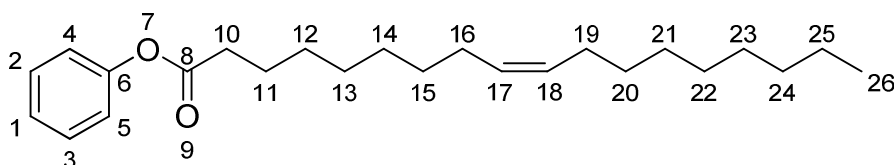
2.2.1. Phenyl undec-10-enoate (3a)



The reaction of 10-undecenoic acid **2a** (50.0 g, 271 mmol) with DPC **1** (58.1 g, 271 mmol) in the presence of catalytic amounts of DBU (1.24 g, 8.14 mmol, 3.0 mol%), was finished after eight hours at 160 °C. After purification by column chromatography (increasing gradient of polarity, *n*-hexane / ethyl acetate 49 : 1 to 9 : 1), pure phenyl undec-10-enoate **3a** was obtained as colorless oil (63.2 g, 89%). TLC (*n*-hexane / ethyl acetate 9 : 1) R_f = 0.93; ^1H NMR (CDCl_3 , 300 MHz) δ = 1.26 – 1.48 (m, 10 H, 5 CH_2^{12-16}), 1.75 (quint., J = 7.3 Hz, 2 H, CH_2^{11}), 2.05 (q, J = 7.0 Hz, 2 H, CH_2^{17}), 2.55 (t, J = 7.5 Hz, 2 H, CH_2^{10}), 4.90 – 5.04 (m, 2 H, CH_2^{19}), 5.81 (tdd, J = 17.0 Hz, 10.2 Hz, 6.8 Hz, 1 H, CH^{18}), 7.02 (dt, J = 7.4 Hz, 1.1 Hz, 2 H, 2 $\text{CH}^{4,5}$), 7.22 (tt, J = 7.5 Hz, 1.1 Hz, 1 H, CH^1), 7.38 (t, J = 8.2 Hz, 2 H, 2 $\text{CH}^{2,3}$) ppm; ^{13}C NMR (CDCl_3 , 75 MHz) δ = 24.9 (CH_2^{11}), 28.8 (CH_2^{16}), 29.0 (CH_2^{12-15}), 29.0 (CH_2^{12-15}), 29.1 (CH_2^{12-15}), 29.2 (CH_2^{12-15}), 33.7 (CH_2^{17}), 34.3 (CH_2^{10}), 114.1 (CH_2^{19}), 121.5 (2 $\text{CH}^{4,5}$), 125.6 (CH^1), 129.3 (2 $\text{CH}^{2,3}$), 139.1 (CH^{18}), 150.7 (C^6), 172.2 (CO^8) ppm; FAB of $\text{C}_{17}\text{H}_{24}\text{O}_2$ ($[\text{M}+\text{H}]^+$ = 261.2, $[\text{2M}+\text{H}]^+$ = 521.4); HRMS(FAB) of $\text{C}_{17}\text{H}_{24}\text{O}_2$ $[\text{M}+\text{H}]^+$ calc. 261.1849 found 261.1847; IR (ATR) ν = 3073.8, 2924.1, 2852.8, 1758.4 (ester), 1639.0, 1592.7, 1491.8, 1456.0, 1415.3, 1362.4, 1193.4, 1160.9, 1133.6, 1070.1, 1023.9, 992.8, 908.1, 812.3, 746.6, 688.4 cm^{-1} .

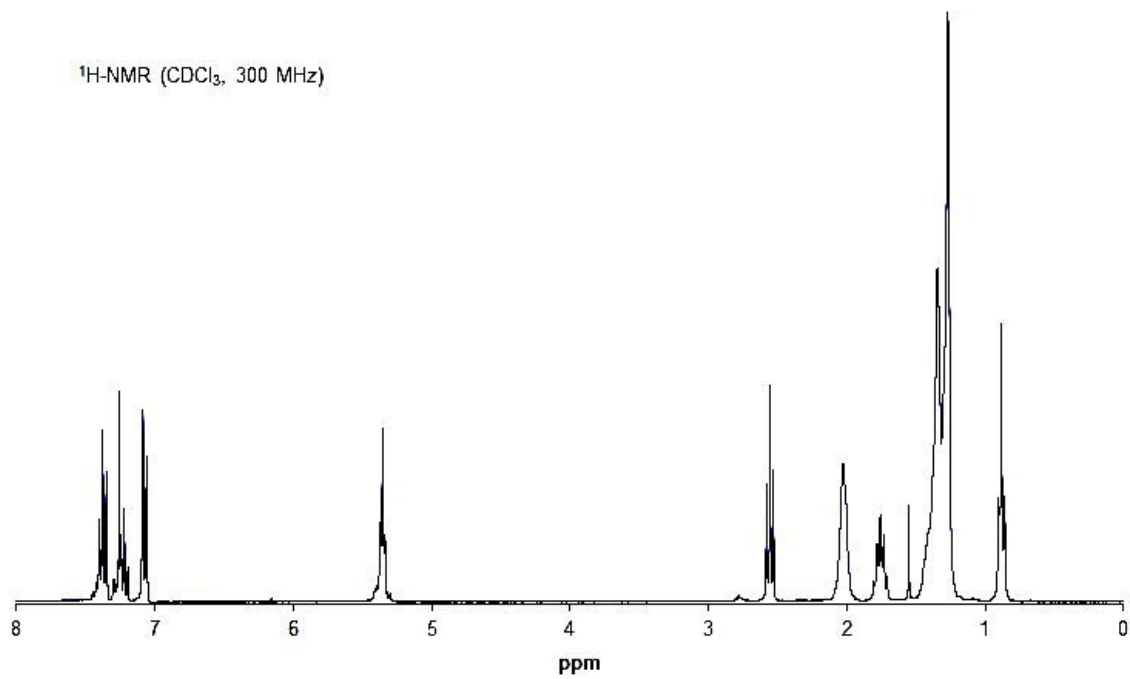


2.2.2. Phenyl oleate (3b)

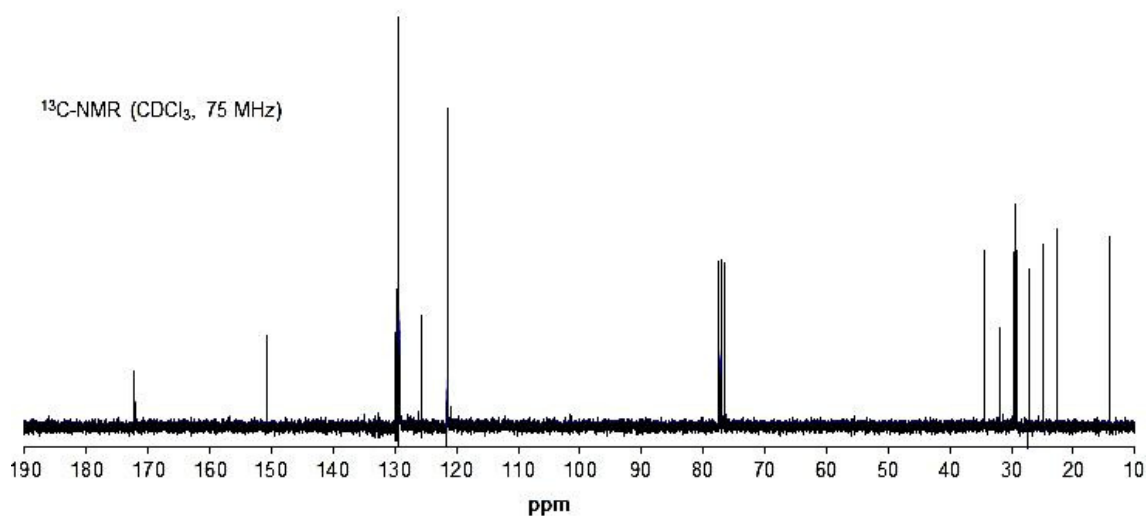


The reaction of oleic acid **2b** (0.77 g, 2.71 mmol) with DPC **1** (0.58 g, 2.71 mmol) in the presence of catalytic amounts of DBU (15.7 mg, 0.14 mmol, 5.0 mol%), was finished after one day at 160 °C. After purification by column chromatography (increasing gradient of polarity, *n*-hexane / ethyl acetate 49 : 1 to 9 : 1), pure phenyl oleate **3b** was obtained as colorless oil (0.80 g, 82%). TLC (*n*-hexane / ethyl acetate 49 : 1) $R_f = 0.83$; $^1\text{H NMR}$ (CDCl_3 , 300 MHz) $\delta = 0.88$ (t, $J = 6.7$ Hz, 3 H, CH_3^{26}), 1.22 – 1.47 (m, 20 H, 10 $\text{CH}_2^{12-15,20-25}$), 1.76 (quint., $J = 7.3$ Hz, 2 H, CH_2^{11}), 1.98 – 2.10 (m, 4 H, 2 $\text{CH}_2^{16,19}$), 2.56 (t, $J = 7.5$ Hz, 2 H, CH_2^{10}), 5.30 – 5.42 (m, 2 H, $\text{CH}_2^{17,18}$), 7.08 (dt, $J = 7.4$ Hz, 1.1 Hz, 2 H, 2 $\text{CH}^{4,5}$), 7.22 (t, $J = 7.5$ Hz, 1 H, CH^1), 7.38 (t, $J = 8.1$ Hz, 2 H, 2 $\text{CH}^{2,3}$) ppm; $^{13}\text{C NMR}$ (CDCl_3 , 75 MHz) $\delta = 14.1$ (CH_3^{26}), 22.6 (CH_2^{25}), 24.9 (CH_2^{11}), 27.1 ($\text{CH}_2^{16,19}$), 27.2 ($\text{CH}_2^{16,19}$), 29.1 ($\text{CH}_2^{12-15,20-23}$), 29.1 ($\text{CH}_2^{12-15,20-23}$), 29.3 ($\text{CH}_2^{12-15,20-23}$), 29.5 ($\text{CH}_2^{12-15,20-23}$), 29.6 ($\text{CH}_2^{12-15,20-23}$), 29.7 ($\text{CH}_2^{12-15,20-23}$), 31.9 (CH_2^{24}), 34.4 (CH_2^{10}), 121.5 (2 $\text{CH}^{4,5}$), 125.6 (CH^1), 129.3 (2 $\text{CH}^{2,3}$), 129.7 ($\text{CH}^{17,18}$), 130.0 ($\text{CH}^{17,18}$), 150.7 (C^6), 172.2 (CO^8) ppm; FAB of $\text{C}_{24}\text{H}_{38}\text{O}_2$ ($[\text{M}+\text{H}]^+ = 359.3$); HRMS(FAB) of $\text{C}_{24}\text{H}_{38}\text{O}_2$ $[\text{M}+\text{H}]^+$ calc. 359.2945 found 359.2944; IR (ATR) $\nu = 3003.5, 2921.5, 2851.8, 1760.0$ (ester), 1593.0, 1491.8, 1456.3, 1363.7, 1226.9, 1194.2, 1160.7, 1132.2, 1023.9, 924.4, 812.1, 746.4, 722.0, 688.4 cm^{-1} .

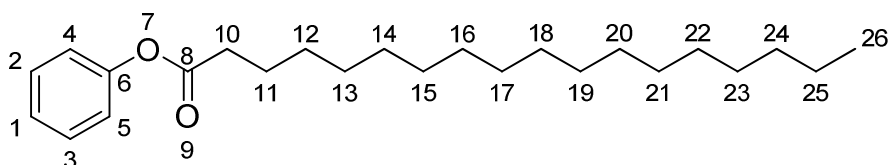
$^1\text{H-NMR}$ (CDCl_3 , 300 MHz)



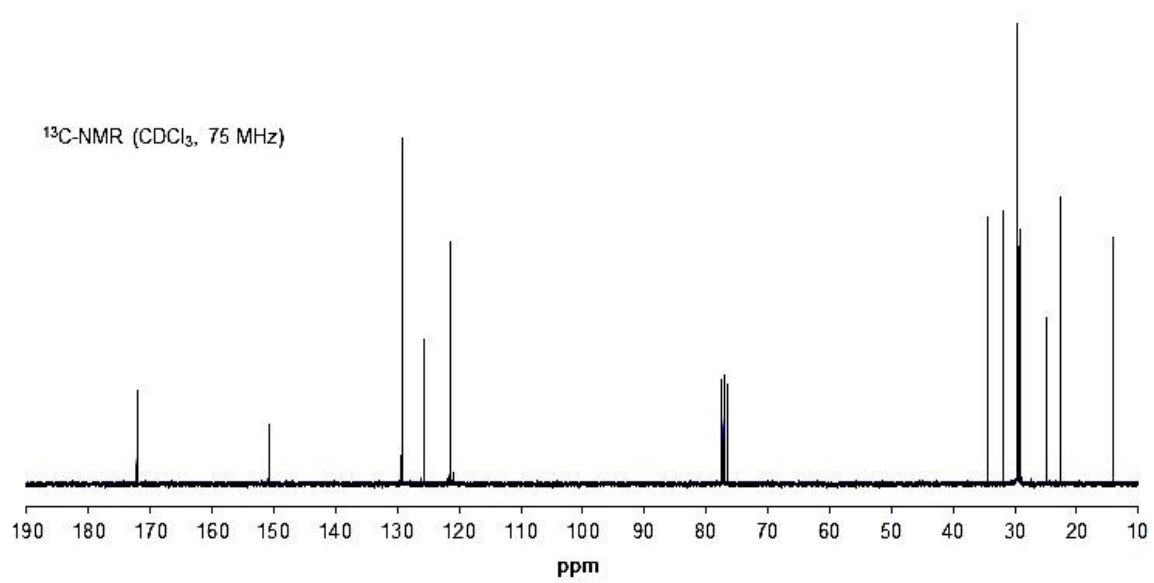
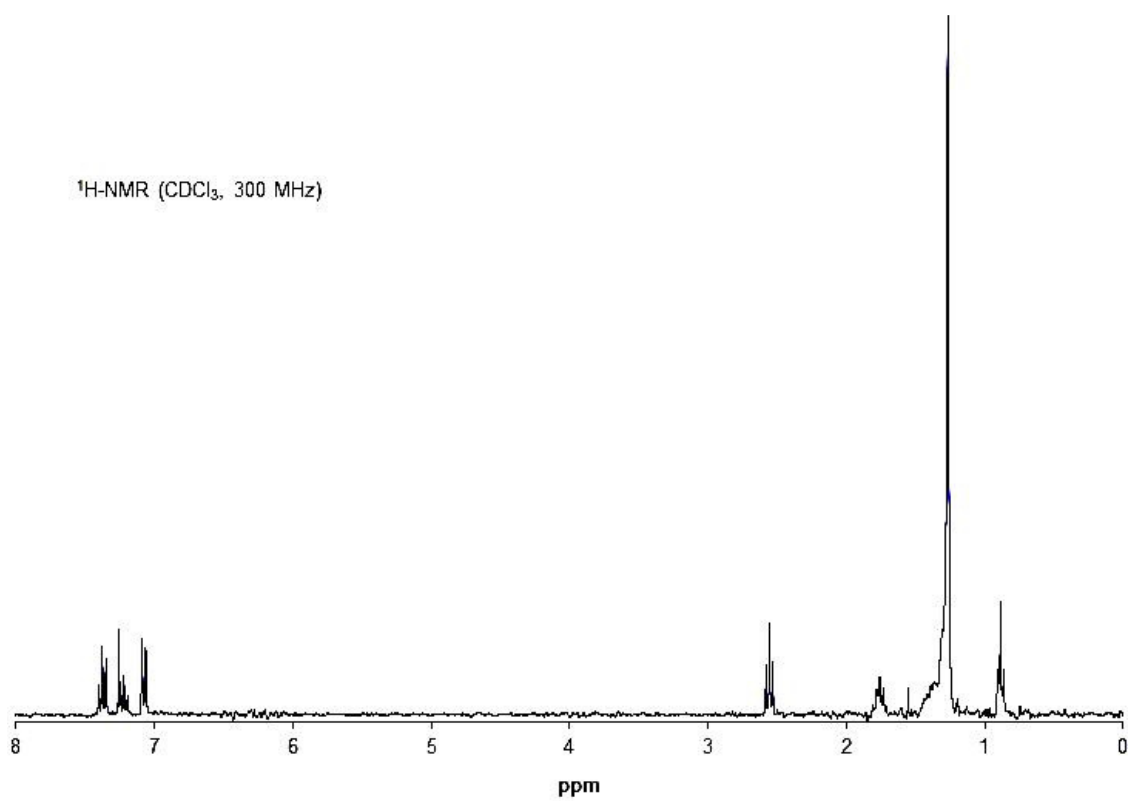
$^{13}\text{C-NMR}$ (CDCl_3 , 75 MHz)



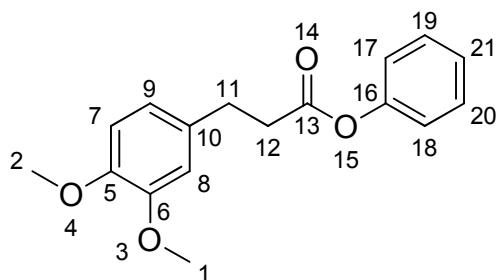
2.2.3. Phenyl stearate (3c)



