Supporting Information:

Highly Active Heterogenous Hydrogenation Catalysts Prepared from Cobalt Complexes and Rice Husk Waste

Felix Unglaube,[a] Janina Schlapp,[a] Antje Quade,[b] Jan Schäfer[b] and Esteban Mejía[a]*

[a] Leibniz-Institut für Katalyse e. V. an der Universität Rostock (LIKAT), Albert-Einstein-Str. 29a, 18059 Rostock, Germany;

b Leibniz-Institut für Plasmaforschung und Technologie e.V., Felix-Hausdorff-Str. 2, 17489 Greifswald (Germany)

*Corresponding E-mail address: Esteban.Mejia@catalysis.de

Contents

1. Experimental Details

1.1 Materials and Methods

Chemicals were purchased from commercial sources and used without purification unless stated otherwise. The purity of the purchased chemicals was controlled by either NMR spectroscopy or GC/MS analysis. If not stated differently, all reactions were performed under Schlenk, air/moisture-free conditions. All solvents were dried, degassed and stored in septum-sealed flasks over molecular sieves under argon atmosphere. Solvents were stored over molecular sieves. The RH samples were received from Vietnamese farmers at the Red River Delta (Nam Đinh Povince, 20°23'27.7"N 106°15'34.7"E) and Mekong Delta (An Giang Provice, 10°24'55.0"N 105°11'52.3"E). The samples were collected between 08.04.2019 and 11.04.2019. All collected samples were harvested within two months.

NMR spectra were recorded deuterated solvents: $CDCl_3$ or Toluene-D_8 by using Bruker Avance 300 spectrometer with QNP probe head (^{1}H: 300 MHz, ^{13}C: 75 MHz) or Bruker Avance 400 spectrometer (^{1}H: 400 MHz, ^{13}C: 100 MHz), respectively. The calibration of the spectra was carried out referenced with residual solvent shifts and were reported as parts per million (ppm) relative to $SiMe_4$. Multiplicities are abbreviated as follows: singlet (s), doublet (d), triplet (t), quartet (q), doublet-doublet (dd), doublet-triplet (dt), multiplet (m). Samples were measured at room temperature (297 K).

Chromatograms were obtained by GC analysis performed on Hewlett-Packard 6890 Series. Samples were dissolved in ethyl acetate and sampled into the GC column. GC/MS analysis was performed on Agilent 6890/5973 GC-MS or on Agilent 7890/5977 GC-MS. Samples were dissolved in ethyl acetate and *n*-octan was used as internal standard.

Morphological analysis was performed by scanning electron microscopy (SEM, JEOL 7500F, Japan). The SEM is equipped with a field emission gun (FEG) and two secondary electron detectors used in this investigation: SEI (in-lens detector, resolution of 1.0 nm) and LEI (lower detector with maximum resolution of at least 2 nm). SEM-FEG was operated at acceleration voltage in the range of 0.5 - 2 kV in a gentle beam modus, thus no additional coating with a conductive layer is required. Working distance and magnification were 8.5 mm an 50x – 2500x, respectively.

The elemental surface composition and chemical binding properties were analyzed by X-ray photoelectron spectroscopy (XPS) using an AXIS Ultra DLD electron spectrometer (Kratos Analytical, Manchester, UK). The spectra were recorded utilizing monochromatic X-rays Al kα (15 kV, 10 mA for general spectra and 15 kV, 15 mA for highly resolved measured C 1s and N 1s spectra) with a medium magnification (field of view 2) lens and by selecting the slot mode. At a pass energy of 160 eV survey spectra were acquired. A pass energy of 80 eV was used for estimating the chemical elemental composition, and 10 eV for the highly resolved measured C 1s and N 1s peaks for investigation of chemical functional groups. Charge neutralization was used for all samples to reduce any potential differential charging effects. Data acquisition and processing were carried out using CasaXPS software, version 2.15 (Casa Software Ltd., UK). After subtraction of a Shirley background the peaks were quantified. For quantification, an average was calculated from data measured in three different sample spots. Highly resolved

measured C 1s peaks were fitted using a Gaussian-Lorentzian GL(30) peak shape for following components: binding energy (BE) @ 285.0 eV: C-C/C-H, BE @ 285.8±0.1 eV: amines and secondary carboxyl groups (-C-NH, -C-COOH), BE @ 286.5±0.1 eV: hydroxyls, ethers (-C-O), BE @ 287.8±0.2 eV: aldehydes, ketones (-C=O), BE @ 289.1±0.2 eV: ester and carboxyl groups (-C-O-C=O, -COOH). In contrast, the sp2 hybridized component was fitted using an asymmetric peak shape, BE @ 284.1±0.1 eV. Highly resolved measured N 1s peaks were fitted using following components: Co-N @ 399.0±0.1 eV, N-pyrrol @ 400.8±0.1 eV, N-amm @ 402.3±0.1 eV, NOx @ 406.2±0.2 eV.

Elemental analysis for C, H, N and S was conducted with an instrument of Leco, model Mikroanalysator -TruSpec CHNS Micro. For other elements, elemental analysis was made by atomic absorption spectroscopy (AAS) with an instrument of Analytik Jena, model AAS – contrAA800D. Inductively coupled plasma - optical emission spectrometry (ICP-OES) analysis was conducted with an instrument of SPECTRO Analytical Instruments, model SPECTROFLAME.

XRD powder pattern were recorded on a Panalytical X'Pert θ/2θ-diffractometer equipped with Xcelerator detector using automatic divergence slits and Cu kα1/α2 radiation (40 kV, 40 mA; λ= 0.15406 nm, 0.154443 nm). Cu beta-radiation was excluded using a nickel filter foil. The measurements were performed with 0.087°s-1. The samples were mounted on silicon zero background holders. The obtained intensities were converted from automatic to fixed divergence slits (0.25°) for further analysis. Peak positions and profile were fitted with Pseudo-Voigt function using the HighScore Plus software package (Panalytical). Phase identification was done by using the PDF-2 database of the International Center of Diffraction Data (ICDD).

IR spectra were recorded on a Nicolet Avatar 370 (Thermo Electron) FTIR spectrometer equipped with a smart endurance ATR accessory.

BET surface areas were determined on aNOVA 4200e instrument by N2-physisorption at −196 °C. Prior to the measurements, the known amount of the catalyst was evacuated for 2 h at 400 °C to remove physically adsorbed water.

1.2 Catalysts Synthesis

The rice husk was dried under the sun at the harvesting sites in Vietnam by local farmers. All samples were shredded with a SM 200 (1000 rpm, 2 mm sieve sizes) cutting mill and milled for 3 h in a ball mill PM 200 in steel cups using steel balls at 400 rpm.

Co1@RH-E1 Was prepared as follows: 0.5 g (2.1 mmol) of $Co(II)Cl_2*6H_2O$, were dissolved in 50 mL of ethanol and 0.5 g (1.0 mmol) of phthalocyanine were added, followed by 2 g of grounded RH. The suspension was stirred for 24 h at 21 °C. After that, the solvent was removed *in vacuo* with a rotary evaporator. The dried sample was pyrolyzed under N_2 atmosphere at 600 °C in an Al_2O_3 pot inside a quartz tube furnace at a heating rate of 10 °C/min. After reaching the aspired temperature it was maintained for 1 h. The quartz tube was flushed using nitrogen at 50 ml/min and after cooling down to room temperature the prepared material was stored under ambient conditions. For the base etching, a sample of the material was suspended in an aqueous 1M NaOH solution, stirred at room temperature for 24h, filtered, washed with water, and dried in an oven.

Co2@RH-E1 was prepared following the same procedure as for Co1@RH-E1, using 0.3 g of $Co(II)Cl_2*6H_2O$ (1.3 mmol), 0.55 g (3.1 mmol) of 1,10-phenanthroline and 2.04 g of RH.

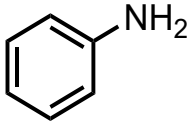
Co3@RH-E1 was prepared following the same procedure as for Co1@RH-E1, using 0.5 g of $Co(II)Cl_2*6H_2O$ (2.1 mmol), 0.75 g (4.2 mmol) of phenylbiguanidine and 2.02 g of RH.

Co4@RH-E1 was prepared following the same procedure as for Co1@RH-E1, using 0.5 g of $Co(II)Cl_2*6H_2O$ (2.1 mmol), 0.8 g (2.3 mmol) of bis(tetramethylguanidino)naphthalene and 2.07 g of RH.

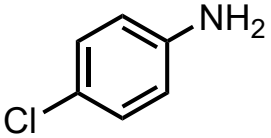
Co5@RH-E1 was prepared following the same procedure as for Co1@RH-E1, using 0.5 g of $Co(II)Cl_2*6H_2O$ (2.1 mmol), 1.06 g (4.2 mmol) of 1-(2-pyridylazo)-2-naphtol and 2.04 g of RH.

1.3 Catalytic Hydrogenation

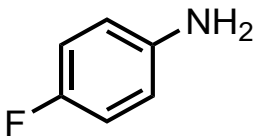
The general procedure for the product preparation is given exemplarily for aniline, other products were synthesized following the general procedure if not stated differently.



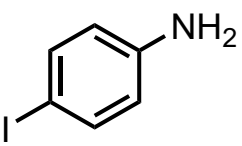
Aniline (2a): Nitrobenzene (1 mmol, 102 µl), 25 mg of Co1@RH-E1and isopropanol/water (1:1) (1 ml) were added together in a 12 ml vial, equipped with a Teflon coated magnetic stirrer. The lid of the vial was pierced through with a steel cannula (0.45× 12 mm) to equalize pressure and ensure gas exchange. The prepared vial was placed in a steal autoclave. The autoclave was flushed three times with 10 bar of hydrogen and the required reaction pressure was adjusted. The pressurized autoclave was placed in an aluminium heating block. After completing the desired reaction time**,** the system was cooled down using an ice bath. The crude mixture was filtered through a syringe filter after adding 2 ml of ethyl acetate. Finally, the crude product was purified by flash-column chromatography on silica gel (heptane/ethyl acetate 10:1). The reaction product was a yellowish liquid. Yield: 90 mg (97 %). ^{1}H NMR (300 MHz, Chloroform-d) δ 3.76 (s, 2H), 7.36 (tq, J = 7.4, 1.4 Hz, 2H), 6.97 (ddt, J = 8.8, 7.4, 1.4 Hz, 1H), 6.87 – 6.78 (m, 2H). ^{13}C NMR (75 MHz, CDCl3) δ 146.41, 129.16, 118.27, 114.96. The obtained NMR spectra match previous reports.[1]



4-chloroaniline (2b): Following the general procedure, using 1-chloro-4-nitrobenzene (127 mg, 1 mmol). The reaction product was purified by column chromatography on silica gel using a mixture of pentane and ethyl acetate. Yield: 124 mg (yield 98 %). ^{1}H NMR (300 MHz, Benzene-d_6) δ 7.02 – 6.94 (m, 2H), 6.07 – 6.00 (m, 2H), 2.74 (s, 2H). ^{13}C NMR (75 MHz, C_6D_6) δ 145.71, 129.27, 122.79, 116.17. The obtained NMR spectra match previous reports.[2]



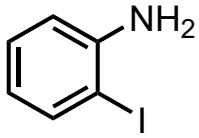
4-fluoroaniline (2c): Following the general procedure, using and 1-fluoro-4-nitrobenzene (111 mg, 1 mmol). Yield: 108 mg (98 %). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 6.90 – 6.82 (m, 2H), 6.65 – 6.58 (m, 2H), 3.51 (s, 2H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 158.10, 154.98, 142.52, 116.22, 116.12, 115.91, 115.61. ^{19}F NMR (282 MHz, Chloroform-*d*) δ -126.83. The obtained NMR spectra match previous reports.[2]



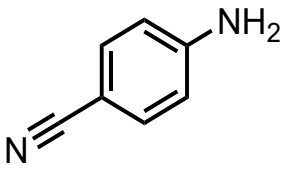
4-iodoaniline (2d): Following the general procedure, using 1-iodo-4-nitrobenzene (248 mg, 1 mmol). Yield: 209 mg (96 %). ^{1}H NMR (300 MHz,

Chloroform-d) δ 6.83 – 6.70 (m, 2H), 5.93 – 5.74 (m, 2H), 3.11 (s, 2H). ^{13}C NMR (75 MHz, CDCl3) δ 171.19, 146.13, 145.79, 138.99, 137.91, 129.36, 119.97, 117.32, 116.28. The obtained spectra match previous reports.[3]

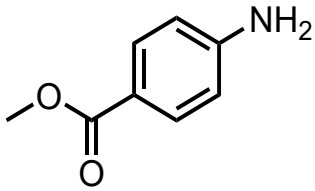
2-iodoaniline (2e): Following the general procedure, using 2-iodo-4-nitrobenzene (111 mg, 1 mmol). Yield: 185 mg (85 %). ^{1}H NMR (300 MHz, Chloroform-d) δ 7.64 (dd, J = 7.9, 1.5 Hz, 1H), 7.14 (ddd, J = 8.0, 7.2, 1.5 Hz, 1H), 6.76 (dd, J = 8.0, 1.5 Hz, 1H), 6.48 (ddd, J = 7.9, 7.3, 1.5 Hz, 1H), 4.46 – 3.75 (m, 2H). ^{13}C NMR (75 MHz, CDCl3) δ 139.14, 129.47, 120.18, 114.93.



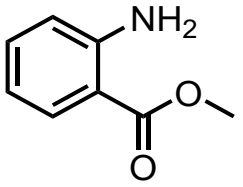
4-aminobenzonitrile (2f): Following the general procedure, using 4-nitrobenzonitrile (148 mg, 1 mmol). Yield: 115 mg (98 %). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.45 – 7.31 (m, 2H), 6.70 – 6.53 (m, 2H), 4.20 (s, 2H). ^{13}C NMR (75 MHz, CDCl3) δ 150.59, 133.87, 120.38, 114.51, 112.13, 100.09. The obtained spectra match previous reports.[4]



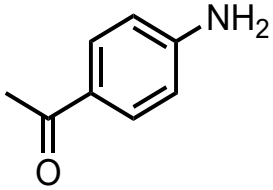
methyl 4-aminobenzoate (2g): Following the general procedure, using methyl 4-nitrobenzoate (181 mg, 1 mmol). Yield: 144 mg (96 %). ^{1}H NMR (300 MHz, Chloroform-d) δ 7.86 – 7.79 (m, 2H), 6.65 – 6.58 (m, 2H), 4.27 – 3.92 (m, 2H), 3.84 (d, J = 0.3 Hz, 3H). ^{13}C NMR (75 MHz, CDCl3) δ 167.31, 151.06, 131.65, 119.59, 113.84, 51.67. The obtained spectra match previous reports.[5]



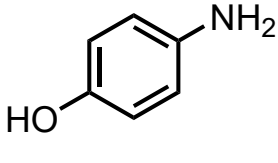
methyl 2-aminobenzoate (2h): Following the general procedure, using methyl 2-nitrobenzoate (181 mg, 1 mmol). Yield: 140 mg (94 %). ^{1}H NMR (400 MHz, Chloroform-d) δ 7.88 – 7.83 (m, 1H), 7.29 – 7.23 (m, 1H), 6.69 – 6.62 (m, 2H), 5.61 (s, 2H), 3.87 (s, 3H). ^{13}C NMR (75 MHz, CDCl3) δ 168.66, 150.43, 134.18, 131.31, 116.82, 116.43, 110.90, 51.60. The obtained spectra match previous reports.[5]



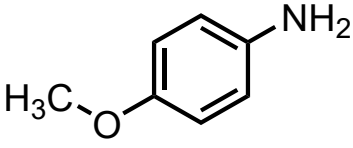
1-(4-aminophenyl)ethan-1-one (2i): Following the general procedure, using 1-(4-nitrophenyl)ethan-1-one (165 mg, 1 mmol). Yield: 132 mg (98 %). ^{1}H NMR (300 MHz, Chloroform-d) δ 7.33 – 7.20 (m, 2H), 6.20 – 6.03 (m, 2H), 3.71 (s, 2H), 1.98 (s, 3H). ^{13}C NMR (75 MHz, CDCl3) δ 196.70, 151.45, 130.85, 127.63, 113.72, 113.29, 77.58, 77.16, 76.74, 26.12. The obtained spectra matches previous reports.[4]



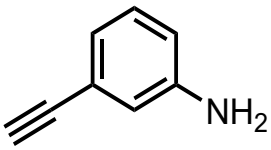
4-aminophenol (2j): Following the general procedure, using 4-nitrophenol (140 mg, 1 mmol). Yield: 95 mg (98 %). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.33 (d, J = 1.7 Hz, 1H), 6.57 – 6.25 (m, 4H), 4.36 (s, 2H). ^{13}C NMR (101 MHz, DMSO) δ 148.23, 140.68, 115.54, 115.23. The obtained spectra match previous literature reports.[6-7]



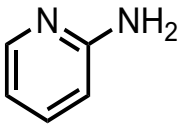
4-methoxyaniline (2k): Following the general procedure, using 1-methoxy-4-nitrobenzene (153 mg, 1 mmol). Yield: 120 mg (98 %). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 6.78 – 6.61 (m, 4H), 3.75 (s, 3H), 3.32 (s, 2H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 152.97, 140.03, 116.56, 114.95, 77.36, 55.88. The obtained spectra match previous reports.[4]



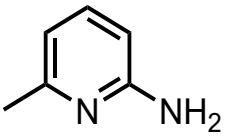
3-ethynylaniline (2l): Following the general procedure, using 1-ethynyl-3-nitrobenzene (147 mg, 1 mmol) were added together with isopropanol/water (1:1) (32 mmol, 1 ml). Yield: 112 mg (96 %). ^{1}H NMR (300 MHz, Benzene-d_6) δ 8.18 (ddd, *J* = 5.1, 1.9, 0.9 Hz, 1H), 7.09 (dd, *J* = 15.4, 2.0 Hz, 1H), 6.41 (ddd, *J* = 7.2, 5.0, 1.0 Hz, 1H), 6.11 (dt, *J* = 8.3, 0.9 Hz, 1H), 4.52 (s, 2H), ^{13}C NMR (75 MHz, Benzene-d_6) δ 159.62, 148.49, 137.34, 113.40, 108.40. The obtained spectra match previous reports.[8]



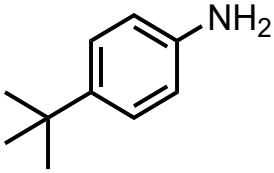
pyridin-2-amine (2m): Following the general procedure, using 2-nitropyridine (127 mg, 1 mmol). Yield: 92 mg (95 %). ^{1}H NMR (300 MHz, Benzene-d_6) δ 8.18 (ddd, *J* = 5.1, 1.9, 0.9 Hz, 1H), 7.09 (dd, *J* = 15.4, 2.0 Hz, 1H), 6.41 (ddd, *J* = 7.2, 5.0, 1.0 Hz, 1H), 6.11 (dt, *J* = 8.3, 0.9 Hz, 1H), 4.52 (s, 2H), ^{13}C NMR (75 MHz, Benzene-d_6) δ 159.62, 148.49, 137.34, 113.40, 108.40. The obtained spectra match previous reports.[3]



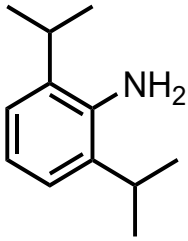
2-amino-4-methylpyridin (2n): Following the general procedure, using 4-methyl-2-nitropyridine (138 mg, 1 mmol). Yield: 105 mg (98 %). ^{1}H NMR (300 MHz, Chloroform-d) δ 6.67 – 6.55 (m, 2H), 6.48 (ddd, J = 7.9, 2.1, 0.8 Hz, 1H), 3.82 (s, 4H), 2.21 (d, J = 0.7 Hz, 3H). ^{13}C NMR (75 MHz, CDCl3) δ 131.18, 119.99, 118.01, 115.34, 77.58, 77.16, 76.74, 20.84. The obtained spectra match previous reports.[3]



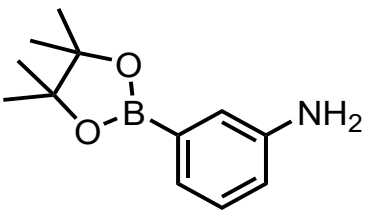
4-(tert-butyl)aniline (2o): Following the general procedure, using 1-(tert-butyl)-4-nitrobenzene (149 mg, 1 mmol). Yield: 116 mg (99 %). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.35 – 7.27 (m, 2H), 6.78 – 6.68 (m, 2H), 3.63 (s, 2H), 1.42 (d, *J* = 1.0 Hz, 9H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 143.83, 141.30, 126.03, 114.95, 31.57. The obtained spectra match previous reports.[9]



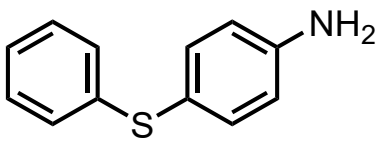
2,6-diisopropylaniline (2p): Following the general procedure, using 1,3-diisopropyl-2-nitrobenzene (207 mg, 1 mmol) in acetonitrile (1 ml). Yield: 169 mg (96 %). ^{1}H NMR (300 MHz, Chloroform-d) δ 7.08 (d, J = 7.6 Hz, 2H), 6.84 (dd, J = 8.0, 7.3 Hz, 1H), 3.77 (s, 2H), 2.97 (hept, J = 6.8 Hz, 2H), 1.34 – 1.29 (m, 12H). ^{13}C NMR (75 MHz, CDCl3) δ 171.24, 140.35, 132.53, 122.87, 118.62, 60.50, 28.03, 24.43, 22.56, 21.15, 14.31. The obtained spectra match previous reports.[10]



3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (2q): Following the general procedure, using 4,4,5,5-tetramethyl-2-(3-nitrophenyl)-1,3,2-dioxaborolane (249 mg, 1 mmol). Yield: 210 mg (96 %). ^{1}H NMR (300 MHz, Chloroform-d) δ 7.25 – 7.10 (m, 3H), 6.80 (ddd, J = 7.5, 2.6, 1.6 Hz, 1H), 3.65 (s, 2H), 1.34 (s, 12H). ^{13}C NMR (75 MHz, CDCl3) δ 145.70, 128.89, 125.25, 121.36, 118.25, 83.85, 77.58, 77.16, 76.74, 24.99. The obtained spectra match previous reports.[11]

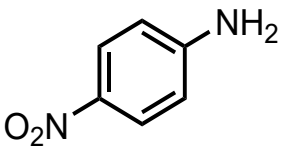


4-(phenylthio)aniline (2r): Following the general procedure, using (4-nitrophenyl)(phenyl)sulfane (350 mg, 1 mmol). Yield: 332 mg (95 %). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.35 – 7.29 (m, 2H), 7.26 – 7.18 (m, 2H), 7.16 – 7.07 (m, 3H), 6.74 – 6.64

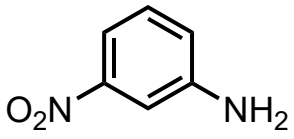


(m, 2H), 3.88 (s, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 146.70, 139.66, 136.11, 128.94, 127.50, 125.42, 120.97, 116.17. The obtained spectra match previous reports.[12]

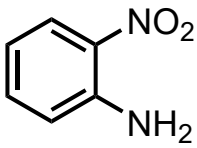
4-nitroaniline (2s): Following the general procedure, using 1,4-dinitrobenzene (168 mg, 1 mmol). Yield: 161 mg (96 %). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.43 (s, 1H), 8.13 – 8.02 (m, 2H), 6.69 – 6.58 (m, 2H), 4.36 (s, 1H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 126.37, 124.90, 113.40. The obtained spectra match previous reports.[13]



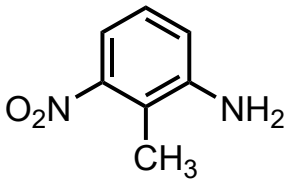
3-nitroaniline (2t): Following the general procedure, using 1,3-dinitrobenzene (168 mg, 1 mmol). Yield: 164 mg (98 %). ^{1}H NMR (300 MHz, Chloroform-d) δ 7.56 (ddd, J = 8.1, 2.2, 0.9 Hz, 1H), 7.47 (td, J = 2.3, 0.4 Hz, 1H), 7.34 – 7.19 (m, 1H), 6.94 (ddd, J = 8.0, 2.4, 0.9 Hz, 1H), 3.99 (s, 1H). ^{13}C NMR (75 MHz, CDCl3) δ 147.58, 130.03, 120.75, 113.23, 109.12. The obtained spectra match previous reports.[14]



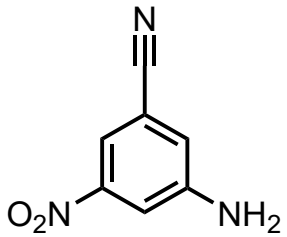
2-nitroaniline (2u): Following the general procedure, using 1,2-dinitrobenzene (168 mg, 1 mmol). Yield: 156 mg (yield 93 ^{1}H NMR (300 MHz, Chloroform-d) δ 8.11 (ddd, J = 8.7, 1.6, 0.4 Hz, 1H), 7.35 (ddd, J = 8.5, 7.0, 1.6 Hz, 1H), 6.85 – 6.77 (m, 1H), 6.70 (ddd, J = 8.6, 7.0, 1.3 Hz, 1H), 6.02 (s, 2H). ^{13}C NMR (75 MHz, CDCl3) δ 135.76, 126.34, 118.87, 117.09. %). The obtained spectra match previous reports.[13]



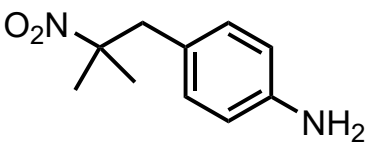
2-methyl-3-nitroaniline (2v): Following the general procedure, using and 2-methyl-1,3-dinitrobenzene (182 mg, 1 mmol). Yield: 144 mg (95 %). ^{1}H NMR (300 MHz, Chloroform-d) δ 7.21 – 7.02 (m, 2H), 6.85 (ddd, J = 7.8, 1.4, 0.5 Hz, 1H), 3.89 (s, 2H), 2.24 (d, J = 0.5 Hz, 3H). ^{13}C NMR (75 MHz, CDCl3) δ 146.44, 126.87, 118.51, 115.99, 114.04, 77.58, 77.16, 76.74, 12.73. The obtained spectra match previous reports.[15]



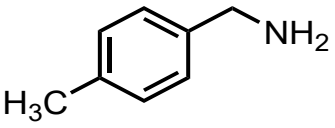
3-amino-5-nitrobenzonitrile (2w): Following the general procedure, using 3,5-dinitrobenzonitrile (193 mg, 1 mmol). Yield: 156 mg (96 %). ^{1}H NMR (300 MHz, Chloroform-d) δ 7.82 (dd, J = 2.1, 1.3 Hz, 1H), 7.67 (t, J = 2.2 Hz, 1H), 7.16 (dd, J = 2.3, 1.3 Hz, 1H), 4.27 (s, 2H). The obtained spectra match previous reports.[15]



4-(2-methyl-2-nitropropyl)aniline (2x): Following the general procedure, using 1-(2-methyl-2-nitropropyl)-4-nitrobenzene (224 mg, 1 mmol). Yield: 192 mg (99 %). ^{1}H NMR (300 MHz, Chloroform-d) δ 6.95 – 6.82 (m, 2H), 6.69 – 6.50 (m, 2H), 3.43 (d, J = 86.0 Hz, 2H), 3.07 (s, 2H), 1.54 (s, 6H). ^{13}C NMR (75 MHz, CDCl3) δ 207.13, 145.81, 131.05, 124.83, 115.17, 89.04, 46.27, 31.04, 25.53. The obtained spectra match previous reports.[16]

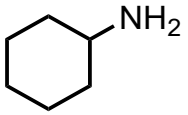


4-methylbenzylamine (2y): Following the general procedure, using 1-methyl-4-(nitromethyl)benzene (151 mg, 1 mmol). The reaction product was purified by column chromatography on silica gel using a mixture of pentane and ethyl acetate (10:1), Rf = 0.8.

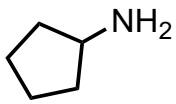


Yield: 116 mg (96 %). ^{1}H NMR (300 MHz, Chloroform-d) δ 7.18 (p, J = 8.0, 7.5 Hz, 4H), 3.79 (d, J = 1.5 Hz, 2H), 2.34 (s, 3H), 1.89 (s, 2H). ^{13}C NMR (75 MHz, CDCl3) δ 161.45, 140.67, 139.99, 136.17, 136.11, 135.99, 129.05, 128.93, 128.26, 128.02, 127.91, 127.71, 126.79, 77.58, 77.17, 76.73, 45.86, 20.83. The obtained spectra match previous reports.[17]

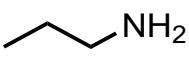
cyclohexylamine (2z): Following the general procedure, using nitrocyclohexane (111 mg, 1 mmol). Yield: 94 mg (95 %). ^{1}H NMR (300 MHz, Chloroform-d) δ 2.18 (q, J = 11.2, 10.2 Hz, 1H), 1.46 – 1.04 (m, 5H), 0.73 (dp, J = 34.2, 13.1, 11.6 Hz, 7H). ^{13}C NMR (75 MHz, CDCl3) δ 49.75, 36.22, 25.02, 24.42. The obtained spectra match previous reports.[17]



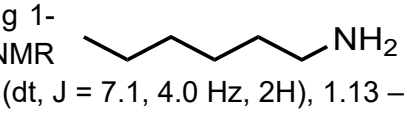
cyclopentanamine (2aa): Following the general procedure, using nitrocyclopentane (115 mg, 1 mmol). Yield: 80 mg (95 %). ^{1}H NMR (300 MHz, Chloroform-d) δ 3.25 (p, J = 6.3 Hz, 1H), 1.75 (dddd, J = 17.9, 8.2, 4.8, 1.7 Hz, 2H), 1.68 – 1.56 (m, 2H), 1.56 – 1.38 (m, 2H), 1.28 – 1.05 (m, 4H). ^{13}C NMR (75 MHz, CDCl3) δ 77.58, 77.16, 76.74, 53.30, 36.24, 23.89. The obtained spectra match previous reports.[17]



propylamine (2ab): Following the general procedure, using 1-nitropropane (89 mg, 1 mmol). Yield: 57 mg (97 %). ^{1}H NMR (300 MHz, Chloroform-d) δ 2.25 – 2.17 (m, 2H), 1.02 (h, J = 7.3 Hz, 2H), 0.64 (s, 2H), 0.48 (t, J = 7.4 Hz, 3H). ^{13}C NMR (75 MHz, CDCl3) δ 43.50, 26.49, 10.53. The obtained spectra match previous reports.[18]

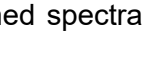


Hexan-1-amine (2ac): Following the general procedure, using 1-nitrohexane (1139 mg, 1 mmol). Yield: 98 mg (99 %). 1H NMR (300 MHz, Chloroform-d) δ 2.44 (td, J = 6.8, 2.5 Hz, 2H), 1.19 (dt, J = 7.1, 4.0 Hz, 2H), 1.13 – 1.03 (m, J = 4.4 Hz, 6H), 0.84 (d, J = 2.4 Hz, 2H), 0.66 (td, J = 6.8, 2.7 Hz, 3H). 13C NMR (75 MHz, CDCl3) δ 42.00, 33.62, 31.45, 26.30, 22.35, 13.68. The obtained spectra match previous reports.[19]



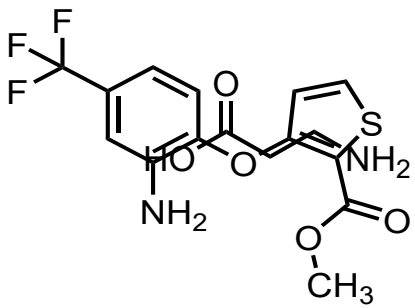
heptan-1-amine (2ad): Following the general procedure, using 1-nitroheptane (145 mg, 1 mmol). Yield: 104 mg (91 %). ^{1}H NMR (300 MHz, Chloroform-d) δ 2.60 (t, J = 6.9 Hz, 2H), 1.49 – 1.29 (m, 2H), 1.22 (dq, J = 7.6, 5.3, 3.6 Hz, 8H), 1.05 (s, 2H), 0.91 – 0.71 (m, 3H).^{13}C NMR (75 MHz, CDCl3) δ 60.35, 42.30, 33.94, 31.87, 31.64, 29.19, 26.87, 22.63, 20.99, 14.17, 14.06. The obtained spectra match previous reports.[20]

decylamine (2ae): Following the general procedure, using 1-nitrodecane (159 mg, 1 mmol). Yield: 104 mg (81 %). ^{1}H NMR (300 MHz, Chloroform-d) δ 2.56 (t, J = 6.8 Hz, 2H), 1.31 (p, J = 7.0 Hz, 2H), 1.16 (d, J = 4.5 Hz, 15H), 1.04 (s, 2H), 0.76 (t, J = 6.4 Hz, 3H). ^{13}C NMR (75 MHz, CDCl3) δ 41.80, 33.44, 31.42, 29.17, 29.10, 29.04, 28.85, 26.42, 22.18, 13.57. The obtained spectra match previous reports.[21]



propan-2-amine (2af): Following the general procedure, using 2-nitropropane (89 mg, 1 mmol). Yield: 57 mg (97 %). ^{1}H NMR (300 MHz, Chloroform-d) δ 2.92 (heptd, J = 6.3, 0.6 Hz, 1H), 0.96 (dd, J = 1.9, 1.2 Hz, 2H), 0.88 (dd, J = 6.3, 0.7 Hz, 6H). ^{13}C NMR (75 MHz, CDCl3) δ 42.52, 25.91 The obtained spectra match previous literature reports.[7]

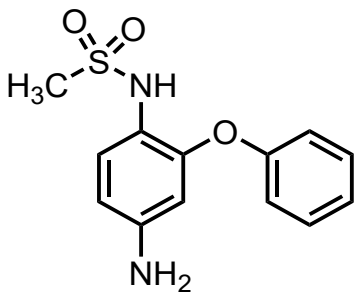
β-alanine (2ag): Following the general procedure, using 3-nitropropanoic acid (119 mg, 1 mmol). Yield: 80 mg (91 %).



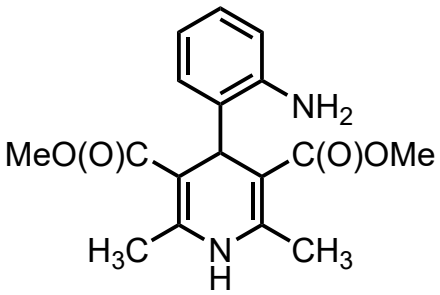
^{1}H NMR (300 MHz, Deuterium Oxide) δ 3.12 (p, J = 6.8 Hz, 2H), 2.49 (p, J = 6.7 Hz, 2H). ^{13}C NMR (75 MHz, D2O) δ 179.18, 37.91, 34.95. The obtained spectra match previous reports.[22]

methyl3-(2-amino-4-(trifluoromethyl)phenoxy) thiophene-2-carboxylate (2ah): Following the general procedure, using methyl 3-(2-nitro-4-(trifluoromethyl)phenoxy)thiophene-2-carboxylate (347 mg, 1 mmol). Yield: 301 mg (95 %). ^{1}H NMR (300 MHz, Chloroform-d) δ 7.37 (dd, J = 8.7, 7.3 Hz, 3H), 7.25 – 7.11 (m, 1H), 7.11 – 6.93 (m, 2H), 6.42 (dd, J = 8.5, 2.5 Hz, 1H), 6.33 (s, 1H), 6.17 (d, J = 2.5 Hz, 1H), 3.66 (s, 2H), 2.92 (s, 3H). ^{13}C NMR (75 MHz, CDCl3) δ 155.89, 150.60, 146.28, 130.27, 127.28, 124.46, 118.99, 117.97, 110.72, 104.59, 77.58, 77.16, 76.73, 39.06. The obtained spectra match previous reports.[23]

N-(4-amino-2-phenoxyphenyl)methanesulfonamide (2ai): Following the general procedure, using N-(4-nitro-2-phenoxyphenyl)methanesulfonamide (308 mg, 1 mmol) in isopropanol/water (1:1) (2 ml). 5 ml ethyl acetate was added after the reaction was finished. The reaction product was obtained by filtrating the catalyst of over Celite and removing the solvent in vacuum. The crude product was dissolved in ethyl acetate and hexane was added and the mixture was stored at 5°C for 12 h. The precipitate was collected, washed with diethyl ether, and dried under reduced pressure. Yield: 274 mg (99 %). ^{1}H NMR (300 MHz, Chloroform-d) δ 7.44 – 7.31 (m, 3H), 7.22 – 7.13 (m, 1H), 7.06 – 6.96 (m, 2H), 6.51 – 6.42 (m, 1H), 6.34 (s, 1H), 6.21 (dd, J = 2.5, 0.9 Hz, 1H), 4.12 (s, 2H), 2.93 (s, 3H). ^{13}C NMR (75 MHz, CDCl3) δ 130.31, 126.95, 124.54, 119.00, 77.58, 77.16, 76.74, 39.13. The obtained spectra match previous reports.[23]



dimethyl 4-(2-aminophenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (2aj): Following the general procedure, using dimethyl 2,6-dimethyl-4-(2-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (345 mg, 1 mmol). Yield: 292 mg (93 %) ^{1}H NMR (300 MHz, Chloroform-d) δ 12.07 (s, 1H), 8.98 (s, 1H), 7.47 – 7.39 (m, 2H), 7.34 (ddd, J = 8.4, 6.9, 1.1 Hz, 1H), 7.16 (ddd, J = 8.0, 6.9, 1.1 Hz, 1H), 3.88 (s, 3H), 3.56 (s, 3H), 2.82 (s, 1H), 2.23 (s, 3H), 2.20 (s, 3H). ^{13}C NMR (75 MHz, CDCl3) δ 153.69, 135.79, 128.24, 125.89, 124.90, 121.47, 121.08, 112.16, 100.94, 77.59, 77.16, 76.74, 52.14, 51.81.



2. SEM Analysis

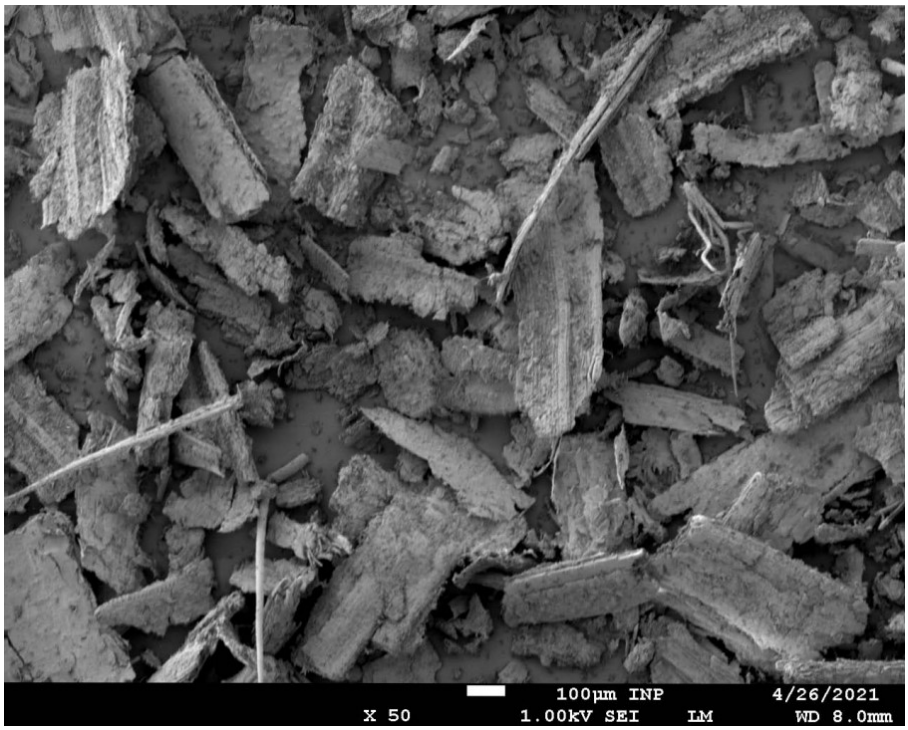


Figure S1: SEM image of raw RH at 50 times magnification.

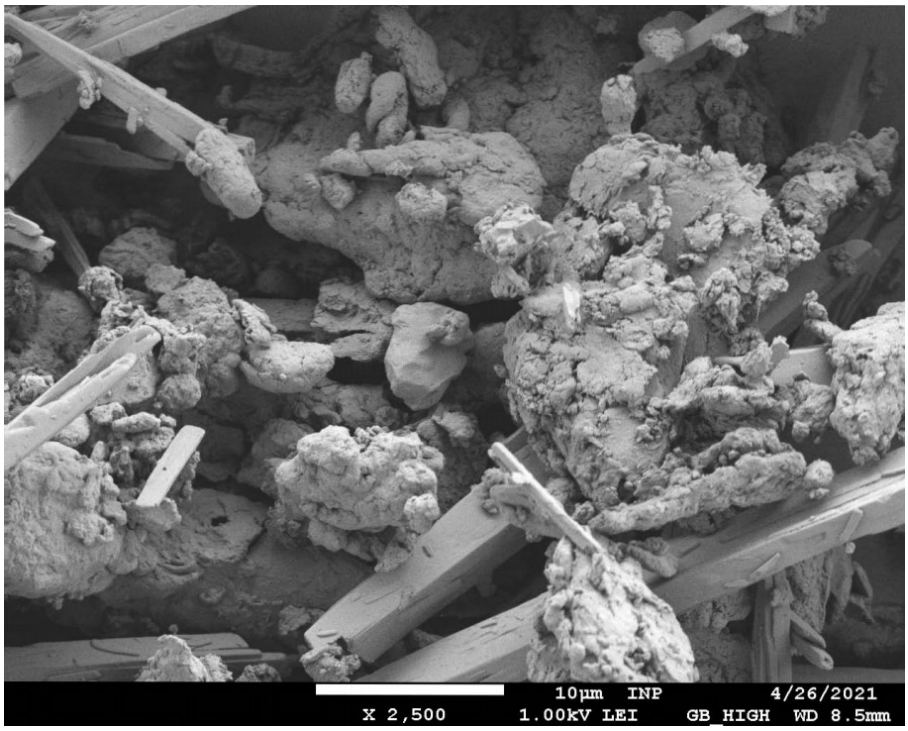


Figure S2: SEM image of washed and milled RH impregnated with Co1 at 2500 times magnification.

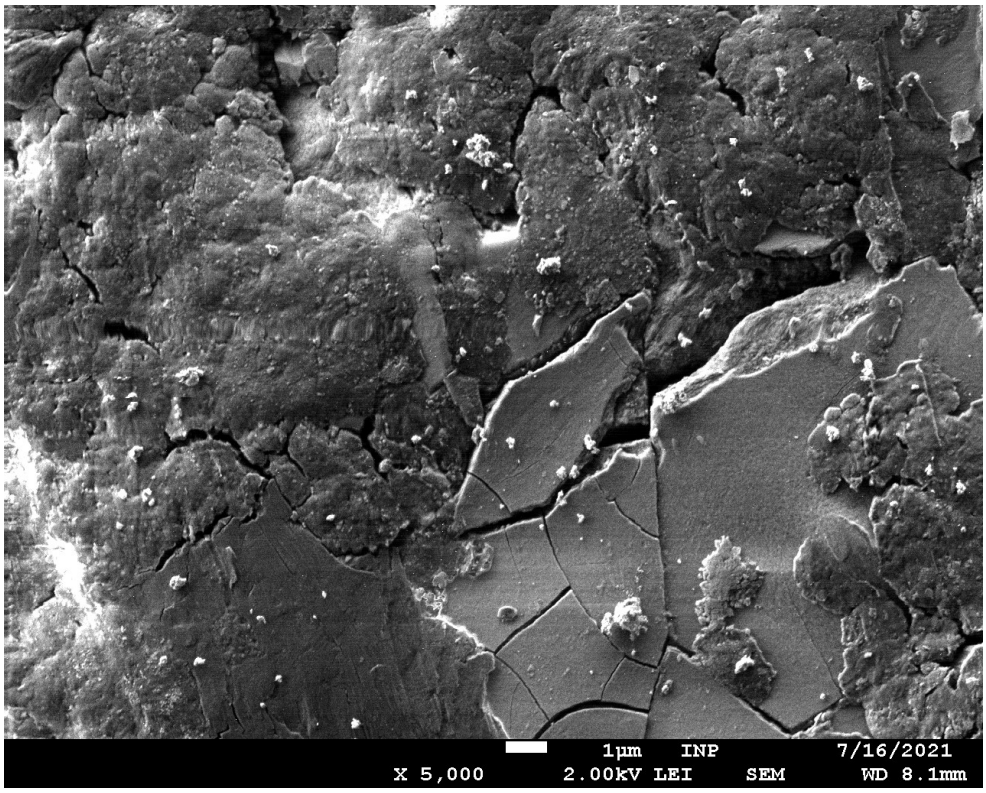


Figure S3: SEM image of washed and milled RH impregnated with Co1 at 5000 times magnification.

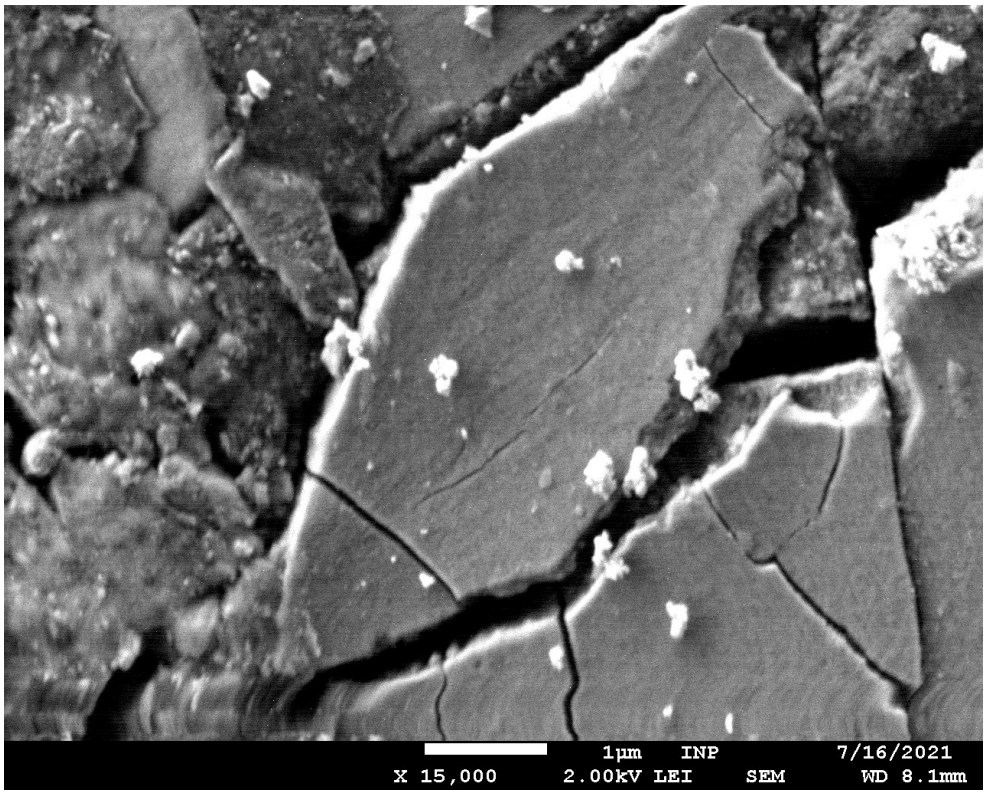


Figure S4: SEM image of washed and milled RH impregnated with Co1 at 15000 times magnification.

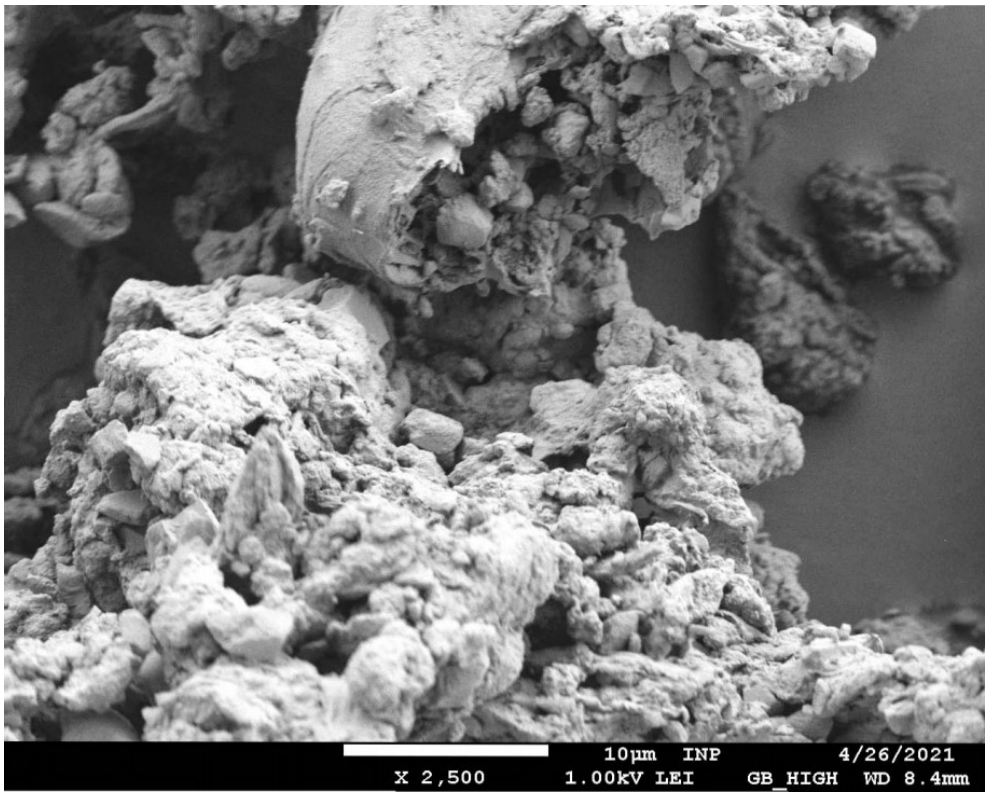


Figure S5: SEM image of pyrolyzed RH at 2500 times magnification.

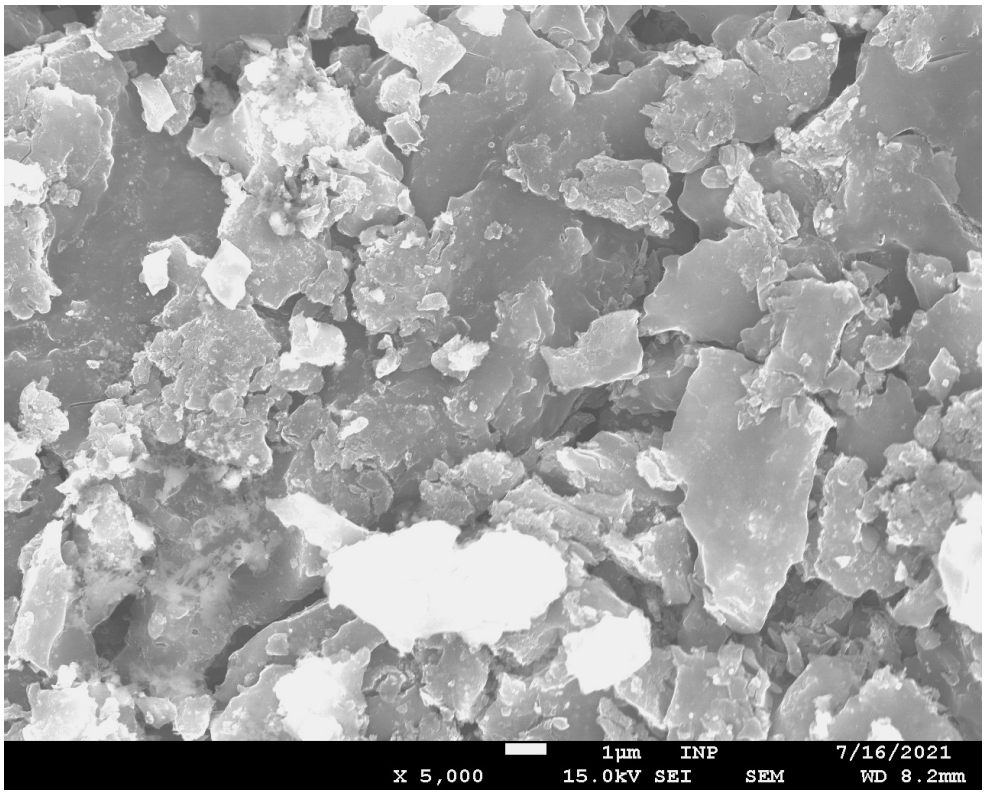


Figure S6: SEM image of washed and milled RH impregnated with Co1 at 5000 times magnification.

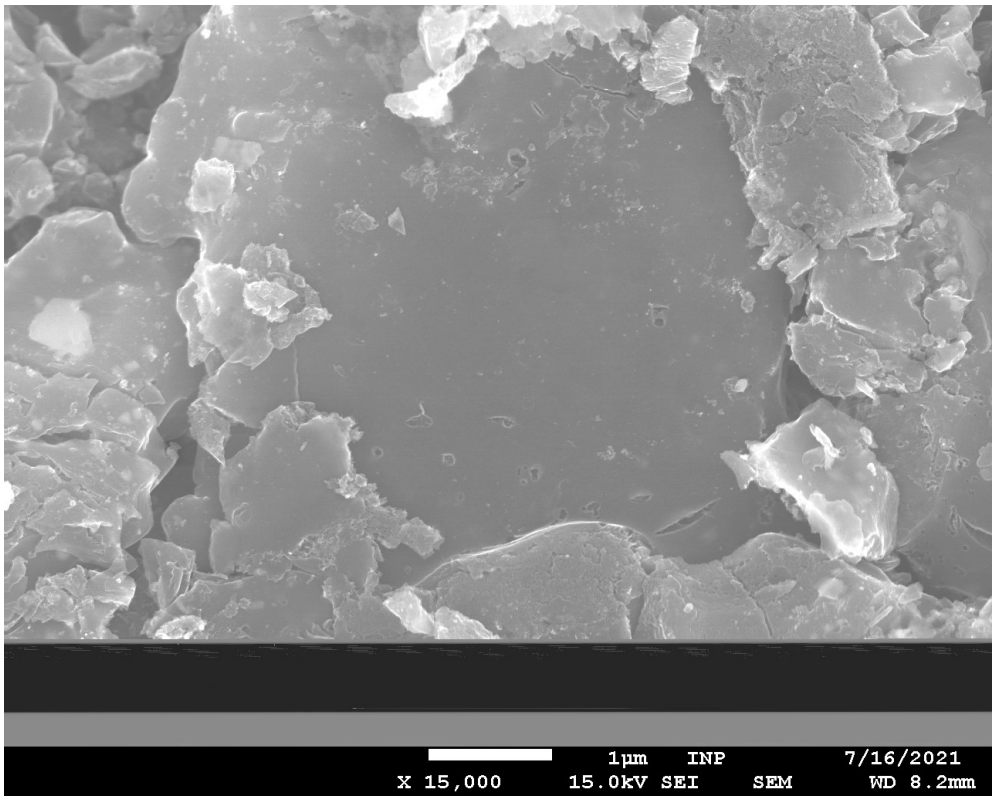


Figure S7: SEM image of washed and milled RH impregnated with Co1 at 15000 times magnification.

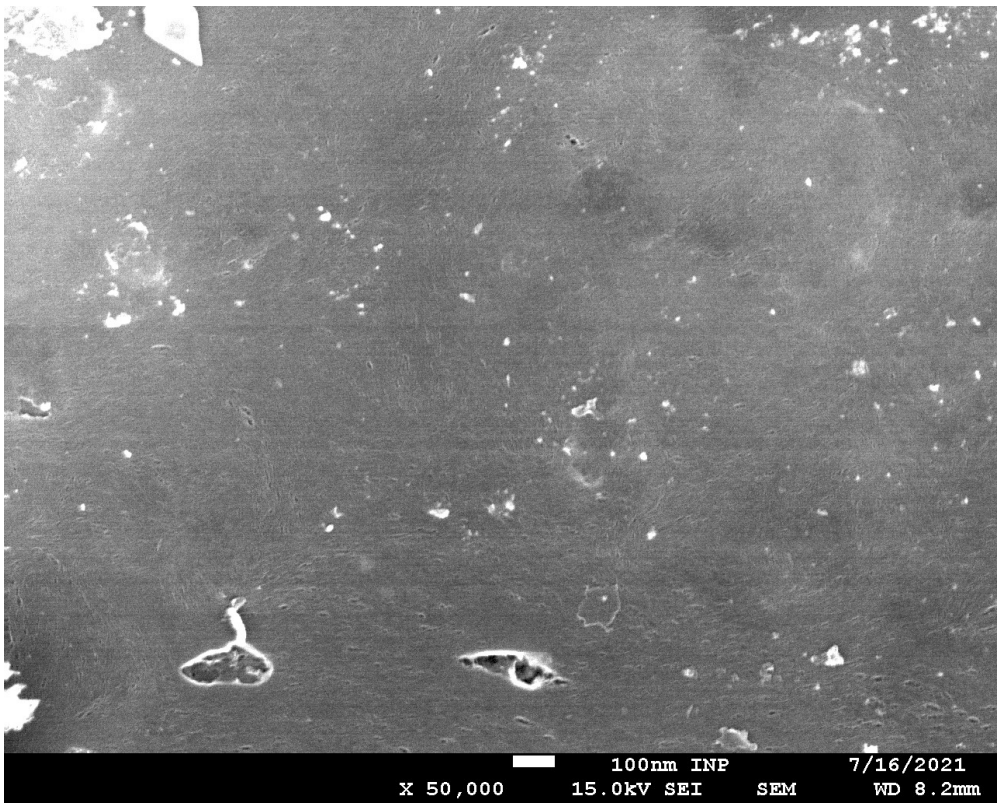


Figure S8: SEM image of washed and milled RH impregnated with Co1 at 50000 times magnification.

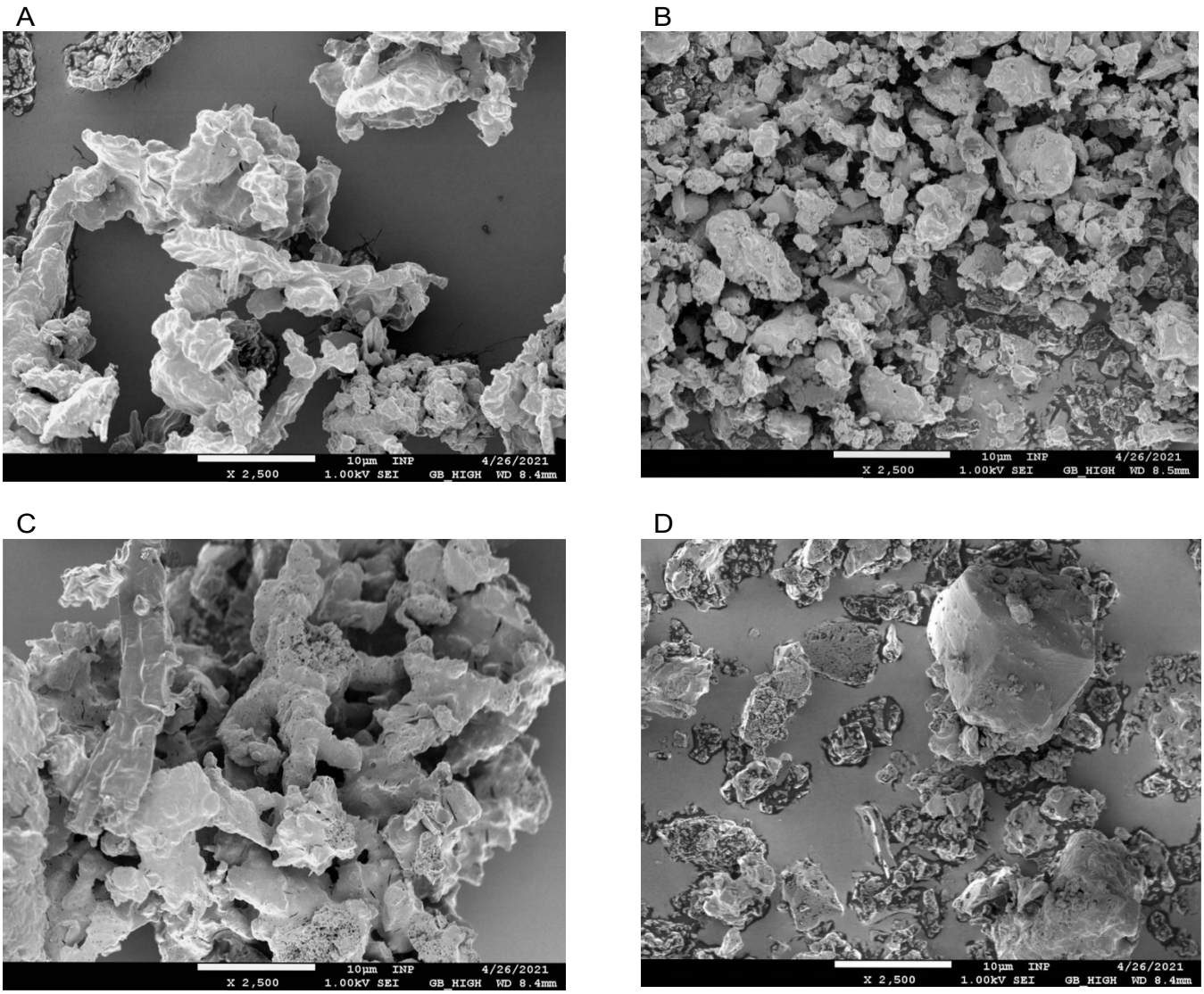


Figure S9: SEM image of Co1@RH before (A) and after (B) recycling experiments as well as Co1@RH-E1 before (C) and after (B) recycling experiments at 2500 times magnification.

3. XPS and elemental analysis (AAS and ICP-OES)

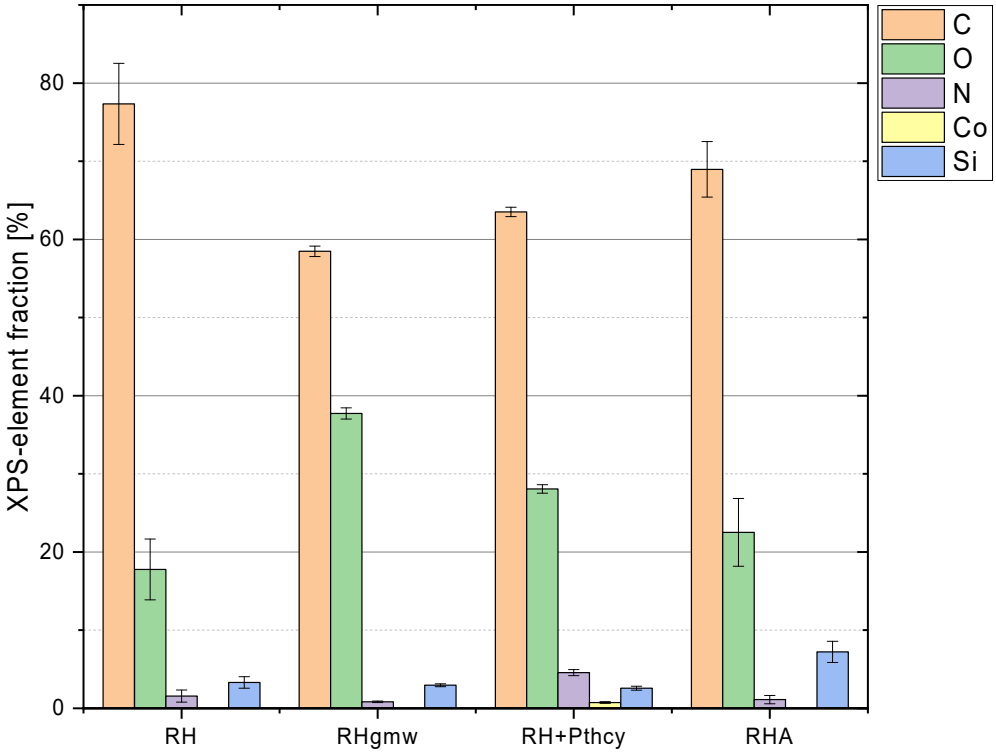


Figure S10: XPS-element fraction of raw RH.

