Supporting Information

Synthesis of Cobalt Nanoparticles by Pyrolysis of Vitamin B_{12}: A Non-noble Catalyst for Efficient Hydrogenation of Nitriles

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General information. Cyanocobalamine was supplied by Fisher BioReagents and Cerium(IV) oxide nanopowder was obtained from Sigma-Aldrich; both solids were used as received.
The substrates and solvents were used without any further purification prior to use.
All hydrogenation reactions were conducted in 8 mL glass vials which were placed in a 300 mL autoclave (PARR Instrument Company).
Conversions and yields of the hydrogenation reactions were determined by a GC-FID device (HP 6890), column HP530 m x 250 mm x 0.25 μm. Mass spectra were recorded on an Agilent 5973 GC-MS spectrograph.
^{1}H NMR spectra of the compounds were recorded on a 300 MHz (Bruker AV-300) or 400 MHz (Bruker AV-400) spectrometer; $^{13}C\{^{1}H\}$ NMR spectra were obtained at 75 MHz or 101 MHz, respectively. NMR chemical shifts are reported in parts per million downfield from tetramethylsilane and are referenced to the residual proton resonance and the natural ^{13}C resonance of DMSO-d_6 at 2.50 ppm (^{1}H) and 39.5 ppm (^{13}C), respectively. All chemical shifts (δ) are reported in ppm and coupling constants (J) in Hz. Abbreviations used in the reported NMR experiments: b, broad; s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. All measurements were carried out at room temperature.

S1 *Catalyst preparation.*
B_{12}@CeO_2-X (X: 7; 8; 9; 10 refers to 700, 800, 900 and 1000 °C pyrolysis temperature, respectively). To a deep purple solution of cyanocobalamin (338.8 mg, 0.25 mmol, is equivalent to 15 mg of cobalt) in EtOH (50 mL) was added Cerium(IV)oxide nanopowder (1.0 g) to obtain a material containing 1.5 w% of Co/CeO_2. The mixture was heated at reflux under magnetic stirring for 4 h. After cooling to room temperature the solvent was evaporated under reduced pressure. The solid residue was dried under vacuum for 4 h at r.t. The dry solid was grinded to a fine powder, transferred into a ceramic crucible and placed in the oven. The oven was evacuated to 5 mbar and then flushed with argon. The furnace was then heated to 800 (or 700, 900, 1000) °C at the rate of 25 °C per minute and held at the required temperature for 2 hours under an argon atmosphere. After that heating was switched off and the oven was allowed to reach room temperature. During the whole process argon was constantly passed through the interior of the furnace.
B_{12}@CeO_2-8 (3%). A mixture of cyanocobalamin (170 mg, 0.125 mmol, is equivalent to 7.4 mg of cobalt) and Cerium(IV)oxide nanopowder (250 mg) in EtOH (25 mL) was heated at reflux under magnetic stirring for 4 h. After the work-up procedure of the thus obtained suspension as described the resulting dried fine powder (3 w%, Co/CeO_2) was pyrolysed at 800 °C for 2 hours under argon atmosphere. The catalyst has been successfully used in the model reaction to check actvity (>99 conversion; >99 selectivity, GC Y: 84%). Reaction conditions: PhCN (0.25 mmol), catalyst (1.6 mol%, 10 mg assuming a cobalt content about 2.2 %), 0.2 mL aqueous NH_3, *i*-PrOH (2 mL), 120 °C, 15 h.
B_{12}-8 was prepared by pyrolysis at 800 °C of pure cyanocobalamine without using any support. Elemental analysis of the new materials are reported in Table S1.

S2 *Catalyst characterization.*
CHN analyses were performed using a Leco Microanalysator TruSpec. Metal content of the catalysts was determined by atom absorption spectroscopy using a PerkinElmer AAS Analyst

300 or by emissions spectroscopy (ICP) using a Varian 715-ES after fusion melts and acidic dissolving of the sample.

XRD pattern of the materials were recorded on a PANalytical X'Pert Pro diffractometer in reflection mode with Cu Kα radiation (λ=1.5406 Å) and a silicon strip detector (X'Celerator).

XPS data were obtained with a VG ESCALAB220iXL (ThermoScientific) with mono-chromatic Al Kα (1486.6 eV) radiation. The electron binding energies E_B were obtained without charge compensation. For quantitative analysis the peaks were deconvoluted with Gaussian-Lorentzian curves, the peak area was divided by a sensitive factor obtained from the element specific Scofield factor and the transmission function of the spectrometer.

Table S1. Catalyst elemental analysis (w%).

		Co (%)	C (%)	H (%)	N (%)	P (%)	O (%)	Ce (%)
1	B_{12}@CeO_2-7	1.24	4.84	0.13	0.77	0.68	18.69	73.65
2	B_{12}@CeO_2-8	1.18	4.42	0.11	0.48	0.43	10.66	82.72
3	B_{12}@CeO_2-9	1.18	3.18	0.09	0.24	0.68	18.48	76.15
4	B_{12}@CeO_2-10	1.13	4.21	0.03	0.09	0.44	11.16	82.94
5	B_{12}@CeO_2-8(3%)	2.29	3.84	0.05	0.15	1.00	12.02	80.65
6	B_{12}-8[a]	11.59	56.12	1.11	8.03	5.88	17.27	-

[a]B_{12}-8 is vitamin B_{12} pyrolysed at 800 °C.

S3 *General procedure for the hydrogenation of nitriles* **1** (**Table 4**)

A reaction glass vial fitted with a magnetic stirring bar and a septum cap penetrated with a needle was charged with the B_{12}@CeO_2-8 catalyst (1.6 mol%, 20 mg), nitrile (0.25 mmol), internal standard (*n*-hexadecane, 25 μL), solvent (2 mL) and a 25% aqueous solution of NH_3 (200 μL) in that order. The vial was then placed into a 300 mL Parr steel autoclave equipped with a drilled aluminium plate that accommodates up to 7 uniform reaction glasses (8 mL). The autoclave was then flushed with hydrogen twice at 30 bar, pressurized with hydrogen and placed into an aluminium block which was heated to the required temperature. On completion of the reaction the autoclave was put into a water bath to accelerate cooling to room temperature. After releasing non-consumed H_2 gas the vials were removed from the autoclave whereupon the catalyst was separated by centrifugation. A sample of the clear supernatant was collected, diluted with ethyl acetate and analyzed by GC (all GC-yields are average values from at least 2 runs; the calibration curve of the starting materials as well as the products were obtained using the commercially available materials).

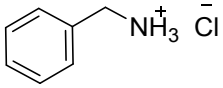
Isolation of amines as the hydrochloride salt (Table 5). The supernatant obtained after separating the catalyst by centrifugation was evaporated to dryness under reduced pressure. Unless otherwise stated the residue was dissolved in AcOEt (2 mL), cooled in an ice bath and treated with a 1.25 M solution of HCl in methanol (0.2-0.3 mL). The formed precipitate was filtered, washed with *n*-hexane (2 x 0.5 mL) and dried *in vacuo*.

As reported in Table 5 the hydrogenation of 2-furonitrile produced a mixture of the desired amine and 2-furoic acid in a 9/1 molar ratio (NMR analysis) (entry 13). To isolate the amine as a pure HCl salt, the crude residue obtained after evaporation *i*-PrOH was dissolved in

AcOEt (2 mL) and washed with a saturated solution of K_2CO_3 (2 mL). Hereafter, the organic layer was separated and treated with a solution of HCl in methanol according to the procedure reported above.
In the case of 3- and 4-(aminomethyl)pyridine (Table 5, entries 11 and 12) the residue obtained after evaporating *i*-PrOH was purified by filtration over a short pad of silica gel using MeOH as eluent.

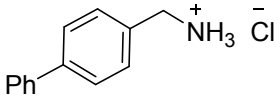
S4 *General procedure for the hydrogenation of* **5**, **7, 8** (**Scheme 2**)
A reaction glass vial fitted with a magnetic stirring bar and a septum cap penetrated with a needle was charged with the B_{12}@CeO_2-8 catalyst (1.6 mol%, 20 mg), substrate (0.25 mmol), internal standard (*n*-hexadecane, 25 μL) and solvent (2 mL) (Scheme 2). Then, substrate hydrogenation was carried out at the required H_2 pressure and temperature according to the procedure reported in **S3**. On completion of the reaction (15 h) a sample was analysed by GC.
Reductive amination reactions of **7** and **8** (0.25 mmol) were carried out in *i*-PrOH and under addition of 25% aqueous ammonia solution (0.2 mL) according to the procedure described in **S3**.

S5 *Characterization of* **2** *(GC MS analysis) and the corresponding ammonium chloride salts (NMR analysis)*



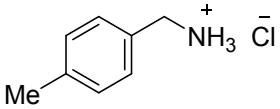
Benzylamine hydrochloride. **^{1}H NMR** (300 MHz, DMSO-d_6): 3.98 (b s, 2H); 7.31-7.41 (m, 3H); 7.41-7.48 (m, 2H); 8.61 (b s, 3H). **^{13}C NMR** (75 MHz, DMSO-d_6): 42.6 (CH_2), 128.9 (CH), 129.0 (CH), 129.4 (CH), 134.5 (Cq).

GCMS-EI (70eV): m/z (%): 106 (M-1, 100), 91 (10), 79 (38), 65 (14), 51 (14), 39 (5), 30 (14).



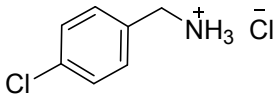
4-Phenylbenzylamine hydrochloride. **^{1}H NMR** (300 MHz, DMSO-d_6): 4.05 (q, J = 6.0 Hz, 2H), 7.37 (dt, J = 6.0, 3.0 Hz, 1H), 7.44-7.49 (m, 2H), 7.58 (d, J = 6.0 Hz, 2H), 7.66-7.72 (m, 4H), 8.52 (b s, 3H). **^{13}C NMR** (75 MHz, DMSO-d_6): 41.7 (CH_2), 126.7 (CH), 126.8 (CH), 127.6 (CH), 129.0 (CH), 129.6 (CH), 133.3 (Cq), 139.5 (Cq), 140.1 (Cq).

GCMS-EI (70 eV): m/z (%) = 182 (M-1, 100), 166 (90), 152 (45), 128 (9), 106 (36), 91 (4), 77 (18), 63 (4), 51 (5), 30 (8).



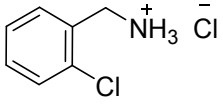
4-Methylbenzylamine hydrochloride. **^{1}H NMR** (300 MHz, DMSO-d_6): 2.30 (s, 3H), 3.94 (s, 2H), 7.21 (d, J = 6.0 Hz, 2H), 7.37 (d, J = 6.0 Hz, 2H), 8.43 (b s, 3H). **^{13}C NMR** (101 MHz, DMSO-d_6): 20.7 (Me), 41.8 (CH_2), 128.9 (CH), 129.0 (CH), 131.0 (Cq), 137.6 (Cq).

GCMS-EI (70eV): m/z (%) = 120 (M-1, 78), 104 (100), 91 (50), 77 (30), 65 (20), 51 (10), 39 (9), 30 (13).



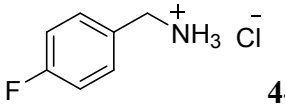
4-Chlorobenzylamine hydrochloride. ^{1}H NMR (300 MHz, DMSO-d_6): 4.0 (s, 2H); 7.46 (d, J = 9.0 Hz, 2H), 7.56 (d, *J* = 9.0 Hz, 2H), 8.65 (b s, 3H). **^{13}C NMR** (75 MHz, DMSO-d_6): 41.8 (CH_2), 128.9 (CH), 131.5 (CH), 133.5 (Cq), 133.6 (Cq).

GCMS-EI (70eV): m/z (%) = 140 (M-1, 52), 125 (13), 113 (9), 106 (100), 89 (8), 77 (35), 51 (10), 28 (17).



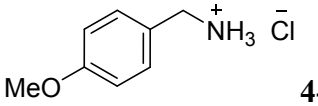
2-Chlorobenzylamine hydrochloride. **^{1}H NMR** (300 MHz, DMSO-d_6): 4.09 (s, 2H), 7.38-7.41 (m, 2H), 7.50-7.52 (m, 1H), 7.66-7.68 (m, 1H), 8.80 (b s, 3H). **^{13}C NMR** (75 MHz, DMSO-d_6): 39.8 (CH_2), 127.9 (CH), 129.9 (CH), 130.7 (CH), 131.1 (CH), 132.1 (Cq), 133.3 (Cq).

GCMS-EI (70eV): m/z (%) = 140 (M-1, 44), 125 (9), 112 (5), 106 (100), 89 (6), 77 (32), 51 (12), 30 (16).



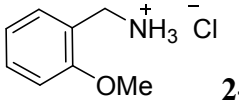
4-Fluorobenzylamine hydrochloride. **^{1}H-NMR**: (300 MHz, DMSO-d_6): 3.99 (s, 2H), 7.29-7.17 (m, 2H), 7.62-7.52 (m, 2H), 8.60 (b s, 3H). **^{13}C-NMR** (75 MHz, DMSO-d_6): 41.3 (CH_2), 115.3 (d, J = 21.5 Hz, CH), 130.4 (d, J = 3.0 Hz, Cq), 131.4 (d, J = 8.4 Hz, CH), 162.0 (d, J = 244.6 Hz, Cq).

GC/MS (EI, 70eV): m/z (%) = 124 (M-1, 100), 105 (45), 95 (32), 75 (10), 51 (6), 28 (15).



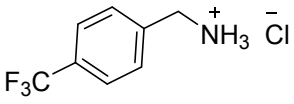
4-Methoxybenzylamine hydrochloride. **^{1}H NMR** (300 MHz, DMSO-d_6): 3.75 (s, 3H), 3.92 (m, 2H), 6.96 (d, J = 9.0 Hz, 2H), 7.42 (d, J = 9.0 Hz, 2H), 8.42 (b s, 3H). **^{13}C NMR** (101 MHz, DMSO-d_6): 41.5 (CH_3), 55.2 (CH_2), 113.8 (CH), 126.0 (Cq), 130.5 (CH), 159.2 (Cq).

GCMS-EI (70eV): m/z (%) = 136 (M-1, 100), 121 (38), 106 (39), 94 (20), 77 (21), 65 (10), 51 (7), 39 (5), 30 (9).



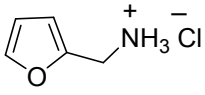
2-Methoxybenzylamine hydrochloride: ^{1}H NMR (300 MHz, DMSO-d_6): 3.82 (s, 3H), 3.92-3.95 (m, 2H), 6.96 (dt, J = 9.0, 3.0 Hz, 2H), 7.05 (d, J = 6.0 Hz, 1H), 7.33-7.42 (m, 2H), 8.40 (b s, 3H). **^{13}C NMR** (75 MHz, DMSO-d_6): 37.9 (CH_3), 56.0 (CH_2), 111.3 (CH), 120.7 (CH), 122.2 (Cq), 130.6 (CH), 130.7 (CH), 157.6 (Cq).

GCMS-EI (70eV): 136 (M-1, 100), 121 (44), 106 (50), 91 (40), 77 (32), 65 (18), 51 (14), 39 (10), 30 (18).



