Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Electronic Supplementary Information for

Recyclable Cobalt(0) Nanoparticle Catalysts for Hydrogenations

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1 General information

Analytical Thin-Layer Chromatography: TLC was performed using aluminium plates with silica gel and fluorescent indicator (*Merck*, 60, F254). Thin layer chromatography plates were visualized by exposure to ultraviolet light (366 or 254 nm) or by immersion in a staining solution of molybdatophosphoric acid in ethanol or potassium permanganate in water.

Chemicals and Solvents: Commercially available olefins were distilled under reduced pressure prior to use. Solvents (THF, Et_2O, *n*-hexane, toluene) were distilled over sodium and benzophenone and stored over molecular sieves (4 Å). Oleylamine was stored over molecular sieve (4 Å) for 30 days and degassed in vacuum. Cobalt(II)chloride (99.999%, ABCR), lithium (99%, Alfa Aesar) and naphthalene (99%, Alfa Aesar) were used as received.

Column Chromatography: Flash column chromatography with silica gel 60 from *KMF* (0.040-0.063 mm). Mixtures of solvents used are noted in brackets.

High Pressure Reactor: Hydrogenation reactions were carried out in 160 and 300 mL high pressure reactors (*Parr*™) in 4 mL glass vials. The reactors were loaded under argon, purged with H_2 (1 min), then three times with 2 bar H_2, sealed and the internal pressure was adjusted. Hydrogen (99.9992%) was purchased from *Linde*.

^{1}H- und ^{13}C-NMR-Spectroscopy: Nuclear magnetic resonance spectra were recorded on a *Bruker* Avance 300 (300 MHz) and *Bruker* Avance 400 (400 MHz). ^{1}H-NMR: The following abbreviations are used to indicate multiplicities: s = singlet; d = doublet; t = triplet, q = quartet; m = multiplet, dd = doublet of doublet, dt = doublet of triplet, dq = doublet of quartet, ddt = doublet of doublet of quartet. Chemical shift δ is given in ppm to tetramethylsilane.

Fourier-Transformations-Infrared-Spectroscopy (FT-IR): Spectra were recorded on a *Agilent* Cary 630 FTIR with ATR-device. All spectra were recorded at room temperature. Wave number is given in cm^{-1}. Bands are marked as s = strong, m = medium, w = weak and b = broad.

Gas chromatography with FID (GC-FID): HP6890 GC-System with injector 7683B and *Agilent* 7820A System. Column: HP-5, 19091J-413 (30 m × 0.32 mm × 0.25 µm),

carrier gas: N_2. GC-FID was used for reaction control and catalyst screening (Calibration with internal standard *n*-pentadecane and analytically pure samples).

Gas chromatography with mass-selective detector (GC-MS): Agilent 6890N Network GC-System, mass detector 5975 MS. Column: HP-5MS (30 m × 0.25 mm × 0.25 µm, 5% phenylmethylsiloxane, carrier gas: H_2. Standard heating procedure: 50 °C (2 min), 25 °C/min -> 300 °C (5 min)

High resolution mass spectrometry (HRMS): The spectra were recorded by the Central Analytics Lab at the Department of Chemistry, University of Regensburg, on a MAT SSQ 710 A from *Finnigan.*

Inductively coupled plasma optical emission spectrometry (ICP-OES): ICP-OES measurements were carried out on a *Spectro Analytical Instruments* Spectroflame (Type: FSMEA85C).

Inductively coupled plasma mass spectrometry (ICP-MS): ICP-MS measurements were carried out on a *Perkin Elmer* Elan 9000.

Gas-uptake reaction monitoring: Gas-uptake was monitored with a *Man On the Moon X201* kinetic system to maintain a constant reaction pressure. The system was purged with hydrogen prior to use. Reservoir pressure was set to about 9 bar H_2. Calibration of the reservoir pressure drop in relation to H_2 consumption was performed by quantitative hydrogenation of various amounts of *α*-methylstyrene with a Pd/C catalyst in 1 mL of THF.

Transmission electron microscopy (TEM): TEM, high-resolution (HR)TEM, and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) were conducted with an aberration-corrected FEI Titan^3 80-300 microscope operating at 300 and 80 kV, a FEI Osiris microscope at 200 kV, and a Philips CM 200 FEG/ST microscope at 200 kV. TEM samples were prepared by evaporating DME, THF or *n*-heptane suspensions on amorphous carbon (lacey-)film suspended on copper grids. The deposition of the samples on the carbon (lacey-)film copper grids was performed under argon atmosphere in a glovebox. The grids were thereafter transferred with a suitable vacuum/inert gas transfer module into the transmission electron microscope without any contact to air. Average particle diameters were calculated by statistical evaluation of at least 150 particles (ImageJ 1.47v software).

X-ray powder diffraction (XRD): X-ray powder diffraction was carried out with a Stoe STADI-P diffractometer operating with Ge-monochromatized Cu-Kα radiation. Co^0 powder samples sintered at 800 °C for 7 h in vacuum for crystallization of the metal and eventual oxide impurities. The powder samples were measured on a Stoe IPDS II image plate diffractometer using Mo-Kα radiation (graphite monochromator). Samples were diluted with glass spheres (9-13 µm, Sigma-Aldrich) to reduce the X-ray absorption of the metal nanoparticles and prepared in glass capillaries under argon. Since the scattering power of the small-sized metal nanoparticles (diameter ≤10 nm) is low, certain non-specific background is observed for all nanoparticles. This non-specific scattering was fitted by background correction.

2 General procedures

Synthesis of Co nanoparticles

Cobalt(II)chloride (519 mg, 4.0 mmol), lithium (56 mg, 8.0 mmol) and naphthalene (1.20 g, 9.4 mmol) were stirred in 20 mL THF for 24 h. The resultant nanoparticles were separated by centrifugation (20.000 rpm) and purified by redispersion and centrifugation (3×20 mL THF). Subsequently, the solids were dried in vacuum (for storage as powder) or redispersed in 40 mL THF (Co-NPs, for catalytic applications). The preparation of amine-stabilized nanoparticles (aCo-NPs) was effected by treatment of the dried solids with 38 mL THF and 2 mL oleylamine (aCo-NP). As an alternative to the separation by centrifugation, the particles can be separated by an external commercial neodymium magnet (mCo-NPs). The preparation of related nanoparticles followed the same reduction protocol but without the washing procedures (*in situ* Co-NPs). The primary THF solutions (containing the by-products LiCl, naphthalene) were directly employed in catalytic reactions. The removal of the magnetic stir bar appeared to important to ensure long-term catalyst stability. After extended periods of storage of the catalysts suspensions, ultrasonification for 15-60 min effected complete redispersion and secured highest reproducibility.

General procedure for hydrogenation

Under an atmosphere of argon, a 5 mL screw cap vial with a PTFE septum and magnetic stir bar was charged with the substrate (0.25 mmol) and THF (875 µL). The catalyst suspension (125 µL; 0.0125 mmol Co) was added and the septum punctured with a short needle (Braun). The vial was placed into a high-pressure reactor (Parr Instr.), which was sealed, removed from the glove box, placed on a magnetic stirrer plate, and purged with H_2. After 3 h at r.t. under an atmosphere of H_2 (2 bar), the pressure was released, the vial retrieved, and the reaction quenched with saturated aqueous NH_4Cl (1 mL). For quantitative GC-FID analyses, *n*-pentadecane was added as internal standard. The mixture was extracted with ethyl acetate and the combined organic layers were dried (Na_2SO_4). For isolation of the products, the reaction mixture was filtered through a Pasteur pipette filled with SiO_2. The pipette was washed with *n*-pentane (3 x 1 mL) and the solvents evaporated. Amines were isolated as the corresponding ammonium salts after addition of $HCl{\cdot}Et_2O$.

General method for kinetic examination in catalytic hydrogenation

A flame-dried 10 mL two-neck flask was connected to a *Man on the Moon X201* gas-uptake system. After purging with H_2, the system was set to a reaction pressure of 1.9 bar. The catalyst mixture in THF (2 ml) was added using a Teflon septum. Monitoring of the hydrogen uptake started with the addition of the substrate (0.5 mmol). The pressure was recorded every two seconds until the pressure in the reaction vessel remained stationary.

3 Synthesis of starting materials

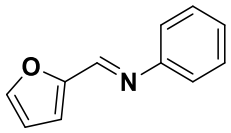
General procedure for the synthesis of imines

Silica (6 g) was weighed into a 100 ml round-bottom flask and suspended in ethanol (35 ml). After addition of the aldehyde (20 mmol) and amine (20 mmol, 1 equiv.), the flask was put into an ultrasonic bath for 20 min at room temperature.

The mixture was stirred overnight, filtered and the solvent removed. The crude product mixture was vacuum distilled (80 °C, 0.02 mbar) and the imines collected.

Modified procedure according to K. P. Guzen, A. S. Guarezemini, A. T. Órfão, R. Cella, C. M. Pereira, H. A. Stefani, *Tetrahedron Lett.* **2007**, *48*, 1845.

N-(2-Furanylmethylene)-benzenamine



$C_{11}H_9NO$

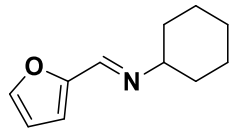
171.20 g/mol

Pale yellow liquid

Yield	1.72 g, 10.0 mmol (50%)
^{1}H-NMR	(300 MHz, MeOD) δ 8.37 (s, 1H), 7.77 (d, *J* = 1.8 Hz, 1H), 7.44 – 7.33 (m, 2H), 7.29 – 7.19 (m, 3H), 7.12 (dd, *J* = 3.5, 0.7 Hz, 1H), 6.64 (dd, *J* = 3.5, 1.8 Hz, 1H).
^{13}C-NMR	(75 MHz, MeOD) δ 153.08, 151.98, 150.21, 147.68, 130.38, 127.63, 122.05, 118.77, 113.52.
GC-MS	t_R = 8.044 min, (EI, 70 eV): *m/z* = 171 [M^+], 142, 115, 104, 93, 77, 66, 51.

Analytical data were in full agreement with H. Naka, D. Koseki, Y. Kondo, *Adv. Synth. Catal.* **2008**, *350*, 1901.

***N*-(2-Furanylmethylene)-cyclohexylamine**



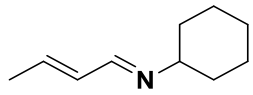
$C_{11}H_{15}NO$

177.25 g/mol

Yellow liquid

Yield	2.68 g, 15.1 mmol (76%)
^{1}H-NMR	(300 MHz, MeOD) δ 8.16 (s, 1H), 7.67 (d, *J* = 1.8 Hz, 1H), 6.91 (dd, *J* = 3.6, 0.8 Hz, 1H), 6.56 (dd, *J* = 3.5, 1.8 Hz, 1H), 3.18 (tt, *J* = 10.8, 4.1 Hz, 1H), 1.88 – 1.78 (m, 1H), 1.78 – 1.66 (m, 2H), 1.62 – 1.46 (m, 2H), 1.46 – 1.15 (m, 3H).
^{13}C-NMR	(75 MHz, MeOD) δ 152.56, 150.41, 146.59, 116.23, 112.95, 70.97, 35.25, 26.56, 25.89.
GC-MS	t_R = 7.46 min, (EI, 70 eV): *m/z* = 177 [M^+], 162, 148, 134, 122, 107, 94, 81, 67, 53.
HRMS	found 177.11437 (calculated: 177.11482)

(*rac*)-*N*-(2-Butenylidene)-cyclohexlyamine



$C_{10}H_{17}N$

151.25 g/mol

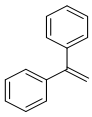
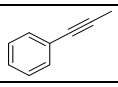
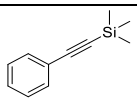
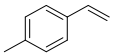
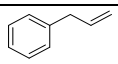
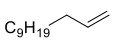
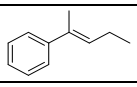
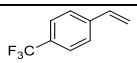
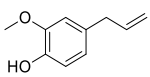
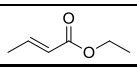
Yield	2.04 g, 13.5 mmol (68%)
^{1}H-NMR	(300 MHz, MeOD) δ 7.93 – 7.87 (m, 1H), 7.76 (t, *J* = 2.8 Hz, 1H), 6.43 – 6.29 (m, 1H), 6.19 (ddq, *J* = 15.4, 8.8, 1.4 Hz, 1H), 3.67 – 3.56 (m, 1H), 3.08 – 2.95 (m, 2H), 1.89 (d, J = 6.7 Hz, 3H), 1.84 – 1.61 (m, 11H), 1.50 – 1.31 (m, 7H), 1.17 (d, J = 6.2 Hz, 3H).
^{13}C-NMR	(75 MHz, MeOD) δ 164.2, 163.6, 163.6, 143.6, 143.5, 132.0, 75.8, 70.5, 70.0, 36.9, 35.4, 35.3, 35.3, 26.6, 26.3, 25.8, 25.8, 19.5, 18.6, 18.5.
GC-MS	t_R = 6.26 min, (EI, 70 eV): *m/z* = 150 [M^+-H], 136, 122, 110, 94, 82, 68, 55.

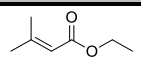
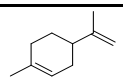
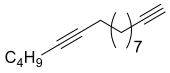
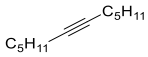
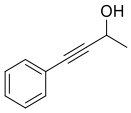
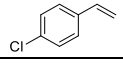
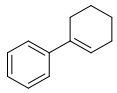
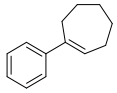
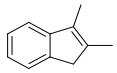
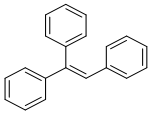
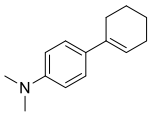
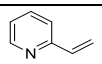
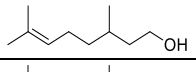
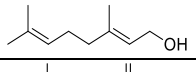
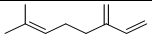
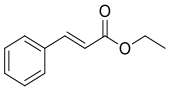
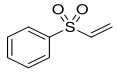
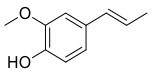
Analytical data were in full agreement with A. Saoudi, A. Benguedach, H. Benhaoua, *Synth. Commun.* **1995**, *25*, 2349.

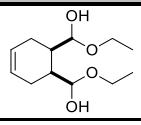
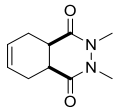
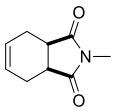
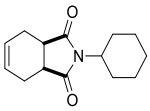
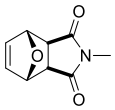
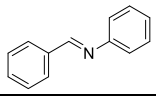
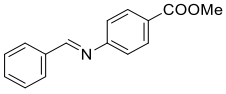
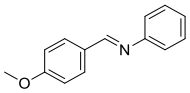
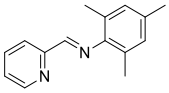
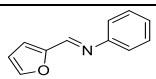
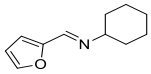
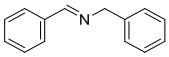
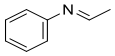
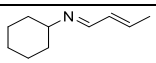
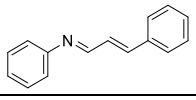
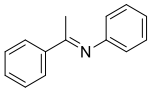
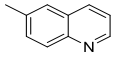
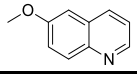
4 Hydrogenation reactions

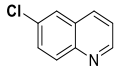
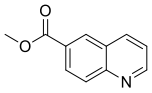
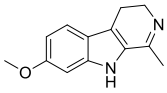
4.1 Catalyst & substrate screening

Table S1. Hydrogenation of alkenes, alkynes, imines, and quinolines catalyzed by cobalt(0) nanoparticles isolated by centrifugation (Co-NP), isolated by magnetic separation (mCo-NP), prepared and used in situ (in situ Co-NP), and isolated by centrifugation and stabilized by oleyl amine (aCo-NP). Standard conditions: 0.25 mmol substrate, 1 mL in THF or 0.5 mmol substrate, 2 mL THF. If not otherwise noted, yields were determined by GC-FID vs. internal n-pentadecane.

Substrate		[Co]	[mol%]	[bar]	[°C]	[h]	Yield [%]	Comment
1a		Co-NP	1	2	20	3	>99	-
		Co-NP	5			0,5	>99	-
		mCo-NP	5			0,5	98	-
		In situ Co-NP	5			0,5	97	-
		aCo-NP	1			3	16 (26)	-
1b		Co-NP	1	2	20	3	>99	-
		Co-NP	5			1	98	-
		mCo-NP	5			0,5	>99	-
		In situ Co-NP	5			0,5	>99	-
		aCo-NP	1			3	16 (26)	-
1c		Co-NP	1	2	20	3	>99	-
		In situ Co-NP	5				99	-
1d		Co-NP	5	2	20	8	>99	-
		mCo-NP	1			24	88	-
		mCo-NP	5			3	90	-
1e		Co-NP	5	2	20	8	98	-
1f		mCo-NP	5	2	20	3	96 (isol.)	-
1g		mCo-NP	1	2	20	3	58	-
1h		mCo-NP	1	2	20	3	94	-
1i		mCo-NP	1	2	20	3	72 (isol.)	100% according to ^{1}H-NMR of the mixture
1j		Co-NP	1	2	20	3	>99	-
		In situ Co-NP	5				97	-
1k		Co-NP	1	2	20	3	>96	-
		Co-NP	5			0,5	92	-
		mCo-NP	5			0,5	>99	-
		In situ Co-NP	5			0,5	>99	-
1l		mCo-NP	5	2	20	24	69 (isol.)	-
1m		mCo-NP	5	2	20	3	98	-
1n		mCo-NP	5	2	20	3	89 (isol.)	-
1o		mCo-NP	5	2	20	3	98	-

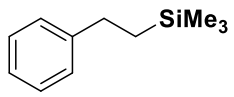
Substrate		[Co]	[mol%]	[bar]	[°C]	[h]	Yield [%]	Comment
1p		mCo-NP mCo-NP	5 10	2	20	3	42 94	- -
1q		mCo-NP	5	2	20	24	74 (isol.)	residual solvent (*vide infra*)
1r		mCo-NP	5	2	20	3	87	Yield refers to: ethylcyclohexane (100% conversion). Rest: M = 100
1s		mCo-NP	5	2	20	3	53	See **1q**
1t		mCo-NP	5	2	20	8	99 (isol.)	-
1u		Co-NP m-CoNP	5 5	2	20	8 24	>99 93 (isol.)	- -
1v		mCo-NP	5	2	20	3	96 (isol.)	-
1w		Co-NP	5	10	20	24	58	-
1x		Co-NP Co-NP	5 5	10 60	60 20	3 24	>99 >99	- -
1y		Co-NP aCo-NP	5 5	10	60	24	98 80	- -
1z		Co-NP aCo-NP	5 5	10	60	24	98 79	- -
1aa		Co-NP	5	10	60	24	86	-
1ab		Co-NP Co-NP	5 5	10	20 60	3	71 92	- -
1ac		mCo-NP	5	10	60	24	99 (isol.)	-
1ad		mCo-NP	5	2	20	3	99 (isol.)	-
1ae		mCo-NP	5	20	80	24	88 (isol.)	-
1af		mCo-NP	5	10	60	24	99 (isol.)	-
1ag		mCo-NP	5	20	80	24	79 (isol.)	-
1ah		mCo-NP mCo-NP	5	2 10	20 60	3 24	49 88	-
1ai		mCo-NP	5	10	60	24	81	Purity: *vide infra*
1aj		mCo-NP	5	10	60	24	91 (isol.)	-

Substrate	[Co]	[mol%]	[bar]	[°C]	[h]	Yield [%]	Comment
1ak 	mCo-NP	5	10	60	24	95 (isol.)	-
1al 	mCo-NP	5	20	80	24	81 (isol.)	-
1am 	mCo-NP	5	10	60	24	93 (isol.)	-
1an 	mCo-NP	5	10	60	24	96 (isol.)	-
1ao 	mCo-NP	5	10	60	24	94	-
2a 	Co-NP Co-NP mCo-NP	5 5 5	10	60	6 24	87 >99 91 (isol.)	- - -
2b 	mCo-NP	5	10	60	24	83 (isol.)	-
2c 	mCo-NP	5	10	60	24	88 (isol.)	-
2d 	mCo-NP	5	10	60	24	98 (isol.)	mixture (*vide infra*)
2e 	mCo-NP	5	10	60	24	99 (isol.)	mixture (*vide infra*)
2f 	mCo-NP	5	10	60	24	67 (isol.)	mixture (*vide infra*)
2g 	mCo-NP	5	10	60	24	84 (isol.)	-
2h 	mCo-NP	5	10	60	24	63 (isol.)	-
2i 	mCo-NP	5	10	60	24	92 (isol.)	-
2j 	mCo-NP	5	10	60	24	96 (isol.)	-
2k 	mCo-NP	5	20	80	48	89 (isol.)	Purity: *vide infra*
2l 	mCo-NP	5	10	100	24	99 (isol.)	-
2m 	mCo-NP	5	20	80	48	75 (isol.)	-
2n 	mCo-NP	5	20	80	24	39 (isol.)	
2o 	mCo-NP	5	20	80	24	77 (isol.)	

Substrate		[Co]	[mol%]	[bar]	[°C]	[h]	Yield [%]	Comment
2p		mCo-NP	5	20	80	48	62 (isol.)	-
2q		mCo-NP	5	20	80	24	98 (isol.)	-
2r		mCo-NP	5	20	80	24	95 (isol.)	-
2s		mCo-NP	5	10	60	24	97 (isol)	-

4.2 Isolated hydrogenation reaction products

Trimethyl(phenethyl)silane (**1f**)



$C_{11}H_{18}Si$

178.35 g/mol

Yield 85.2 mg, 0.48 mmol (96%)

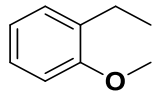
^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.30 – 7.10 (m, 5H), 2.66 – 2.56 (m, 2H), 0.91 – 0.80 (m, 2H), 0.00 (s, 9H).

^{13}C-NMR (75 MHz, $CDCl_3$) δ 145.5, 128.4, 127.9, 125.6, 30.2, 18.8, -1.6.

GC-MS t_R = 6.16 min, (EI, 70 eV): *m/z* = 178 [M^+], 163, 135, 104, 91, 73, 59, 51.

Analytical data were in full agreement with E. Negishi, D. R. Swanson, C. J. Rousset, *J. Org. Chem.* **1990**, *55*, 5406.

1-Ethyl-2-methoxybenzene (**1i**)



$C_9H_{12}O$

136.19 g/mol

Yield 52.2 mg, 0.38 mmol (72%)

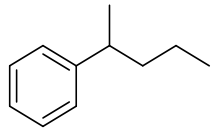
^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.22 – 7.13 (m, 2H), 6.91 (td, *J* = 7.4, 1.1 Hz, 1H), 6.86 (dd, *J* = 8.0, 1.1 Hz, 1H), 3.84 (s, 3H), 2.66 (q, *J* = 7.5 Hz, 2H), 1.21 (t, *J* = 7.5 Hz, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$) δ 157.5, 132.7, 129.0, 126.9, 120.6, 110.3, 55.4, 23.4, 14.3.

GC-MS t_R = 5.30 min, (EI, 70 eV): *m/z* = 136 [M^+], 121, 103, 91, 77, 65, 51.

Analytical data were in full agreement with M. Mirza-Aghayan, R. Boukherroub, M. Rahimifard, *J. Organomet. Chem.* **2008**, *693*, 3567.

2-Phenylpentane (**1l**)



$C_{11}H_{16}$

148.25 g/mol

Yield 53.4 mg, 0.36 mmol (69%)

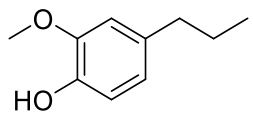
^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.33 – 7.26 (m, 2H), 7.22 – 7.14 (m, 3H), 2.70 (h, *J* = 7.0 Hz, 1H), 1.65 – 1.43 (m, 2H), 1.36 – 1.09 (m, 5H), 0.87 (t, *J* = 7.3 Hz, 3H)

^{13}C-NMR (75 MHz, $CDCl_3$) δ 148.1, 128.4, 127.1, 125.9, 40.9, 39.8, 22.4, 21.0, 14.3.

GC-MS t_R = 5.42 min, (EI, 70 eV): *m/z* = 148 [M^+], 105, 91, 77, 65, 51.

Analytical data were in full agreement with R. B. Bedford, P. B. Brenner, E. Carter, T. W. Carvell, P. M. Cogswell, T. Gallagher, J. N. Harvey, D. M. Murphy, E. C. Neeve, J. Nunn et al., *Chem. Eur. J.* **2014**, *20*, 7935.

2-Methoxy-4-propylphenol (**1n/1aj**)



$C_{10}H_{14}O_2$

166.22 g/mol

Yield From eugenol: 75.6 mg, 0.45 mmol (89%)

from isoeugenol: 75.7 mg, 0.46 mmol (91%)

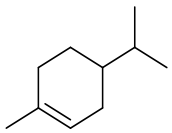
^{1}H-NMR (300 MHz, $CDCl_3$) δ 6.86 – 6.81 (m, 1H), 6.71 – 6.65 (m, 2H), 5.48 (brs, 1H), 3.88 (s, 3H), 2.52 (t, J = 7.8 Hz, 2H), 1.69 – 1.55 (m, 2H), 0.94 (t, J = 7.3 Hz, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$) δ 146.4, 143.6, 134.8, 121.1, 114.2, 111.1, 56.0, 37.9, 25.0, 14.0.

GC-MS t_R = 7.038 min, (EI, 70 eV): *m/z* = 166 [M^+], 137, 122, 107, 94, 77, 65, 51.

Analytical data were in full agreement with C. Smit, M. W. Fraaije, A. J. Minnaard, *J. Org. Chem.* **2008**, *73*, 9482.

4-Isopropyl-1-methylcyclohexene (**1q**)



$C_{10}H_{18}$

138.25 g/mol

Yield 33.7 mg, 0.24 mmol (95%; 78% purity)

Due to the volatile nature of the product, the solvents could not be removed completely. NMR-analysis showed 74% hydrogenation product, 14% THF, 7% *n*-pentane

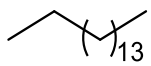
^{1}H-NMR (400 MHz, $CDCl_3$) δ 5.46 – 5.28 (m, 1H), 2.08 – 1.91 (m, 3H), 1.80 – 1.67 (m, 2H), 1.64 (s, 3H), 1.46 (dq, J = 13.1, 7.1, 6.5 Hz, 1H), 1.35 – 1.16 (m, 2H), 0.92 – 0.84 (m, 6H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ 134.1, 121.2, 40.2, 32.4, 31.0, 29.1, 26.6, 23.6, 20.2, 19.9.

GC-MS t_R = 4.84 min, (EI, 70 eV): *m/z* = 138 [M^+], 123, 109, 95, 81, 67, 55.

Analytical data were in full agreement with G. Villa, G. Povie, P. Renaud, *J. Am. Chem. Soc.* **2011**, *133*, 5913.

n-Hexadecane (**1t**)



$C_{16}H_{34}$

226.45 g/mol

Yield 59.3 mg, 0.26 mmol (99%)

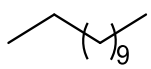
^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.26 (s, 28H), 0.94 – 0.82 (m, 6H).

^{13}C-NMR (75 MHz, $CDCl_3$) δ 32.1, 29.9, 29.8, 29.6, 22.9, 14.3.

GC-MS t_R = 8.185 min, (EI, 70 eV): *m/z* = 226 [M^+], 197, 183, 169, 155, 141, 127, 113, 99, 85, 71, 57.

Analytical data were in full agreement with T. Brenstrum, D. A. Gerristma, G. M. Adjabeng, C. S. Frampton, J. Britten, A. J. Robertson, J. McNulty, A. Capretta, *J. Org. Chem.* **2004**, *69*, 7635.

n-Dodecane (**1u**)



$C_{12}H_{26}$

170.34 g/mol

Yield 78.6 mg, 0.46 mmol (93%)

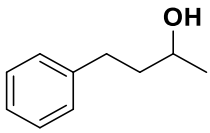
^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.26 (s, 20H), 0.94 – 0.84 (m, 6H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ 32.1, 29.9, 29.8, 29.5, 22.9, 14.3.

GC-MS t_R = 6.01 min, (EI, 70 eV): *m/z* = 170 [M^+], 141, 127, 112, 98, 85, 71, 57.

Analytical data were in full agreement with X. Xu, D. Cheng, W. Pei, *J. Org. Chem.* **2006**, *71*, 6637.

4-Phenylbutan-2-ol (**1v**)



$C_{10}H_{14}O$

150.22 g/mol

Yield 73.9 mg, 0.49 mmol (96%)

Purity: 93%; 7% semihydrogenation product

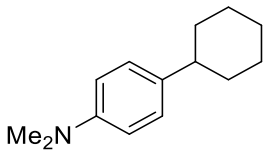
^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.26 – 7.31 (m, 2H), 7.17 – 7.24 (m, 3H), 3.84 (dq, 1H, *J* = 6.22, 12.10 Hz), 2.61 – 2.83 (m, 2H), 1.73 – 1.83 (m, 2H), 1.53 (br s, 1H), 1.24 (d, 3H, *J* = 6.17 Hz).

^{13}C-NMR (75 MHz, $CDCl_3$) δ 142.2, 128.5, 125.9, 67.6, 41.0, 32.3, 23.8.

GC-MS t_R = 6.51 min, (EI, 70 eV): *m/z* = 150 [M^+], 132, 117, 91, 77, 65, 51.

Analytical data were in full agreement with Z. E. Clarke, P. T. Maragh, T. P. Dasgupta, D. G. Gusev, A. J. Lough, K. Abdur-Rashid, *Organometallics* **2006**, *25*, 4113.

4-Cyclohexyl-N,N-dimethylaniline (**1ac**)



$C_{14}H_{21}N$

203.33 g/mol

Yield 100.7 mg, 0.50 mmol (99%)

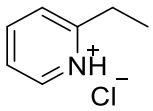
^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.15 – 7.08 (m, 2H), 6.77 – 6.70 (m, 2H), 2.93 (s, 6H), 2.43 (tq, *J* = 9.0, 3.3 Hz, 1H), 1.92 – 1.81 (m, 4H), 1.75 (dtt, *J* = 12.6, 3.1, 1.4 Hz, 1H), 1.47 – 1.33 (m, 4H), 1.27 (ddt, *J* = 14.5, 9.0, 3.3 Hz, 1H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ 149.1, 136.8, 127.4, 113.1, 43.6, 41.1, 34.9, 27.2, 26.4.

GC-MS t_R = 9.15 min, (EI, 70 eV): *m/z* = 203 [M^+], 160, 146, 134, 115, 103, 93, 77, 51.

Analytical data were in full agreement with W. M. Czaplik, M. Mayer, A. Jacobi von Wangelin, *Angew. Chem. Int. Ed.* **2009**, *48*, 607.

2-Ethylpyridine hydrochloride (**1ad**)



$C_7H_{10}ClN$

143.61 g/mol

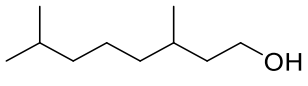
Yield 36.1 mg, 0.25 mmol (99%)

^{1}H-NMR (300 MHz, MeOD) δ 8.75 (dt, *J* = 4.8, 2.3 Hz, 1H), 8.65 – 8.53 (m, 1H), 8.04 (d, *J* = 8.1 Hz, 1H), 8.00 – 7.90 (m, 1H), 3.21 – 3.06 (m, 2H), 2.02 (s, 1H), 1.50 – 1.41 (m, 3H).