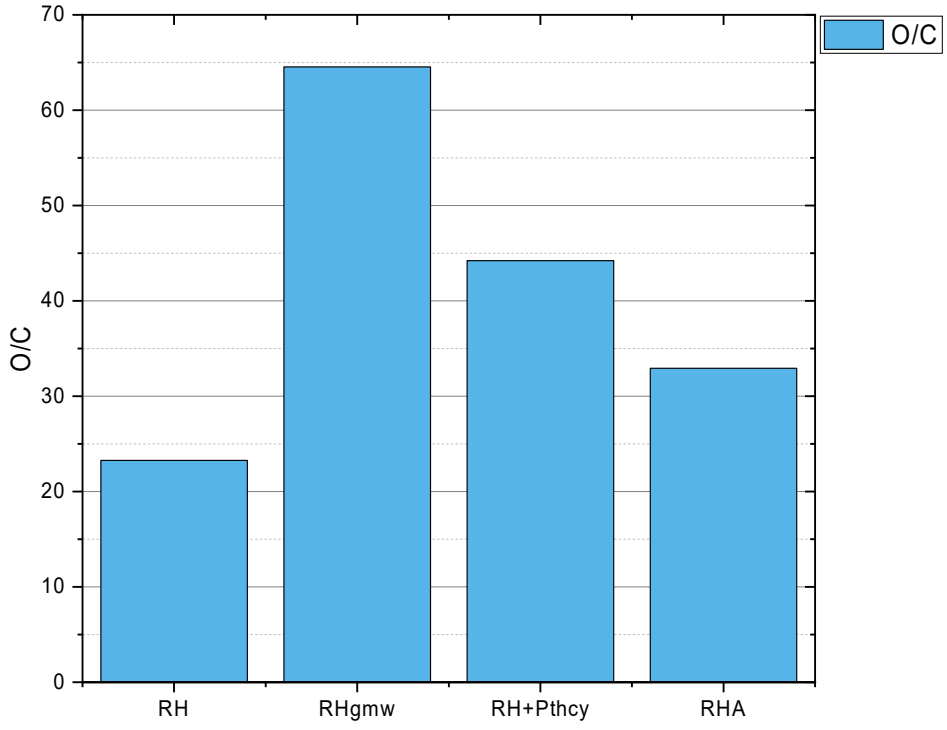


Figure S11: XPS-analysis of oxygen/carbon ratio in raw RH.

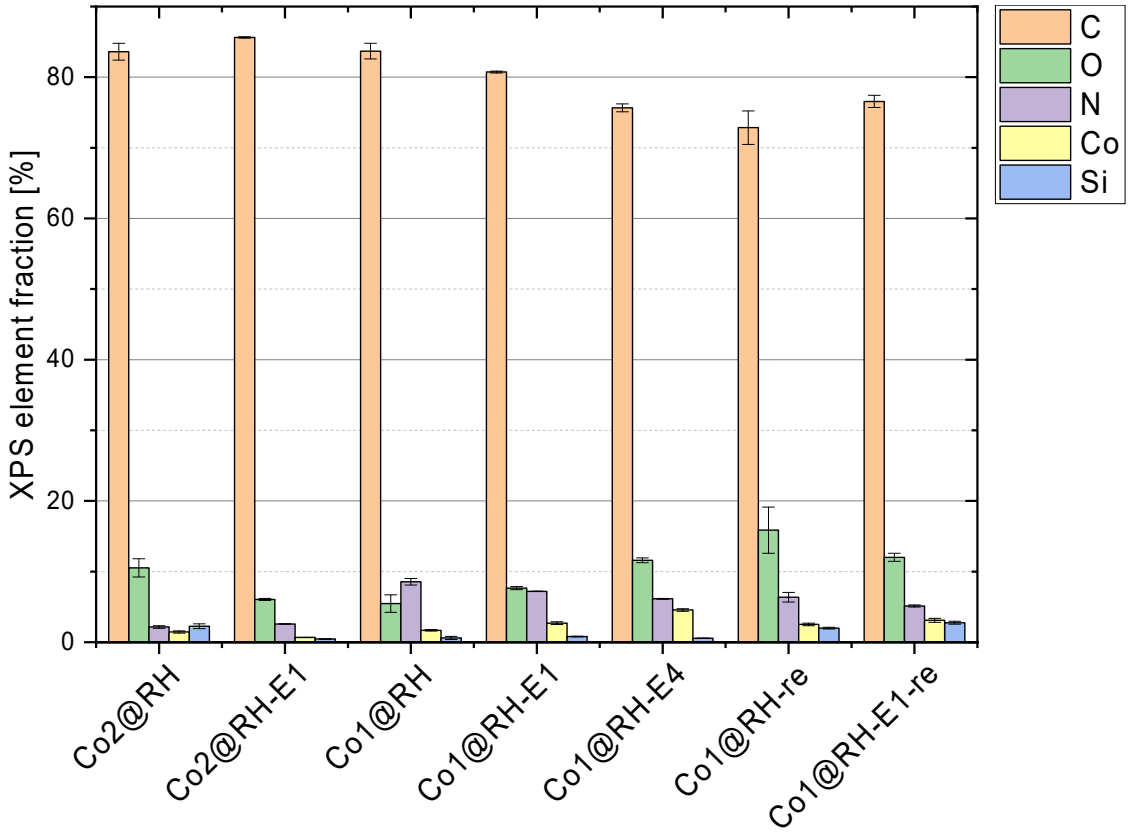


Figure S12: XPS-element fraction of different RH-derived catalysts.

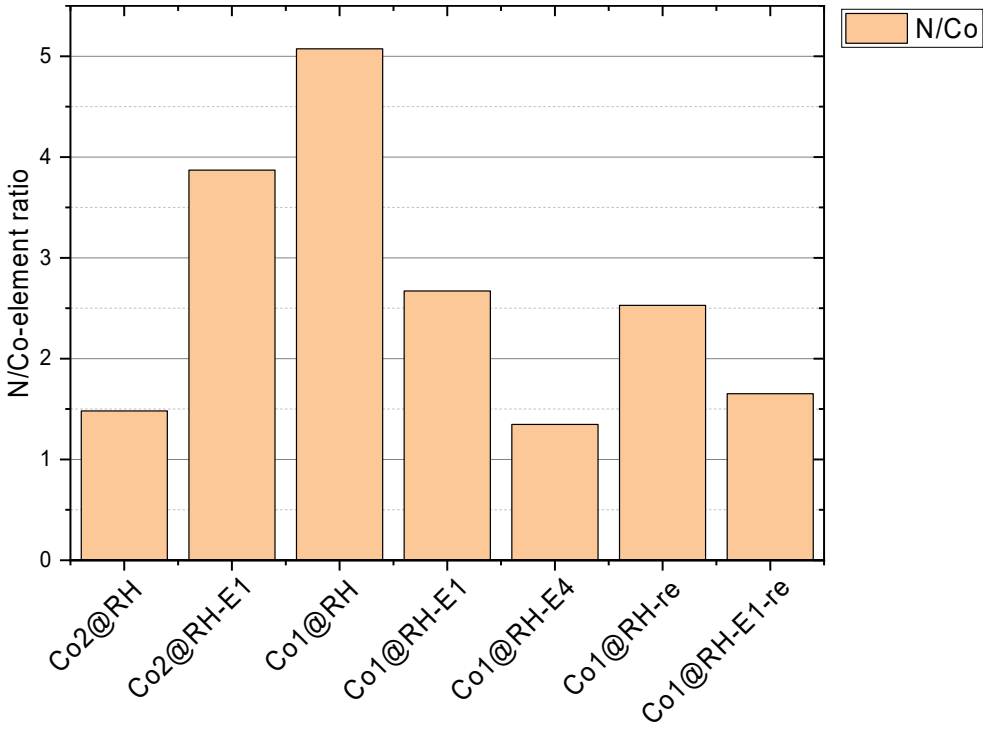


Figure S13: XPS-analysis of nitrogen/cobalt ratio in RH-derived catalysts.

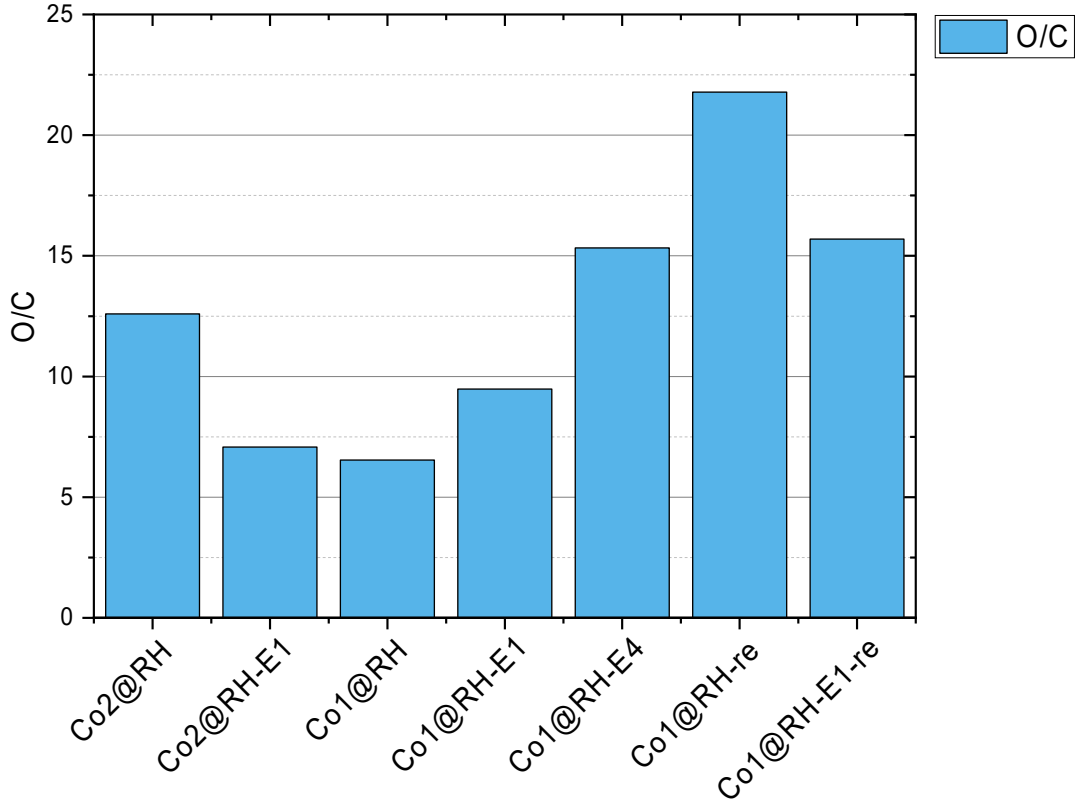


Figure S14: XPS-analysis of oxygen/carbon ratio in RH-derived catalysts.

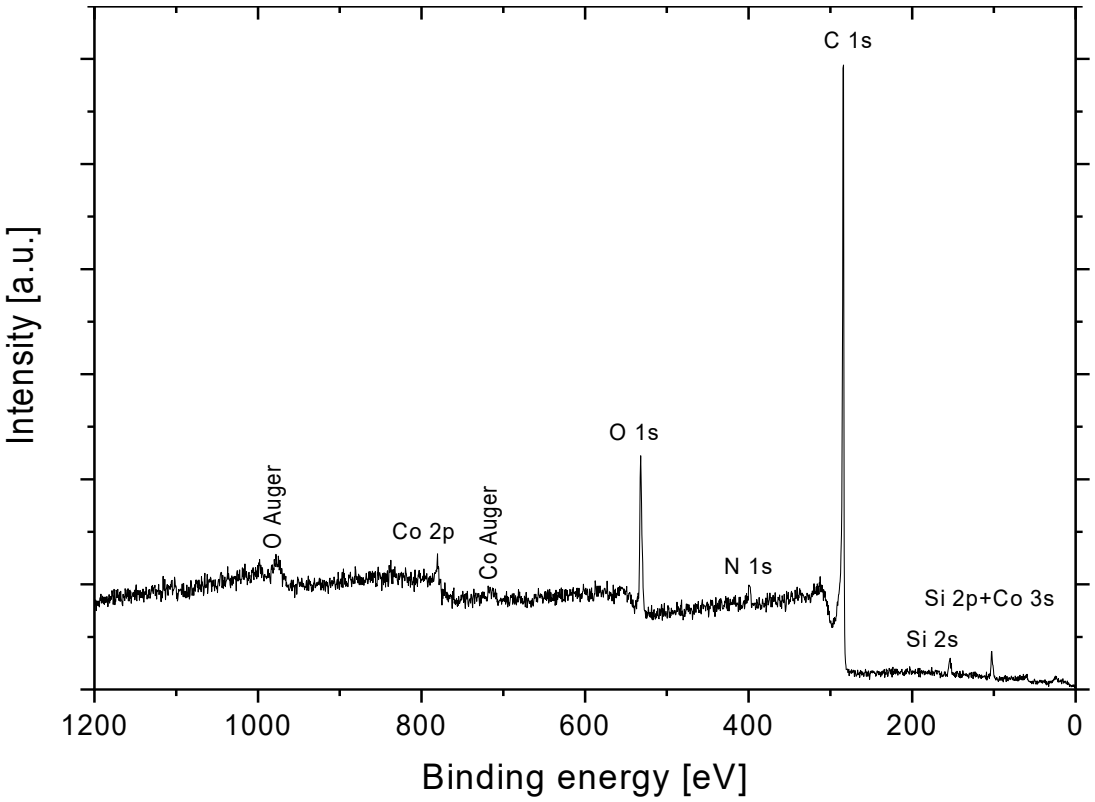


Figure S15: XPS survey scan of Co2@RH.

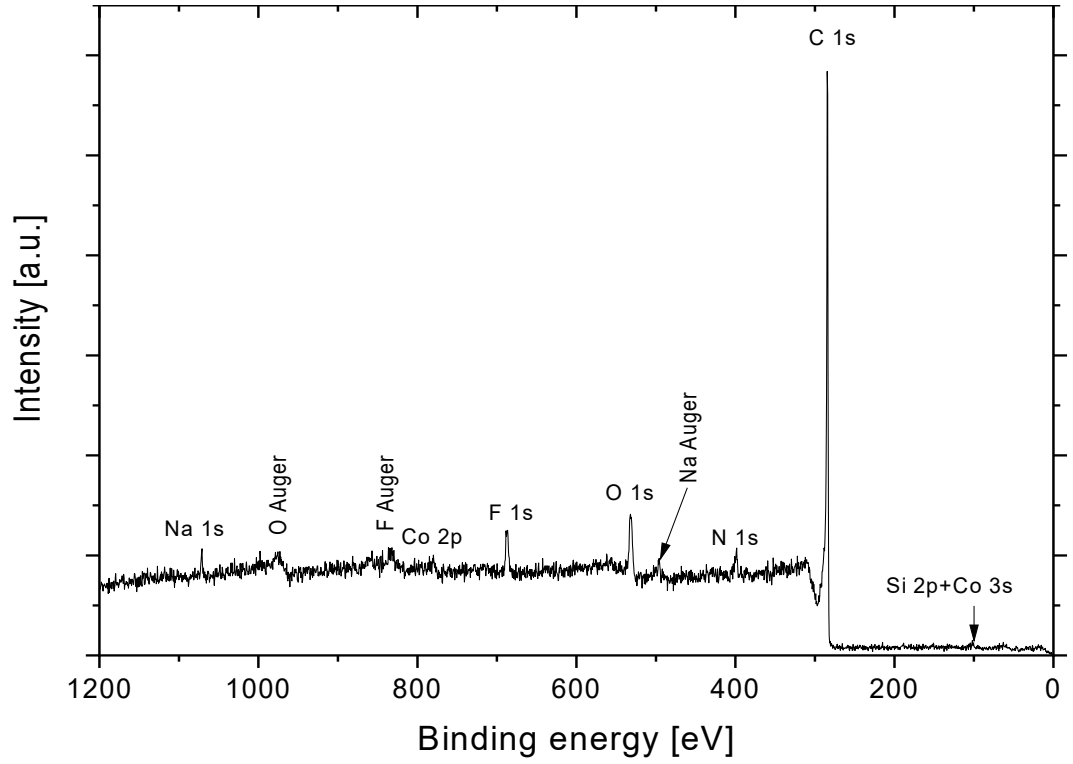


Figure S16: XPS survey scan of Co2@RH-E1.

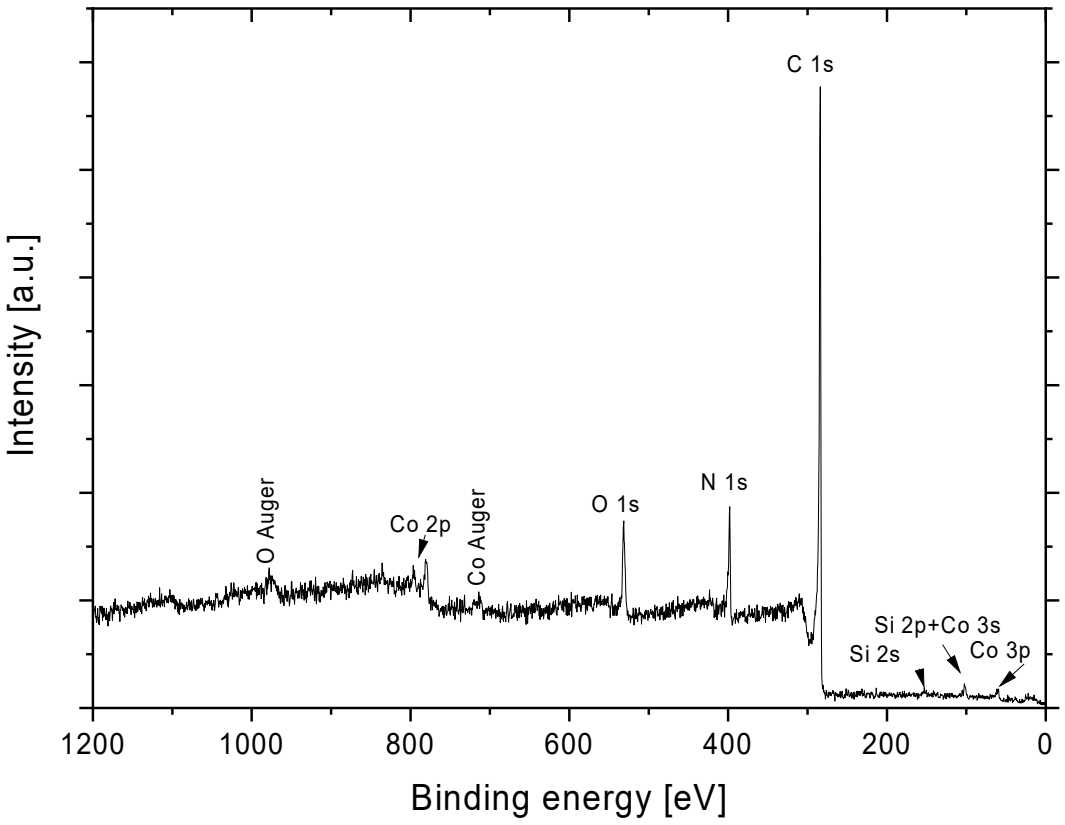


Figure S17: XPS survey scan of Co1@RH.

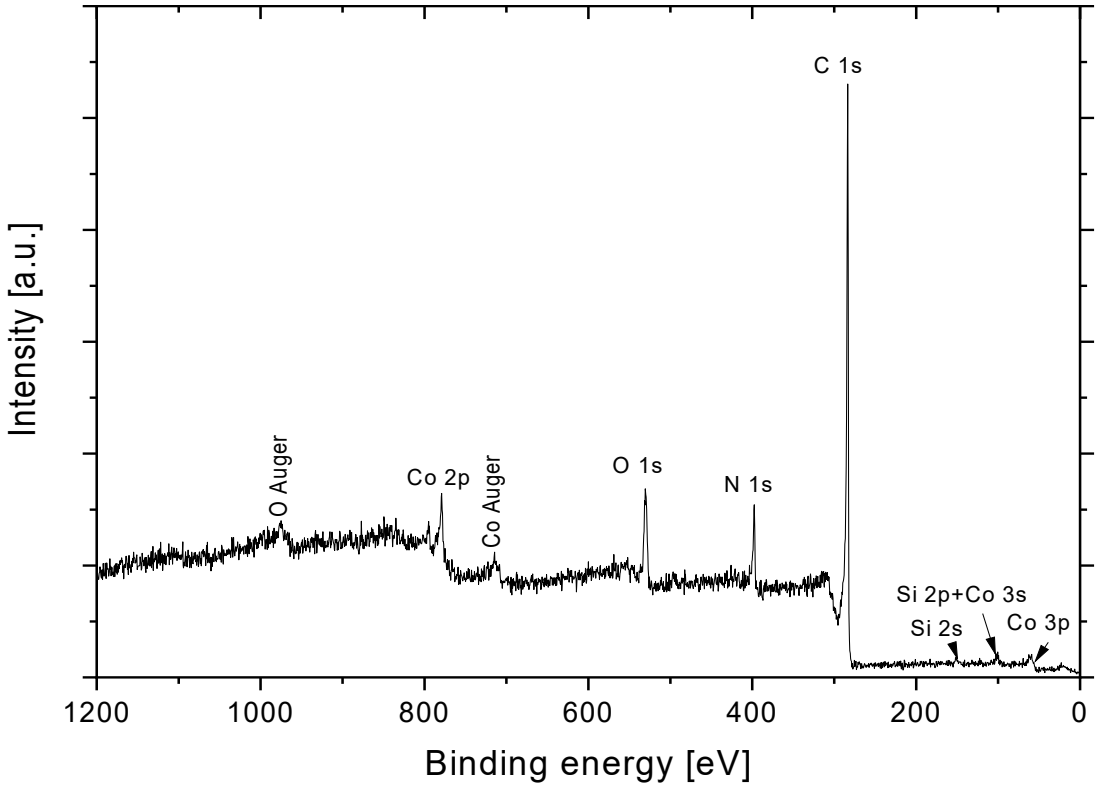


Figure S18: XPS survey scan of Co1@RH-E1.

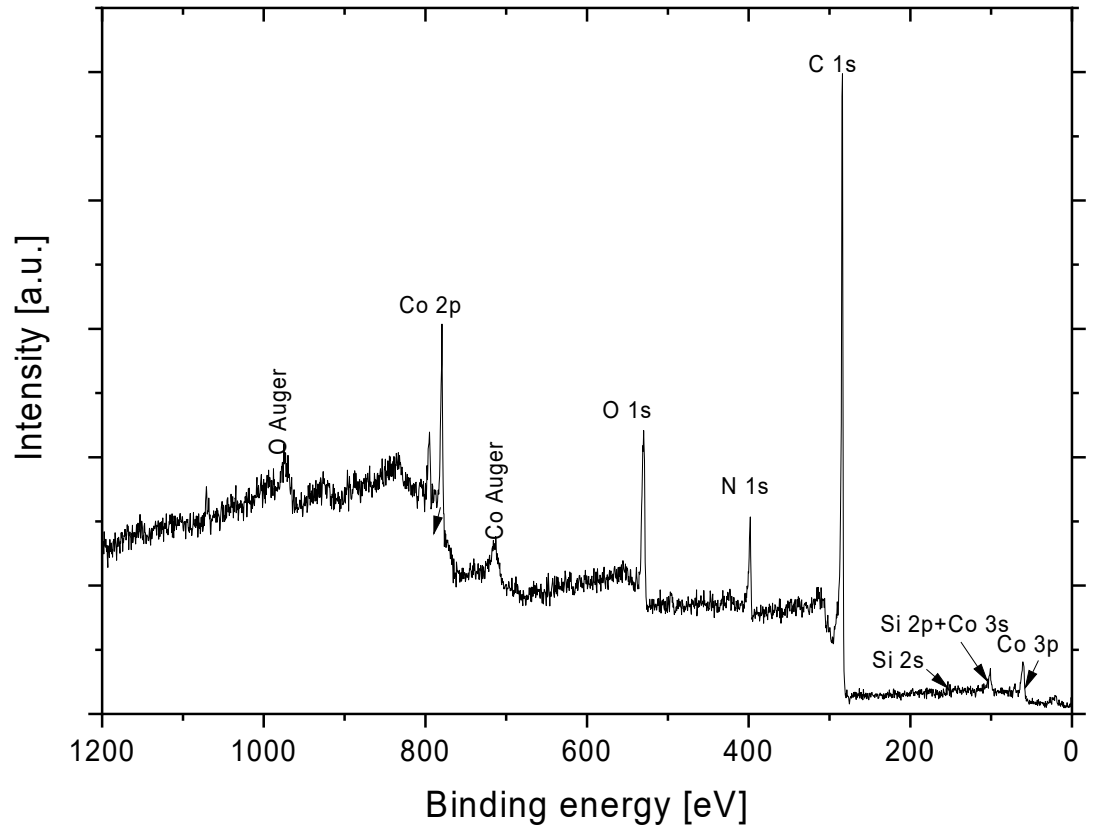


Figure S19: XPS survey scan of Co1@RH-E4.

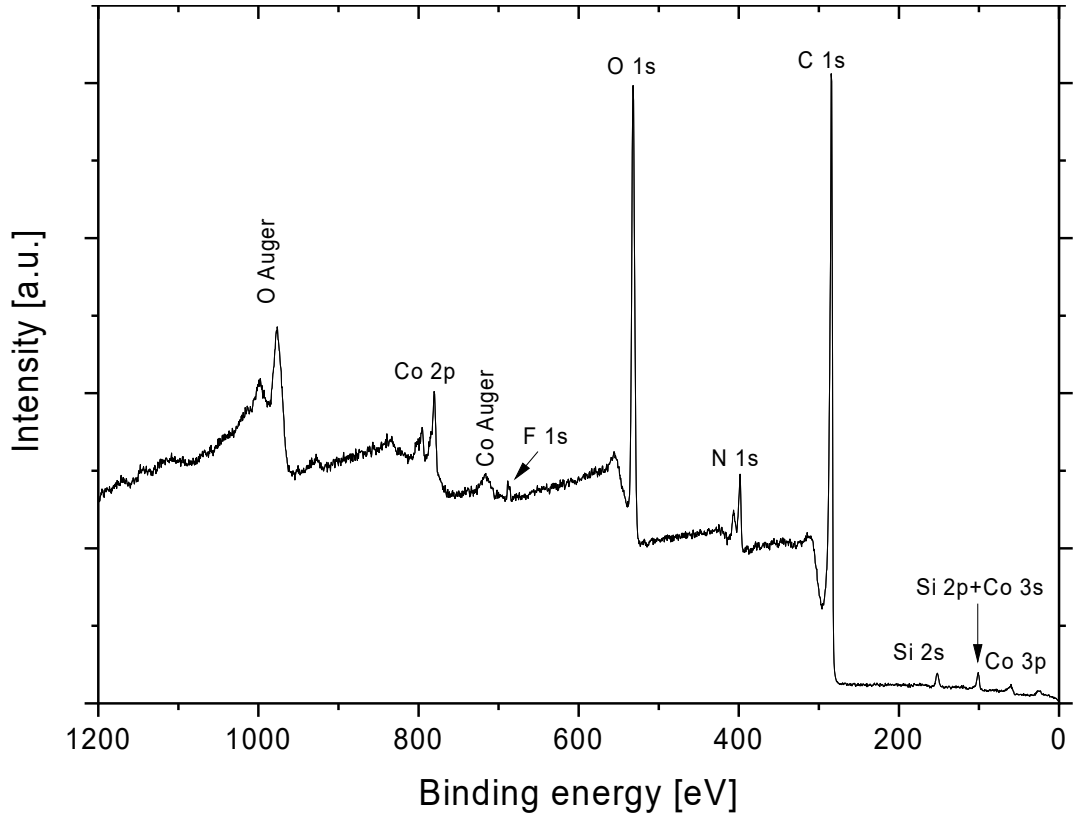


Figure S20: XPS survey scan of Co1@RH after 5 recycling runs.

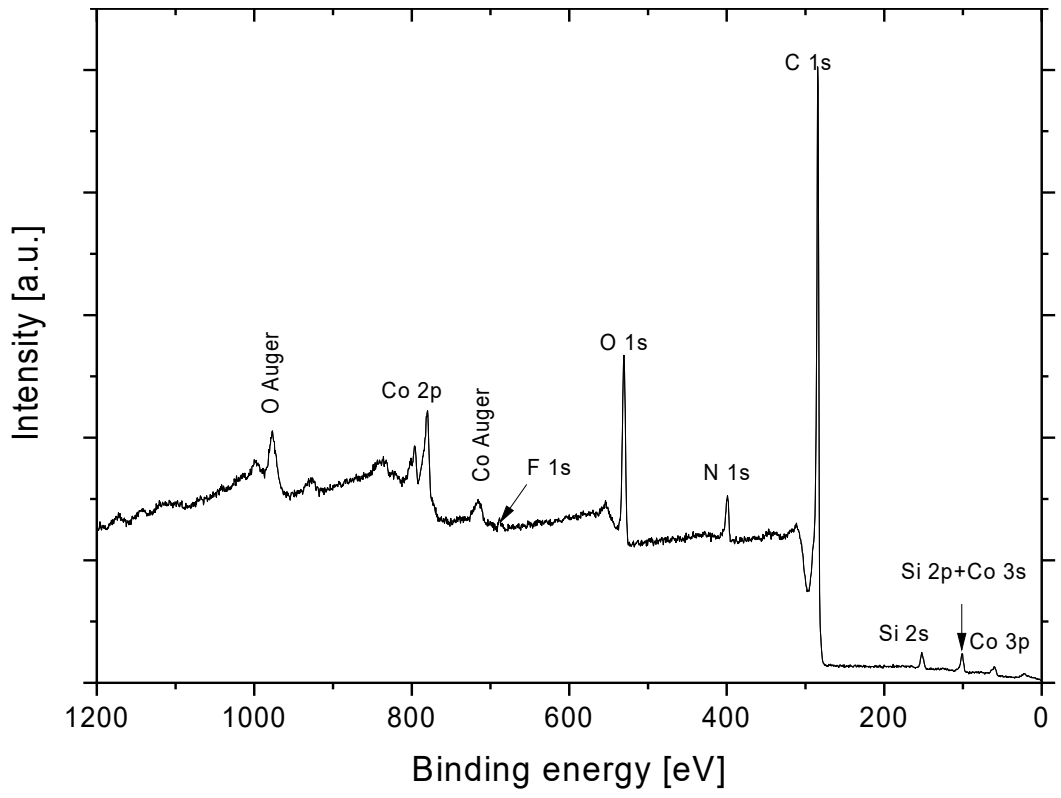


Figure S21: XPS survey scan of Co1@RH-E1 after 5 recycling runs.

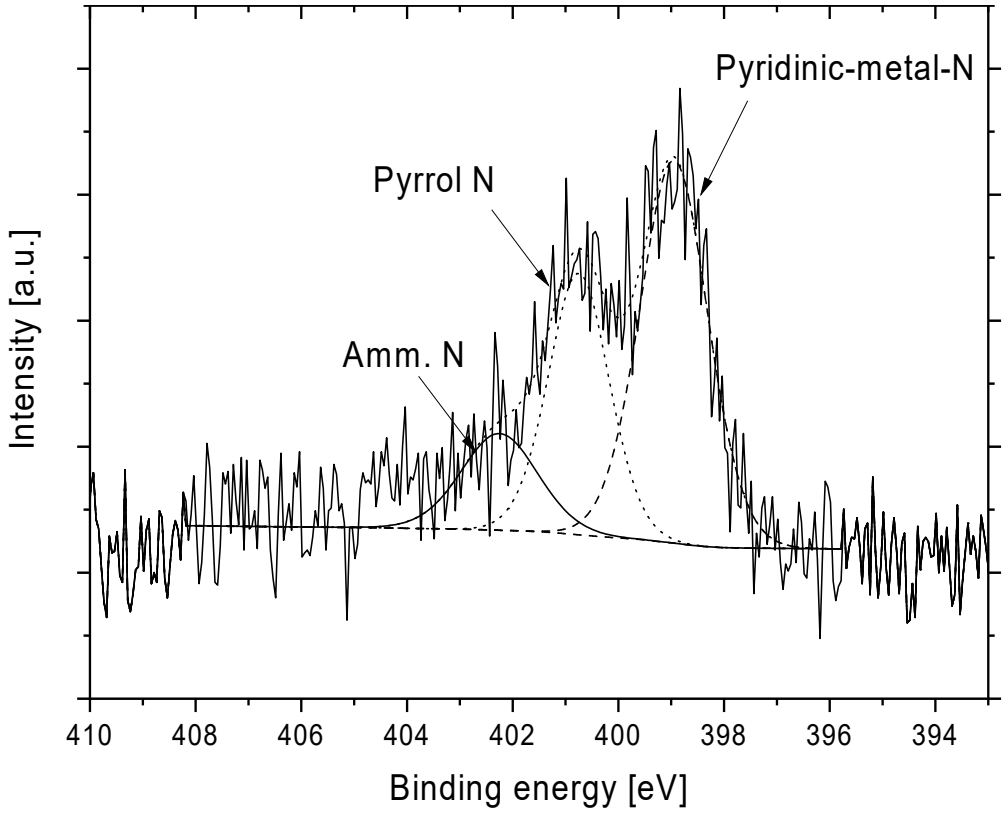


Figure S22: XPS analysis of N1s signal in Co2@RH.

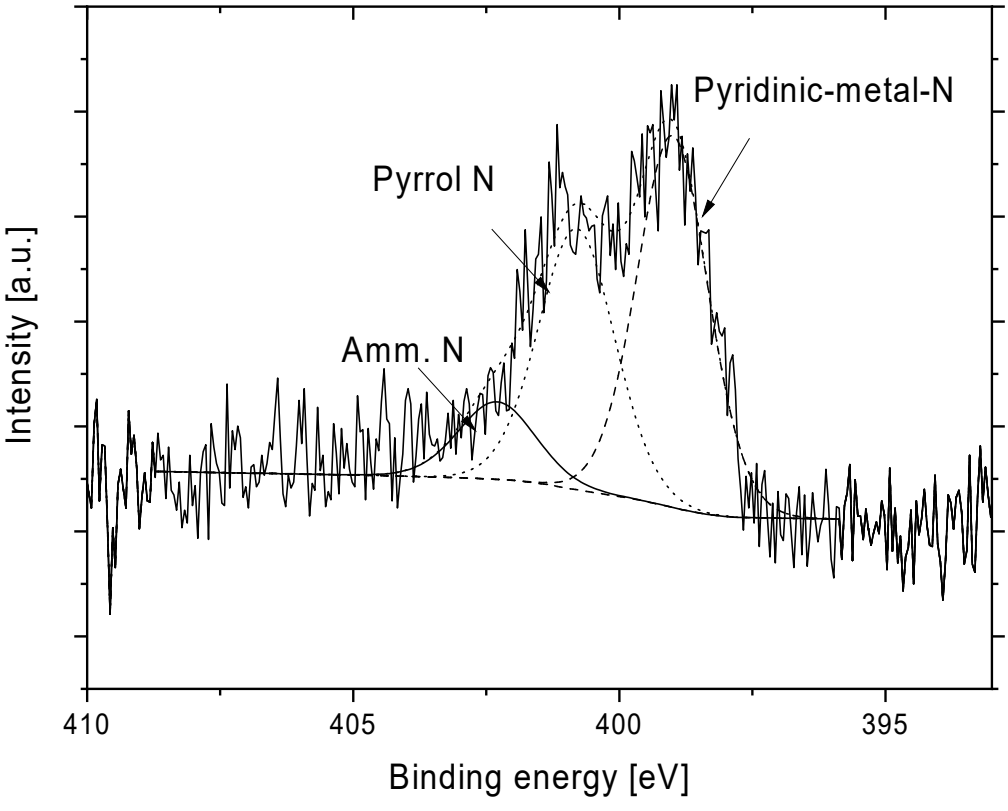


Figure S23: XPS analysis of N1s signal in Co2@RH-E1.

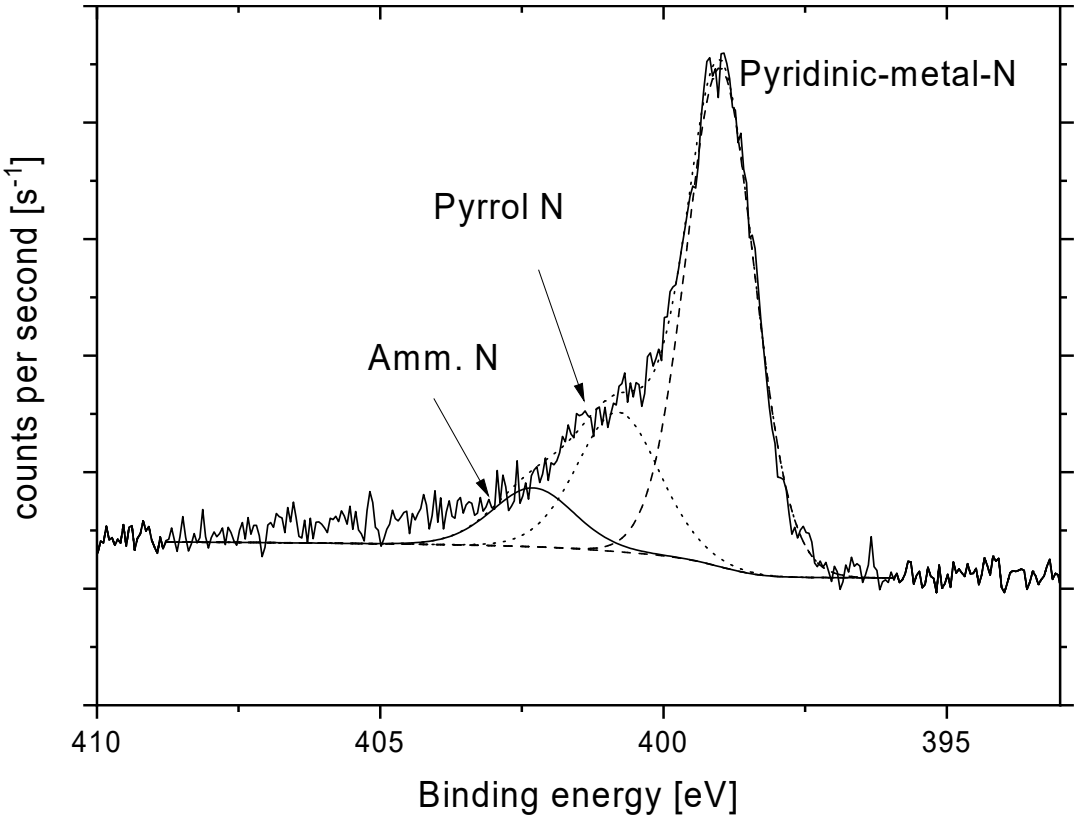


Figure S24: XPS analysis of N1s signal in Co1@RH.

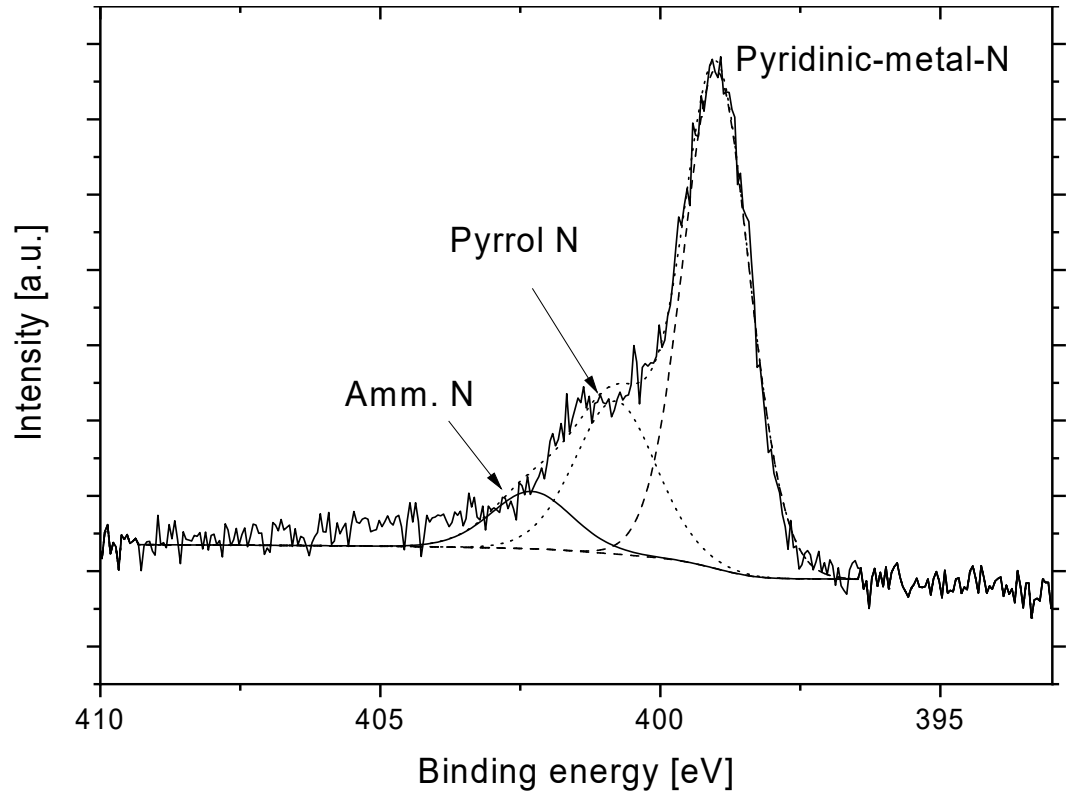


Figure S25: XPS analysis of N1s signal in Co1@RH-E1.

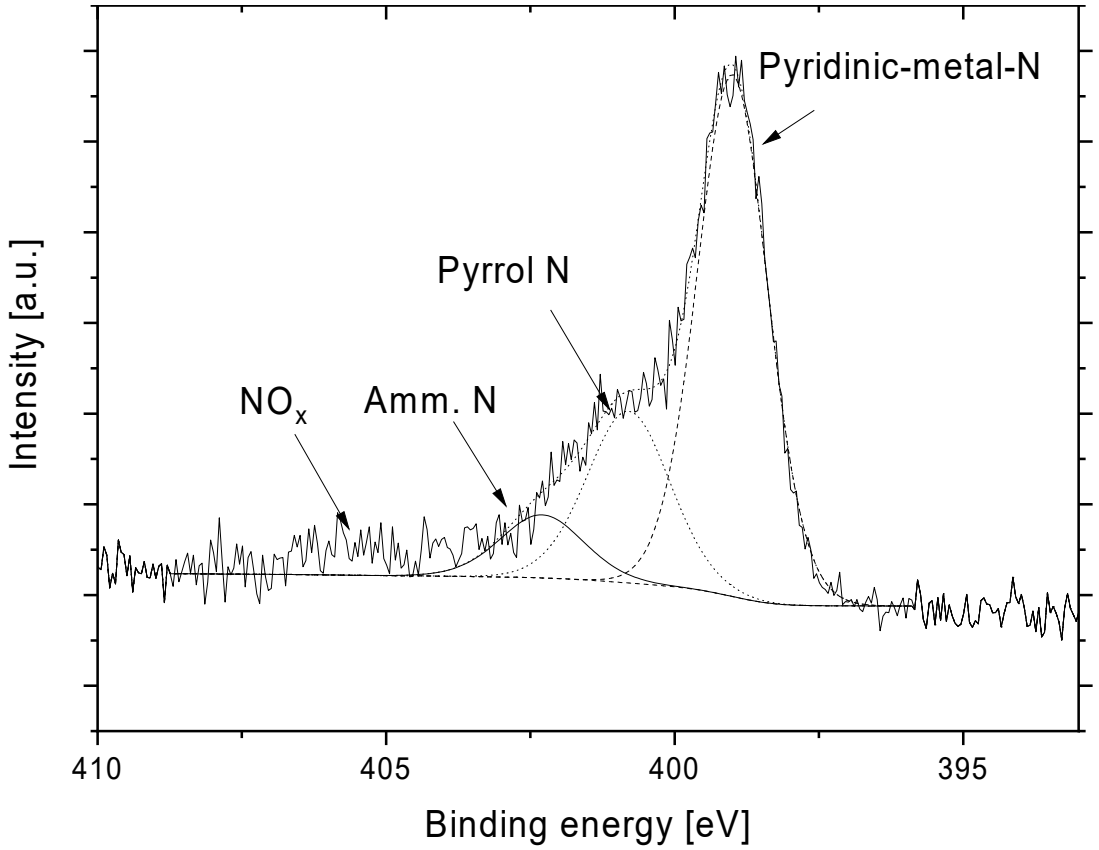


Figure S26: XPS analysis of N1s signal in Co1@RH-E4.

Table S1: Elemental analysis of catalysts by ICP-OES.

	Co wt-%	Si wt-%	C wt-%	H wt-%	N wt-%
Co1@RH	4.92	11.77	44.66	1.19	2.38
Co1@RH-E1	5.52	3.02	68.46	1.57	2.81
Co1@RH-E2	5.65	2.07	68.51	1.23	2.75
Co1@RH-E4	5.76	1.46	61.07	1.31	2.41
Co2@RH	7.69	9.74	48.97	0.69	1.82
Co2@RH-E1	6.74	3.71	57.70	0.75	2.72
Co3@RH	8.59	10.28	32.86	0.45	1.63
Co3@RH-E1	9.18	4.31	47.44	1.04	3.12
Co4@RH	9.32	10.25	53.25	0.76	2.26
Co4@RH-E1	7.44	5.35	63.55	1.04	2.41
Co5@RH	10.33	9.42	46.58	0.56	1.15
Co5@RH-E1	11.73	4.66	57.25	0.43	1.49

4. XRD, IR and BET experiments

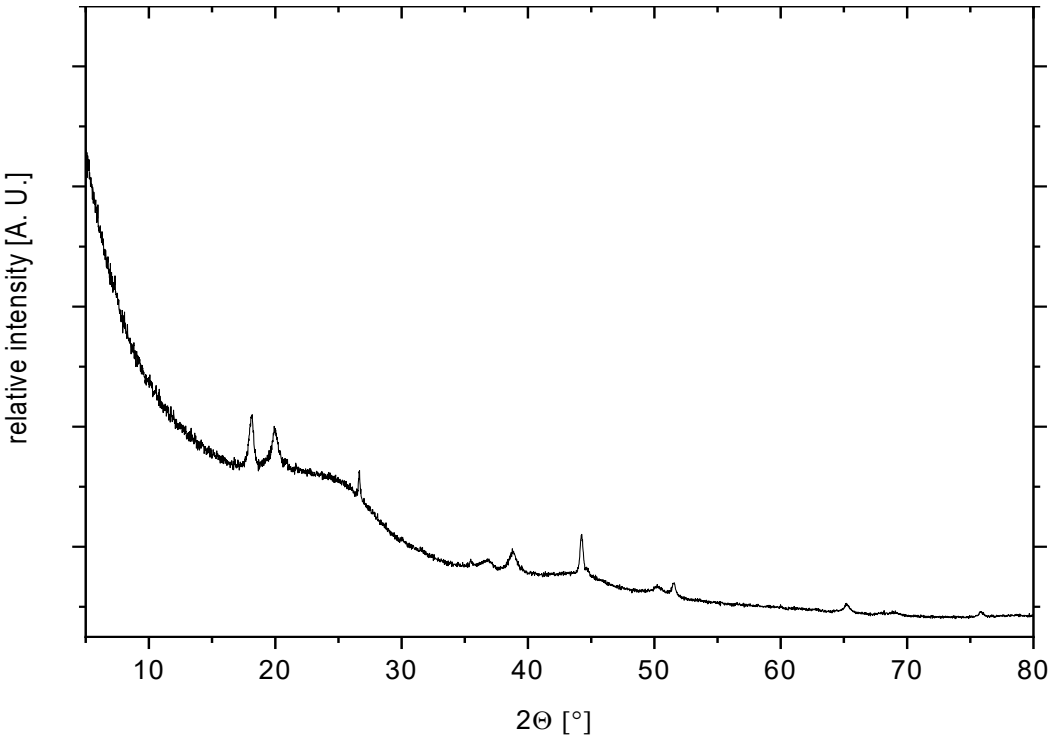


Figure S27: XRD pattern of Co1@RH-E2.

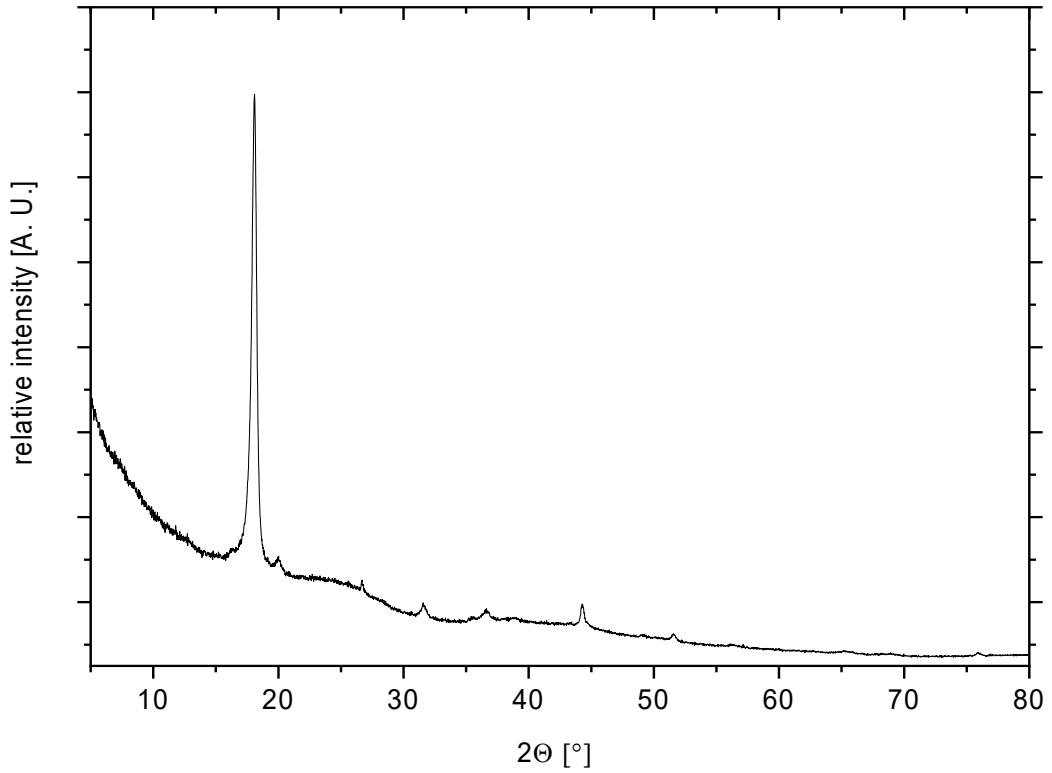


Figure S28: XRD pattern of Co1@RH-E4.

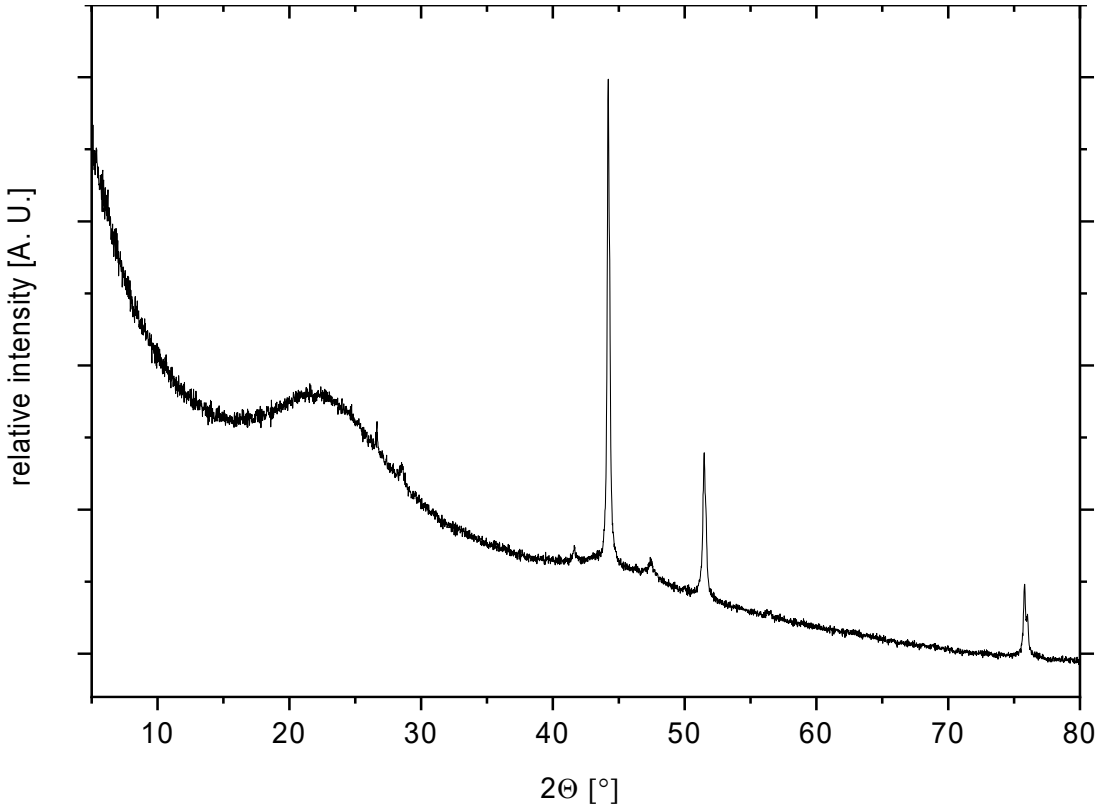


Figure S29: XRD pattern of Co2@RH.

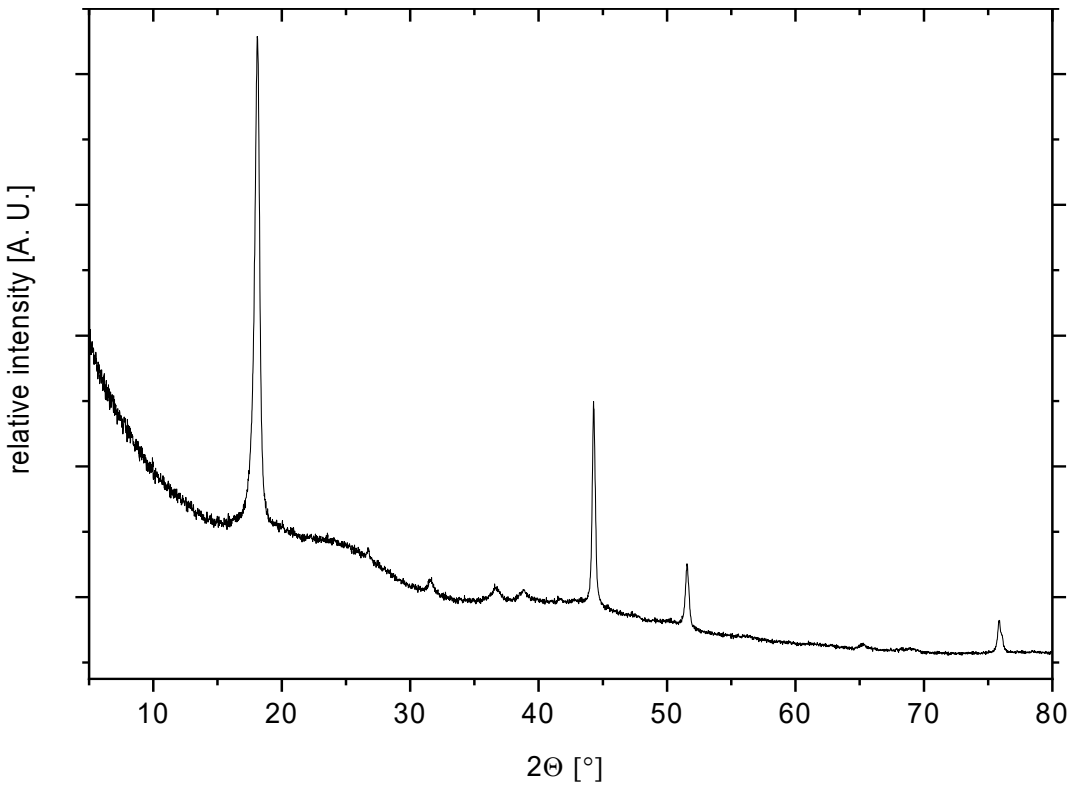


Figure S30: XRD pattern of Co2@RH-E1.fresh

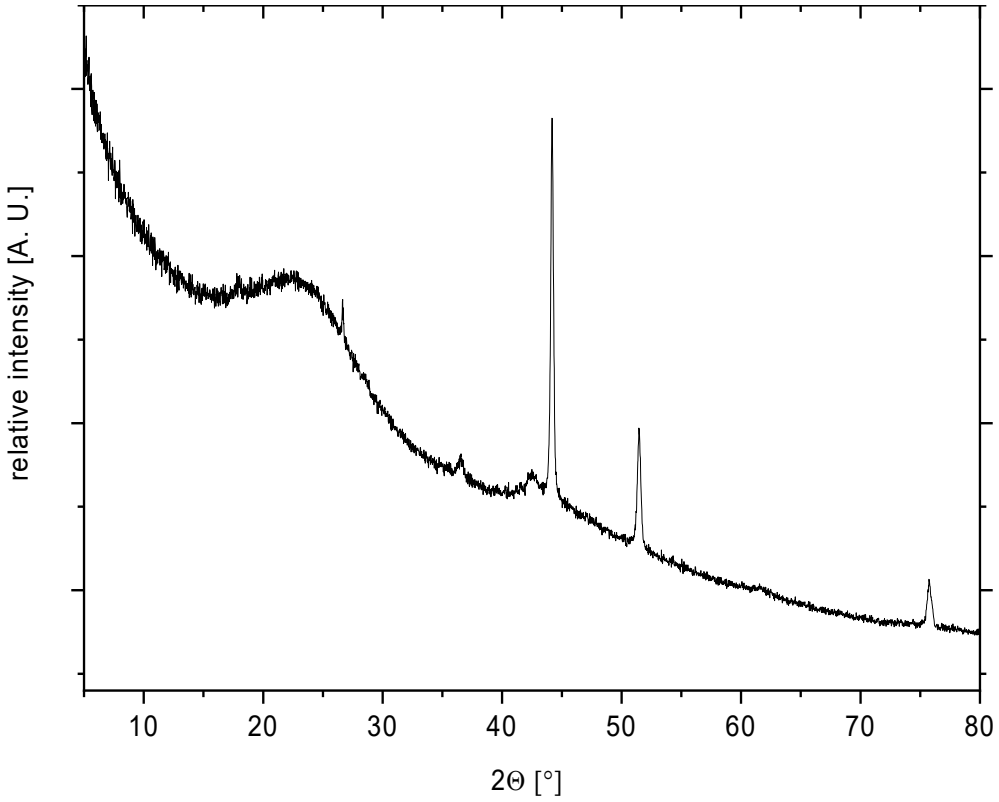


Figure S31: XRD pattern of Co2@RH-E1.washed

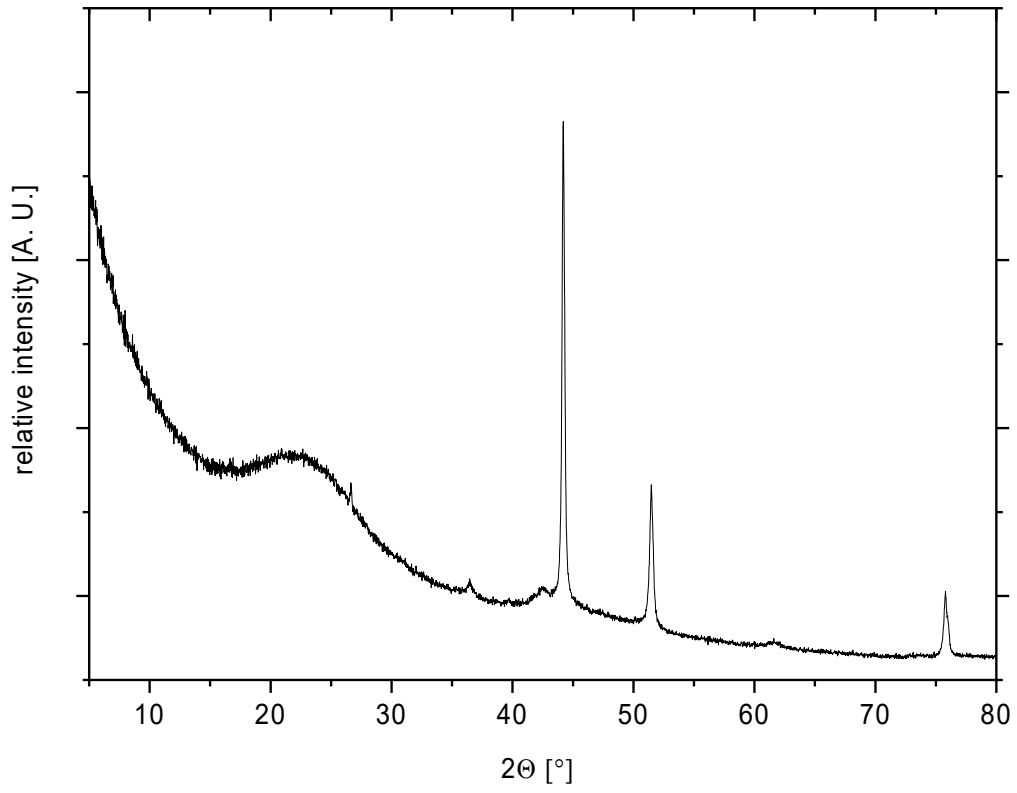


Figure S32: XRD pattern of Co3@RH.

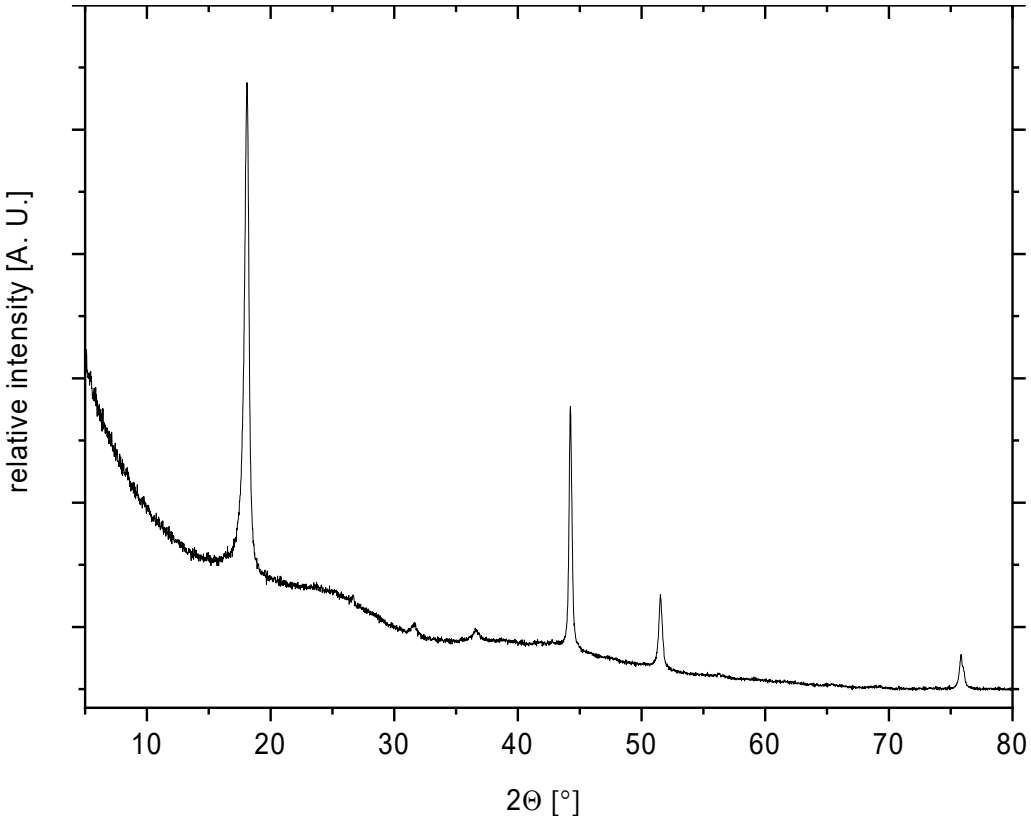


Figure S33: XRD pattern of Co3@RH-E1.

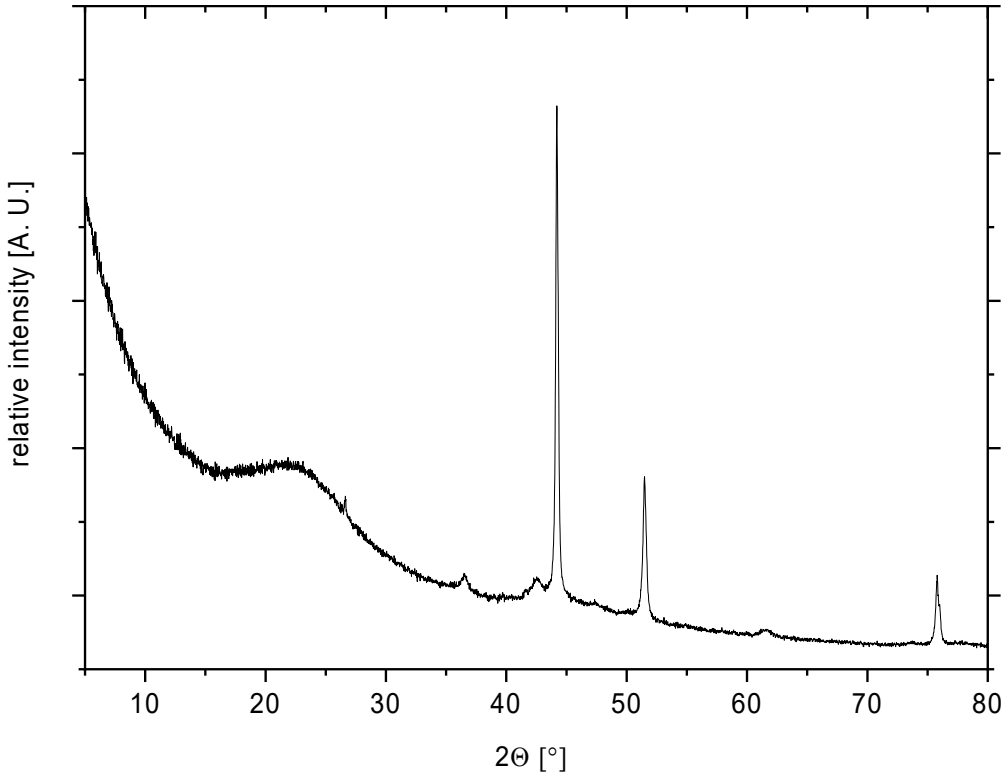


Figure S34: XRD pattern of Co4@RH.