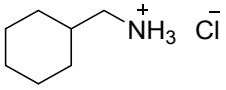
4-Trifluoromethylbenzylamine hydrochloride. **^{1}H NMR** (300 MHz, DMSO-d_6): 4.1 (m, 2H), 7.72-7.79 (m, 4H), 8.79 (s, 3H). **^{13}C NMR** (75 MHz, DMSO-d_6,): 41.5 (CH_2), 124.1 (q, J = 272 Hz, Cq), 125.3 (q, J = 3.8 Hz, CH), 128.8 (q, J = 30 Hz, Cq), 129.8 (CH), 138.8 (Cq).

GCMS-EI (70eV): m/z (%) = 174 (M-1, 100), 156 (16), 145 (11), 127 (36), 106 (45), 77 (99), 50 (6), 30 (27).



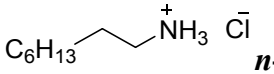
Furfurylamine hydrochloride. **^{1}H NMR** (DMSO-d_6, 300 MHz): 4.03 (s, 2H), 6.48 (dd, J = 3.0, 1.8 Hz, 1H), 6.55 (d, J = 3.0 Hz, 1H), 7.71 (dd, J = 1.8, 0.6 Hz, 1H), 8.62 (b s, 3H). **^{13}C NMR** (DMSO-d_6, 75 MHz): 35.4 (CH_2), 110.7 (CH), 111.4 (CH), 144.0 (CH), 148.2 (Cq).

GCMS-EI (70 eV): m/z (%) = 97 (M, 61), 81 (27), 69 (100), 53 (40), 41 (43), 39 (60), 30 (31).



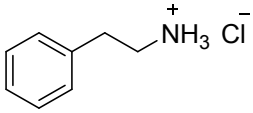
Cyclohexanemethylamine hydrochloride. **^{1}H-NMR** (300 MHz, DMSO-d_6): 0.80-0.97 (m, 2H), 1.01-1.26 (m, 3H), 1.46-1.77 (m, 6H), 2.59 (quintet, J = 6.1 Hz, 2H), 8.06 (b s, 3H). **^{13}C-NMR** (75 MHz, DMSO-d_6): 25.5 (CH_2), 26.1 (CH_2), 30.2 (CH_2), 35.8 (CH), 44.8 (CH_2).

GC/MS: (EI, 70eV): m/z = 113 (M+1, 12), 96 (6), 81 (5), 67 (14), 55 (13), 41 (13), 30 (100).



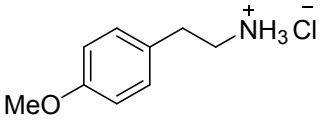
***n*-Octylamine hydrochloride**. **^{1}H-NMR**: (300 MHz, DMSO-d_6): 0.79-0.88 (m, 3 H), 1.15-1.33 (m, 10 H), 1.45-1.60 (m, 2H), 2.63-2.77 (m, 2H), 8.09 (b s, 3H). **^{13}C-NMR:** (75 MHz, DMSO-d_6): 14.4 (CH_3), 22.5 (CH_2), 26.3 (CH_2), 27.4 (CH_2), 29.0 (CH_2), 31.6 (CH_2), 39.1 (CH_2).

GC/MS: (EI, 70eV): m/z = 129 (M, 2), 100 (3), 86 (5), 69 (3), 55 (5), 41 (12), 30 (100).



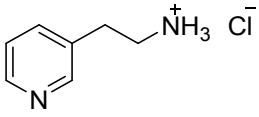
2-Phenylethylamine hydrochloride. **^{1}H-NMR** (300 MHz, DMSO-d_6): 2.84-3.07 (m, 4H), 7.17-7.36 (m, 5H), 8.07-8.45 (b s, 3H). **^{13}C-NMR** (75 MHz, DMSO-d_6): 33.4 (CH_2), 40.3 (CH_2), 127.1 (CH), 129.0 (CH), 129.1 (CH), 137.9 (Cq).

GC/MS: (EI, 70eV): m/z = 121 (M, 5), 104 (4), 91 (31), 77 (4), 65 (11), 51 (8), 30 (100).



2-(4-Methoxyphenyl)ethylamine hydrochloride. **^{1}H-NMR** (400 MHz, DMSO-d_6): 2.81-2.88 (m, 2H), 2.91-3.00 (m, 2H), 3.73 (s, 3H), 6.86-6.91 (m, 2H), 7.15-7.20 (m, 2H), 8.23 (b s, 3H). **^{13}C-NMR** (101 MHz, DMSO-d_6): 32.0 (CH_2), 40.1 (CH_2), 55.0 (CH_3), 114.0 (CH), 129.2 (Cq), 129.6 (CH), 158.0 (Cq).

GC/MS (EI, 70eV): m/z (%) = 151 (M, 4), 122 (100), 107 (7), 91 (10), 78 (13), 65 (4), 51 (4), 30 (33).



2-(3-Pyridyl)ethylamine hydrochloride. **^{1}H-NMR** (300 MHz, DMSO-d_6): 3.15 (s, 4H), 7.98 (dd, J = 8.0, 5.7 Hz, 1H), 8.34 (b s, 3H), 8.46-8.53 (m, 1H), 8.76-8.83 (m, 1H), 8.88 (s, 1H). **^{13}C-NMR** (101 MHz, DMSO-d_6): 29.6 (CH_2), 39.2 (CH_2), 125.9 (CH), 136.2 (Cq), 142.3 (CH), 143.5 (CH), 144.2 (CH).

GC/MS (EI, 70eV): m/z (%) = 121 (M-1, 1), 93 (100), 65 (7), 39 (9), 30 (22).

S6 *Catalyst recycling experiments* (**Table 3**)

The catalytic hydrogenations were carried with 0.25 mmol and 0.50 mmol of benzonitrile, respectively. The reactions followed the practical guidelines as outlined in **S3**. After each run the catalyst was separated from the reaction mixture by centrifugation. The recovered solid was washed with *i*-PrOH (3 x 2-3 mL) and then dried *in vacuo* at room temperature overnight. All yields are average values obtained from at least 2 runs. The supernatant collected after each cycle was subjected to GC- and ICP analysis. Elemental analyses of the recycled catalysts are reported in Table S2.

Table S2. Recycled catalyst elemental analysis (w%).

	Co (%)	C (%)	H (%)	N (%)	P (%)	O (%)	Ce (%)
B_{12}@CeO_2-8	1.18	4.42	0.11	0.48	0.43	10.67	82.72
Re-B_{12}@CeO_2-8 (8 h)[a]	0.97	8.38	0.10	0.69	0.47	18.08	71.31
Re-B_{12}@CeO_2-8 (8 h)[a]	0.79	8.31	0.16	0.53	0.57	18.02	71.62
Re-B_{12}@CeO_2-8 (15 h)[b]	0.42	9.06	0.17	0.39	3.65	16.28	70.03

[a]Recycled catalyst after 8h. [b]Recycled catalyst after 15 h.

S6 *Time-concentration profile*

Table S3. Conversion of benzonitrile as a function of the reaction time (Fig 1).[a]

	catalyst	time (h)	Conv (%)[b]	**2**/**3**+**4** Molar ratio[b]	GY yield (%)[b]
1	B_{12}@CeO_2-7	2	6	47/53	0
2	B_{12}@CeO_2-8	2	13	48/52	3
3	B_{12}@CeO_2-9	2	0	-	0

4	B_{12}@CeO_2-7	4	46	67/33	27
5	B_{12}@CeO_2-8	4	68	70/30	42
6	B_{12}@CeO_2-9	4	32	56/44	15
7	B_{12}@CeO_2-7	5	69	65/35	41
8	B_{12}@CeO_2-8	5	93	76/24	67
9	B_{12}@CeO_2-9	5	40	47/53	16
10	B_{12}@CeO_2-7	8	>99	>99	92
11	B_{12}@CeO_2-8	8	>99	>99	93
12	B_{12}@CeO_2-9	8	66	60/40	50

[a]*Reaction conditions*: benzonitrile (0.25 mmol), catalyst (1.6 mol%), aqueous NH_3 (0.2 mL), *i*-PrOH (2 mL), *n*-hexadecane as an internal standard (25 µL).
[b]Determined by gas chromatography (GC).

S8 *Hot filtration test*

The catalytic hydrogenation of benzonitrile was interrupted after a period of 2 h whereupon the catalyst was removed from the reaction mixture by hot filtration at 120 °C (Fig. **S1**). The solid was then washed with hot *i*-PrOH (2 x 0.5 mL) and the catalytic hydrogenation was resumed with the clear filtrate. No catalytic activity of the liquid portion was observed after 15 h at 30 bar and 120 °C.

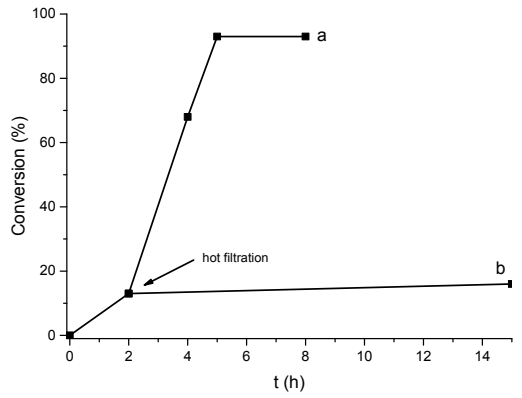


Fig. **S1**. Hot filtration test. Benzonitrile (0.25 mmol), B_{12}@CeO_2-8 catalyst (1.6 mol%), *n*-hexadecane (25 µL) at 30 bar hydrogen pressure and 120 °C in *i*-PrOH. (a) Without filtration. (b) With filtration of the solid after 2 h.

S9 *Copy of ICP analysis:*

ICP-LABOR

Catalysis
Leibniz-Institut für Katalyse e.V.

A. Simmula, Tel. 0381 1281 315
18059 Rostock
Albert-Einstein-Str. 29a

ANALYSENERGEBNIS / KURZBERICHT

AUFTRAG *Datum:26.01.2016*

MS-Auftragsnummer:	**7593**		
Probenbezeichnung:	**RE 1-1**		
Auftraggeber:	**Ferraccioli**		
Institution/Projekt:	LIKAT	*Tel:*	*262*

ANALYSE

Methode: ICP

durchgeführt von: AS

Ergebnis (in g/l):

Element	*erwartet**	*1. Messung*	*2. Messung*
Co	-	nn	nn

** ev.zusätzliche Messung, s. Bemerkungen*

Bemerkungen:

Unterschrift / Datum:

Anlagen (Erläuterungen / Abildungen ☐

ICP-LABOR

A. Simmula, Tel. 0381 1281 315
ANALYSENERGEBNIS / KURZBERICHT

18059 Rostock
Albert-Einstein-Str. 29a

AUFTRAG

Datum:26.01.2016

MS-Auftragsnummer:	**7594**	
Probenbezeichnung:	**RE 1-2**	
Auftraggeber:	**Ferraccioli**	
Institution/Projekt:	LIKAT	*Tel: 262*

ANALYSE

Methode: ICP

durchgeführt von: AS

Ergebnis (in g/l):

Element	*erwartet**	*1. Messung*	*2. Messung*
Co	-	nn	nn

** ev.zusätzliche Messung, s. Bemerkungen*

Bemerkungen:

Unterschrift / Datum:

Anlagen (Erläuterungen / Abildungen ☐

ICP-LABOR

A. Simmula, Tel. 0381 1281 315
ANALYSENERGEBNIS / KURZBERICHT

18059 Rostock
Albert-Einstein-Str. 29a

AUFTRAG

Datum:26.01.2016

MS-Auftragsnummer:	**7595**		
Probenbezeichnung:	**RE 1-3**		
Auftraggeber:	**Ferraccioli**		
Institution/Projekt:	LIKAT	*Tel:*	*262*

ANALYSE

Methode: ICP

durchgeführt von: AS

Ergebnis (in g/l):

Element	*erwartet**	*1. Messung*	*2. Messung*
Co	-	nn	nn

** ev.zusätzliche Messung, s. Bemerkungen*

Bemerkungen:

Unterschrift / Datum:

Anlagen (Erläuterungen / Abildungen ☐

ICP-LABOR

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ANALYSENERGEBNIS / KURZBERICHT

18059 Rostock
Albert-Einstein-Str. 29a

AUFTRAG

Datum:26.01.2016

MS-Auftragsnummer:	**7596**		
Probenbezeichnung:	**RE 1-4**		
Auftraggeber:	**Ferraccioli**		
Institution/Projekt:	LIKAT	*Tel:*	*262*

ANALYSE

Methode: ICP

durchgeführt von: AS

Ergebnis (in g/l):

Element	*erwartet**	*1. Messung*	*2. Messung*
Co	-	nn	nn

** ev.zusätzliche Messung, s. Bemerkungen*

Bemerkungen:

Unterschrift / Datum:

Anlagen (Erläuterungen / Abildungen ☐

ICP-LABOR

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ANALYSENERGEBNIS / KURZBERICHT

18059 Rostock
Albert-Einstein-Str. 29a

AUFTRAG

Datum:26.01.2016

MS-Auftragsnummer:	**7597**	
Probenbezeichnung:	**RE 1-5**	
Auftraggeber:	**Ferraccioli**	
Institution/Projekt:	LIKAT	*Tel: 262*

ANALYSE

Methode: ICP

durchgeführt von: AS

Ergebnis (in g/l):

Element	*erwartet**	*1. Messung*	*2. Messung*
Co	-	nn	nn

* *ev.zusätzliche Messung, s. Bemerkungen*

Bemerkungen:

Unterschrift / Datum:

Anlagen (Erläuterungen / Abildungen ☐

ICP-LABOR

A. Simmula, Tel. 0381 1281 315
ANALYSENERGEBNIS / KURZBERICHT

18059 Rostock
Albert-Einstein-Str. 29a

AUFTRAG

Datum:03.02.2016

MS-Auftragsnummer:	**7603**	
Probenbezeichnung:	**213 recycling exp (hot filtration)**	
Auftraggeber:	**Ferraccioli**	
Institution/Projekt:	LIKAT	*Tel: 262*

ANALYSE

Methode: ICP

durchgeführt von: AS

Ergebnis (in g/l):

Element	*erwartet**	*1. Messung*	*2. Messung*
Co	-	nn	nn

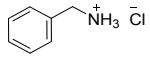
** ev.zusätzliche Messung, s. Bemerkungen*