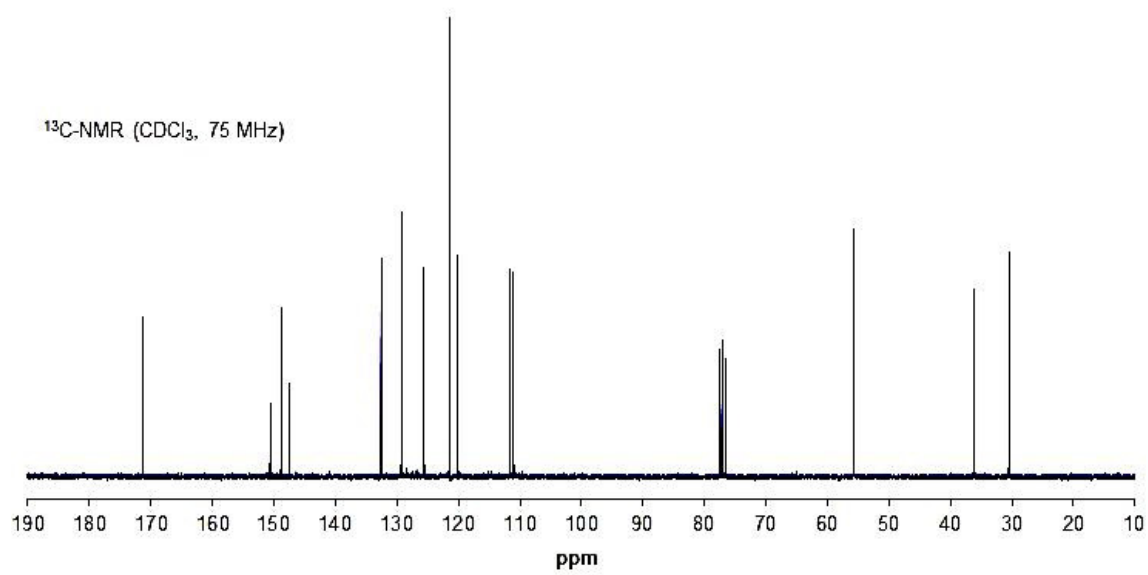
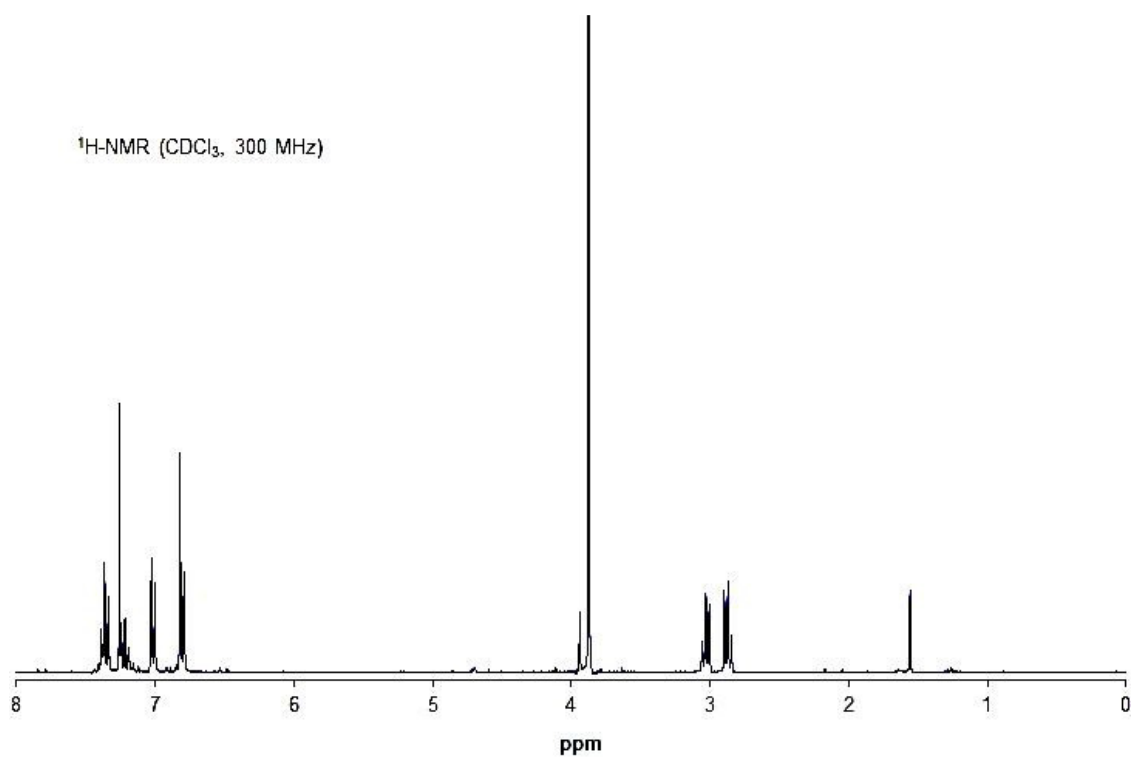
The reaction of stearic acid **2c** (5.00 g, 17.6 mmol) with DPC **1** (3.77 g, 17.6 mmol) in the presence of catalytic amounts of DBU (0.13 g, 0.88 mmol, 5.0 mol%), was finished after one day at 160 °C. After purification by column chromatography (increasing gradient of polarity, *n*-hexane / ethyl acetate 49 : 1 to 9 : 1), pure phenyl stearate **3c** was obtained as colorless solid (5.73 g, 90%). TLC (*n*-hexane / ethyl acetate 19 : 1) $R_f = 0.92$; $T_m = 43.5^\circ \text{C}$ (ethyl acetate); $^1\text{H NMR}$ (CDCl_3 , 300 MHz) $\delta = 0.89$ (t, $J = 6.6$ Hz, 3 H, CH_3^{26}), 1.20 – 1.46 (m, 28 H, 14 CH_2^{12-25}), 1.76 (quint., $J = 7.2$ Hz, 2 H, CH_2^{11}), 2.56 (tt, $J = 7.5$ Hz, 2 H, CH_2^{10}), 7.08 (dt, $J = 7.4$ Hz, 1.1 Hz, 2 H, 2 $\text{CH}^{4,5}$), 7.22 (t, $J = 7.5$ Hz, 1.1 Hz, 1 H, CH^1), 7.38 (t, $J = 8.1$ Hz, 2 H, 2 $\text{CH}^{2,3}$) ppm; $^{13}\text{C NMR}$ (CDCl_3 , 75 MHz) $\delta = 14.1$ (CH_3^{26}), 22.7 (CH_2^{25}), 24.9 (CH_2^{11}), 29.1 (CH_2^{12-23}), 29.2 (CH_2^{12-23}), 29.3 (CH_2^{12-23}), 29.4 (CH_2^{12-23}), 29.6 (CH_2^{12-23}), 29.6 (CH_2^{12-23}), 29.6 (CH_2^{12-23}), 29.7 (CH_2^{12-23}), 31.9 (CH_2^{24}), 34.3 (CH_2^{10}), 121.5 (2 $\text{CH}^{4,5}$), 125.6 (CH^1), 129.3 (2 $\text{CH}^{2,3}$), 150.7 (C^6), 172.2 (CO^8) ppm; FAB of $\text{C}_{24}\text{H}_{40}\text{O}_2$ ($[\text{M}+\text{H}]^+ = 361.4$); HRMS(FAB) of $\text{C}_{24}\text{H}_{40}\text{O}_2$ $[\text{M}+\text{H}]^+$ calc. 361.3101 found 361.3099; IR (ATR) $\nu = 2913.1, 2847.5, 1745.5$ (ester), 1589.1, 1470.9, 1416.2, 1379.3, 1309.6, 1263.0, 1199.6, 1166.4, 1145.7, 1072.4, 1023.5, 933.7, 906.9, 813.6, 763.3, 714.8, 689.8 cm^{-1} .



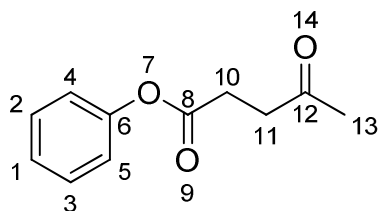
2.2.4. Phenyl 3-(3,4-dimethoxyphenyl)propanoate (**3d**)



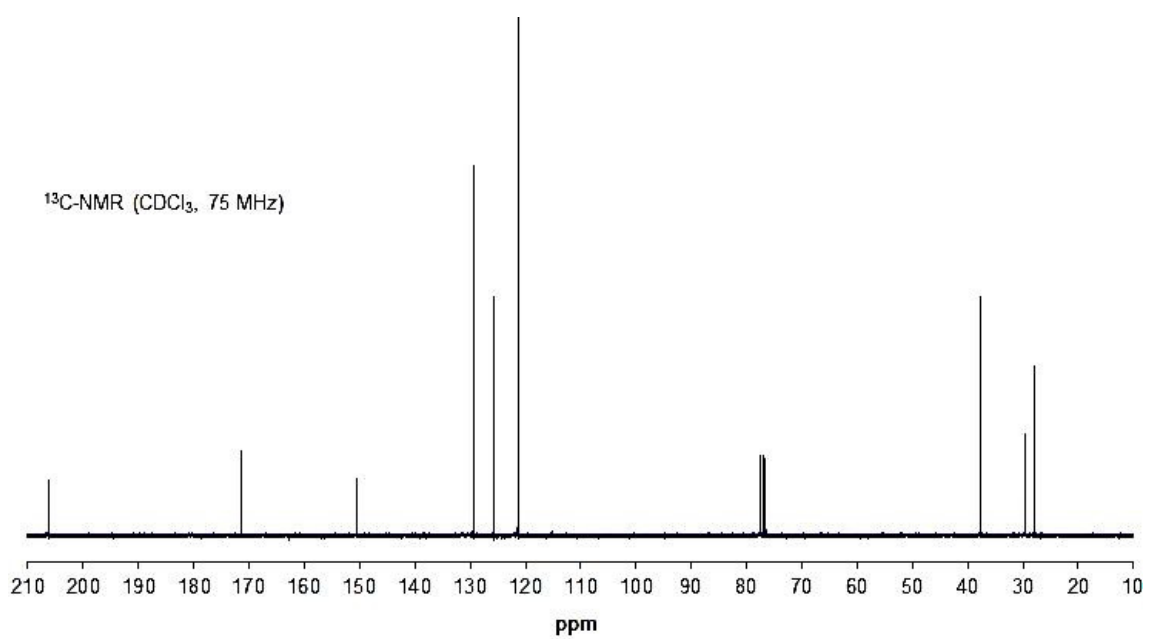
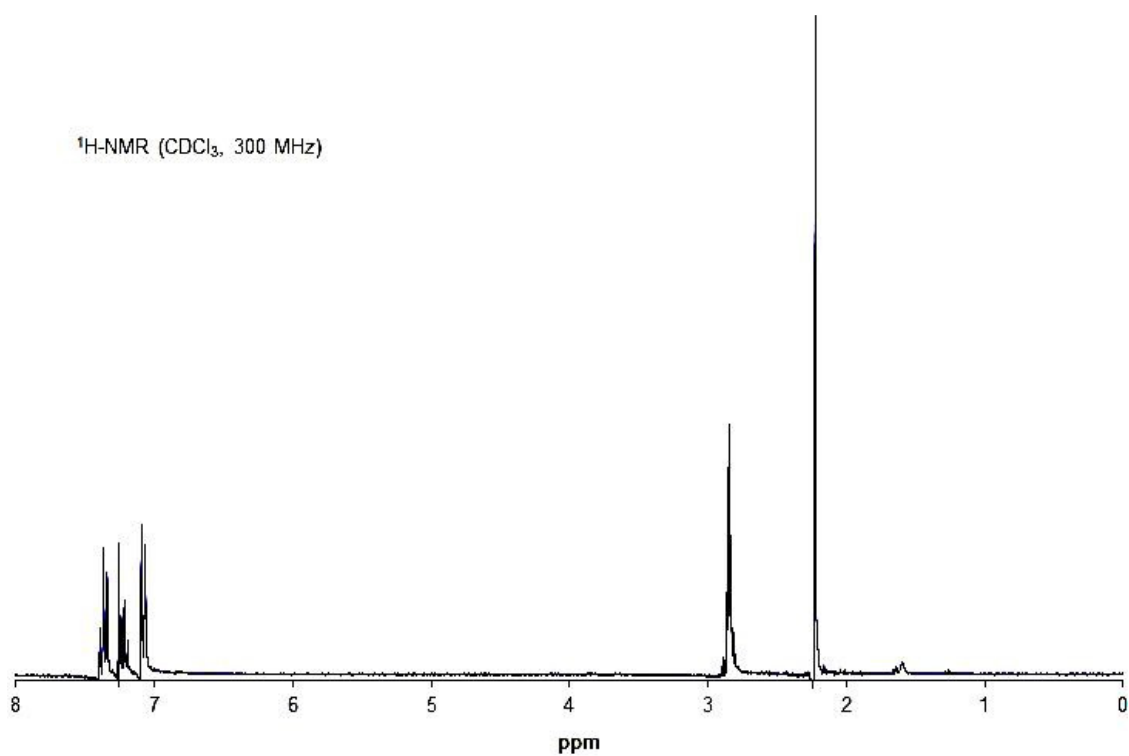
The reaction of 3-(3,4-dimethoxyphenyl)propanoic acid **2d** (0.50 g, 2.38 mmol) with DPC **1** (0.51 g, 2.38 mmol) in the presence of catalytic amounts of DBU (18.1 mg, 0.12 mmol, 5.0 mol%), was finished after one day at 160 °C. After purification by column chromatography (increasing gradient of polarity, *n*-hexane / ethyl acetate 4 : 1 to pure ethyl acetate), phenyl 3-(3,4-dimethoxyphenyl)propanoate **3d** was obtained as yellowish oil (0.54 g, 79%). TLC (*n*-hexane / ethyl acetate 2 : 1) $R_f = 0.70$; $^1\text{H NMR}$ (CDCl_3 , 300 MHz) $\delta = 2.87$ (t, $J = 7.7$ Hz, 2 H, CH_2^{12}), 3.03 (t, $J = 7.5$ Hz, 2 H, CH_2^{11}), 3.88 (s, 6 H, 2 $\text{CH}_3^{1,2}$), 6.78 – 6.84 (m, 3 H, 3 CH^{7-9}), 7.02 (dt, $J = 7.5$ Hz, 1.1 Hz, 2 H, 2 $\text{CH}^{17,18}$), 7.22 (tt, $J = 7.5$ Hz, 1.7 Hz, 1 H, CH^{21}), 7.37 (t, $J = 8.1$ Hz, 2 H, 2 $\text{CH}^{19,20}$) ppm; $^{13}\text{C NMR}$ (CDCl_3 , 75 MHz) $\delta = 30.4$ (CH_2^{11}), 36.1 (CH_2^{12}), 55.7 ($\text{CH}_3^{1,2}$), 55.7 ($\text{CH}_3^{1,2}$), 111.2 ($\text{CH}^{7,8}$), 111.6 ($\text{CH}^{7,8}$), 120.1 (CH^9), 121.4 (2 $\text{CH}^{17,18}$), 125.7 (CH^{21}), 129.2 (2 $\text{CH}^{19,20}$), 132.6 (C^{10}), 147.4 (C^5), 148.8 (C^6), 150.5 (C^{16}), 171.3 (CO^{13}) ppm; FAB of $\text{C}_{17}\text{H}_{18}\text{O}_4$ ($\text{M}^+ = 286.1$, $[\text{M}+\text{H}]^+ = 287.1$); HRMS(FAB) of $\text{C}_{17}\text{H}_{18}\text{O}_4$ M^+ calc. 286.1200 found 286.1201; IR (ATR) $\nu = 2933.0$, 2833.0, 1753.6 (ester), 1590.5, 1513.4, 1491.8, 1453.3, 1417.3, 1344.6, 1259.2, 1235.0, 1190.6, 1157.8, 1124.9, 1025.9, 929.1, 850.9, 807.6, 751.1, 692.4 cm^{-1} .



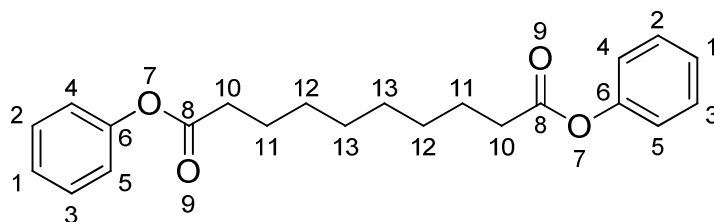
2.2.5. Phenyl 4-oxopentanoate (phenyl levulinate, **3e**)