^{13}C-NMR (75 MHz, MeOD) δ 160.0, 148.3, 142.1, 128.0, 126.0, 27.8, 13.3.

GC-MS (freebase) t_R = 3.792 min, (EI, 70 eV): *m/z* = 106 [M^+], 92, 79, 65, 51.

3,7-Dimethyl-1-octanol (**1ae**: from citronellol; **1af**: from geraniol)

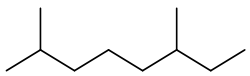


$C_{10}H_{22}O$

158.29 g/mol

Yield	From citronellol: 68.3 mg, 0.43 mmol (88%), from geraniol: 40.4 mg, 0.26 mmol (99%)
^{1}H-NMR	(300 MHz, $CDCl_3$) δ 3.76 – 3.57 (m, 2H), 1.67 – 1.46 (m, 3H), 1.43 – 1.32 (m, 2H), 1.32 – 1.21 (m, 3H), 1.19 – 1.06 (m, 3H), 0.87 (dd, *J* = 8.0, 6.5 Hz, 9H).
^{13}C-NMR	(75 MHz, $CDCl_3$) δ 61.4, 40.1, 39.4, 37.5, 29.6, 28.1, 24.8, 22.8, 22.7, 19.7.
GC-MS	t_R = 6.016 min, (EI, 70 eV): *m/z* = 140 [M^+-OH_2], 125, 112, 97, 83, 70, 55.
HRMS	Calcd. for $C_{10}H_{21}O$ 157.15869; found: 157.15836.
IR	3324 (b), 2955 (s), 2926 (s), 2870 (s), 1461 (m), 1379 (m), 1260 (m), 1051 (s), 805 (s) cm^{-1}.

2,6-Dimethyloctane (**1ag**)



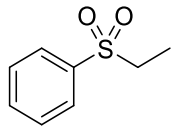
$C_{10}H_{22}$

142.29 g/mol

Yield	57.6 mg, 0.40 mmol (79%)
^{1}H-NMR	(300 MHz, $CDCl_3$) δ 1.52 (dp, J = 13.1, 6.6 Hz, 1H), 1.38 – 1.22 (m, 5H), 1.18 – 1.01 (m, 4H), 0.85 (t, J = 6.8 Hz, 12H).
^{13}C-NMR	(75 MHz, $CDCl_3$) δ 39.5, 37.0, 34.6, 29.7, 28.2, 25.0, 22.9, 22.8, 19.4, 11.6.
GC-MS	t_R = 4.03 min, (EI, 70 eV): *m/z* = 142 [M^+], 127, 113, 97, 85, 71, 57.

Analytical data were in full agreement with R. V. Ottenbacher, D. G. Samsonenko, E. P. Talsi, K. P. Bryliakov, *Org. Lett.* **2012**, *14*, 4310.

(Ethylsulfonyl)benzene (**1ai**)



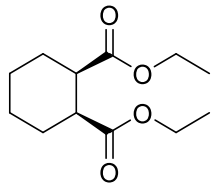
$C_8H_{10}O_2S$

170.23 g/mol

Yield	77.1 mg, 0.45 mmol (91%) Purity: 89%; 12% starting material
^{1}H-NMR	(300 MHz, $CDCl_3$) δ 7.93 – 7.86 (m, 2H), 7.72 – 7.59 (m, 1H), 7.60 – 7.53 (m, 2H), 3.11 (q, J = 7.4 Hz, 2H), 1.26 (t, J = 7.4 Hz, 3H).
^{13}C-NMR	(75 MHz, $CDCl_3$) δ 138.6, 133.8, 129.4, 128.3, 50.7, 7.6.
GC-MS	t_R = 9.00 min, (EI, 70 eV): *m/z* = 170 [M^+], 154, 141, 125, 105, 94, 77, 65, 51.

Analytical data were in full agreement with R. V. Kupwade, S. S. Khot, U. P. Lad, U. V. Desai, P. P. Wadgaonkar, *Res. Chem. Intermed.* **2017**, *43*, 6875.

Diethyl *cis*-1,2-cyclohexanedicarboxylate (**1ak**)



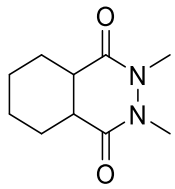
$C_{12}H_{20}O_4$

228.29 g/mol

Yield	107.8 mg, 0.47 mmol (95%)
^{1}H-NMR	(300 MHz, $CDCl_3$) δ 4.12 (q, J = 7.1 Hz, 4H), 2.85 – 2.74 (m, 2H), 2.10 – 1.89 (m, 2H), 1.83 – 1.66 (m, 2H), 1.58 – 1.30 (m, 4H), 1.23 (t, J = 7.2 Hz, 6H).
^{13}C-NMR	(75 MHz, $CDCl_3$) δ 173.8, 60.4, 42.8, 26.4, 23.9, 14.3.
GC-MS	t_R = 9.33 min, (EI, 70 eV): *m/z* = 228 [M^+], 183, 154, 140, 125, 108, 99, 81, 67, 55.

Analytical data were in full agreement with T. Volk, D. Bernicke, J. W. Bats, H.-G. Schmalz, *Eur. J. Inorg. Chem.* **1998**, 1883..

2,3-Dimethyloctahydrophthalazine-1,4-dione (**1al**)

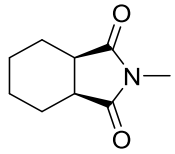


$C_{10}H_{16}N_2O_2$

196.25 g/mol

Yield	79.5 mg, 0.41 mmol (81%)
^{1}H-NMR	(300 MHz, $CDCl_3$) δ 3.24 (s, 6H), 2.79 – 2.62 (m, 2H), 1.97 – 1.49 (m, 6H), 1.49 – 1.29 (m, 2H).
^{13}C-NMR	(75 MHz, $CDCl_3$) δ 170.4, 32.7, 24.3.
GC-MS	t_R = 8.78 min, (EI, 70 eV): *m/z* = 196 [M^+], 180, 166, 153, 141, 125, 109, 96, 81, 67, 59.

(3a*R*,7a*S*)-2-Methylhexahydro-1H-isoindole-1,3(2H)-dione (**1am**)



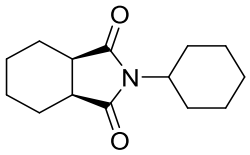
$C_9H_{13}NO_2$

167.21 g/mol

Yield	78.3 mg, 0.47 mmol (93%)
^{1}H-NMR	(300 MHz, $CDCl_3$) δ 2.96 (s, 3H), 2.90 – 2.79 (m, 2H), 1.93 – 1.66 (m, 4H), 1.51 – 1.34 (m, 4H).
^{13}C-NMR	(75 MHz, $CDCl_3$) δ 180.1, 39.9, 24.8, 23.8, 21.7.
GC-MS	t_R = 7.46 min, (EI, 70 eV): *m/z* = 167 [M^+], 152. 138. 125. 113. 82. 67. 54.

Analytical data were in full agreement with T. N. Gieshoff, U. Chakraborty, M. Villa, A. Jacobi von Wangelin, *Angew. Chem. Int. Ed.* **2017**, *56*, 3585.

(3a*R*,7a*S*)-2-Cyclohexylhexahydro-1H-isoindole-1,3(2H)-dione (**1an**)



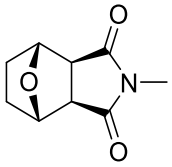
$C_{14}H_{21}NO_2$

235.33 g/mol

Yield	111.0 mg, 0.47 mmol (96%)
^{1}H-NMR	(300 MHz, $CDCl_3$) δ 3.92 (tt, J = 12.3, 3.9 Hz, 1H), 2.77 (ddd, J = 6.4, 4.4, 2.1 Hz, 2H), 2.11 (qd, J = 12.3, 3.4 Hz, 2H), 1.89 – 1.76 (m, 4H), 1.75 – 1.51 (m, 5H), 1.49 – 1.34 (m, 4H), 1.34 – 1.15 (m, 3H).
^{13}C-NMR	(75 MHz, $CDCl_3$) δ 180.0, 51.3, 39.7, 28.9, 26.0, 25.2, 24.0, 21.8.
GC-MS	t_R = 9.83 min, (EI, 70 eV): *m/z* = 235 [M^+], 207, 192, 178, 164, 154, 136, 124, 108, 98, 81, 67, 55.

Analytical data were in full agreement with M. Ostendorf, R. Romagnoli, I. C. Pereiro, E. C. Roos, M. J. Moolenaar, W. Speckamp, H. Hiemstra, *Tetrahedron: Asymmetry* **1997**, *8*, 1773.

exo-3,6-Epoxy-*N*-methyl-hexahydrophthalimide (**1ao**)

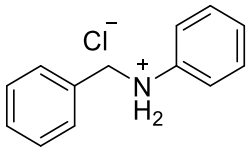


$C_9H_{11}NO_3$

181.19 g/mol

Yield	85.2 mg, 0.47 mmol (94%)
^{1}H-NMR	(300 MHz, $CDCl_3$) δ 4.86 (dd, J = 3.3, 2.1 Hz, 2H), 2.95 (s, 3H), 2.87 (s, 2H), 1.92 – 1.80 (m, 2H), 1.64 – 1.53 (m, 2H).
^{13}C-NMR	(75 MHz, $CDCl_3$) δ 177.4, 79.1, 50.1, 28.7, 25.2.
GC-MS	t_R = 9.65 min, (EI, 70 eV): *m/z* = 181 [M^+], 152, 140, 125, 108, 99, 81, 67, 55.

N-Benzylaniline hydrochloride (**2a**)



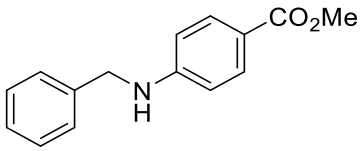
$C_{13}H_{14}ClN$

219.71 g/mol

Yield	99.4 mg, 0.45 mmol (91%)
^{1}H-NMR	(300 MHz, MeOD) δ 7.59 – 7.50 (m, 3H), 7.48 – 7.38 (m, 7H), 4.61 (s, 2H).
^{13}C-NMR	(75 MHz, MeOD) δ 136.2, 131.9, 131.5, 131.4, 131.0, 130.9, 130.2, 124.3, 57.0.
GC-MS (freebase)	t_R = 8.97 min, (EI, 70 eV): *m/z* = 183 [M^+], 154, 107, 91, 77, 65, 51.
Elemental Analysis	Calcd: 71.07% C, 6.42% H, 6.38% N; found: 70.57% C, 6.80% H, 6.27% N

Analytical data were in full agreement with T. Li, X. Cui, L. Sun, C. Li, *RSC Adv.* **2014**, *4*, 33599.

Methyl 4-(benzylamino)benzoate (**2b**)



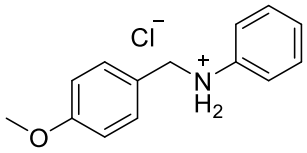
$C_{15}H_{15}NO_2$

241.29 g/mol

Yield	49.0 mg, 0.20 mmol (83%)
^{1}H-NMR	(300 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.8 Hz, 2H), 7.41 – 7.27 (m, 5H), 6.61 (d, *J* = 8.8 Hz, 2H), 4.81 (br s, 1H), 4.39 (s, 2H), 3.85 (s, 3H).
^{13}C-NMR	(75 MHz, $CDCl_3$) δ 167.4, 151.6, 138.3, 131.7, 128.9, 127.7, 127.6, 119.0, 112.0, 51.7, 48.0.
GC-MS	t_R = 11.24 min, (EI, 70 eV): *m/z* = 241 [M^+], 210, 180, 164, 151, 135, 119, 104, 91, 78, 65, 51.
Elemental Analysis	Calculated: 74.67% C, 6.27% H, 5.81% N; found: 73.82% C, 6.37% H, 5.63% N.

Analytical data were in full agreement with L. Fan, J. Jia, H. Hou, Q. Lefebvre, M. Rueping, *Chem. Eur. J.* **2016**, *22*, 16437.

N-(4-Methoxybenzyl)aniline hydrochloride (**2c**)

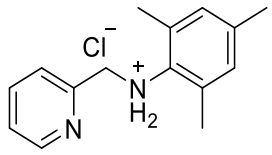


$C_{14}H_{16}ClNO$

249.74 g/mol

Yield	110.1 mg, 0.44 mmol (88%)
^{1}H-NMR	(400 MHz, MeOD) δ 7.59 – 7.48 (m, 3H), 7.45 – 7.36 (m, 2H), 7.35 – 7.30 (m, 2H), 6.97 – 6.92 (m, 2H), 4.54 (s, 2H), 3.80 (s, 3H).
^{13}C-NMR	(101 MHz, MeOD) δ 162.29, 136.10, 133.05, 131.34, 130.97, 124.34, 123.53, 115.41, 56.77, 55.82.
GC-MS (freebase)	t_R = 10.12 min, (EI, 70 eV): *m/z* = 213 [M^+], 196, 180, 168, 152, 142, 121, 106, 91, 77, 65, 51.
HRMS	Calcd. for $C_{14}H_{16}NO$: 214,1226; found: 214.1226.
IR	3060 (w), 2896 (m), 2840 (m), 2669 (s), 2550 (s), 2423 (s), 1595 (s), 1513 (s), 1305 (m), 1249 (s), 1033 (s), 815 (s), 795 (s) cm^{-1}.

N-(2,4,6-Trimethylphenyl)-2-pyridinemethanamine hydrochloride (**2d**)

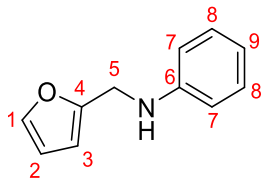


$C_{15}H_{19}ClN_2$

262.78 g/mol

Yield	128.2 mg, 0.49 mmol (98%) 23% pyridine hydrogenation
^{1}H-NMR	(300 MHz, MeOD) δ 8.85 (ddd, *J* = 5.5, 1.6, 0.8 Hz, 1H), 8.37 (td, *J* = 7.9, 1.7 Hz, 1H), 7.93 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.93 – 6.99 (m, 1H), 7.03 (s, 2H), 4.77 (s, 2H), 2.41 (s, 6H), 2.29 (s, 3H).
^{13}C-NMR	(75 MHz, MeOD) δ 151.3, 146.4, 144.4, 139.8, 132.8, 131.8, 127.5, 127.3, 52.7, 20.8, 18.0.
GC-MS (freebase)	t_R = 9.839 min, (EI, 70 eV): *m/z* = 226 [M^+], 211, 196, 181, 148, 134, 120, 107, 93, 79, 65, 51.
HRMS	Calcd. for $C_{15}H_{19}N_2$ 227.1543; found: 227.1543; Calcd. for $C_{15}H_{25}N_2$ 223.2012; found: 223.2011.

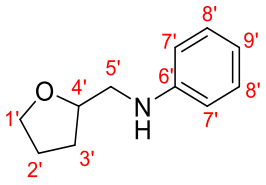
N-(2-Furanylmethyl)aniline (**2e**)



$C_{11}H_{11}NO$

173.22 g/mol

Yield 88.8 mg, 0.51 mmol (99%); Selectivity: 81%

Only detectable side product: 

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.38 (dd, *J* = 1.9, 0.8 Hz, 1H, 1), 7.20 (qd, *J* = 6.6, 6.1, 1.7 Hz, 3H, 8), 6.76 (t, *J* = 7.3 Hz, 1H, 9), 6.73 – 6.62 (m, 2H, 7), 6.34 (dd, *J* = 3.2, 1.9 Hz, 1H, 2), 6.25 (dd, *J* = 3.2, 0.9 Hz, 1H, 3), 4.33 (s, 2H, 5).

Side product (400 MHz, $CDCl_3$) δ 7.18 – 7.15 (m, 2H, 8'), 6.67 – 6.63 (m, 3H, 7'/9'), 4.15 (qd, *J* = 7.2, 3.8 Hz, 1H, 4'), 3.91 (dt, *J* = 8.3, 6.7 Hz, 1H, 1'), 3.80 (dt, *J* = 8.2, 6.8 Hz, 1H, 1'), 3.28 (dd, *J* = 12.3, 3.8 Hz, 1H, 5'), 3.10 (dd, *J* = 12.3, 7.5 Hz, 1H, 5'), 2.10 – 2.00 (m, 1H, 3'), 1.99 – 1.89 (m, 2H, 2'), 1.67 (ddt, *J* = 11.6, 8.3, 7.0 Hz, 1H, 3').

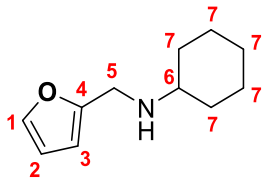
^{13}C-NMR (101 MHz, $CDCl_3$) δ 152.9 (6), 147.8 (4), 142.0 (1), 129.4 (8), 118.1 (9), 113.3 (7), 110.5 (2), 107.1 (3), 41.6 (5).

Side product (101 MHz, $CDCl_3$) δ 148.5 (6'), 129.3 (8'), 117.6 (9'), 113.2 (7'), 77.7 (4'), 68.2 (1'), 48.3 (5'), 29.2 (3'), 25.9 (2').

GC-MS t_R = 7.97 min, (EI, 70 eV): *m/z* = 173 [M^+], 144, 130, 115, 104, 91, 81, 65, 53.

Analytical data were in full agreement with M. L. Kantam, G. T. Venkanna, C. Sridhar, B. Sreedhar, B. M. Choudary, *J. Org. Chem.* **2006**, *71*, 9522.

N-(2-Furanylmethyl)cyclohexylamine (**2f**)

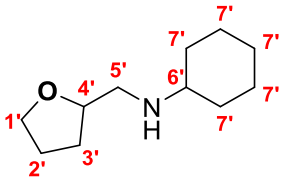


$C_{11}H_{17}NO$

179.26 g/mol

Yield 58.8 mg, 0.33 mmol (67%); Selectivity 53%

Only detectable side product:



^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.34 (dd, *J* = 1.9, 0.8 Hz, 1H, 1), 6.29 (dd, *J* = 3.2, 1.9 Hz, 1H, 2), 6.15 (d, *J* = 3.1 Hz, 1H, 3), 3.80 (s, 2H, 5), 2.44 (tt, *J* = 10.4, 3.8 Hz, 1H, 6), 1.91 – 1.83 (m, 5H, 7/7'), 1.72 (dt, J = 12.5, 3.6 Hz, 4H, 7/7'), 1.63 – 1.57 (m, 2H, 7/7'), 1.30 – 1.02 (m, 8H, 7/7').

Side product (400 MHz, $CDCl_3$) δ 3.99 (ddt, J = 11.1, 7.4, 3.7 Hz, 1H, 4'), 3.84 (dt, J = 8.4, 6.7 Hz, 1H, 1'), 3.73 (dt, J = 8.2, 6.8 Hz, 1H, 1'), 2.74 (dd, J = 11.8, 3.7 Hz, 1H, 5'), 2.63 (dd, J = 11.8, 8.1 Hz, 1H, 5'), 2.44 (tt, J = 10.4, 3.8 Hz, 1H, 6'), 2.03 – 1.92 (m, 1H, 3'), 1.91 – 1.83 (m, 2H, 2'), 1.91 – 1.83 (m, 5H, 7/7'), 1.72 (dt, J = 12.5, 3.6 Hz, 4H, 7/7'), 1.63 – 1.57 (m, 2H, 7/7'), 1.57 – 1.47 (m, 1H, 3'), 1.30 – 1.02 (m, 8H, 7/7').

^{13}C-NMR (101 MHz, $CDCl_3$) δ 154.4 (4), 141.8 (1), 110.2 (3), 106.7 (2), 55.9 (6), 43.5 (5), 33.5 (7/7'), 33.5 (7/7'), 33.4 (7/7'), 26.3 (7/7'), 25.2 (7/7'), 25.2 (7/7'), 25.1 (7/7').

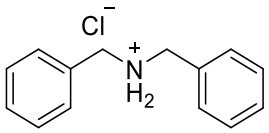
Side product (101 MHz, $CDCl_3$) δ 78.6 (4'), 68.0 (1'), 57.1 (6'), 51.6 (5'), 33.5 (7/7'), 33.5 (7/7'), 33.4 (7/7'), 29.6 (3'), 26.3 (7/7'), 25.9 (2'), 25.2 (7/7'), 25.2 (7/7'), 25.1 (7/7').

GC-MS t_R = 7.24 min, (EI, 70 eV): *m/z* = 179 [M^+], 150, 136, 122, 96, 81, 67, 53.

Side product: t_R = 7.65 min, (EI, 70 eV): *m/z* = 183 [M^+], 140, 122, 112, 105, 96, 83, 68, 55.

HRMS	Calcd. for $C_{11}H_{18}NO$ 180,1383; found: 180.1386;
	Calcd. for $C_{11}H_{22}NO$ (side product) 184,1696; found: 184.1700.

N,*N*-Dibenzylamine hydrochloride (**2g**)



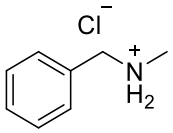
$C_{14}H_{16}ClN$

233.10 g/mol

Yield	49.0 mg, 0.21 mmol (84%)
^{1}H-NMR	(400 MHz, MeOD) δ 7.55 – 7.49 (m, 4H), 7.49 – 7.44 (m, 6H), 4.25 (s, 4H).
^{13}C-NMR	(101 MHz, MeOD) δ 132.4, 131.1, 130.7, 130.3, 52.0.
GC-MS (freebase)	t_R = 10.9 min, (EI, 70 eV): *m/z* = 196 [M-H$^+$], 179, 165, 152, 139, 120, 106, 91, 77, 65 ,51.

Analytical data were in full agreement with L. Xing, C. Cheng, R. Zhu, B. Zhang, X. Wang, Y. Hu, *Tetrahedron* **2008**, *64*, 11783.

N-Benzylmethylamine hydrochloride (**2h**)



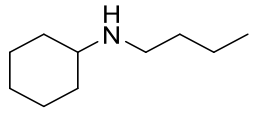
$C_8H_{12}ClN$

157.64 g/mol

Yield	52.7 mg, 0.33 mmol (63%)
^{1}H-NMR	(400 MHz, MeOD) δ 7.53 – 7.43 (m, 5H), 4.19 (s, 2H), 2.72 (s, 3H).
^{13}C-NMR	(101 MHz, MeOD) δ 132.56, 130.90, 130.72, 130.31, 53.61, 33.12.
GC-MS	t_R = 5.22 min, (EI, 70 eV): *m/z* = 120 [M$^+$], 104, 91, 78, 65, 51.

Analytical data were in full agreement with N. L. Lampland, M. Hovey, D. Mukherjee, A. D. Sadow, *ACS Catal.* **2015**, *5*, 4219.

N-Butyl-cyclohexylamine (**2i**)



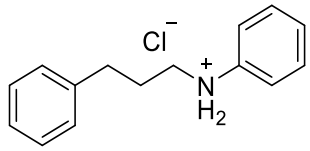
$C_{10}H_{21}N$

155.29 g/mol

Yield	72.0 mg, 0.46 mmol (92%)
^{1}H-NMR	(400 MHz, MeOD) δ 3.12 – 2.95 (m, 3H), 2.20 – 2.03 (m, 2H), 1.93 – 1.82 (m, 2H), 1.78 – 1.61 (m, 3H), 1.45 (dt, J = 15.1, 7.5 Hz, 2H), 1.42 – 1.31 (m, 4H), 1.31 – 1.15 (m, 1H), 0.99 (t, *J* = 7.4 Hz, 3H).
^{13}C-NMR	(101 MHz, MeOD) δ 58.39, 45.58, 30.35, 29.52, 26.12, 25.48, 20.90, 13.92.
GC-MS	t_R = 6.00 min, (EI, 70 eV): *m/z* = 155 [M^+], 126, 112, 98, 84, 70, 56.

Analytical data were in full agreement with R. Nacario, S. Kotakonda, D. M. D. Fouchard, L. M. V. Tillekeratne, R. A. Hudson, *Org. Lett.* **2005**, *7*, 471.

N-(3-Phenylpropyl)aniline hydrochloride (**2j**)

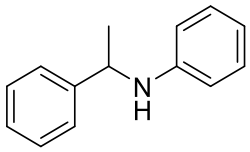


$C_{15}H_{18}ClN$

247.77 g/mol

Yield	58.2 mg, 0.23 mmol (96%)
^{1}H-NMR	(300 MHz, MeOD) δ 7.69 – 7.46 (m, 5H), 7.34 – 7.17 (m, 5H), 3.53 – 3.36 (m, 2H), 2.75 (t, *J* = 7.6 Hz, 2H), 2.14 – 1.98 (m, 2H).
^{13}C-NMR	(75 MHz, MeOD) δ 141.5, 136.7, 131.6, 131.1, 129.7, 129.4, 127.5, 123.8, 52.9, 33.4, 28.9.
GC-MS (freebase)	t_R = 9.88 min, (EI, 70 eV): *m/z* = 211 [M^+], 118, 106, 91, 77, 65, 51.
HRMS	Calcd. for $C_{15}H_{18}N$ 212.1434; found: 212.1436.
IR	3370 (b), 3063 (w), 3026 (m), 2870 (m), 2646 (m), 2017 (m), 1603 (m), 1491 (m), 749 (s), 690 (s) cm^{-1}.

N-(1-Phenylethyl)aniline (**2k**)



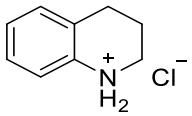
$C_{14}H_{15}N$

197.28 g/mol

Yield	87.5 mg, 0.44 mmol (89%) Starting material could not be separated (5%)
^{1}H-NMR	(400 MHz, $CDCl_3$) δ 7.41 – 7.37 (m, 2H), 7.38 – 7.29 (m, 2H), 7.28 – 7.22 (m, 1H), 7.11 (dd, J = 8.6, 7.3 Hz, 2H), 6.68 (tt, J = 7.3, 1.1 Hz, 1H), 6.57 – 6.52 (m, 2H), 4.51 (q, J = 6.7 Hz, 1H), 4.20 (brs, 1H), 1.54 (d, J = 6.7 Hz, 3H).
^{13}C-NMR	(101 MHz, $CDCl_3$) δ 147.2, 145.2, 129.2, 128.8, 127.0, 126.0, 117.5, 113.6, 53.7, 25.1.
GC-MS	t_R = 8.83 min, (EI, 70 eV): *m/z* = 197 [M^+], 182, 167, 152, 120, 105, 93, 77, 65, 51.

Analytical data were in full agreement with A. H. Vetter, A. Berkessel, *Synthesis* **1995**, 419.

1,2,3,4-Tetrahydroquinoline hydrochloride (**2l**)



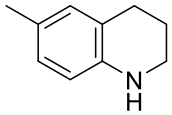
$C_9H_{12}ClN$

169.65 g/mol

Yield	43.8 mg, 0.26 mmol (99%)
^{1}H-NMR	(300 MHz, $CDCl_3$) δ 7.46 – 7.33 (m, 3H), 7.30 (dd, *J* = 8.2, 1.7 Hz, 1H), 3.56 – 3.50 (m, 2H), 2.97 (t, *J* = 6.5 Hz, 2H), 2.25 – 2.07 (m, 2H).
^{13}C-NMR	(75 MHz, $CDCl_3$) δ 132.9, 132.2, 131.3, 130.4, 128.7, 124.1, 43.8, 25.8, 20.7.
GC-MS (freebase)	t_R = 7.01 min, (EI, 70 eV): *m/z* = 132 [M^+-H], 118, 104, 91, 77, 65, 51.

Analytical data were in full agreement with M. Ortiz-Marciales, L. D. Rivera, M. de Jesús, S. Espinosa, J. A. Benjamin, O. E. Casanova, I. G. Figueroa, S. Rodríguez, W. Correa, *J. Org. Chem.* **2005**, *70*, 10132.

6-Methyl-1,2,3,4-tetrahydroquinoline (**2m**)



$C_{10}H_{13}N$

147.22 g/mol

Yield 53.2 mg, 0.36 mmol (73%)

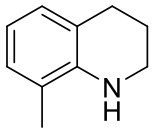
^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.82 – 6.77 (m, 2H), 6.43(d, *J* = 8.6 Hz, 1H), 3.48 (brs, 1H), 3.31 – 3.25 (m, 2H), 2.75 (t, *J* = 6.4 Hz, 2H), 2.22 (s, 3H), 2.00 – 1.89 (m, 2H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ 142.4, 130.2, 127.4, 126.5, 121.8, 114.7, 42.3, 27.0, 22.5, 20.5.

GC-MS t_R = 7.53 min, (EI, 70 eV): *m/z* = 147 [M^+], 132, 117, 103, 91, 77, 65, 51.

Analytical data were in full agreement with R. Adam, J. R. Cabrero-Antonino, A. Spannenberg, K. Junge, R. Jackstell, M. Beller, *Angew. Chem. Int. Ed.* **2017**, *56*, 3216.

8-Methyl-1,2,3,4-tetrahydroquinoline (**2n**)



$C_{10}H_{13}N$

147.22 g/mol

Yield 28.4 mg, 0.19 mmol (39%)

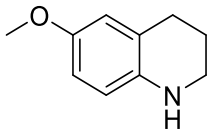
^{1}H-NMR (300 MHz, $CDCl_3$) δ 6.92 – 6.82 (m, 2H), 6.57 (t, J = 7.4 Hz, 1H), 3.59 (brs, 1H), 3.41 – 3.35 (m, 2H), 2.80 (t, J = 6.4 Hz, 2H), 2.09 (s, 3H), 2.00 – 1.90 (m, 2H).

^{13}C-NMR (75 MHz, $CDCl_3$) δ 142.6, 128.0, 127.5, 121.5, 121.2, 116.7, 42.5, 27.4, 22.3, 17.3.

GC-MS t_R = 7.48 min, (EI, 70 eV): *m/z* = 147 [M^+], 132, 117, 103, 91, 77, 65, 51.

Analytical data were in full agreement with Y.-G. Ji, K. Wei, T. Liu, L. Wu, W.-H. Zhang, *Adv. Synth. Catal.* **2017**, *359*, 933..

6-Methoxy-1,2,3,4-tetrahydroquinoline (**2o**)



$C_{10}H_{13}NO$

163.22 g/mol

Yield 31.9 mg, 0.20 mmol (77%)

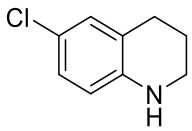
^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.62 – 6.55 (m, 2H), 6.45 (d, *J* = 8.5 Hz, 1H), 3.73 (s, 3H), 3.44 (brs, 1H), 3.26 (t, *J* = 5.4 Hz, 2H), 2.76 (t, *J* = 6.5 Hz, 2H), 1.98 – 1.89 (m, 2H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ 151.9, 139.0, 123.0, 115.7, 115.0, 113.0, 55.9, 42.5, 27.3, 22.6.

GC-MS t_R = 8.31 min, (EI, 70 eV): *m/z* = 163 [M^+], 148, 130, 118, 103, 91, 77, 65, 51.

Analytical data were in full agreement with R. Adam, J. R. Cabrero-Antonino, A. Spannenberg, K. Junge, R. Jackstell, M. Beller, *Angew. Chem. Int. Ed.* **2017**, *56*, 3216.