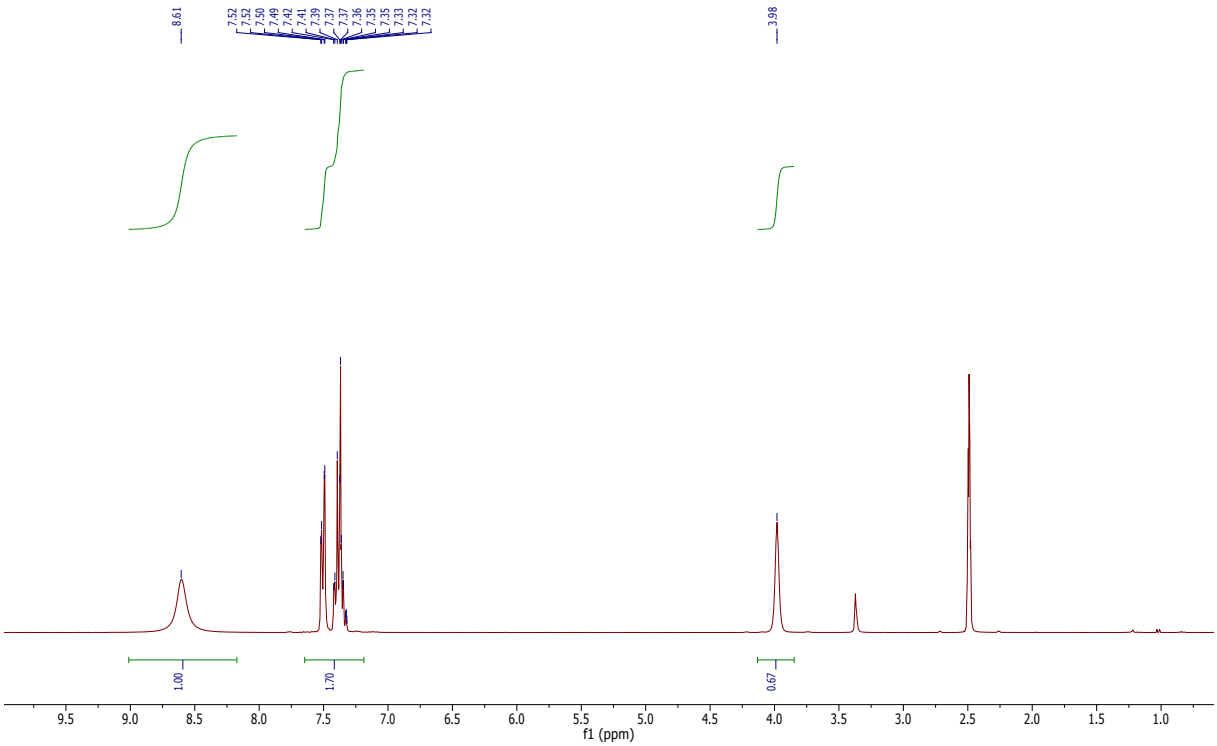
Bemerkungen:

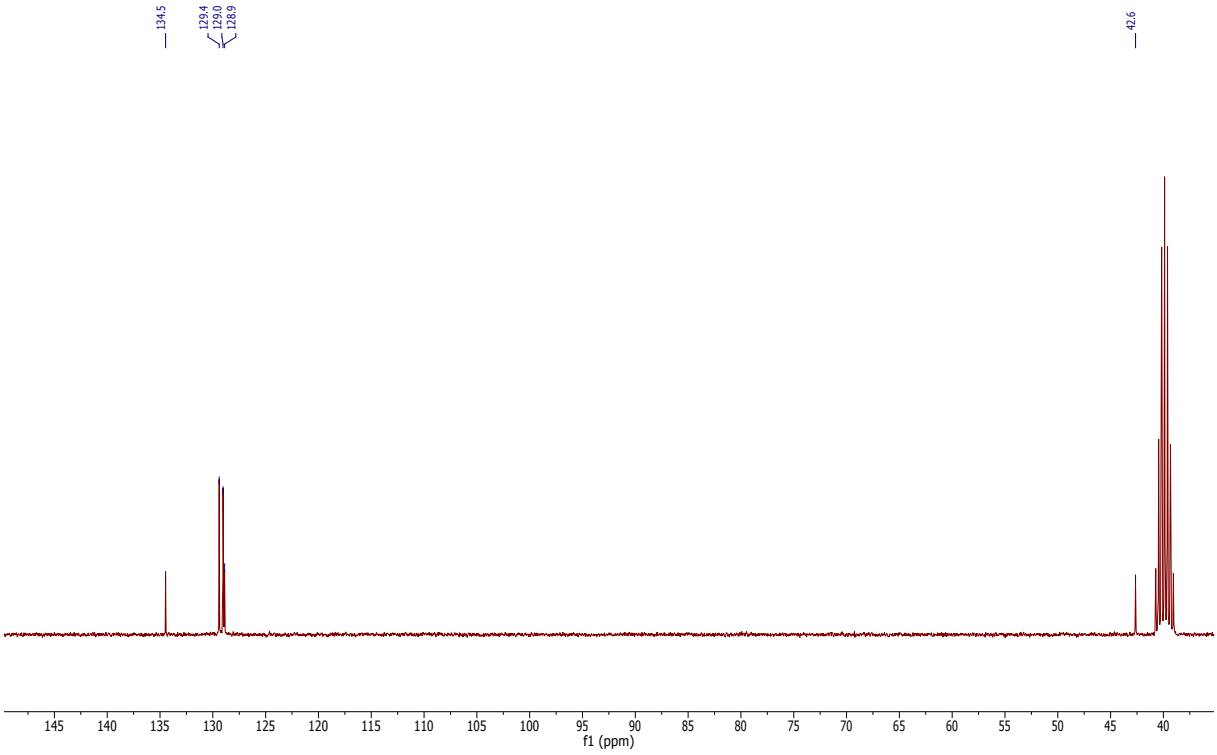
Unterschrift / Datum:

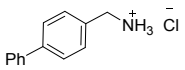
Anlagen (Erläuterungen / Abildungen ☐

S10 *Copy of [1]H and [13]C NMR spectra of the ammonium chloride salts of* **2**.





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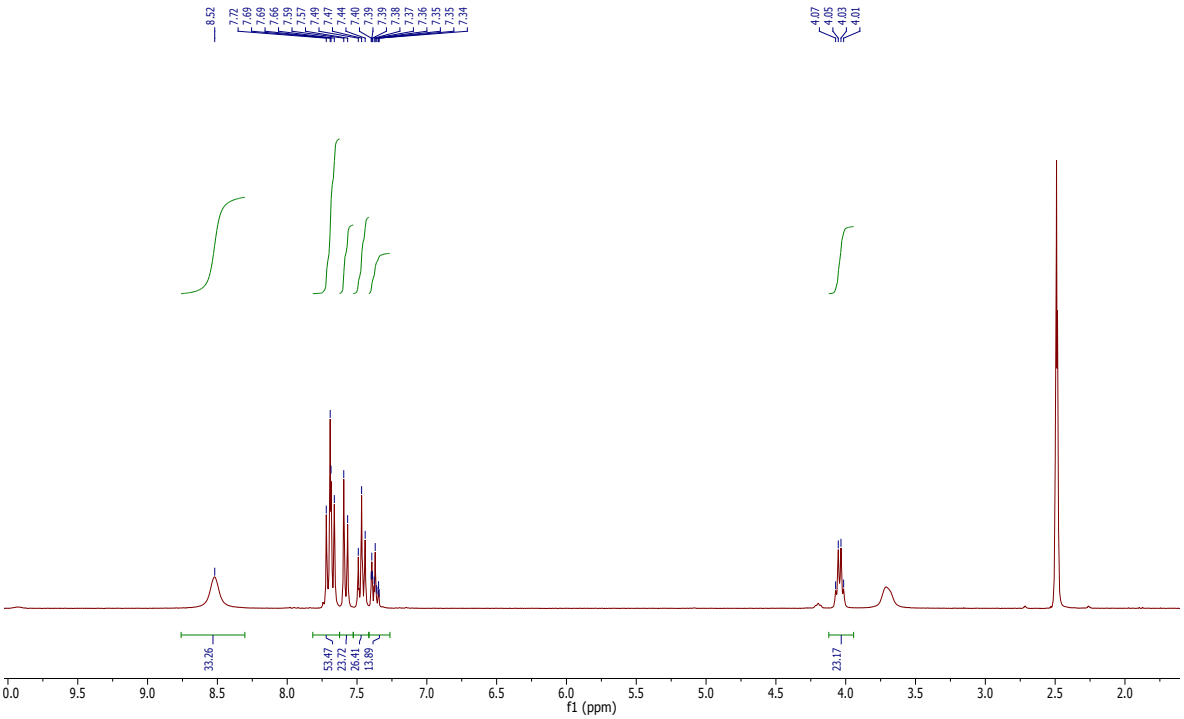
NH3
Cl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7.39
7.38
7.37
7.36
7.35
7.35
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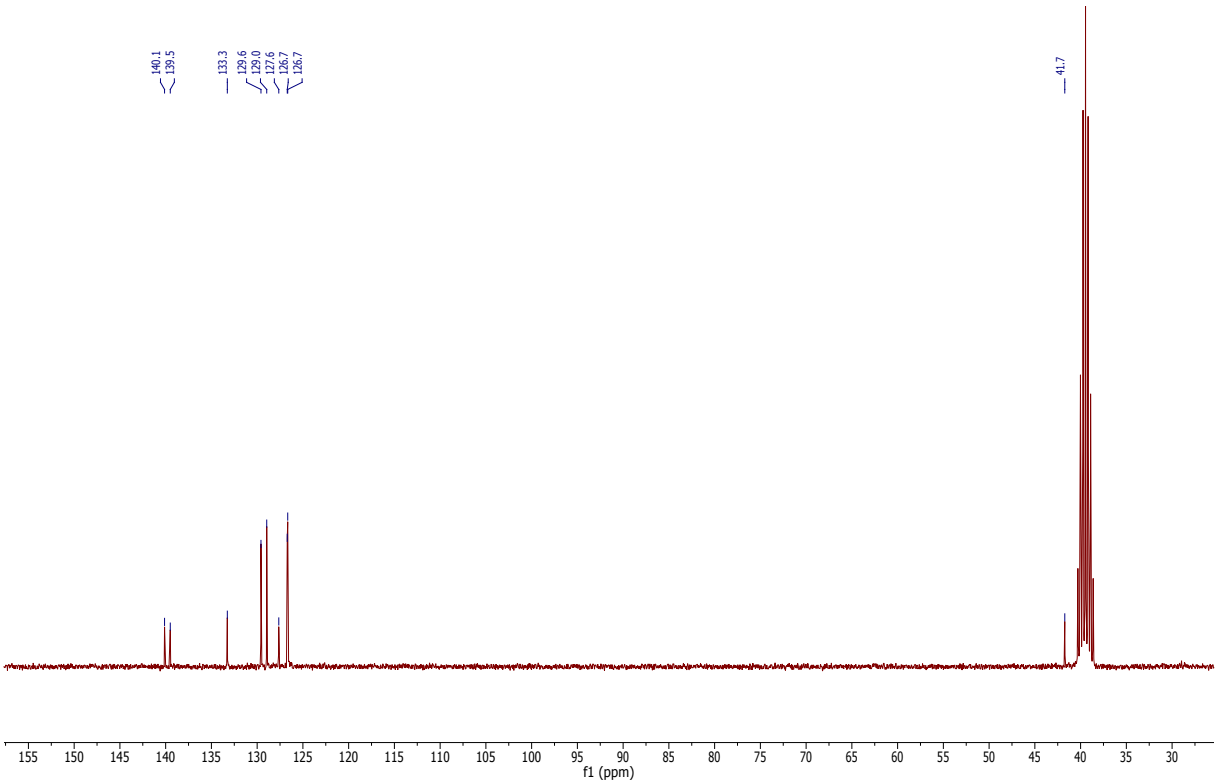
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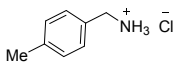
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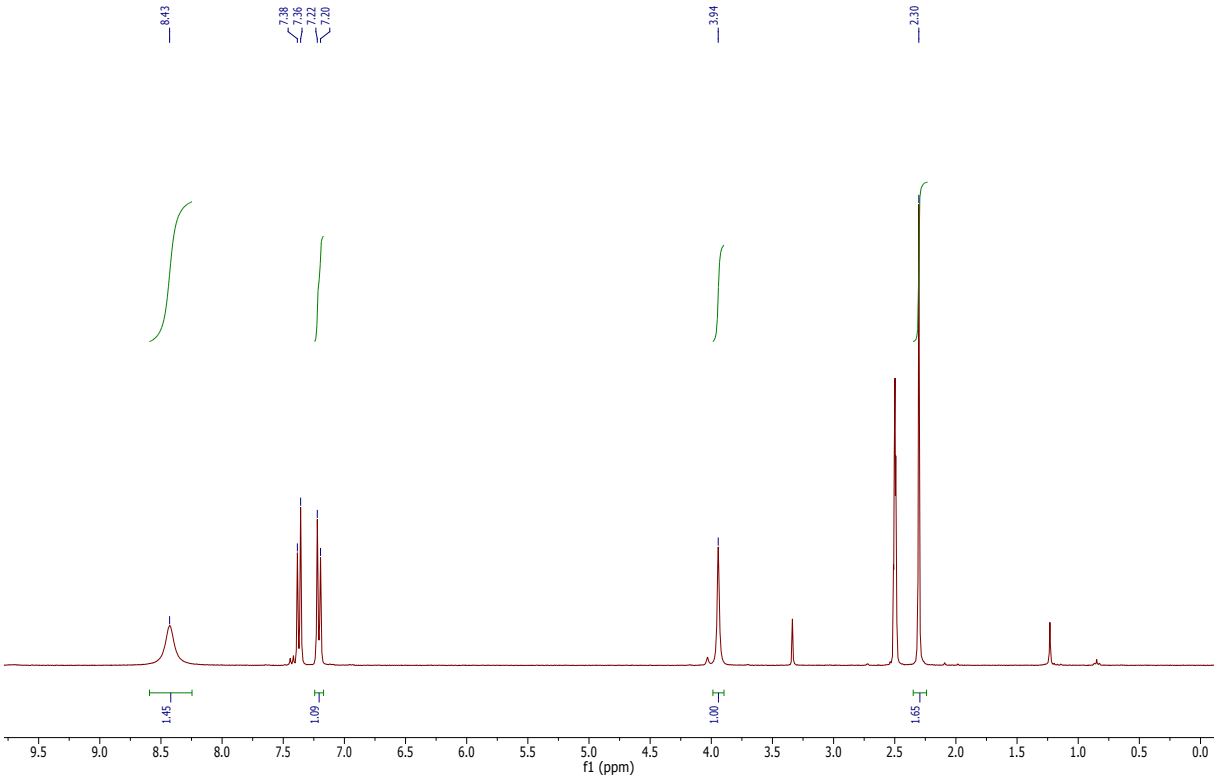
Cl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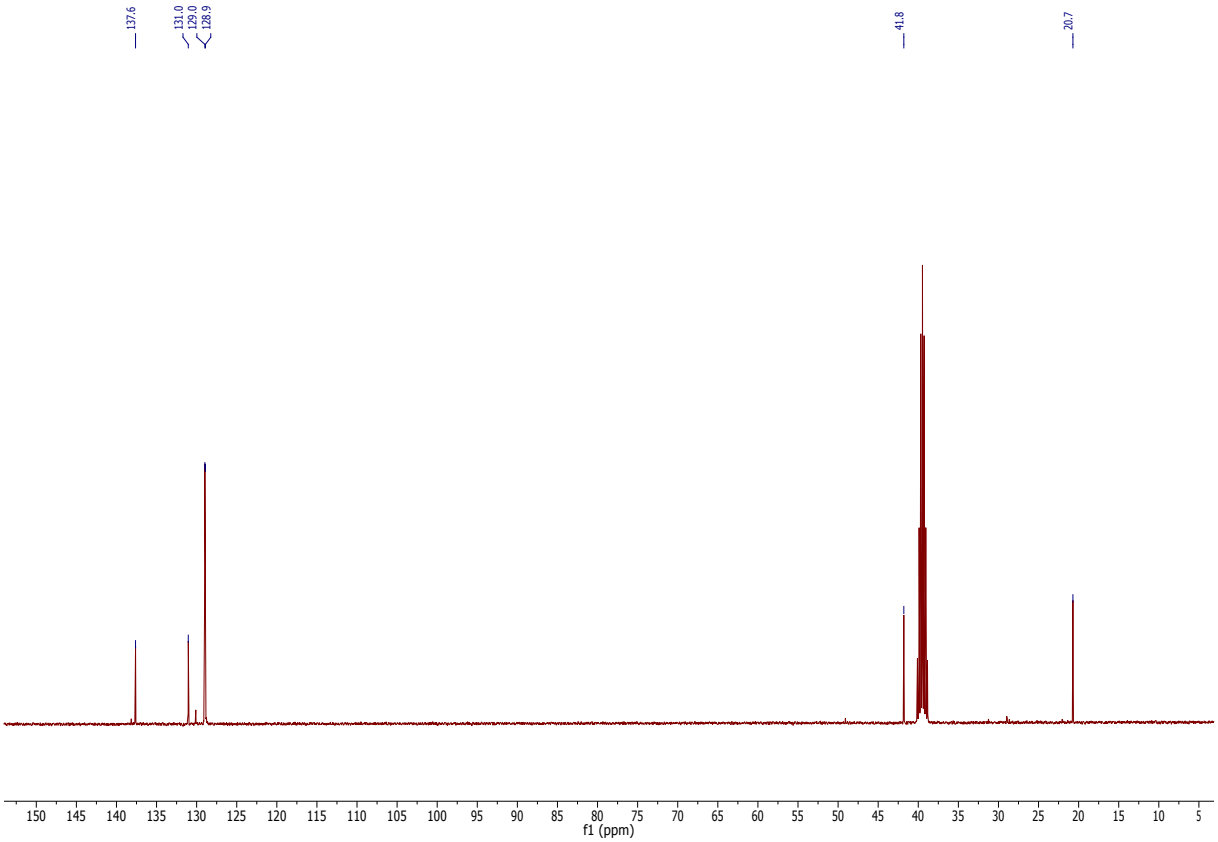
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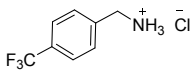
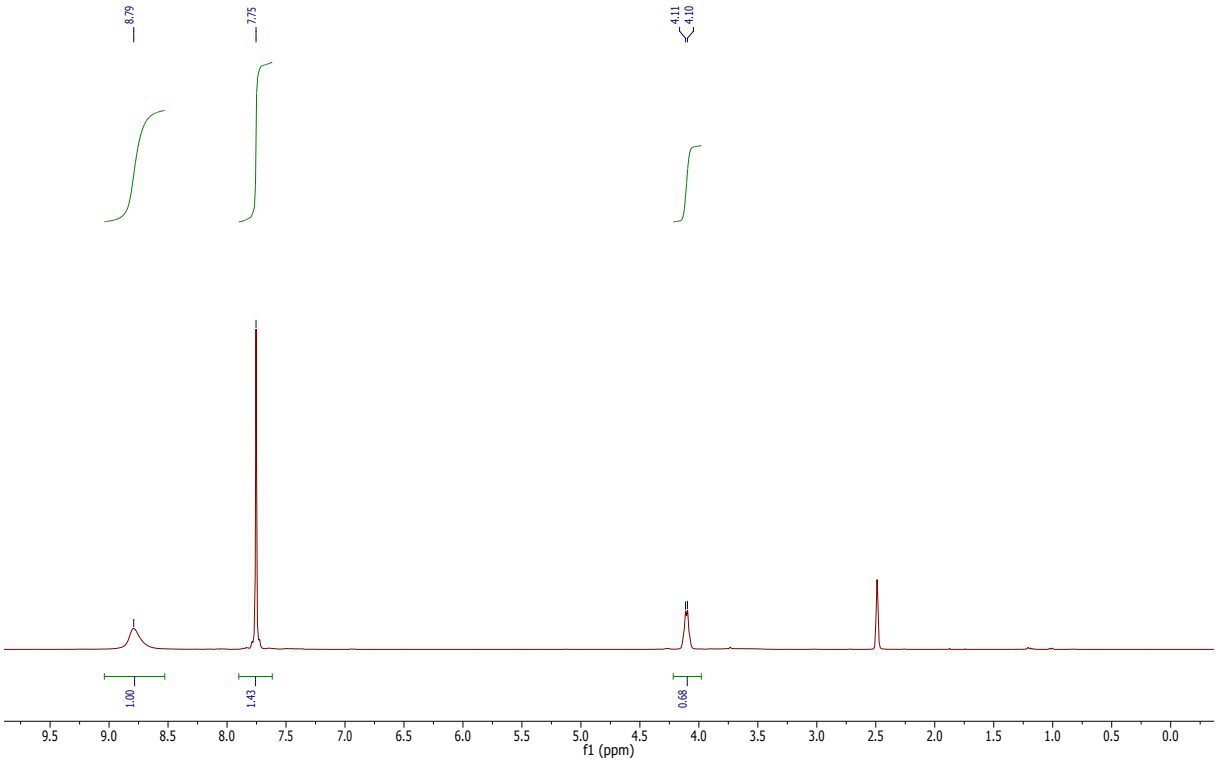