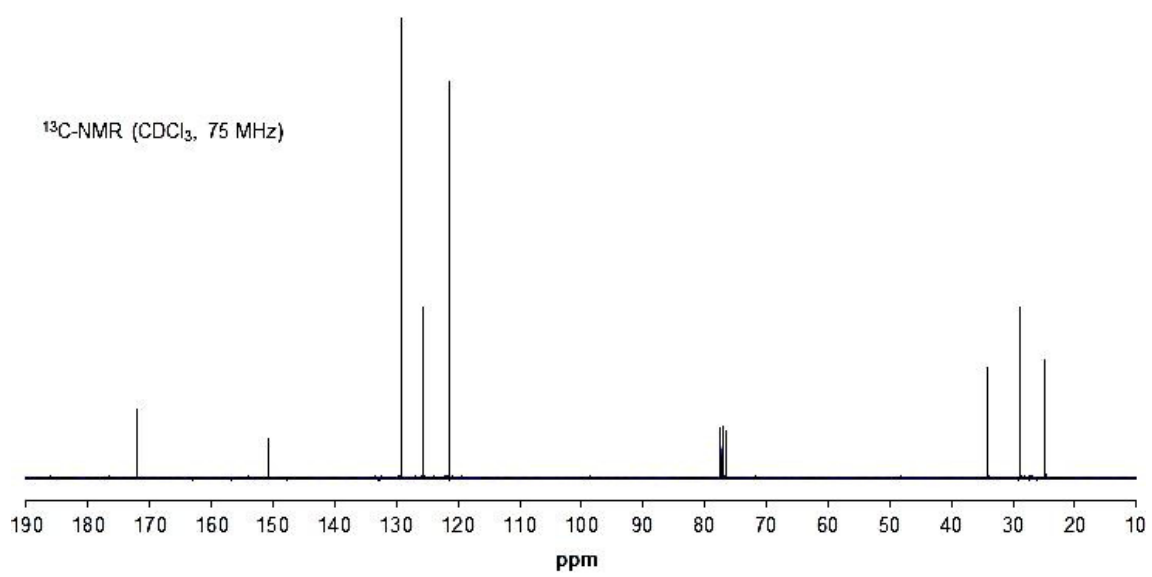
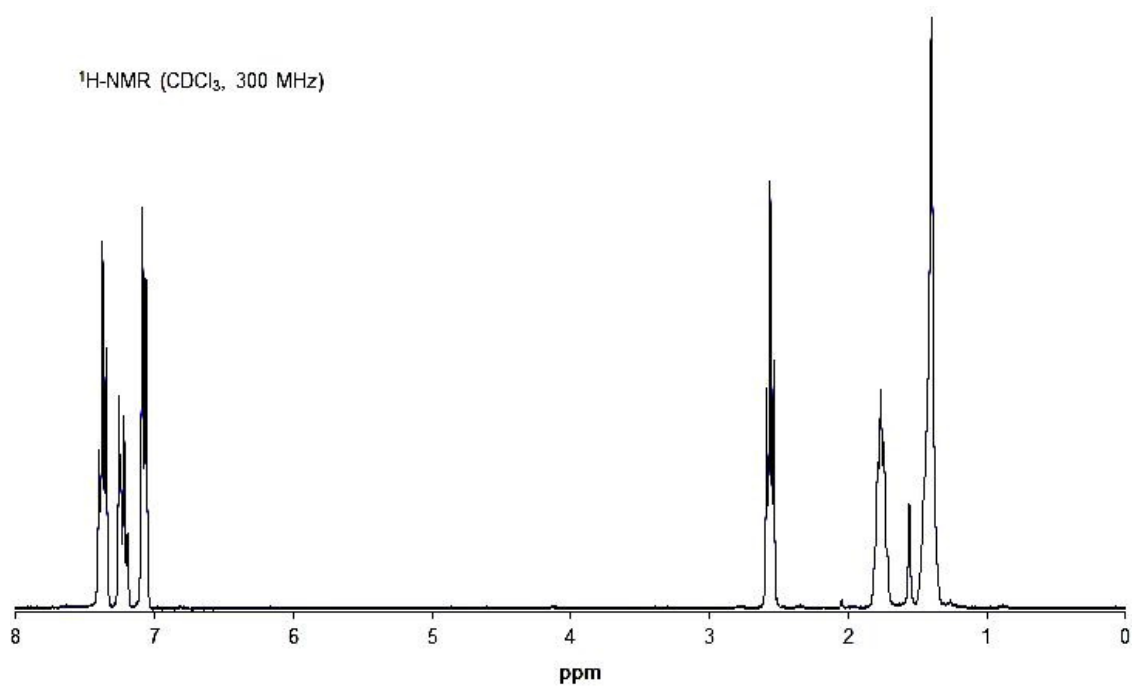
The reaction of levulinic acid **2e** (1.00 g, 8.61 mmol) with DPC **1** (1.84 g, 8.61 mmol) in the presence of catalytic amounts of DBU (65.5 mg, 0.43 mmol, 5.0 mol%), was finished after one day at 160 °C. After purification by column chromatography (increasing gradient of polarity, *n*-hexane / ethyl acetate 9 : 1 to 2 : 1), phenyl levulinate **3e** was obtained as yellowish oil (0.73 g, 44%). TLC (*n*-hexane / ethyl acetate 1 : 1) R_f = 0.80; ^1H NMR (CDCl_3 , 300 MHz) δ = 2.23 (s, 3 H, CH_3^{13}), 2.80 – 2.90 (m, 4 H, 2 $\text{CH}_2^{10,11}$), 7.08 (dt, J = 7.4 Hz, 1.3 Hz, 2 H, 2 $\text{CH}^{4,5}$), 7.22 (tt, J = 7.5 Hz, 1.7 Hz, 1 H, CH^1), 7.37 (t, J = 8.1 Hz, 2 H, 2 $\text{CH}^{2,3}$) ppm; ^{13}C NMR (CDCl_3 , 75 MHz) δ = 28.0 (CH_2^{10}), 29.7 (CH_3^{13}), 37.7 (CH_2^{11}), 121.4 (2 $\text{CH}^{4,5}$), 125.7 (CH^1), 129.2 (2 $\text{CH}^{2,3}$), 150.5 (C^6), 171.3 (CO^8), 206.3 (CO^{12}) ppm; FAB of $\text{C}_{11}\text{H}_{12}\text{O}_3$ ($[\text{M}+\text{H}]^+$ = 193.1); HRMS(FAB) of $\text{C}_{11}\text{H}_{12}\text{O}_3$ $[\text{M}+\text{H}]^+$ calc. 193.0859 found 193.0860; IR (ATR) ν = 2920.2, 1754.8 (ester), 1714.6 (ketone), 1591.4, 1492.0, 1404.2, 1357.6, 1231.1, 1193.0, 1161.1, 1133.3, 1065.3, 1023.4, 928.6, 814.3, 750.3, 691.6 cm^{-1} .



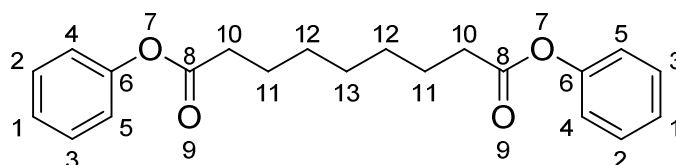
2.2.6. Diphenyl decanedioate (diphenyl sebacate, **3f**)



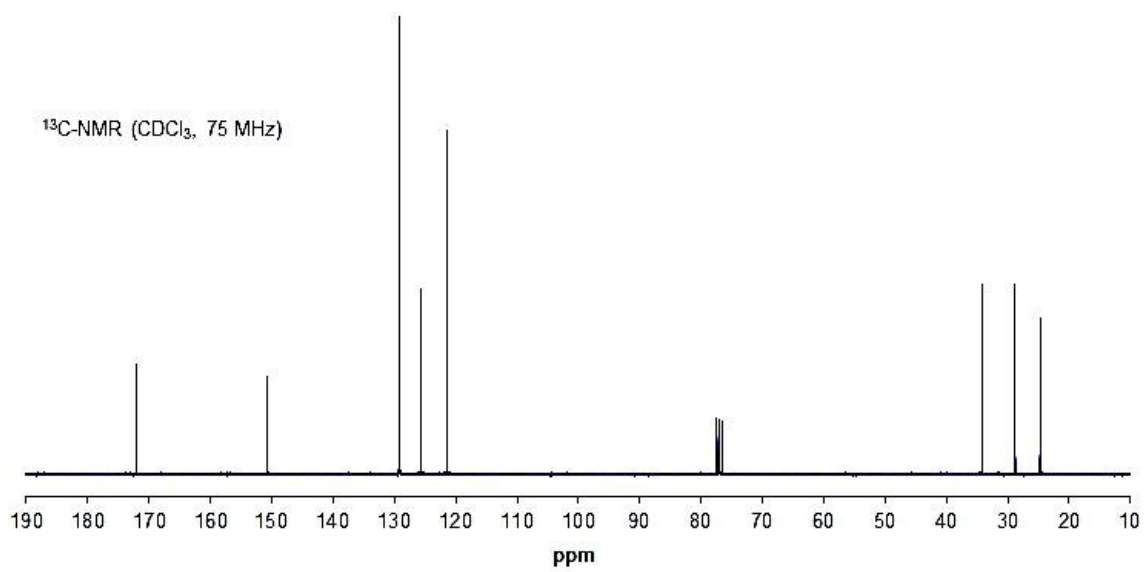
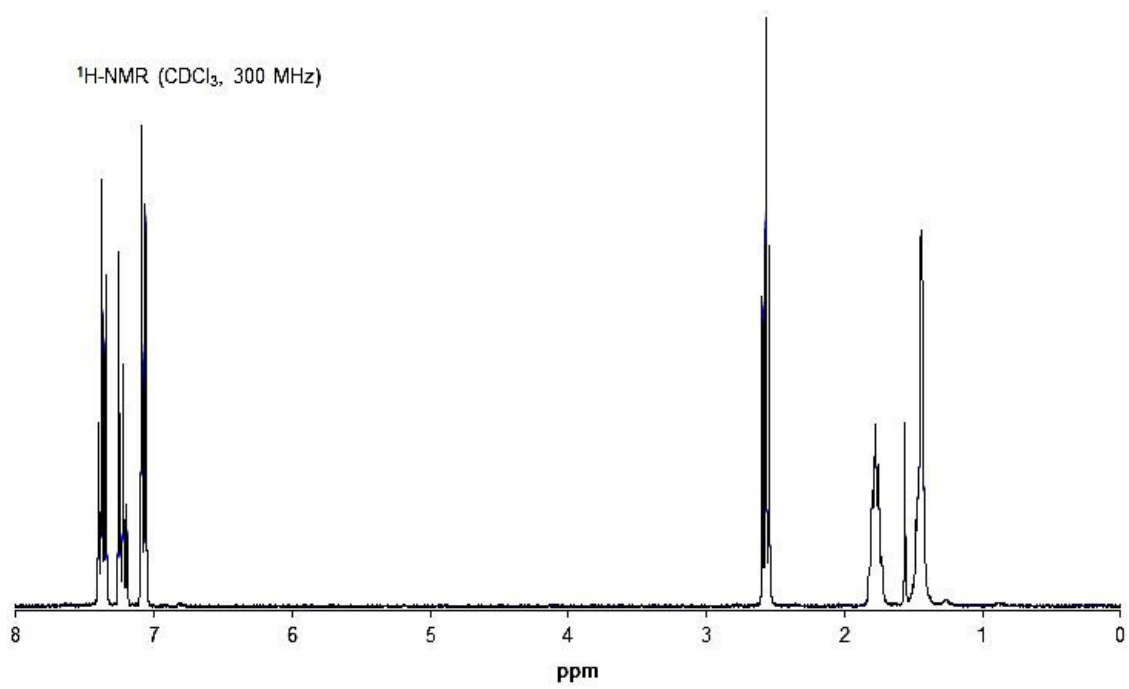
The reaction of sebacic acid **2f** (20.0 g, 98.9 mmol) with DPC **1** (42.4 g, 198 mmol, 2.0 eq.) in the presence of catalytic amounts of DBU (1.51 g, 9.89 mmol, 10 mol%), was finished after one day at 160 °C. Phenol as by-product was removed *via* vacuum distillation (80 °C, 7.0 mbar) to obtain it in a yield of 90% (16.7 g). The crude product was recrystallized in ethyl acetate / *n*-hexane (~1 : 3) to obtain diphenyl sebacate **3f** as colorless solid (27.3 g, 78%). TLC (*n*-hexane / ethyl acetate 9 : 1) $R_f = 0.54$; $T_m = 66.7$ °C (ethyl acetate); $^1\text{H NMR}$ (CDCl_3 , 300 MHz) $\delta = 1.34 - 1.49$ (m, 8 H, 4 $\text{CH}_2^{12,13}$), 1.77 (quint., $J = 7.0$ Hz, 4 H, 2 CH_2^{11}), 2.56 (t, $J = 7.5$ Hz, 4 H, 2 CH_2^{10}), 7.07 (d, $J = 7.6$ Hz, 4 H, 4 $\text{CH}^{4,5}$), 7.22 (t, $J = 7.5$ Hz, 2 H, 2 CH^1), 7.38 (t, $J = 7.8$ Hz, 4 H, 4 $\text{CH}^{2,3}$) ppm; $^{13}\text{C NMR}$ (CDCl_3 , 75 MHz) $\delta = 24.8$ (2 CH_2^{11}), 28.9 (2 CH_2^{12}), 29.0 (2 CH_2^{13}), 34.2 (2 CH_2^{10}), 121.5 (4 $\text{CH}^{4,5}$), 125.6 (2 CH^1), 129.3 (4 $\text{CH}^{2,3}$), 150.7 (2 C^6), 172.1 (2 CO^8) ppm; FAB of $\text{C}_{22}\text{H}_{26}\text{O}_4$ ($[\text{M}+\text{H}]^+ = 355.2$); HRMS(FAB) of $\text{C}_{22}\text{H}_{26}\text{O}_4$ $[\text{M}+\text{H}]^+$ calc. 355.1904 found 355.1906; IR (ATR) $\nu = 2929.3, 2850.5, 1744.9$ (ester), 1588.3, 1483.2, 1455.7, 1416.6, 1380.6, 1359.3, 1288.8, 1197.0, 1166.1, 1130.9, 1071.7, 1042.0, 931.8, 906.3, 813.1, 762.5, 711.7, 688.9 cm^{-1} .



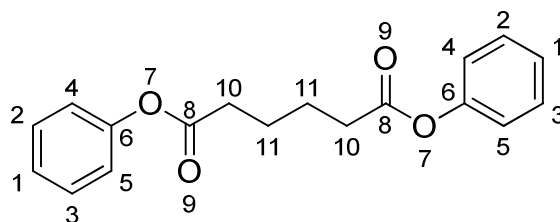
2.2.7. Diphenyl nonanedioate (diphenyl azelate, **3g**)



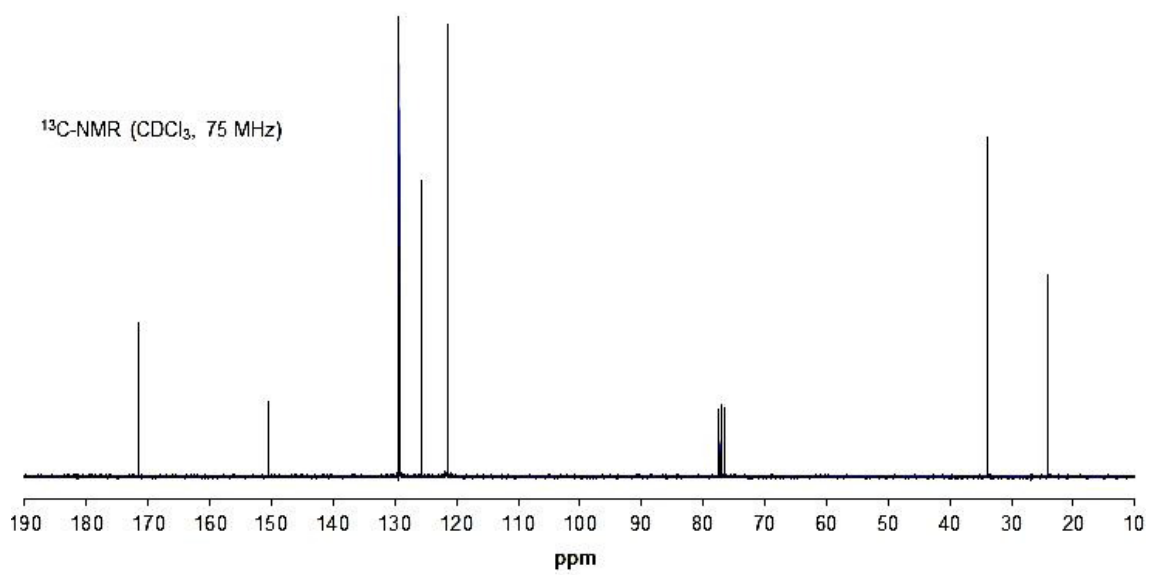
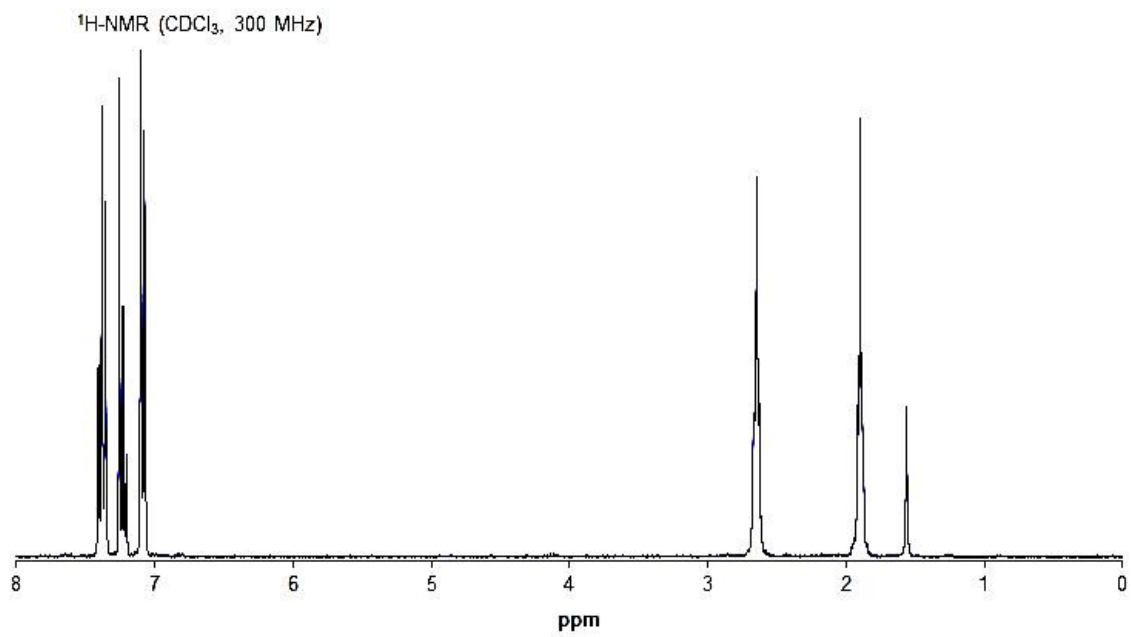
The reaction of azelaic acid **2g** (14.9 g, 79.4 mmol) with DPC **1** (34.1 g, 159 mmol, 2.0 eq.) in the presence of catalytic amounts of DBU (1.21 g, 7.94 mmol, 10 mol%), was finished after one day at 160 °C. Phenol as by-product was removed *via* vacuum distillation (75 °C, 4.0 mbar) to obtain it in a yield of 91% (13.6 g). The crude product was recrystallized in ethyl acetate / *n*-hexane (~1 : 3) to obtain diphenyl azelate **3g** as colorless solid (20.8 g, 77%). TLC (*n*-hexane / ethyl acetate 9 : 1) $R_f = 0.47$; $T_m = 61.5$ °C (ethyl acetate); $^1\text{H NMR}$ (CDCl_3 , 300 MHz) $\delta = 1.39 - 1.51$ (m, 6 H, 3 $\text{CH}_2^{12,13}$), 1.78 (quint., $J = 7.0$ Hz, 4 H, 2 CH_2^{11}), 2.57 (t, $J = 7.5$ Hz, 4 H, 2 CH_2^{10}), 7.05 – 7.10 (m, 4 H, 4 $\text{CH}^{4,5}$), 7.22 (tt, $J = 7.5$ Hz, 1.1 Hz, 2 H, 2 CH^1), 7.34 – 7.41 (m, 4 H, 4 $\text{CH}^{2,3}$) ppm; $^{13}\text{C NMR}$ (CDCl_3 , 75 MHz) $\delta = 24.7$ (2 CH_2^{11}), 28.8 (3 $\text{CH}_2^{12,13}$), 34.2 (2 CH_2^{10}), 121.5 (4 $\text{CH}^{4,5}$), 125.6 (2 CH^1), 129.3 (4 $\text{CH}^{2,3}$), 150.6 (2 C^6), 172.1 (2 CO^8) ppm; FAB of $\text{C}_{21}\text{H}_{24}\text{O}_4$ ($[\text{M}+\text{H}]^+ = 341.2$); HRMS(FAB) of $\text{C}_{21}\text{H}_{24}\text{O}_4$ $[\text{M}+\text{H}]^+$ calc. 341.1747 found 341.1750; IR (ATR) $\nu = 2925.1, 2846.5, 1746.9$ (ester), 1590.2, 1493.3, 1377.8, 1307.8, 1202.1, 1138.1, 1069.5, 1006.5, 934.9, 900.7, 814.4, 763.5, 707.6, 687.1 cm^{-1} .