6-Chloro-1,2,3,4-tetrahydroquinoline (**2p**)



$C_9H_{10}ClN$

167.64 g/mol

Yield 51.7 mg, 0.31 mmol (62%)

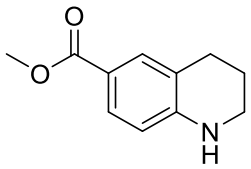
^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.94 – 6.84 (m, 2H), 6.38 (dd, *J* = 7.9, 0.9 Hz, 1H), 3.82 (brs, 1H), 3.28 (t, *J* = 5.5 Hz, 2H), 2.72 (t, *J* = 6.4 Hz, 2H), 1.97 – 1.84 (m, 2H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ 143.4, 129.2, 126.6, 123.0, 121.3, 115.2, 42.0, 27.0, 21.9.

GC-MS t_R = 8.35 min, (EI, 70 eV): *m/z* = 167 [M^+], 152, 130, 117, 103, 89 ,77, 65, 51.

Analytical data were in full agreement with R. Adam, J. R. Cabrero-Antonino, A. Spannenberg, K. Junge, R. Jackstell, M. Beller, *Angew. Chem. Int. Ed.* **2017**, *56*, 3216.

Methyl 1,2,3,4-tetrahydroquinoline-6-carboxylate (**2q**)



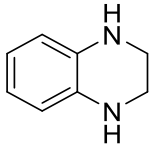
$C_{11}H_{13}NO_2$

191.23 g/mol

Yield	93.4 mg, 0.49 mmol (98%)
^{1}H-NMR	(300 MHz, $CDCl_3$) δ 7.66 – 7.61 (m, 2H), 6.41 – 6.37 (m, 1H), 4.35 (brs, 1H), 3.83 (s, 3H), 3.35 (t, J = 5.7 Hz, 2H), 2.76 (t, J = 6.3 Hz, 2H), 2.00 – 1.85 (m, 2H).
^{13}C-NMR	(75 MHz, $CDCl_3$) δ 167.6, 148.8, 131.4, 129.2, 120.0, 117.6, 112.8, 51.6, 41.8, 27.0, 21.5.
GC-MS	t_R = 9.68 min, (EI, 70 eV): *m/z* = 191 [M^+], 176, 160, 144, 132, 117, 104, 89, 77, 64, 51.

Analytical data were in full agreement with R. Adam, J. R. Cabrero-Antonino, A. Spannenberg, K. Junge, R. Jackstell, M. Beller, *Angew. Chem. Int. Ed.* **2017**, *56*, 3216.

1,2,3,4-tetrahydroquinoxaline (**2r**)



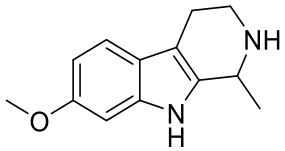
$C_8H_{10}N_2$

134.18 g/mol

Yield	64.2 mg, 0.48 mmol (95%)
^{1}H-NMR	(400 MHz, XX) δ 6.59 (dd, J = 5.8, 3.4 Hz, 2H), 6.50 (dd, J = 5.8, 3.4 Hz, 2H), 3.59 (brs, 2H), 3.42 (s, 4H).
^{13}C-NMR	(101 MHz, XX) δ 133.8, 118.9, 114.8, 41.5.
GC-MS	t_R = 7.94 min, (EI, 70 eV): *m/z* = 134 [M^+], 119, 104, 92, 77, 66, 51.

Analytical data were in full agreement with R. Adam, J. R. Cabrero-Antonino, A. Spannenberg, K. Junge, R. Jackstell, M. Beller, *Angew. Chem. Int. Ed.* **2017**, *56*, 3216.

Tetrahydroharmine (**2s**)



$C_{13}H_{16}N_2O$

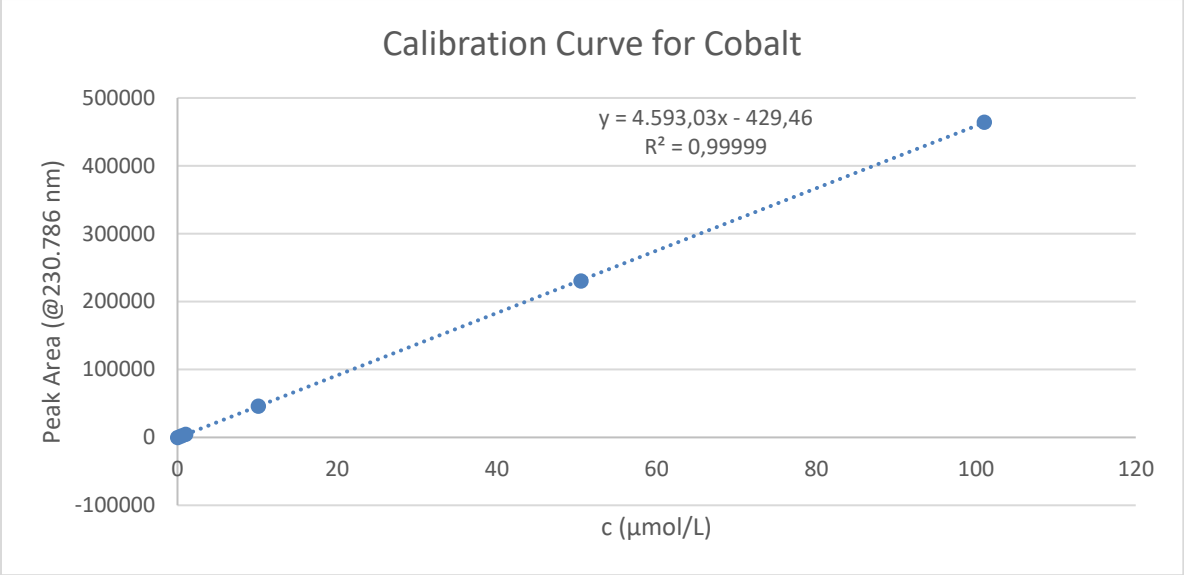
216.28 g/mol

Yield	104.6 mg, 0.48 mmol (97%)
^{1}H-NMR	(300 MHz, $CDCl_3$) δ 8.06 (brs, 1H), 7.33 (d, J = 8.5 Hz, 1H), 6.83 (d, J = 2.2 Hz, 1H), 6.75 (dd, J = 8.6, 2.3 Hz, 1H), 4.14 (q, J = 6.6 Hz, 1H), 3.81 (s, 3H), 3.32 – 3.27 (m, 1H), 3.01 (ddd, J = 12.9, 8.6, 5.4 Hz, 1H), 2.80 – 2.66 (m, 2H), 2.52 (brs, 1H), 1.43 (d, J = 6.7 Hz, 3H).
^{13}C-NMR	(75 MHz, $CDCl_3$) δ 156.2, 136.5, 135.8, 122.0, 118.7, 108.9, 108.2, 95.2, 55.9, 48.3, 42.7, 22.7, 20.8.
GC-MS	t_R = 10.76 min, (EI, 70 eV): *m/z* = 216 [M^+], 201, 186, 172, 158, 144, 130, 115, 100, 89, 77, 63, 51.

Analytical data were in full agreement with J. Wu, D. Talwar, S. Johnston, M. Yan, J. Xiao, *Angew. Chem. Int. Ed.* **2013**, *52*, 6983..

5 ICP-OES measurement

The cobalt concentration in the organic layer after hydrogenation was determined by ICP-OES. Five stock solutions of $CoCl_2$ in 35% HNO_3 were prepared and a calibration curve was measured by integration of the emission signal of cobalt at 230.786 nm. Each data point corresponds to the mean value of three consecutive measurements correcting for the observed background signals.



For the actual measurement, styrene (0.25 mmol) was hydrogenated using 5 mol% of the cobalt nanoparticles (12.5 mmol/L Co) under standard conditions (2 bar H_2, 3 h in 1 ml THF). After reaction, two reaction vials were placed on separate neodymium magnets and allowed to settle down for 2 and 24 h respectively. The organic phase was removed with a Pasteur Pipette, the solvent removed under vacuum and the residue dissolved in 5 ml dilute HNO_3.

PBcat135_2h	Peak Area	c (µmol/L)
Run 1	41231	9,07
Run 2	42226	9,29
Run 3	41338,2	9,09
Average	41598,4	9,15
StdDev	546,15	0,12

PBcat135_24h	Peak Area	c (µmol/L)
Run 1	31624,5	6,98
Run 2	31439,7	6,94
Run 3	31299,3	6,91
Average	31454,5	6,94
StdDev	163,10	0,04

This results in a cobalt concentration of 45.75±0.6 and 34.7±0.2 µmol/L in the organic phase after 2 and 24 h settle time respectively, which corresponds to 0.37 and 0.28% of the cobalt concentration in the reaction vessel.

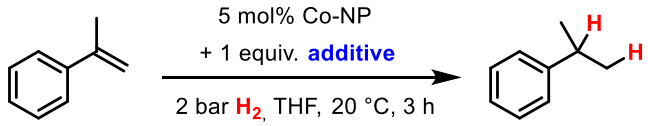
6 ICP-MS measurement

In preparation for the measurement, half of the vials were charged with styrene (1 mmol) and 5 mol% of the cobalt nanoparticles (12.5 mmol/L Co), the other vials omitting the cobalt catalyst (blank reaction solution). All were hydrogenated under standard conditions (2 bar H_2, 3 h in 4 ml THF). After the reaction, each vial was put on a neodymium magnet and the organic phase was transferred to a new vial, leaving behind most of the cobalt metal. The vials were washed twice with an additional 1 ml of ethyl acetate. To the first set of vials (Co-reaction and blank) was then added 1 ml saturated ammonium chloride solution which was extracted three times with ethyl acetate, the second set was eluted through a short silica plug inside a Pasteur pipette using ethyl acetate. The solvent was subsequently removed from all vials under vacuum and the residue dissolved in 50 ml dilute HNO_3.

Reactions	Peak Area	c (ng/mL)	nCo (nmol)
Extraction	838524.5	0.80	0.6780
Extraction (blank)	23595.3	0.02	0.01696
Silica	52582.7	0.05	0.0424
Silica (blank)	13541.0	0.01	0.00848

This results in a cobalt concentration of 165 nmol/L and 8.5 nmol/L in the organic phase after extraction and elution respectively, which corresponds to 13.2 and 0.68 ppm of the cobalt concentration in the reaction vessel.

7 Functional group tolerance tests



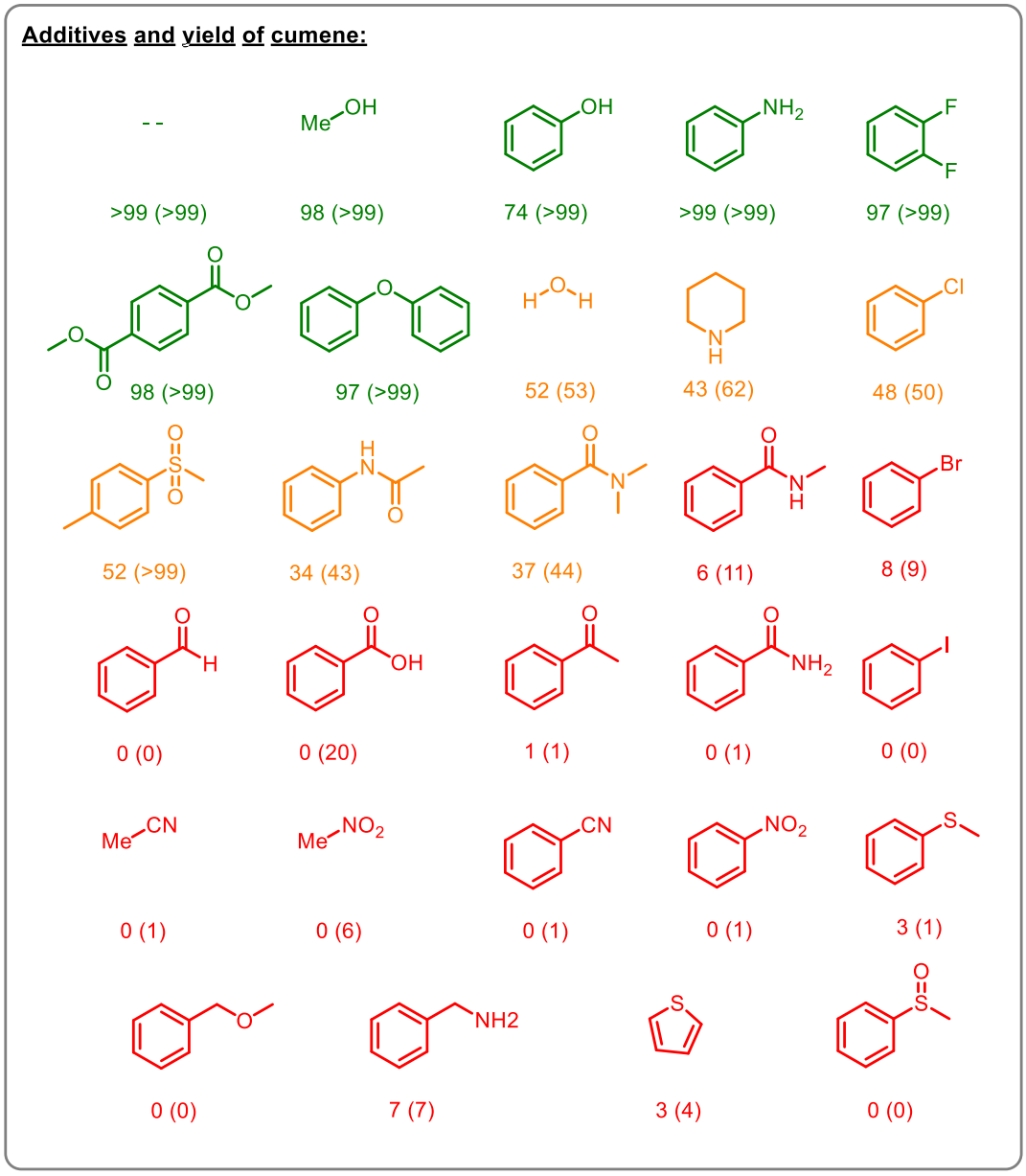


***Figure S1*:** Functional group tolerance of Co-NP catalyzed hydrogenation of α-Methylstyrene in presence of 1 equiv. additive. Standard conditions: 0.25 mmol substrate in 1 mL THF; yields of hydrogenation product (cumene) determined by quantitative GC vs. internal reference n-pentadecane. Conversion of α-Methylstyrene shown in parentheses.

8 Comparison of different Co-Np preparations

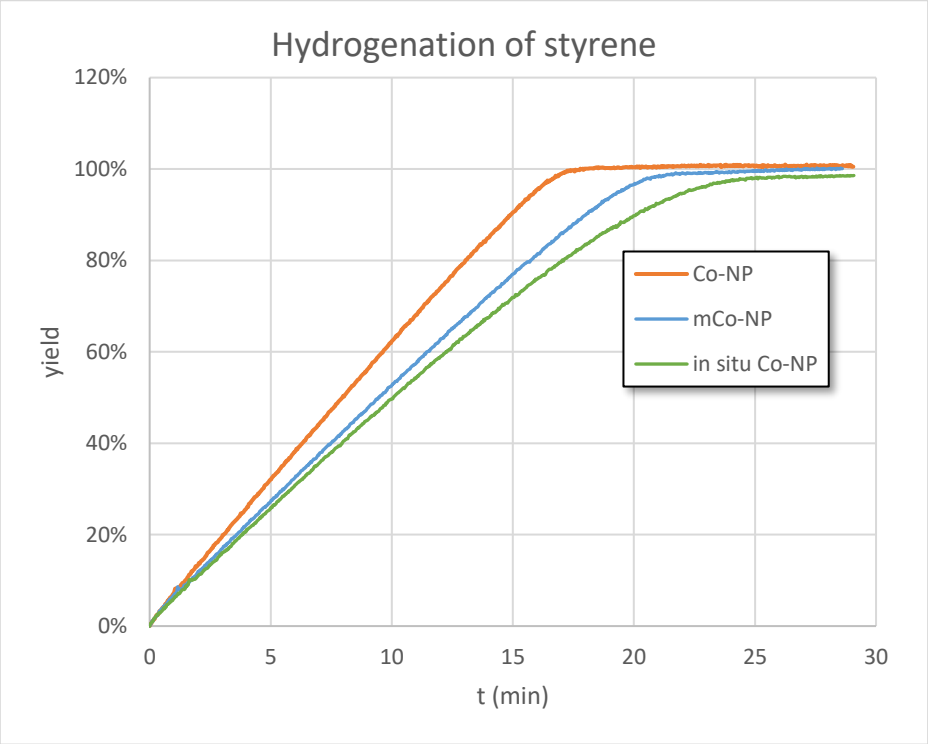


Figure S2. Hydrogenation of styrene using the nanoparticles isolated by centrifugation, separation by a magnet and using the *in situ* protocol. The conditions were 1.9 bar H_2, 5 mol% [Co], r.t., THF. The reaction yield was determined by measuring the consumption of H_2.

Kinetic experiments were carried out to compare the catalytic activity of the different catalyst systems described previously. **Figure S2** shows a similar catalytic activity of the various nanoparticles, yielding complete conversion after 17 to 24 minutes.

9 Recycling experiments

The reactions were set up according to the general hydrogenation procedure with styrene (0.5 mmol) as substrate in 2 ml THF. The hydrogenations were carried out for 30 min each (2 bar H_2, r.t., 5 mol% Co-NP). After reaction, the autoclave was introduced into the glovebox and the reaction vial put on top of a neodymium magnet (cylindrical, 10 x 20 mm (height x diameter), N45) for 5 min. The solvent was removed using a Pasteur pipette and the particles washed once with 2 ml THF. New substrate and solvent were added, the vial was put back into the autoclave and a new hydrogenation reaction started. The organic phase was analyzed using quantitative GC-FID. After nine consecutive reactions, the particles were dissolved in 1 mL THF and stirred inside the glovebox overnight. The next day, three more runs were carried out. After these three reactions the particles were stirred again inside the glovebox for another 72 hours before a last hydrogenation reaction was started.

10 Particle Analyses

Purity and crystallinity

The purity of the as-prepared Co(0) nanoparticles was proven by X-ray powder diffraction (XRD) after powder sintering (800 °C, Ar). This treatment ensured crystallization of all products including potentially amorphous residual components (e.g. oxides and hydroxides). Despite the resultant non-nanoparticulate state, the presence of pure cobalt (cubic modification as majority phase with traces of a hexagonal phase) and the absence of any cobalt oxide impurities was validated (Figure S2).

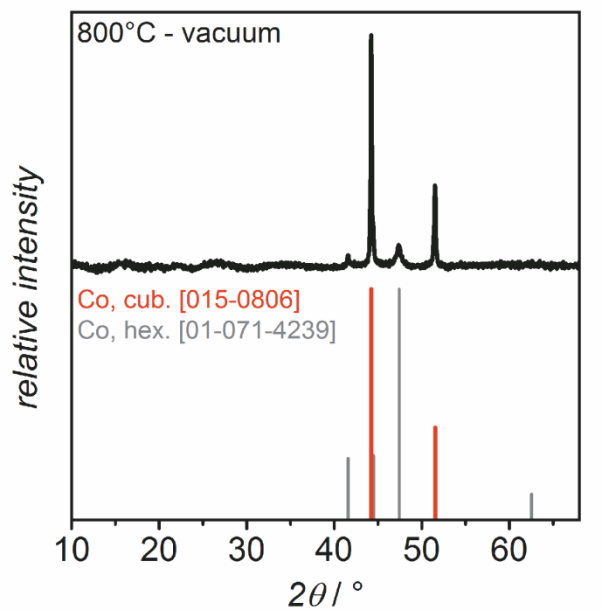


Figure S3. XRD Co(0) powder samples after annealing (800 °C, Ar).

Particle size distribution

Average particle diameters of the Co(0) nanoparticles before and after the hydrogenation reaction were calculated by statistical evaluation of >200 particles on TEM images using the ImageJ 1.47v software. Figure S2 shows the results for [NaNaph]-made Co(0) nanoparticles (Co-NPs) isolated by centrifugation. Figure S3 shows the results for *in situ*-generated cobalt nanoparticles (*in situ* Co-NPs). It should be noted that dynamic light scattering (DLS) as an alternative analytical tool gives less conclusive results due to the magnetic interaction of the nanoparticles.

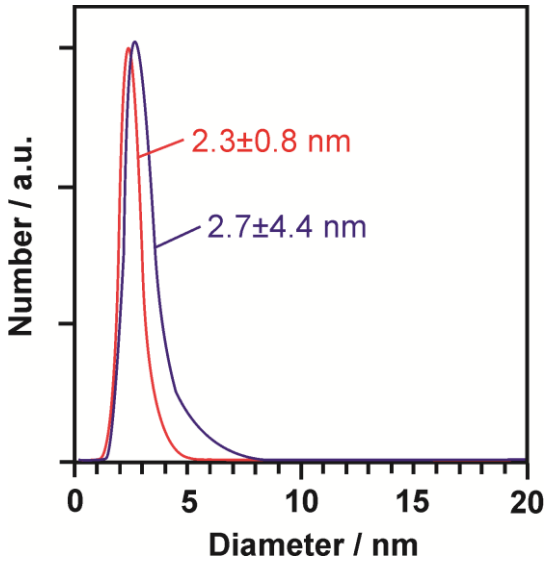


Figure S4. Particle size distribution according to statistical evaluation of TEM images (>200 particles) of cobalt nanoparticles (Co-NPs) before (red) and after (blue) hydrogenation reaction.

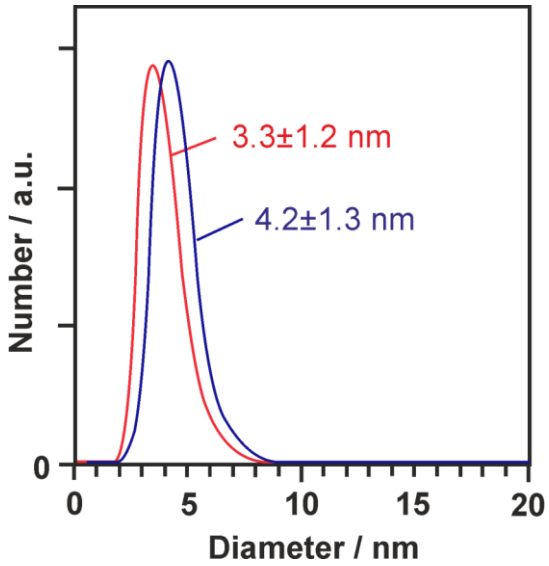


Figure S5. Particle size distribution according to statistical evaluation of TEM images (>200 particles) of *in situ* generated cobalt nanoparticles (*in situ* Co-NPs) before (red) and after (blue) hydrogenation reaction.

TEM Measurements

TEM images of Co(0) nanoparticles before and after the catalytical reaction are shown in Figure S5 and Figure S6 for ex situ and in situ generated nanoparticles.

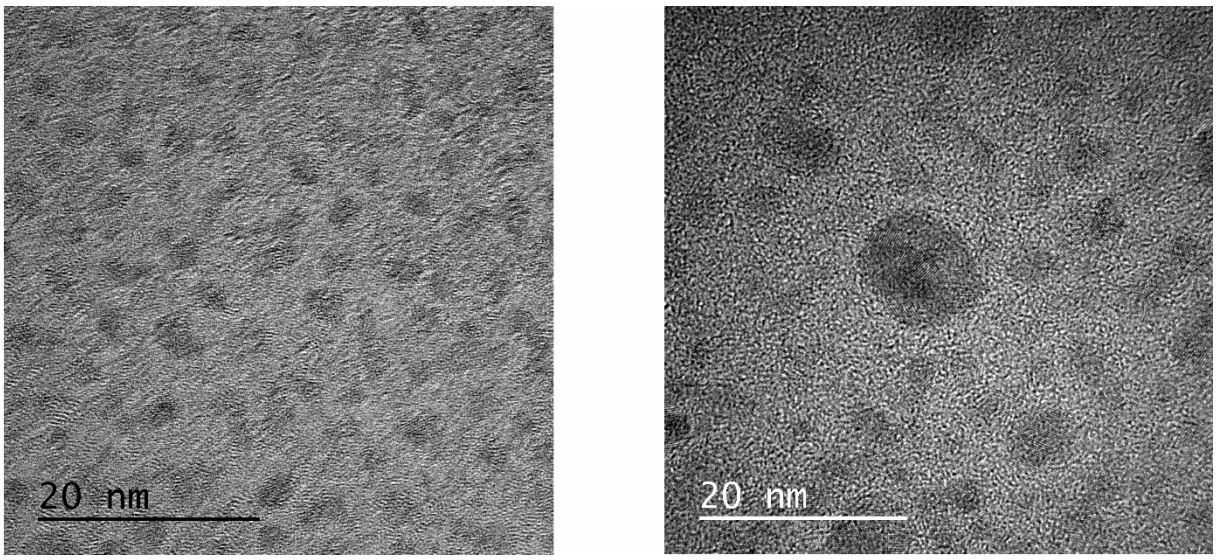


Figure S6. TEM measurement of cobalt nanoparticles (Co-NP) before (left) and after (right) hydrogenation reaction.

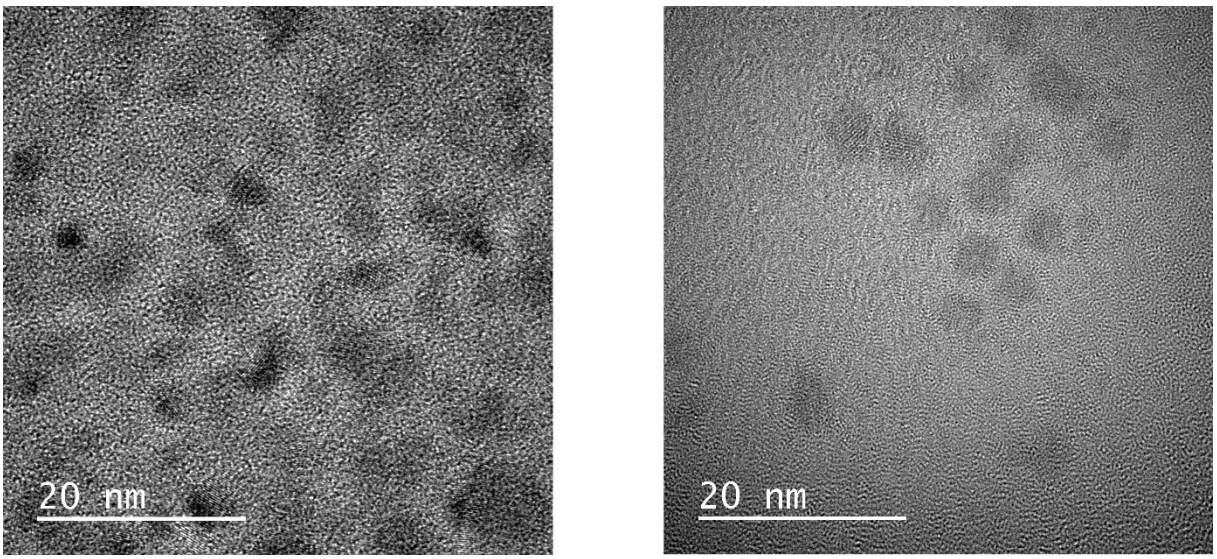
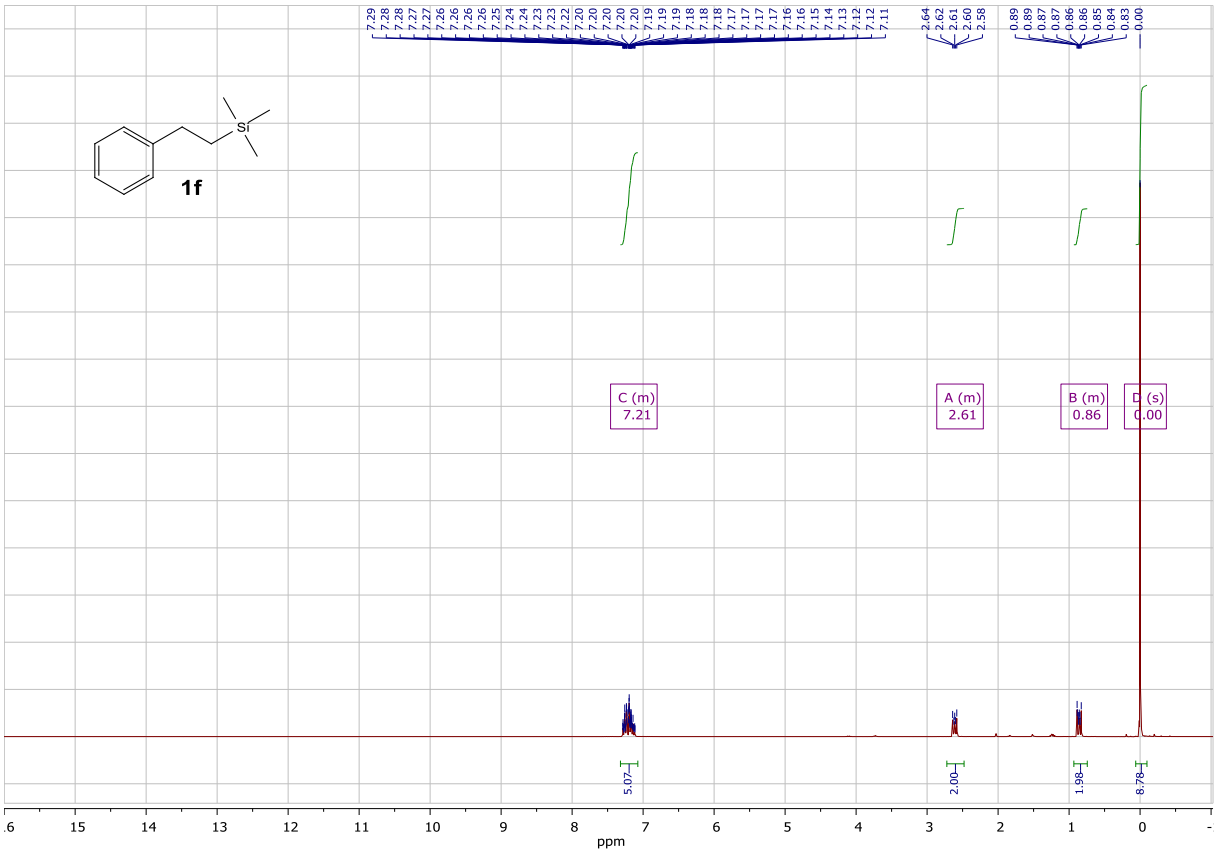
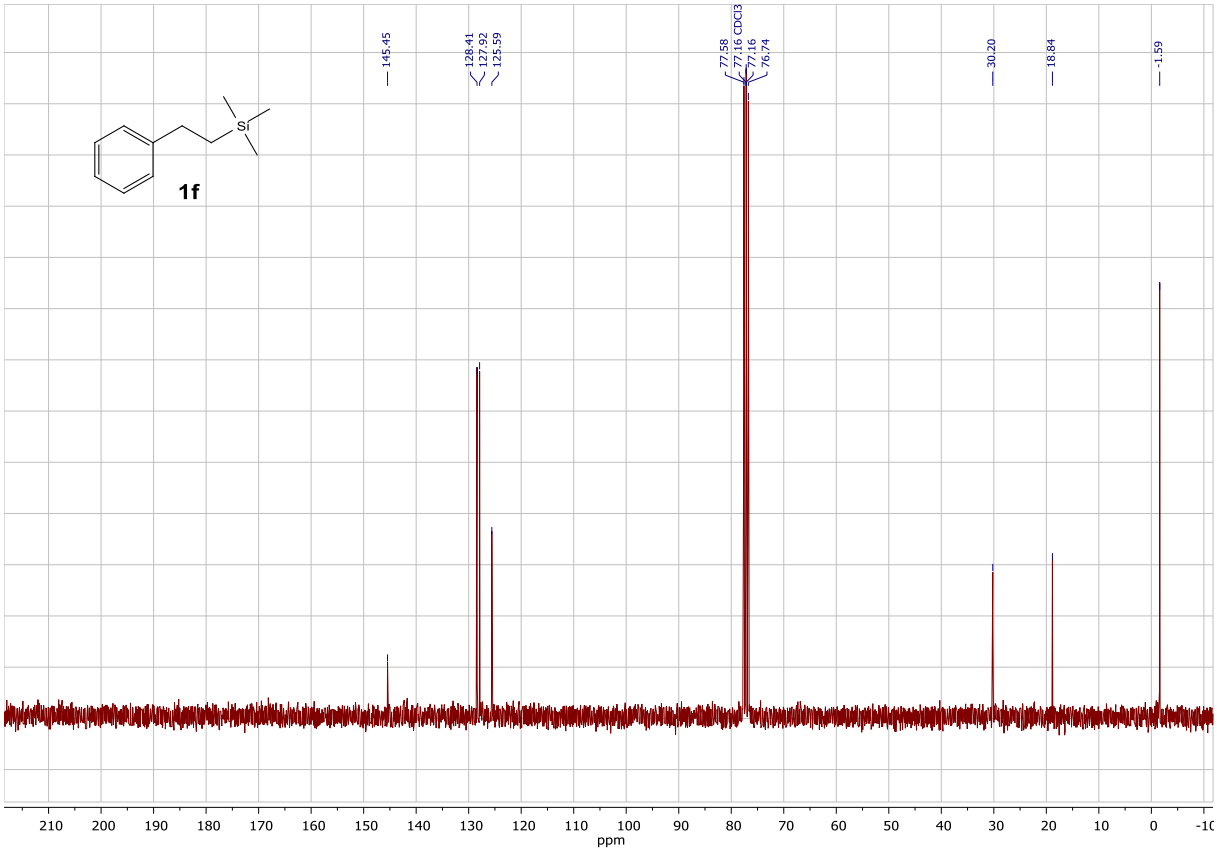
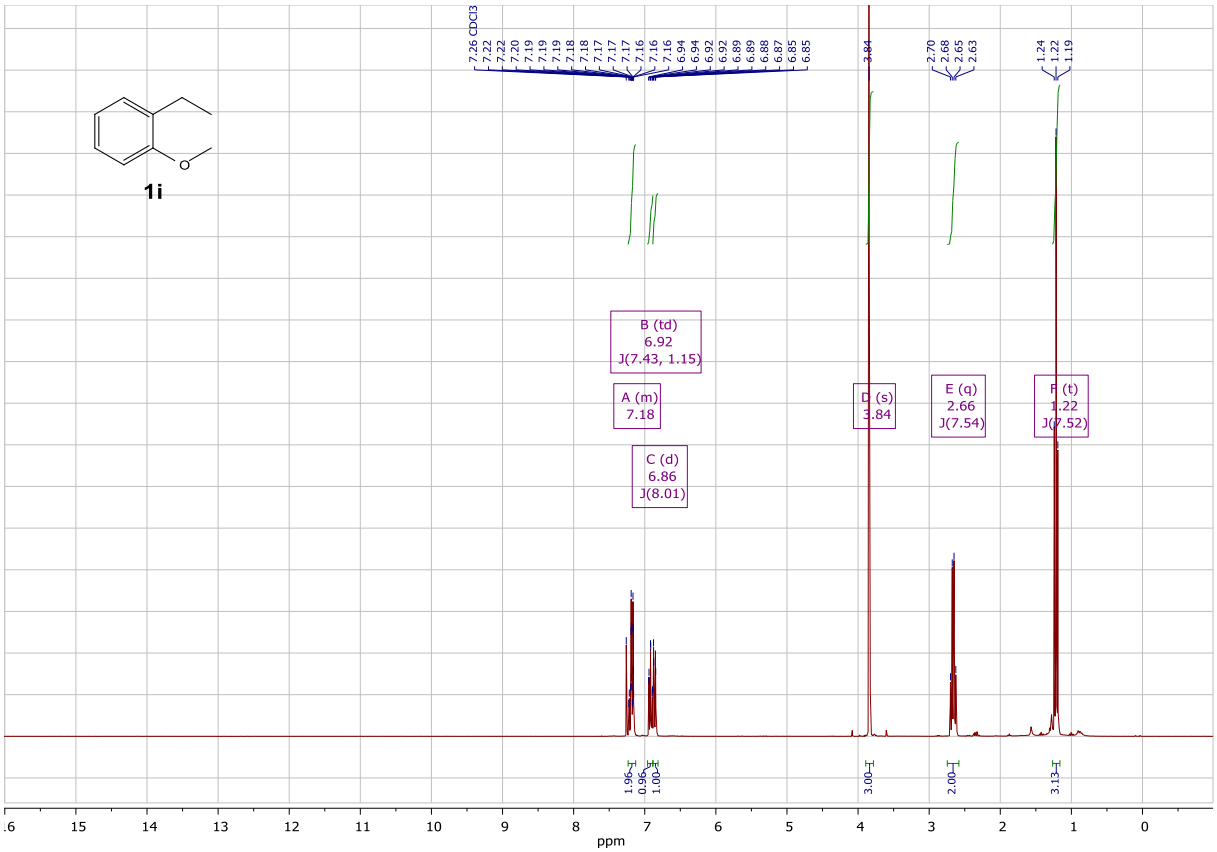


