Supporting Information for

Examples of Xylochemistry: Colorants and Polymers

Jonas Kühlborn[a], Ann-Kathrin Danner[a,b], Holger Frey[a], Rishab Iyer[c], Anthony J. Arduengo III[c,*], and Till Opatz.[a,*]

a Institute of Organic Chemistry, Johannes Gutenberg University, Duesbergweg 10−14, 55128 Mainz, Germany

b Graduate School Materials Science in Mainz, Staudingerweg 9, 55128 Mainz

c Department of Chemistry, The University of Alabama, Tuscaloosa, Alabama 35487, United States

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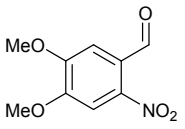
1 General methods

Solvents were dried and purified, where necessary, by appropriate standard procedures. All other chemicals were purchased from commercial sources (Sigma-Aldrich, Alfa Aesar, Carbolution Chemicals, Acros Organics) and used as received unless mentioned otherwise. All reactions were performed under an inert atmosphere of argon in oven-dried glassware using standard Schlenk techniques unless mentioned otherwise. Reactions under increased pressures were carried out in a type T316 autoclave (Parr Instruments). Deuterated solvents for NMR measurements were obtained from Deutereo and used as received. NMR spectra were recorded on a Bruker Avance III HD 300 and Bruker Avance III HD 400 spectrometer. Chemical shifts (δ) are reported as parts per million (ppm) downfield from TMS. FT-IR spectra were recorded on a Tensor 27 spectrometer (Bruker) equipped with a diamond ATR unit. UV spectra were recorded on an Evolution 201 spectrometer (Thermo Scientific). HPLC-ESI-MS was performed on a 1200 series HPLC system with a UV diode array detector coupled with a LC/MSD trap XCT mass spectrometer (Agilent Technologies). High-resolution masses (ESI) were recorded on a Q-ToF-Ultima 3 instrument (Waters) with a LockSpray™ interface and a suitable external calibrant. Size exclusion chromatography (SEC) measurements in DMF (containing 0.25 g L^{-1} potassium bromide as additive) were carried out on an Agilent 1100 Series integrated instrument, including a PSS HEMA column ($300/100/40 \cdot 10^{-10}$ porosity), a UV-detector (detection at 275 nm) and a RI-detector. Poly(ethylene glycol) standards purchased from Polymer Standards Service were used for calibrations. Matrix-assisted laser desorption/ionization-time-of-flight-MS (MALDI-ToF-MS) spectra were measured on an Axima CFR MALDI-ToF spectrometer (Shimadzu) equipped with a nitrogen laser delivering 3 ns laser pulses at 337 nm using CHCA (α-cyano-4-hydroxycinnamic acid) or HABA (4'-hydroxyazobenzene-2-carboxylic acid) as the matrix. The samples were prepared from pyridine and ionized by adding lithium chloride or potassium trifluoroacetate. DSC measurements were carried out on a PerkinElmer DSC 8500 instrument heating from 0 to 170 °C at 10 °C min^{-1} under nitrogen using about 3 mg of the respective polymer for analysis. Melting points were determined in open capillary tubes on a KSP I N (Krüss). Thin-layer chromatography (TLC) was carried out on silica gel 60 F_{254} plates (Merck). Compounds were visualized using UV light and/or by immersion in a solution of $KMnO_4$ (3 g), K_2CO_3 (20 g), 5% aqueous NaOH (5 mL) and water (300 mL) followed by heating. Preparative normal-phase chromatography was performed on silica gel (35-70 µm, Acros Organics) using manual flash chromatography. For dialysis regenerated cellulose membranes with a molecular weight cut-off (MWCO) of 1000 g mol^{-1} (Cellu Sep) were used.

2 Experimental procedures

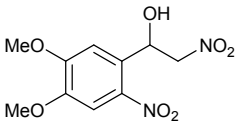
2.1 Indigo dye syntheses

4,5-dimethoxy-2-nitrobenzaldehyde (9)



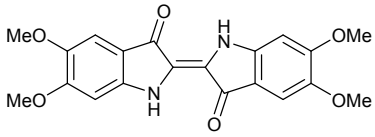
In contrast to a procedure of Kumar et al.[1] The procedure was carried out in the presence of normal laboratory lighting. Nitric acid (65%, 100 mL) was cooled to 0 °C and veratraldehyde (**8**, 20.0 g, 120 mmol) was added with stirring. The mixture was brought to room temperature, stirred for 3 h and then poured into ice-water (200 mL). The resulting yellow precipitate was collected by filtration and washed with cold water and ethanol. The crude material was dried and recrystallized from ethanol. The product was obtained as a yellow solid and is not light sensitive. Product melting point was checked for subsequent months to identify any chemical transformations that may have occurred due to laboratory light exposure. Melting point remained at the literature value indicating that the desired product was still present. (23.1 g, 10.9 mmol, 91%), mp = 131–132 °C (from EtOH). **IR** (ATR): $\tilde{\nu}_{max}$ 2947, 1682, 1571, 1514, 1397, 1354, 1224, 1189, 1058, 793 cm^{-1}. **^{1}H-NMR, COSY** (400 MHz, $CDCl_3$): δ = 10.45 (s, 1H, C*H*O), 7.61 (s, 1H, H-3), 7.41 (s, 1H, H-6), 4.03 (s, 3H, OCH_3-4), 4.02 (s, 3H, OCH_3-5) ppm. **^{13}C-NMR, HSQC, HMBC** (101 MHz, $CDCl_3$): δ = 187.8 (*C*HO), 153.4 (C-4), 152.5 (C-5), 144.0 (C-2), 125.7 (C-1), 109.9 (C-6), 107.3 (C-3), 57.0 (O*C*H$_3$), 56.9 (O*C*H$_3$) ppm.. **ESI-MS** (pos.): *m/z* (%) = 212.0 (100) $[M + H]^+$, 234.0 (3) $[M + Na]^+$. The analytical data are in accordance with the literature.[1]

1-(4,5-dimethoxy-2-nitrophenyl)-2-nitroethanol (10)



The procedure was conducted following Pandi et al.[2] Aldehyde **9** (100 mg, 0.47 mmol), $Ba(OH)_2 \cdot 8H_2O$ (7.60 mg, 224 µmol) and nitromethane (253 µL, 4.73 mmol) were suspended in water (1.5 mL) and stirred at ambient temperature for 3 h. The reaction mixture was extracted with ethyl acetate (3x5 mL), the combined organic extracts were dried over Na_2SO_4 and evaporated. The yellow product thus obtained (120 mg, 0.44 mmol, 94%) was used without further purification, mp = 139–141 °C. IR (ATR): $\tilde{\nu}_{max}$ 3511, 2942, 1579, 1555, 1333, 1274, 1219, 1088, 799 cm^{-1}. **^{1}H-NMR, COSY** (300 MHz, $CDCl_3$): δ = 7.67 (s, 1H, H-3), 7.39 (s, 1H, H-6), 6.16 (dd, *J* = 8.94, 2.28 Hz, 1H, H-1'), 4.84 (dd, *J* = 13.70, 2.28 Hz, 1H, H_a-2'), 4.50 (dd, *J* = 13.70, 9.94 Hz, 1H, H_b-2'), 4.02 (s, 3H, C5-OCH_3), 3.97 (s, 3H, C4-OCH_3) ppm. **^{13}C-NMR, HSQC, HMBC** (76 MHz, $CDCl_3$): δ = 154.1 (C-5), 148.8 (C-4), 139.4 (C-2), 129.1 (C-1), 109.3 (C-6), 108.0 (C-3), 80.0 (C-2'), 66.9 (C-1'), 56.6 (C5-O*C*H$_3$), 56.5 (C4-O*C*H$_3$) ppm.. **ESI-MS** (pos.): *m/z* (%) = 255.6 (100) $[M - H_2O + H]^+$, 295.3 (95) $[M + Na]^+$. **ESI-HRMS** (pos.) calcd ($C_{10}H_{12}N_2O_7Na$) 295.0542; found 295.0550. The analytical data are in accordance with the literature.[3]

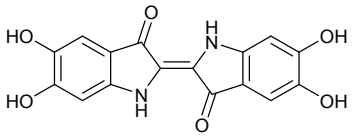
5,5',6,6'-tetramethoxyindigo (3)



Method A: According to a procedure from Harley-Mason.[4] To a stirred suspension of 4,5-dimethoxy-2-nitrobenzaldehyde (**9**, 2.00 g, 9.47 mmol) in acetone (5.00 mL, 68.0 mmol) were added 5 drops of 10% aqueous NaOH under exclusion of light. After 1 h, water (30 mL) and more 10% aqueous NaOH (5 mL) were added. The resulting mixture was stirred over night at room temperature and left standing without stirring for two more days. The precipitate was collected by filtration, washed with boiling ethanol (50 mL) and dried in order to obtain a dark blue solid (415 mg, 1.09 mmol, 23%).

Method B: The procedure was conducted following Harley-Mason et al.[5] Compound **10** (89.0 mg, 0.33 mmol) was suspended in water (1.4 mL), 2 M aqueous NaOH solution (383 µL) and sodium dithionite (172 mg, 0.99 mmol) were added slowly. A dark precipitate of indigo **3** was formed at once and air was bubbled through the reaction mixture for 15 minutes. The precipitate was collected by filtration, washed with ethanol (2x10 mL) and diethyl ether (2x10 mL) and dried. The product was obtained as a dark blue solid (51.0 mg, 0.13 mmol, 81%), mp = 325–326 °C. λ_{max} (DMSO)/nm 606 (ε,/dm^3 mol^{-1} cm^{-1} 13383). IR (ATR): $\tilde{\nu}_{max}$ 3416, 1612, 1485, 1438, 1294, 1144, 1060, 991, 850, 654 cm^{-1}. **^{1}H-NMR, COSY** (400 MHz, DMSO-d_6): δ = 10.00 (s, 2H, H-1, H-1'), 7.01 (s, 2H, H-4, H-4'), 6.94 (s, 2H, H-7, H-7'), 3.85 (s, 6H, C-6OCH_3, C-6'OCH_3), 3.75 (s, 6H, C-5OCH_3, C-5'OCH_3) ppm. **^{13}C-NMR, HSQC, HMBC** (101 MHz, DMSO-d_6): δ = 185.8 (2C, C-3, C-3'), 156.7 (2C, C-6, C-6'), 150.3 (2C, C-7a, C-7a'), 144.1 (2C, C-5, C-5'), 121.5 (2C, C-2, C-2'), 110.3 (2C, C-3a, C-3a'), 104.3 (2C, C-4, C-4'), 96.2 (2C, C-7, C-7'), 55.8 (4C, OCH$_3$) ppm. **ESI-MS** (pos.): *m/z* (%) = 383.1 (100) [M + H]$^+$, 405.1 (0.4) [M + Na]$^+$. **ESI-HRMS** (pos.) calcd ($C_{20}H_{18}N_2O_6$) 383.1243; found 383.1230.

5,5',6,6'-tetrahydroxyindigo (4)



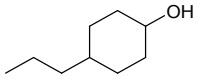
The procedure was conducted following Bai et al.[6] and modified according to Harley-Mason.[4] A suspension of 5,5',6,6'-tetramethoxyindigo (**3**, 2.00 g, 5.23 mmol) in acetic acid (92.0 mL, 1.61 mol) and 48% aqueous HBr solution (92.0 mL, 0.81 mol) was stirred for three days under reflux. After cooling to room temperature the mixture was poured into ice-water (200 mL) and the precipitate was collected by filtration, washed with ethanol (50 mL) and diethyl ether (50 mL). The residue was dissolved in 1% aqueous NaOH (50 mL) and the resulting violet solution was filtered. An equal volume of acetic acid was added to the filtrate. The solution was evaporated and the residue was suspended in water (20 mL) and filtrated. The residue was again washed with ethanol (20 mL) and diethyl ether (20 mL). The product was obtained as a black solid (537 mg, 1.65 mmol, 32%), mp = >370 °C. λ_{max} (DMSO)/nm 610 (ε,/dm^3 mol^{-1} cm^{-1} 5887). IR (ATR): $\tilde{\nu}_{max}$ 3424, 1659, 1051, 1023, 1002, 823, 760, 614 cm^{-1}. **^{1}H-NMR, COSY** (400 MHz, DMSO-d_6): δ = 11.95 (s, 2H, H-1, H-1'), 9.75 (s, 2H, OH), 9.25 (s, 2H, H-4, H-4'), 9.11 (s, 2H, OH), 6.82 (s, 2H, H-7, H-7') ppm.

^{13}C-NMR, HSQC, HMBC (101 MHz, DMSO-d_6): δ = 160.7 (2C, C-3, C-3'), 148.5 (2C, C-6, C-6'), 141.7 (2C, C-5, C-5'), 131.7 (2C, C-7a, C-7a'), 125.2 (2C, C-2, C-2'), 112.6 (2C, C-4, C-4'), 110.4 (2C, C-3a, C-3a'), 100.3 (2C, C-7, C-7') ppm.; **ESI-HRMS** (pos.) calcd ($C_{16}H_{11}N_2O_6$) 327.0617; found 327.0626.

2.2 Polyamide syntheses

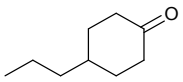
2.2.1 Monomer syntheses

4-propylcyclohexanol (2)



The procedure was conducted following Ellwood et al.[7] A stainless steel autoclave equipped with a magnetic stirring bar was charged with 4'-hydroxypropiophenone (**11**, 30.0 g, 222 mmol). Distilled water (17 mL, 942 mmol), lactic acid, (85% aq. solution, 1.13 mL, 13.3 mmol) and palladium on activated charcoal (10%, 510 mg) were added. After purging with nitrogen and hydrogen three times, the stirring mixture was set under a hydrogen pressure of 20 bar. With the help of an external oil bath, the autoclave was heated to 100 °C. At this temperature, the mixture was stirred for 3 h. The pressure was raised to 50 bar before heating to 150 °C. The mixture was stirred for about 15 h under these conditions. After cooling to room temperature, the pressure was released and, after purging with nitrogen, the mixture was taken up in ethyl acetate (200 mL). In order to remove the catalyst the mixture was filtered through Celite. The residue was washed with ethyl acetate (200 mL) and the filtrate was washed with saturated $NaHCO_3$ solution (100 mL). The organic layer was dried over Na_2SO_4 and evaporated to obtain a colorless liquid (29.0 g, 204 mmol, 92%). The product was obtained as a 1:1-mixture of diastereomers (see ^{1}H-NMR-spectrum S18). These could be seperated by coloumn chromatography (eluent: cyclohexane/ethyl acetate 3:1) in order to characterize the single diastereomers, but all further syntheses was conducted using the mixture. *cis*-**2**: IR (ATR): $\tilde{\nu}_{max}$ 3329, 2956, 2924, 2855, 1451, 1368, 1096, 1050, 1011, 951 cm^{-1}. **^{1}H-NMR, COSY, NOESY** (400 MHz, $CDCl_3$): δ = 3.54 (tt, J = 10.9, 4.3 Hz, 1H, H-1), 1.98–1.93 (m, 2H, H_a-2, H_a-6), 1.78–1.70 (m, 2H, H_{eq}-3, H_{eq}-5), 1.33–1.13 (m, 7H, H_b-2, H-4, H_b-6, H-1', H-2'), 0.97–0.91 (m, 2H, H_{ax}-3, H_{ax}-5), 0.87 (t, J = 7.3 Hz, 3H, H-3') ppm. **^{13}C-NMR, HSQC, HMBC** (101 MHz, $CDCl_3$): δ = 71.5 (C-1), 39.1 (C-1'), 36.6 (C-4), 35.8 (2C, C-2, C-6), 31.4 (2C, C-3, C-5), 20.4 (C-2'), 14.5 (C-3') ppm.. *trans*-**2**: IR (ATR): $\tilde{\nu}_{max}$ 3346, 2955, 2922, 2854, 1456, 1443, 1143, 1049, 1034, 961 cm^{-1}. **^{1}H-NMR, COSY, NOESY** (400 MHz, $CDCl_3$): δ = 3.95 (m, 1H, H-1), 1.72–1.66 (m, 2H, H_a-2, H_a-6), 1.59–1.47 (m, 4H, H_b-2, H_a-3, H_a-5, H_b-6), 1.35–1.20 (m, 7H, H_b-3, H-4, H_b-5, H-1', H-2'), 0.88 (t, J = 7.2 Hz, 3H, H-3') ppm. **^{13}C-NMR, HSQC, HMBC** (101 MHz, $CDCl_3$): δ = 67.5 (C-1), 38.5 (C-1'), 36.1 (C-4), 32.4 (2C, C-2, C-6), 27.2 (2C, C-3, C-5), 20.2 (C-2'), 14.5 (C-3') ppm. Diastereomeric **2**: **FD-MS** (pos.): *m/z* (%) = 142.4 (100) $[M]^{+\bullet}$. bp = 78 °C (1.5 mbar). The analytical data are in accordance with the literature.[8, 9]

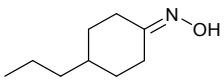
4-propylcyclohexanone (12)



Method A: The procedure was conducted following Schultz et al.[10] To a 250-mL Schlenk flask equipped with a magnetic stirring bar was added $Pd(OAc)_2$ (379 mg, 1.68 mmol) and powdered, freshly activated 3 Å molecular sieves (11 g). THF (23 mL), toluene (150 mL) and TEA (0.48 mL, 3.36 mmol) were added and the flask was evacuated and refilled with oxygen three times before stirring for 30 min under an atmosphere of oxygen at room temperature. To this mixture was added alcohol **2** (8.00 g, 56.2 mmol) and stirring was continued for 2 days at room temperature. The reaction mixture was filtered through a plug of silica and the residue was washed with diethyl ether (1 L). The eluate was evaporated in order to obtain a colorless liquid (6.86 g, 48.9 mmol, 87%).

Method B: The procedure was conducted following Stevens et al.[11] To a stirred and cooled (0 °C) solution of cyclohexanol **2** (10.3 g, 72.4 mmol) in acetic acid (50 ml) was added dropwise sodium hypochlorite solution (1.74 M, 50.0 mL, 84.4 mmol). The resulting solution was stirred for 2 h at 0 °C and for 1 h at room temperature. Subsequently, saturated aqueous sodium bisulfite solution (4 mL) was added until the color of the reaction mixture changed from yellow to colorless. The mixture was poured into an ice-brine mixture (150 mL) and extracted with diethyl ether (6x100 mL). The ether layer was washed with aqueous 5% NaOH solution (600 mL) until the aqueous washes were basic (checked with pH test paper). The combined aqueous layers were then extracted with diethyl ether (5x50 mL), the organic layers were combined and dried over Na_2SO_4. After evaporation of the solvent and distillation under reduced pressure (bp = 47 °C, 1.5 mbar) the product was obtained as a colorless liquid (9.95 g, 71.0 mmol, 98%). IR (ATR): $\tilde{\nu}_{max}$ 2956, 2926, 2861, 1716, 1460, 1421, 1332, 1173, 1124, 944, 738 cm^{-1}. **^{1}H-NMR, COSY** (300 MHz, $CDCl_3$): δ = 2.42–2.26 (m, 4H, H-2, H-6), 2.09–1.99 (m, 2H, H_a-3, H_a-5), 1.76–1.65 (m, 1H, H-4), 1.45–1.23 (m, 6H, H_b-3, H_b-5, H-1', H-2'), 0.92 (t, J = 7.0 Hz, 3H, H-3') ppm. **^{13}C-NMR, HSQC, HMBC** (76 MHz, $CDCl_3$): δ = 212.8 (C-1), 41.0 (2C, C-2, C-6), 38.0 (C-1'), 35.9 (C-4), 32.9 (2C, C-3, C-5), 20.6 (C-2'), 14.4 (C-3') ppm. **ESI-MS** (pos.): *m/z* (%) = 141.1 (100) $[M + H]^+$, 163.0 (7) $[M + Na]^+$. bp = 47 °C (1.5 mbar). The analytical data are in accordance with the literature.[8, 9]

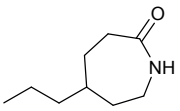
***N*-hydroxy-4-propylcyclohexanimine (13)**



In accordance to a procedure from Hardy et al.[12] A solution of **12** (240 mg, 1.71 mmol), hydroxylamine hydrochloride (238 mg, 3.43 mmol) and Na_2CO_3 (544 mg, 5.14 mmol) in MeOH (2 mL) and water (1 mL) was stirred at room temperature for 2.5 h. The reaction mixture was evaporated and the residue was taken up in ethyl acetate (15 mL) and water (15 mL). The layers were separated and the aqueous layer was extracted with ethyl acetate (3x10 mL). The combined organic extracts were washed with brine (15 mL), dried over Na_2SO_4 and evaporated to obtain a colorless oil (252 mg, 1.62 mmol, 96%). IR (ATR): $\tilde{\nu}_{max}$ 3225, 3116, 2954, 2920, 1667, 1441,

1008, 971, 914 cm^{-1}. **^{1}H-NMR, COSY, NOESY** (400 MHz, $CDCl_3$): δ = 8.51 (s, 1H, O*H*), 3.29–3.20 (m, 1H, H_{eq}-6), 2.44–2.38 (m, 1H, H_{eq}-2), 2.08 (dt, J = 13.6, 4.8 Hz, 1H, H_{ax}-2), 1.93–1.85 (m, 2H, H_{eq}-3, H_{eq}-5), 1.79 (dt, J = 14.5, 5.3 Hz, 1H, H_{ax}-6), 1.55–1.45 (m, 1H, H-4), 1.38–1.28 (m, 2H, H-2'), 1.26–1.18 (m, 2H, H-1'), 1.17–1.04 (m, 2H, H_{ax}-3, H_{ax}-5), 0.89 (t, J = 7.2 Hz, 3H, H-3') ppm. **^{13}C-NMR, HSQC, HMBC** (101 MHz, $CDCl_3$): δ = 160.9 (C-1), 38.5 (C-1'), 36.7 (C-4), 32.9 (C-3), 31.7 (C-5), 31.5 (C-2), 24.0 (C-6), 20.3 (C-2'), 14.4 (C-3') ppm. **ESI-MS** (pos.): *m/z* (%) = 156.0 (100) $[M + H]^+$, 178.0 (1) $[M + Na]^+$. **ESI-HRMS** (pos.) calcd ($C_9H_{18}NO$) 156.1388; found 156.1389. The analytical data are in accordance with the literature.[13]

5-propylazepan-2-one (5)

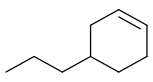


The procedure was conducted following Powell et al.[14] Oxime **13** (120 mg, 0.77 mmol) was dissolved in polyphosphoric acid (4.4 g) under gentle warming. The resulting solution was stirred at 55 °C for 18 h. After cooling to room temperature, the mixture was quenched with ice-cold water (2.2 mL) and neutralized with 4 M NaOH (25 mL). The solution was extracted with DCM (3x15 mL), the combined organic extracts were dried over Na_2SO_4 and evaporated. The product was obtained as a colorless solid (104 mg, 0.67 mmol, 87%), mp = 80–81 °C. IR (ATR): $\tilde{\nu}_{max}$ 3199, 3072, 2954, 2910, 2852, 1660, 1440, 1356, 1225, 1120, 851 cm^{-1}. **^{1}H-NMR, COSY** (400 MHz, $CDCl_3$): δ = 6.65 (s, 1H, H-1), 3.29–3.22 (m, 2H, H-7), 2.54–2.43 (m, 2H, H-3), 1.90–1.82 (m, 2H, H_a-4, H_a-6), 1.58–1.50 (m, 1H, H-5), 1.36–1.18 (m, 6H, H_b-4, H_b-6, H-1', H-2'), 0.89 (t, J = 7.1 Hz, 3H, H-3') ppm. **^{13}C-NMR, HSQC, HMBC** (101 MHz, $CDCl_3$): δ = 179.5 (C-2), 42.2 (C-7), 41.4 (C-5), 39.4 (C-1'), 35.6 (C-6), 34.9 (C-3), 29.1 (C-4), 20.0 (C-2'), 14.3 (C-3') ppm. **ESI-MS** (pos.): *m/z* (%) = 156.1 (85) $[M + H]^+$, 178.1 (14) $[M + Na]^+$, 311.3 (100) $[2M + H]^+$, 333.2 (16.4) $[2M + Na]^+$. **ESI-HRMS** (pos.) calcd ($C_9H_{18}NO$) 156.1388; found 156.1385. The analytical data are in accordance with the literature.[15]

3-propylhexanedioic acid (6)

Method A:

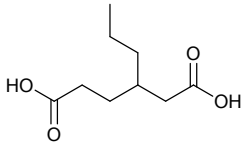
Step 1: 4-propylcyclohex-1-ene



The procedure was conducted following Coleman et al.[16] Cyclohexanol **2** (13.0 g, 91.4 mmol) and concentrated sulfuric acid (274 µL, 483 µmol) were placed in a 50-mL round-bottom flask equipped with a distillation attachment. The mixture was placed in a preheated oil bath at 150 C and was stirred under diminished pressure of 200 mbar. The receiver was kept cold through an external ice bath and the distillation was continued until only a small residue remained. The distillate was dissolved in DCM (200 mL) and washed with brine (50 mL). The organic layer was dried over Na_2SO_4 and concentrated under a pressure of 350 mbar. The product was obtained as a

colorless liquid (6.55 g, 48.0 mmol, containing 9 mol% DCM, see ^{1}H-NMR-spectrum S35) and was used without further purification in the next step.

Step 2: 3-propylhexanedioic acid (**6**)

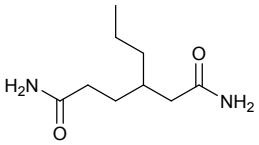


The procedure was conducted following Zimmermann et al.[17] To a stirred suspension of 4-propylcyclohex-1-ene (6.55 g, 48.0 mmol, containing 9 mol% DCM) and sodium periodate (42.4 g, 198 mmol) in water (240 mmol), ethyl acetate (95 mL) and acetonitrile (95 mL) was added $RuCl_3 \cdot xH_2O$ (48% Ru, 240 mg, 1.14 mmol). The resulting mixture was stirred vigorously for 2 h at room temperature. After phase separation, the aqueous layer was extracted with ethyl acetate (3x100 mL). The combined organic extracts were concentrated under diminished pressure to 50 mL, quickly extracted with 1 M NaOH (3x25 mL) and the aqueous extracts were again acidified with 2 M hydrochloric acid. This solution was extracted with ethyl acetate (3x50 mL) and the combined organic extracts were dried over Na_2SO_4 and evaporated. The black residue was eluted through a plug of silica (eluent: cyclohexane:ethyl acetate:acetic acid = 100:100:1) in order to remove inorganic salts. The product was obtained as a colorless oil (8.54 g, 45.4 mmol, 74% over two steps).

Method B:

The procedure was conducted following Rokhum et al.[18] A suspension of Oxone® (70.2 g, 228 mmol) in water (86 mL) was added to cyclohexanone **12** (8.00 g, 57.1 mmol) and $RuCl_3 \cdot xH_2O$ (48% Ru, 59.2 mg, 0.29 mmol). The resulting mixture was allowed to stir over night at room temperature and was subsequently extracted with ethyl acetate (3x100mL). The combined organic extracts were dried over Na_2SO_4 and evaporated. The resulting black oil was eluted through a plug of silica (eluent: cyclohexane:ethyl acetate:acetic acid = 100:100:1) in order to remove inorganic salts and the product was obtained as a colorless oil (7.54 g, 39.9 mmol, 70%). IR (ATR): $\tilde{\nu}_{max}$ 2958, 2932, 2874, 1702, 1456, 1412, 1381, 1286, 1235, 1162, 934 cm^{-1}. **^{1}H-NMR, COSY** (300 MHz, $CDCl_3$): δ = 11.01 (s, 2H, O*H*), 2.44–2.36 (m, 2H, H-5), 2.36–2.25 (m, 2H, H-2), 1.96–1.88 (m, 1H, H-3), 1.73–1.63 (m, 2H, H-4), 1.37–1.27 (m, 4H, H-1', H-2'), 0.90 (t, J = 6.3 Hz, 3H, H-3') ppm. **^{13}C-NMR, HSQC, HMBC** (76 MHz, $CDCl_3$): δ = 180.3 (C-6), 179.9 (C-1), 38.7 (C-2), 35.9 (C-1'), 34.1 (C-3), 31.5 (C-5), 28.6 (C-4), 19.7 (C-2'), 14.3 (C-3') ppm. **ESI-MS** (pos.): *m/z* (%) = 189.0 (8.6) $[M + H]^+$, 211.0 (100) $[M + Na]^+$. **ESI-HRMS** (pos.) calcd ($C_9H_{16}O_4Na$) 211.0946; found 211.0952.

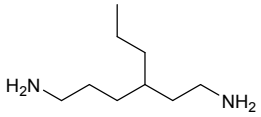
3-propylhexanediamide (15)



The procedure was conducted following Treibs et al.[19] A solution of diacid **6** (5.78 g, 30.8 mmol) in freshly distilled thionyl chloride (6.70 mL, 92.4 mmol) was stirred for 1 h under reflux. After cooling to room temperature, excess thionyl chloride was removed under reduced pressure to obtain the crude acyl chloride which was used directly. The crude acyl chloride was added to an ice-cold solution of a 25%

aqueous ammonia solution (27.9 mL, 370 mmol) over 15 min. After removal of the ice bath, the mixture was stirred for 15 min at room temperature and the precipitate was collected by filtration. The residue was washed with water and dried in order to obtain a colorless solid (4.3 g, 23.1 mmol, 75% over two steps), mp = 147–149 °C. IR (ATR): $\tilde{\nu}_{max}$ 3385, 3189, 2955, 2927, 2872, 1649, 1412, 1170 cm^{-1}. **^{1}H-NMR, COSY** (400 MHz, DMSO-d_6): δ = 7.25 (s, 1H, C-1NH_a), 7.23 (s, 1H, C-6NH_a), 6.71 (s, 1H, C-1NH_b), 6.68 (s, 1H, C-6NH_b), 2.04–1.98 (m, 2H, H-5), 1.95 (d, J = 7.6 Hz, 2H, H-2), 1.77–1.70 (m, 1H, H-3), 1.49–1.40 (m, 2H, H-4), 1.29–1.15 (m, 4H, H-1‘, H-2‘), 0.84 (t, J = 7.0 Hz, 3H, H-3‘) ppm. **^{13}C-NMR, HSQC, HMBC** (101 MHz, DMSO-d_6): δ = 174.5 (C-6), 173.9 (C-1), 39.9 (C-2), 35.4 (C-1’), 34.0 (C-3), 32.5 (C-5), 29.2 (C-4), 19.0 (C-2’), 14.3 (C-3’) ppm. **ESI-MS** (pos.): *m/z* (%) = 187.1 (30) [M + H]$^+$, 209.1 (100) [M + Na]$^+$, 395.2 (80) [2M + Na]$^+$. **ESI-HRMS** (pos.) calcd ($C_9H_{18}O_2N_2Na$) 209.1266; found 209.1261. The analytical data are in accordance with the literature.[20]

3-propylhexane-1,6-diamine (7)



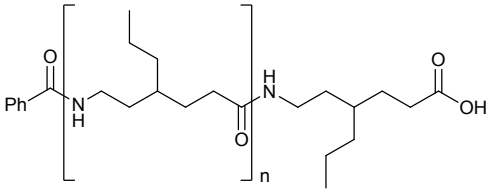
Method A: The procedure was conducted following Reynolds et al.[21] To a stirred suspension of lithium aluminium hydride (1.42 g, 37.6 mmol) in dry MTBE (280 mL) was added diamide **15** (2.00 g, 10.7 mmol) over a period of 10 minutes. The resulting mixture was stirred for 16 h under reflux. After cooling to 0 °C 1 M potassium sodium tartrate solution (90 mL) was added slowly. The resulting precipitate was removed by filtration and the residue was washed with ethyl acetate (200 mL). After separation of the layers the aqueous phase was extracted with ethyl acetate (3x30 mL) and the combined organic layers were dried over Na_2SO_4 and evaporated. In order to obtain a pure product the residue was distilled using a Kugelrohr apparatus under vacuum (bp 120–135 °C, 1 mbar). The product was obtained as a yellow liquid (1.20 g, 7.60 mmol, 71%).