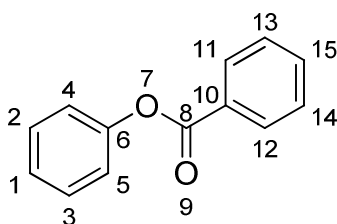
2.2.8. Diphenyl hexanedioate (Diphenyl adipate, **3h**)



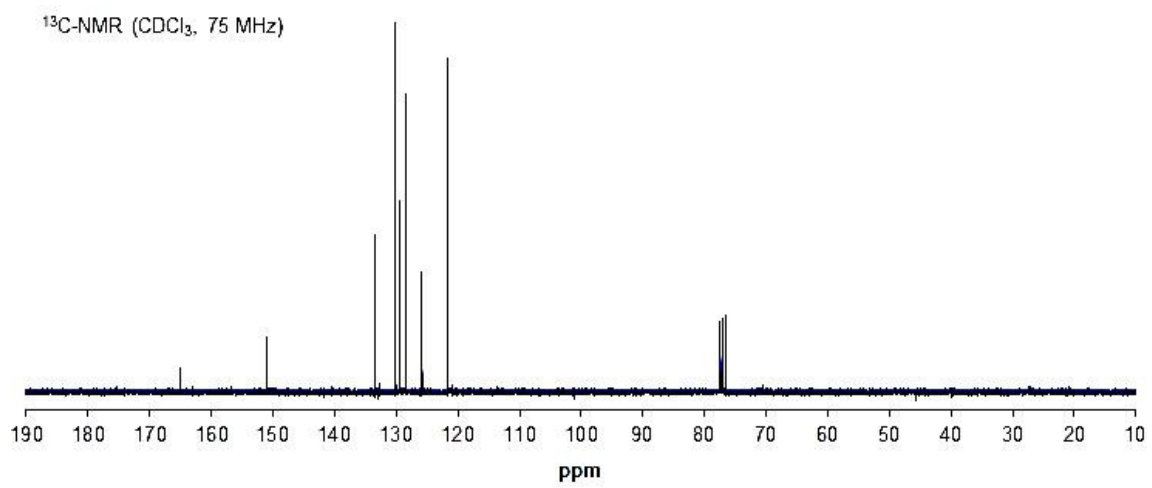
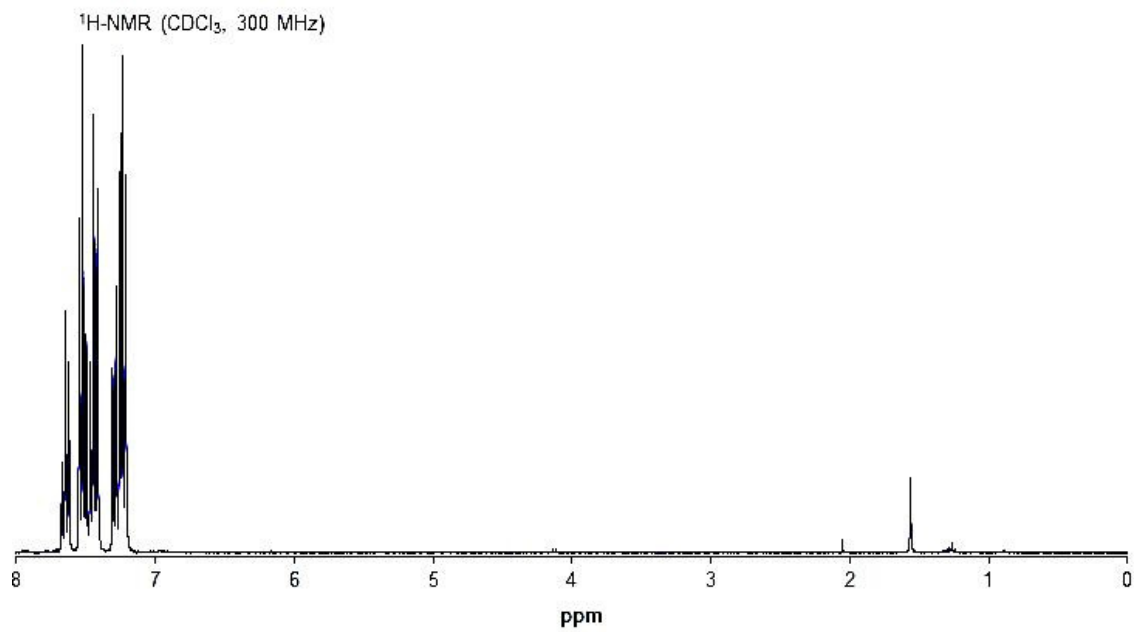
The reaction of adipic acid **2h** (15.0 g, 103 mmol) with DPC **1** (44.0 g, 205 mmol, 2.0 eq.) in the presence of catalytic amounts of DBU (1.56 g, 10.3 mmol, 10 mol%), was finished after one day at 160 °C. Phenol as by-product was removed *via* vacuum distillation (75 °C, 4.0 mbar) to obtain it in a yield of 93% (8.98 g). The crude product was recrystallized in ethyl acetate / *n*-hexane (~1 : 3) to obtain diphenyl adipate **3h** as colorless solid (24.2 g, 79%). TLC (*n*-hexane / ethyl acetate 2 : 1) R_f = 0.78; T_m = 108.6 °C (ethyl acetate); $^1\text{H NMR}$ (CDCl_3 , 300 MHz) δ = 1.90 (quint., J = 3.2 Hz, 4 H, 2 CH_2^{11}), 2.65 (t, J = 7.0 Hz, 4 H, 2 CH_2^{10}), 7.09 (dt, J = 7.6 Hz, 1.3 Hz, 4 H, 4 $\text{CH}^{4,5}$), 7.23 (tt, J = 7.4 Hz, 1.8 Hz, 2 H, 2 CH^1), 7.38 (t, J = 8.0 Hz, 4 H, 4 $\text{CH}^{2,3}$) ppm; $^{13}\text{C NMR}$ (CDCl_3 , 75 MHz) δ = 24.2 (2 CH_2^{11}), 33.9 (2 CH_2^{10}), 121.5 (4 $\text{CH}^{4,5}$), 125.7 (2 CH^1), 129.3 (4 $\text{CH}^{2,3}$), 150.6 (2 C^6), 171.6 (2 CO^8) ppm; FAB of $\text{C}_{18}\text{H}_{18}\text{O}_4$ ($[\text{M}+\text{H}]^+$ = 299.1); HRMS(FAB) of $\text{C}_{18}\text{H}_{18}\text{O}_4$ $[\text{M}+\text{H}]^+$ calc. 299.1278 found 299.1280; IR (ATR) ν = 2955.6, 2871.7, 1751.3 (ester), 1587.5, 1481.2, 1454.7, 1412.4, 1374.1, 1245.8, 1191.5, 1162.4, 1122.7, 1067.9, 1042.4, 1019.9, 1006.0, 929.4, 906.6, 813.0, 766.1, 735.0, 710.9, 684.8 cm^{-1} .



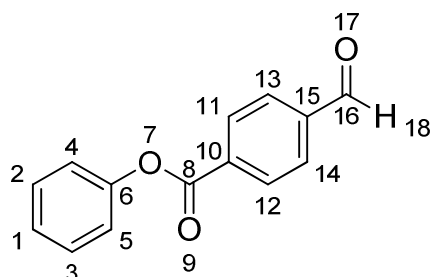
2.2.9. Phenyl benzoate (3i)



The reaction of benzoic acid **2i** (0.66 g, 5.42 mmol) with DPC **1** (1.16 g, 5.42 mmol) in the presence of catalytic amounts of DBU (41.3 mg, 0.27 mmol, 5.0 mol%), was finished after one day at 160 °C. After purification by column chromatography (increasing gradient of polarity, *n*-hexane / ethyl acetate 49 : 1 to 9 : 1), phenyl benzoate **3i** was obtained as colorless solid (0.78 g, 73%). TLC (*n*-hexane / ethyl acetate 19 : 1) $R_f = 0.64$; $T_m = 70.2$ °C (ethyl acetate), Lit. $T_m = 68 - 70$ °C; $^1\text{H NMR}$ (CDCl_3 , 300 MHz) $\delta = 7.20 - 7.32$ (m, 3 H, 3 $\text{CH}^{1,4,5}$), 7.40 – 7.56 (m, 4 H, 4 $\text{CH}^{2,3,13,14}$), 7.65 (tt, $J = 7.5$ Hz, 2.1 Hz, 1 H, CH^{15}), 8.19 – 8.25 (m, 2 H, $\text{CH}^{11,12}$) ppm; $^{13}\text{C NMR}$ (CDCl_3 , 75 MHz) $\delta = 121.7$ (2 $\text{CH}^{4,5}$), 125.8 (CH^1), 128.5 (2 $\text{CH}^{13,14}$), 129.4 (2 $\text{CH}^{2,3}$), 129.5 (2 $\text{CH}^{11,12}$), 130.1 (C^{10}), 133.5 (CH^{15}), 150.9 (C^6), 165.1 (CO^8) ppm; FAB of $\text{C}_{13}\text{H}_{10}\text{O}_2$ ($[\text{M}+\text{H}]^+ = 199.1$, $[2\text{M}+\text{H}]^+ = 397.2$); HRMS(FAB) of $\text{C}_{13}\text{H}_{10}\text{O}_2$ $[\text{M}+\text{H}]^+$ calc. 199.0754 found 199.0753; IR (ATR) $\nu = 3057.1$, 1725.1 (ester), 1589.6, 1485.1, 1449.2, 1310.7, 1256.3, 1194.7, 1165.3, 1078.6, 1060.2, 1023.5, 998.9, 914.9, 851.7, 815.4, 749.3, 690.9 cm^{-1} .

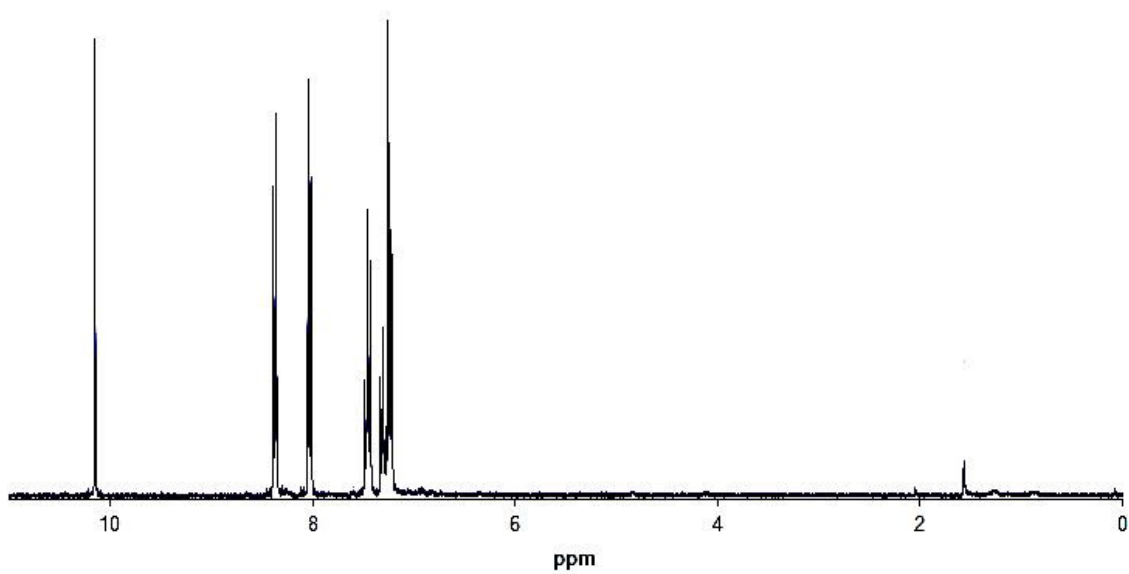


2.2.10. Phenyl 4-formylbenzoate (**3j**)

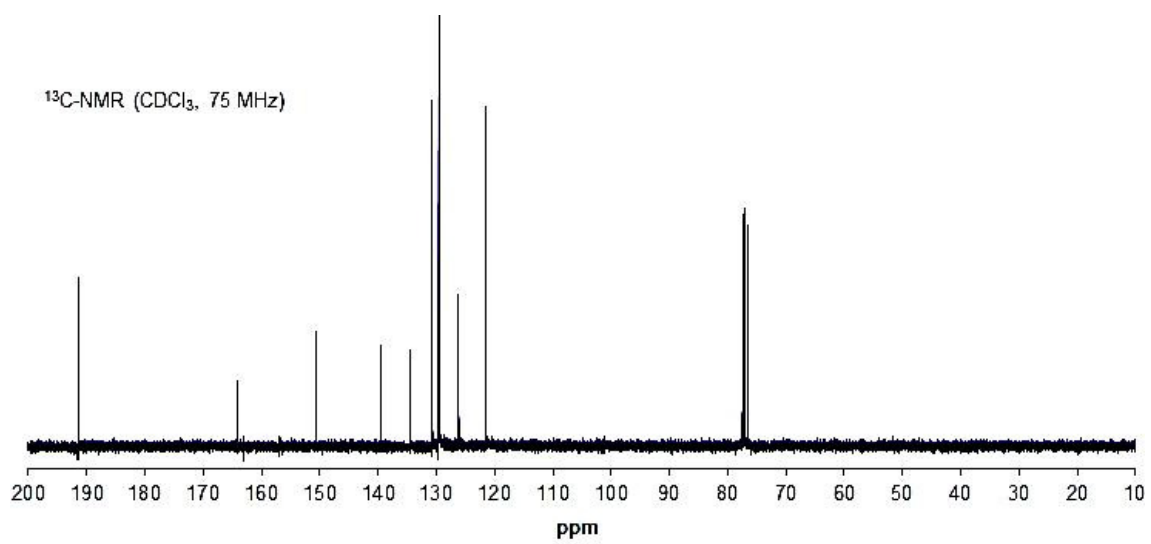


The reaction of 4-formylbenzoic acid **2j** (1.00 g, 6.66 mmol) with DPC **1** (1.43 g, 6.66 mmol) in the presence of catalytic amounts of DBU (50.7 mg, 0.33 mmol, 5.0 mol%), was finished after one day at 160 °C. After purification by column chromatography (increasing gradient of polarity, *n*-hexane / ethyl acetate 19 : 1 to 4 : 1), phenyl 4-formylbenzoate **3j** was obtained as colorless solid (0.80 g, 53%). TLC (*n*-hexane / ethyl acetate 5 : 1) $R_f = 0.53$; $T_m = 87.2$ °C (ethyl acetate); $^1\text{H NMR}$ (CDCl_3 , 300 MHz) $\delta = 7.20 - 7.27$ (m, 2 H, 2 $\text{CH}^{4,5}$), 7.31 (tt, $J = 7.5$ Hz, 1.1 Hz, 1 H, CH^1), 7.46 (t, $J = 8.0$ Hz, 2 H, 2 $\text{CH}^{2,3}$), 8.03 (d, $J = 8.2$ Hz, 2 H, 2 $\text{CH}^{13,14}$), 8.37 (d, $J = 8.5$ Hz, 2 H, 2 $\text{CH}^{11,12}$), 10.15 (s, 1 H, CHO^{18}) ppm; $^{13}\text{C NMR}$ (CDCl_3 , 75 MHz) $\delta = 121.5$ (2 $\text{CH}^{4,5}$), 126.2 (CH^1), 129.6 (2 $\text{CH}^{13,14}$), 129.6 (2 $\text{CH}^{2,3}$), 130.7 (2 $\text{CH}^{11,12}$), 134.5 (C^{10}), 139.5 (C^{15}), 150.6 (C^6), 164.1 (CO^8), 191.5 (CHO^{16}) ppm; FAB of $\text{C}_{14}\text{H}_{10}\text{O}_3$ ($[\text{M}+\text{H}]^+ = 227.1$); HRMS(FAB) of $\text{C}_{14}\text{H}_{10}\text{O}_3$ $[\text{M}+\text{H}]^+$ calc. 227.0703 found 227.0701; IR (ATR) $\nu = 3379.6, 3041.9, 2840.6, 1731.0$ (ester), 1700.7 (aldehyde), 1591.8, 1573.6, 1484.1, 1414.0, 1374.7, 1298.1, 1259.7, 1189.2, 1160.0, 1074.7, 1007.8, 921.3, 854.4, 827.3, 811.9, 748.0, 685.3 cm^{-1} .