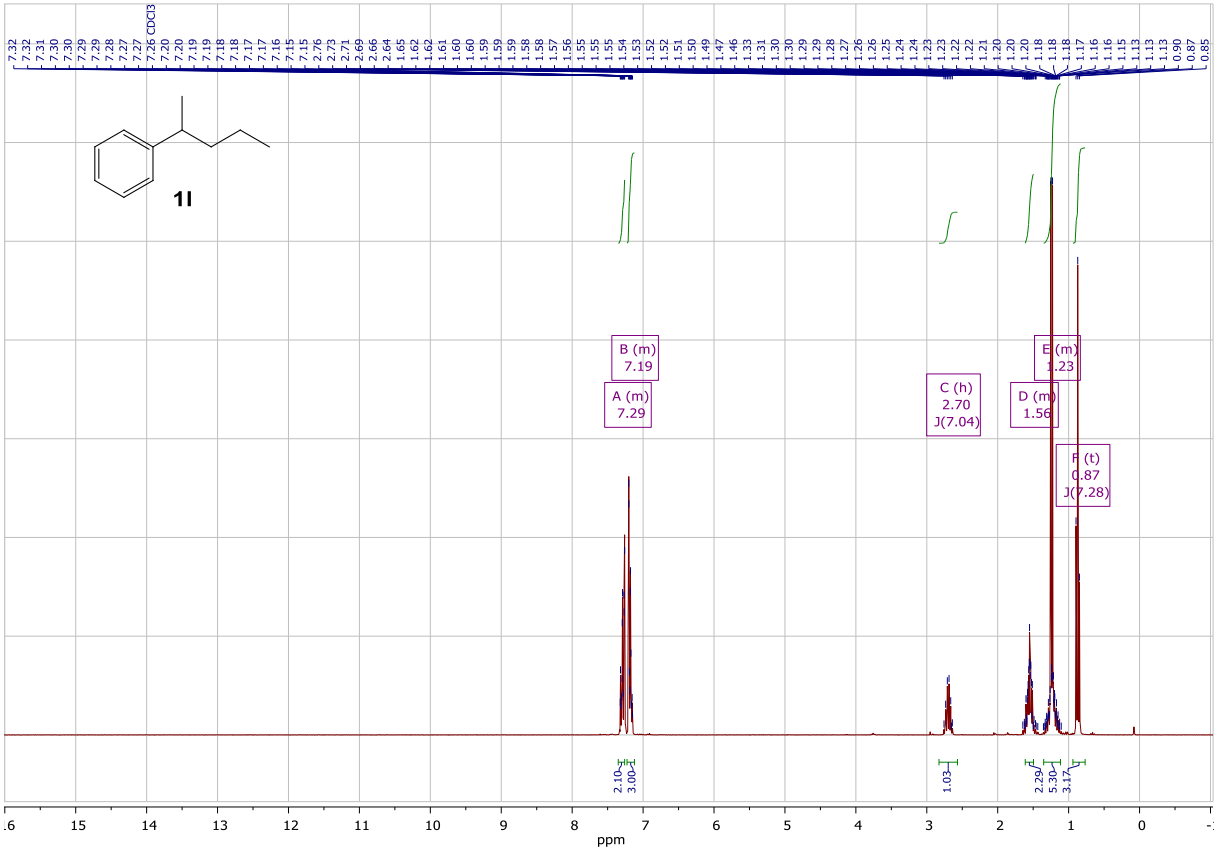
Figure S7. TEM measurement of in situ generated cobalt nanoparticles (*in situ* Co-NP) before (left) and after (right) hydrogenation reaction.

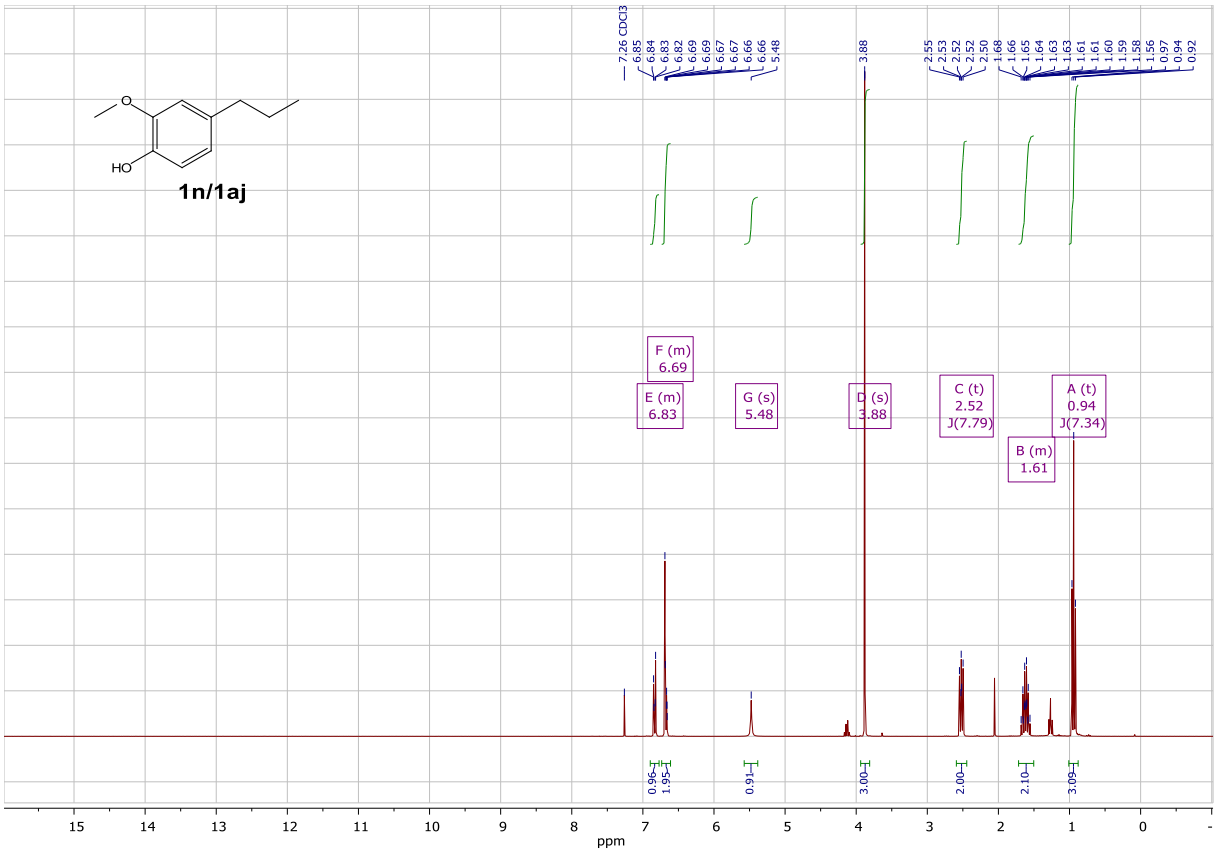
11 Selected NMR-Spectra

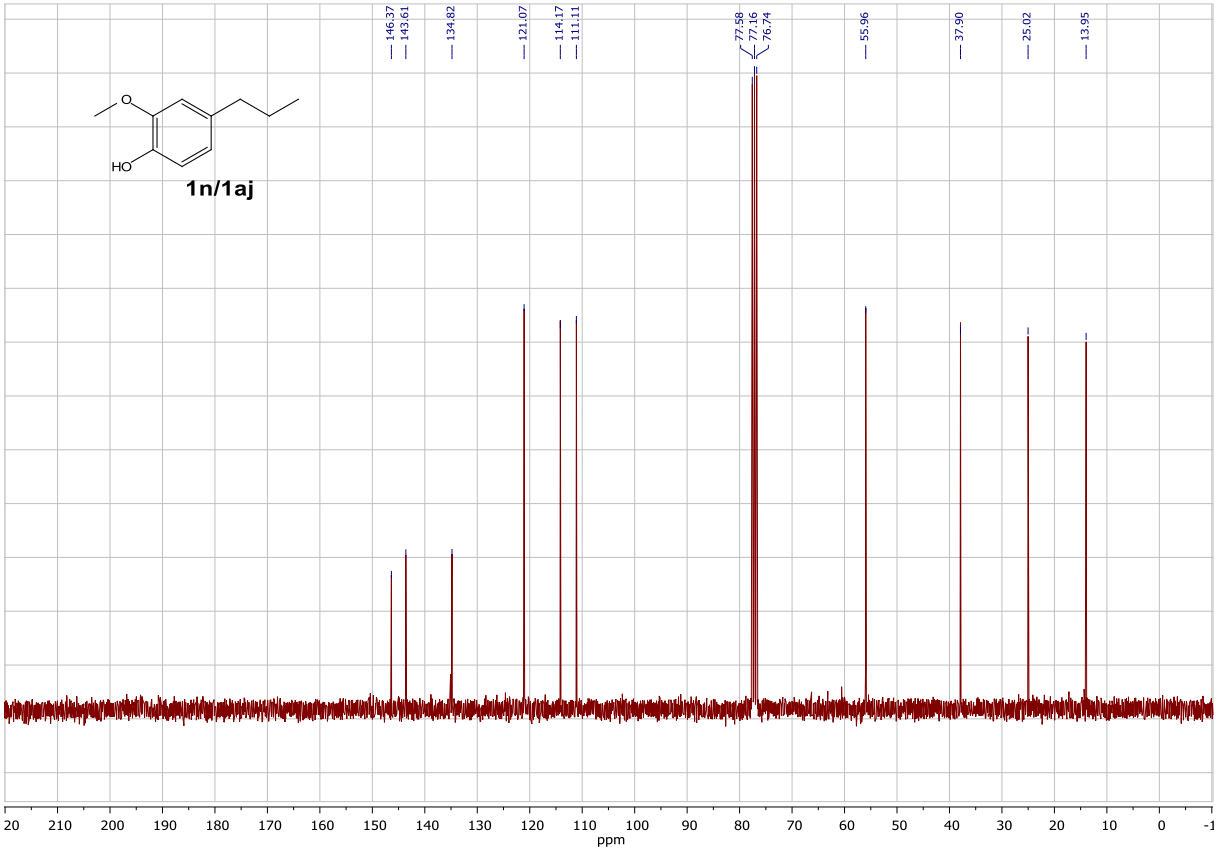


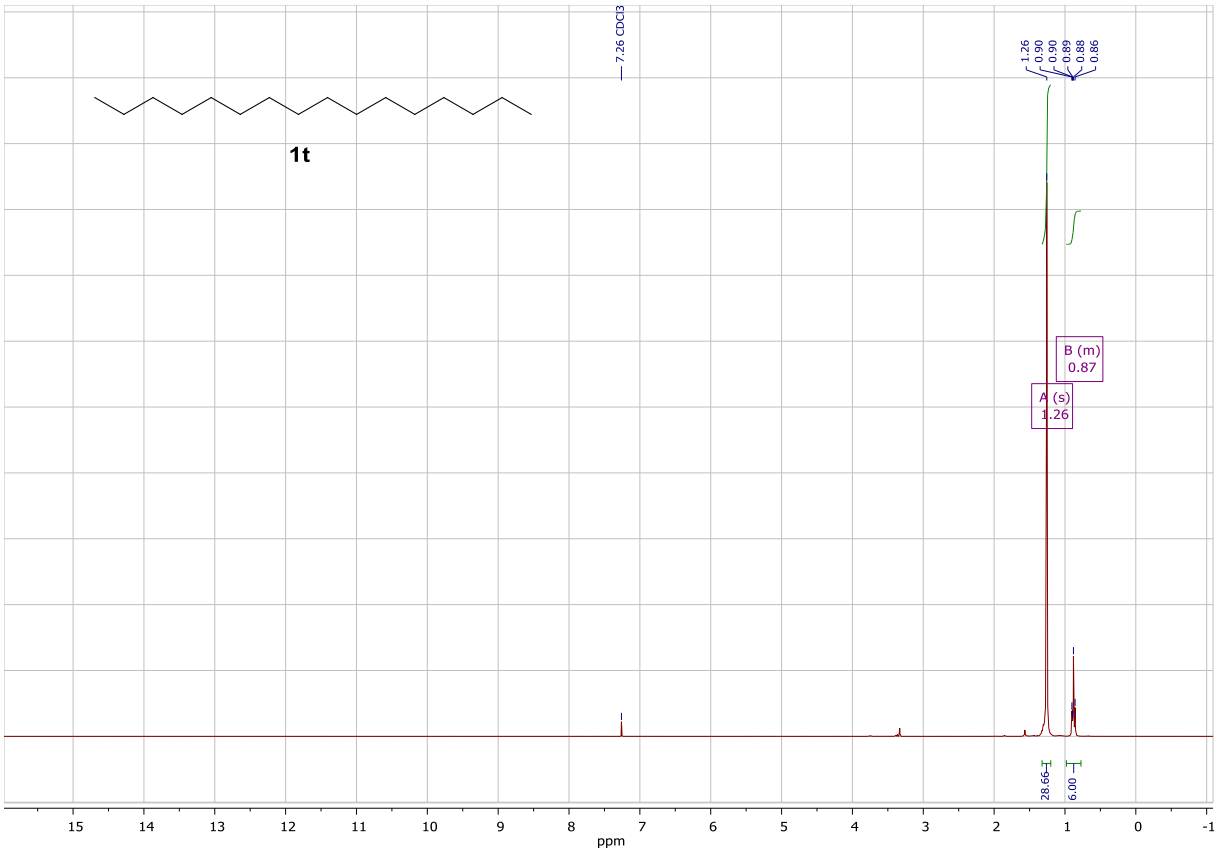


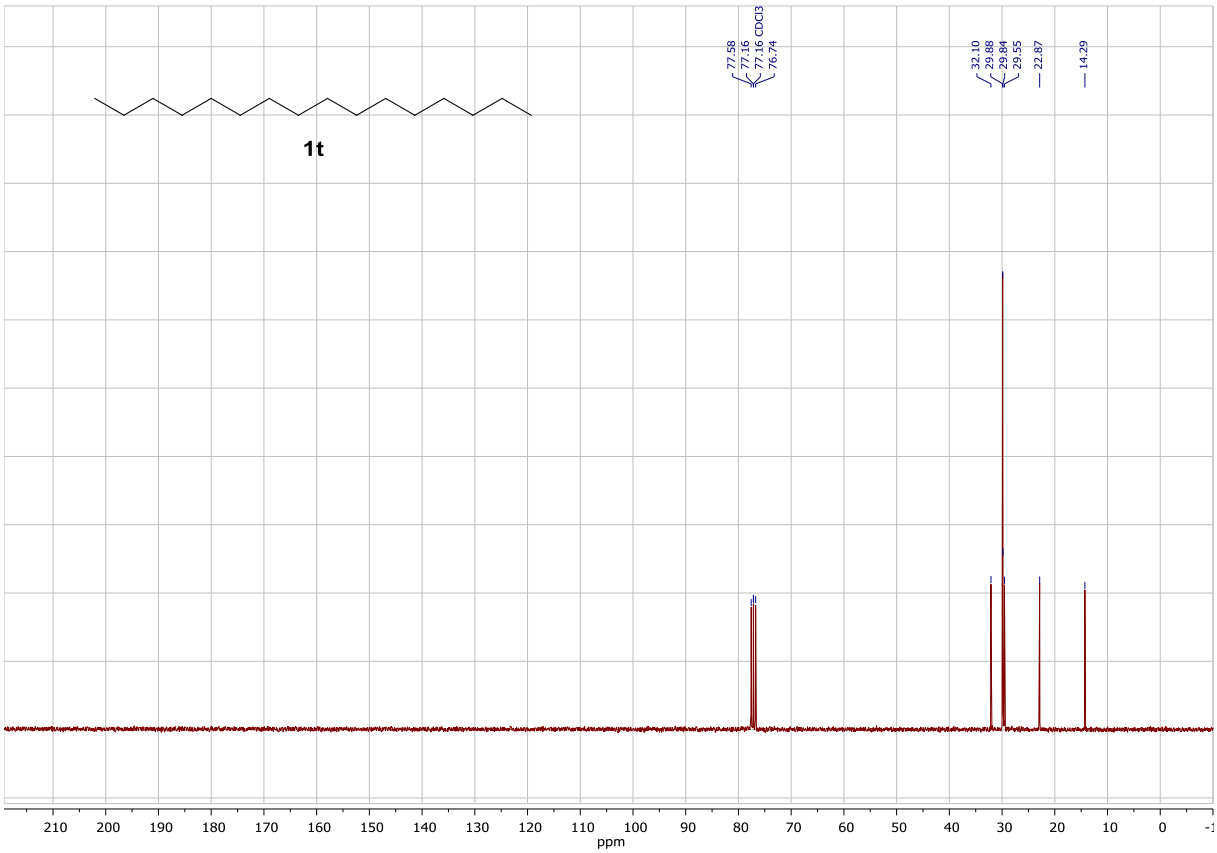

1i
B (td)
6.92
J(7.43, 1.15)
A (m)
7.18
C (d)
6.86
J(8.01)
D (s)
3.84
E (q)
2.66
J(7.54)
F (t)
1.22
J(7.52)
ppm

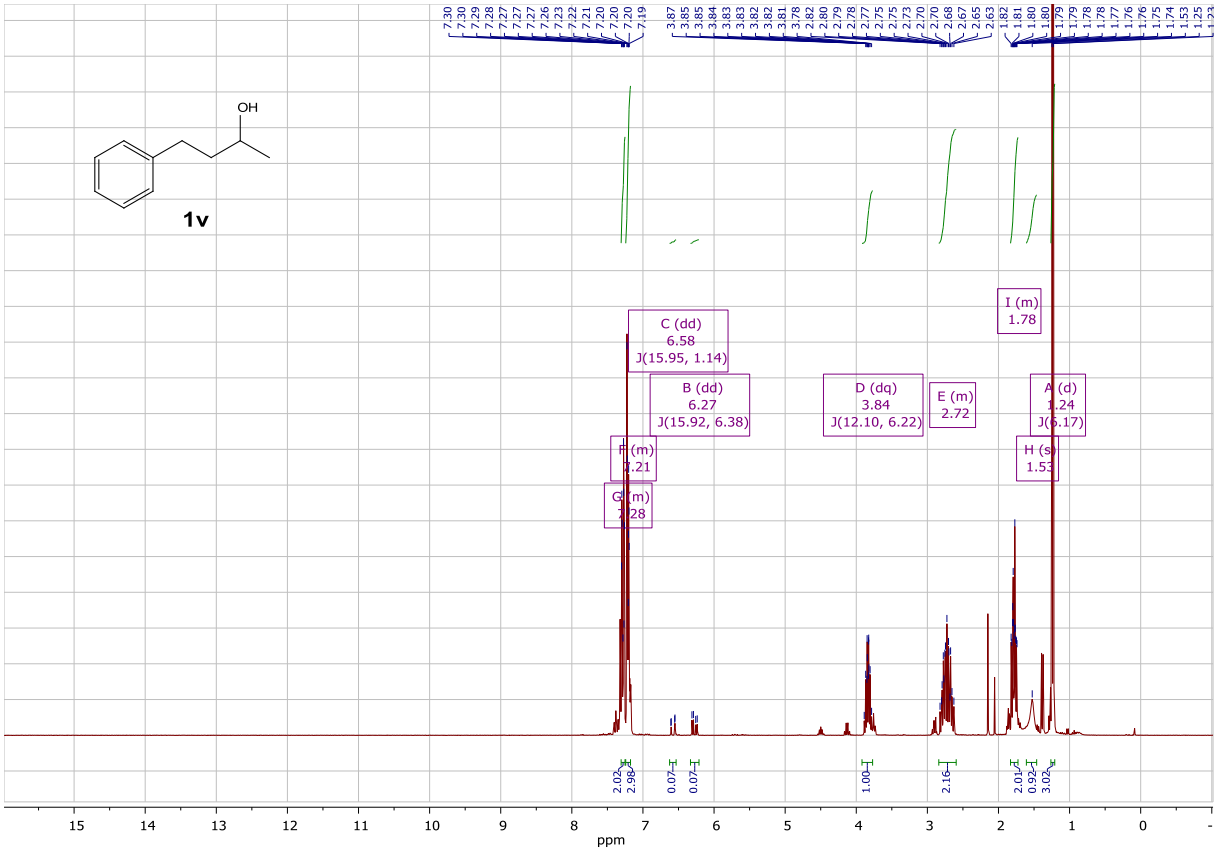

1l
B (m)
7.19
A (m)
7.29
C (h)
2.70
J(7.04)
D (m)
1.56
E (m)
1.23
F (t)
0.87
J(7.28)
ppm

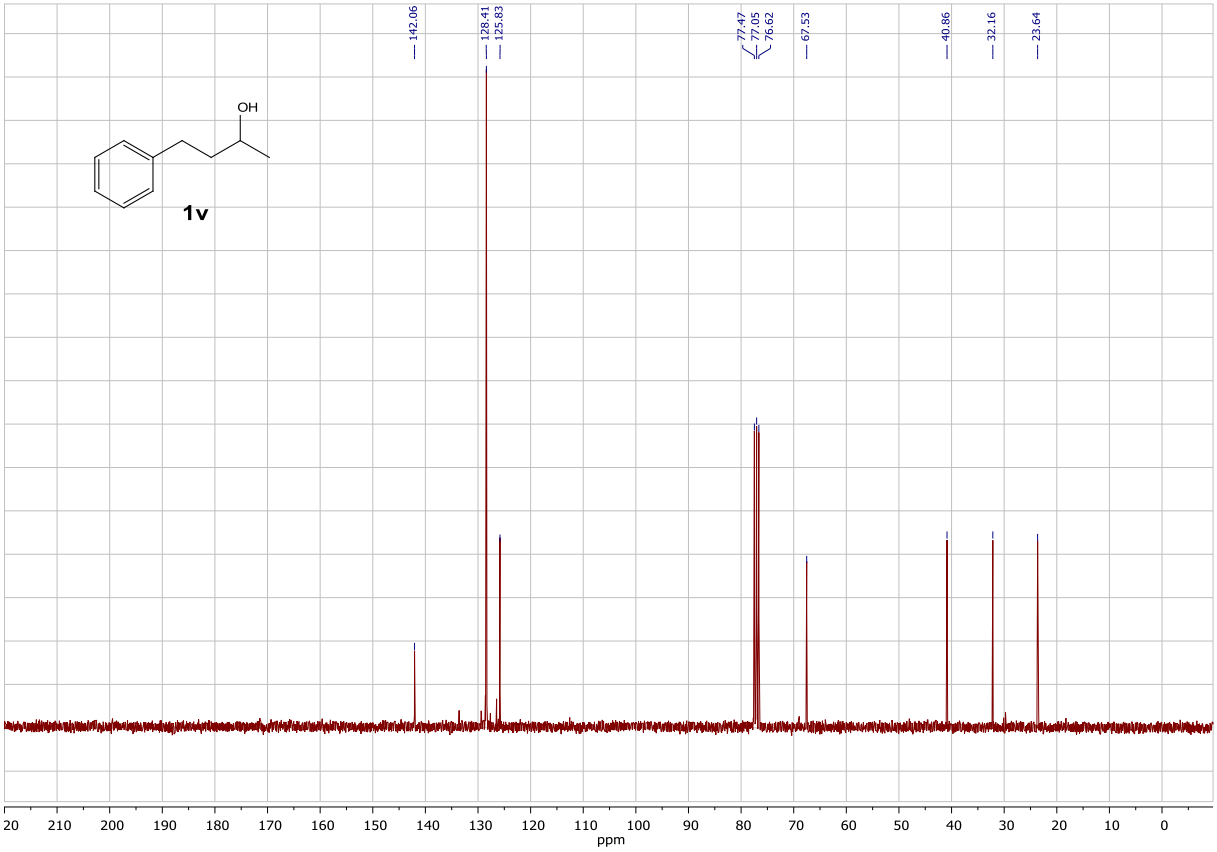

1n/1aj
7.26 CDCl3
6.85
6.84
6.83
6.82
6.69
6.69
6.67
6.67
6.66
6.66
5.48
3.88
2.55
2.53
2.52
2.52
2.50
1.68
1.66
1.65
1.64
1.63
1.63
1.61
1.61
1.60
1.59
1.58
1.56
0.97
0.94
0.92
F (m)
6.69
E (m)
6.83
G (s)
5.48
D (s)
3.88
C (t)
2.52
J(7.79)
B (m)
1.61
A (t)
0.94
J(7.34)
0.96
1.95
0.91
3.00
2.00
2.10
3.09
ppm


1n/1aj
146.37
143.61
134.82
121.07
114.17
111.11
77.58
77.16
76.74
55.96
37.90
25.02
13.95
ppm


1t
7.26 CDCl3
1.26
0.90
0.90
0.89
0.88
0.86
B (m)
0.87
A (s)
1.26
28.66
6.00
ppm


1t
77.58
77.16
77.16 CDCl3
76.74
32.10
29.88
29.84
29.55
22.87
14.29
ppm


OH
1v
C (dd)
6.58
J(15.95, 1.14)
B (dd)
6.27
J(15.92, 6.38)
D (dq)
3.84
J(12.10, 6.22)
E (m)
2.72
I (m)
1.78
A (d)
1.24
H (s)
1.53
ppm