Method B: The procedure was conducted following Malkov et al.[22] To a stirred solution of diamide **15** (500 mg, 2.68 mmol) in dry THF (6.30 mL) was added a 1 M solution of BH_3·THF complex in THF (25.5 mL, 25.5 mmol). The resulting solution was stirred for 1 h at room temperature and for 5 h at 70 °C. The mixture was then cooled to 0 °C and MeOH (5 mL) was added. After stirring over night at room temperature, the solvent was evaporated, 6 M aqueous HCl (50 mL) was added to the residue and the mixture was stirred for 4 h under reflux. The solvent was removed with a constant stream of nitrogen overnight and the residue was extracted with MeOH (3x15 mL). After evaporation of the solvent the residue was taken up with 1 M aqueous KOH (70 mL) and extracted with diethyl ether (6x20 mL). The combined organic layers were dried over Na_2SO_4 and evaporated to give a yellow oil (314 mg, 1.99 mmol, 74%). IR (ATR): $\tilde{\nu}_{max}$ 3281, 2954, 2923, 2858, 1669, 1601, 1456, 1378, 1296, 1070, 817 cm^{-1}. **^{1}H-NMR, COSY** (300 MHz, $CDCl_3$): δ = 2.71–2.64 (m, 4H, H-1, H-6), 1.56 (s, 4H, N*H*), 1.54–1.22 (m, 12H, H-2, H-3, H-4, H-5, H-1‘, H-2‘), 0.87 (t, J = 6.8 Hz, 3H, H-3‘) ppm. **^{13}C-**

NMR, HSQC, HMBC (76 MHz, $CDCl_3$): δ = 42.8, 40.0, 38.0, 36.2 (C-1'), 35.0 (C-3), 30.9, 30.8, 19.9 (C-2'), 14.6 (C-3') ppm. **ESI-HRMS** (pos.) calcd ($C_9H_{23}N_2$) 159.1861; found 159.1865.

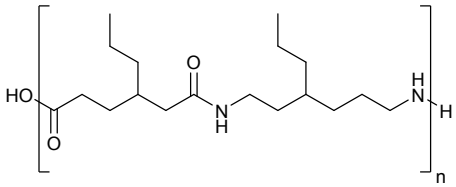
2.2.2 Polymerizations

Anionic polymerization of lactam 5 with potassium



The procedure was conducted following Winnacker et al.[23] The dried lactam **5** (560 mg, 3.60 mmol) and potassium (7.5 mg, 0.18 mmol) were placed in a Schlenk flask under argon. The stirred mixture was evacuated and heated to 150 °C. Upon reaching this temperature, the flask was flushed with argon again and benzoyl chloride (12 µL, 0.09 mmol) was added. The mixture was evacuated and stirred for 7 hours at 150 °C. After cooling to room temperature, the residue was washed with hexane:ethyl acetate 1:1 (3x10 mL) and water. The remaining brown solid was dissolved in methanol (0.5 mL) and purred into cold (–20 °C) diethyl ether (30 mL) in order to precipitate the polyamide which was separated by centrifugation. The insoluble fraction was taken up in MeOH (4 mL) and dialysed in MeOH (1 L) for 24 h using regenerated cellulose membranes (MWCO 1000 g mol^{-1}). After drying, the polyamide was obtained as a yellowish solid (291 mg, 1.88 mmol, 52%), DSC T_g = 15 °C. **IR** (ATR): $\tilde{\nu}_{max}$ 3282, 2955, 2927, 2869, 1637, 1546, 1454, 1377, 1313, 697 cm^{-1}. **^{1}H-NMR, COSY** (400 MHz, DMSO-d_6): δ = 7.84–7.81 (m, benzoyl *o*-positions), 7.74 (s, NH), 7.51–7.48 (m, benzoyl *p*-position), 7.45–7.42 (m, benzoyl *m*-positions), 3.03–2.97 (m, NH-CH_2), 2.01–1.99 (m, CO-CH_2), 1.46–1.44 (m, CO-CH$_2$-CH_2), 1.33–1.15 (m, H-1', H-2', C*H*, NH-CH$_2$-CH_2), 0.83 (t, J = 7.0 Hz, H-3') ppm. **^{13}C$_{\text{inverse gated}}$-NMR, HSQC, HMBC** (101 MHz, DMSO-d_6): δ = 172.5 (*C*O), 166.5 (terminal benzoyl CO), 135.2 (terminal benzoyl C-1), 131.4 (terminal benzoyl *p*-position), 128.7 (2C, terminal benzoyl *m*-position), 127.5 (2C, terminal benzoyl *o*-position), 36.8 (NH-*C*H$_2$), 35.5 (C-1'), 34.6 (*C*H), 33.3 (NH-CH$_2$-*C*H$_2$), 33.2 (CO-*C*H$_2$), 29.1 (CO-CH$_2$-*C*H$_2$), 19.5 (C-2'), 14.7 (C-3') ppm.

Polycondensation of 7 with the acid chloride of 6



The procedure was conducted following Wu et al.[24] and modified according to Sudo et al.[25] The dicarboxylic acid **6** (250 mg, 1.33 mmol) was converted to the corresponding acyl chloride by refluxing in freshly distilled thionyl chloride (575 µL, 7.98 mmol) for an hour. Excess thionyl chloride was removed by evaporation at room temperature. This crude acyl chloride was then dissolved in dry DMAc (2.5 mL) and added to a solution of diamine **7** (210 mg, 1.33 mmol) and dry triethylamine (374 µL, 2.66 mmol) in dry DMAc (2.5 mL). The reaction mixture was stirred overnight at room temperature and then poured into 5% aqueous $NaHCO_3$ solution (25 mL). The precipitate was collected by filtration and washed with water and acetone. The residue was taken up in MeOH, concentrated by evaporation (to 1 mL) and poured

into cold (–20 °C) diethyl ether (30 mL). After centrifugation, the insoluble fraction was taken up with MeOH (3.5 mL) and dialysis in MeOH (1 L) was conducted for 24 hours using regenerated cellulose membranes (MWCO 1000 g mol^{-1}). The polyamide was obtained as a yellowish solid (254 mg, 0.84 mmol, 62%), DSC T_g = 28 °C. **IR** (ATR): $\tilde{\nu}_{max}$ 3284, 2955, 2927, 2869, 1638, 1547, 1454, 1376, 1251, 737 cm^{-1}. **^{1}H-NMR, COSY** (400 MHz, DMSO-d_6): δ = 7.85–7.73 (m, 2H, N*H*), 3.03–2.94 (m, 4H, NH-CH_2), 2.03–1.94 (m, 4H, CO-CH_2), 1.74–1.70 (m, 1H, CO-CH$_2$-C*H*), 1.46–1.13 (m, 17H, H-1', H-2', H-1'', H-2'', 2xNH-CH$_2$-CH_2, NH-CH$_2$-CH$_2$-C*H*, NH-CH$_2$-CH$_2$-CH_2, CO-CH$_2$-CH_2), 0.85–8.80 (m, 6H, H-3', H-3'') ppm. **^{13}C-NMR, HSQC, HMBC** (101 MHz, DMSO-d_6): δ = 172.0 (*C*O-CH$_2$-CH$_2$), 171.3 (*C*O-CH$_2$-CH), 40.1 (CO-*C*H$_2$-CH), 38.7 (NH-*C*H$_2$), 36.2 (NH-*C*H$_2$), 35.2 (2C, C-1', C-1''), 34.1 (CO-CH$_2$-*C*H), 33.9 (*C*H), 33.0, 32.8 (CO-*C*H$_2$-CH$_2$), 30.1, 29.3 (CO-CH$_2$-*C*H$_2$), 26.0, 19.0 (C-2'), 18.9 (C-2''), 14.2 (2C, C-3', C-3'') ppm.

3 References

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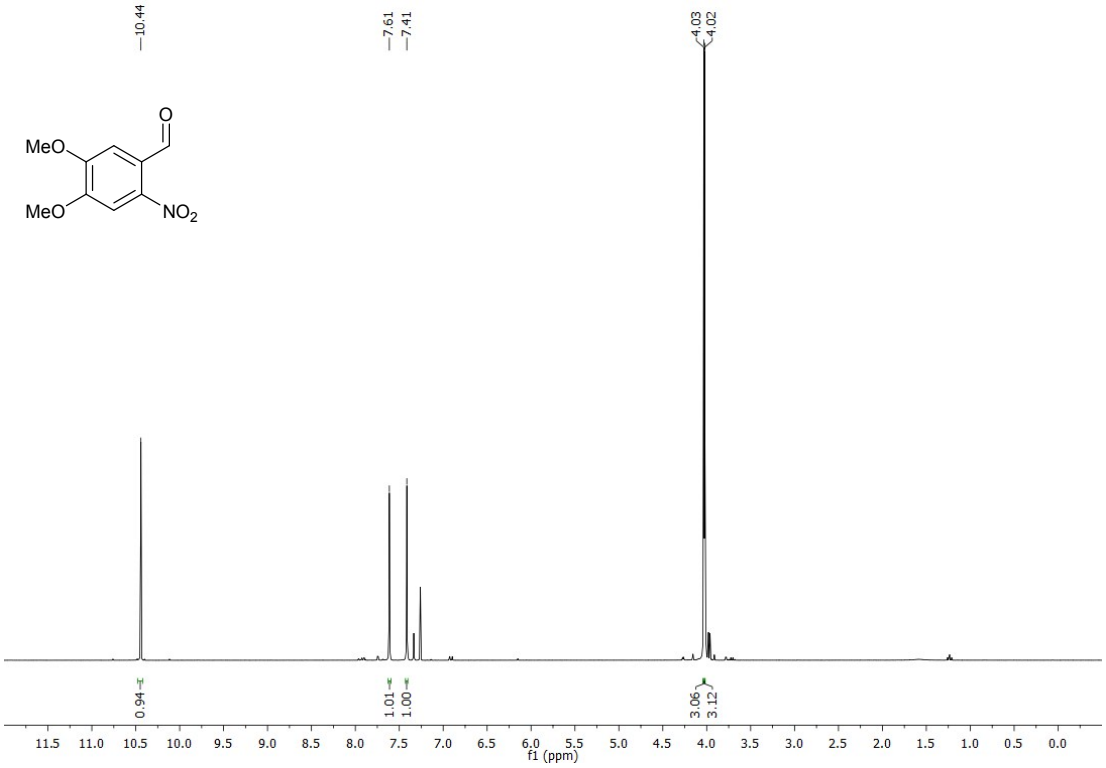
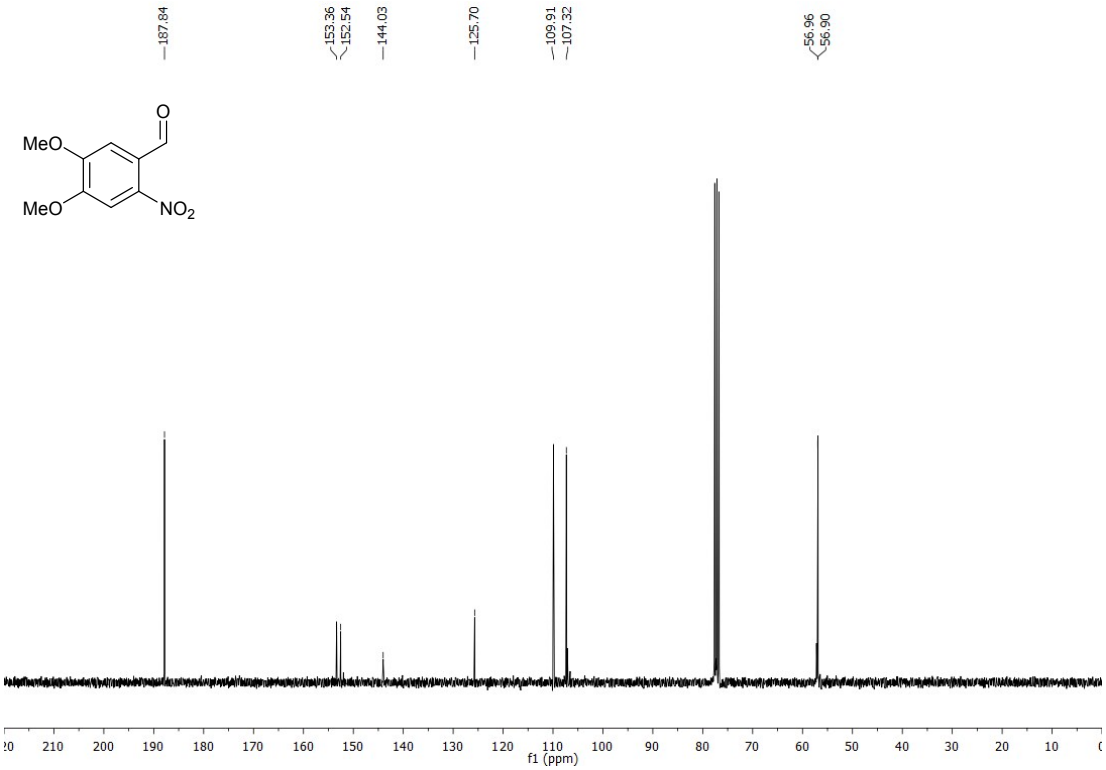
4 NMR spectra

4.1 Spectra of the indigo dye syntheses

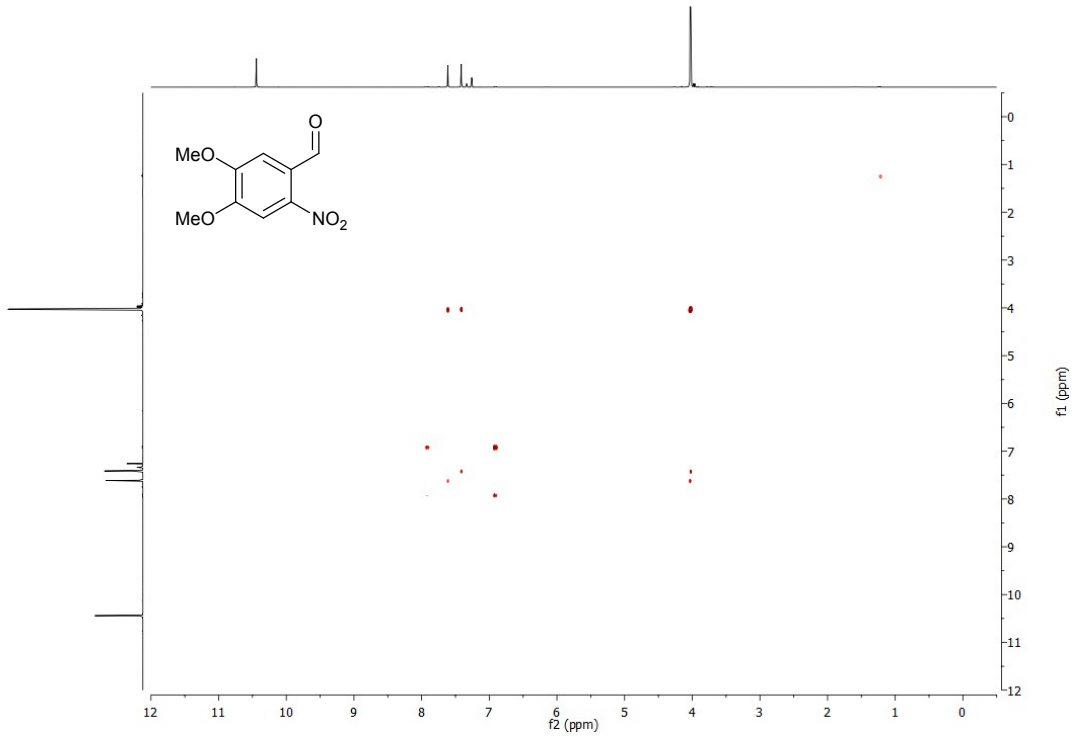
^{1}H-spectrum of 4,5-dimethoxy-2-nitrobenzaldehyde (**9**) in $CDCl_3$ (400 MHz)



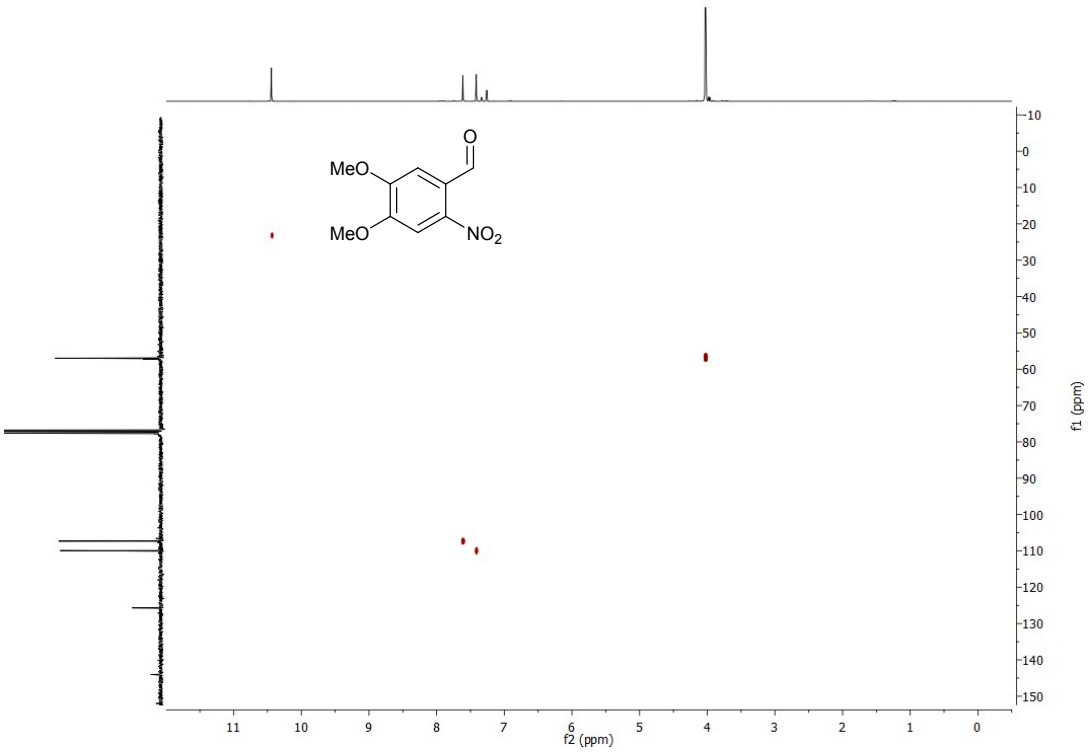
^{13}C-spectrum of 4,5-dimethoxy-2-nitrobenzaldehyde (**9**) in $CDCl_3$ (101 MHz)



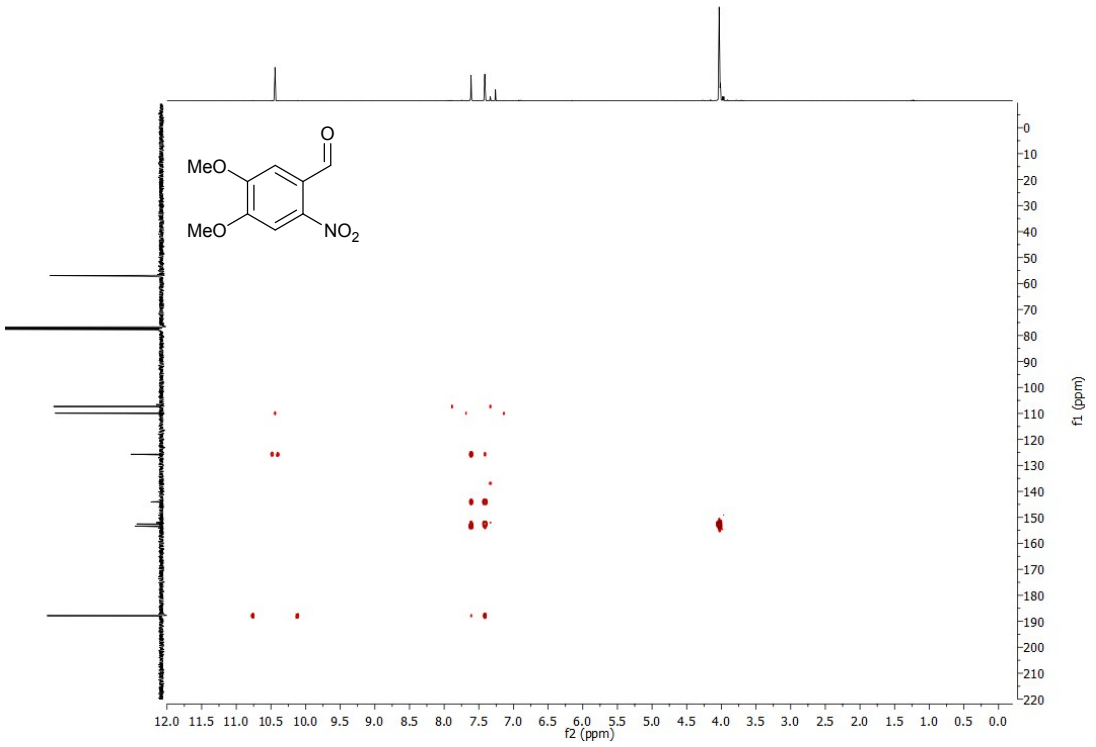
^{1}H-COSY-spectrum of 4,5-dimethoxy-2-nitrobenzaldehyde (**9**) in $CDCl_3$ (400 MHz)



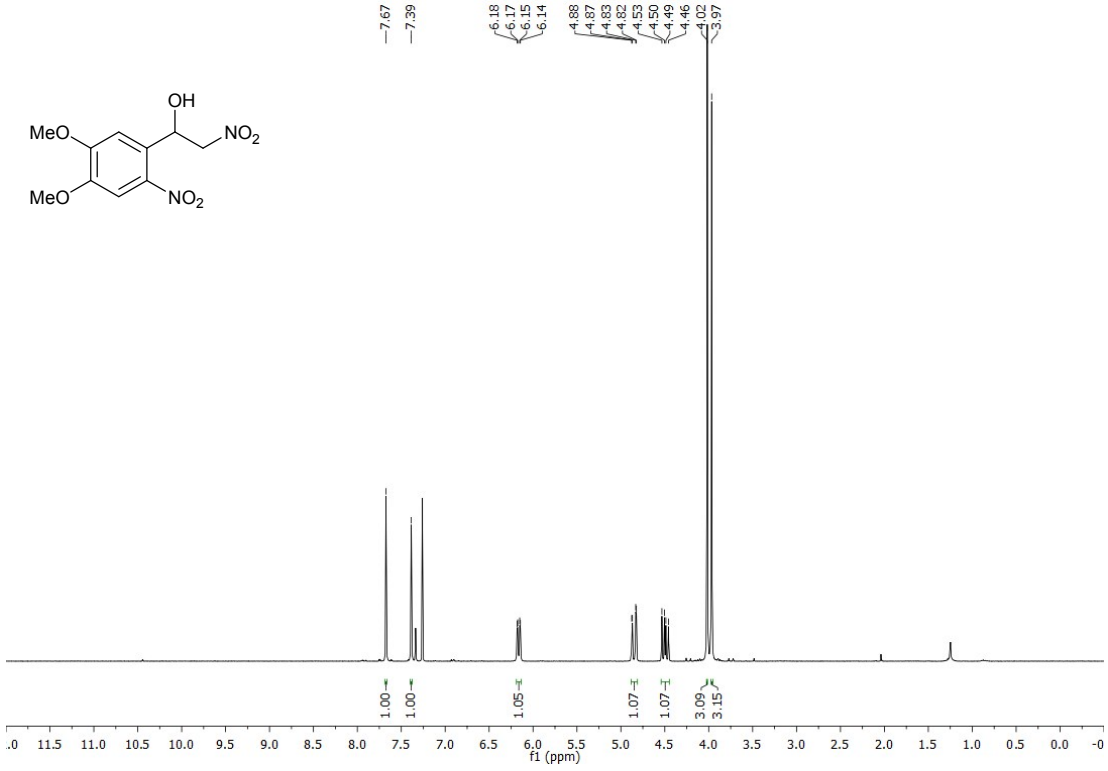
^{1}H-^{13}C-HSQC-spectrum of 4,5-dimethoxy-2-nitrobenzaldehyde (**9**) in $CDCl_3$ (400 MHz, 101 MHz)



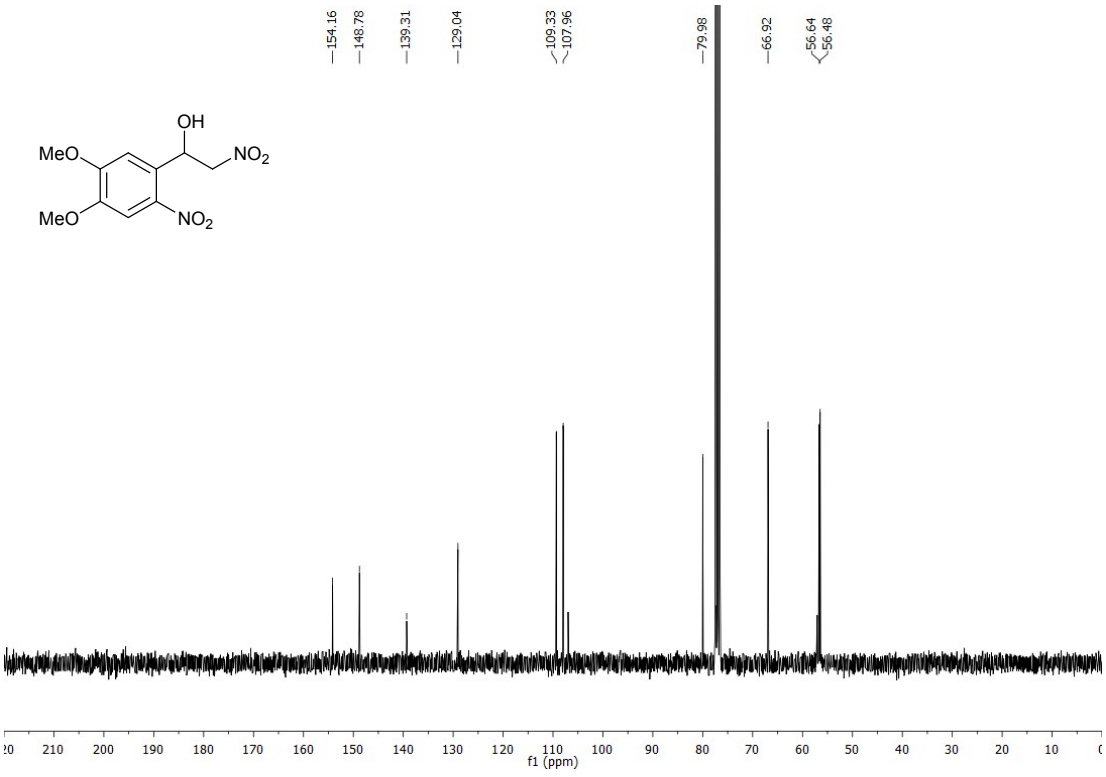
^{1}H-^{13}C-HMBC-spectrum of 4,5-dimethoxy-2-nitrobenzaldehyde (**9**) in $CDCl_3$ (400 MHz, 101 MHz)



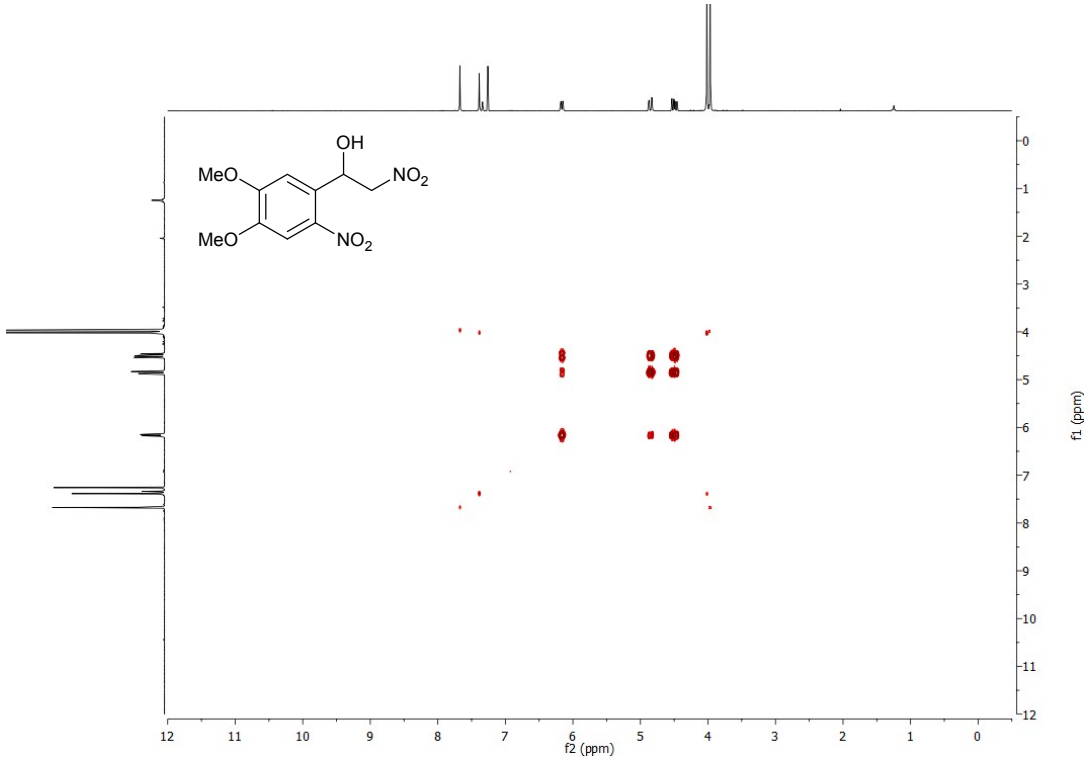
^{1}H-spectrum of 1-(4,5-dimethoxy-2-nitrophenyl)-2-nitroethanol (**10**) in $CDCl_3$ (300 MHz)



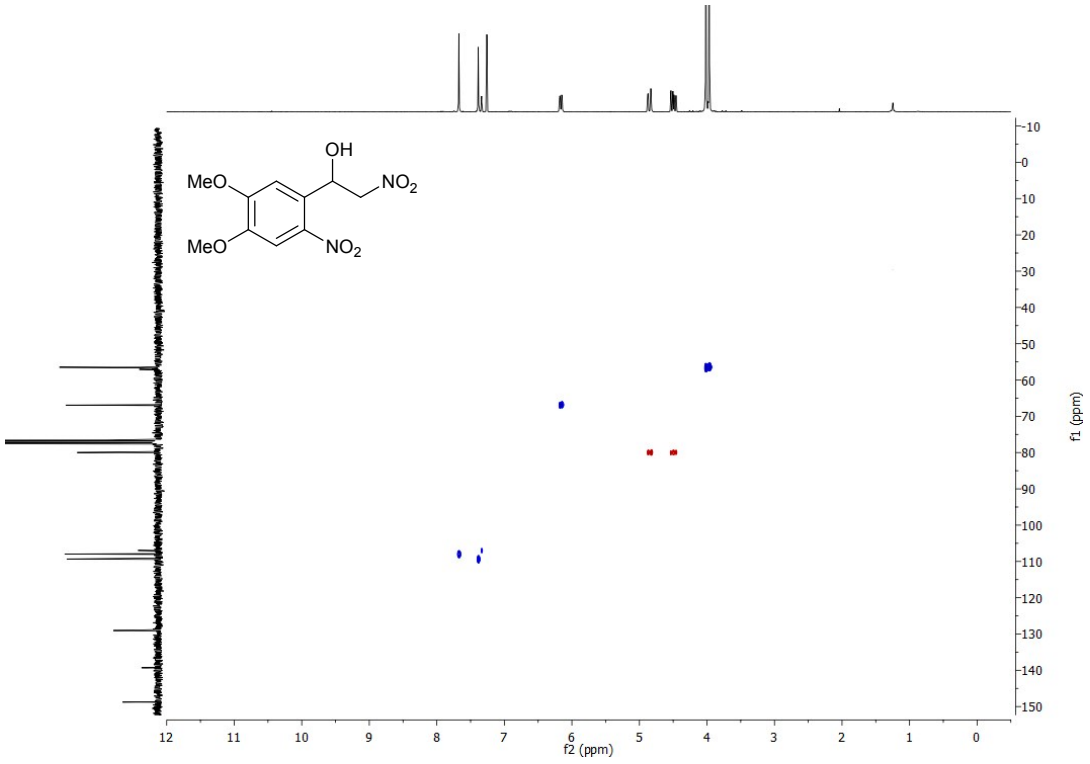
^{13}C-spectrum of 1-(4,5-dimethoxy-2-nitrophenyl)-2-nitroethanol (**10**) in $CDCl_3$ (76 MHz)