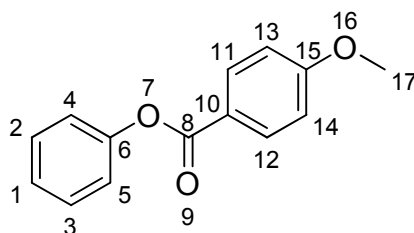
$^1\text{H-NMR}$ (CDCl_3 , 300 MHz)



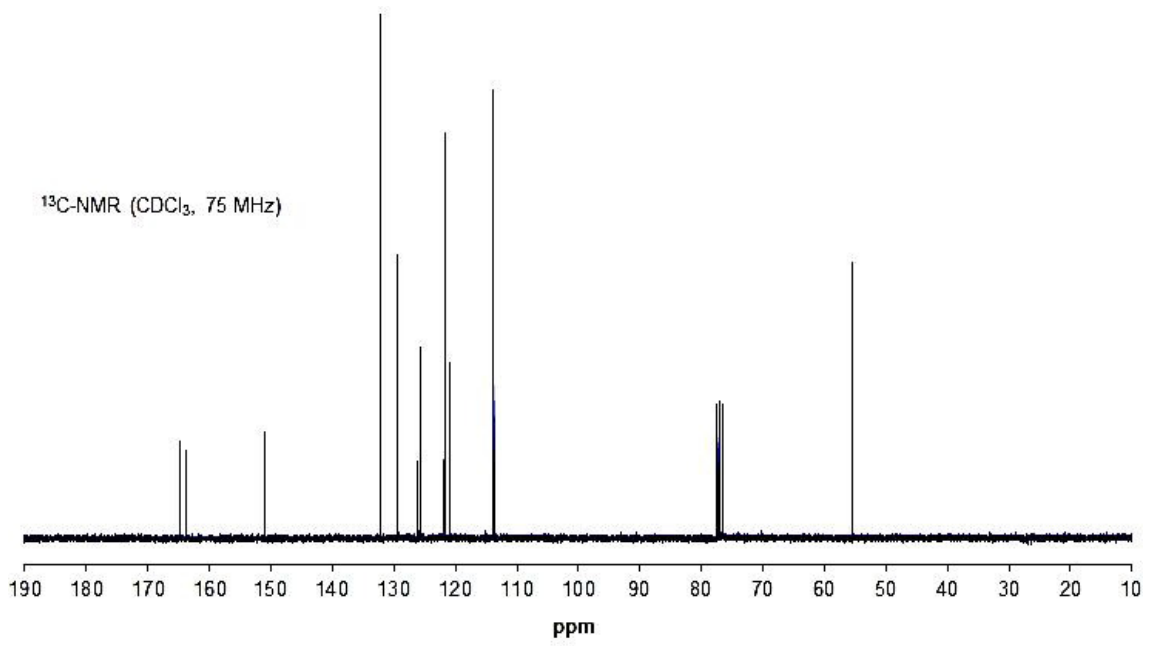
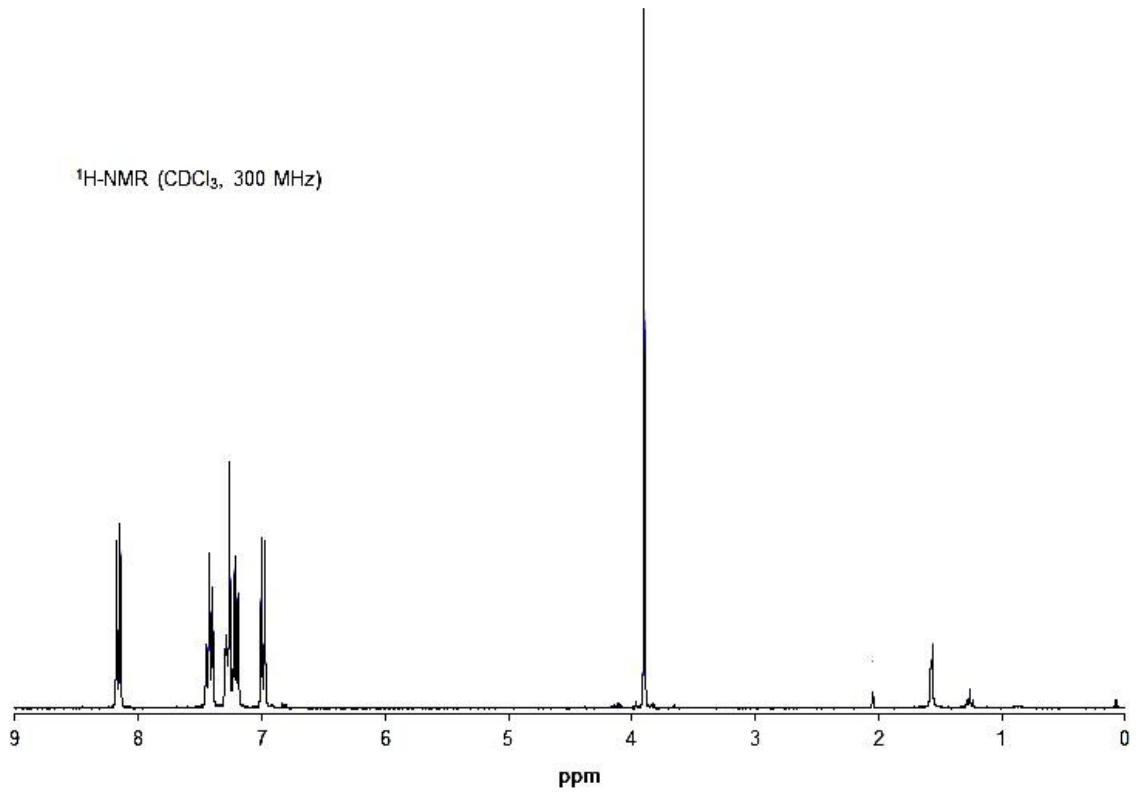
$^{13}\text{C-NMR}$ (CDCl_3 , 75 MHz)



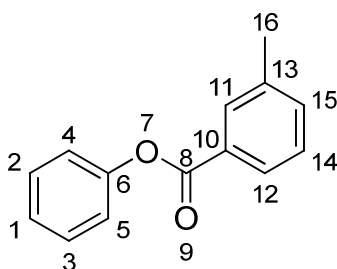
2.2.11. Phenyl 4-methoxybenzoate (3k)



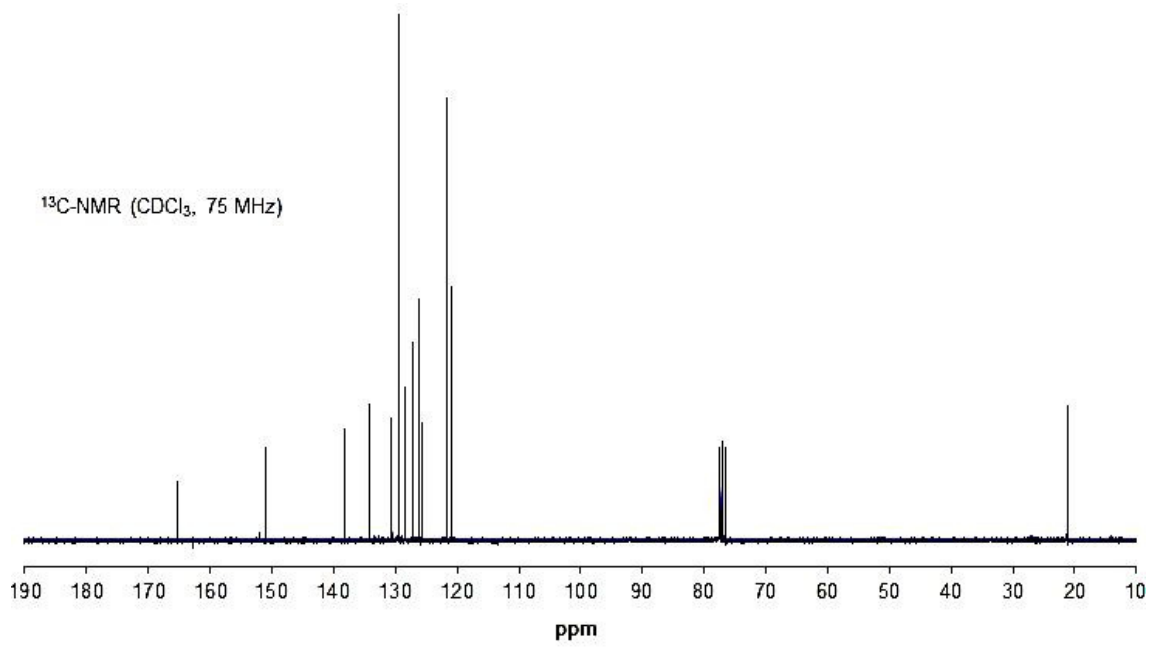
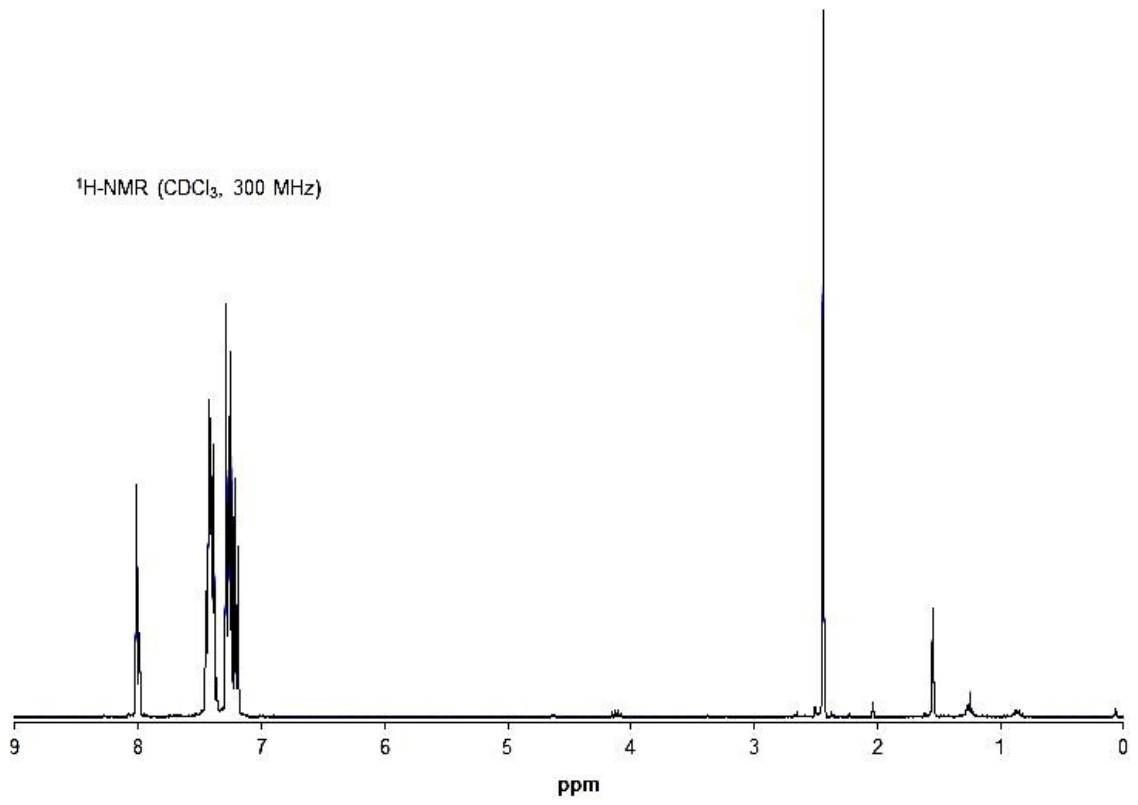
The reaction of 4-methoxybenzoic acid **2k** (1.00 g, 6.57 mmol) with DPC **1** (1.41 g, 6.57 mmol) in the presence of catalytic amounts of DBU (50.0 mg, 0.33 mmol, 5.0 mol%), was finished after one day at 160 °C. After purification by column chromatography (increasing gradient of polarity, *n*-hexane / ethyl acetate 49 : 1 to 9 : 1), phenyl 4-methoxybenzoate **3k** was obtained as colorless solid (1.21 g, 81%). TLC (*n*-hexane / ethyl acetate 9 : 1) $R_f = 0.65$; $T_m = 66.5$ °C (ethyl acetate); $^1\text{H NMR}$ (CDCl_3 , 300 MHz) $\delta = 3.90$ (s, 3 H, CH_3^{17}), 6.99 (dt, $J = 9.1$ Hz, 2.1 Hz, 2 H, 2 $\text{CH}^{13,14}$), 7.21 (dt, $J = 7.5$ Hz, 1.3 Hz, 2 H, 2 $\text{CH}^{4,5}$), 7.25 – 7.32 (m, 1 H, CH^1), 7.43 (t, $J = 7.9$ Hz, 2 H, 2 $\text{CH}^{2,3}$), 8.16 (dt, $J = 9.1$ Hz, 2.1 Hz, 2 H, 2 $\text{CH}^{11,12}$) ppm; $^{13}\text{C NMR}$ (CDCl_3 , 75 MHz) $\delta = 55.4$ (CH_3^{17}), 113.8 (2 $\text{CH}^{13,14}$), 120.8 (C^{10}), 121.7 (2 $\text{CH}^{4,5}$), 125.6 (CH^1), 129.4 (2 $\text{CH}^{2,3}$), 132.2 (2 $\text{CH}^{11,12}$), 151.0 (C^6), 163.8 (C^{15}), 164.8 (CO^8) ppm; FAB of $\text{C}_{14}\text{H}_{12}\text{O}_3$ ($[\text{M}+\text{H}]^+ = 229.1$); IR (ATR) $\nu = 3057.9, 3015.5, 2929.3, 2838.0, 1722.2$ (ester), 1603.6, 1508.0, 1484.3, 1451.9, 1438.2, 1317.0, 1253.4, 1191.7, 1161.1, 1074.2, 1022.0, 920.2, 841.0, 788.3, 762.0, 742.7, 689.4 cm^{-1} .



2.2.12. Phenyl 3-methylbenzoate (3I)



The reaction of *m*-toluic acid **2I** (1.00 g, 7.34 mmol) with DPC **1** (1.57 g, 7.34 mmol) in the presence of catalytic amounts of DBU (55.9 mg, 0.37 mmol, 5.0 mol%), was finished after one day at 160 °C. After purification by column chromatography (increasing gradient of polarity, *n*-hexane / ethyl acetate 49 : 1 to 9 : 1), phenyl 3-methylbenzoate **3I** was obtained as colorless oil (1.21 g, 78%). TLC (*n*-hexane / ethyl acetate 9 : 1) $R_f = 0.83$; $^1\text{H NMR}$ (CDCl_3 , 300 MHz) $\delta = 2.44$ (s, 3 H, CH_3^{16}), 7.16 – 7.30 (m, 4 H, 5 $\text{CH}^{1,4,5,14}$), 7.36 – 7.47 (m, 3 H, 3 $\text{CH}^{2,3,15}$), 7.98 – 8.03 (m, 2 H, 2 $\text{CH}^{11,12}$) ppm; $^{13}\text{C NMR}$ (CDCl_3 , 75 MHz) $\delta = 21.2$ (CH_3^{16}), 120.8 (CH^{12}), 121.7 (2 $\text{CH}^{4,5}$), 126.2 (CH^1), 127.2 (CH^{14}), 128.4 (CH^{11}), 129.5 (2 $\text{CH}^{2,3}$), 131.6 (C^{10}), 134.3 (CH^{15}), 138.3 (C^{13}), 150.9 (C^6), 165.2 (CO^8) ppm; FAB of $\text{C}_{14}\text{H}_{12}\text{O}_2$ ($[\text{M}+\text{H}]^+ = 213.1$); HRMS(FAB) of $\text{C}_{14}\text{H}_{12}\text{O}_2$ $[\text{M}+\text{H}]^+$ calc. 213.0910 found 213.0911; IR (KBr) $\nu = 3447.4, 3065.2, 2923.5, 1781.6, 1736.2$ (ester), 1592.3, 1492.9, 1457.2, 1275.6, 1234.5, 1182.6, 1160.7, 1087.5, 1066.7, 1023.1, 891.9, 789.8, 740.0, 689.2 cm^{-1} .

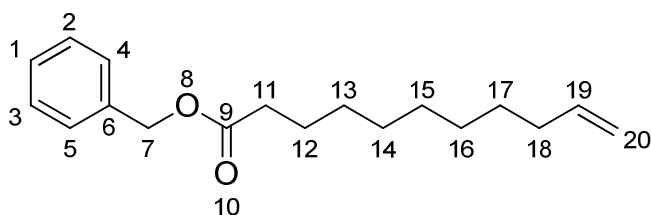


2.3. Transesterification reactions of phenyl esters

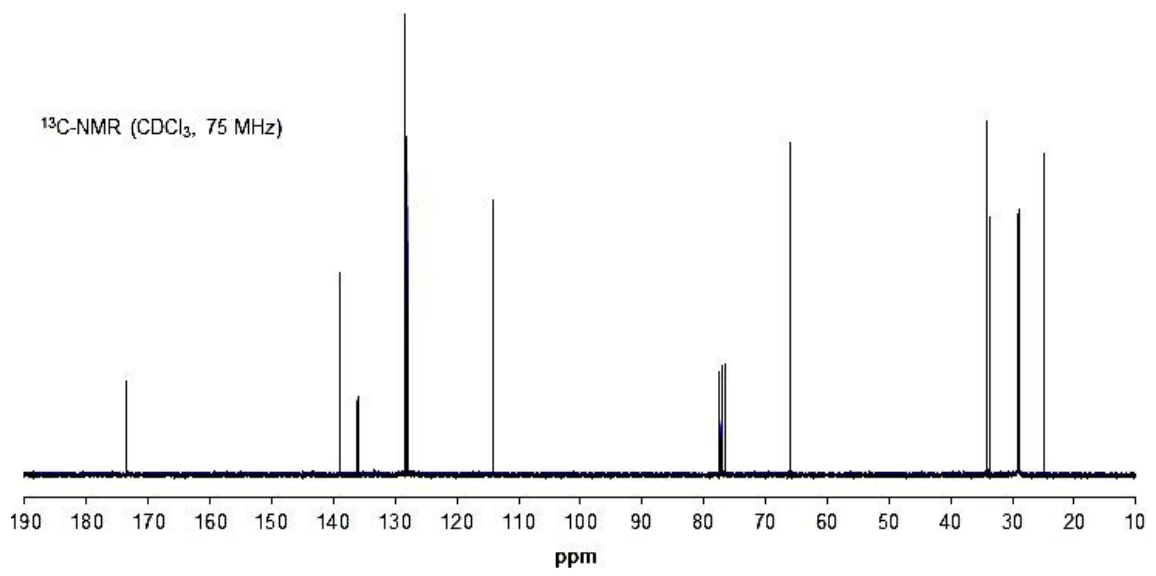
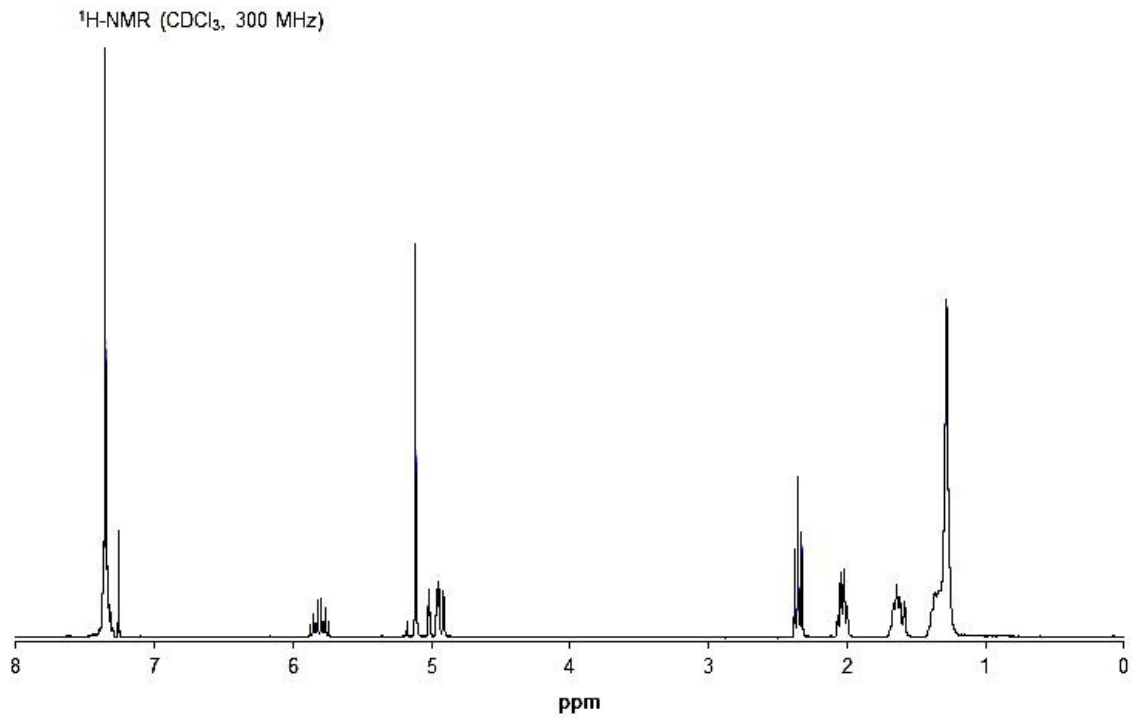
Representative procedure for the synthesis of alkyl esters 6a-d from phenyl 10-undecenoate 3a:

Phenyl 10-undecenoate **3a** (2.00 g, 7.68 mmol), benzyl alcohol **5a** (1.08 g, 9.99 mmol, 1.3 eq.) and catalytic amounts of TBD (0.11 g, 0.77 mmol, 10 mol%) were mixed and heated to 120 °C while stirring. After 90 minutes, TLC (*n*-hexane / ethyl acetate 19 : 1) and ¹H NMR spectroscopy indicated a full conversion. The crude product was purified by column chromatography (increasing gradient of polarity, *n*-hexane / ethyl acetate 49 : 1 to 9 : 1) to obtain pure benzyl undec-10-enoate **6a** as colorless oil (1.91 g, 91%).