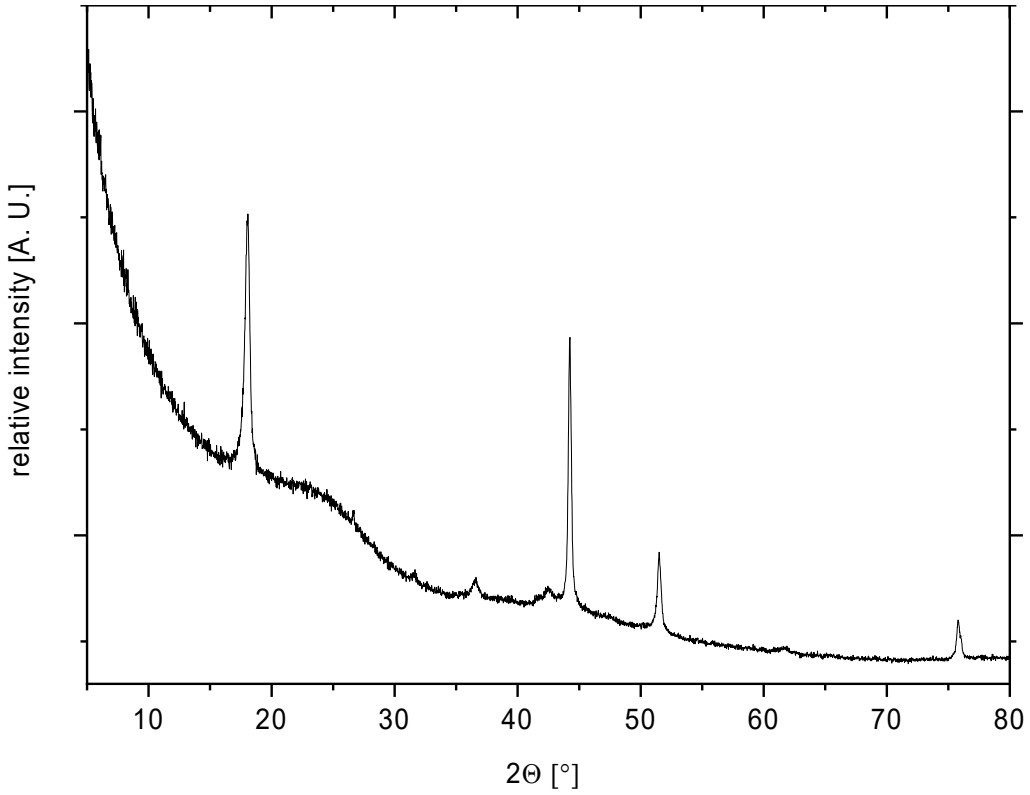


Figure S35: XRD pattern of Co4@RH-E1.

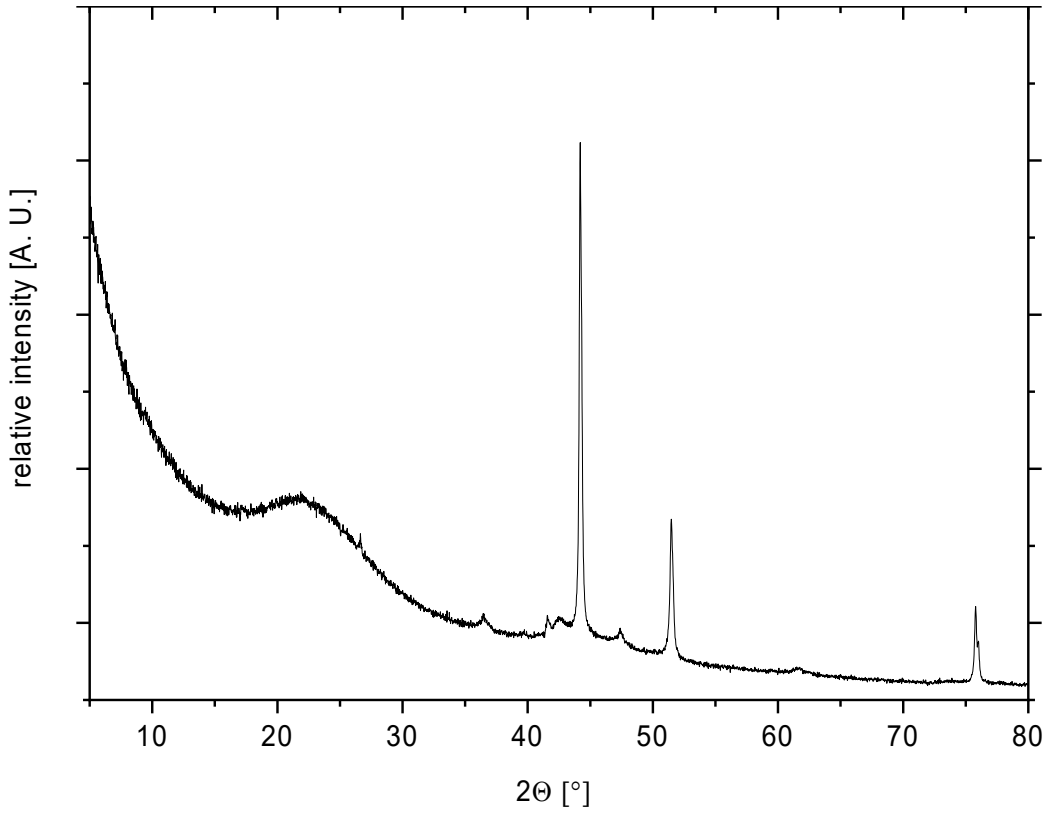


Figure S36: XRD pattern of Co5@RH.

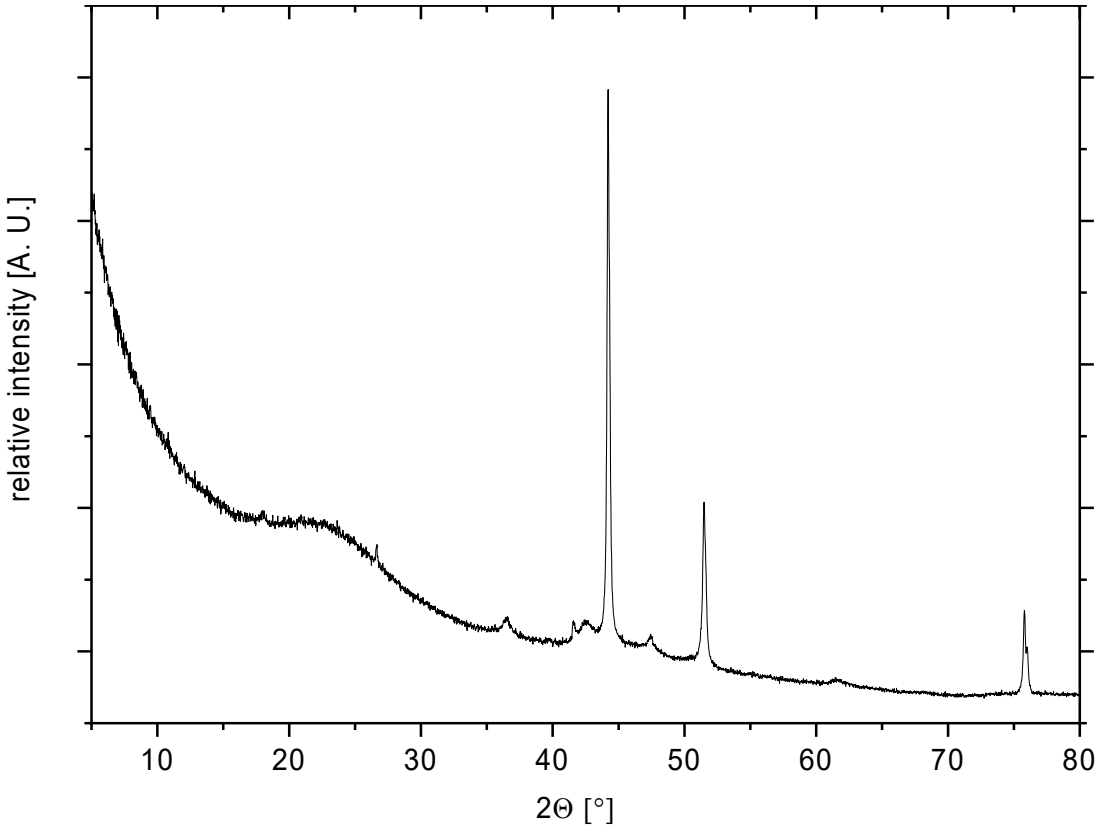


Figure S37: XRD pattern of Co5@RH-E1.

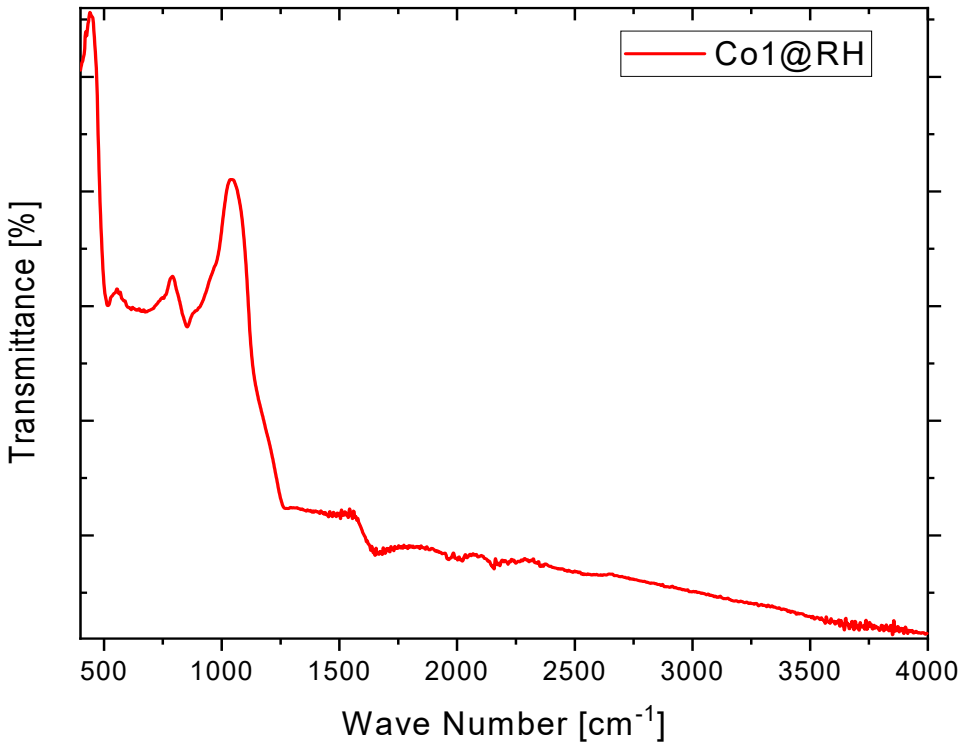


Figure S38: IR spectrum of Co1@RH.

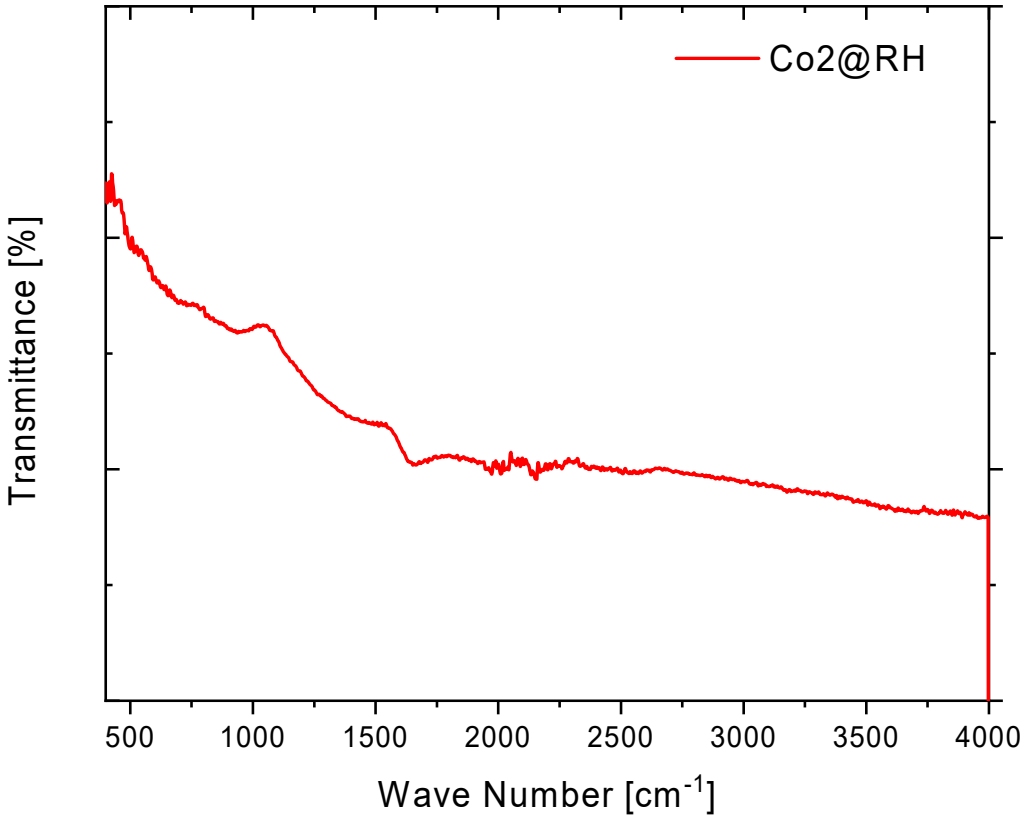


Figure S39: IR spectrum of Co2@RH.

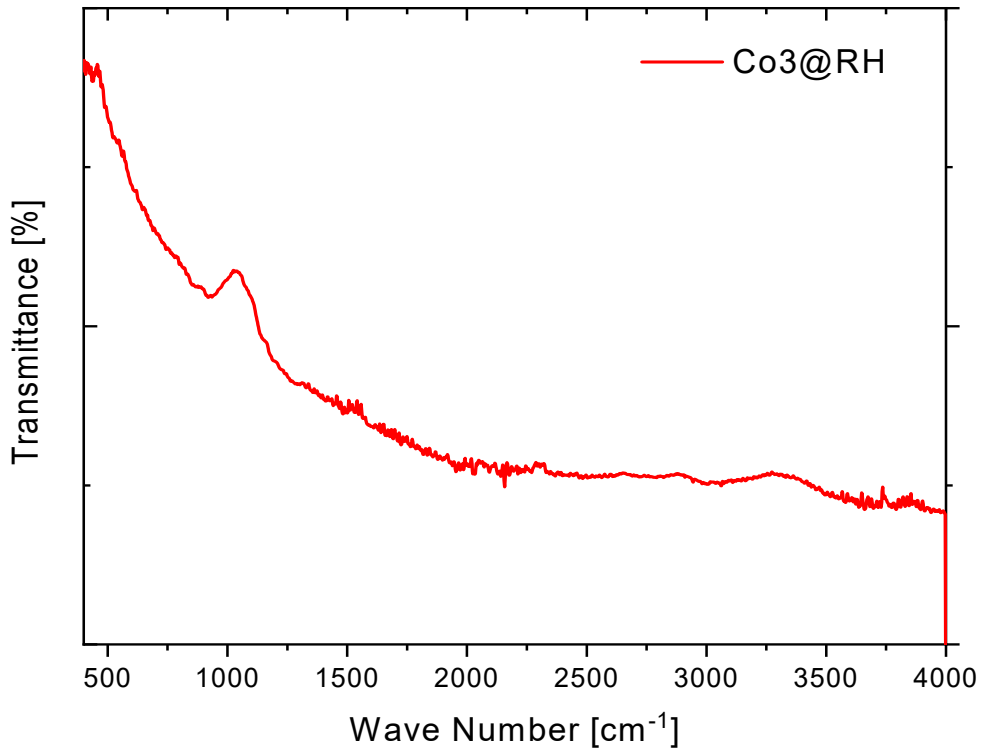


Figure S40: IR spectrum of Co3@RH.

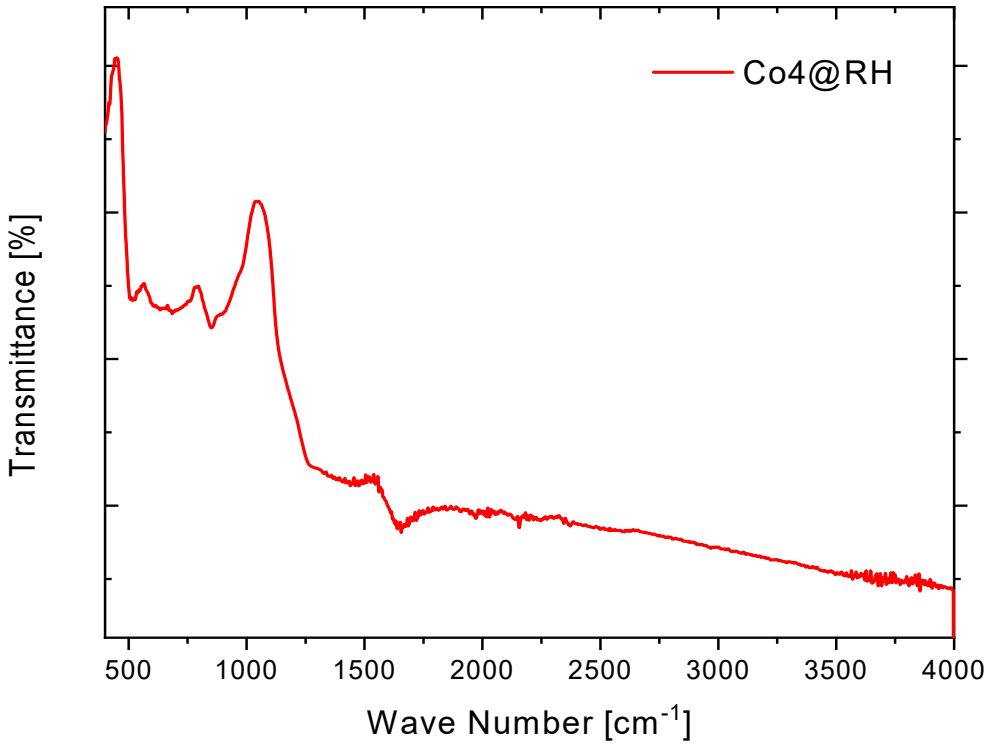


Figure S41: IR spectrum of Co4@RH.

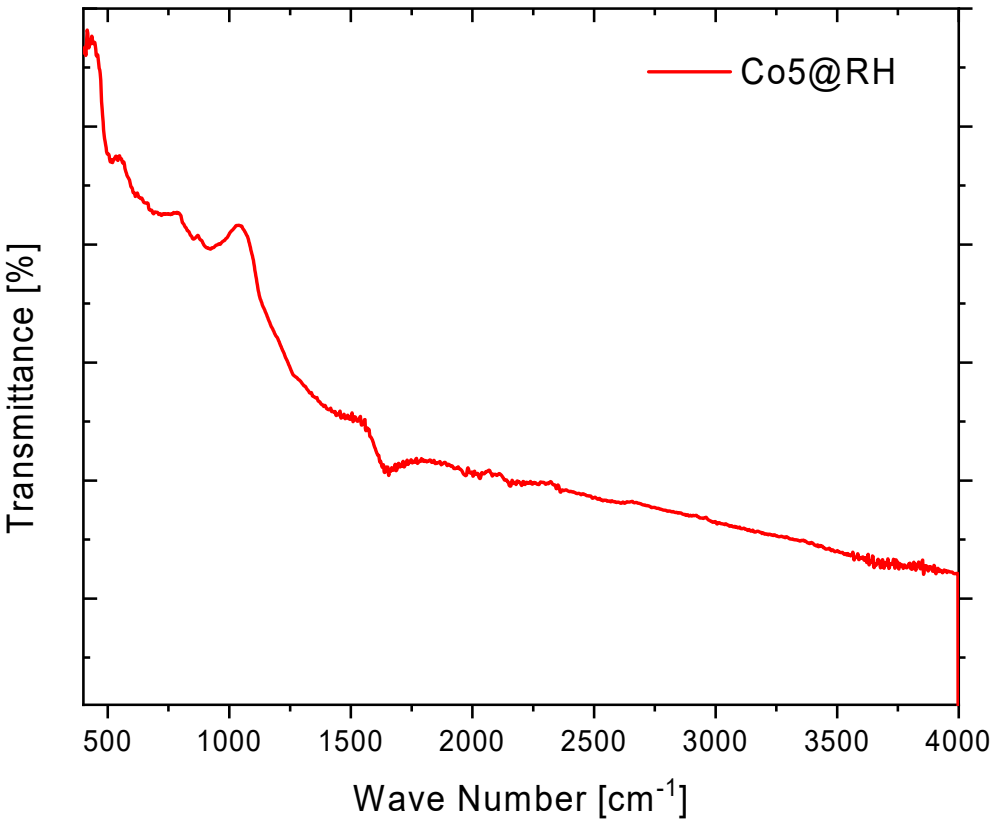


Figure S42: IR spectrum of Co5@RH.

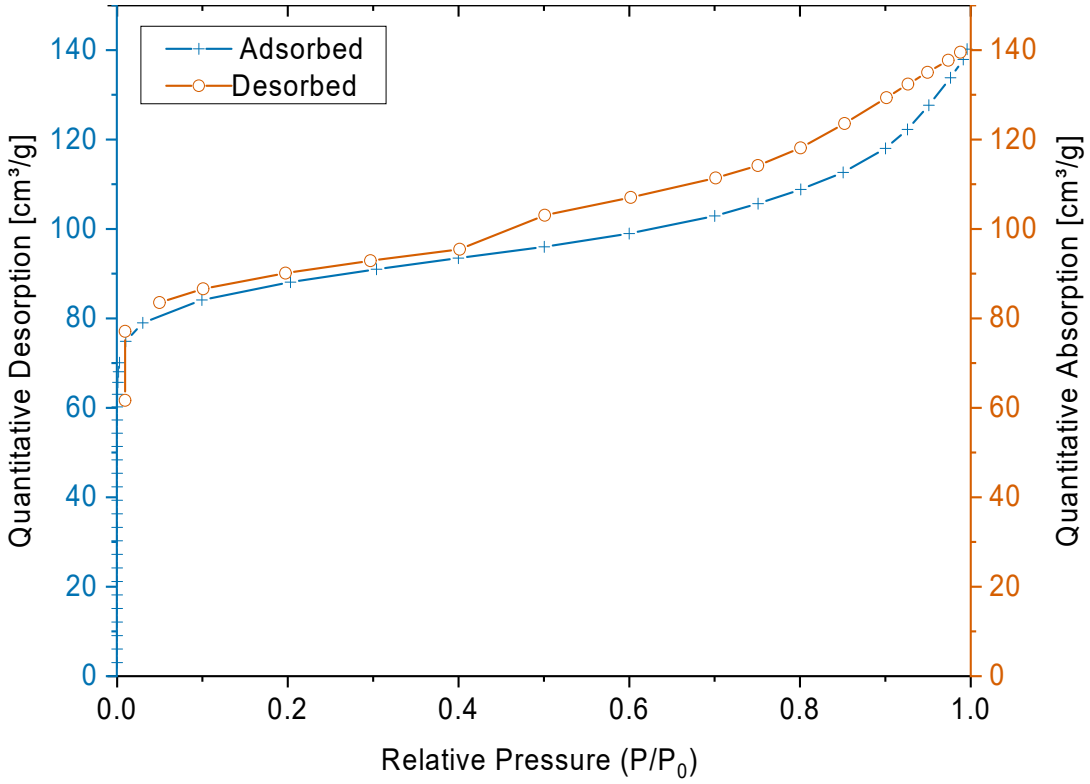


Figure S43: Isotherm Linear Plot of BET measurements of Co1@RH.

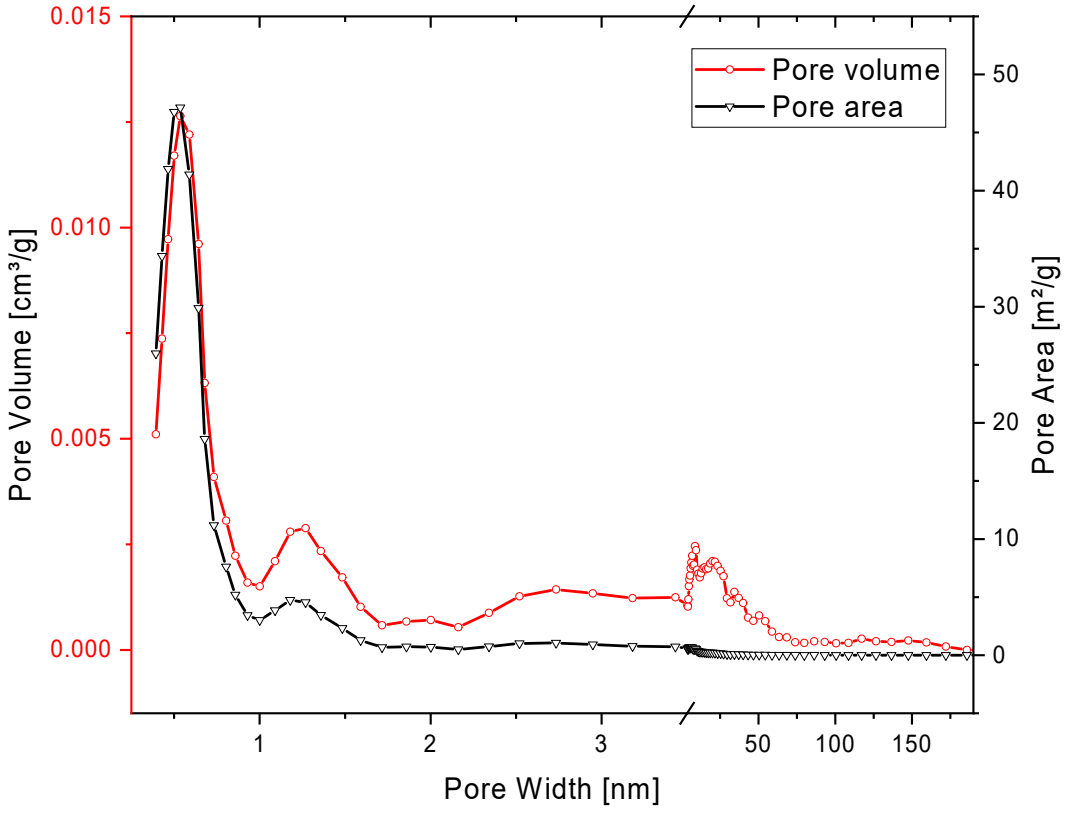


Figure S44: Desorption pore volume and area vs pore width of Co1@RH.

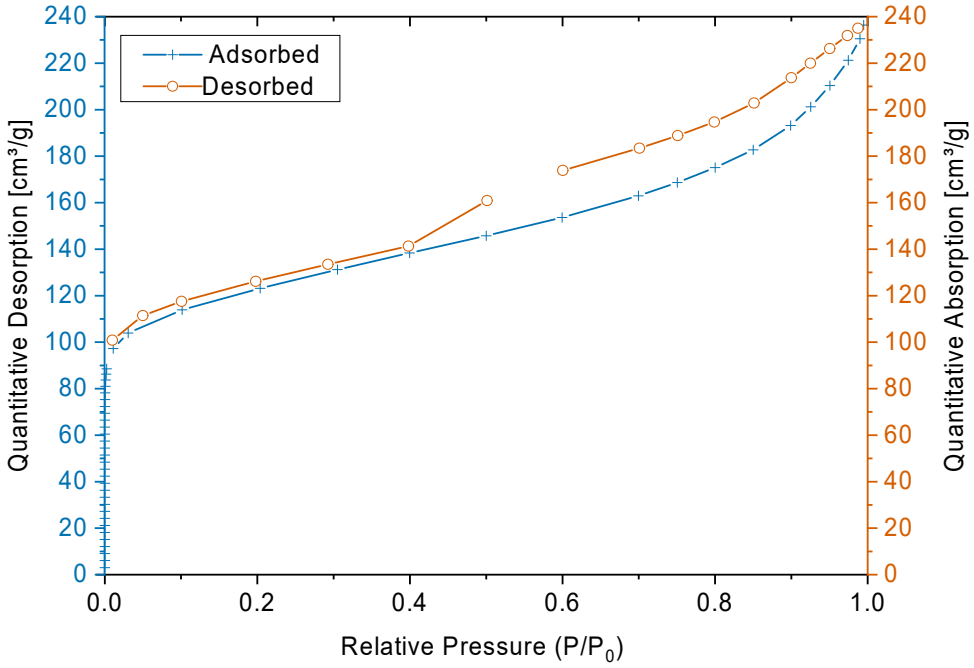


Figure S45: Isotherm Linear Plot of BET measurements of Co1@RH-E1.

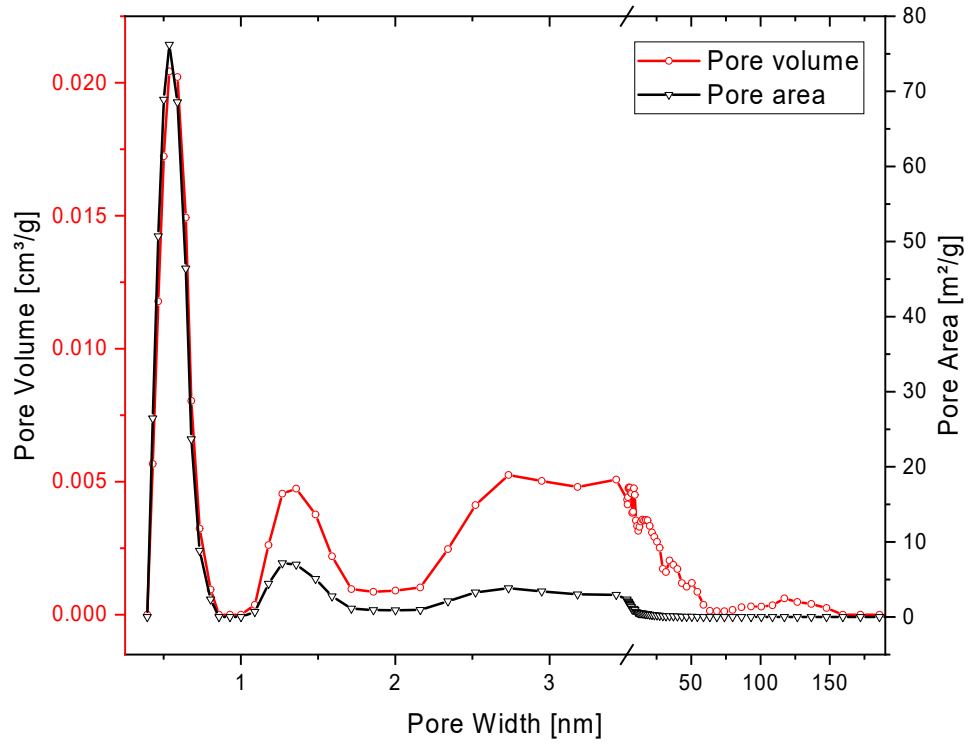


Figure S46: Desorption pore volume and area vs pore width of Co1@RH-E1.

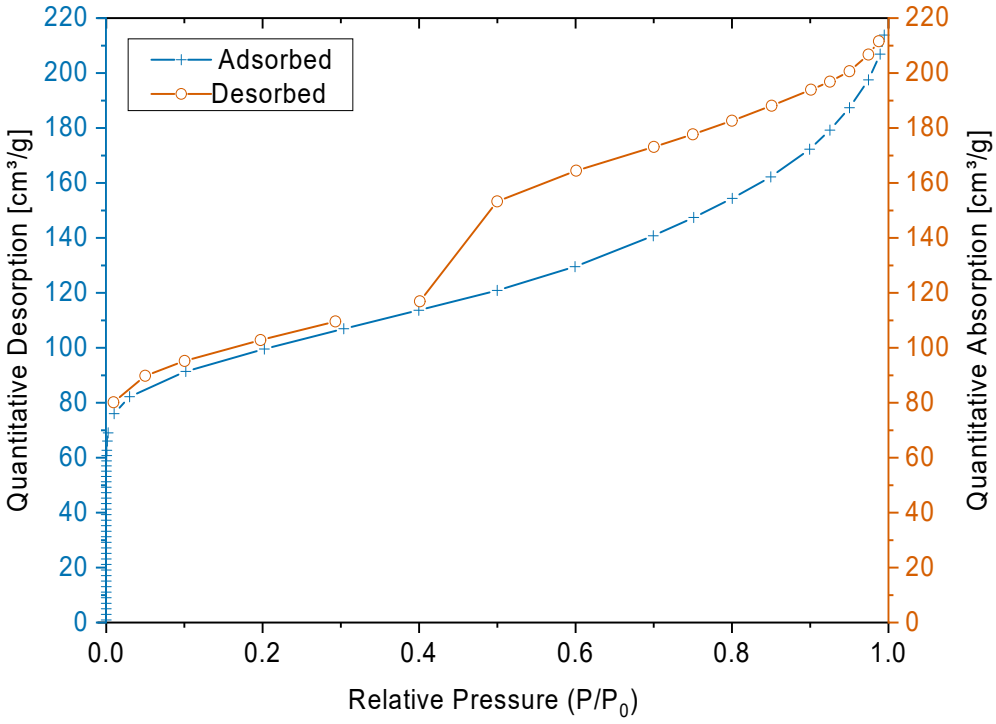


Figure S47: Isotherm Linear Plot of BET measurements of Co1@RH-E4.

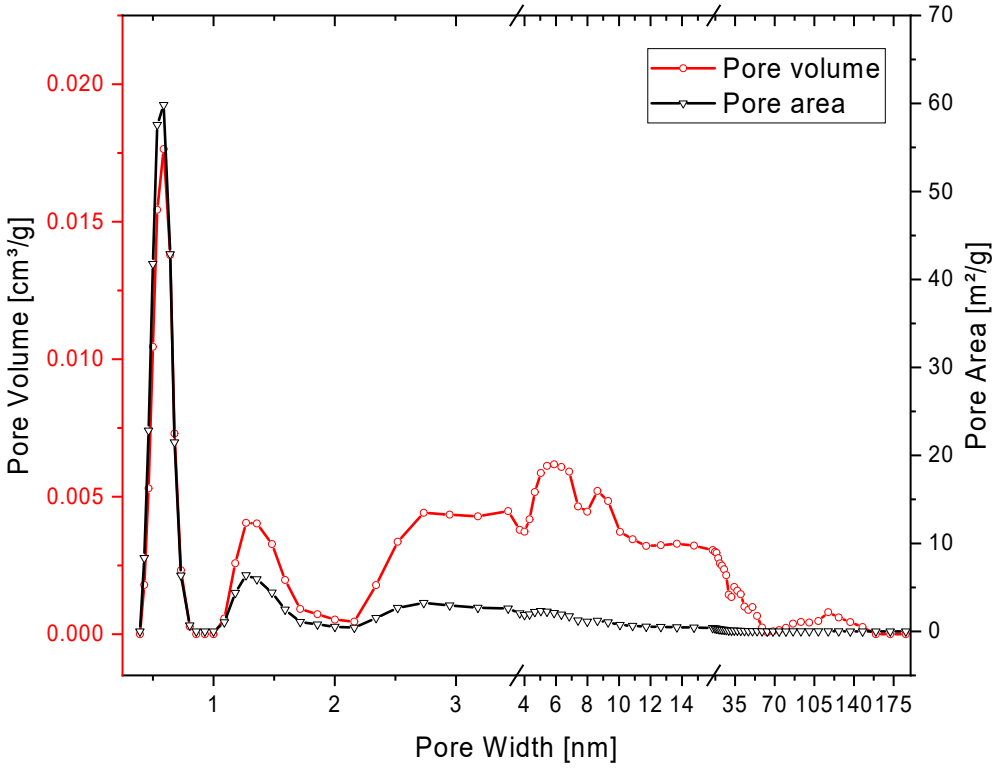


Figure S48: Desorption pore volume and area vs pore width of Co1@RH-E4.

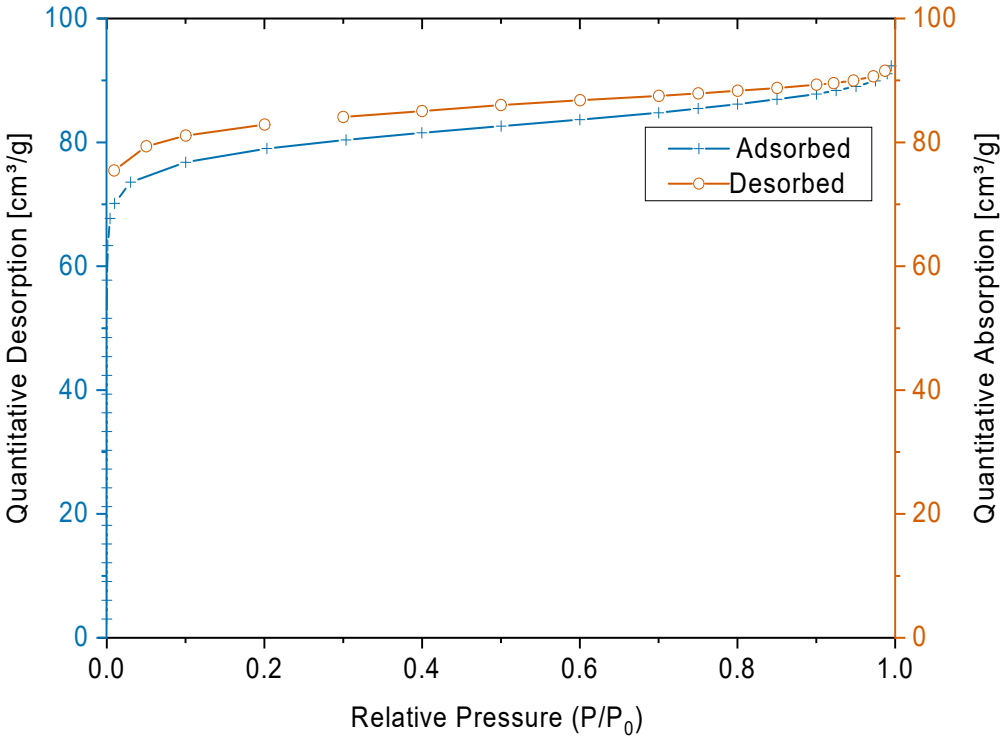


Figure S49: Isotherm Linear Plot of BET measurements of Co2@RH.

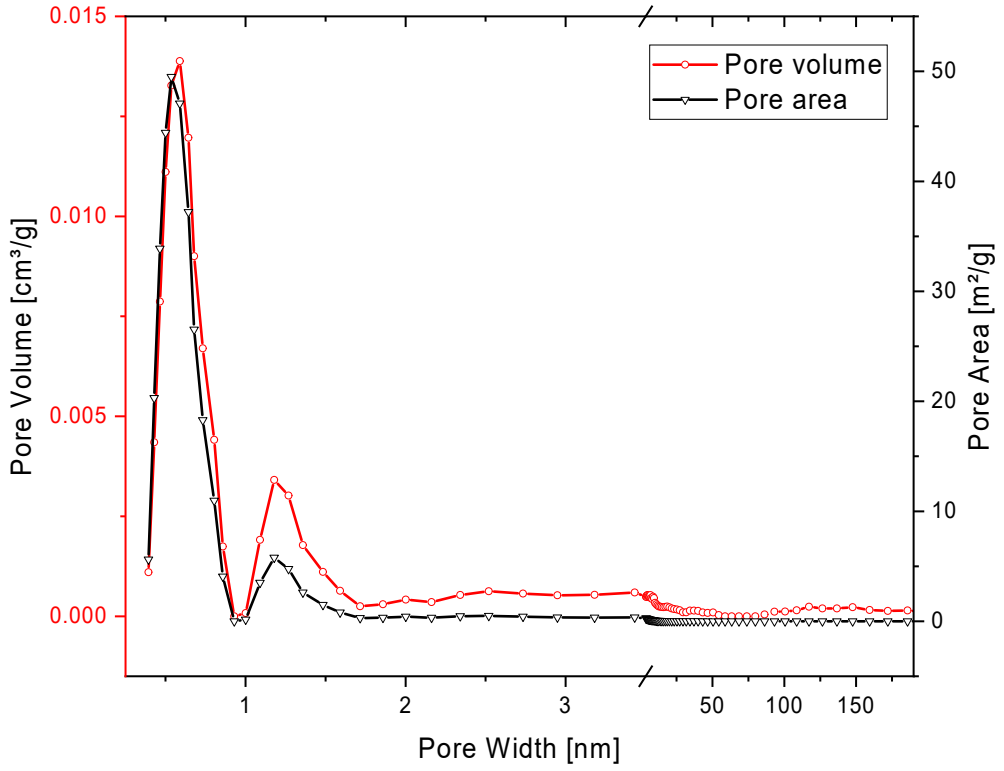


Figure S50: Desorption pore volume and area vs pore width of Co2@RH.

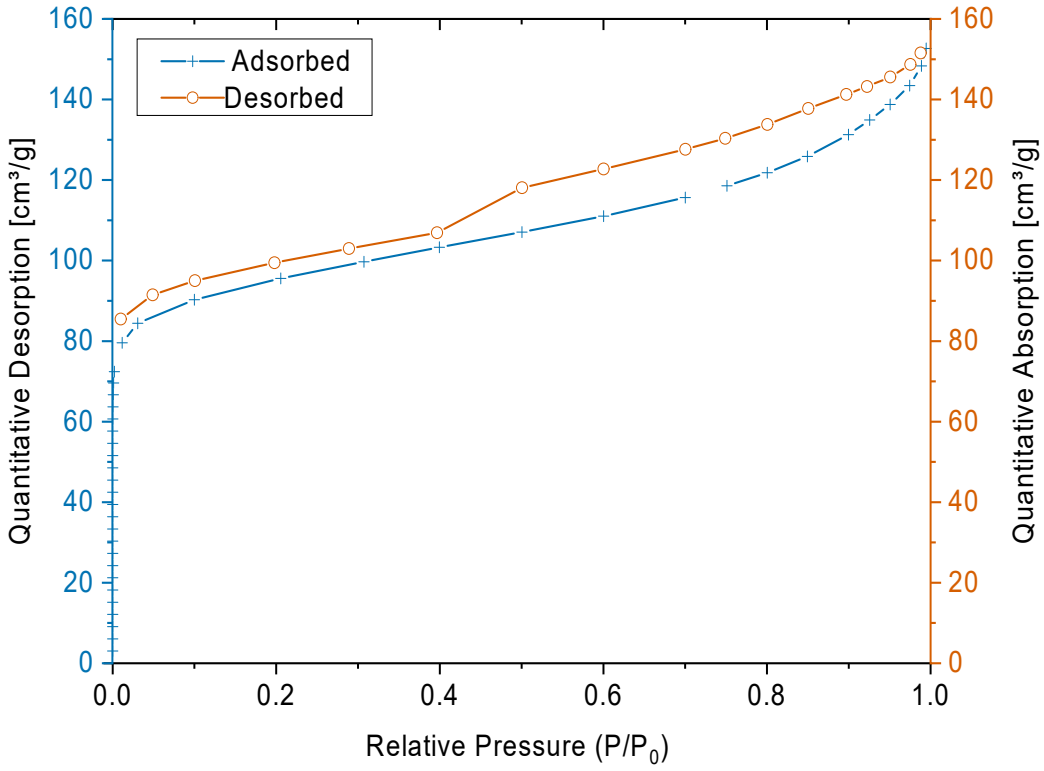


Figure S51: Isotherm Linear Plot of BET measurements of Co2@RH-E1.

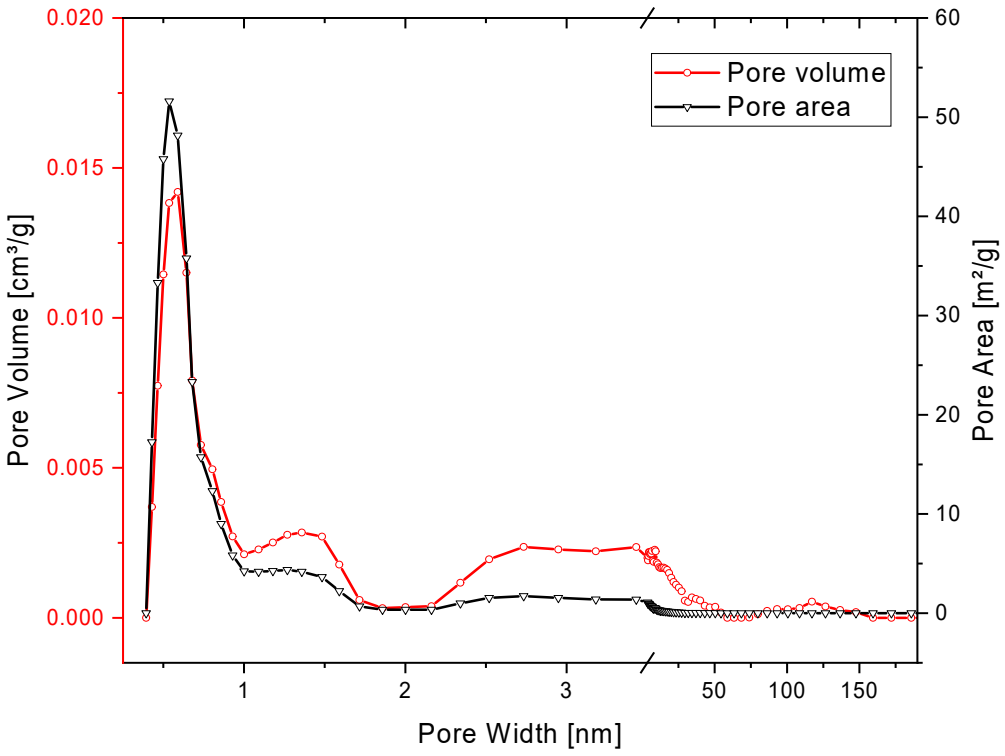


Figure S52: Desorption pore volume and area vs pore width of Co2@RH-E1.

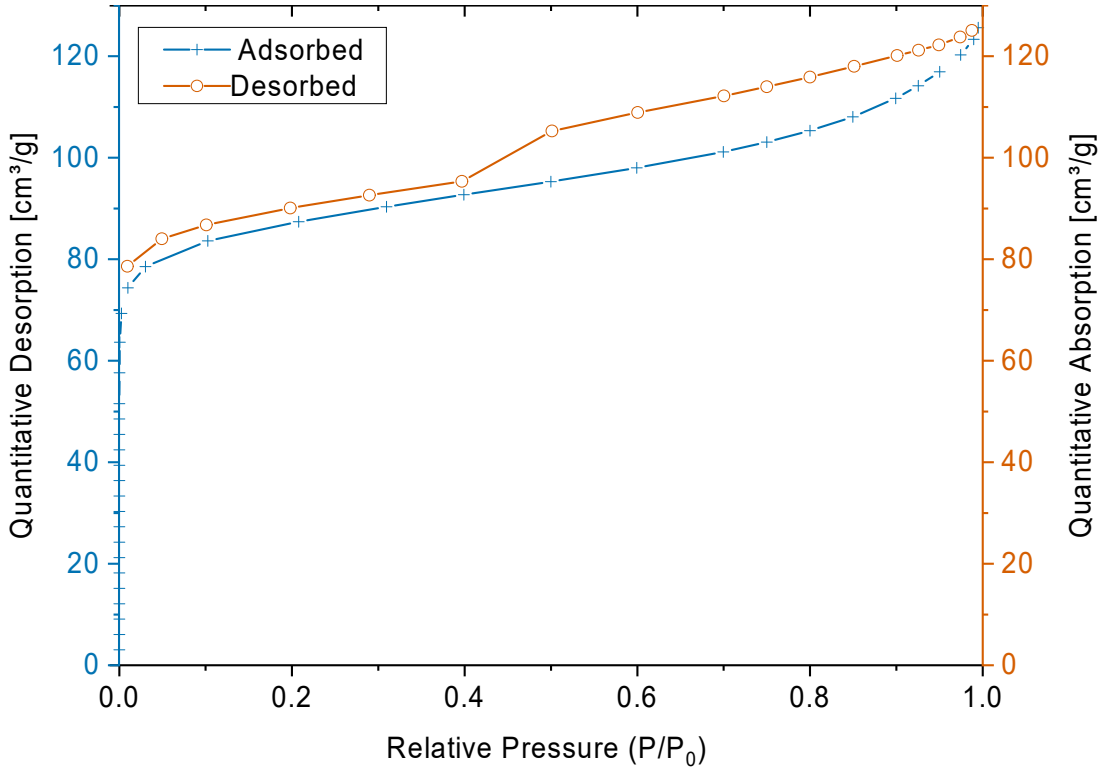


Figure S53: Isotherm Linear Plot of BET measurements of Co3@RH.

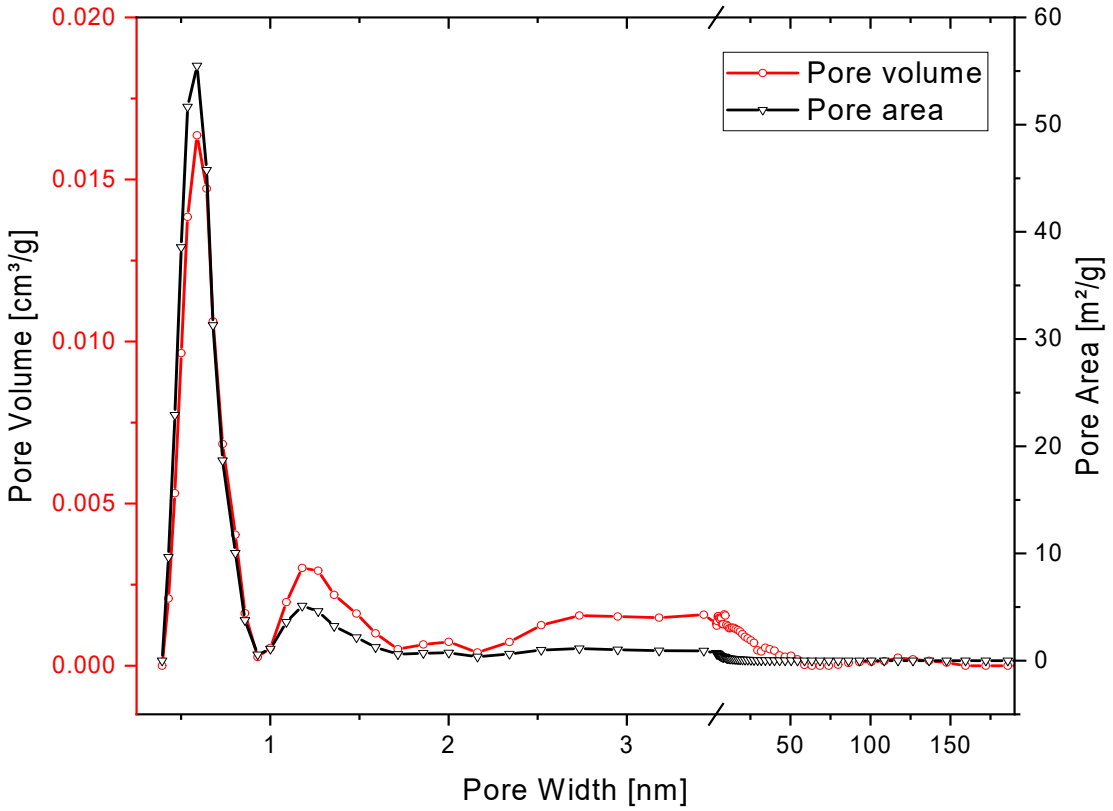


Figure S54: Desorption pore volume and area vs pore width of Co3@RH.

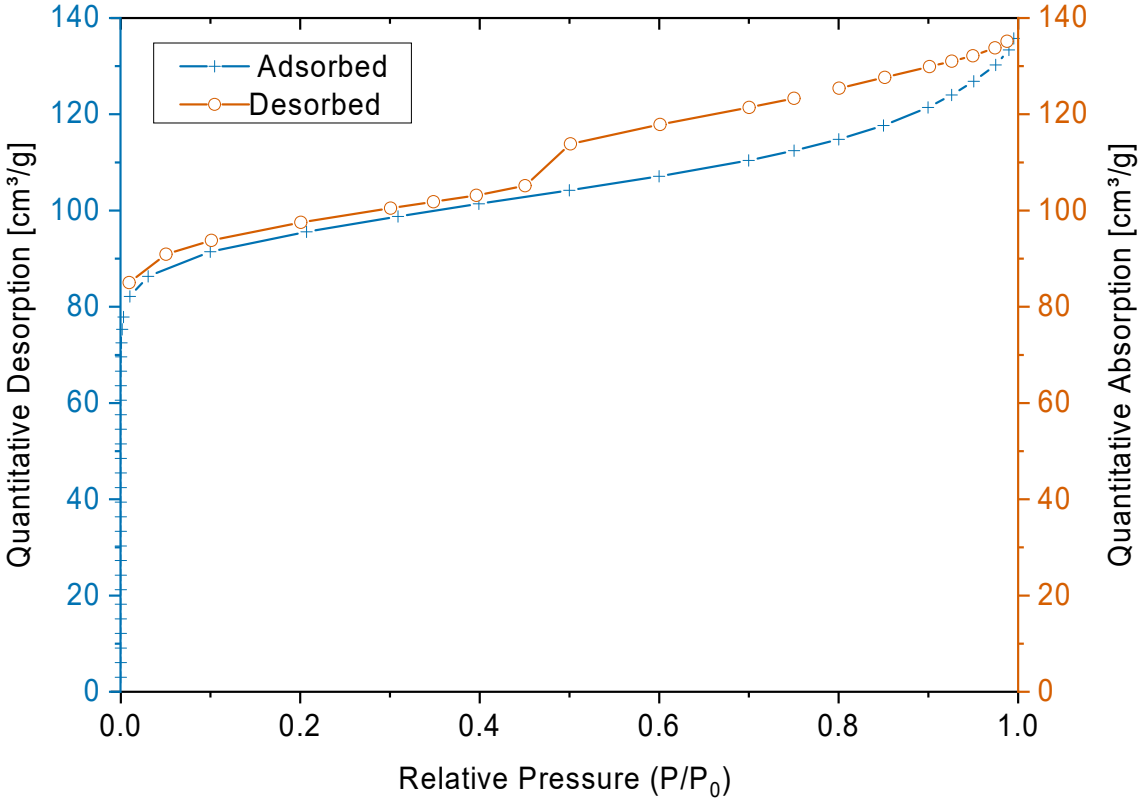


Figure S55: Isotherm Linear Plot of BET measurements of Co3@RH-E1.

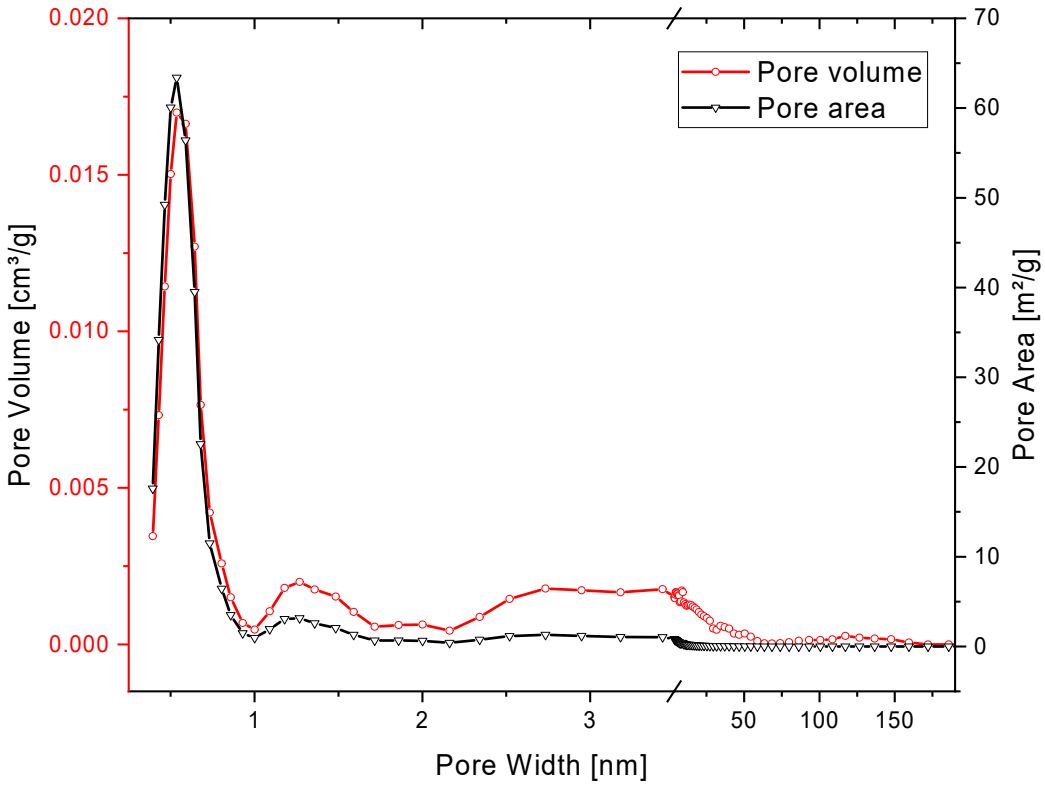


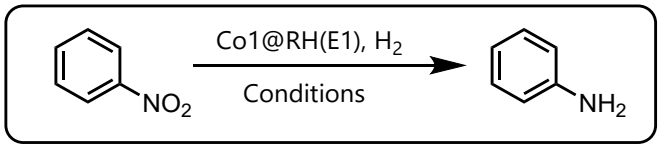
Figure 56 Desorption pore volume and area vs pore width of Co3@RH-E1.

Table S2: BET Measurements of RH based catalysts.

Catalyst	BET Surface Area m^2/g	Micropore volume cm^3/g	Cumulative volume of pores between 2 nm and 100 nm width cm^3/g
Co1@RH	323.6259	0.115657	0.108750
Co1@RH-E1	347.1341	0.115864	0.268478
Co1@RH-E4	427.8690	0.155368	0.254334
Co2@RH	302.0532	0.120379	0.021826
Co2@RH-E1	344.9881	0.130140	0.123560
Co3@RH	321.1991	0.123380	0.086954
Co3@RH-E1	329.4469	0.135952	0.193609

5. Screening of Catalytic Conditions

Nitrobenzene was chosen as model substrate for the optimization of the reaction conditions. The general catalysis procedure described in section 1.3 was followed, with the corresponding variations on each case (temperature, solvent, concentration, and pressure).



Product yields were calculated by gas chromatography. An exemplary calibration curve for nitrobenzene within a concentration range from $3.71 \cdot 10^{-3}$ mol l^{-1} to $4{,}75 \cdot 10^{-1}$ mol l^{-1} is shown in Figure S57. It was made using ethyl acetate as solvent and octane as internal standard.

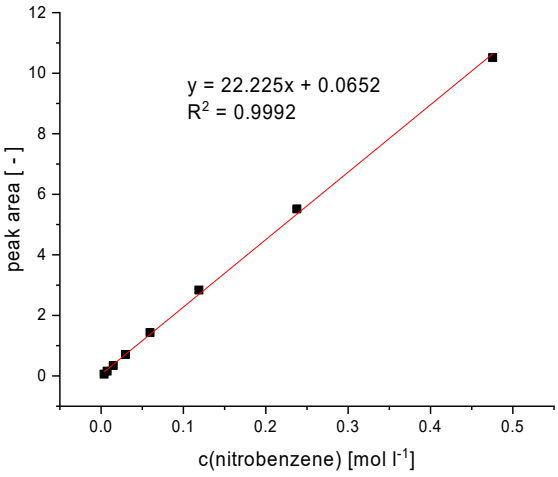


Figure S57: Exemplary calibration curve for nitrobenzene used for optimization of reaction conditions.

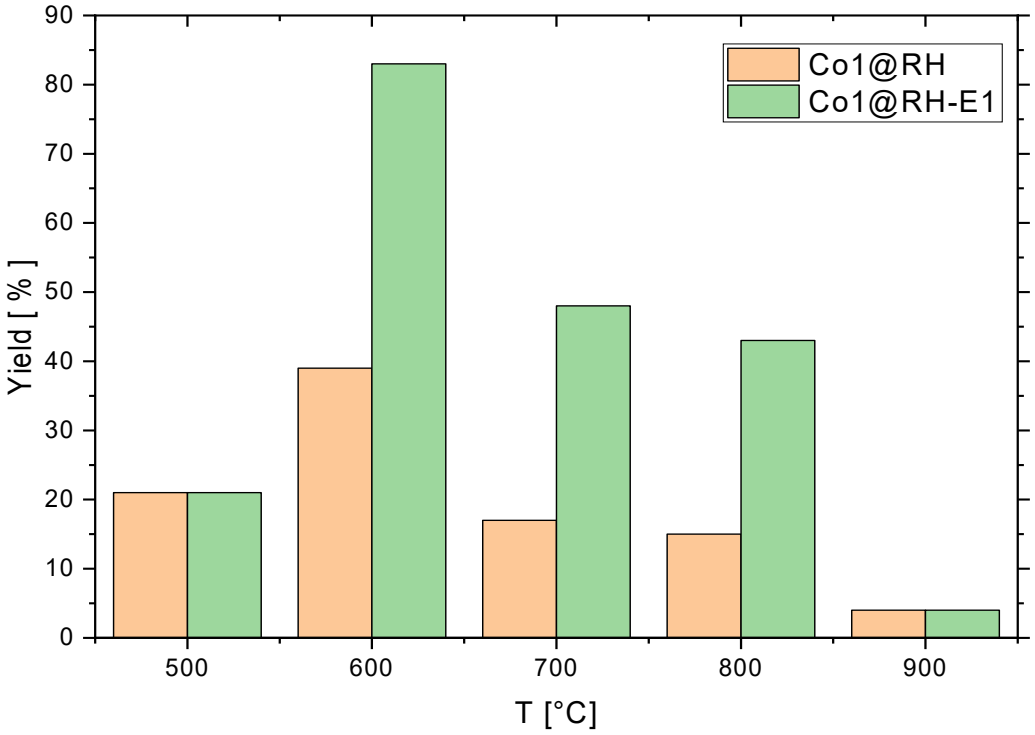


Figure S58: Screening of pyrolysis temperature with Co1@RH and Co1@RH-E1.

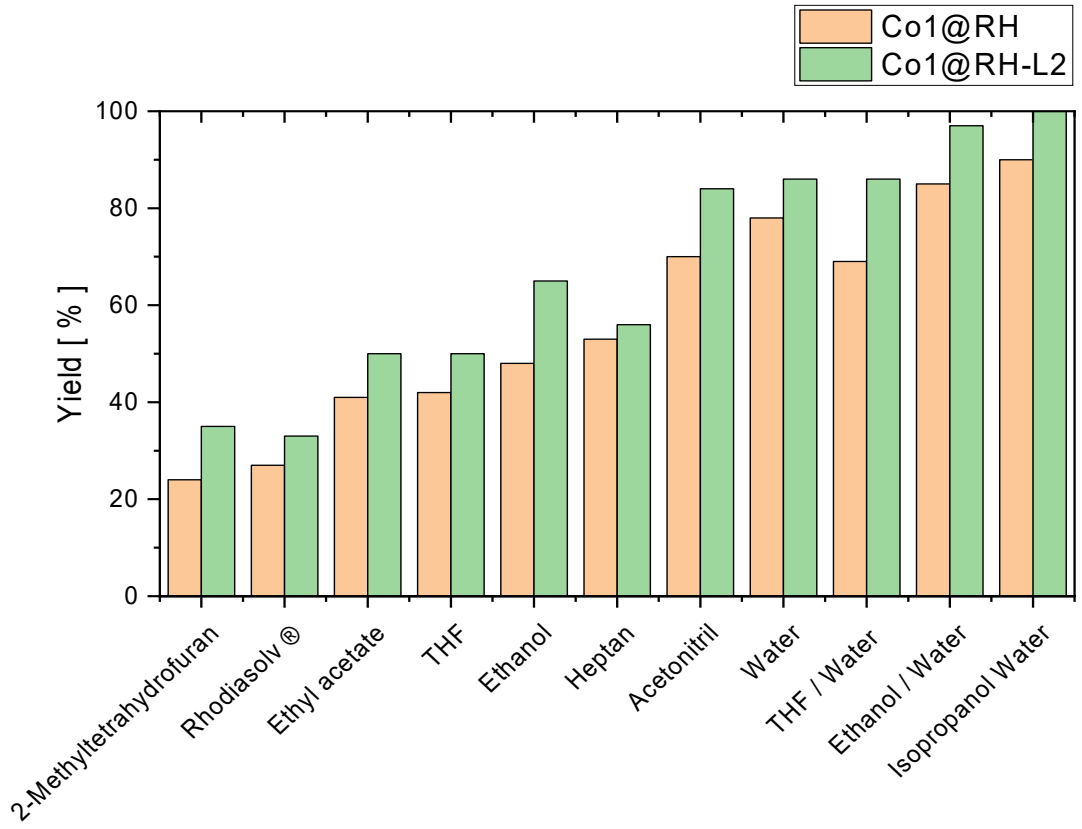


Figure S59: Solvent screening with Co1@RH and Co1@RH-E1.