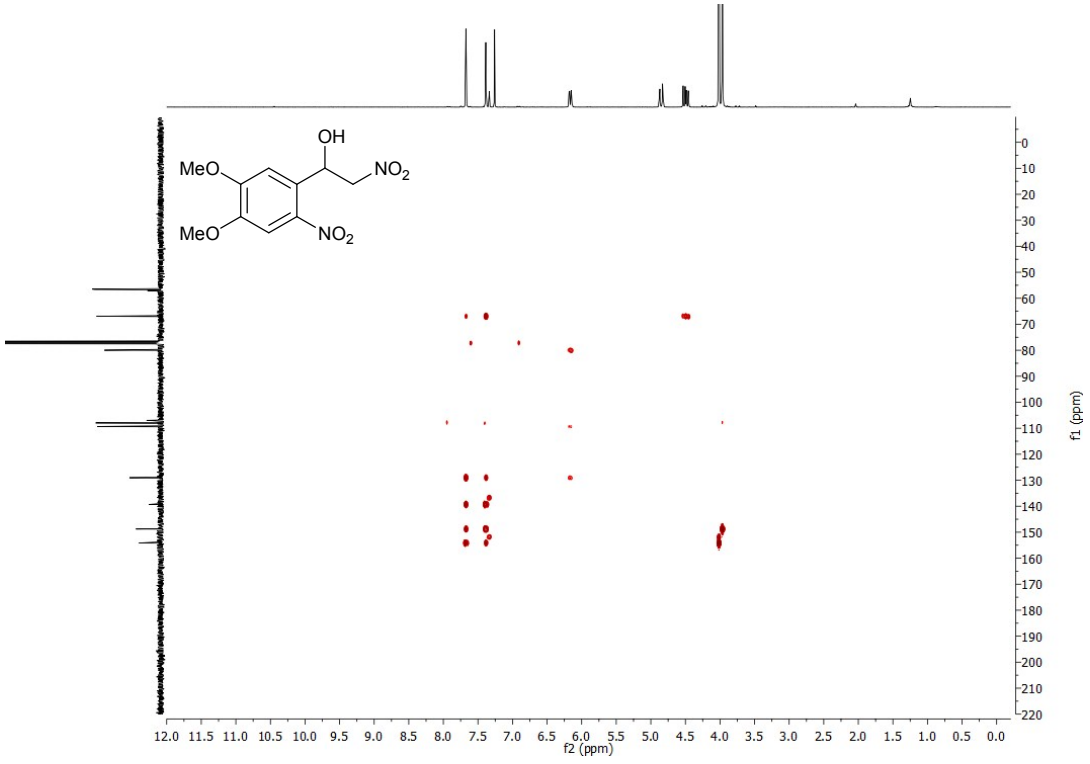
^{1}H-COSY-spectrum of 1-(4,5-dimethoxy-2-nitrophenyl)-2-nitroethanol (**10**) in $CDCl_3$ (300 MHz)



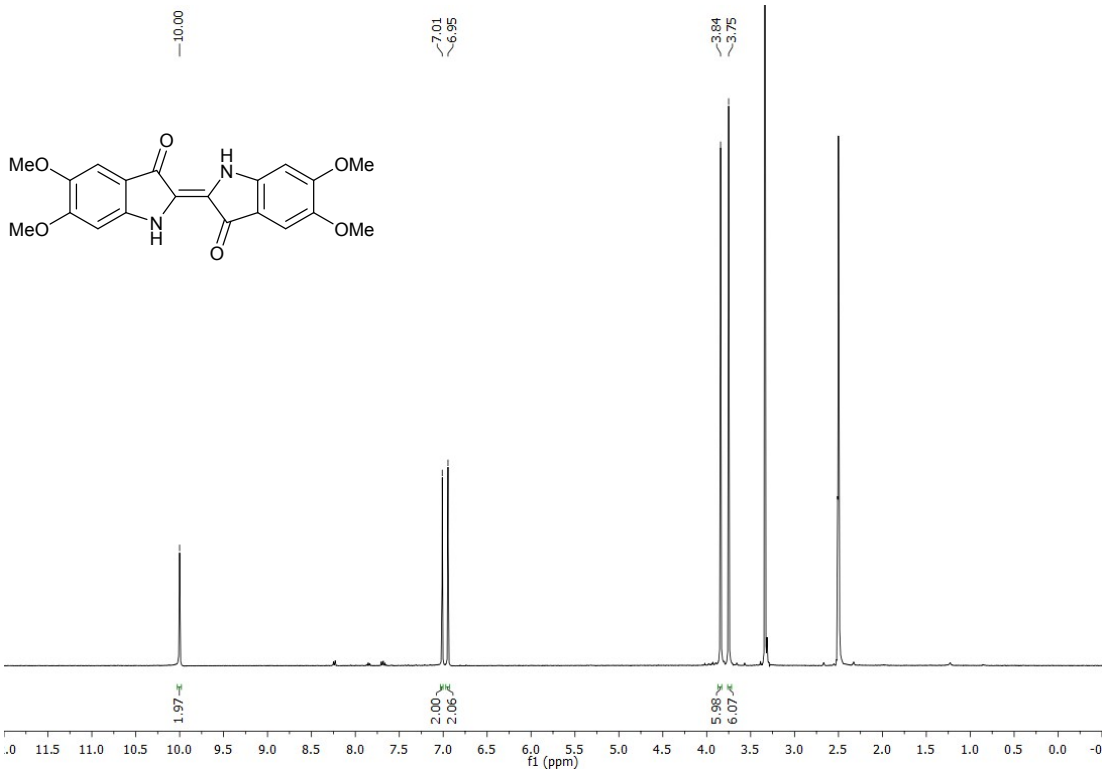
^{1}H-^{13}C-HSQC-spectrum of 1-(4,5-dimethoxy-2-nitrophenyl)-2-nitroethanol (**10**) in $CDCl_3$ (300 MHz, 76 MHz)



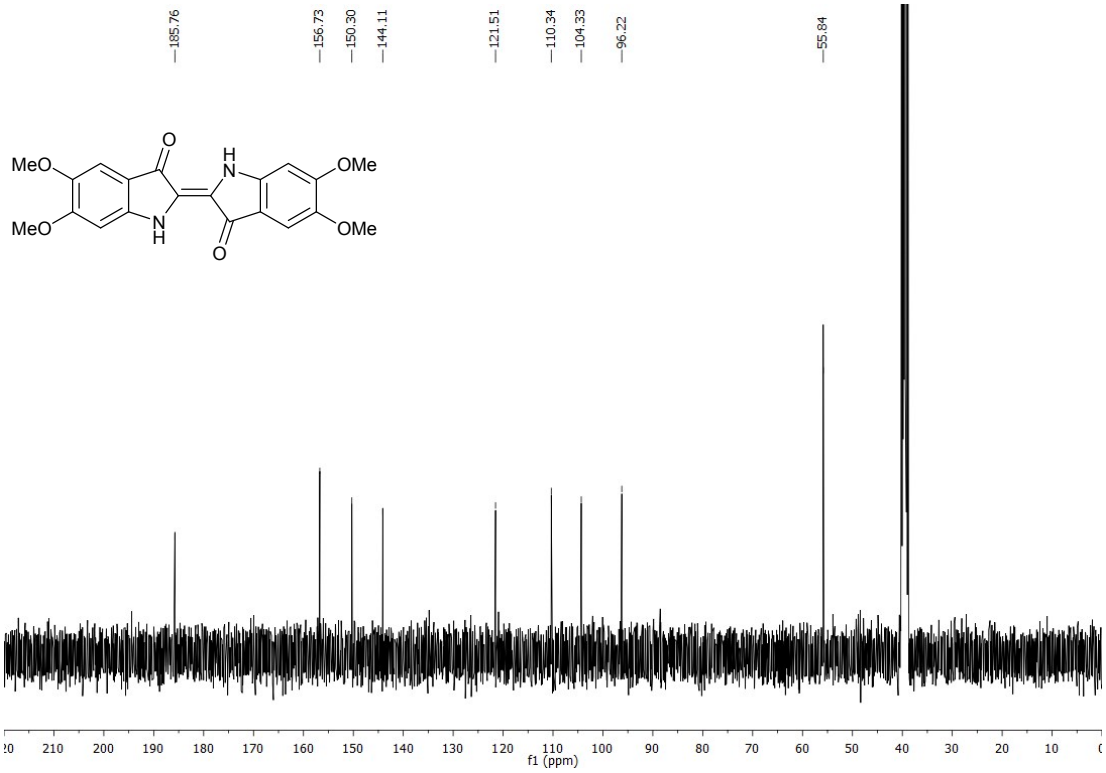
^{1}H-^{13}C-HMBC-spectrum of 1-(4,5-dimethoxy-2-nitrophenyl)-2-nitroethanol (**10**) in $CDCl_3$ (300 MHz, 76 MHz)



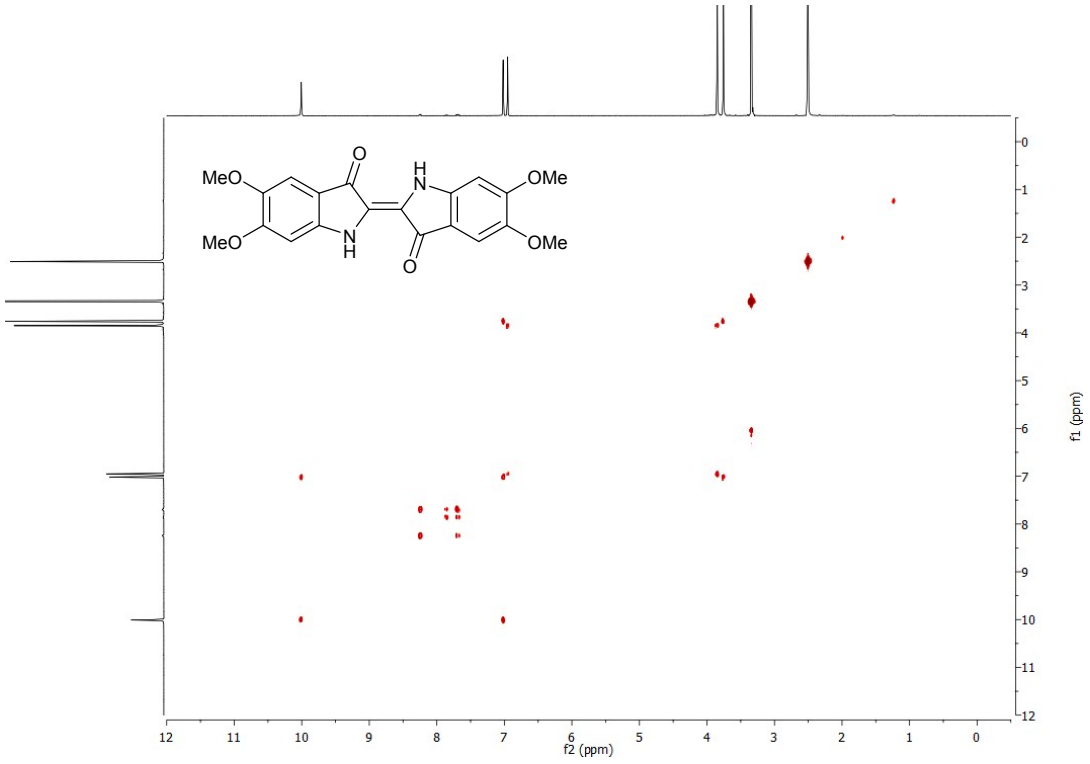
^{1}H-spectrum of 5,5',6,6'-tetramethoxyindigo (**3**) in DMSO-d_6 (400 MHz)



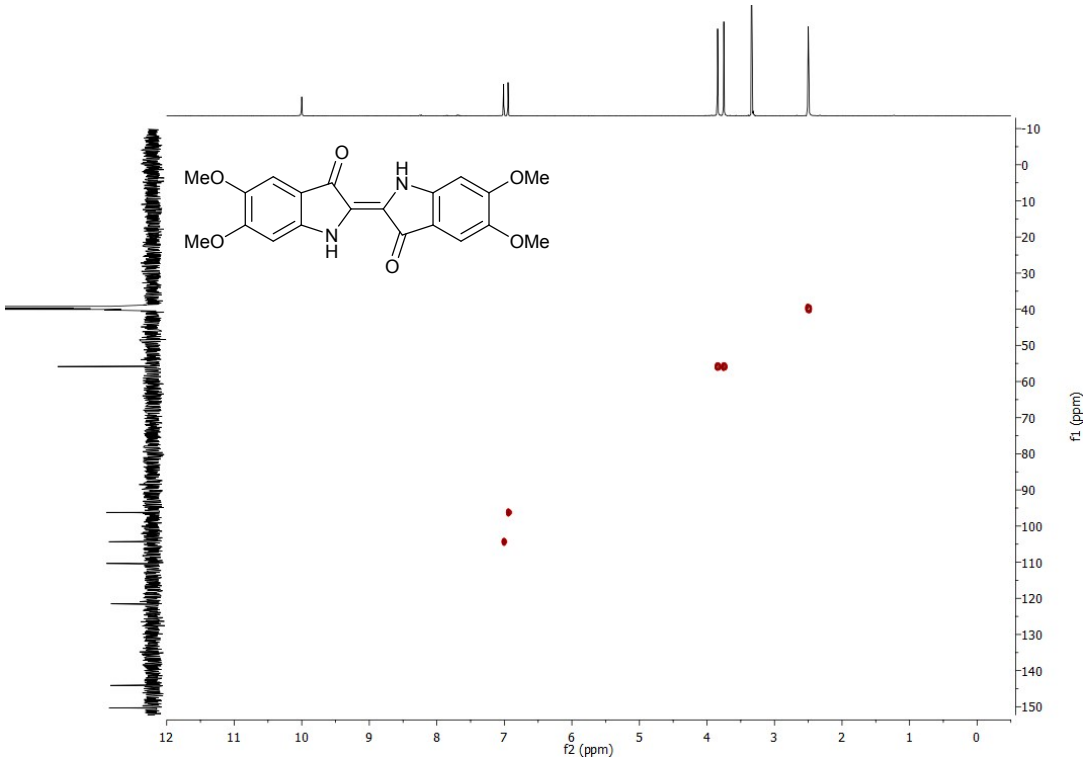
^{13}C-spectrum of 5,5',6,6'-tetramethoxyindigo (**3**) in DMSO-d_6 (101 MHz)



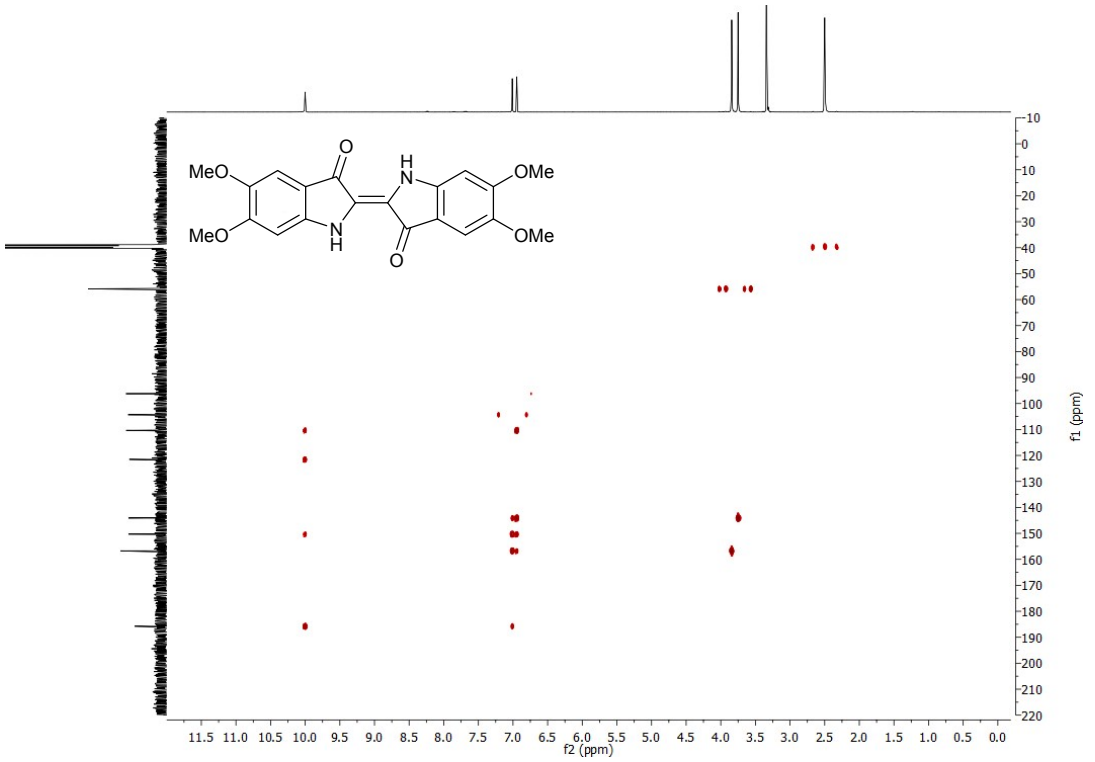
^{1}H-COSY-spectrum of 5,5',6,6'-tetramethoxyindigo (**3**) in DMSO-d_6 (400 MHz)



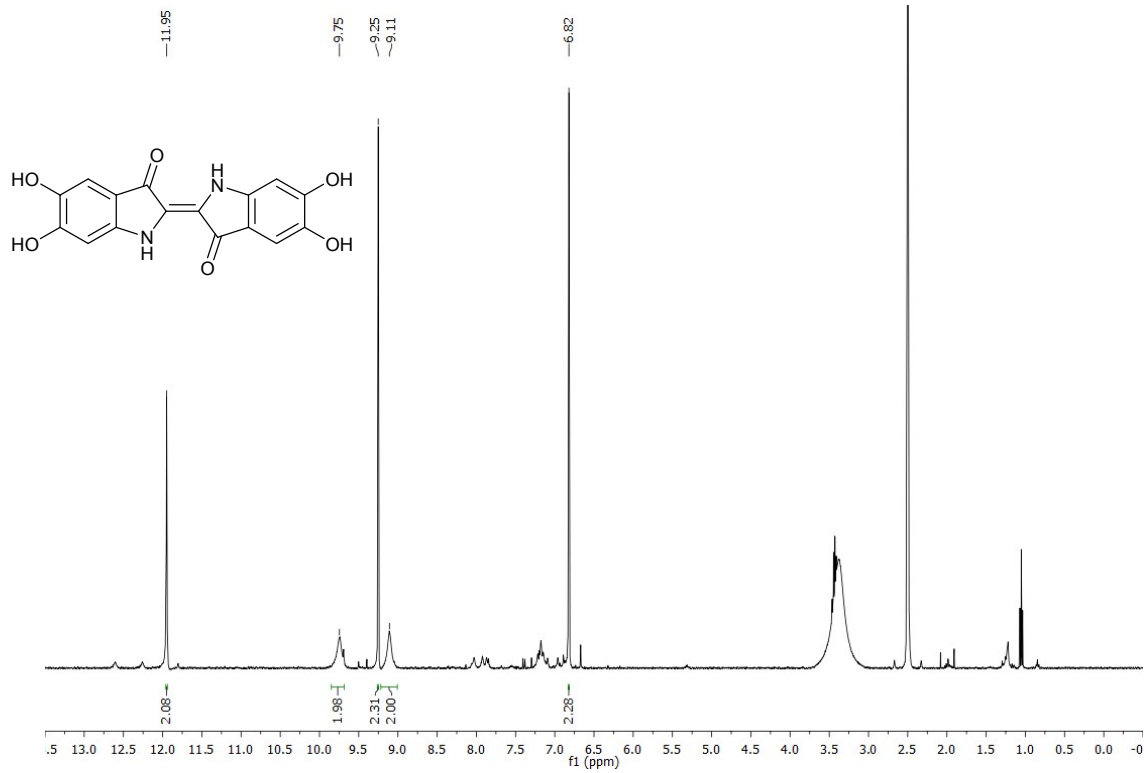
^{1}H-^{13}C-HSQC-spectrum of 5,5’,6,6’-tetramethoxyindigo (**3**) in DMSO-d_6 (400 MHz, 101 MHz)



^{1}H-^{13}C-HMBC-spectrum of 5,5’,6,6’-tetramethoxyindigo (**3**) in DMSO-d_6 (400 MHz, 101 MHz)

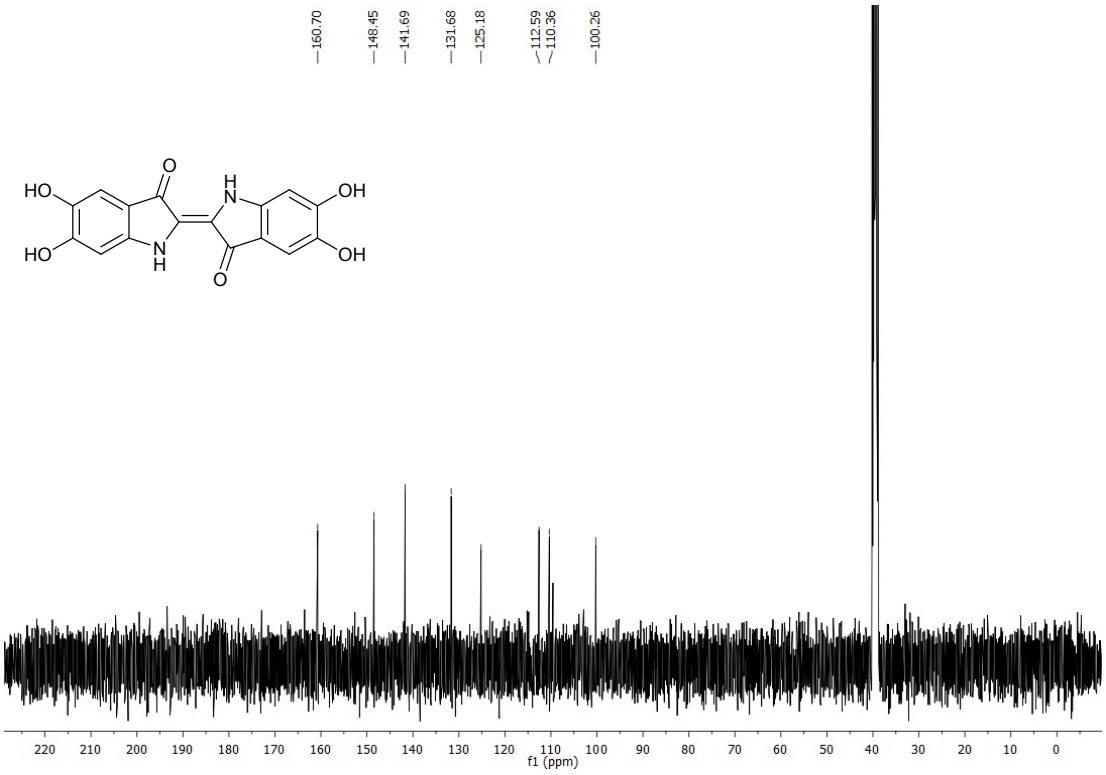


^{1}H-spectrum of 5,5',6,6'-tetrahydroxyindigo (**4**) in DMSO-d_6 (400 MHz)



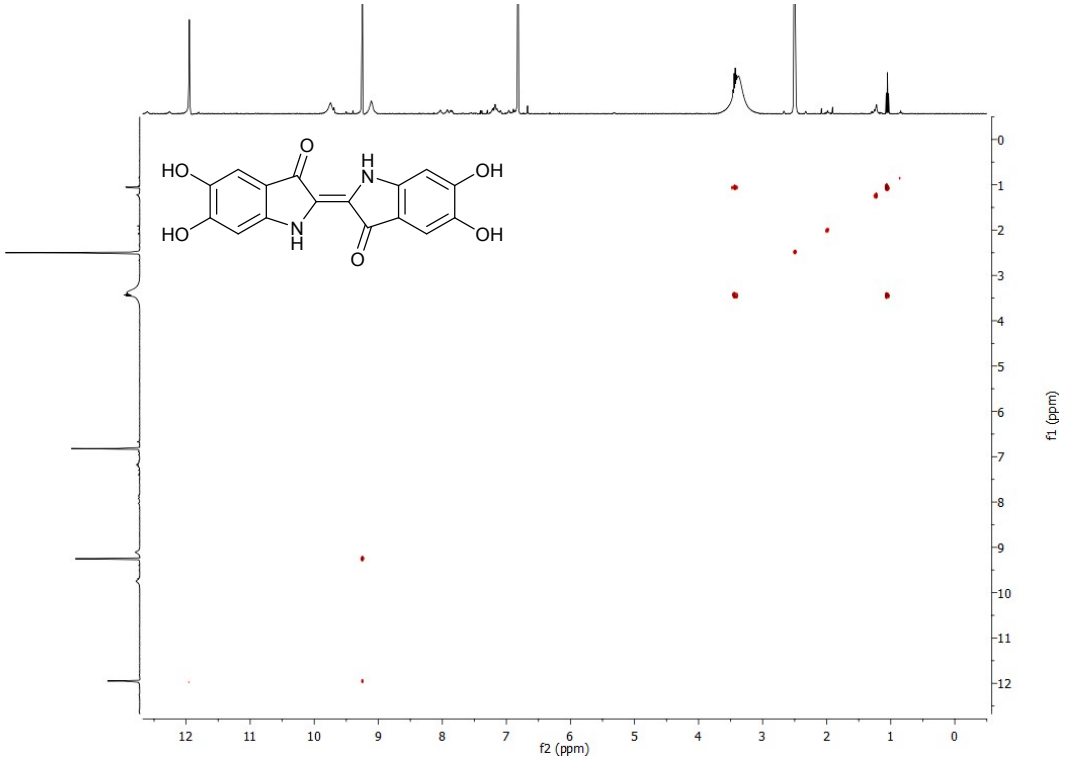
Compound poorly soluble in DMSO-d_6

^{13}C-Spectrum of 5,5',6,6'-tetrahydroxyindigo (**4**) in DMSO-d_6 (101 MHz)

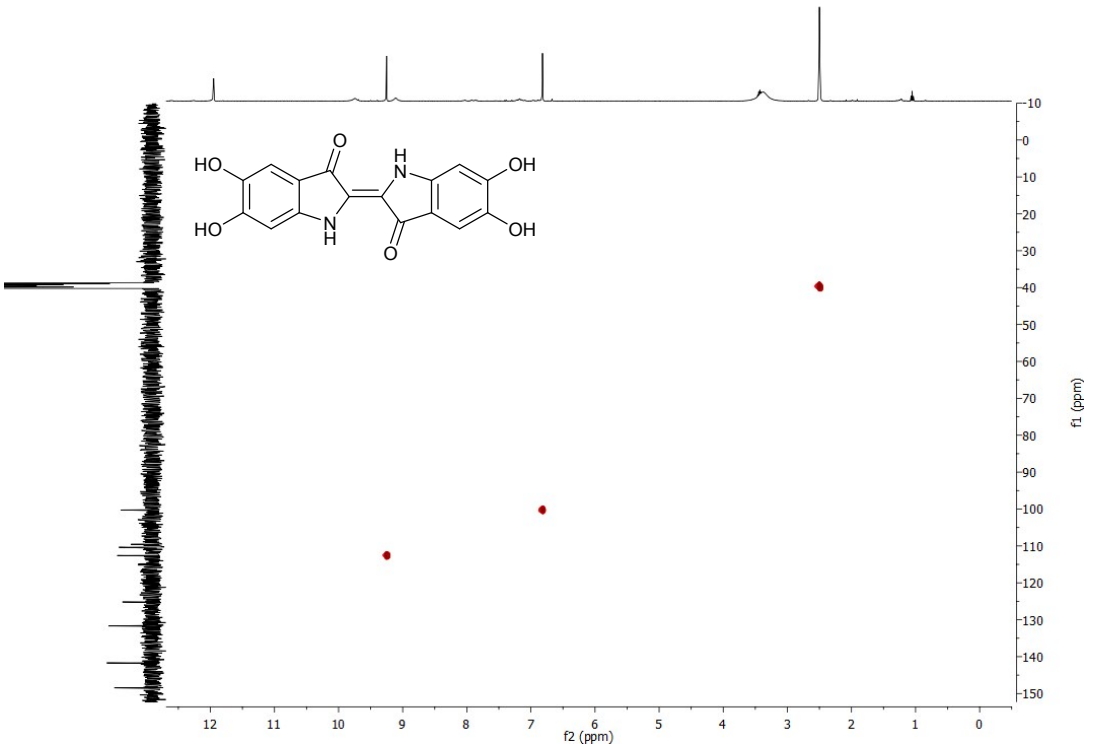


Compound poorly soluble in DMSO-d_6

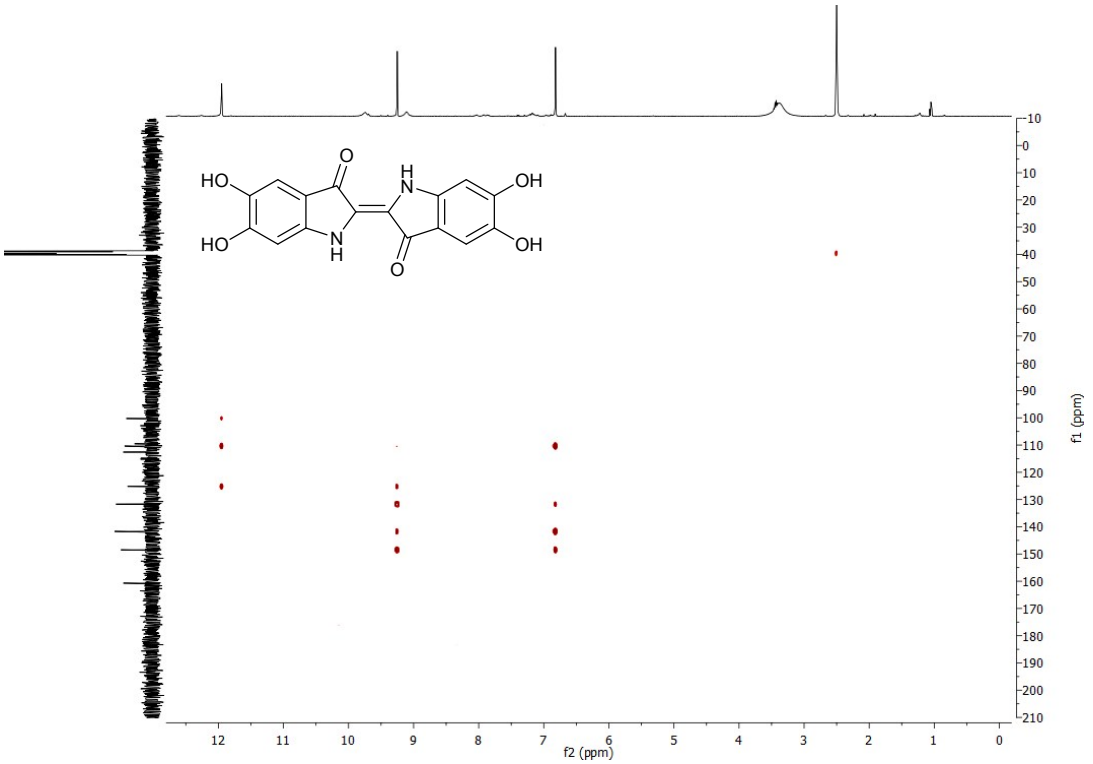
^{1}H-COSY-spectrum of 5,5',6,6'-tetrahydroxyindigo (**4**) in DMSO-d_6 (400 MHz)