OH
1v
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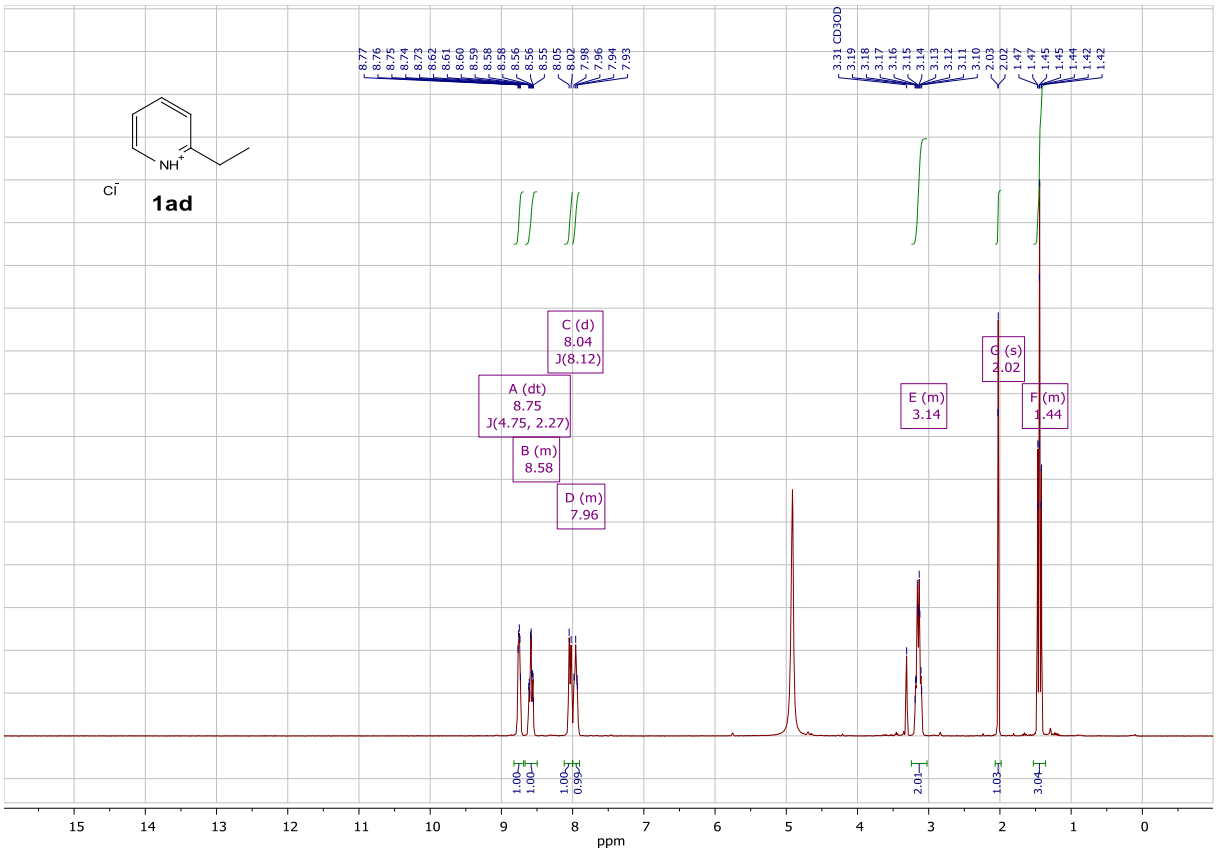
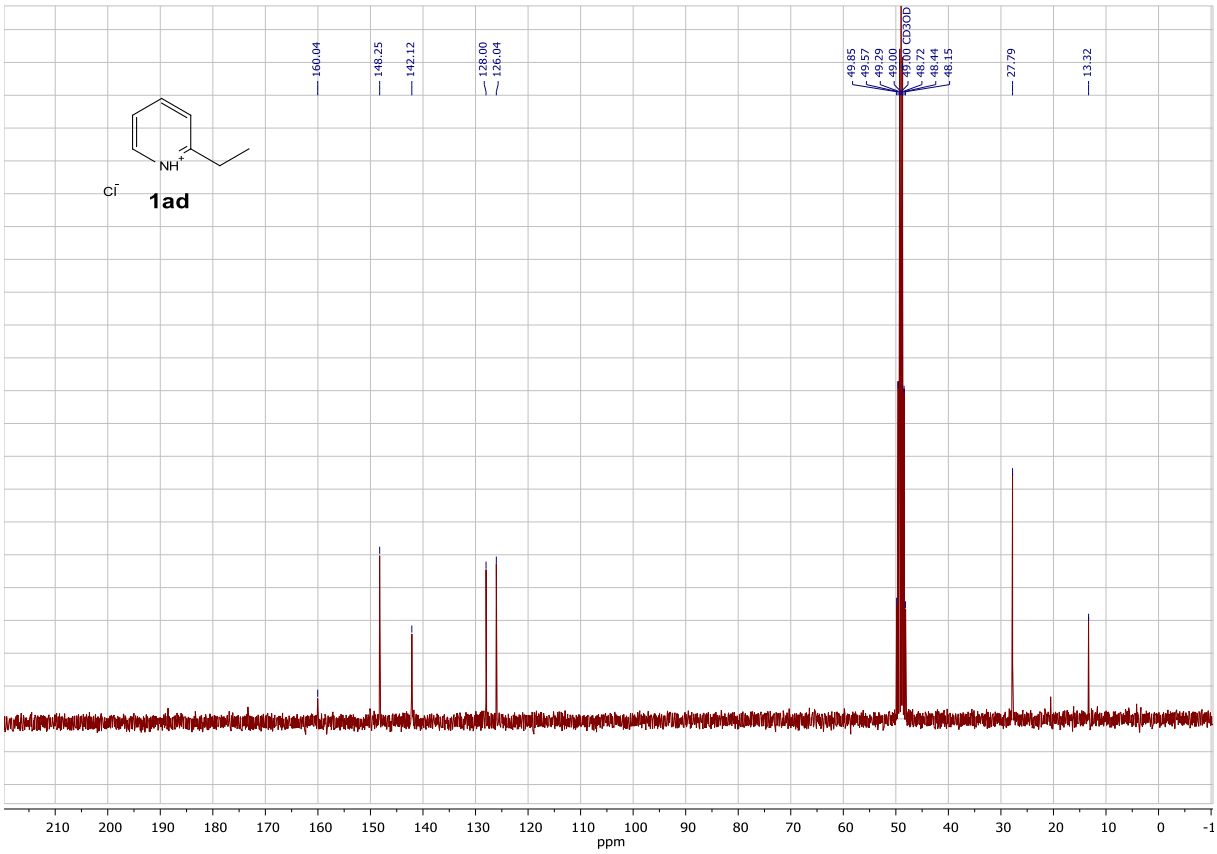
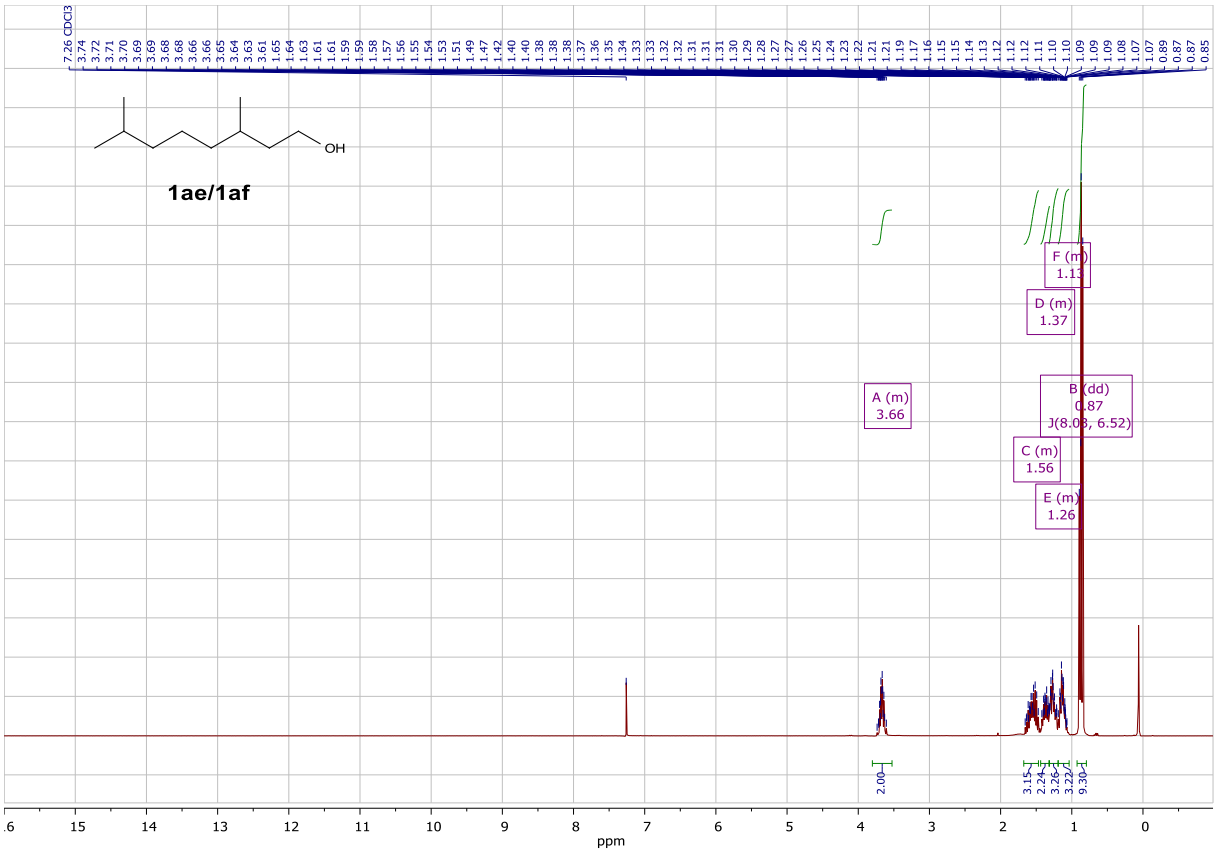
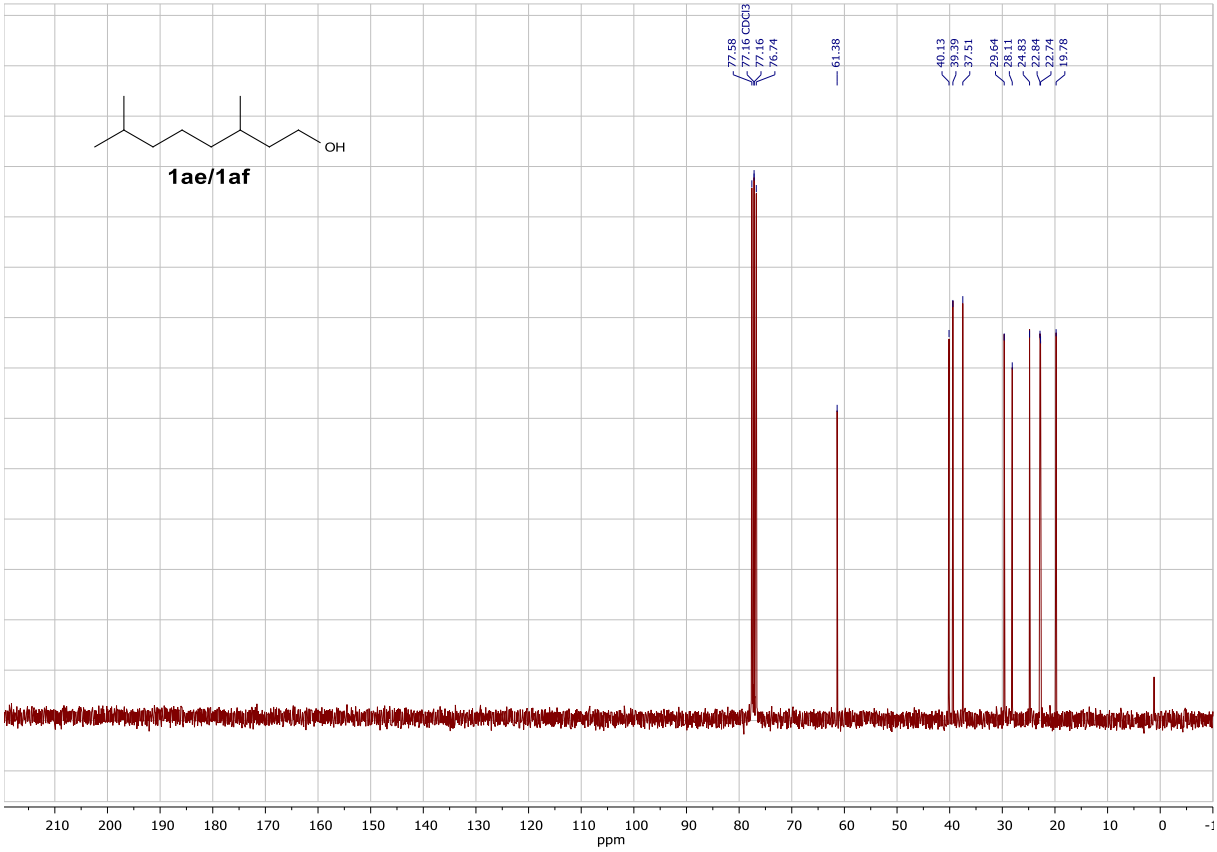
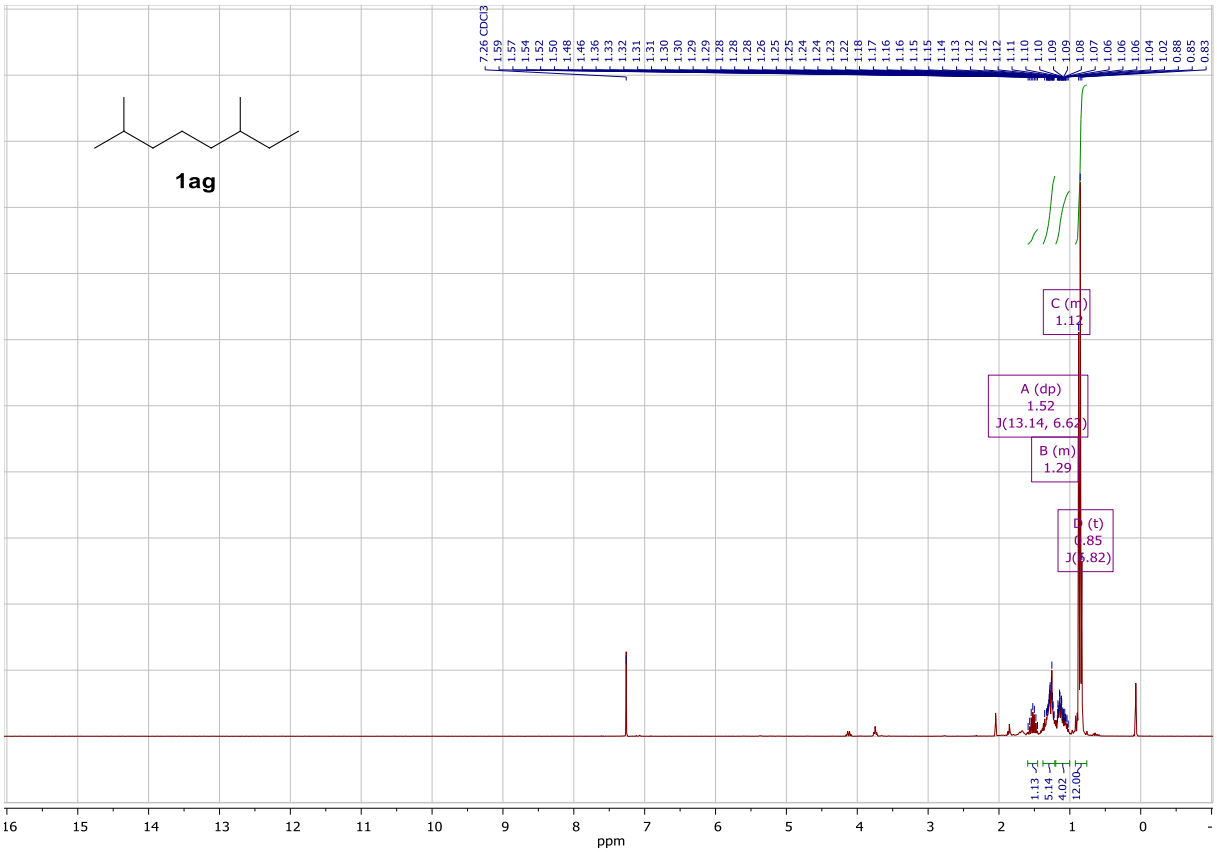
128.41
125.83
77.47
77.05
76.62
67.53
40.86
32.16
23.64
ppm

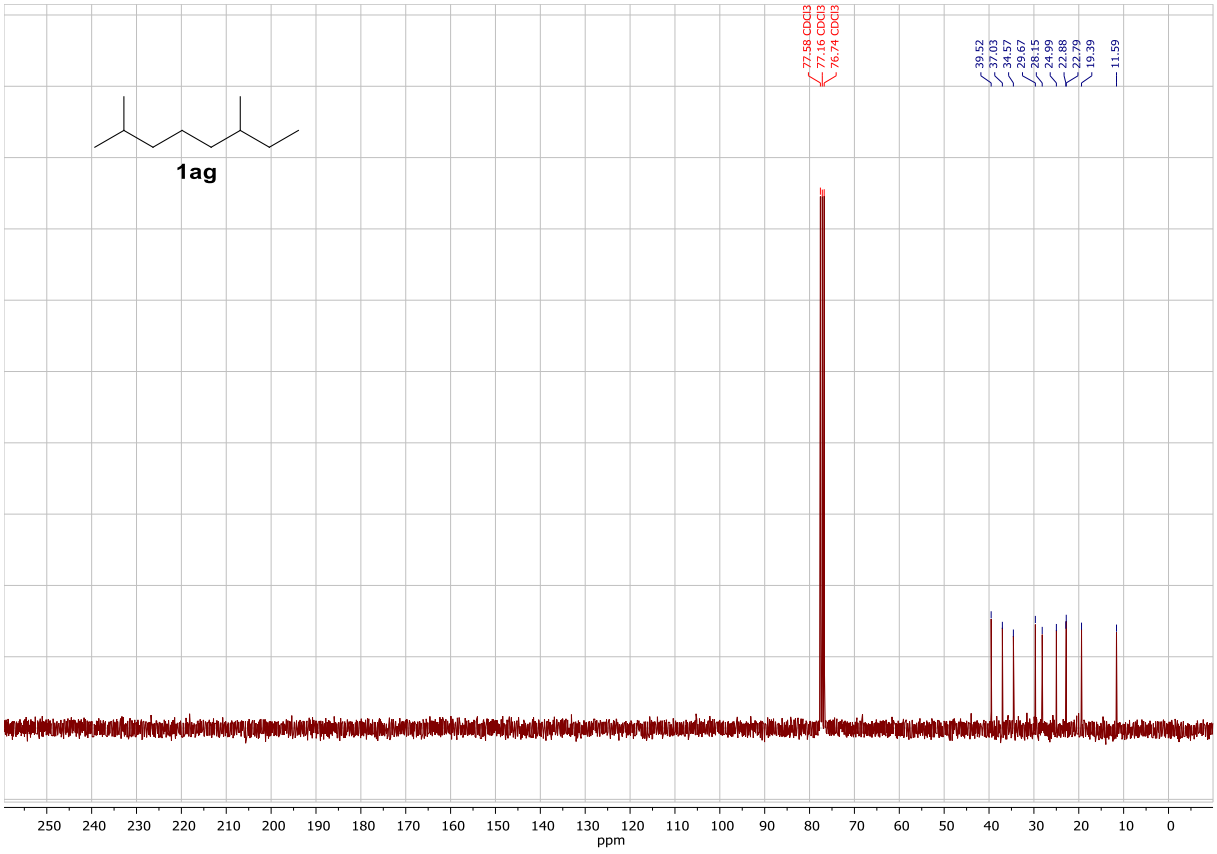

1ad
C (d)
8.04
J(8.12)
A (dt)
8.75
J(4.75, 2.27)
B (m)
8.58
D (m)
7.96
E (m)
3.14
G (s)
2.02
F (m)
1.44
ppm

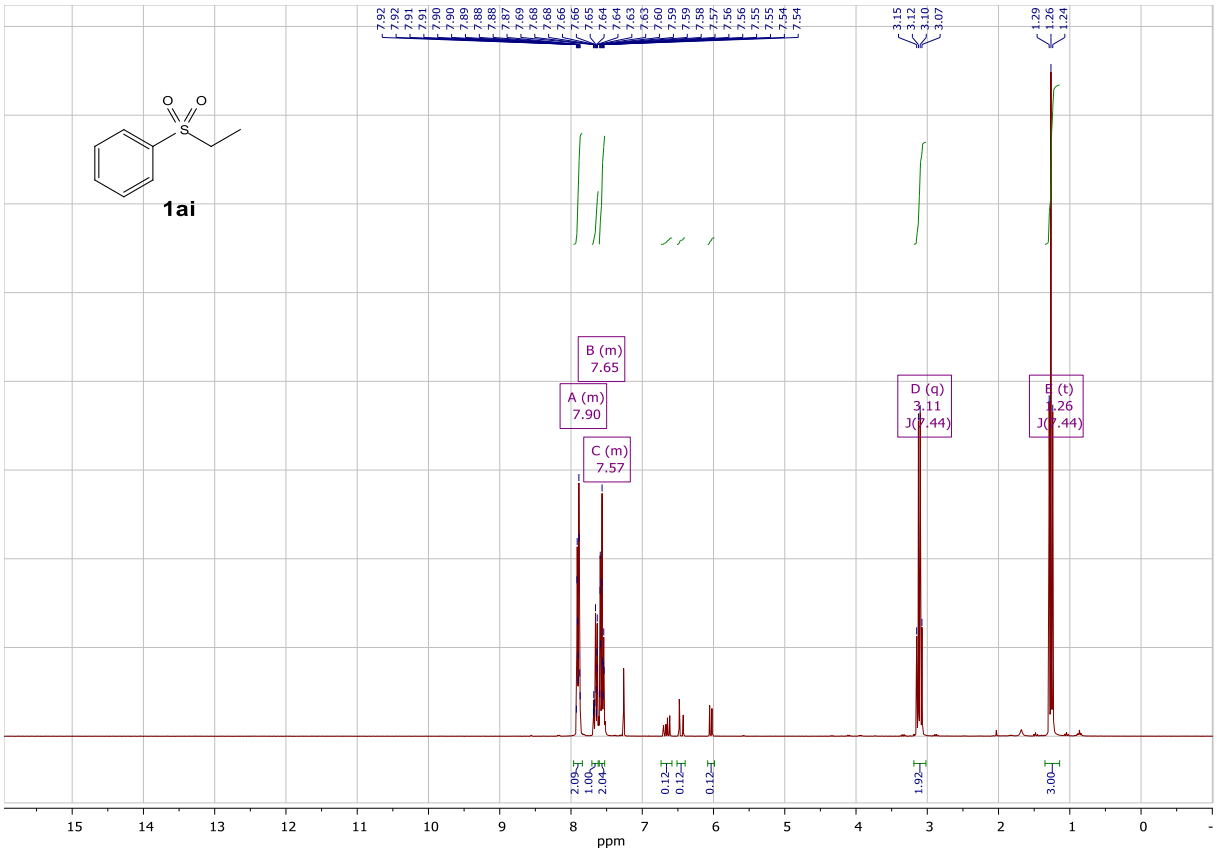

1ad
160.04
148.25
142.12
128.00
126.04
49.00 CD3OD
27.79
13.32
ppm

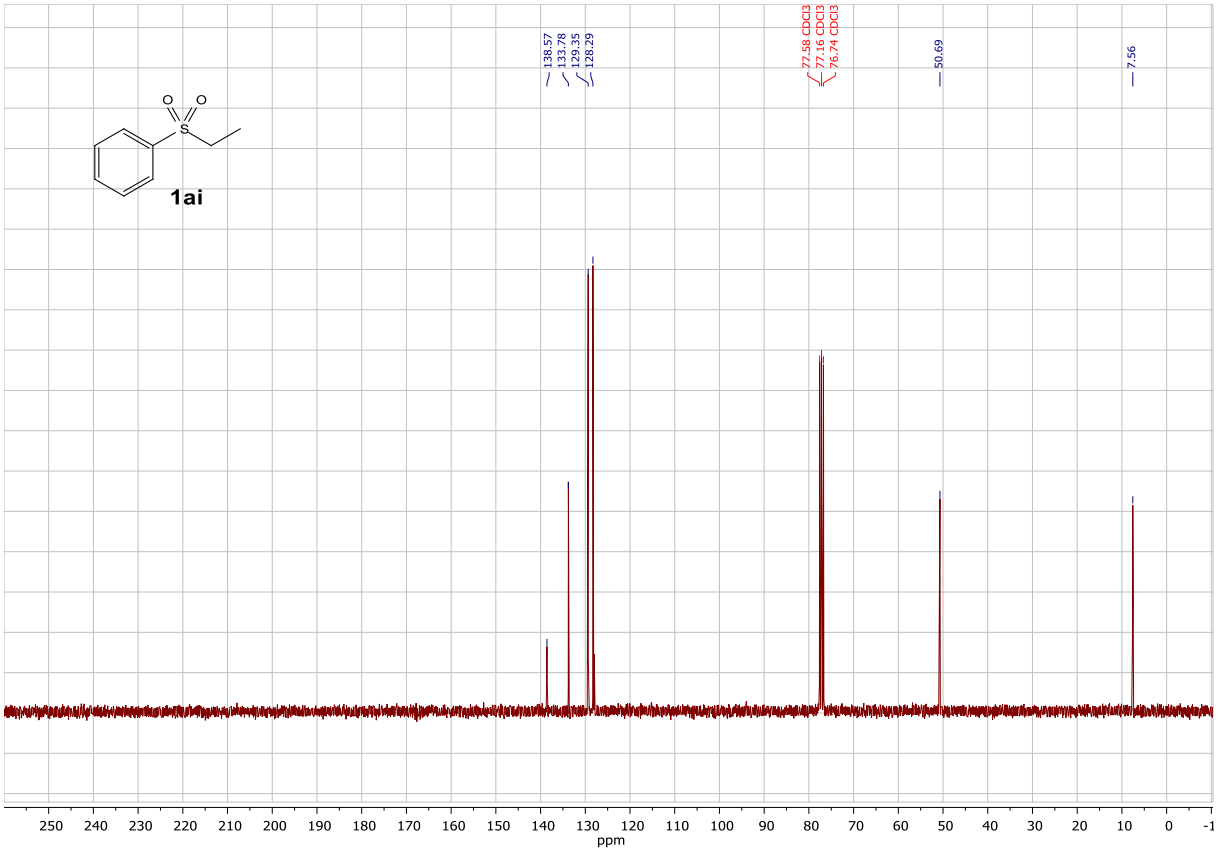

OH
1ae/1af
A (m)
3.66
B (dd)
0.87
J(8.08, 6.52)
C (m)
1.56
D (m)
1.37
E (m)
1.26
F (m)
1.11
ppm

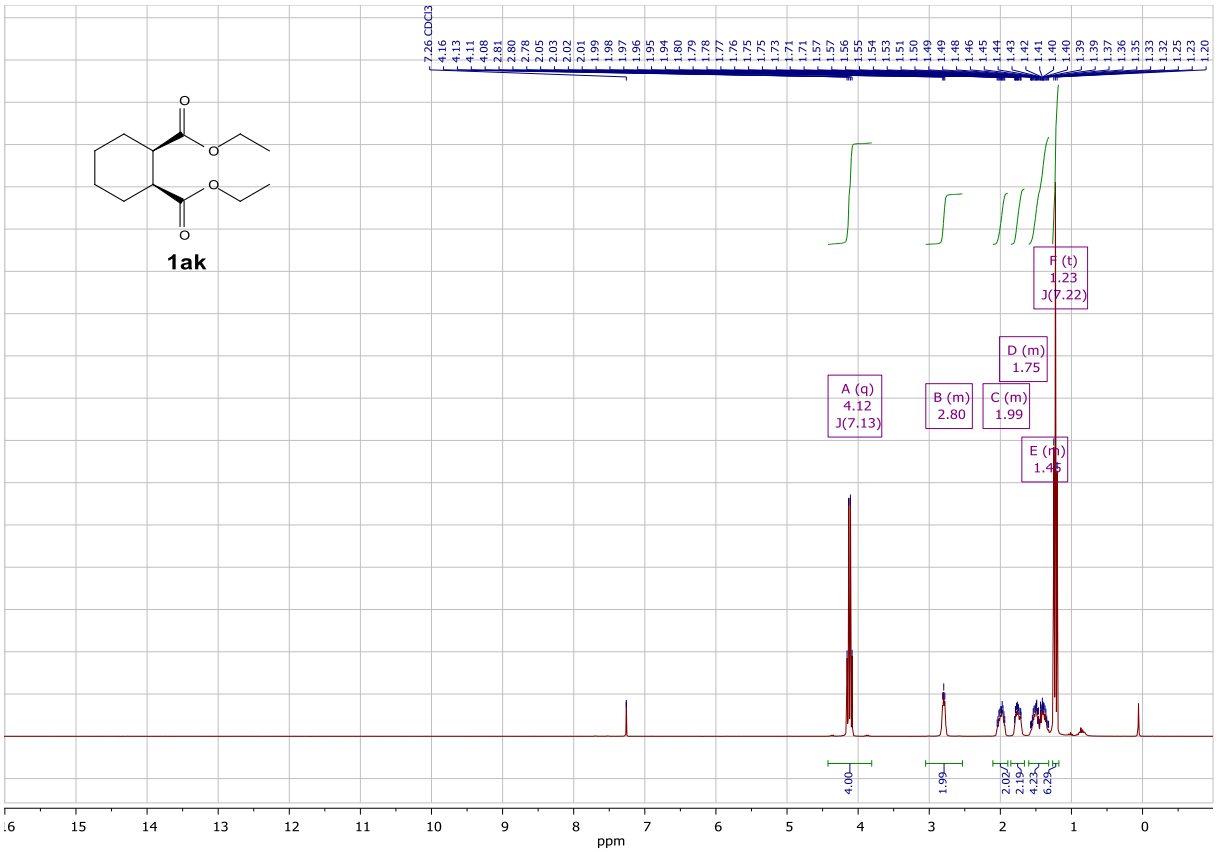

OH
1ae/1af
77.58
77.16 CDCl3
77.16
76.74
61.38
40.13
39.39
37.51
29.64
28.11
24.83
22.84
22.74
19.78
ppm