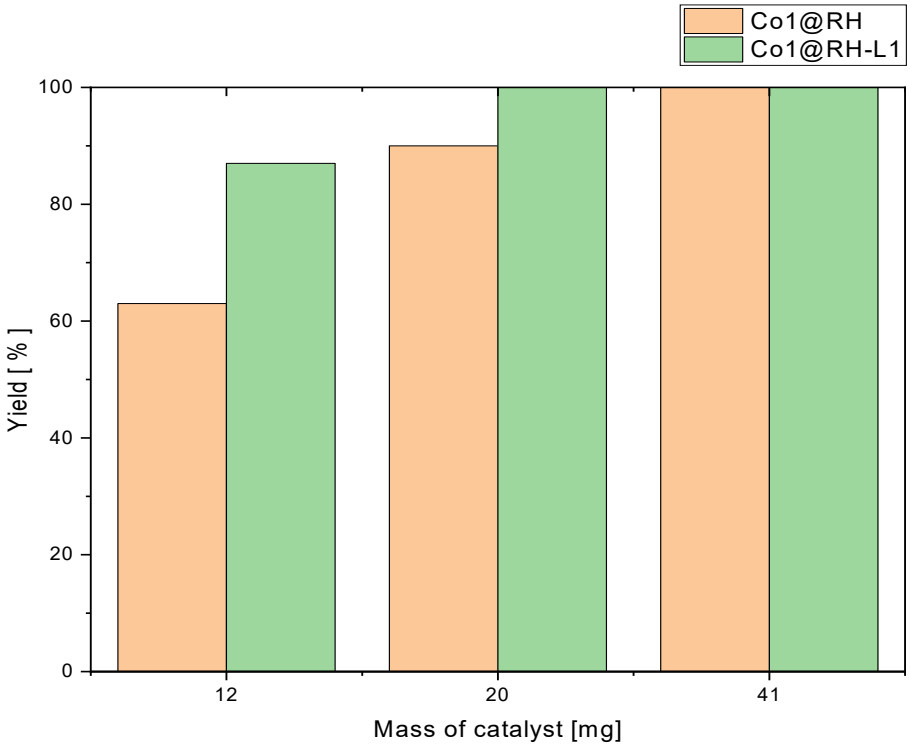


Figure S60: Screening of necessary catalyst amount for full conversion of the substrate with Co1@RH and Co1@RH-E1.

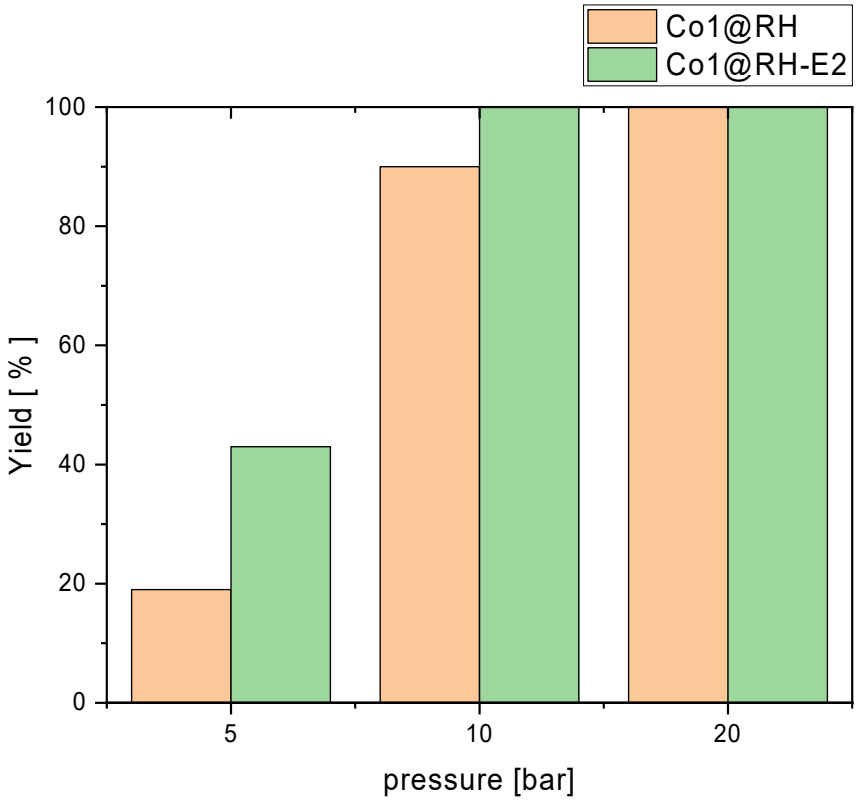


Figure S61: Hydrogen pressure screening with Co1@RH and Co1@RH-E1.

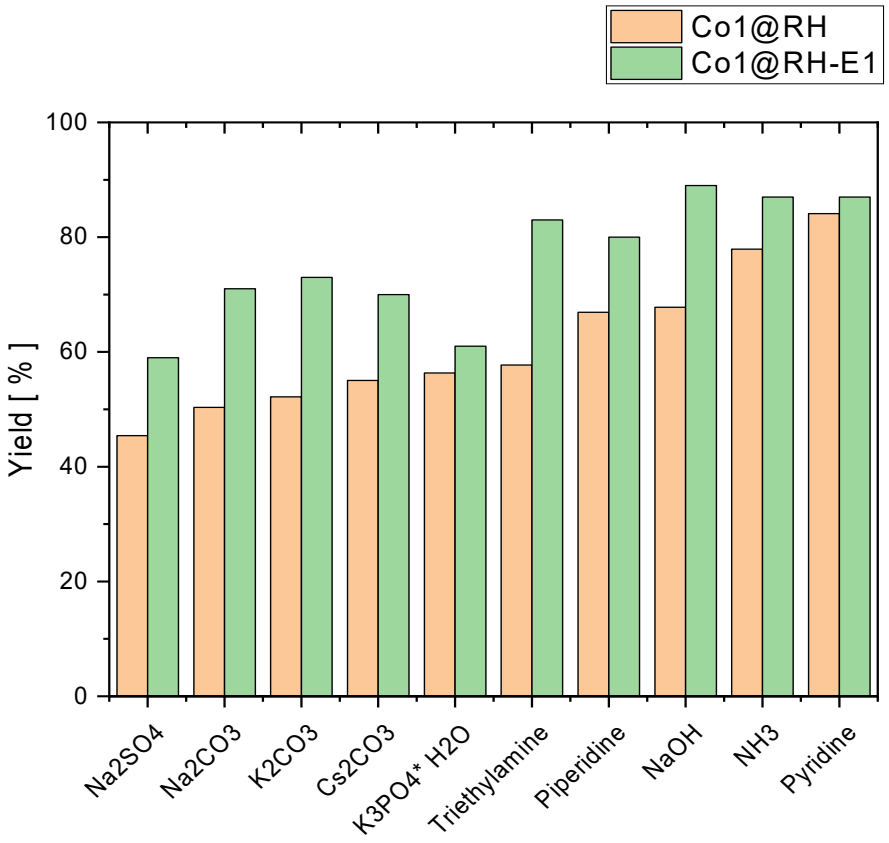


Figure S62: Base screening with Co1@RH and Co1@RH-E1.

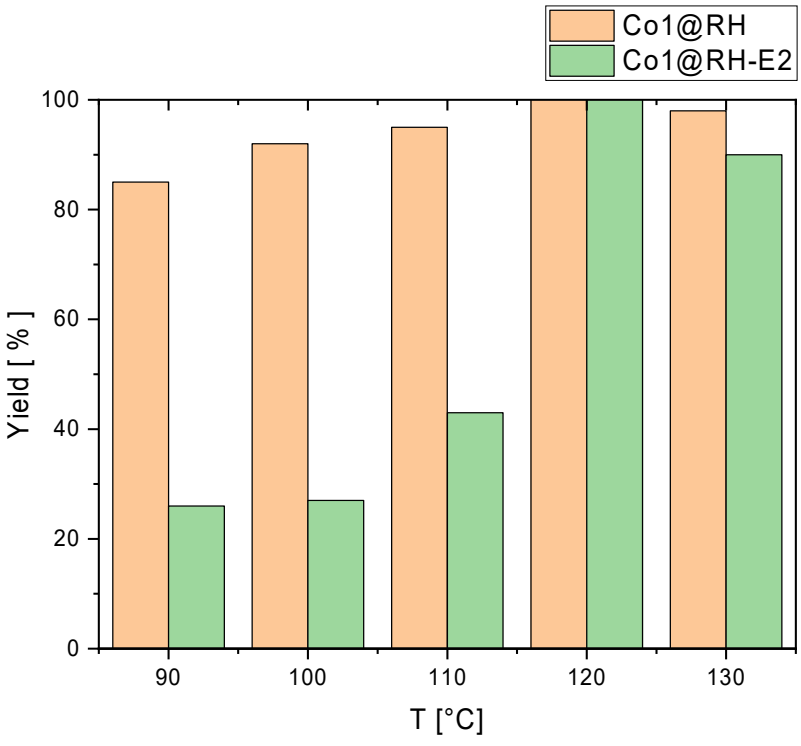


Figure S63: Temperature screening with Co1@RH and Co1@RH-E1.

6. Kinetic experiments

Nitrobenzene was chosen as model substrate for the kinetic investigations. See the main text for further details.

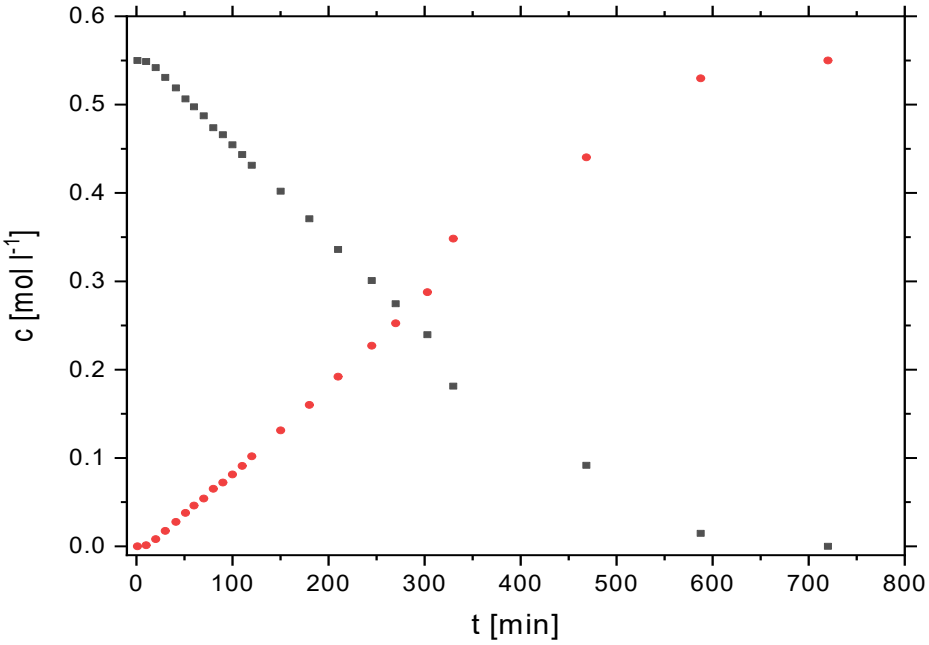


Figure S64: Concentration/time profile using 200 mg of Co1@RH at 120°C.

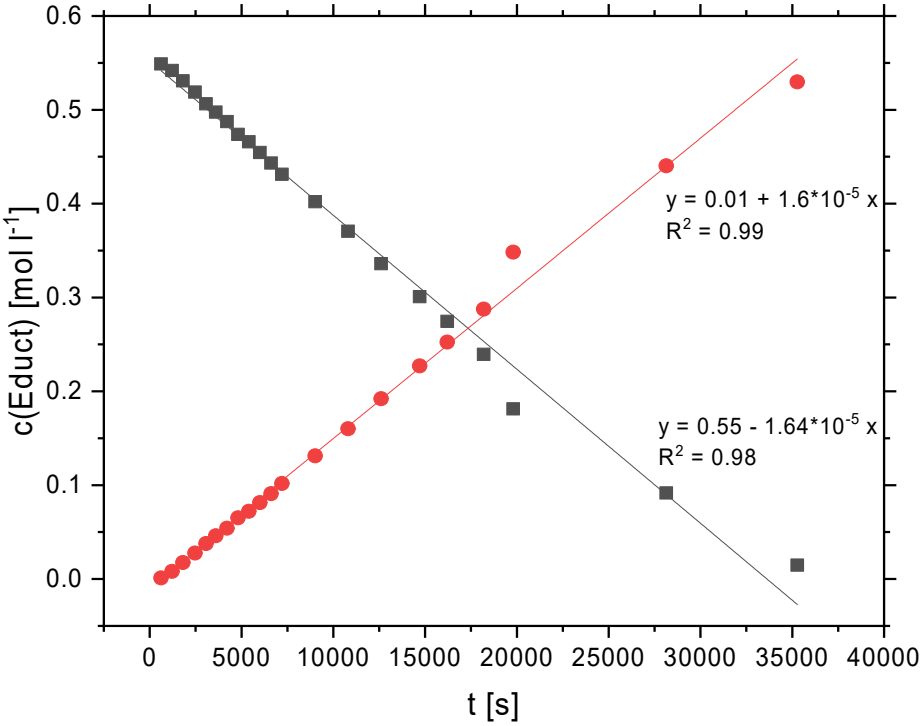


Figure S65: Concentration/time profile using 200 mg of Co1@RH at 120°C in linear range with linear equation and coefficient of determination.

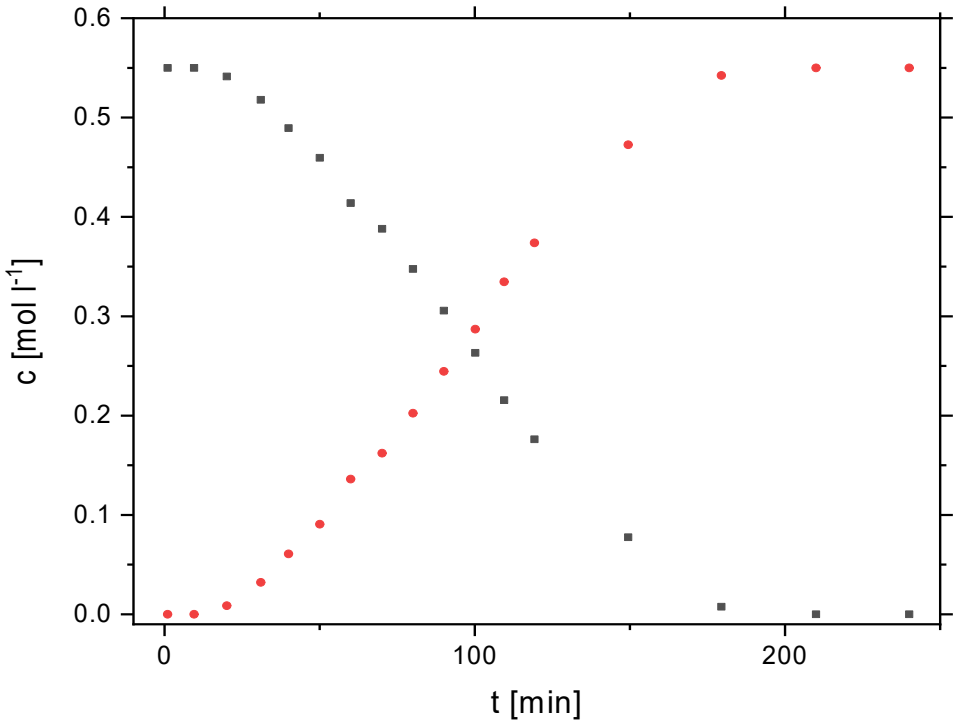


Figure S66: Concentration/time profile using 100 mg of Co1@RH-E1 at 120°C.

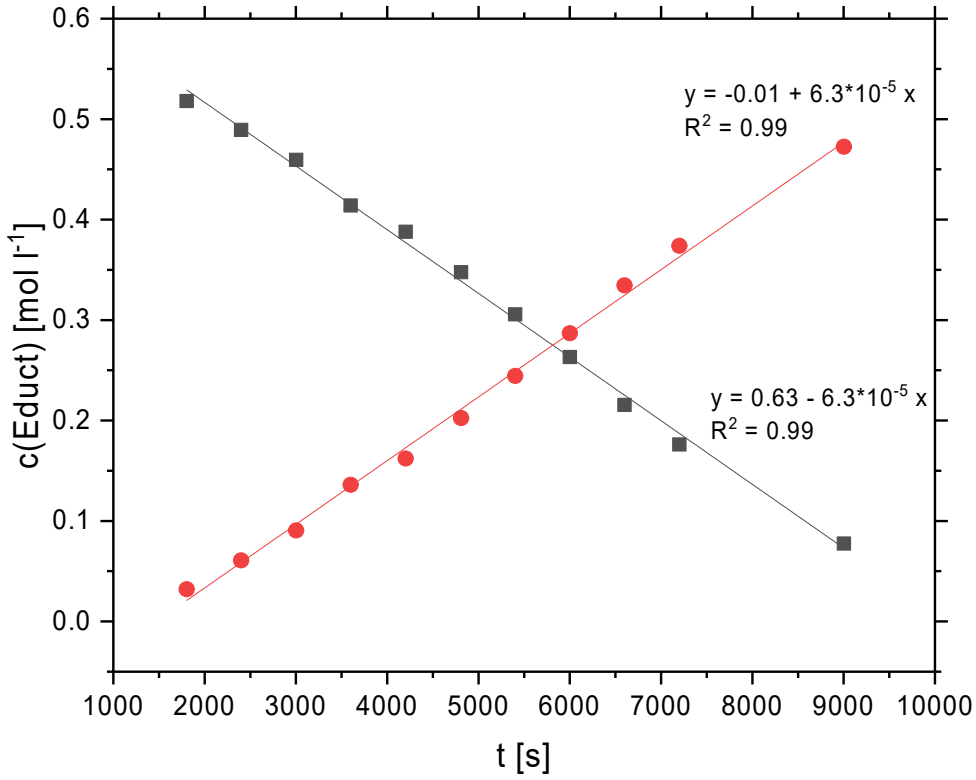


Figure S67: Concentration/time profile using 100 mg of Co1@RH-E1 at 120°C in linear range with linear equation and coefficient of determination.

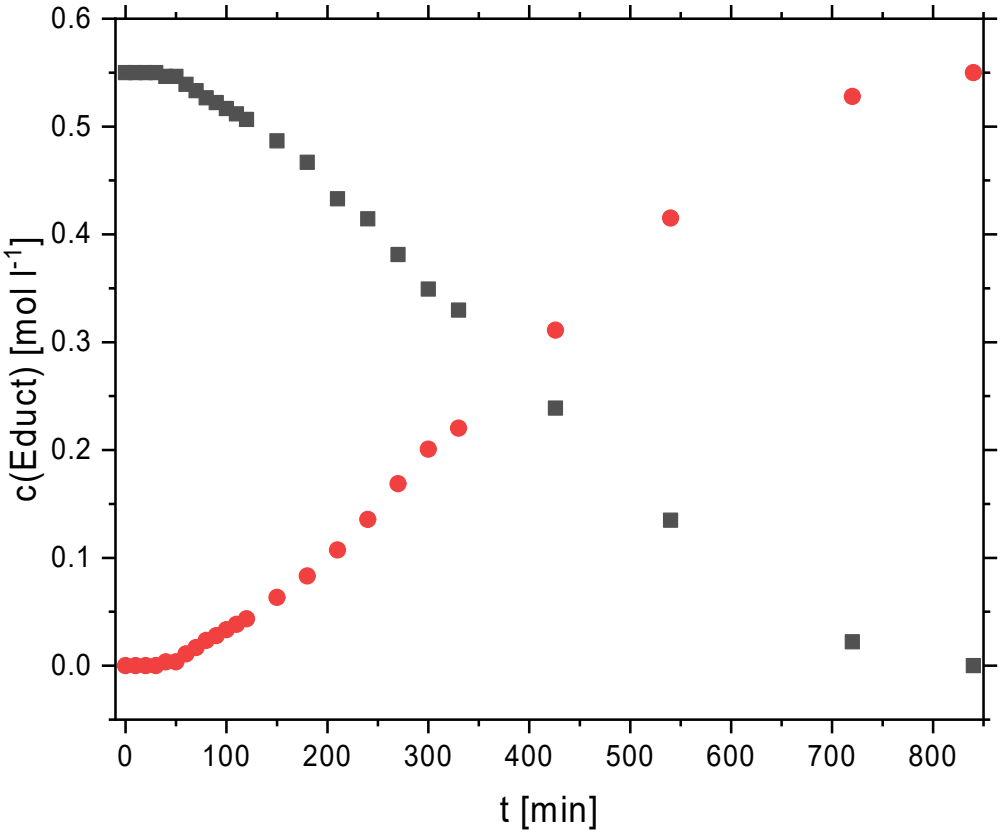


Figure S68: Concentration/time profile using 100 mg of Co1@RH-E1 at 80°C.

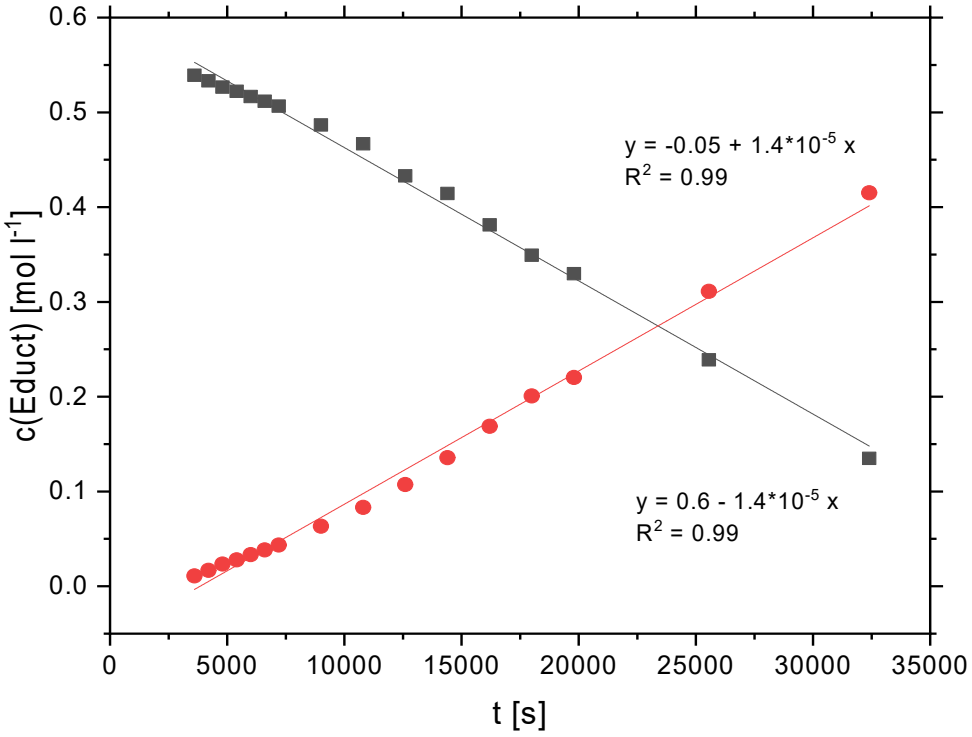


Figure S69: Concentration/time profile using 100 mg of Co1@RH-E1 at 80°C in linear range with linear equation and coefficient of determination.

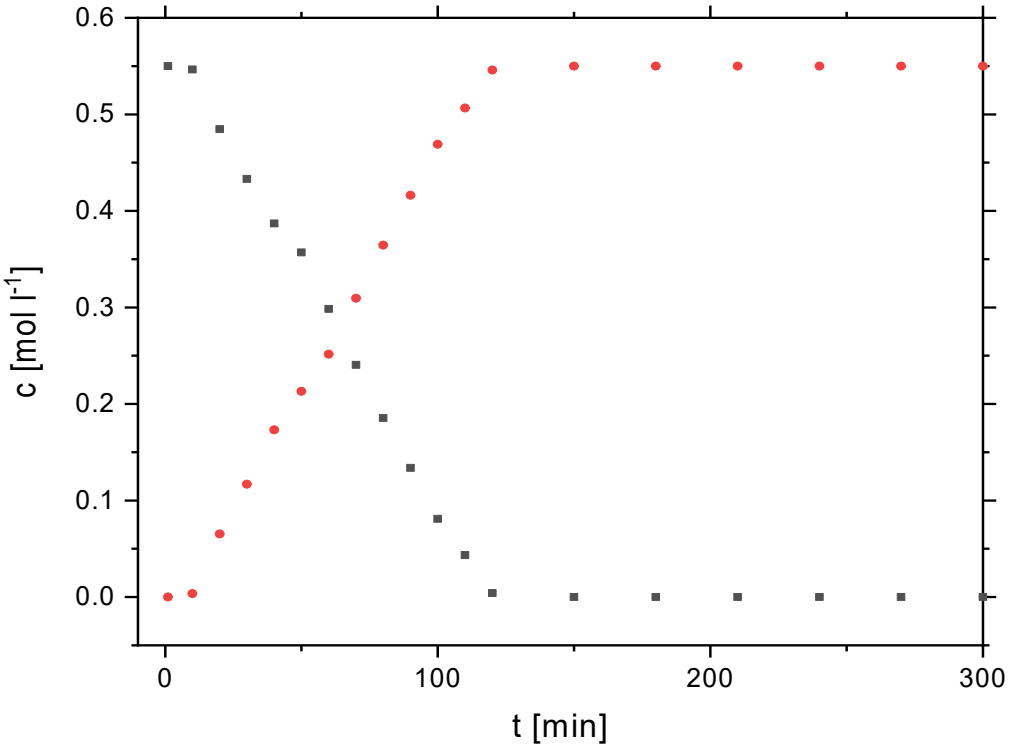


Figure S70: Concentration/time profile using 100 mg of Co1@RH-E1 at 160°C.

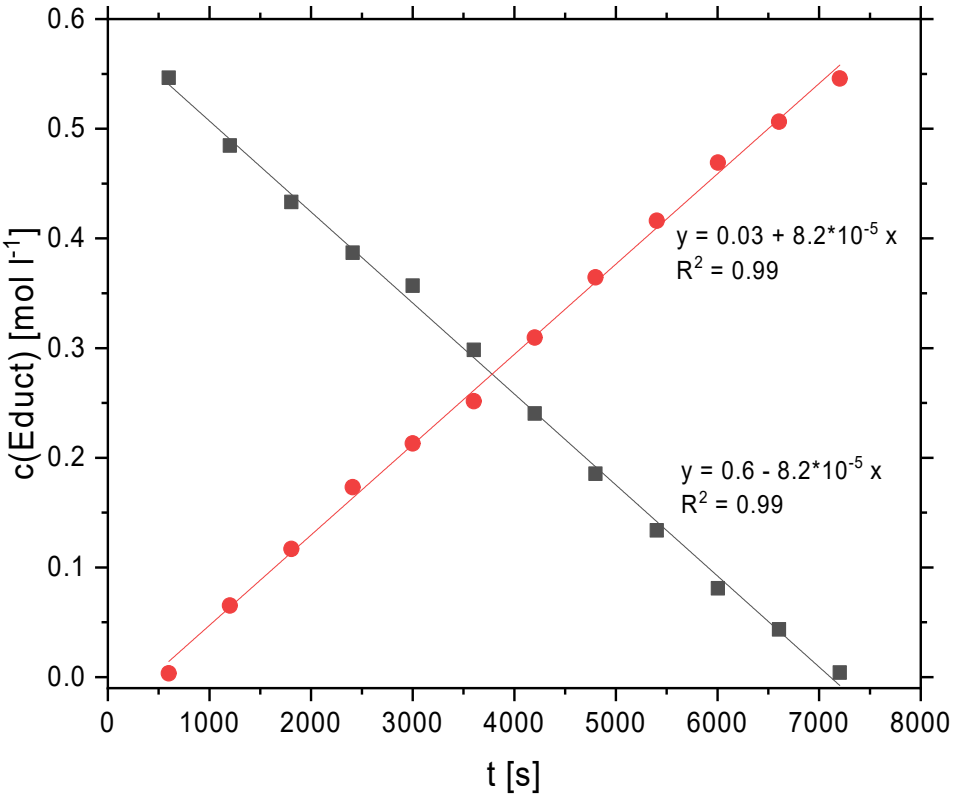


Figure S71: Concentration/time profile using 100 mg of Co1@RH-E1 at 160°C in linear range with linear equation and coefficient of determination.

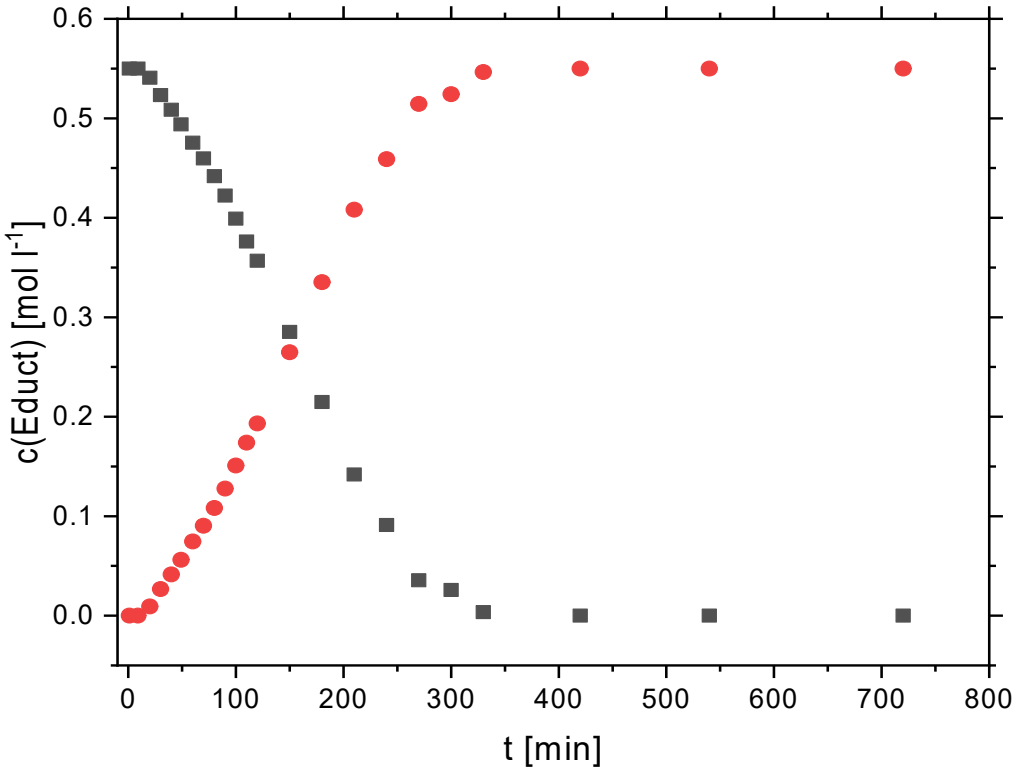


Figure S72: Concentration/time profile using 50 mg of Co1@RH-E1 at 120°C.

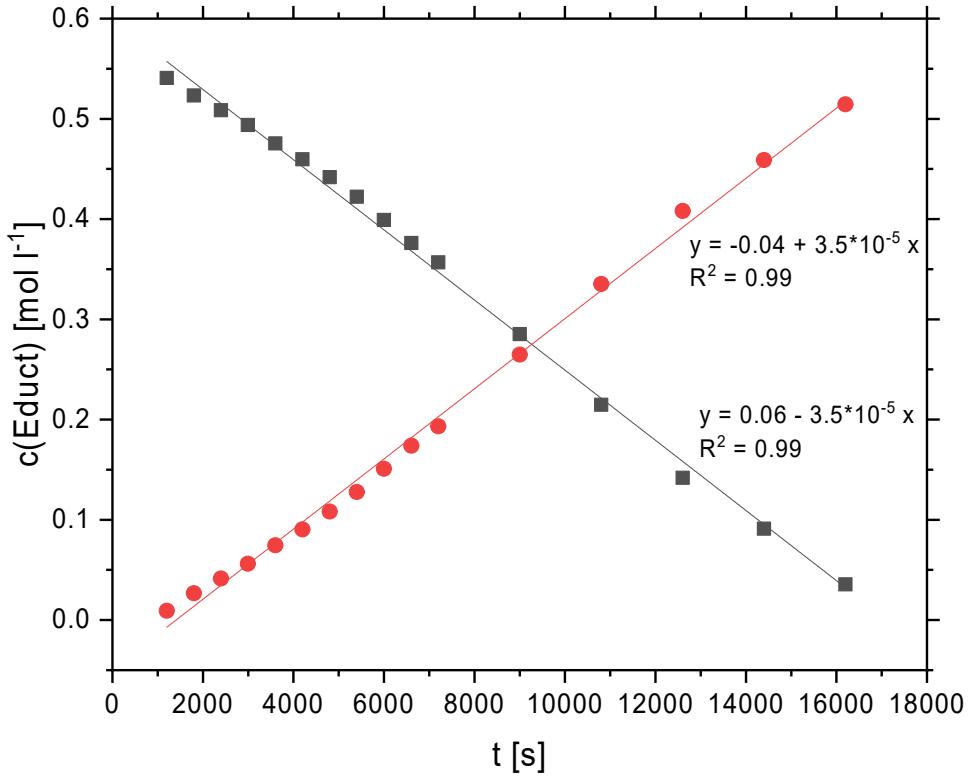


Figure S73: Concentration/time profile using 50 mg of Co1@RH-E1 at 120°C in linear range with linear equation and coefficient of determination.

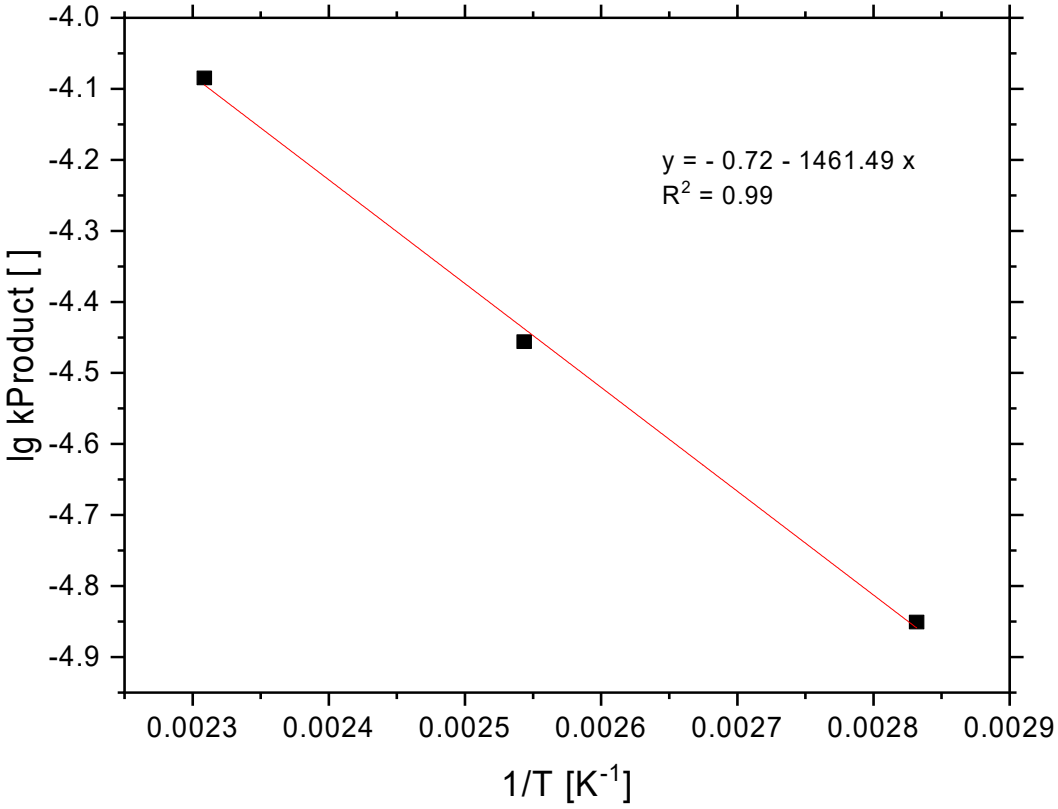


Figure S74: Arrhenius plot for activation energy determination.

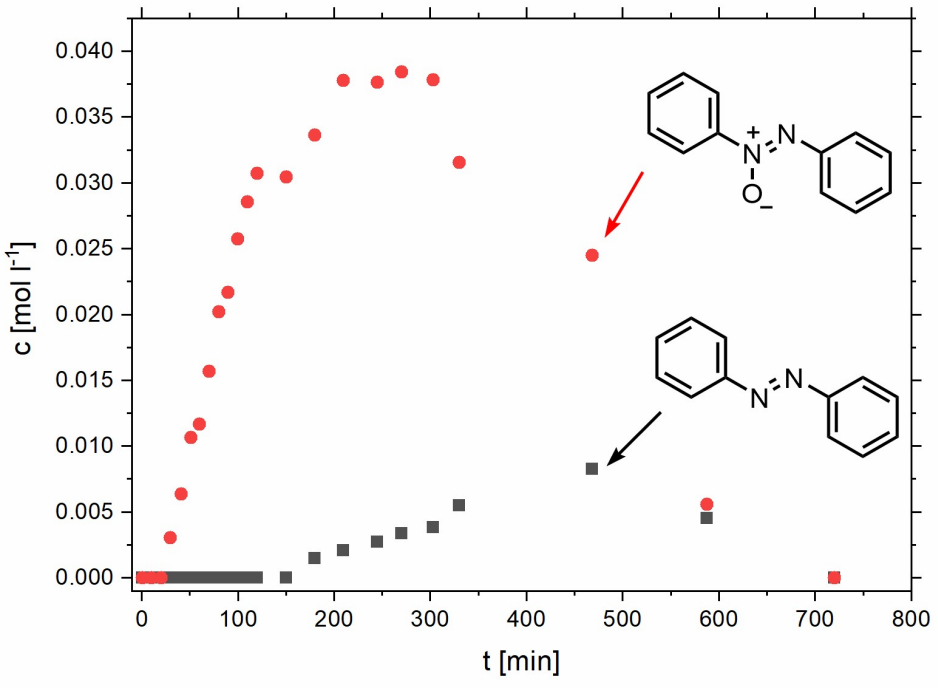


Figure S75: Concentration/time profile of azoxy and azo intermediates in kinetic experiment using 100 mg of Co1@RH-E1 at 120°C

7. MR Spectra

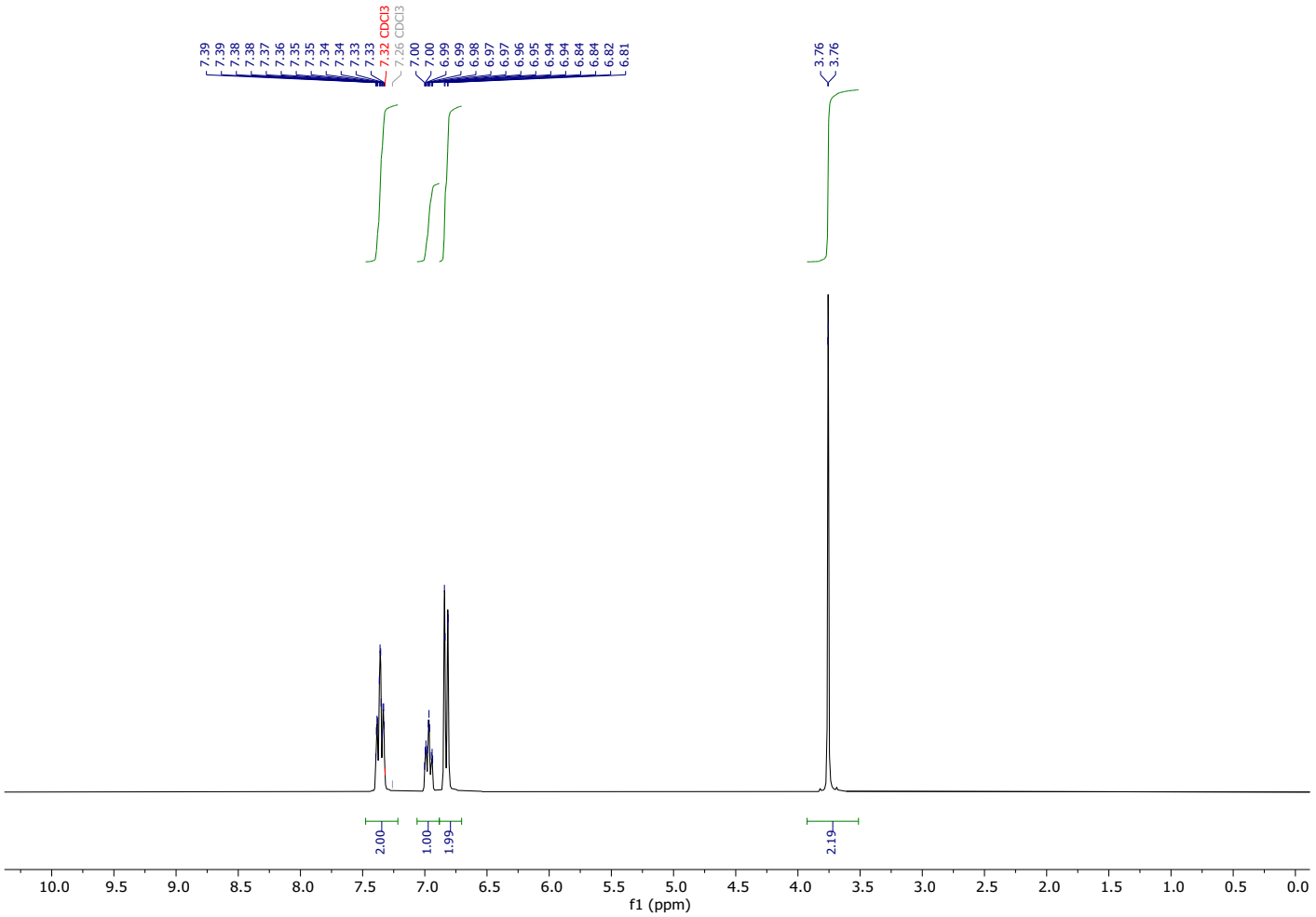


Figure S76: ^{1}H-NMR (300 MHz, DMSO-d6) for Aniline (2a)

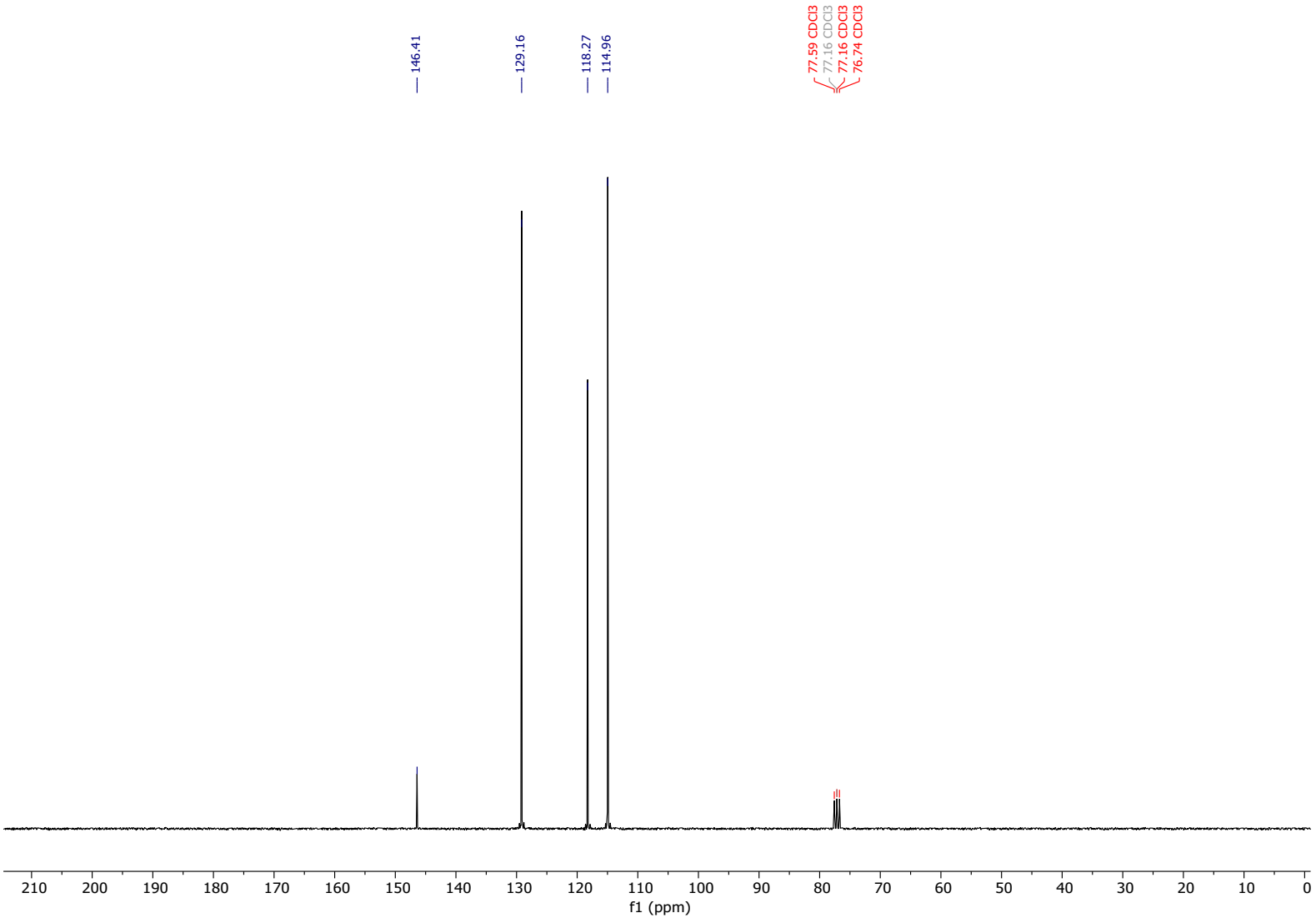


Figure S77: ^{13}C-NMR (75 MHz, DMSO-d6) for Aniline (2a)

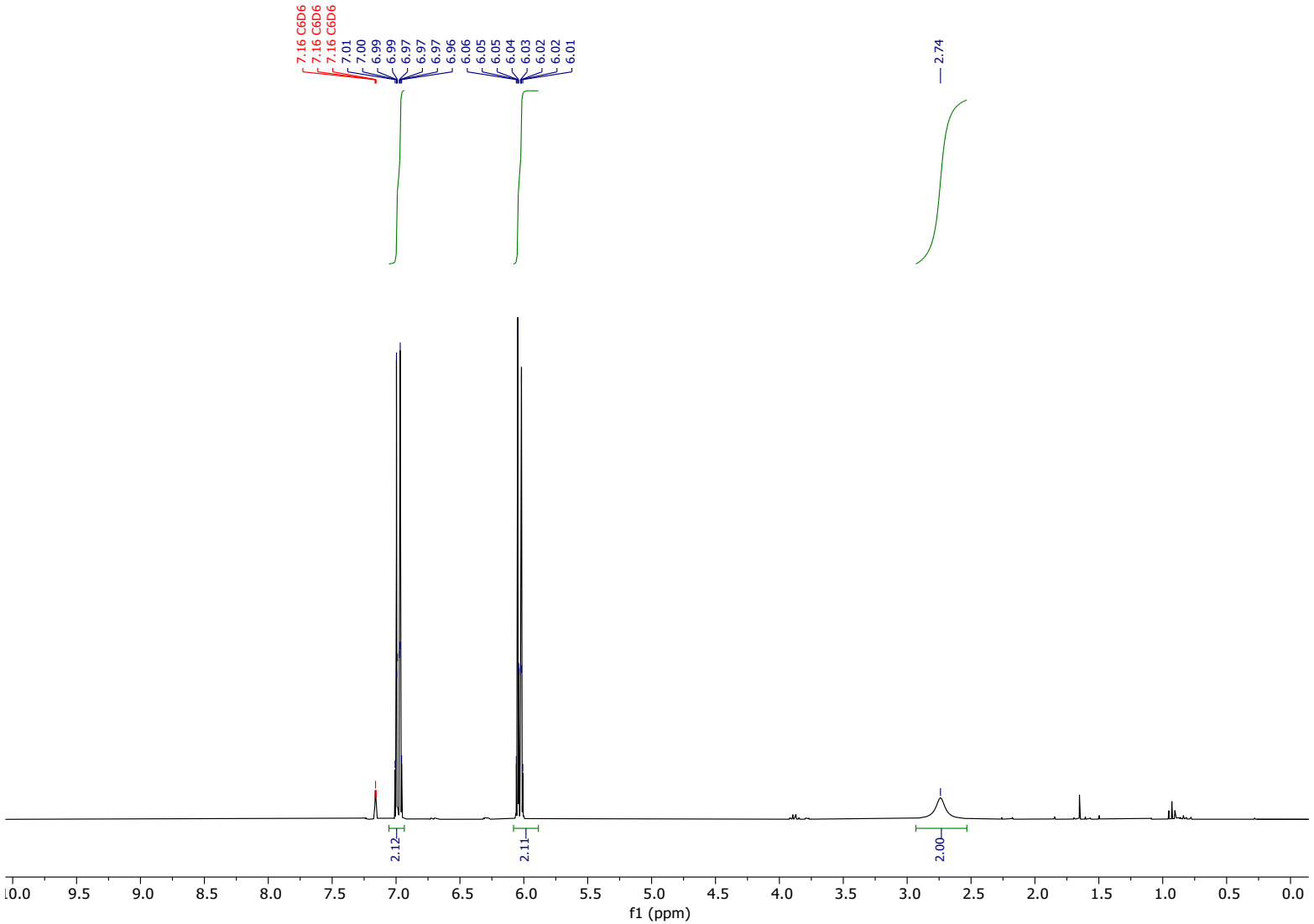


Figure S78: ^{1}H-NMR (300 MHz, DMSO-d6) for 4-chloroaniline (2b)

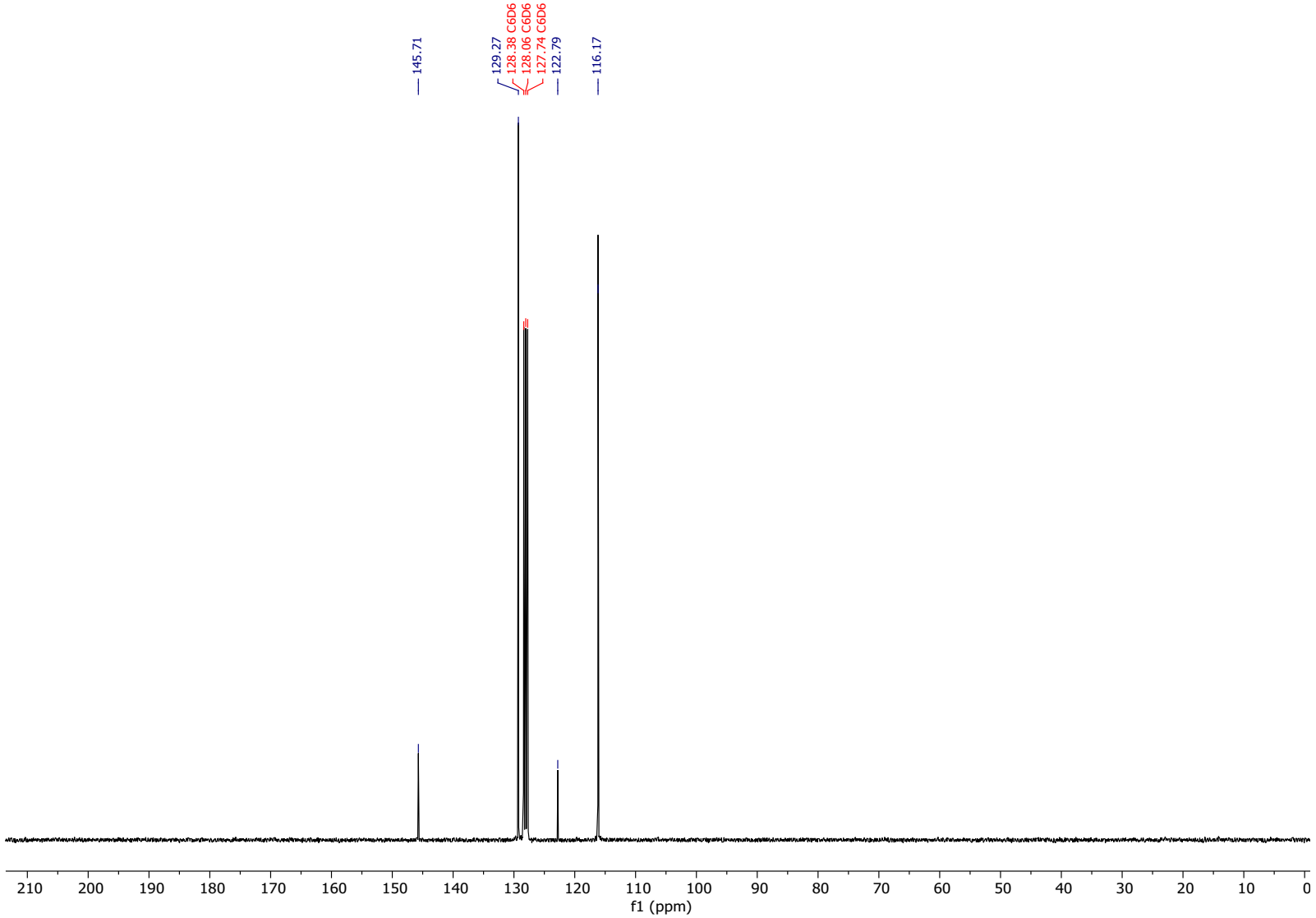


Figure S79: ^{13}C-NMR (75 MHz, DMSO-d6) for 4-chloroaniline (2b)

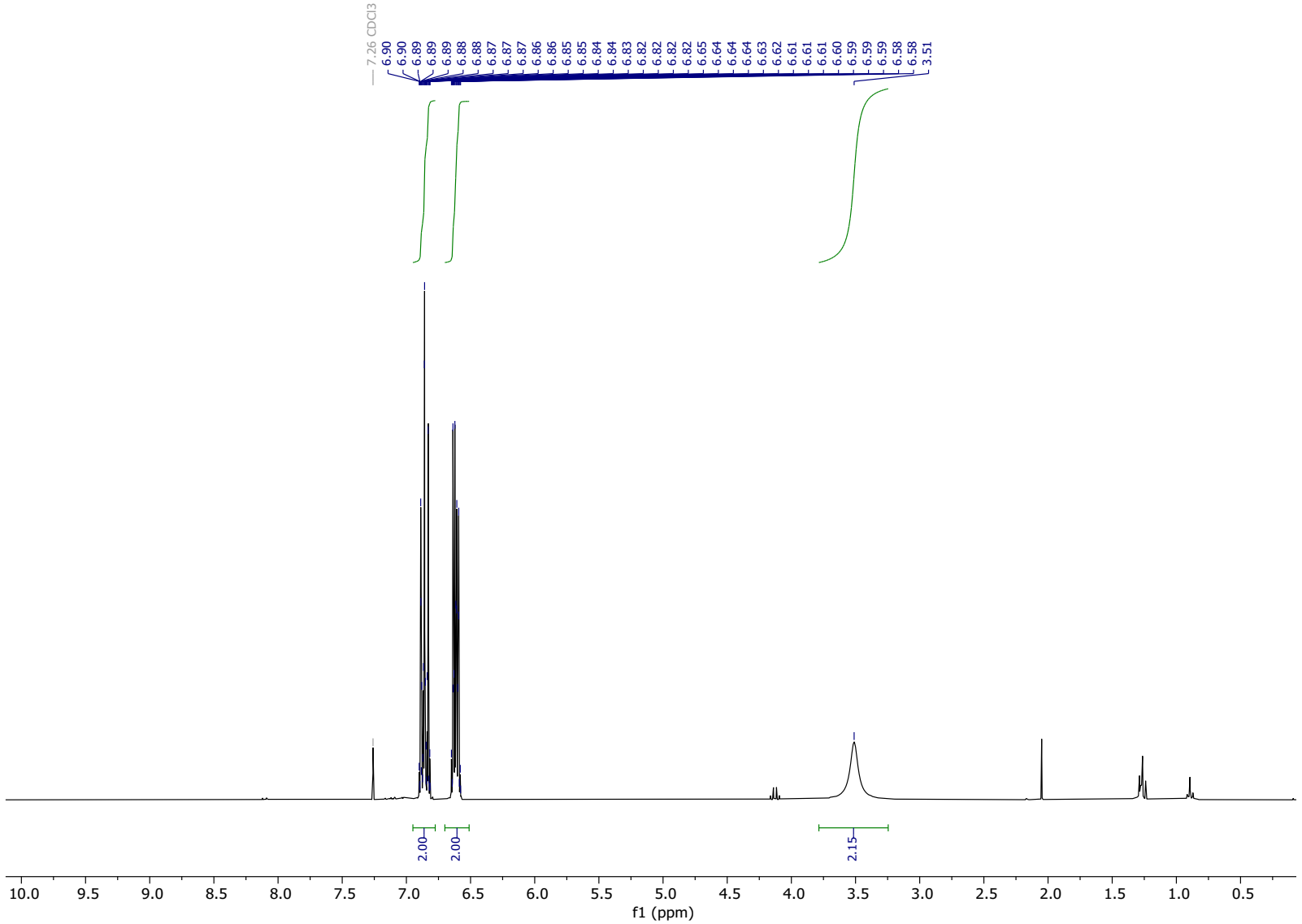


Figure S80: ^{1}H-NMR (300 MHz, $CDCl_3$) for 4-fluoroaniline (2c)

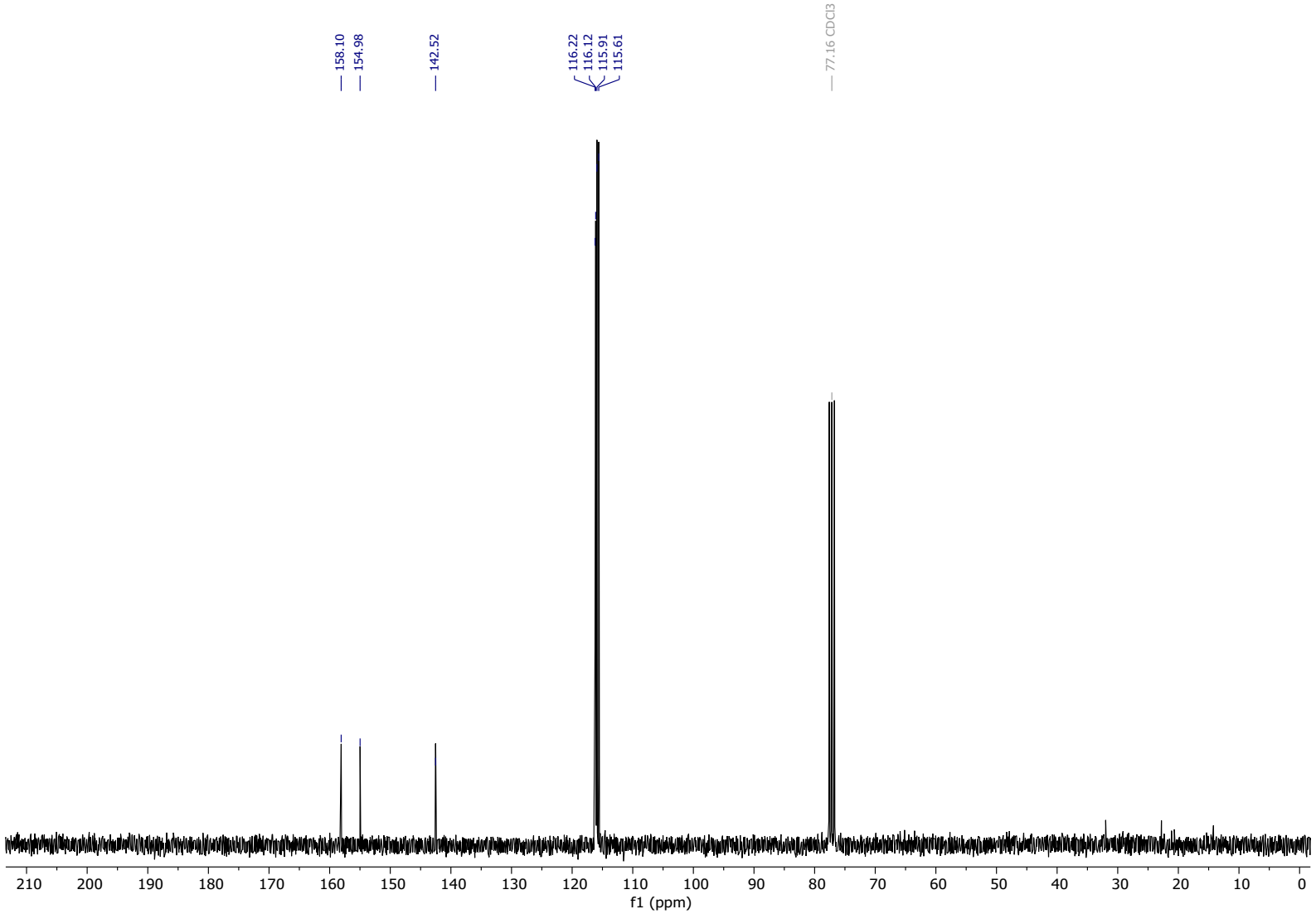


Figure S81: ^{13}C-NMR (75 MHz, $CDCl_3$) for 4-fluoroaniline (2c)

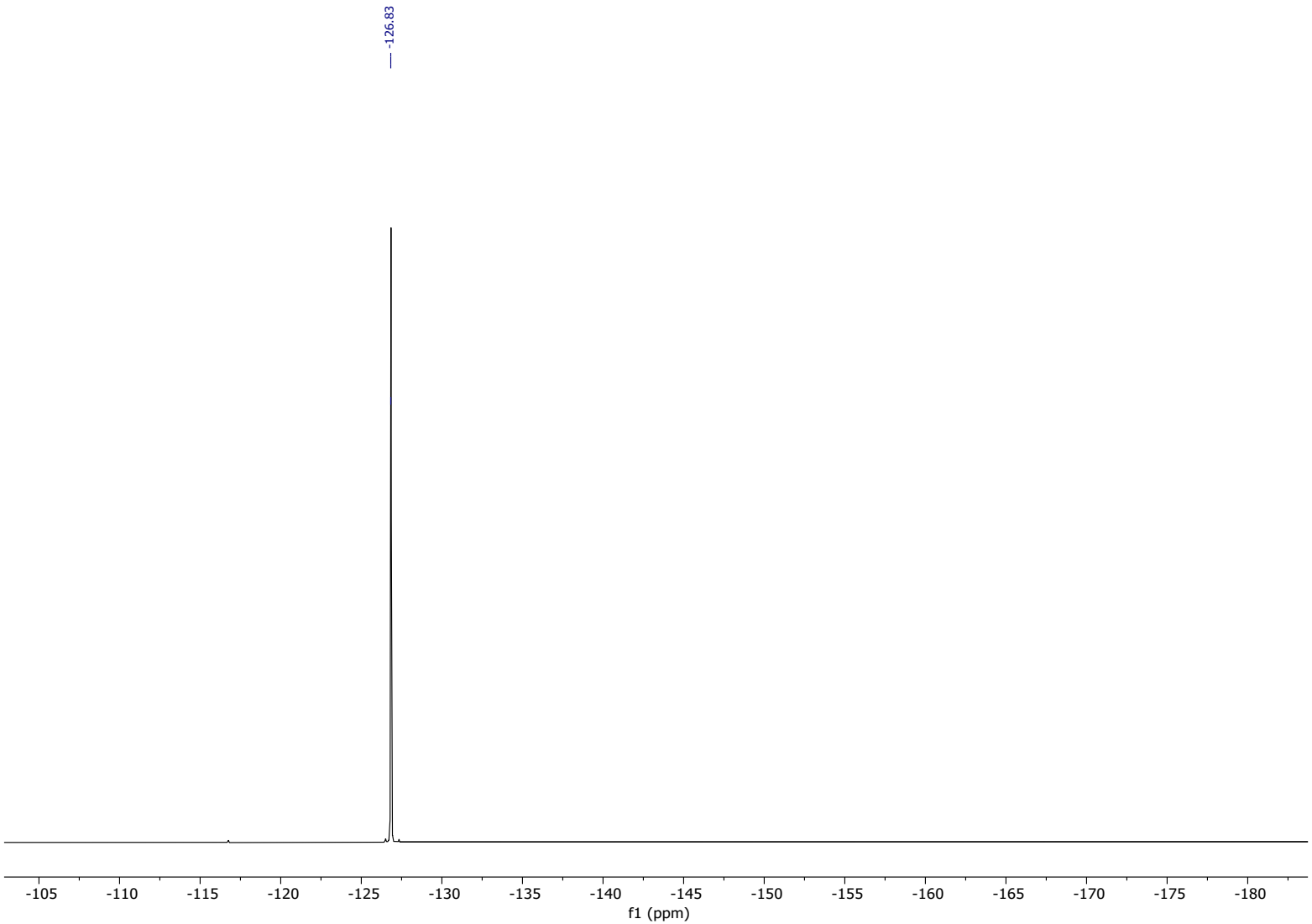


Figure S82: ^{19}F-NMR (300 MHz, $CDCl_3$) for 4-fluoroaniline (2c)

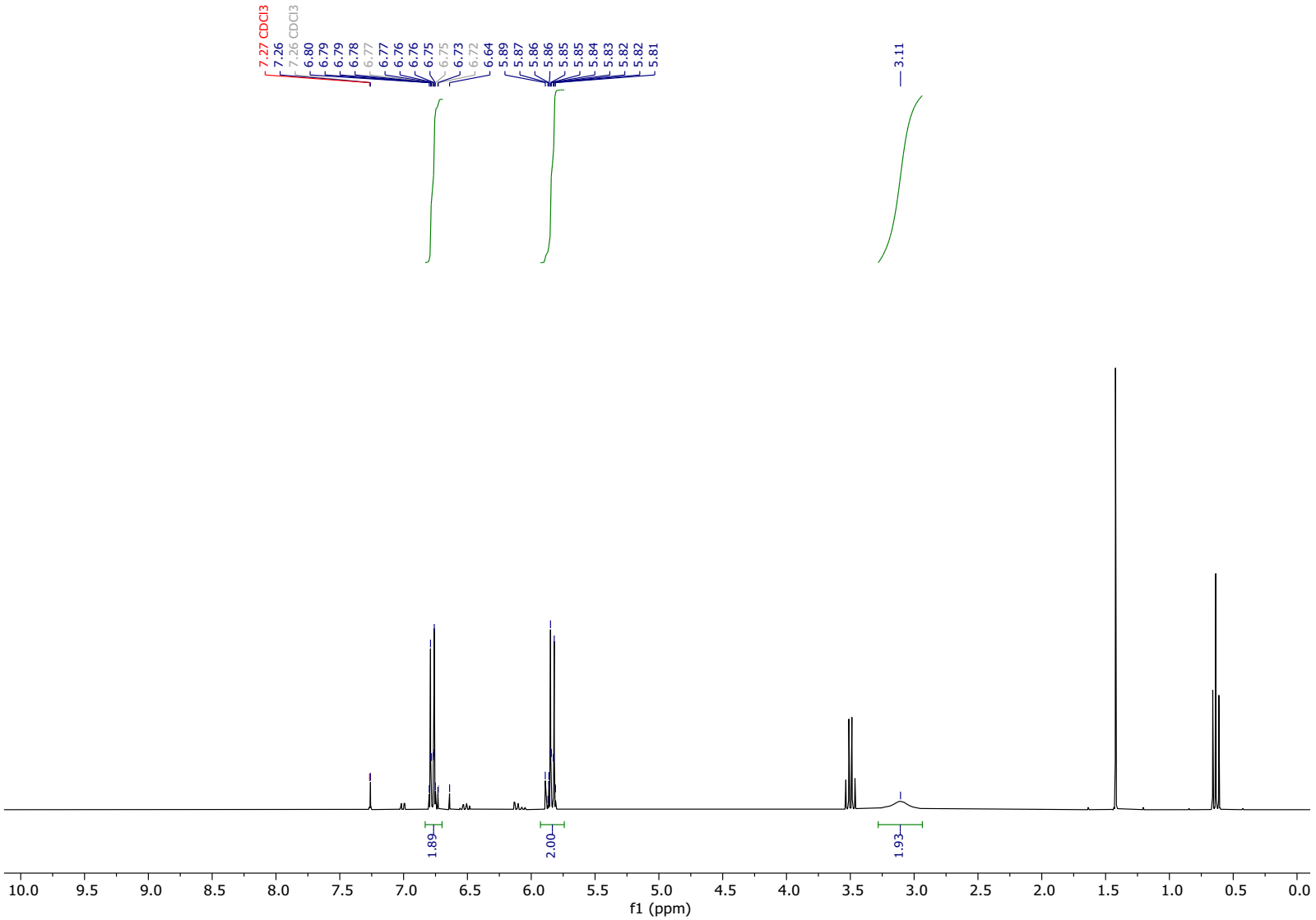


Figure S83: ^{1}H-NMR (300 MHz, $CDCl_3$) for 4-iodoaniline (2d) with impurities of ethyl acetate.

