Supporting Information

Metal-Free, Visible-Light-Mediated, Decarboxylative Alkylation of Biomass-Derived Compounds

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1. General information

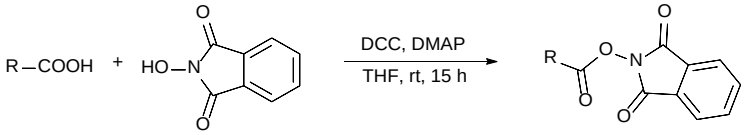
Commercially available reagents and solvents were used without further purification. Dry solvents were used for all photoreactions. Industrial grade of solvents was used for automated flash column chromatography. All NMR spectra were measured at room temperature using a Bruker Avance 300 (300 MHz for ^{1}H, 75 MHz for ^{13}C) or a Bruker Avance 400 (400 MHz for ^{1}H, 101 MHz for ^{13}C)[1] NMR spectrometer. All chemical shifts are reported in δ-scale as parts per million [ppm] (multiplicity, coupling constant *J*, number of protons) relative to the solvent residual peaks as the internal standard.[2] The spectra were analyzed by first order and coupling constants *J* are given in Hertz [Hz]. Abbreviations used for signal multiplicity: ^{1}H-NMR: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets and m = multiplet; ^{13}C-NMR: (+) = primary/tertiary, (–) = secondary, (C_q) = quaternary carbon. The mass spectrometrical measurements were performed at the Central Analytical Laboratory of the University of Regensburg. All mass spectra were recorded on a Finnigan MAT 95, ThermoQuest Finnigan TSQ 7000, Finnigan MAT SSQ 710 A or an Agilent Q-TOF 6540 UHD instrument. GC measurements were performed on a GC 7890 from Agilent Technologies. Data acquisition and evaluation was done with Agilent ChemStation Rev.C.01.04. GC-MS measurements were performed on a 7890A GC system from Agilent Technologies with an Agilent 5975 MSD Detector. Data acquisition and evaluation was done with MSD ChemStation E.02.02.1431. A capillary column HP-5MS/30 m x 0.25 mm/0.25 μM film and helium as carrier gas (flow rate of 1 mL/min) were used. The injector temperature (split injection: 40:1 split) was 280 °C, detection temperature 300 °C (FID). GC measurements were performed and investigated via integration of the signal obtained. The GC oven temperature program was adjusted as follows: initial temperature 40 °C was kept for 3 min, the temperature was increased at a rate of 15 °C/min over a period of 16 min until 280 °C was reached and kept for 5 min, the temperature was again increased at a rate of 25 °C/min over a period of 48 seconds until the final temperature (300 °C) was reached and kept for 5 min. Naphthalene was chosen as internal standard. Analytical TLC was performed on silica gel coated alumina plates (MN TLC sheets ALUGRAM® Xtra SIL G/UV254). UV light (254 or 366 nm) was used for visualization. If necessary, potassium permanganate, ninhydrin, bromocresol green or ceric ammonium molybdate was used for chemical staining. Purification by column chromatography was performed with silica gel 60 M (40-63 μm, 230-440 mesh, Merck) or pre-packed Biotage® SNAP Ultra HP-Sphere columns (25 μm spherical silica gel) on a Biotage® Isolera™ Spektra One device. UV-vis absorption spectroscopy was performed

on a Varian Cary BIO 50 UV-vis/NIR spectrometer with a 10 mm Hellma® quartz fluorescence cuvette at room temperature. Fluorescence spectra were recorded on a HORIBA FluoroMax®-4 Spectrofluorometer with a 10 mm Hellma® quartz fluorescence cuvette at room temperature. FluorEssence Version 3.5.1.20 was used as software. Fluorescence measurements were performed under nitrogen atmosphere. For irradiation with blue light, OSRAM Oslon SSL 80 LDCQ7P-1U3U (blue, λ_{max} = 455 nm, I_{max} = 1000 mA, 1.12 W) was used. For irradiation with green light, Cree XPEGRN G4 Q4 (green, λ_{max} = 535 nm, I_{max} = 1000 mA, 1.12 W) was used.

2. Synthesis of *N*-(acyloxy)phthalimides (1) as starting materials

2.1. General procedure for the synthesis of *N*-(acyloxy)phthalimides (1)

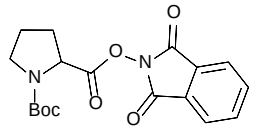
N-(Acyloxy)phthalimides (**1**) were synthesized by a slightly modified procedure based on Reiser *et al.*[3] and Overman *et al.*[4]



The respective carboxylic acid (8.00 mmol, 1.0 equiv.), *N*-hydroxyphthalimide (1.43 g, 8.80 mmol, 1.1 equiv.), *N*,*N´*-dicyclohexylcarbodiimide (1.98 g, 9.60 mmol, 1.2 equiv.) and 4-dimethylaminopyridine (0.98 g, 0.80 mmol, 0.1 equiv.) were mixed in a flask with a magnetic stirring bar. Dry THF (40 mL) was added and the orange reaction mixture was stirred for 15 h at rt. The white precipitate was filtered off and the solution was concentrated by evaporation of the solvent. Purification by column chromatography on flash silica gel (CH_2Cl_2 or CH_2Cl_2/CH_3OH = 9:1) gave a white solid (**1a-q**) or a clear liquid (**1r** and **1s**).

2.2. Characterization of *N*-(acyloxy)phthalimides (1)

1-(*tert*-Butyl) 2-(1,3-dioxoisoindolin-2-yl) pyrrolidine-1,2-dicarboxylate (1a)[5]



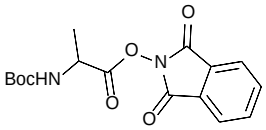
Yield: 2.16 g, 5.99 mmol, 75%.

^{1}H NMR (300 MHz, $CDCl_3$): (rotamers around the tertiary amide);[6] δ [ppm] = 7.89 – 7.81 (m, 2H), 7.80–7.72 (m, 2H), 4.68 (dd, *J* = 7.0 Hz, 5.1 Hz, 0.2H), 4.59 (dd, *J* = 8.6 Hz, 3.9 Hz, 0.8H), 3.65 – 3.35 (m, 2H), 2.50 – 2.27 (m, 2H), 2.12 – 1.89 (m, 2H), 1.54 – 1.40 (m, 9H).

^{13}C NMR (75 MHz, $CDCl_3$): δ [ppm] = 169.7 and 169.4 (C_q), 161.8 and 161.7 (C_q), 153.5 (C_q), 134.9 and 134.8 (+), 128.9 (C_q), 124.0 (+), 81.2 and 80.4 (C_q), 57.24 and 57.15 (+), 46.5 and 46.3 (–), 31.5 and 30.3 (–), 28.4 and 28.2 (+), 24.5 and 23.6 (–).

HRMS (ESI) (m/z): $[M + H]^+$ ($C_{18}H_{21}N_2O_6$) calc.: 361.1394, found: 361.1397.
MF: $C_{18}H_{20}N_2O_6$
MW: 360.37 g/mol

1,3-Dioxoisoindolin-2-yl (*tert*-butoxycarbonyl)alaninate (1b)[5]



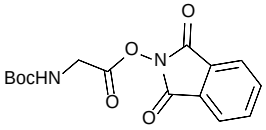
Yield: 1.83g, 5.46 mmol, 68%.

^{1}H NMR (300 MHz, $CDCl_3$): (rotamers around the tertiary amide); δ [ppm] = 7.91 – 7.81 (m, 2H), 7.80 – 7.73 (m, 2H), 5.29 – 4.93 (m, 1H), 4.87 – 4.33 (m, 1H), 1.60 (d, *J* = 7.3 Hz, 3H), 1.53 – 1.40 (m, 9H).

^{13}C NMR (75 MHz, $CDCl_3$): δ [ppm] = 170.1 (C_q), 161.6 (C_q), 154.8 (C_q), 134.9 (+), 128.9 (C_q), 124.1 (+), 80.6 (C_q), 47.8 (+), 28.3 (+) and 28.1 (+), 18.9 (+).

HRMS (ESI) (m/z): $[M + H]^+$ ($C_{16}H_{19}N_2O_6$) calc.: 335.1238, found: 335.1238.
MF: $C_{16}H_{18}N_2O_6$
MW: 334.33 g/mol

1,3-Dioxoisoindolin-2-yl (*tert*-butoxycarbonyl)glycinate (1c)[5]



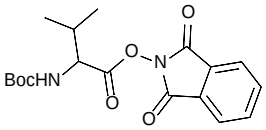
Yield: 668 mg, 2.09 mmol, 26%.

^{1}H NMR (300 MHz, $CDCl_3$): (rotamers around the tertiary amide); δ [ppm] = 7.94 – 7.85 (m, 2H), 7.84 – 7.76 (m, 2H), 5.22 – 4.76 (m, 1H), 4.43 – 4.15 (m, 2H), 1.55 – 1.40 (m, 9H).

^{13}C NMR (75 MHz, $CDCl_3$): δ [ppm] = 167.3 (C_q), 161.6 (C_q), 155.4 (C_q), 135.0 (+), 128.9 (C_q), 124.2 (+), 80.8 (C_q), 40.5 (–), 28.4 (+).

HRMS (ESI) (m/z): $[M + H]^+$ ($C_{15}H_{17}N_2O_6$) calc.: 321.1081, found: 321.1084.
MF: $C_{15}H_{16}N_2O_6$
MW: 320.30 g/mol

1,3-Dioxoisoindolin-2-yl (*tert*-butoxycarbonyl)valinate (1d)



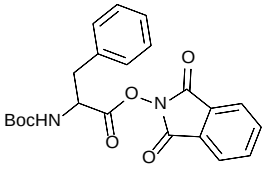
Yield: 2.26 g, 6.24 mmol, 78%.

^{1}H NMR (300 MHz, $CDCl_3$): (rotamers around the tertiary amide); δ [ppm] = 7.90 – 7.82 (m, 2H), 7.81 – 7.74 (m, 2H), 5.25 – 4.76 (m, 1H), 4.75 – 4.15 (m, 1H), 2.43 – 2.24 (m, 1H), 1.56 – 1.39 (m, 9H), 1.08 (t, *J* = 7.2 Hz, 6H).

^{13}C NMR (75 MHz, $CDCl_3$): δ [ppm] = 169.0 (C_q), 161.6 (C_q), 155.3 (C_q), 134.9 (+), 128.9 (C_q), 124.1 (+), 81.5 and 80.5 (C_q), 58.8 and 57.2 (+), 31.8 and 31.2 (+), 28.3 and 28.1 (+), 18.8 (+), 17.5 (+).

HRMS (ESI) (m/z): $[M + H]^+$ ($C_{18}H_{23}N_2O_6$) calc.: 363.1551, found: 363.1551.
MF: $C_{18}H_{22}N_2O_6$
MW: 362.38 g/mol

1,3-Dioxoisoindolin-2-yl (*tert*-butoxycarbonyl)phenylalaninate (1e)



Yield: 2.68 g, 6.52 mmol, 82%.

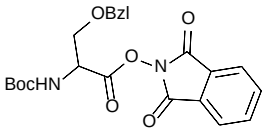
^{1}H NMR (300 MHz, DMSO-d_6): (rotamers around the tertiary amide); δ [ppm] = 8.03 – 7.91 (m, 4H), 7.84 – 7.70 (m, 1H), 7.42 – 7.22 (m, 5H), 4.76 – 4.39 (m, 1H), 3.30 – 3.00 (m, 2H), 1.41 – 1.28 (m, 9H).

^{13}C NMR (75 MHz, DMSO-d_6): δ [ppm] = 169.6 and 169.3 (C_q), 161.7 and 161.6 (C_q), 155.3 and 154.0 (C_q), 136.6 (C_q), 135.6 (+), 129.4 and 129.3 (+), 128.4 and 128.3 (+), 128.2 (C_q),

126.9 and 126.8 (+), 124.1 and 123.0 (+), 79.6 and 78.9 (C_q), 55.0 and 53.6 (+), 36.4 and 36.2 (–), 28.1 and 27.6 (+).

HRMS (ESI) (m/z): $[M + H]^+$ ($C_{22}H_{23}N_2O_6$) calc.: 411.1551, found: 411.1551.
MF: $C_{22}H_{22}N_2O_6$
MW: 410.43 g/mol

1,3-Dioxoisoindolin-2-yl *O*-benzyl-*N*-(*tert*-butoxycarbonyl)serinate (1f)



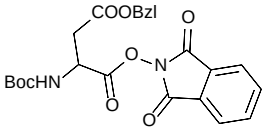
Yield: 2.94 g, 6.67 mmol, 83%.

^{1}H NMR (300 MHz, $CDCl_3$): (rotamers around the tertiary amide); δ [ppm] = 7.94 – 7.83 (m, 2H), 7.83 – 7.74 (m, 2H), 7.46 – 7.27 (m, 5H), 5.50 (d, *J* = 9.1 Hz, 1H), 5.32 – 5.12 (m, 0.2H), 4.98 – 4.83 (m, 0.8H), 4.74 – 4.57 (m, 2H), 4.15 – 3.99 (m, 1H), 3.86 (dd, *J* = 9.7 Hz, 3.4 Hz, 1H), 1.54 – 1.40 (m, 9H).

^{13}C NMR (75 MHz, $CDCl_3$): δ [ppm] = 167.8 (C_q), 161.5 (C_q), 155.1 (C_q), 137.4 (C_q), 134.9 (+), 129.0 (C_q), 128.6 (+), 128.0 (+), 124.1 (+), 80.7 (C_q), 73.8 (–), 69.9 (–), 54.1 and 52.8 (+), 28.4 and 28.1 (+).

HRMS (ESI) (m/z): $[M + H]^+$ ($C_{23}H_{25}N_2O_7$) calc.: 441.1656, found: 441.1656.
MF: $C_{23}H_{24}N_2O_7$
MW: 440.45 g/mol

4-Benzyl 1-(1,3-dioxoisoindolin-2-yl) (*tert*-butoxycarbonyl)aspartate (1g)



Yield: 2.84 g, 6.07 mmol, 76%.

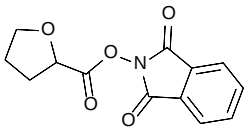
^{1}H NMR (400 MHz, $CDCl_3$): (rotamers around the tertiary amide); δ [ppm] = 7.92 – 7.83 (m, 2H), 7.82 – 7.76 (m, 2H), 7.43 – 7.27 (m, 5H), 5.77 – 5.30 (m, 1H), 5.28 – 5.19 (m, 2H), 5.12 – 4.84 (m, 1H), 3.27 – 2.98 (m, 2H), 1.54 – 1.40 (m, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 170.2 (C_q), 168.0 (C_q), 161.4 (C_q), 155.0 (C_q), 135.4 (C_q), 134.9 (+), 128.9 (C_q), 128.7 (+), 128.60 (+), 128.55 (+), 124.1 and 123.5 (+), 80.9 (C_q), 67.4 (–), 48.8 (+), 37.1 (–), 28.3 (+).

HRMS (ESI) (m/z): $[M + H]^+$ ($C_{24}H_{25}N_2O_8$) calc.: 469.1605, found: 469.1606.
MF: $C_{24}H_{24}N_2O_8$

MW: 468.46 g/mol

1,3-Dioxoisoindolin-2-yl tetrahydrofuran-2-carboxylate (1h)[7]



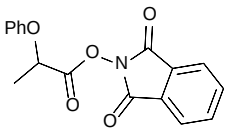
Yield: 996 mg, 3.81 mmol, 48%.

^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm] = 7.91 – 7.82 (m, 2H), 7.82 – 7.75 (m, 2H), 4.86 (dd, *J* = 8.4 Hz, 5.1 Hz, 1H), 4.12 – 3.95 (m, 2H), 2.50 – 2.30 (m, 2H), 2.15 – 1.93 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): δ [ppm] = 169.9 (C_q), 161.8 (C_q), 135.0 (+), 128.9 (C_q), 124.1 (+), 75.0 (+), 70.0 (–), 31.0 (–), 25.2 (–).

HRMS (APCI) (m/z): $[M + H]^+$ ($C_{13}H_{12}NO_5$) calc.: 262.0710, found: 262.0713.
MF: $C_{13}H_{11}NO_5$
MW: 261.23 g/mol

1,3-Dioxoisoindolin-2-yl 2-phenoxypropanoate (1i)



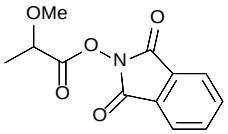
Yield: 1.90 g, 6.10 mmol, 76%.

^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm] = δ 7.90 – 7.83 (m, 2H), 7.81 – 7.74 (m, 2H), 7.39 – 7.31 (m, 2H), 7.08 – 6.96 (m, 3H), 5.12 (q, *J* = 6.9 Hz, 1H), 1.87 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ [ppm] = 168.8 (C_q), 161.7 (C_q), 157.0 (C_q), 135.0 (+), 129.8 (+), 128.9 (C_q), 124.2 (+), 122.4 (+), 115.4 (+), 71.0 (+), 19.0 (+).

HRMS (ESI) (m/z): $[M + H]^+$ ($C_{17}H_{14}NO_5$) calc.: 312.0866, found: 312.0874.
MF: $C_{17}H_{13}NO_5$
MW: 311.29 g/mol

1,3-Dioxoisoindolin-2-yl 2-methoxypropanoate (1j)



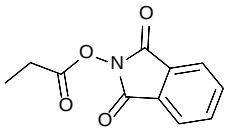
Yield: 1.33 g, 5.32 mmol, 67%.

^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm] = 7.90 – 7.81 (m, 2H), 7.80 – 7.72 (m, 2H), 4.26 (q, *J* = 6.9 Hz, 1H), 3.49 (s, 3H), 1.61 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ [ppm] = 169.6 (C_q), 161.7 (C_q), 134.9 (+), 128.9 (C_q), 124.1 (+), 74.9 (+), 58.2 (+), 18.8 (+).

HRMS (APCI) (m/z): $[M + H]^+$ ($C_{12}H_{12}NO_5$) calc.: 250.0710, found: 250.0715.
MF: $C_{12}H_{11}NO_5$
MW: 249.06 g/mol

1,3-Dioxoisoindolin-2-yl propionate (1k)[8]



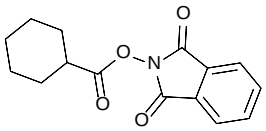
Yield: 1.32 g, 6.01 mmol, 75%.

^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm] = 7.93 – 7.84 (m, 2H), 7.82 – 7.75 (m, 2H), 2.70 (q, *J* = 7.5 Hz, 2H), 1.30 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 170.5 (C_q), 162.1 (C_q), 134.9 (+), 129.1 (C_q), 124.1 (+), 24.7 (–), 8.8 (+).

HRMS (ESI) (m/z): $[M + Na]^+$ ($C_{11}H_9NNaO_4$) calc.: 242.0424, found: 242.0425.
MF: $C_{11}H_9NO_4$
MW: 219.20 g/mol

1,3-Dioxoisoindolin-2-yl cyclohexanecarboxylate (1l)[7]



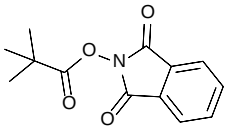
Yield: 1.83 g, 6.69 mmol, 84%.

^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm] = 7.92 – 7.80 (m, 2H), 7.80 – 7.67 (m, 2H), 2.71 (tt, *J* = 10.9 Hz, 3.7 Hz, 1H), 2.14 – 2.01 (m, 2H), 1.86 – 1.74 (m, 2H), 1.71 – 1.55 (m, 3H), 1.44 – 1.22 (m, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ [ppm] = 171.9 (C_q), 162.1 (C_q), 134.8 (+), 129.0 (C_q), 123.9 (+), 40.5 (+), 28.8 (–), 25.5 (–), 25.1 (–).

HRMS (ESI) (m/z): $[M + H]^+$ ($C_{15}H_{16}NO_4$) calc.: 274.1074, found: 274.1075.
MF: $C_{15}H_{15}NO_4$
MW: 273.29 g/mol

1,3-Dioxoisoindolin-2-yl pivalate (1m)[9]



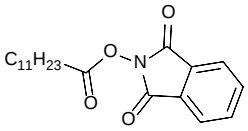
Yield: 1.63 g, 6.60 mmol, 83%.

^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm] = 7.92 – 7.81 (m, 2H), 7.81 – 7.73 (m, 2H), 1.43 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$): δ [ppm] = 174.5 (C_q), 162.2 (C_q), 134.8 (+), 129.1 (C_q), 124.0 (+), 38.5 (C_q), 27.1 (+).

HRMS (APCI) (m/z): $[M + NH_4]^+$ ($C_{13}H_{17}N_2O_4$) calc.: 265.1183, found: 265.1189.
MF: $C_{13}H_{13}NO_4$
MW: 247.25 g/mol

1,3-Dioxoisoindolin-2-yl dodecanoate (1n)



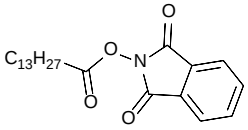
Yield: 2.43 g, 7.04 mmol, 88%.

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.90 – 7.79 (m, 2H), 7.79 – 7.69 (m, 2H), 2.63 (t, *J* = 7.5 Hz, 2H), 1.81 – 1.71 (m, 2H), 1.46 – 1.21 (m, 16H), 0.85 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 169.7 (C_q), 162.0 (C_q), 134.8 (+), 129.0 (C_q), 124.0 (+), 32.0 (–), 31.0 (–), 29.7 (–), 29.6 (–), 29.43 (–), 29.39 (–), 29.2 (–), 28.9 (–), 24.7 (–), 22.7 (–), 14.2 (+).

HRMS (ESI) (m/z): $[M + H]^+$ ($C_{20}H_{28}NO_4$) calc.: 346.2013, found: 346.2014.
MF: $C_{20}H_{27}NO_4$
MW: 345.44 g/mol

1,3-Dioxoisoindolin-2-yl tetradecanoate (1o)[10]



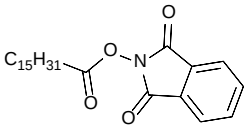
Yield: 2.61 g, 7.00 mmol, 87%.

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.92 – 7.80 (m, 2H), 7.80 – 7.72 (m, 2H), 2.65 (t, *J* = 7.5 Hz, 2H), 1.82 – 1.73 (m, 2H), 1.47 – 1.21 (m, 20H), 0.87 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ [ppm] = 169.8 (C_q), 162.1 (C_q), 134.8 (+), 129.0 (C_q), 124.1 (+), 32.0 (–), 31.1 (–), 29.79 (–), 29.76 (–), 29.75 (–), 29.68 (–), 29.49 (–), 29.48 (–), 29.2 (–), 24.8 (–), 22.8 (–), 14.3 (+).

HRMS (APCI) (m/z): $[M + H]^+$ ($C_{22}H_{32}NO_4$) calc.: 374.2326, found: 374.2332.
MF: $C_{22}H_{31}NO_4$
MW: 373.49 g/mol

1,3-Dioxoisoindolin-2-yl palmitate (1p)[11]



Yield: 1.90 g, 4.74 mmol, 59%.

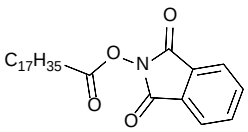
^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm] = 7.92 – 7.81 (m, 2H), 7.81 – 7.72 (m, 2H), 2.66 (t, *J* = 7.5 Hz, 2H), 1.84 – 1.71 (m, 2H), 1.48 – 1.21 (m, 24H), 0.87 (t, *J* = 6.7 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ [ppm] = 169.8 (C_q), 162.1 (C_q), 134.9 (+), 129.1 (C_q), 124.1 (+), 32.1 (–), 31.1 (–), 29.82 (–), 29.80 (–), 29.76 (–), 29.7 (–), 29.5 (–), 29.3 (–), 29.0 (–), 24.8 (–), 22.8 (–), 14.3 (+).

HRMS (APCI) (m/z): $[M + H]^+$ ($C_{24}H_{36}NO_4$) calc.: 402.2639, found: 402.2641.

MF: $C_{24}H_{35}NO_4$
MW: 401.55 g/mol

1,3-Dioxoisoindolin-2-yl stearate (1q)[10]



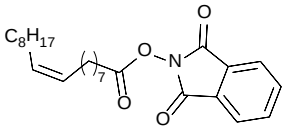
Yield: 2.88 g, 6.69 mmol, 84%.

^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm] = 7.93 – 7.81 (m, 2H), 7.81 – 7.72 (m, 2H), 2.65 (t, *J* = 7.5 Hz, 2H), 1.83 – 1.72 (m, 2H), 1.48 – 1.21 (m, 28H), 0.87 (t, *J* = 6.7 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ [ppm] = 169.8 (C_q), 162.1 (C_q), 134.8 (+), 129.1 (C_q), 124.1 (+), 32.1 (–), 31.1 (–), 29.83 (–), 29.80 (–), 29.76 (–), 29.7 (–), 29.5 (–), 29.3 (–), 29.0 (–), 24.8 (–), 22.8 (–), 14.3 (+).

HRMS (CI) (m/z): $[M + H]^+$ ($C_{26}H_{40}NO_4$) calc.: 430.2952, found: 430.2953.
MF: $C_{26}H_{39}NO_4$
MW: 429.60 g/mol

1,3-Dioxoisoindolin-2-yl oleate (1r)[11]



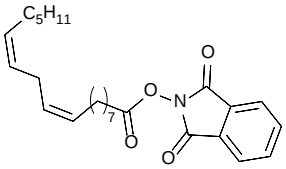
Yield: 3.18 g, 7.44 mmol, 93%.

^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm] = 7.91 – 7.80 (m, 2H), 7.80 – 7.68 (m, 2H), 5.40 – 5.27 (m, 2H), 2.64 (t, *J* = 7.5 Hz, 2H), 2.14 – 1.88 (m, 4H), 1.82 – 1.71 (m, 2H), 1.50 – 1.18 (m, 20H), 0.86 (t, *J* = 6.7 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ [ppm] = 169.7 (C_q), 162.0 (C_q), 134.8 (+), 130.1 (+), 129.8 (+), 129.0 (C_q), 124.0 (+), 32.0 (–), 31.0 (–), 29.8 (–), 29.7 (–), 29.6 (–), 29.4 (–), 29.10 (–), 29.09 (–), 28.9 (–), 27.3 (–), 27.2 (–), 24.7 (–), 22.8 (–), 14.2 (+).

HRMS (ESI) (m/z): $[M + Na]^+$ ($C_{26}H_{37}NNaO_4$) calc.: 450.2615, found: 450.2617.
MF: $C_{26}H_{37}NO_4$
MW: 427.59 g/mol

1,3-Dioxoisoindolin-2-yl (9*Z*,12*Z*)-octadeca-9,12-dienoate (1s)



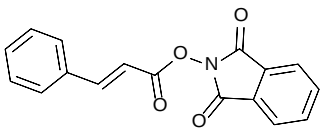
Yield: 2.54 g, 5.97 mmol, 75%.

^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm] = 7.92 – 7.81 (m, 2H), 7.81 – 7.71 (m, 2H), 5.43 – 5.25 (m, 4H), 2.77 (t, *J* = 5.8 Hz, 2H), 2.65 (t, *J* = 7.5 Hz, 2H), 2.10 – 1.98 (m, 4H), 1.83 – 1.69 (m, 2H), 1.48 – 1.23 (m, 14H), 0.87 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ [ppm] = 169.7 (C_q), 162.1 (C_q), 134.8 (+), 130.3 (+), 130.1 (+), 129.0 (C_q), 128.2 (+), 128.0 (+), 124.0 (+), 31.6 (–), 31.1 (–), 29.6 (–), 29.4 (–), 29.1 (–), 28.9 (–), 27.28 (–), 27.26 (–), 25.7 (–), 24.7 (–), 22.7 (–), 14.2 (+).

HRMS (APCI) (m/z): $[M + NH_4]^+$ ($C_{26}H_{39}N_2O_4$) calc.: 443.2904, found: 443.2903.
MF: $C_{26}H_{35}NO_4$
MW: 425.57 g/mol

1,3-Dioxoisoindolin-2-yl cinnamate (1t)[12]



Yield: 2.03 g, 6.93 mmol, 87%.

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.96 (d, *J* = 16.1 Hz, 1H), 7.94 – 7.87 (m, 2H), 7.83 – 7.77 (m, 2H), 7.62 – 7.57 (m, 2H), 7.50 – 7.39 (m, 3H), 6.66 (d, *J* = 16.1 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 163.1 (C_q), 162.2 (C_q), 150.1 (+), 134.9 (+), 133.7 (C_q), 131.7 (+), 129.3 (+), 129.1 (C_q), 128.8 (+), 124.1 (+), 111.9 (+).

HRMS (APCI) (m/z): $[M + H]^+$ ($C_{17}H_{12}NO_4$) calc.: 294.0761, found: 294.0767.
MF: $C_{17}H_{11}NO_4$
MW: 293.28 g/mol

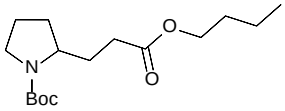
3. Photocatalytic decarboxylative alkylation

3.1. General procedure for the photocatalytic decarboxylative alkylation

In a 5 mL crimp cap vial with a stirring bar, eosin Y (**A**, 19.4 mg, 0.03 mmol, 0.1 equiv.) and *N*-(acyloxy)phthalimide **1** (0.30 mmol, 1.0 equiv.) were added. After addition of DIPEA (102 µL, 0.60 mmol, 2.0 equiv.), the corresponding olefin **2** (1.50 mmol, 5.0 equiv.) and dry CH_2Cl_2 (4 mL), the vial was capped to prevent evaporation. The reaction mixture was stirred and irradiated through the vials´ plane bottom side using green LEDs (535 nm) for 18 h at rt. The reaction mixture of two vials with the same content was combined and diluted with saturated aqueous solution of $NaHCO_3$ (20 mL). It was extracted with EA (3 x 20 mL) and the combined organic phases were washed with brine (20 mL), dried over Na_2SO_4 and concentrated in vacuum. Purification of the crude product was performed by automated flash column chromatography (PE/EA = 19:1 to 1:1) yielding the corresponding product as colorless oil.

3.2. Characterization of photocatalytic products 3 and 4

***tert*-Butyl 2-(3-butoxy-3-oxopropyl)pyrrolidine-1-carboxylate (3a)**



Yield: 144 mg, 0.48 mmol, 80%.

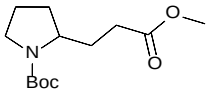
^{1}H NMR (400 MHz, $CDCl_3$): (rotamers around the tertiary amide); δ [ppm] = 4.04 (t, *J* = 6.6 Hz, 2H), 3.77 (brs, 1H), 3.54 – 3.16 (m, 2H), 2.28 (brs, 2H), 2.01 – 1.76 (m, 4H), 1.71 – 1.54 (m, 4H), 1.44 (s, 9H), 1.35 (q, *J* = 7.4 Hz, 2H), 0.91 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 173.6 and 173.1 (C_q), 154.8 (C_q), 79.4 and 79.1 (C_q), 64.4 (–), 56.7 (+), 46.6 and 46.2 (–), 31.5 (–), 30.8 (–), 30.1 and 29.8 (–), 28.6 (+), 23.8 (–), 23.2 (–), 19.2 (–), 13.8 (+).

HRMS (APCI) (m/z): $[M + H]^+$ ($C_{16}H_{30}NO$) calc.: 300.2169, found: 300.2170.
MF: $C_{16}H_{29}NO$

MW: 299.41 g/mol

***tert*-Butyl 2-(3-methoxy-3-oxopropyl)pyrrolidine-1-carboxylate (3b)**[13]



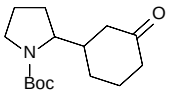
Yield: 120 mg, 0.47 mmol, 78%.

^{1}H NMR (400 MHz, $CDCl_3$): (rotamers around the tertiary amide); δ [ppm] = 3.80 (brs, 1H), 3.65 (s, 3H), 3.52 – 3.16 (m, 2H), 2.31 (brs, 2H), 2.03 – 1.59 (m, 6H), 1.45 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 174.0 (C_q), 154.9 (C_q), 79.5 and 79.2 (C_q), 56.7 (+), 51.7 (+), 46.6 and 46.2 (–), 31.2 and 30.9 (–), 30.1 and 29.8 (–), 28.6 (+), 23.9 (–), 23.2 (–).

HRMS (APCI) (m/z): $[M + H]^+$ ($C_{13}H_{24}NO_4$) calc.: 258.1700, found: 258.1706.
MF: $C_{13}H_{23}NO_4$
MW: 257.33 g/mol

***tert*-Butyl 2-(3-oxocyclohexyl)pyrrolidine-1-carboxylate (3c)**[14]



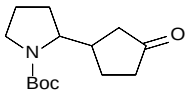
Yield: 122 mg, 0.46 mmol, 76%.

^{1}H NMR (400 MHz, $CDCl_3$): (rotameric and diasteromeric mixture); δ [ppm] = 3.83 (brs, 1H), 3.46 (brs, 1H), 3.29 – 3.14 (m, 1H), 2.41 – 1.97 (m, 6H), 1.96 – 1.50 (m, 7H), 1.49 – 1.42 (m, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): (rotameric and diastereomeric mixture); δ [ppm] = 211.6 (C_q), 155.3 (C_q), 79.5 (C_q), 61.0 and 61.1 (+), 46.9 (–), 45.4 (–), 43.9 (–), 43.1 (+), 41.5 (–), 28.7 (+), 28.6 (–), 27.9 (–), 25.5 (–).

HRMS (APCI) (m/z): $[M + H]^+$ ($C_{15}H_{26}NO_3$) calc.: 268.1907, found: 268.1911.
MF: $C_{15}H_{25}NO_3$
MW: 267.37 g/mol

***tert*-Butyl 2-(3-oxocyclopentyl)pyrrolidine-1-carboxylate (3d)**



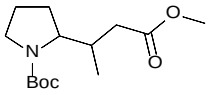
Yield: 111 mg, 0.44 mmol, 73%.

^{1}H NMR (400 MHz, $CDCl_3$): (rotameric and diasteromeric mixture); δ [ppm] = 3.91 (brs, 1H), 3.44 (brs, 1H), 3.30 – 3.22 (m, 1H), 2.45 – 1.62 (m, 11H), 1.49 – 1.41 (m, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 219.0 (C_q), 155.5 (C_q), 79.5 (C_q), 60.3 and 60.1 (+), 46.9 and 46.6 (–), 43.0 and 42.2 (–), 41.7 (+), 38.8 and 38.5 (–), 29.6 and 28.6 (+), 26.9 (–), 26.4 (–), 24.0 and 23.2 (–).

HRMS (ESI) (m/z): $[M + H]^+$ ($C_{14}H_{24}NO_3$) calc.: 254.1751, found: 254.1751.
MF: $C_{14}H_{23}NO_3$
MW: 253.34 g/mol

***tert*-Butyl 2-(4-methoxy-4-oxobutan-2-yl)pyrrolidine-1-carboxylate (3e)**[15]



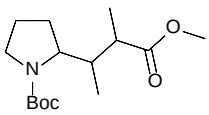
Yield: 119 mg, 0.44 mmol, 73%.

^{1}H NMR (300 MHz, $CDCl_3$): (rotameric and diasteromeric mixture); δ [ppm] = 3.87 – 3.28 (m, 5H), 3.24 – 3.04 (m, 1H), 2.69 – 2.15 (m, 2H), 2.14 – 1.95 (m, 1H), 1.91 – 1.58 (m, 4H), 1.43 (s, 9H), 0.87 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 173.9 and 173.7 and 173.5 (C_q), 155.4 and 155.2 (C_q), 79.5 and 79.1 (C_q), 61.5 and 61.4 (+), 51.6 and 51.5 (+), 47.4 and 47.2 and 46.9 and 46.7 (–), 38.9 and 38.7 (–), 33.9 and 33.8 and 33.4 (+), 28.6 (+), 27.7 (–), 24.0 and 23.4 (–), 17.0 and 16.3 and 15.7 (+).

HRMS (ESI) (m/z): $[M + H]^+$ ($C_{14}H_{26}NO_4$) calc.: 272.1856, found: 272.1861.
MF: $C_{14}H_{25}NO_4$
MW: 271.36 g/mol

***tert*-Butyl 2-(4-methoxy-3-methyl-4-oxobutan-2-yl)pyrrolidine-1-carboxylate (3f)**



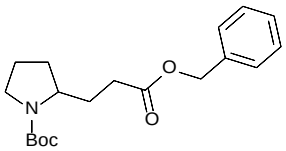
Yield: 102 mg, 0.36 mmol, 59%.

^{1}H NMR (400 MHz, $CDCl_3$): (rotameric and diasteromeric mixture); δ [ppm] = 4.06 – 3.23 (m, 5H), 3.23 – 3.01 (m, 1H), 2.57 – 1.61 (m, 6H), 1.44 (s, 9H), 1.21 – 1.05 (m, 3H), 0.91 – 0.72 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 176.6 and 176.2 (C_q), 155.4 and 154.8 (C_q), 79.5 and 79.1 (C_q), 61.0 and 60.6 and 59.6 (+), 51.6 and 51.5 and 51.4 (+), 47.0 and 46.8 and 46.3 (–), 43.6 and 41.8 and 41.1 and 40.7 (+), 39.0 and 38.8 (+), 29.8 and 28.6 (+), 28.1 and 27.7 (–), 24.2 and 24.0 and 23.6 and 23.3 (–), 16.1 and 15.7 and 15.3 and 14.1 (+),12.3 and 11.9 (+).

HRMS (APCI) (m/z): $[M + H]^+$ ($C_{15}H_{28}NO_4$) calc.: 286.2013, found: 286.2017.
MF: $C_{15}H_{27}NO_4$
MW: 285.38 g/mol

***tert*-Butyl 2-(3-(benzyloxy)-3-oxopropyl)pyrrolidine-1-carboxylate (3g)**[16]



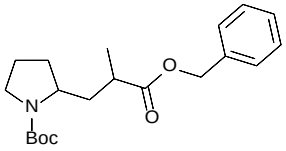
Yield: 138 mg, 0.41 mmol, 69%.

^{1}H NMR (400 MHz, DMSO-*d*$_6$): (rotamers around the tertiary amide); δ [ppm] = 7.38 – 7.30 (m, 5H), 5.08 (s, 2H), 3.69 (brs, 1H), 3.31 – 3.04 (m, 2H), 2.42 – 2.25 (m, 2H), 1.97 – 1.50 (m, 6H), 1.37 (s, 9H).

^{13}C NMR (101 MHz, DMSO-*d*$_6$): δ [ppm] = 172.5 (C_q), 153.7 and 153.6 (C_q), 136.2 (C_q), 128.4 (+), 128.0 (+), 127.9 (+), 78.2 (C_q), 65.4 (–), 56.1 (+), 46.2 and 45.9 (–), 30.5 and 30.0 (–), 29.3 and 28.9 (–), 28.1 (+), 23.2 (–), 22.5 (–).

HRMS (ESI) (m/z): $[M + H]^+$ ($C_{19}H_{28}NO_4$) calc.: 334.2015, found: 334.2013.
MF: $C_{19}H_{27}NO_4$
MW: 333.43 g/mol

***tert*-Butyl 2-(3-(benzyloxy)-2-methyl-3-oxopropyl)pyrrolidine-1-carboxylate (3h)**



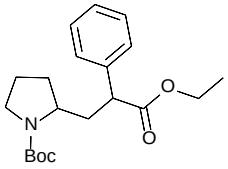
Yield: 178 mg, 0.51 mmol, 85%.

^{1}H NMR (300 MHz, $CDCl_3$): (rotameric and diasteromeric mixture); δ [ppm] = 7.43 – 7.26 (m, 5H), 5.20 – 5.02 (m, 2H), 4.15 – 3.50 (m, 1H), 3.46 – 3.15 (m, 2H), 2.85 – 1.95 (m, 2H), 1.95 – 1.48 (m, 5H), 1.46 – 1.38 (m, 9H), 1.21 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ [ppm] = 176.2 (C_q), 154.8 and 154.6 (C_q), 136.2 and 136.1 (C_q), 128.57 (+), 128.55 (+), 128.2 (+), 79.3 and 79.1 (C_q), 66.5 and 66.2 and 66.1 (–), 55.6 and 55.3 (+), 46.0 (–), 38.9 and 38.3 (–), 37.2 and 37.1 (+), 30.9 and 30.5 (–), 28.6 (+), 23.7 and 23.1 (–), 17.9 and 17.3 and 17.1 (+).

HRMS (ESI) (m/z): $[M + H]^+$ ($C_{20}H_{30}NO_4$) calc.: 348.2169, found: 348.2175.
MF: $C_{20}H_{29}NO_4$
MW: 347.46 g/mol

***tert*-Butyl 2-(3-ethoxy-3-oxo-2-phenylpropyl)pyrrolidine-1-carboxylate (3i)**



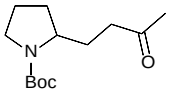
Yield: 191 mg, 0.55 mmol, 92%.

^{1}H NMR (400 MHz, acetone-d_6): (rotameric and diasteromeric mixture); δ [ppm] = 7.39 – 7.22 (m, 5H), 4.18 – 4.03 (m, 2H), 3.95 – 3.40 (m, 2H), 3.40 – 3.09 (m, 2H), 2.60 (brs, 0.8H), 2.32 – 2.23 (m, 0.2H), 2.01 – 1.55 (m, 5H), 1.55 – 1.34 (m, 9H), 1.17 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, acetone-d_6): δ [ppm] = 174.2 and 174.1 (C_q), 155.3 and 155.0 (C_q), 141.2 (C_q), 129.6 (+), 129.1 and 128.9 (+), 128.1 (+), 79.3 (C_q), 61.6 and 61.3 (–), 57.0 and 56.3 (+), 49.9 and 49.8 (+), 47.2 and 46.9 (–), 40.0 and 39.7 and 39.5 and 39.4 (–), 31.4 (–), 29.0 (+), 24.6 and 23.7 (–), 14.7 and 14.4 (+).

HRMS (ESI) (m/z): $[M + Na]^+$ ($C_{20}H_{29}NNaO_4$) calc.: 370.1989, found: 390.1992.
MF: $C_{20}H_{29}NO_4$
MW: 347.46 g/mol

***tert*-Butyl 2-(3-oxobutyl)pyrrolidine-1-carboxylate (3j)**[14]



Yield: 79 mg, 0.33 mmol, 55%.

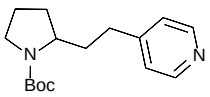
^{1}H NMR (400 MHz, $CDCl_3$): (rotamers around the tertiary amide); δ [ppm] = 3.79 (brs, 1H), 3.48 – 3.22 (m, 2H), 2.44 (t, *J* = 7.5 Hz, 2H), 2.14 (s, 3H), 1.94 – 1.75 (m, 4H), 1.69 – 1.56 (m, 2H), 1.45 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 208.6 (C_q), 155.0 (C_q), 79.3 (C_q), 56.7 (+), 46.4 (–), 41.0 and 40.8 (–), 30.7 (–), 30.0 and 29.8 (+), 28.9 (–), 28.7 (+), 24.0 and 23.6 (–).

HRMS (APCI) (m/z): $[M + H]^+$ ($C_{13}H_{24}NO_3$) calc.: 242.1751, found: 242.1755.

MF: $C_{13}H_{23}NO_3$
MW: 241.33 g/mol

tert-Butyl 2-(2-(pyridin-4-yl)ethyl)pyrrolidine-1-carboxylate (3k)



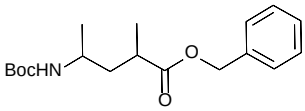
Yield: 66 mg, 0.24 mmol, 40%.

^{1}H NMR (400 MHz, $CDCl_3$): (rotamers around the tertiary amide); δ [ppm] = 8.44 (brs, 2H), 7.09 (brs, 2H), 3.95 – 3.60 (m, 1H), 3.47 – 3.21 (m, 2H), 2.64 – 2.49 (m, 2H), 2.15 – 1.55 (m, 6H), 1.42 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 154.7 (C_q), 151.2 and 151.0 (C_q), 149.8 (+), 123.9 (+), 79.3 and 79.1 (C_q), 57.0 and 56.7 (+), 46.7 and 46.3 (–), 35.3 and 34.8 (–), 32.2 (–), 30.7 and 30.2 (–), 28.6 (+), 23.9 and 23.2 (–).

HRMS (ESI) (m/z): $[M + H]^+$ ($C_{16}H_{25}N_2O_2$) calc.: 277.1911, found: 277.1914.
MF: $C_{16}H_{24}N_2O_2$
MW: 276.38 g/mol

Benzyl 4-((*tert*-butoxycarbonyl)amino)-2-methylpentanoate (4b)



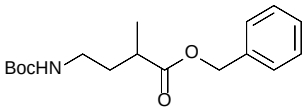
Yield: 132 mg, 0.41 mmol, 68%.

^{1}H NMR (300 MHz, $CDCl_3$): (rotameric and diasteromeric mixture); δ [ppm] = 7.39 – 7.30 (m, 5H), 5.20 – 5.02 (m, 2H), 4.52 – 3.96 (m, 1H), 3.74 (brs, 1H), 2.67 – 2.46 (m, 1H), 1.89 – 1.48 (m, 2H), 1.45 – 1.36 (m, 9H), 1.23 – 1.16 (m, 3H), 1.12 (t, *J* = 6.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 176.8 and 176.3 (C_q), 155.5 and 155.3 (C_q), 136.23 and 136.18 (C_q), 128.69 and 128.66 (+), 128.3 (+), 128.25 and 128.22 (+), 79.2 (C_q), 66.7 and 66.41 and 66.39 (–), 44.9 (+), 41.2 and 40.8 (–), 37.1 and 36.7 (+), 28.5 (+), 22.3 and 21.4 (+), 17.7 and 17.3 (+).

HRMS (ESI) (m/z): $[M + H]^+$ ($C_{18}H_{28}NO_4$) calc.: 322.2013, found: 322.2017.
MF: $C_{18}H_{27}NO_4$
MW: 321.42 g/mol

Benzyl 4-((*tert*-butoxycarbonyl)amino)-2-methylbutanoate (4c)



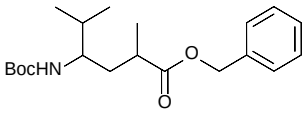
Yield: 114 mg, 0.37 mmol, 62%.

^{1}H NMR (400 MHz, $CDCl_3$): (rotamers around the tertiary amide); δ [ppm] = 7.38 – 7.31 (m, 5H), 5.21 – 5.07 (m, 2H), 4.75 – 4.19 (m, 1H), 3.37 – 2.97 (m, 2H), 2.60 – 2.49 (m, 1H), 1.93 – 1.78 (m, 1H), 1.80 – 1.58 (m, 1H), 1.45 – 1.40 (m, 9H), 1.23 (d, *J* = 5.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 176.5 and 176.2 (C_q), 156.0 and 155.8 (C_q), 136.2 and 136.0 (C_q), 128.71 and 128.68 (+), 128.37 and 128.35 (+), 128.2 (+), 79.4 (C_q), 66.8 and 66.4 (–), 38.6 (–), 37.3 (+), 33.9 (–), 28.5 (+), 17.2 (+).

HRMS (ESI) (m/z): $[M + H]^+$ ($C_{17}H_{26}NO_4$) calc.: 308.1856, found: 308.1857.
MF: $C_{17}H_{25}NO_4$
MW: 307.39 g/mol

Benzyl 4-((*tert*-butoxycarbonyl)amino)-2,5-dimethylhexanoate (4d)[17]



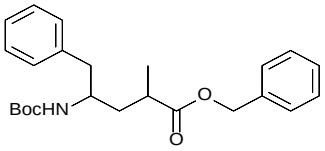
Yield: 187 mg, 0.54 mmol, 89%.

^{1}H NMR (300 MHz, $CDCl_3$): (rotameric and diasteromeric mixture); δ [ppm] = 7.38 – 7.29 (m, 5H), 5.20 – 4.94 (m, 2H), 4.45 – 3.88 (m, 1H), 3.88 – 3.20 (m, 1H), 2.75 – 1.44 (m, 4H), 1.44 – 1.34 (m, 9H), 1.22 – 1.10 (m, 3H), 0.93 – 0.76 (m, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ [ppm] = 177.1 and 176.9 and 176.5 and 176.3 (C_q), 156.0 and 155.8 and 155.4 (C_q), 136.3 and 136.2 and 136.99 and 135.98 (C_q), 128.66 and 128.63 and 128.60 and 128.56 (+), 128.23 and 128.22 and 128.19 (+), 128.1 and 128.0 (+), 79.04 and 78.97 (C_q), 66.6 and 66.5 and 66.4 and 66.3 (–), 53.73 and 53.65 and 51.84 and 51.79 (+), 45.0 and 44.6 and 44.4 and 44.2 (–), 37.1 and 36.7 and 36.4 and 35.8 (+), 33.7 and 33.1 and 32.4 (+), 28.5 (+), 20.1 and 19.1 and 19.0 and 18.9 (+), 18.0 and 17.9 (+), 17.7 and 17.6 and 17.1 (+).

HRMS (APCI) (m/z): $[M + H]^+$ ($C_{20}H_{32}NO_4$) calc.: 350.2326, found: 350.2334.
MF: $C_{20}H_{31}NO_4$
MW: 349.47 g/mol

Benzyl 4-((*tert*-butoxycarbonyl)amino)-2-methyl-5-phenylpentanoate (4e)[18]



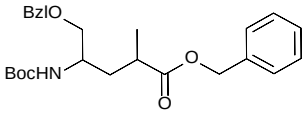
Yield: 120 mg, 0.34 mmol, 57%.

^{1}H NMR (300 MHz, CD_2Cl_2) (rotameric and diasteromeric mixture); δ [ppm] = 7.53 – 6.95 (m, 10H), 5.18 – 4.92 (m, 2H), 4.56 – 4.13 (m, 1H), 4.13 – 3.68 (m, 1H), 2.90 – 1.44 (m, 5H), 1.43 – 1.22 (m, 9H), 1.20 – 1.08 (m, 3H).

^{13}C NMR (101 MHz, CD_2Cl_2): δ [ppm] = 176.9 and 176.8 and 176.5 and 176.2 (C_q), 155.6 and 155.5 and 155.1 (C_q), 138.8 and 138.64 and 138.58 (C_q), 136.81 and 136.77 and 136.66 and 136.5 (C_q), 129.88 and 129.84 and 129.80 (+), 128.89 and 128.87 (+), 128.67 and 128.65 and 128.62 (+), 128.47 and 128.44 (+), 128.40 and 128.37 and 128.33 (+), 126.68 and 126.65 (+), 79.22 and 79.19 (C_q), 66.9 and 66.8 and 66.54 and 66.49 (–), 50.4 and 50.3 and 48.9 (+), 44.5 and 43.5 and 42.5 and 41.9 (–), 38.6 and 38.4 (–), 37.3 and 36.9 and 36.1 (+), 30.1 and 28.5 (+), 20.3 and 20.1 and 18.0 and 17.2 (+).