^{1}H-^{13}C-HSQC-spectrum of 5,5',6,6'-tetrahydroxyindigo (**4**) in DMSO-d_6 (400 MHz, 101 MHz)



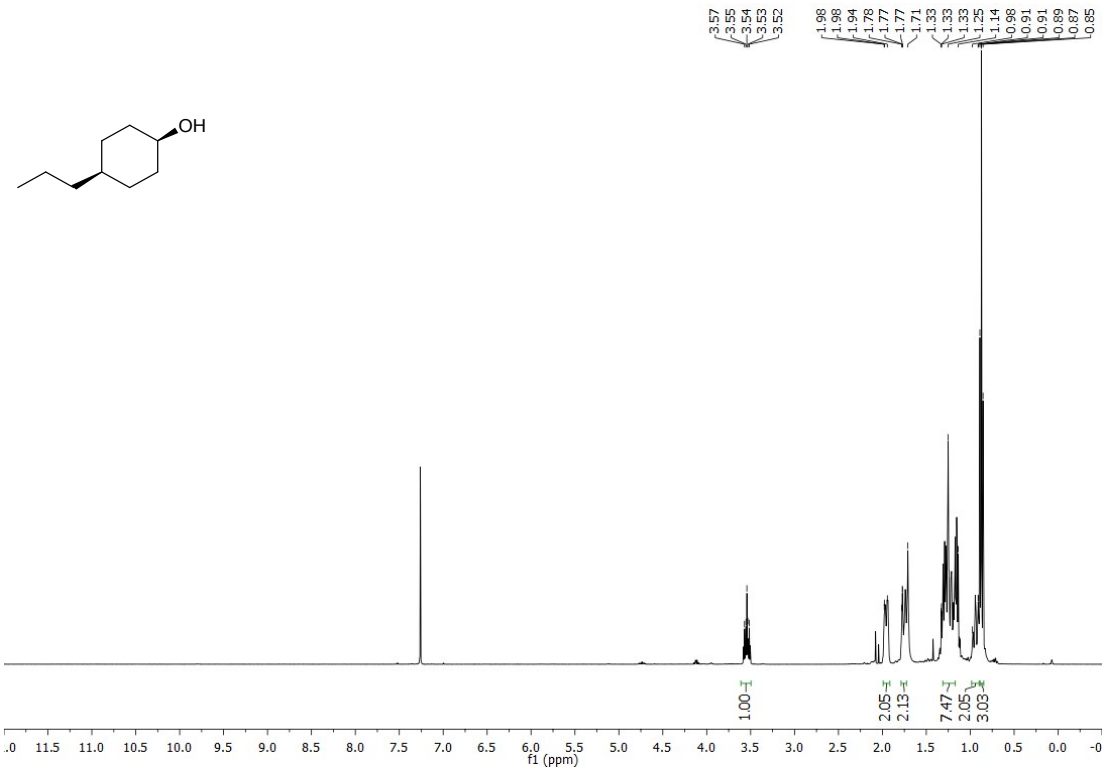
^{1}H-^{13}C-HMBC-spectrum of 5,5',6,6'-tetrahydroxyindigo (**4**) in DMSO-d_6 (400 MHz, 101 MHz)



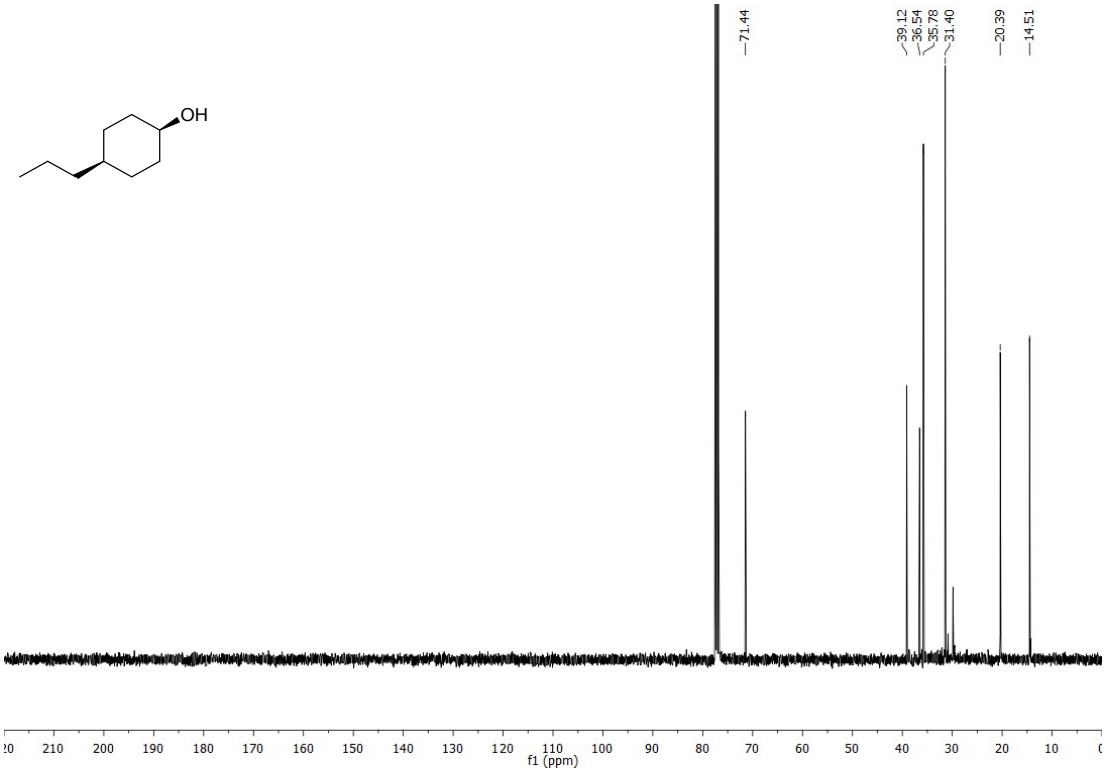
4.2 Spectra of the polyamide syntheses

4.2.1 Spectra of 4-propylcyclohexanol (**2**)

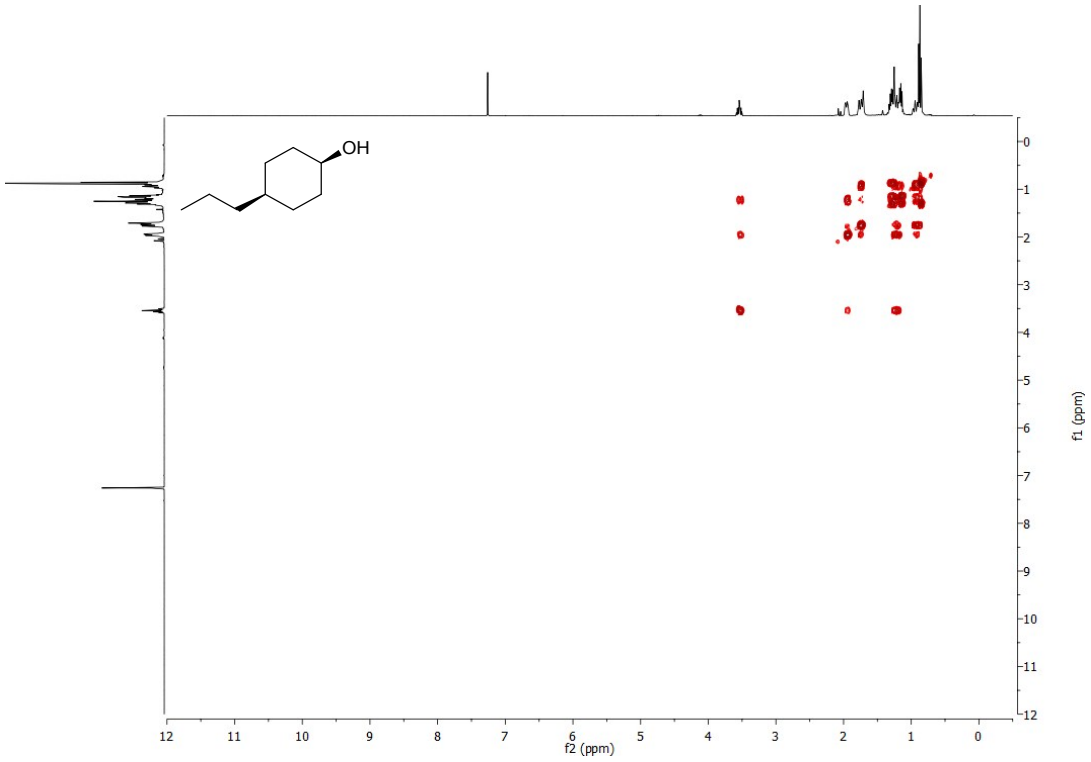
^{1}H-spectrum of *cis*-4-propylcyclohexanol (*cis*-**2**) in $CDCl_3$ (400 MHz)



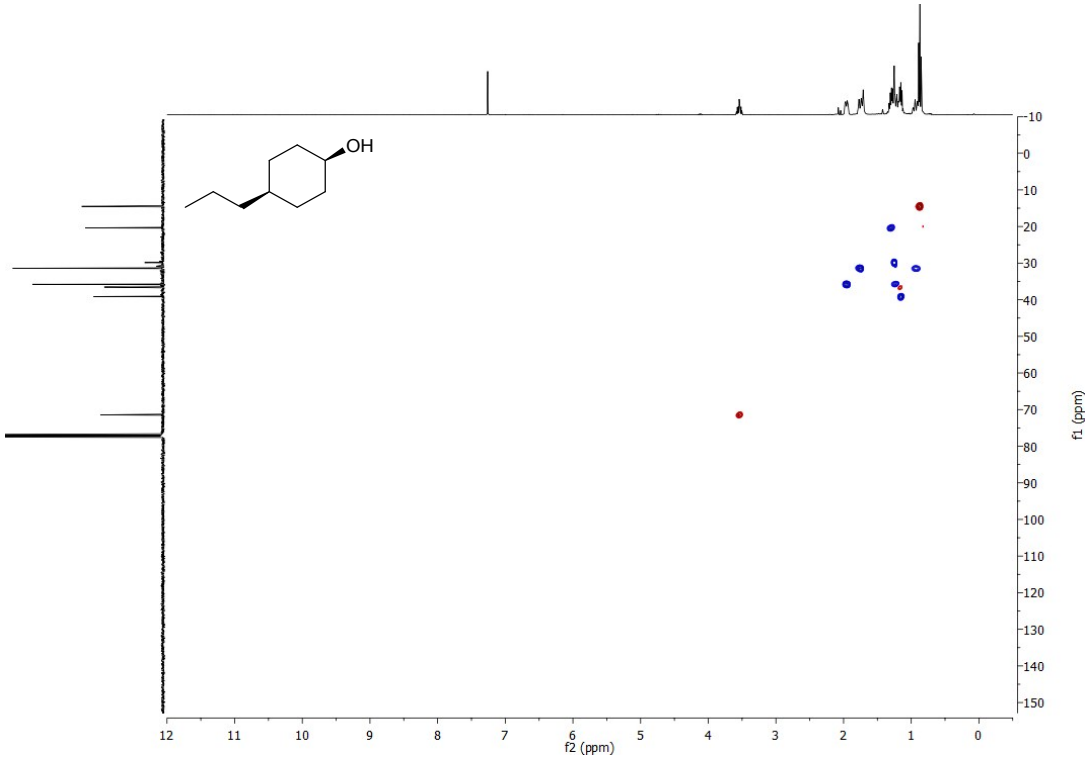
^{13}C-spectrum of *cis*-4-propylcyclohexanol (*cis*-**2**) in $CDCl_3$ (101 MHz)



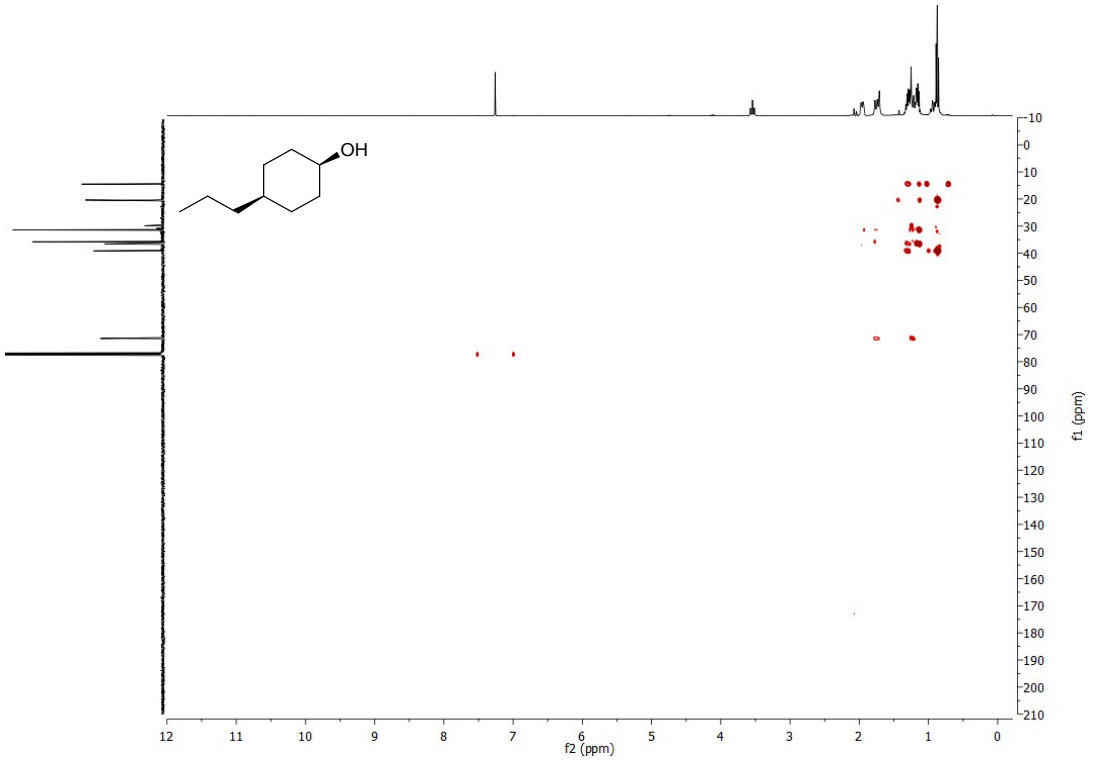
^{1}H-COSY-spectrum of *cis*-4-propylcyclohexanol (*cis*-**2**) in $CDCl_3$ (400 MHz)



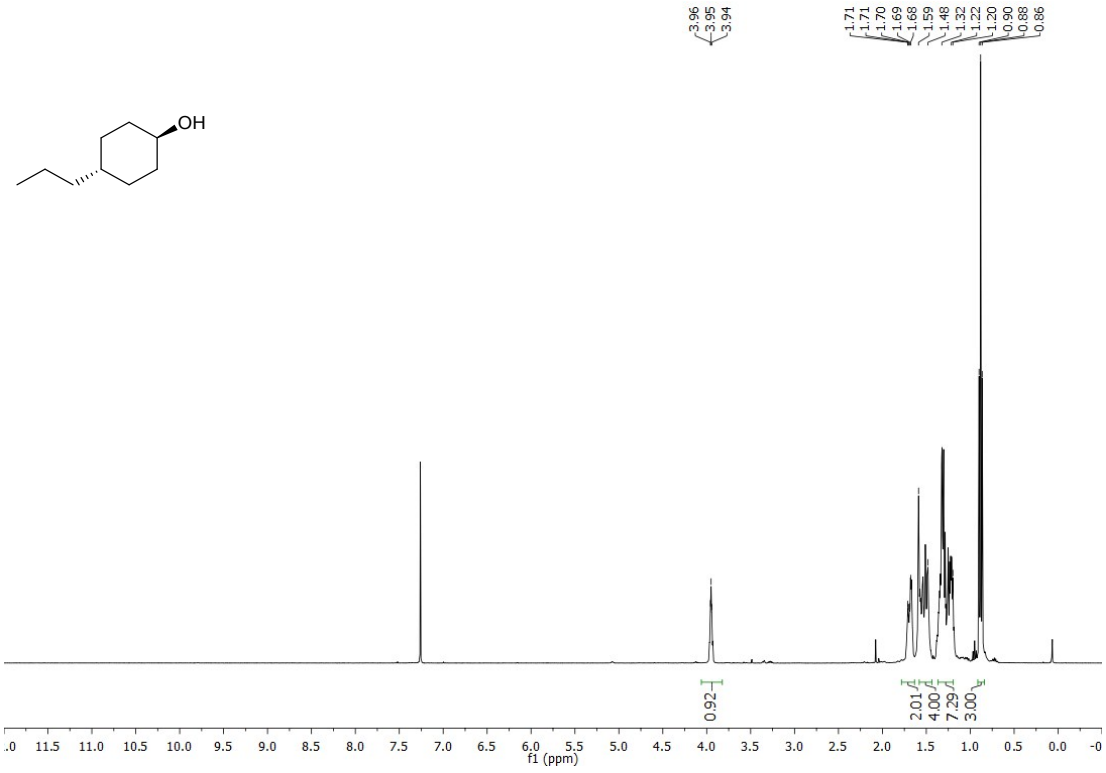
^{1}H-^{13}C-HSQC-spectrum of *cis*-4-propylcyclohexanol (*cis*-**2**) in $CDCl_3$ (400 MHz, 101 MHz)



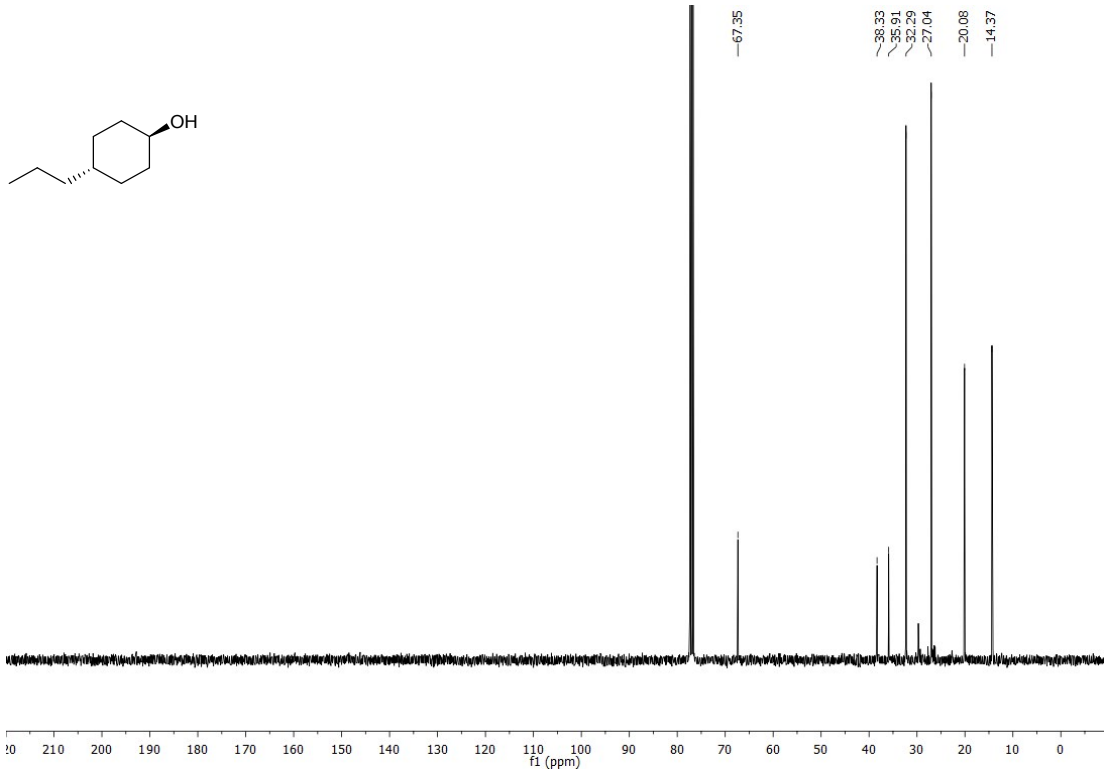
^{1}H-^{13}C-HMBC-spectrum of *cis*-4-propylcyclohexanol (*cis*-**2**) in $CDCl_3$ (400 MHz, 101 MHz)



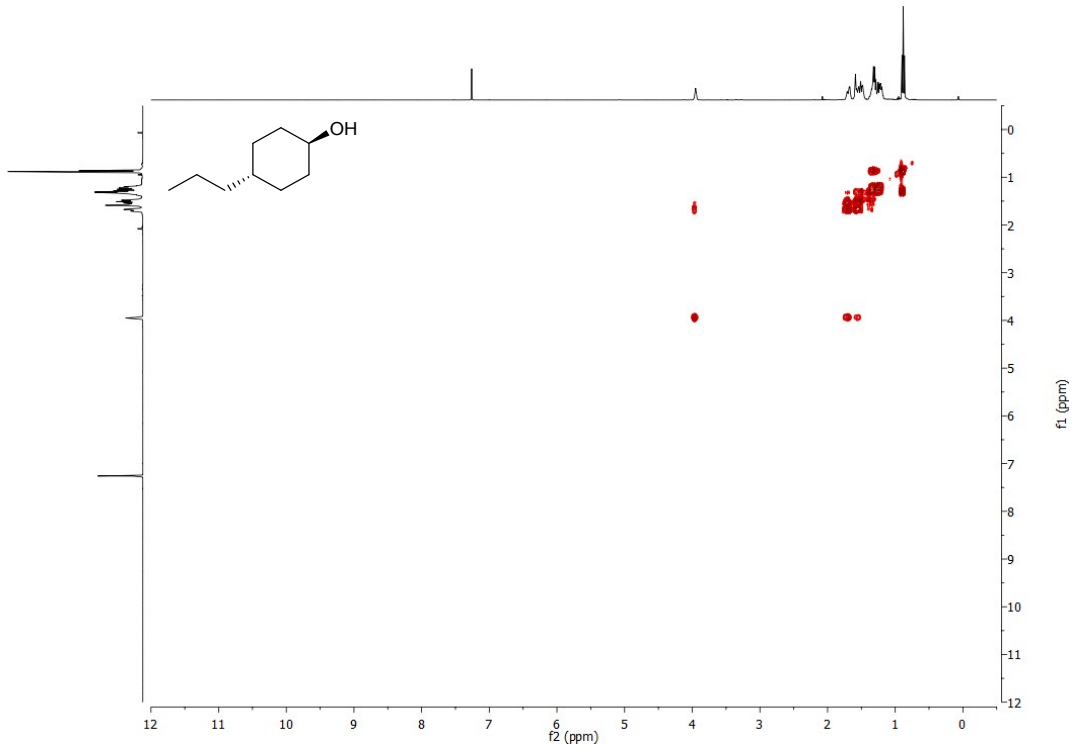
^{1}H-spectrum of *trans*-4-propylcyclohexanol (*trans*-**2**) in $CDCl_3$ (400 MHz)



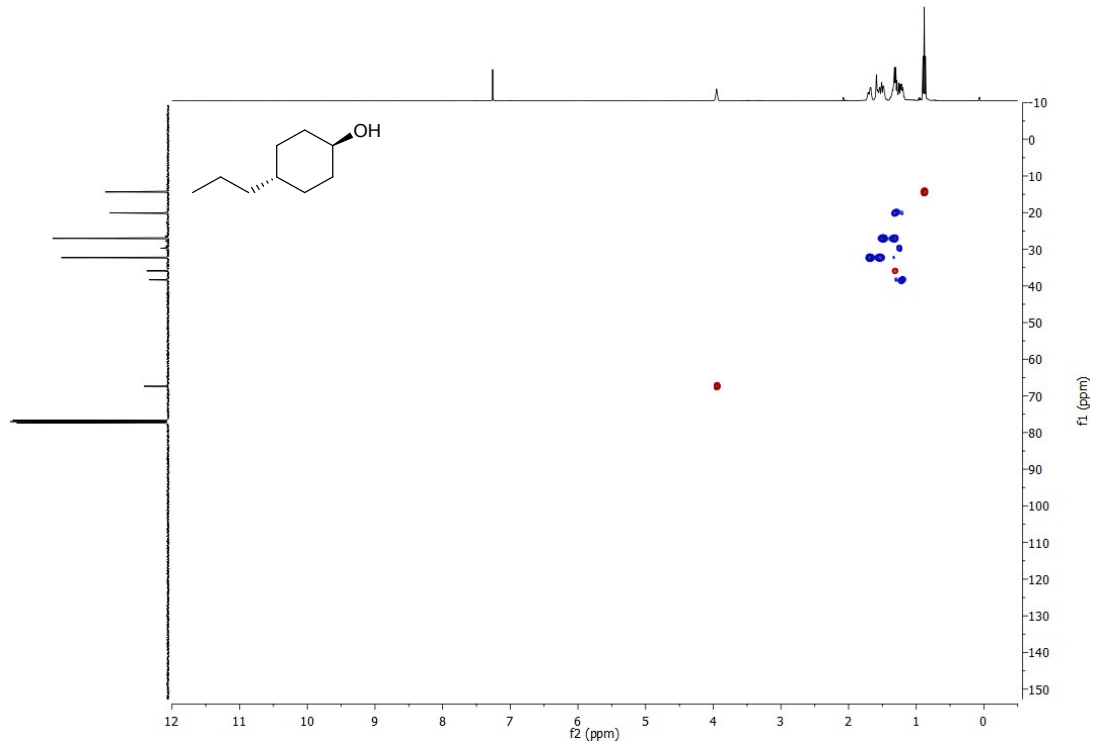
^{13}C-spectrum of *trans*-4-propylcyclohexanol (*trans*-**2**) in $CDCl_3$ (101 MHz)



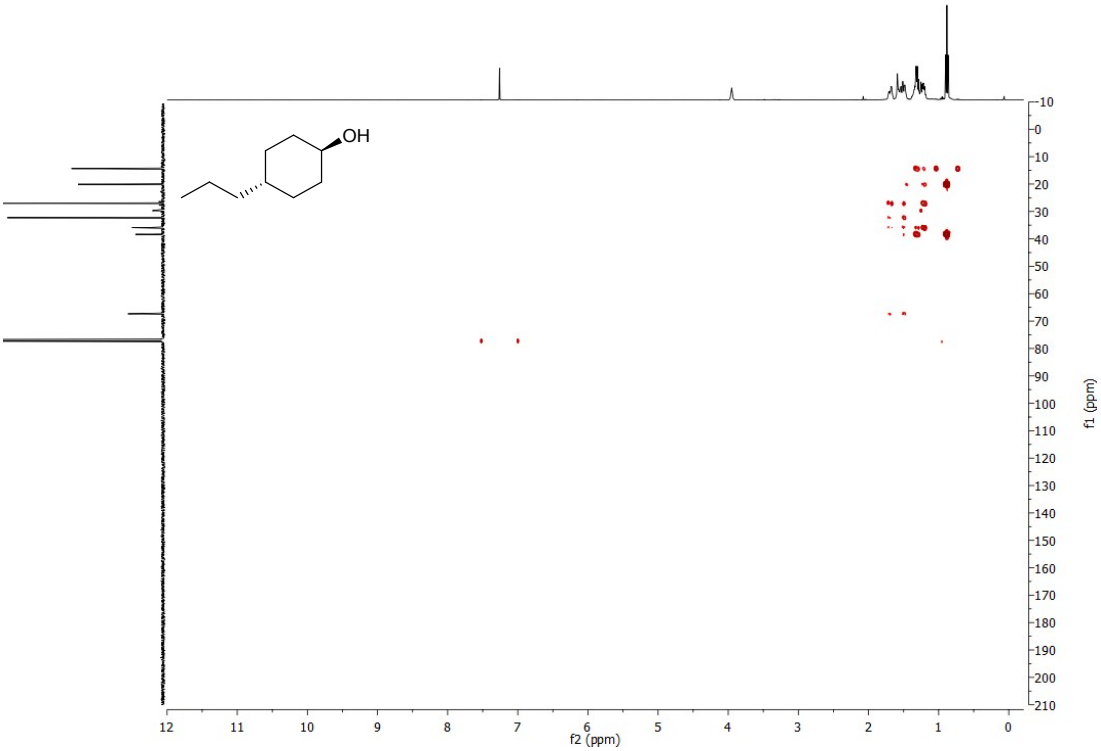
^{1}H-COSY-spectrum of *trans*-4-propylcyclohexanol (*trans*-**2**) in $CDCl_3$ (400 MHz)



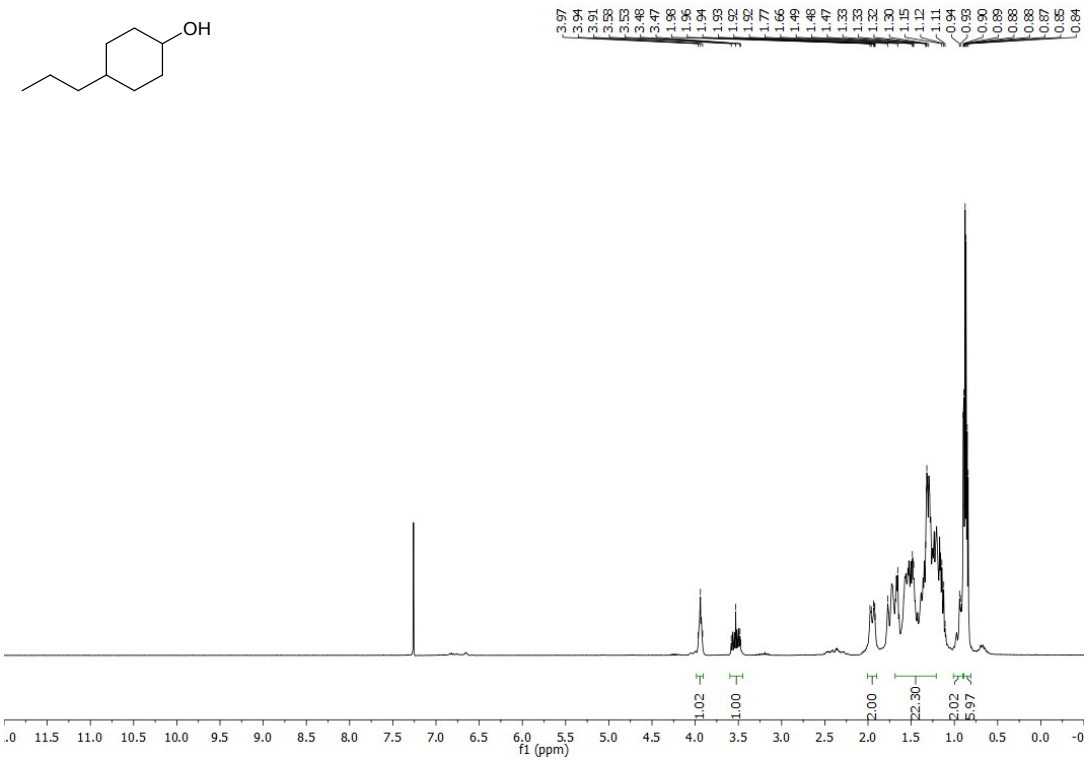
^{1}H-^{13}C-HSQC-spectrum of *trans*-4-propylcyclohexanol (*trans*-**2**) in $CDCl_3$ (400 MHz, 101 MHz)