NH3 Cl
F3C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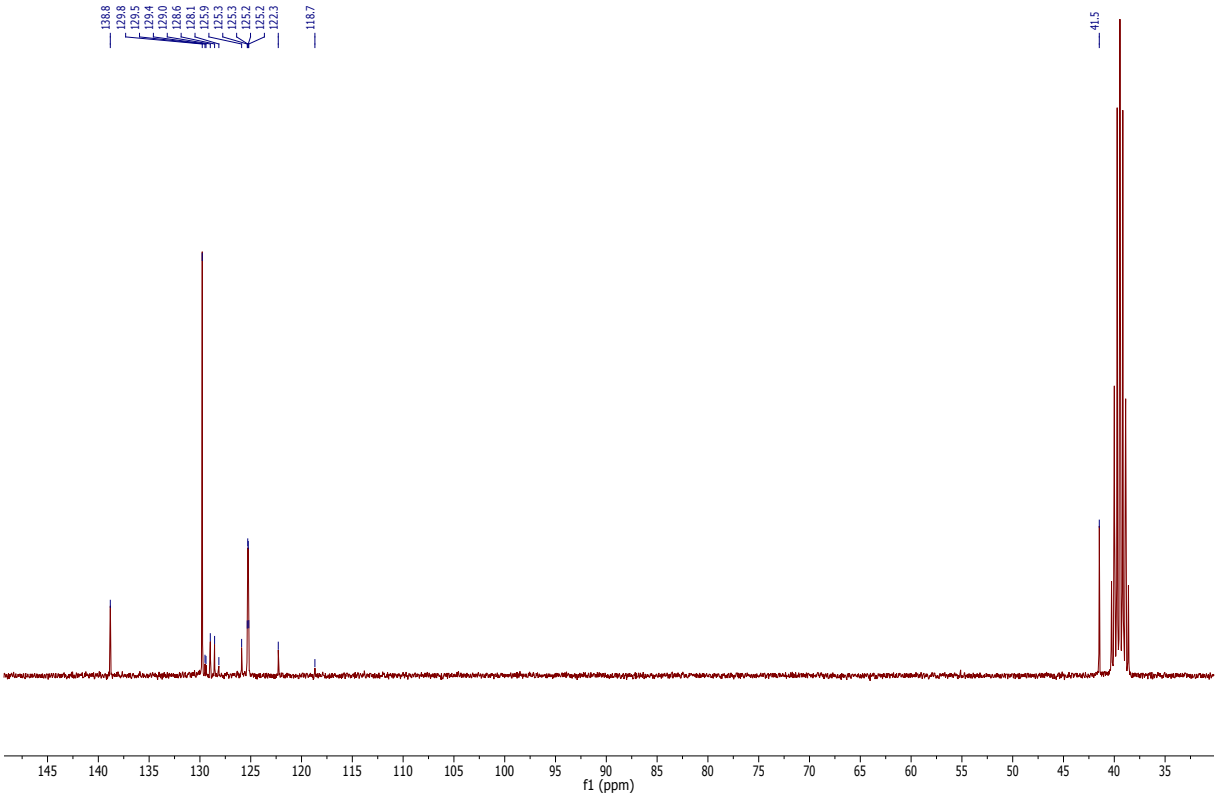
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41.5
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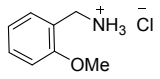
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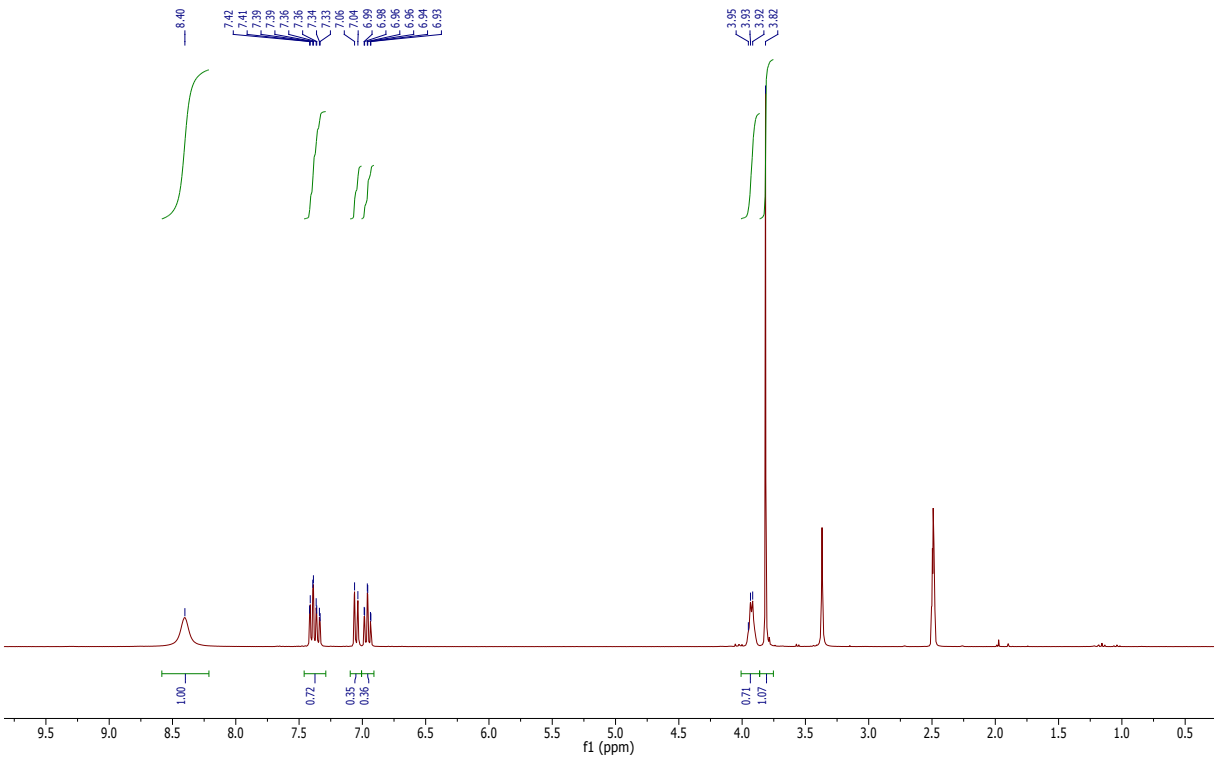
Cl
OMe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6.96
6.96
6.94
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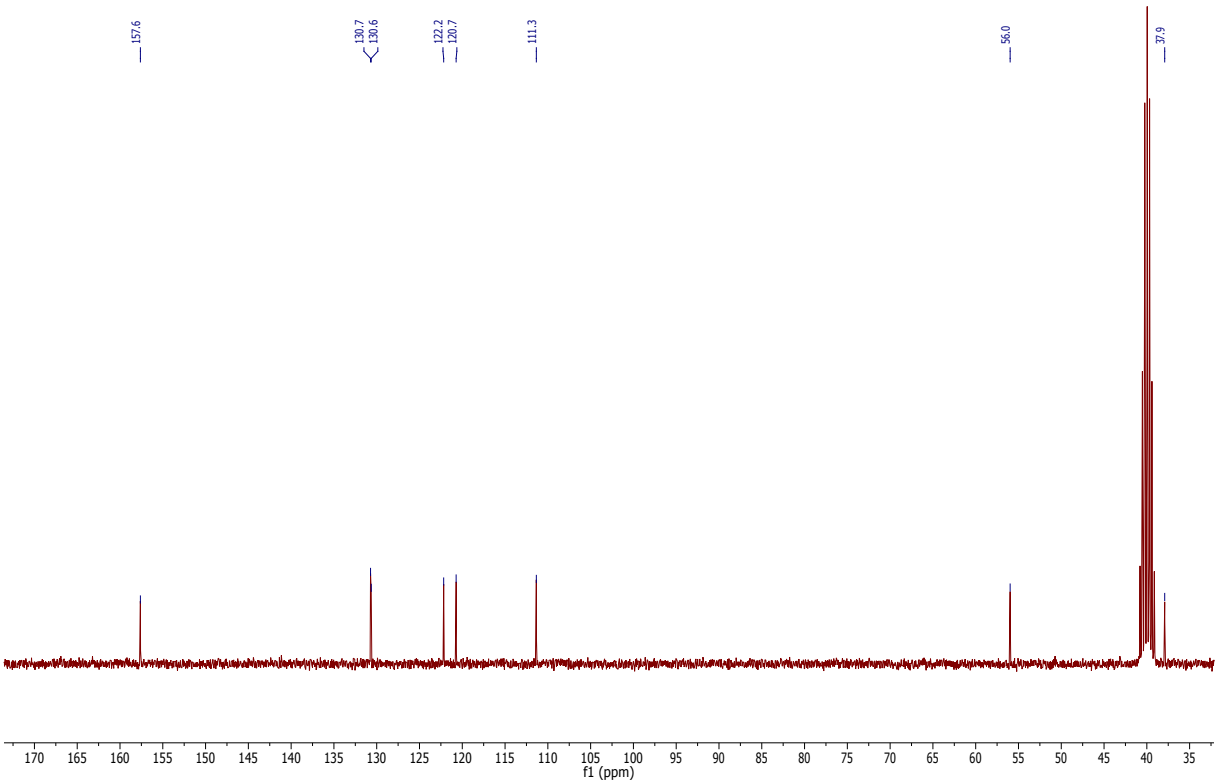
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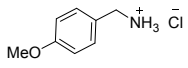
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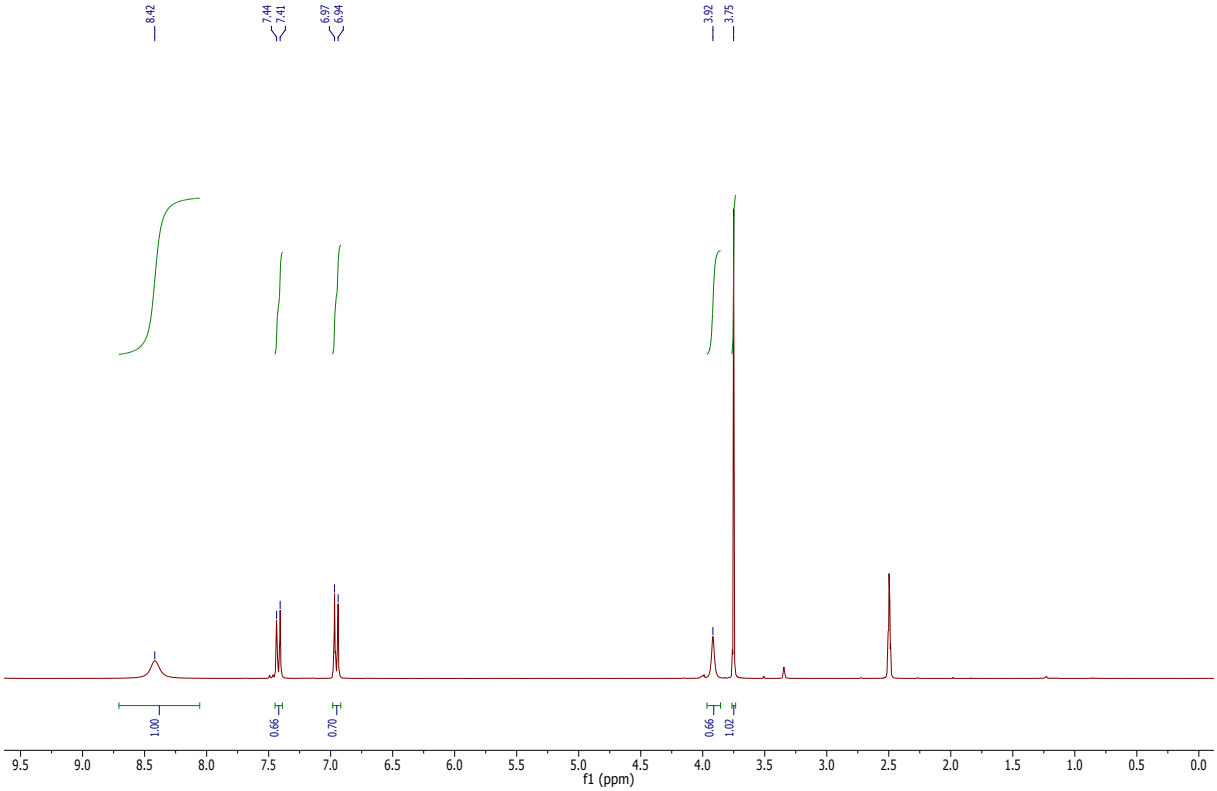
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1.02
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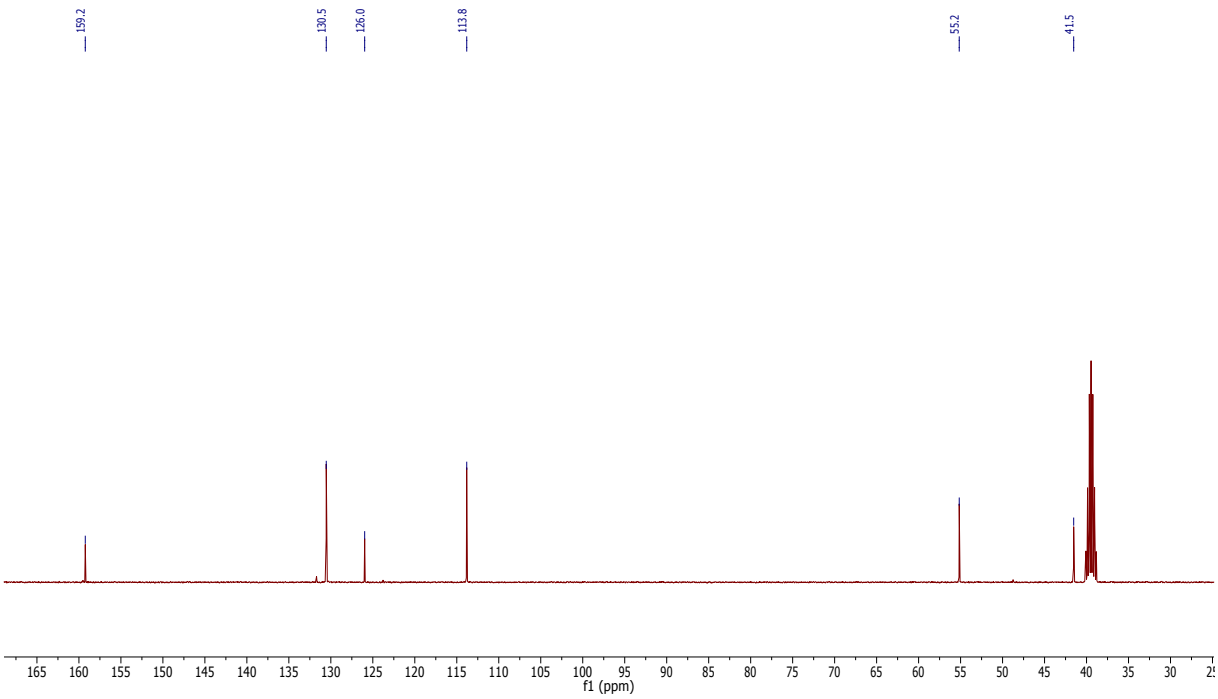
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113.8
55.2
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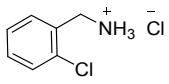
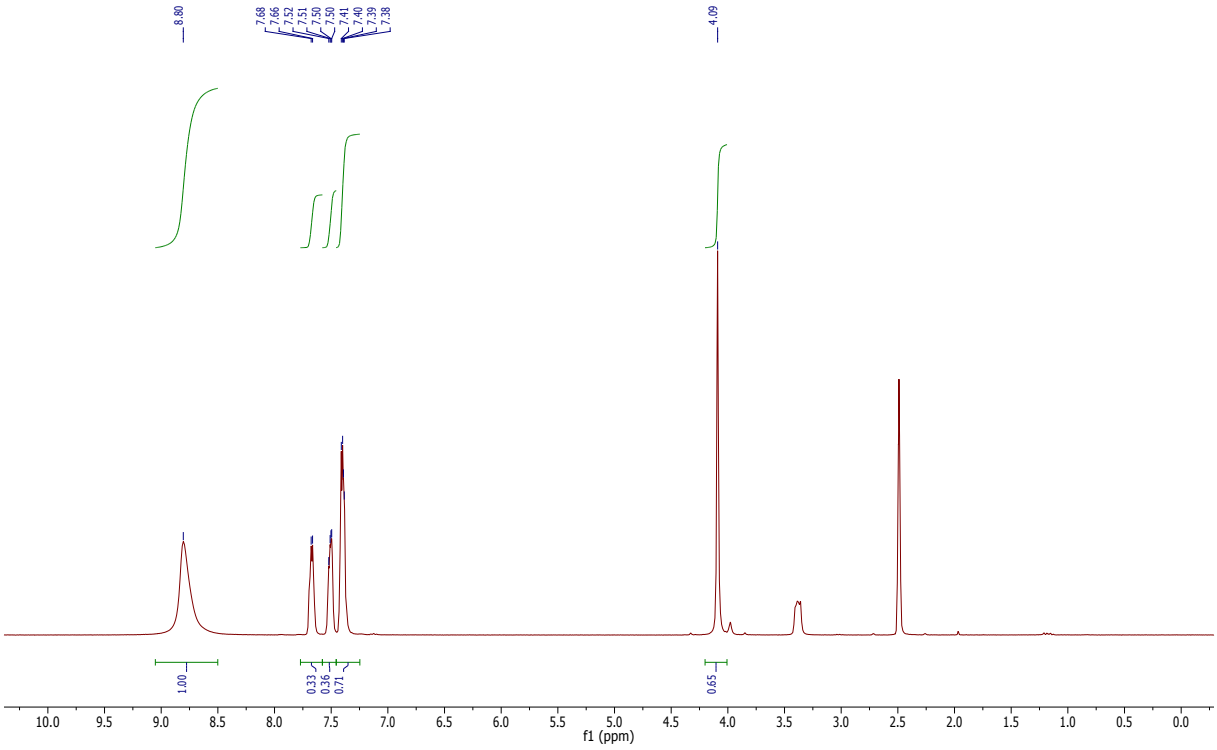