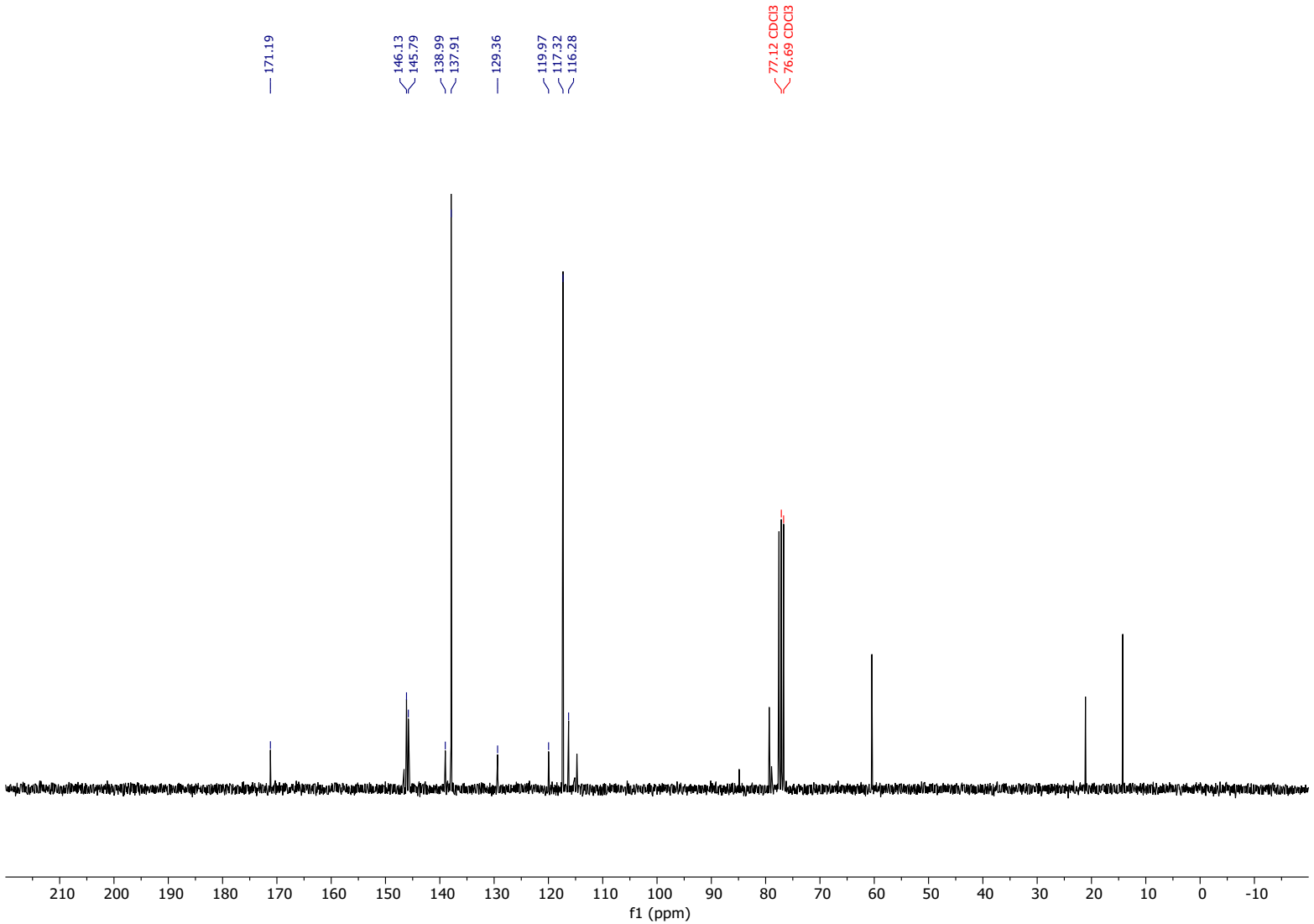


Figure S84: ^{13}C-NMR (75 MHz, $CDCl_3$) for 4-iodoaniline (2d)

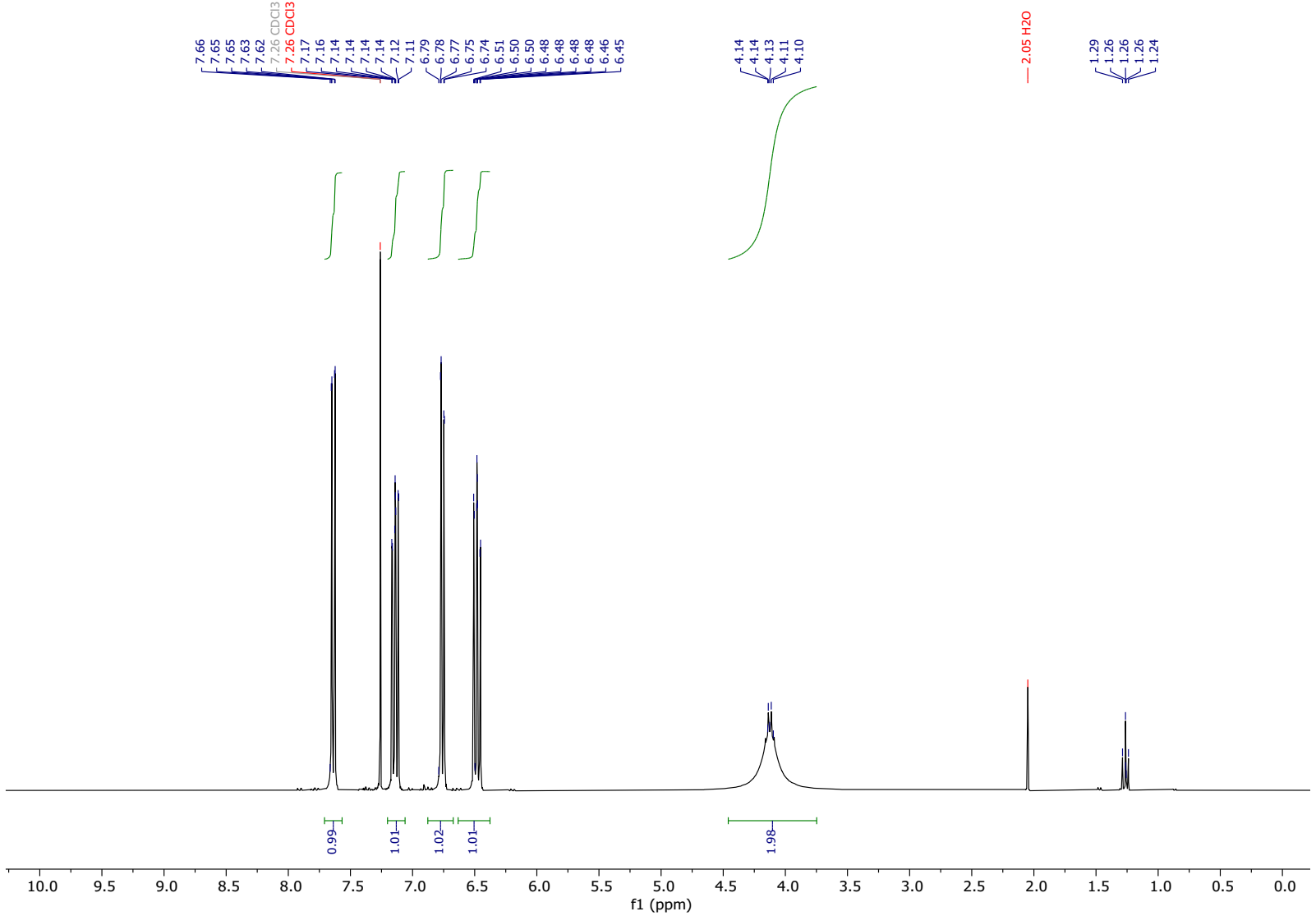


Figure S85: ^{1}H-NMR (300 MHz, $CDCl_3$) for 2-iodoaniline (2e)

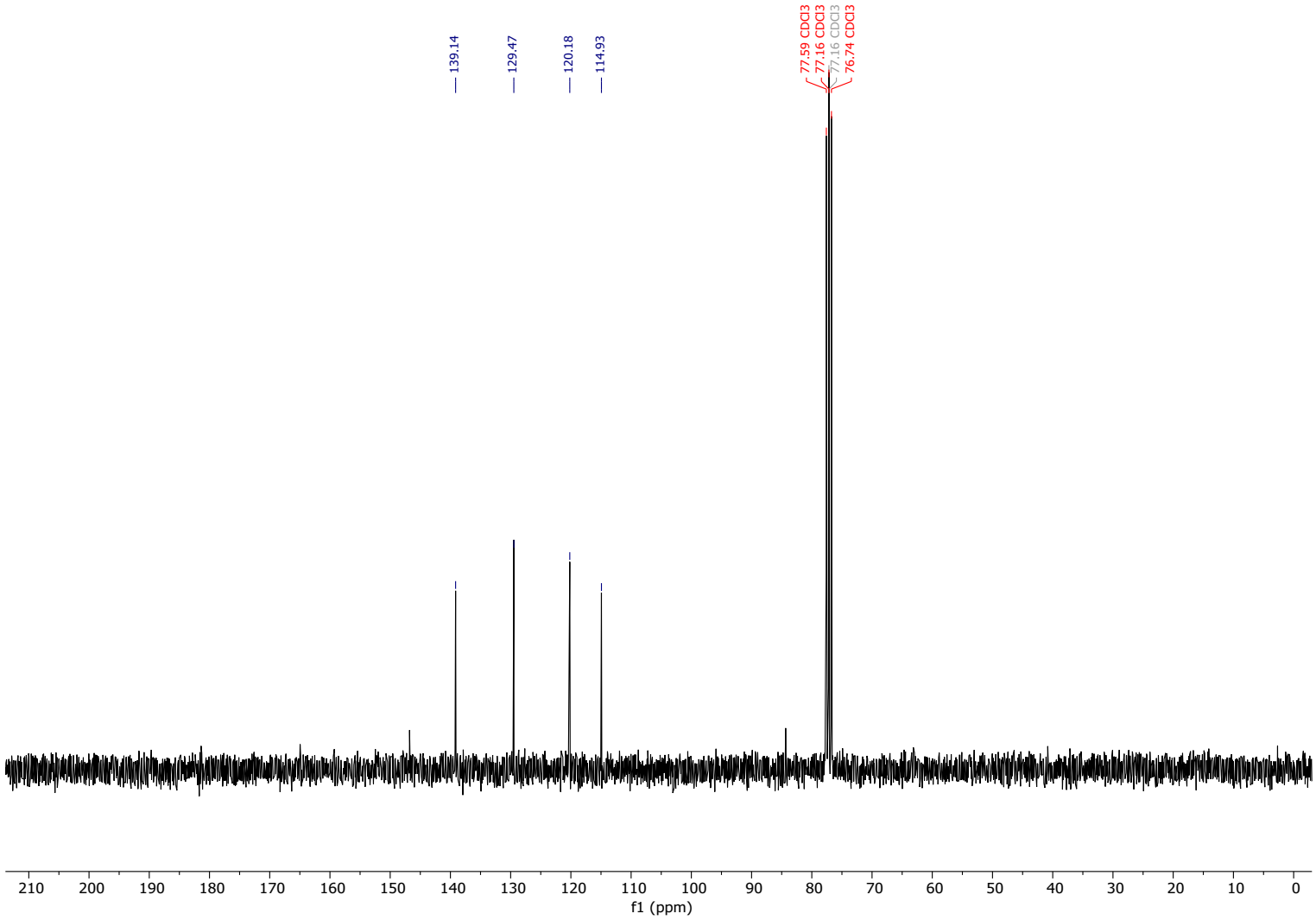


Figure S86: ^{13}C-NMR (75 MHz, $CDCl_3$) for 2-iodoaniline (2e)

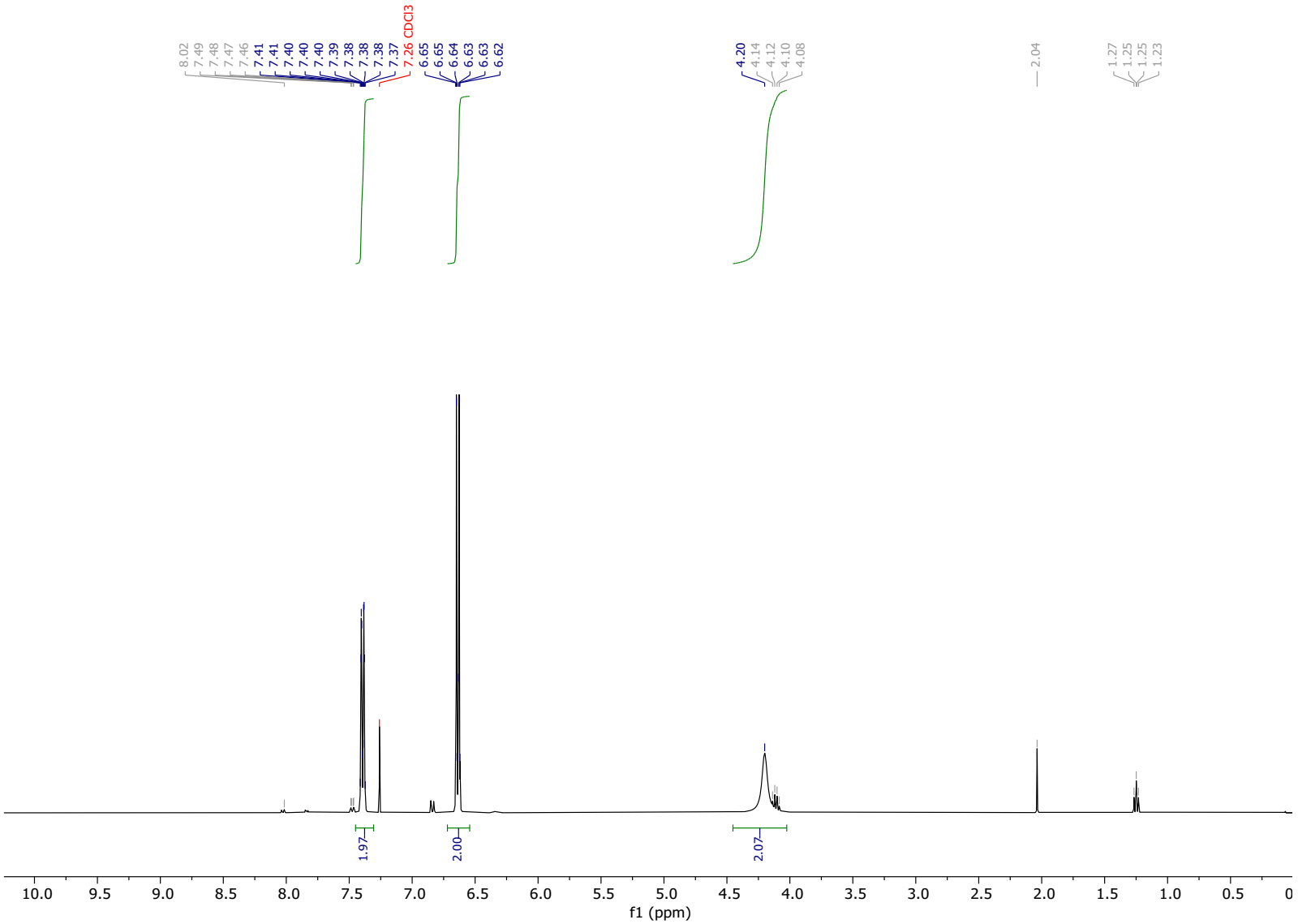


Figure S87: ^{1}H-NMR (300 MHz, $CDCl_3$) for 4-aminobenzonitrile (2f)

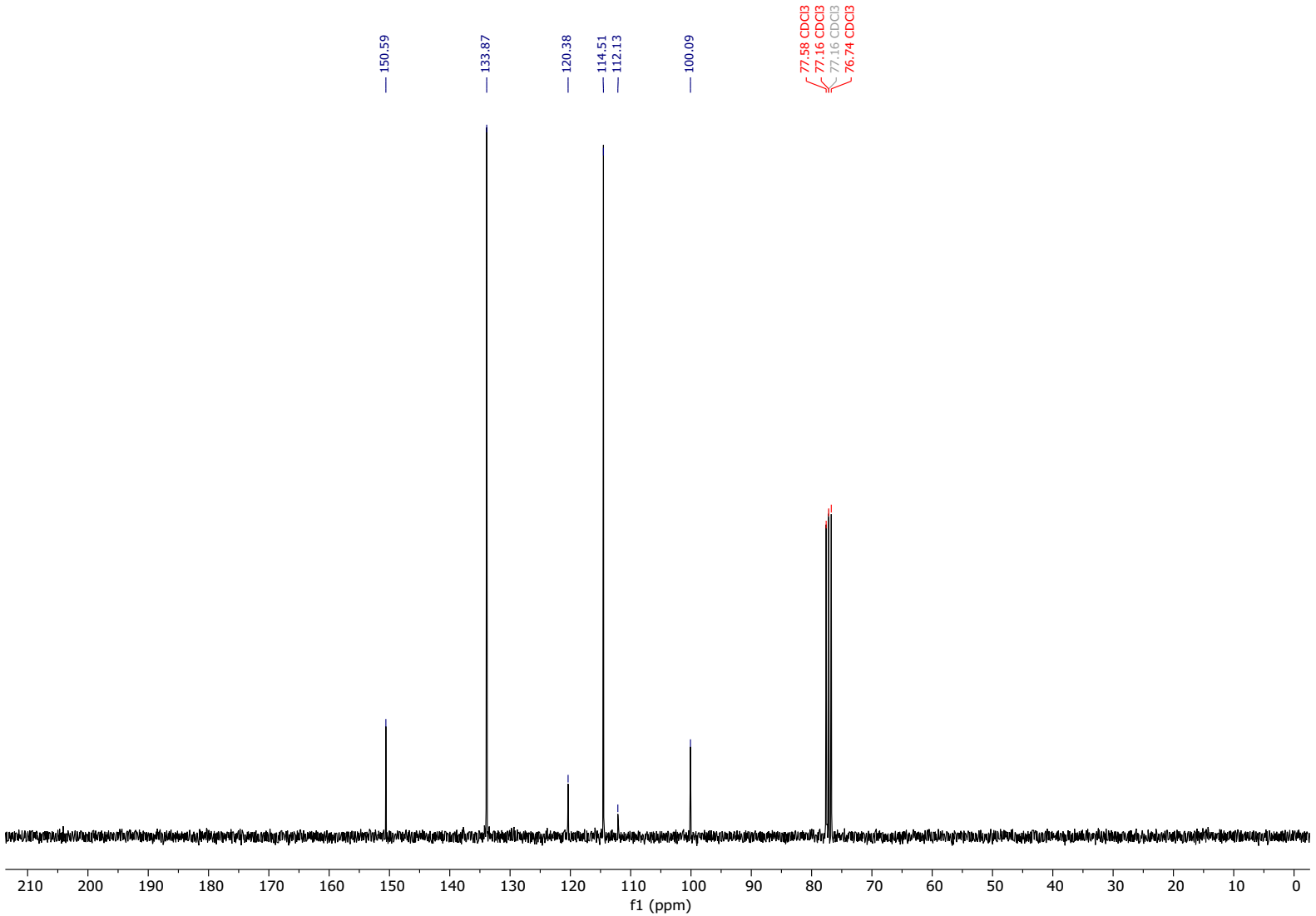


Figure S88: ^{13}C-NMR (75 MHz, $CDCl_3$) for 4-aminobenzonitrile (2f)

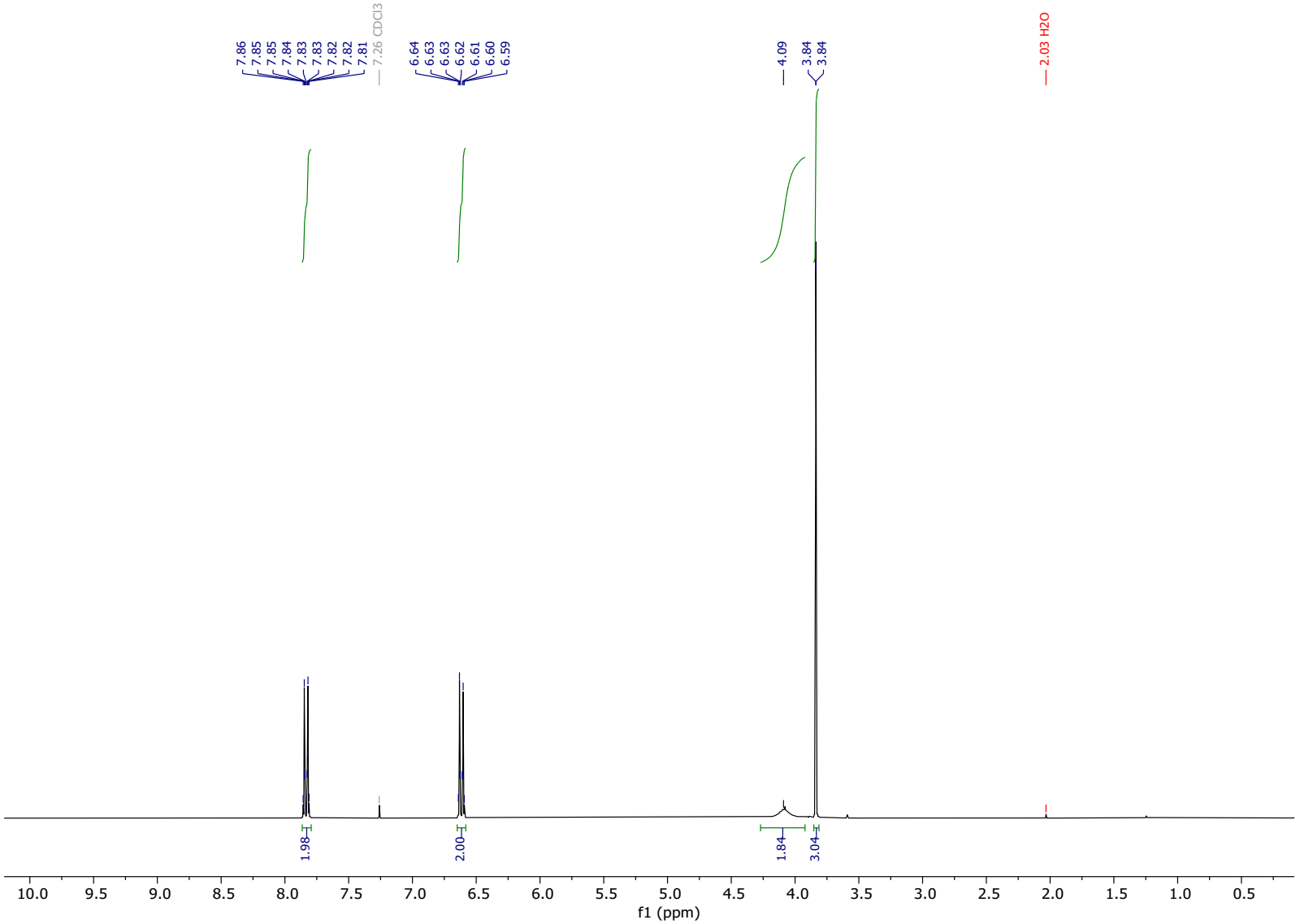


Figure S89: ^{1}H-NMR (300 MHz, $CDCl_3$) for methyl 4-aminobenzoate (2g)

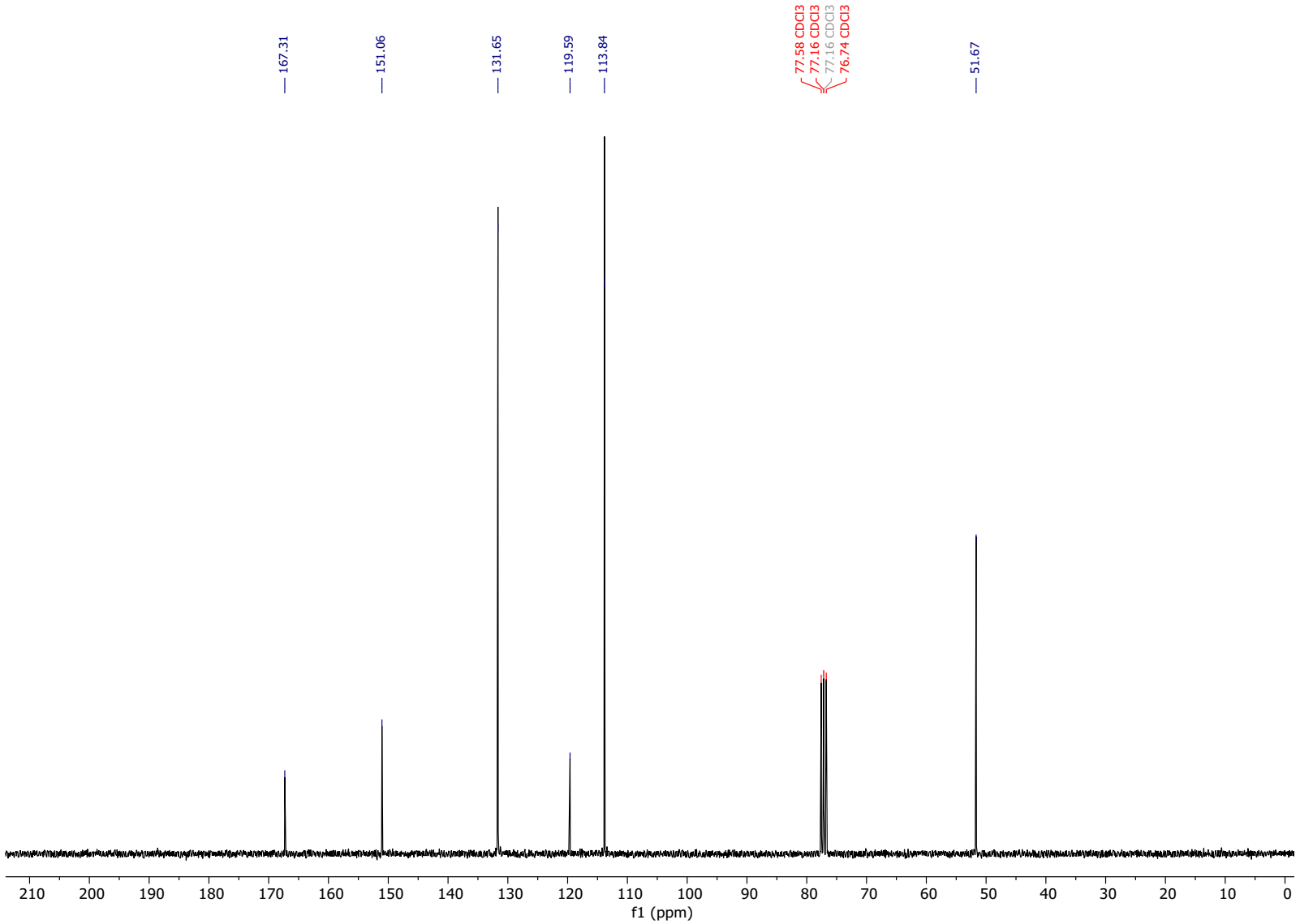


Figure S90: ^{13}C-NMR (75 MHz, $CDCl_3$) for methyl 4-aminobenzoate (2g)

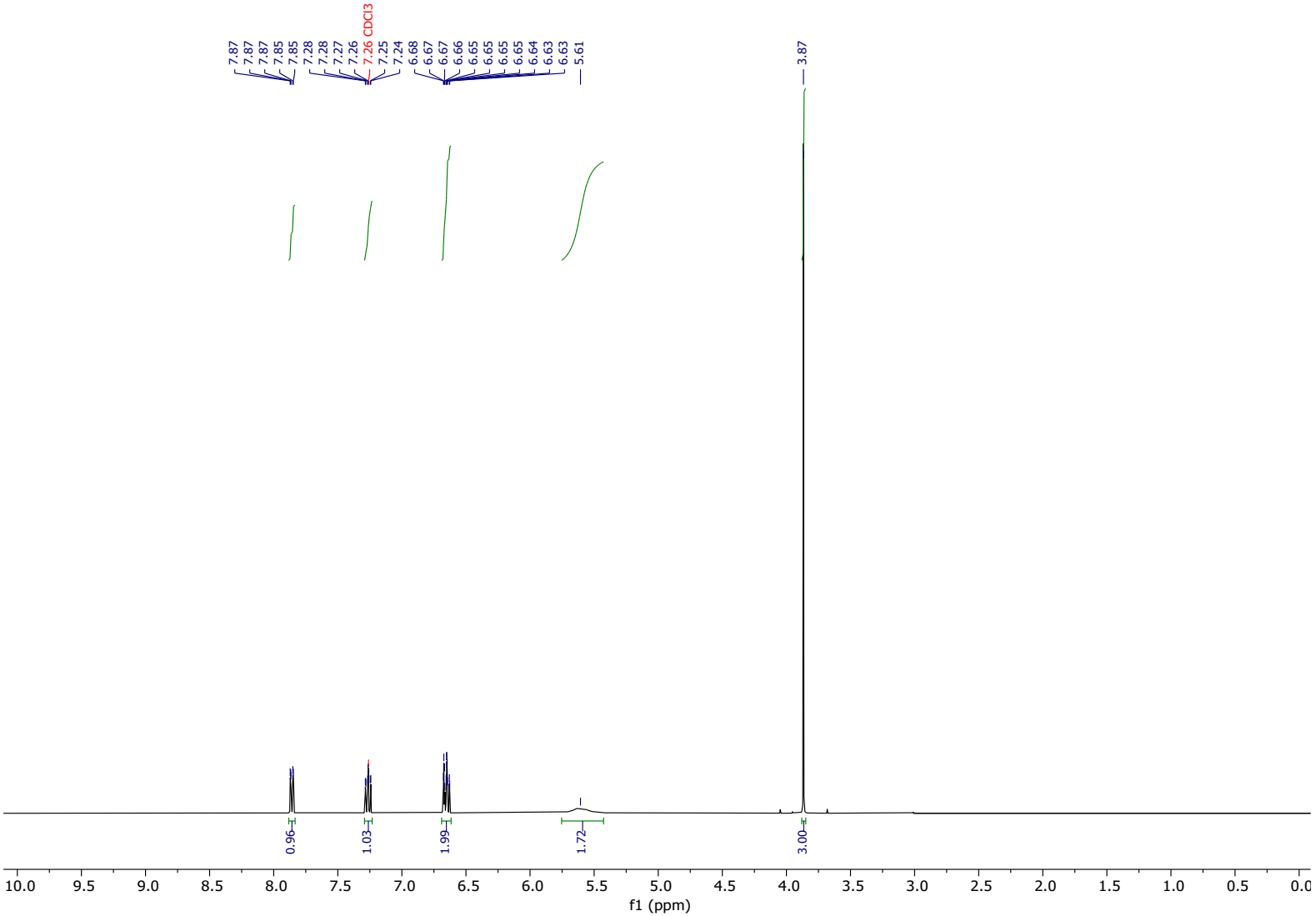


Figure S91: ^{1}H-NMR (300 MHz, $CDCl_3$) for methyl 2-aminobenzoate (2h)

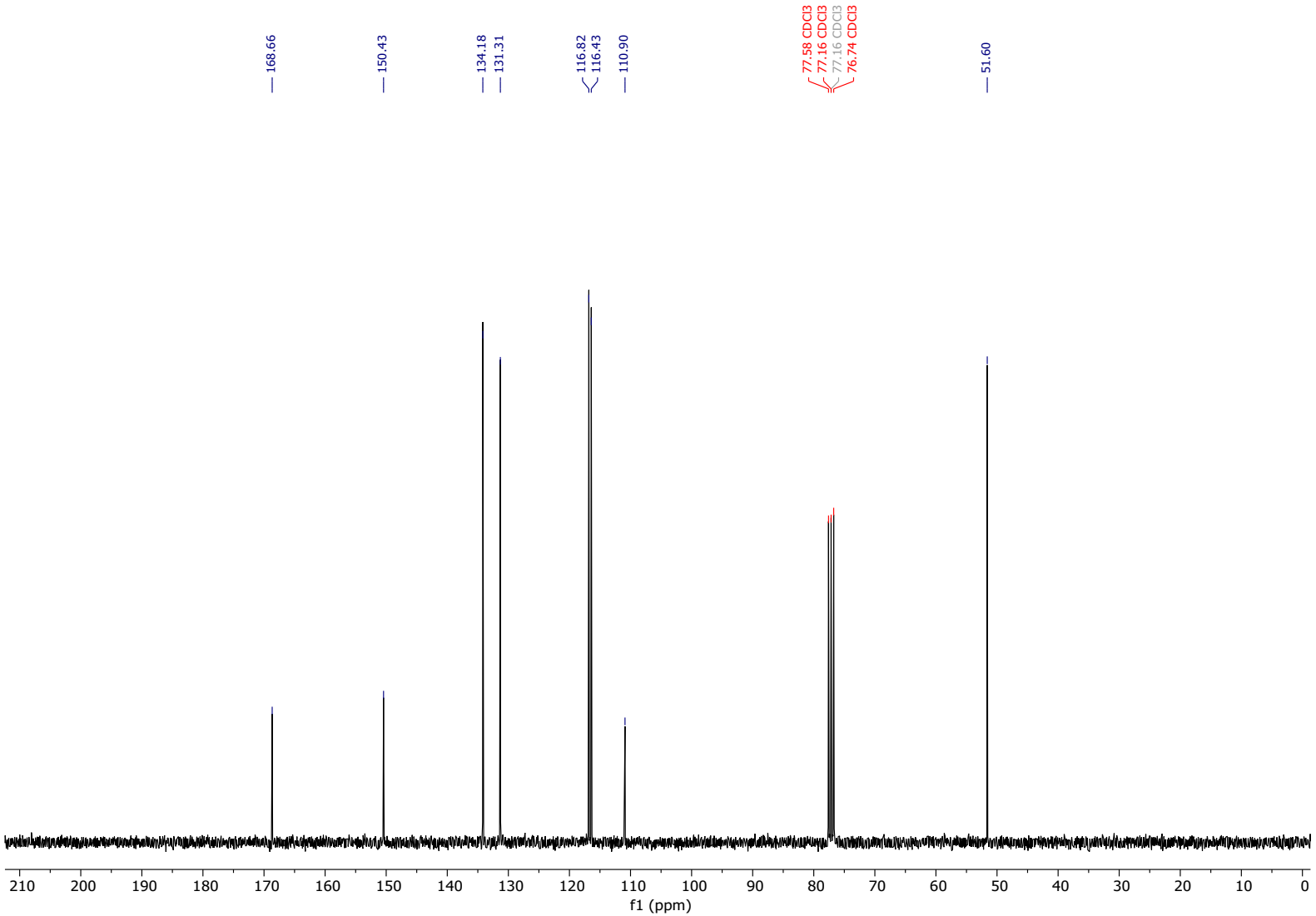


Figure S92: ^{13}C-NMR (75 MHz, $CDCl_3$) for methyl 2-aminobenzoate (2h)

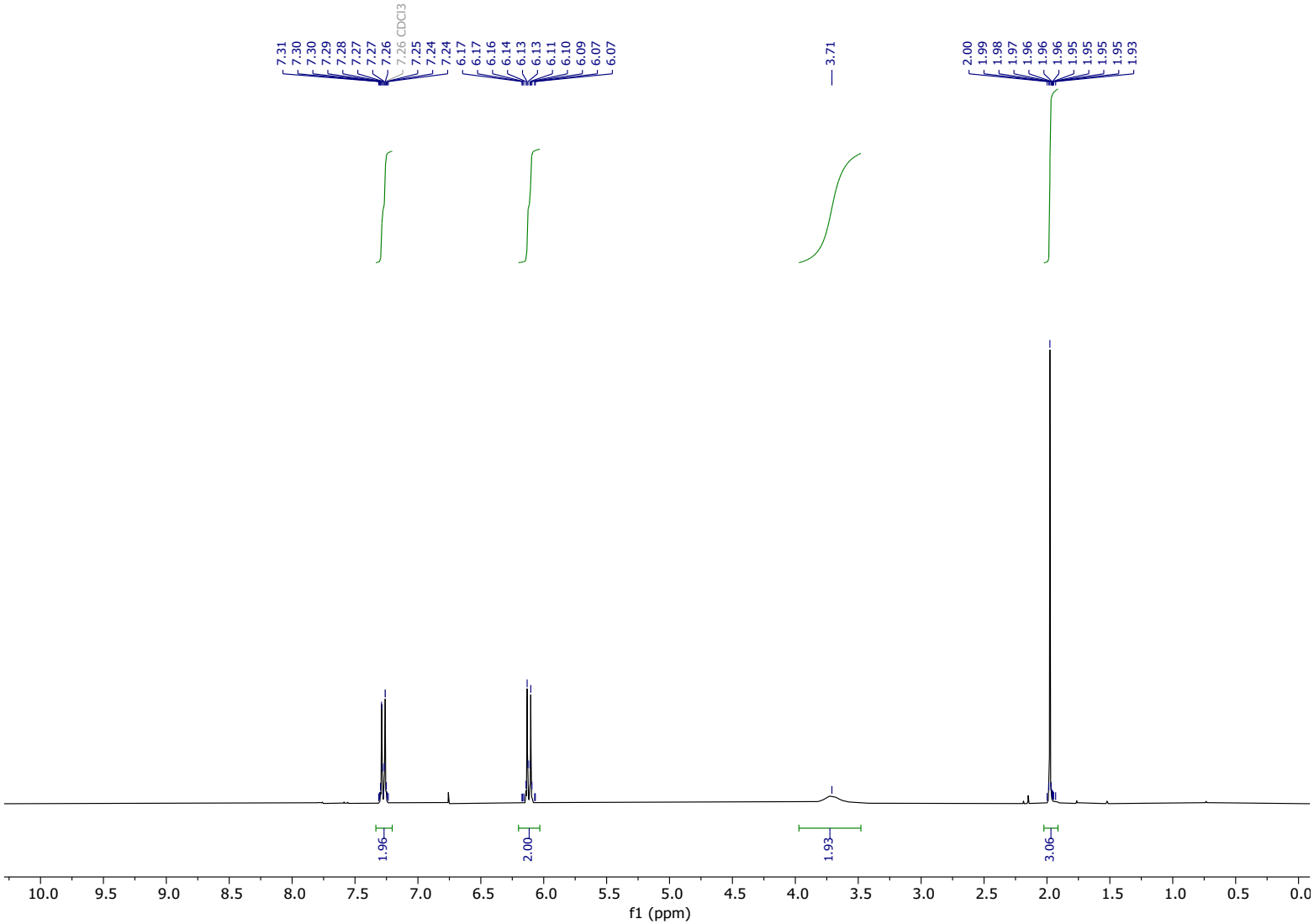


Figure S93: ^{1}H-NMR (300 MHz, $CDCl_3$) for 1-(4-aminophenyl)ethan-1-one (2i)

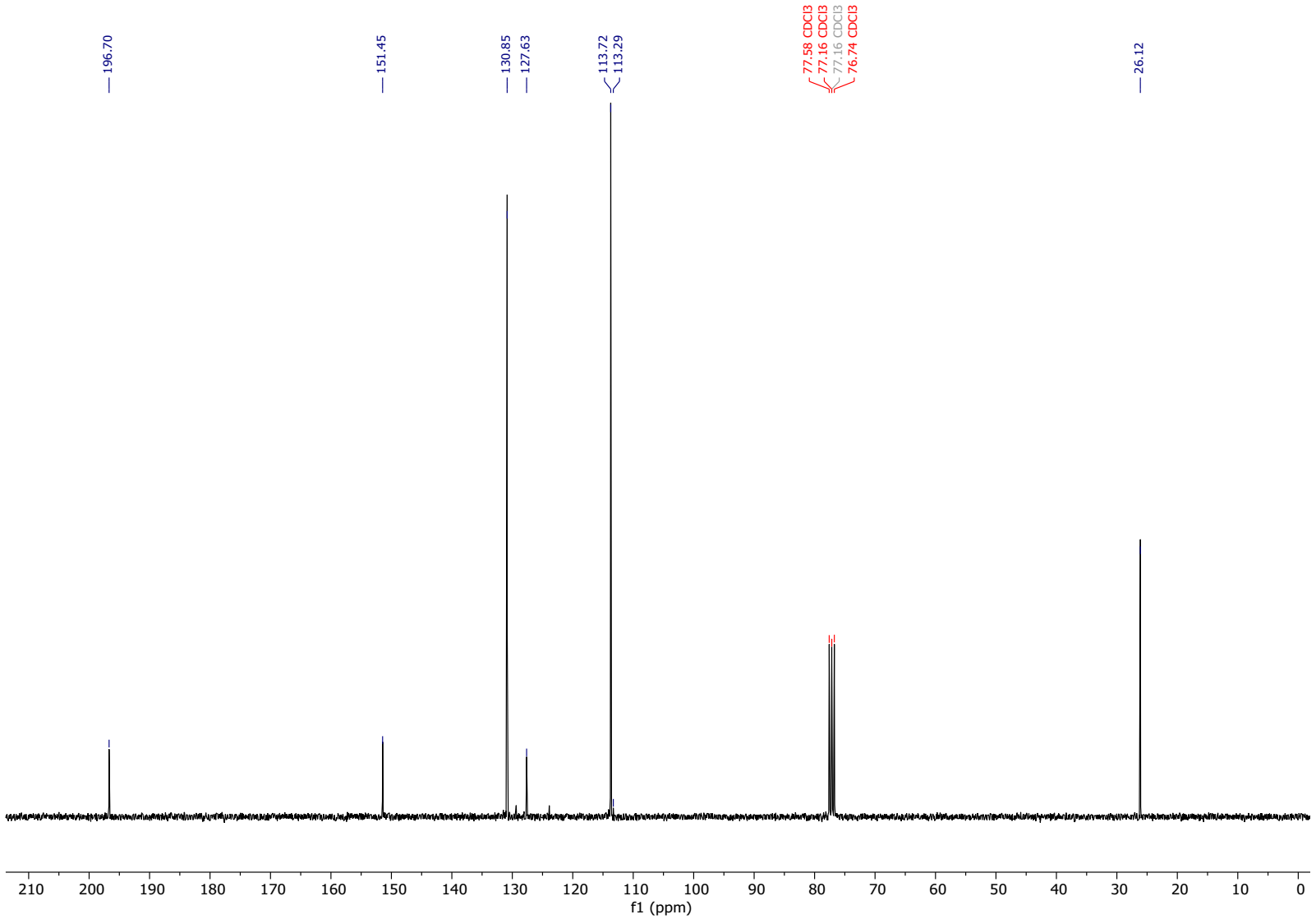


Figure S94: ^{13}C-NMR (75 MHz, $CDCl_3$) for 1-(4-aminophenyl)ethan-1-one (2i)

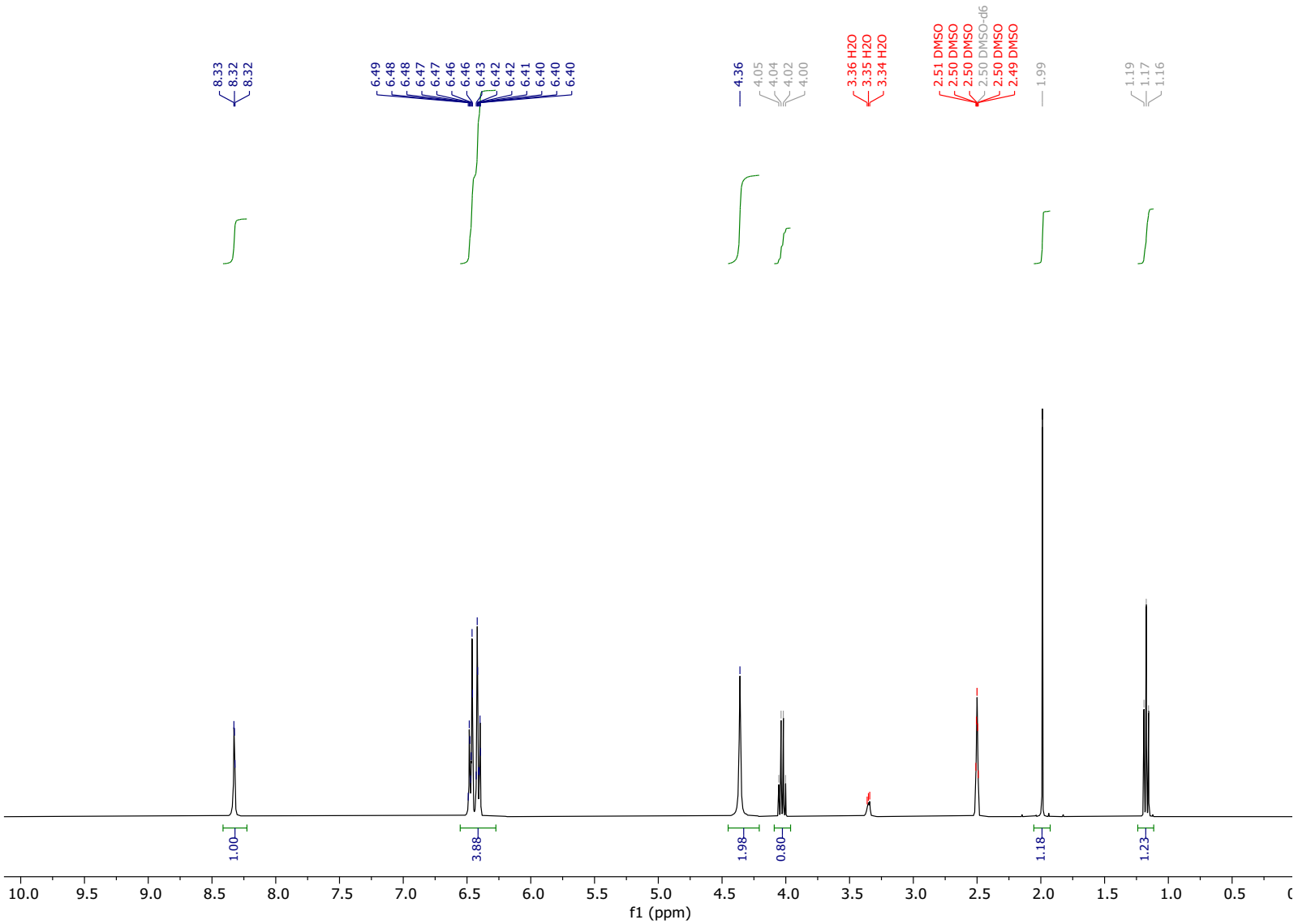


Figure S95: ^{1}H-NMR (300 MHz, $CDCl_3$) for 4-aminophenol (2j)

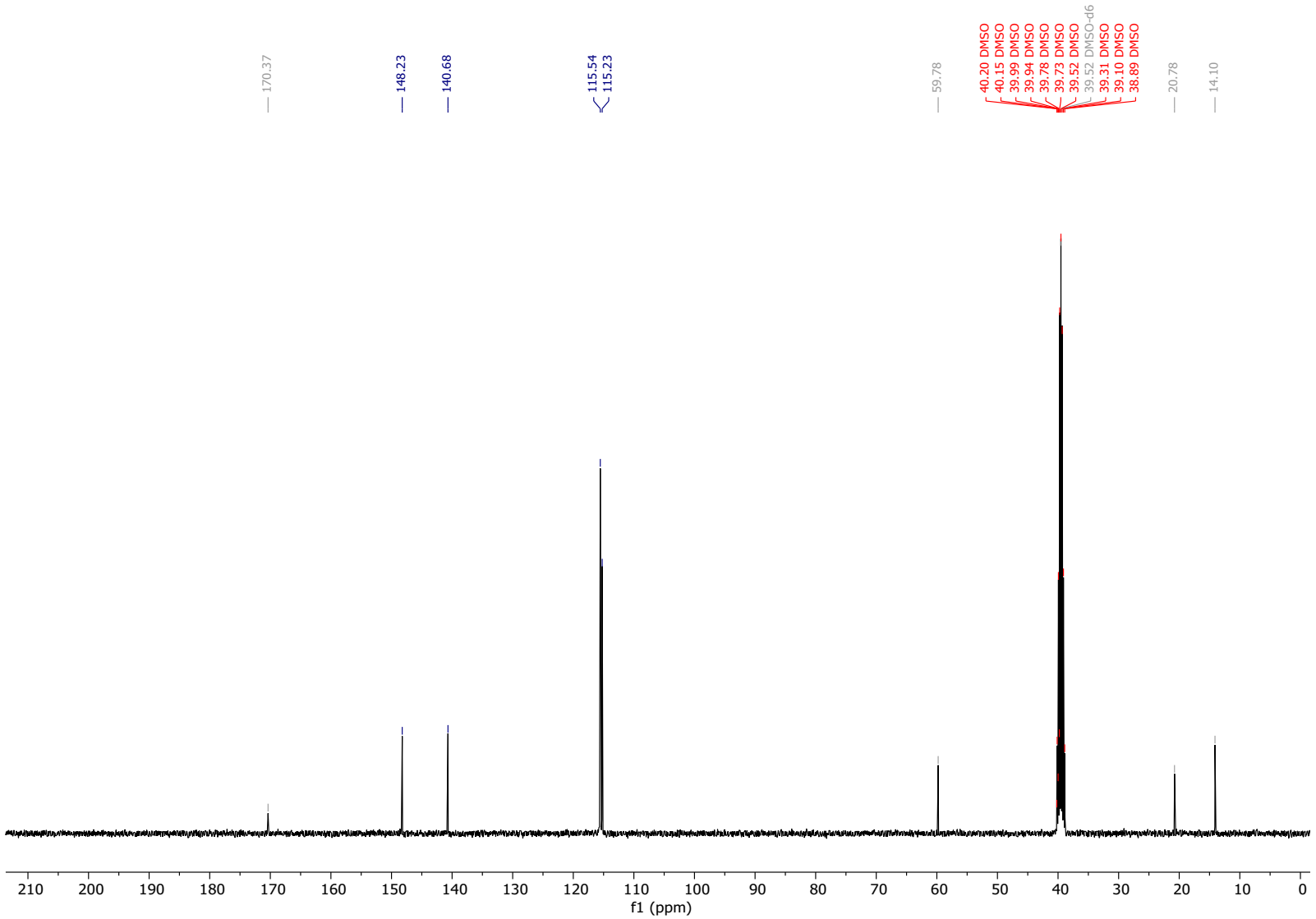


Figure S96: ^{13}C-NMR (75 MHz, $CDCl_3$) for 4-aminophenol (2j)

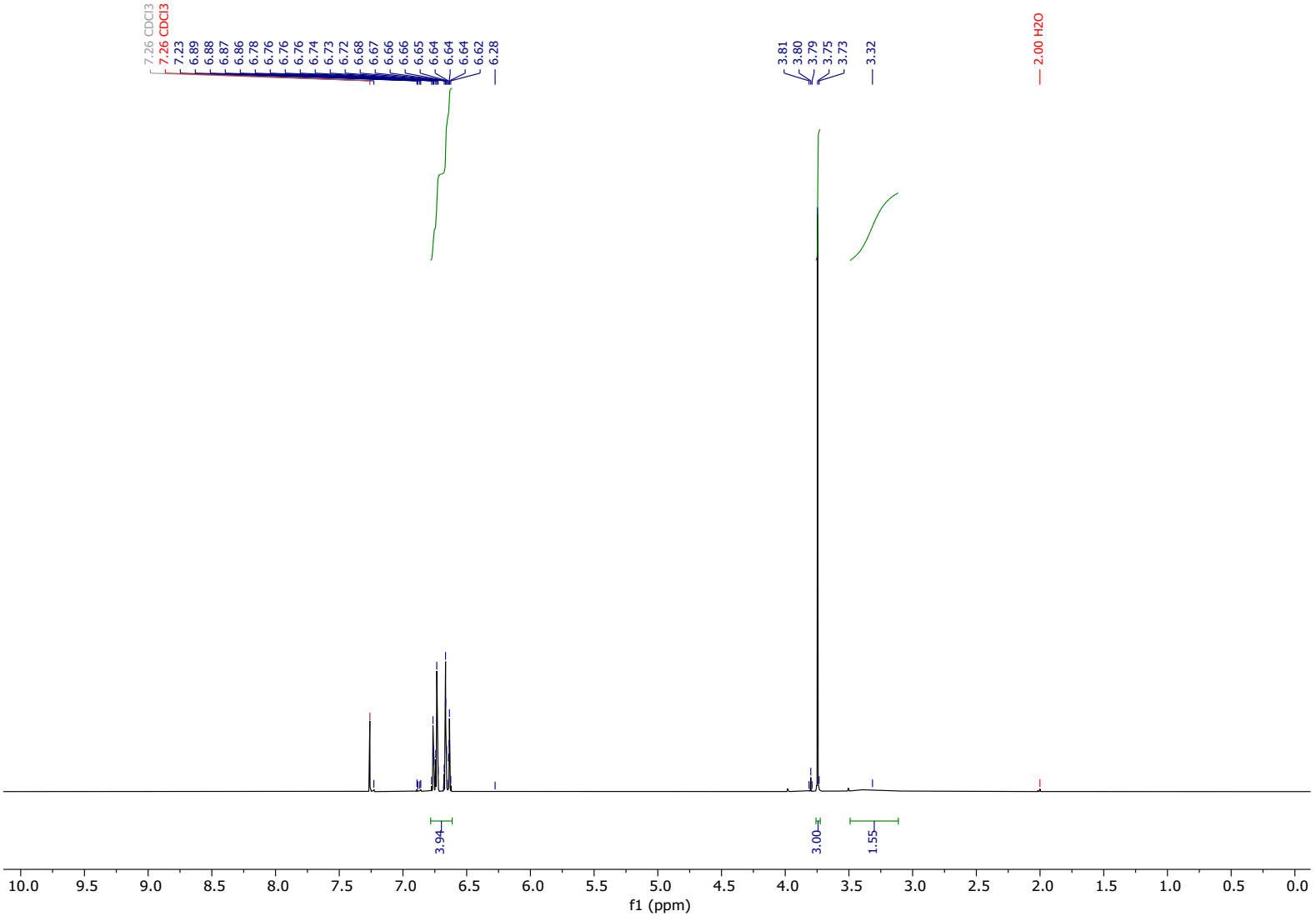


Figure S97: ^{1}H-NMR (300 MHz, $CDCl_3$) for 4-methoxyaniline (2k)

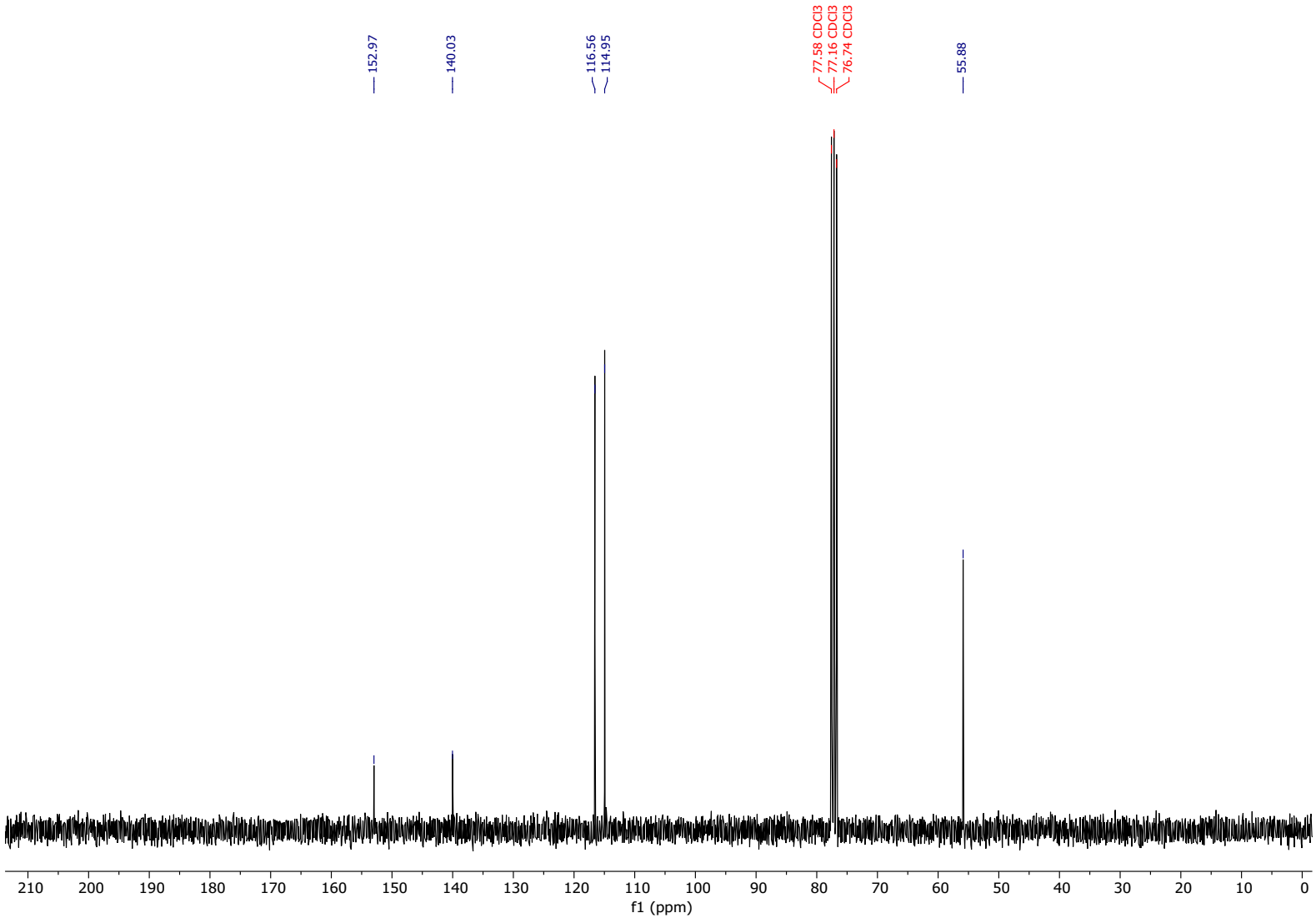


Figure S98: ^{13}C-NMR (75 MHz, $CDCl_3$) for 4-methoxyaniline (2k)