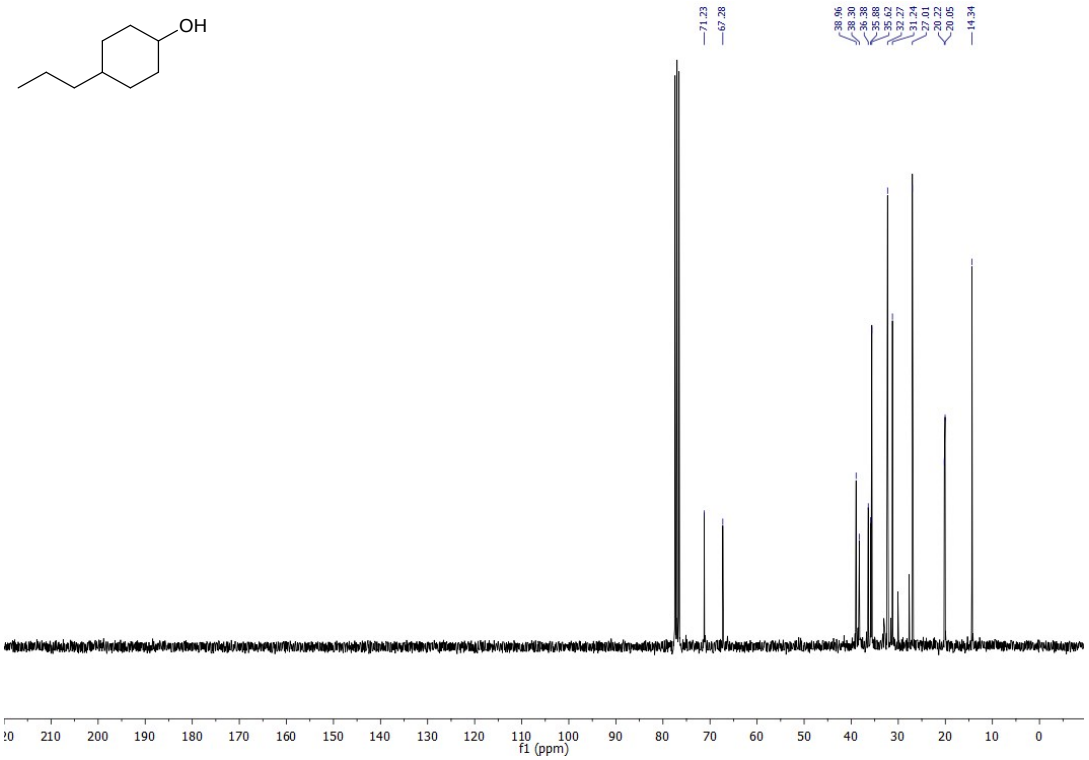
^{1}H-^{13}C-HMBC-spectrum of *trans*-4-propylcyclohexanol (*trans*-**2**) in $CDCl_3$ (400 MHz, 101 MHz)



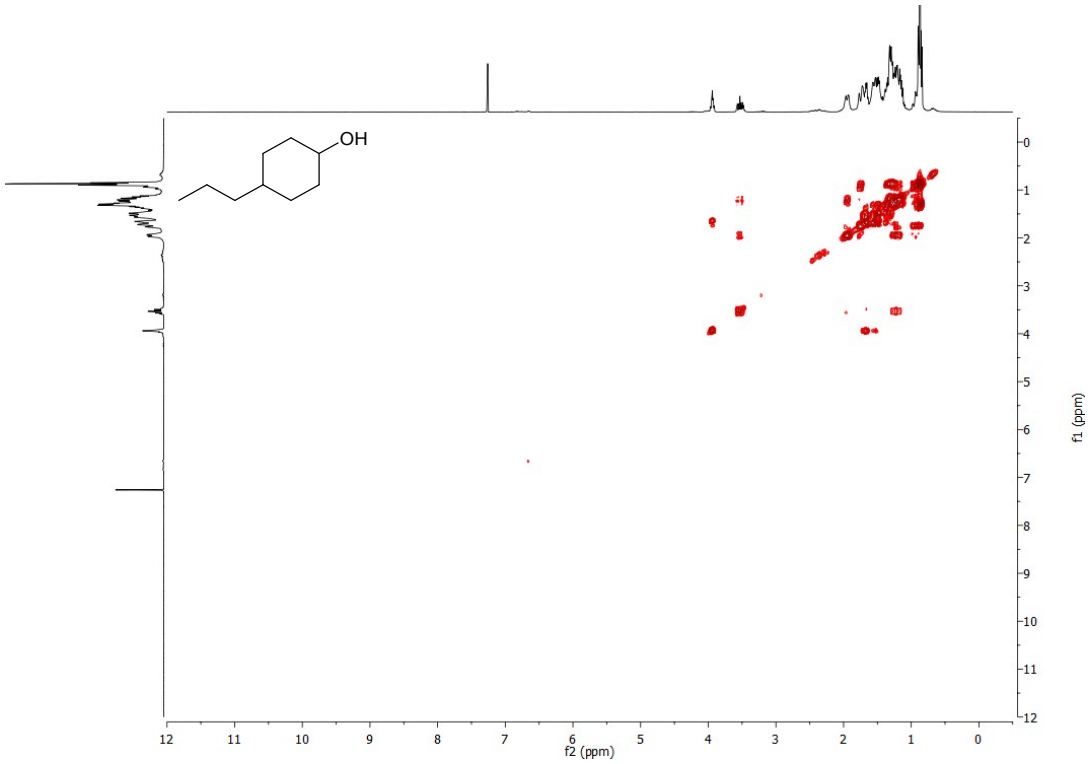
^{1}H-spectrum of the mixture of diastereomers of 4-propylcyclohexanol (**2**) in $CDCl_3$ (300 MHz)



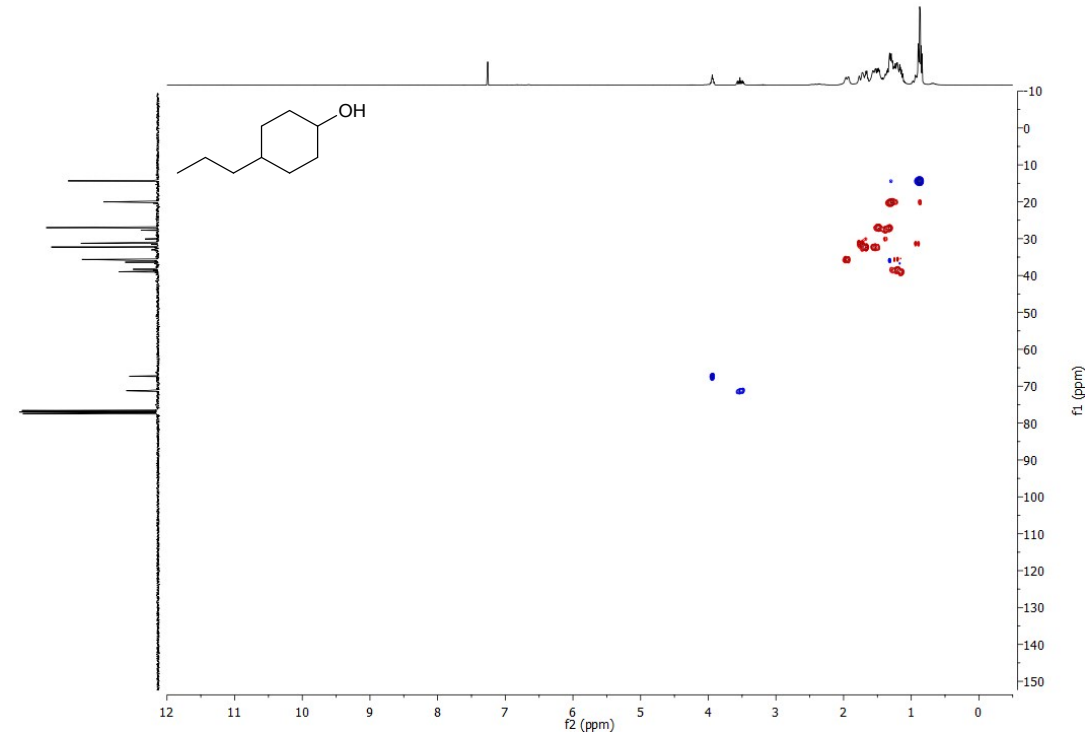
^{13}C-spectrum of the mixture of diastereomers of 4-propylcyclohexanol (**2**) in $CDCl_3$ (76 MHz)



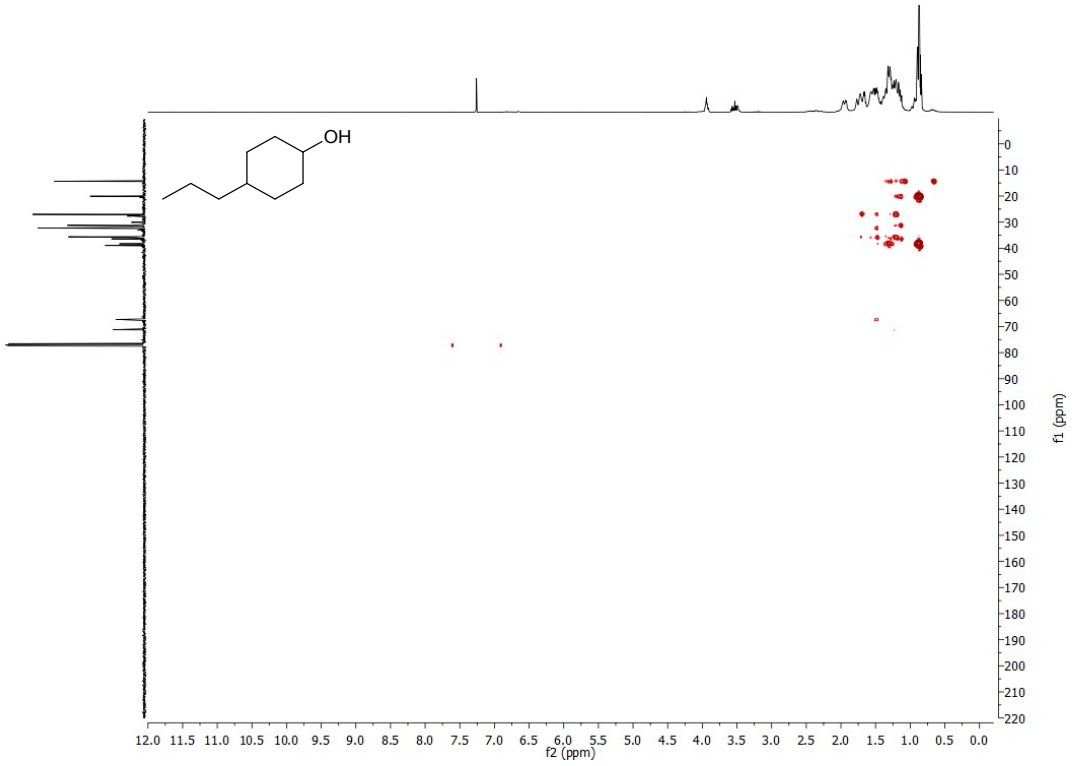
^{1}H-COSY-spectrum of the mixture of diastereomers of 4-propylcyclohexanol (**2**) in $CDCl_3$ (300 MHz)



^{1}H-^{13}C-HSQC-spectrum of the mixture of diastereomers of 4-propylcyclohexanol (**2**) in $CDCl_3$ (300 MHz, 76 MHz)

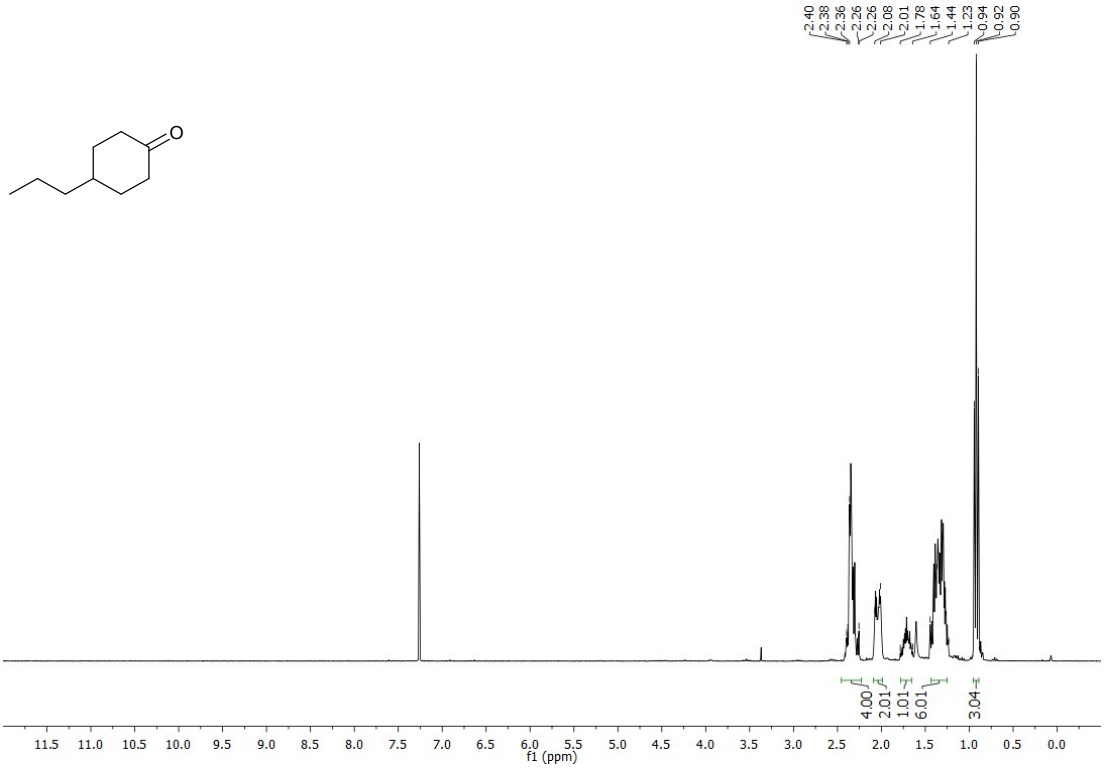


^{1}H-^{13}C-HMBC-spectrum of the mixture of diastereomers of 4-propylcyclohexanol (**2**) in $CDCl_3$ (300 MHz, 76 MHz)

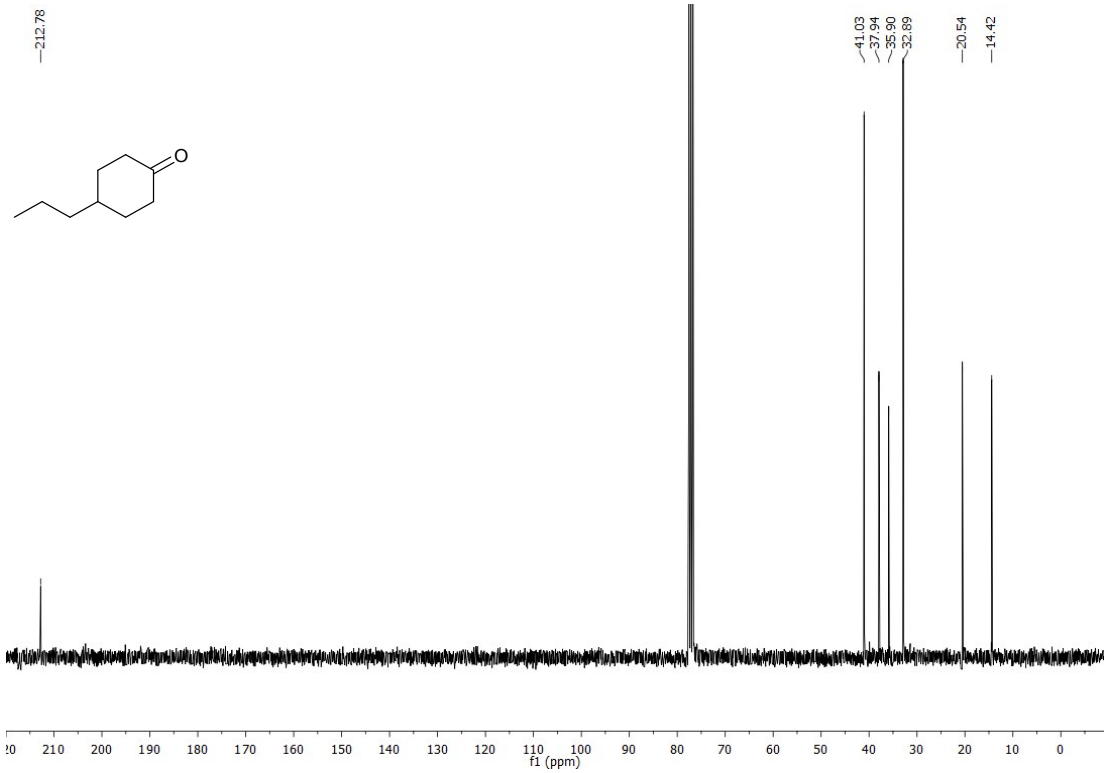


4.2.2 Spectra of the monomer syntheses

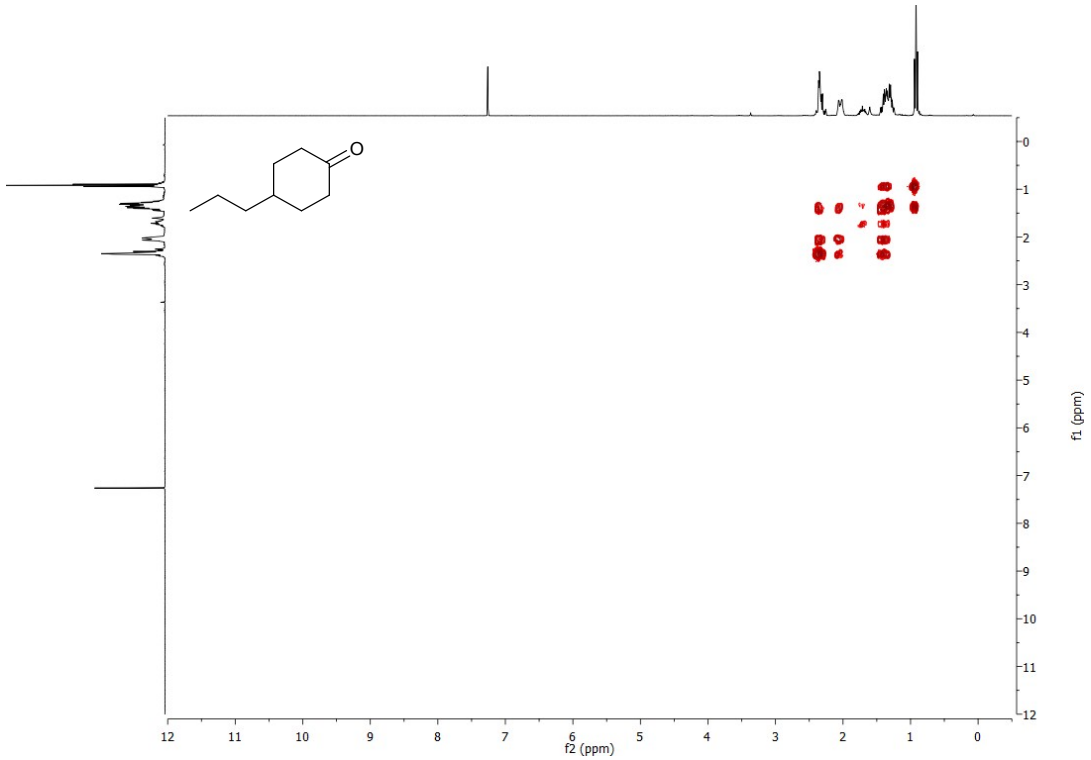
^{1}H-spectrum of 4-propylcyclohexanone (**12**) in $CDCl_3$ (300 MHz)



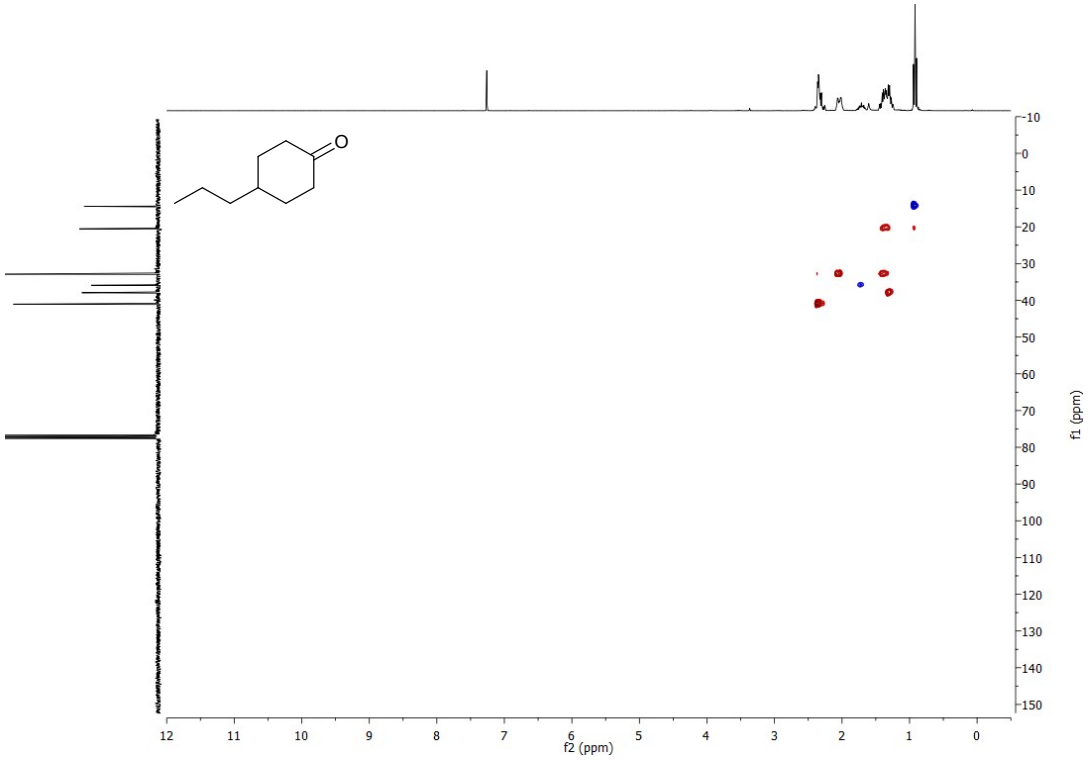
^{13}C-spectrum of 4-propylcyclohexanone (**12**) in $CDCl_3$ (76 MHz)



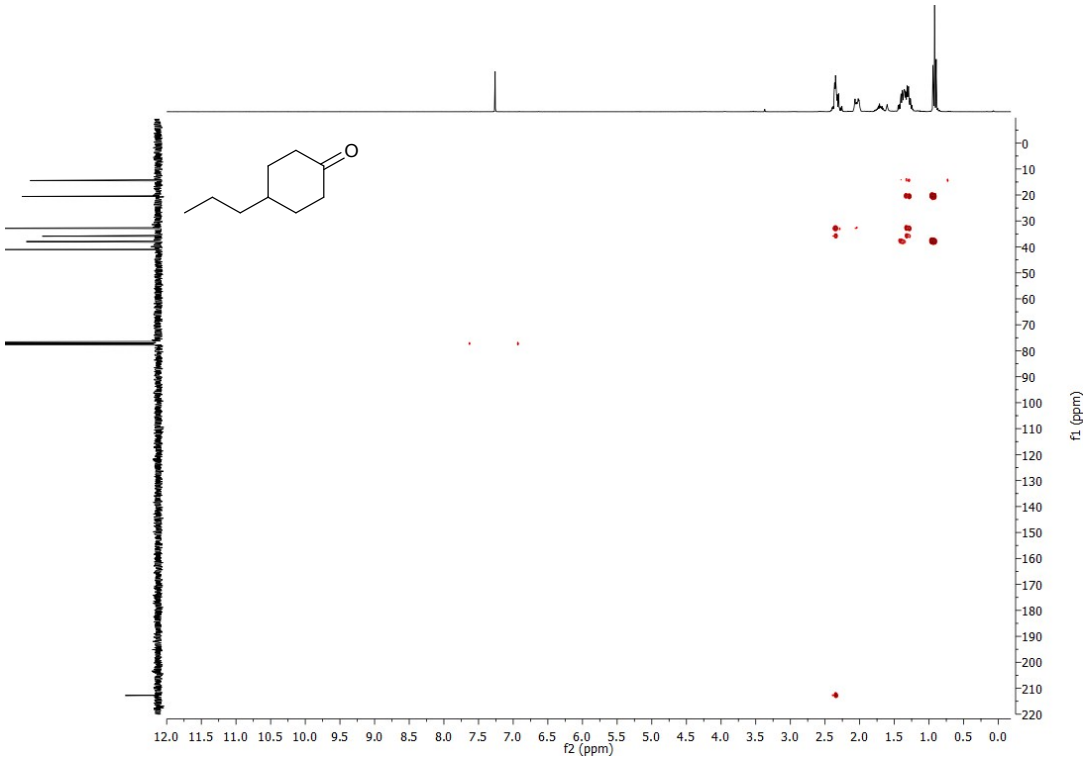
^{1}H-COSY-spectrum of 4-propylcyclohexanone (**12**) in $CDCl_3$ (300 MHz)



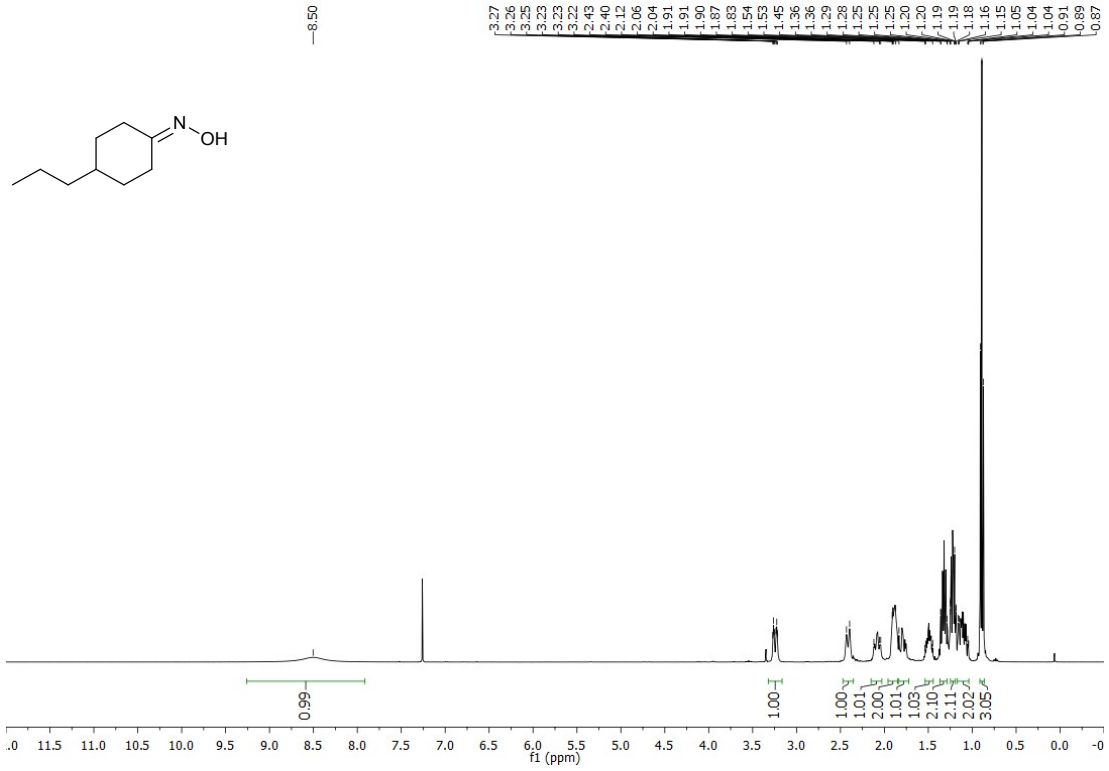
^{1}H-^{13}C-HSQC-spectrum of 4-propylcyclohexanone (**12**) in $CDCl_3$ (300 MHz, 76 MHz)



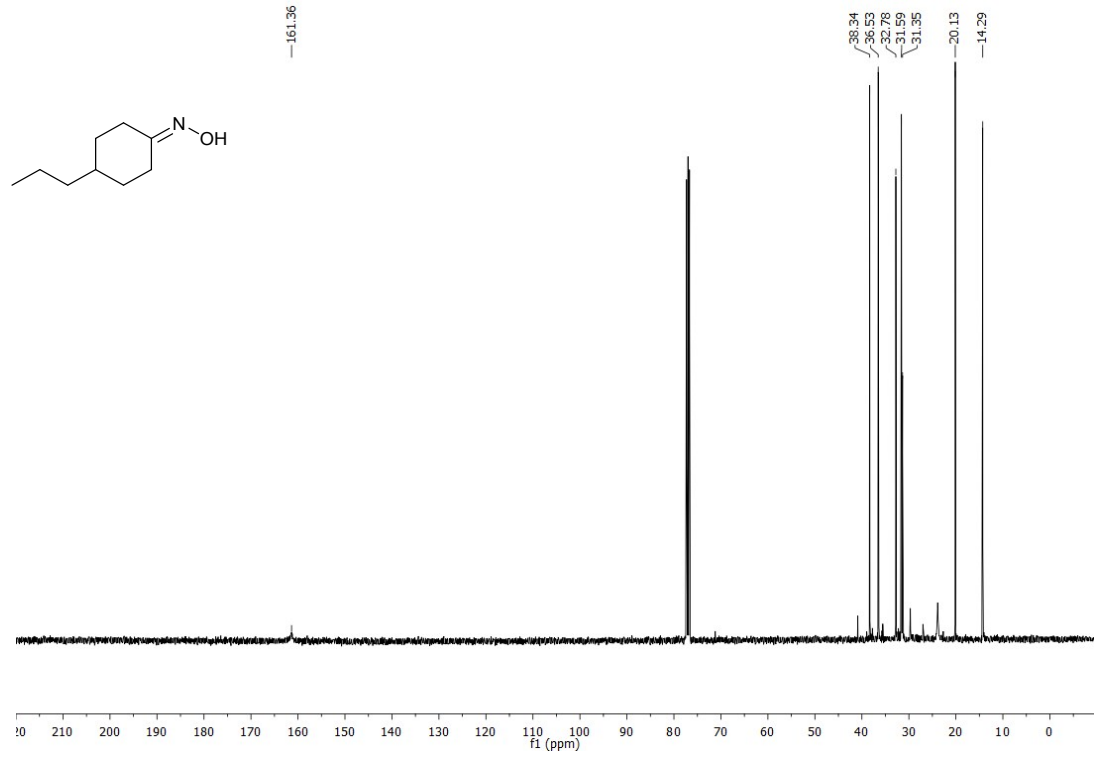
^{1}H-^{13}C-HMBC-spectrum of 4-propylcyclohexanone (**12**) in $CDCl_3$ (300 MHz, 76 MHz)