+
NH3
−
Cl
Cl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0.71
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9.0
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8.0
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7.0
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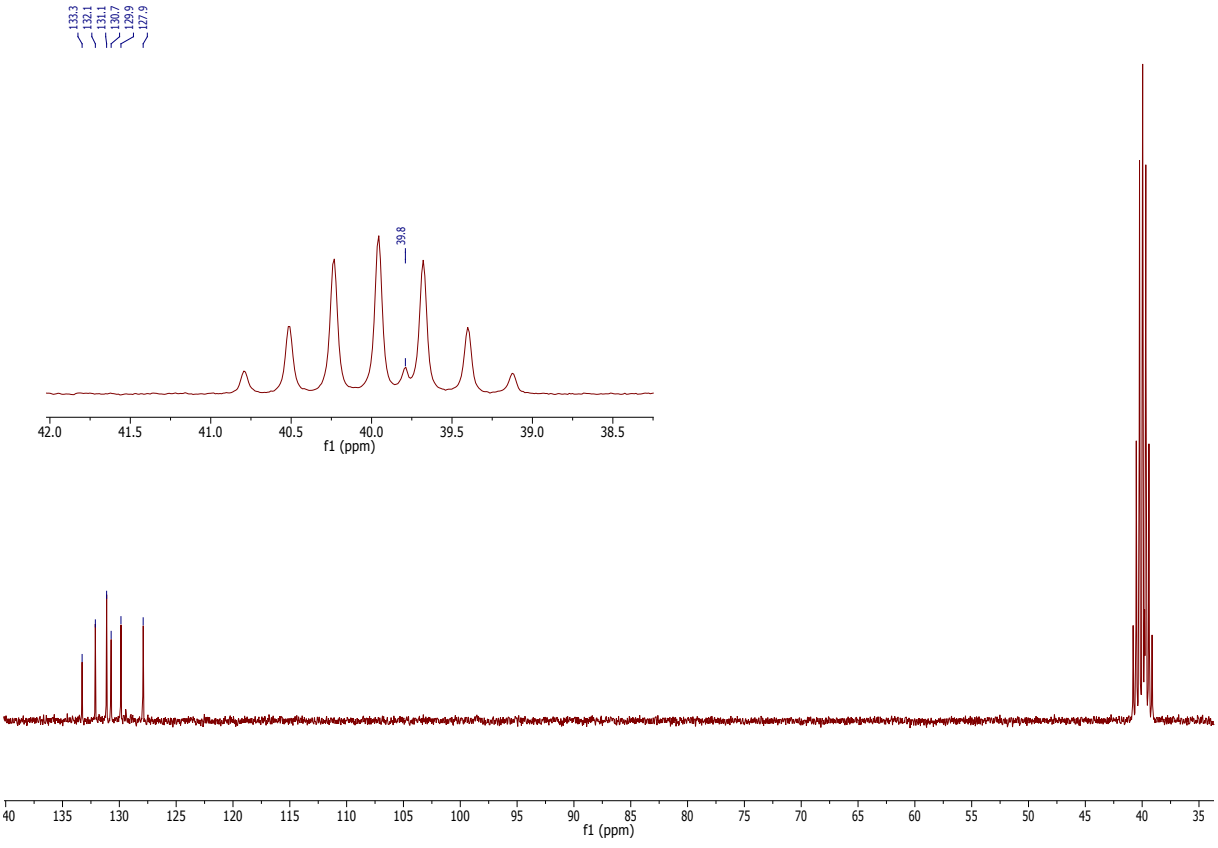
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41.0
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39.5
39.0
38.5
f1 (ppm)
40
135
130
125
120
115
110
105
100
95
90
85
80
75
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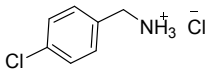
60
55
50
45
40
35
f1 (ppm)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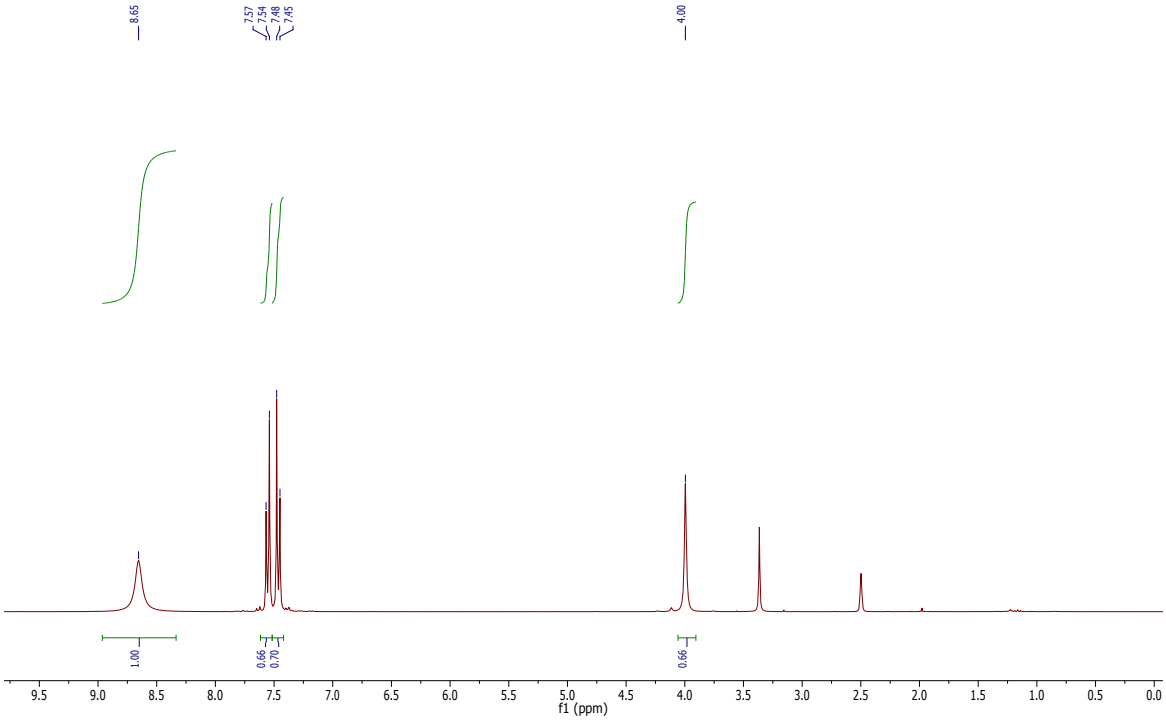
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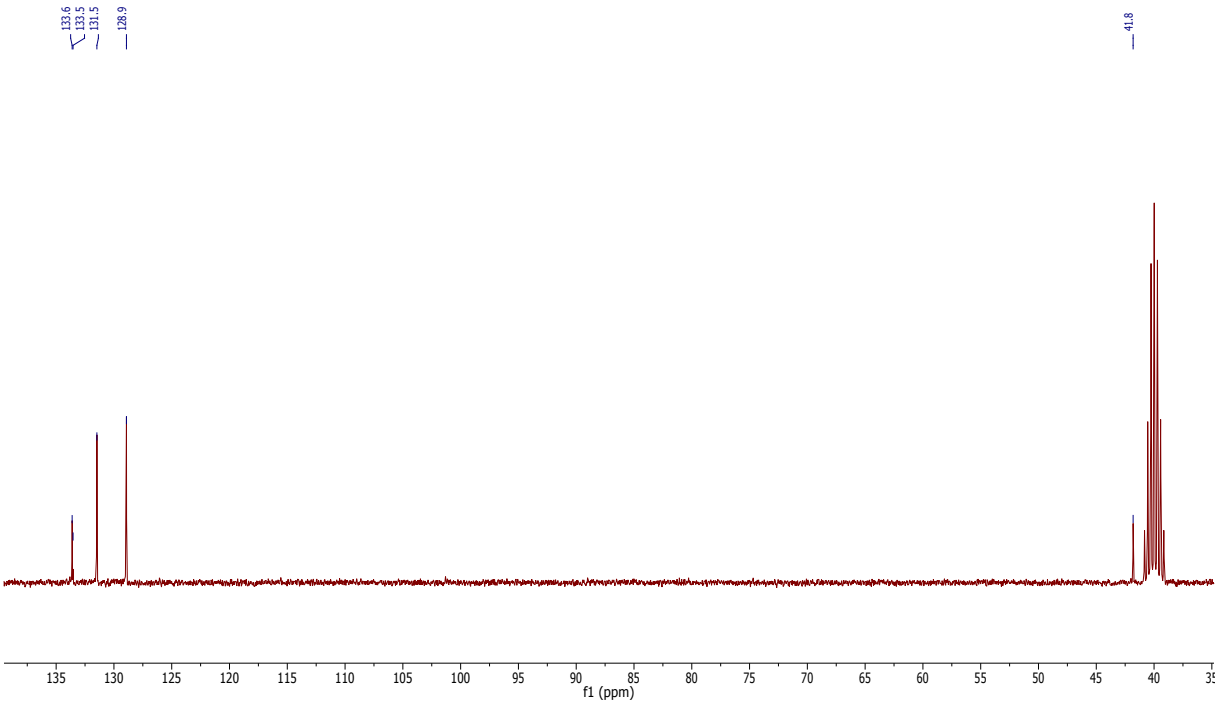
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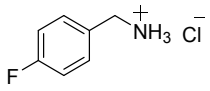
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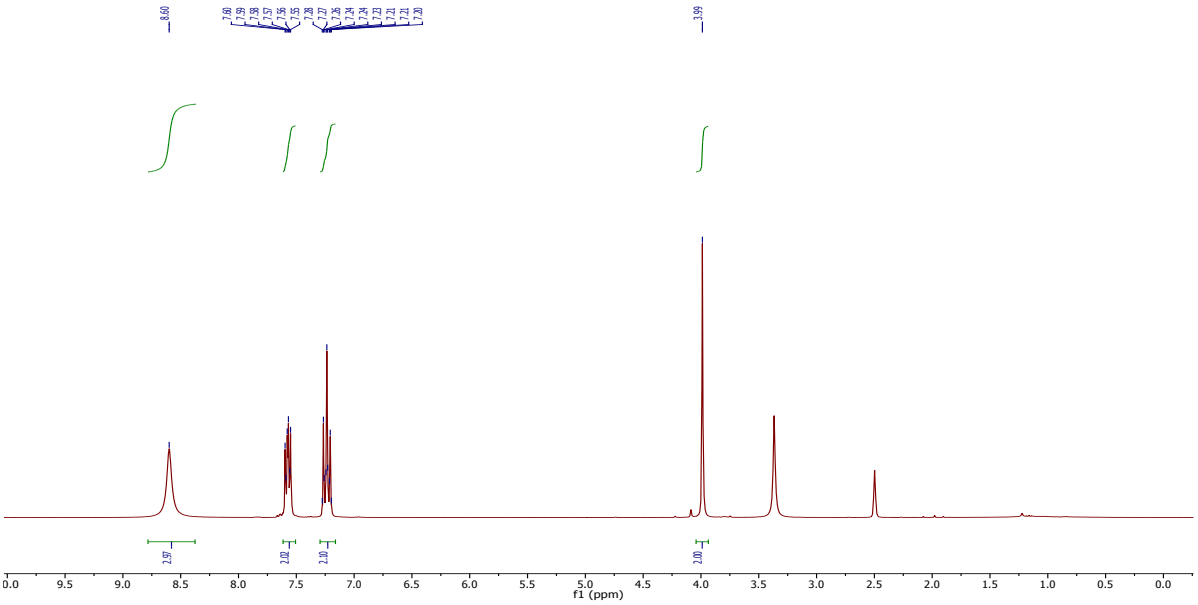
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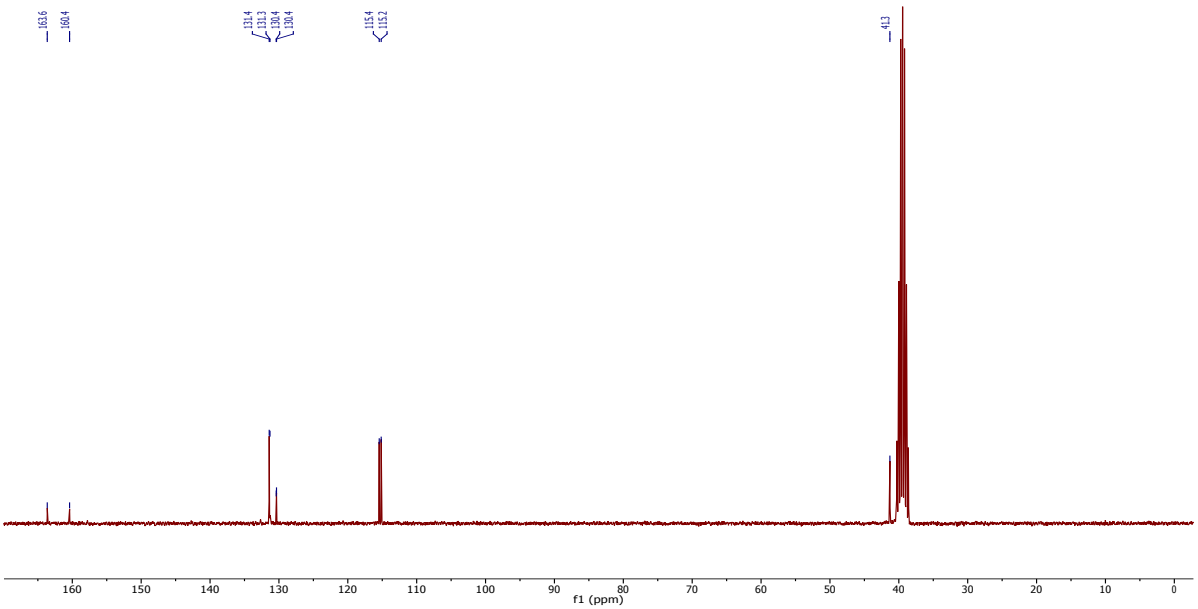
2.00
f1 (ppm)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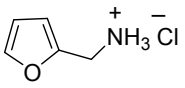
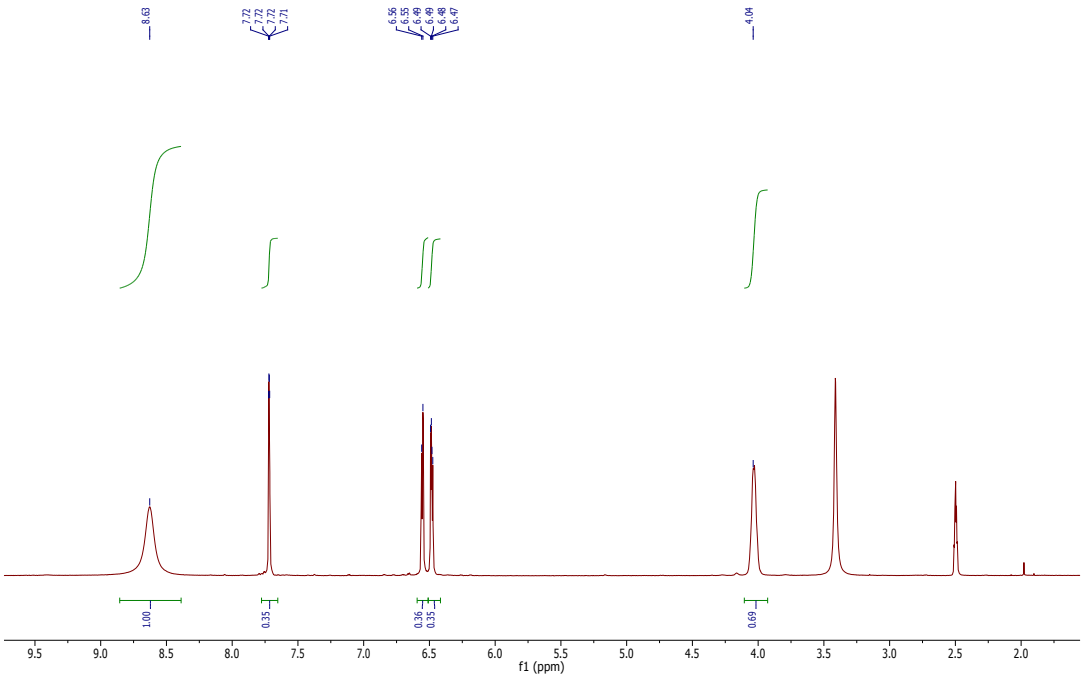