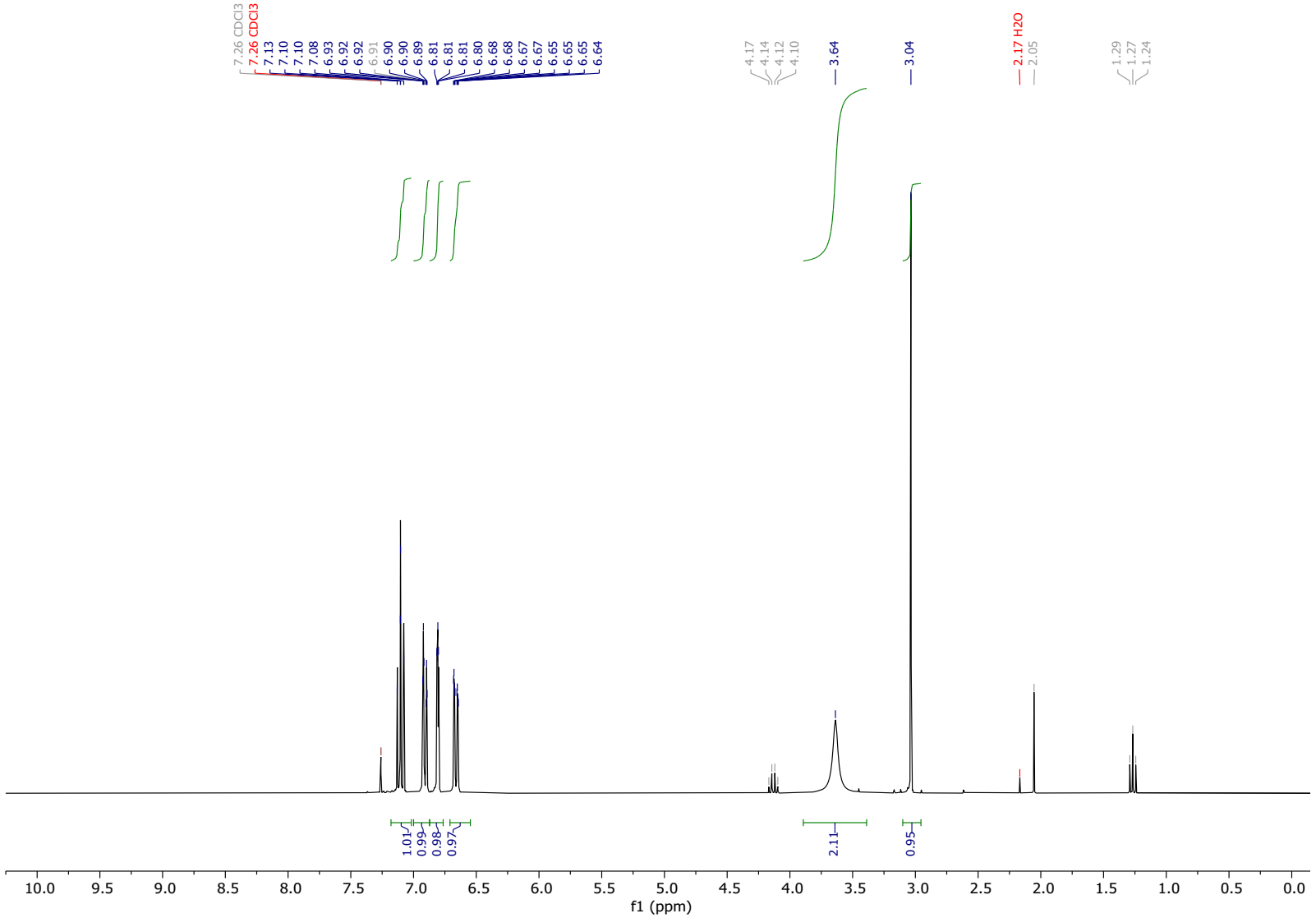


Figure S99: ^{1}H-NMR (300 MHz, $CDCl_3$) for 3-ethynylaniline (2l)

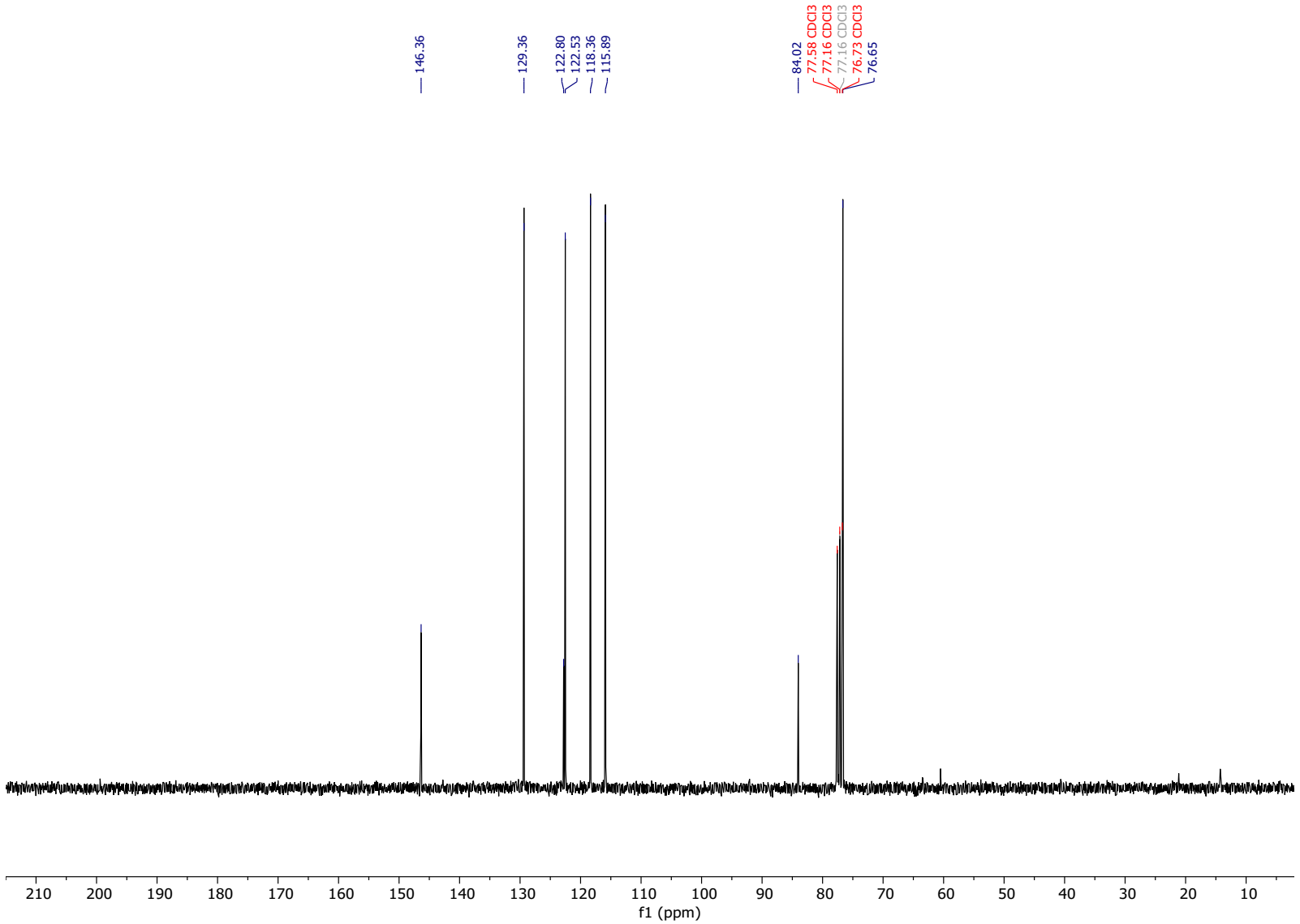


Figure S100: ^{13}C-NMR (75 MHz, $CDCl_3$) for 3-ethynylaniline (2l)

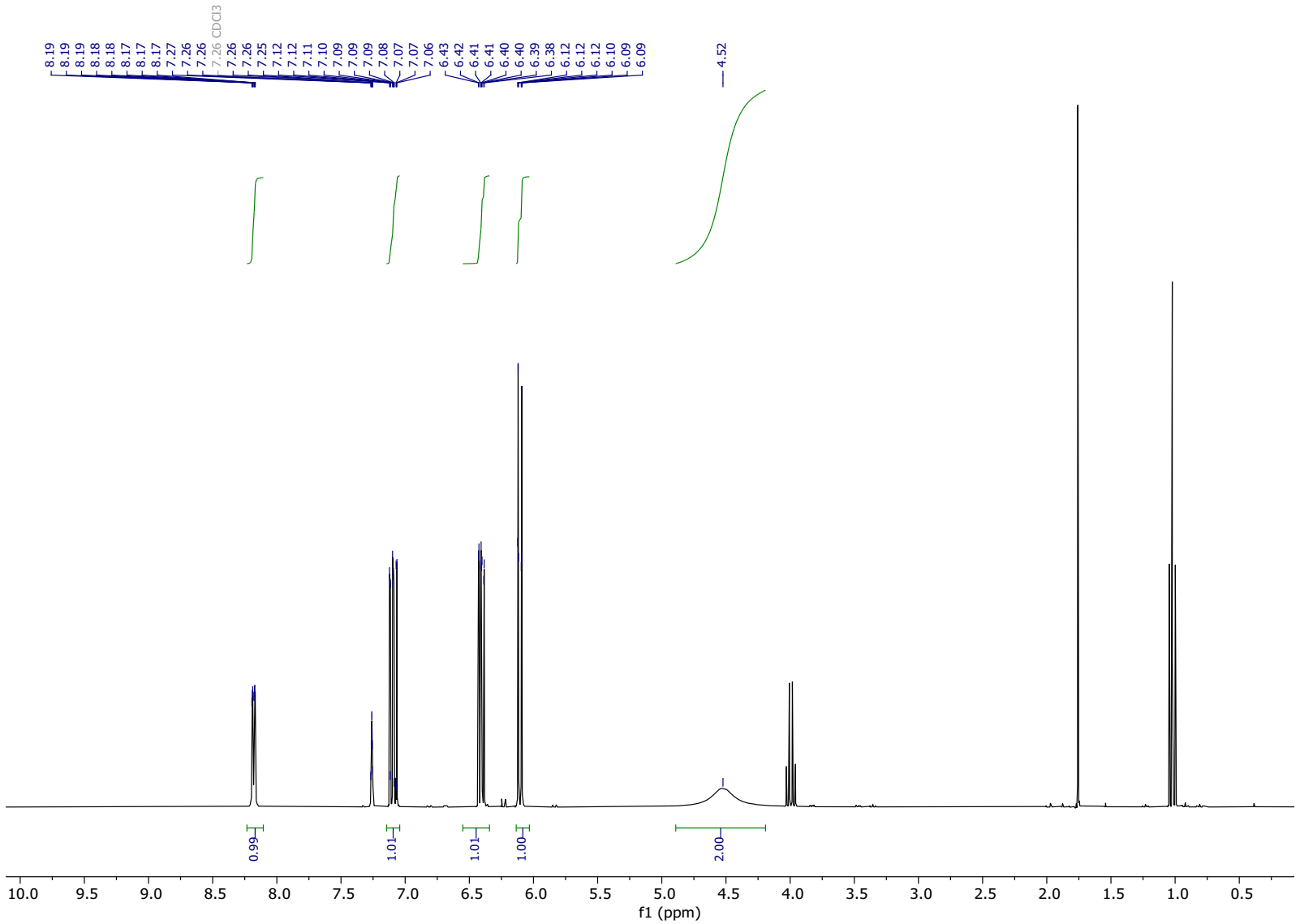


Figure S101: ^{1}H-NMR (300 MHz, $CDCl_3$) for pyridin-2-amine (2m)

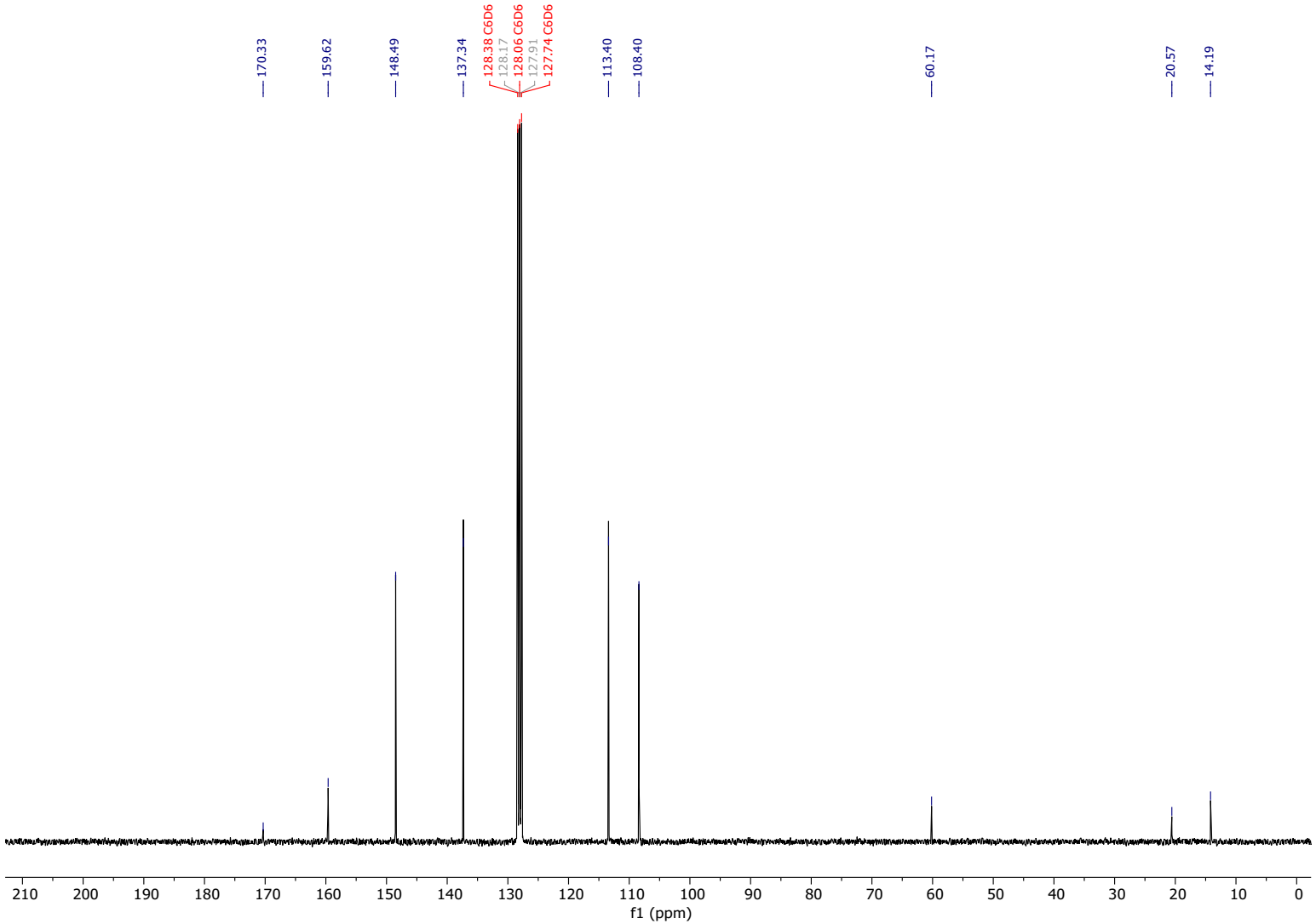


Figure S102: ^{13}C-NMR (75 MHz, $CDCl_3$) for pyridin-2-amine (2m)

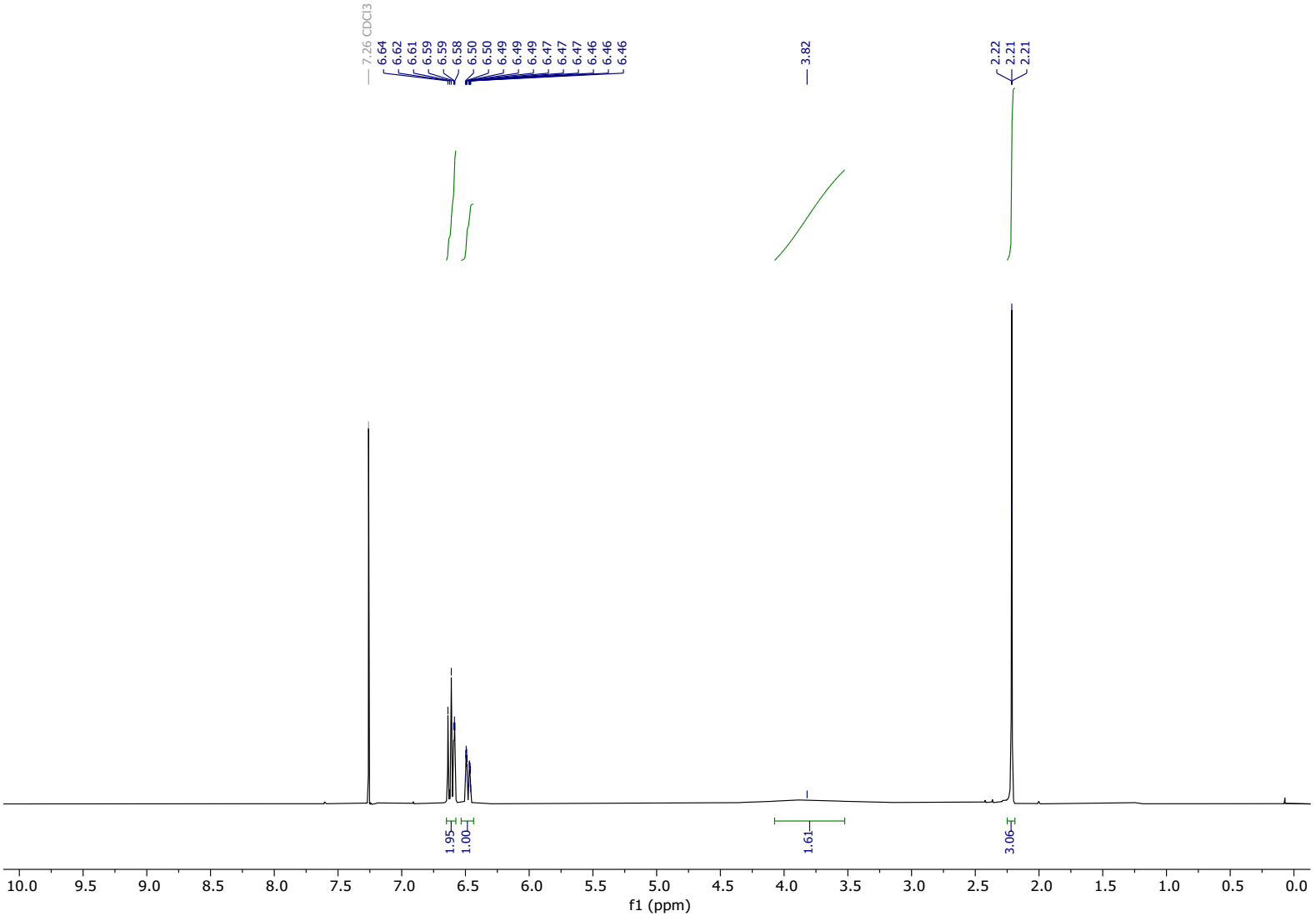


Figure S103: ^{1}H-NMR (300 MHz, $CDCl_3$) for 2-amino-4-methylpyridin (2n)

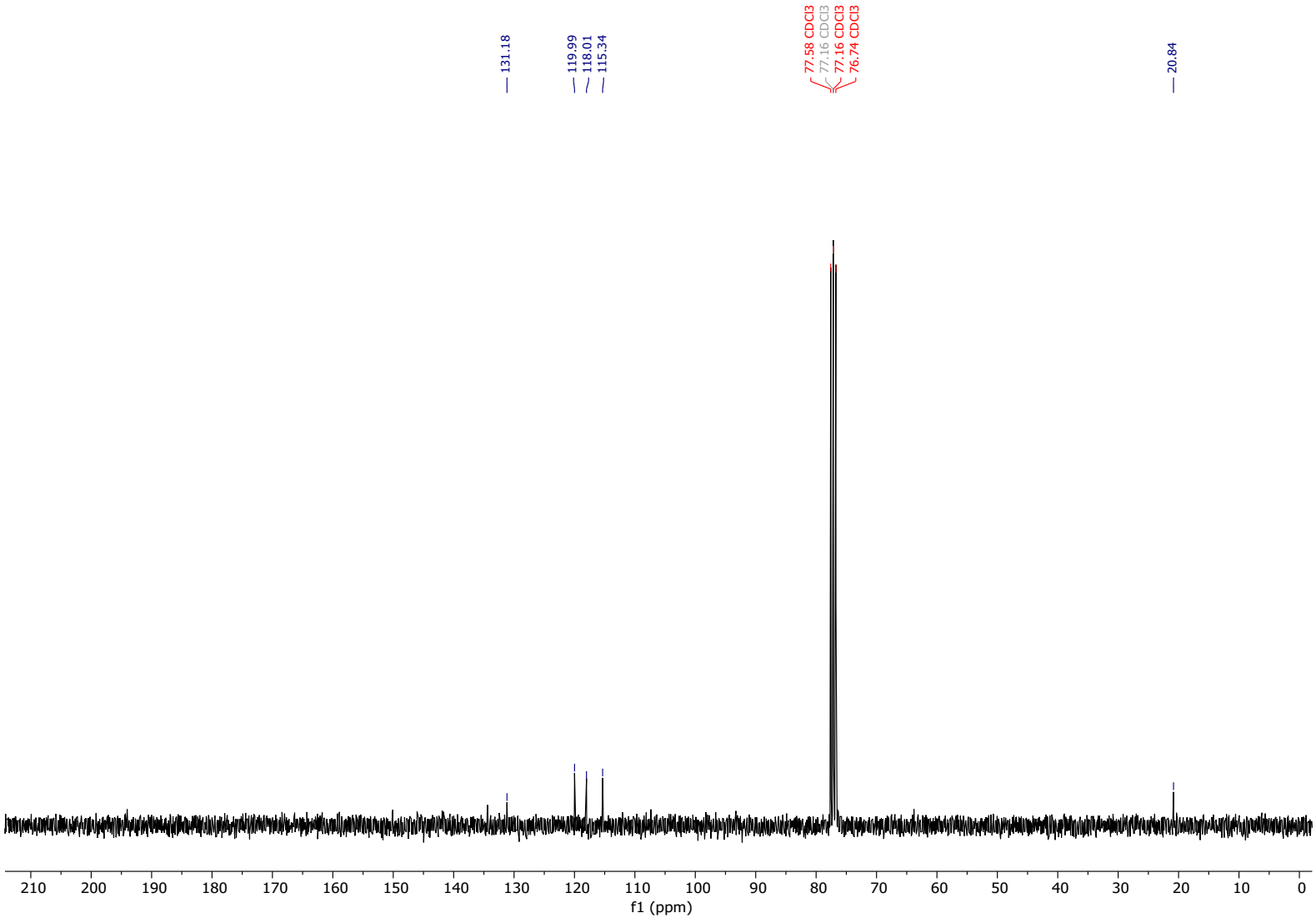


Figure S104: ^{13}C-NMR (75 MHz, $CDCl_3$) for 2-amino-4-methylpyridin(2n).

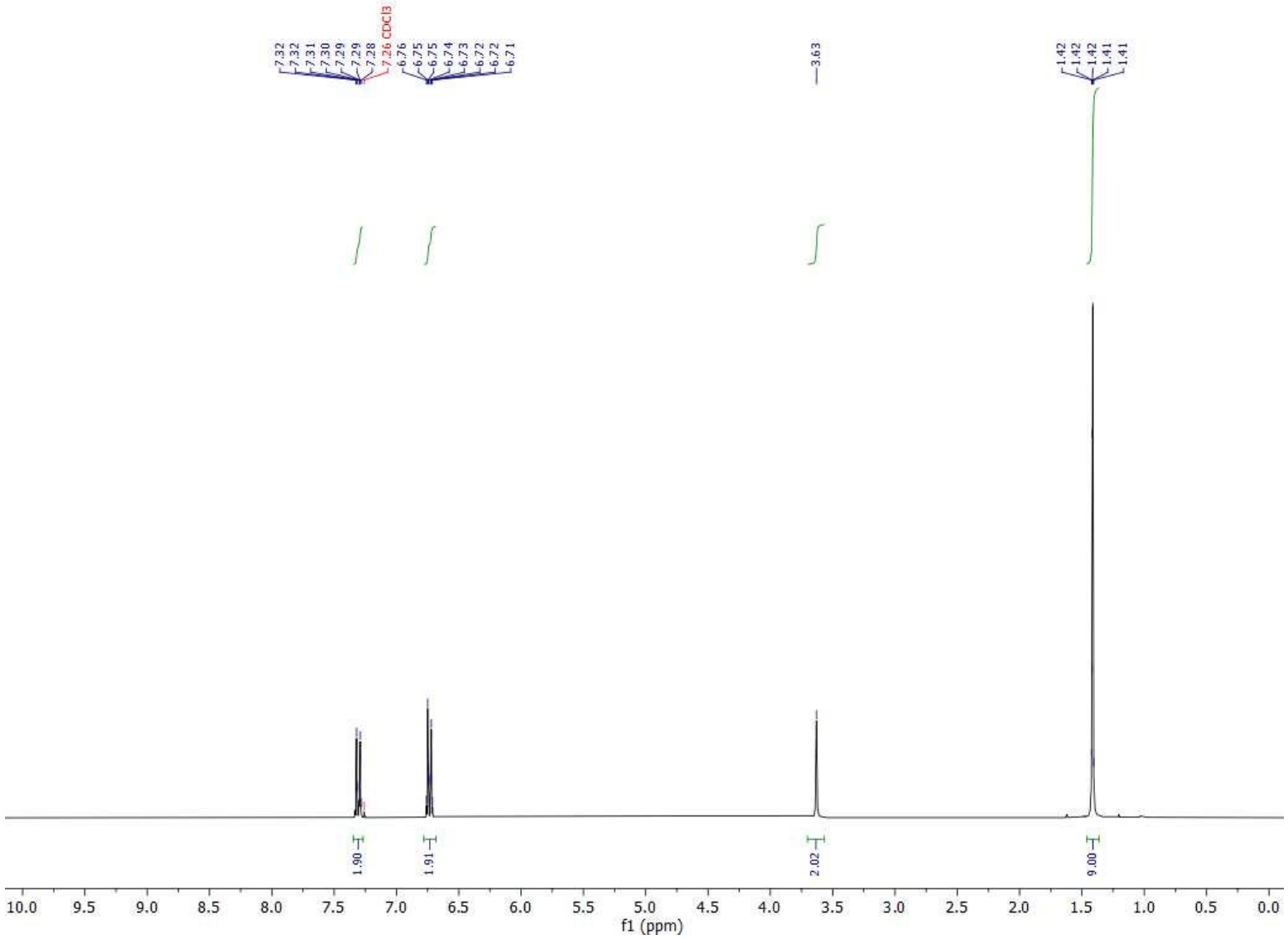


Figure S105 ^{1}H-NMR (300 MHz, $CDCl_3$) for 4-(tert-butyl)aniline (2o)

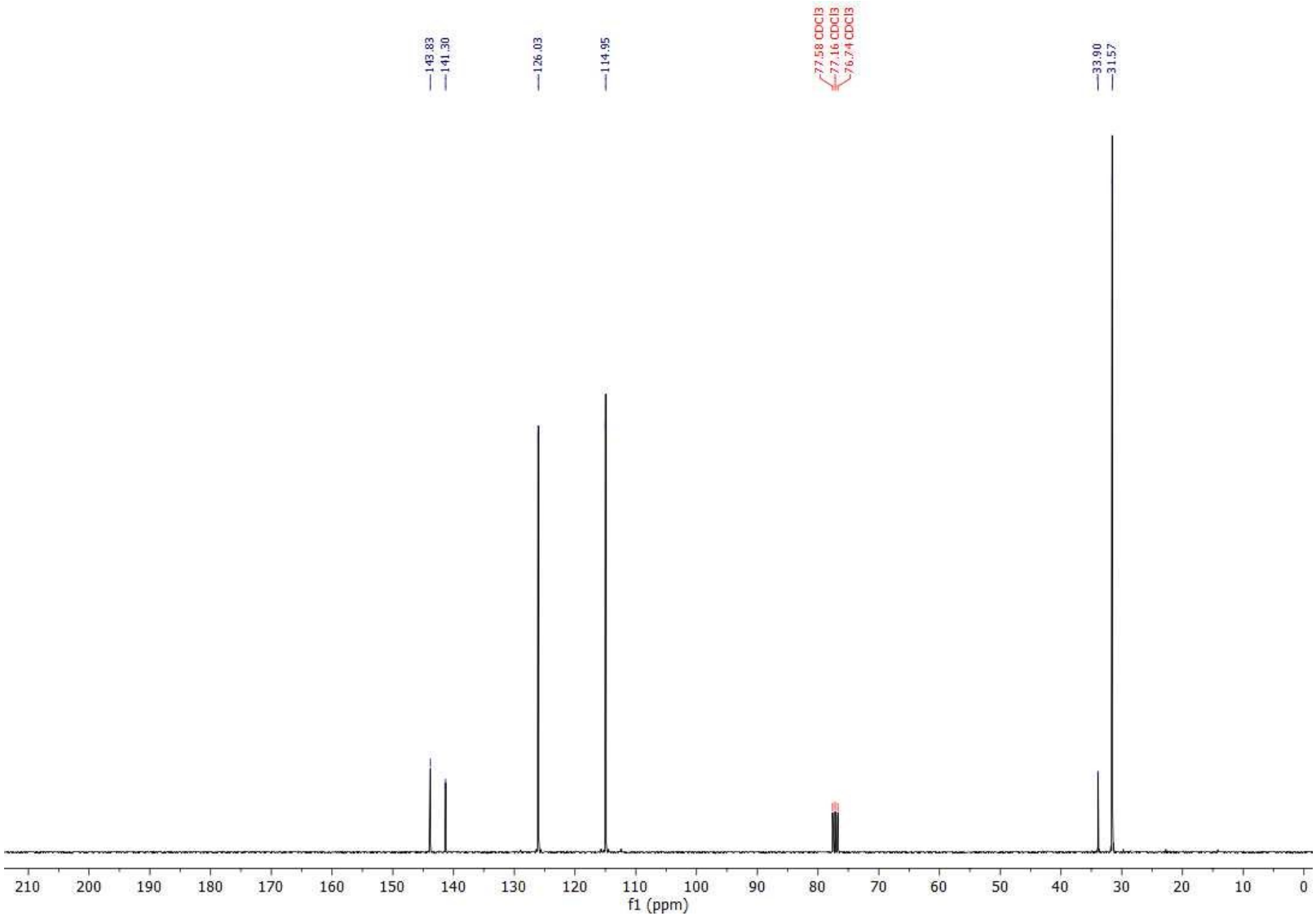


Figure S106: ^{13}C-NMR (75 MHz, $CDCl_3$) for 4-(tert-butyl)aniline (2o)

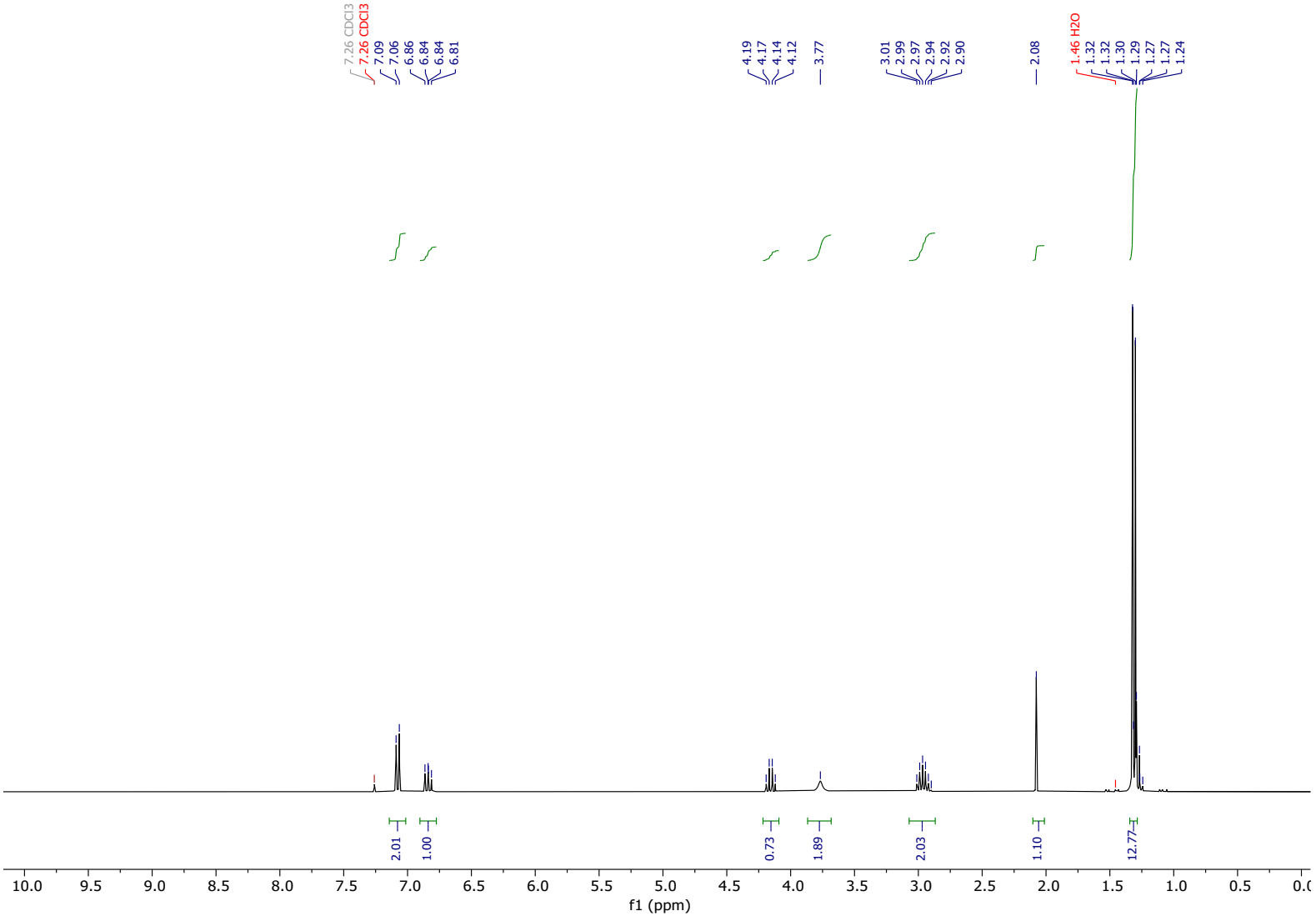


Figure S107: ^{1}H-NMR (300 MHz, $CDCl_3$) for 2,6-diisopropylaniline (2p)

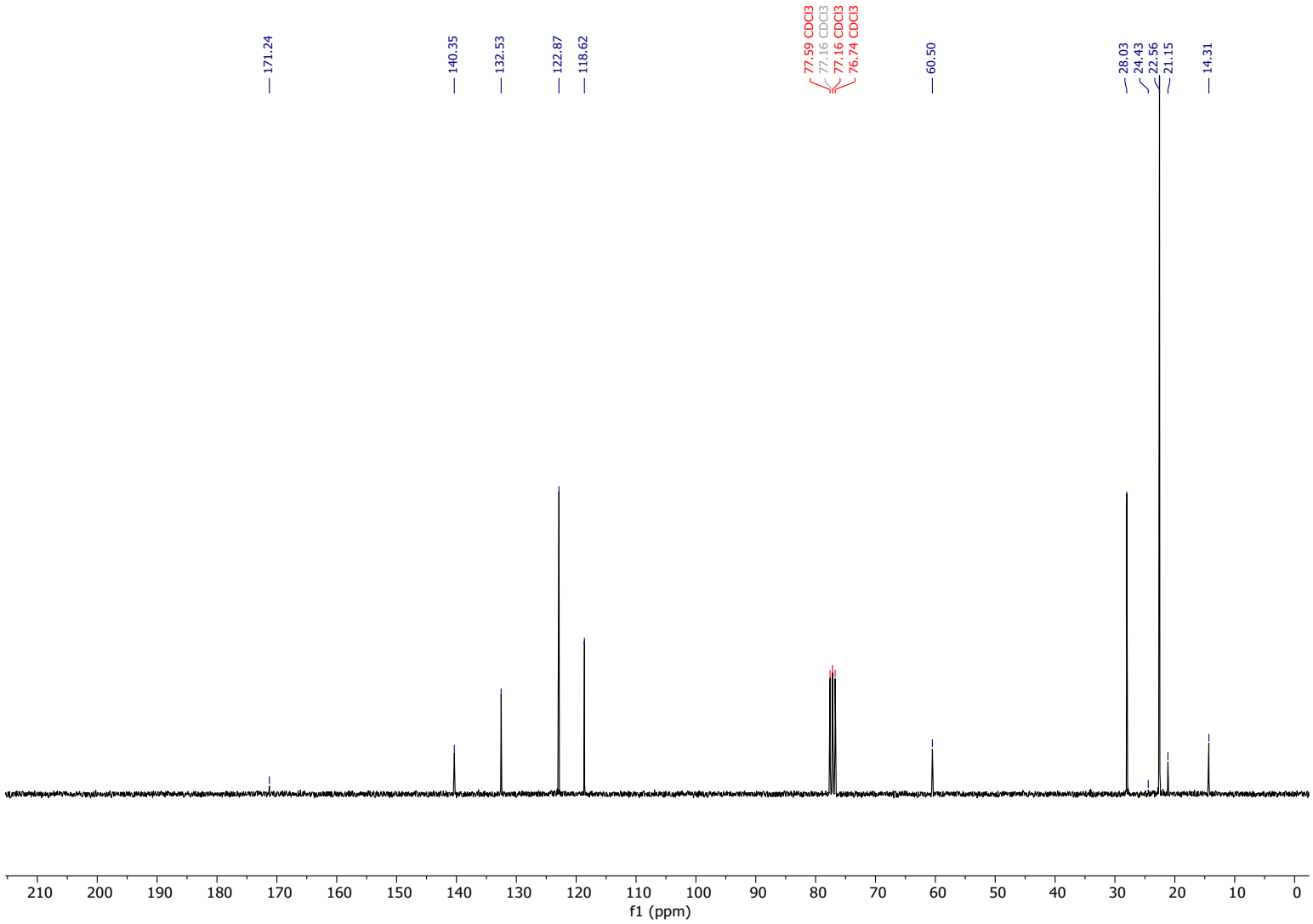


Figure S108: ^{13}C-NMR (75 MHz, $CDCl_3$) for 2,6-diisopropylaniline (2p)

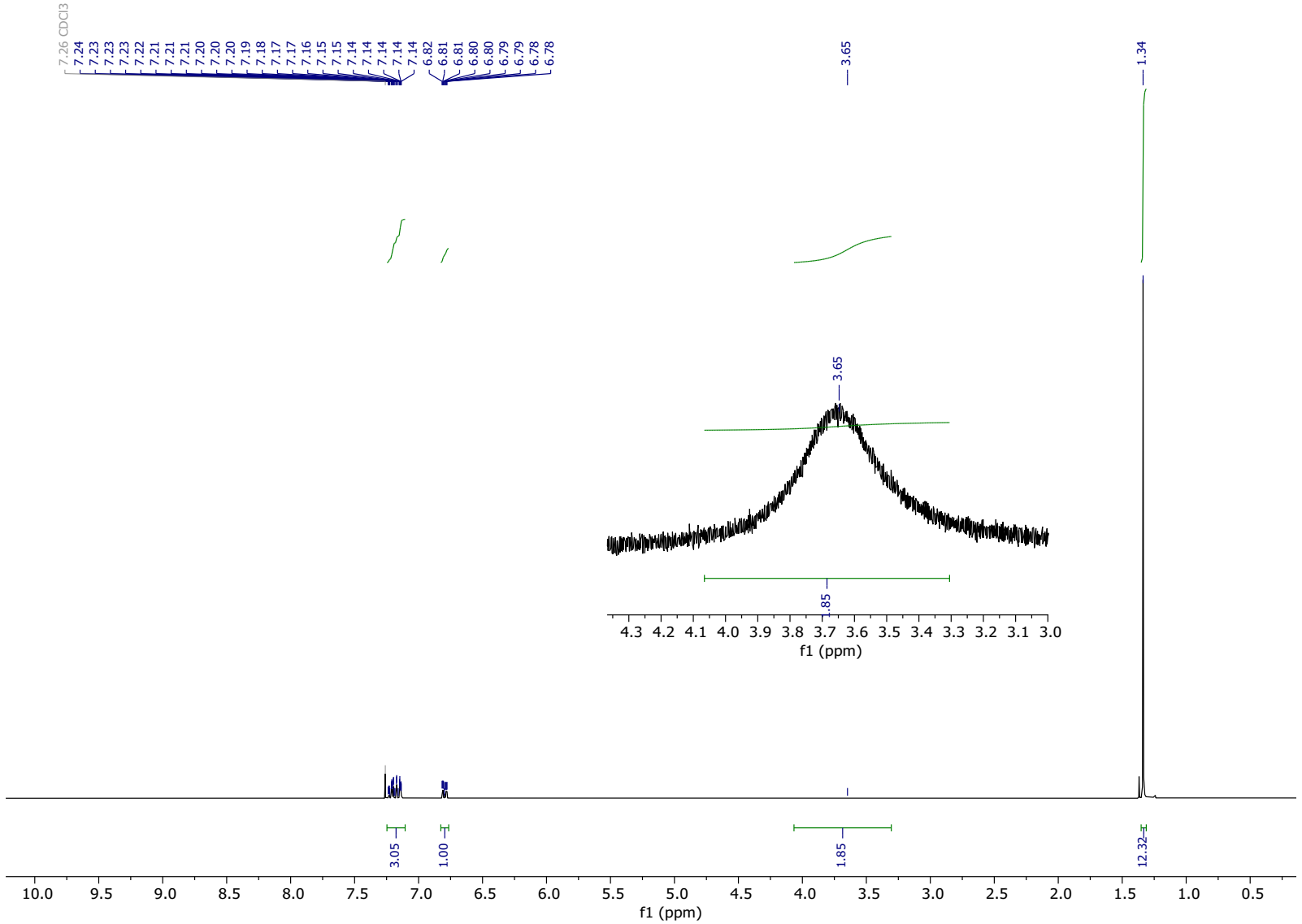


Figure S109: ^{1}H-NMR (300 MHz, $CDCl_3$) for 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (2q)

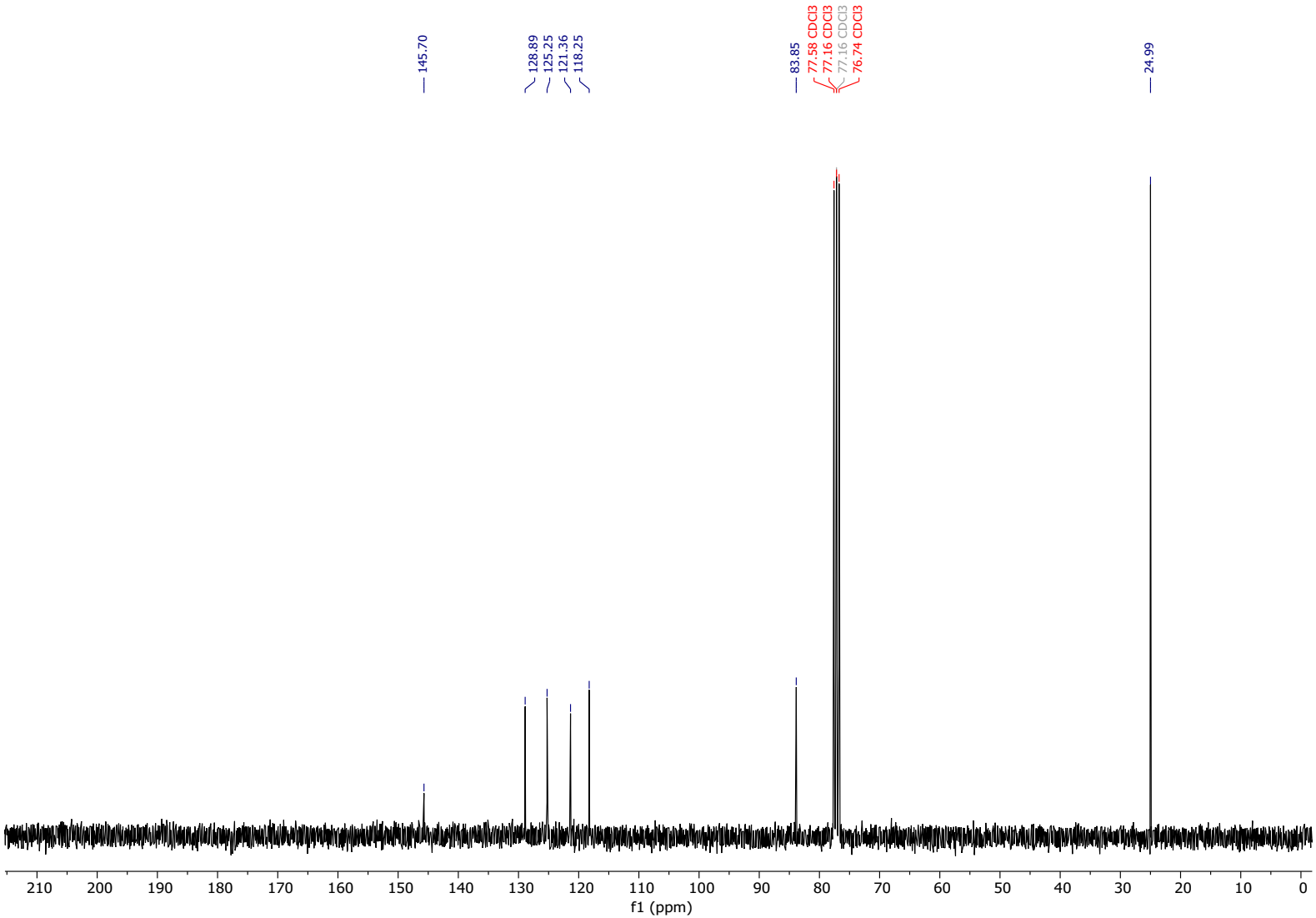


Figure S110: ^{13}C-NMR (75 MHz, $CDCl_3$) for 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (2q)

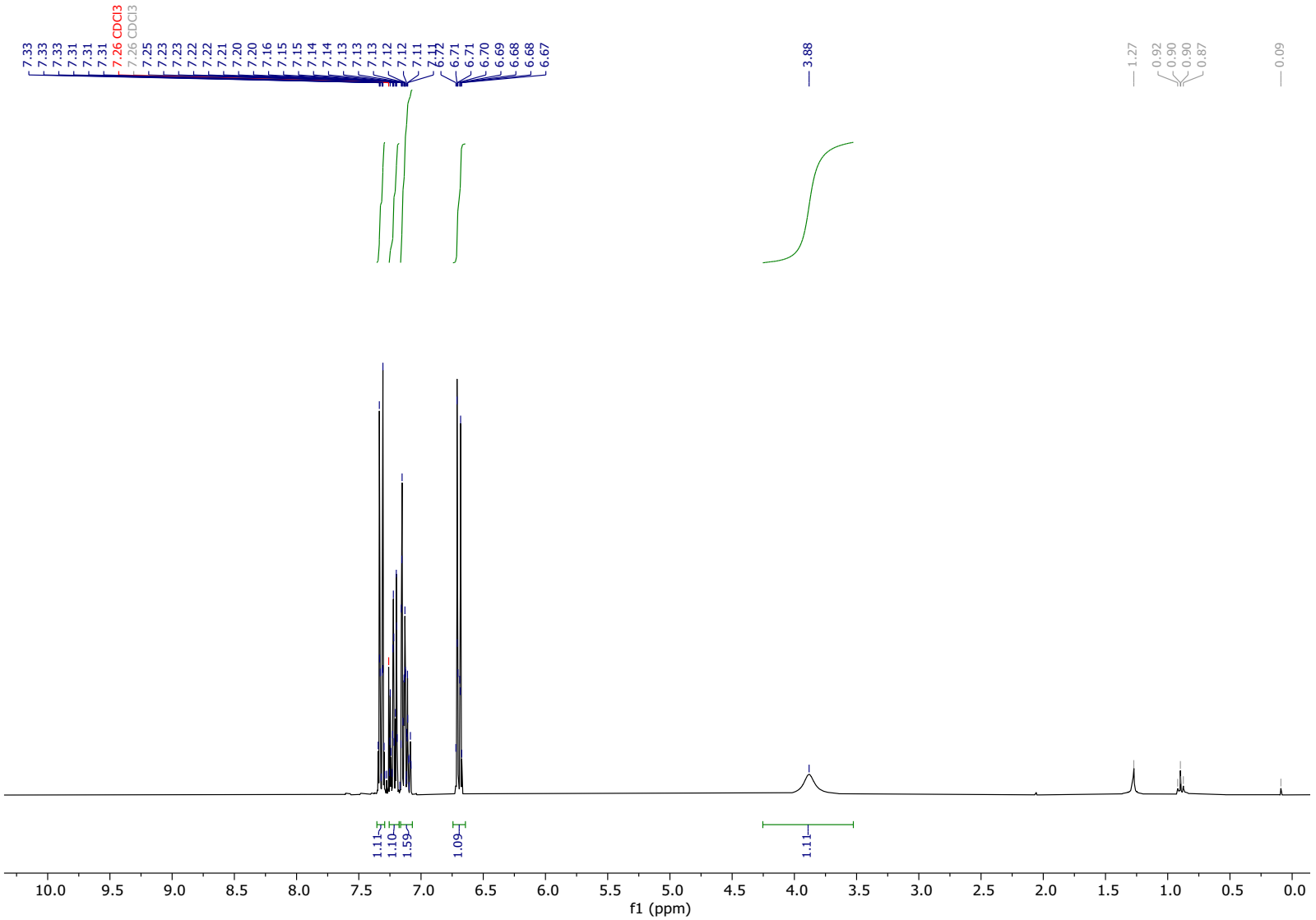


Figure 111: ^{1}H-NMR (300 MHz, $CDCl_3$) for 4-(phenylthio)aniline (2r)

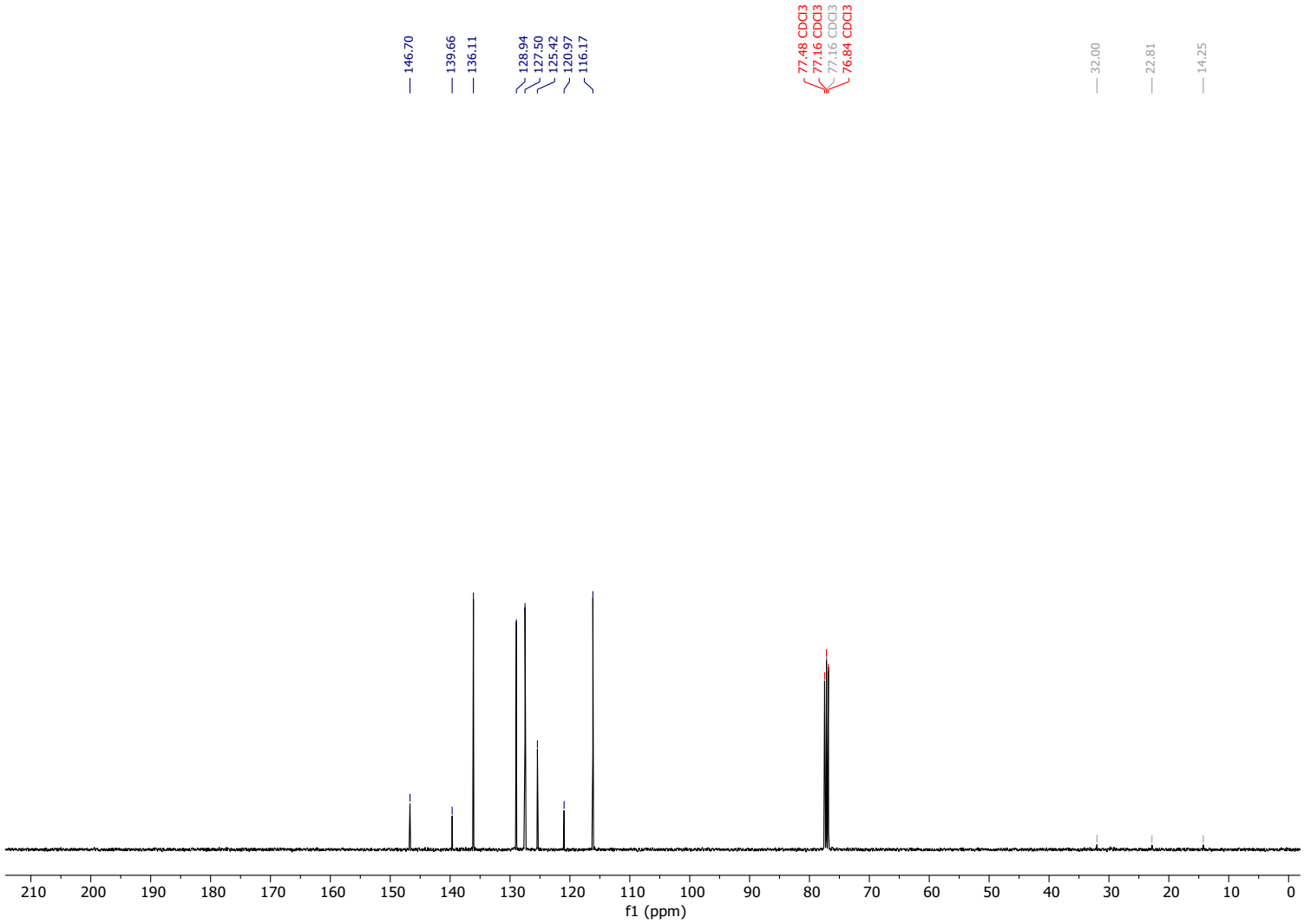


Figure S112: ^{13}C-NMR (75 MHz, $CDCl_3$) for 4-(phenylthio)aniline (2r)

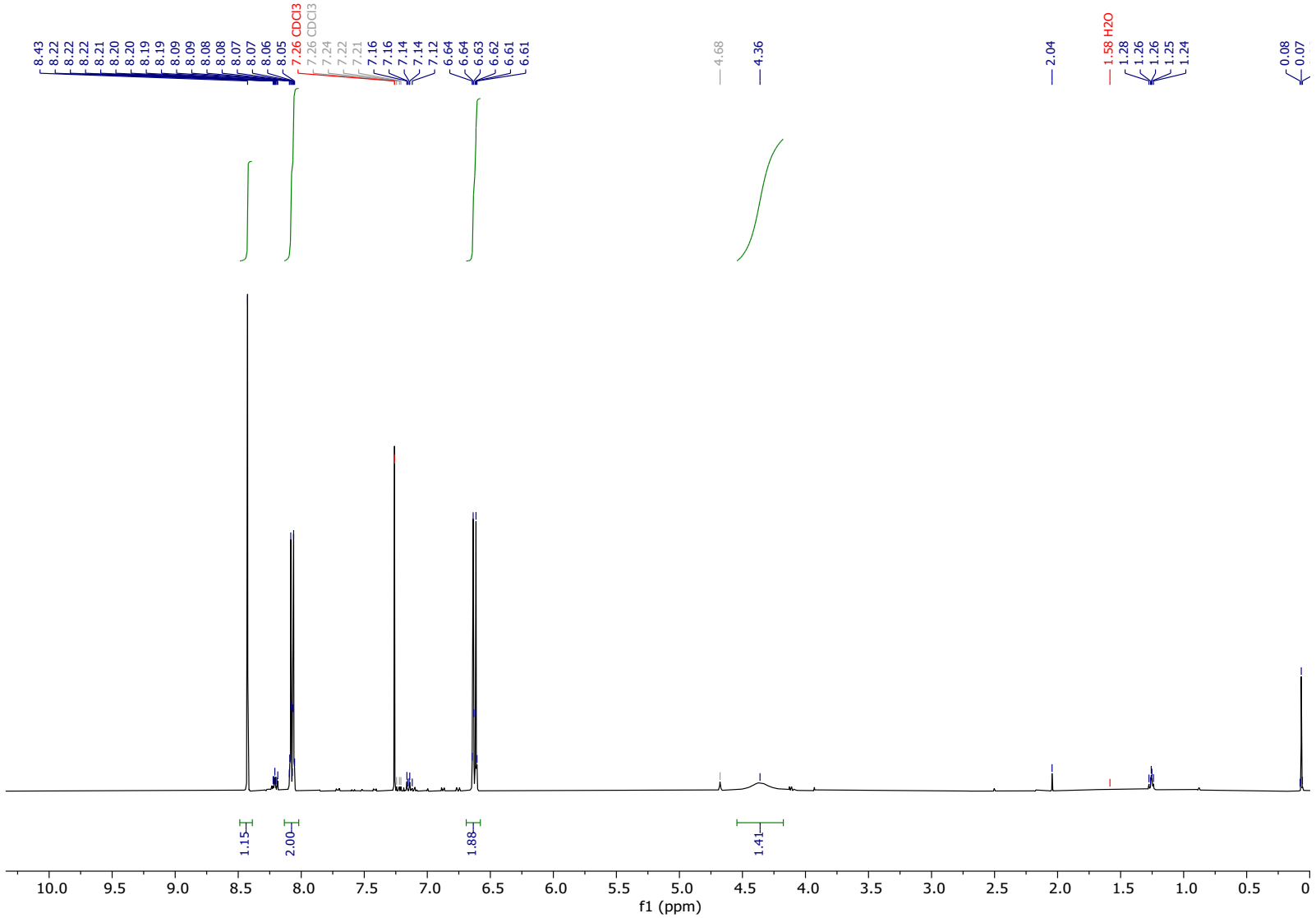


Figure S113: ^{1}H-NMR (300 MHz, $CDCl_3$) for 4-nitroaniline (2s)

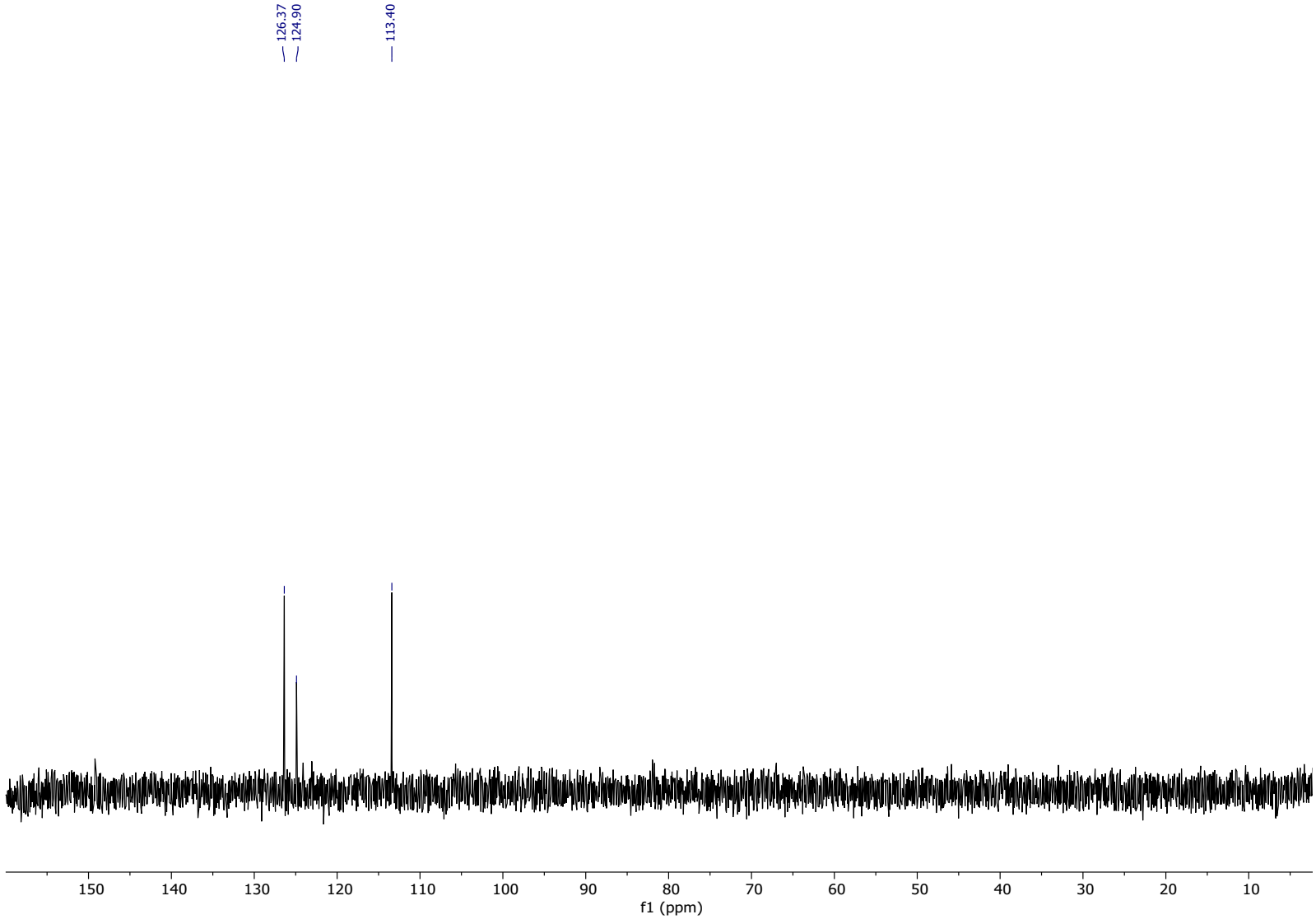


Figure S114: ^{13}C-NMR (75 MHz, $CDCl_3$) for 4-nitroaniline (2s)

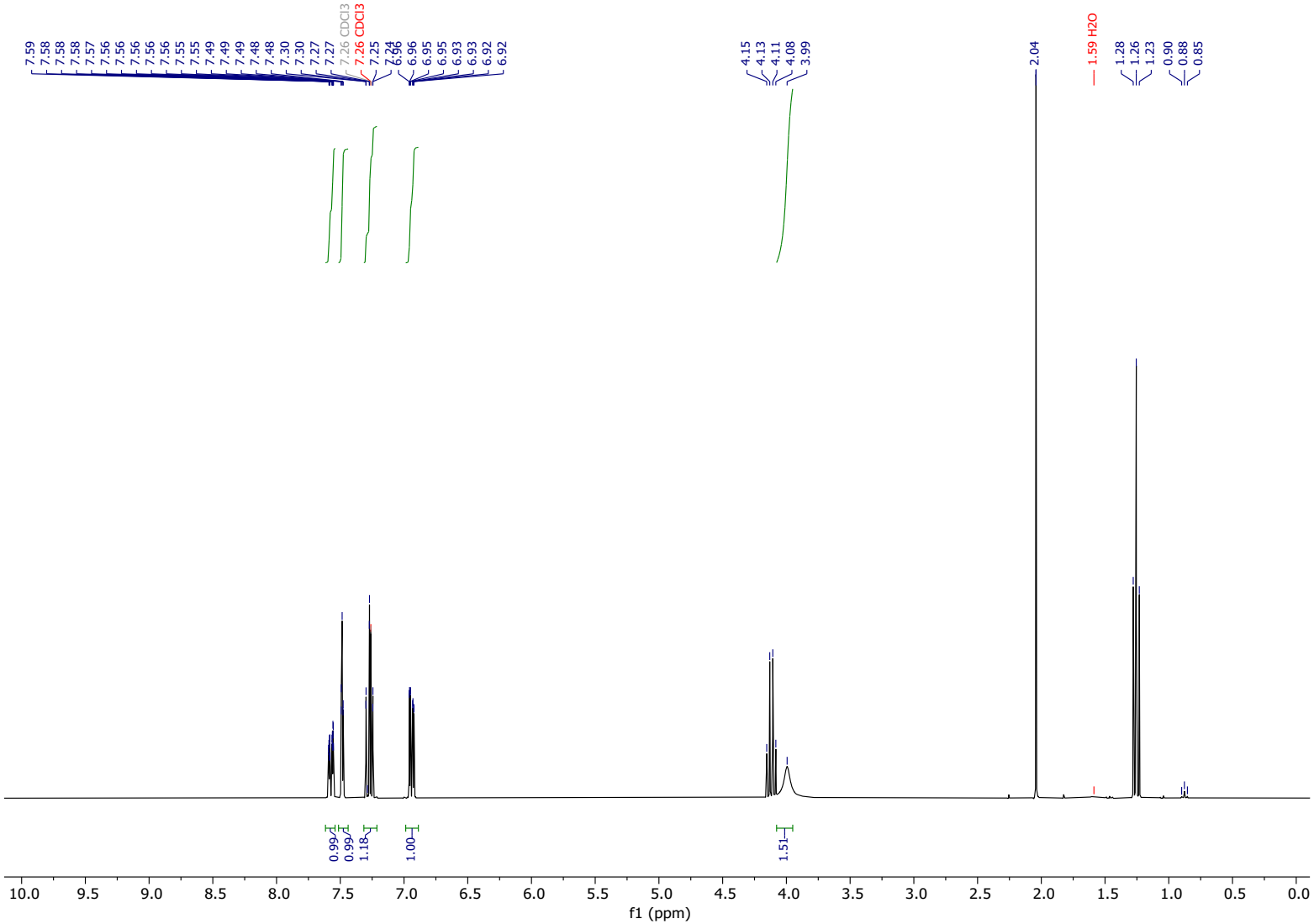


Figure S115: ^{1}H-NMR (300 MHz, $CDCl_3$) for 3-nitroaniline (2t) with impurities of ethyl acetate.