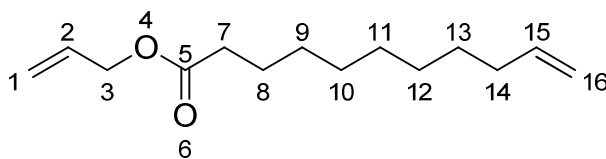
2.3.1. Benzyl undec-10-enoate (6a)



The reaction of phenyl 10-undecenoate **3a** (2.00 g, 7.68 mmol), benzyl alcohol **5a** (1.00 g, 9.22 mmol, 1.2 eq.) and catalytic amounts of TBD (57.8 mg, 0.38 mmol, 5.0 mol%), was finished after 90 minutes at 120 °C. After purification by column chromatography (increasing gradient of polarity, *n*-hexane / ethyl acetate 49 : 1 to 9 : 1), pure benzyl undec-10-enoate **6a** was obtained as colorless oil (1.91 g, 91%). TLC (*n*-hexane / ethyl acetate 19 : 1) $R_f = 0.65$; $^1\text{H NMR}$ (CDCl_3 , 300 MHz) $\delta = 1.24 - 1.42$ (m, 10 H, 5 CH_2^{13-17}), 1.64 (quint., $J = 7.2$ Hz, 2 H, CH_2^{12}), 2.04 (q, $J = 7.0$ Hz, 2 H, CH_2^{18}), 2.35 (t, $J = 7.5$ Hz, 2 H, CH_2^{11}), 4.90 – 5.03 (m, 2 H, CH_2^{20}), 5.12 (s, 2 H, CH_2^7), 5.81 (tdd, $J = 17.0$ Hz, 10.4 Hz, 6.6 Hz, 1 H, CH^{19}), 7.29 – 7.40 (m, 5 H, 5 CH^{1-5}) ppm; $^{13}\text{C NMR}$ (CDCl_3 , 75 MHz) $\delta = 24.9$ (CH_2^{12}), 28.8 (CH_2^{17}), 29.0 (CH_2^{13-16}), 29.0 (CH_2^{13-16}), 29.1 (CH_2^{13-16}), 29.2 (CH_2^{13-16}), 33.7 (CH_2^{18}), 34.2 (CH_2^{11}), 66.0 (CH_2^7), 114.1 (CH_2^{20}), 128.1 (2 $\text{CH}^{4,5}$), 128.1 (CH^1), 128.5 (2 $\text{CH}^{2,3}$), 136.1 (C^6), 139.1 (CH^{19}), 173.6 (CO^9) ppm; FAB of $\text{C}_{18}\text{H}_{26}\text{O}_2$ ($[\text{M}+\text{H}]^+ = 275.2$, $[\text{2M}+\text{H}]^+ = 549.5$); HRMS(FAB) of $\text{C}_{18}\text{H}_{26}\text{O}_2$ $[\text{M}+\text{H}]^+$ calc. 275.2006 found 275.2006; IR (ATR) $\nu = 2923.7$, 2852.6, 1735.1 (ester), 1454.6, 1158.0, 992.8, 908.1, 734.4, 696.3 cm^{-1} .

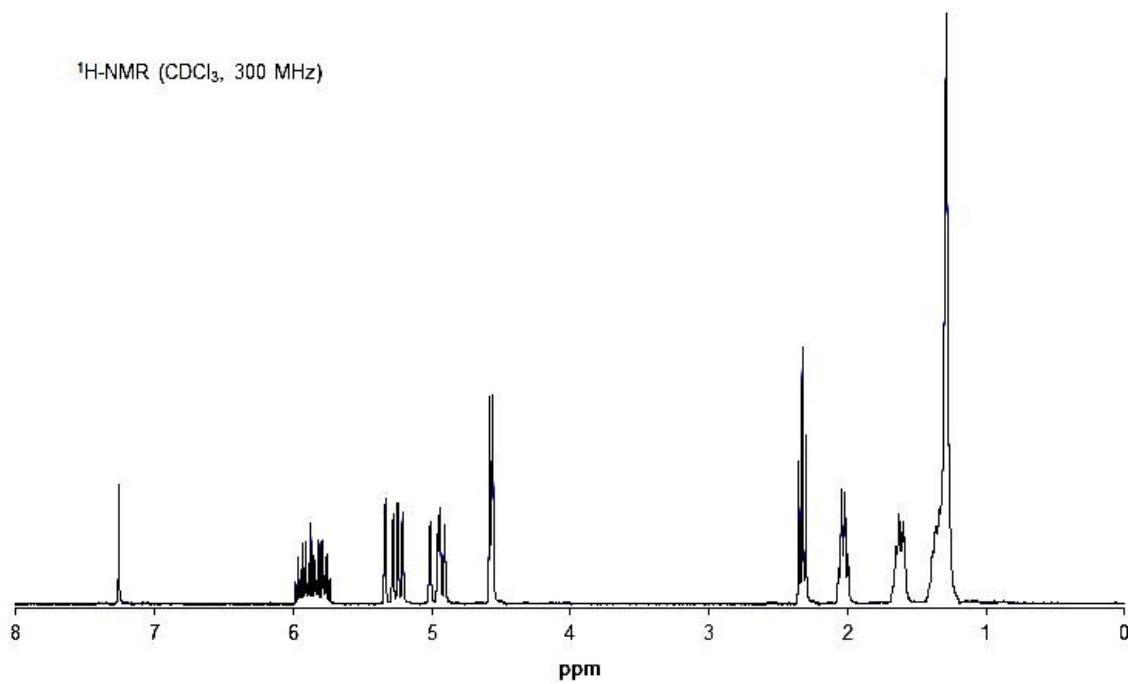


2.3.2. Allyl undec-10-enoate (**6b**)

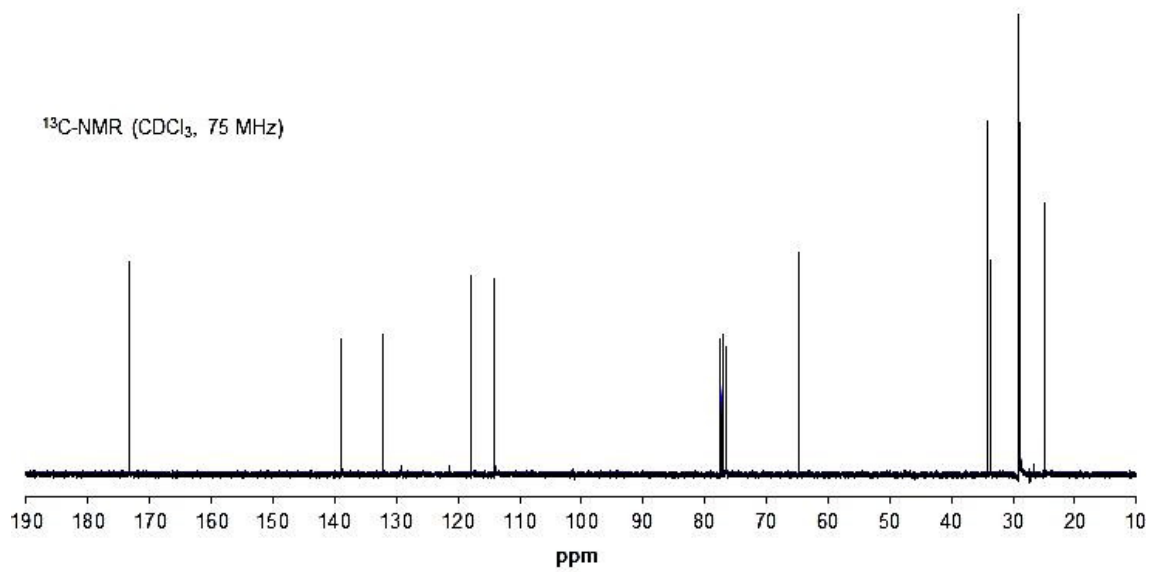


The reaction of phenyl 10-undecenoate **3a** (2.00 g, 7.68 mmol), allyl alcohol **5b** (0.54 g, 9.22 mmol, 1.2 eq.) and catalytic amounts of TBD (57.8 mg, 0.38 mmol, 5.0 mol%), was finished after 60 minutes at 140 °C in a microwave reactor. After purification by column chromatography (increasing gradient of polarity, *n*-hexane / ethyl acetate 49 : 1 to 9 : 1), pure benzyl undec-10-enoate **6b** was obtained as colorless oil (1.63 g, 95%). TLC (*n*-hexane / ethyl acetate 19 : 1) $R_f = 0.69$; $^1\text{H NMR}$ (CDCl_3 , 300 MHz) $\delta = 1.24 - 1.42$ (m, 10 H, 5 CH_2^{9-13}), 1.63 (quint., $J = 7.2$ Hz, 2 H, CH_2^8), 2.03 (q, $J = 7.0$ Hz, 2 H, CH_2^{14}), 2.33 (t, $J = 7.5$ Hz, 2 H, CH_2^7), 4.57 (dt, $J = 5.7$ Hz, 1.3 Hz, 2 H, CH_2^3), 4.89 – 5.03 (m, 2 H, CH_2^{16}), 5.20 – 5.35 (m, 2 H, CH_2^1), 5.73 – 5.99 (m, 2 H, 2 $\text{CH}^{2,15}$) ppm; $^{13}\text{C NMR}$ (CDCl_3 , 75 MHz) $\delta = 24.8$ (CH_2^8), 28.8 (CH_2^{13}), 29.0 (CH_2^{9-12}), 29.0 (CH_2^{9-12}), 29.1 (CH_2^{9-12}), 29.2 (CH_2^{9-12}), 33.7 (CH_2^{14}), 34.2 (CH_2^7), 64.8 (CH_2^3), 114.1 (CH_2^{16}), 117.9 (CH_2^1), 132.3 (CH^2), 139.0 (CH^{15}), 173.4 (CO^5) ppm; FAB of $\text{C}_{14}\text{H}_{24}\text{O}_2$ ($[\text{M}+\text{H}]^+ = 225.2$, $[2\text{M}+\text{H}]^+ = 449.4$); HRMS(FAB) of $\text{C}_{14}\text{H}_{24}\text{O}_2$ $[\text{M}+\text{H}]^+$ calc. 225.1849 found 225.1851; IR (ATR) $\nu = 3077.2$, 2924.5, 2853.5, 1736.4 (ester), 1640.0, 1456.7, 1374.5, 1234.2, 1162.3, 1115.2, 988.7, 908.8, 722.6 cm^{-1} .

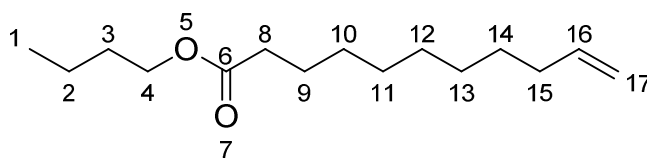
$^1\text{H-NMR}$ (CDCl_3 , 300 MHz)



$^{13}\text{C-NMR}$ (CDCl_3 , 75 MHz)

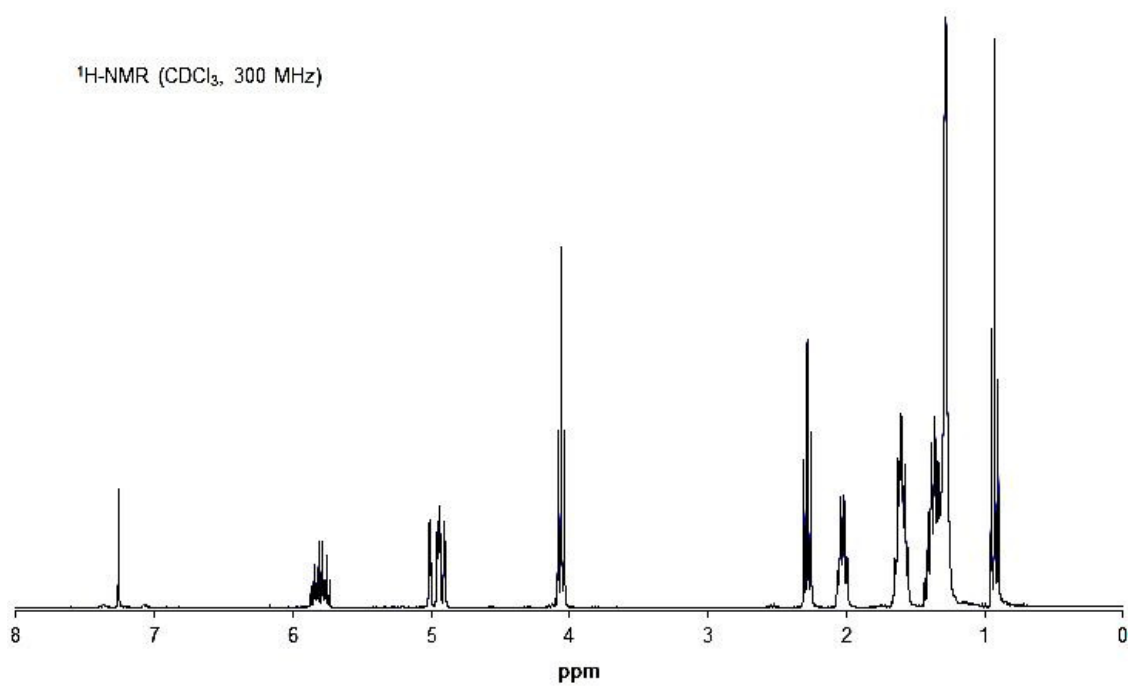


2.3.3. *n*-Butyl undec-10-enoate (**6c**)

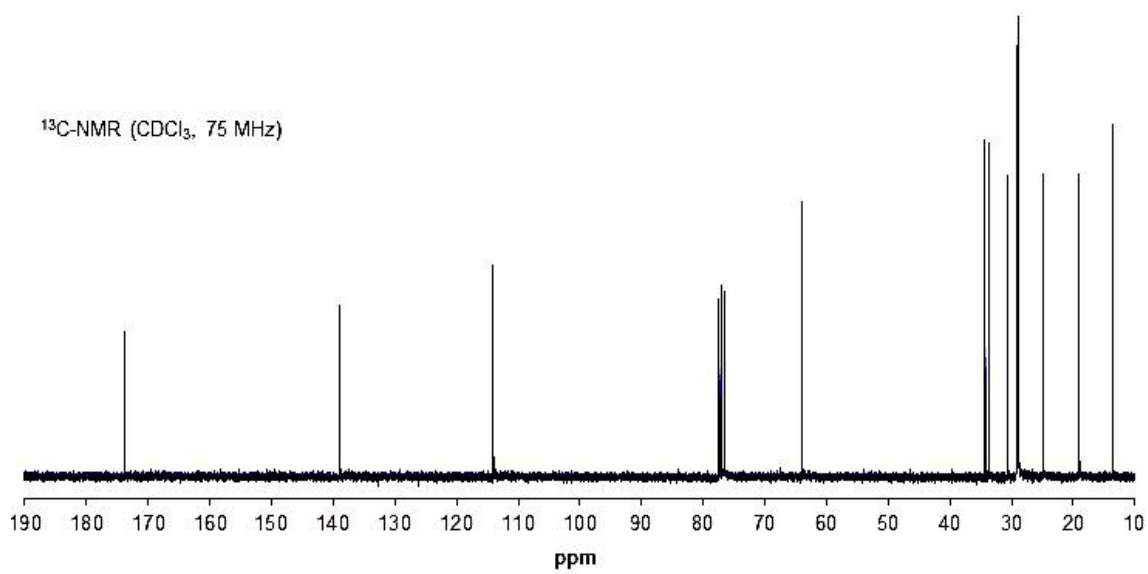


The reaction of phenyl 10-undecenoate **3a** (2.00 g, 7.68 mmol), *n*-butanol **5c** (0.68 g, 9.22 mmol, 1.2 eq.) and catalytic amounts of TBD (57.8 mg, 0.38 mmol, 5.0 mol%), was finished after 60 minutes at 140 °C in a microwave reactor. After purification by column chromatography (increasing gradient of polarity, *n*-hexane / ethyl acetate 49 : 1 to 9 : 1), pure *n*-butyl undec-10-enoate **6c** was obtained as colorless oil (1.80 g, 95%). TLC (*n*-hexane / ethyl acetate 19 : 1) $R_f = 0.67$; $^1\text{H NMR}$ (CDCl_3 , 300 MHz) $\delta = 0.93$ (t, $J = 7.4$ Hz, 3 H, CH_3^1), 1.23– 1.44 (m, 12 H, 6 $\text{CH}_2^{2,10-14}$), 1.54 – 1.67 (m, 4 H, 2 $\text{CH}_2^{3,9}$), 2.03 (q, $J = 7.0$ Hz, 2 H, CH_2^{15}), 2.28 (t, $J = 7.5$ Hz, 2 H, CH_2^8), 4.06 (t, $J = 6.7$ Hz, 2 H, CH_2^4), 4.89 – 5.03 (m, 2 H, CH_2^{17}), 5.81 (tdd, $J = 17.0$ Hz, 10.4 Hz, 6.8 Hz, 1 H, CH^{16}) ppm; $^{13}\text{C NMR}$ (CDCl_3 , 75 MHz) $\delta = 13.6$ (CH_3^1), 19.1 (CH_2^2), 24.9 (CH_2^9), 28.8 (CH_2^{14}), 29.0 (CH_2^{10-13}), 29.1 (CH_2^{10-13}), 29.1 (CH_2^{10-13}), 29.2 (CH_2^{10-13}), 30.6 (CH_2^3), 33.7 (CH_2^{15}), 34.3 (CH_2^8), 64.0 (CH_2^4), 114.1 (CH_2^{17}), 139.0 (CH^{16}), 173.9 (CO^6) ppm; FAB of $\text{C}_{15}\text{H}_{28}\text{O}_2$ ($[\text{M}+\text{H}]^+ = 241.2$, $[2\text{M}+\text{H}]^+ = 481.5$); HRMS(FAB) of $\text{C}_{15}\text{H}_{28}\text{O}_2$ $[\text{M}+\text{H}]^+$ calc. 241.2162 found 241.2165; IR (ATR) $\nu = 3076.3$, 2924.9, 2853.7, 1735.2 (ester), 1639.7, 1459.5, 1352.7, 1239.0, 1170.1, 1115.5, 1064.0, 992.3, 907.9, 723.5 cm^{-1} .