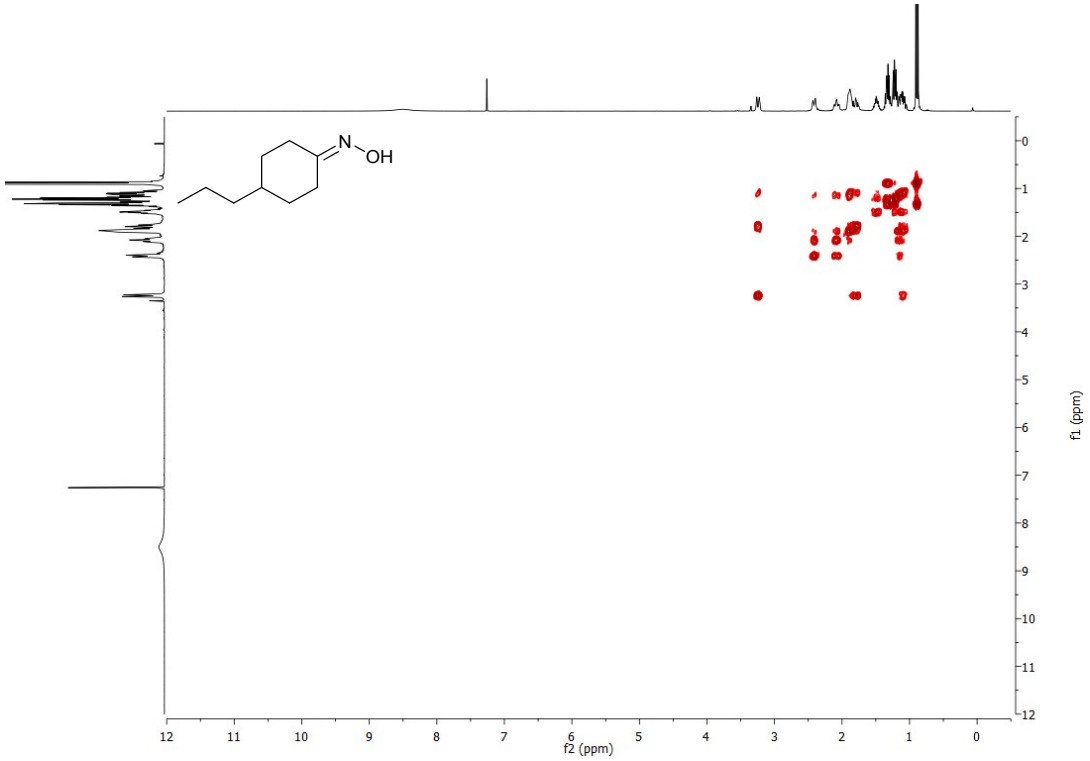
^{1}H-spectrum of *N*-hydroxy-4-propylcyclohexanimine (**13**) in $CDCl_3$ (400 MHz)



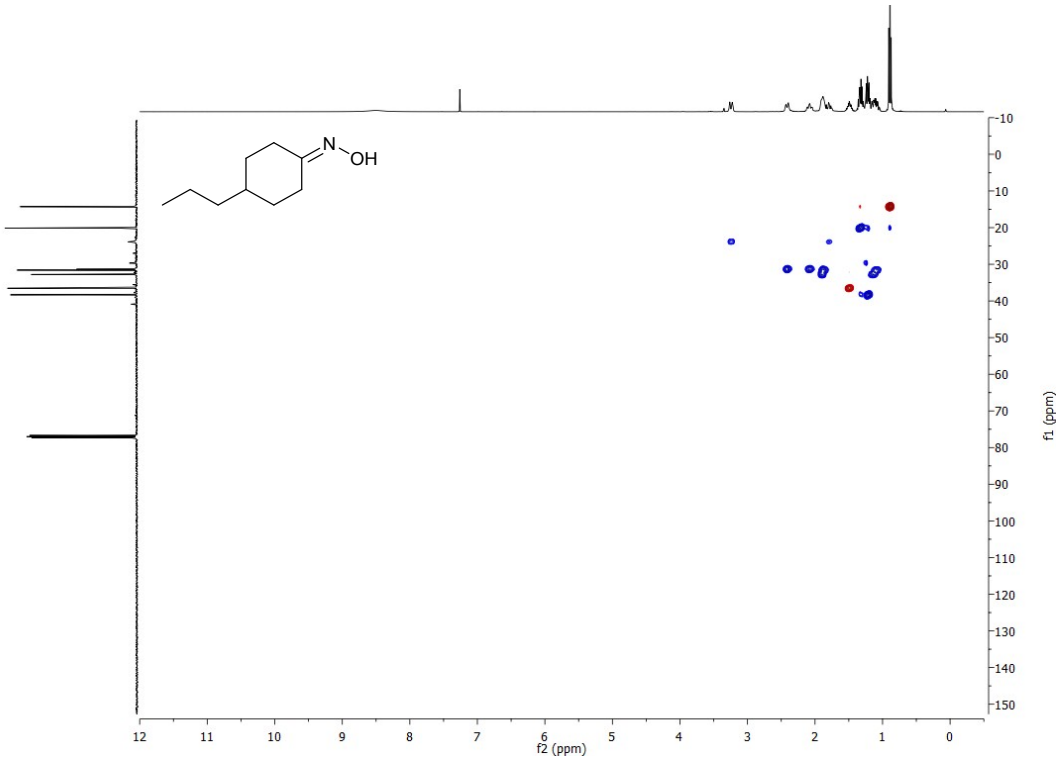
^{13}C-spectrum of *N*-hydroxy-4-propylcyclohexanimine (**13**) in $CDCl_3$ (101 MHz)



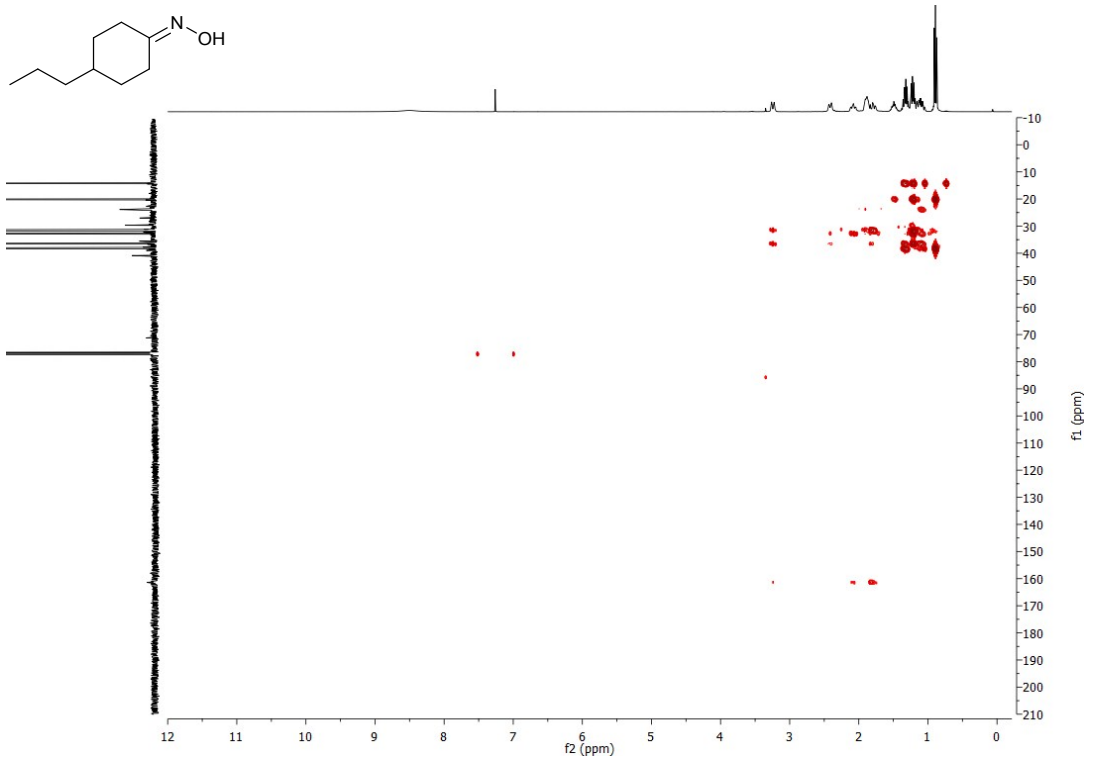
^{1}H-COSY-spectrum of *N*-hydroxy-4-propylcyclohexanimine (**13**) in $CDCl_3$ (400 MHz)



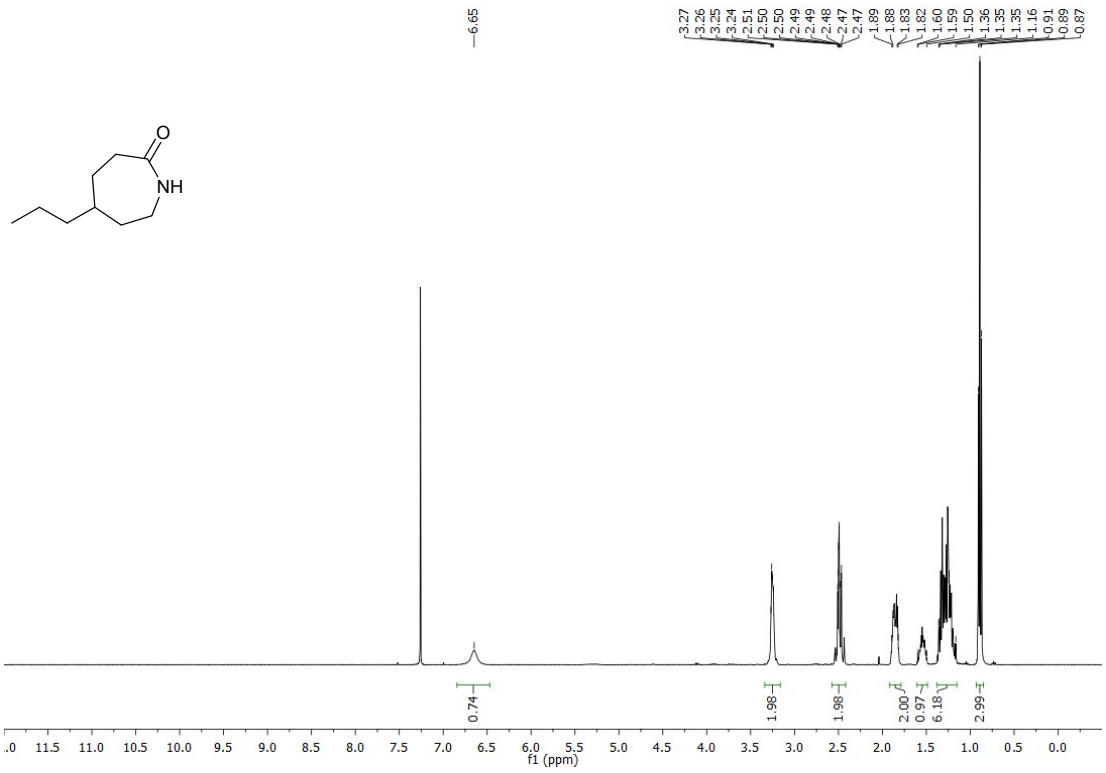
^{1}H-^{13}C-HSQC-spectrum of *N*-hydroxy-4-propylcyclohexanimine (**13**) in $CDCl_3$ (400 MHz, 101 MHz)



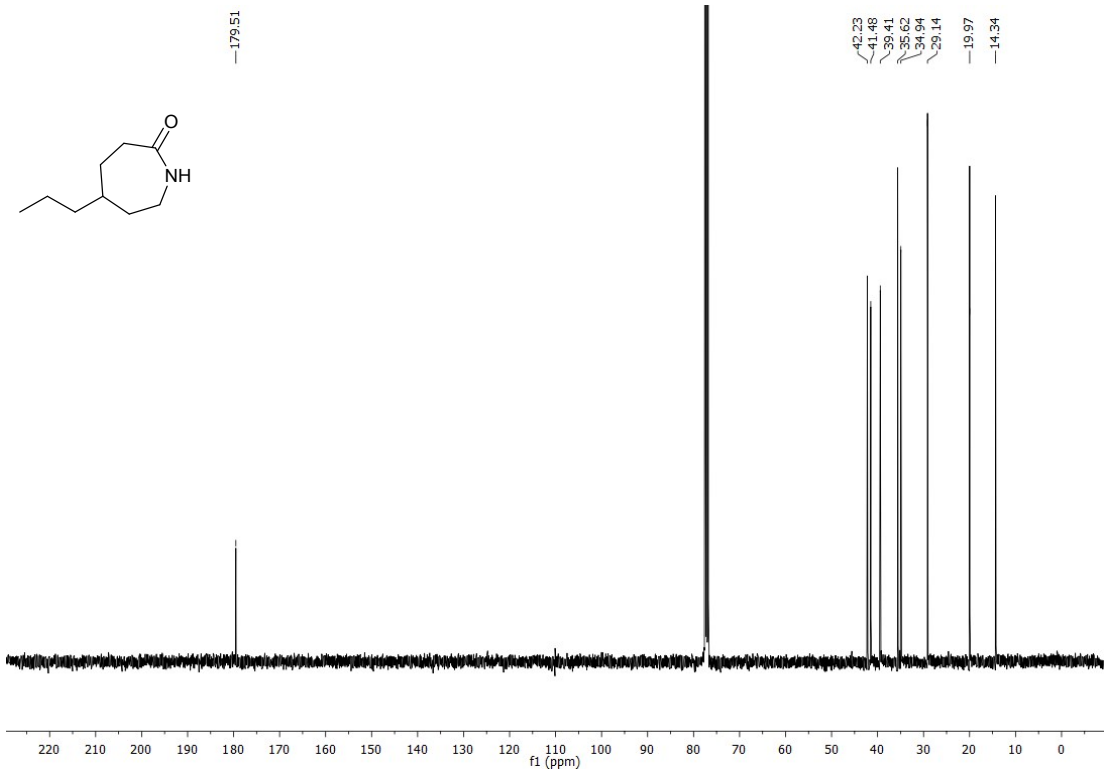
^{1}H-^{13}C-HMBC-spectrum of *N*-hydroxy-4-propylcyclohexanimine (**13**) in $CDCl_3$ (400 MHz, 101 MHz)



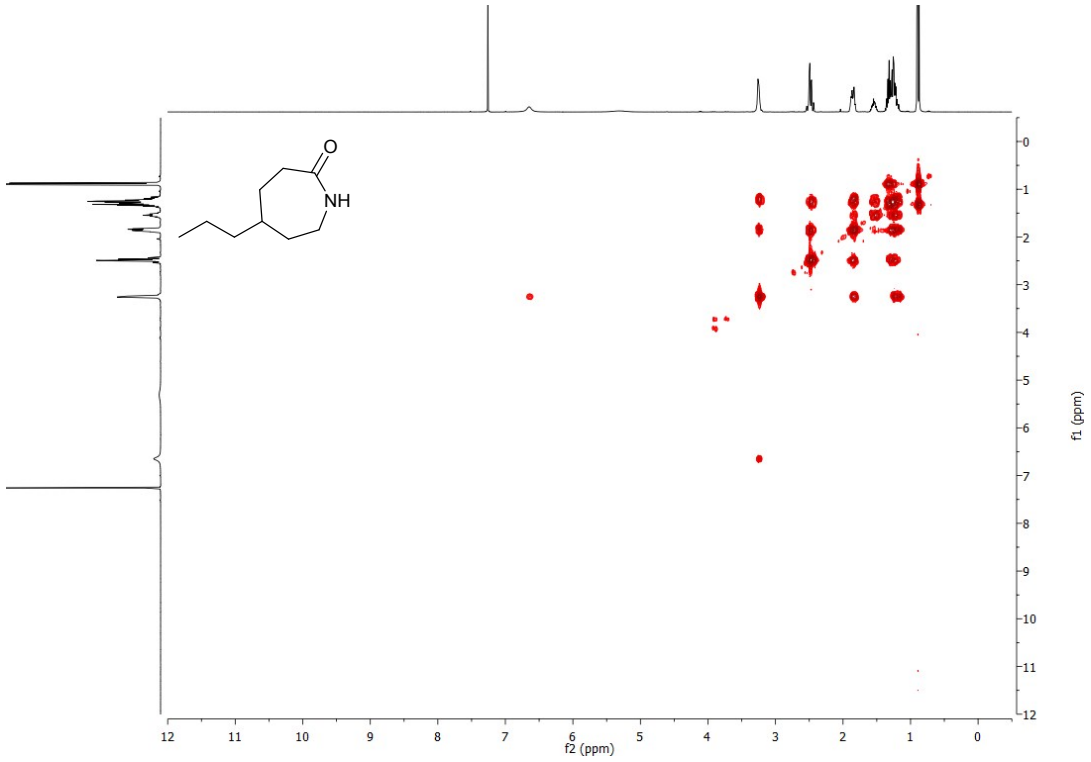
^{1}H-spectrum of 5-propylazepan-2-one (**5**) in $CDCl_3$ (300 MHz)



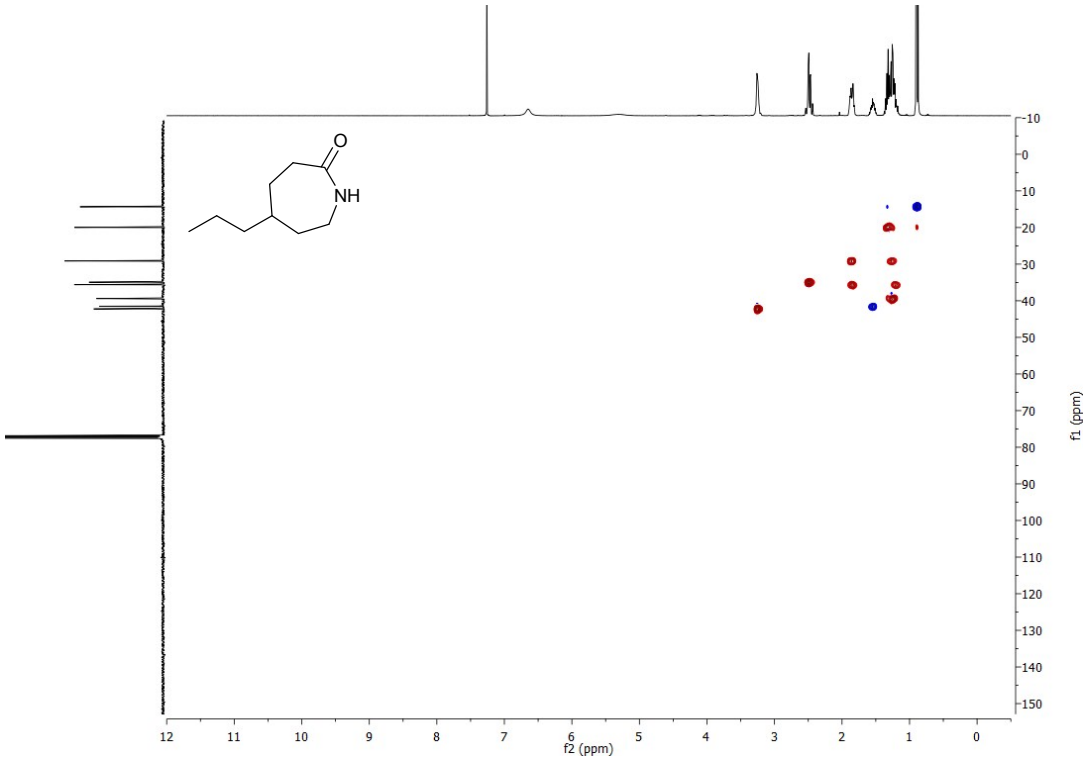
^{13}C-spectrum of 5-propylazepan-2-one (**5**) in $CDCl_3$ (76 MHz)



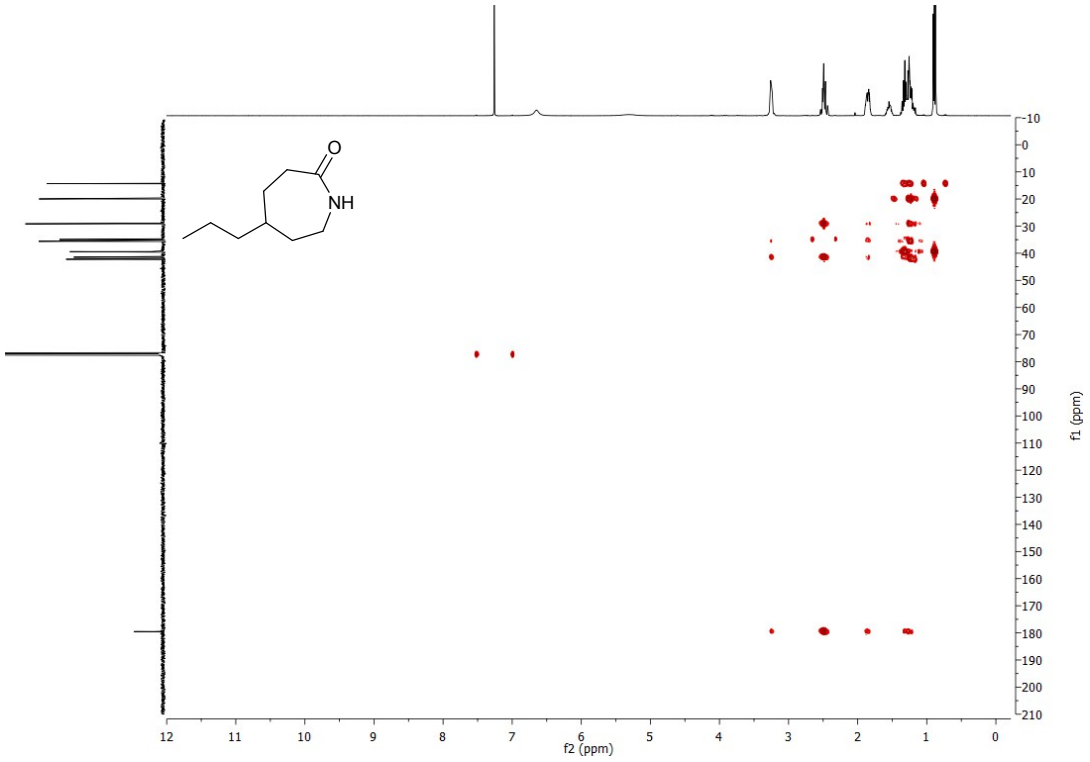
^{1}H-COSY-spectrum of 5-propylazepan-2-one (**5**) in $CDCl_3$ (300 MHz)



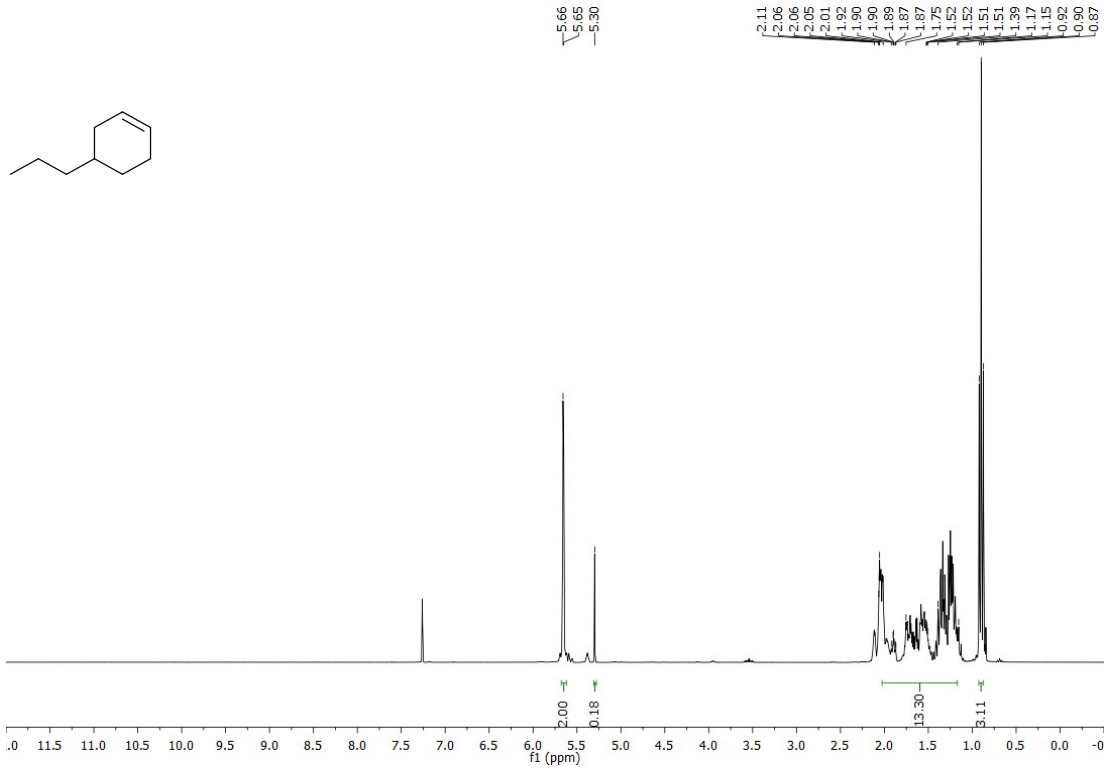
^{1}H-^{13}C-HSQC-spectrum of 5-propylazepan-2-one (**5**) in $CDCl_3$ (300 MHz, 76 MHz)



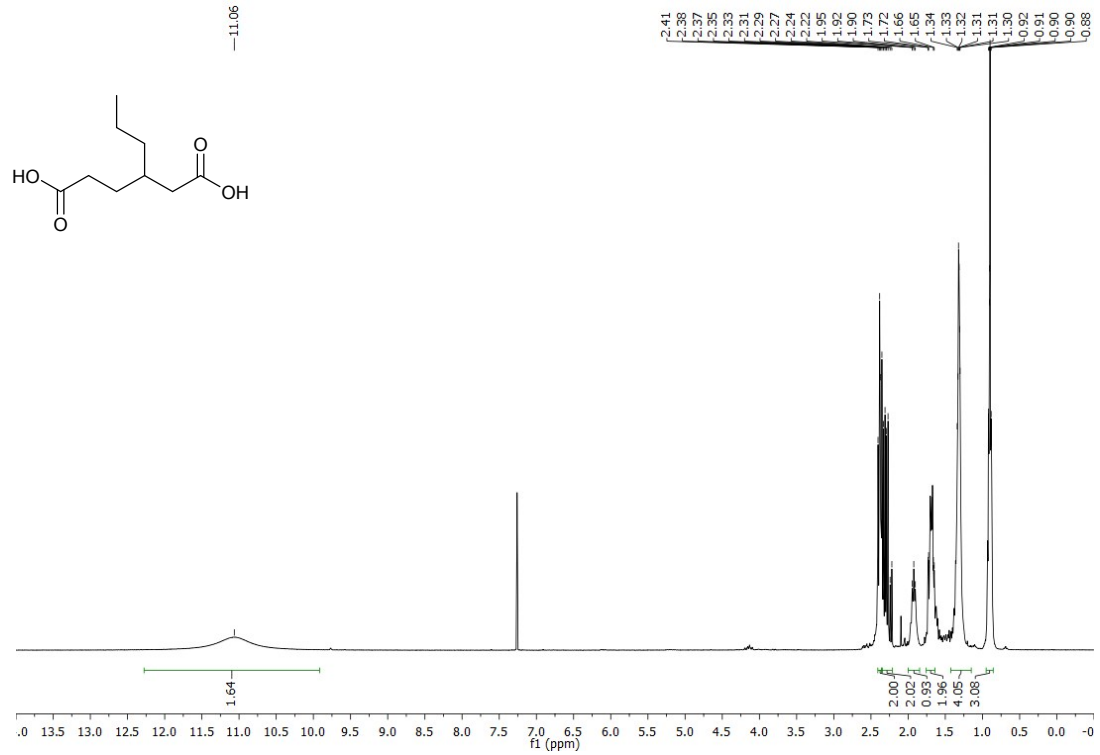
^{1}H-^{13}C-HMBC-spectrum of 5-propylazepan-2-one (**5**) in $CDCl_3$ (300 MHz, 76 MHz)



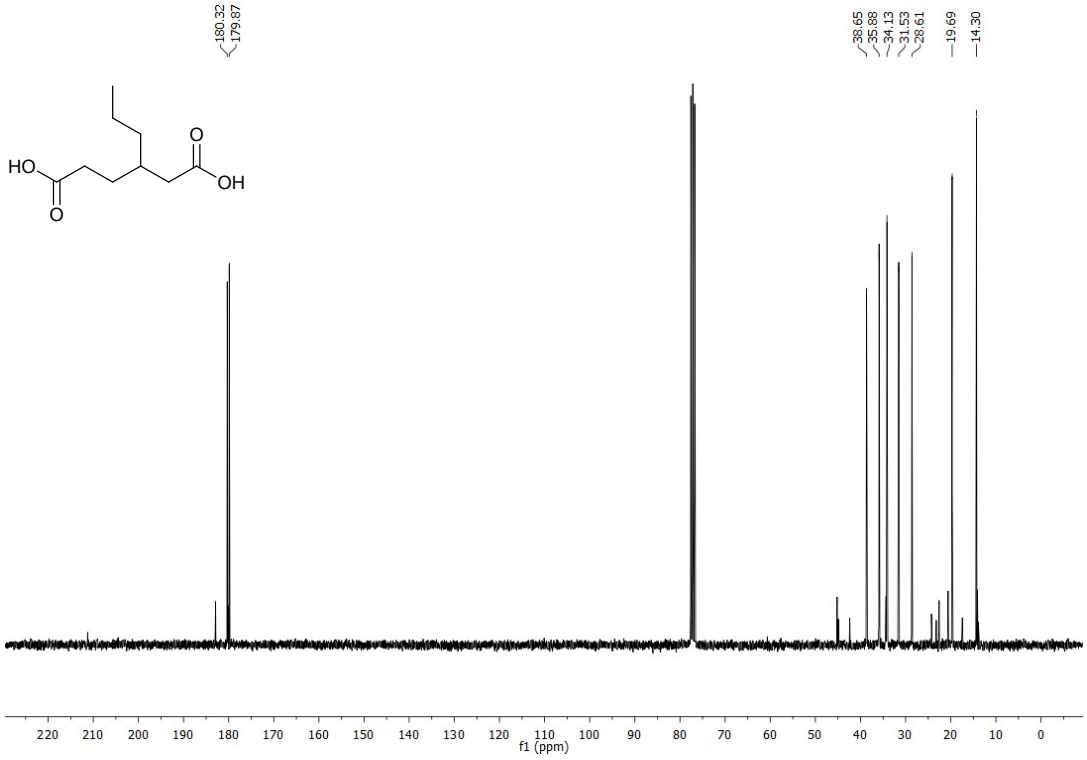
^{1}H-sepctrum of 4-propylcyclohex-1-ene in $CDCl_3$ (300 MHz)