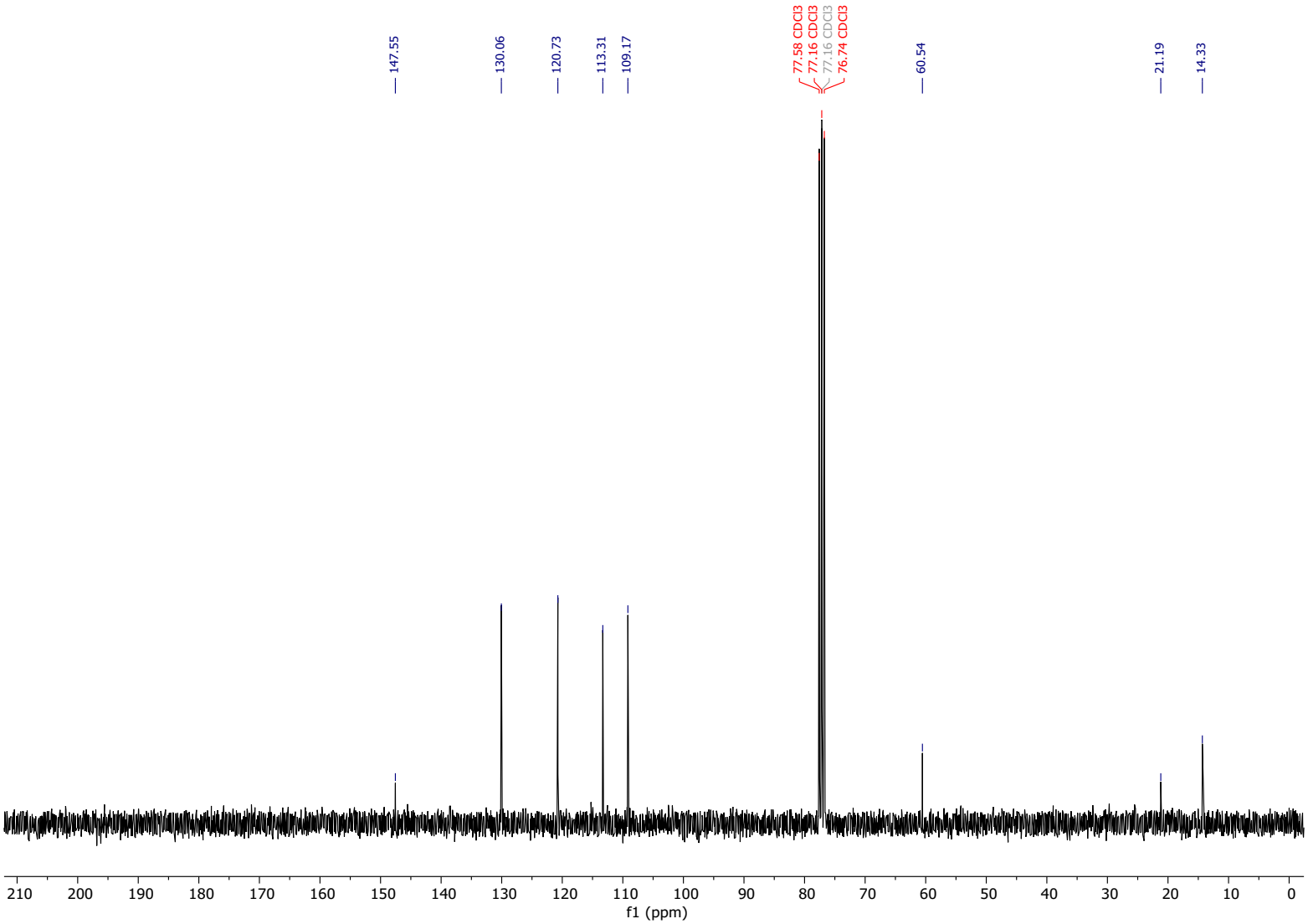


Figure S116: ^{13}C-NMR (75 MHz, $CDCl_3$) for 3-nitroaniline (2t)

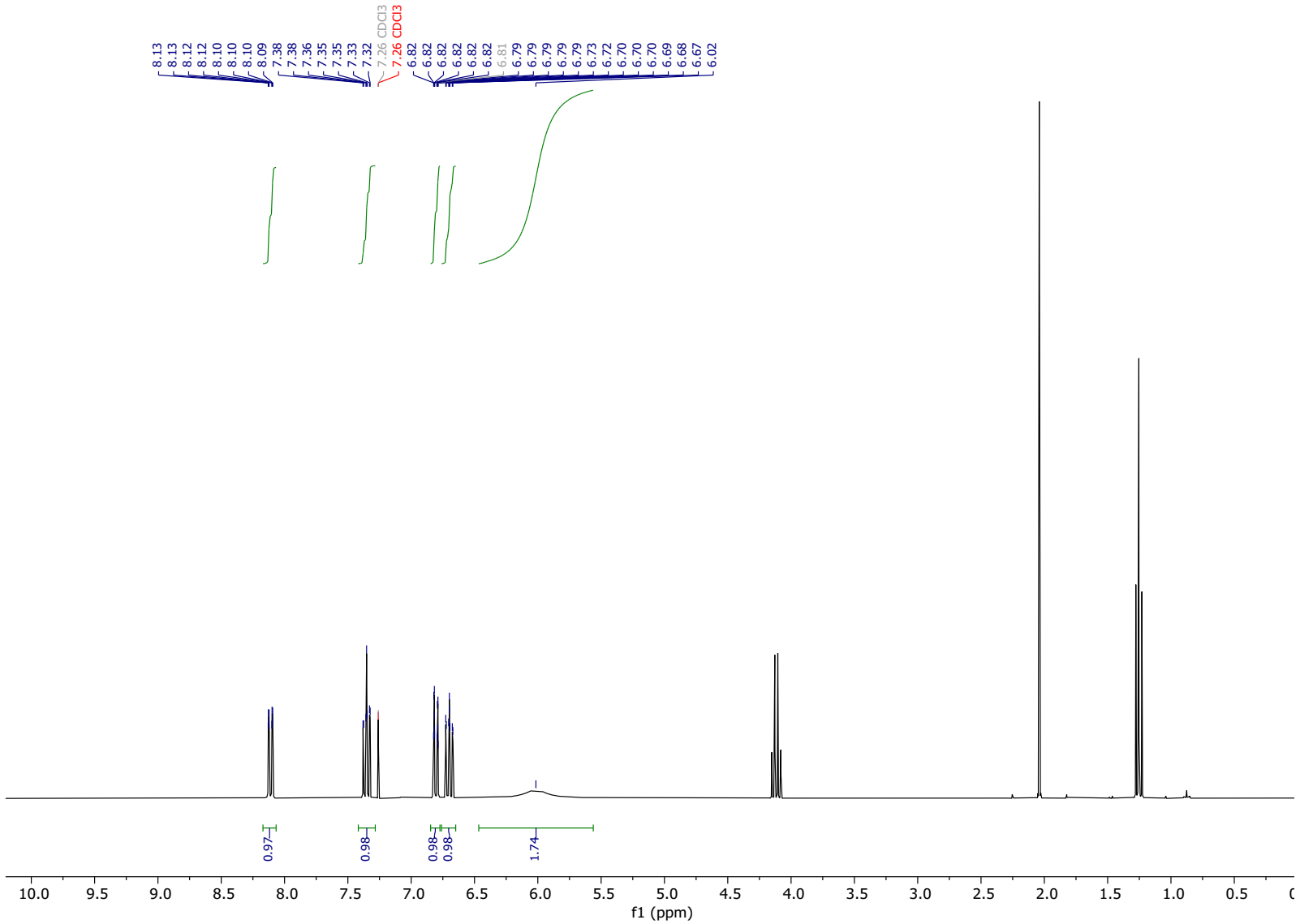


Figure S117: ^{1}H-NMR (300 MHz, $CDCl_3$) for 2-nitroaniline (2u)

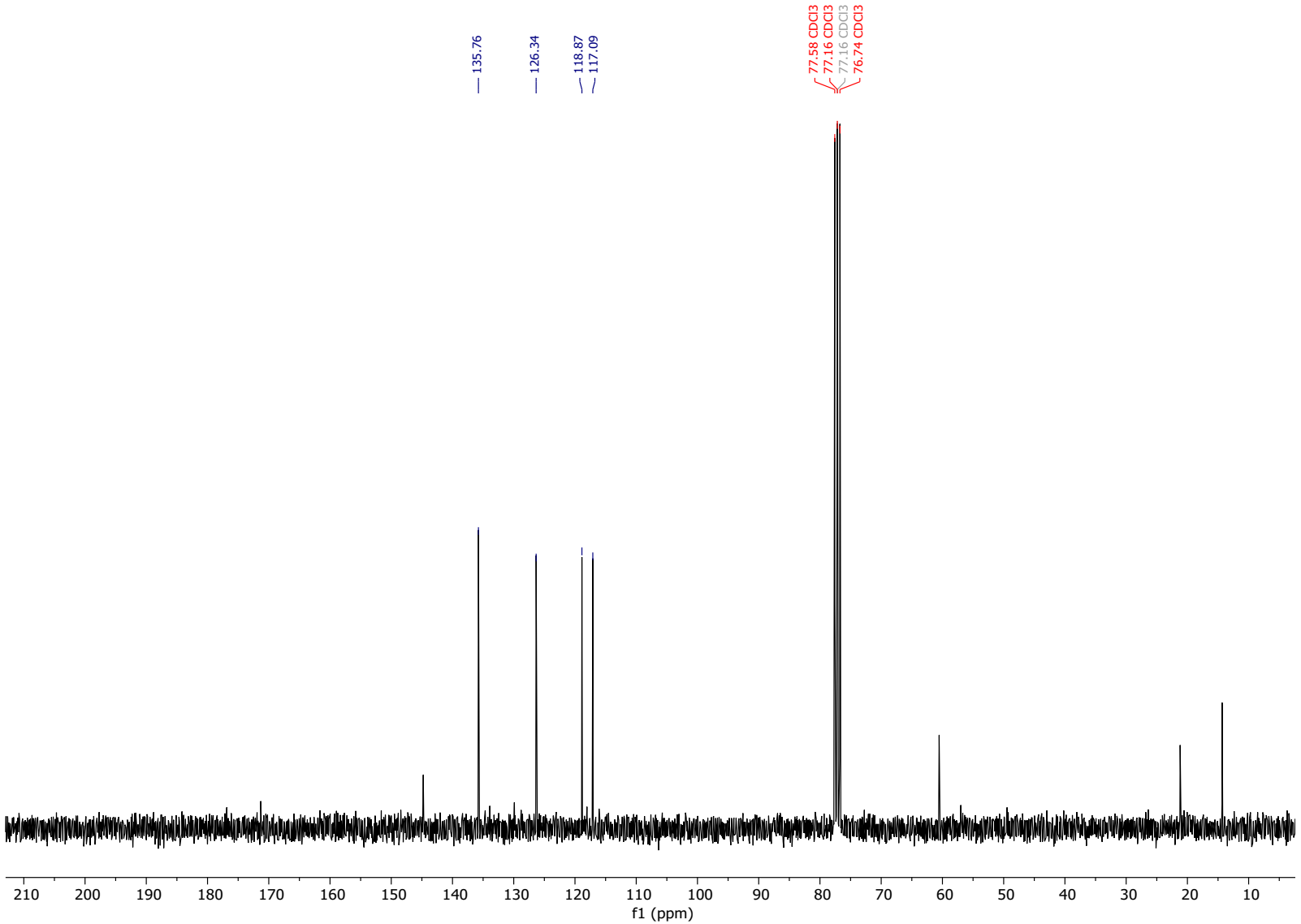


Figure S118: ^{13}C-NMR (75 MHz, $CDCl_3$) for 2-nitroaniline (2u)

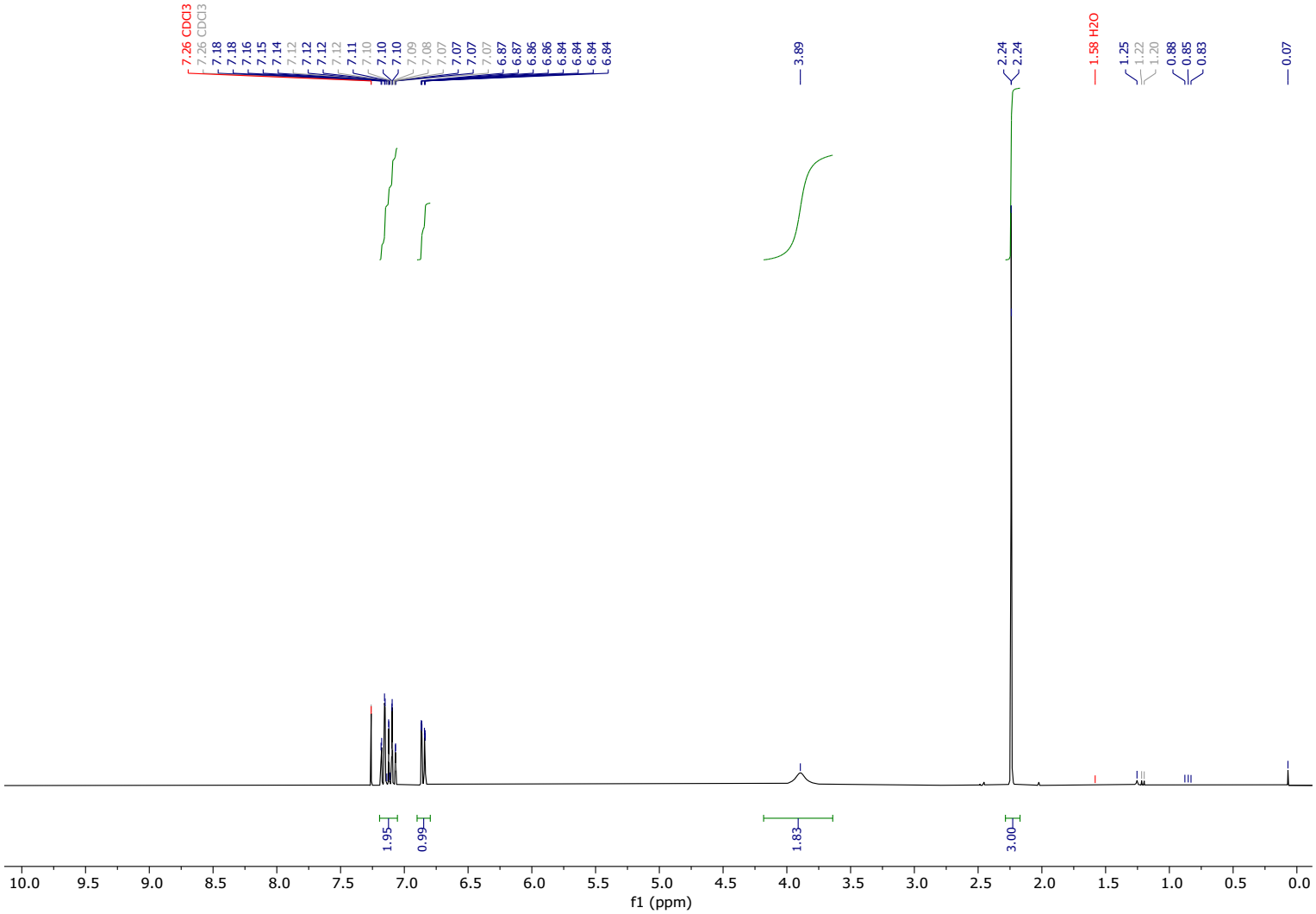


Figure S119: ^{1}H-NMR (300 MHz, $CDCl_3$) for 2-methyl-3-nitroaniline (2v)

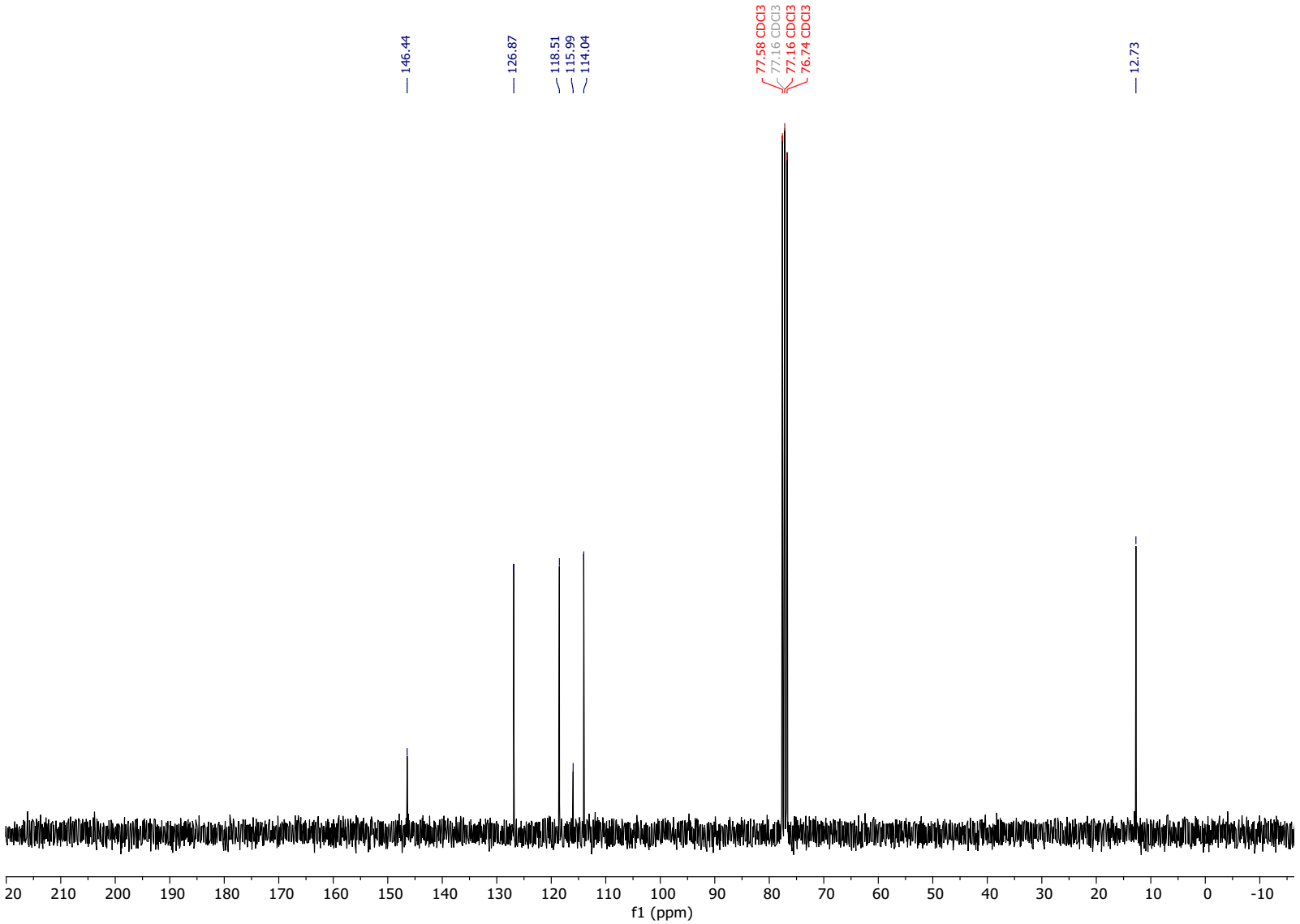


Figure S120: ^{13}C-NMR (75 MHz, $CDCl_3$) for 2-methyl-3-nitroaniline (2v)

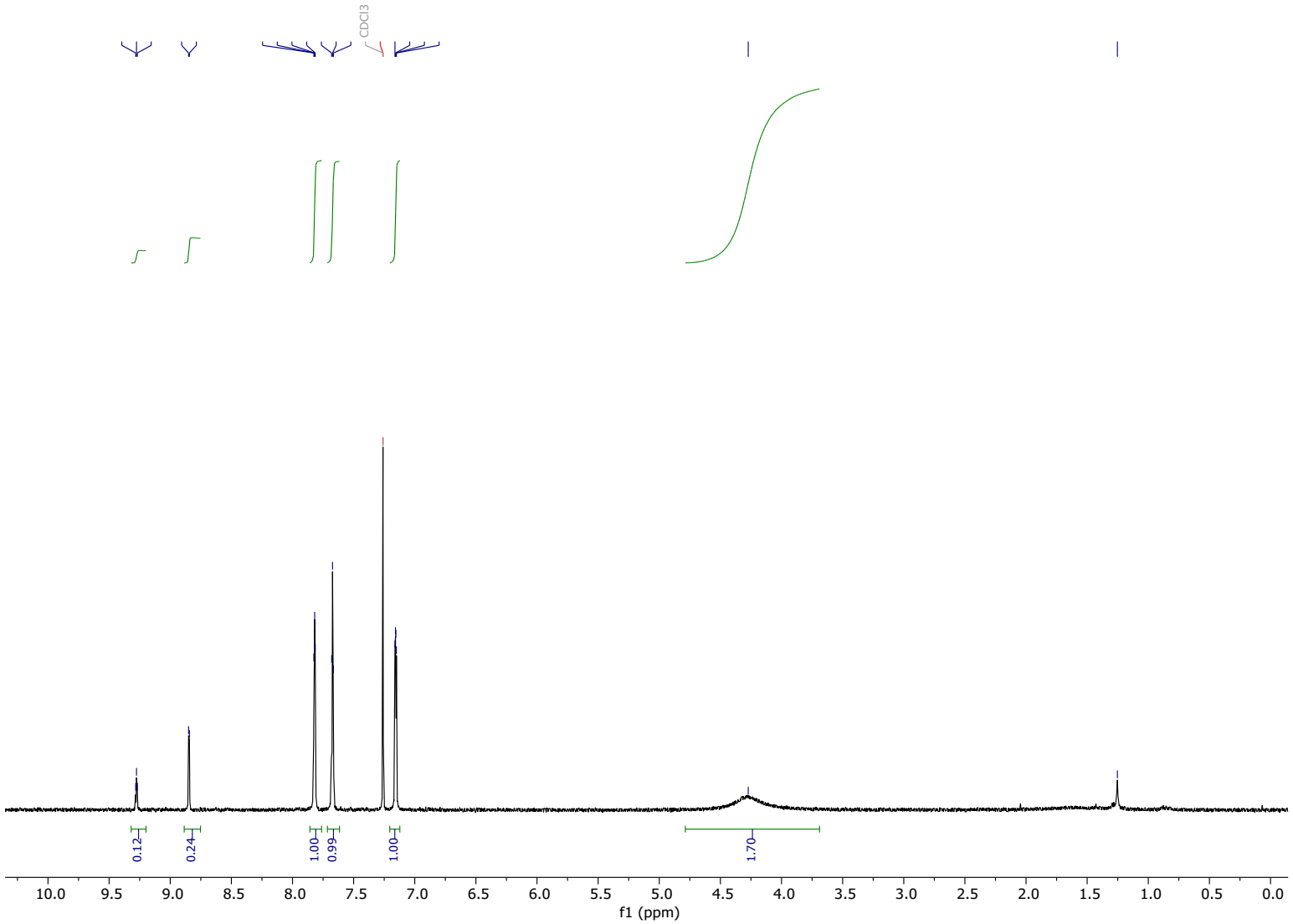


Figure S121: ^{1}H-NMR (300 MHz, $CDCl_3$) for 3-amino-5-nitrobenzonitrile (2w)

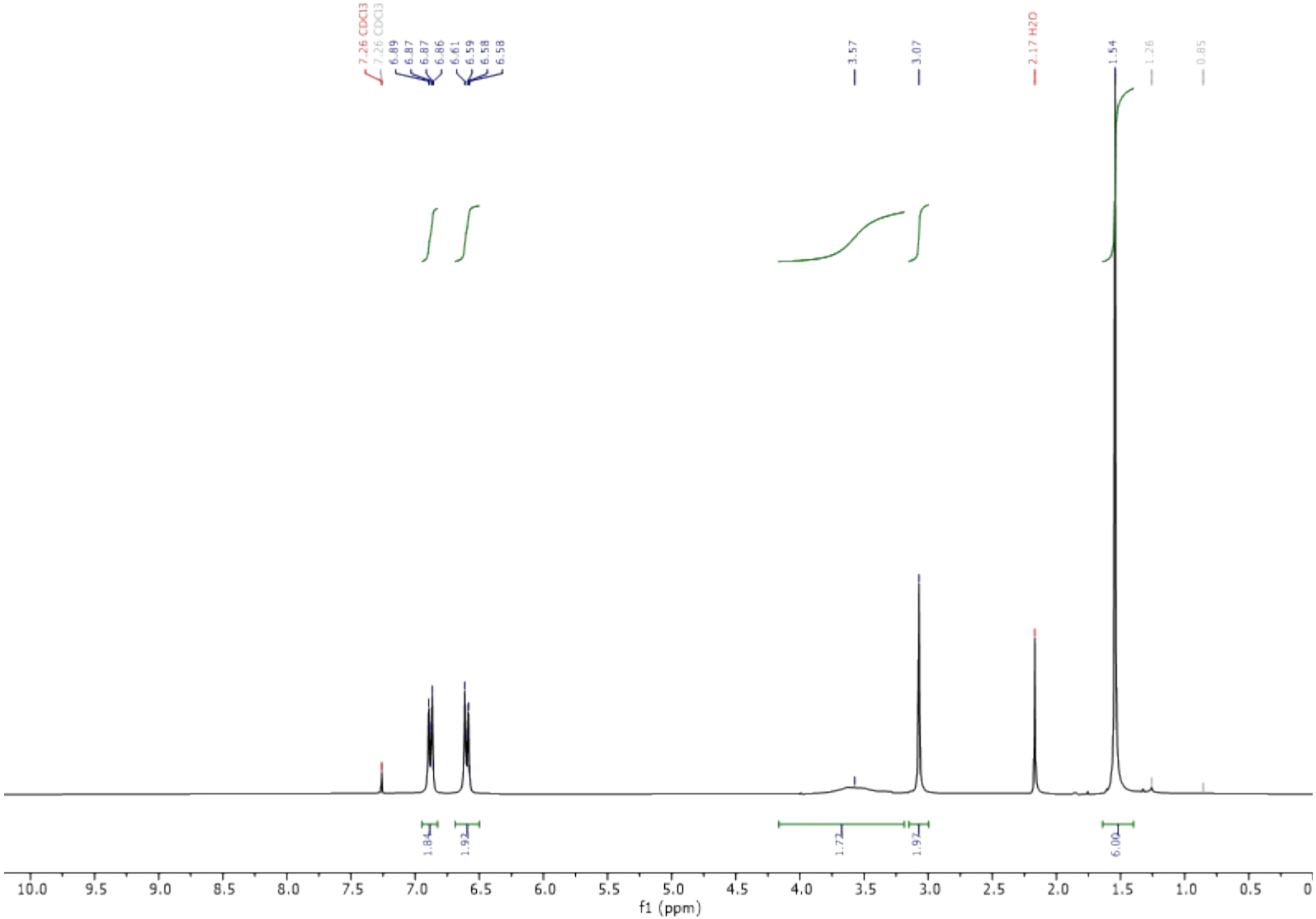


Figure S122: ^{1}H-NMR (300 MHz, $CDCl_3$) for 4-(2-methyl-2-nitropropyl)aniline (2x)

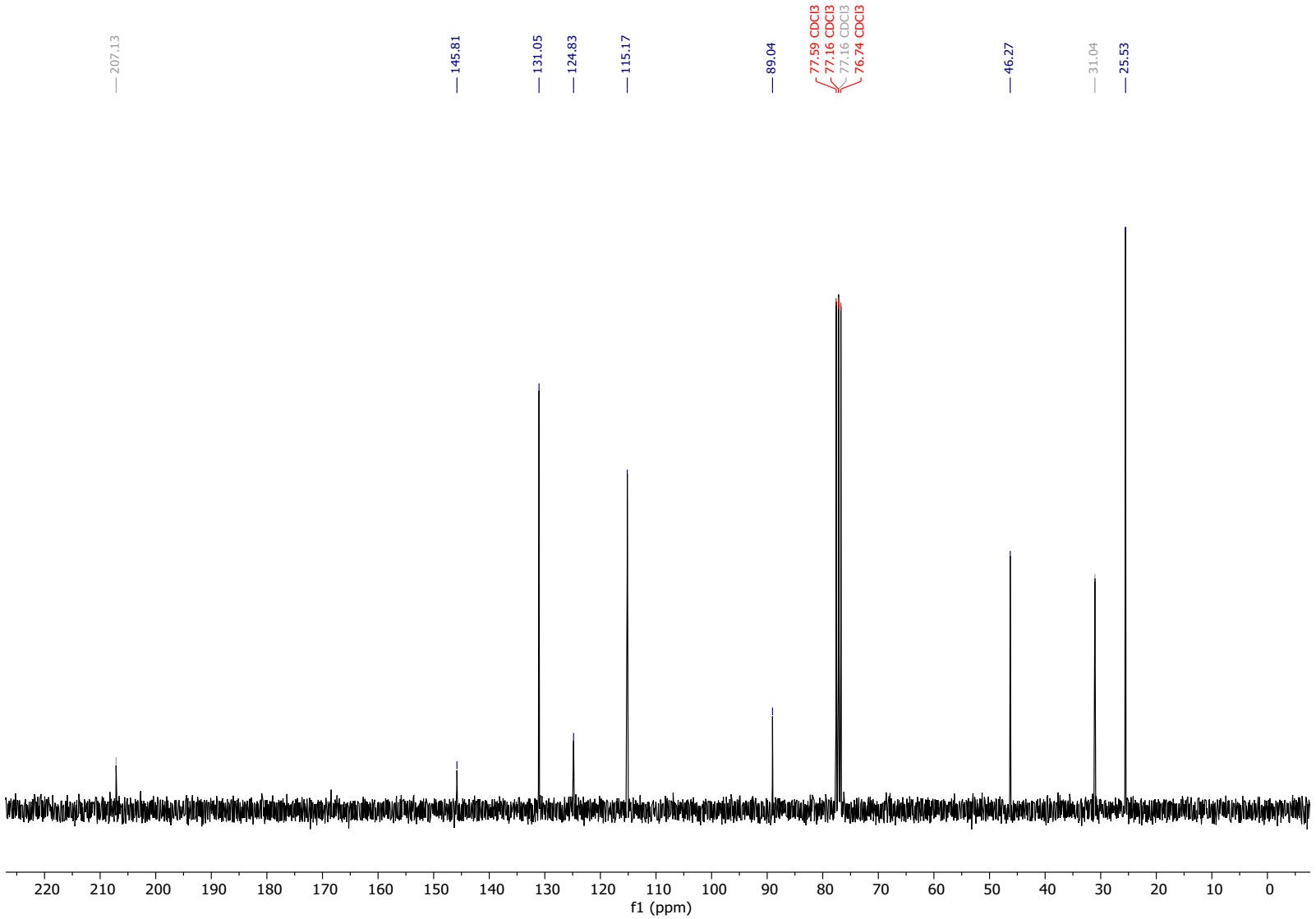


Figure S123: ^{13}C-NMR (75 MHz, $CDCl_3$) for 4-(2-methyl-2-nitropropyl)aniline (2x)

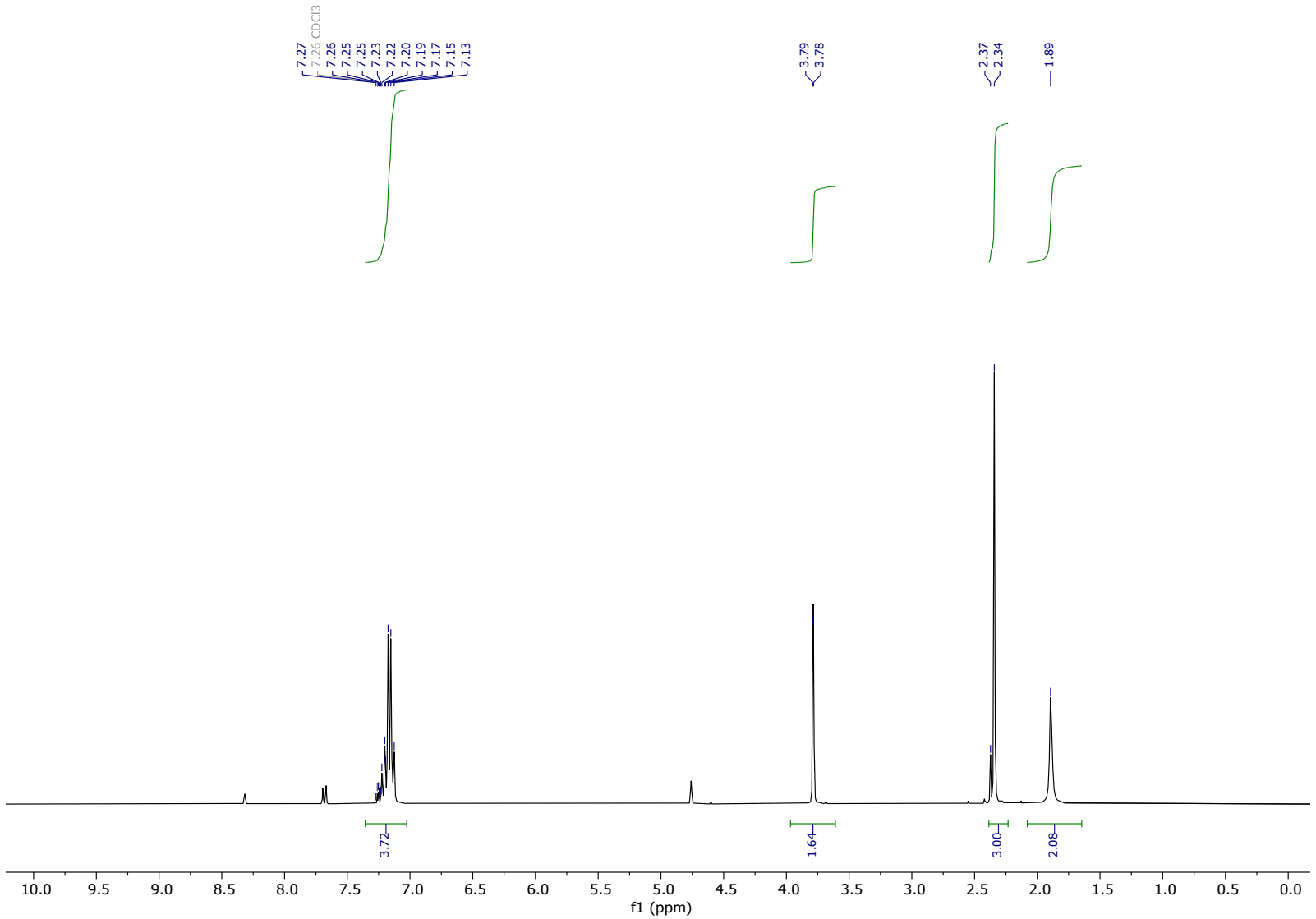


Figure S124: ^{1}H-NMR (300 MHz, $CDCl_3$) for 4-methylbenzylamine (2y)

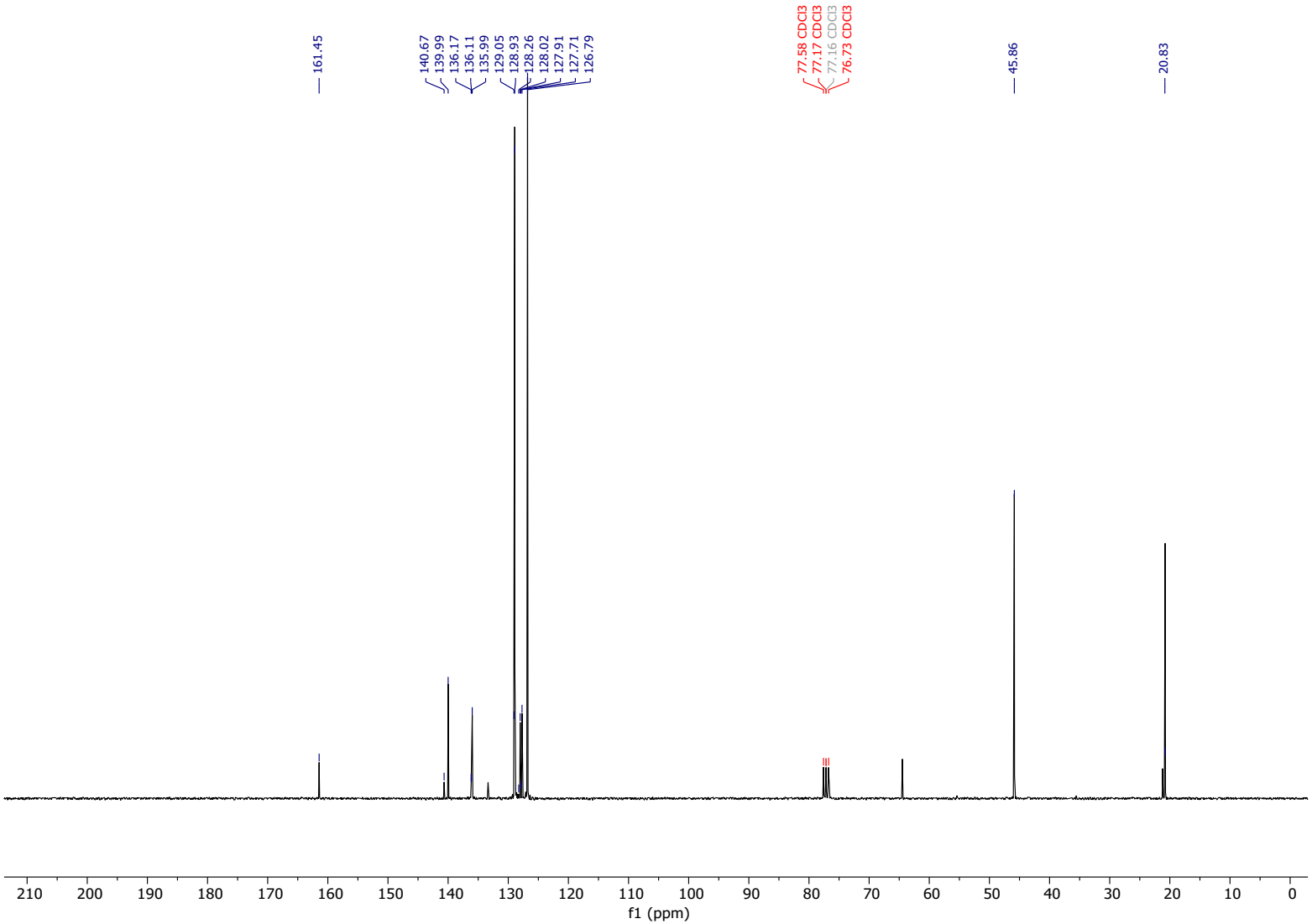


Figure S125: ^{13}C-NMR (75 MHz, $CDCl_3$) for 4-methylbenzylamine (2y)

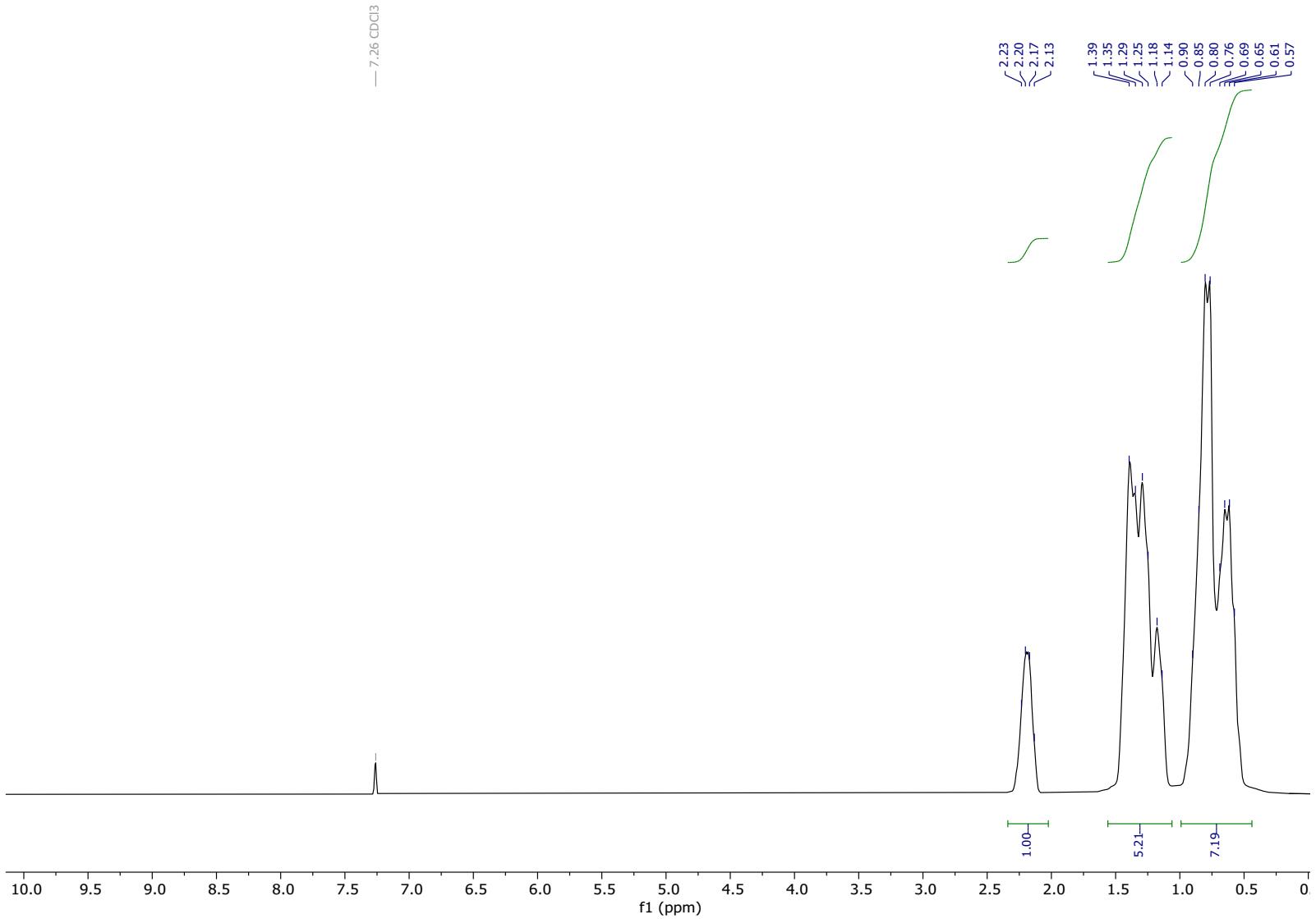


Figure S126: ^{1}H-NMR (300 MHz, $CDCl_3$) for cyclohexylamine (2z)

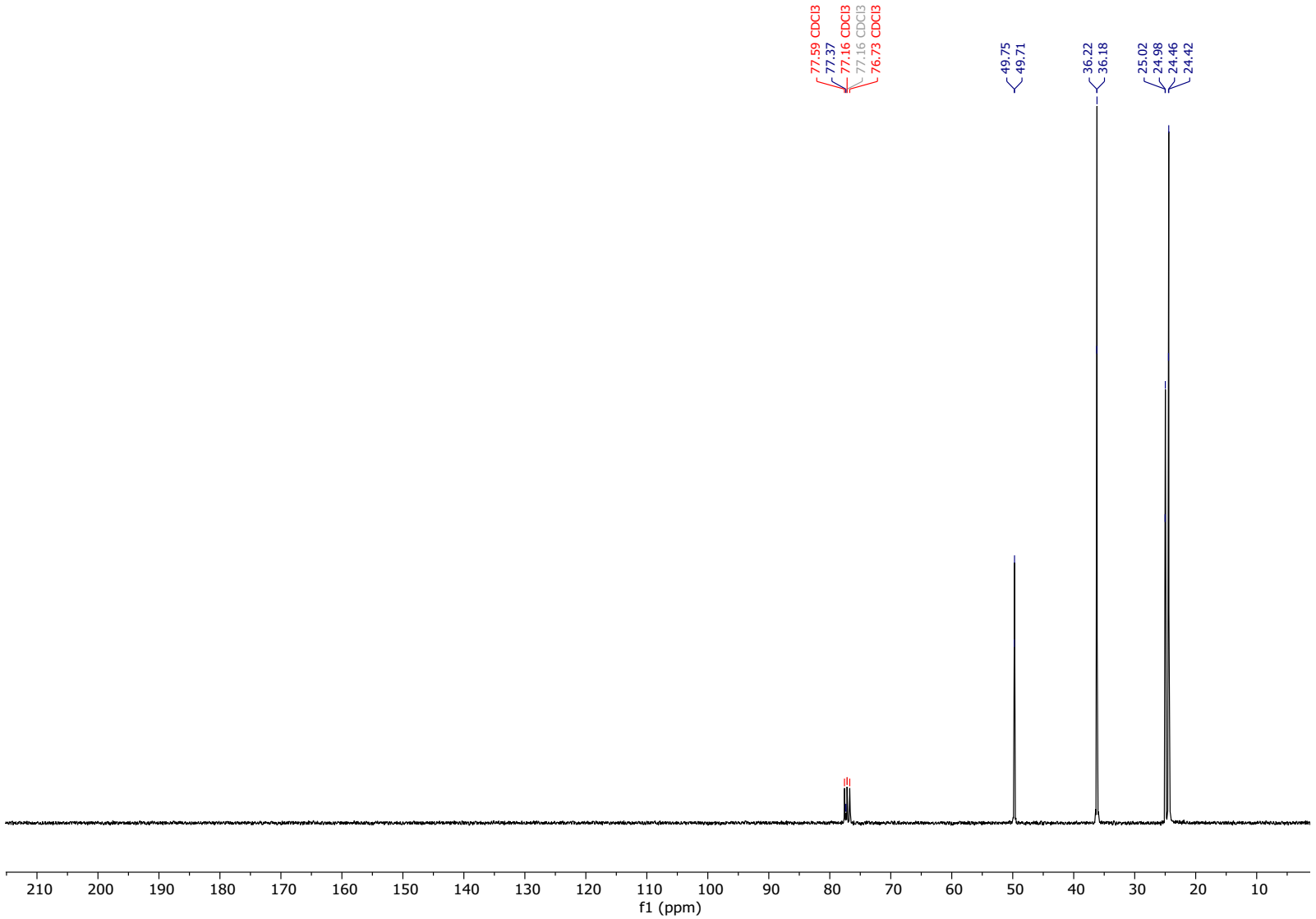


Figure S127: ^{13}C-NMR (75 MHz, $CDCl_3$) for cyclohexylamine (2z)

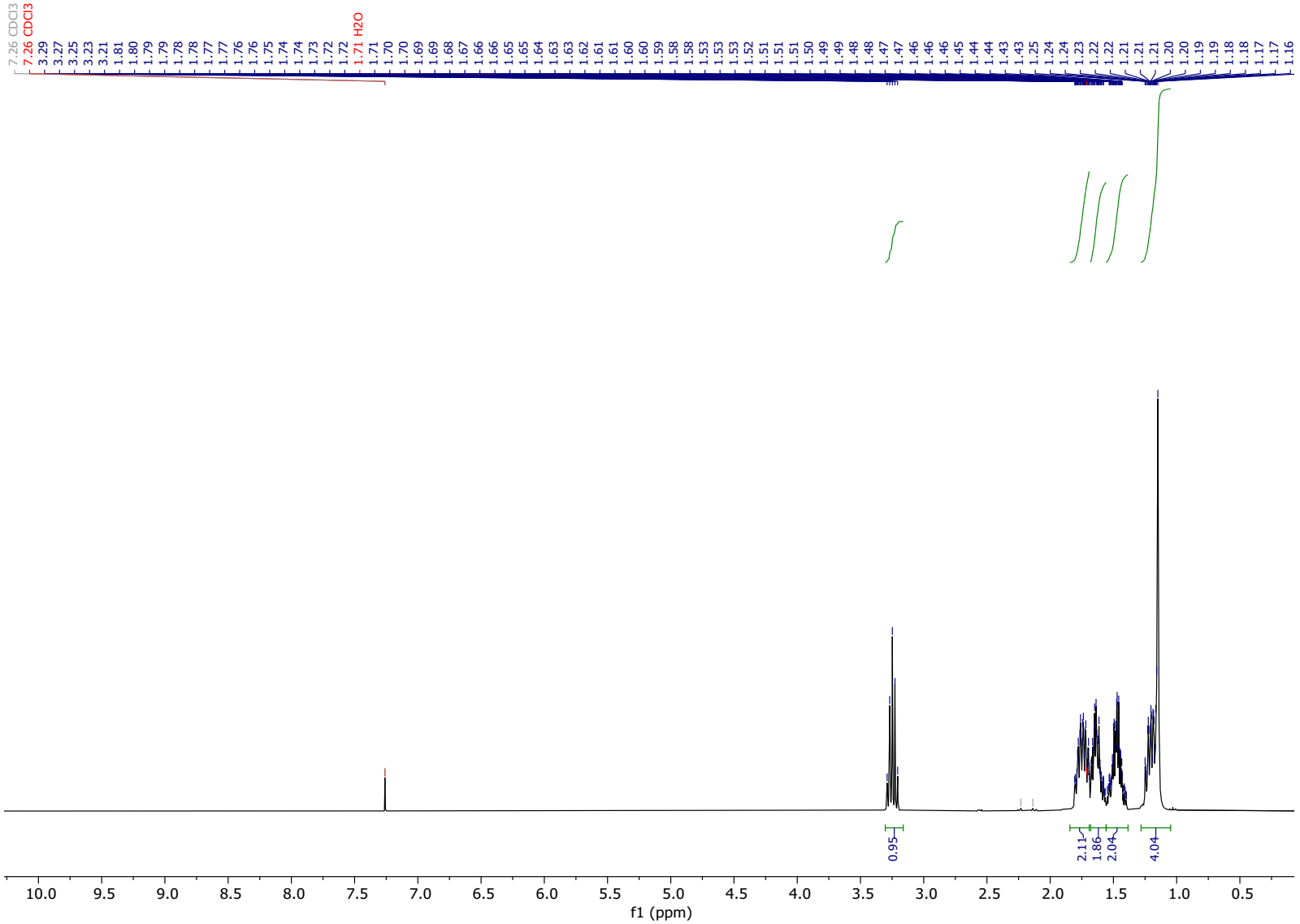


Figure S128: ^{1}H-NMR (300 MHz, $CDCl_3$) for cyclopentanamine (2aa)

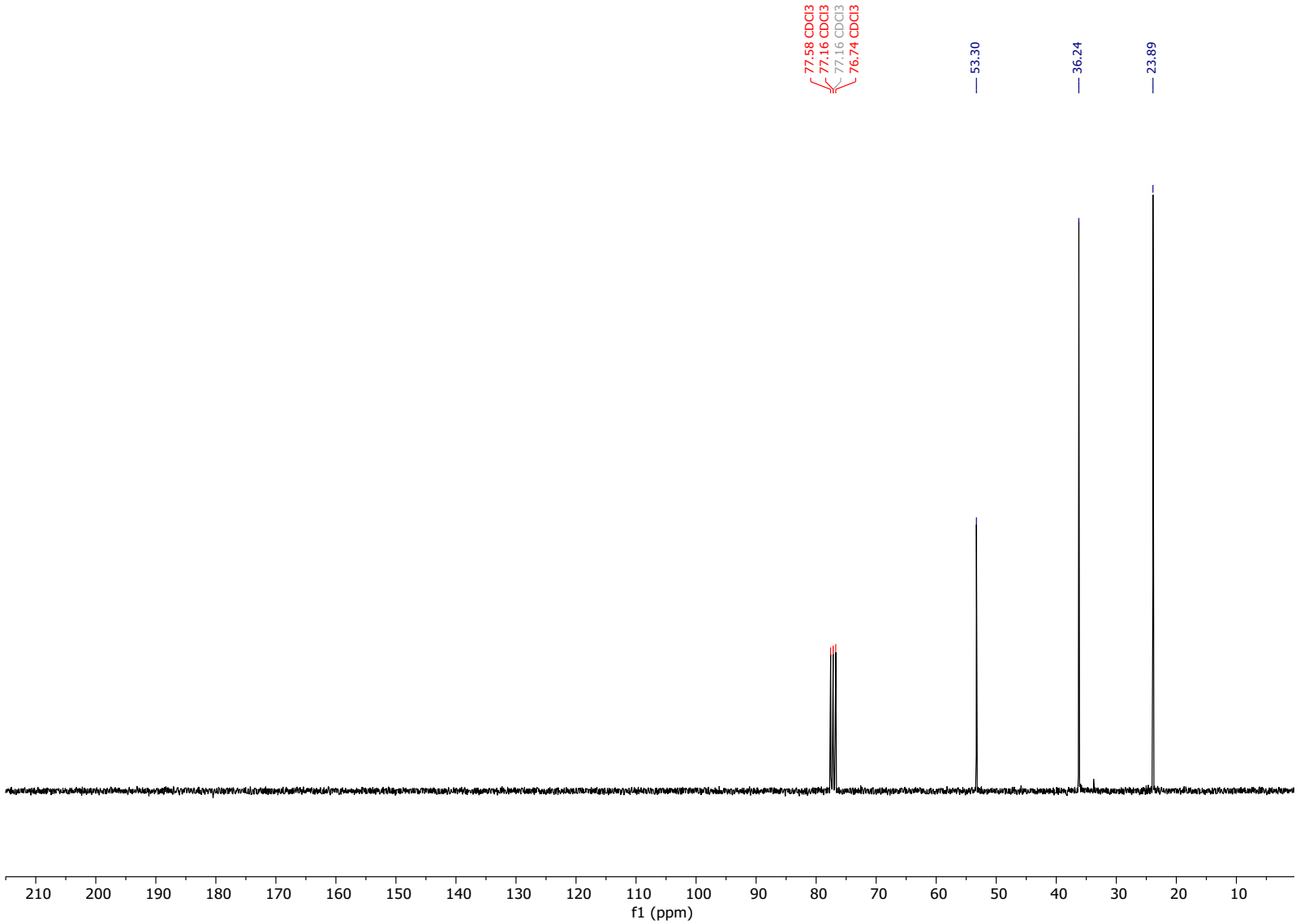


Figure S129: ^{13}C-NMR (75 MHz, $CDCl_3$) for cyclopentanamine (2aa)

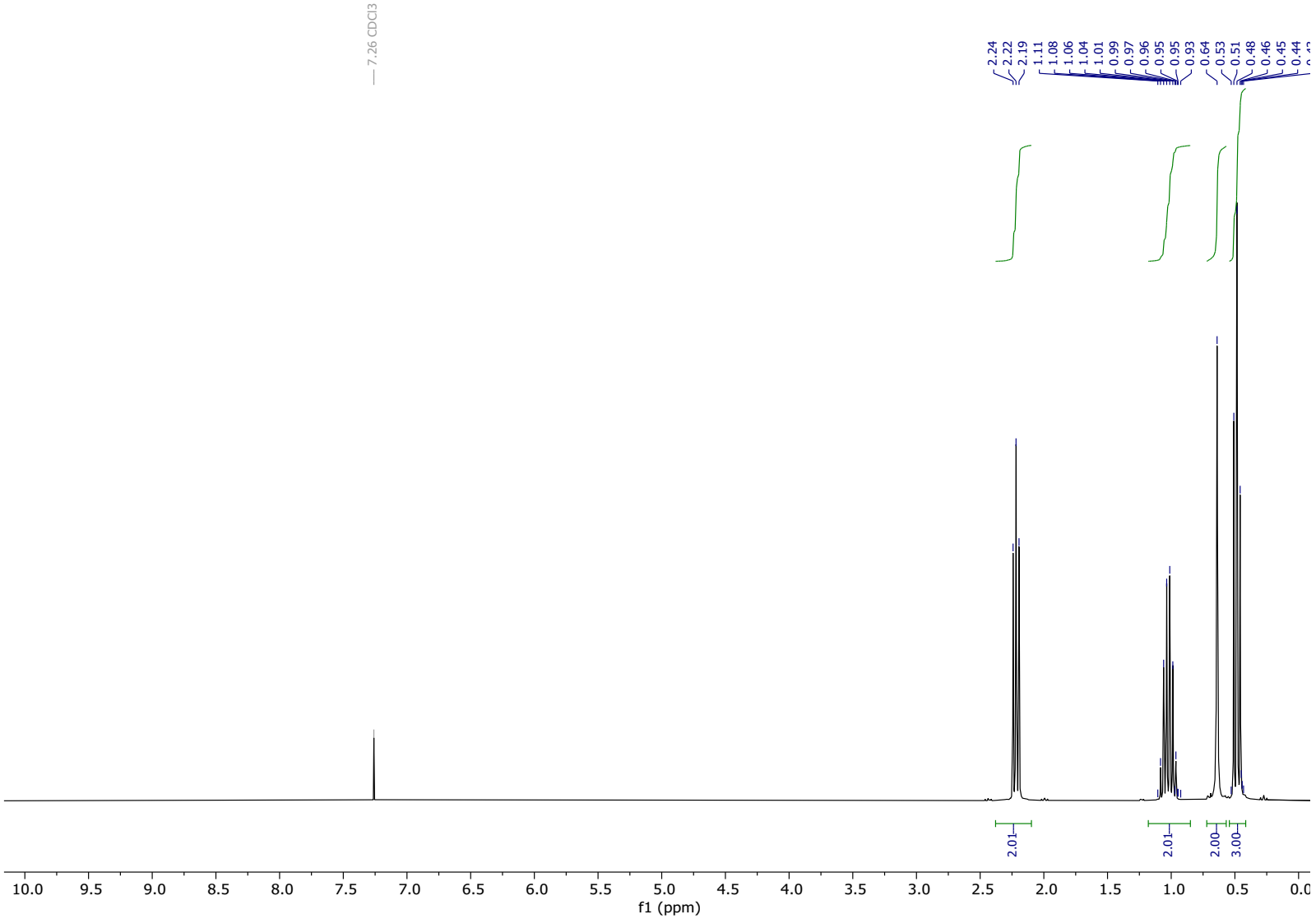


Figure S130: ^{1}H-NMR (300 MHz, $CDCl_3$) for propylamine (2ab)

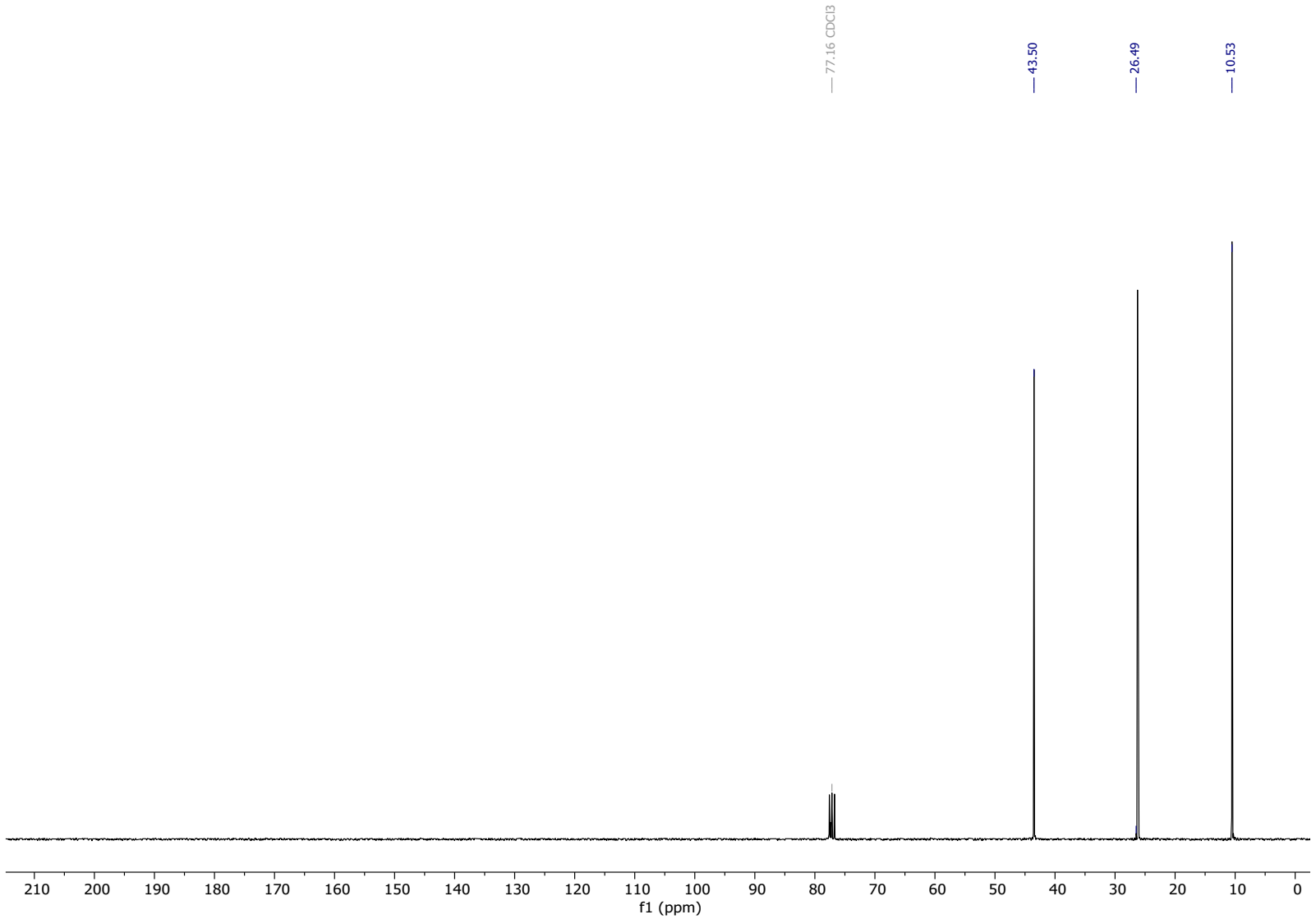


Figure S131: ^{13}C-NMR (75 MHz, $CDCl_3$) for propylamine (2ab)

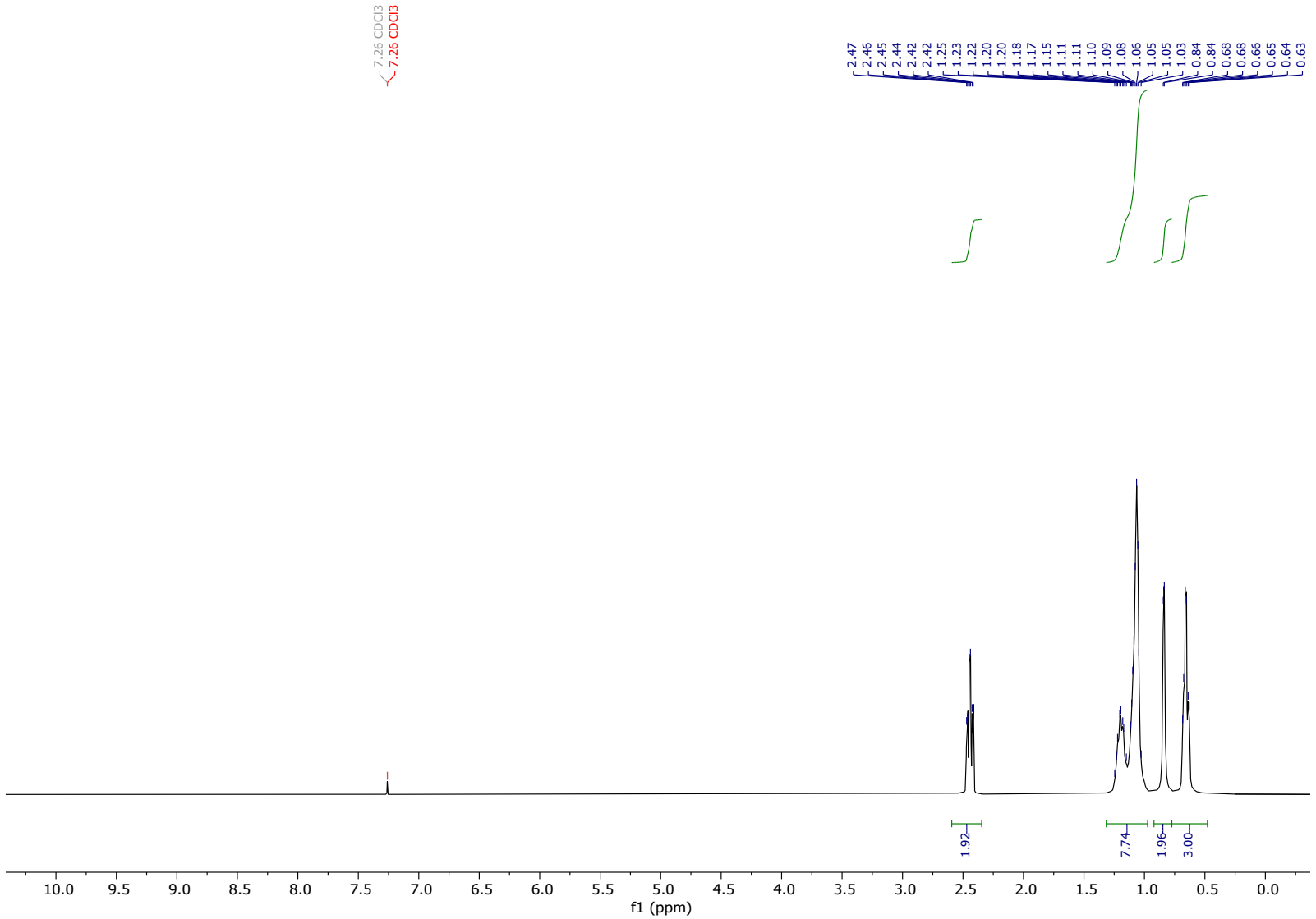


Figure S132: ^{1}H-NMR (300 MHz, $CDCl_3$) for hexan-1-amine (2ac)