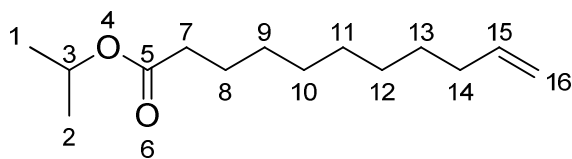
$^1\text{H-NMR}$ (CDCl_3 , 300 MHz)



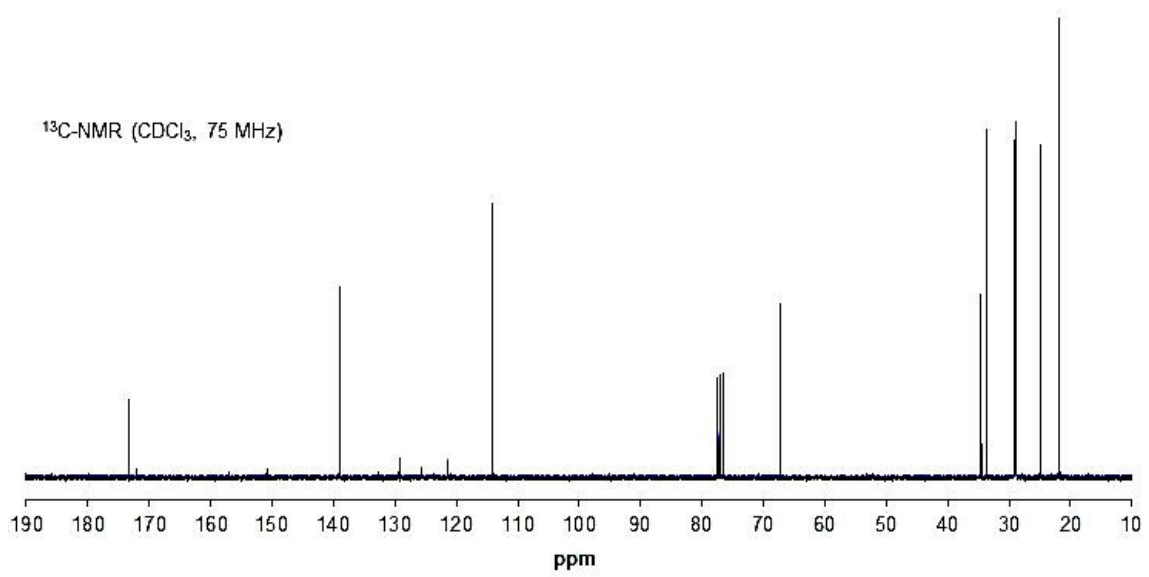
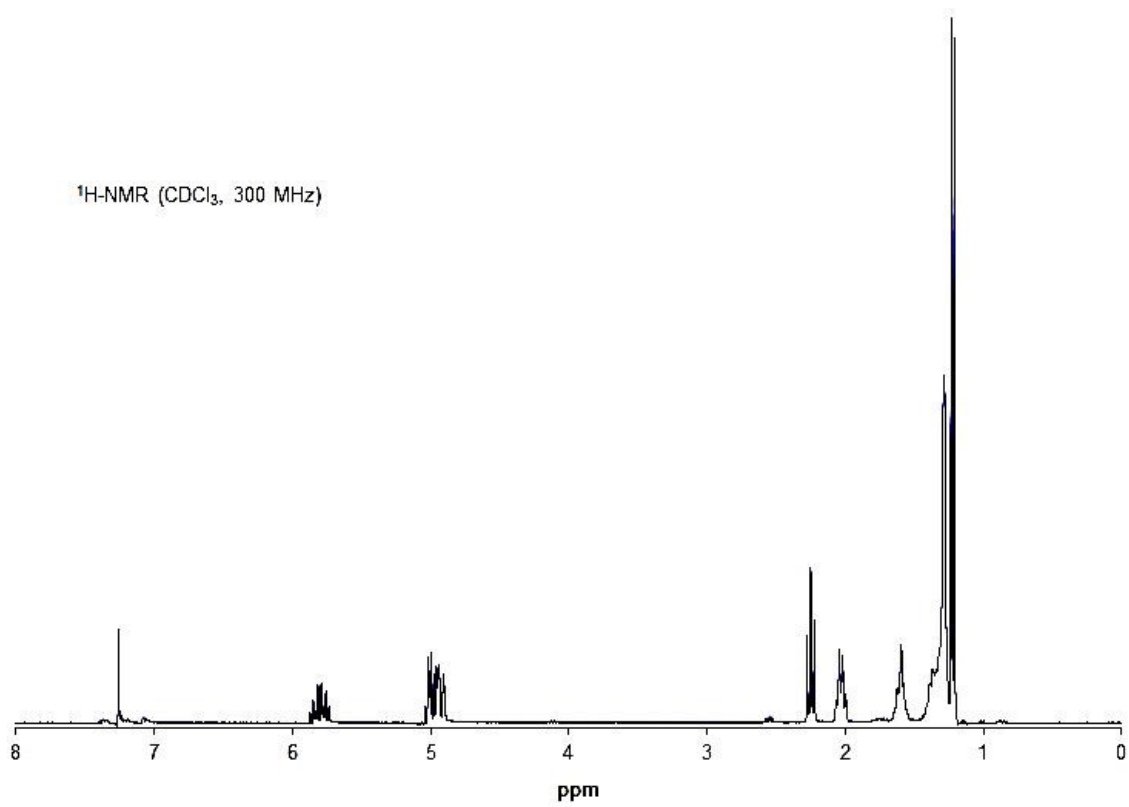
$^{13}\text{C-NMR}$ (CDCl_3 , 75 MHz)



2.3.4. Isopropyl undec-10-enoate (**6d**)

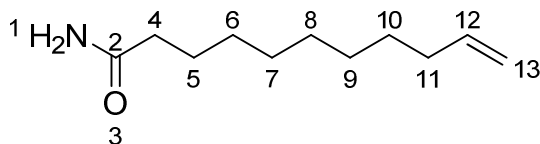


The reaction of phenyl 10-undecenoate **3a** (2.00 g, 7.68 mmol), isopropanol **5d** (0.55 g, 9.22 mmol, 1.2 eq.) and catalytic amounts of TBD (57.8 mg, 0.38 mmol, 5.0 mol%), was finished after three hours at 140 °C in a microwave reactor. After purification by column chromatography (increasing gradient of polarity, *n*-hexane / ethyl acetate 49 : 1 to 9 : 1), pure isopropyl undec-10-enoate **6d** was obtained as colorless oil (1.62 g, 93%). TLC (*n*-hexane / ethyl acetate 19 : 1) $R_f = 0.44$; $^1\text{H NMR}$ (CDCl_3 , 300 MHz) $\delta = 1.21$, 1.23 (2s, 6 H, 2 $\text{CH}_3^{1,2}$), 1.24 – 1.42 (m, 10 H, 5 CH_2^{9-13}), 1.59 (quint., $J = 7.2$ Hz, 2 H, CH_2^8), 2.03 (q, $J = 7.0$ Hz, 2 H, CH_2^{14}), 2.25 (t, $J = 7.5$ Hz, 2 H, CH_2^7), 4.89 – 5.05 (m, 3 H, CH_2^{16} , CH^3), 5.81 (tdd, $J = 16.8$ Hz, 10.2 Hz, 6.8 Hz, 1 H, CH^{15}) ppm; $^{13}\text{C NMR}$ (CDCl_3 , 75 MHz) $\delta = 21.8$ (2 $\text{CH}_3^{1,2}$), 25.0 (CH_2^8), 28.8 (CH_2^{13}), 29.0 (CH_2^{9-12}), 29.0 (CH_2^{9-12}), 29.1 (CH_2^{9-12}), 29.2 (CH_2^{9-12}), 33.7 (CH_2^{14}), 34.6 (CH_2^7), 67.2 (CH^3), 114.1 (CH_2^{16}), 139.1 (CH^{15}), 173.3 (CO^5) ppm; FAB of $\text{C}_{14}\text{H}_{26}\text{O}_2$ ($[\text{M}+\text{H}]^+ = 227.2$, $[\text{2M}+\text{H}]^+ = 453.4$); HRMS(FAB) of $\text{C}_{14}\text{H}_{26}\text{O}_2$ $[\text{M}+\text{H}]^+$ calc. 227.2006 found 227.2004; IR (ATR) $\nu = 2977.4$, 2924.5, 2853.6, 1730.6 (ester), 1639.9, 1492.7, 1465.5, 1372.6, 1240.8, 1177.6, 1144.0, 1107.6, 992.0, 962.1, 907.6, 823.2, 722.7, 689.0 cm^{-1} .

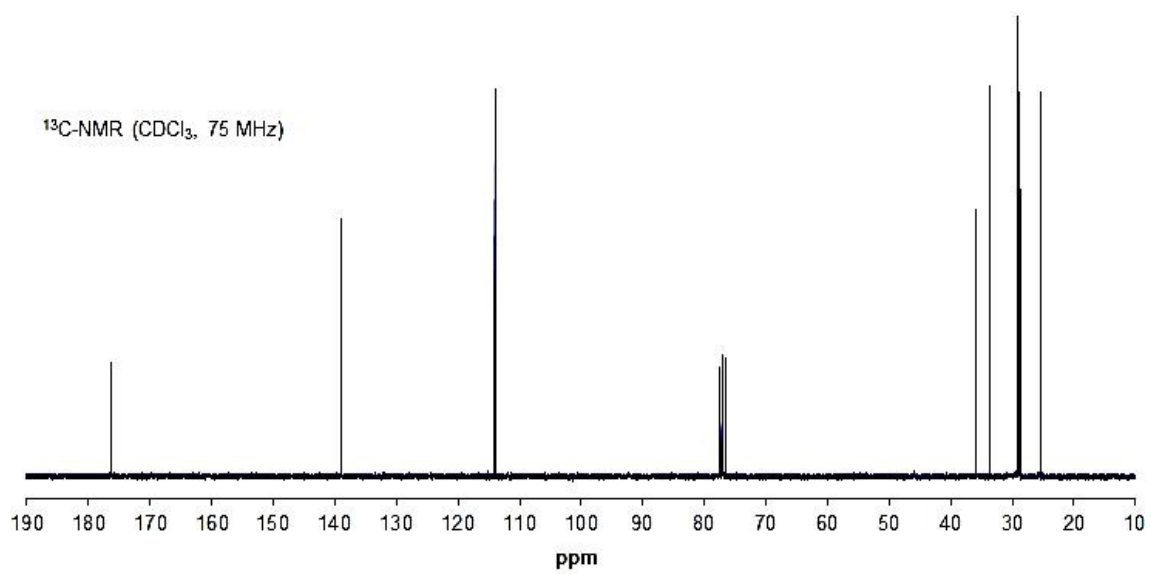
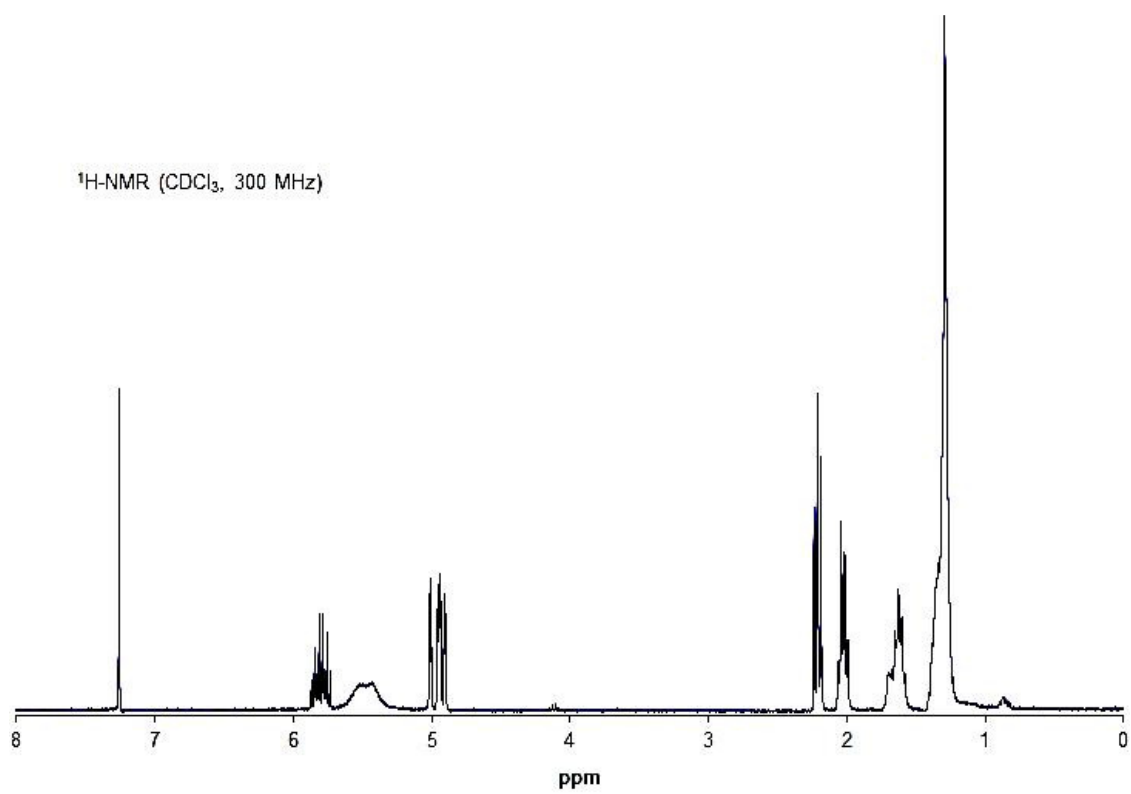


2.4. Conversion of phenyl esters with amine compounds

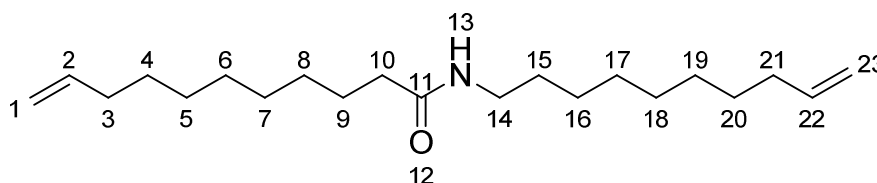
2.4.1. Undec-10-enamide (**8a**)



Phenyl 10-undecenoate **3a** (reaction scale: 163 mmol, 30.0 g of 10-undecenoic acid **2a**) was synthesized according to the before mentioned procedure without work-up and purification. After the crude reaction mixture was cooled to room temperature, a 7N methanolic ammonia solution **7a** (~60 mL) was added *via* syringe and stirred for additional three hours, until TLC (ethyl acetate) indicated a full conversion. Then, the reaction mixture was concentrated on a rotary evaporator. The crude product was recrystallized in ethyl acetate / *n*-hexane (~1 : 1). Pure undec-10-enamide **8a** was obtained as colorless crystals (20.3 g, 69%). TLC (ethyl acetate) $R_f = 0.33$; $T_m = 89.5$ °C (ethyl acetate); $^1\text{H NMR}$ (CDCl_3 , 300 MHz) $\delta = 1.23 - 1.42$ (m, 10 H, 5 CH_2^{6-10}), 1.63 (quint., $J = 7.3$ Hz, 2 H, CH_2^5), 2.03 (q, $J = 7.0$ Hz, 2 H, CH_2^{11}), 2.21 (t, $J = 7.5$ Hz, 2 H, CH_2^4), 4.89 – 5.03 (m, 2 H, CH_2^{13}), 5.47 (br, s, 2 H, NH_2^1), 5.80 (tdd, $J = 16.8$ Hz, 10.2 Hz, 6.8 Hz, 1 H, CH^{12}) ppm; $^{13}\text{C NMR}$ (CDCl_3 , 75 MHz) $\delta = 25.4$ (CH_2^5), 28.7 (CH_2^{10}), 28.9 (CH_2^{6-9}), 29.1 (CH_2^{6-9}), 29.2 (CH_2^{6-9}), 29.2 (CH_2^{6-9}), 33.6 (CH_2^{11}), 35.9 (CH_2^4), 114.0 (CH_2^{13}), 139.0 (CH^{12}), 176.2 (CO^2) ppm; FAB of $\text{C}_{11}\text{H}_{21}\text{NO}$ ($[\text{M}+\text{H}]^+ = 184.2$, $[\text{2M}+\text{H}]^+ = 367.4$); HRMS(FAB) of $\text{C}_{11}\text{H}_{21}\text{NO}$ $[\text{M}+\text{H}]^+$ calc. 184.1696 found 184.1693; IR (ATR) $\nu = 3351.0$, 3178.7, 2919.8, 2848.6, 1658.5 (amide), 1629.4 (amide), 1467.3, 1422.8, 1410.4, 1330.6, 1305.9, 1267.5, 1232.6, 1198.1, 1136.3, 993.9, 910.2, 879.8, 808.8, 694.2, 635.8 cm^{-1} .