HRMS (ESI) (m/z): $[M + H]^+$ ($C_{24}H_{32}NO_4$) calc.: 398.2326, found: 398.2334.
MF: $C_{24}H_{31}NO_4$
MW: 397.52 g/mol

Benzyl 5-(benzyloxy)-4-((*tert*-butoxycarbonyl)amino)-2-methylpentanoate (4f)



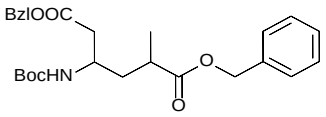
Yield: 141 mg, 0.33 mmol, 55%.

^{1}H NMR (300 MHz, $CDCl_3$): (rotameric and diasteromeric mixture); δ [ppm] = 7.41 – 7.27 (m, 10H), 5.19 – 5.04 (m, 2H), 4.90 – 4.57 (m, 1H), 4.56 – 4.38 (m, 2H), 4.17 – 3.73 (m, 1H), 3.73 – 3.26 (m, 2H), 2.71 – 2.48 (m, 1H), 2.10 – 1.91 (m, 1H), 1.68 – 1.58 (m, 1H), 1.53 – 1.31 (m, 9H), 1.25 – 1.16 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 176.7 and 176.2 (C_q), 155.7 and 155.6 (C_q), 138.3 (C_q), 136.3 and 136.2 (C_q), 128.71 and 128.68 and 128.6 (+), 128.52 and 128.45 (+), 128.34 and 128.28 (+), 128.2 (+), 127.8 (+), 127.70 and 127.69 (+), 79.4 and 79.3 (C_q), 73.3 (–), 72.7 and 72.3 (–), 66.7 and 66.38 and 66.36 (–), 48.71 and 48.66 (+), 36.9 and 36.6 (+), 36.0 and 35.9 (–), 29.8 and 28.5 (+), 17.9 and 17.2 (+).

HRMS (ESI) (m/z): $[M + H]^+$ ($C_{25}H_{34}NO_5$) calc.: 428.2431, found: 428.2437.
MF: $C_{25}H_{33}NO_5$
MW: 427.54 g/mol

Dibenzyl 4-((*tert*-butoxycarbonyl)amino)-2-methylhexanedioate (4g)



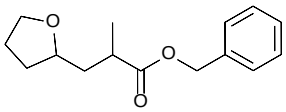
Yield: 174 mg, 0.38 mmol, 64%.

^{1}H NMR (300 MHz, $CDCl_3$): (rotameric and diasteromeric mixture); δ [ppm] = 7.38 – 7.29 (m, 10H), 5.20 – 4.84 (m, 5H), 4.08 (brs, 1H), 2.70 – 2.39 (m, 3H), 2.05 – 1.53 (m, 2H), 1.46 – 1.35 (m, 9H), 1.21 – 1.10 (m, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ [ppm] = 176.4 and 176.0 (C_q), 171.6 and 171.3 (C_q), 155.34 and 155.27 (C_q), 136.2 and 136.1 (C_q), 135.8 (C_q), 128.71 and 128.68 (+), 128.6 (+), 128.5 (+), 128.4 (+), 128.31 and 128.30 (+), 128.2 (+), 79.6 and 79.4 (C_q), 66.58 and 66.55 (–), 66.46 and 66.43 (–), 46.0 (+), 40.0 and 39.3 (–), 38.0 and 37.9 (–), 37.0 and 36.6 (+), 28.5 (+), 17.9 and 17.1 (+).

HRMS (ESI) (m/z): $[M + H]^+$ ($C_{26}H_{34}NO_6$) calc.: 456.2381, found: 456.2384.
MF: $C_{26}H_{33}NO_6$
MW: 455.55 g/mol

Benzyl 2-methyl-3-(tetrahydrofuran-2-yl)propanoate (4h)



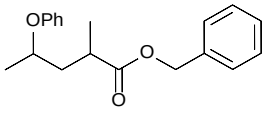
Yield: 108 mg, 0.43 mmol, 72%.

^{1}H NMR (300 MHz, $CDCl_3$): (mixture of diastereomers); δ [ppm] = 7.38 – 7.30 (m, 5H), 5.17 – 5.05 (m, 2H), 3.92 – 3.62 (m, 2H), 2.78 – 1.29 (m, 8H), 1.26 – 1.16 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 176.6 (C_q), 136.4 (C_q), 128.7 and 128.6 (+), 128.5 (+), 128.21 and 128.18 (+), 77.4 (+), 67.8 and 67.7 (–), 66.23 and 66.19 (–), 39.8 and 39.5 (+), 37.3 (–), 31.7 and 29.9 (–), 25.8 (–), 18.2 and 17.2 (+).

HRMS (APCI) (m/z): $[M + H]^+$ ($C_{15}H_{21}O_3$) calc.: 249.1488, found: 249.1493.
MF: $C_{15}H_{20}O_3$
MW: 248.32 g/mol

Benzyl 2-methyl-4-phenoxypentanoate (4i)



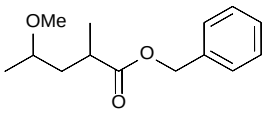
Yield: 90 mg, 0.30 mmol, 50%.

^{1}H NMR (300 MHz, DMSO-*d*$_6$): (mixture of diastereomers); δ [ppm] = 7.39 – 7.19 (m, 7H), 6.93 – 6.78 (m, 3H), 5.22 – 4.96 (m, 2H), 4.70 – 4.30 (m, 1H), 2.82 – 2.52 (m, 1H), 2.13 – 1.84 (m, 1H), 1.84 – 1.54 (m, 1H), 1.27 – 1.04 (m, 6H).

^{13}C NMR (75 MHz, DMSO-*d*$_6$): δ [ppm] = 175.5 and 175.4 (C_q), 157.5 and 157.4 (C_q), 136.2 (C_q), 129.7 and 129.5 (+), 128.44 and 128.41 (+), 128.03 and 127.97 (+), 127.9 (+), 120.5 and 120.4 (+), 115.5 and 115.4 (+), 71.0 and 70.9 (+), 65.6 and 65.5 (–), 40.2 and 39.9 (–), 36.1 and 35.6 (+), 19.6 and 19.5 (+), 17.4 and 17.3 (+).

HRMS (APCI) (m/z): $[M + H]^+$ ($C_{19}H_{23}O_3$) calc.: 299.1642, found: 299.1644.
MF: $C_{19}H_{22}O_3$
MW: 298.38 g/mol

Benzyl 4-methoxy-2-methylpentanoate (4j)



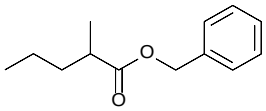
Yield: 82 mg, 0.35 mmol, 58%.

^{1}H NMR (400 MHz, $CDCl_3$): (mixture of diastereomers); δ [ppm] = 7.39 – 7.29 (m, 5H), 5.16 – 5.09 (m, 2H), 3.34 – 3.25 (m, 1H), 3.25 – 3.22 (m, 3H), 2.80 – 2.60 (m, 1H), 2.03 – 1.76 (m, 1H), 1.60 – 1.40 (m, 1H), 1.21 – 1.16 (m, 3H), 1.14 – 1.08 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 176.8 and 176.7 (C_q), 136.4 (C_q), 128.6 (+), 128.3 (+), 128.22 and 128.21 (+), 75.0 and 74.9 (+), 66.17 and 66.15 (–), 56.3 and 56.1 (+), 41.2 and 40.8 (–), 36.8 and 36.3 (+), 19.3 and 19.1 (+), 18.1 and 17.5 (+).

HRMS (APCI) (m/z): $[M + H]^+$ ($C_{14}H_{21}O_3$) calc.: 237.1485, found: 237.1488.
MF: $C_{14}H_{20}O_3$
MW: 236.31 g/mol

Benzyl 2-methylpentanoate (4k)[19]



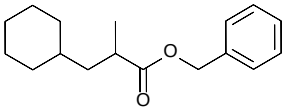
Yield: 36 mg, 0.17 mmol, 29%.[a]

^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm] = 7.38 – 7.31 (m, 5H), 5.12 (s, 2H), 2.59 – 2.40 (m, 1H), 1.73 – 1.58 (m, 1H), 1.48 – 1.37 (m, 1H), 1.34 – 1.25 (m, 2H), 1.16 (d, *J* = 7.0 Hz, 3H), 0.89 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ [ppm] = 176.9 (C_q), 136.4 (C_q), 128.7 (+), 128.22 (+), 128.16 (+), 66.1 (–), 39.5 (+), 36.1 (–), 20.5 (–), 17.2 (+), 14.1 (+).

HRMS (APCI) (m/z): $[M + H]^+$ ($C_{13}H_{19}O_2$) calc.: 207.1380, found: 207.1382.
MF: $C_{13}H_{18}O_2$
MW: 206.29 g/mol

Benzyl 3-cyclohexyl-2-methylpropanoate (4l)[19]



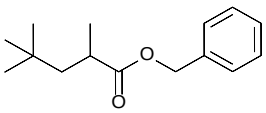
Yield: 63 mg, 0.24 mmol, 40%. [a]

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.39 – 7.29 (m, 5H), 5.20 – 5.08 (m, 2H), 2.68 – 2.53 (m, 1H), 1.75 – 1.57 (m, 6H), 1.27 – 1.19 (m, 8H), 0.90 – 0.80 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 177.2 (C_q), 136.5 (C_q), 128.7 (+), 128.2 (+), 66.1 (–), 41.8 (–), 37.1 (+), 35.5 (+), 33.3 (–), 26.7 (–), 26.4 (–), 17.8 (+).

HRMS (APCI) (m/z): $[M + H]^+$ ($C_{17}H_{25}O_2$) calc.: 261.1849, found: 261.1855.
MF: $C_{17}H_{24}O_2$
MW: 260.38 g/mol

Benzyl 2,4,4-trimethylpentanoate (4m)[20]



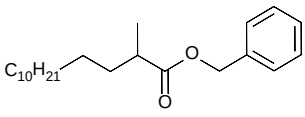
Yield: 63 mg, 0.27 mmol, 45%.[a]

^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm] = 7.39 – 7.33 (m, 5H), 5.09 (s, 2H), 2.65 – 2.46 (m, 1H), 2.02 – 1.80 (m, 2H), 1.18 (d, *J* = 7.1 Hz, 3H), 0.86 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$): δ [ppm] = 177.9 (C_q), 136.2 (C_q), 128.7 (+), 128.32 (+), 128.26 (+), 66.3 (–), 47.9 (–), 36.4 (+), 30.9 (C_q), 29.5 (+), 20.5 (+).

HRMS (ESI) (m/z): $[M + H]^+$ ($C_{15}H_{23}O_2$) calc.: 235.1693, found: 235.1693.
MF: $C_{15}H_{22}O_2$
MW: 234.34 g/mol

Benzyl 2-methyltetradecanoate (4n)



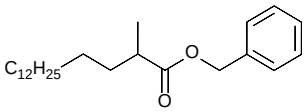
Yield: 62 mg, 0.19 mmol, 31%.[a]

^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm] = 7.45 – 7.26 (m, 5H), 5.12 (s, 2H), 2.58 – 2.25 (m, 1H), 1.74 – 1.59 (m, 1H), 1.51 – 1.38 (m, 1H), 1.36 – 1.21 (m, 20H), 1.17 (d, *J* = 7.0 Hz, 3H), 0.89 (t, *J* = 6.7 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ [ppm] = 176.9 (C_q), 136.4 (C_q), 128.6 (+), 128.21 (+), 128.18 (+), 66.1 (–), 39.7 (+), 34.0 (–), 32.1 (–), 29.81 (–), 29.79 (–), 29.7 (–), 29.64 (–), 29.63 (–), 29.5 (–), 27.3 (–), 22.8 (–), 17.2 (+), 14.3 (+).

HRMS (APCI) (m/z): $[M + H]^+$ ($C_{22}H_{37}O_2$) calc.: 333.2788, found: 333.2788.
MF: $C_{22}H_{36}O_2$
MW: 332.53 g/mol

Benzyl 2-methylhexadecanoate (4o)



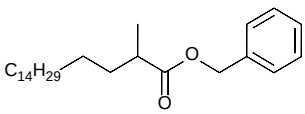
Yield: 69 mg, 0.19 mmol, 32%.[a]

^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm] = 7.44 – 7.26 (m, 5H), 5.12 (s, 2H), 2.55 – 2.29 (m, 1H), 1.74 – 1.59 (m, 1H), 1.51 – 1.39 (m, 1H), 1.36 – 1.21 (m, 24H), 1.17 (d, *J* = 7.0 Hz, 3H), 0.89 (t, *J* = 6.7 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ [ppm] = 176.9 (C_q), 136.4 (C_q), 128.6 (+), 128.21 (+), 128.18 (+), 66.1 (–), 39.7 (+), 34.0 (–), 32.1 (–), 29.84 (–), 29.80 (–), 29.7 (–), 29.6 (–), 29.5 (–), 27.3 (–), 22.8 (–), 17.2 (+), 14.3 (+).

HRMS (APCI) (m/z): $[M + H]^+$ ($C_{24}H_{41}O_2$) calc.: 361.3101, found: 361.3098.
MF: $C_{24}H_{40}O_2$
MW: 360.58 g/mol

Benzyl 2-methyloctadecanoate (4p)



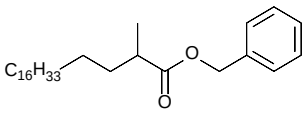
Yield: 72 mg, 0.19 mmol, 31%.[a]

^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm] = 7.40 – 7.26 (m, 5H), 5.12 (s, 2H), 2.56 – 2.29 (m, 1H), 1.74 – 1.58 (m, 1H), 1.50 – 1.39 (m, 1H), 1.33 – 1.22 (m, 28H), 1.17 (d, *J* = 7.0 Hz, 3H), 0.89 (t, *J* = 6.7 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ [ppm] = 176.9 (C_q), 136.4 (C_q), 128.6 (+), 128.20 (+), 128.17 (+), 66.1 (–), 39.7 (+), 34.0 (–), 32.1 (–), 29.9 (–), 29.8 (–), 29.7 (–), 29.6 (–), 29.5 (–), 27.3 (–), 22.8 (–), 17.2 (+), 14.3 (+).

HRMS (APCI) (m/z): $[M + H]^+$ ($C_{26}H_{45}O_2$) calc.: 389.3414, found: 389.3413.
MF: $C_{26}H_{44}O_2$
MW: 388.64 g/mol

Benzyl 2-methylicosanoate (4q)



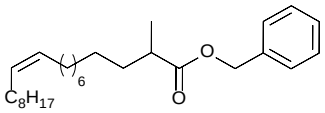
Yield: 75 mg, 0.18 mmol, 30%.[a]

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.39 – 7.29 (m, 5H), 5.12 (s, 2H), 2.57 – 2.41 (m, 1H), 1.73 – 1.61 (m, 1H), 1.47 – 1.39 (m, 1H), 1.31 – 1.23 (m, 32H), 1.17 (d, *J* = 7.0 Hz, 3H), 0.89 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 176.9 (C_q), 136.5 (C_q), 128.6 (+), 128.21 (+), 128.18 (+), 66.1 (–), 39.7 (+), 34.0 (–), 32.1 (–), 29.9 (–), 29.8 (–), 29.73 (–), 29.65 (–), 29.64 (–), 29.5 (–), 27.3 (–), 22.8 (–), 17.2 (+), 14.3 (+).

HRMS (APCI) (m/z): $[M + H]^+$ ($C_{28}H_{49}O_2$) calc.: 417.3727, found: 417.3721.
MF: $C_{28}H_{48}O_2$
MW: 416.69 g/mol

Benzyl (*Z*)-2-methylicos-11-enoate (4r)



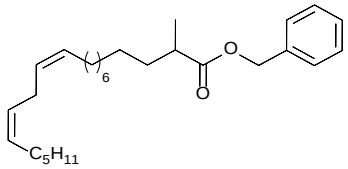
Yield: 69 mg, 0.17 mmol, 28%.[a]

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.42 – 7.26 (m, 5H), 5.44 – 5.26 (m, 2H), 5.22 – 5.00 (m, 2H), 2.54 – 2.29 (m, 1H), 2.10 – 1.93 (m, 4H), 1.76 – 1.57 (m, 1H), 1.49 – 1.38 (m, 1H), 1.37 – 1.21 (m, 24H), 1.16 (d, *J* = 7.0 Hz, 3H), 0.88 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 176.9 (C_q), 136.5 (C_q), 130.1 (+), 130.0 (+), 128.7 (+), 128.22 (+), 128.19 (+), 66.1 (–), 39.7 (+), 34.0 (–), 32.1 (–), 29.92 (–), 29.91 (–), 29.7 (–), 29.64 (–), 29.62 (–), 29.61 (–), 29.5 (–), 29.4 (–), 27.4 (–), 27.3 (–), 22.8 (–), 17.2 (+), 14.3 (+).

HRMS (APCI) (m/z): $[M + H]^+$ ($C_{28}H_{47}O_2$) calc.: 415.3571, found: 415.3569.
MF: $C_{28}H_{46}O_2$
MW: 414.67 g/mol

Benzyl (11*Z*,14*Z*)-2-methylicosa-11,14-dienoate (4s)



Yield: 74 mg, 0.18 mmol, 30%.[a]

^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm] = 7.43 – 7.26 (m, 5H), 5.44 – 5.28 (m, 4H), 5.12 (s, 2H), 2.78 (t, *J* = 5.9 Hz, 2H), 2.57 – 2.40 (m, 1H), 2.10 – 1.99 (m, 4H), 1.76 – 1.60 (m, 1H), 1.50 – 1.22 (m, 19H), 1.16 (d, *J* = 7.0 Hz, 3H), 0.89 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ [ppm] = 176.9 (C_q), 136.4 (C_q), 130.34 (+), 130.29 (+), 128.7 (+), 128.22 (+), 128.19 (+), 128.10 (+), 128.07 (+), 66.1 (–), 39.7 (+), 33.9 (–), 31.7 (–), 29.8 (–), 29.63 (–), 29.61 (–), 29.60 (–), 29.5 (–), 29.4 (–), 27.4 (–), 27.3 (–), 25.8 (–), 22.7 (–), 17.2 (+), 14.2 (+).

HRMS (CI) (m/z): $[M + H]^+$ ($C_{28}H_{45}O_2$) calc.: 413.3414, found: 413.3412.
MF: $C_{28}H_{44}O_2$
MW: 412.66 g/mol

3. Measurement of oxygen concentration during the reaction

For *in situ* monitoring of the oxygen concentration, Fibox 3 fibre optic oxygen sensor (PreSens GmbH) was used. In a 5 mL crimp cap vial were weighed eosin Y (**A**, 4.9 mg, 0.01 mmol, 0.1 equiv.), *N*-(acyloxy)phthalimide **1a** (27.0 mg, 0.08 mmol, 1.0 equiv.), **2a** (53.0 µL, 0.38 mmol, 5.0 equiv.) and DIPEA (26.0 µL, 0.15 mmol, 2.0 equiv.). After addition of a magnetic stirring bar and dry CH_3CN (1 mL), the vessel was capped and the reaction mixture was stirred and irradiated with a green LED (535 nm) for 18 h at rt while the concentration of oxygen was measured.

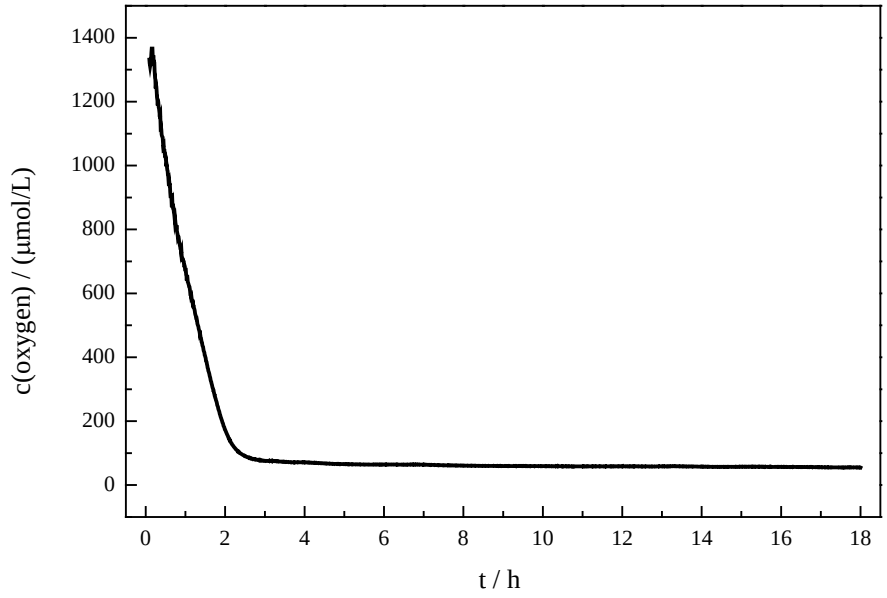


Figure S1. Concentration of oxygen during the reaction of *N*-(acyloxy)phthalimide **1a** with n-butylacrylate (**2a**) in the presence of DIPEA and eosin Y (with CH_3CN as solvent).

4. Stability of eosin Y and time course of the photoreaction

The stability of the photocatalyst and the time course of product formation during the reaction were investigated in parallel. In a 5 mL crimp cap vial were weighed eosin Y (**A**, 19.4 mg, 0.03 mmol, 0.1 equiv.), *N*-(acyloxy)phthalimide **1a** (108 mg, 0.30 mmol, 1.0 equiv.), **2a** (214 µL, 1.50 mmol, 5.0 equiv.) and DIPEA (102 µL, 0.60 mmol, 2.0 equiv.). After addition of a magnetic stirring bar and dry CH_2Cl_2 (4 mL), the vessel was capped and the reaction mixture was stirred and irradiated with green LEDs (535 nm) for 19 h at rt.

The slow degradation of the eosin Y was investigated by hourly measurement of the UV-vis absorption spectrum of the reaction mixture. Therefore, the mixture was diluted to a catalyst concentration of 4.65 µM.

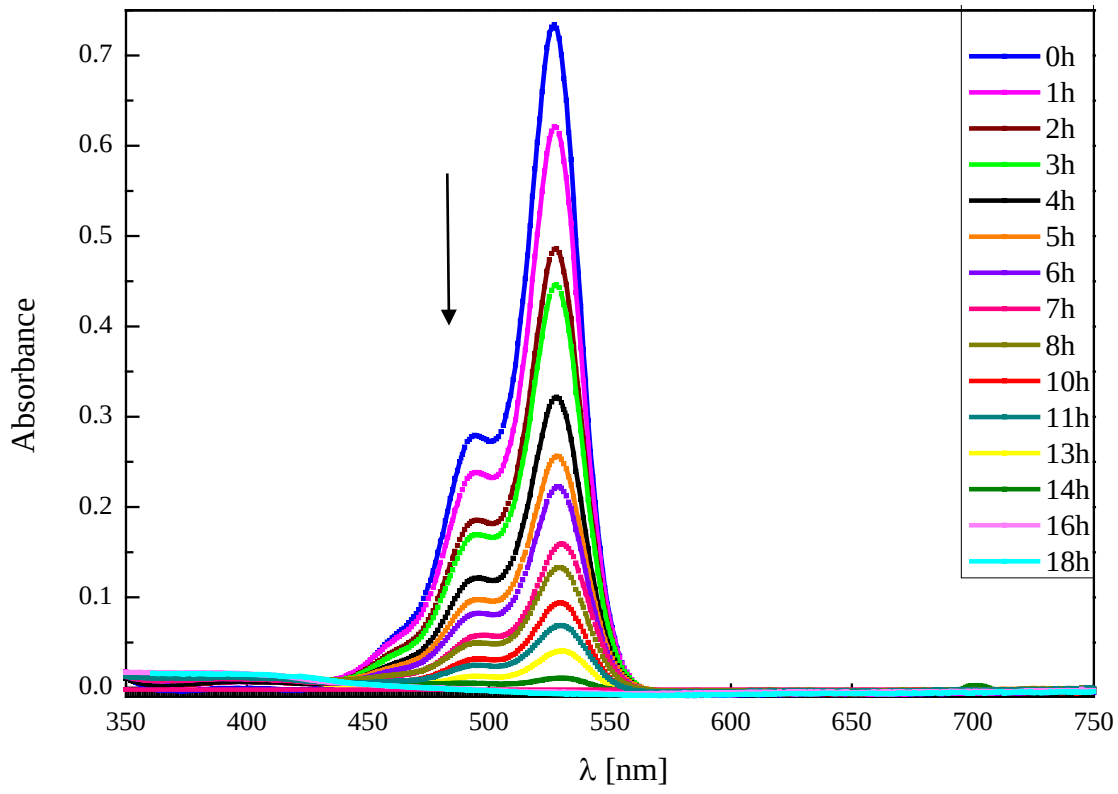


Figure S2. Changes in the UV-Vis absorption spectra of the reaction mixture (4.65 µM eosin Y) upon irradiation with green LEDs.

For determination of the time course of the product formation, the yield was determined every hour by quantitative GC using naphthalene as internal standard.

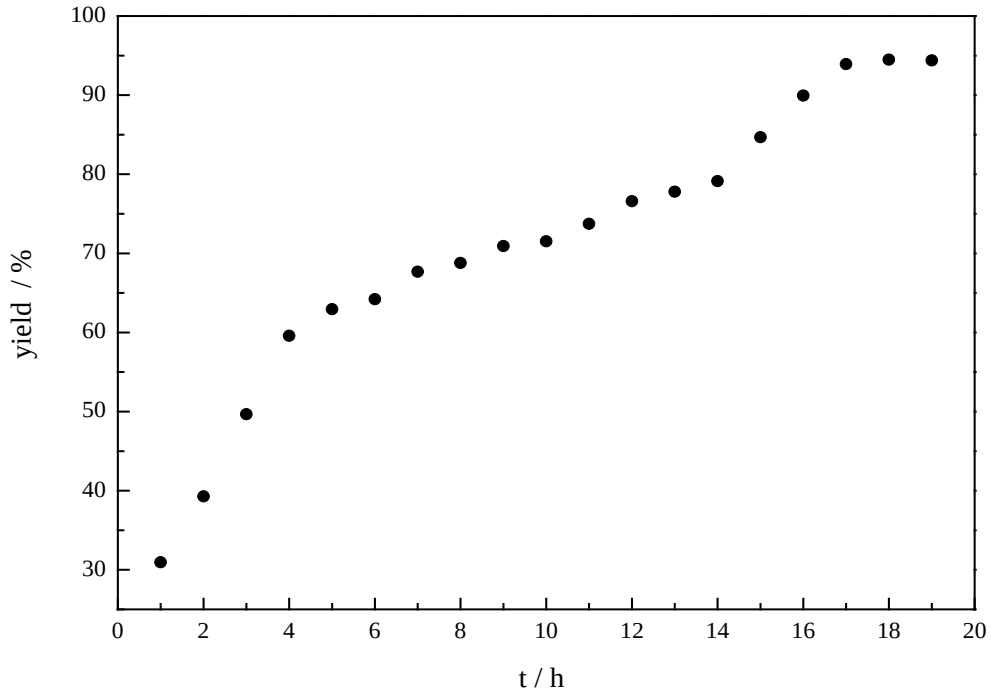


Figure S3. Time course of the photocatalytic product formation determined by quantitative GC using naphthalene as internal standard.

5. Cyclic voltammetry measurement

CV measurements were performed with the three-electrode potentiostat galvanostat PGSTAT302N from Metrohm Autolab using a glassy carbon working electrode, a platinum wire counter electrode, a silver wire as a reference electrode and TBATFB 0.1 M as supporting electrolyte. The potentials were achieved relative to the Fc/Fc^+ redox couple with ferrocene as internal standard.[21] The control of the measurement instrument, the acquisition and processing of the cyclic voltammetric data were performed with the software Metrohm Autolab NOVA 1.10.4. The measurements were carried out as follows: a 0.1 M solution of TBATFB in CH_3CN was added to the measuring cell and the solution was degassed by argon purge for 5 min. After recording the baseline the electroactive compound was added (0.01 M) and the solution was again degassed a stream of argon for 5 min. The cyclic voltammogram was recorded with one to three scans. Afterwards ferrocene (2.20 mg, 12.0 μmol) was added to the solution which was again degassed by argon purge for 5 min and the final measurement was performed with three scans.

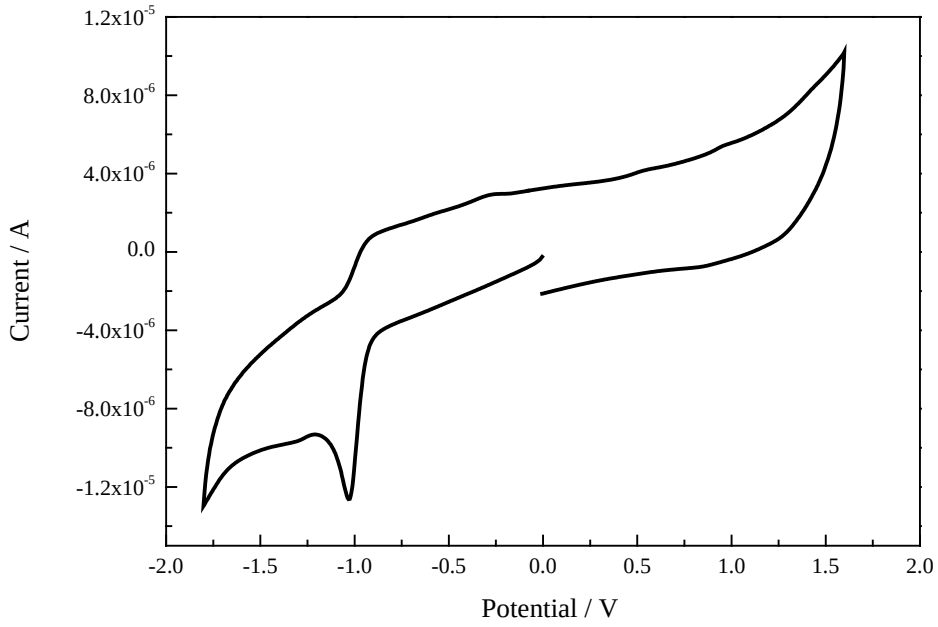
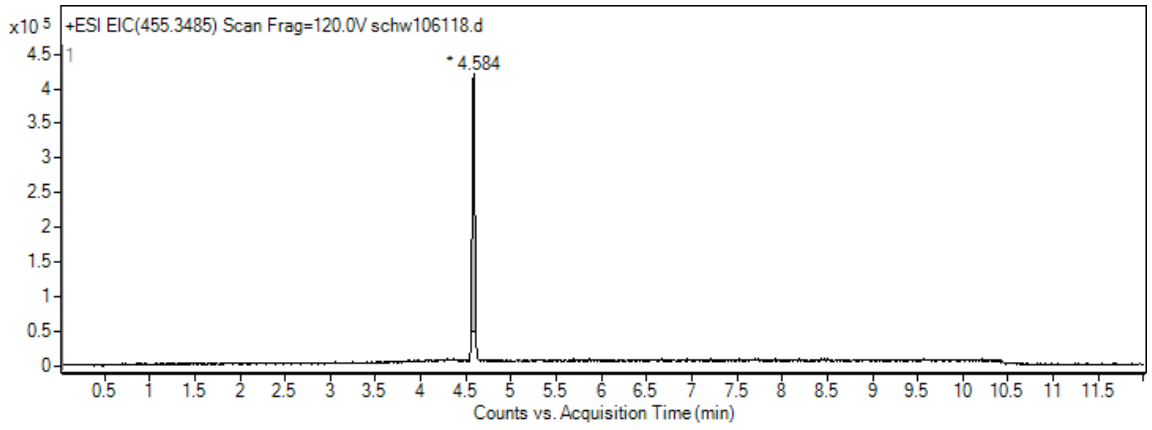
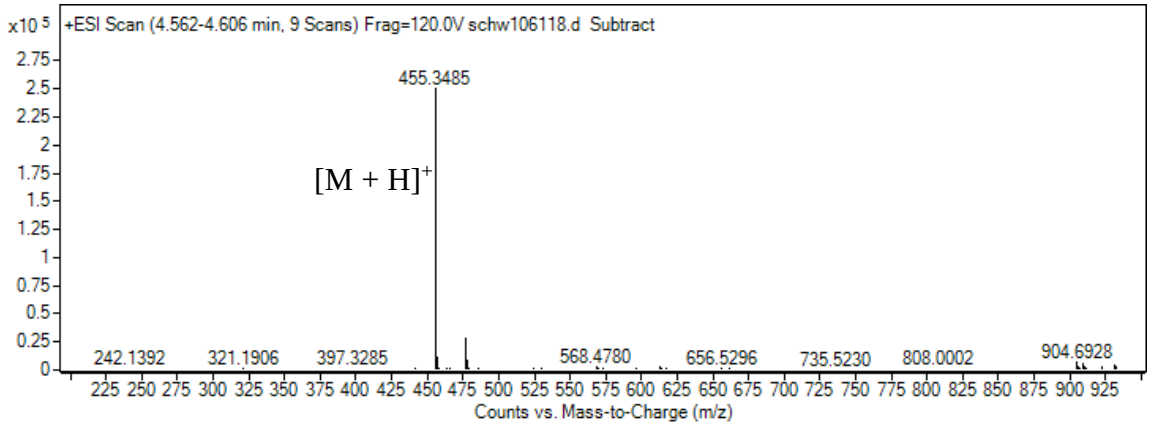


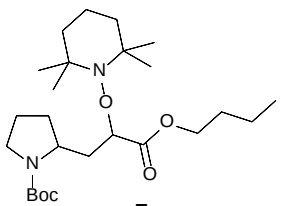
Figure S4. Cyclic voltammogram of Boc-proline-*N*-(acyloxy)phthalimide (**1a**) in CH_3CN under argon. The irreversible peak at -1.03 V shows the reduction of **1a** which corresponds to the reduction potential of -1.20 V vs. SCE.

6. TEMPO trapping of radical intermediates

In a 5 mL crimp cap vial with a stirring bar were weighed eosin Y (**A**, 48.6 mg, 0.08 mmol, 1.0 equiv.), *N*-(acyloxy)phthalimide **1a** (27.0 mg, 0.08 mmol, 1.0 equiv.), **2a** (53.0 µL, 0.38 mmol, 5.0 equiv.), DIPEA (26.0 µL, 0.15 mmol, 2.0 equiv.) and TEMPO (14.6 mg, 0.09 mmol, 1.25 equiv.). After addition of dry CH_2Cl_2 (1 mL), the vessel was capped and the reaction mixture was stirred and irradiated with green LEDs (535 nm) for 18 h at rt. After irradiation, the orange reaction mixture was submitted to mass spectrometry (LC-MS) without any further work-up.







5

MS (ESI) (m/z): $[M + H]^+$ ($C_{25}H_{47}N_2O_5$) calc.: 455.3479, found: 455.3485.

7. Fluorescence titration of photocatalysts

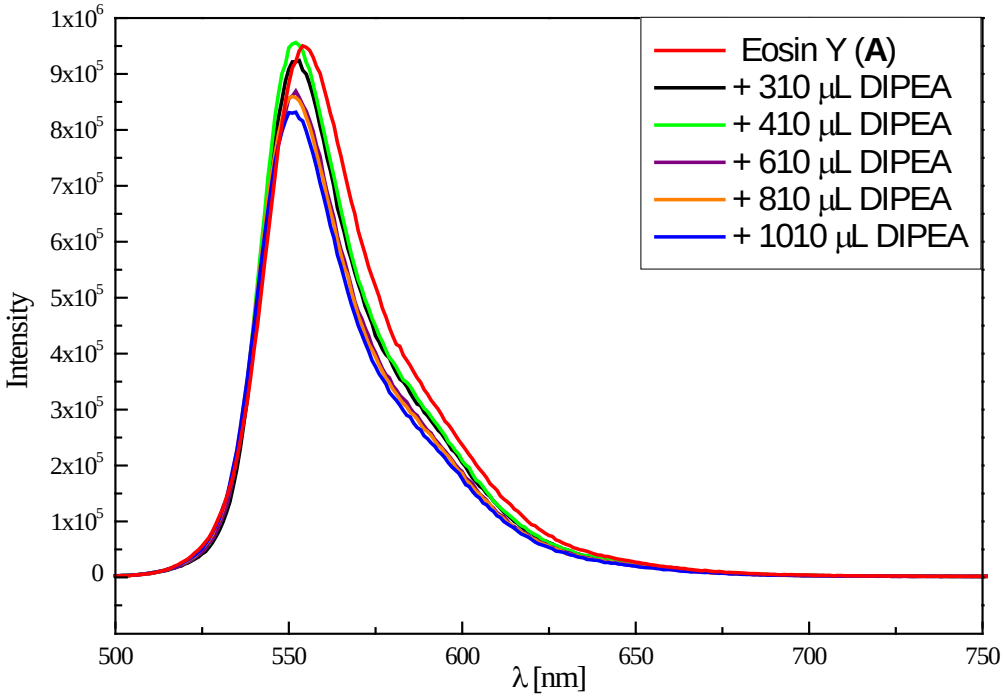


Figure S5. Changes in the fluorescence spectrum of eosin Y (**A**, 15.0 µM in CH_2Cl_2) upon titration with DIPEA (100 mM in CH_2Cl_2).

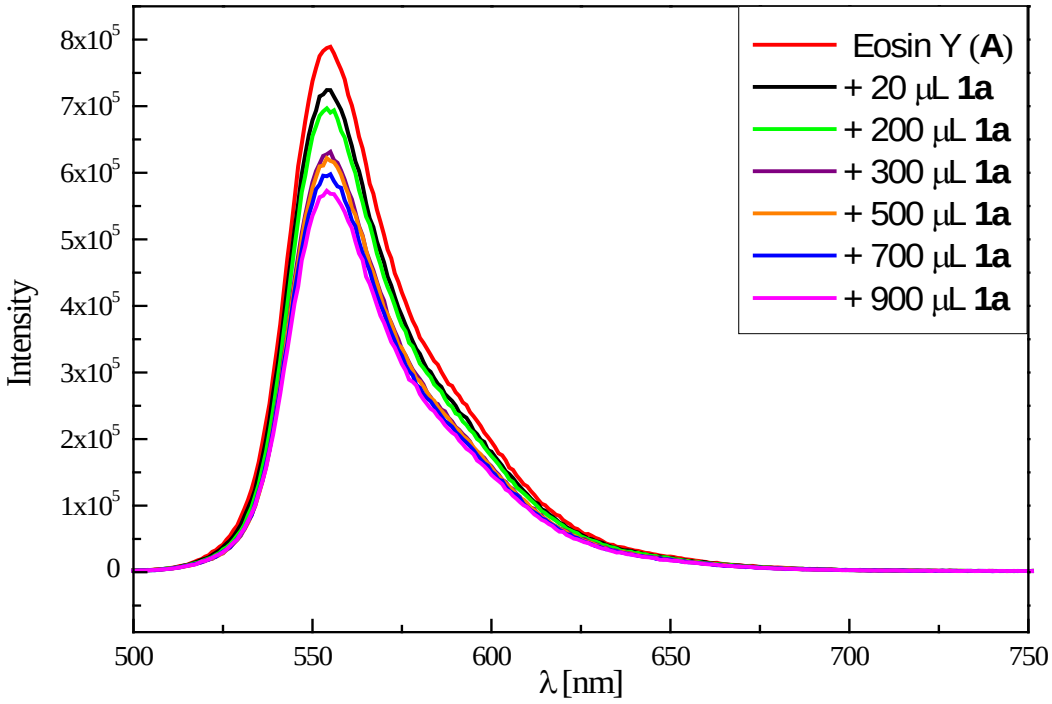


Figure S6. Fluorescence response of eosin Y (**A**, 15.0 µM in CH_2Cl_2) upon successive addition of active ester **1a** (100 mM in CH_2Cl_2).

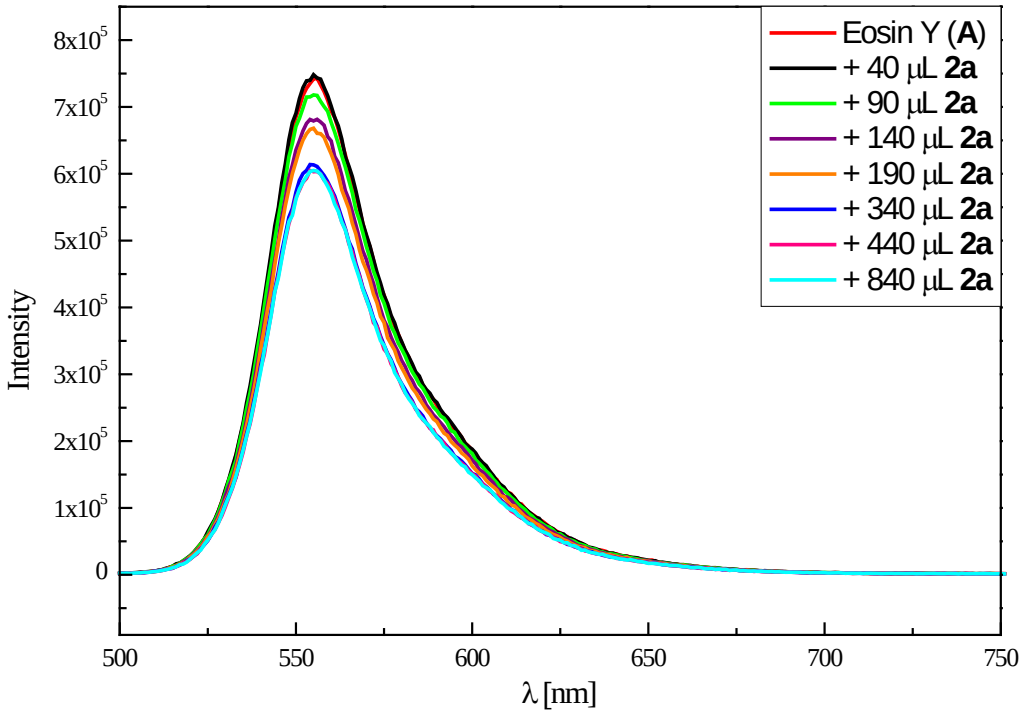


Figure S7. Fluorescence titration of eosin Y (**A**, 15.0 µM in CH_2Cl_2) with n-butylacrylate (**2a**, 100 mM in CH_2Cl_2).

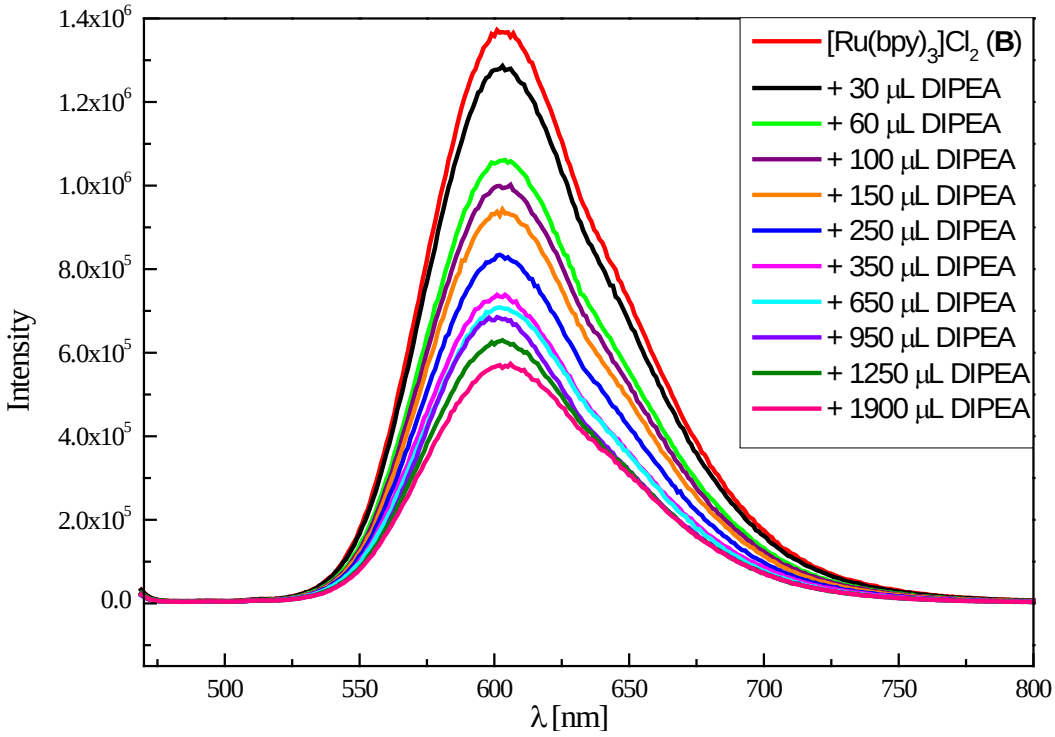


Figure S8. Fluorescence quenching of $[Ru(bpy)_3]Cl_2$ (**B**, 15.0 µM in CH_3CN) upon titration with DIPEA (100 mM in CH_3CN).

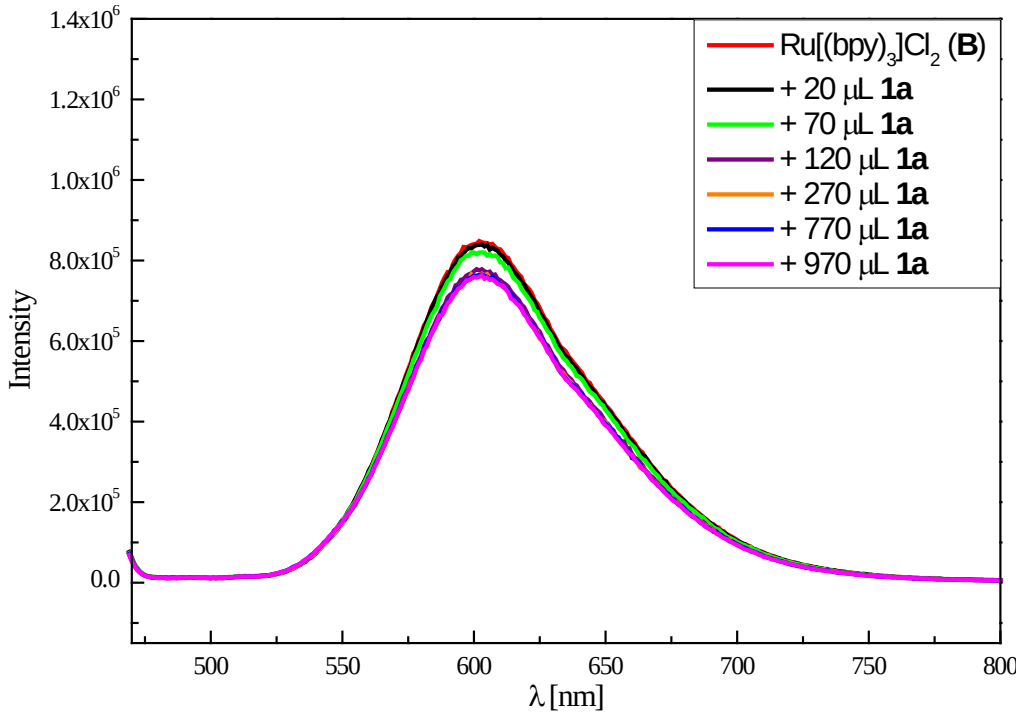


Figure S9. Fluorescence response of $[Ru(bpy)_3]Cl_2$ (**B**, 15.0 µM in CH_3CN) upon successive addition of active ester **1a** (100 mM in CH_3CN).

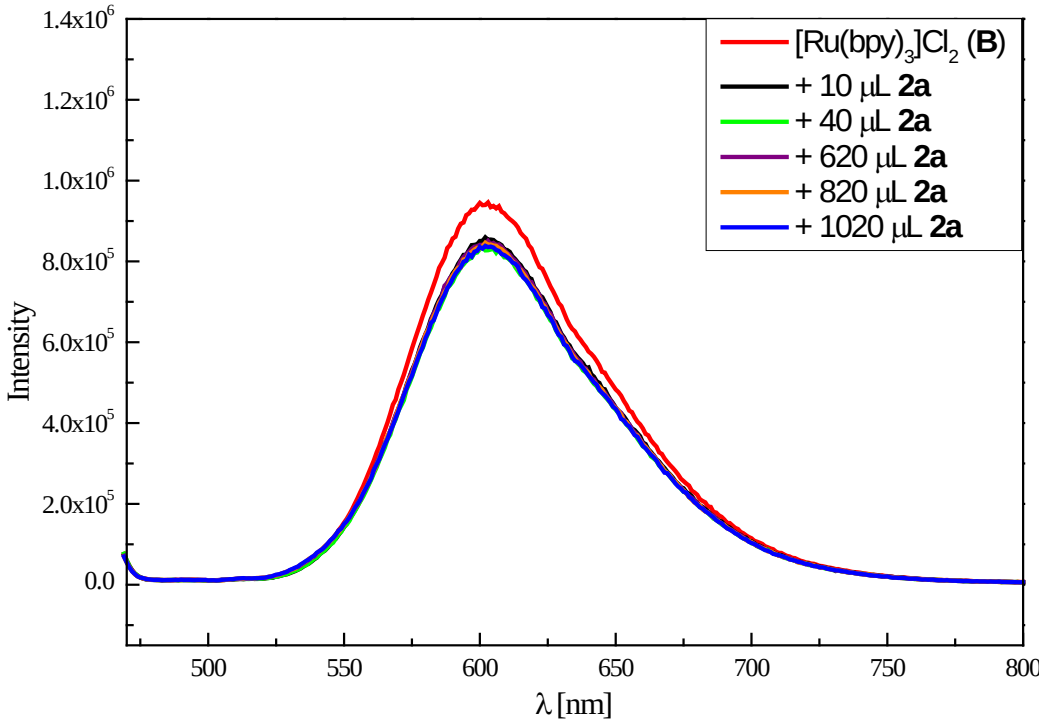


Figure S10. Fluorescence titration of $[Ru(bpy)_3]Cl_2$ (**B**, 15.0 µM in CH_3CN) with n-butylacrylate (**2a**, 100 mM in CH_3CN).

8. Quantum yield determination

The quantum yield was measured with a quantum yield determination setup: translation stages (horizontal and vertical): Thorlabs DT 25/M or DT S25/M; photographic lens with f = 50 mm; magnetic stirrer: Faulhaber motor (1524B024S R) with 14:1 gear (15A); PS19Q power sensor from Coherent; PowerMax software; adjustable power supply "Basetech BT-153 0–15 V/DC 0–3 A 45 W".[22]

The quantum yield of a model photocatalytic reaction was determined by a method developed by our group.[22] A reaction mixture of **1a** (54.1 mg, 0.15 mmol, 1 equiv.), **2a** (107 µL, 0.75 mmol, 5 equiv.), DIPEA (51.0 µL, 0.30 mmol, 2 equiv.), eosin Y (**A**, 9.7 mg, 10 mol%) and CH_2Cl_2 (2 mL) was prepared in a 10 mm Hellma® quartz fluorescence cuvette with a stirring bar. The measurement of quantum yield was accomplished in covered apparatus to minimize the ambient light. The cuvette with solvent (CH_2Cl_2, 2 mL) and a stirring bar was placed in the beam of a 528 nm LED and the transmitted power (P_{ref} = 19.6 mW) was measured by a calibrated photodiode horizontal to the cuvette. The content of the cuvette was changed to the reaction mixture and the transmitted power (P_{sample} = 95.2 µW) was measured analogously to the blank solution. The sample was further irradiated and the transmitted power as well as the respective yield of photocatalytic product (measured by quantitative GC using naphthalene as internal standard) were recorded after different times (Table **S1**).