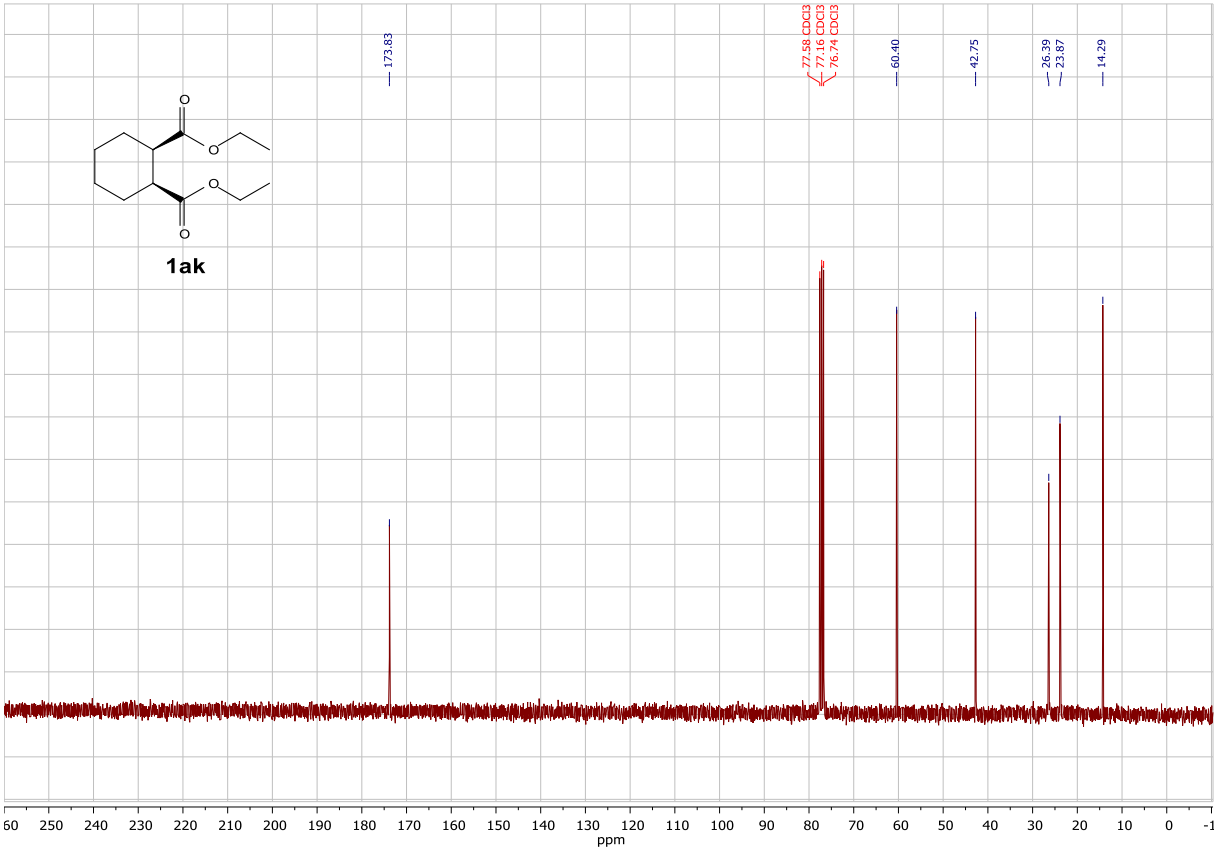

1ag
C (m)
1.12
A (dp)
1.52
B (m)
1.29
D (t)
0.85
ppm

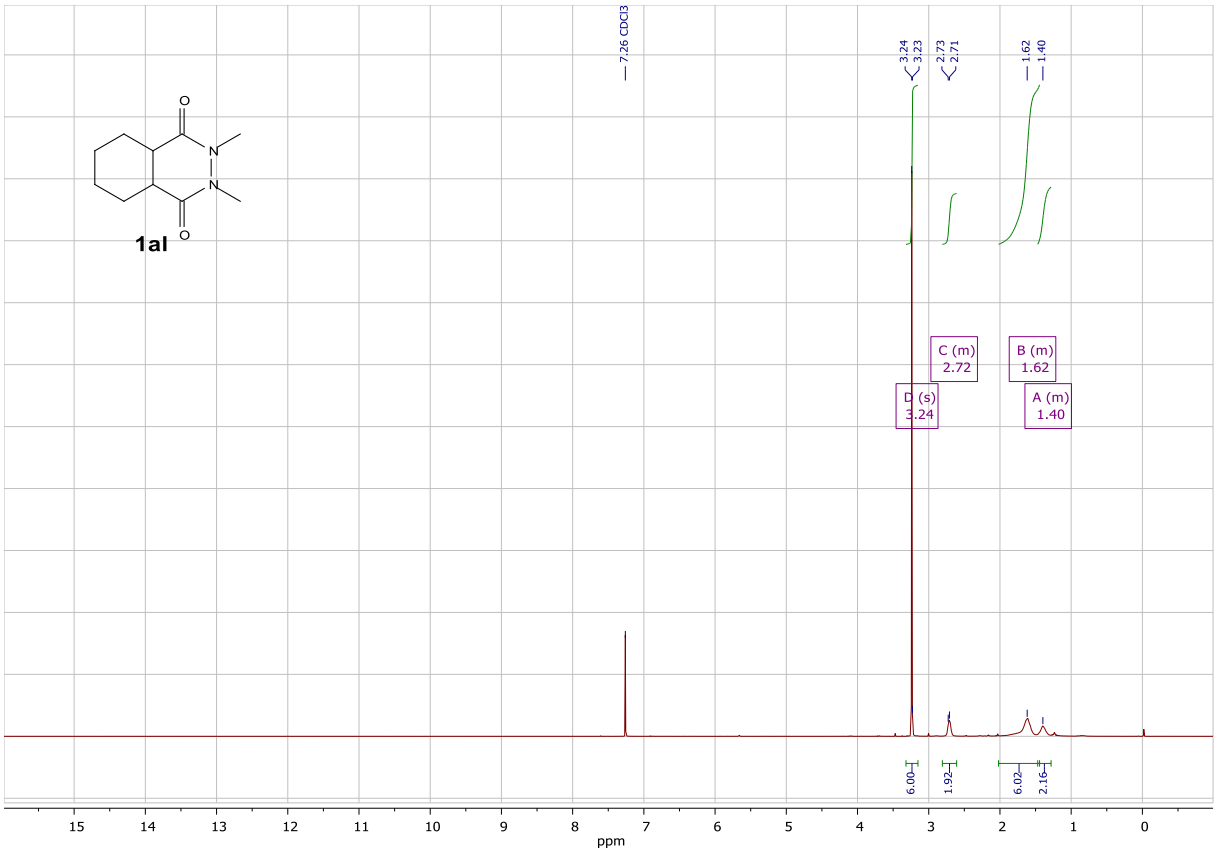

1ag
ppm

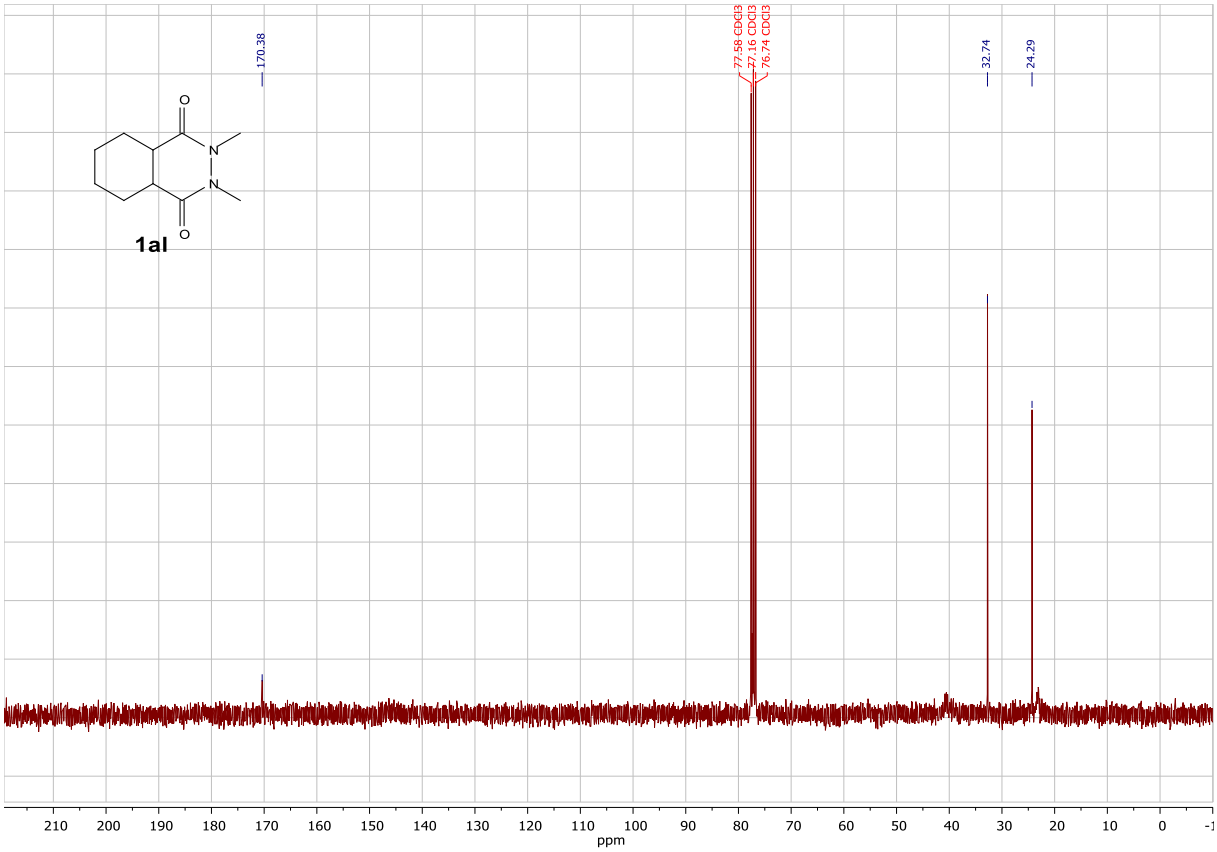

1ai
B (m)
7.65
A (m)
7.90
C (m)
7.57
D (q)
3.11
J(7.44)
E (t)
1.26
J(7.44)
ppm

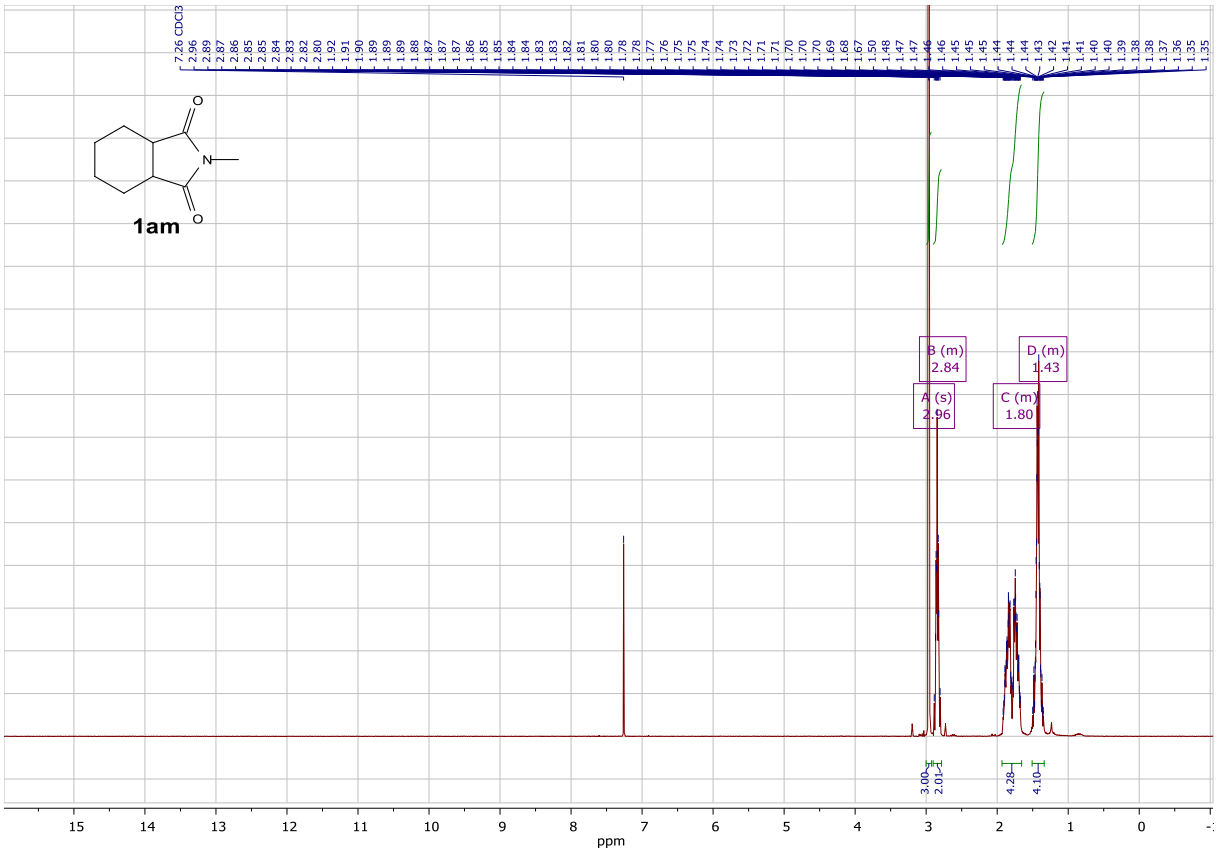

1ai
138.57
133.78
129.35
128.29
77.58 CDCl3
77.16 CDCl3
76.74 CDCl3
50.69
7.56
ppm

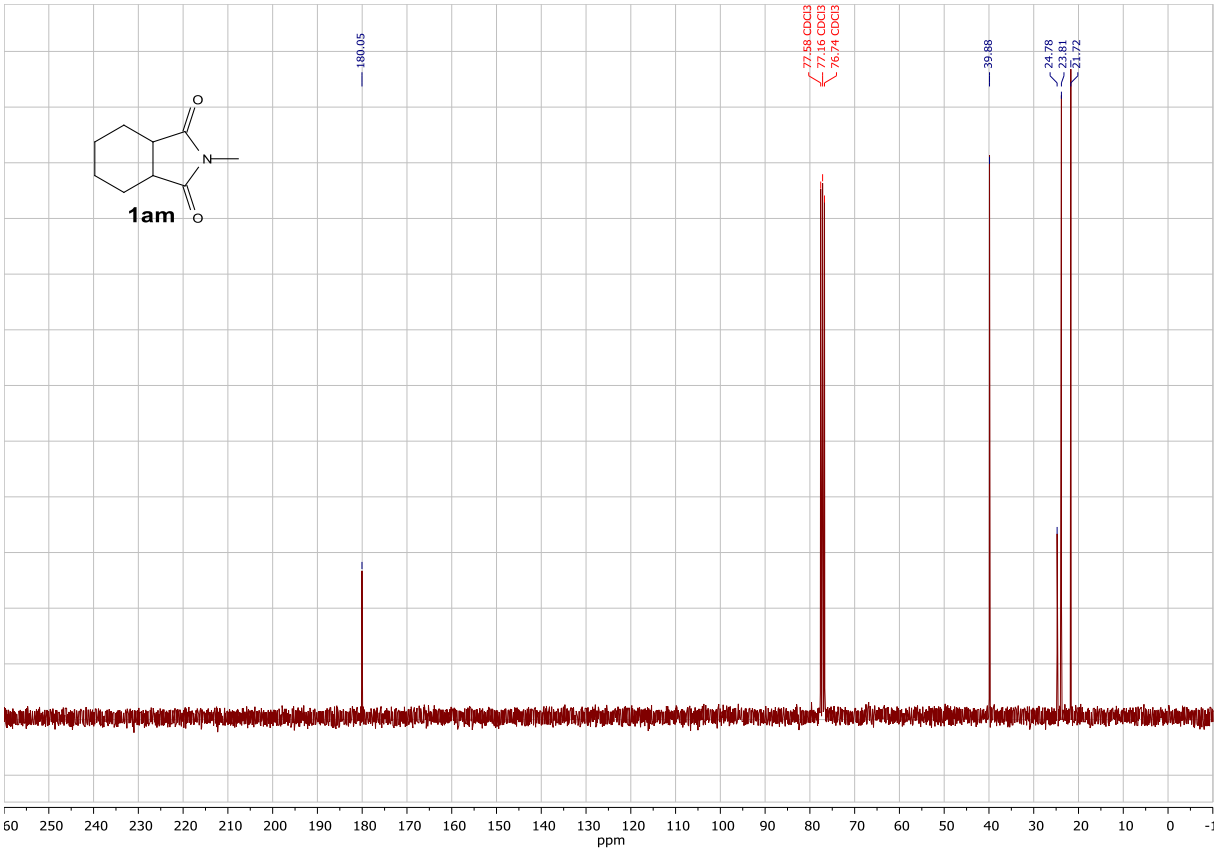

1ak
A (q)
4.12
J(7.13)
B (m)
2.80
C (m)
1.99
D (m)
1.75
E (m)
1.45
F (t)
1.23
J(7.22)
ppm