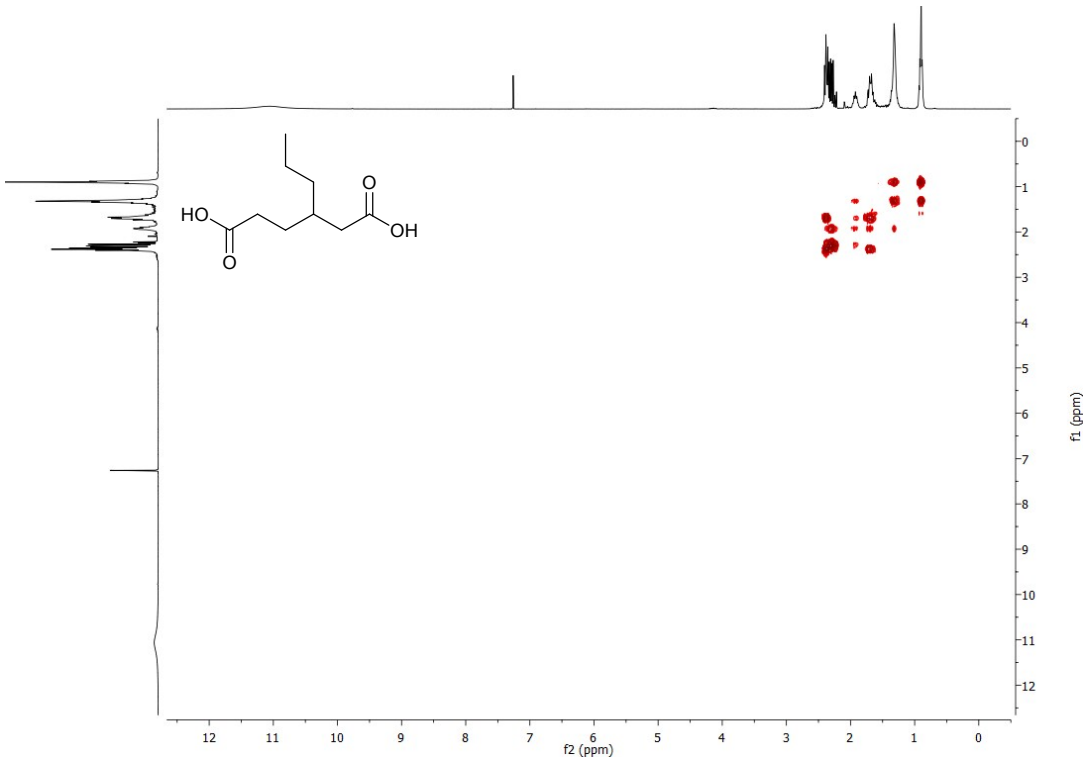
^{1}H-spectrum of 3-propylhexanedioic acid (**6**) in $CDCl_3$ (300 MHz)



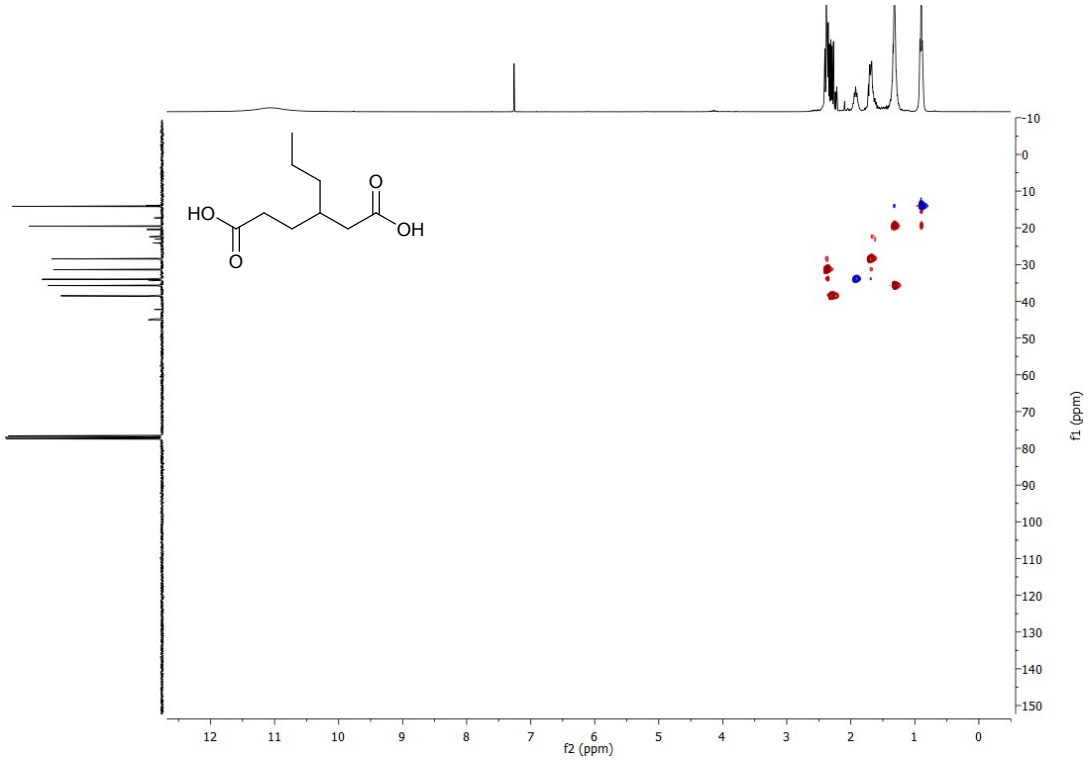
^{13}C-spectrum of 3-propylhexanedioic acid (**6**) in $CDCl_3$ (76 MHz)



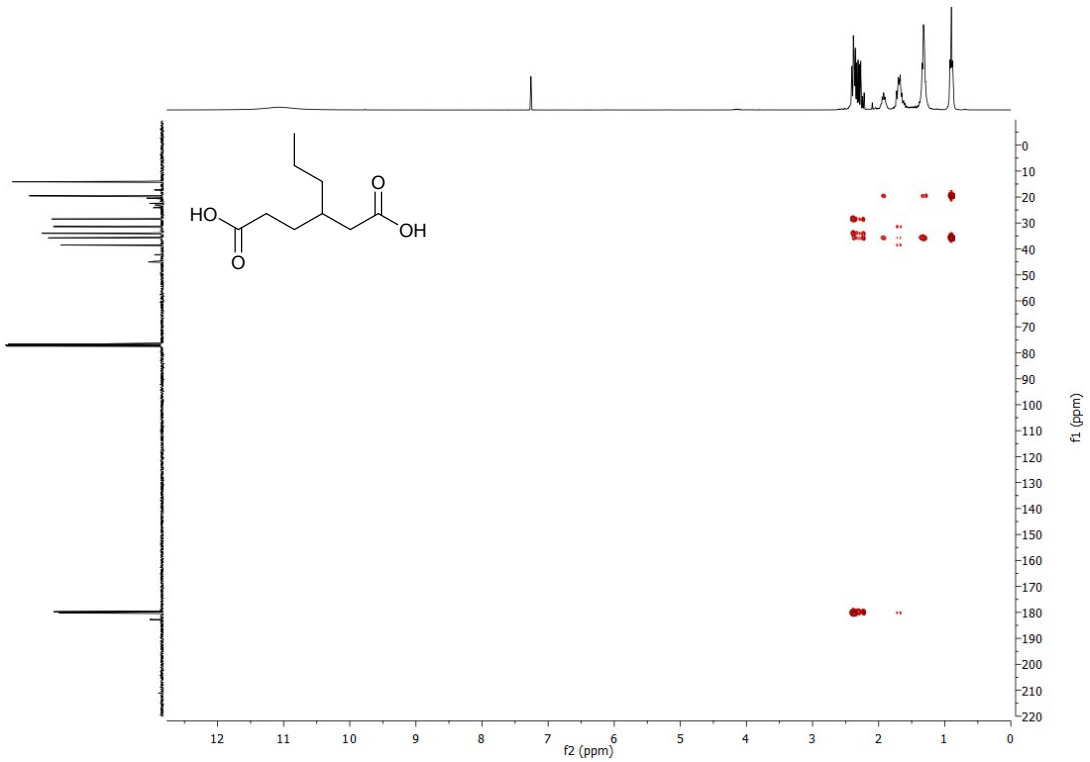
^{1}H-COSY-spectrum of 3-propylhexanedioic acid (**6**) in $CDCl_3$ (300 MHz)



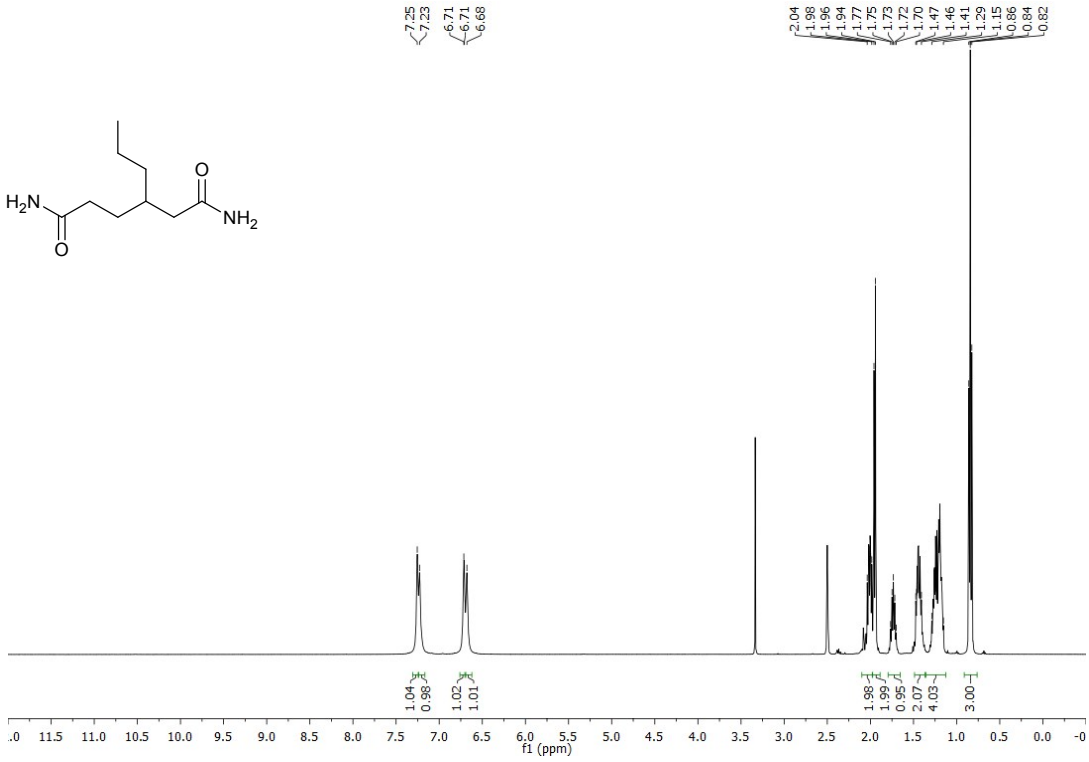
^{1}H-^{13}C-HSQC-spectrum of 3-propylhexanedioic acid (**6**) in $CDCl_3$ (300 MHz, 76 MHz)



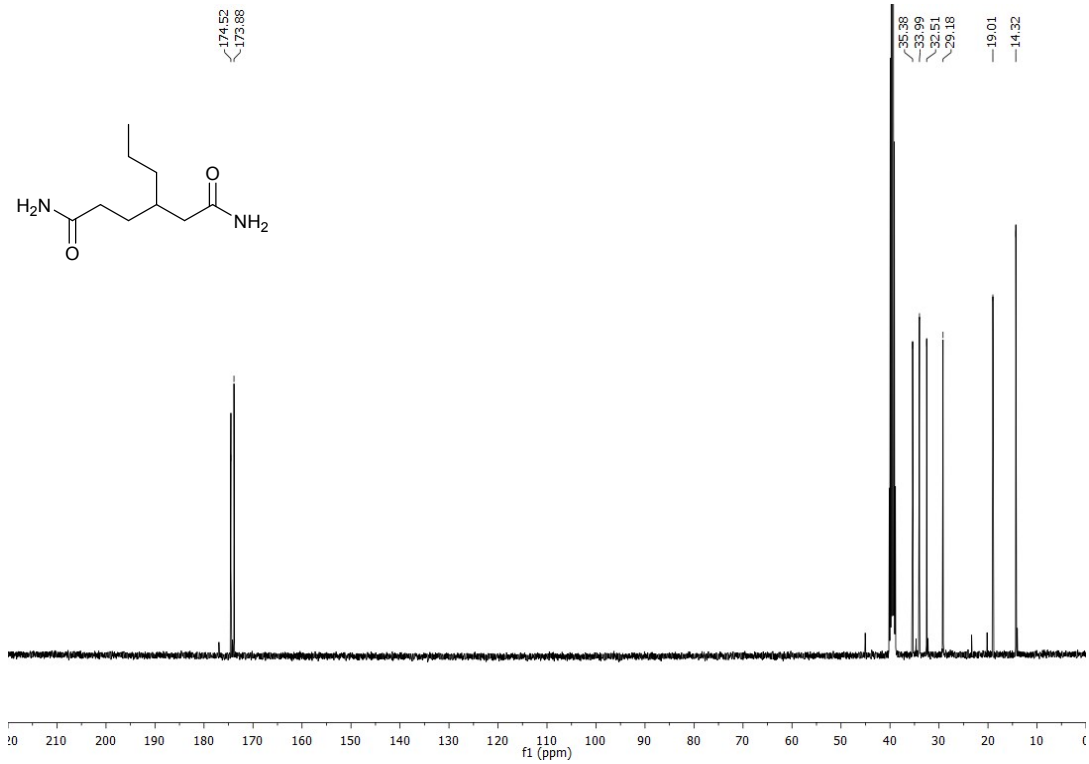
^{1}H-^{13}C-HMBC-spectrum of 3-propylhexanedioic acid (**6**) in $CDCl_3$ (300 MHz, 76 MHz)



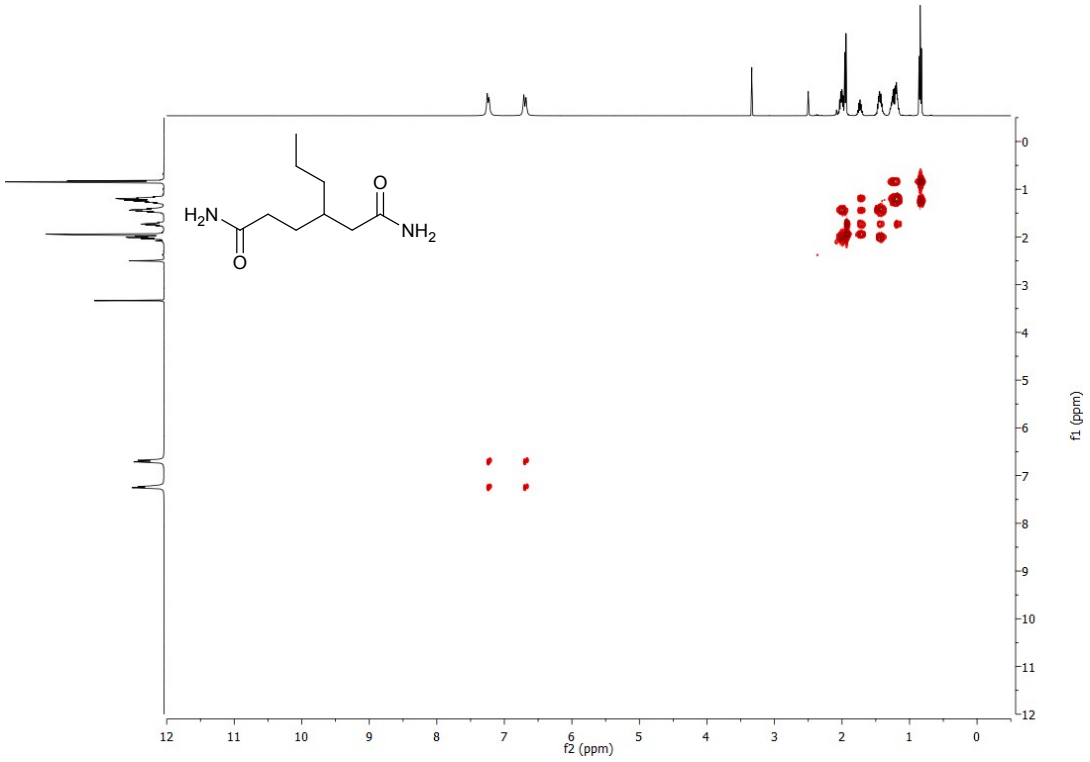
^{1}H-spectrum of 3-propylhexanediamide (**15**) in DMSO-d_6 (400 MHz)



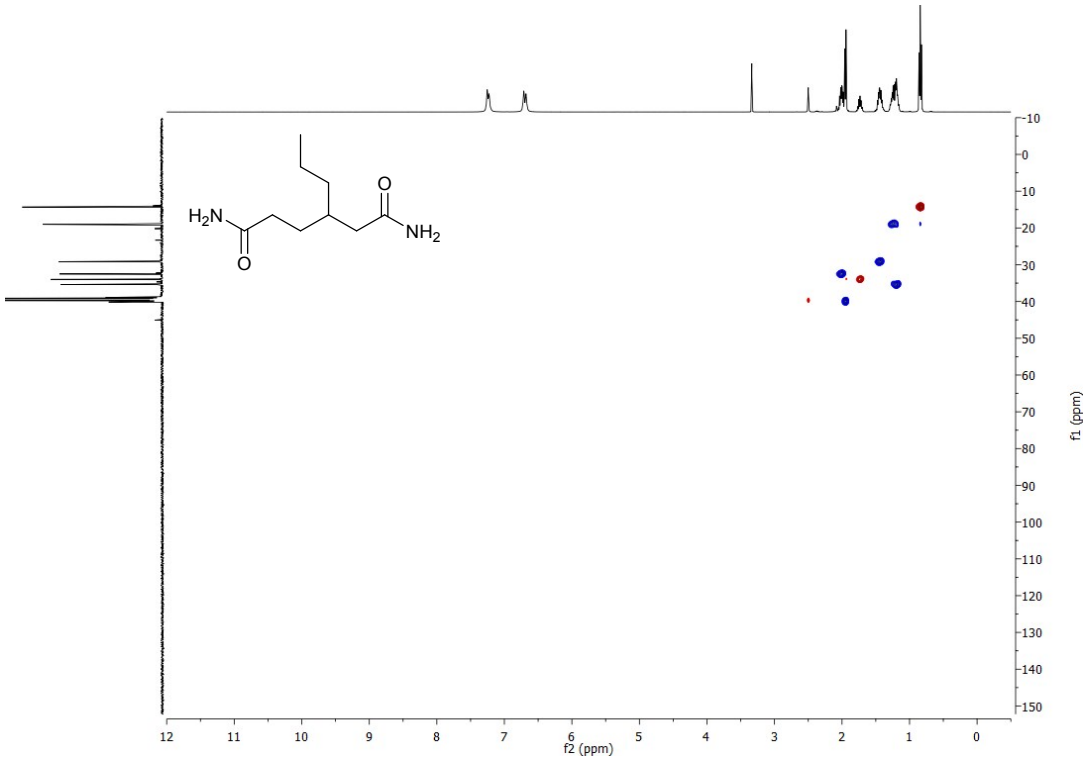
^{13}C-spectrum of 3-propylhexanediamide (**15**) in DMSO-d_6 (101 MHz)



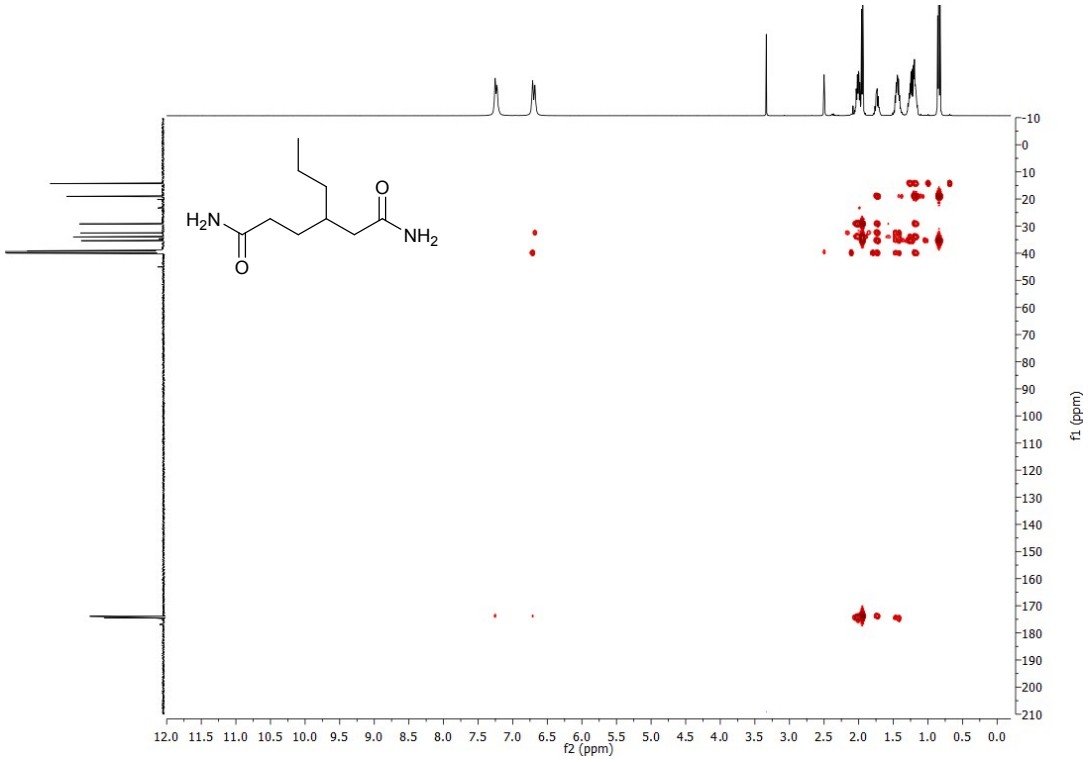
^{1}H-COSY-spectrum of 3-propylhexanediamide (**15**) in DMSO-d_6 (400 MHz)



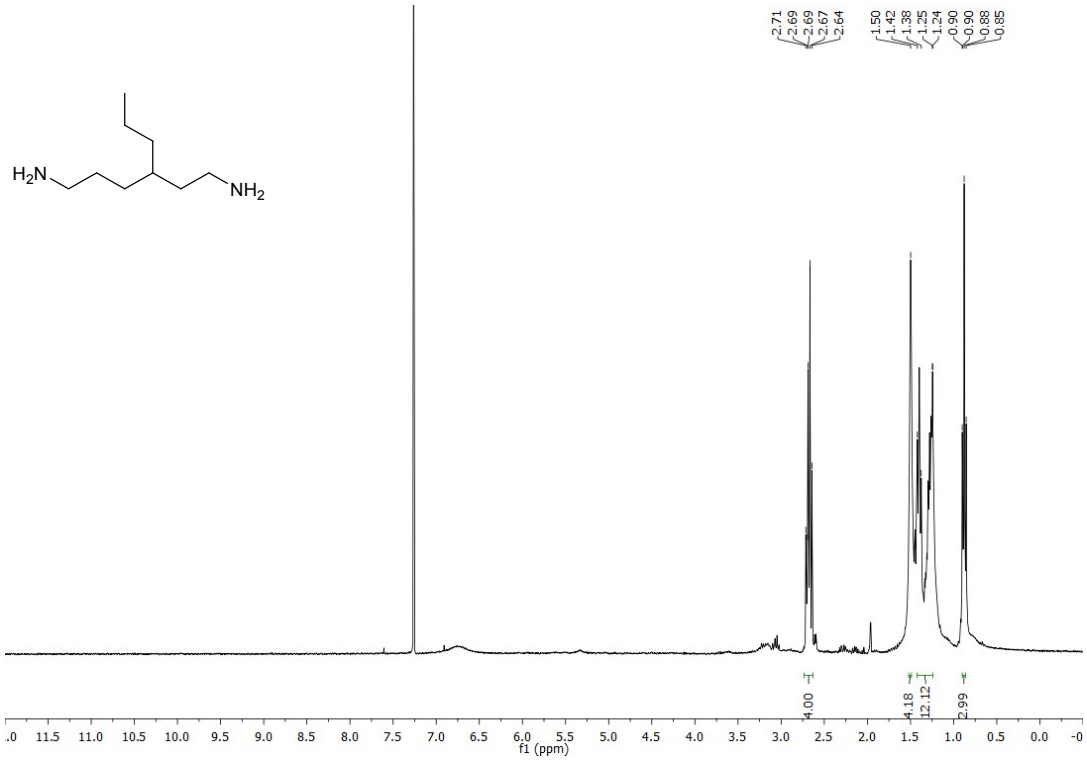
^{1}H-^{13}C-HSQC-spectrum of 3-propylhexanediamide (**15**) in DMSO-d_6 (400 MHz, 101 MHz)



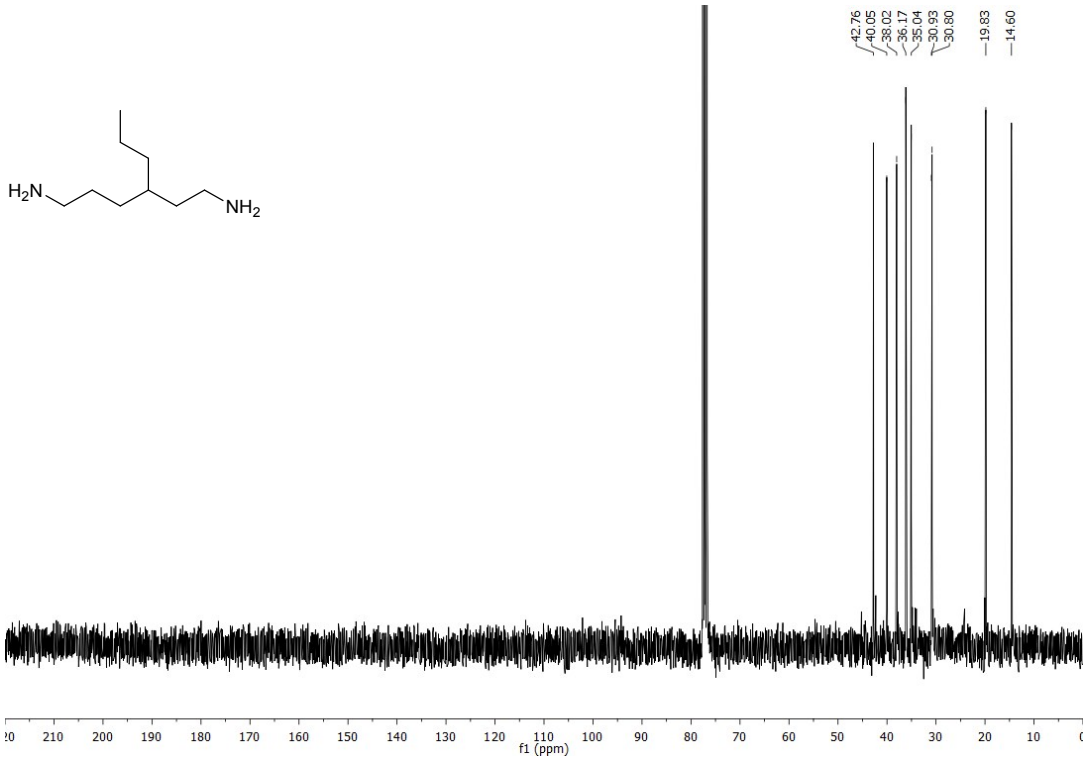
^{1}H-^{13}C-HMBC-spectrum of 3-propylhexanediamide (**15**) in DMSO-d_6 (400 MHz, 101 MHz)



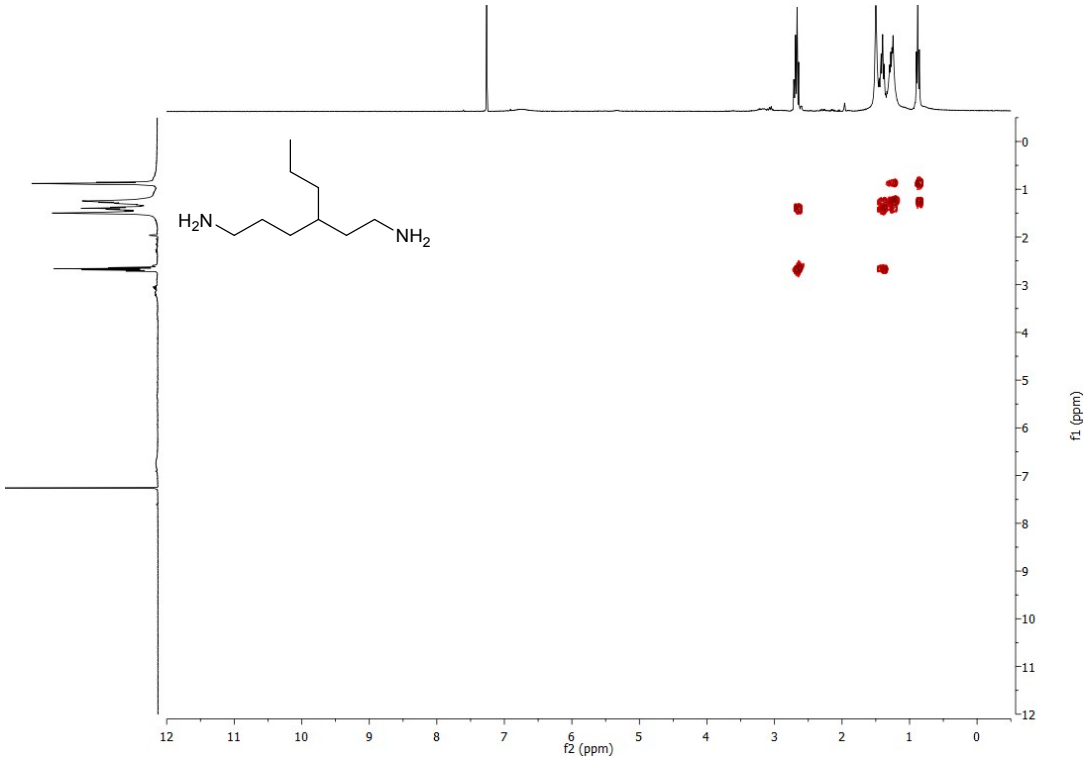
^{1}H-spectrum of 3-propylhexane-1,6-diamine (**7**) in $CDCl_3$ (300 MHz)



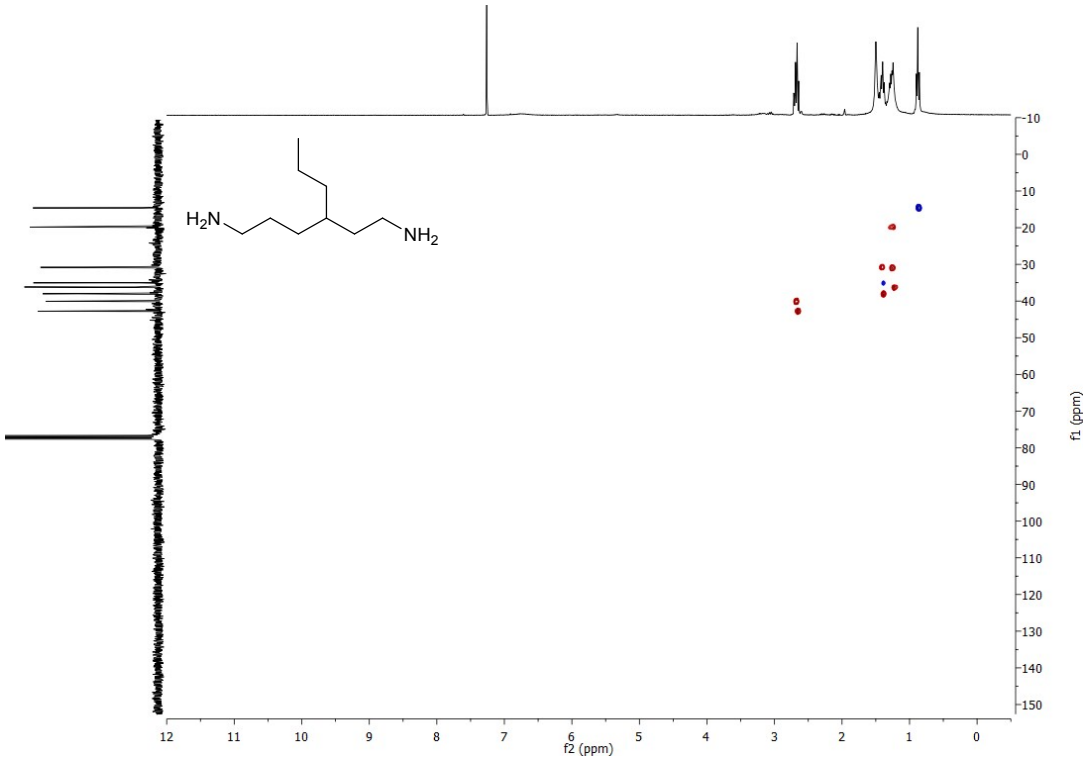
^{13}C-Spectrum of 3-propylhexane-1,6-diamine (**7**) in $CDCl_3$ (76 MHz)