The quantum yield was calculated from equation **E1**:

$$\Phi = \frac{N_{product}}{N_{ph}} = \frac{N_A * n_{product}}{\frac{E_{light}}{E_{ph}}} = \frac{N_A * n_{product}}{\frac{P_{absorbed} * t}{\frac{h*c}{\lambda}}} = \frac{h * c * N_A * n_{product}}{\lambda * \left(P_{ref} - P_{sample}\right) * t} \quad (\mathbf{E1})$$

where Φ is the quantum yield, $N_{product}$ is the number of product molecules created, N_{ph} is the number of photons absorbed, N_A is Avogadro's constant in moles^{-1}, $n_{product}$ is the molar amount of molecules created in moles, E_{light} is the energy of light absorbed in Joules, E_{ph} is the energy of a single photon in Joules, $P_{absorbed}$ is the radiant power absorbed in Watts, t is the irradiation time in sec, h is the Planck's constant in J×s, c is the speed of light in m s^{-1}, λ is the wavelength of irradiation source (528 nm) in meters, P_{ref} is the radiant power transmitted by a blank vial in Watts and P_{sample} is the radiant power transmitted by the vial with reaction mixture in Watts.

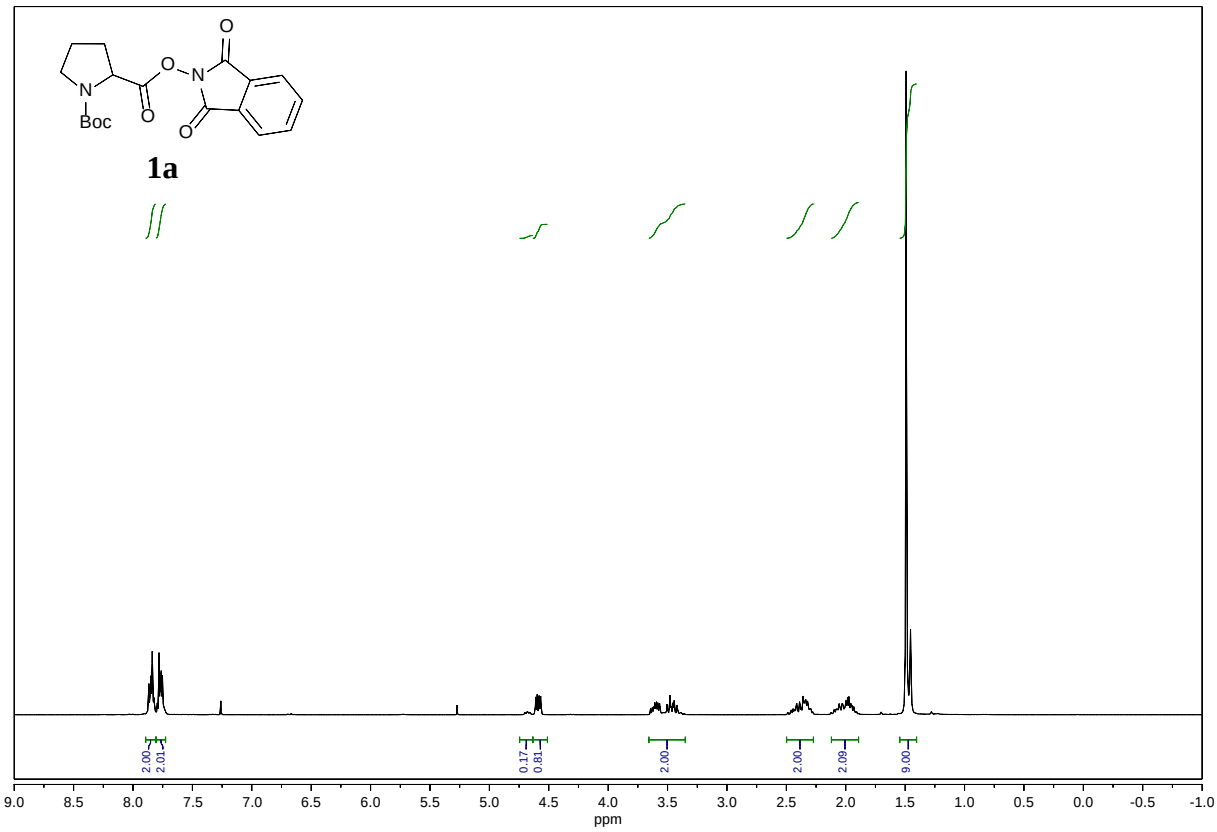
Table S1: Calculation of the quantum yield Φ after different irradiation times.

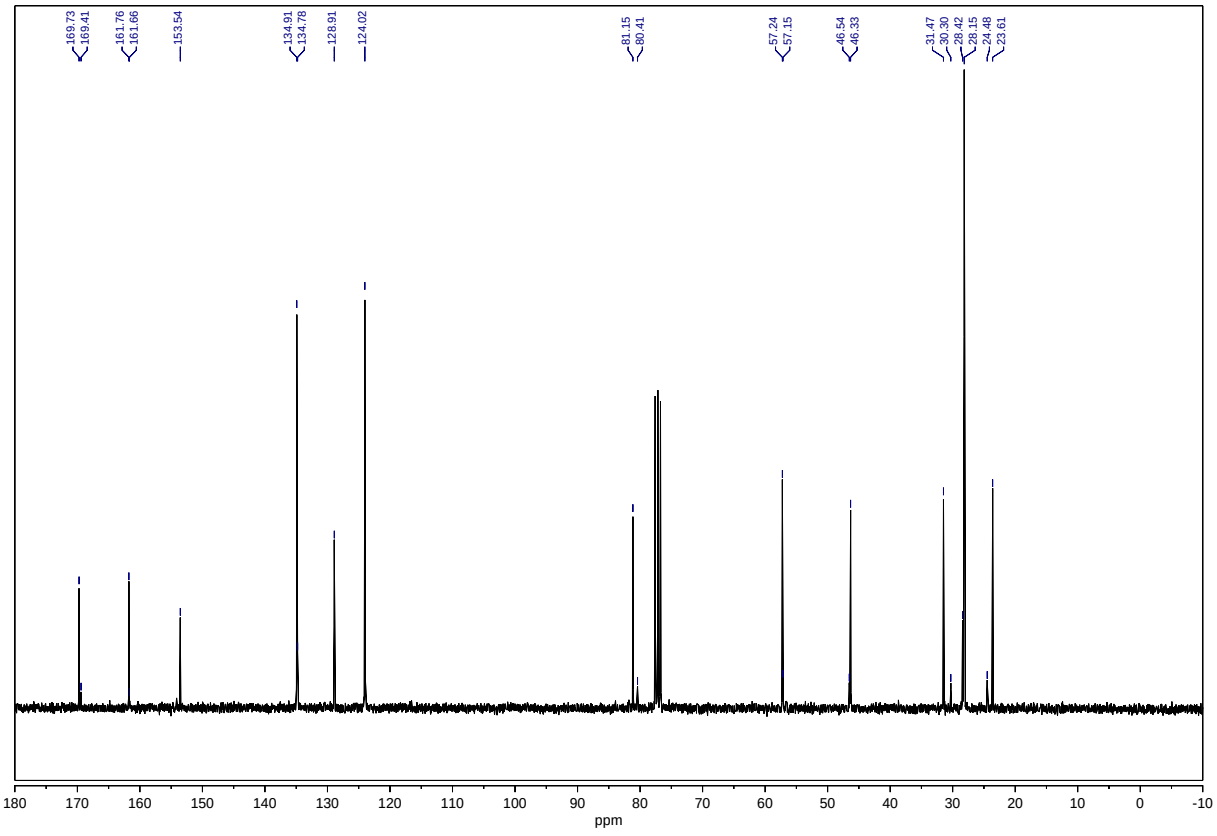
entry	irradiation time / h	P_{sample} / µW	yield / %	Φ / %
1	1	163.5	7	3.2
2	5	5.5	26	2.2
3	8.75	1.1	52	2.5

From these three measurements the mean value for the quantum yield was calculated to be **Φ = 2.6 ± 0.5 %**.

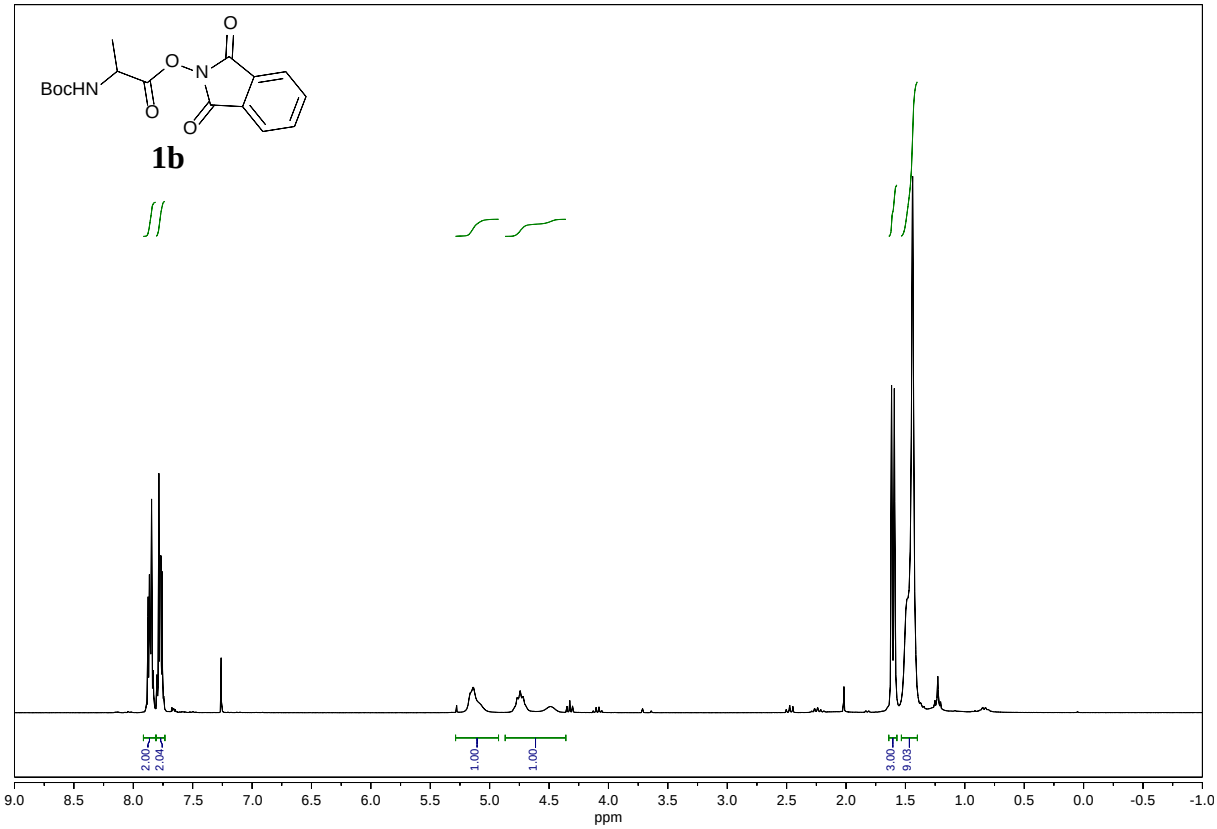
9. ^{1}H- and ^{13}C-NMR spectra

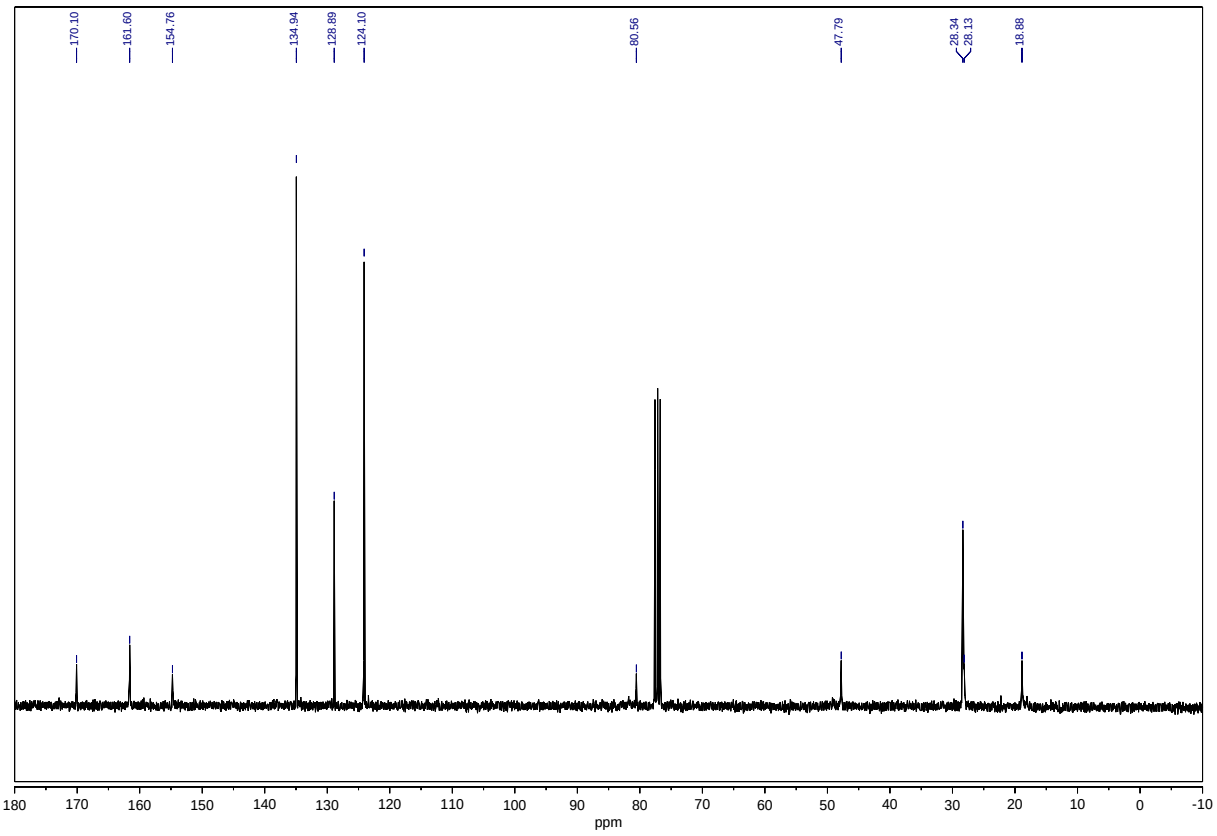
^{1}H- and ^{13}C-NMR in $CDCl_3$ of compound **1a**:



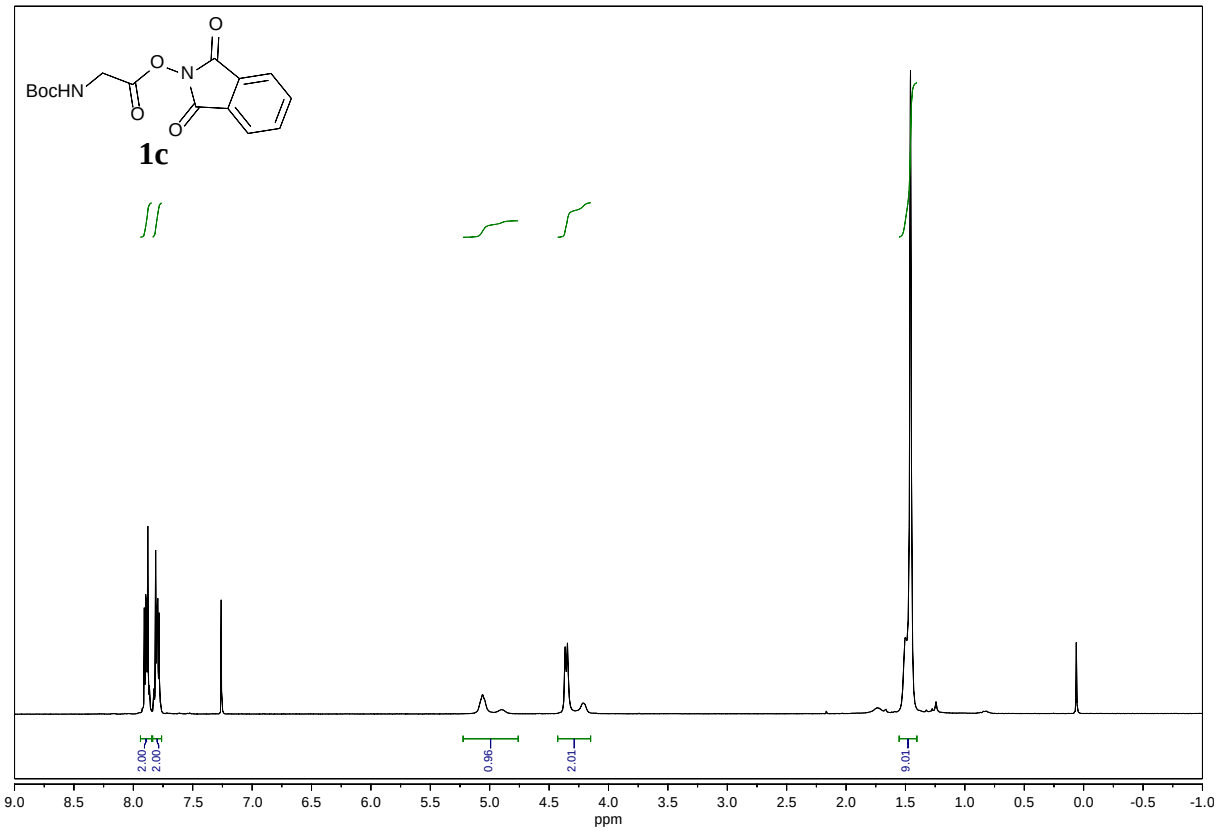


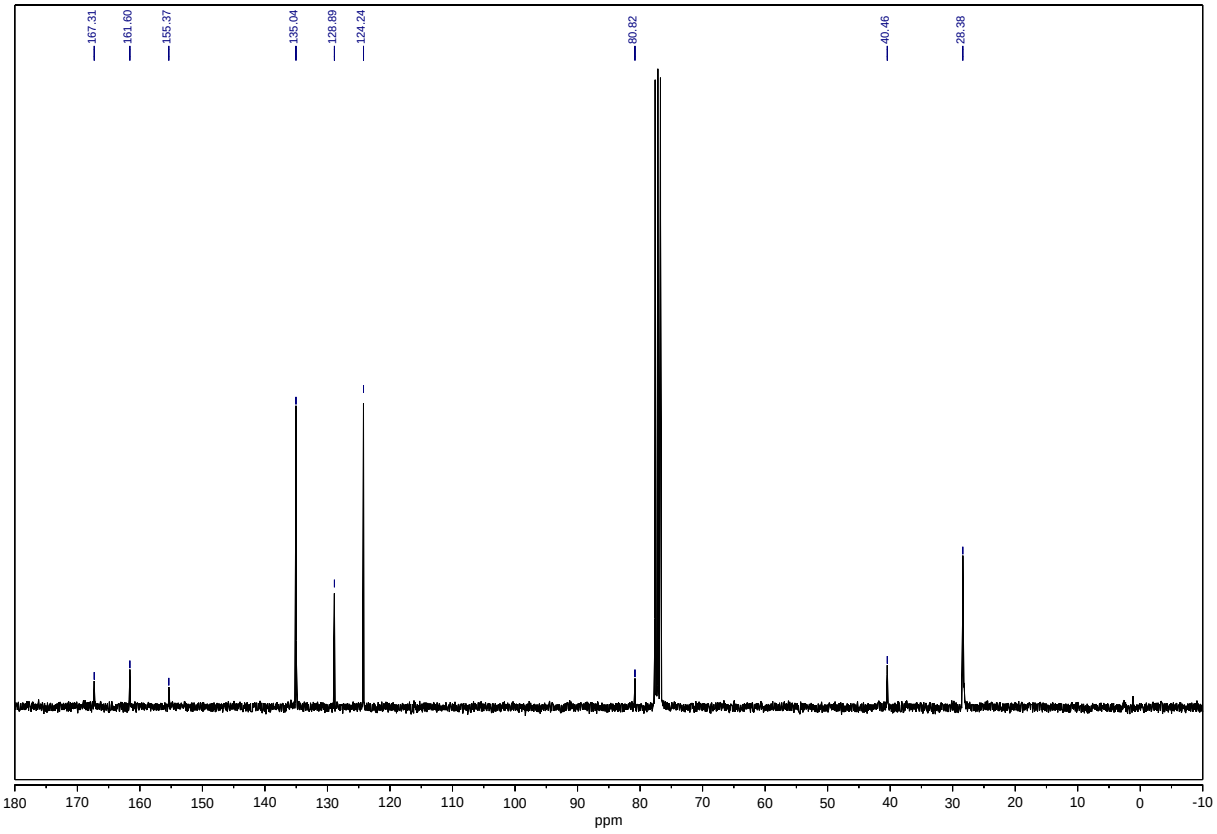
^{1}H- and ^{13}C-NMR in $CDCl_3$ of compound **1b**:



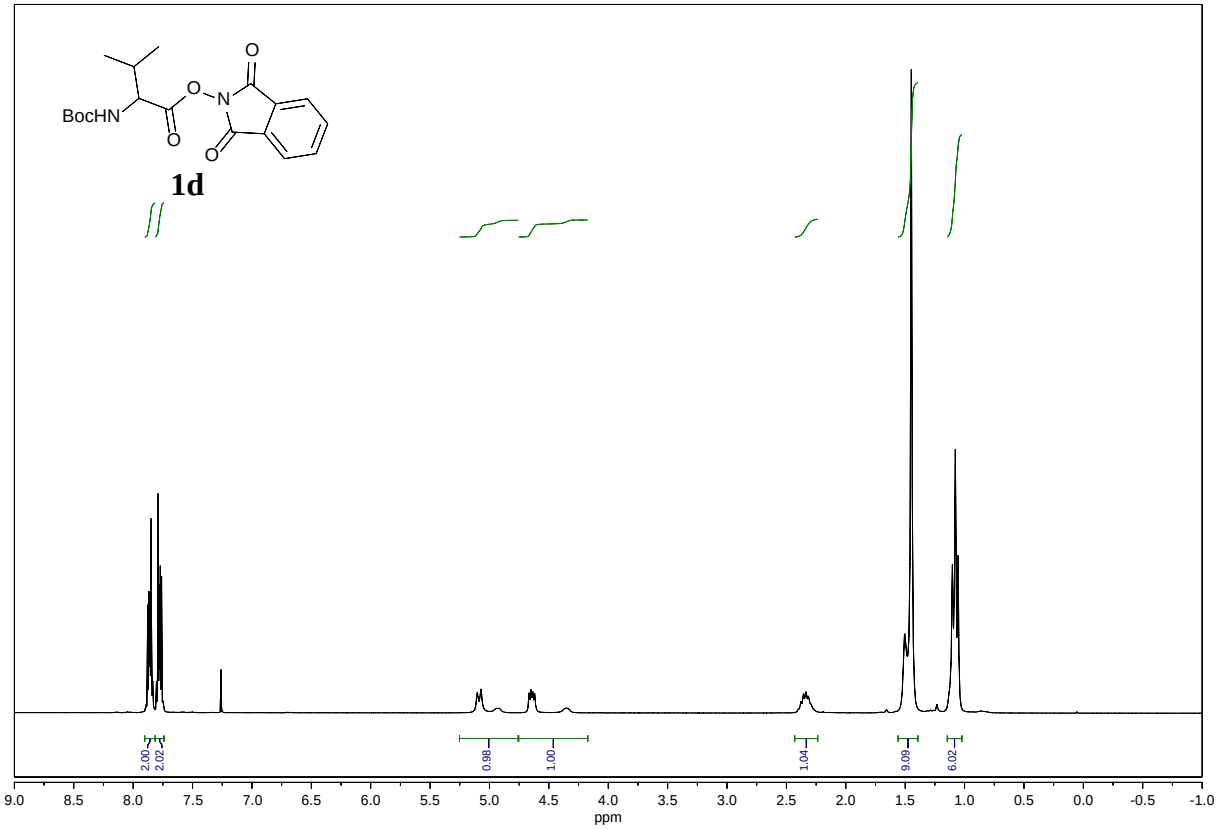


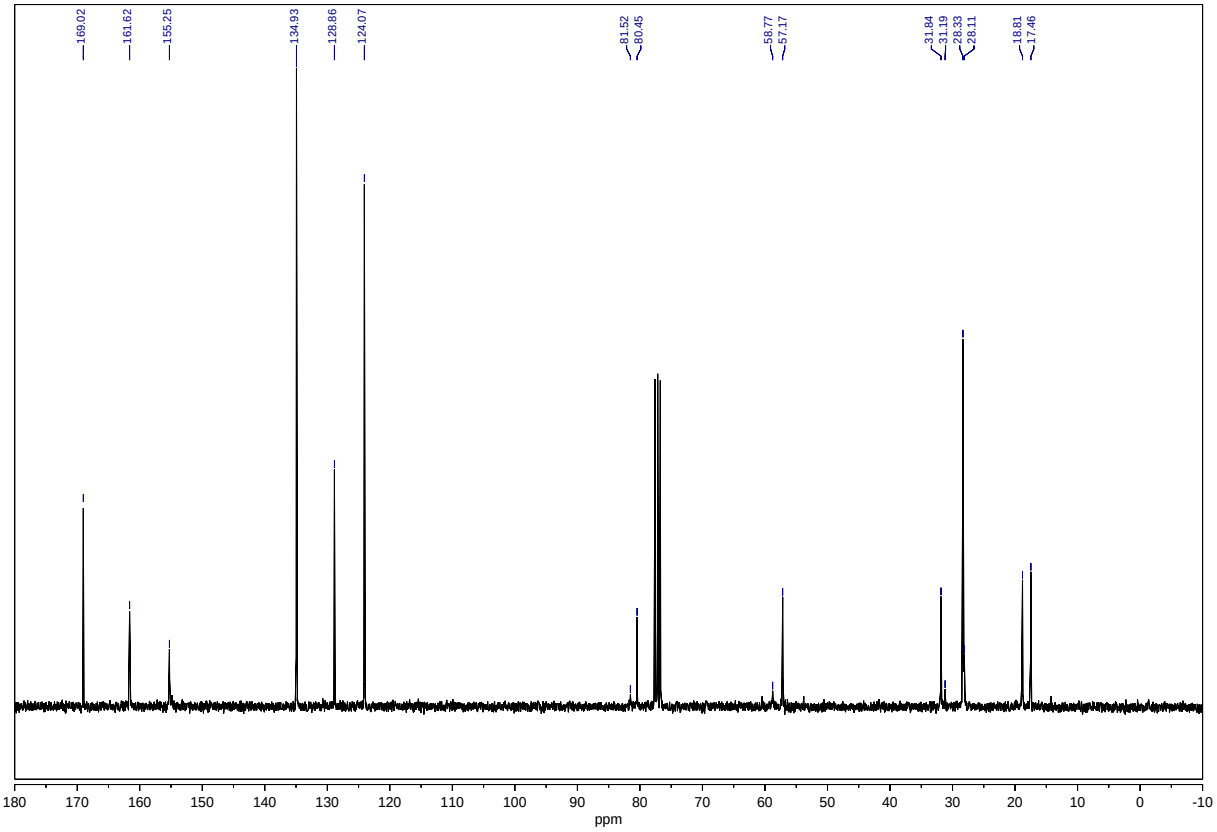
^{1}H- and ^{13}C-NMR in $CDCl_3$ of compound **1c**:



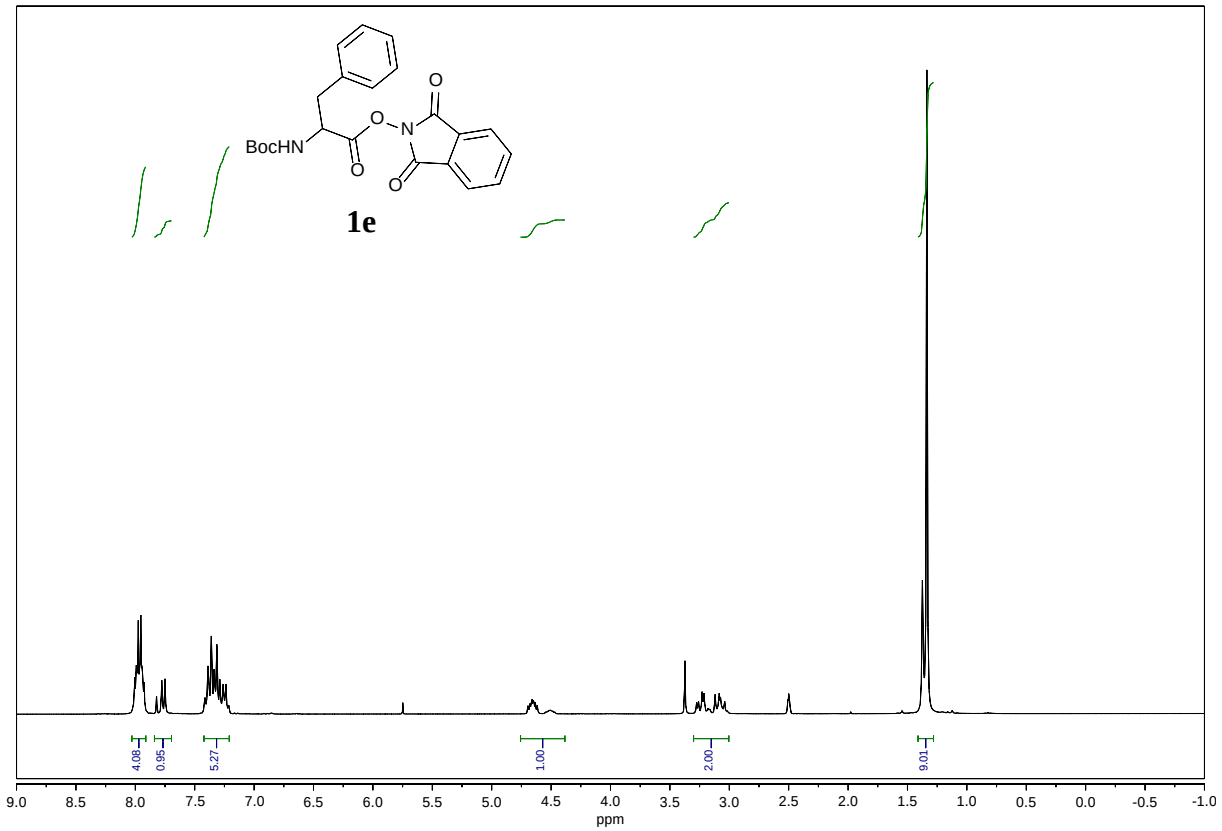


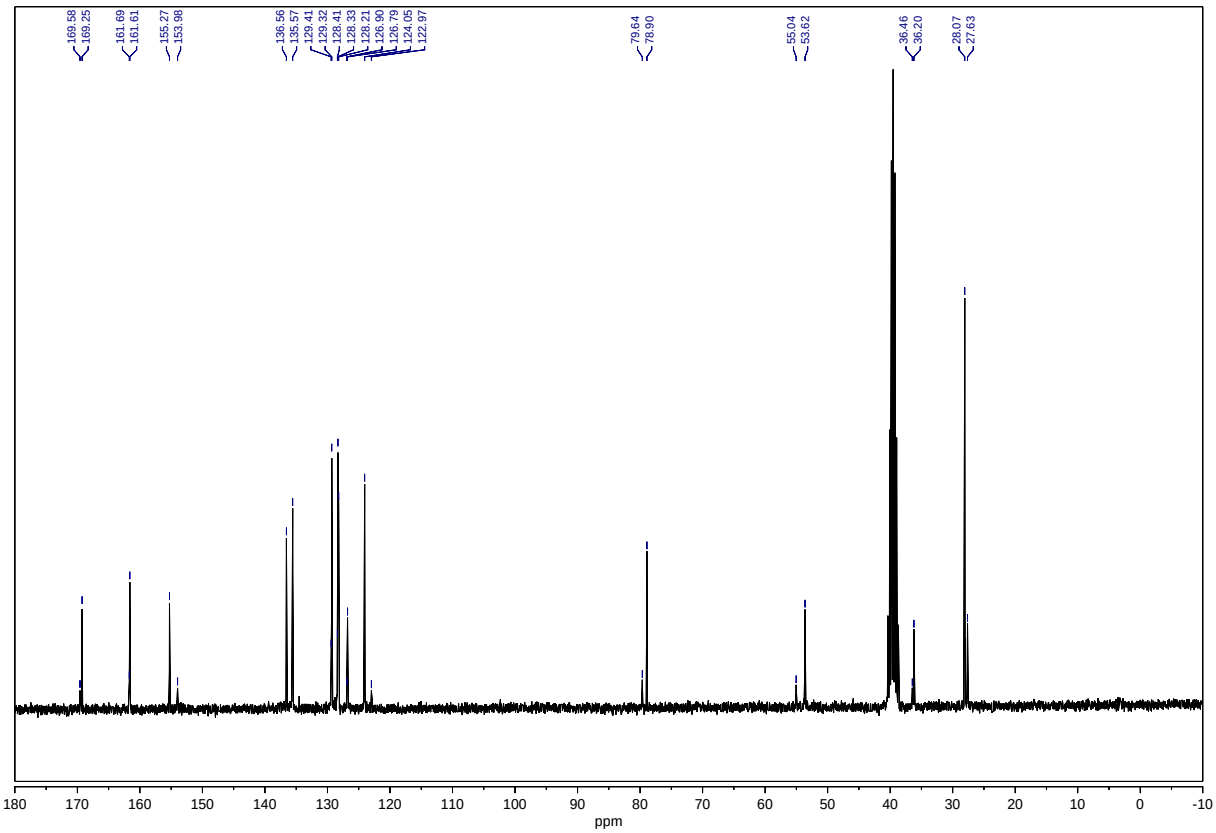
^{1}H- and ^{13}C-NMR in $CDCl_3$ of compound **1d**:



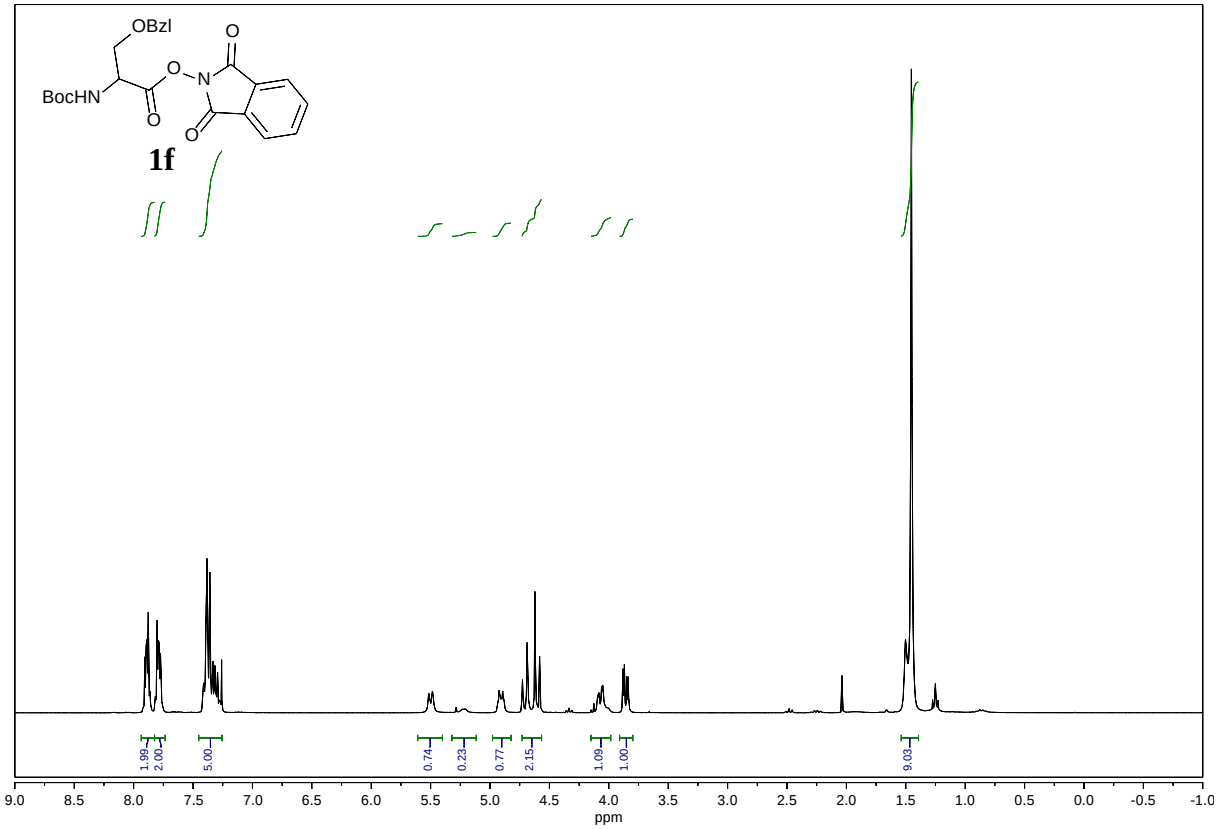


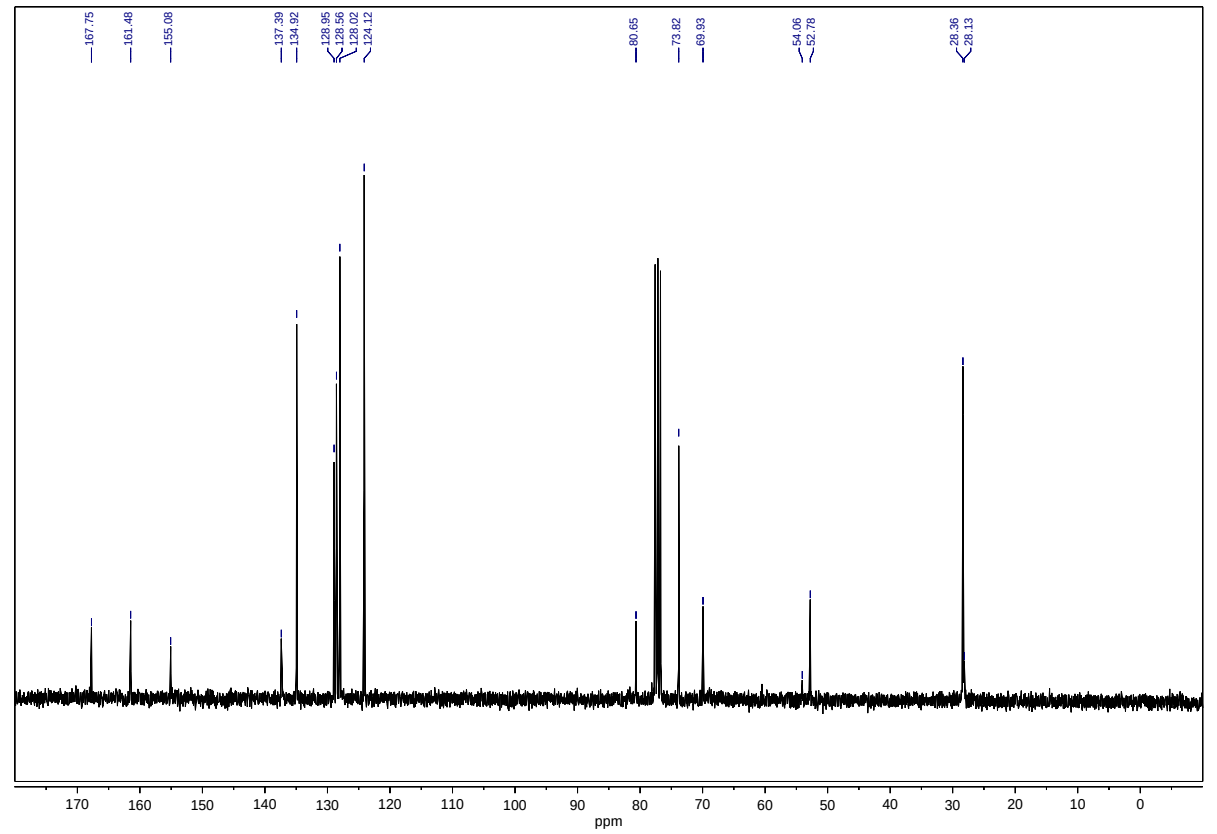
^{1}H- and ^{13}C-NMR in DMSO-d_6 of compound **1e**:



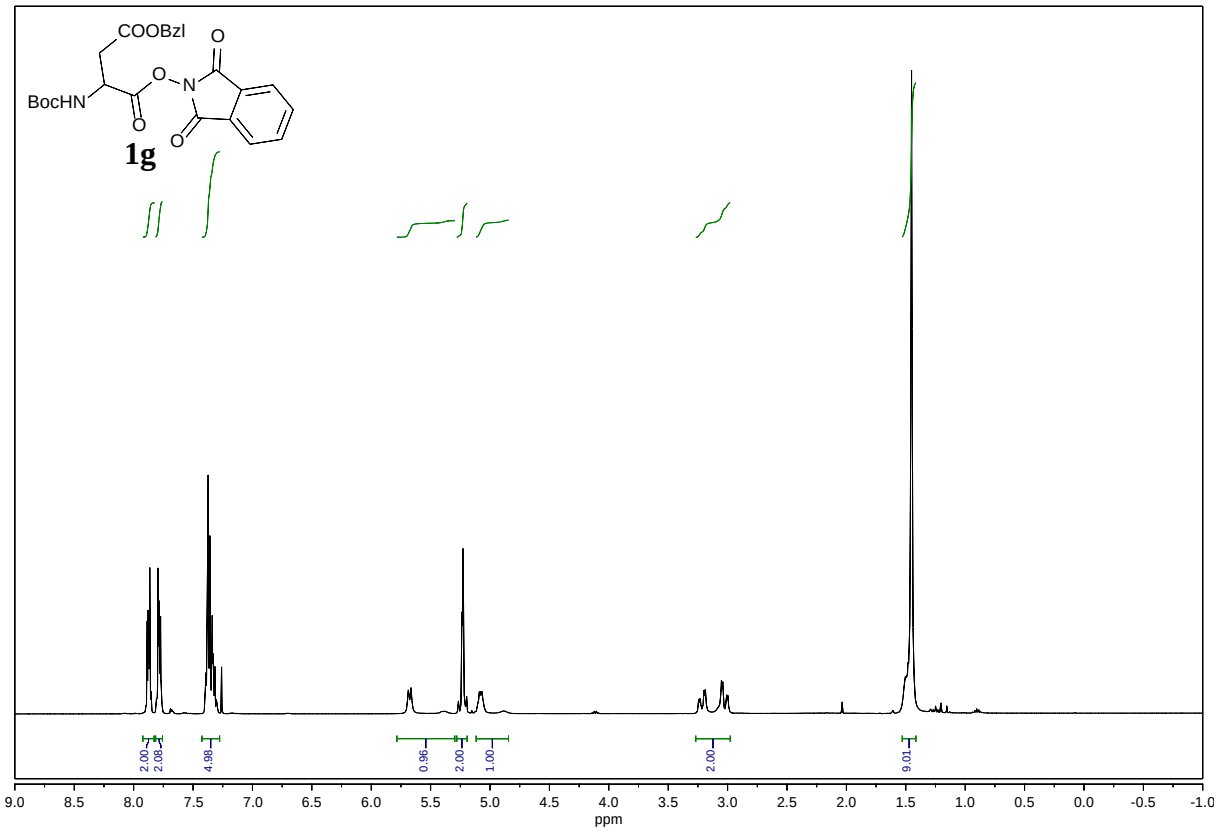


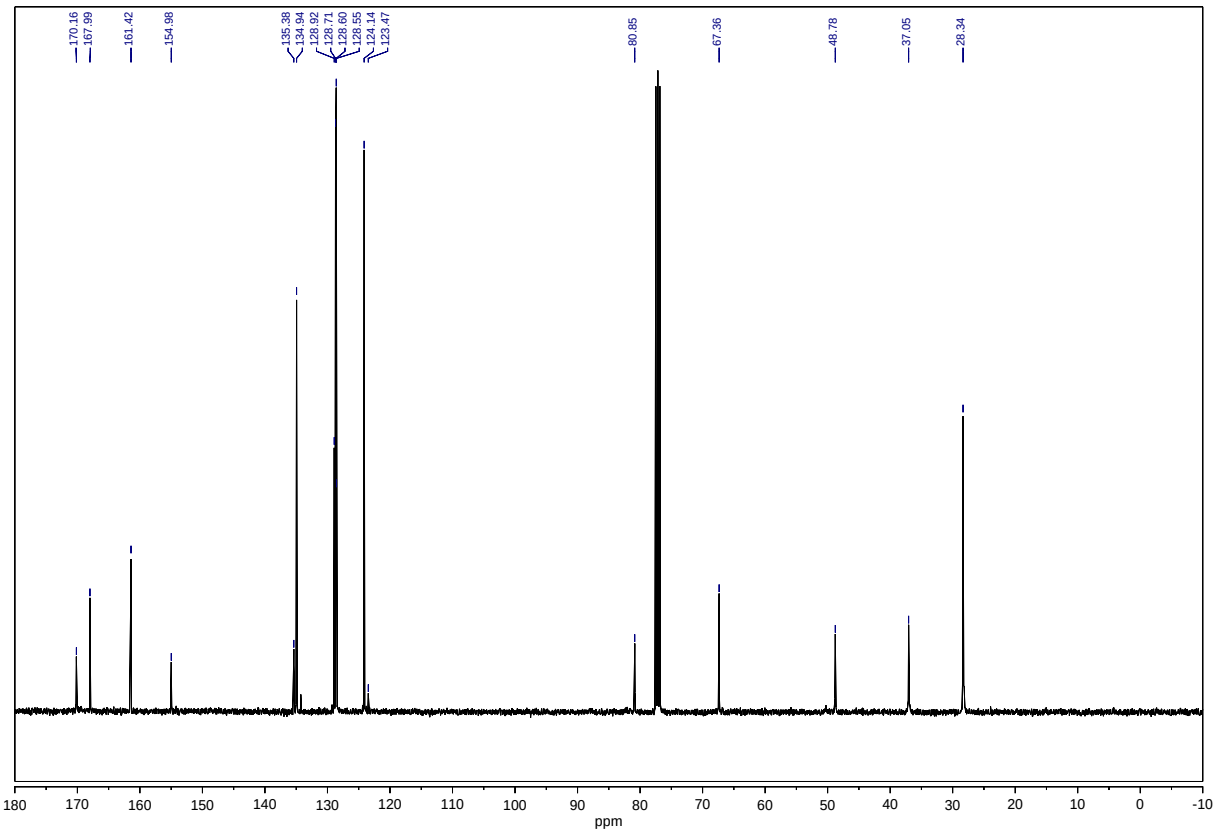
^{1}H- and ^{13}C-NMR in $CDCl_3$ of compound **1f**:



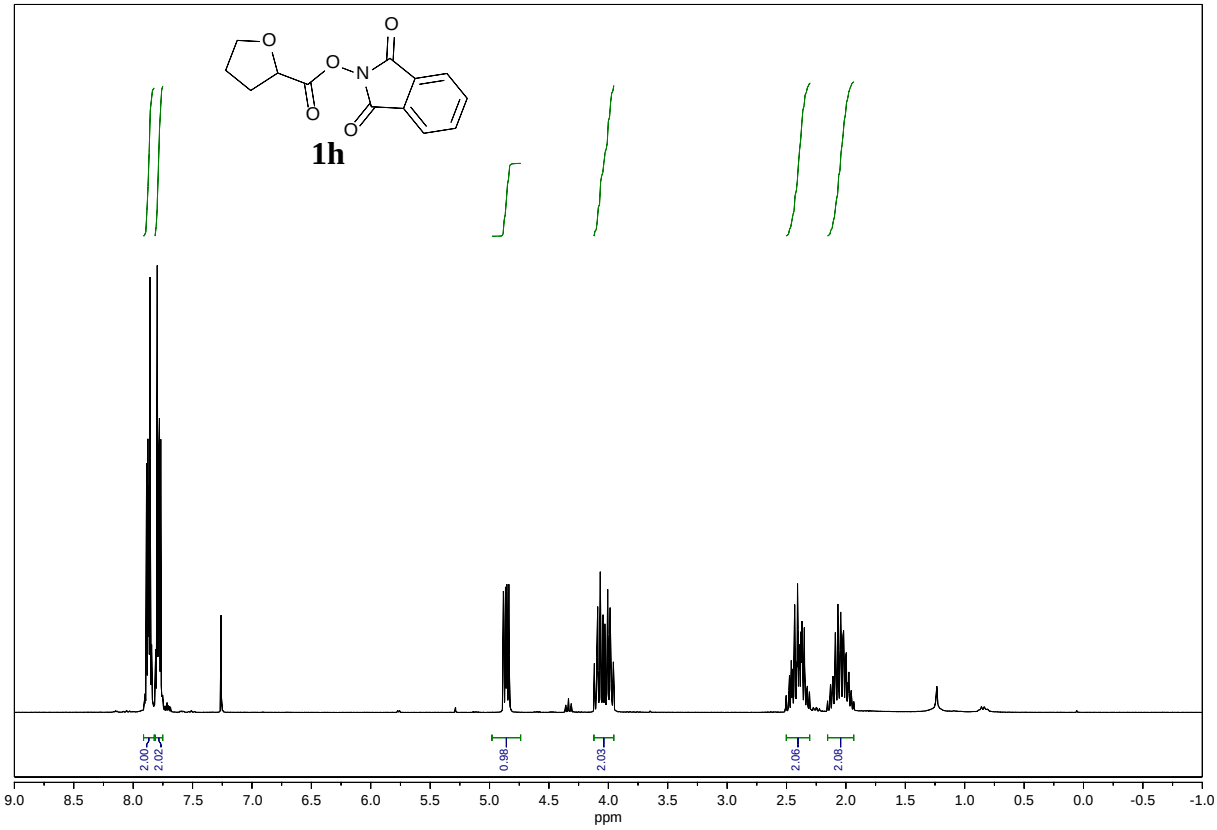


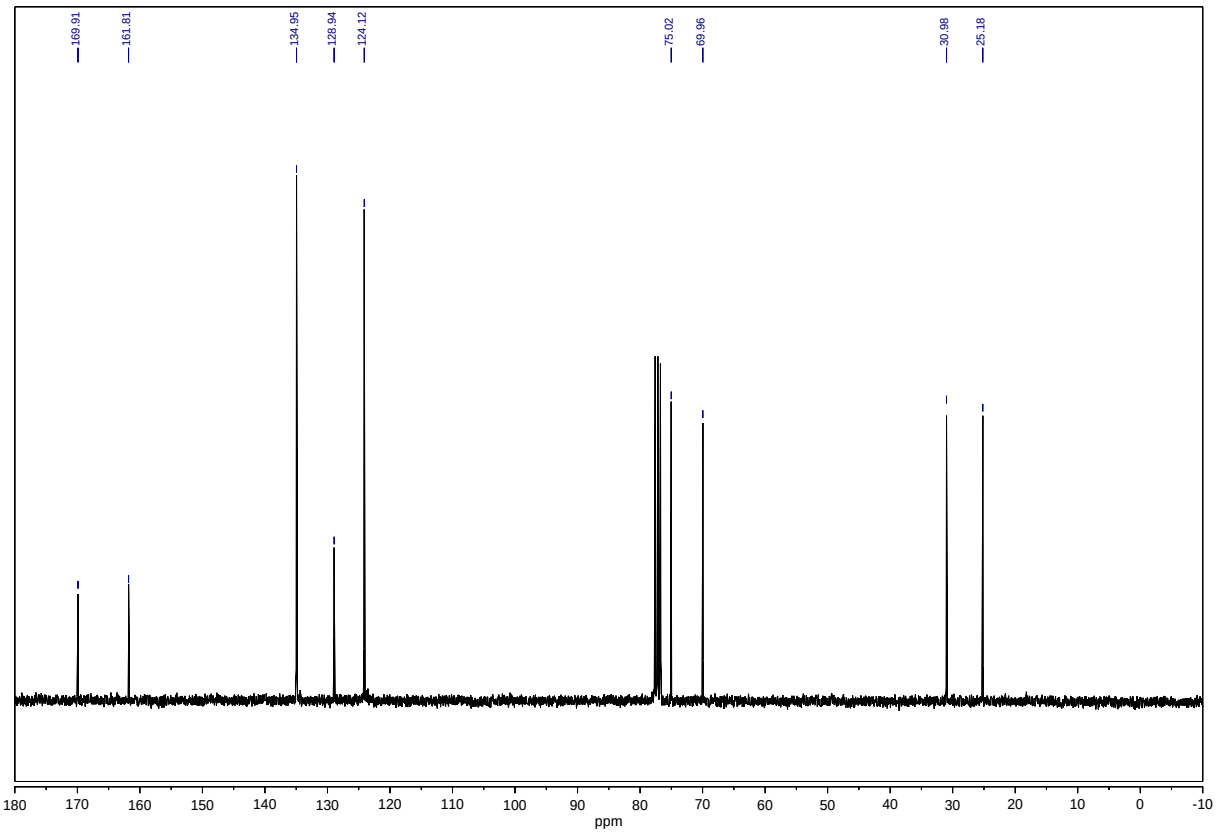
^{1}H- and ^{13}C-NMR in $CDCl_3$ of compound **1g**:



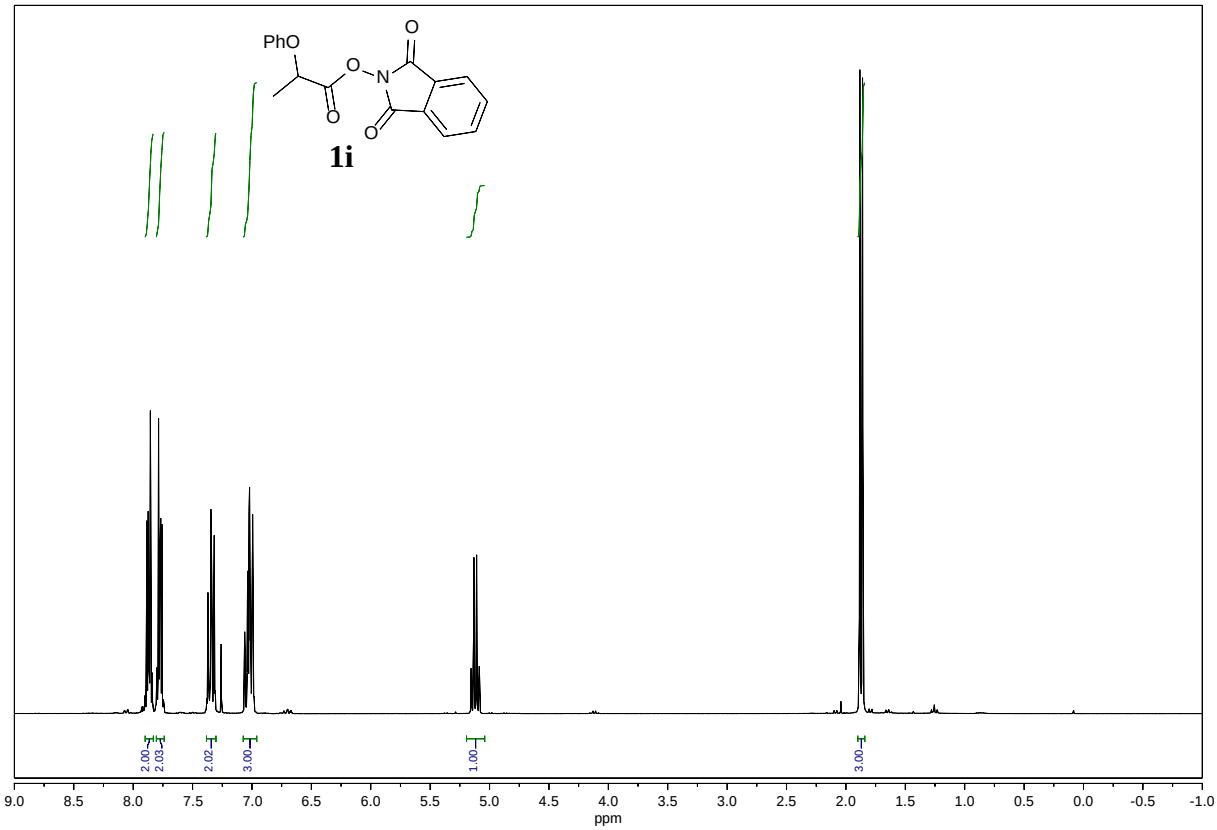


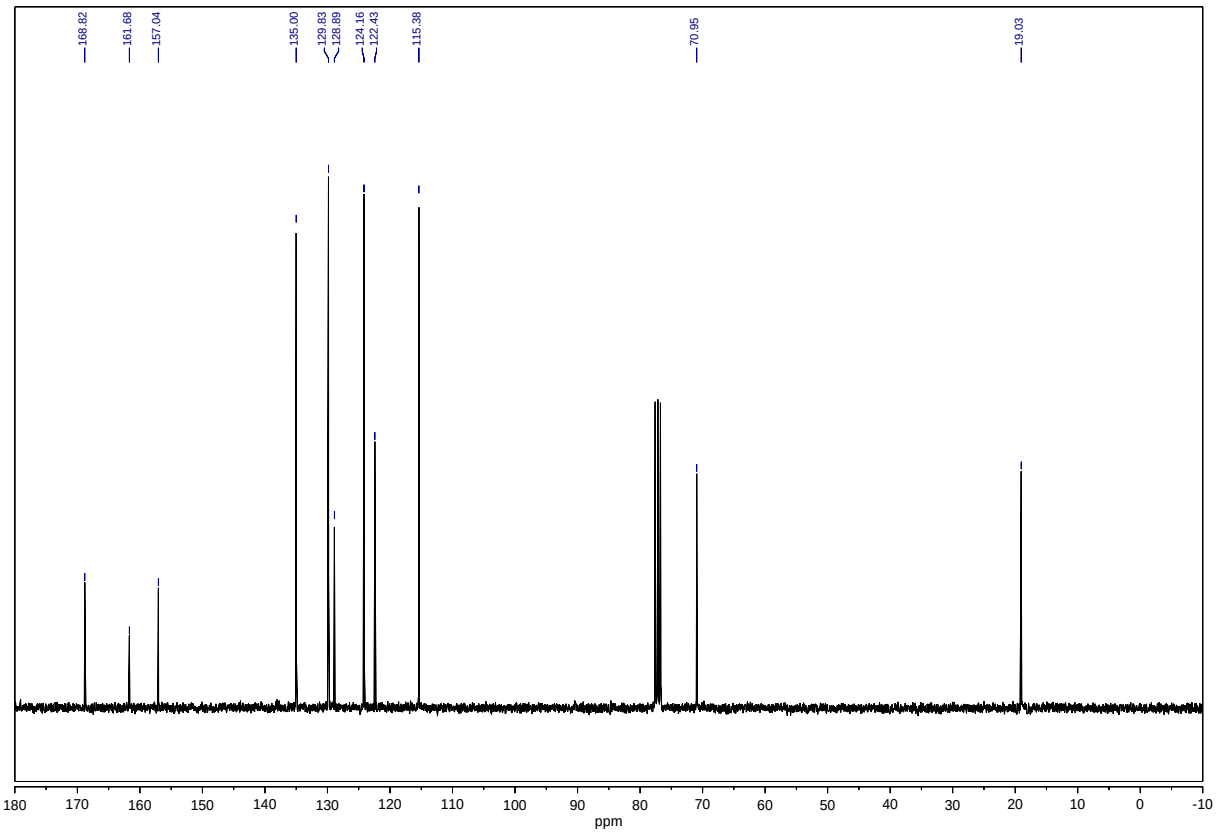
^{1}H- and ^{13}C-NMR in $CDCl_3$ of compound **1h**:



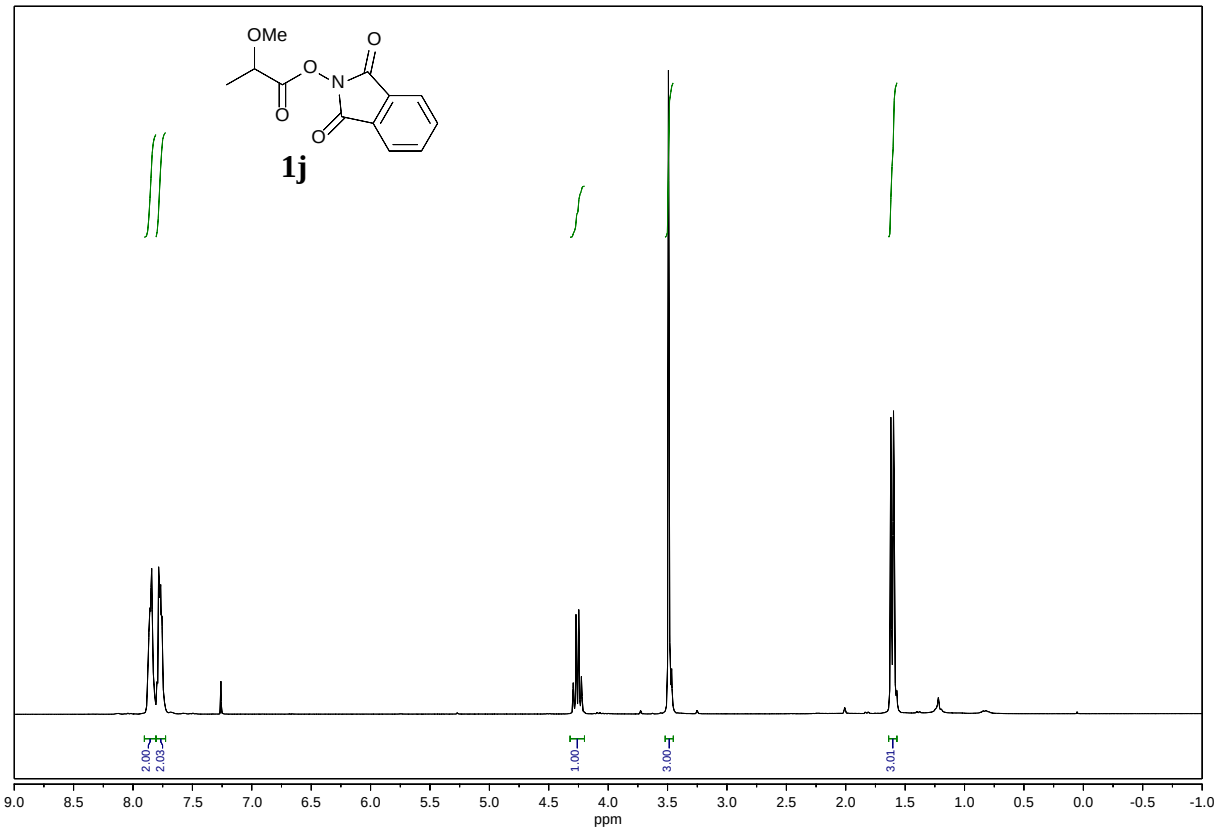


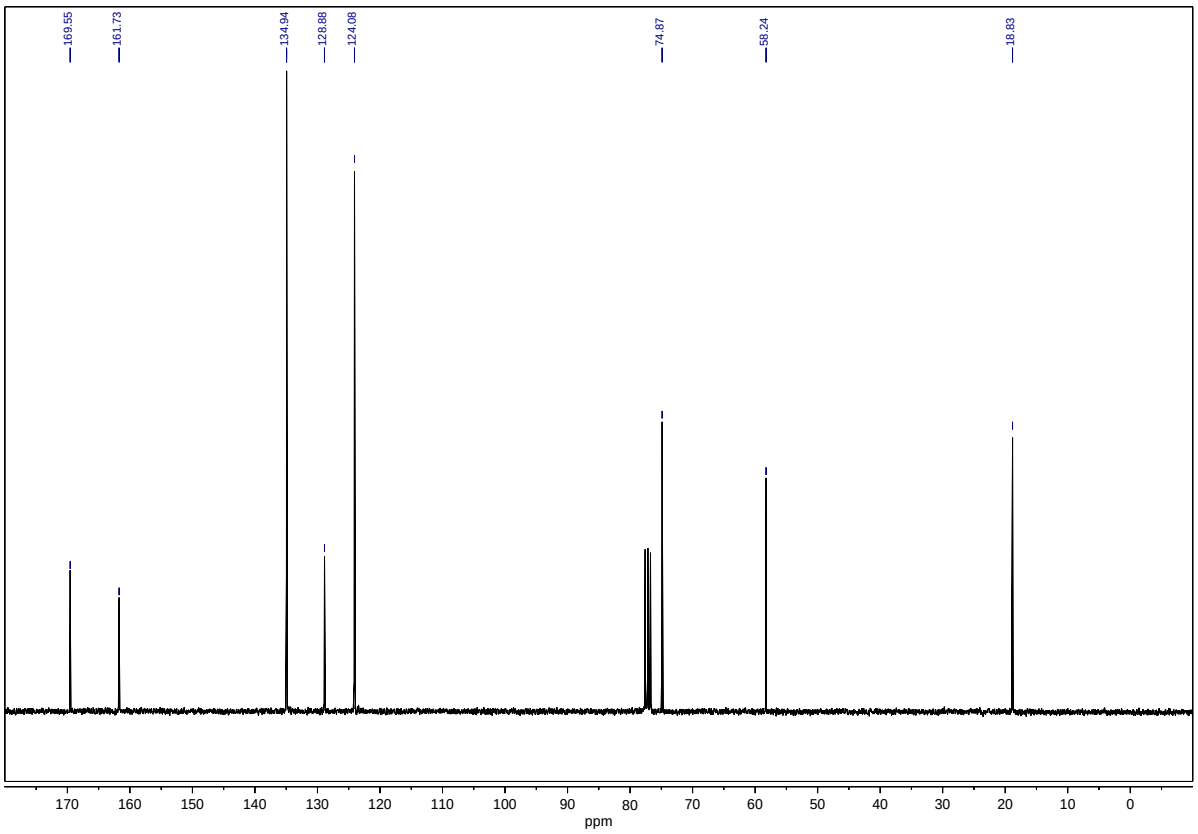
^{1}H- and ^{13}C-NMR in $CDCl_3$ of compound **1i**:



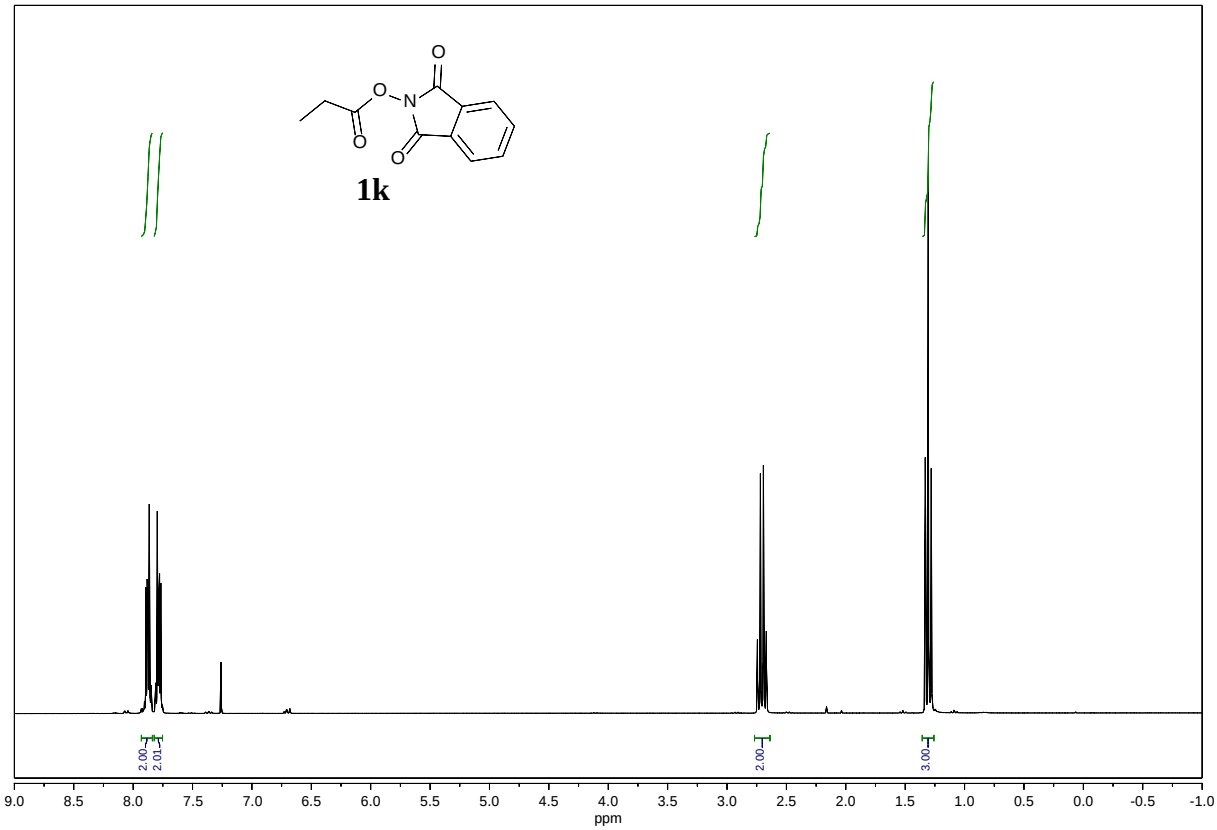


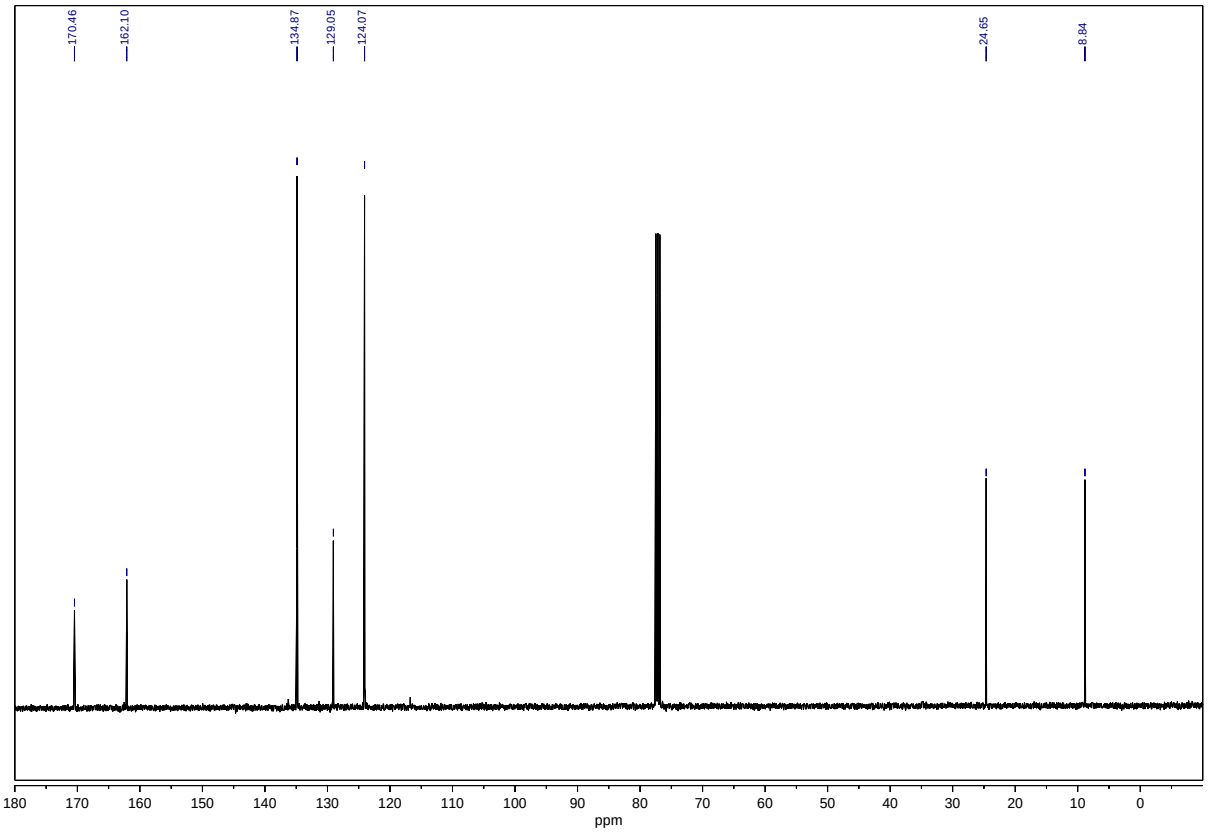
^{1}H- and ^{13}C-NMR in $CDCl_3$ of compound **1j**:



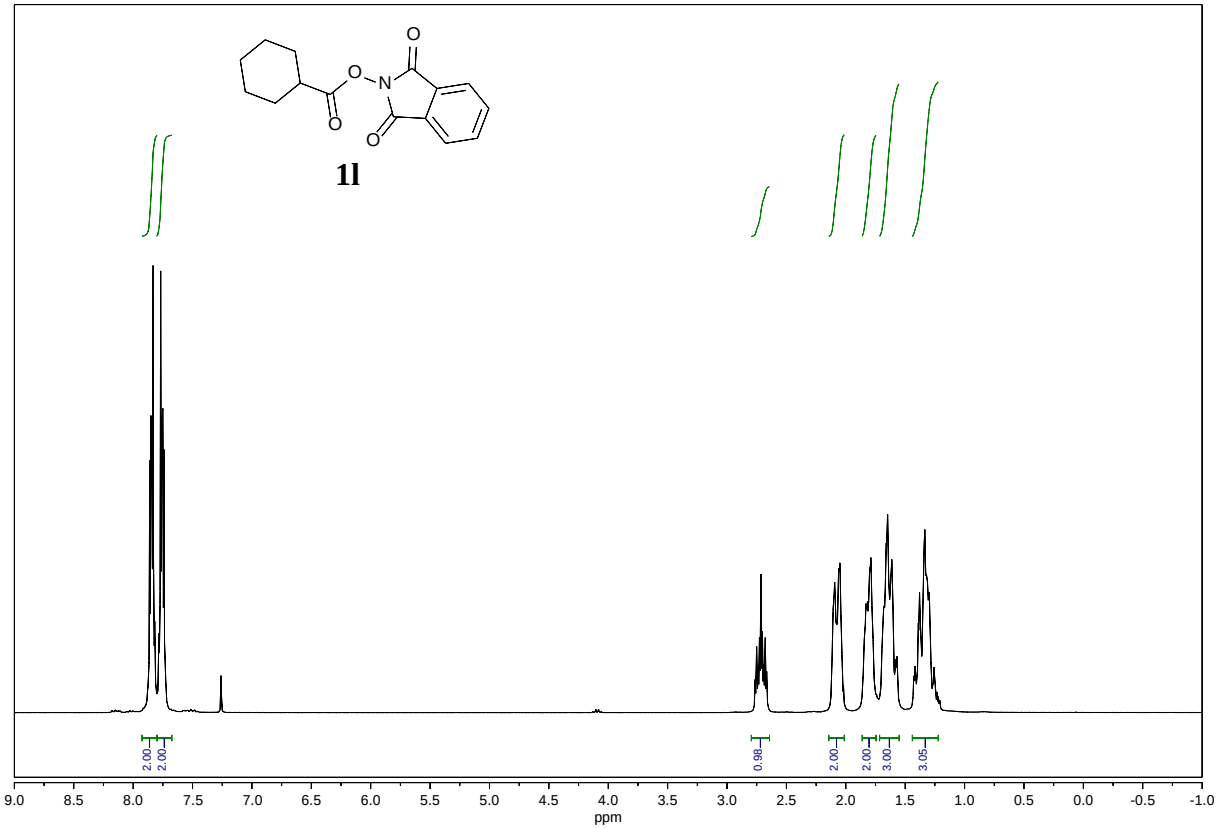


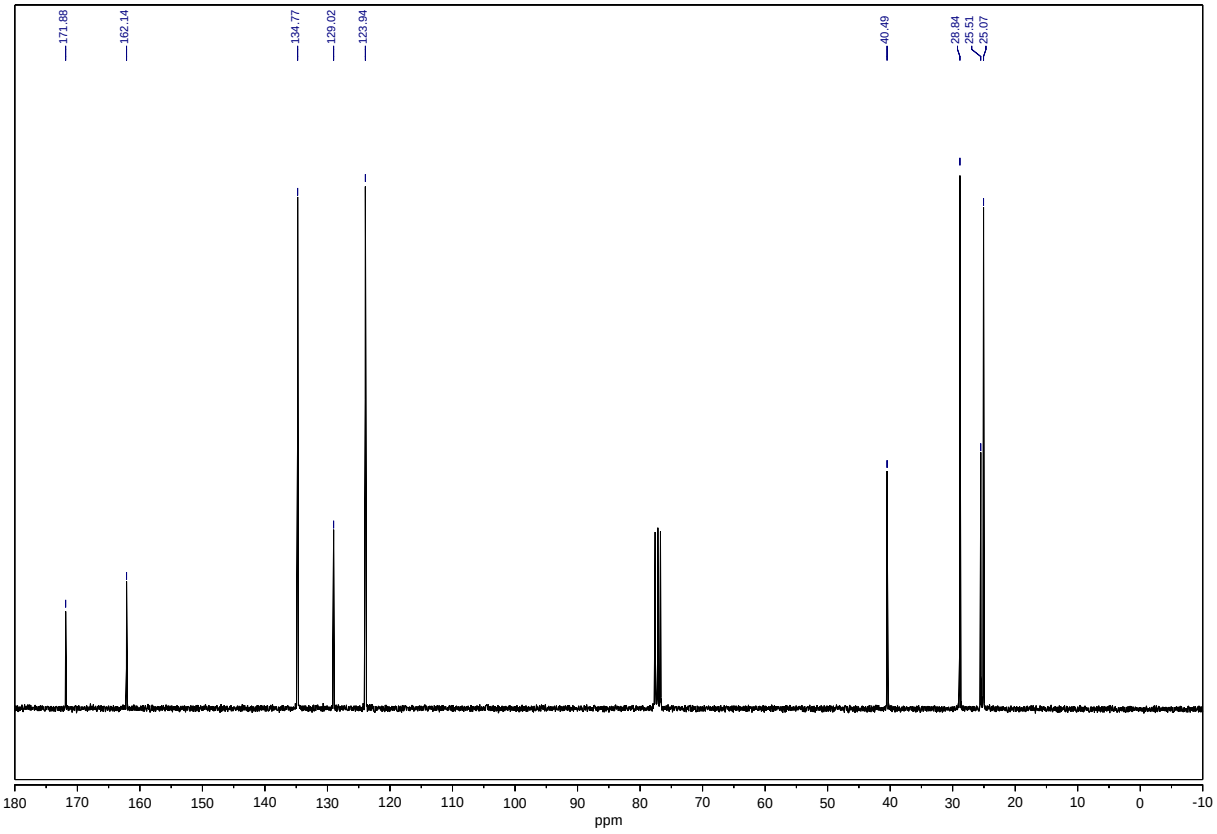
^{1}H- and ^{13}C-NMR in $CDCl_3$ of compound **1k**:



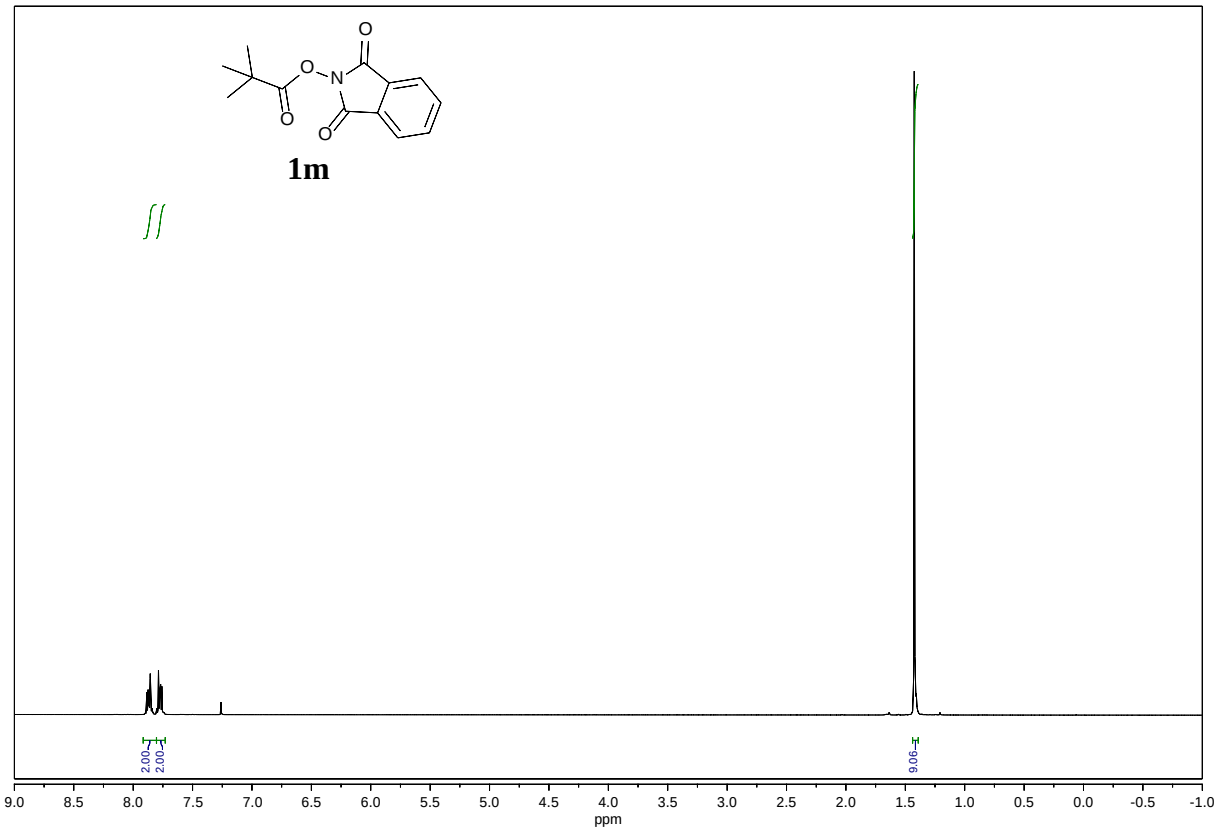


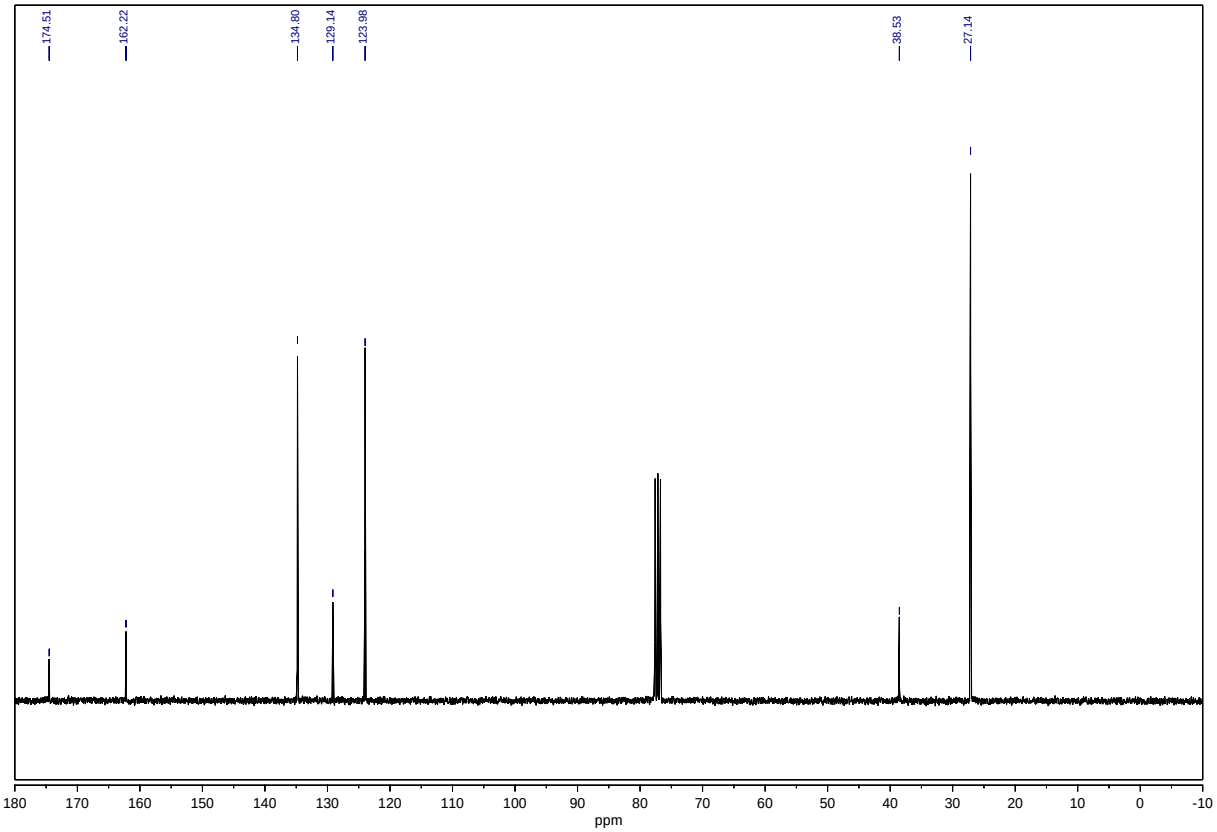
^{1}H- and ^{13}C-NMR in $CDCl_3$ of compound **1l**:



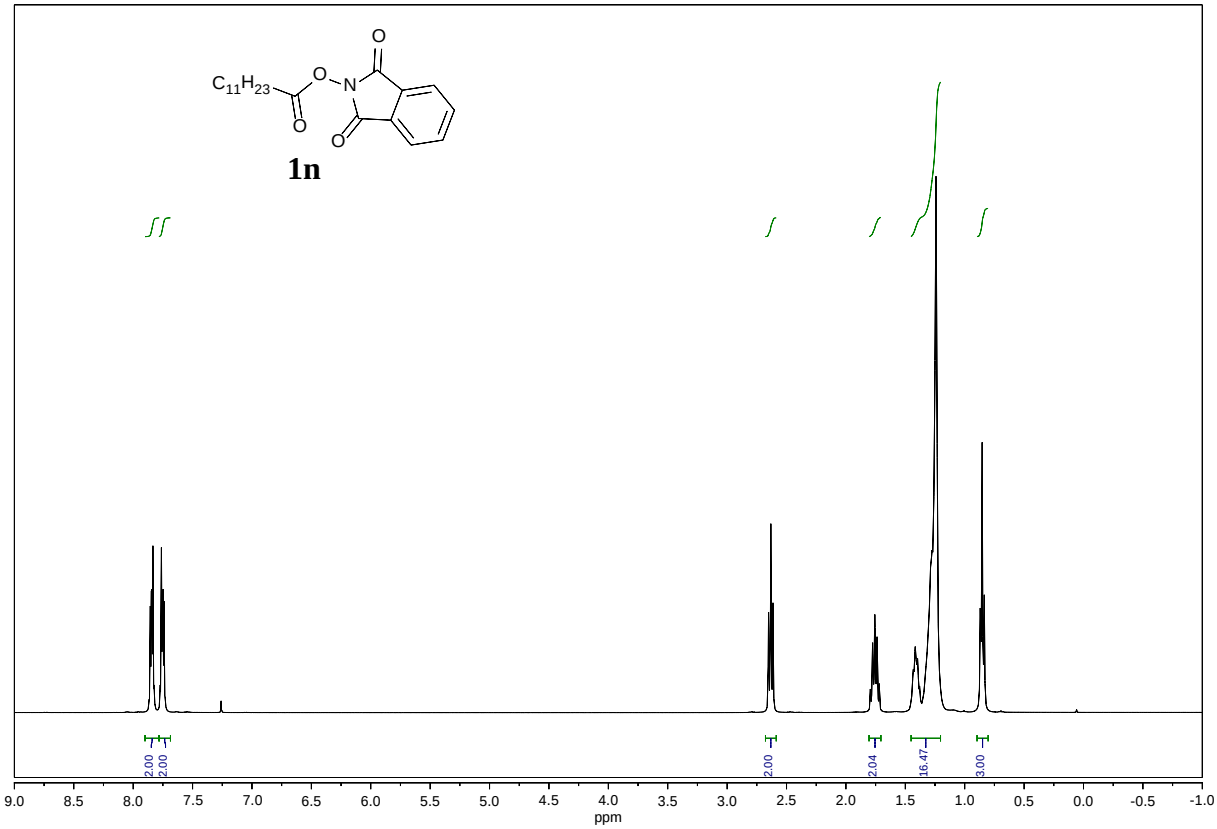


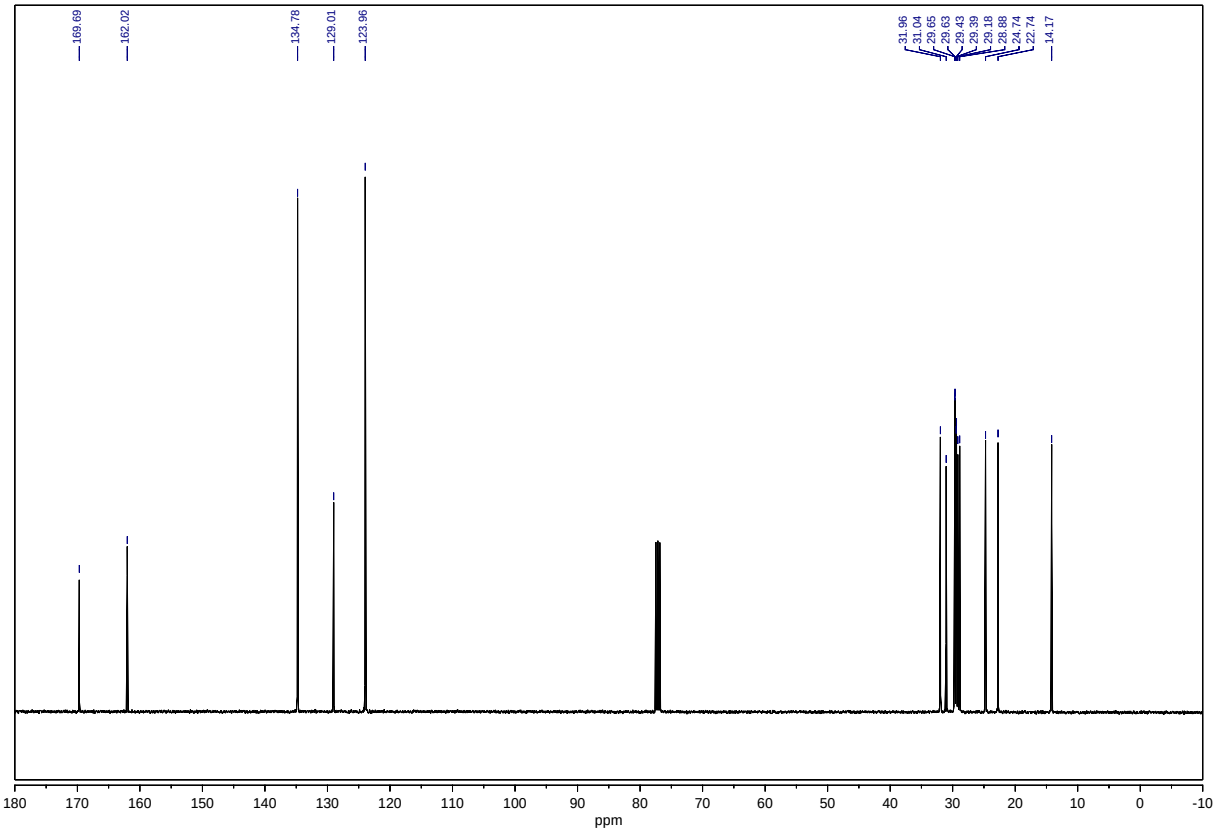
^{1}H- and ^{13}C-NMR in $CDCl_3$ of compound **1m**:



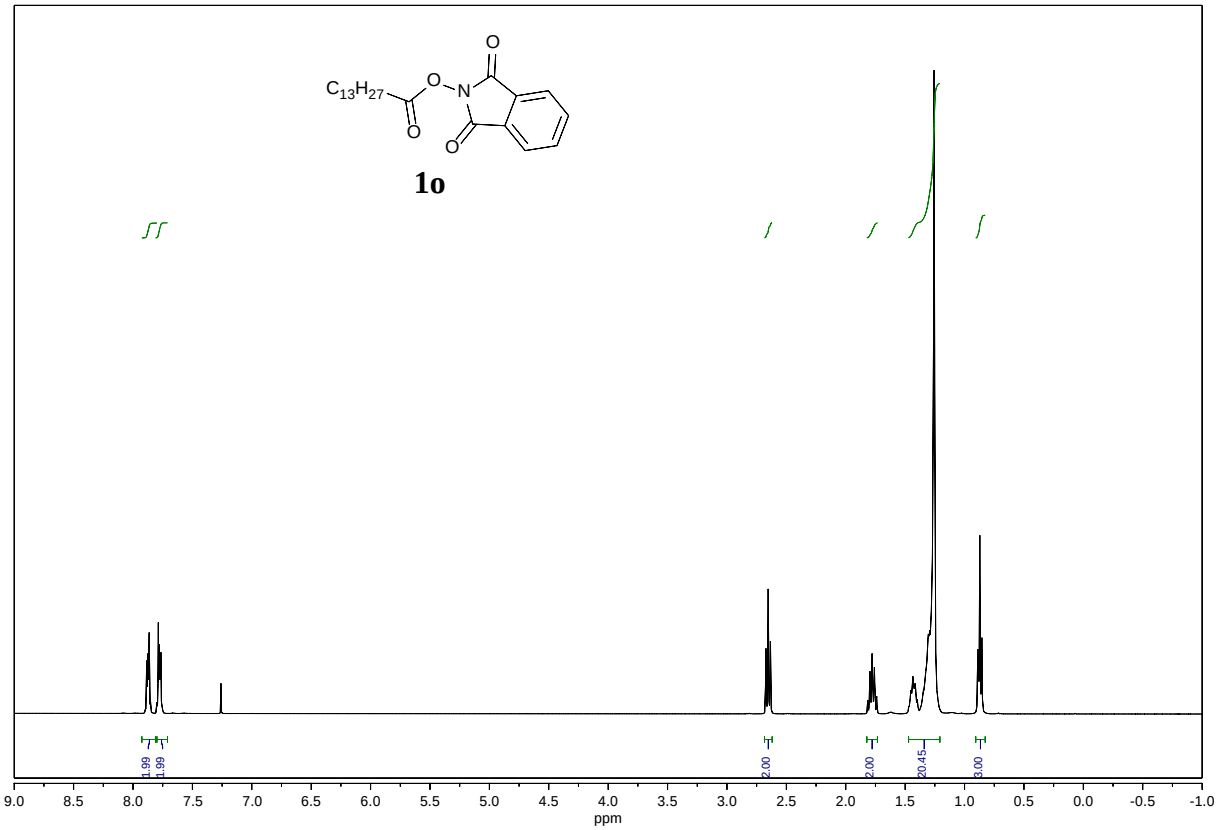


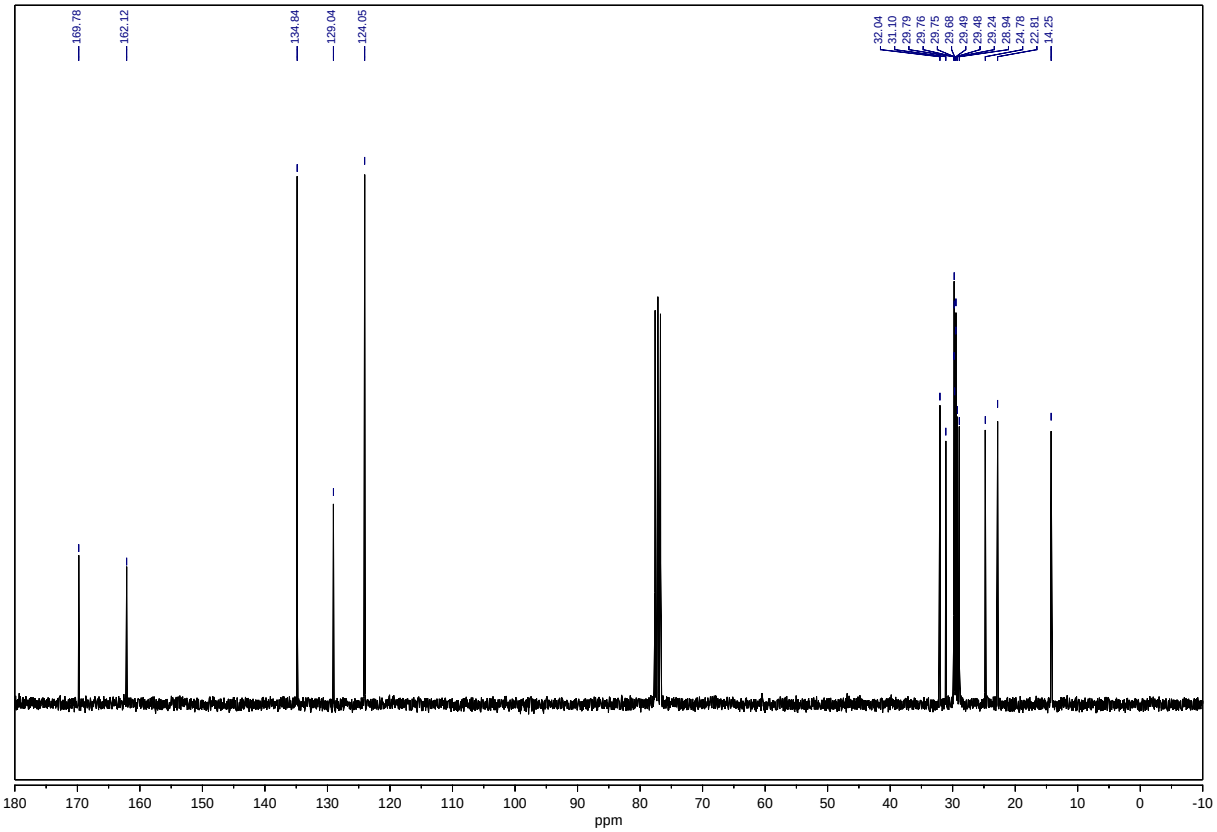
^{1}H- and ^{13}C-NMR in $CDCl_3$ of compound **1n**:



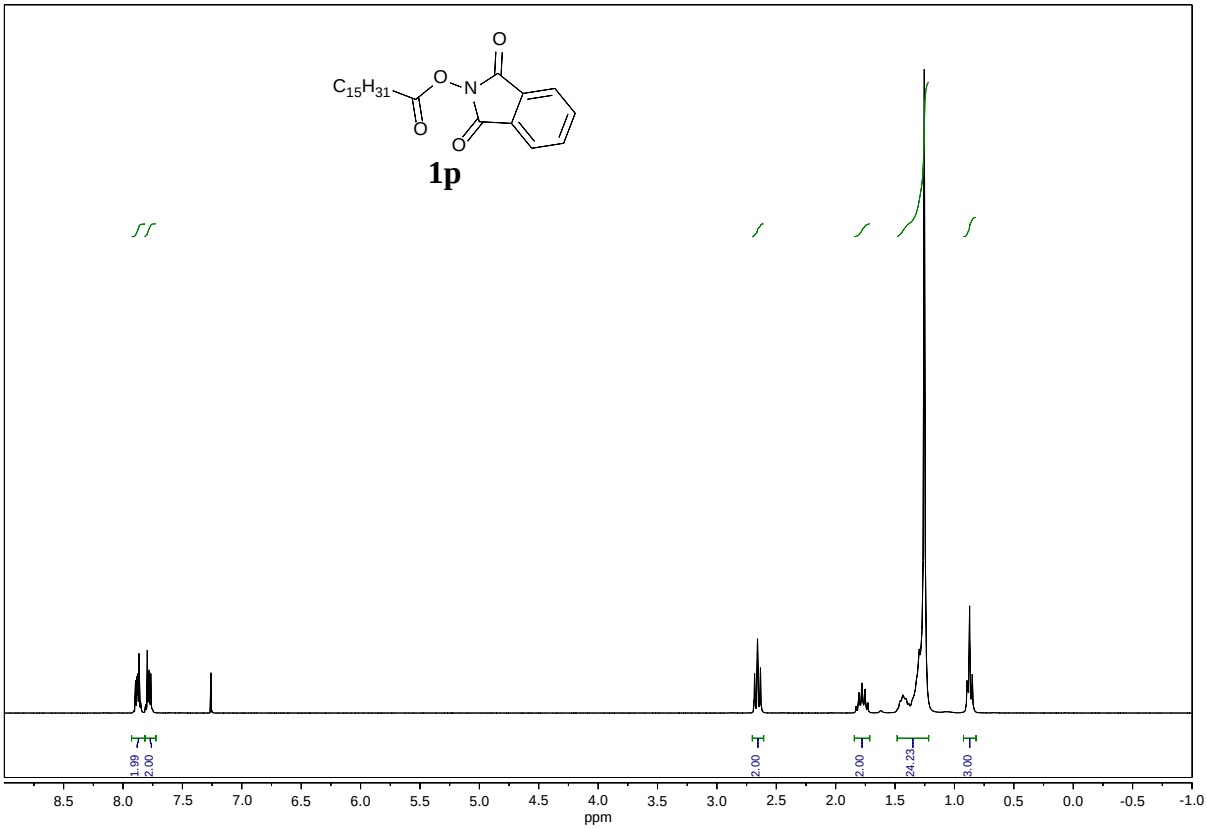


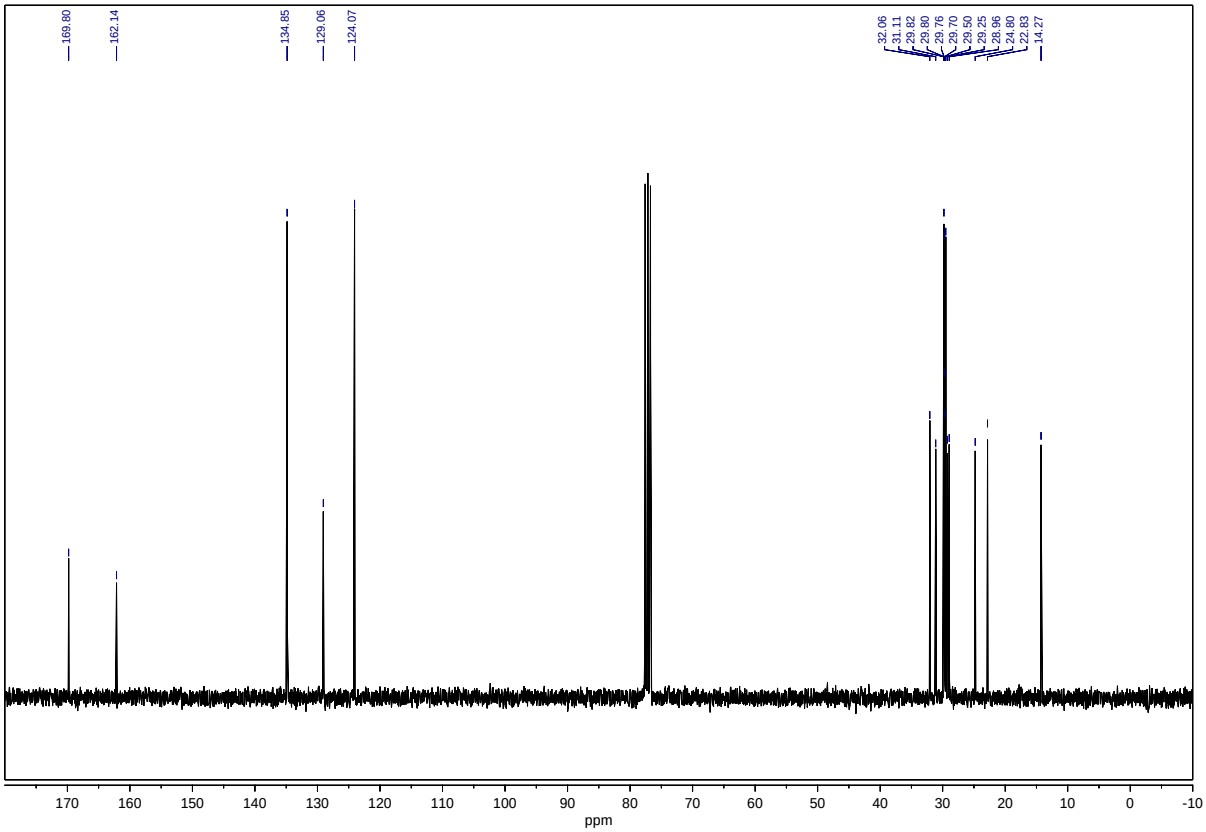
^{1}H- and ^{13}C-NMR in $CDCl_3$ of compound **1o**:



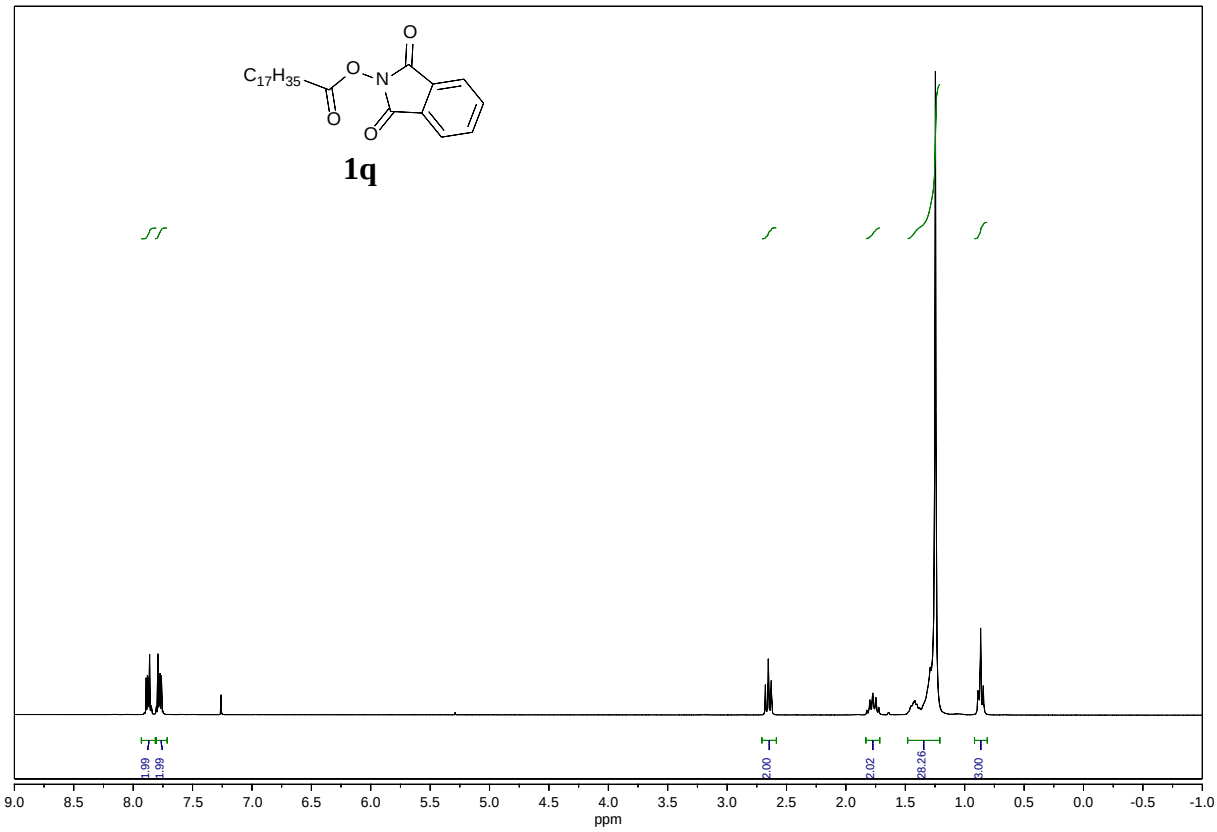


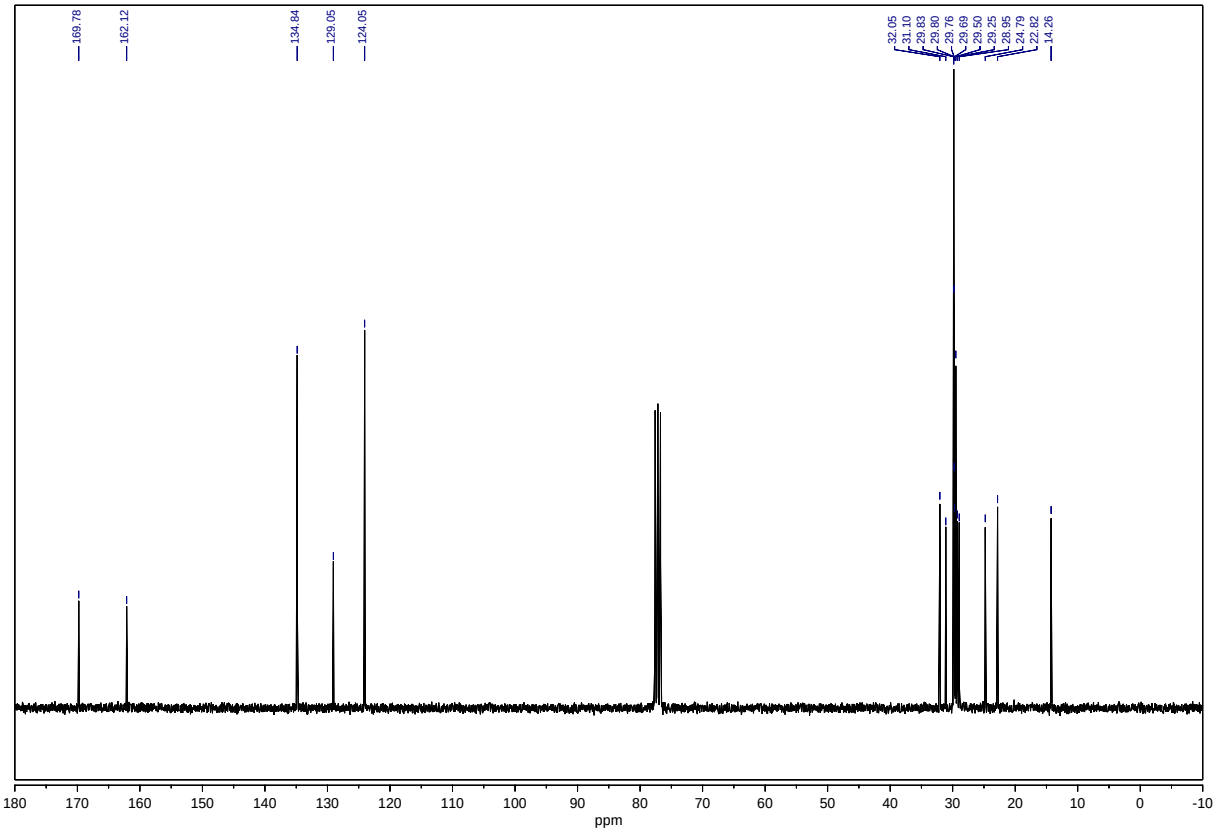
^{1}H- and ^{13}C-NMR in $CDCl_3$ of compound **1p**:



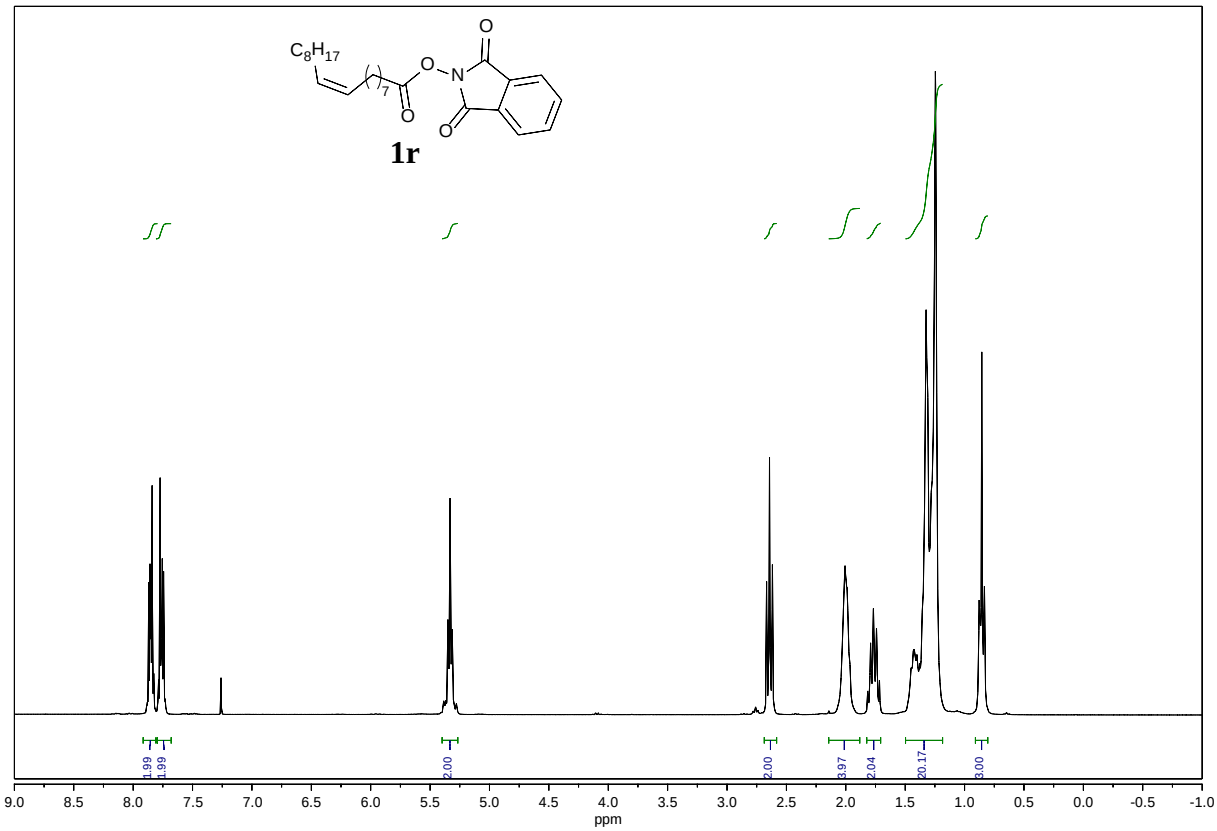


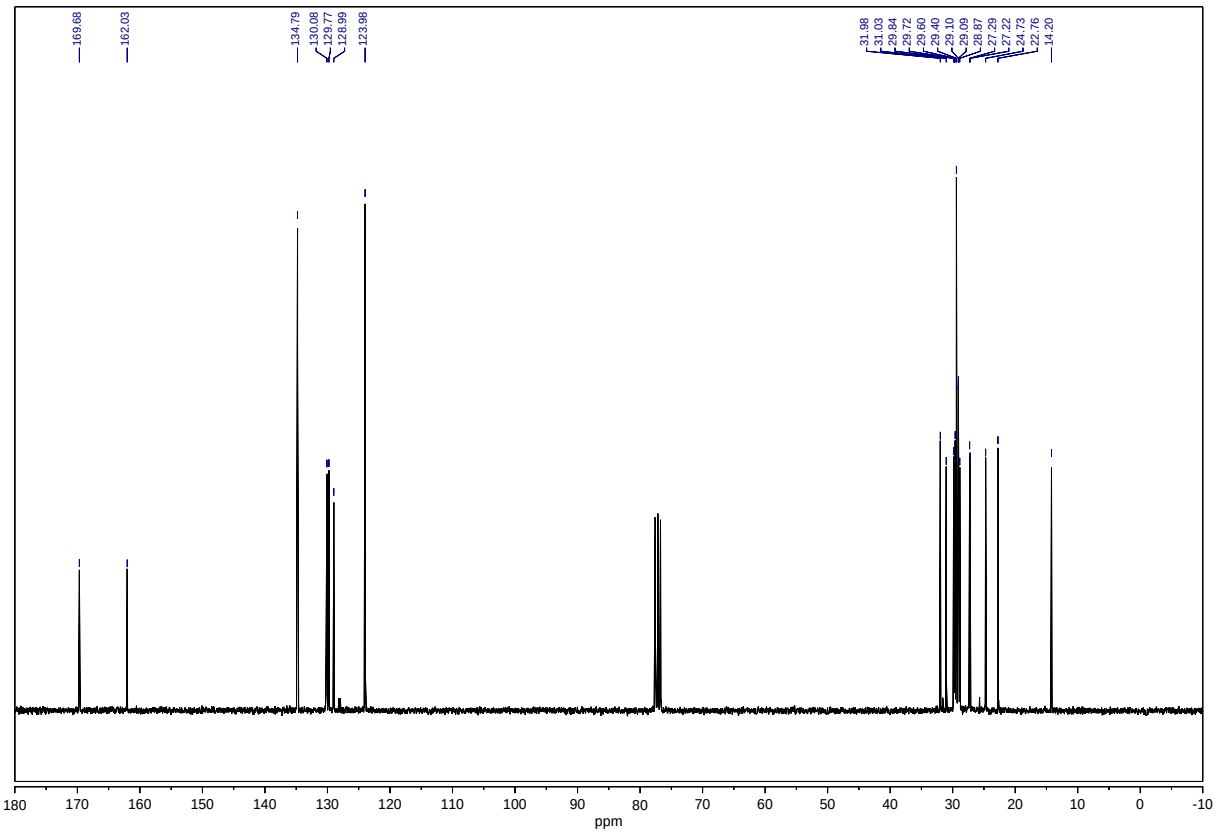
^{1}H- and ^{13}C-NMR in $CDCl_3$ of compound **1q**:



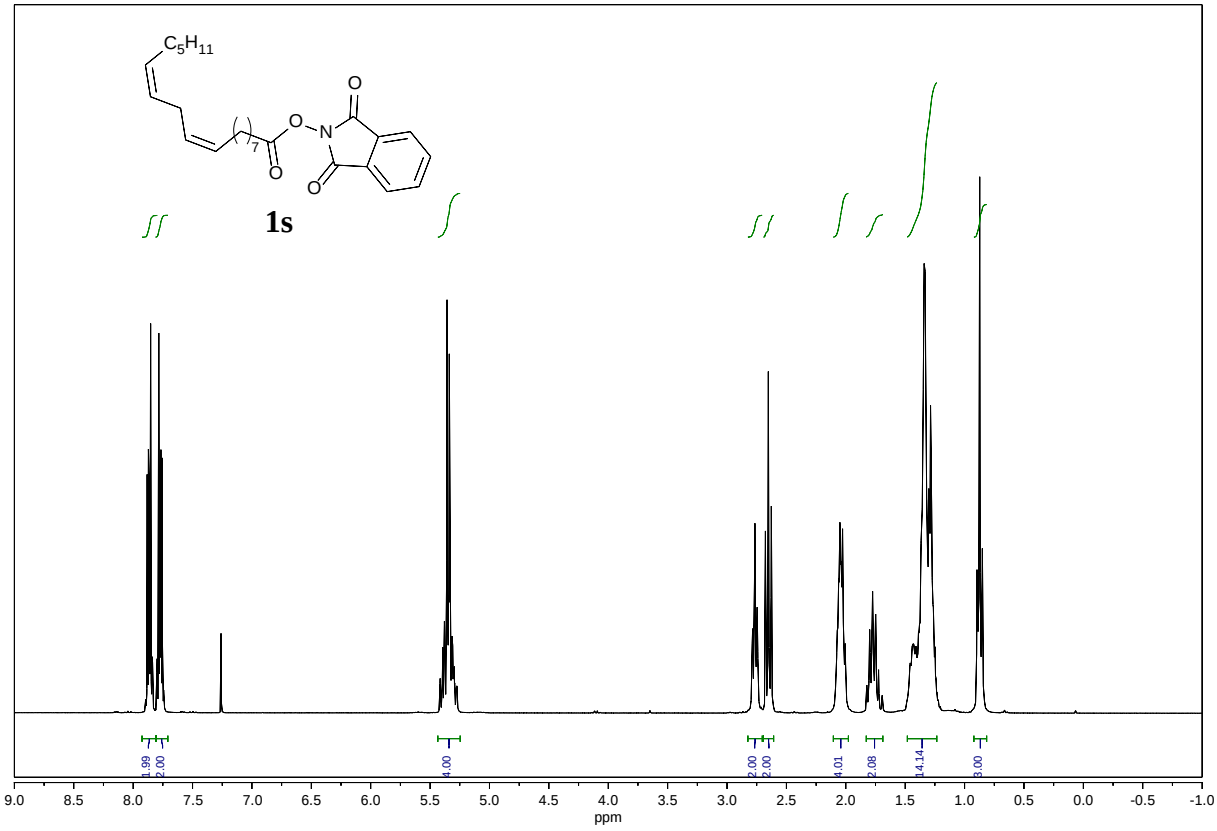


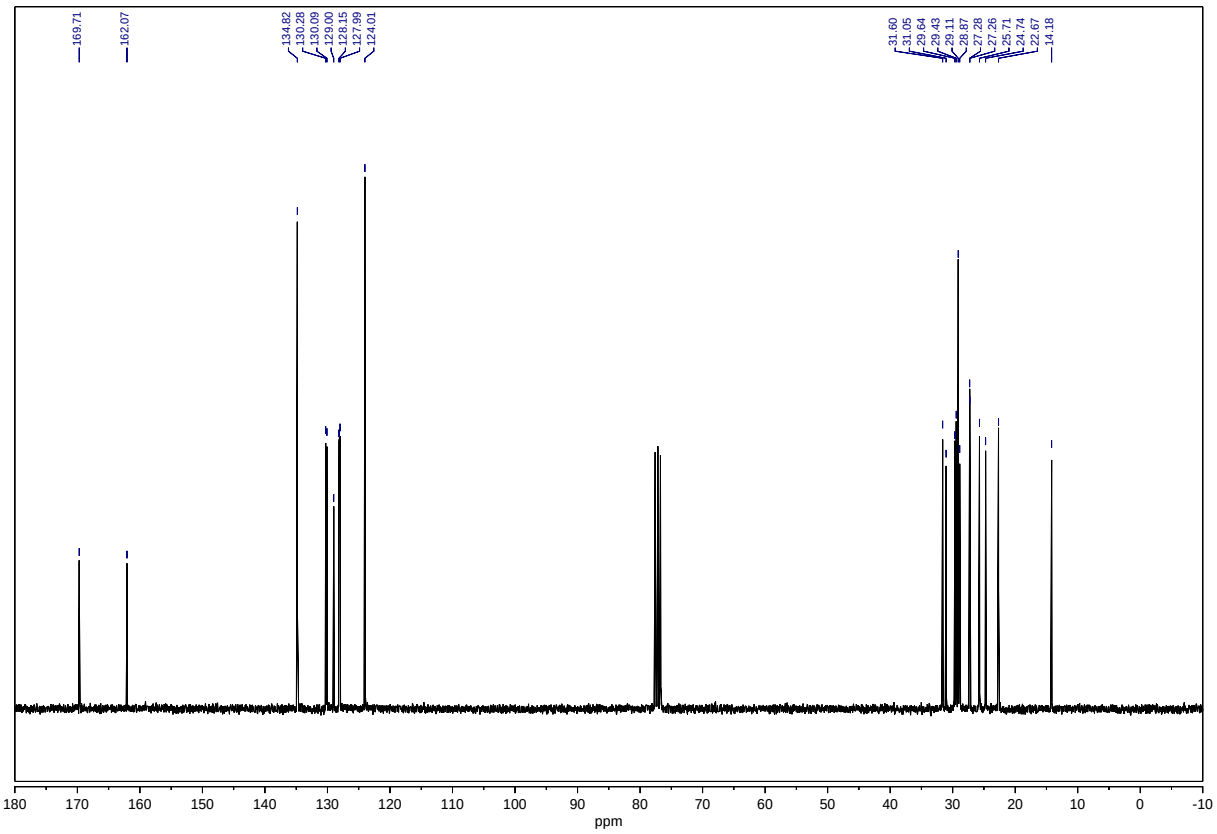
^{1}H- and ^{13}C-NMR in $CDCl_3$ of compound **1r**:



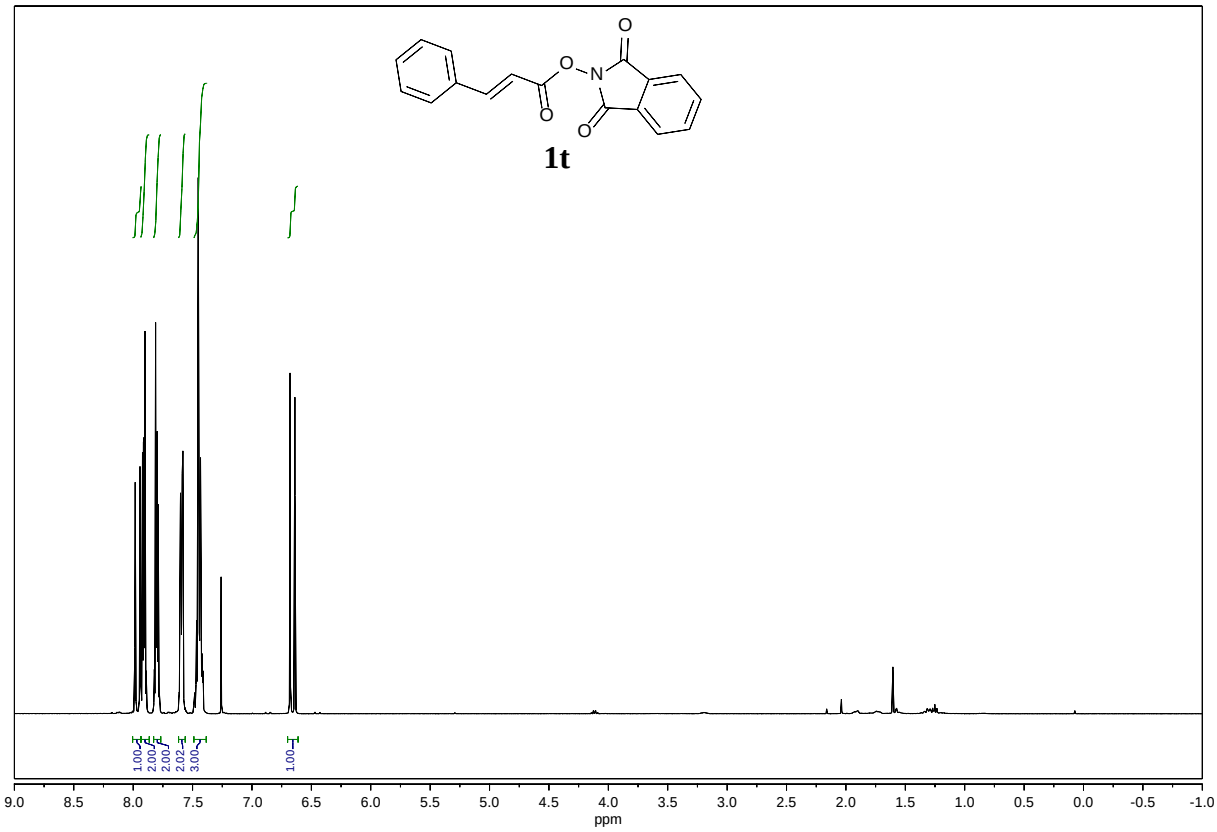


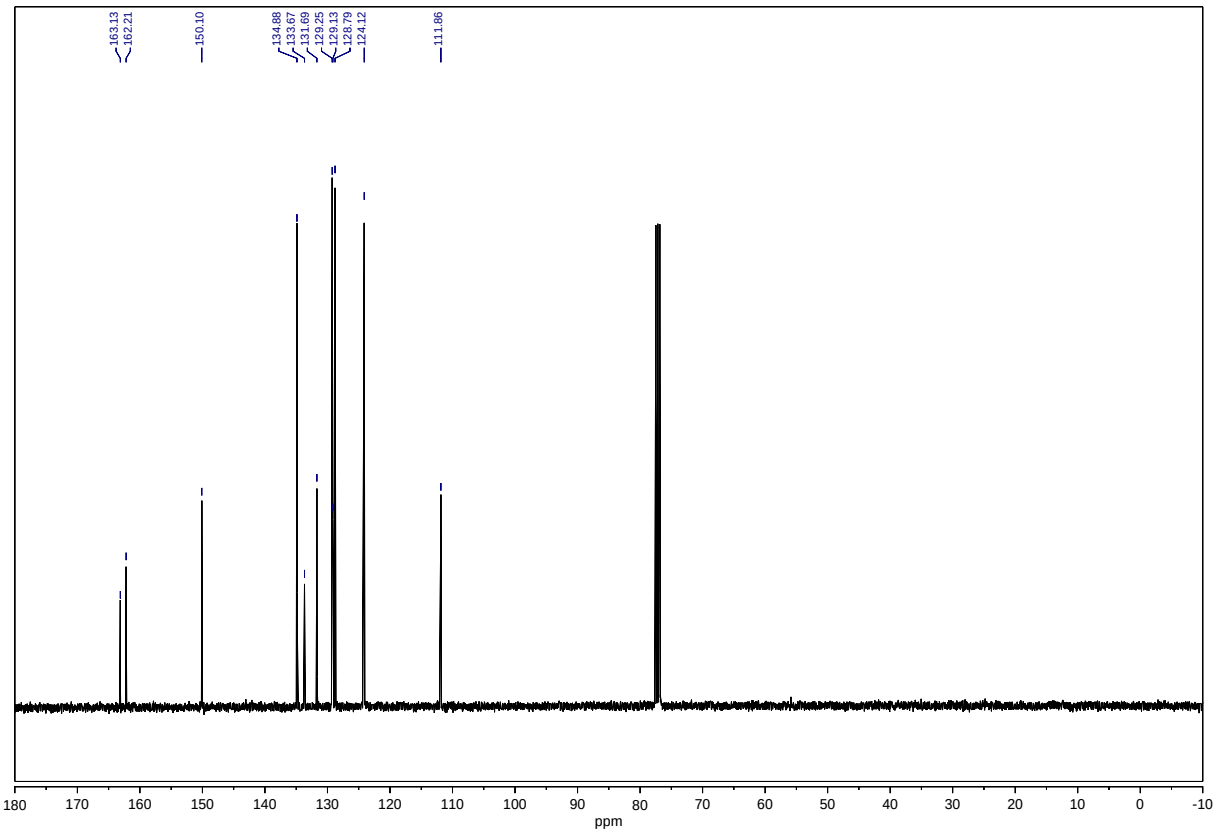
^{1}H- and ^{13}C-NMR in $CDCl_3$ of compound **1s**:



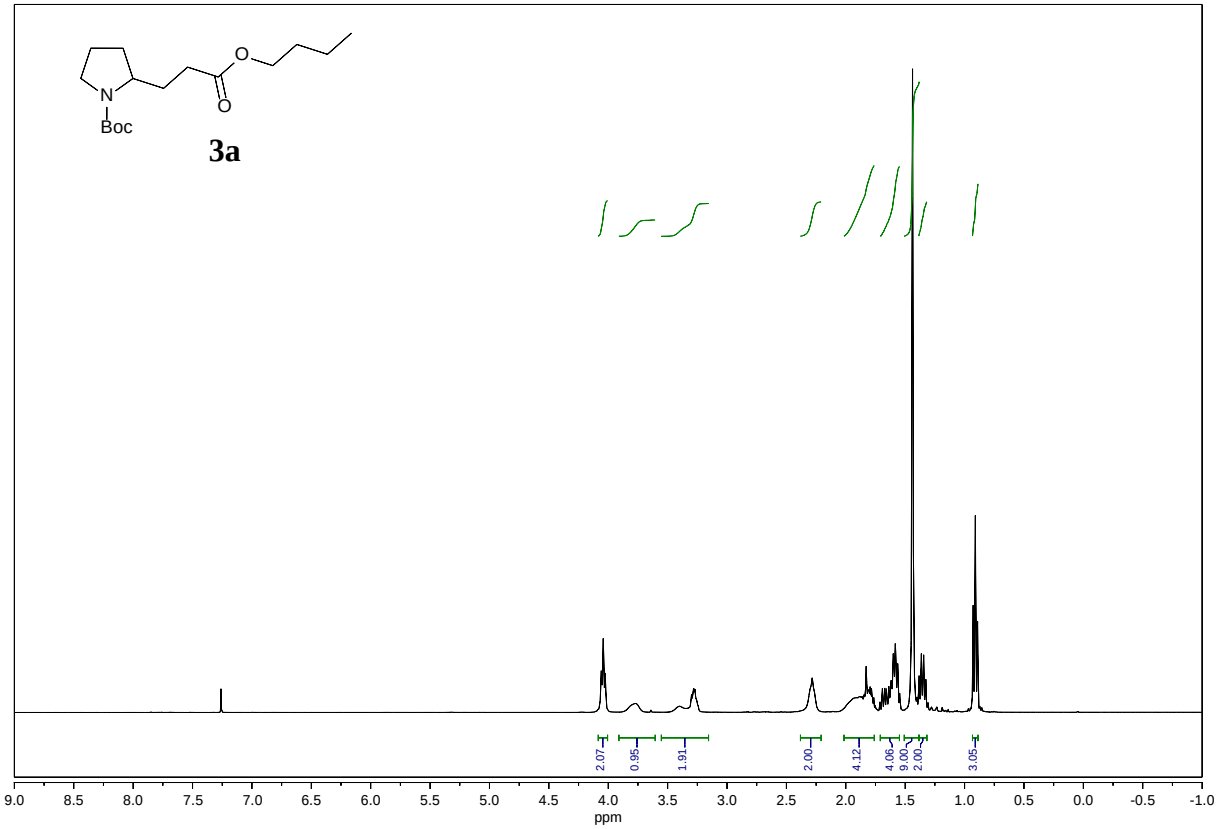


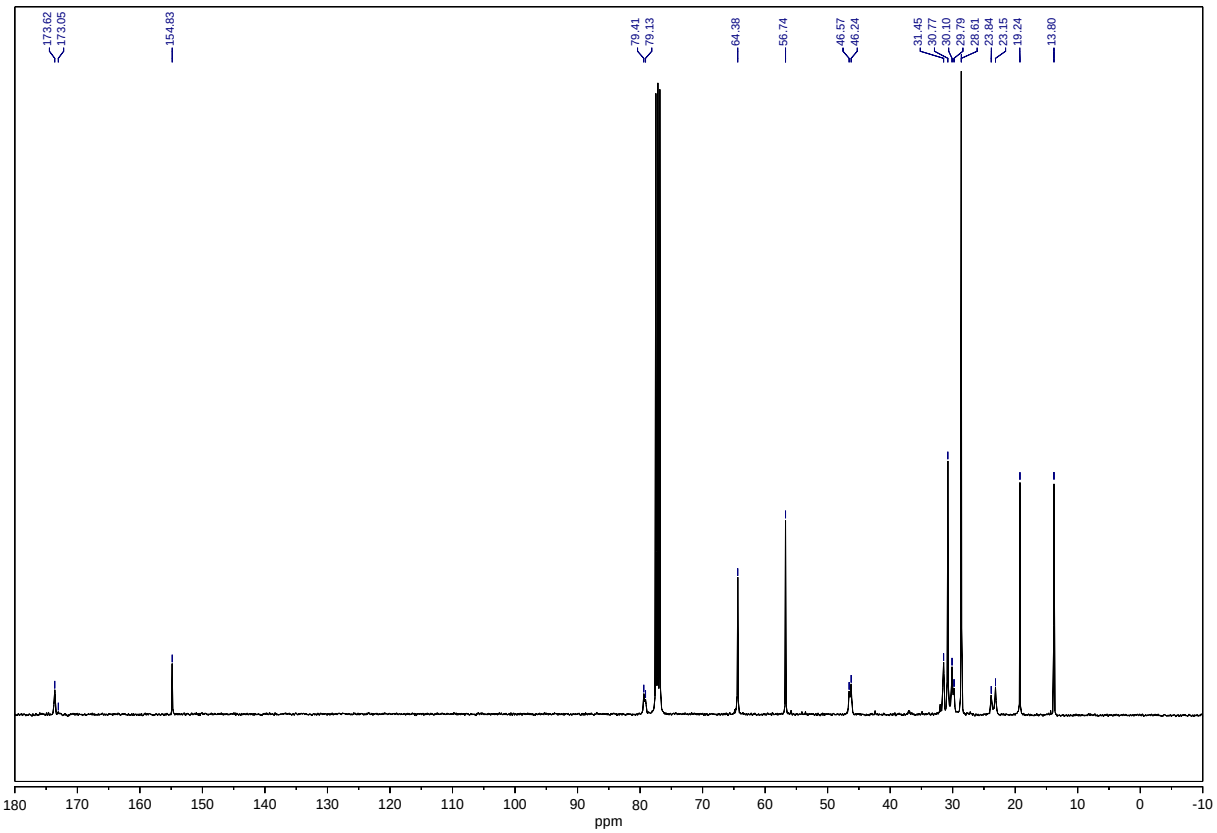
^{1}H- and ^{13}C-NMR in $CDCl_3$ of compound **1t**:



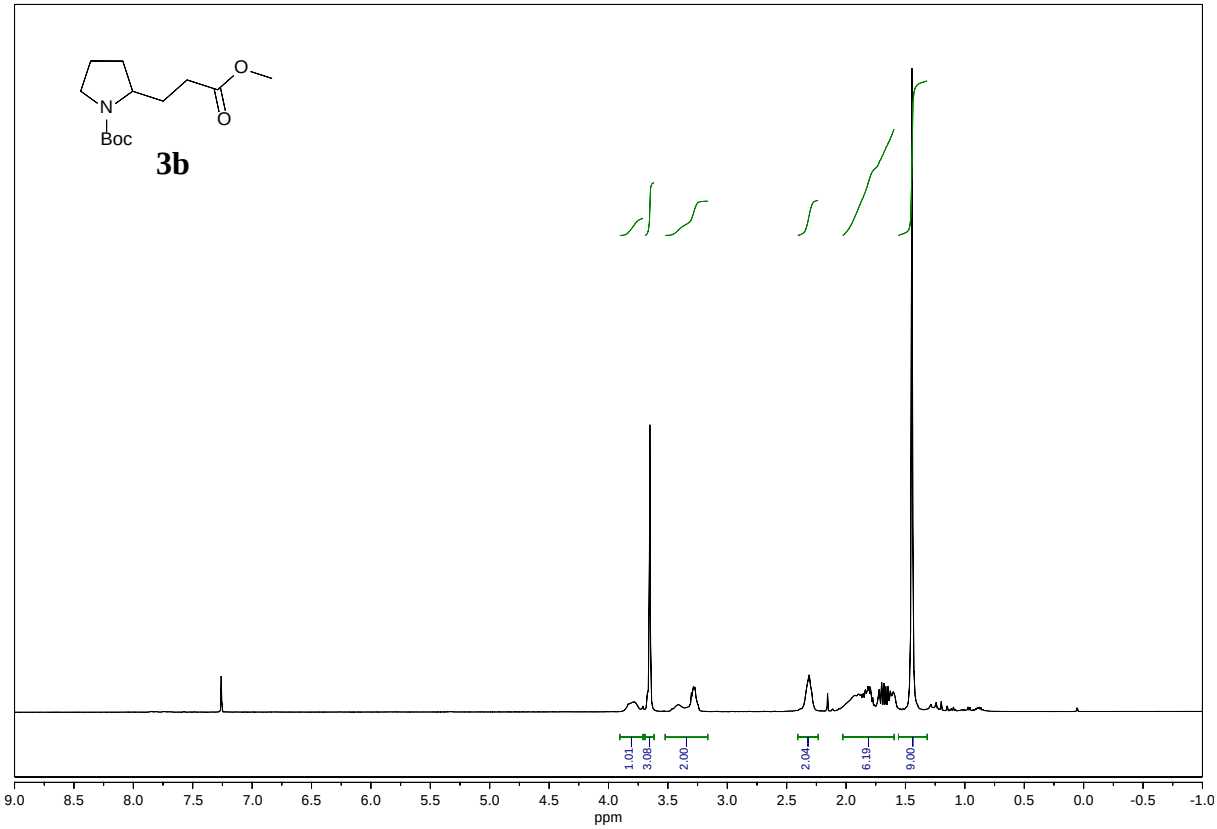


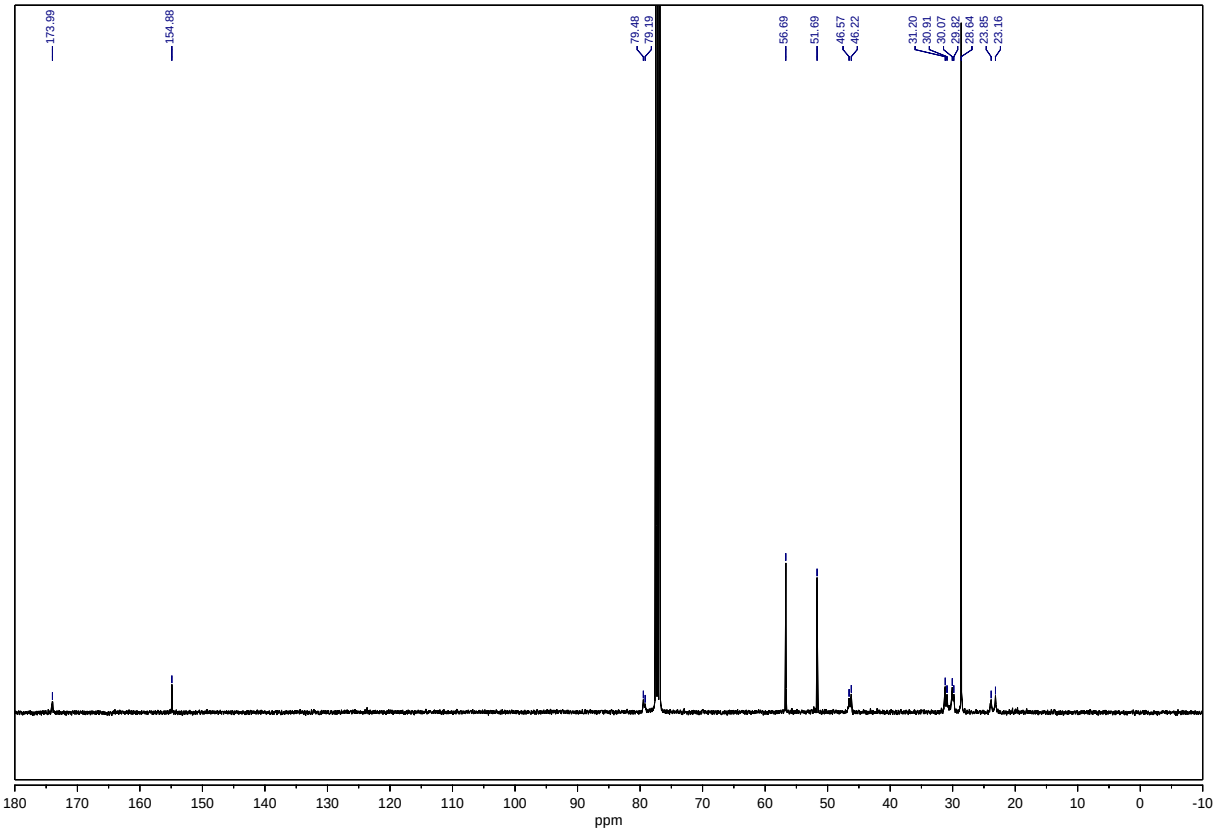
^{1}H- and ^{13}C-NMR in $CDCl_3$ of compound **3a**:



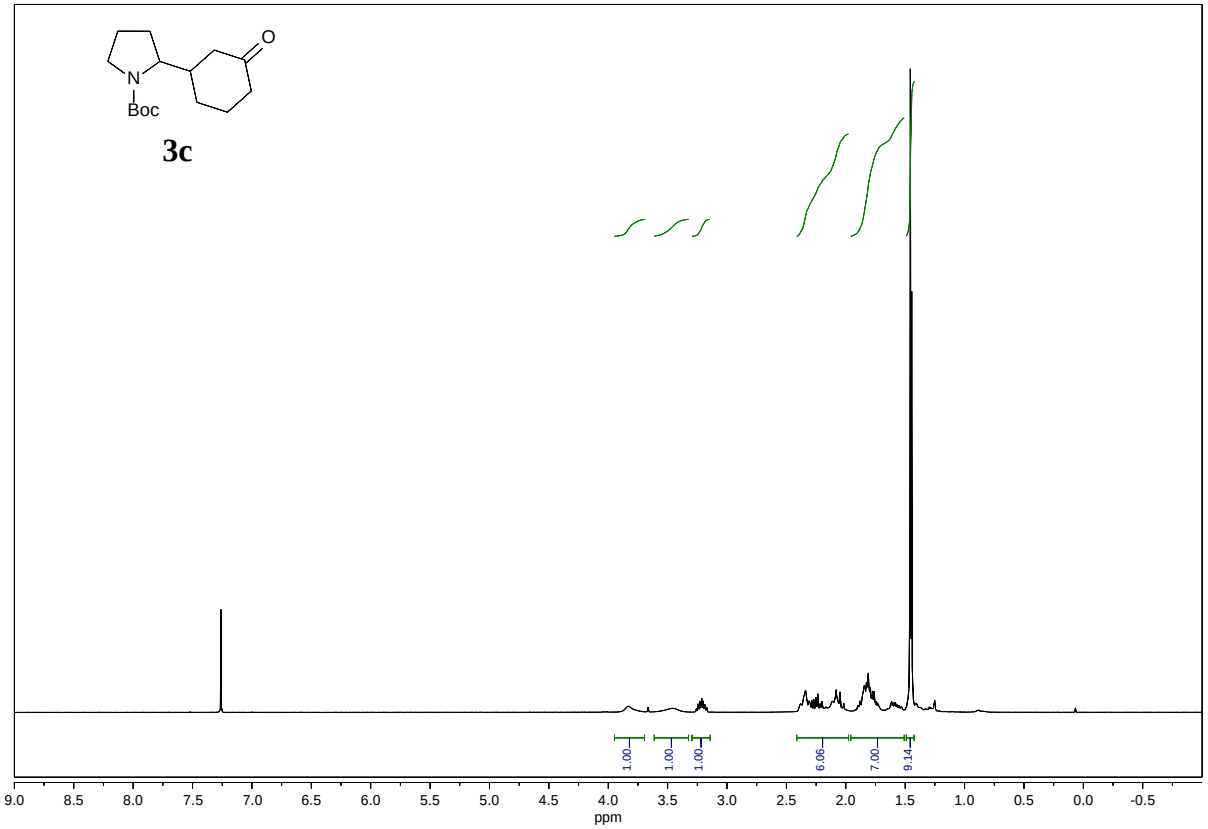


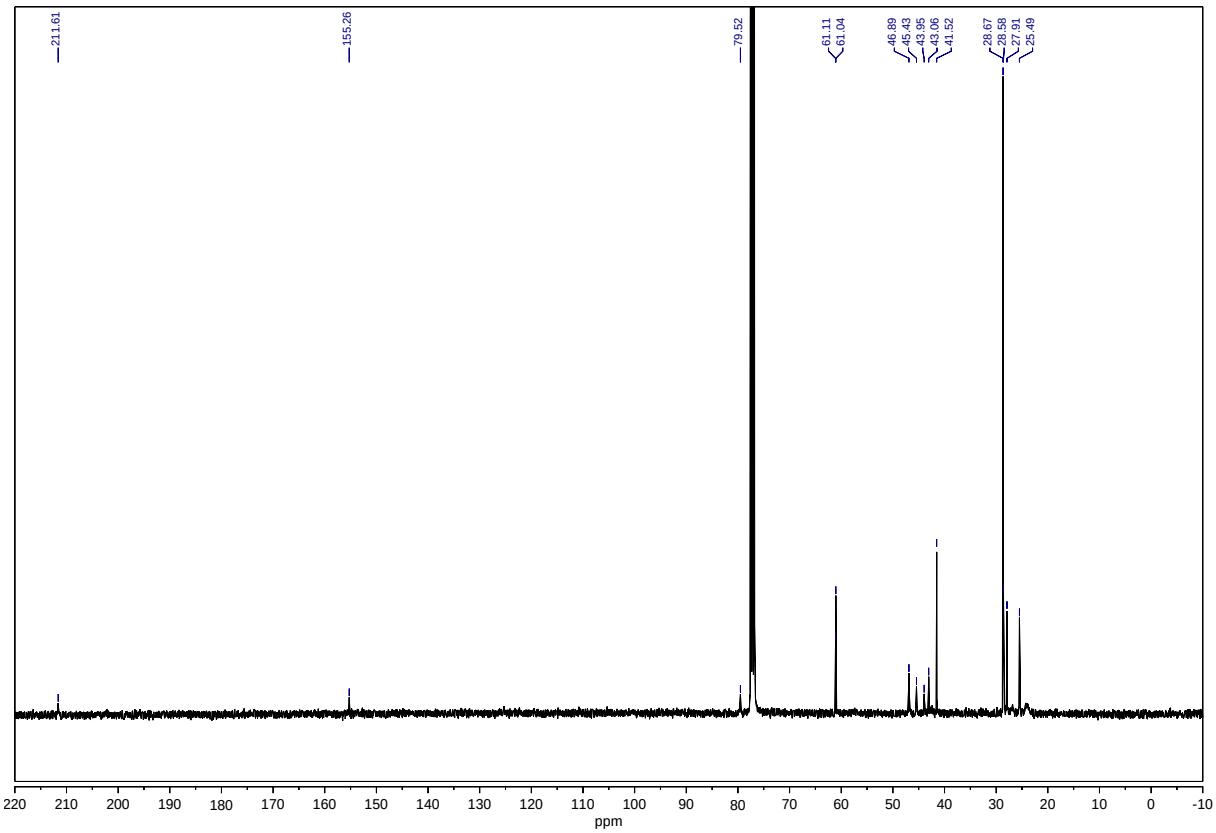
^{1}H- and ^{13}C-NMR in $CDCl_3$ of compound **3b**:



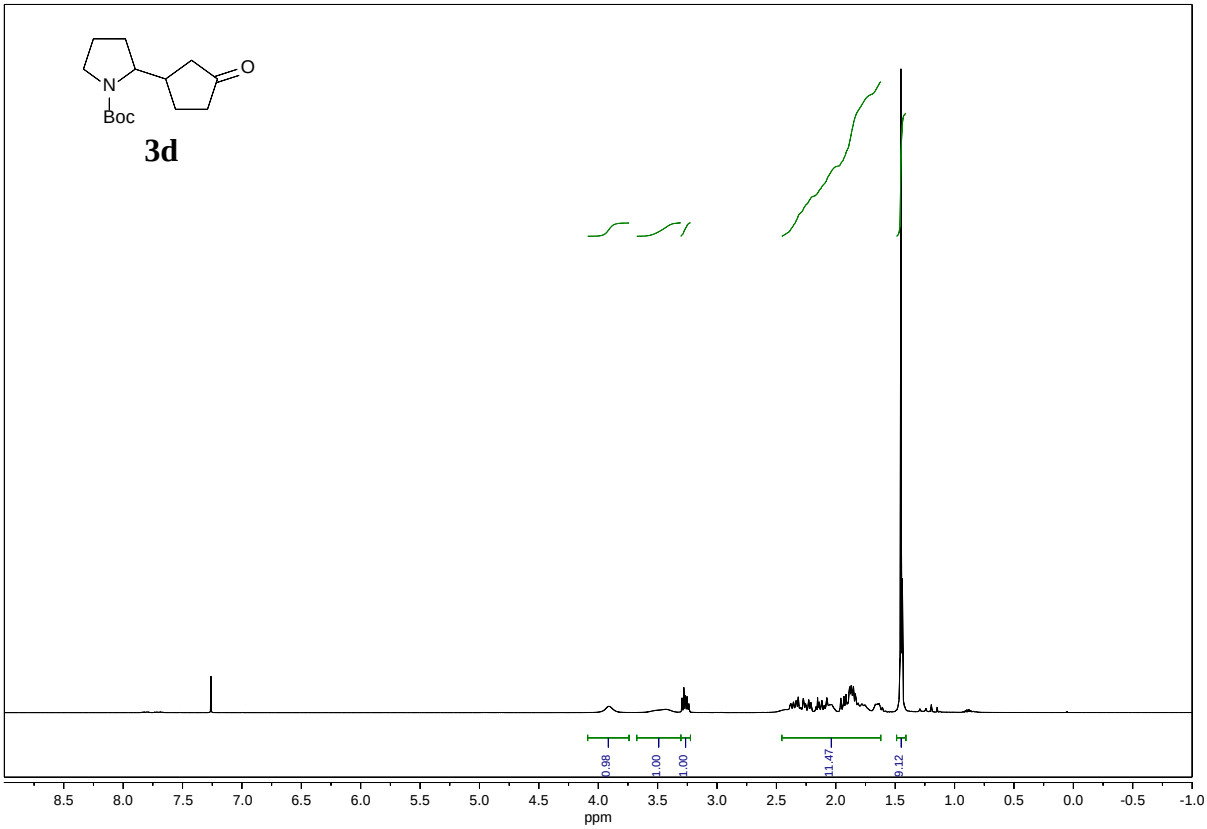


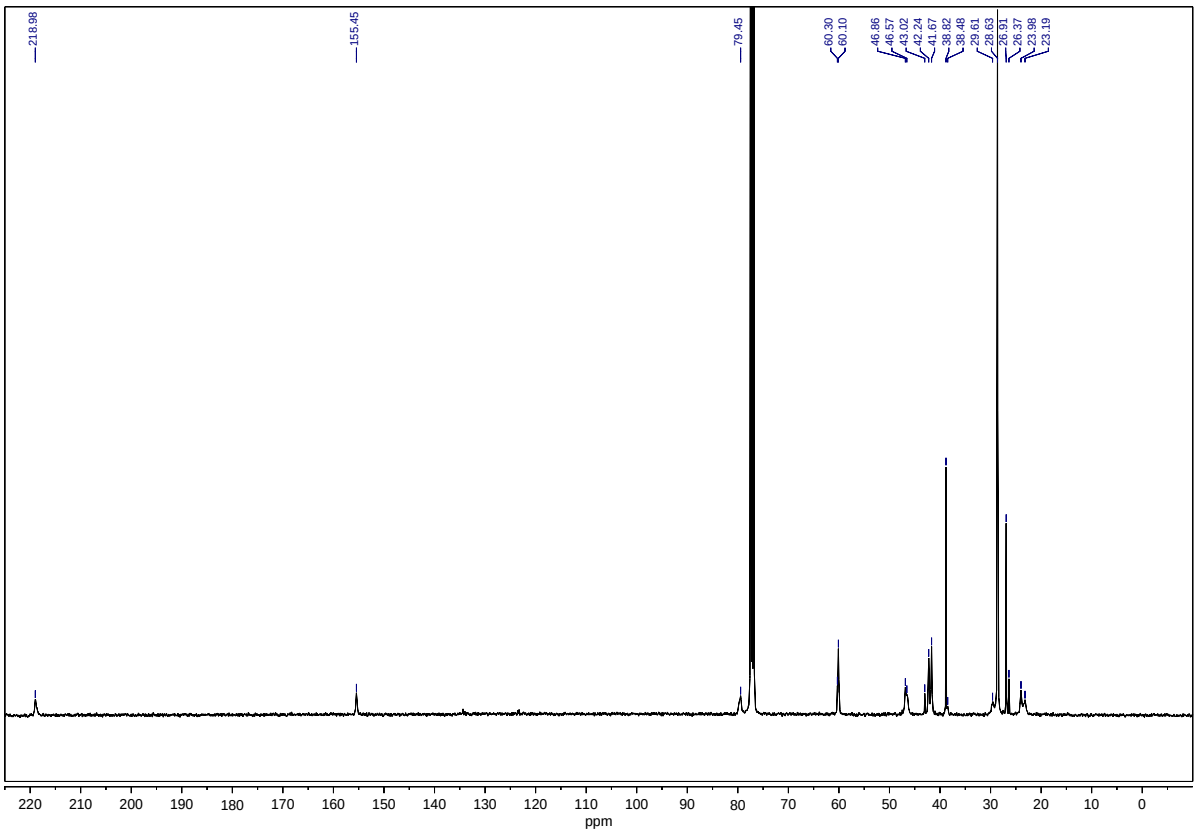
^{1}H- and ^{13}C-NMR in $CDCl_3$ of compound **3c**:



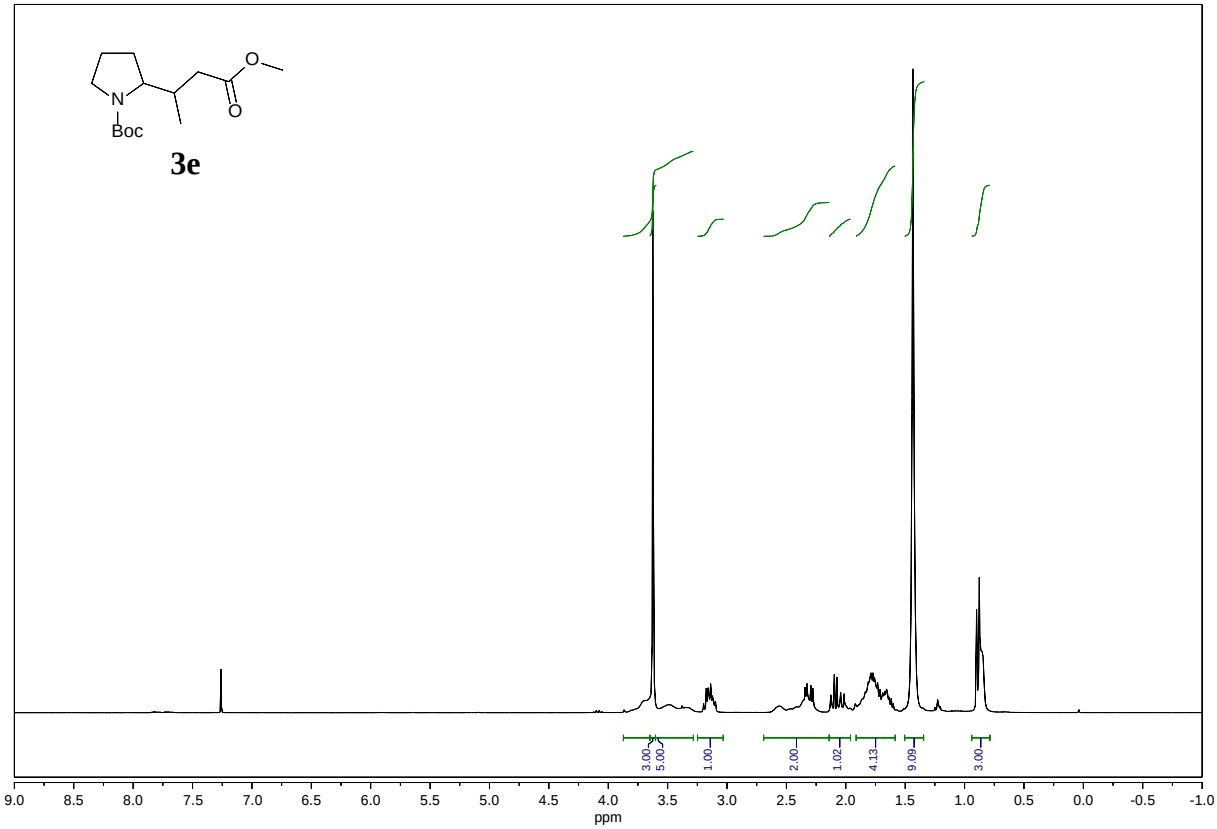


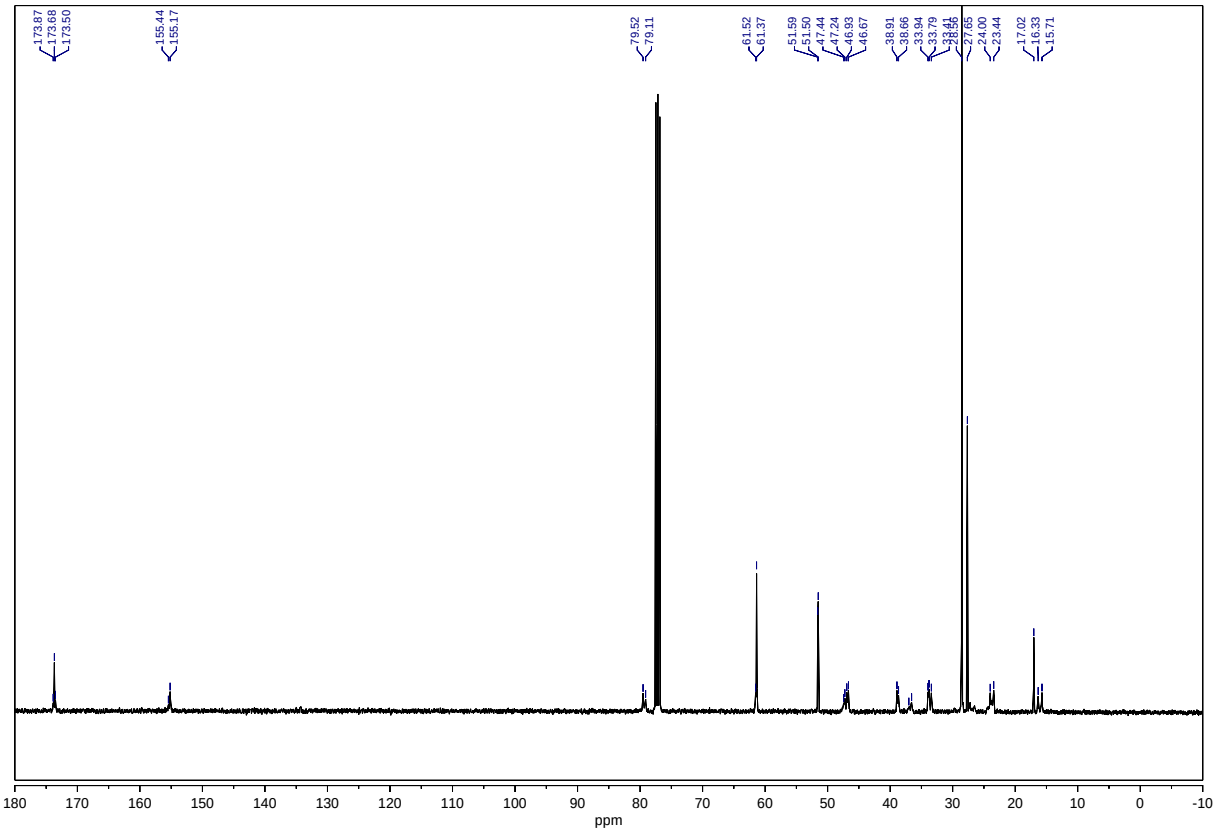
^{1}H- and ^{13}C-NMR in $CDCl_3$ of compound **3d**:



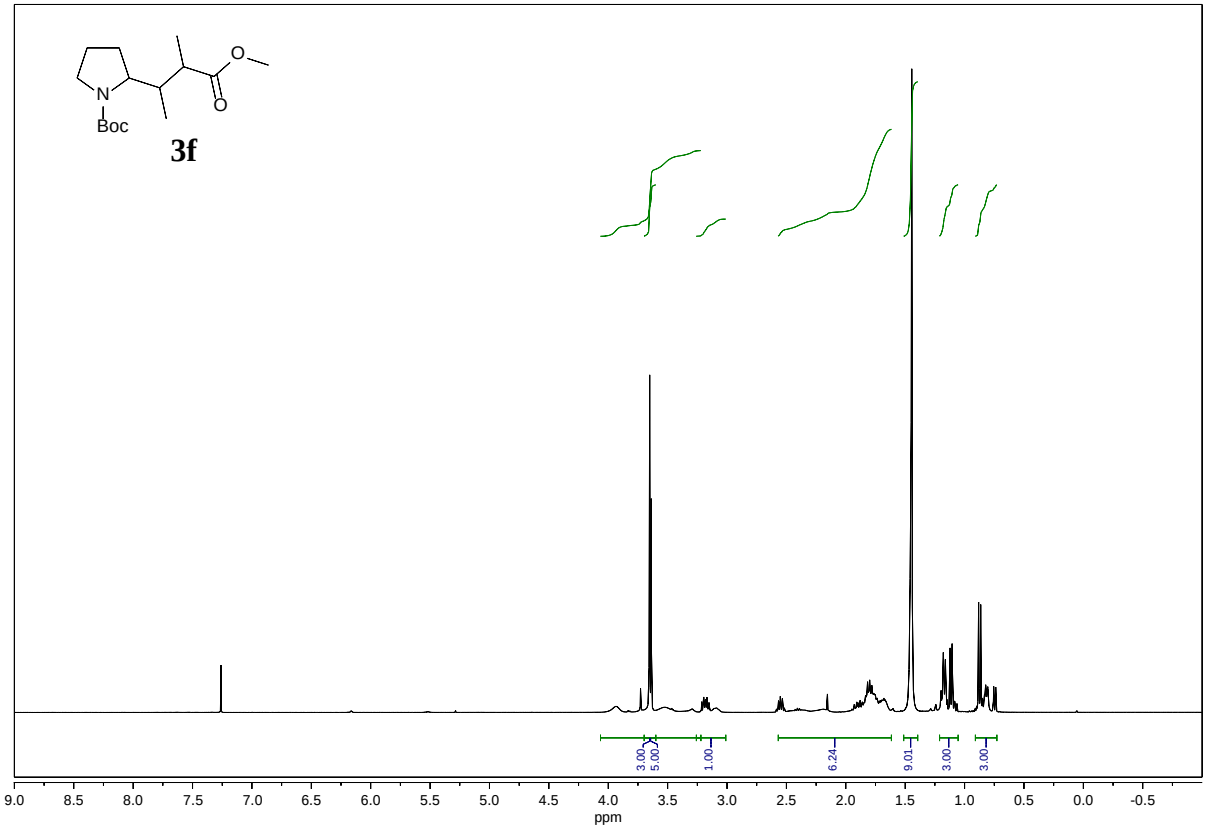


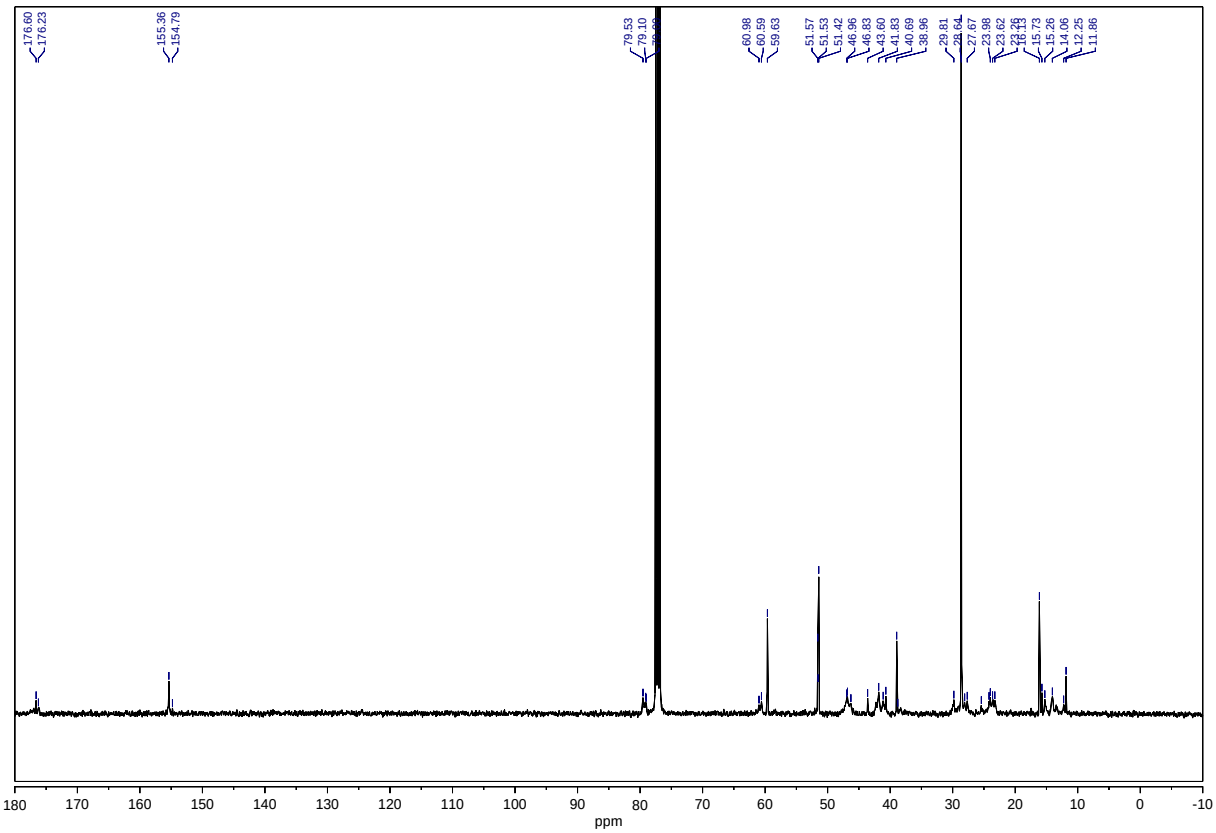
^{1}H- and ^{13}C-NMR in $CDCl_3$ of compound **3e**:



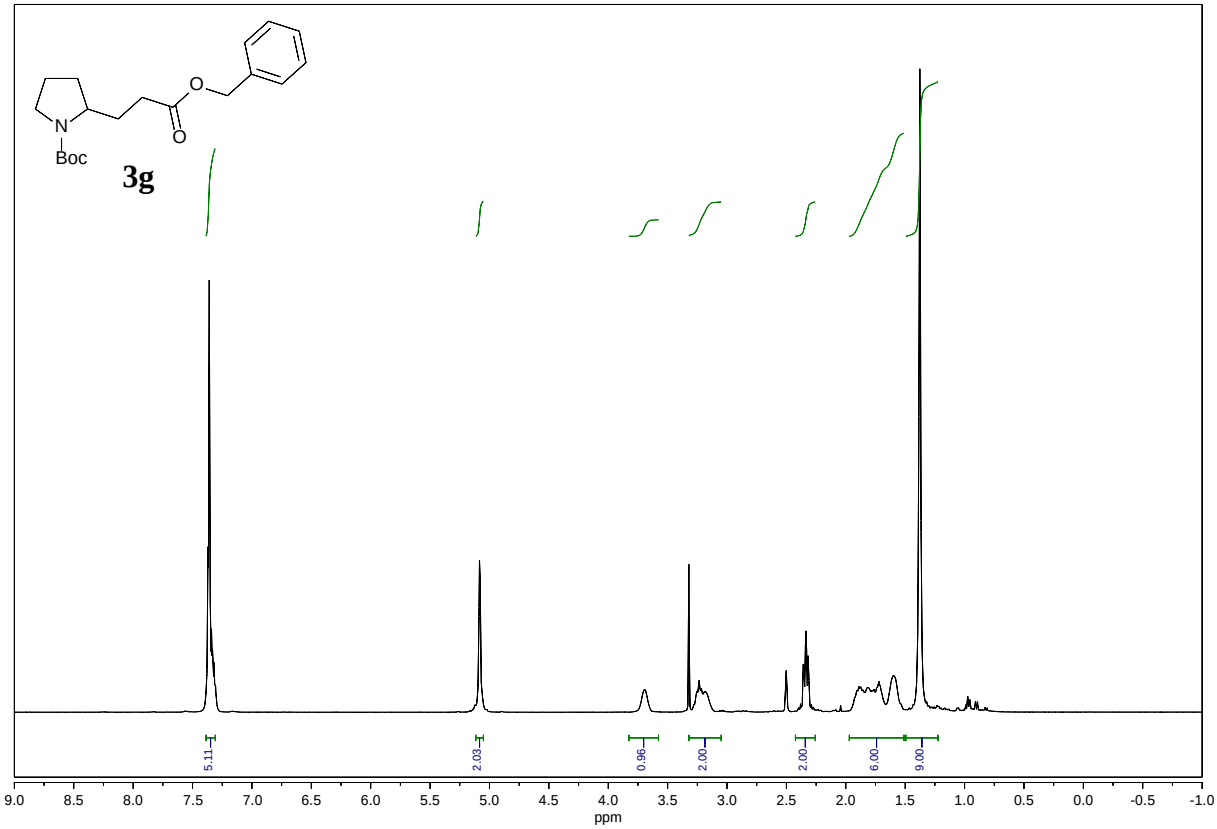


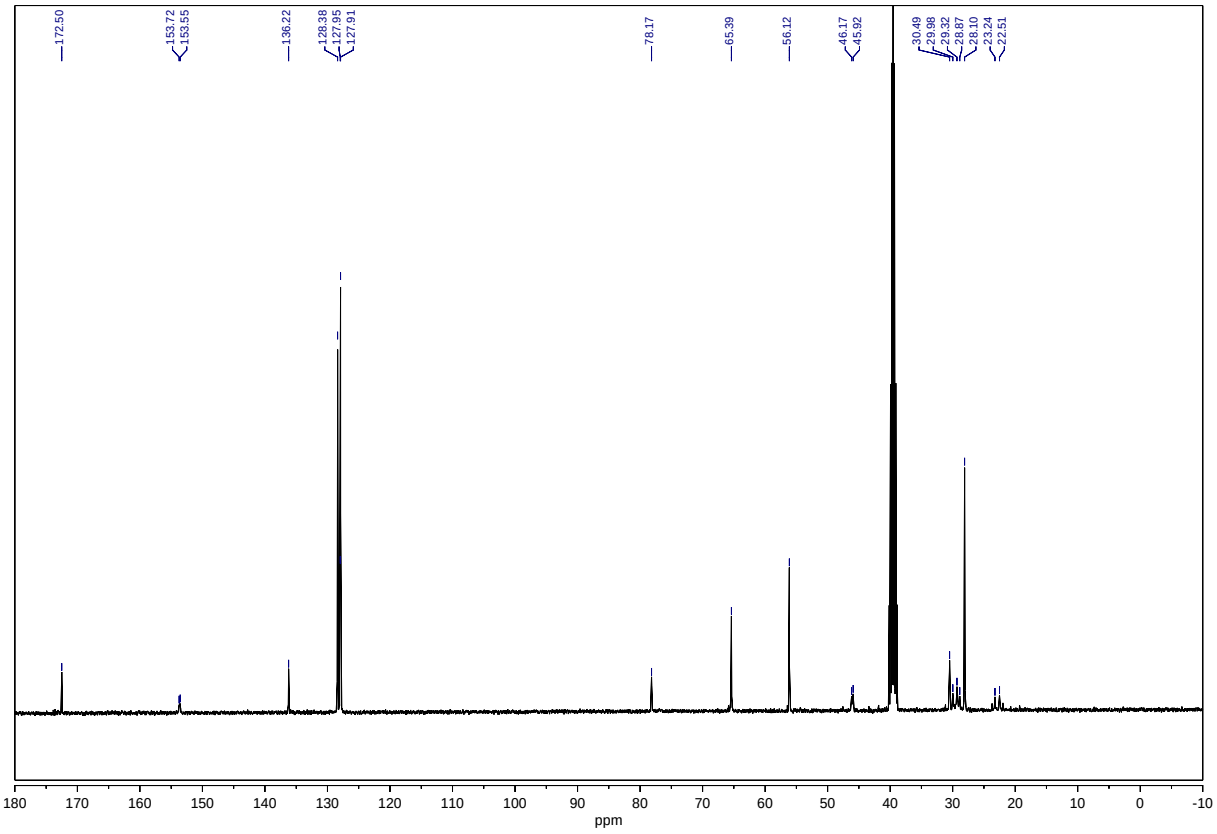
^{1}H- and ^{13}C-NMR in $CDCl_3$ of compound **3f**:



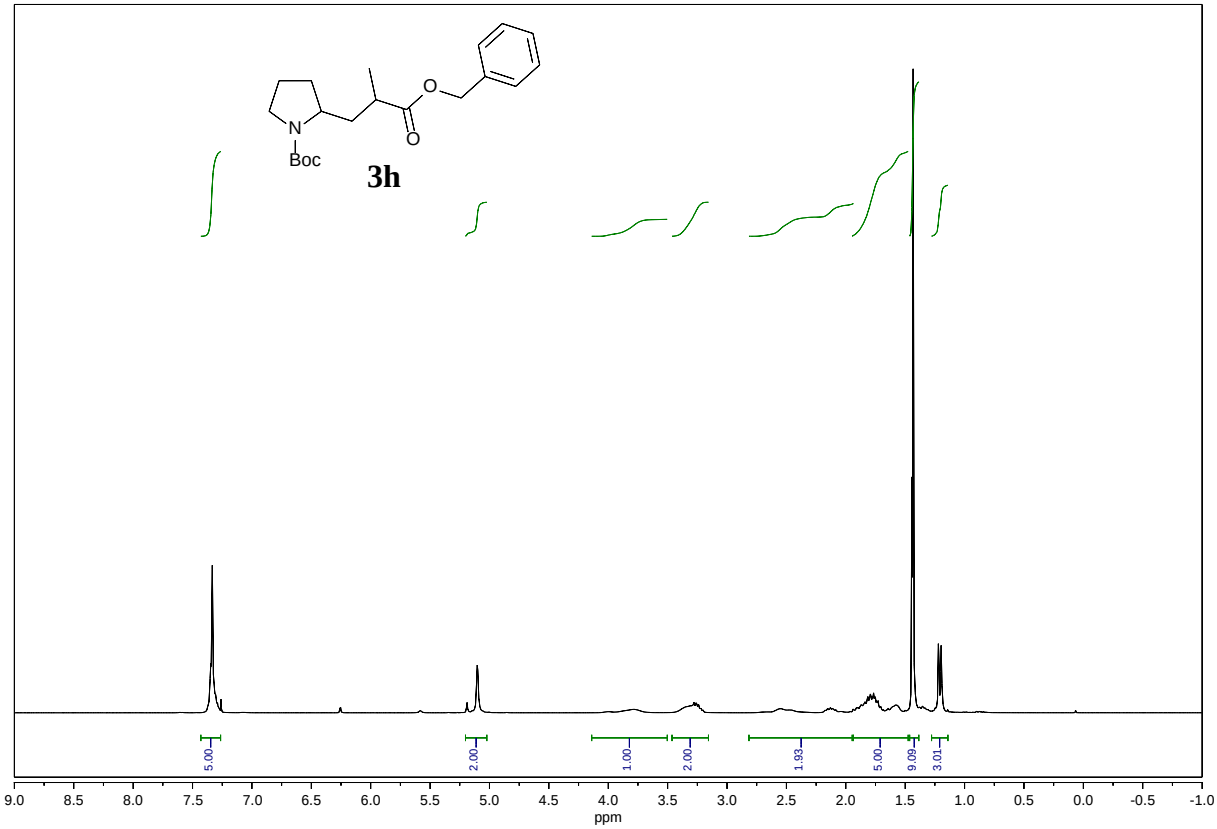


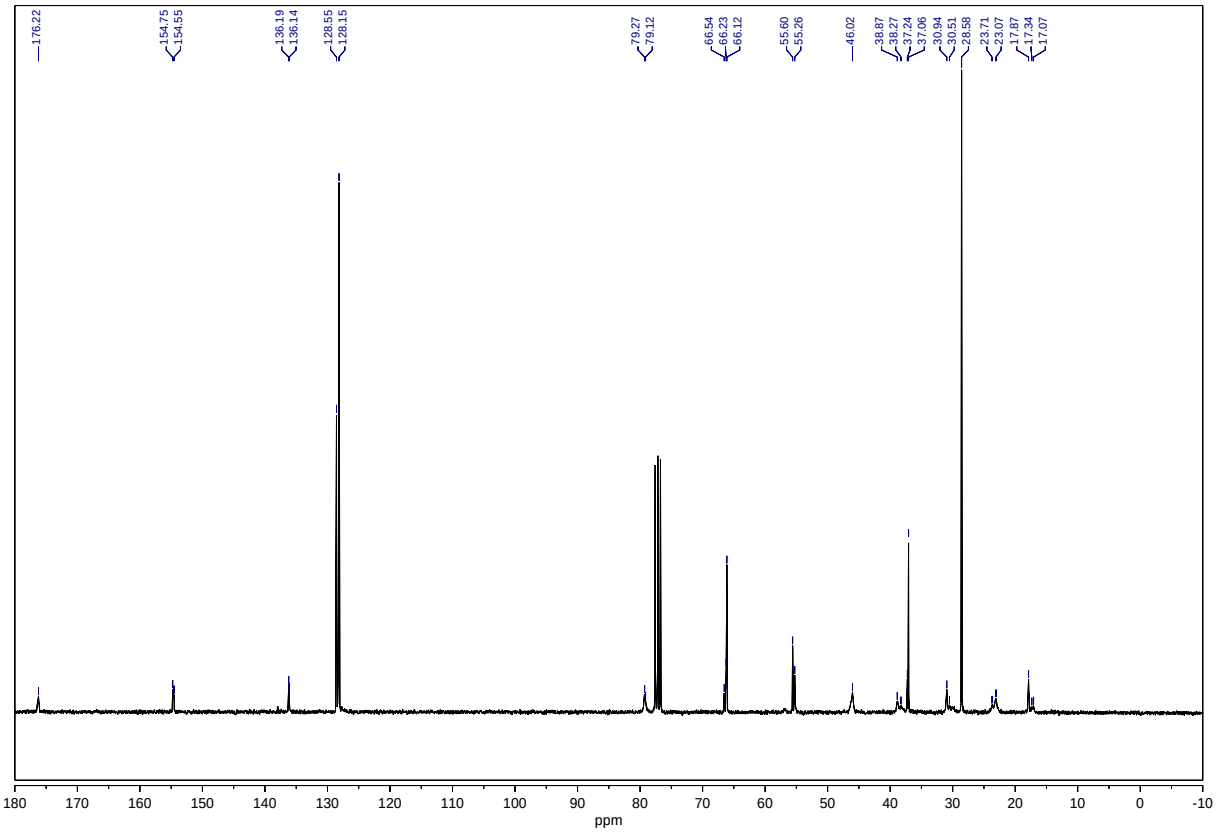
^{1}H- and ^{13}C-NMR in DMSO-d_6 of compound **3g**:



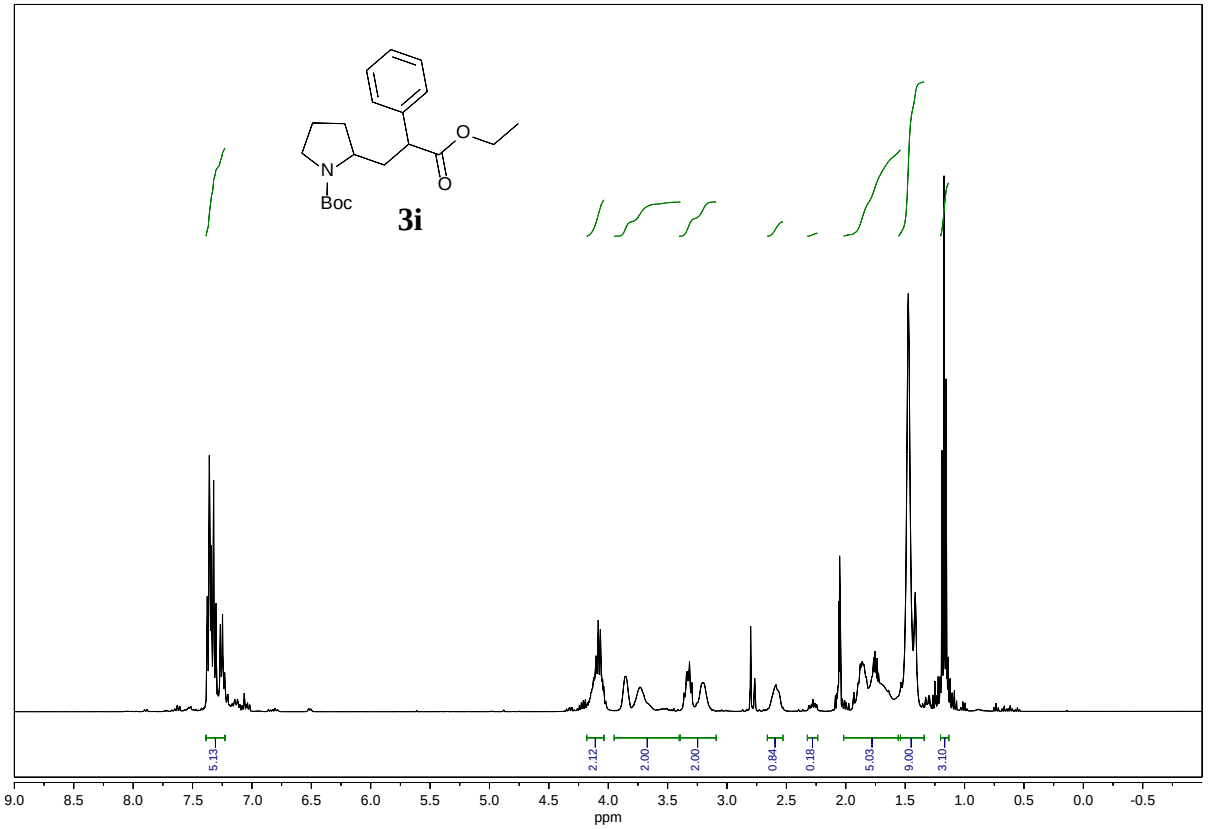


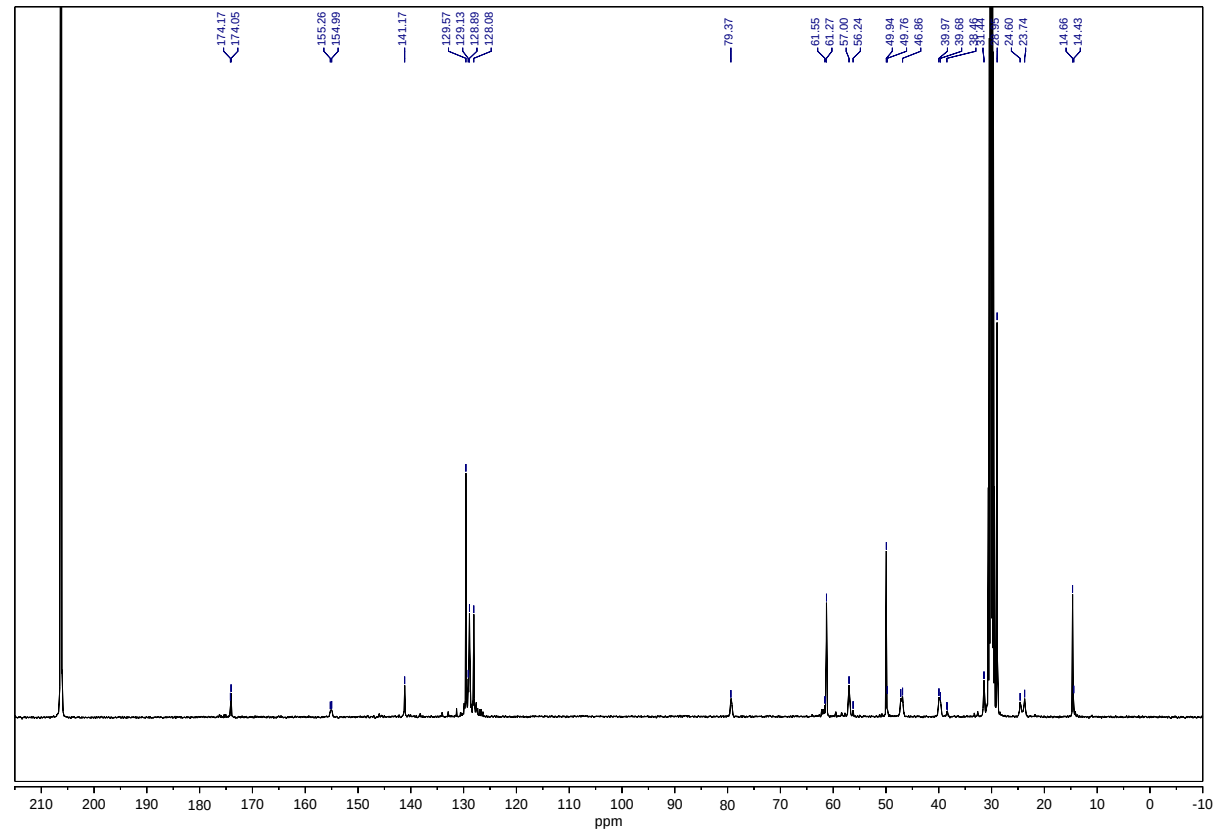
^{1}H- and ^{13}C-NMR in $CDCl_3$ of compound **3h**:



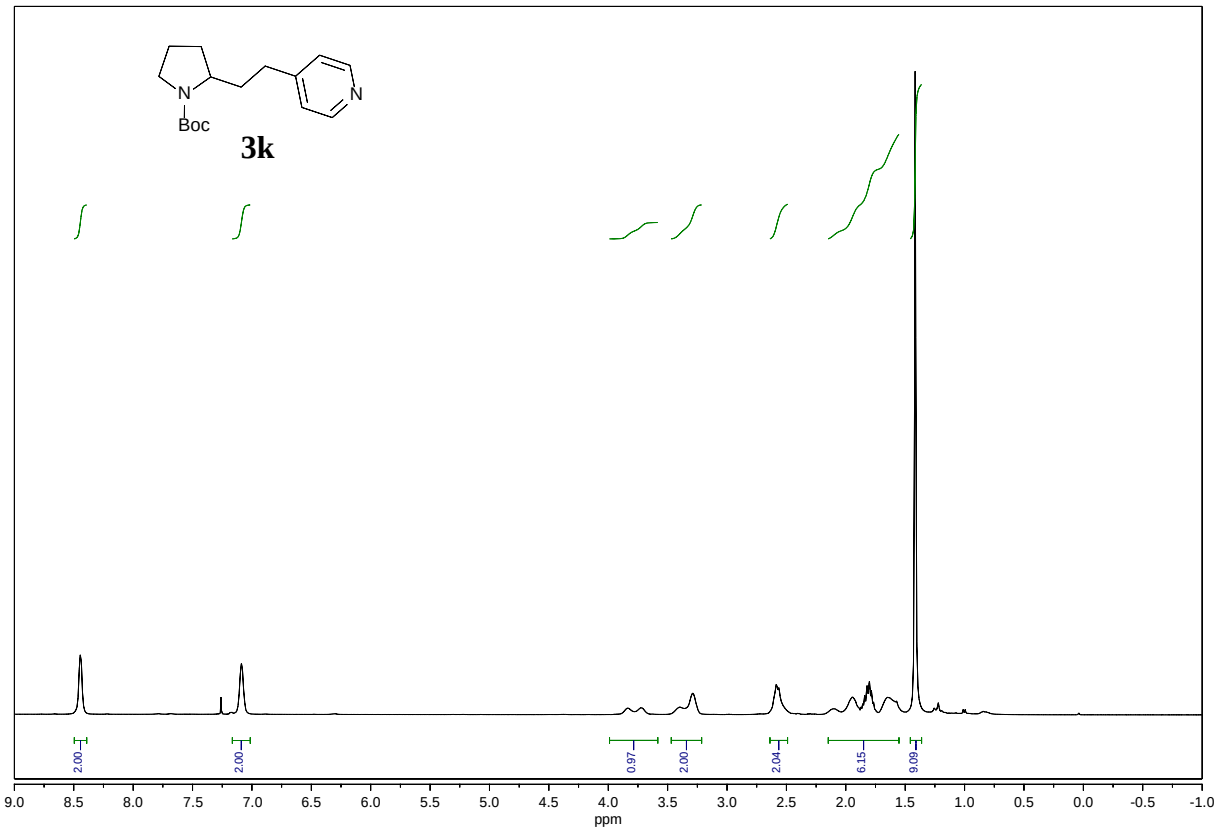


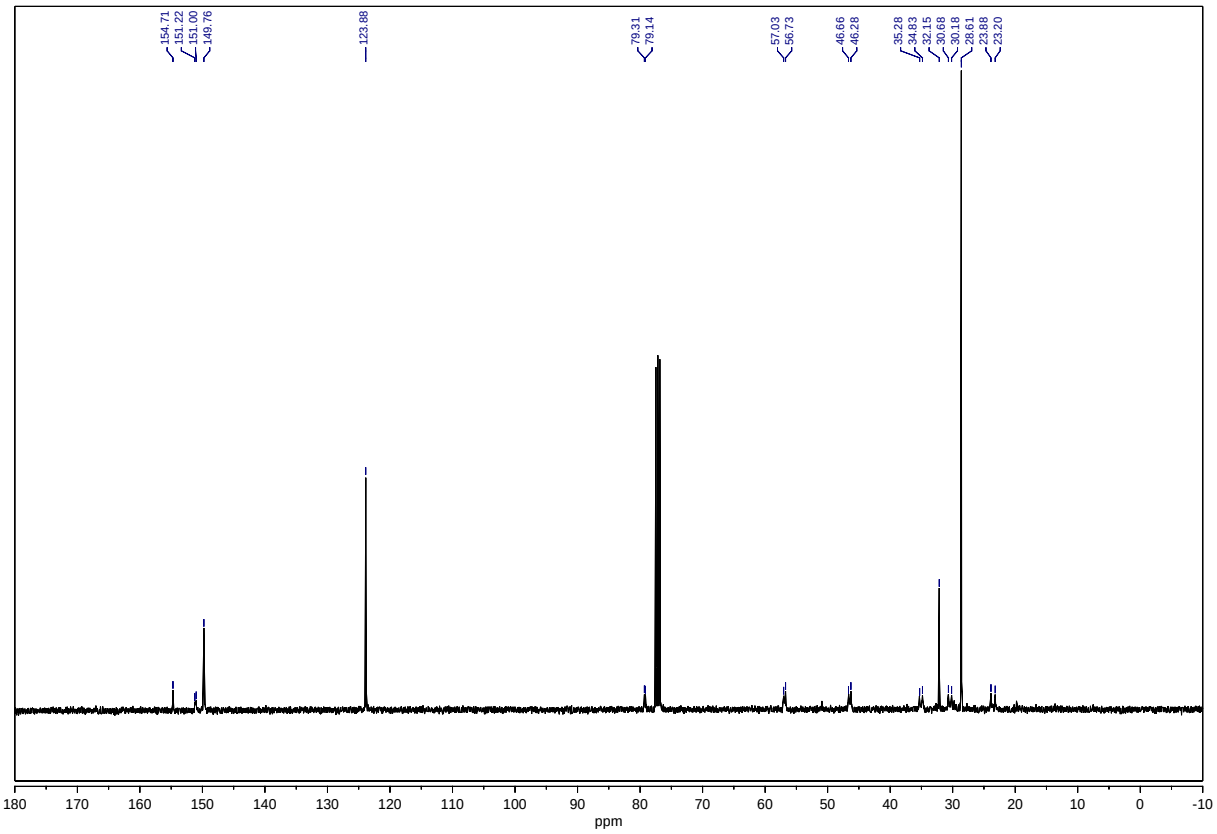
^{1}H- and ^{13}C-NMR in acetone-d_6 of compound **3i**:



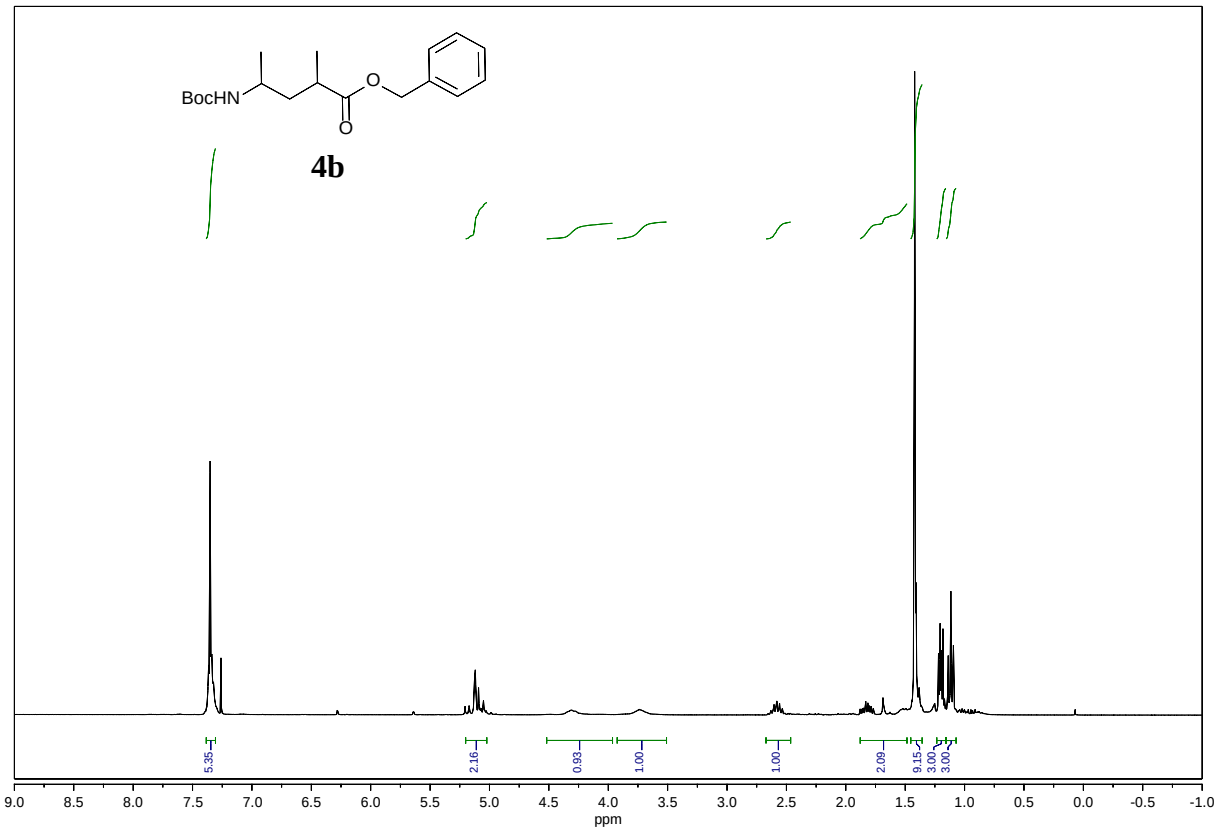


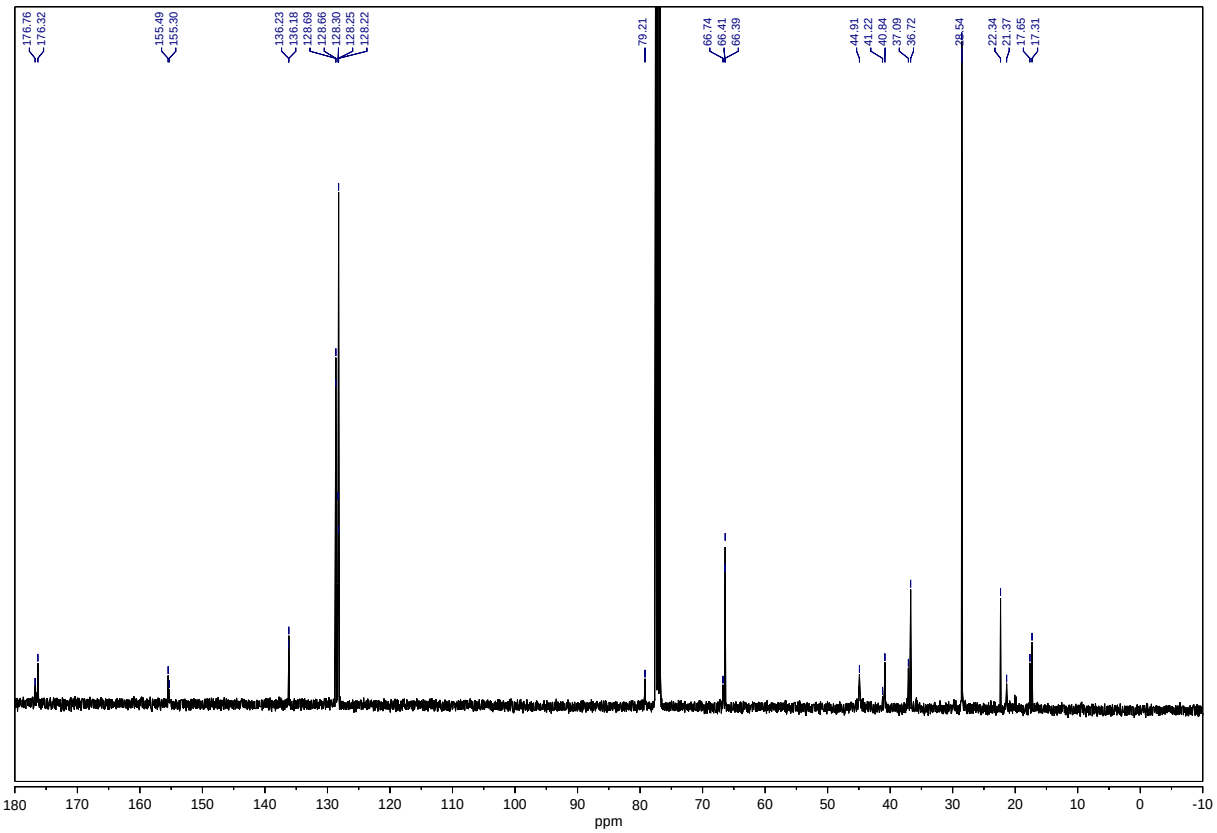
^{1}H- and ^{13}C-NMR in $CDCl_3$ of compound **3k**:



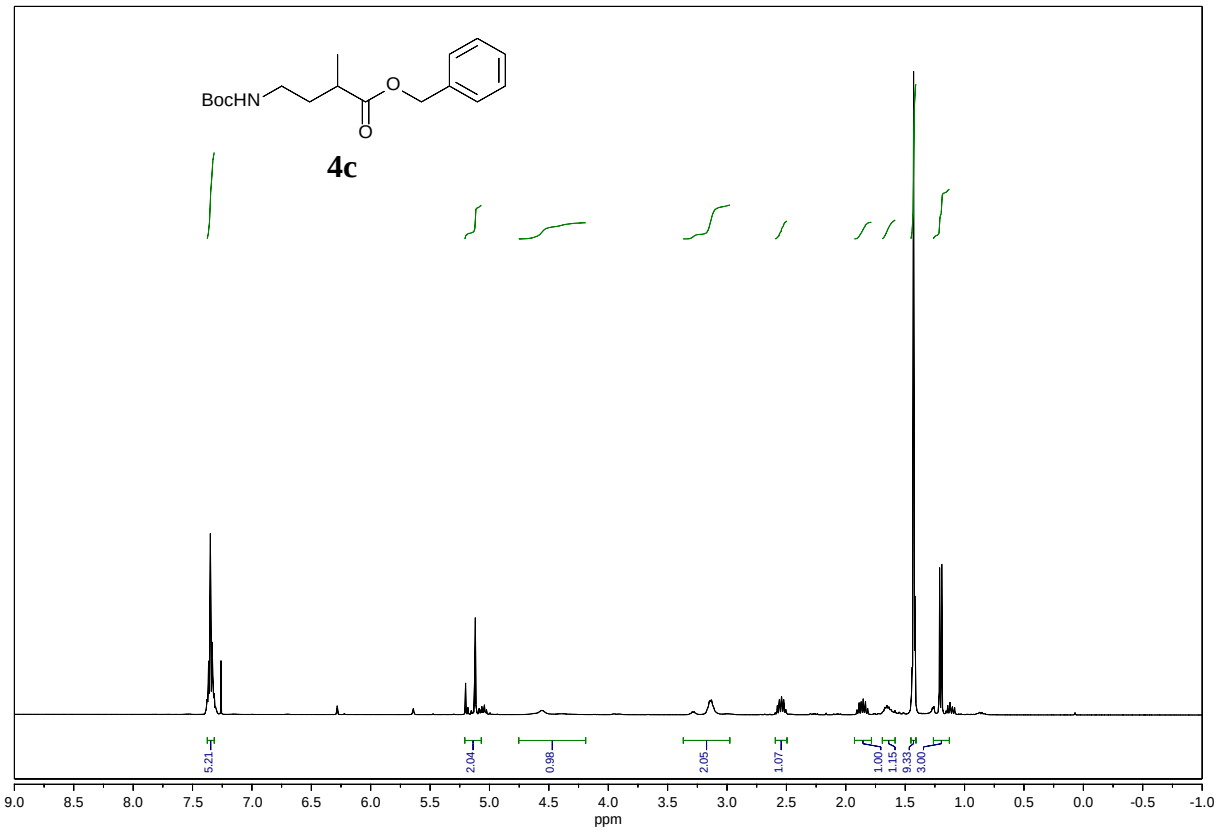


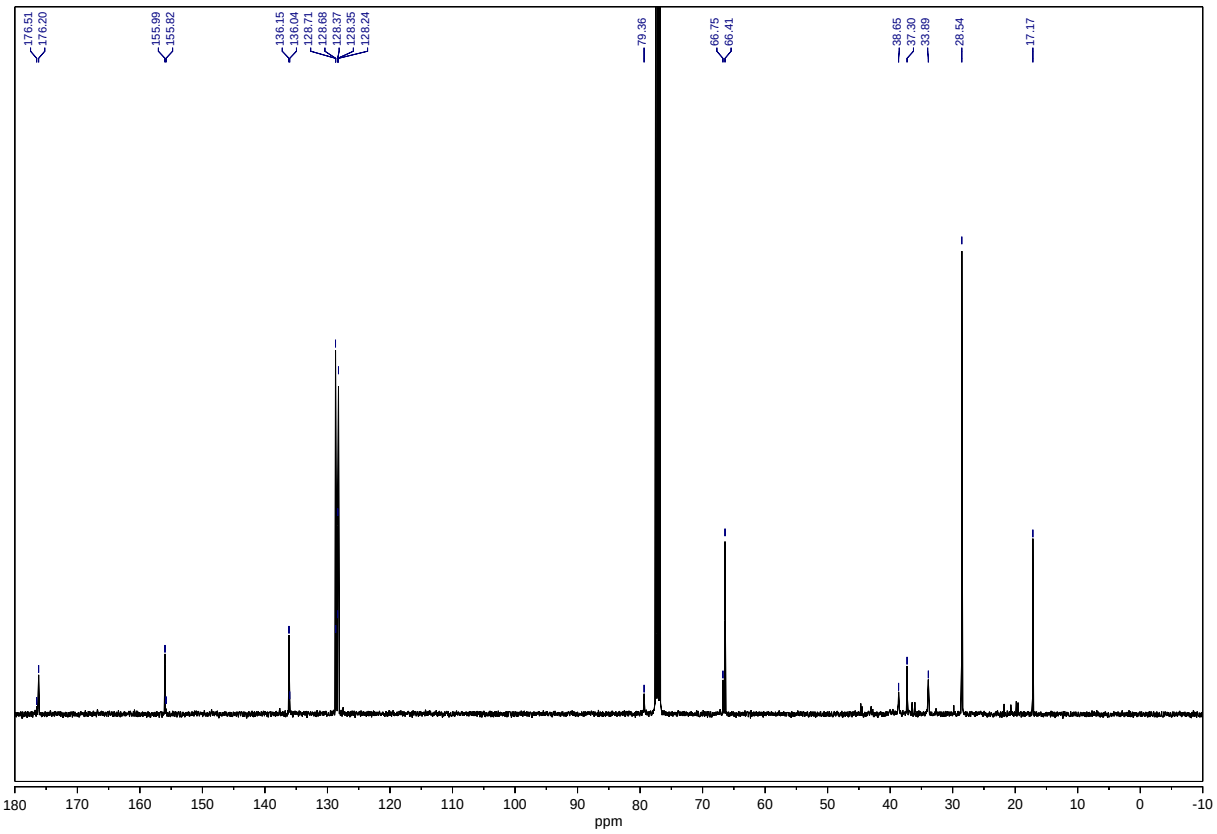
^{1}H- and ^{13}C-NMR in $CDCl_3$ of compound **4b**:



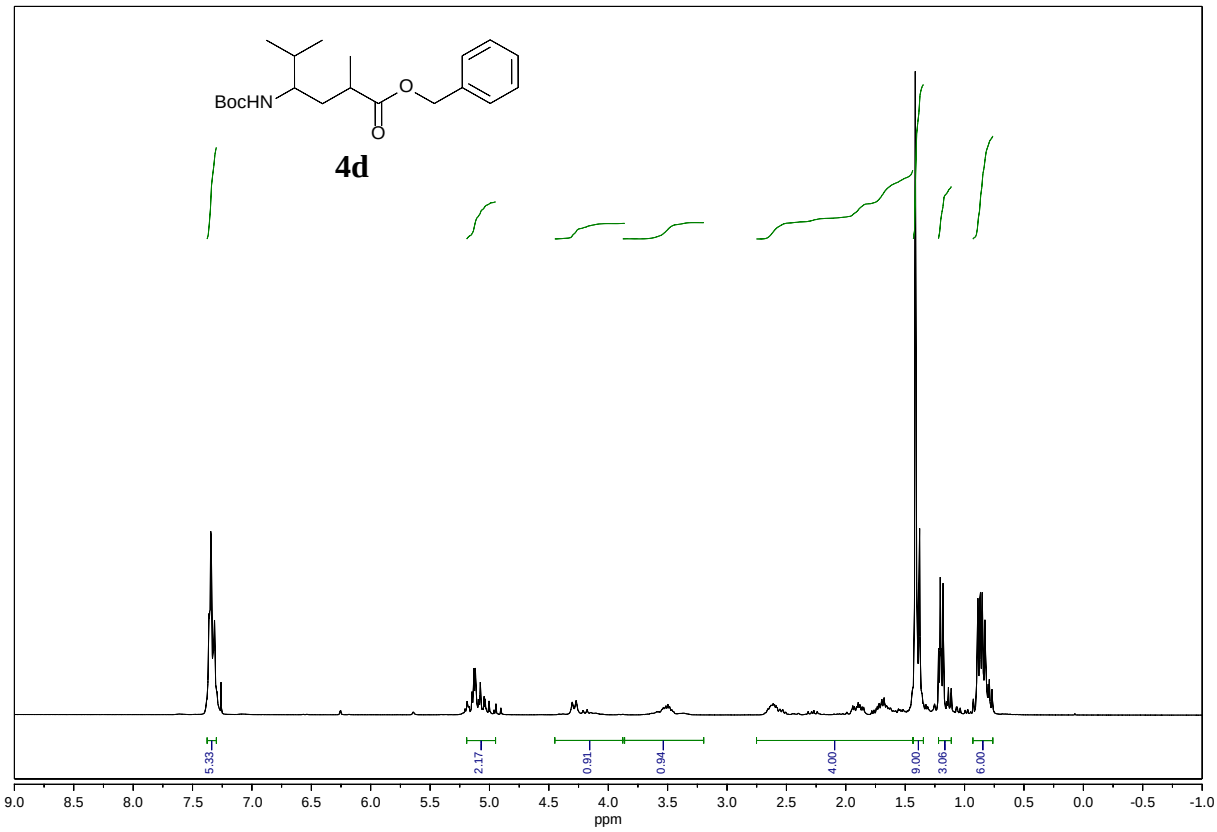


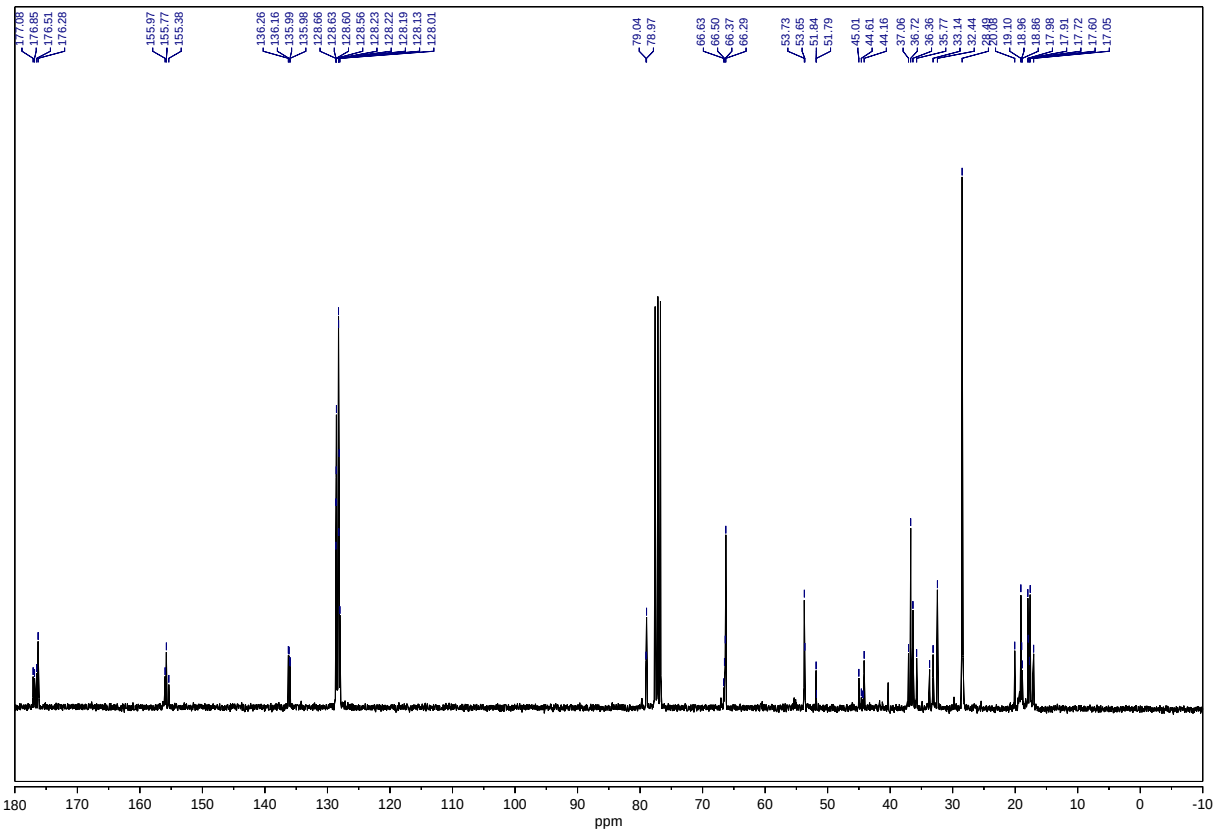
^{1}H- and ^{13}C-NMR in $CDCl_3$ of compound **4c**:



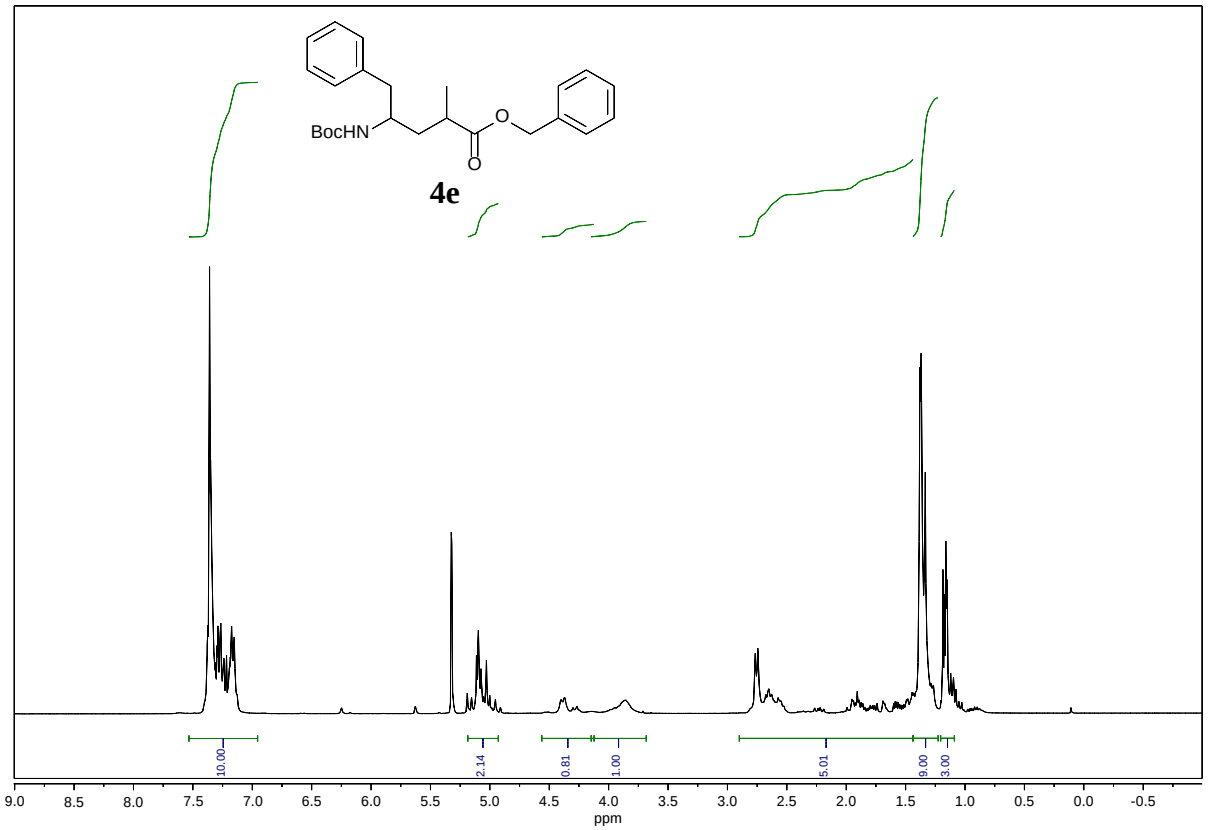


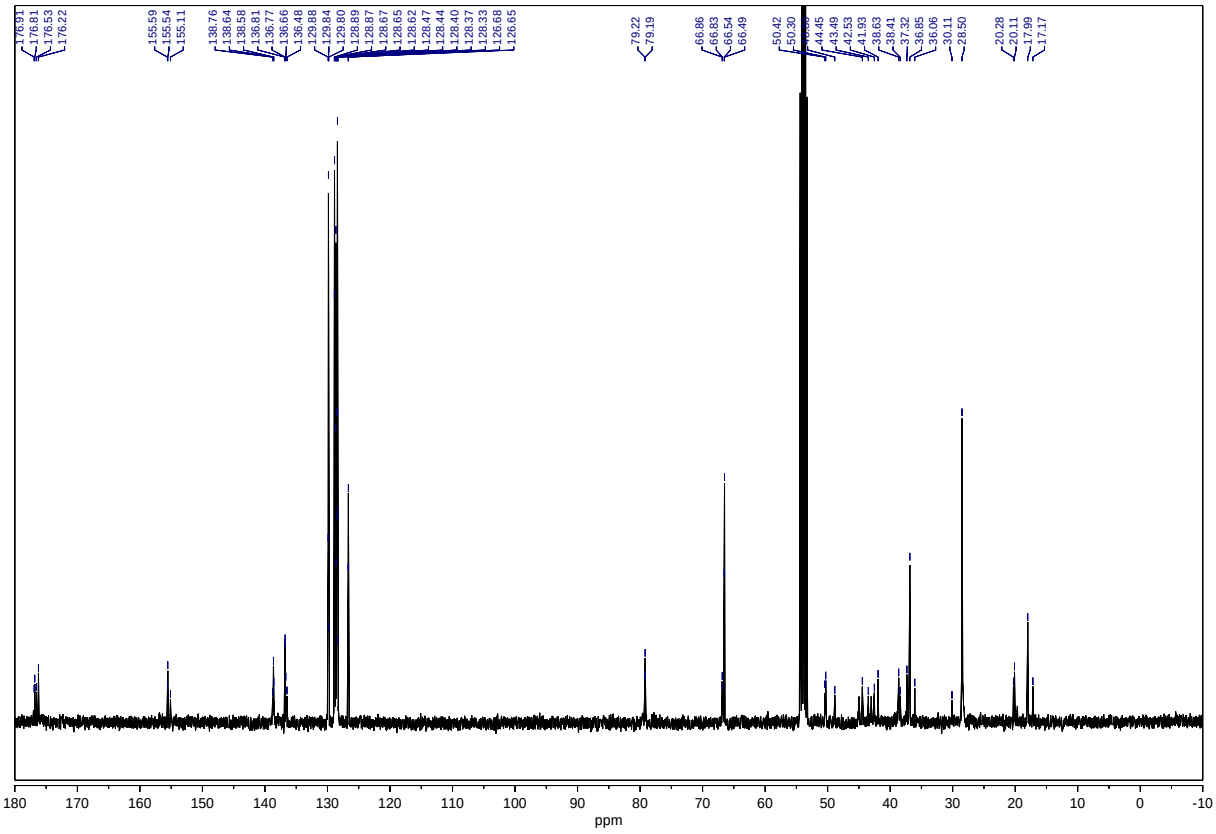
^{1}H- and ^{13}C-NMR in $CDCl_3$ of compound **4d**:



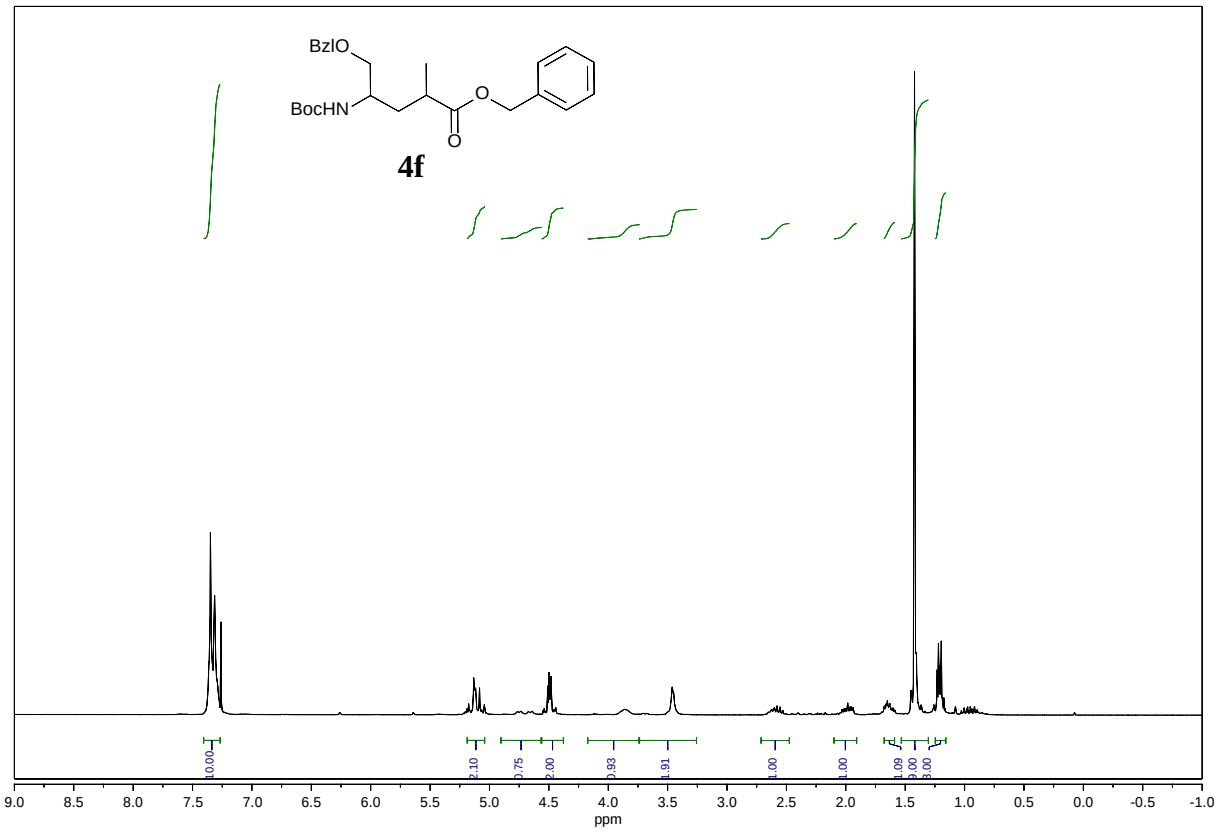


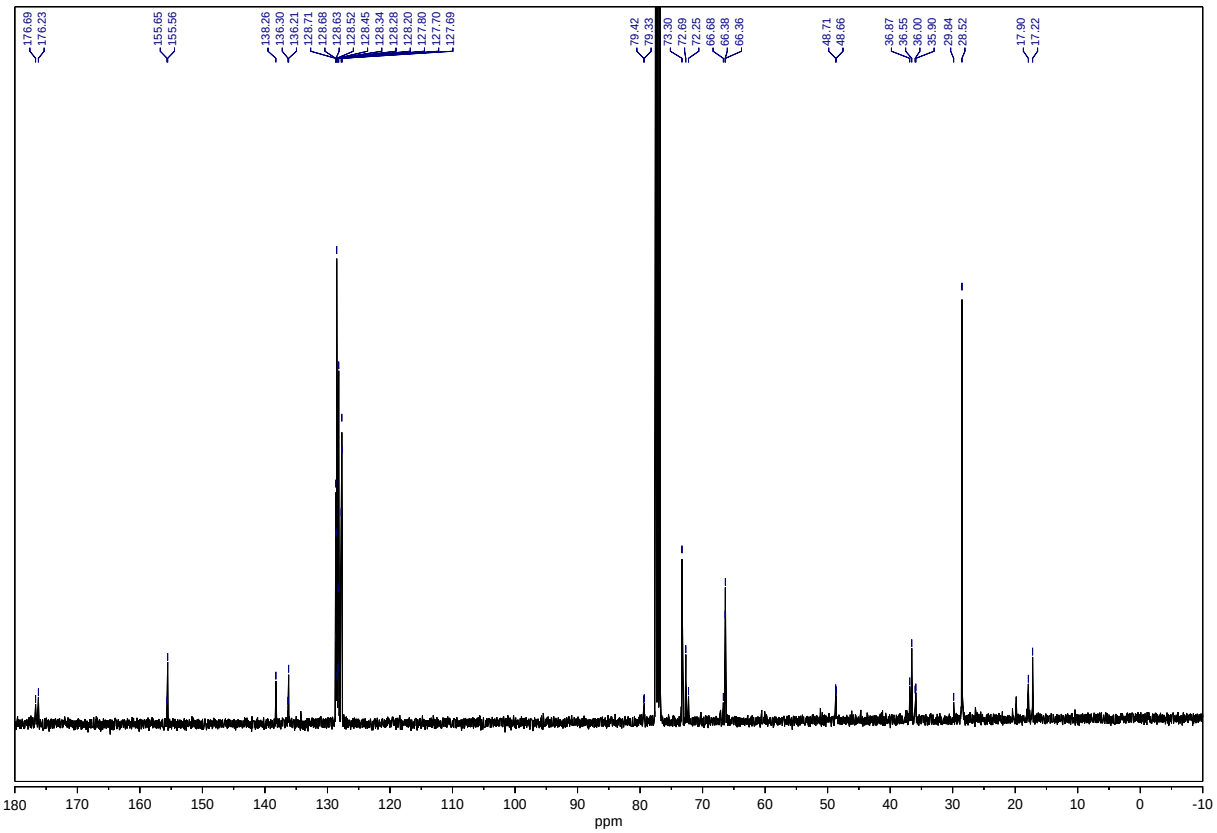
^{1}H- and ^{13}C-NMR in CD_2Cl_2 of compound **4e**:



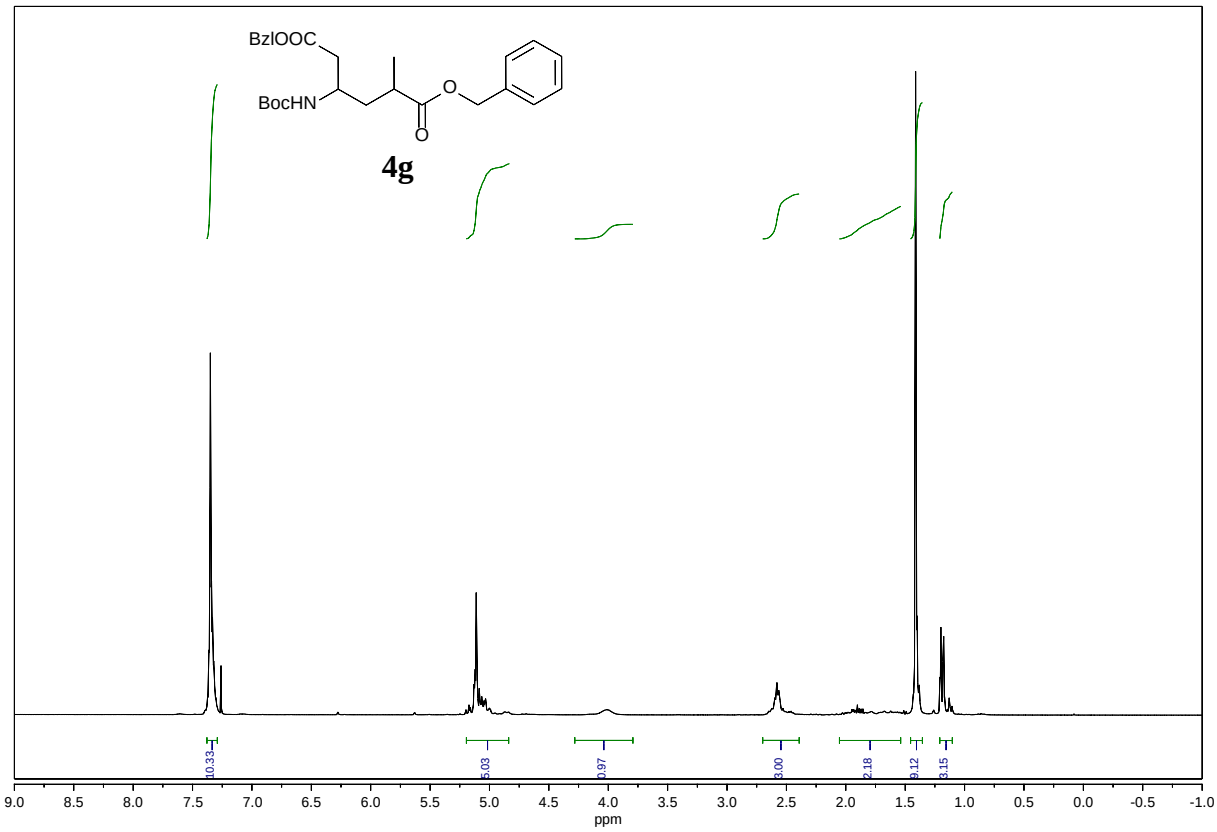


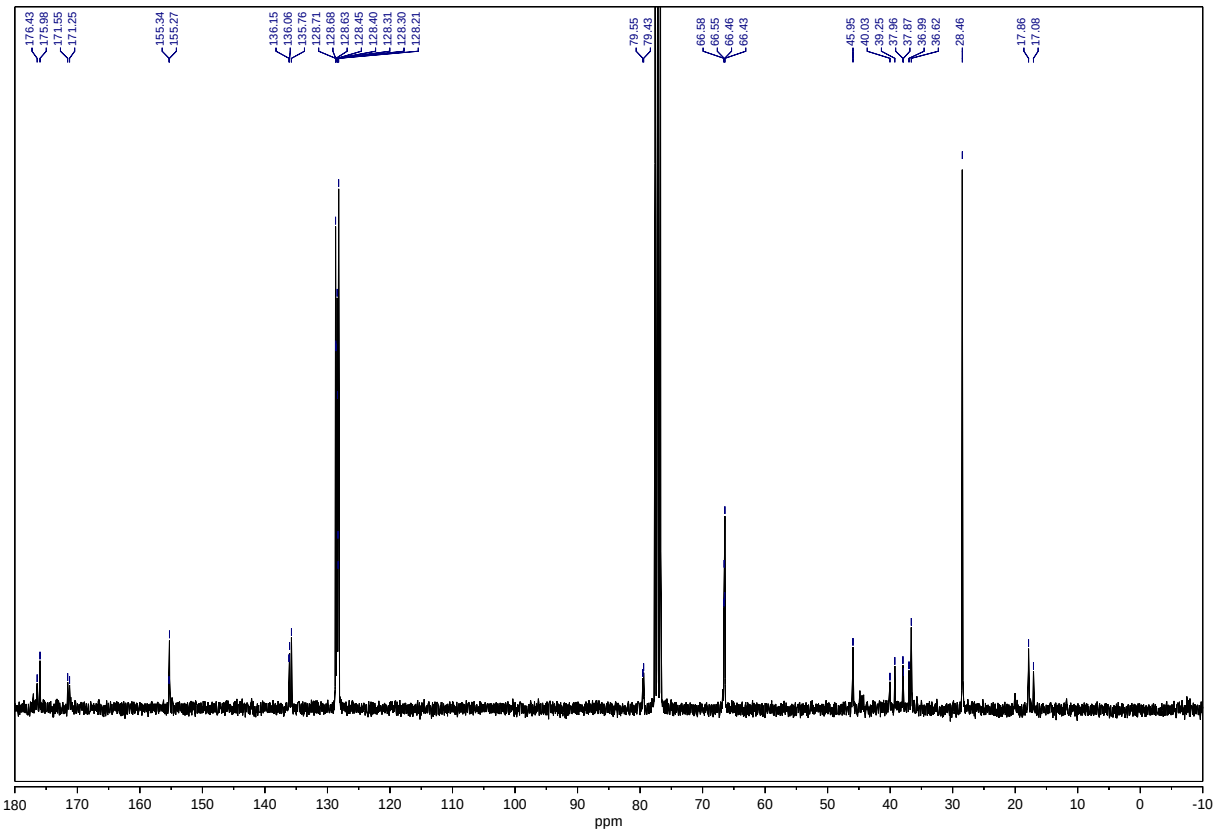
^{1}H- and ^{13}C-NMR in $CDCl_3$ of compound **4f**:



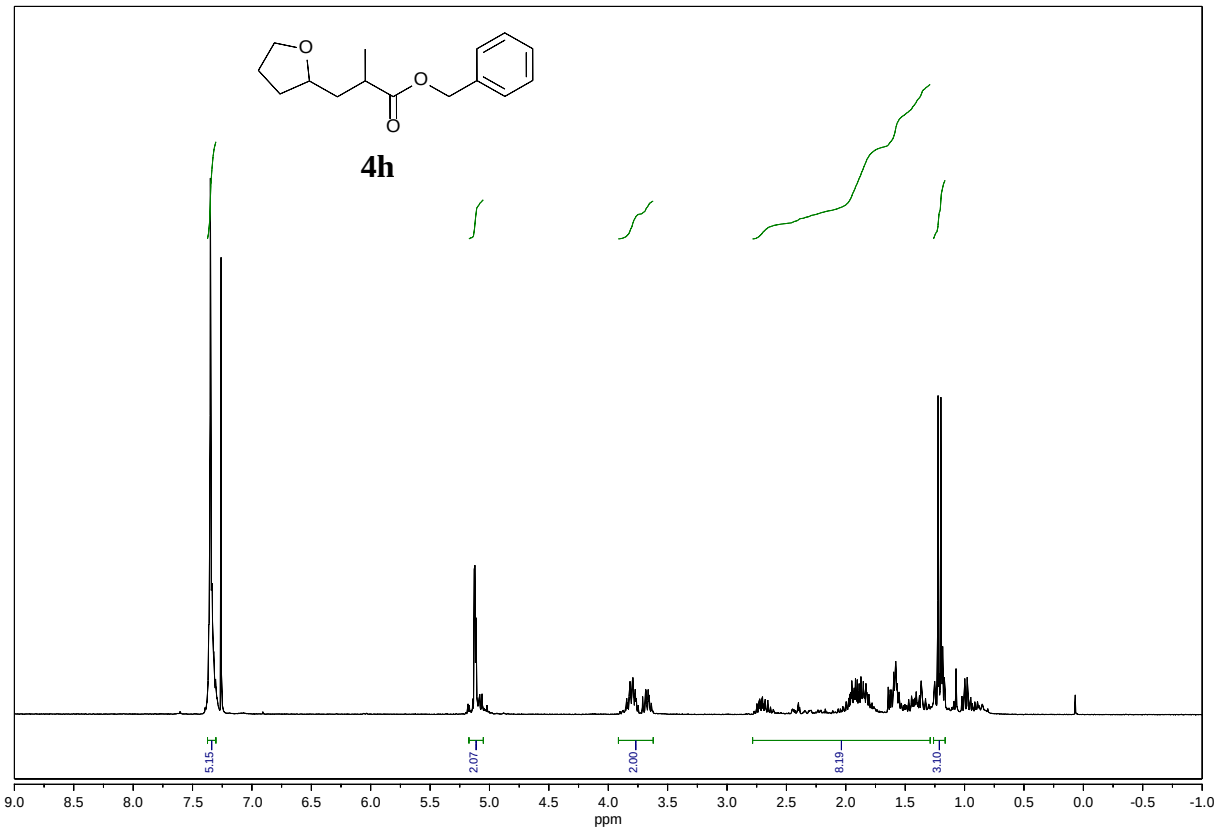


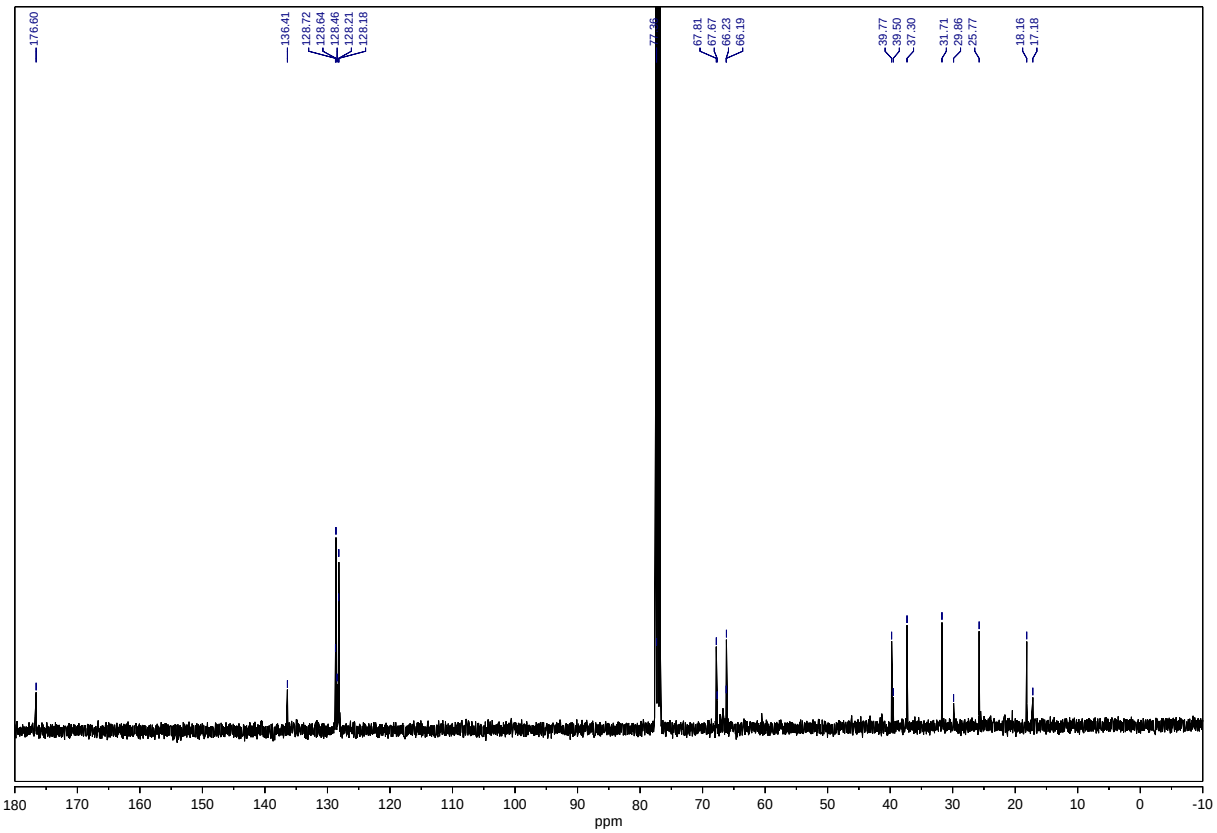
^{1}H- and ^{13}C-NMR in $CDCl_3$ of compound **4g**:



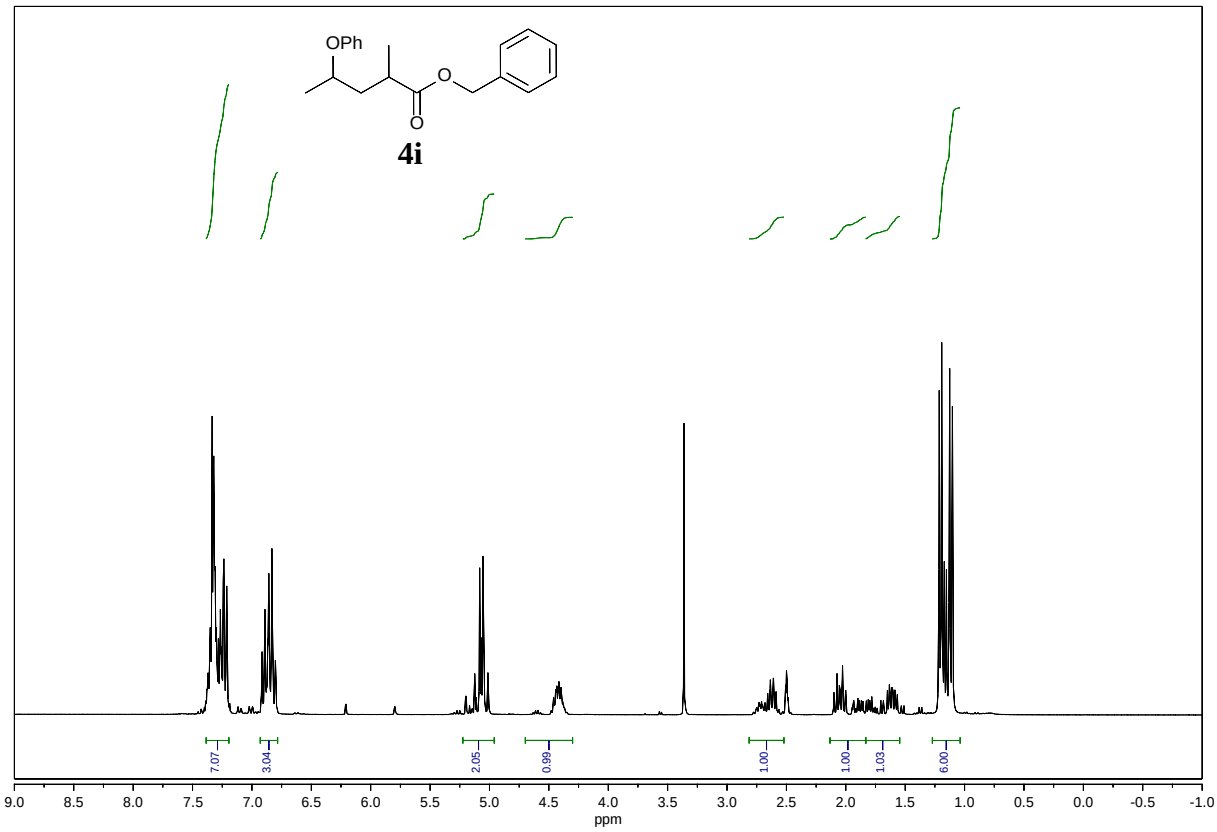


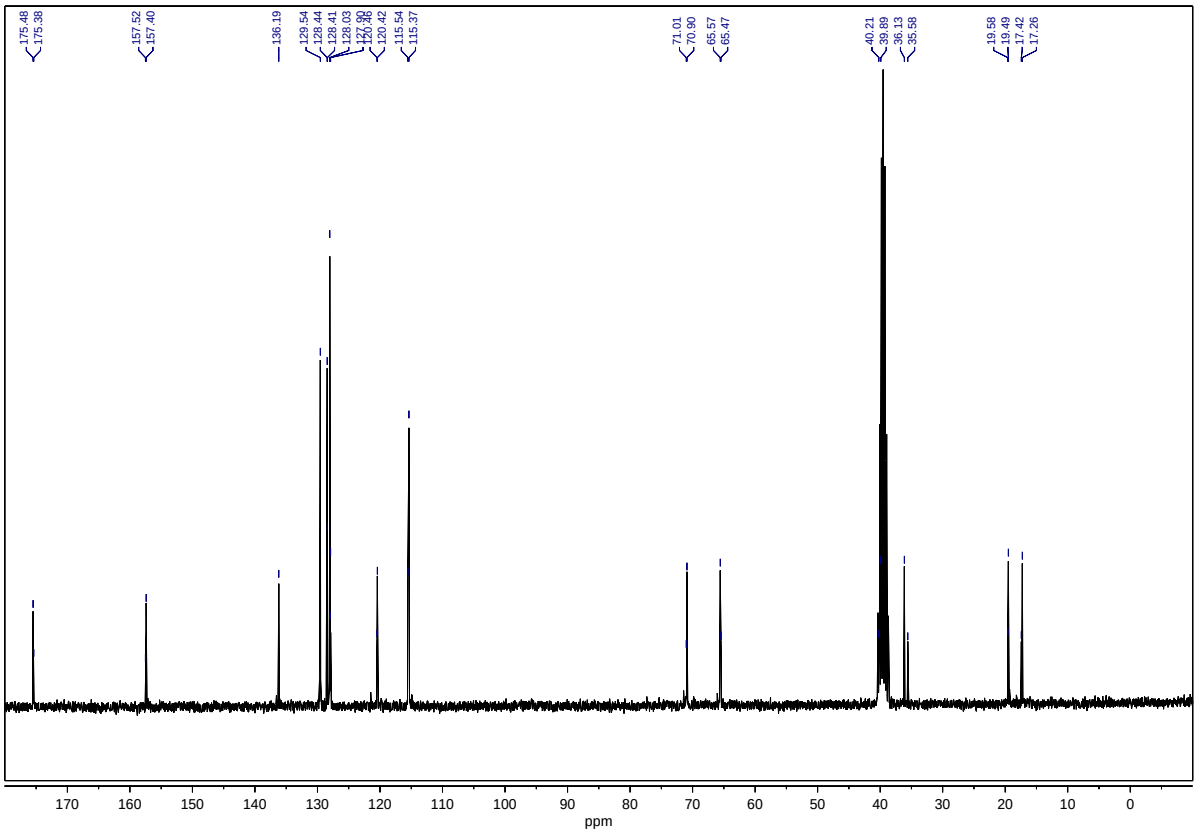
^{1}H- and ^{13}C-NMR in $CDCl_3$ of compound **4h**:



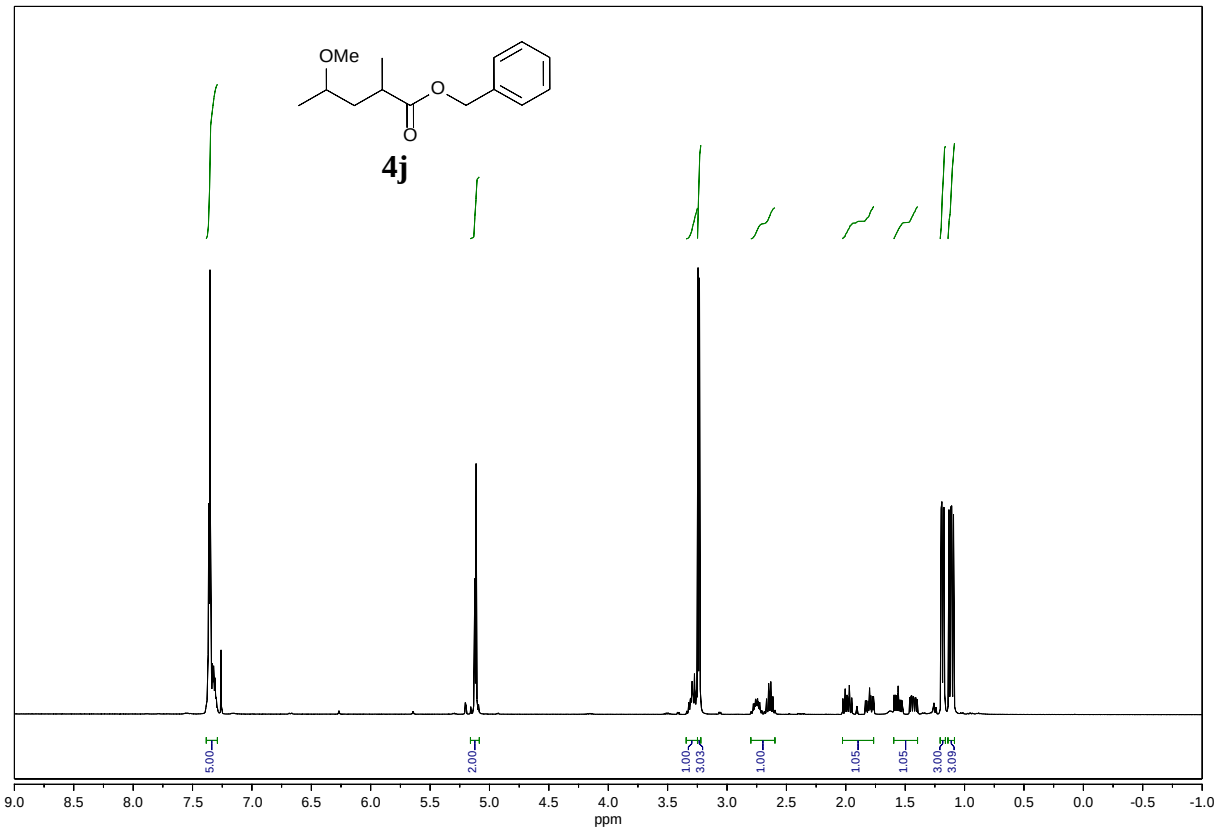


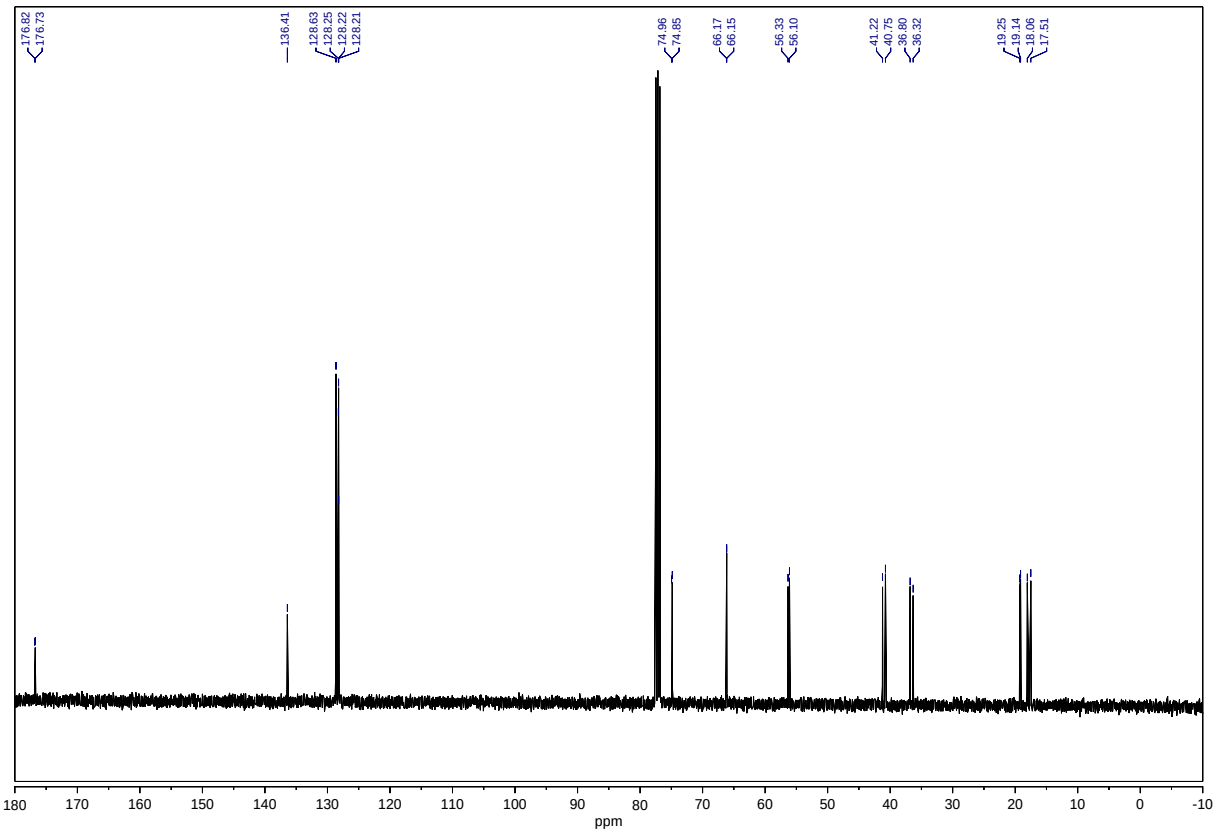
^{1}H- and ^{13}C-NMR in DMSO-d_6 of compound **4i**:



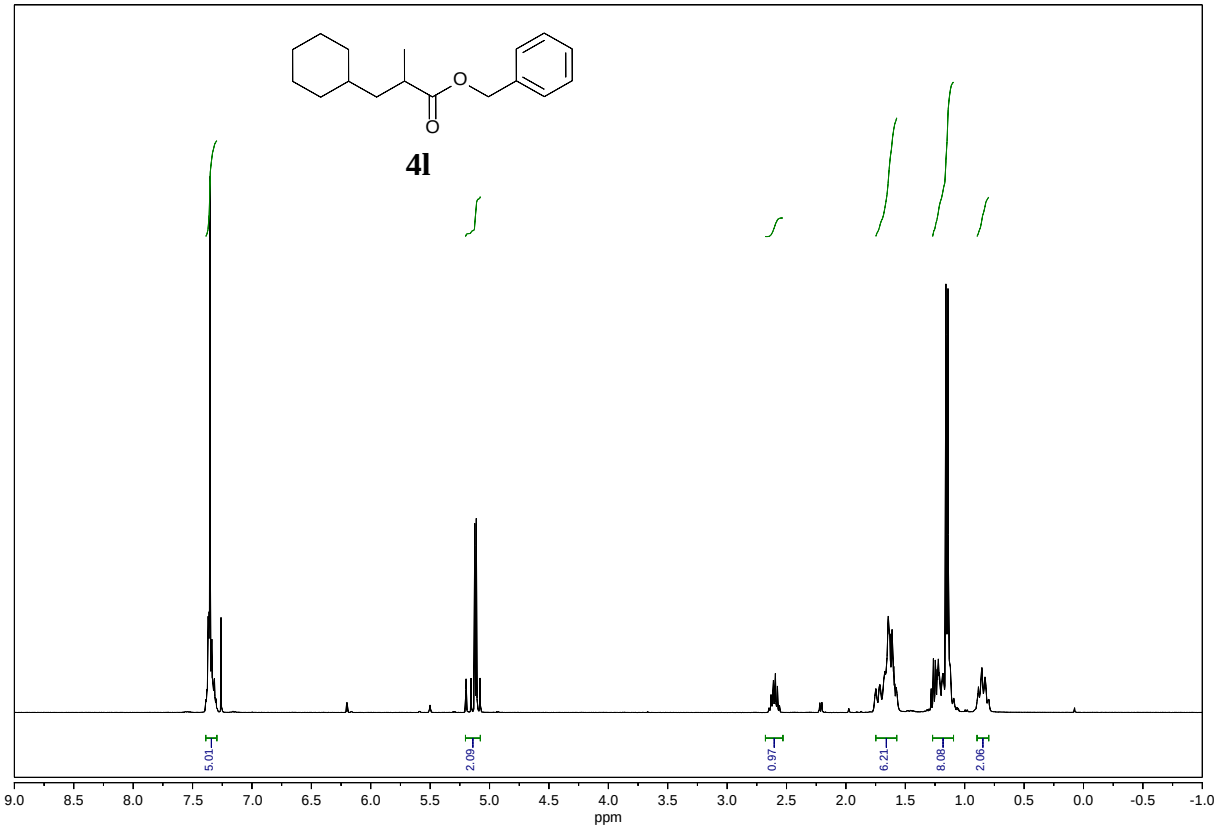


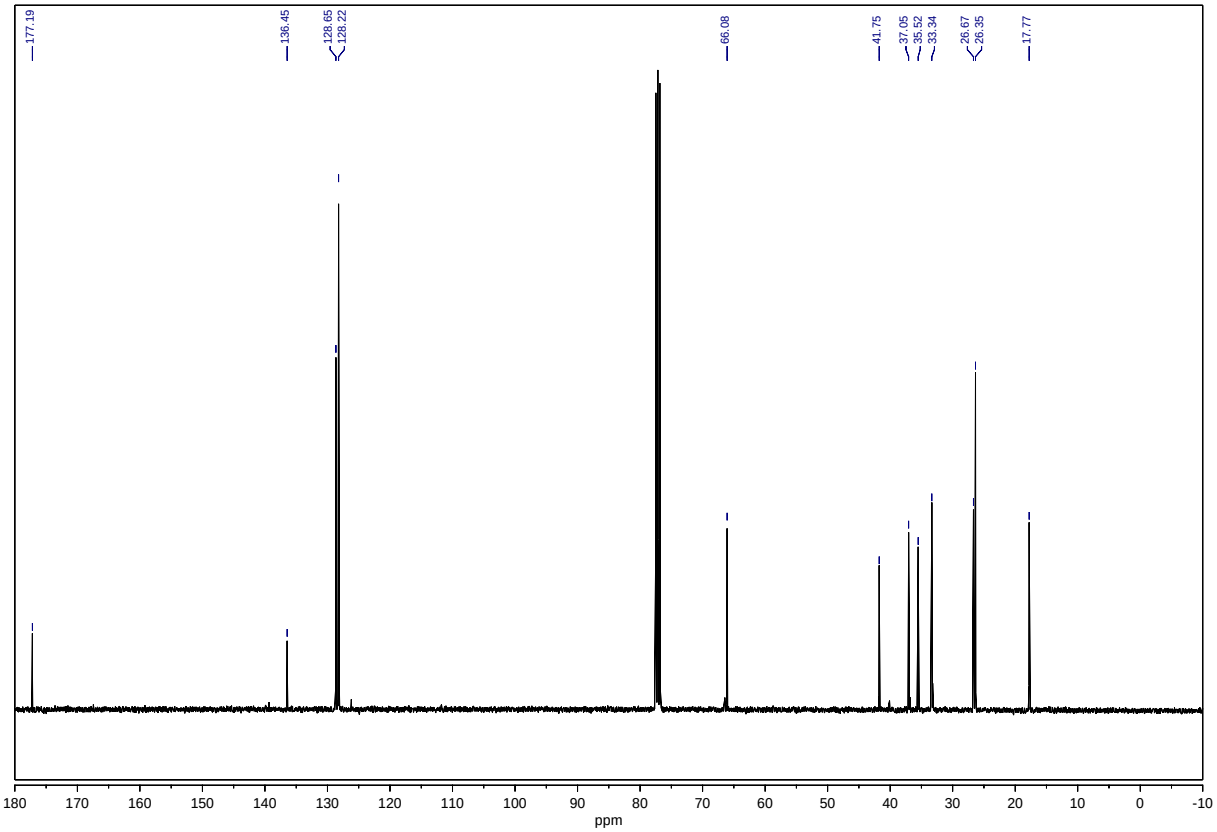
^{1}H- and ^{13}C-NMR in $CDCl_3$ of compound **4j**:



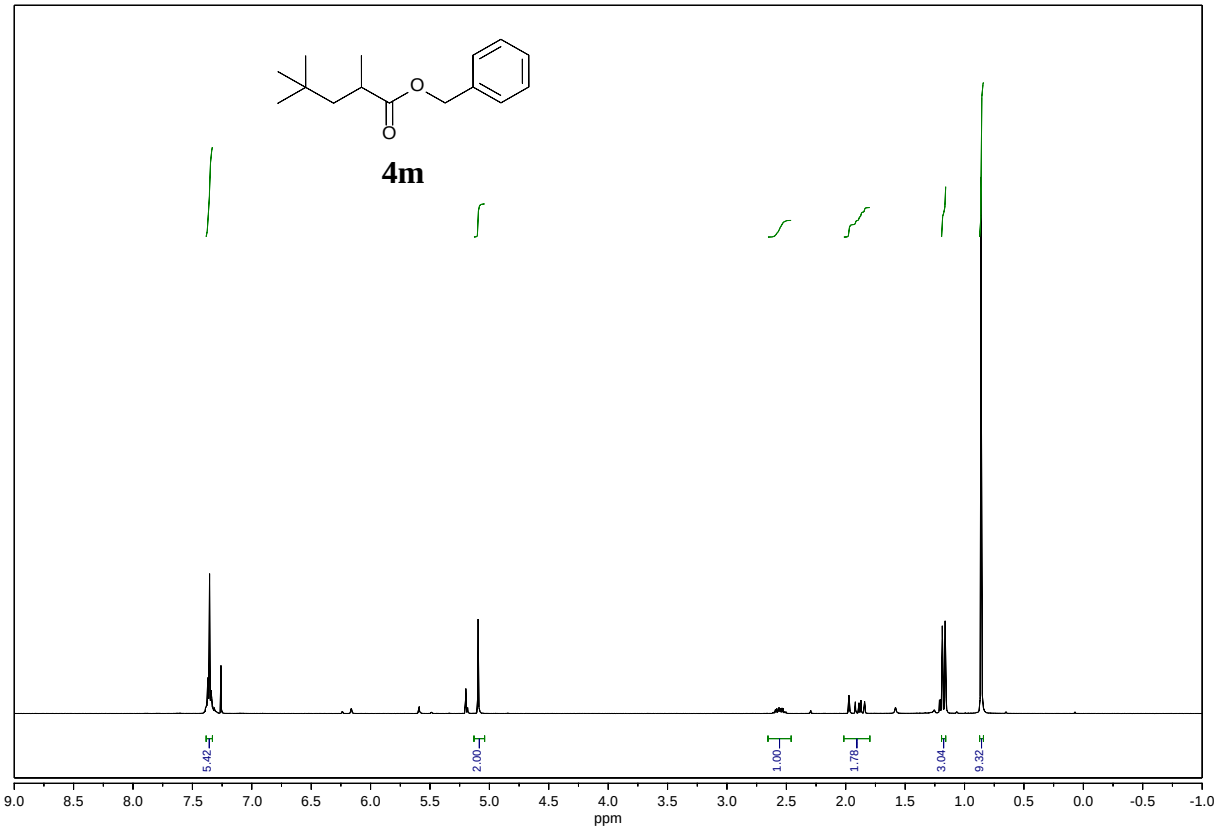


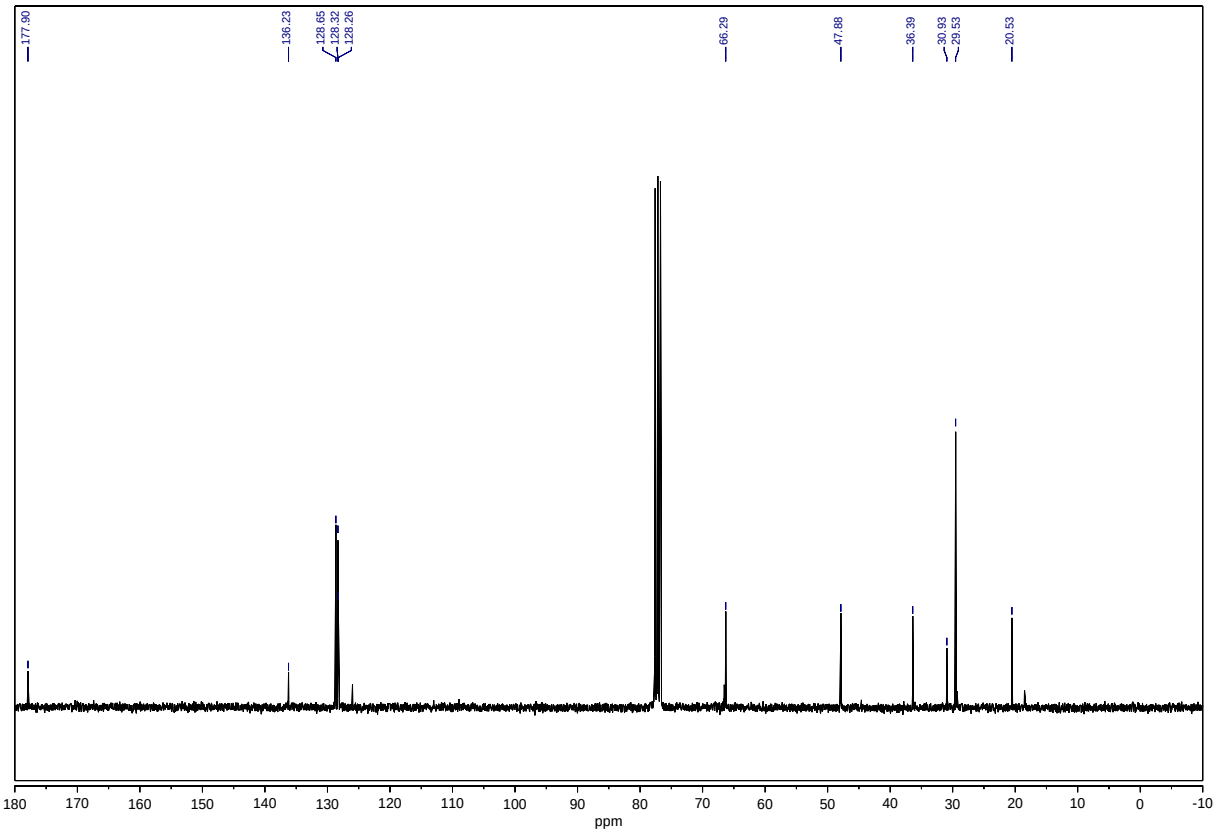
^{1}H- and ^{13}C-NMR in $CDCl_3$ of compound **4l**:



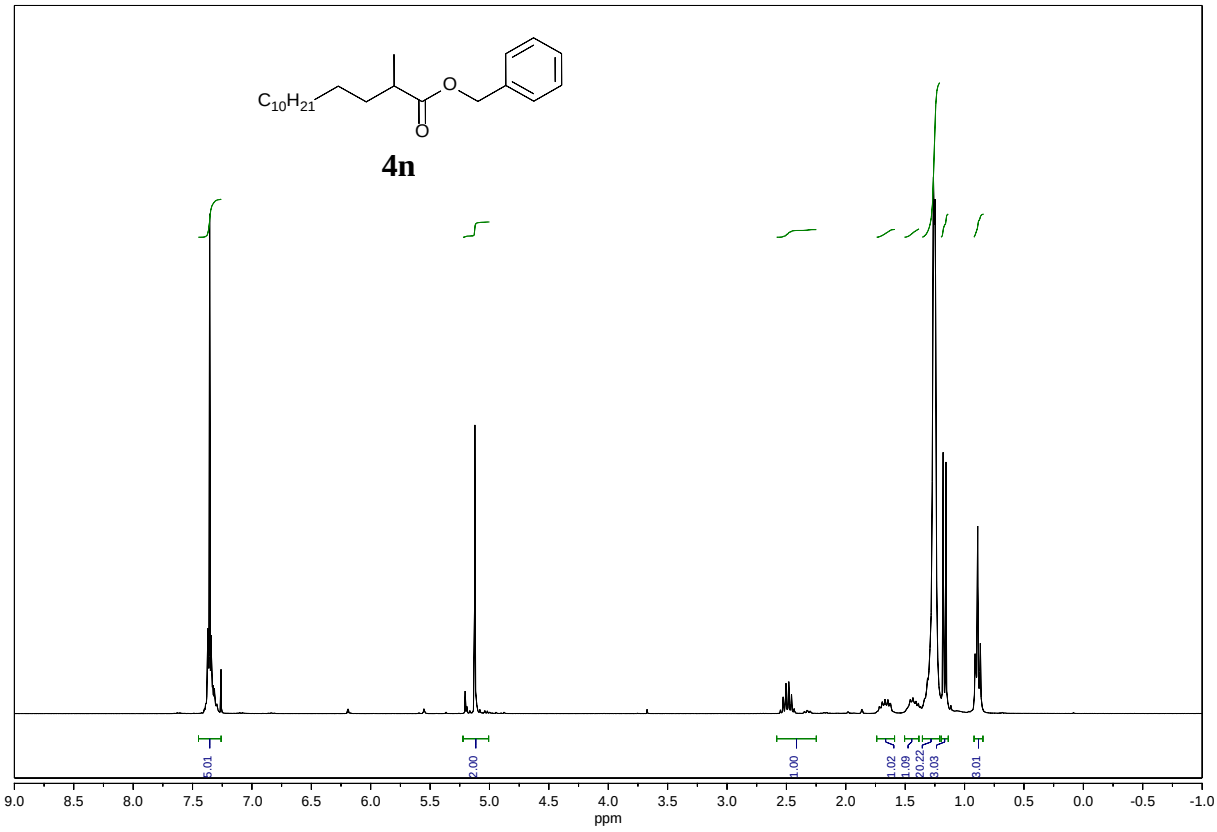


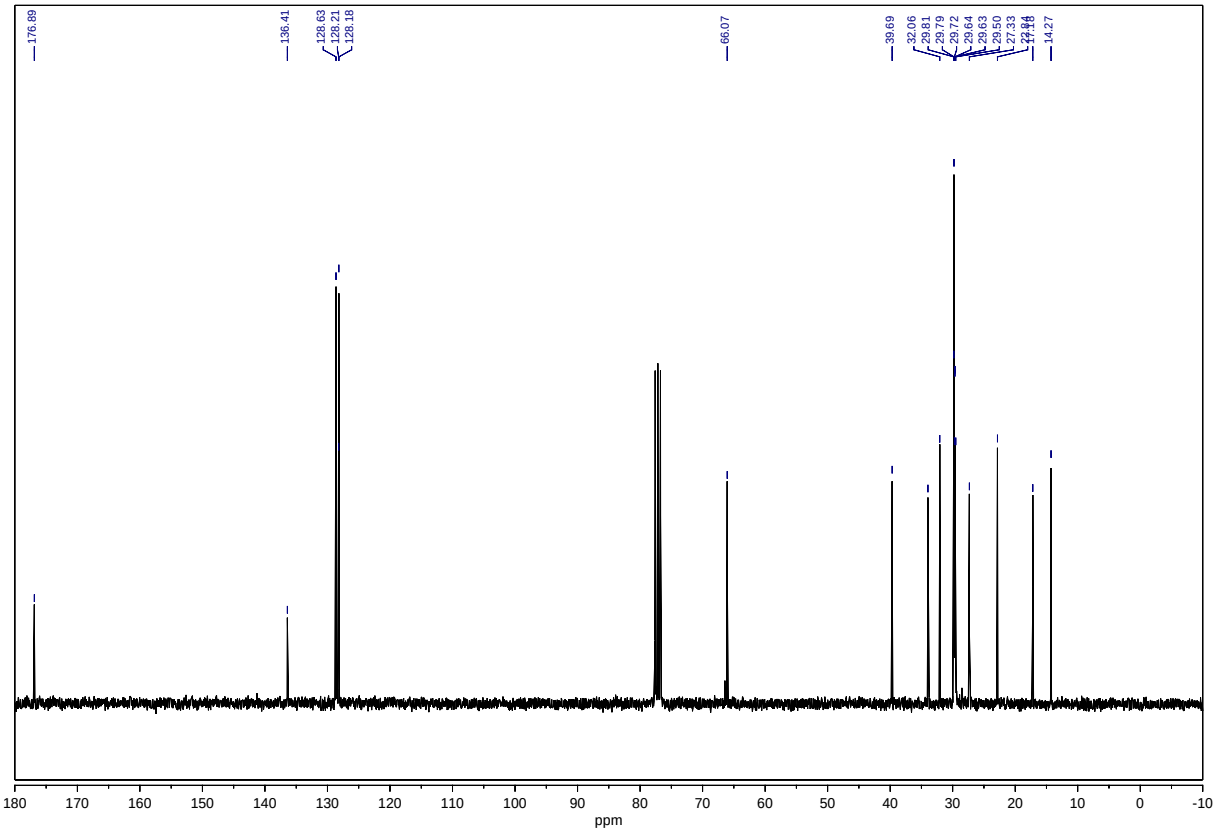
^{1}H- and ^{13}C-NMR in $CDCl_3$ of compound **4m**:



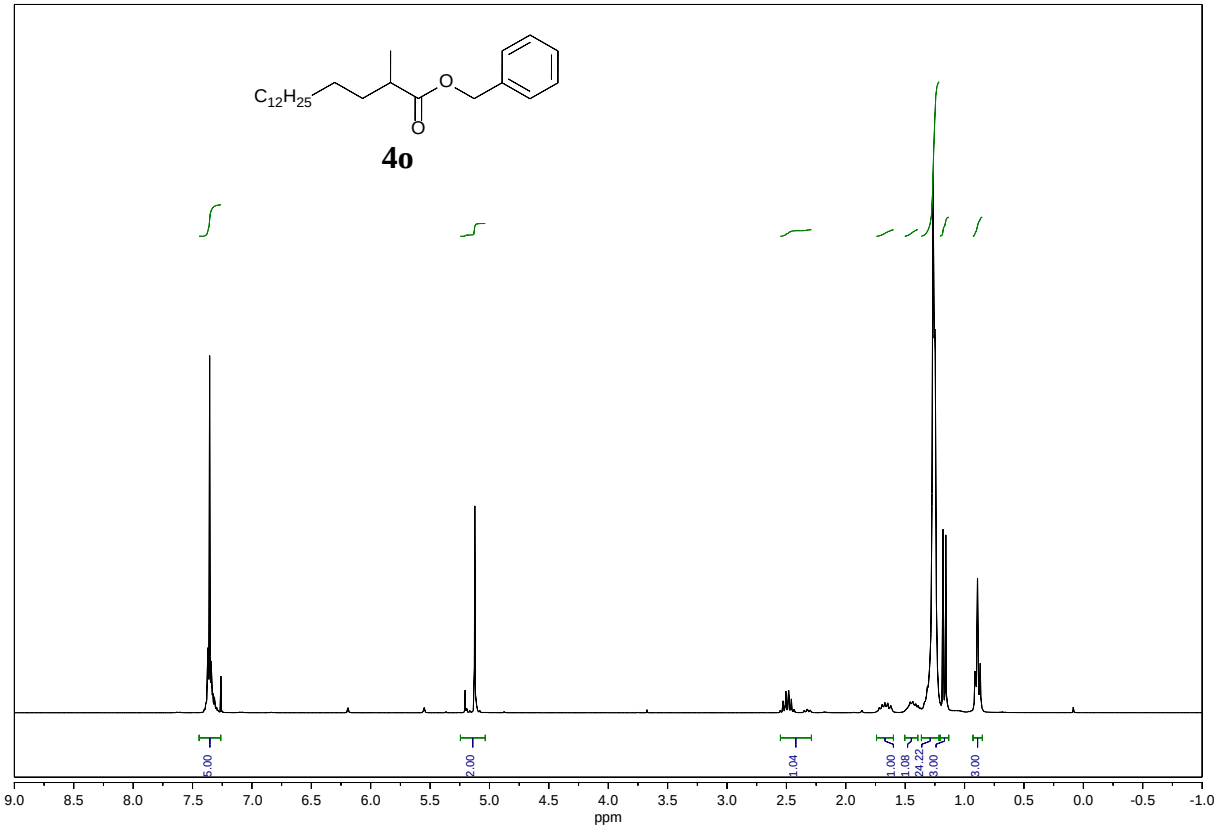


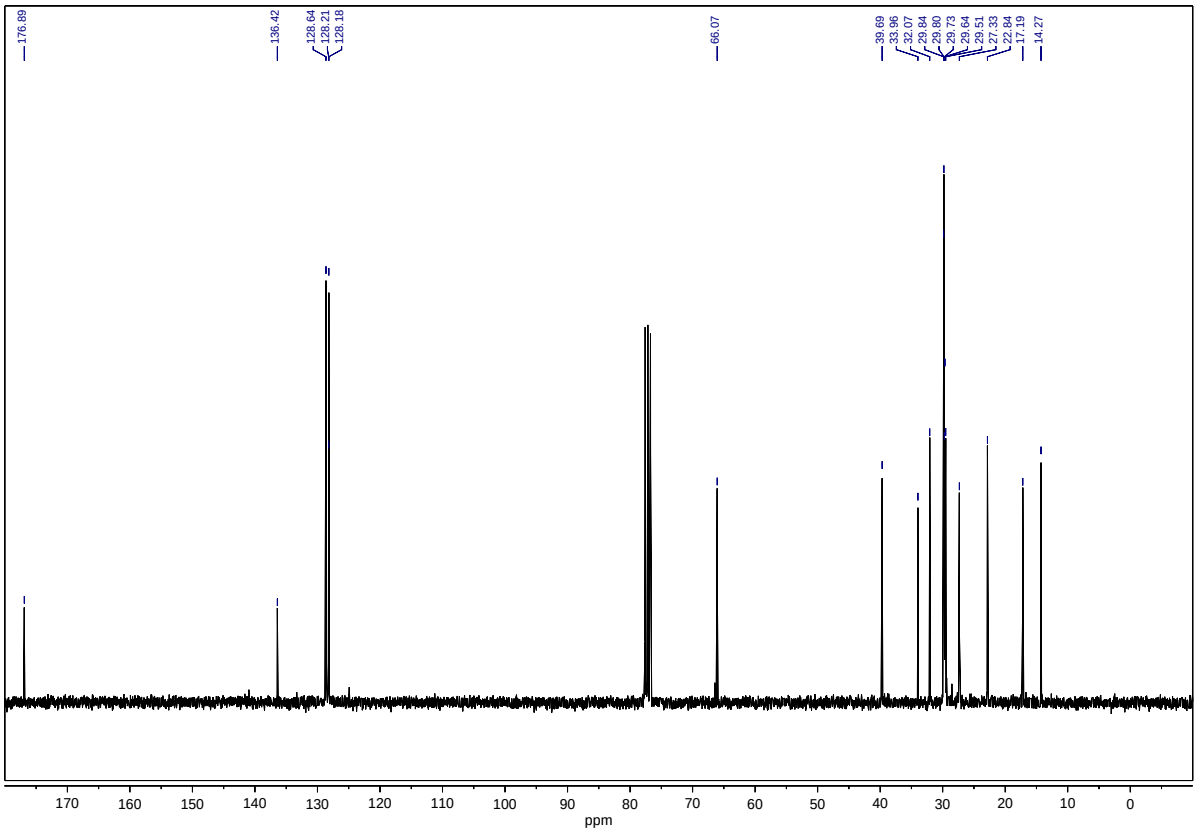
^{1}H- and ^{13}C-NMR in $CDCl_3$ of compound **4n**:



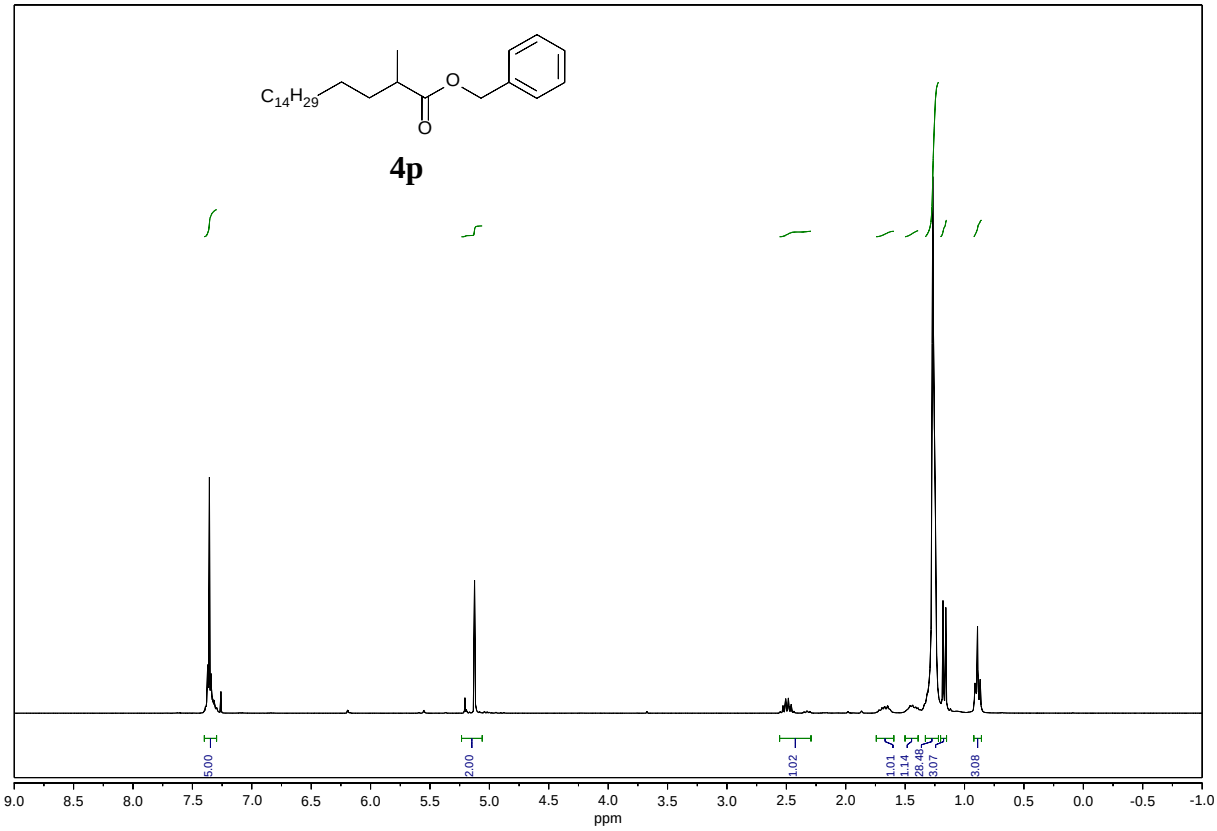


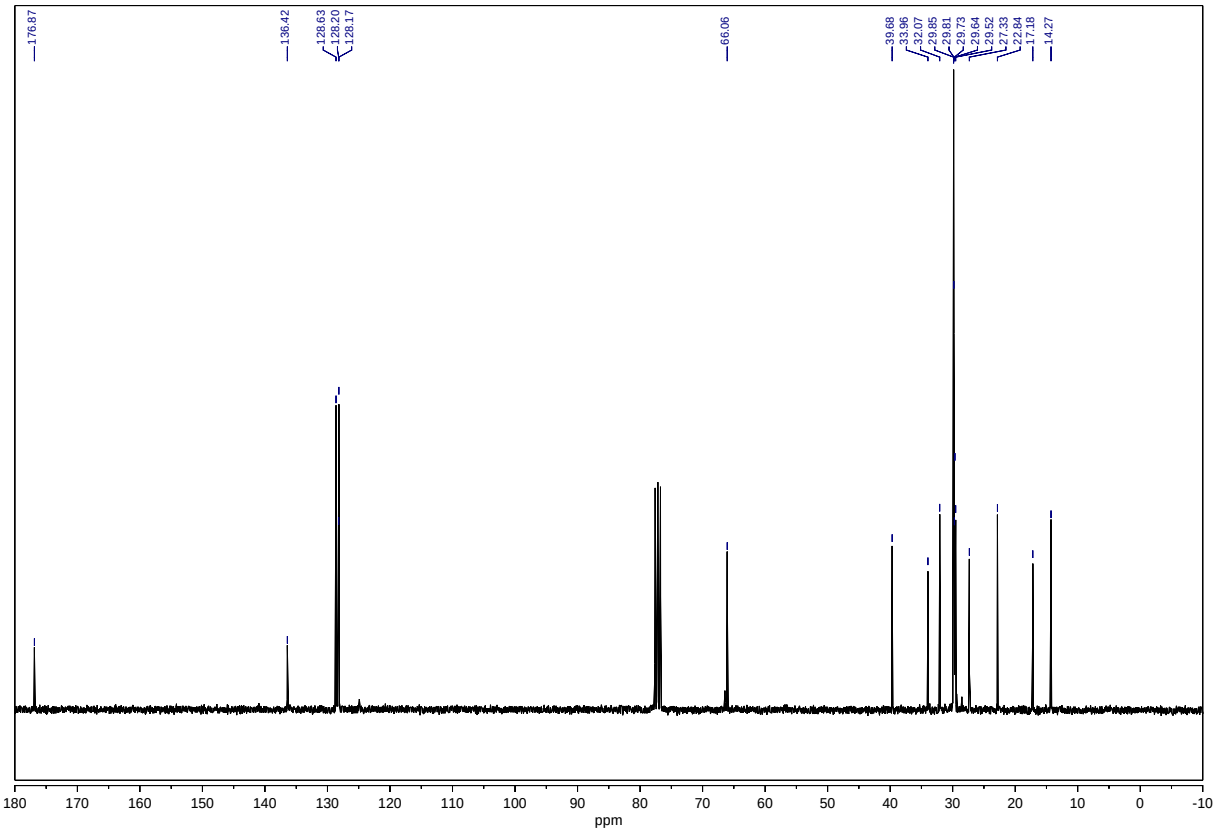
^{1}H- and ^{13}C-NMR in $CDCl_3$ of compound **4o**:





^{1}H- and ^{13}C-NMR in $CDCl_3$ of compound **4p**:





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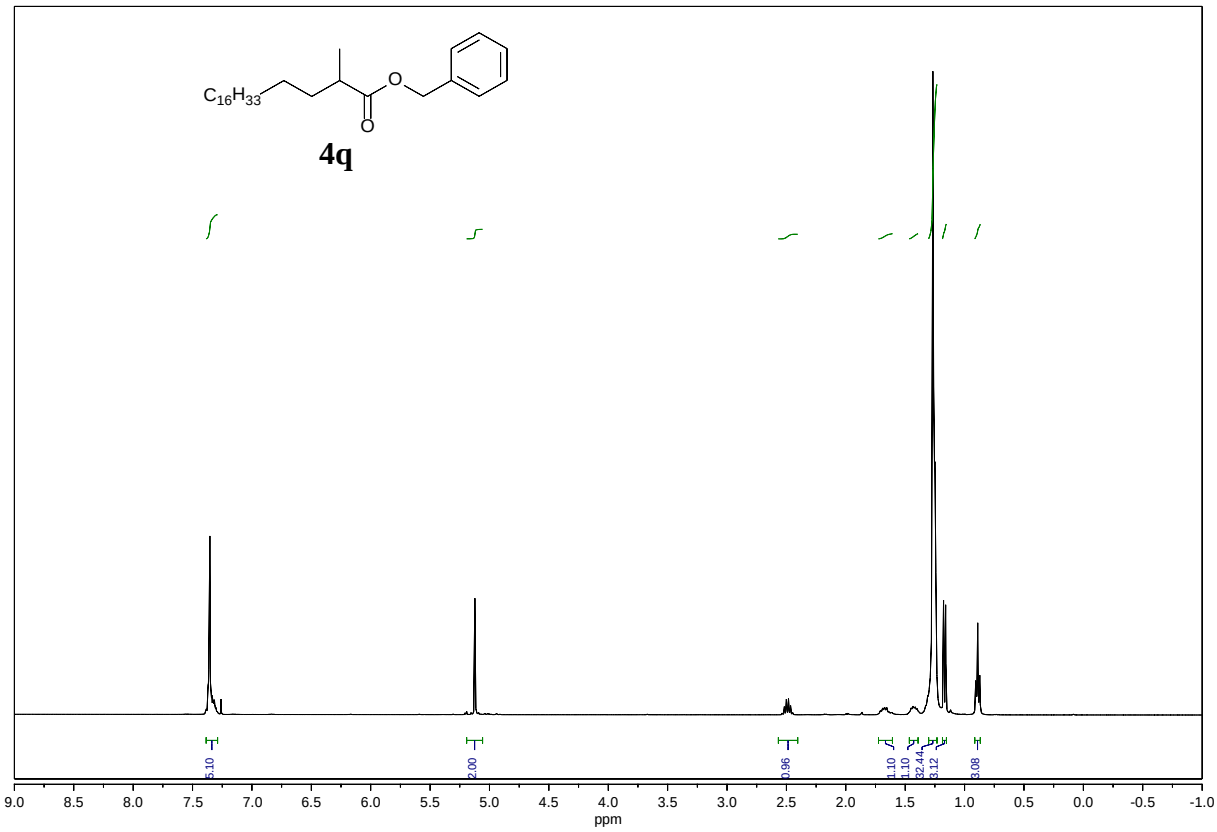

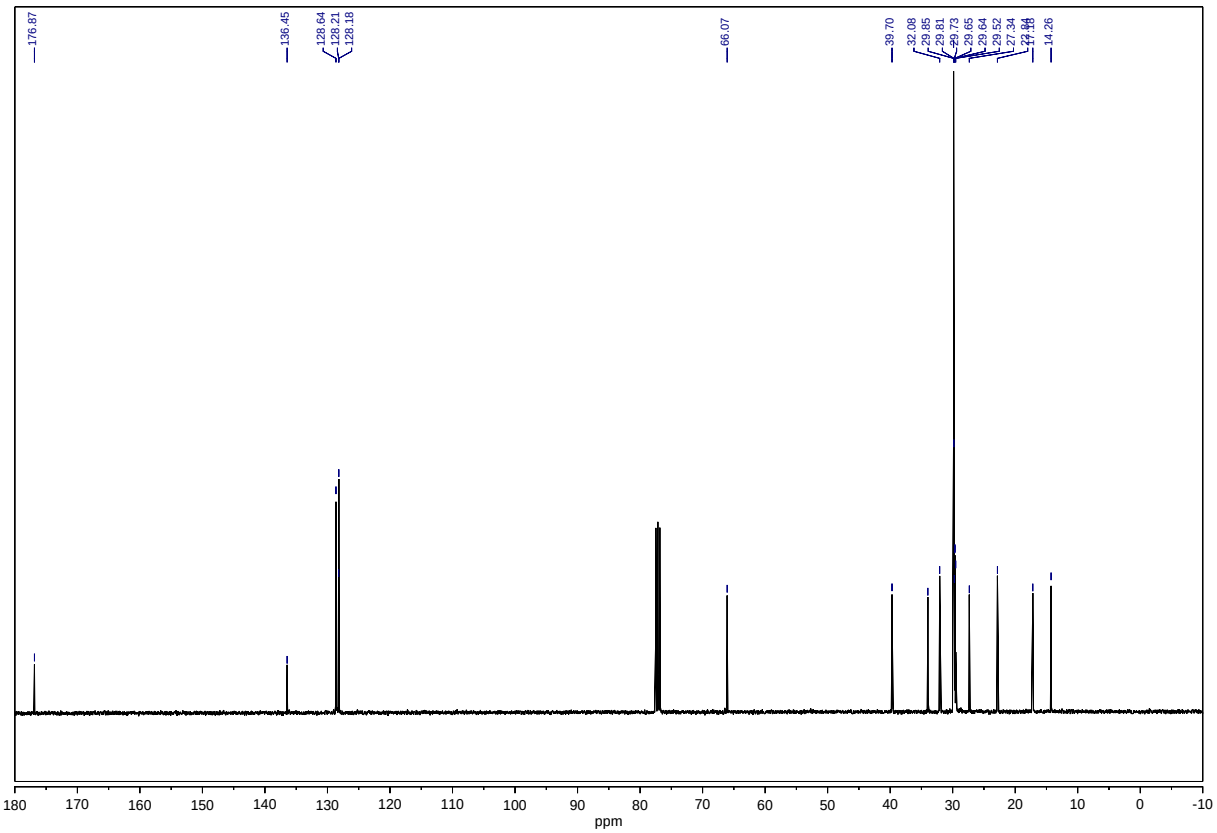

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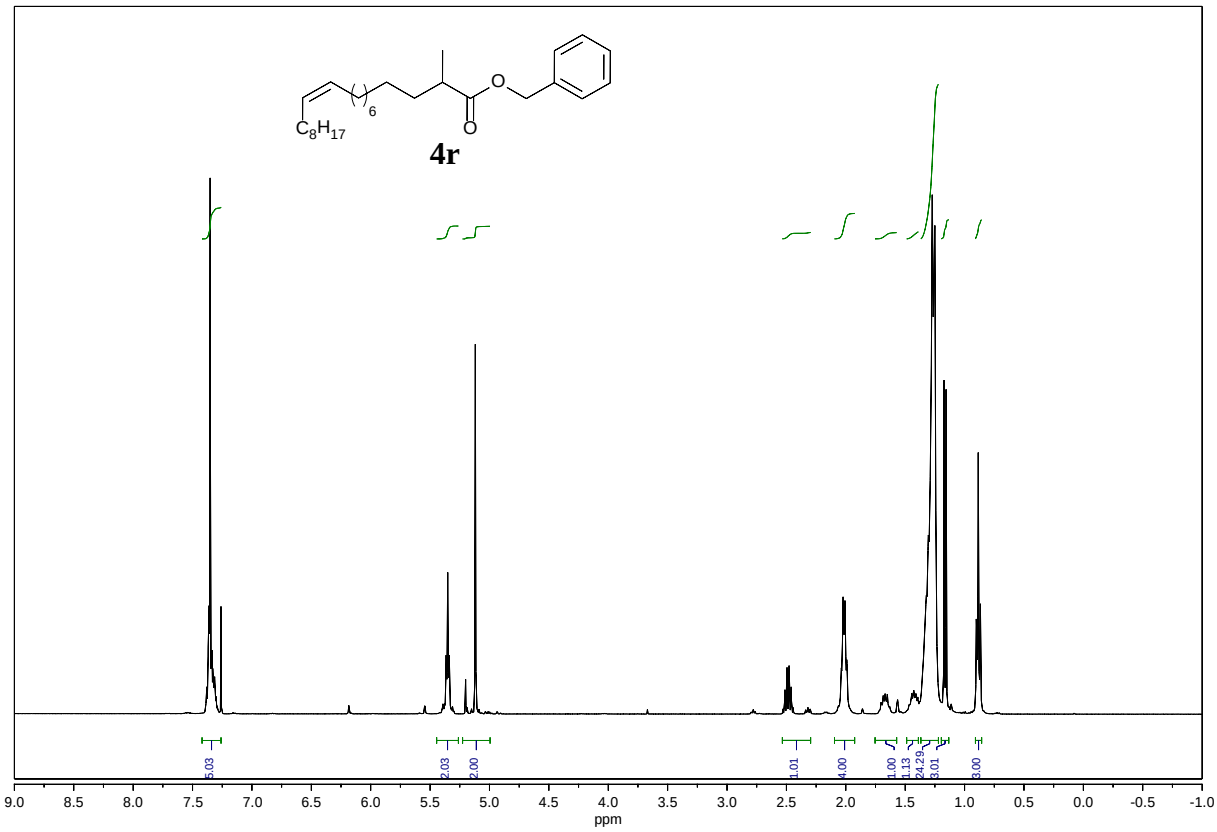
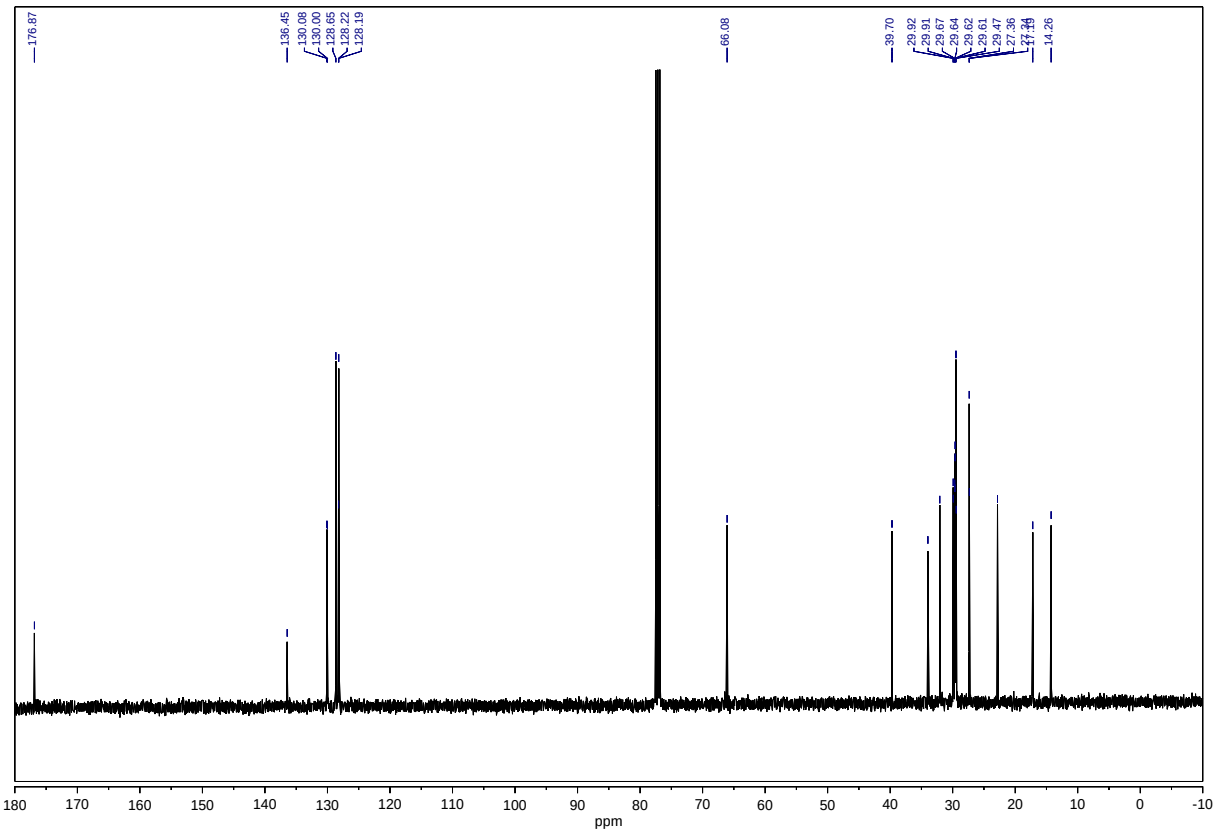
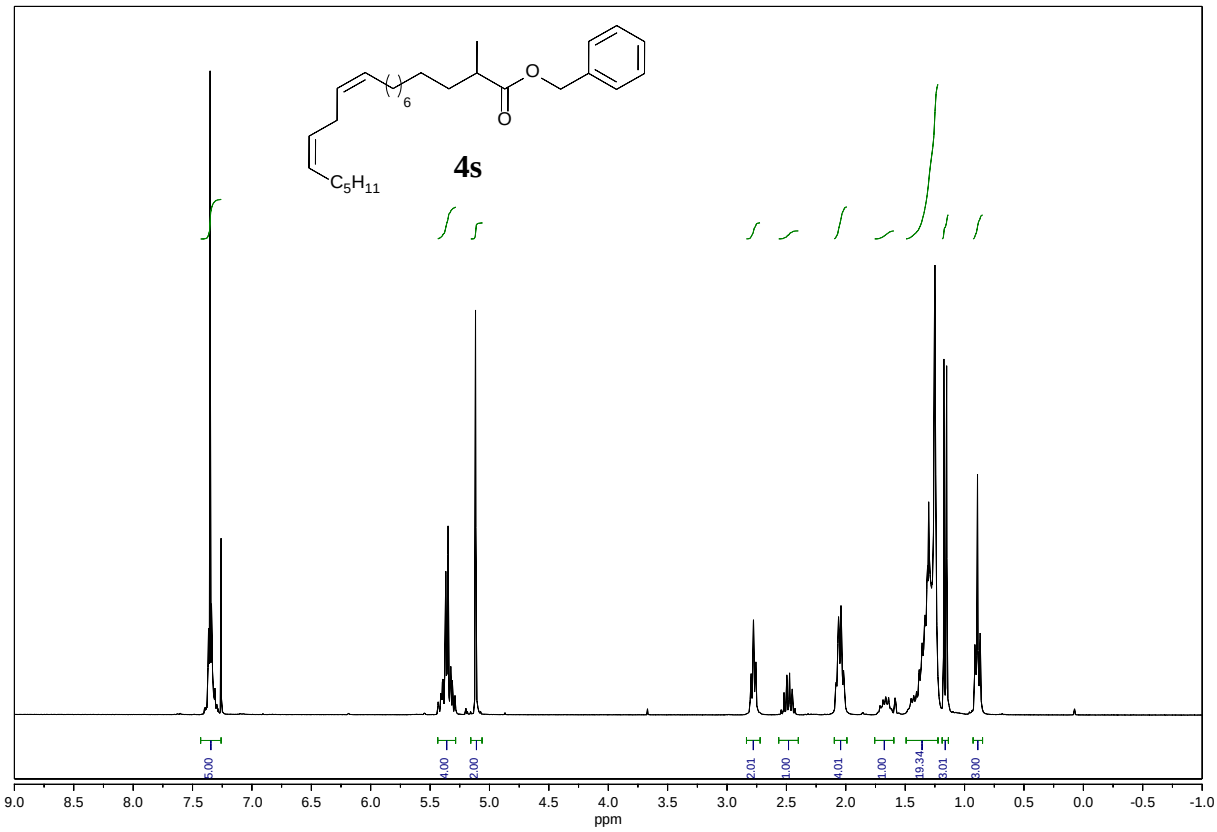
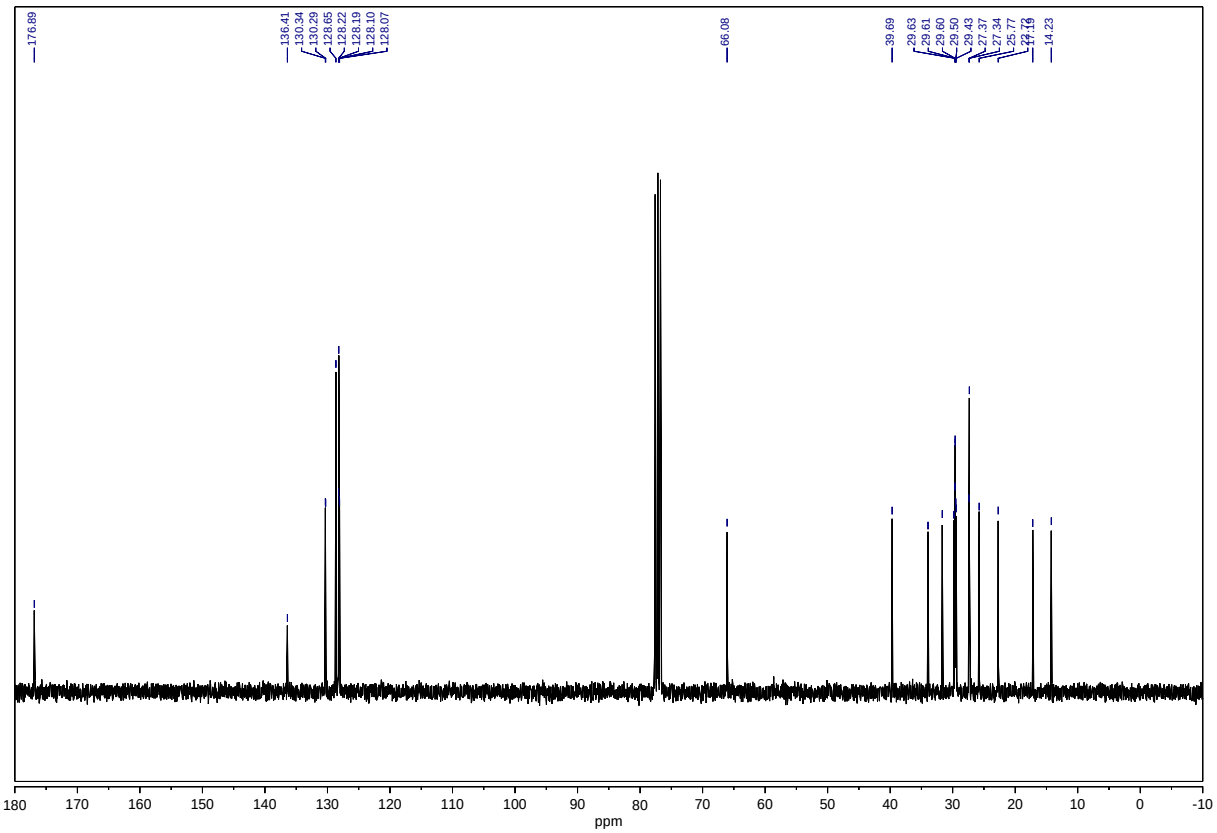




^{1}H- and ^{13}C-NMR in $CDCl_3$ of compound **4s**:





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[a] Isolated with special, pre-packed Biotage SNAP Ultra HP-Sphere columns (see General information).