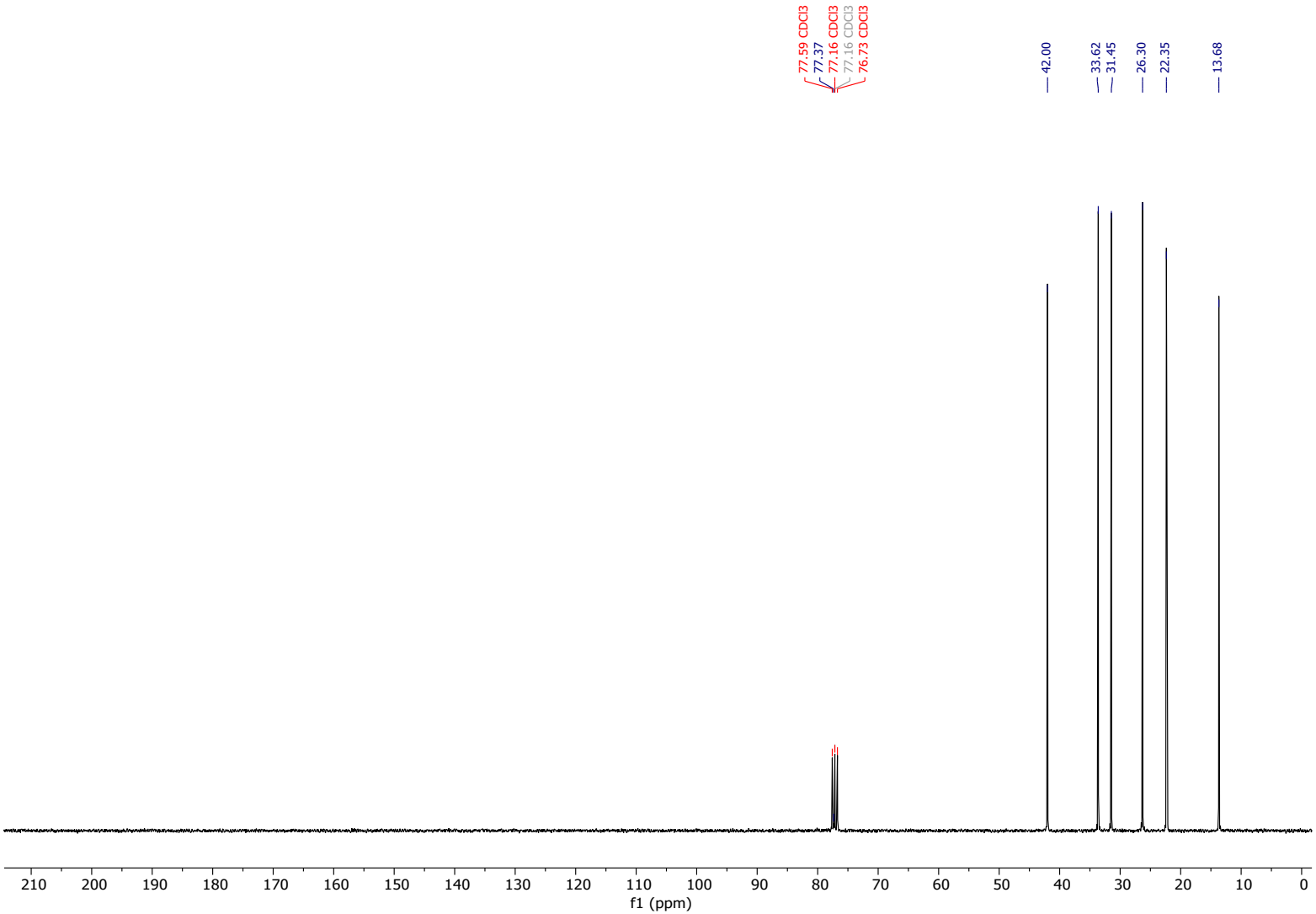


Figure S133: ^{13}C-NMR (75 MHz, $CDCl_3$) for hexan-1-amine (2ac)

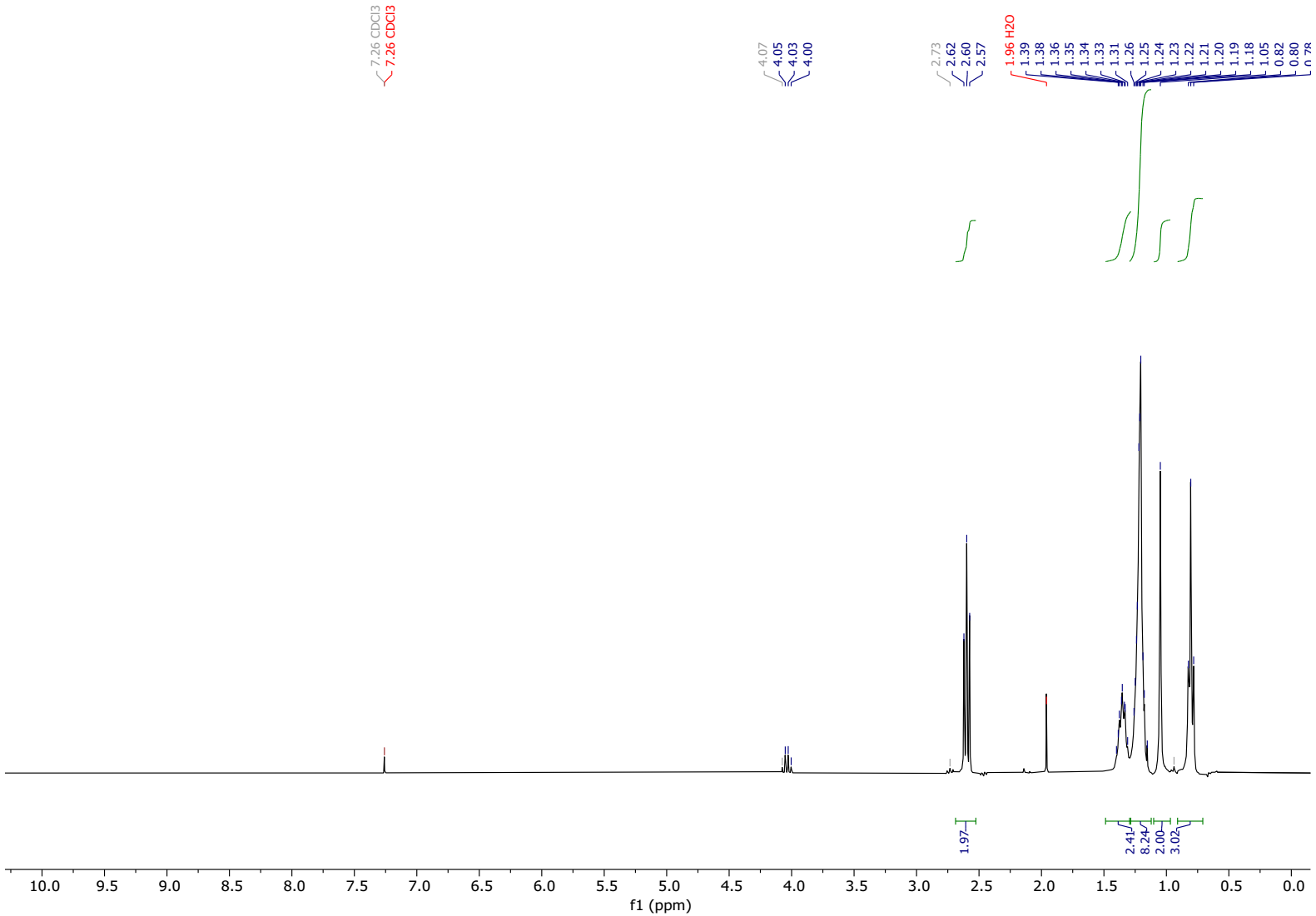


Figure S134: ^{1}H-NMR (300 MHz, $CDCl_3$) for heptan-1-amine (2ad)

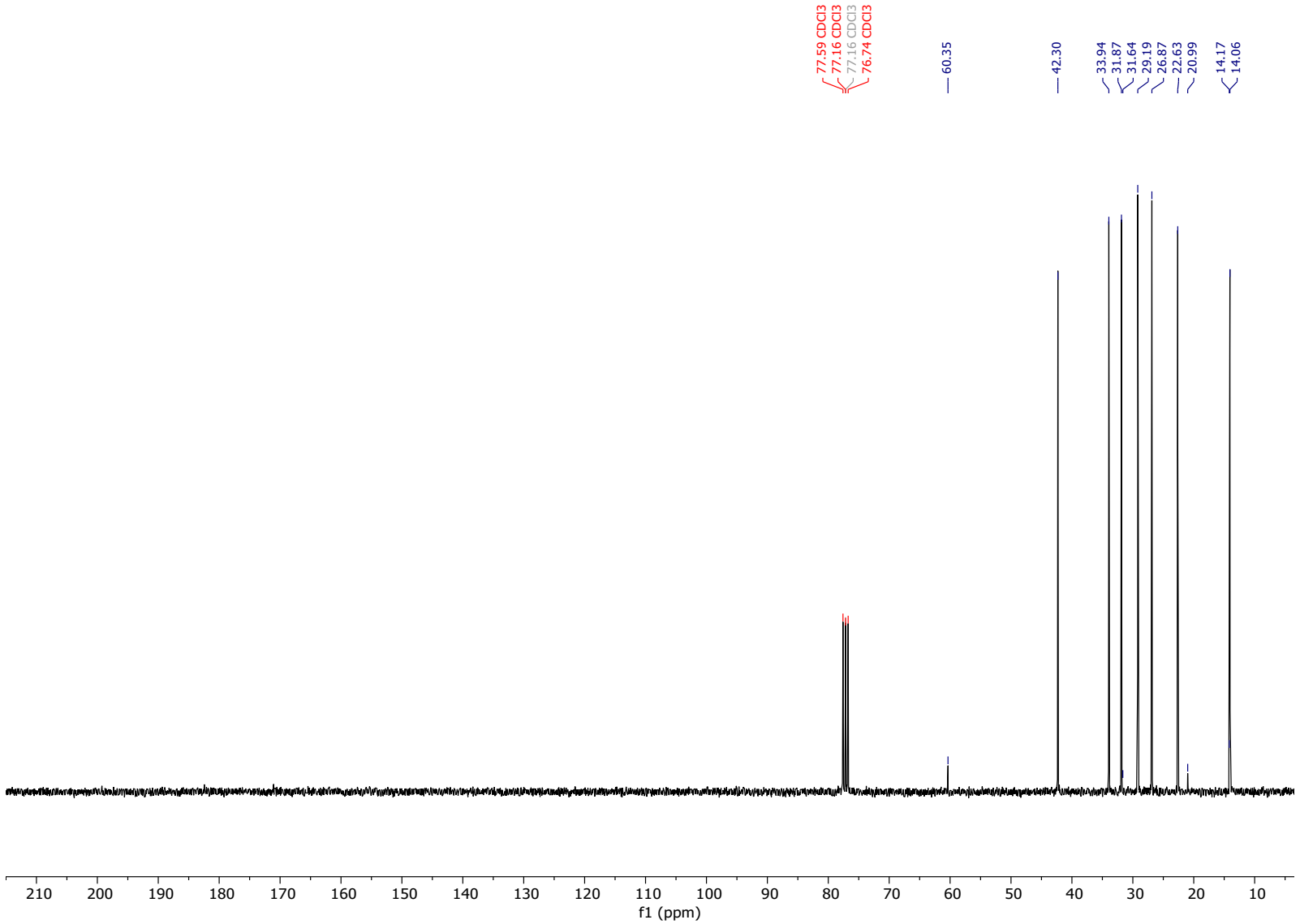


Figure S135: ^{13}C-NMR (75 MHz, $CDCl_3$) for heptan-1-amine (2ad)

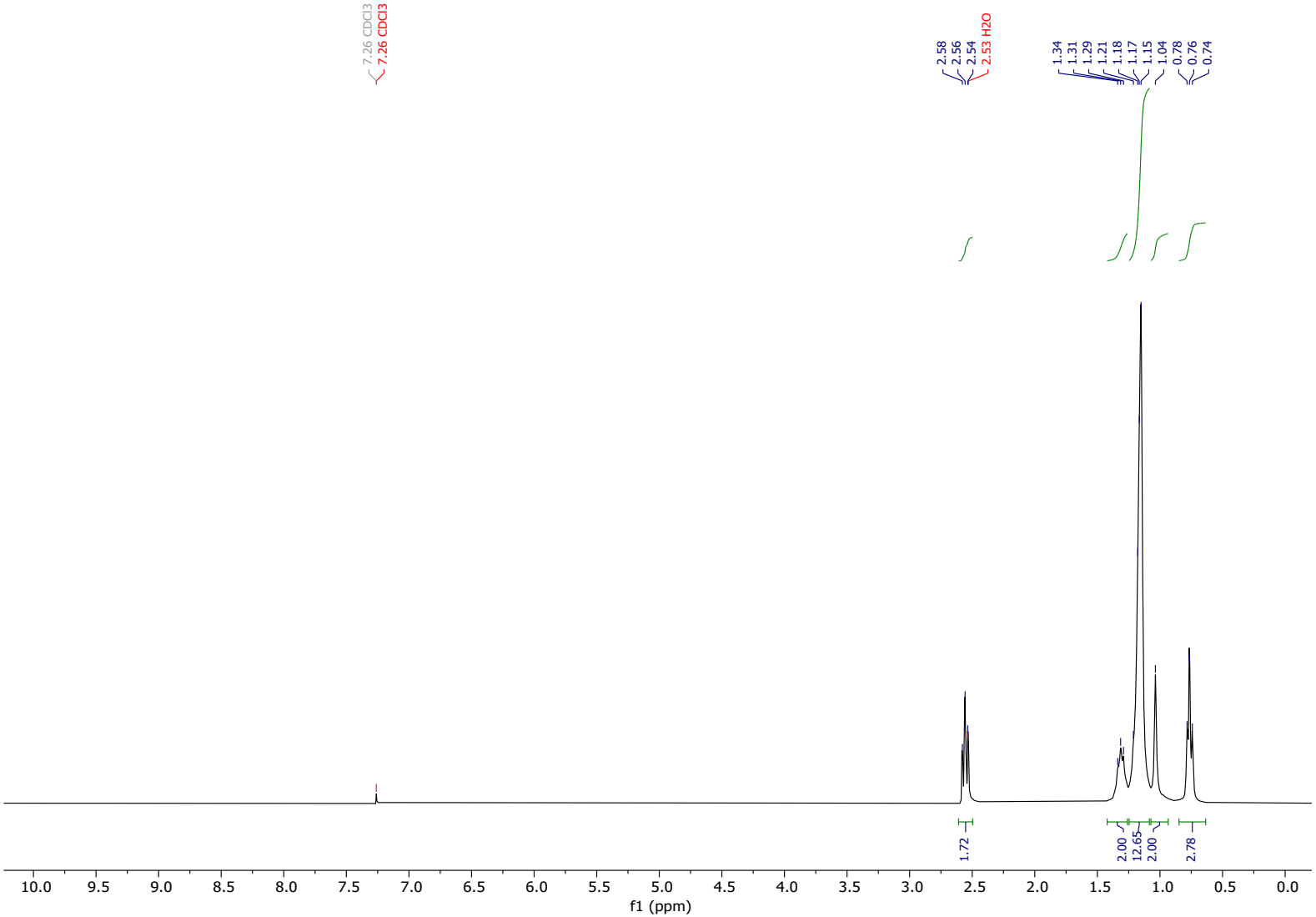


Figure 136: ^{1}H-NMR (300 MHz, $CDCl_3$) for decylamine (2ae)

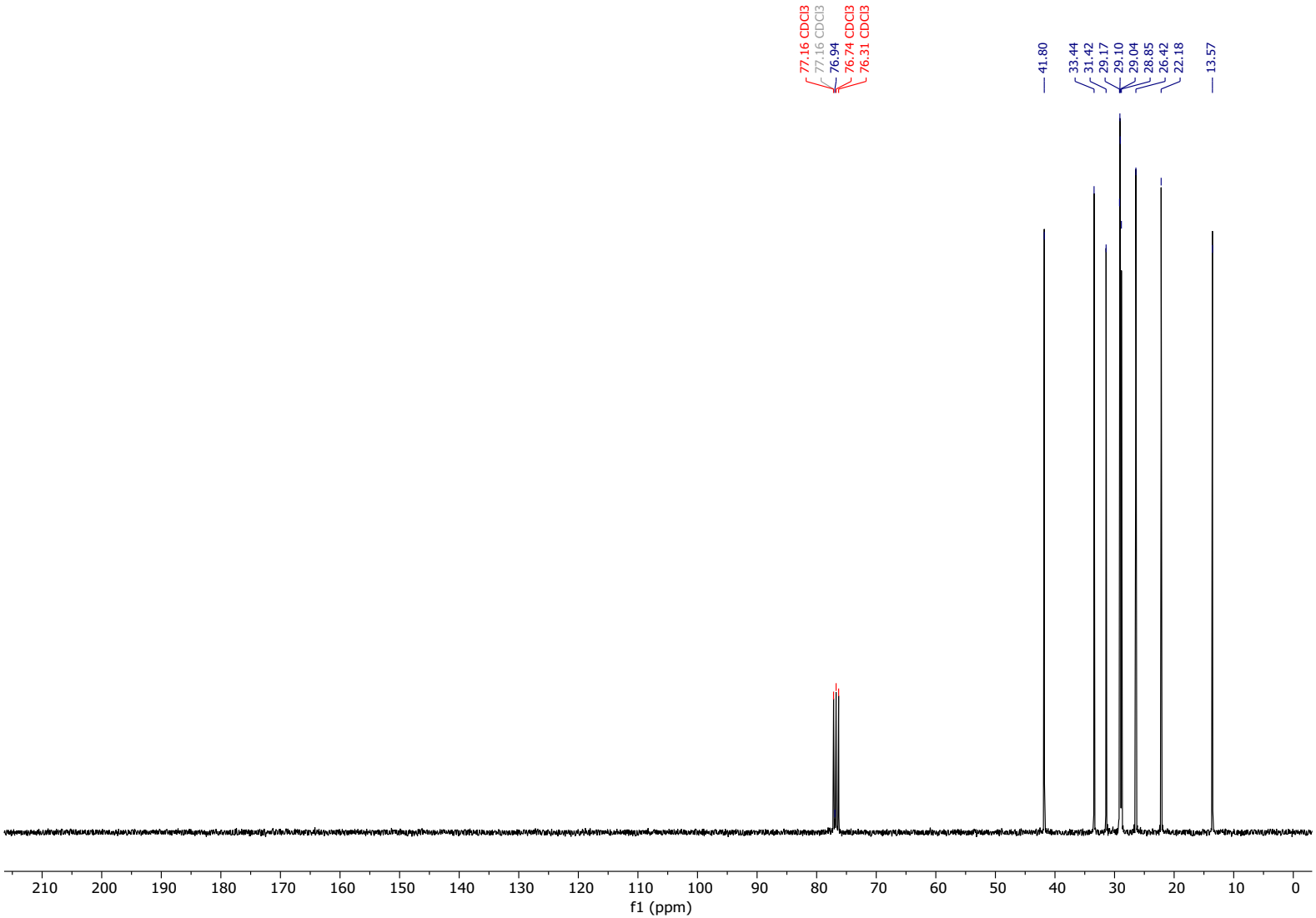


Figure S137: ^{13}C-NMR (75 MHz, $CDCl_3$) for decylamine (2ae)

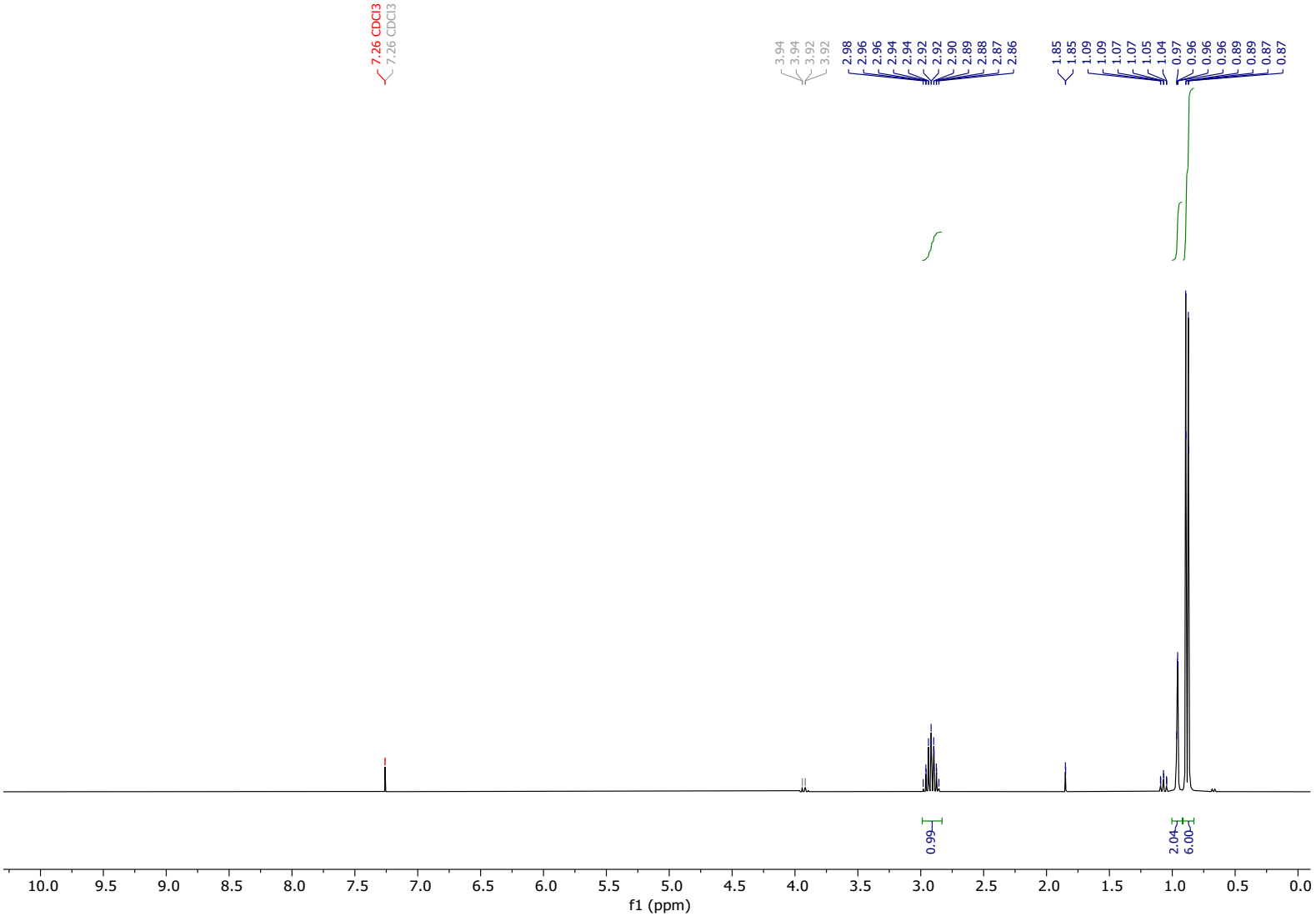


Figure S138: ^{1}H-NMR (300 MHz, $CDCl_3$) for propan-2-amine (2af)

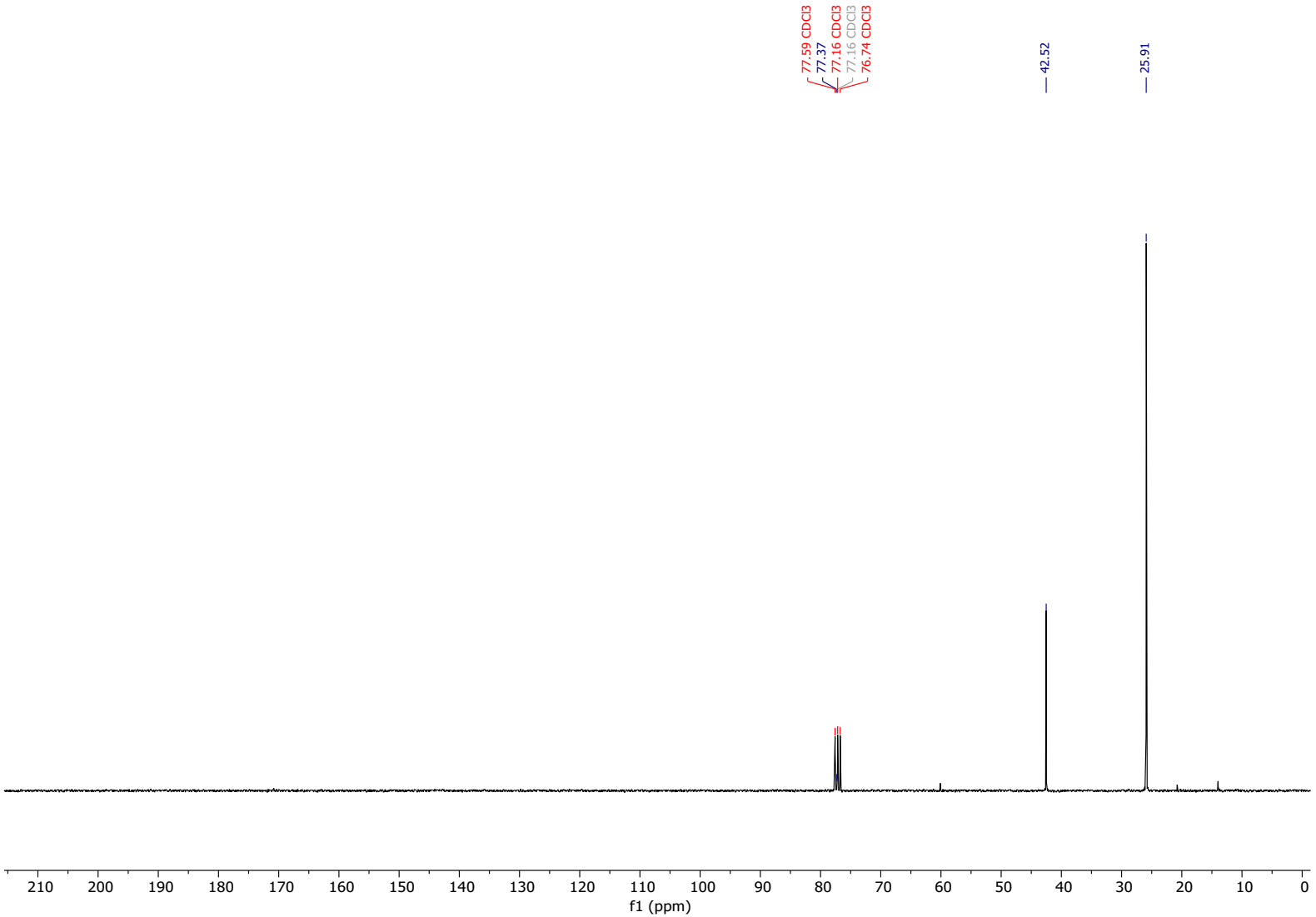


Figure S139: ^{13}C-NMR (75 MHz, $CDCl_3$) for propan-2-amine (2af)

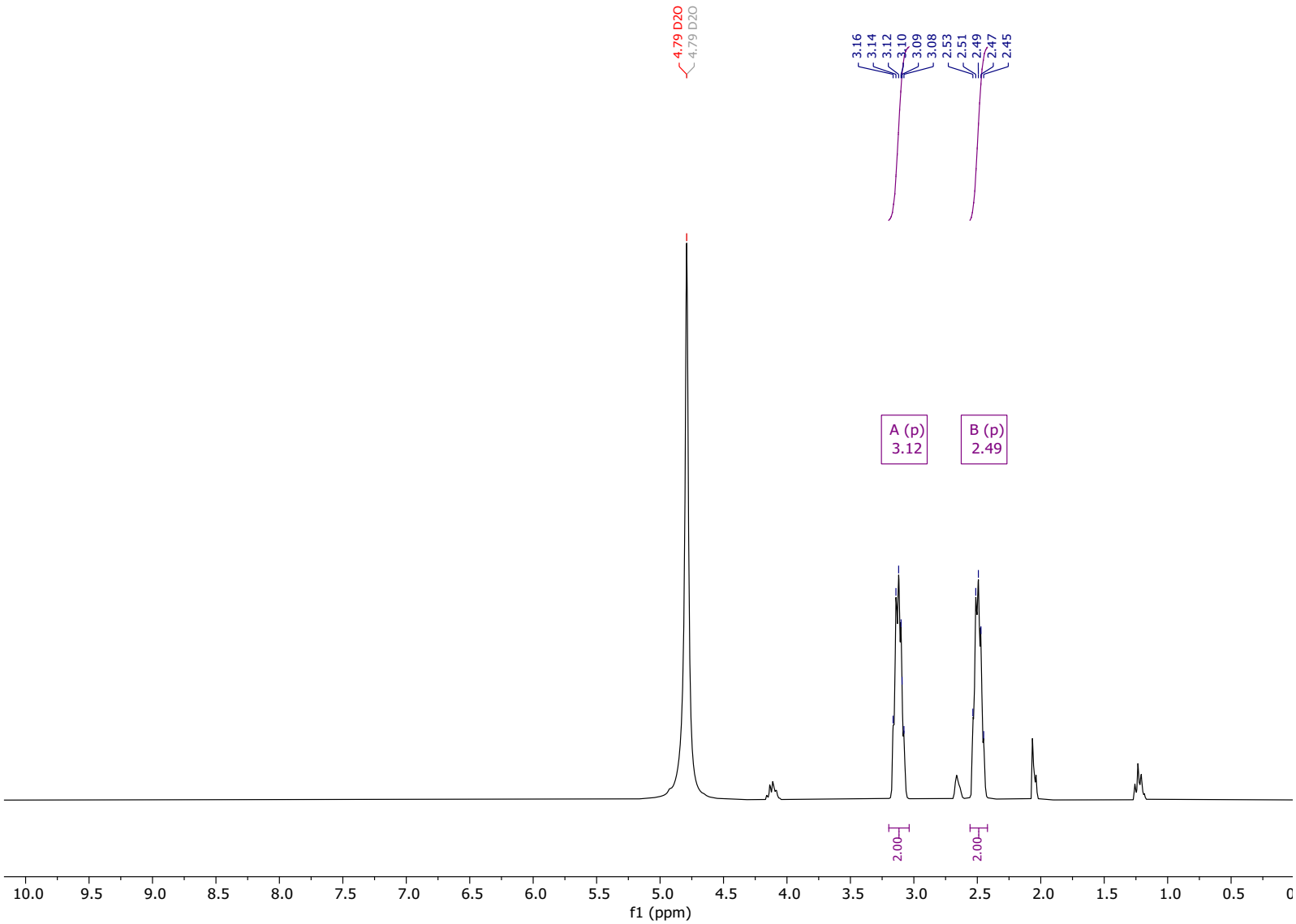


Figure S140: ^{1}H-NMR (300 MHz, $CDCl_3$) for β-alanine (2ag)

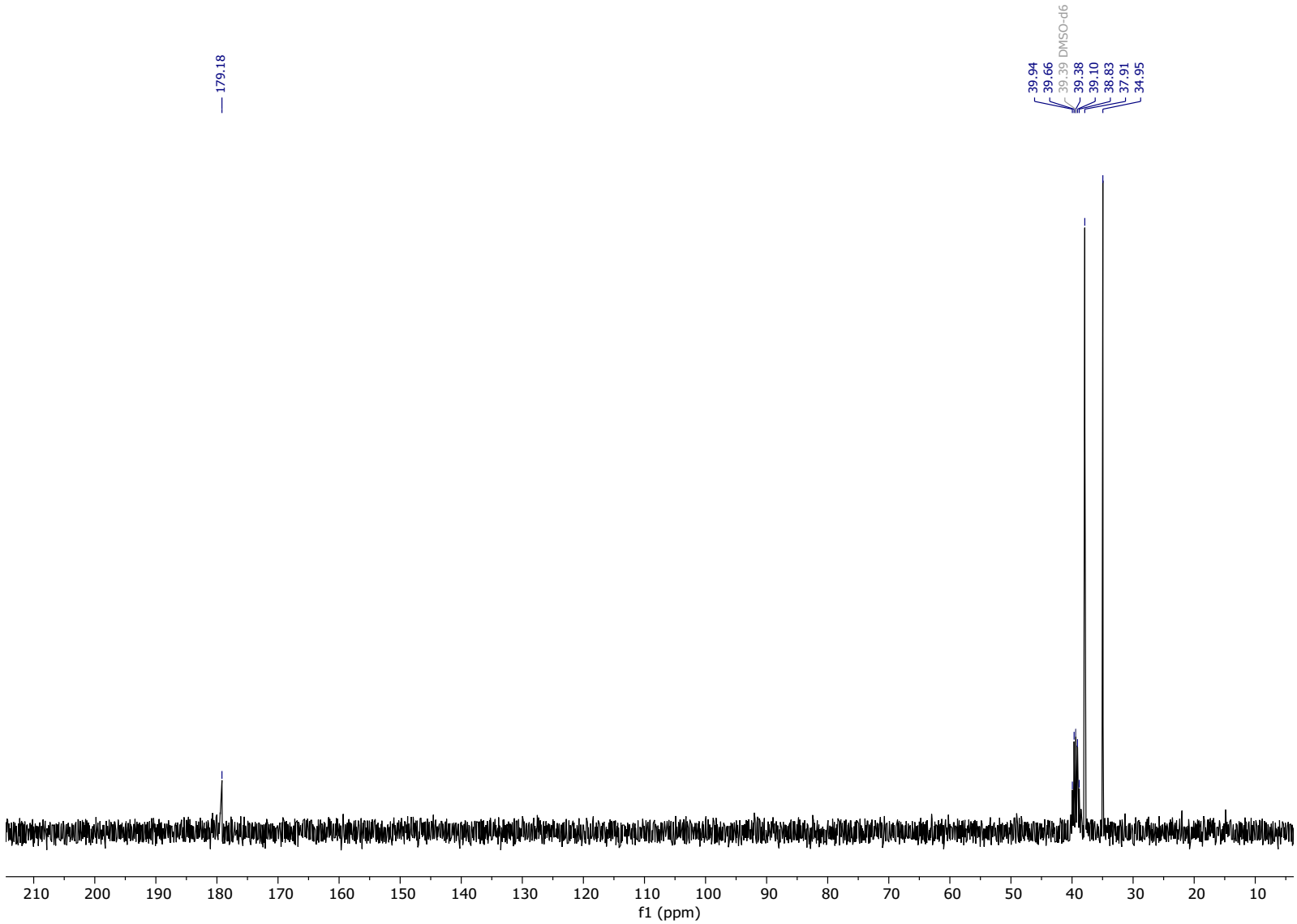


Figure S141: ^{13}C-NMR (75 MHz, $CDCl_3$) for β-alanine (2ag)

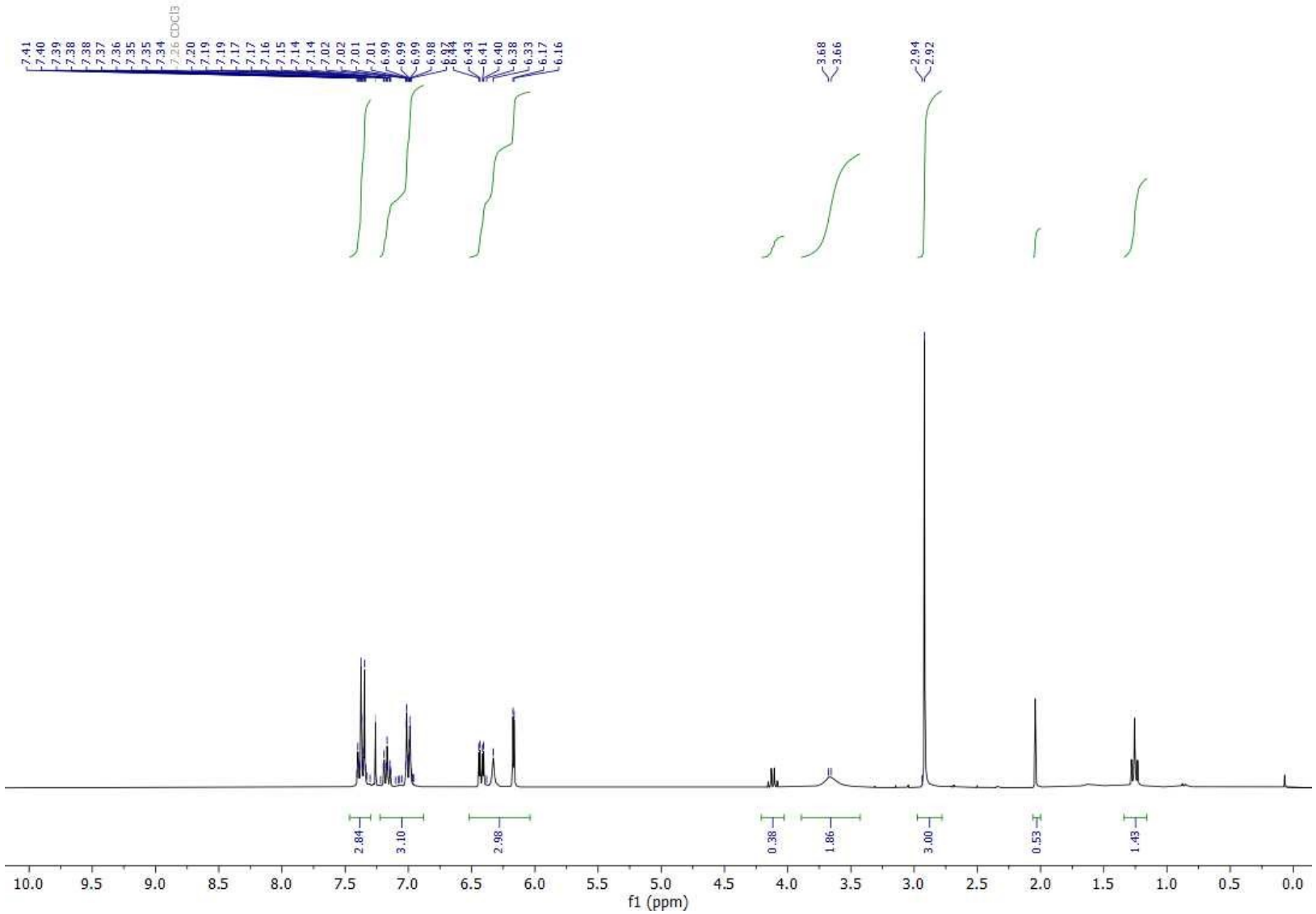


Figure S142: ^{1}H-NMR (300 MHz, $CDCl_3$) for methyl 3-(2-amino-4-(trifluoromethyl)phenoxy)thiophene-2-carboxylate (2ah)

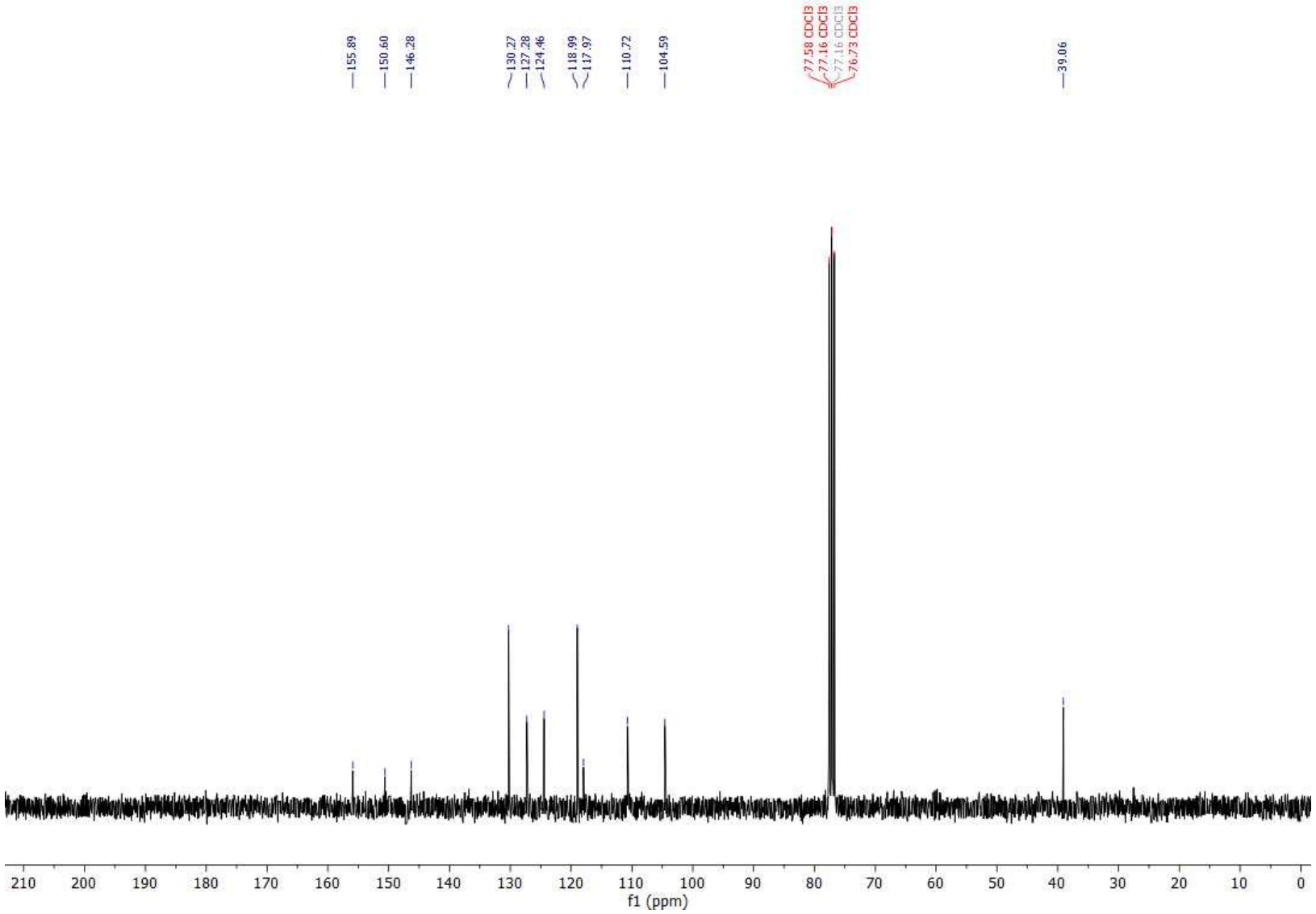


Figure S143: ^{13}C-NMR (75 MHz, $CDCl_3$) for methyl 3-(2-amino-4-(trifluoromethyl)phenoxy)thiophene-2-carboxylate (2ah)

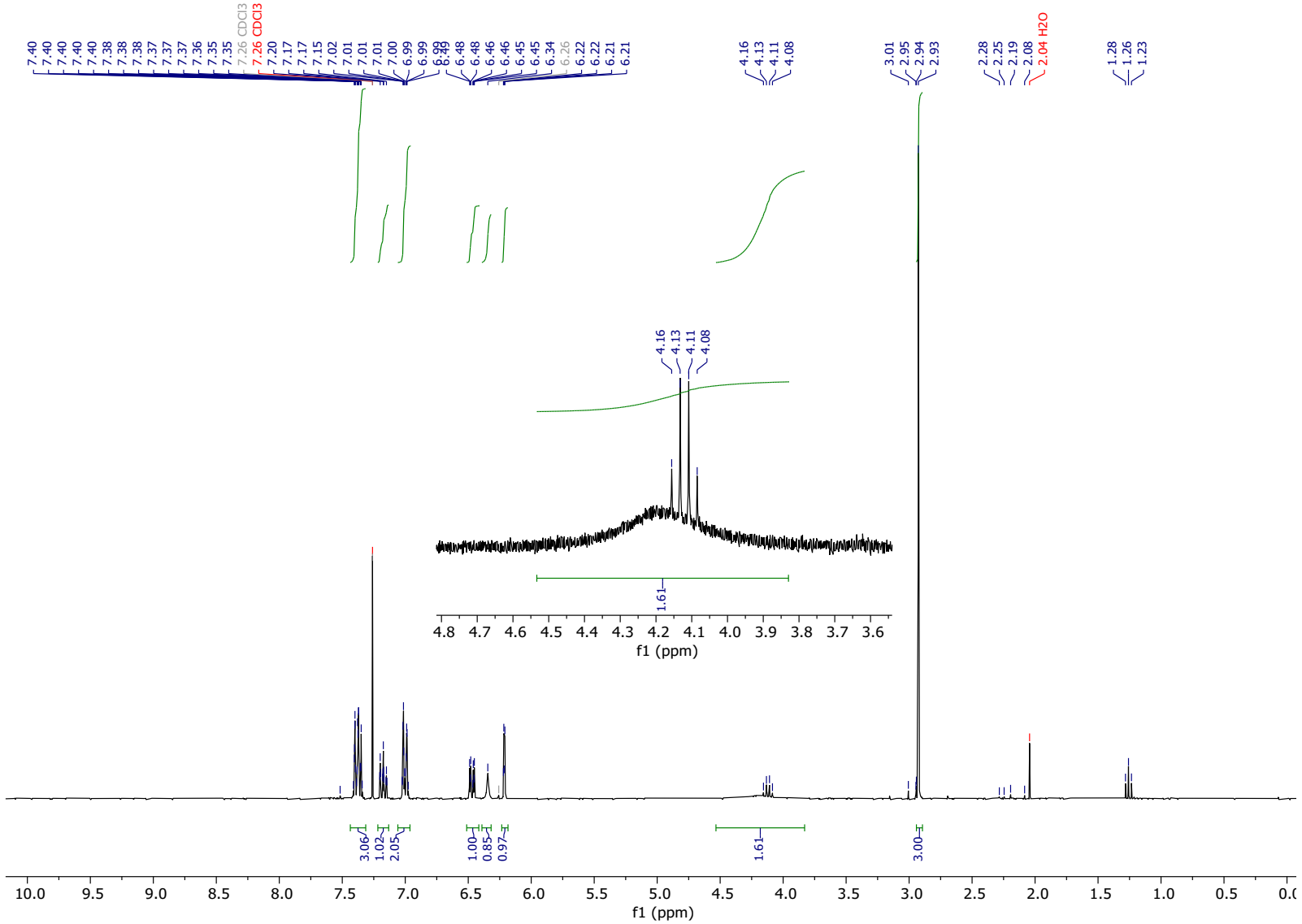


Figure S144: ^{1}H-NMR (300 MHz, $CDCl_3$) for N-(4-amino-2-phenoxyphenyl)methanesulfonamide (2ai)

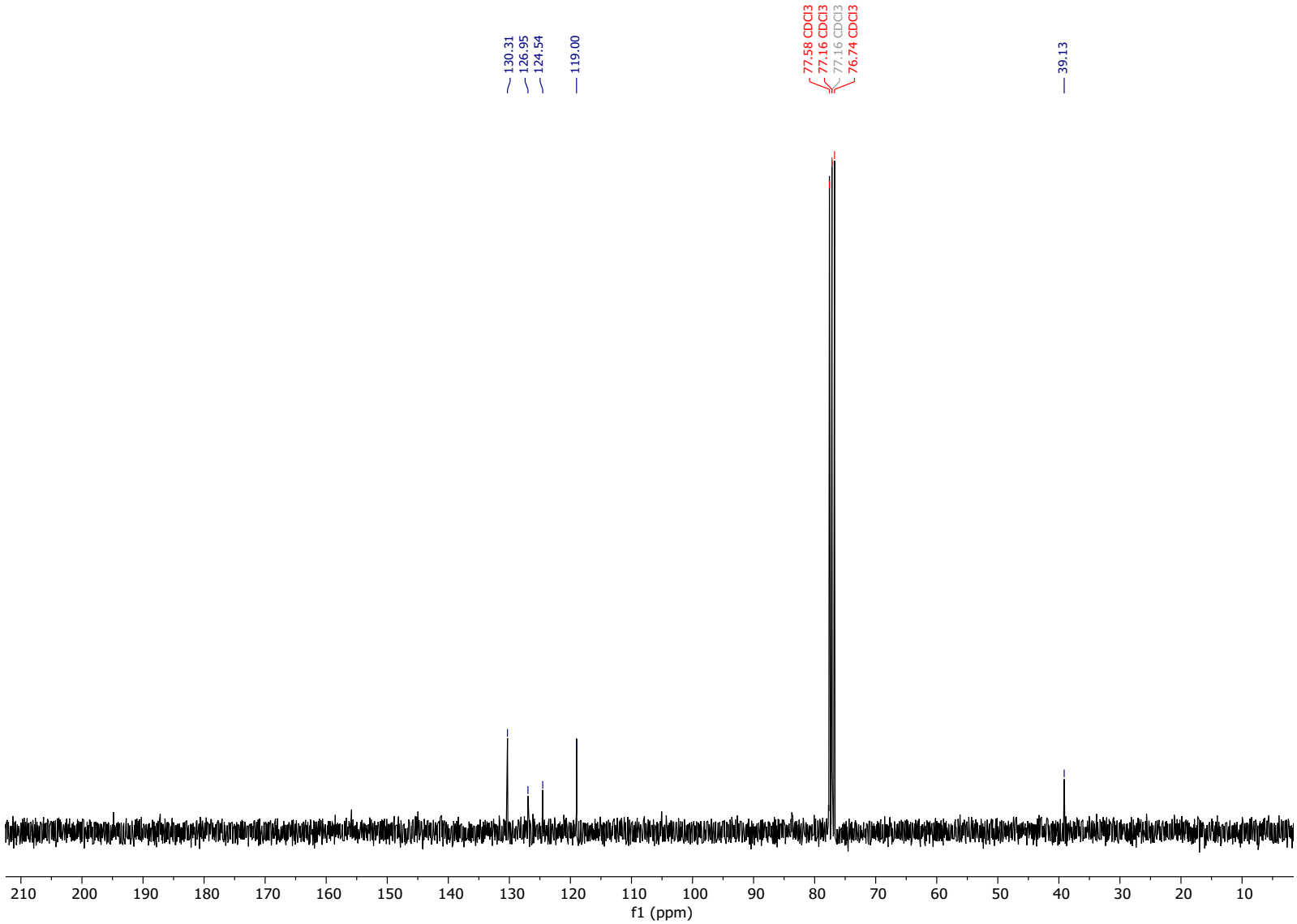


Figure S145: ^{13}C-NMR (75 MHz, $CDCl_3$) for N-(4-amino-2-phenoxyphenyl)methanesulfonamide (2ai)

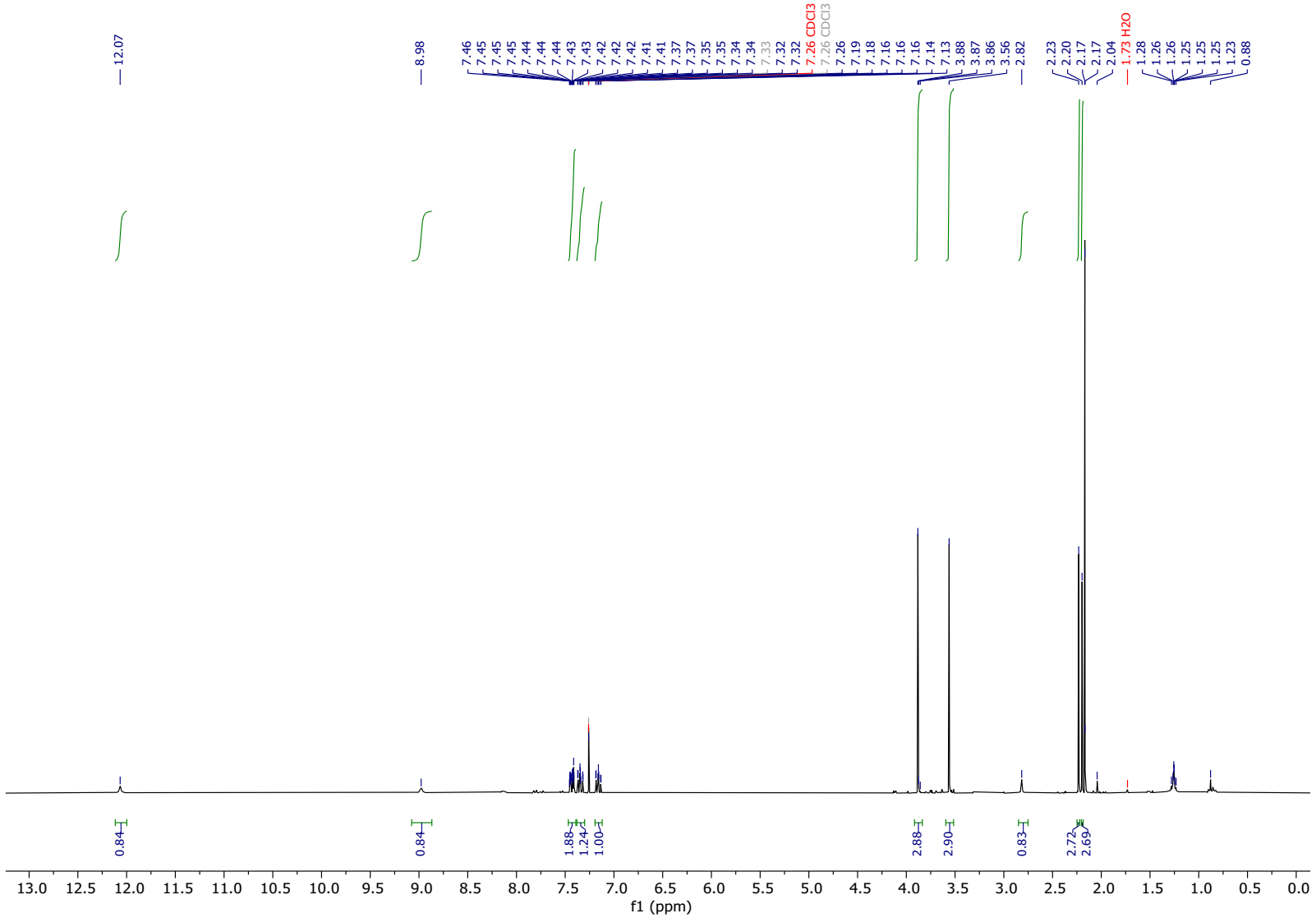


Figure S146: ^{1}H-NMR (300 MHz, $CDCl_3$) for dimethyl 4-(2-aminophenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (2aj)

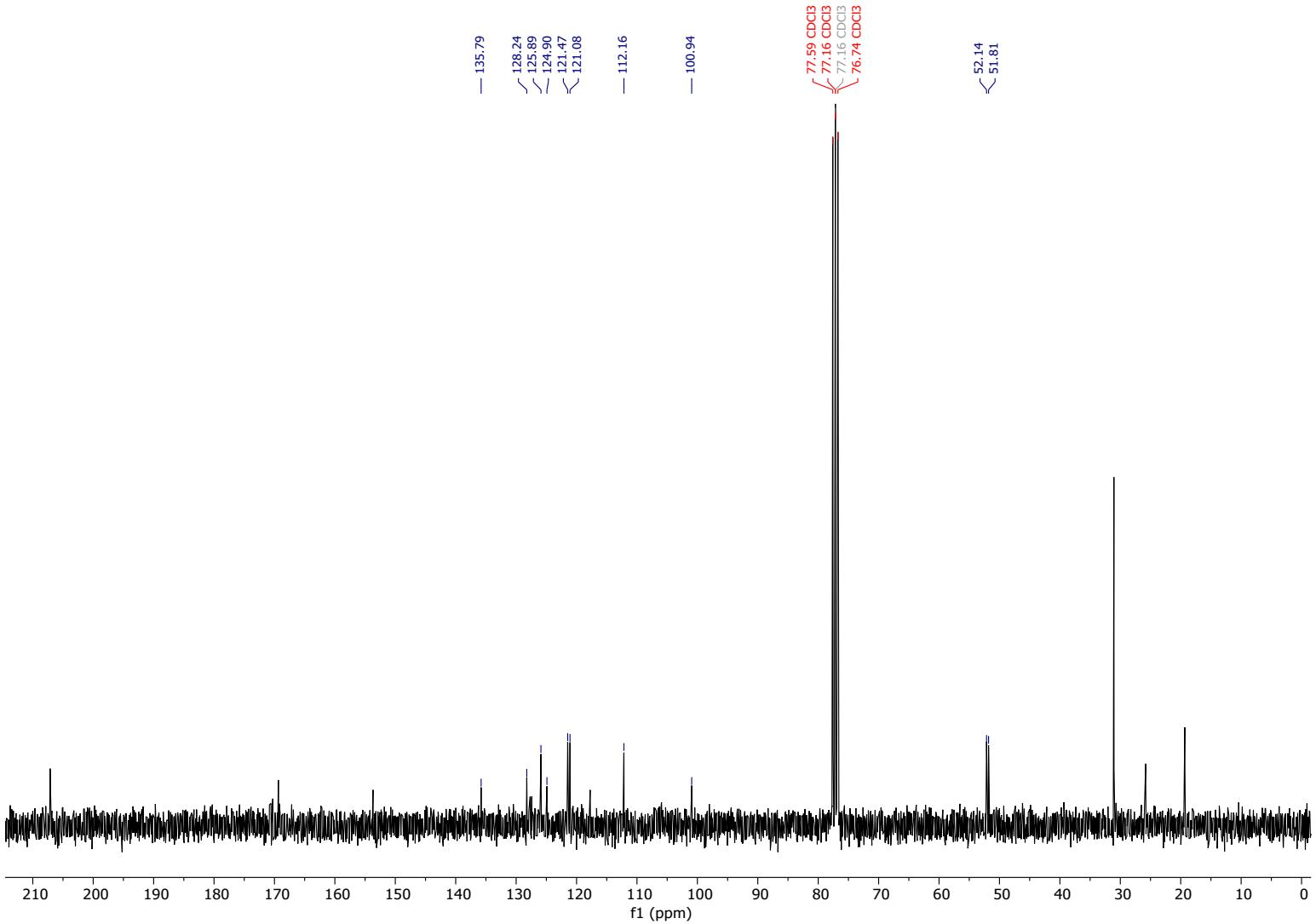


Figure S147: ^{13}C-NMR (75 MHz, $CDCl_3$) for dimethyl 4-(2-aminophenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (2aj)

8. References

1. Redwan, I. N.; Grøtli, M., Method for activation and recycling of trityl resins. *The Journal of organic chemistry* **2012,** *77* (16), 7071-7075.
2. Gawande, M. B.; Rathi, A. K.; Branco, P. S.; Nogueira, I. D.; Velhinho, A.; Shrikhande, J. J.; Indulkar, U. U.; Jayaram, R. V.; Ghumman, C. A. A.; Bundaleski, N., Regio-and Chemoselective Reduction of Nitroarenes and Carbonyl Compounds over Recyclable Magnetic Ferrite□ Nickel Nanoparticles (Fe3O4□ Ni) by Using Glycerol as a Hydrogen Source. *Chemistry–A European Journal* **2012,** *18* (40), 12628-12632.
3. Zhao, L.; Hu, C.; Cong, X.; Deng, G.; Liu, L. L.; Luo, M.; Zeng, X., Cyclic (alkyl)(amino) carbene ligand-promoted nitro deoxygenative hydroboration with chromium catalysis: Scope, mechanism, and applications. *Journal of the American Chemical Society* **2021,** *143* (3), 1618-1629.
4. Krishnan, S.; Patel, P. N.; Balasubramanian, K. K.; Chadha, A., Yeast supported gold nanoparticles: an efficient catalyst for the synthesis of commercially important aryl amines. *New Journal of Chemistry* **2021,** *45* (4), 1915-1923.
5. Xue, D.; Li, G.; Yang, L.; Liu, J.-J.; Zhang, W.; Cao, R.; Wang, C.; Zhang, Z.; Xiao, J., Light-Promoted CN Coupling of Aryl Halides with Nitroarenes. *Angewandte Chemie (International ed. in English)* **2020**.
6. Maddani, M. R.; Moorthy, S. K.; Prabhu, K. R., Chemoselective reduction of azides catalyzed by molybdenum xanthate by using phenylsilane as the hydride source. *Tetrahedron* **2010,** *66* (1), 329-333.
7. Bartoli, G.; Di Antonio, G.; Giovannini, R.; Giuli, S.; Lanari, S.; Paoletti, M.; Marcantoni, E., Efficient Transformation of Azides to Primary Amines Using the Mild and Easily Accessible CeCl3⊙ 7H2O/NaI System. *The Journal of Organic Chemistry* **2008,** *73* (5), 1919-1924.
8. Ferrazzano, L.; Martelli, G.; Fantoni, T.; Daka, A.; Corbisiero, D.; Viola, A.; Ricci, A.; Cabri, W.; Tolomelli, A., Fast Heck–Cassar–Sonogashira (HCS) Reactions in Green Solvents. *Organic letters* **2020,** *22* (10), 3969-3973.
9. Qi, H.-L.; Chen, D.-S.; Ye, J.-S.; Huang, J.-M., Electrochemical technique and copper-promoted transformations: Selective hydroxylation and amination of arylboronic acids. *The Journal of organic chemistry* **2013,** *78* (15), 7482-7487.
10. George, N.; Ofori, S.; Parkin, S.; Awuah, S. G., Mild deprotection of the N-tert-butyloxycarbonyl (N-Boc) group using oxalyl chloride. *RSC advances* **2020,** *10* (40), 24017-24026.
11. Qiu, D.; Wang, S.; Tang, S.; Meng, H.; Jin, L.; Mo, F.; Zhang, Y.; Wang, J., Synthesis of Trimethylstannyl Arylboronate Compounds by Sandmeyer-Type Transformations and Their Applications in Chemoselective Cross-Coupling Reactions. *The Journal of organic chemistry* **2014,** *79* (5), 1979-1988.
12. Duan, Z.; Ranjit, S.; Liu, X., One-pot synthesis of amine-substituted aryl sulfides and benzo [b] thiophene derivatives. *Organic letters* **2010,** *12* (10), 2430-2433.
13. Messaoudi, S.; Brion, J. D.; Alami, M., An Expeditious Copper-Catalyzed Access to 3-Aminoquinolinones, 3-Aminocoumarins and Anilines using Sodium Azide. *Advanced Synthesis & Catalysis* **2010,** *352* (10), 1677-1687.
14. Kim, J.; Chang, S., Ammonium salts as an inexpensive and convenient nitrogen source in the Cu-catalyzed amination of aryl halides at room temperature. *Chemical communications* **2008,** (26), 3052-3054.
15. Liu, S.-S.; Liu, X.; Yu, L.; Liu, Y.-M.; He, H.-Y.; Cao, Y., Gold supported on titania for specific monohydrogenation of dinitroaromatics in the liquid phase. *Green Chemistry* **2014,** *16* (9), 4162-4169.
16. Huber, D.; Andermann, G.; Leclerc, G., Selective reduction of aromatic/aliphatic nitro groups by sodium sulfide. *Tetrahedron letters* **1988,** *29* (6), 635-638.

17. Liu, J.; Zhu, Y.; Wang, C.; Singh, T.; Wang, N.; Liu, Q.; Cui, Z.; Ma, L., Facile synthesis of controllable graphene-co-shelled reusable Ni/NiO nanoparticles and their application in the synthesis of amines under mild conditions. *Green Chemistry* **2020,** *22* (21), 7387-7397.
18. Prathap, K. J.; Wu, Q.; Olsson, R. T.; Dinér, P., Catalytic reductions and tandem reactions of nitro compounds using in situ prepared nickel boride catalyst in nanocellulose solution. *Organic letters* **2017,** *19* (18), 4746-4749.
19. Piazzolla, F.; Mercier, V.; Assies, L.; Sakai, N.; Roux, A.; Matile, S., Fluorescent Membrane Tension Probes for Early Endosomes. *Angewandte Chemie International Edition* **2021,** *60* (22), 12258-12263.
20. Gennen, S.; Grignard, B.; Tassaing, T.; Jérôme, C.; Detrembleur, C., CO2-Sourced α-Alkylidene Cyclic Carbonates: A Step Forward in the Quest for Functional Regioregular Poly (urethane) s and Poly (carbonate) s. *Angewandte Chemie* **2017,** *129* (35), 10530-10534.
21. Formenti, D.; Mocci, R.; Atia, H.; Dastgir, S.; Anwar, M.; Bachmann, S.; Scalone, M.; Junge, K.; Beller, M., A State-of-the-Art Heterogeneous Catalyst for Efficient and General Nitrile Hydrogenation. *Chemistry–A European Journal* **2020,** *26* (67), 15589-15595.
22. Liu, Z.; Huang, C.; Liu, Y.; Lin, D.; Zhao, Y., NMR-based metabolomic analysis of the effects of alanyl-glutamine supplementation on C2C12 myoblasts injured by energy deprivation. *Rsc Advances* **2018,** *8* (29), 16114-16125.
23. Jagadeesh, R. V.; Banerjee, D.; Arockiam, P. B.; Junge, H.; Junge, K.; Pohl, M.-M.; Radnik, J.; Brückner, A.; Beller, M., Highly selective transfer hydrogenation of functionalised nitroarenes using cobalt-based nanocatalysts. *Green Chemistry* **2015,** *17* (2), 898-902.