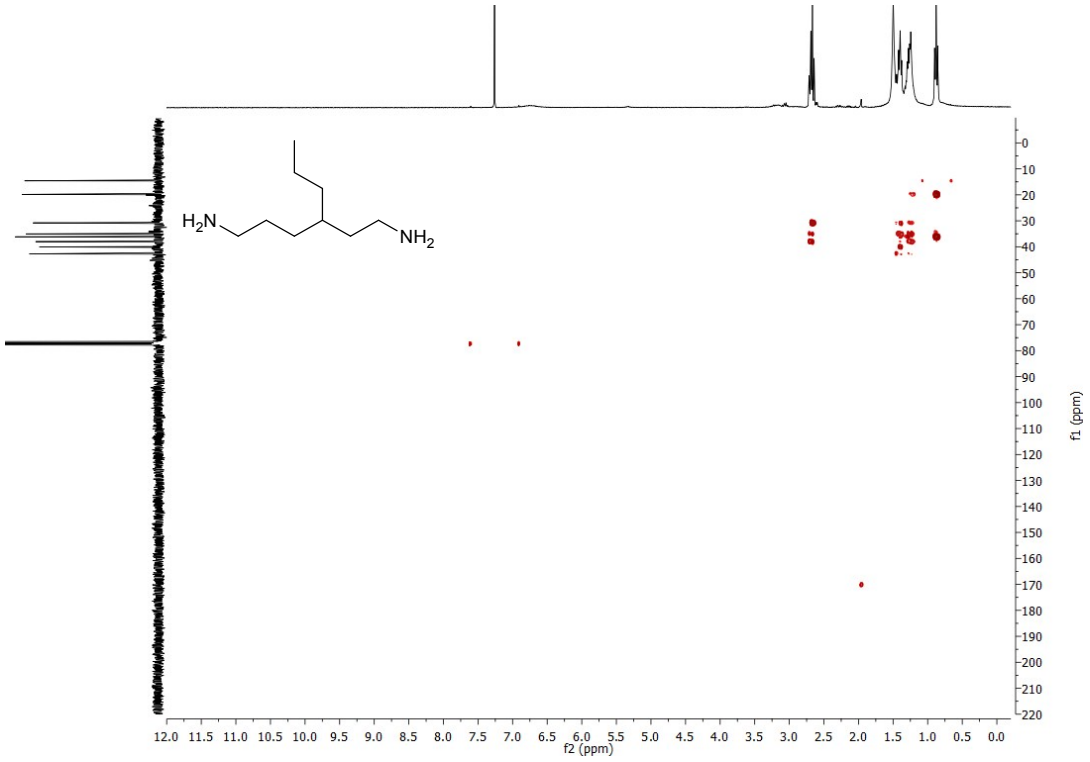
^{1}H-COSY-spectrum of 3-propylhexane-1,6-diamine (**7**) in $CDCl_3$ (300 MHz)



^{1}H-^{13}C-HSQC-spectrum of 3-propylhexane-1,6-diamine (**7**) in $CDCl_3$ (300 MHz, 76 MHz)

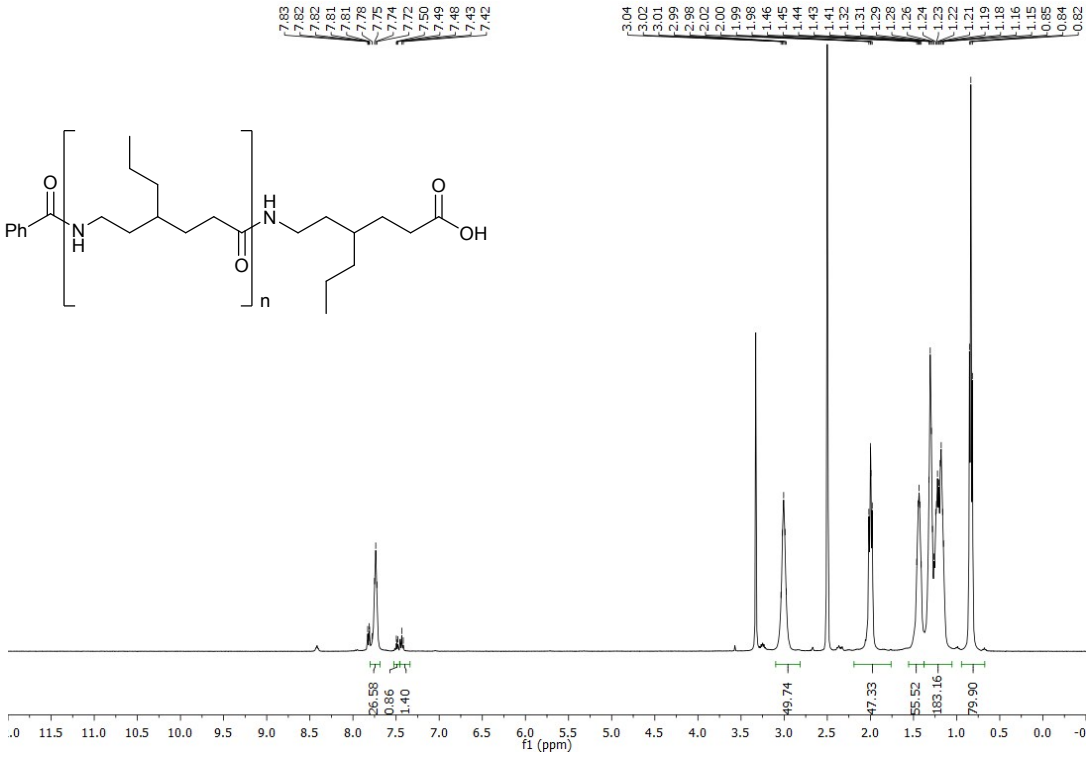


^{1}H-^{13}C-HMBC-spectrum of 3-propylhexane-1,6-diamine (**7**) in $CDCl_3$ (300 MHz, 76 MHz)

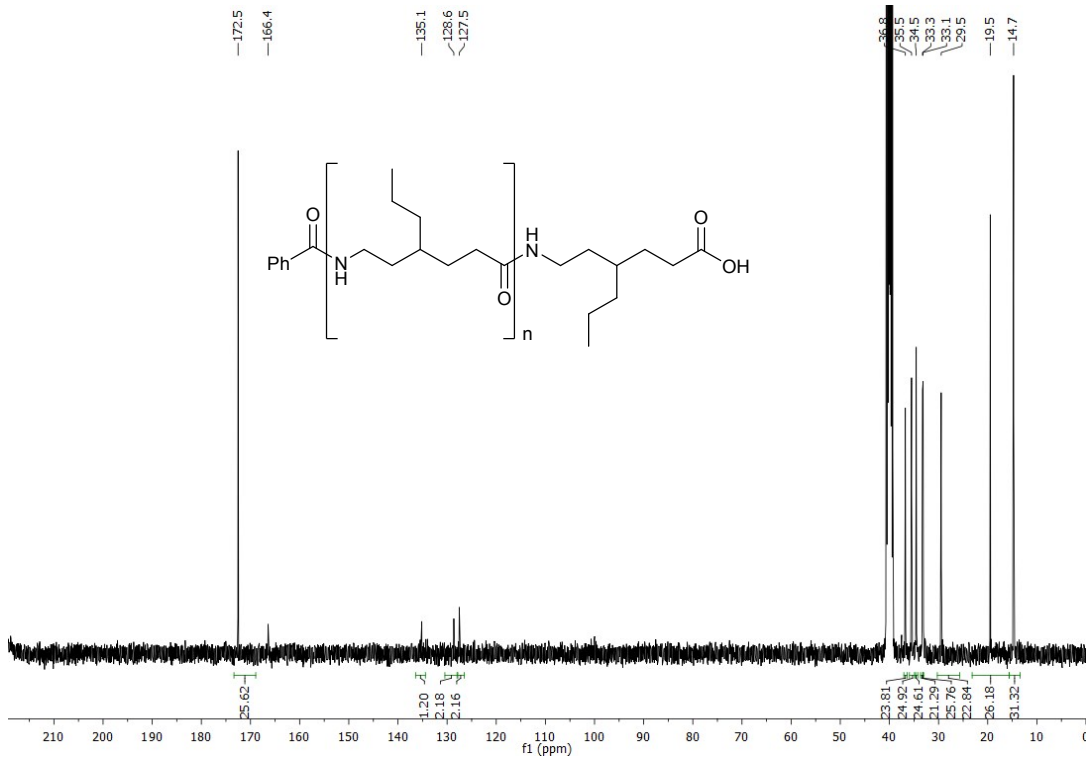


4.2.3 Spectra of the polyamides

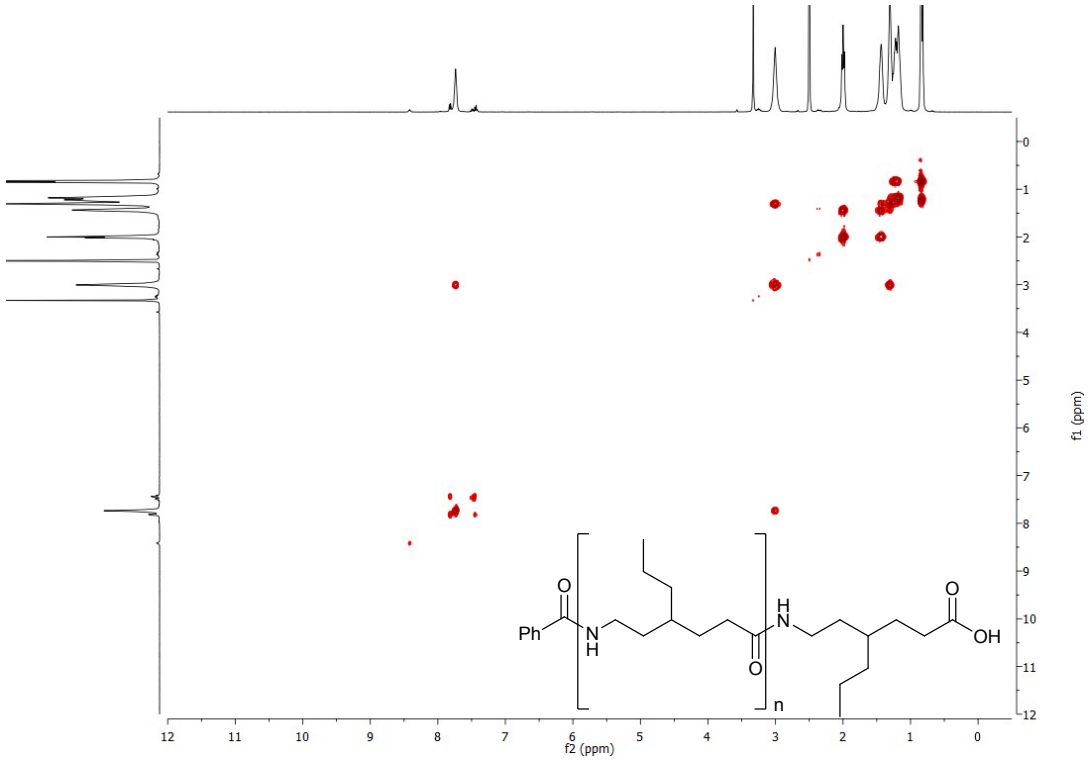
^{1}H-spectrum of AB-type polyamide **16** in DMSO-d_6 (400 MHz)



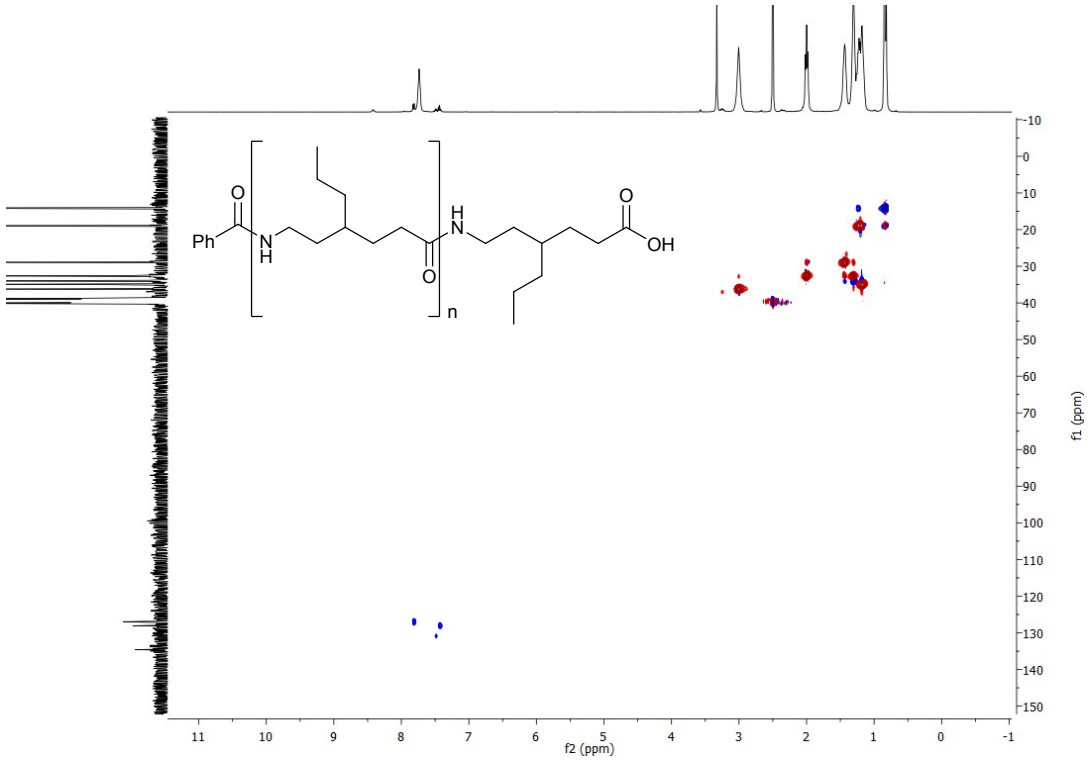
$^{13}C_{\text{inverse gated}}$-spectrum of AB-type polyamide **16** in DMSO-d_6 (101 MHz)



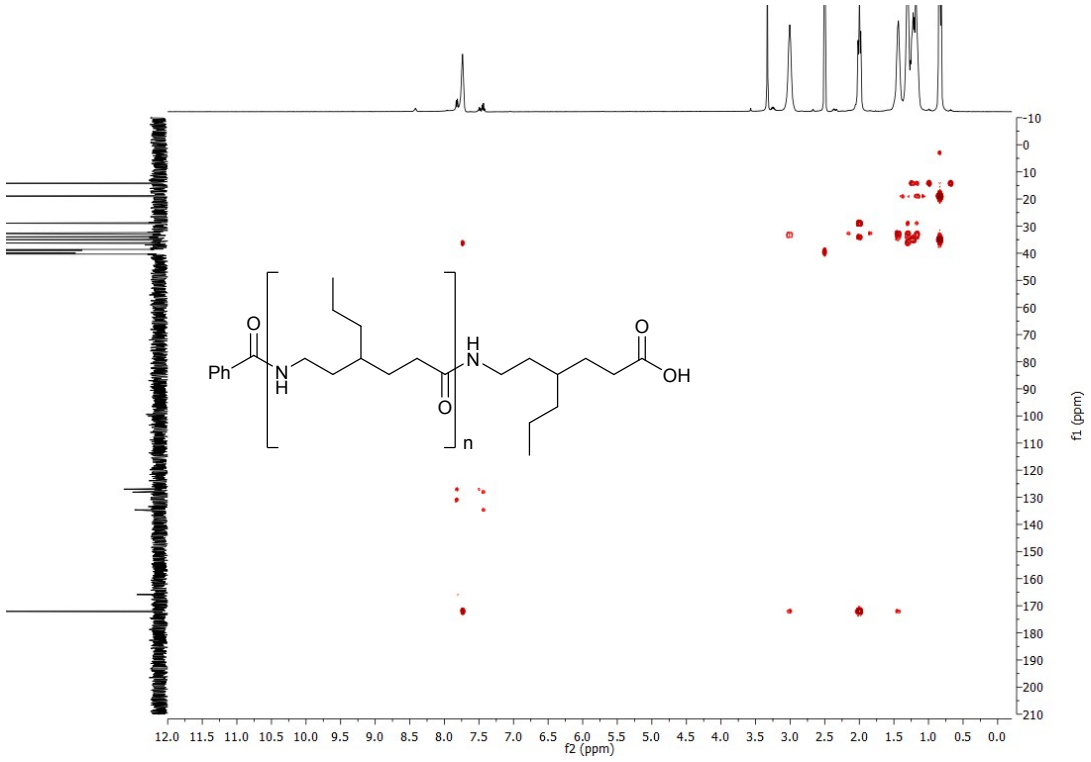
^{1}H-COSY-spectrum of AB-type polyamide **16** in DMSO-d_6 (400 MHz)



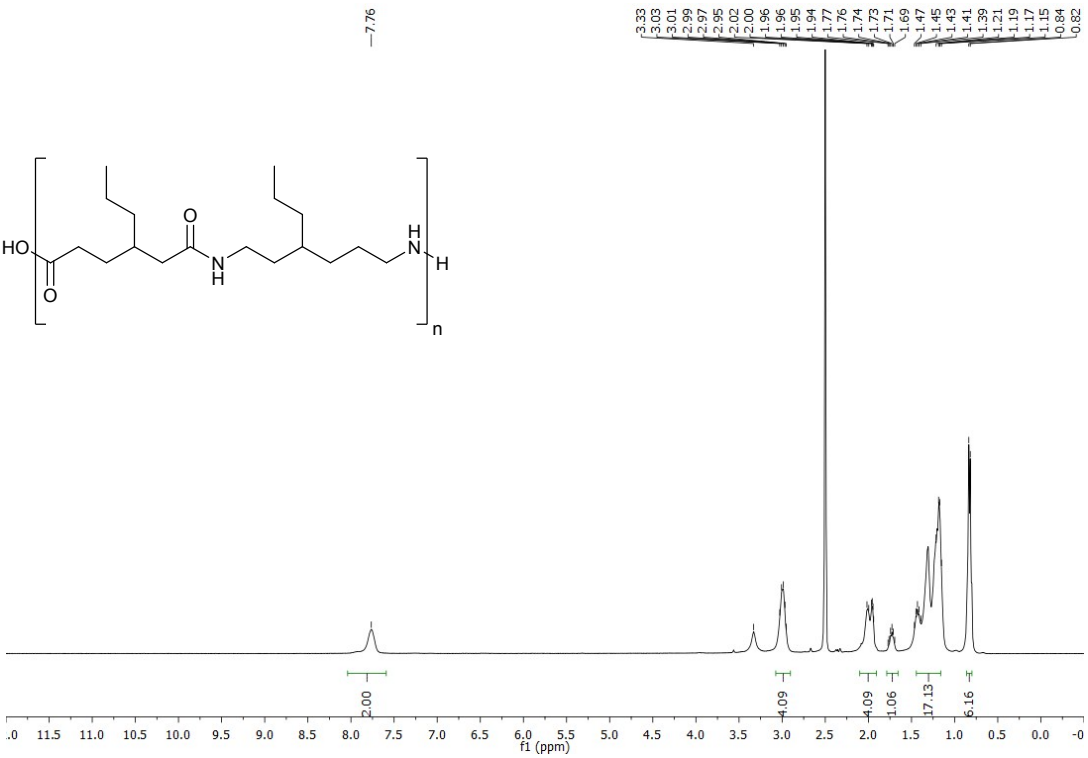
^{1}H-$^{13}C_{\text{inverse gated}}$-HSQC-spectrum of AB-type polyamide **16** in DMSO-d_6 (400 MHz, 101 MHz)



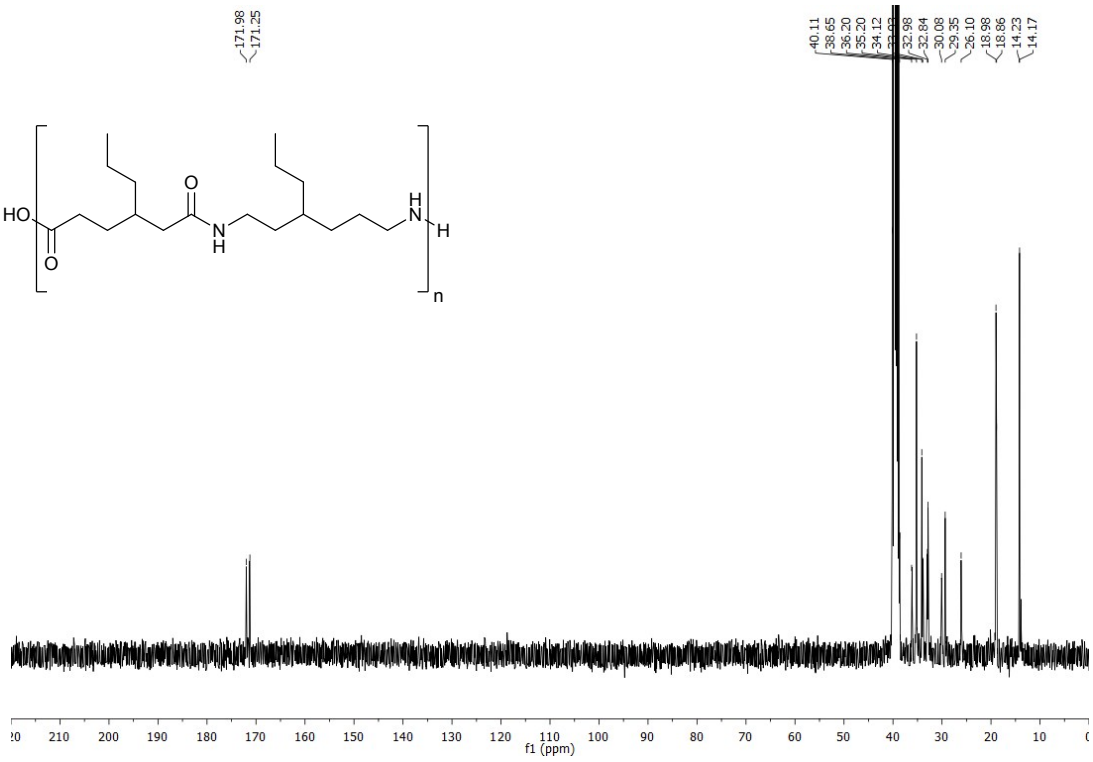
^{1}H-$^{13}C_{\text{inverse gated}}$-HMBC-spectrum of AB-type polyamide **16** in DMSO-d_6 (400 MHz, 101 MHz)



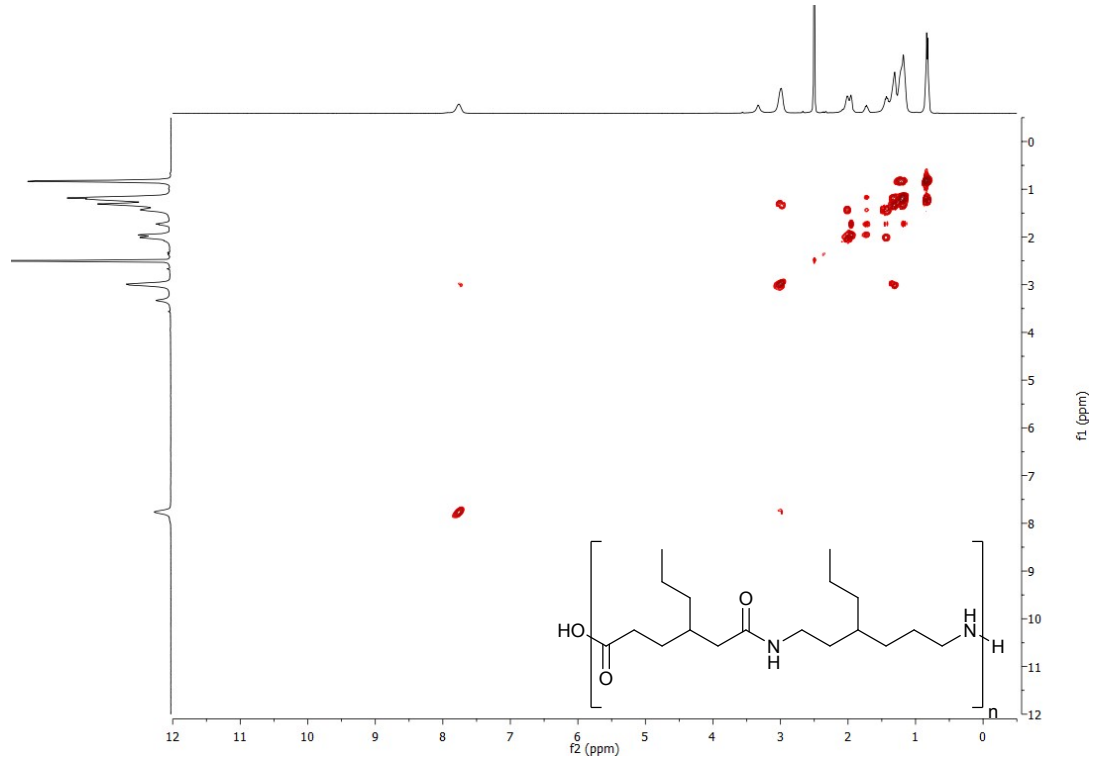
^{1}H-spectrum of A_2/B_2-type polyamide **17** in DMSO-d_6 (400 MHz)



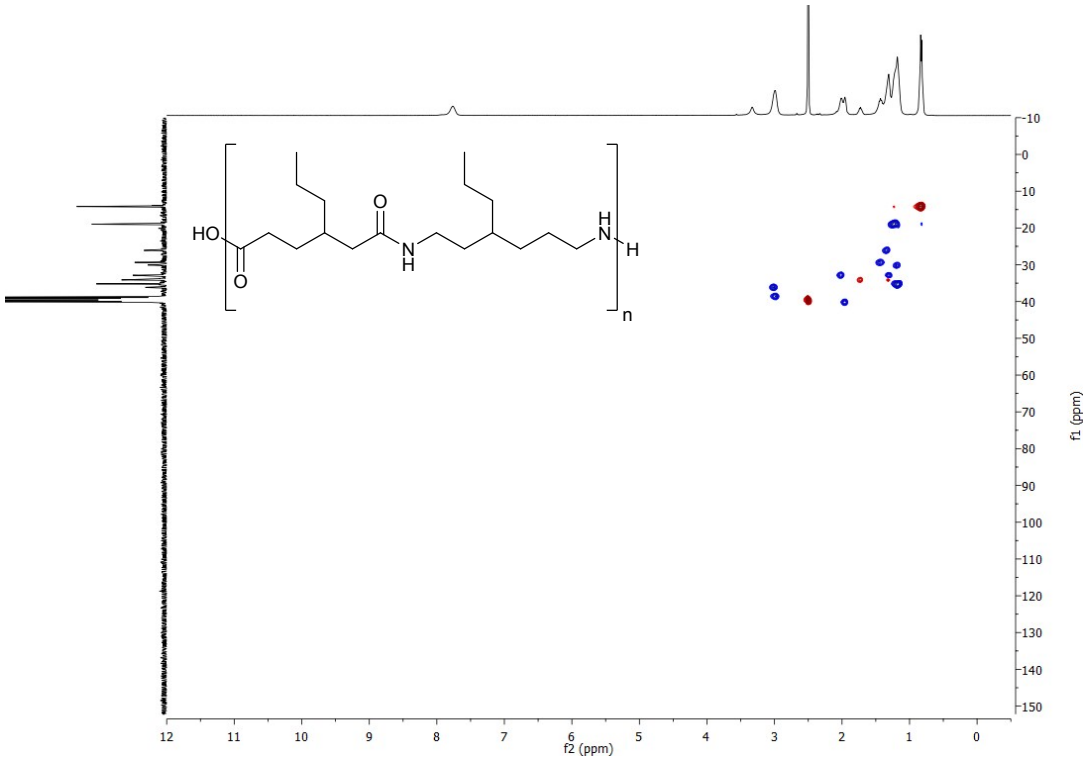
^{13}C-spectrum of A_2/B_2-type polyamide **17** in DMSO-d_6 (101 MHz)



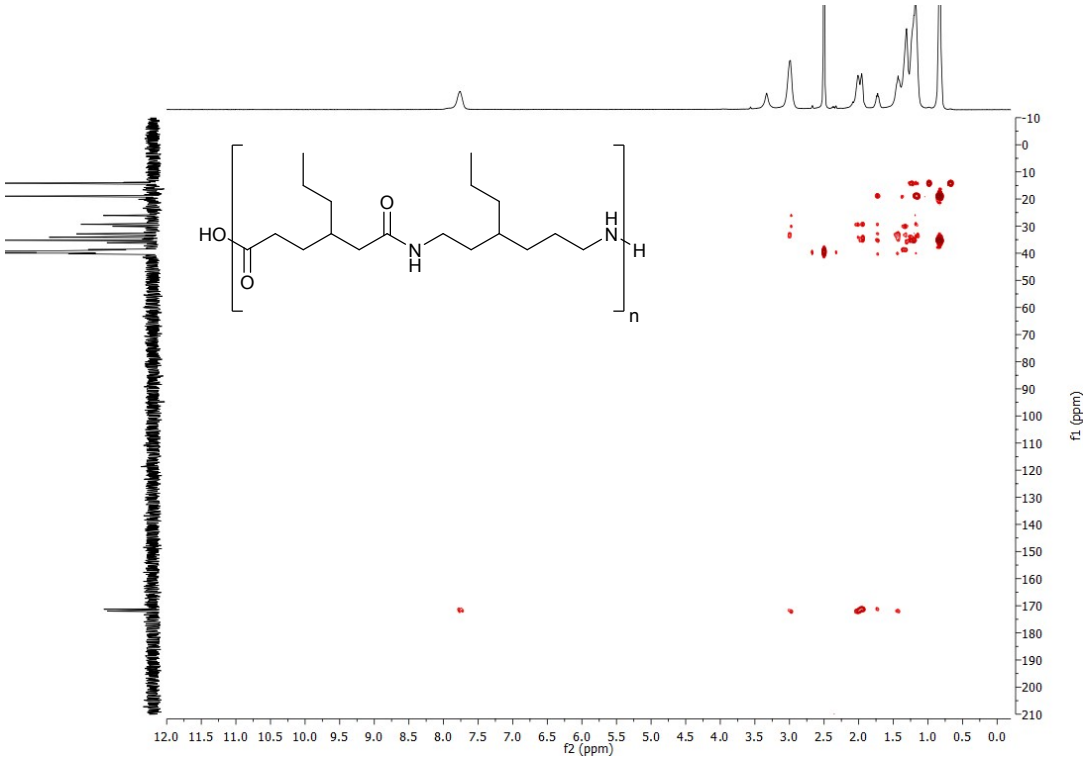
^{1}H-COSY-spectrum of A_2/B_2-type polyamide **17** in DMSO-d_6 (400 MHz)



^{1}H-^{13}C-HSQC-spectrum of A_2/B_2-type polyamide **17** in DMSO-d_6 (400 MHz, 101 MHz)



^{1}H-^{13}C-HMBC-spectrum of A_2/B_2-type polyamide **17** in DMSO-d_6 (400 MHz, 101 MHz)



5 Picture of cotton fabric after vat-dyeing with indigo 3

Cotton fabric after vat-dyeing with indigo **3**.