+
−
NH3 Cl
O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0.36
0.35
0.69
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9.0
8.5
8.0
7.5
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3.5
3.0
2.5
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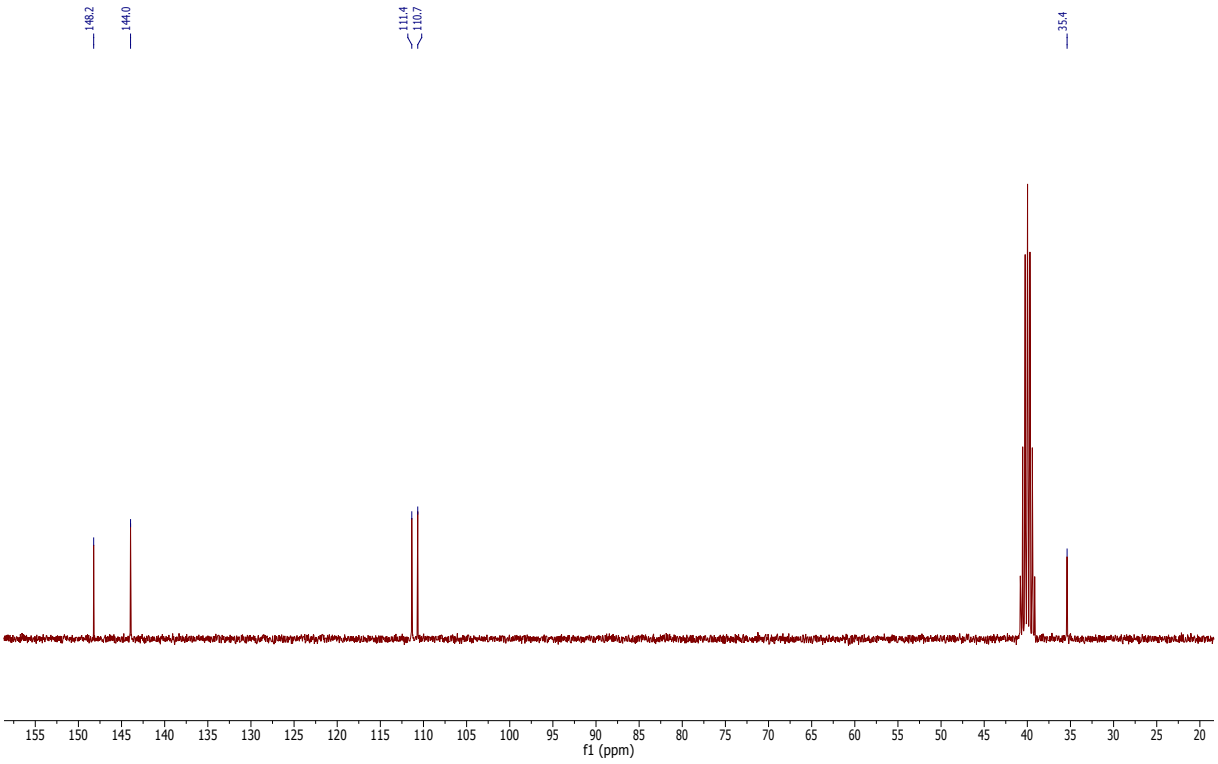
f1 (ppm)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45
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25
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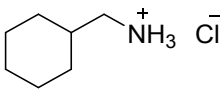
f1 (ppm)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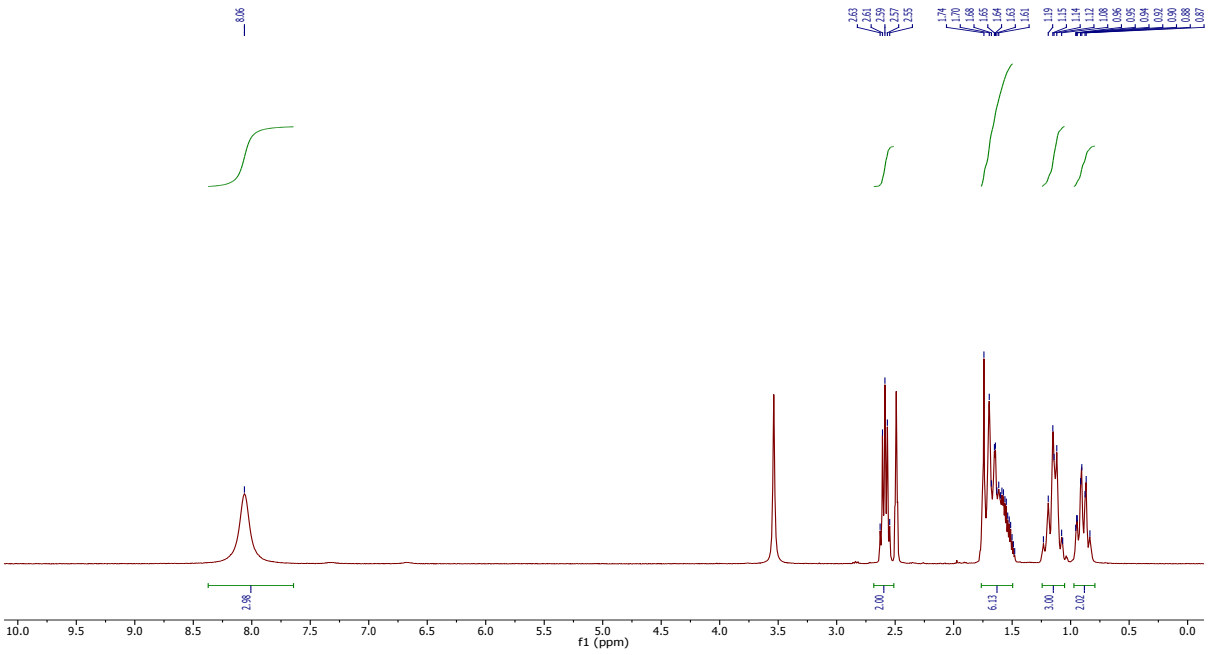
Cl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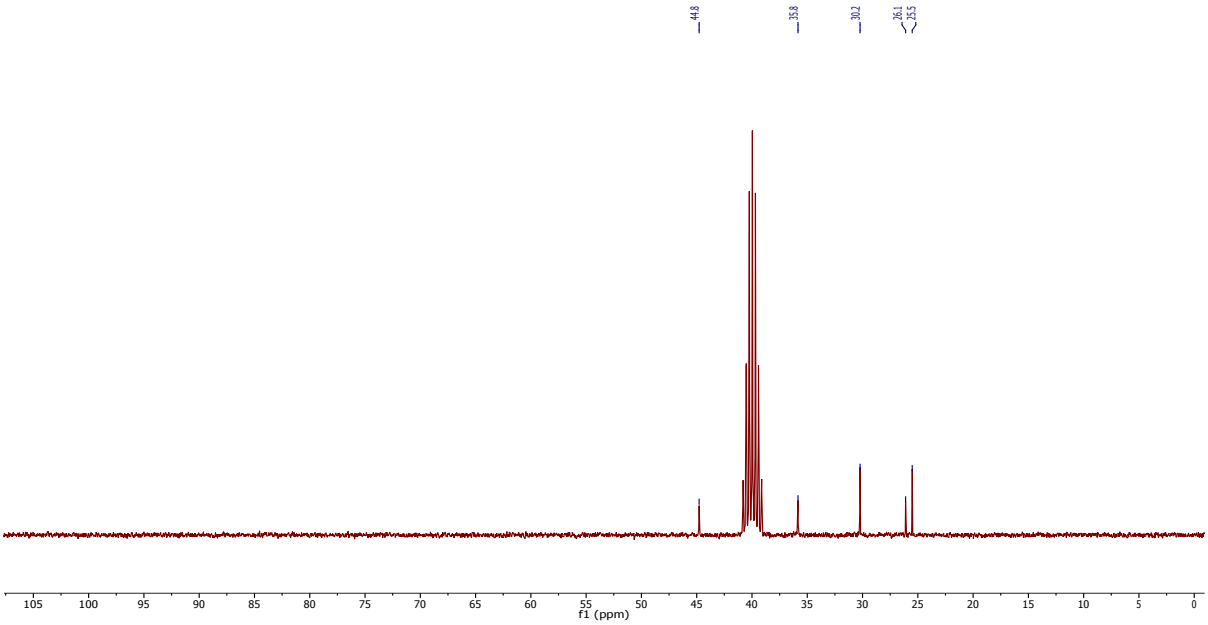
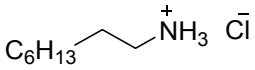
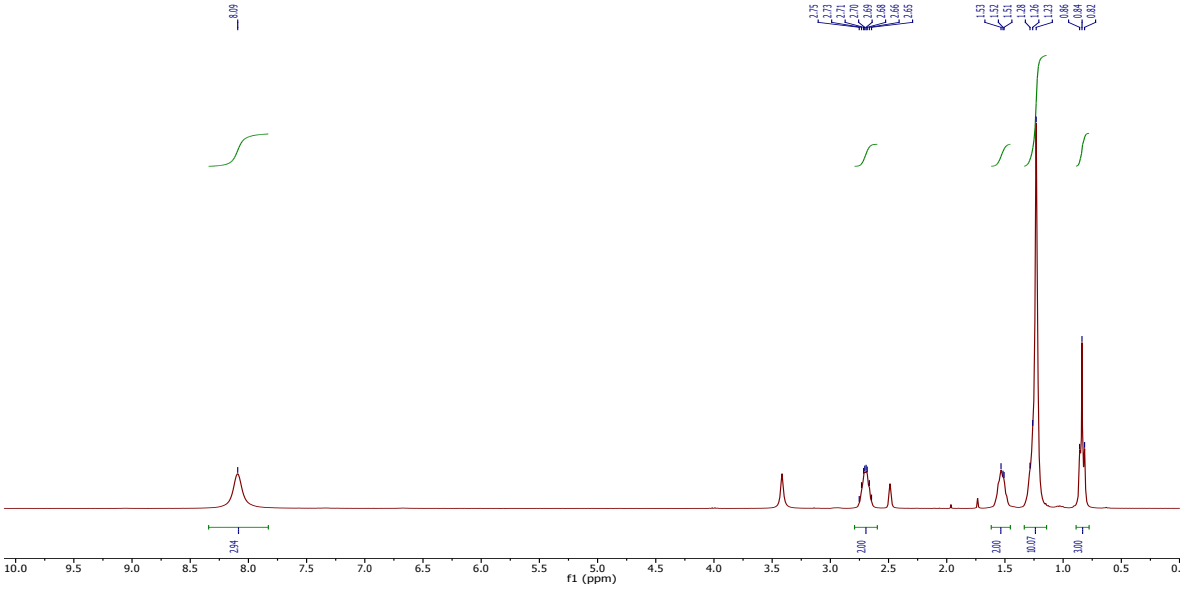
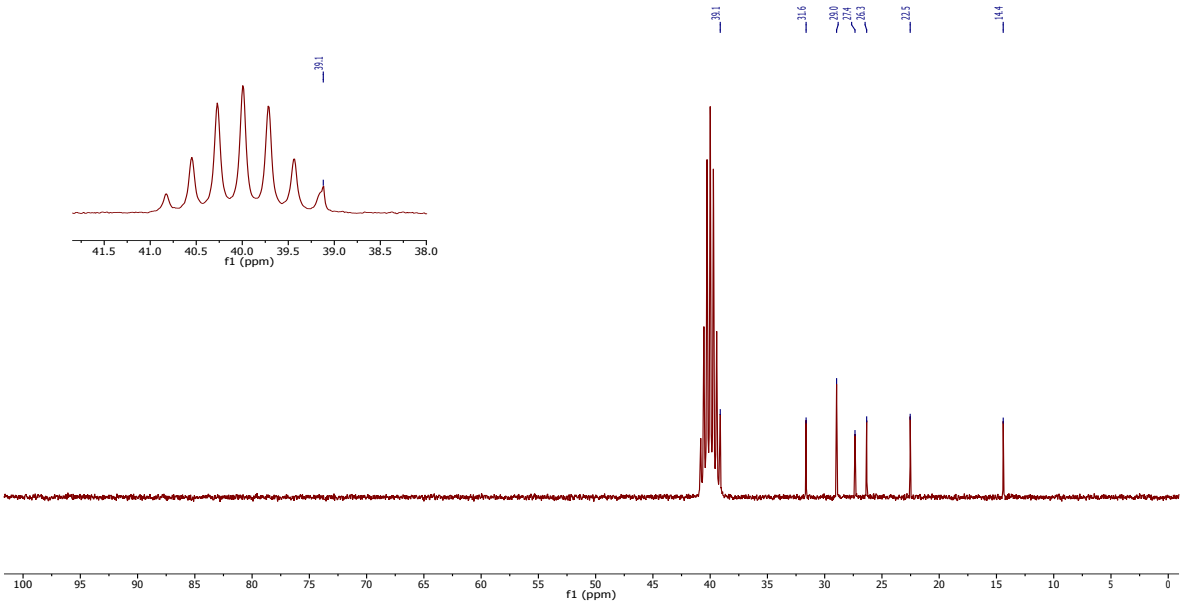
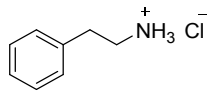
1.15
1.14
1.12
1.08
1.06
1.05
1.04
1.03
1.00
0.98
0.87
2.98
2.00
6.13
3.00
2.02
f1 (ppm)