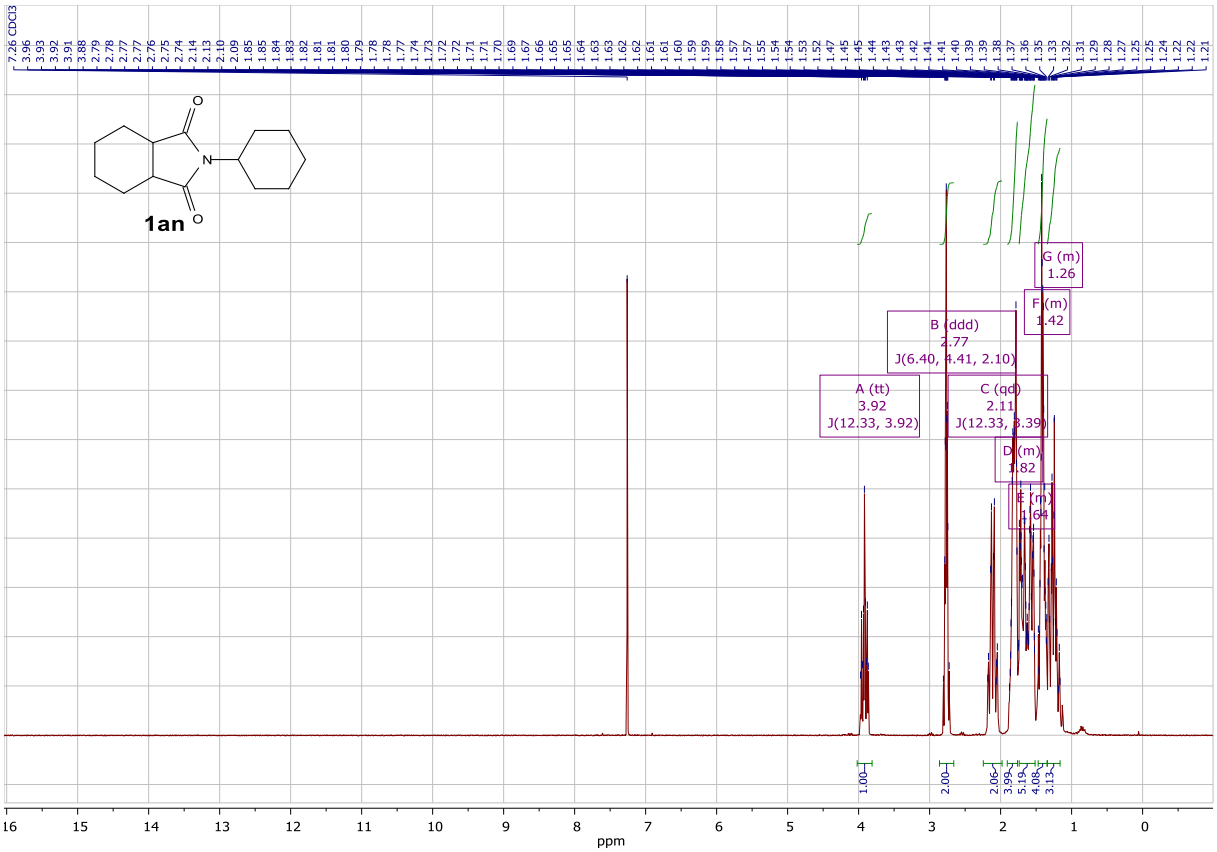

1ak
173.83
77.58 CDCl3
77.16 CDCl3
76.74 CDCl3
60.40
42.75
26.39
23.87
14.29
ppm

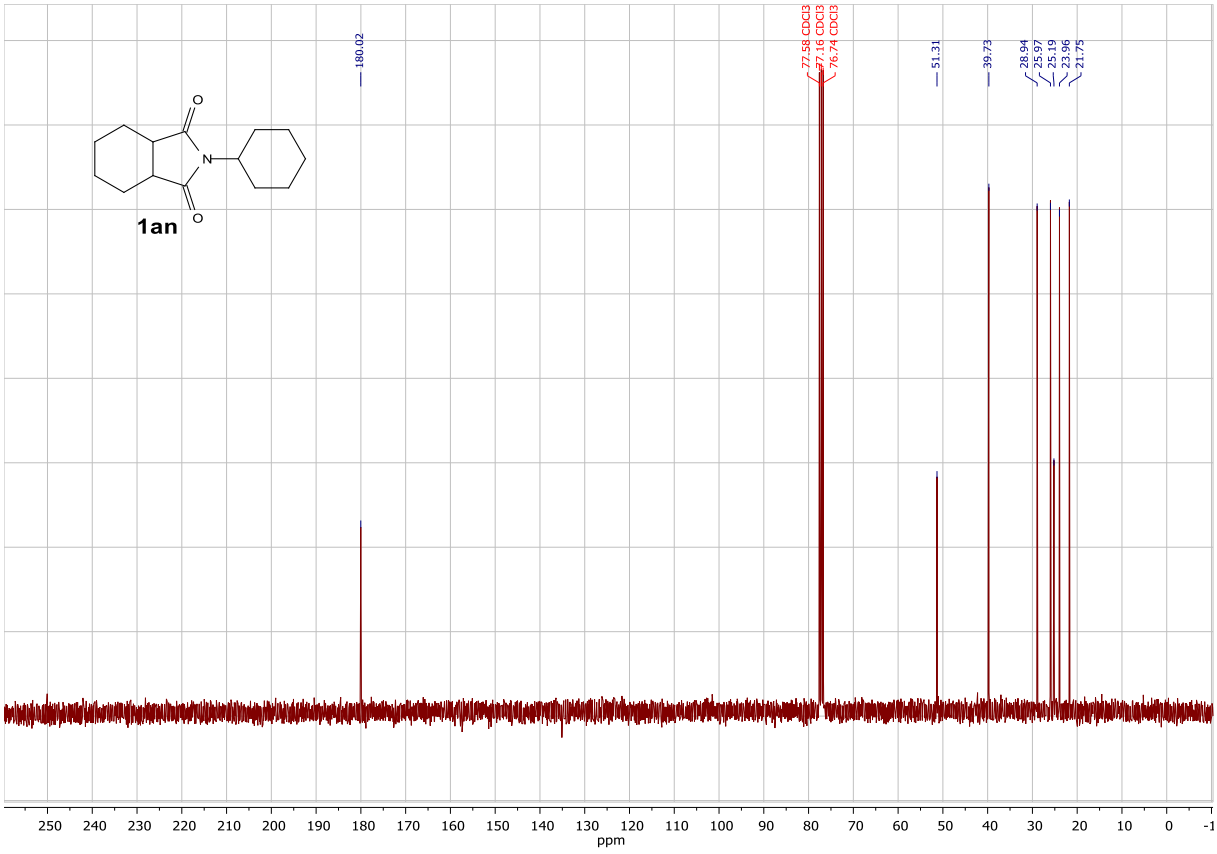

7.26 CDCl3
3.24
3.23
2.73
2.71
1.62
1.40
C (m)
2.72
B (m)
1.62
D (s)
3.24
A (m)
1.40
6.00
1.92
6.02
2.16
ppm
1al

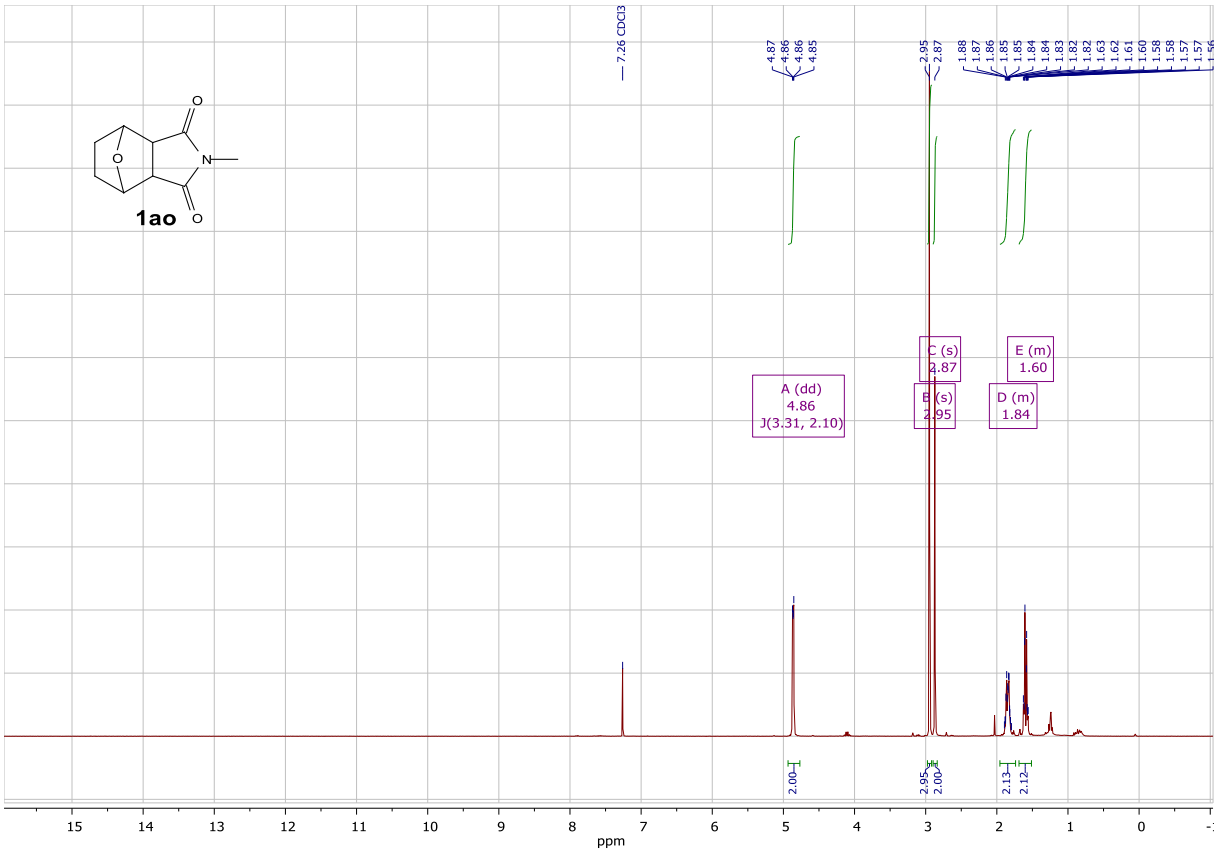

170.38
77.58 CDCl3
77.16 CDCl3
76.74 CDCl3
32.74
24.29
ppm
1al

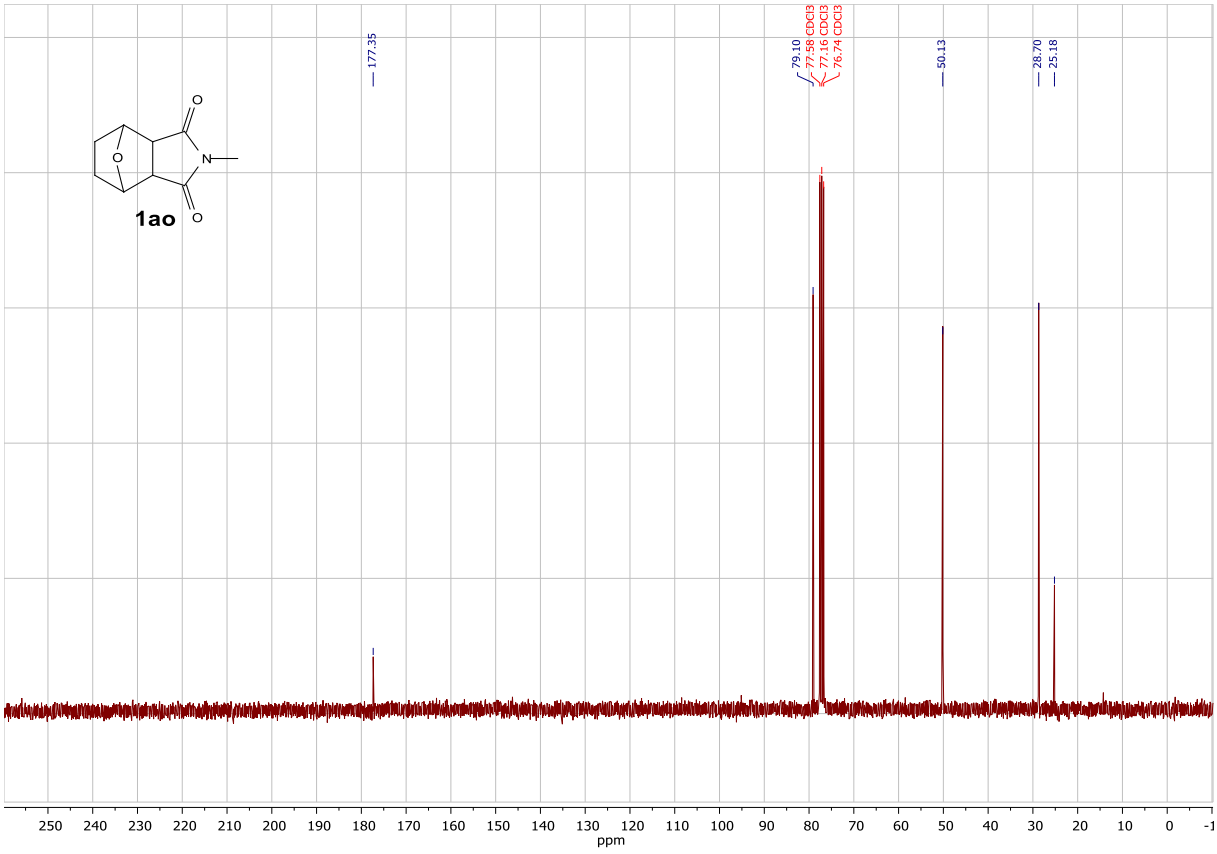

7.26 CDCl3
1am
B (m)
2.84
D (m)
1.43
A (s)
2.96
C (m)
1.80
3.00
2.01
4.28
4.10
ppm

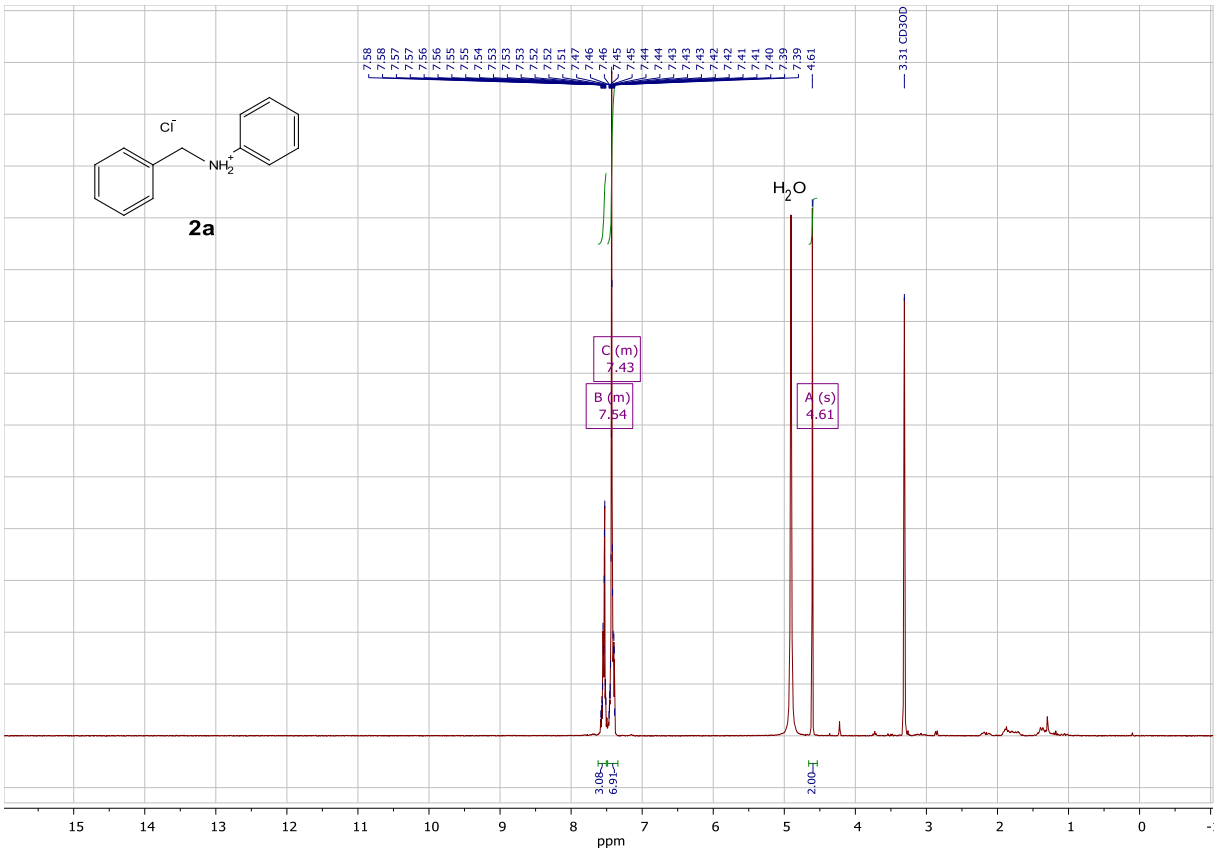

180.05
77.58 CDCl3
77.16 CDCl3
76.74 CDCl3
39.88
24.78
23.81
21.72
1am
ppm

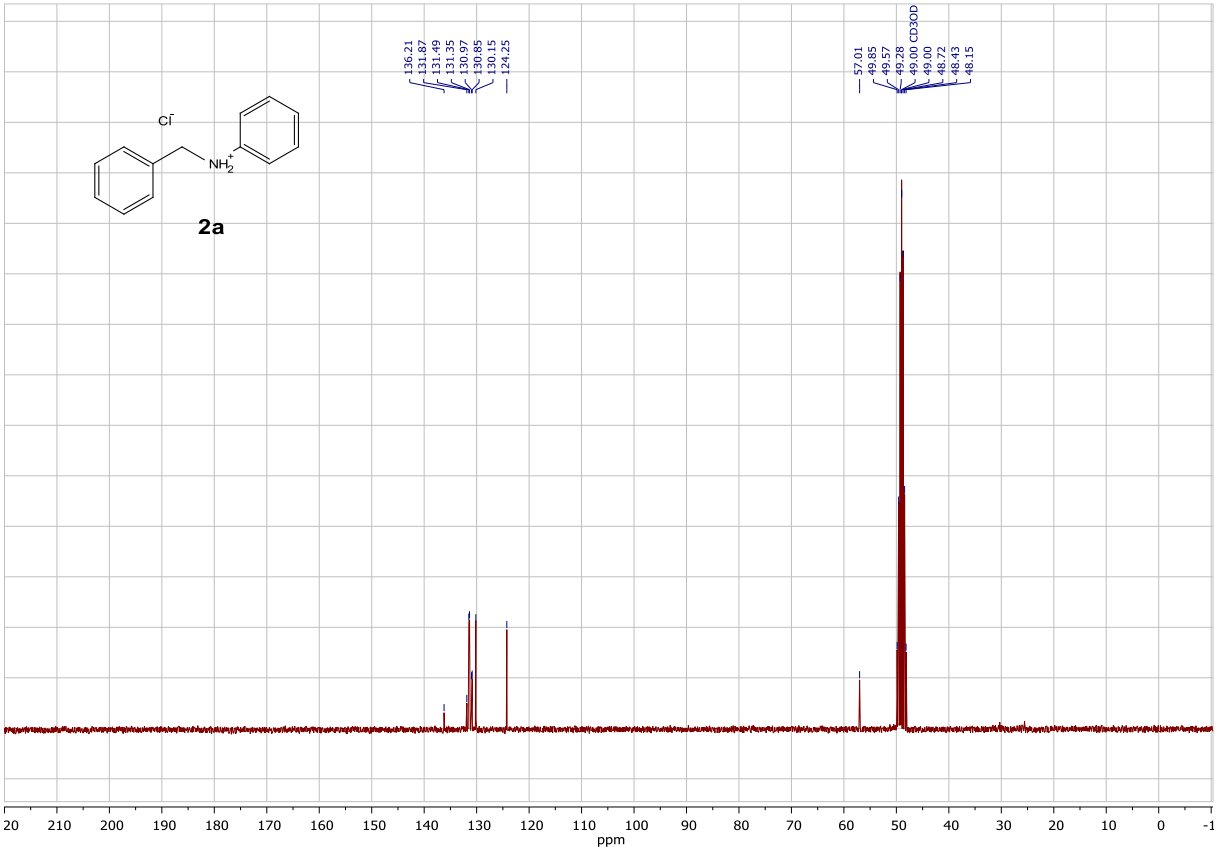

7.26 CDCl3
1an
G (m)
1.26
F (m)
1.42
B (ddd)
2.77
J(6.40, 4.41, 2.10)
A (tt)
3.92
J(12.33, 3.92)
C (qd)
2.11
J(12.33, 3.39)
D (m)
1.82
1.00
2.00
2.06
3.99
5.19
4.08
3.13
ppm

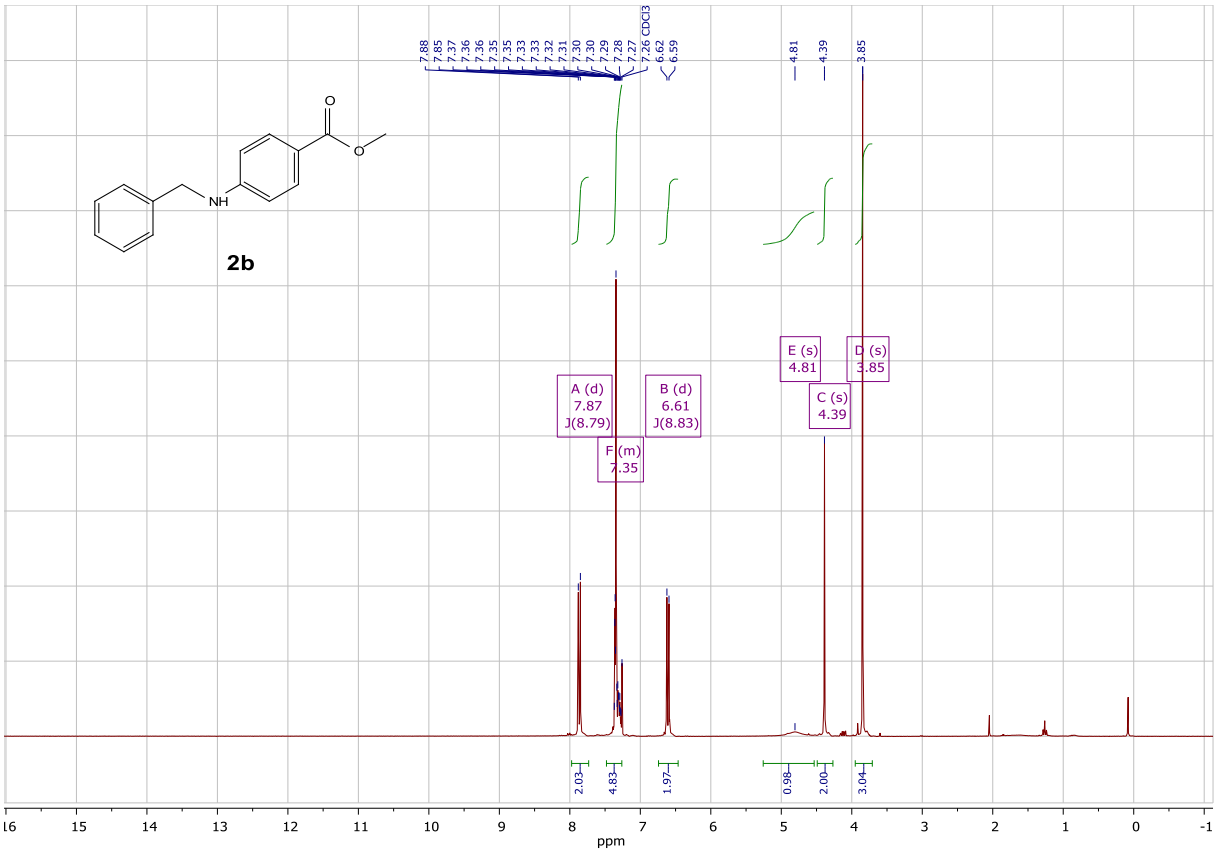

1an
180.02
77.58 CDCl3
77.16 CDCl3
76.74 CDCl3
51.31
39.73
28.94
25.97
25.19
23.96
21.75
ppm

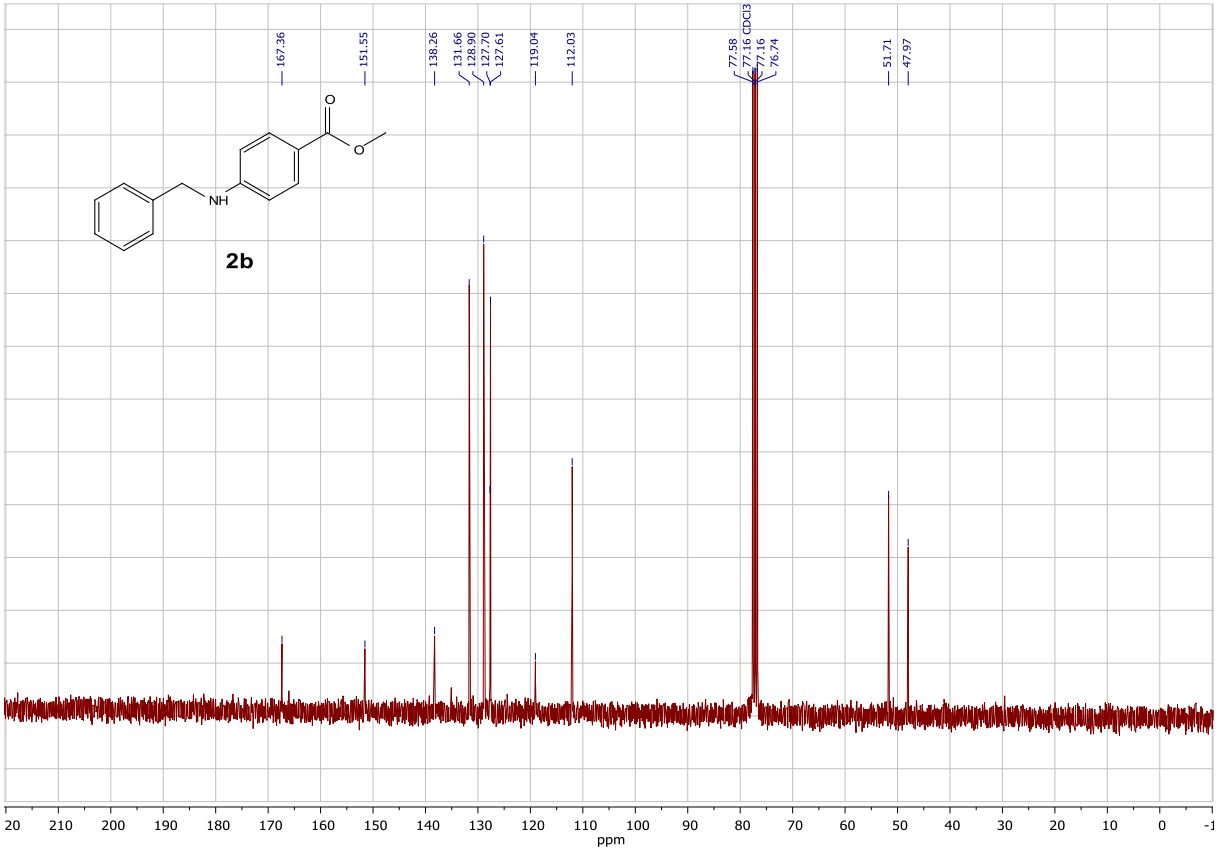

1ao
7.26 CDCl3
4.87
4.86
4.86
4.85
2.95
2.87
1.88
1.87
1.86
1.85
1.85
1.84
1.84
1.83
1.82
1.82
1.63
1.62
1.61
1.60
1.58
1.58
1.57
1.57
A (dd)
4.86
J(3.31, 2.10)
B (s)
2.95
C (s)
2.87
D (m)
1.84
E (m)
1.60
2.00
2.95
2.00
2.13
2.12
ppm

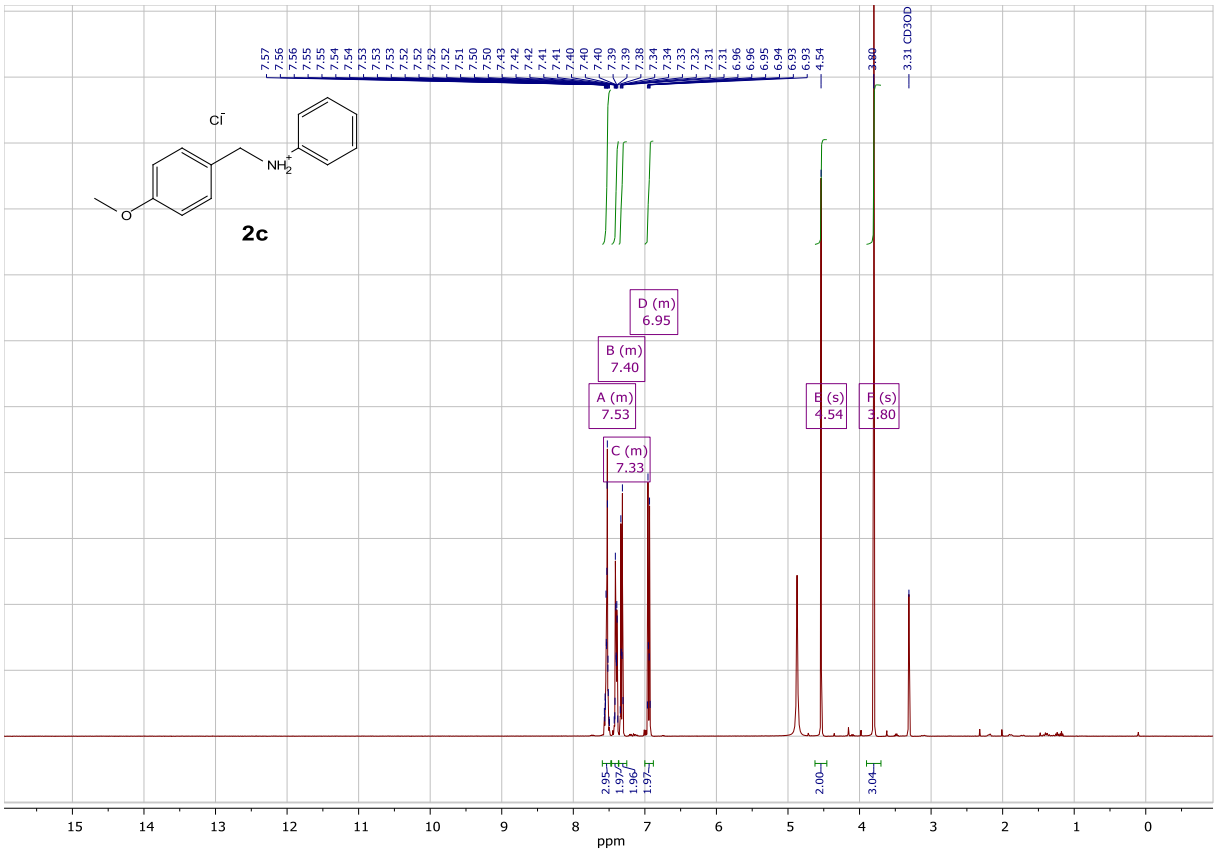

1ao
177.35
79.10
77.58 CDCl3
77.16 CDCl3
76.74 CDCl3
50.13
28.70
25.18
ppm

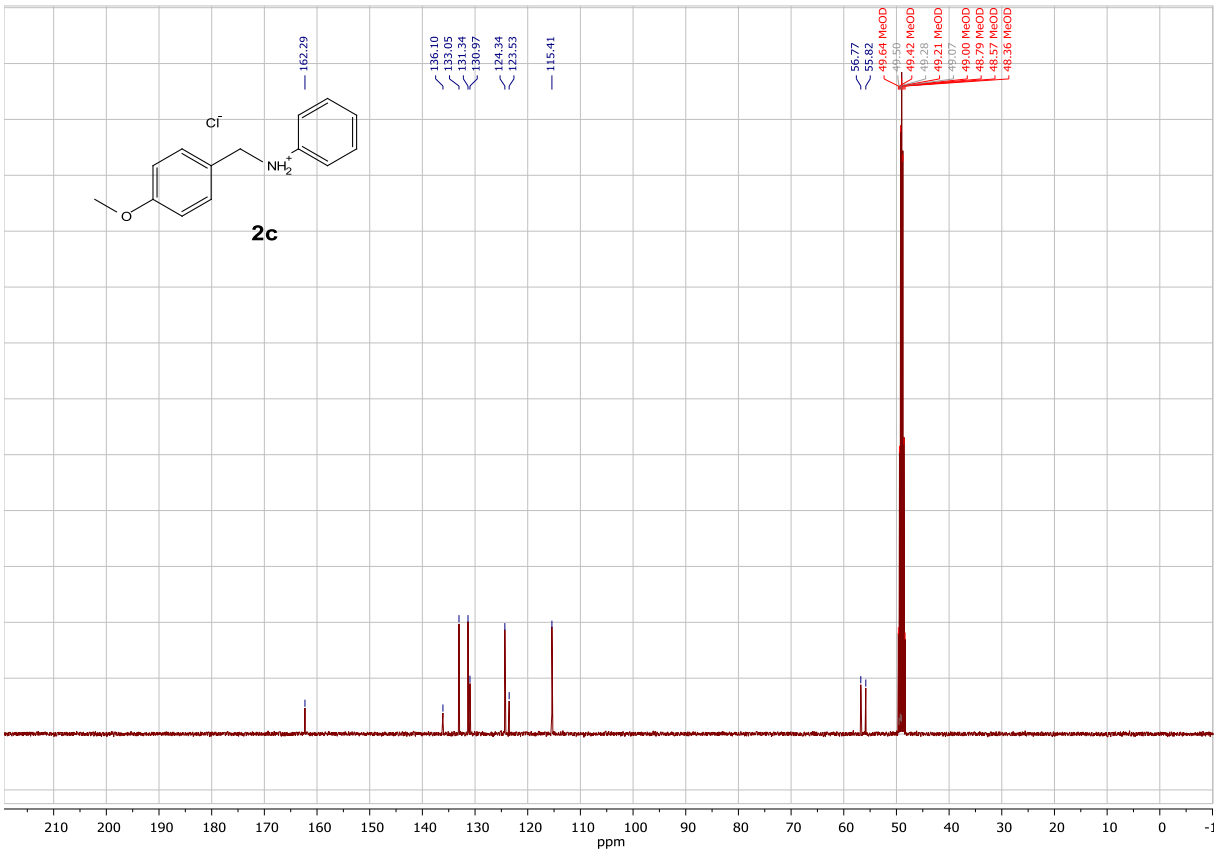

Cl⁻
NH2+
2a
7.58 7.58 7.57 7.57 7.56 7.56 7.55 7.55 7.54 7.53 7.53 7.53 7.52 7.52 7.51 7.47 7.46 7.46 7.45 7.45 7.44 7.44 7.43 7.43 7.43 7.42 7.42 7.41 7.41 7.40 7.39 7.39
4.61
3.31 CD3OD
H2O
C (m) 7.43
B (m) 7.54
A (s) 4.61
3.08
6.91
2.00
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
ppm

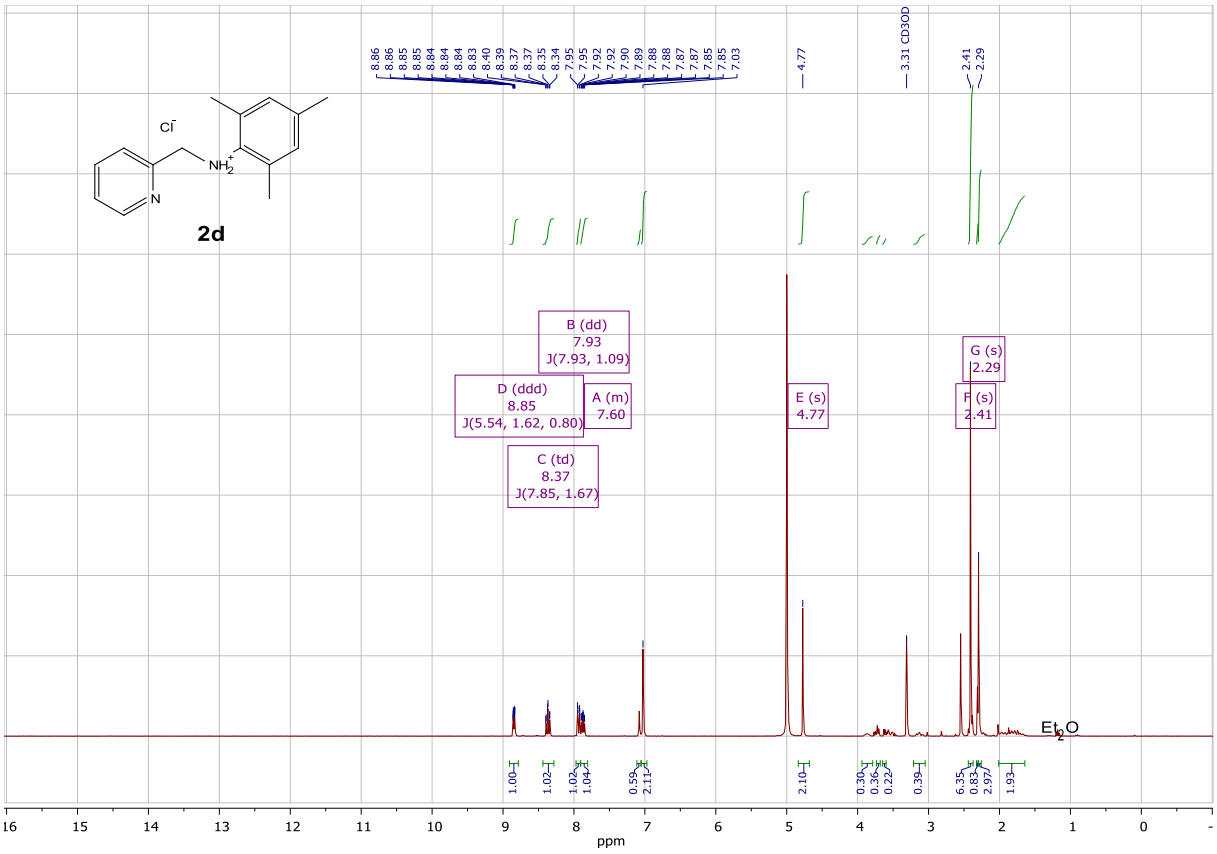

Cl⁻
NH2+
2a
136.21 131.87 131.49 131.35 130.97 130.85 130.15 124.25
57.01 49.85 49.57 49.28 49.00 CD3OD 49.00 48.72 48.43 48.15
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
ppm

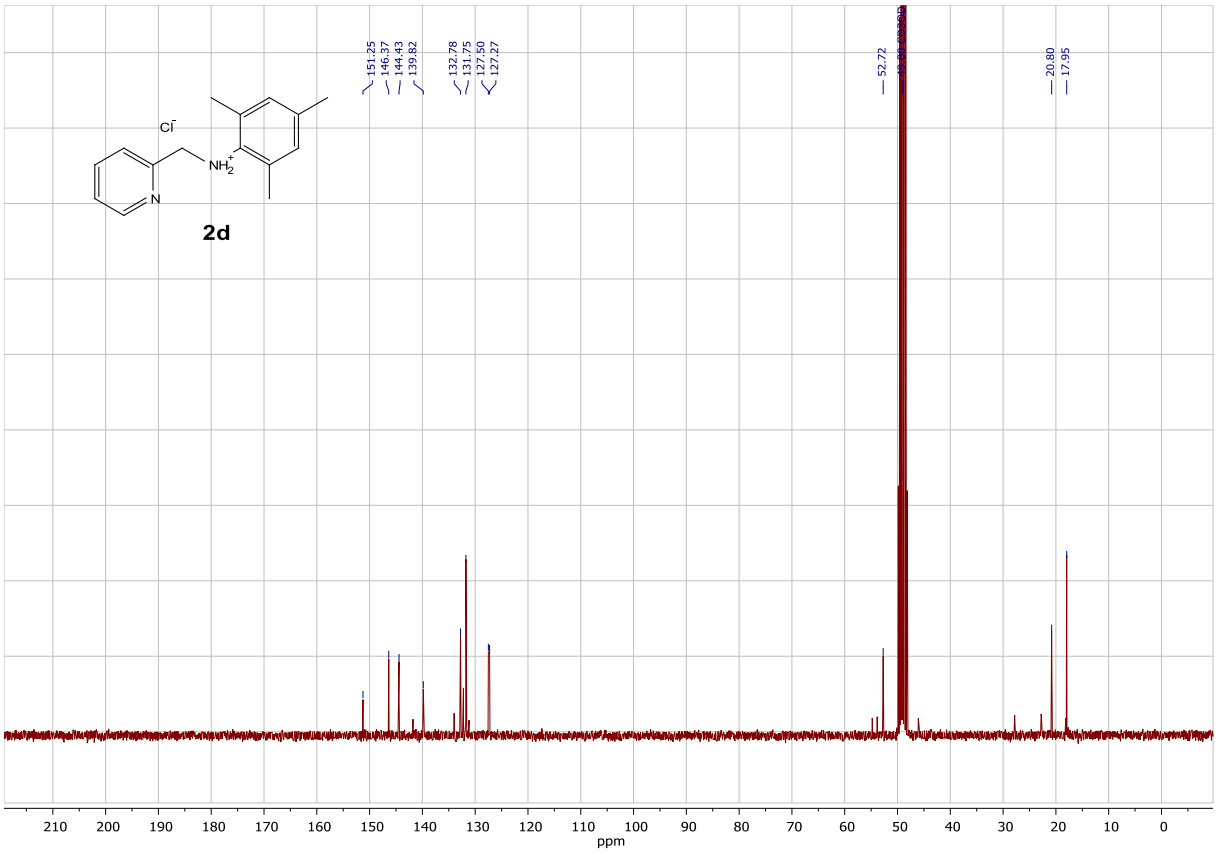

7.88
7.85
7.37
7.36
7.36
7.35
7.35
7.33
7.33
7.32
7.31
7.30
7.30
7.29
7.28
7.27
7.26 CDCl3
6.62
6.59
4.81
4.39
3.85
O
O
NH
2b
A (d)
7.87
J(8.79)
F (m)
7.35
B (d)
6.61
J(8.83)
E (s)
4.81
C (s)
4.39
D (s)
3.85
2.03
4.83
1.97
0.98
2.00
3.04
ppm

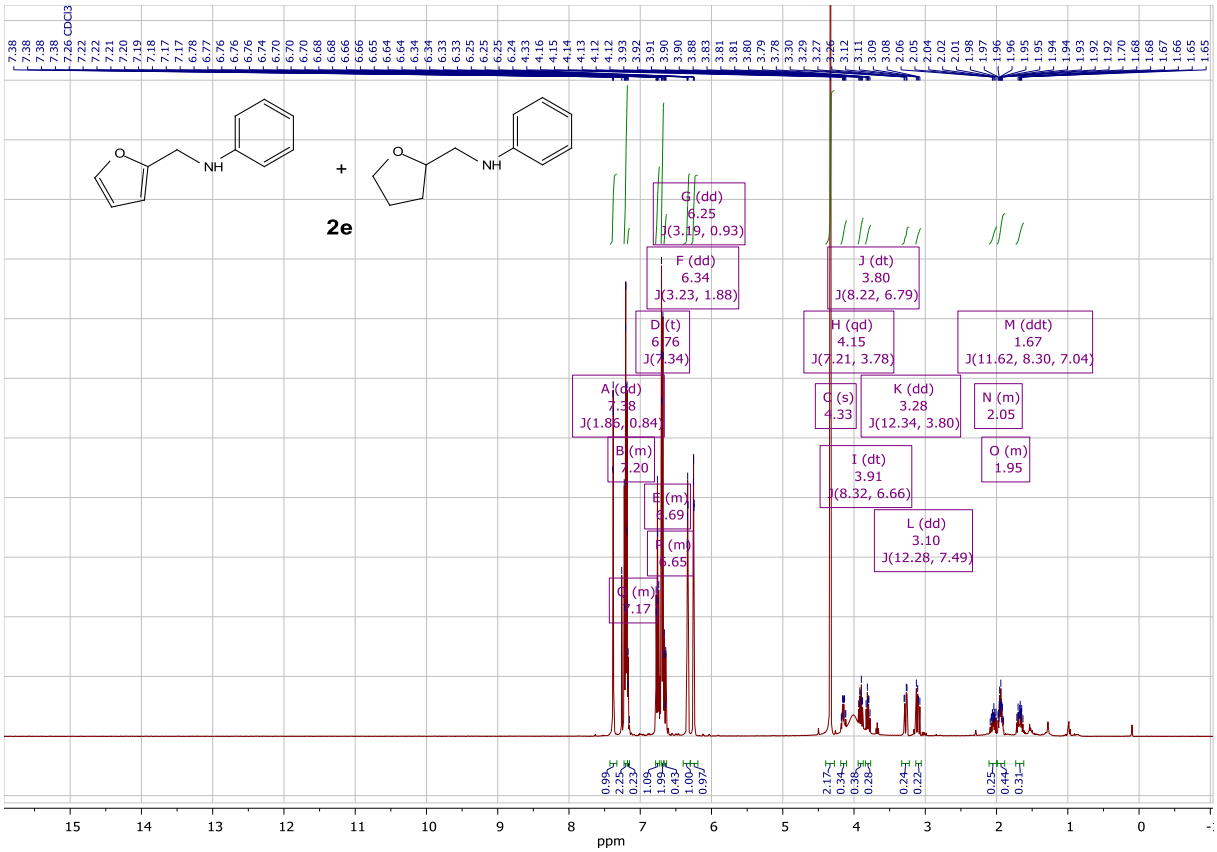

167.36
151.55
138.26
131.66
128.90
127.70
127.61
119.04
112.03
77.58
77.16 CDCl3
77.16
76.74
51.71
47.97
O
O
NH
2b
ppm