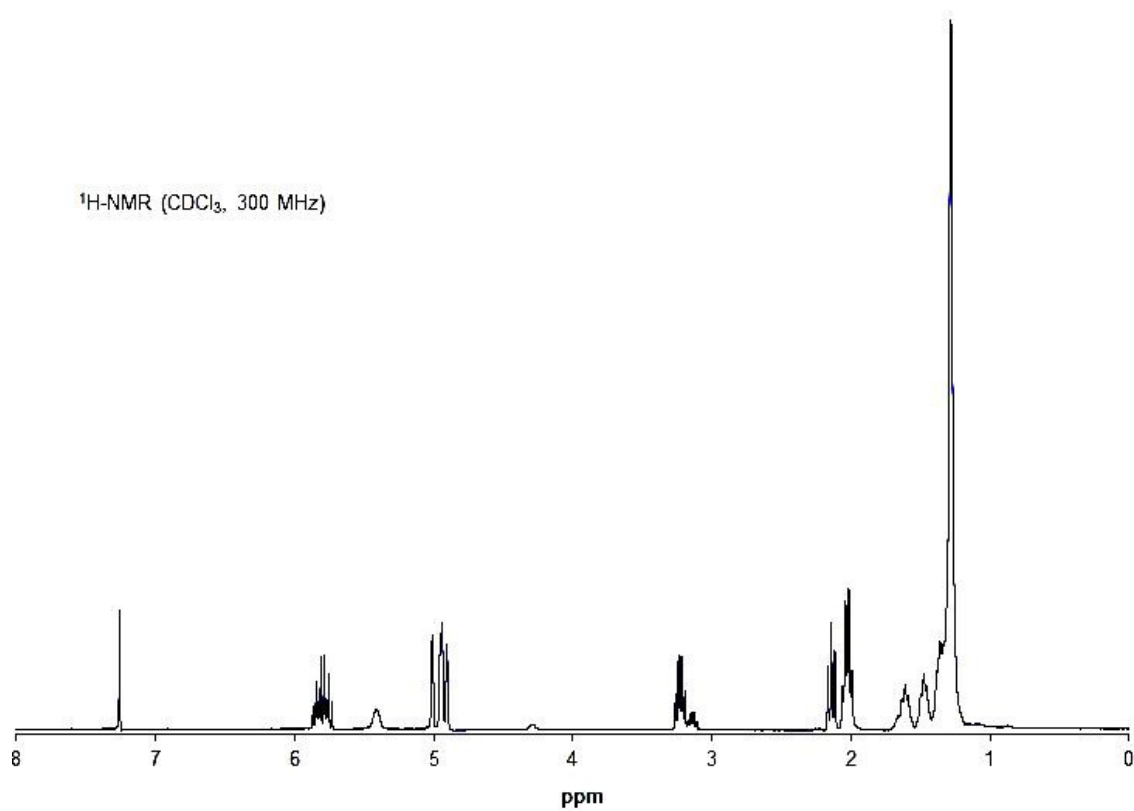


2.4.2. *N*-(Dec-9-en-1-yl)undec-10-enamide (**8b**)

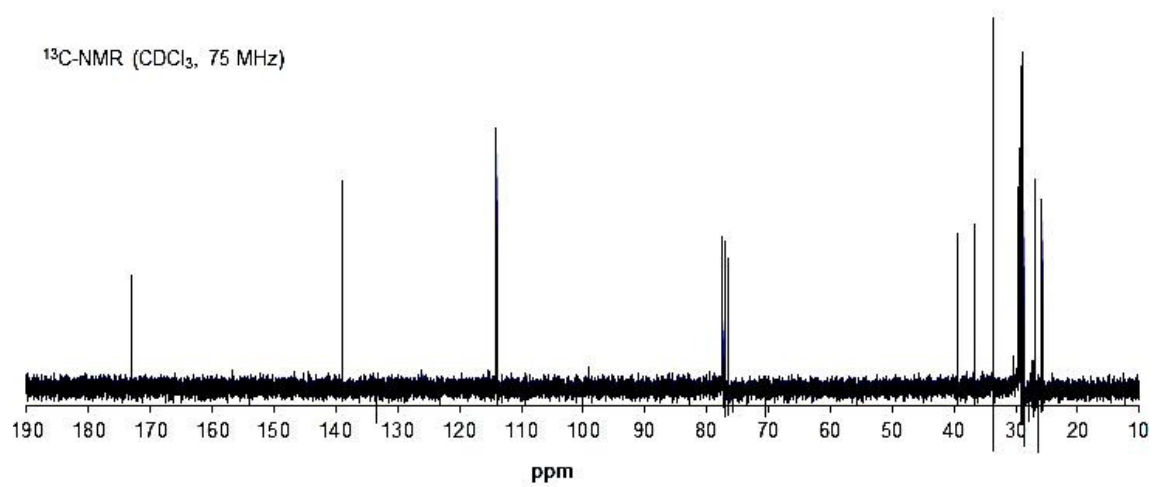


Phenyl 10-undecenoate **3a** (reaction scale: 2.71 mmol, 0.50 g of 10-undecenoic acid **2a**) was synthesized according to the before mentioned procedure without work-up and purification. After the crude reaction mixture was cooled to 100 °C, dec-9-en-1-amine **7b** (0.55 g, 3.52 mmol, 1.3 eq.)¹ was added and after additional 15 minutes, TLC (*n*-hexane / ethyl acetate 5 : 1) indicated a full conversion. Then, the reaction mixture was dissolved in ethyl acetate (30 mL) and washed with 1N HCl (3 x 20 mL), water (20 mL), saturated sodium chloride solution (2 x 20 mL). After drying over sodium sulfate, the solution was concentrated on a rotary evaporator. The crude product was recrystallized in ethyl acetate / *n*-hexane (~1 : 5). Pure *N*-(dec-9-en-1-yl)undec-10-enamide **8b** was obtained as colorless solid (0.80 g, 92%). TLC (*n*-hexane / ethyl acetate 5 : 1) $R_f = 0.26$; $T_m = 59.0$ °C (ethyl acetate); ¹H NMR (CDCl₃, 300 MHz, mixture of *cis/trans*-amide bounds, *ratio* ~1 : 4) $\delta = 1.20 - 1.42$ (m, 20 H, 10 CH₂^{4-8,16-20}), 1.48 (quint., $J = 6.5$ Hz, 2 H, CH₂¹⁵), 1.61 (quint., $J = 7.2$ Hz, 2 H, CH₂⁹), 2.03 (q, $J = 7.0$ Hz, 4 H, 2 CH₂^{3,21}), 2.14 (t, $J = 7.6$ Hz, 2 H, CH₂¹⁰), 3.14 (t, $J = 6.8$ Hz, 2 H, CH₂^{14,cis}), 3.23 (t, $J = 6.8$ Hz, 2 H, CH₂^{14,trans}), 4.29 (br, s, 1 H, NH^{13,cis}), 4.89 – 5.03 (m, 4 H, 2 CH₂^{1,23}), 5.41 (br, s, 1 H, NH^{13,trans}), 5.80 (tdd, $J = 17.0$ Hz, 10.4 Hz, 6.8 Hz, 2 H, CH^{2,22}) ppm; ¹³C NMR (CDCl₃, 75 MHz, mixture of *cis/trans*-amide bounds, *ratio* ~1 : 4) $\delta = 25.8$ (CH₂⁹), 26.8 (CH₂^{16,trans}), 26.9 (CH₂^{16,cis}), 28.8 (CH₂⁸), 28.9 (CH₂^{4-7,17-20}), 29.0 (CH₂^{4-7,17-20}), 29.2 (CH₂^{4-7,17-20}), 29.2 (CH₂^{4-7,17-20}), 29.2 (CH₂^{4-7,17-20}), 29.3 (CH₂^{4-7,17-20}), 29.3 (CH₂^{4-7,17-20}), 29.6 (CH₂^{4-7,17-20}), 30.3 (CH₂¹⁵), 33.7 (CH₂^{3,21}), 36.7 (CH₂¹⁰), 39.4 (CH₂^{14,trans}), 40.2 (CH₂^{14,cis}), 114.0 (CH₂^{1,23}), 114.0 (CH₂^{1,23}), 139.0 (CH^{2,22}), 139.0 (CH^{2,22}), 173.0 (CO¹¹) ppm; FAB of C₂₁H₃₉NO ([M+H]⁺ = 322.3); HRMS(FAB) of C₂₁H₃₉NO [M+H]⁺ calc. 322.3104 found 322.3103; IR (ATR) $\nu = 3287.2, 3079.3, 2918.9, 2848.7, 1637.7$ (amide), 1565.8, 1464.8, 1368.6, 1323.5, 1283.7, 1256.3, 1159.4, 1121.4, 991.2, 912.3, 721.8 cm⁻¹.

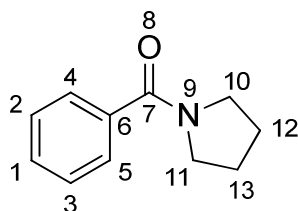
$^1\text{H-NMR}$ (CDCl_3 , 300 MHz)



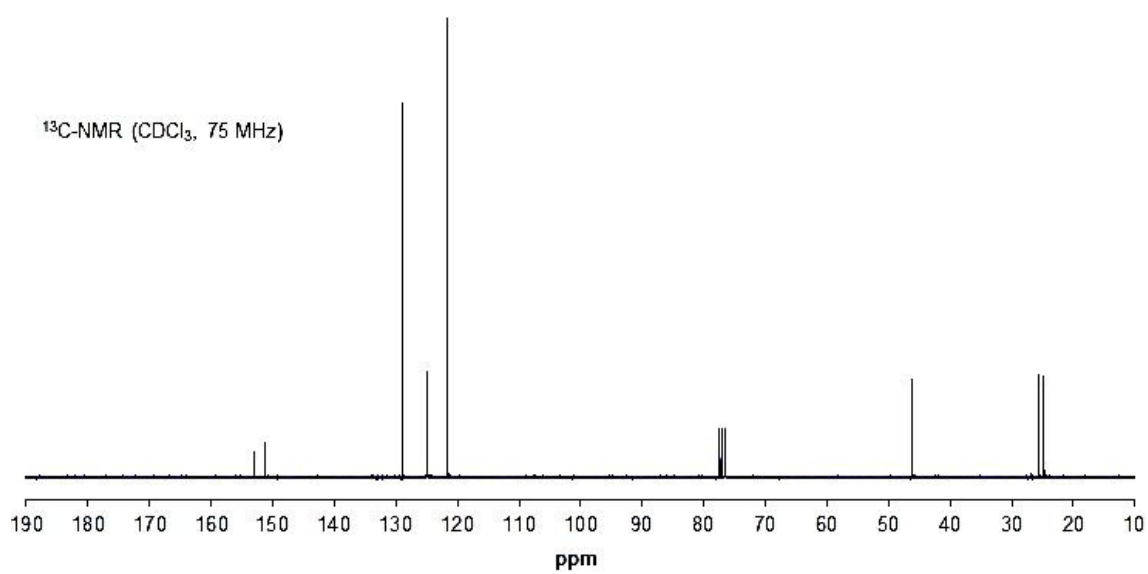
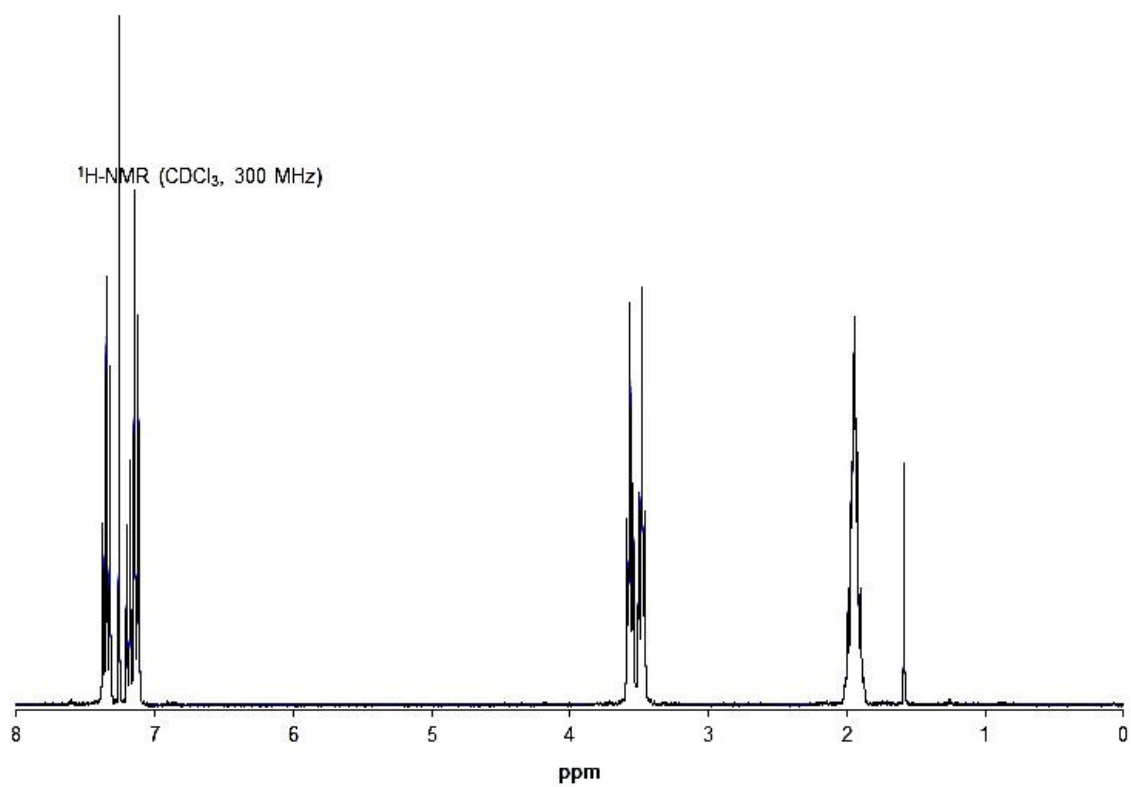
$^{13}\text{C-NMR}$ (CDCl_3 , 75 MHz)



2.4.3. Phenyl(pyrrolidin-1-yl)methanone (**8c**)



Phenyl benzoate **3i** (reaction scale: 40.9 mmol, 5.00 g of benzoic acid **2i**) was synthesized according to the before mentioned procedure without work-up and purification. After the crude reaction mixture was cooled to 80 °C, pyrrolidine **7c** (3.49 g, 49.1 mmol, 1.2 eq.) was added and after one day, TLC (*n*-hexane / ethyl acetate 2 : 1) indicated a full conversion. Then, the reaction mixture was dissolved in ethyl acetate (30 mL) and washed with 1N HCl (3 x 20 mL), water (20 mL) and saturated sodium chloride solution (2 x 20 mL). After drying over sodium sulfate, the solution was concentrated on a rotary evaporator. The crude product was purified by column chromatography (increasing gradient of polarity, *n*-hexane / ethyl acetate 49 : 1 to 9 : 1) to obtain pure phenyl(pyrrolidin-1-yl)methanone **8c** as colorless solid (3.44 g, 48%). TLC (*n*-hexane / ethyl acetate 2 : 1) $R_f = 0.32$; $T_m = 75.5$ °C (ethyl acetate); $^1\text{H NMR}$ (CDCl_3 , 300 MHz) $\delta = 1.87 - 2.02$ (m, 4 H, 2 $\text{CH}_2^{12,13}$), 3.52 (dt, $J = 25.5$ Hz, 6.5 Hz, 4 H, 2 $\text{CH}_2^{10,11}$), 7.10– 7.22 (m, 3 H, 3 CH^{1-3}), 7.35 (t, $J = 8.0$ Hz, 2 H, 2 $\text{CH}^{4,5}$) ppm; $^{13}\text{C NMR}$ (CDCl_3 , 75 MHz) $\delta = 24.8$ ($\text{CH}_2^{12,13}$), 25.6 ($\text{CH}_2^{12,13}$), 46.1 ($\text{CH}_2^{10,11}$), 46.3 ($\text{CH}_2^{10,11}$), 121.6 (2 $\text{CH}^{4,5}$), 124.8 (CH^1), 129.0 (2 $\text{CH}^{2,3}$), 151.3 (C^6), 153.0 (CO^7) ppm; IR (ATR) $\nu = 2976.6, 2878.4, 1708.1$ (amide), 1590.1, 1488.9, 1454.4, 1394.0, 1343.7, 1252.0, 1173.4, 1061.1, 1024.4, 998.4, 969.8, 911.0, 859.6, 815.9, 751.8, 711.2, 689.6 cm^{-1} .



3. References

1 O. Kreye, D. Kugele, L. Faust and M. A. R. Meier, *Macromol. Rapid Commun.*, 2014, **35**, 317.

2 O. Kreye, S. Oelmann and M. A. R. Meier, *Macromol. Chem. Phys.*, 2013, **214**, 1452.

3 <http://www.sigmaaldrich.com/catalog/product/aldrich/142719?lang=de®ion=DE>, accessed on 02.06.2014.