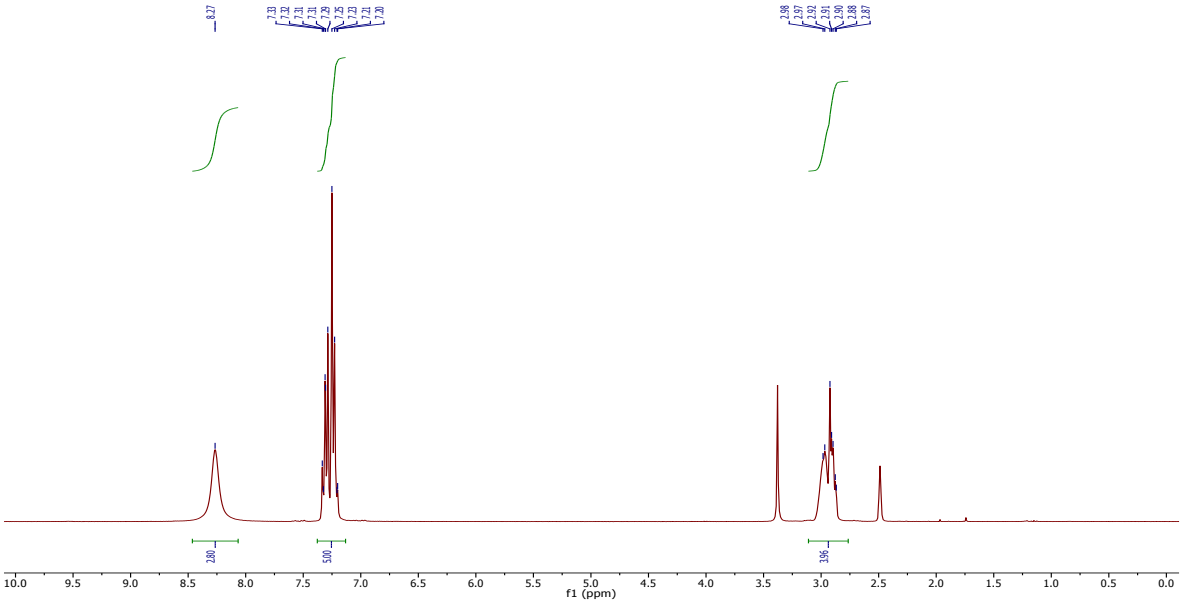

44.8
35.8
30.2
26.1
25.5
f1 (ppm)

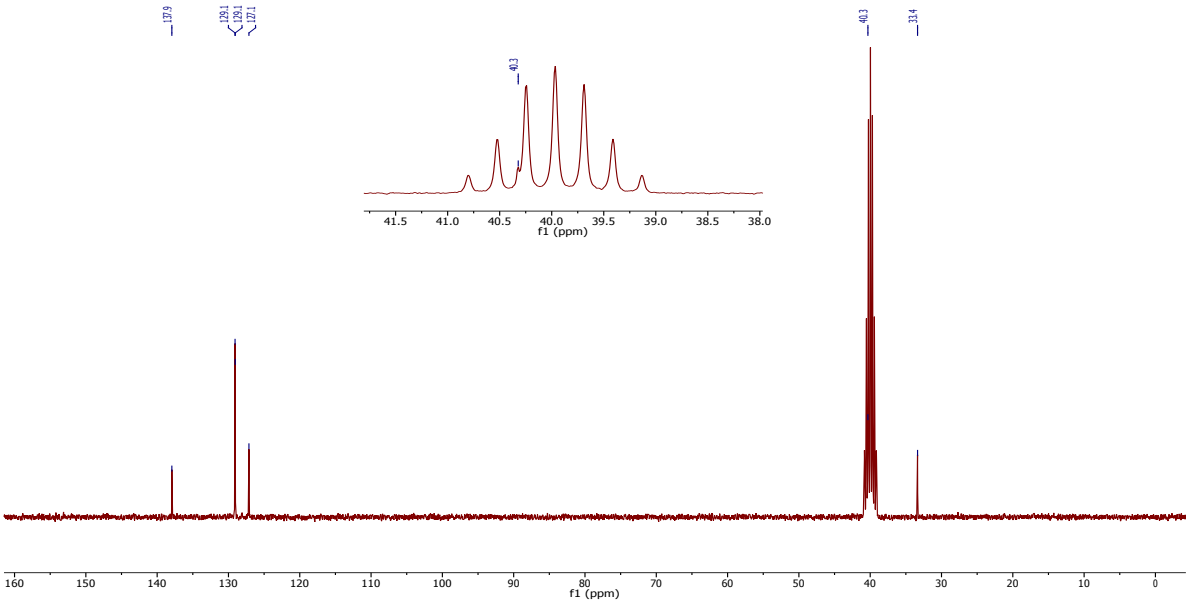

C6H13
NH3
Cl

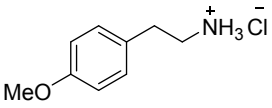

8.09
2.75
2.73
2.71
2.70
2.69
2.68
2.66
2.65
1.53
1.52
1.51
1.28
1.26
1.23
0.86
0.84
0.82
2.94
2.00
2.00
10.07
3.00
f1 (ppm)

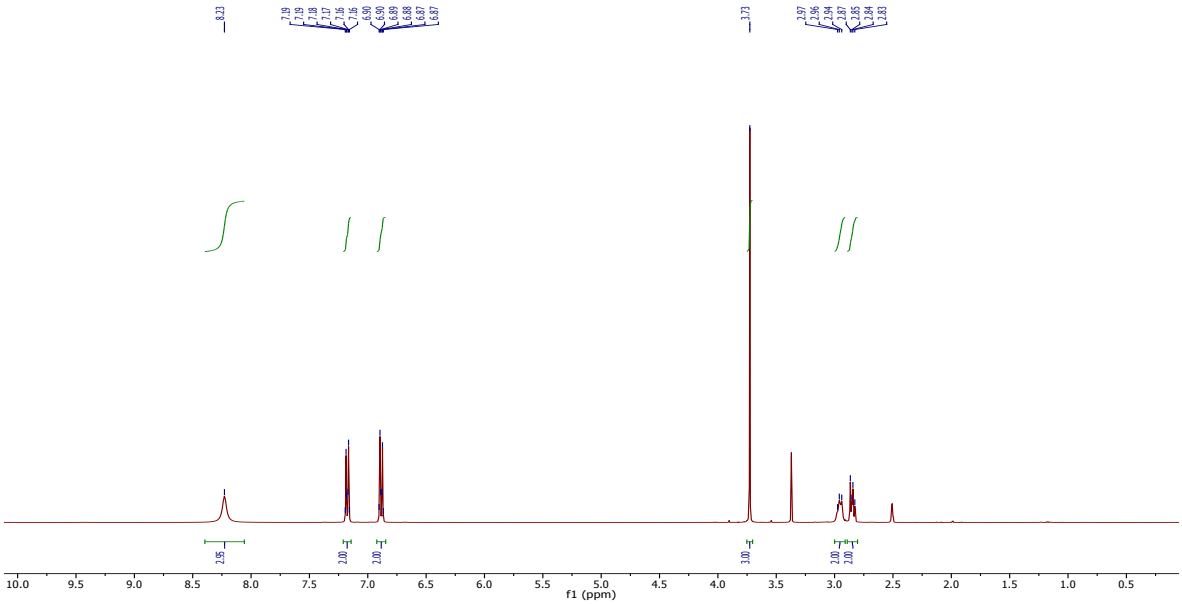

39.1
31.6
29.0
27.4
26.3
22.5
14.4
39.1
f1 (ppm)


NH3 Cl


8.27
7.33
7.32
7.31
7.31
7.29
7.25
7.23
7.21
7.20
2.98
2.97
2.92
2.91
2.90
2.88
2.87
2.80
5.00
3.06
f1 (ppm)


137.9
129.1
129.1
127.1
40.3
33.4
40.3
f1 (ppm)


MeO
NH3 Cl


8.23
7.19
7.19
7.18
7.17
7.16
7.16
6.90
6.90
6.89
6.88
6.87
6.87
3.73
2.97
2.96
2.94
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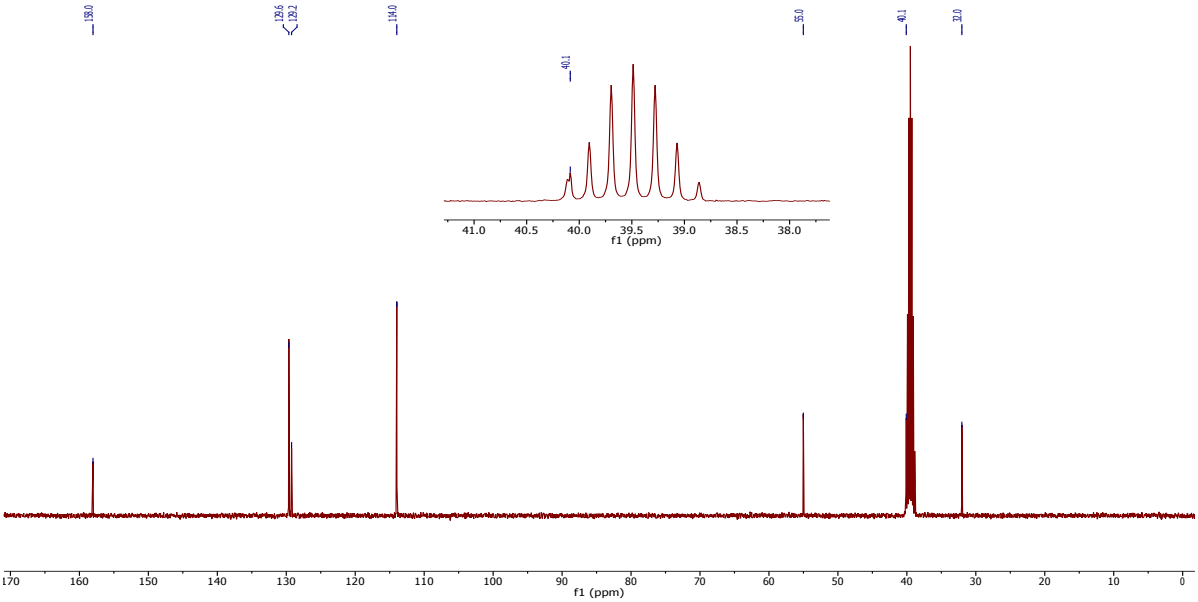
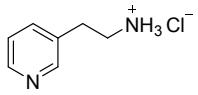
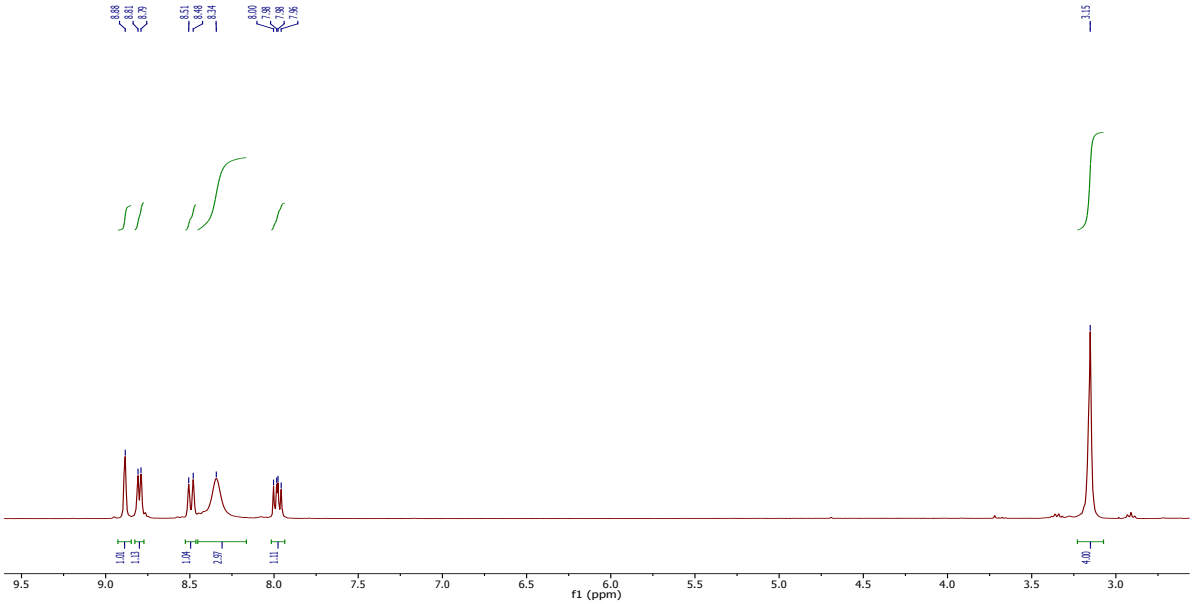
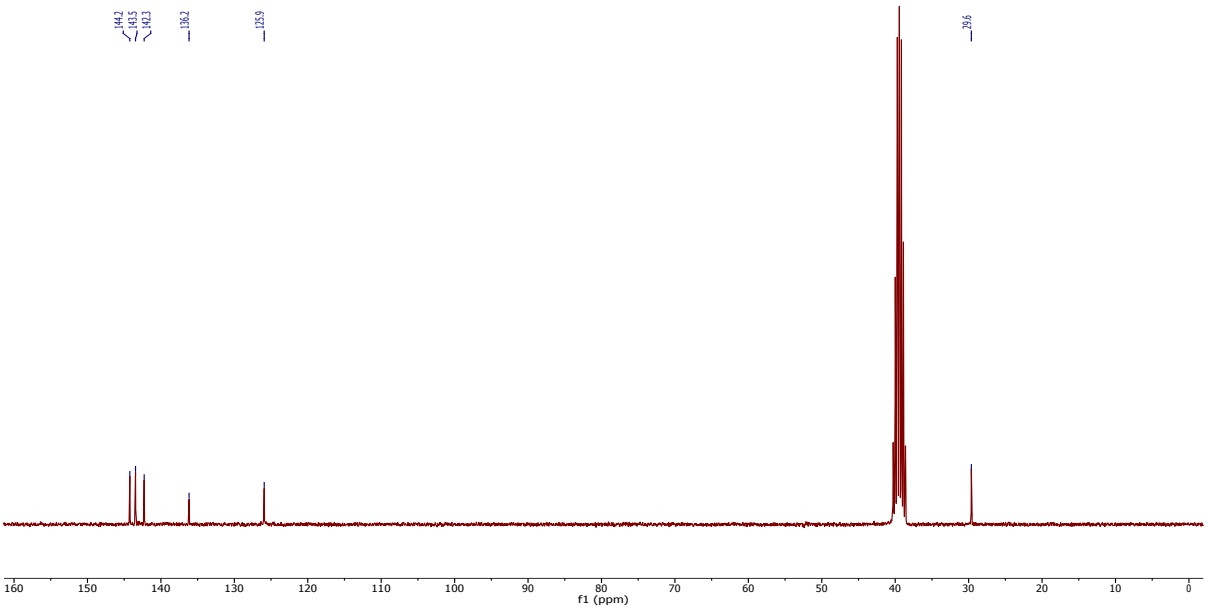
2.00
2.00
3.00
2.00
2.00
f1 (ppm)


158.0
129.6
129.2
114.0
55.0
40.1
32.0
40.1
f1 (ppm)


NH3 Cl
N


8.88
8.81
8.79
8.51
8.48
8.34
8.00
7.98
7.98
7.96
3.15
1.01
1.13
1.04
2.97
1.11
4.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
f1 (ppm)


144.2
143.5
142.3
136.2
125.9
29.6
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

S11 TEM images and analysis

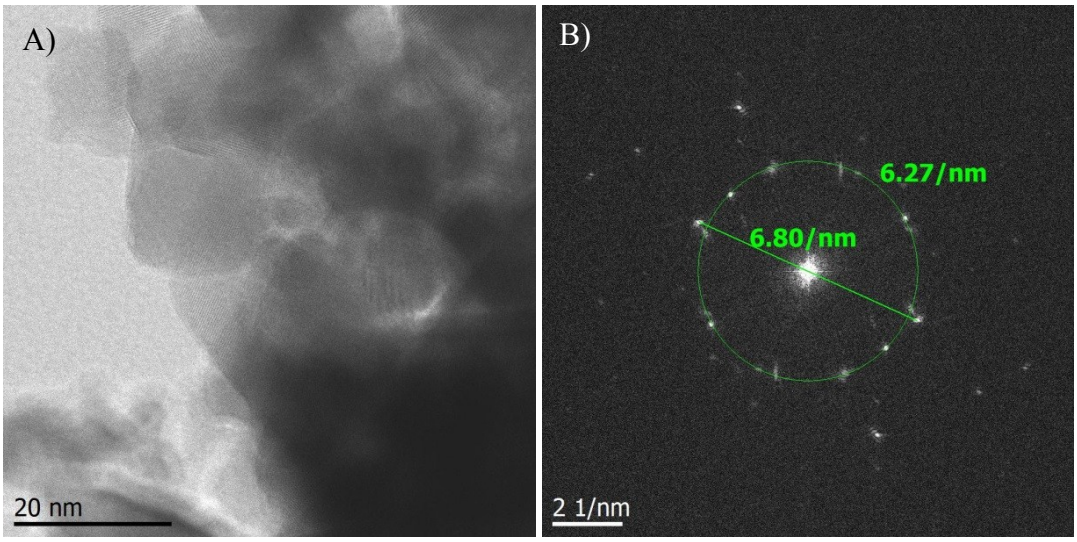


Fig. TEM S1. A) ABF-STEM image of Co containing particle (specimen B_{12}@CeO_2-8, fresh) with higher magnification. Evaluation of Fast Fourier transform of the image (B) shows a reflex different than the ones from the surrounding ceria. The values shown in the image roughly correspond to ceria and Co_3O_4.

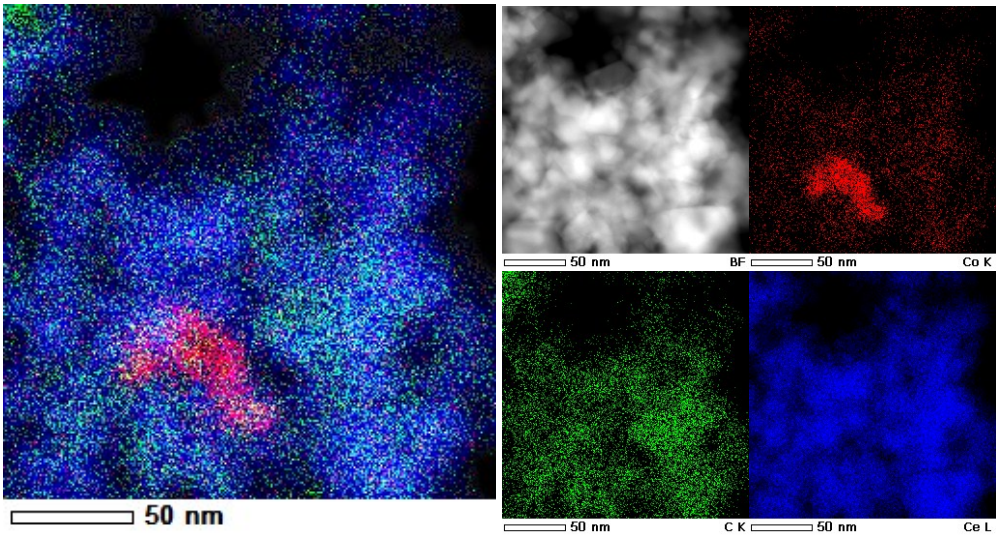


Fig. TEM S2. EDX-elemental Map of specimen B_{12}@CeO_2-8, fresh, showing the distribution of Co (red), C (green) and Ce (blue) together with the corresponding HAADF image.

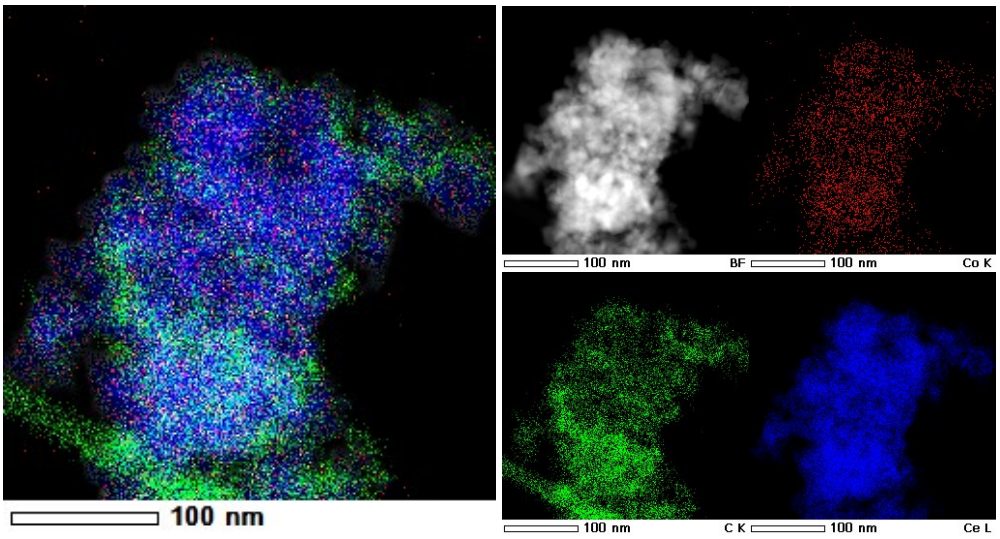


Fig. TEM S3. EDX-elemental Map of specimen B_{12}@CeO_2-8, 5 times recycled, showing the distribution of Co (red), C (green) and Ce (blue) together with the corresponding HAADF image. Note the difference in the carbon signal, here larger local concentration can be observed. The large green stripe in the lower left corner belongs to the TEM-sample grid, supporting the specimen in the microscope.

S12 XPS data for B12@CeO2-8

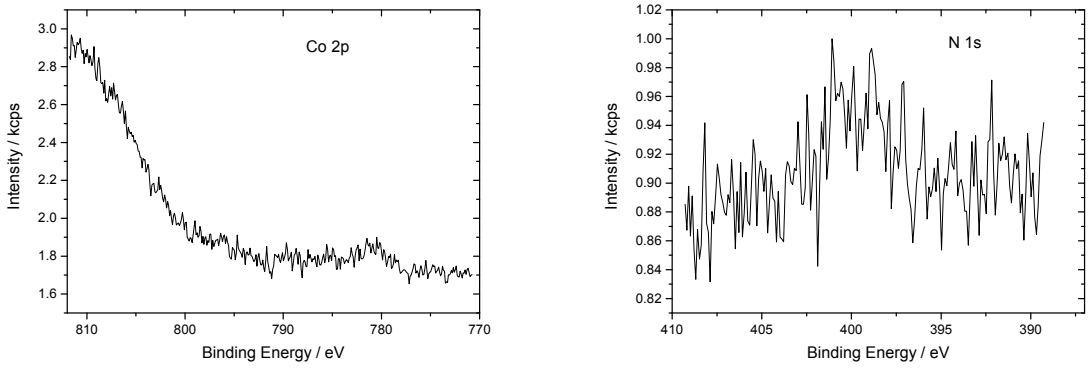


Fig. XPS S1. XPS spectra (Co 2p, N 1s) obtained for B_{12}@CeO_2-8 catalyst not further analyzed due to noisy data. The presence of N and Co in the surface region can however be confirmed at their binding energies of 400 eV respective 781 eV.