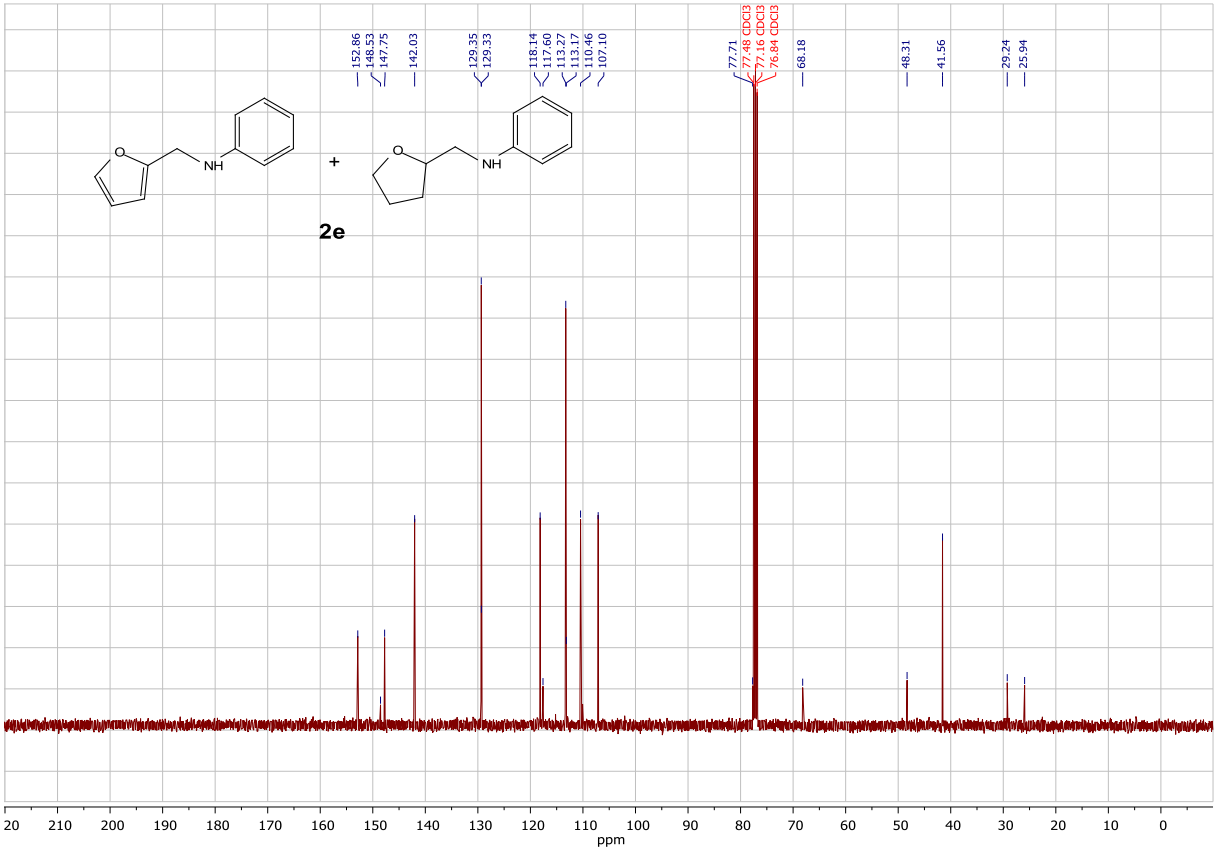

2c
D (m) 6.95
B (m) 7.40
A (m) 7.53
C (m) 7.33
E (s) 4.54
F (s) 3.80
ppm

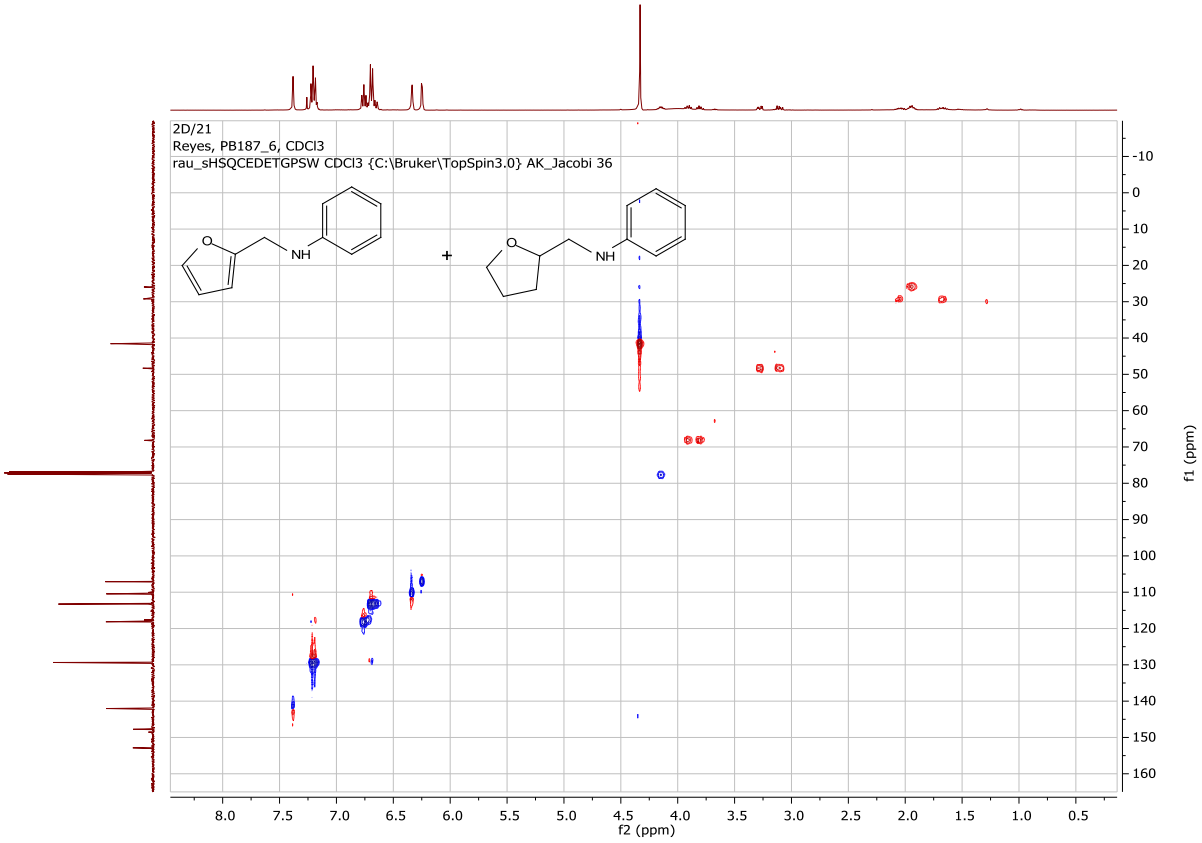

2c
ppm

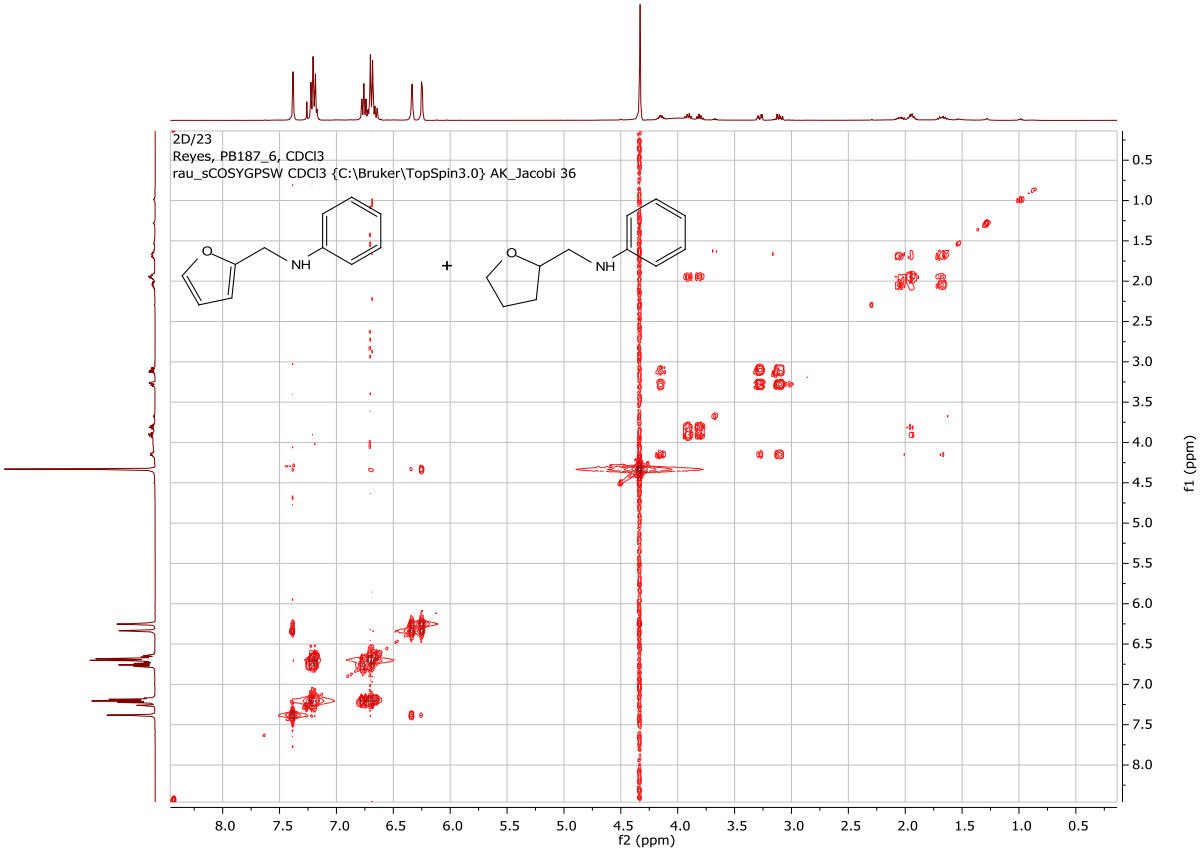

2d
B (dd)
7.93
J(7.93, 1.09)
D (ddd)
8.85
J(5.54, 1.62, 0.80)
A (m)
7.60
C (td)
8.37
J(7.85, 1.67)
E (s)
4.77
G (s)
2.29
F (s)
2.41
Et2O
ppm

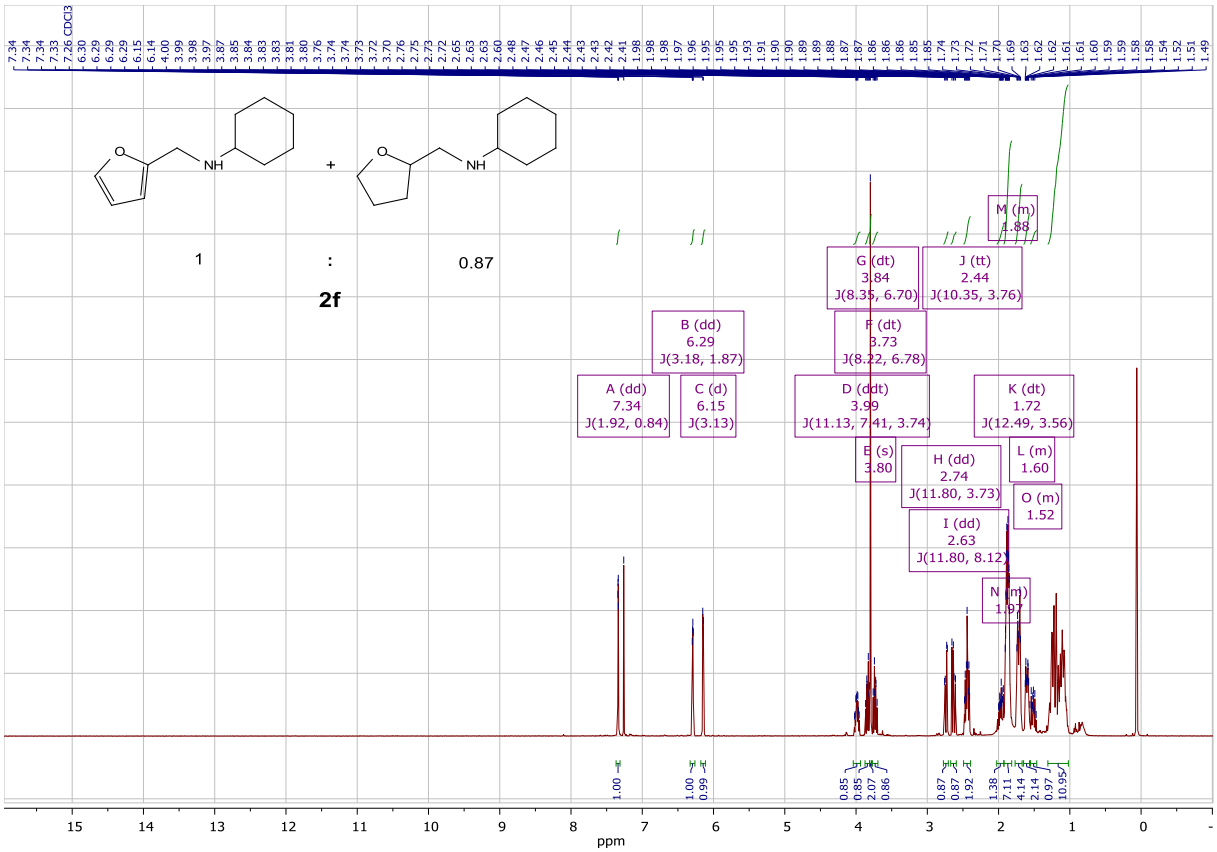

2d
ppm

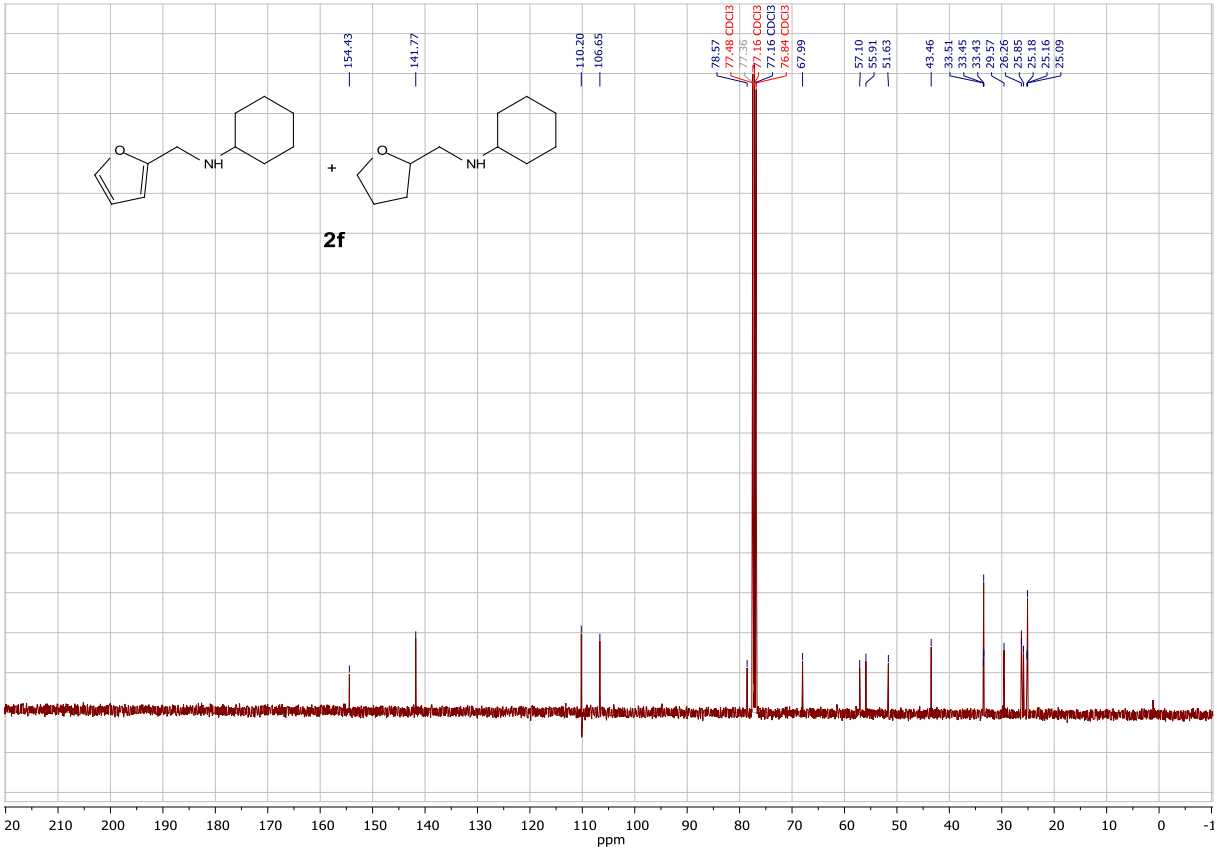

2e
G (dd)
6.25
J(3.19, 0.93)
F (dd)
6.34
J(3.23, 1.88)
J (dt)
3.80
J(8.22, 6.79)
D (t)
6.76
J(7.34)
H (qd)
4.15
J(7.21, 3.78)
M (ddt)
1.67
J(11.62, 8.30, 7.04)
A (dd)
7.38
J(1.85, 0.84)
C (s)
4.33
K (dd)
3.28
J(12.34, 3.80)
N (m)
2.05
B (m)
7.20
O (m)
1.95
I (dt)
3.91
J(8.32, 6.66)
E (m)
6.69
L (dd)
3.10
J(12.28, 7.49)
F (m)
6.65
C (m)
7.17
ppm

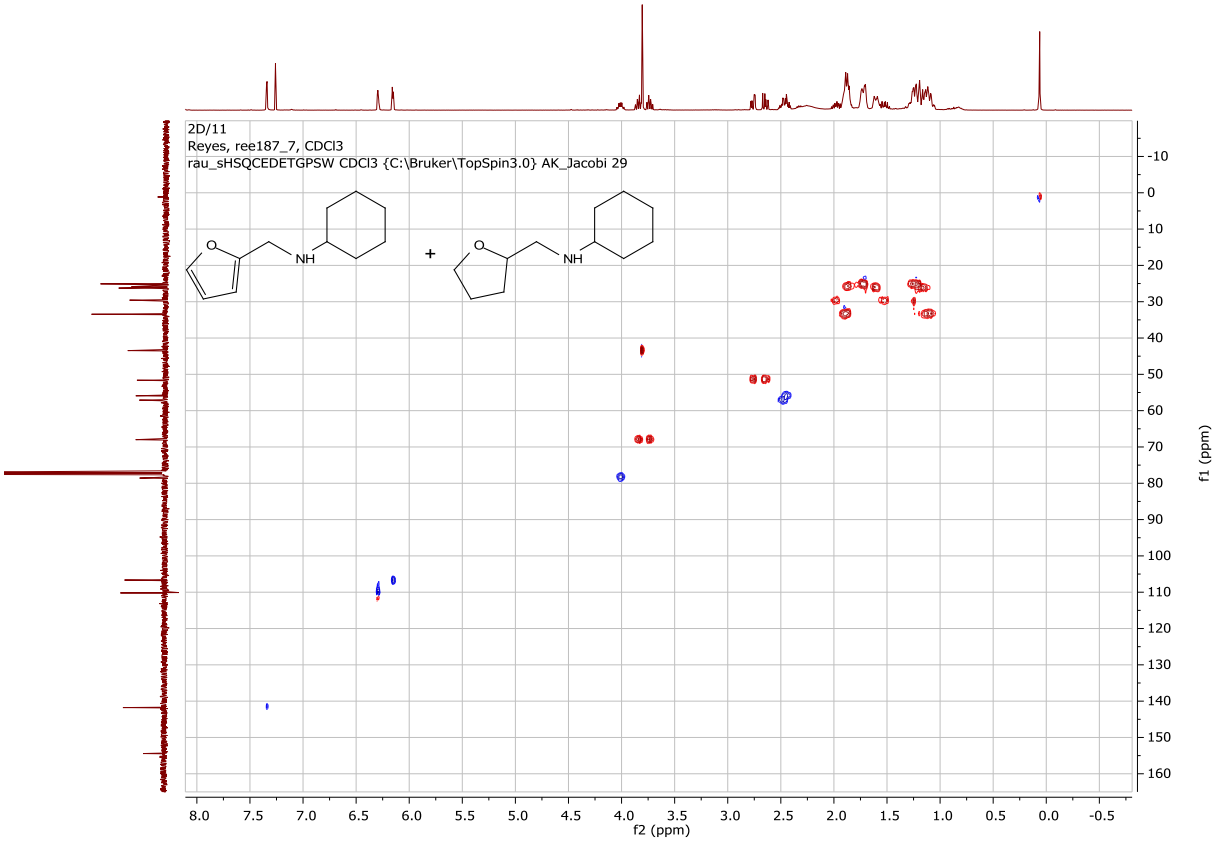

2e
152.86
148.53
147.75
142.03
129.35
129.33
118.14
117.60
113.27
113.17
110.46
107.10
77.71
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
68.18
48.31
41.56
29.24
25.94
ppm

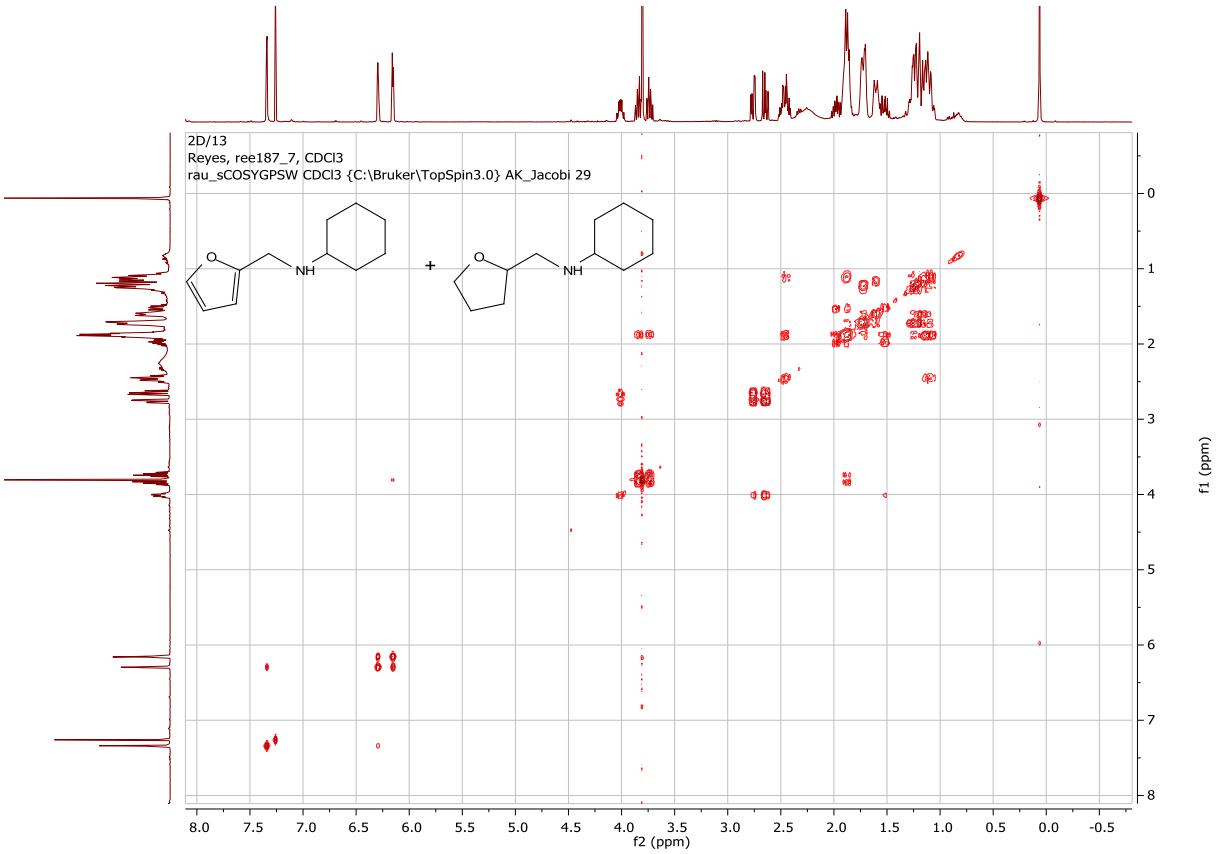

2D/21
Reyes, PB187_6, CDCl3
rau_sHSQCEDETGPSW CDCl3 {C:\Bruker\TopSpin3.0} AK_Jacobi 36
O
NH
+
O
NH
f2 (ppm)
f1 (ppm)

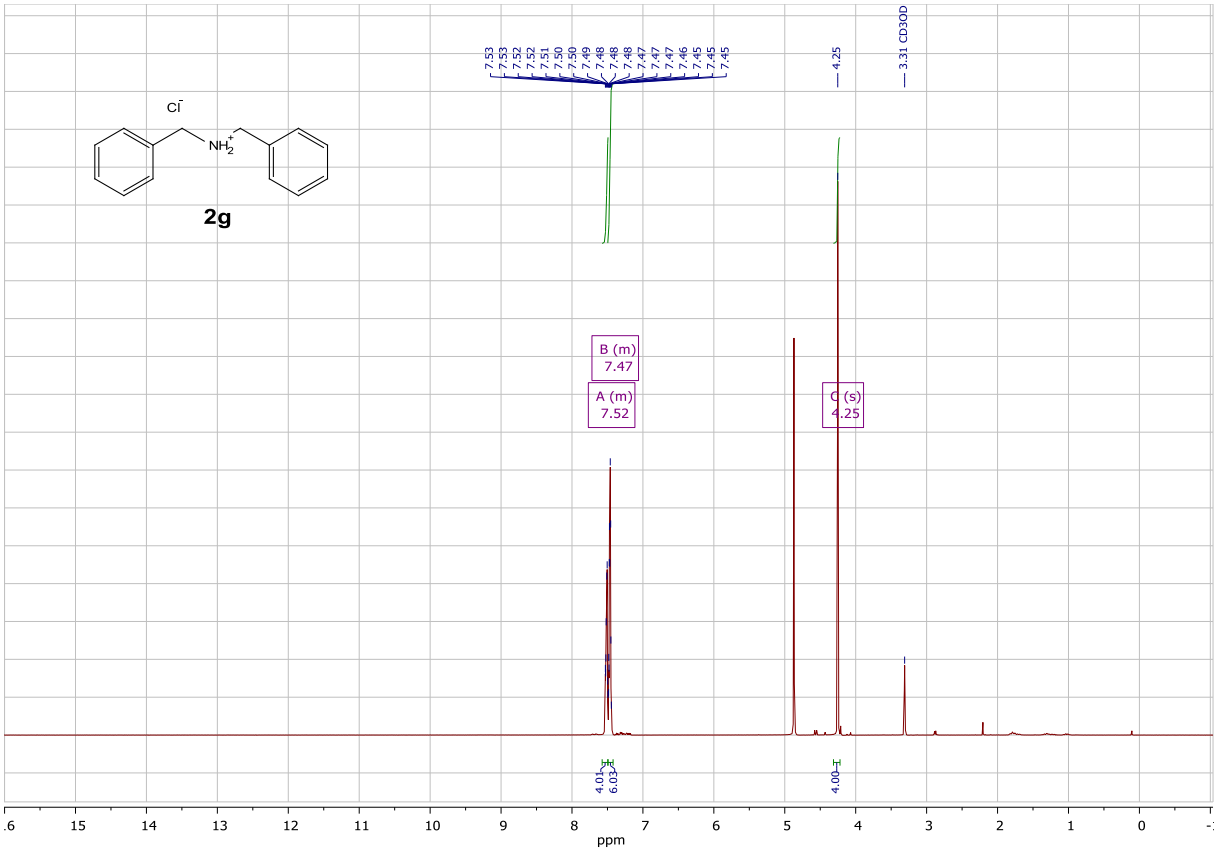

2D/23
Reyes, PB187_6, CDCl3
rau_sCOSYGPSW CDCl3 {C:\Bruker\TopSpin3.0} AK_Jacobi 36
O
NH
+
O
NH
f2 (ppm)
f1 (ppm)

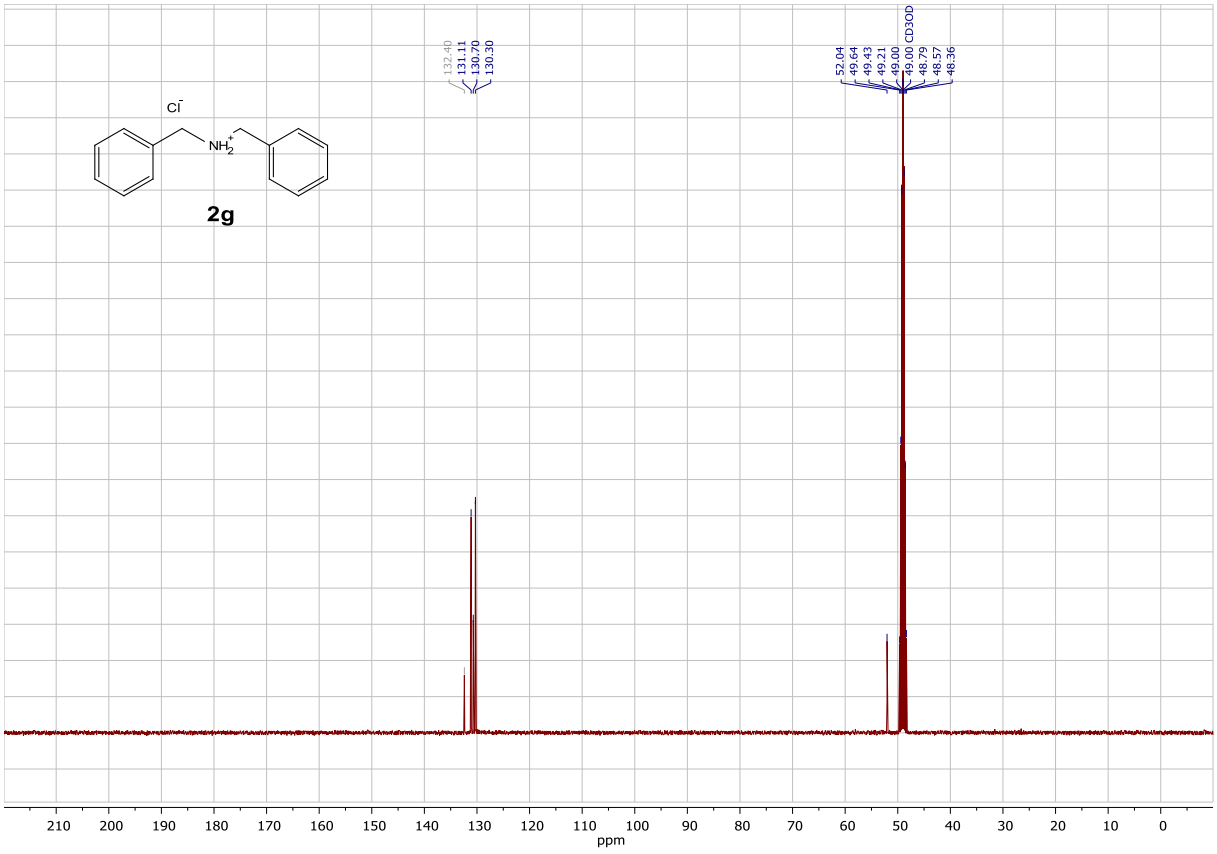

1 : 0.87
2f
A (dd) 7.34 J(1.92, 0.84)
B (dd) 6.29 J(3.18, 1.87)
C (d) 6.15 J(3.13)
D (ddt) 3.99 J(11.13, 7.41, 3.74)
E (s) 3.80
F (dt) 3.73 J(8.22, 6.78)
G (dt) 3.84 J(8.35, 6.70)
H (dd) 2.74 J(11.80, 3.73)
I (dd) 2.63 J(11.80, 8.12)
J (tt) 2.44 J(10.35, 3.76)
K (dt) 1.72 J(12.49, 3.56)
L (m) 1.60
M (m) 1.88
N (m) 1.97
O (m) 1.52
ppm

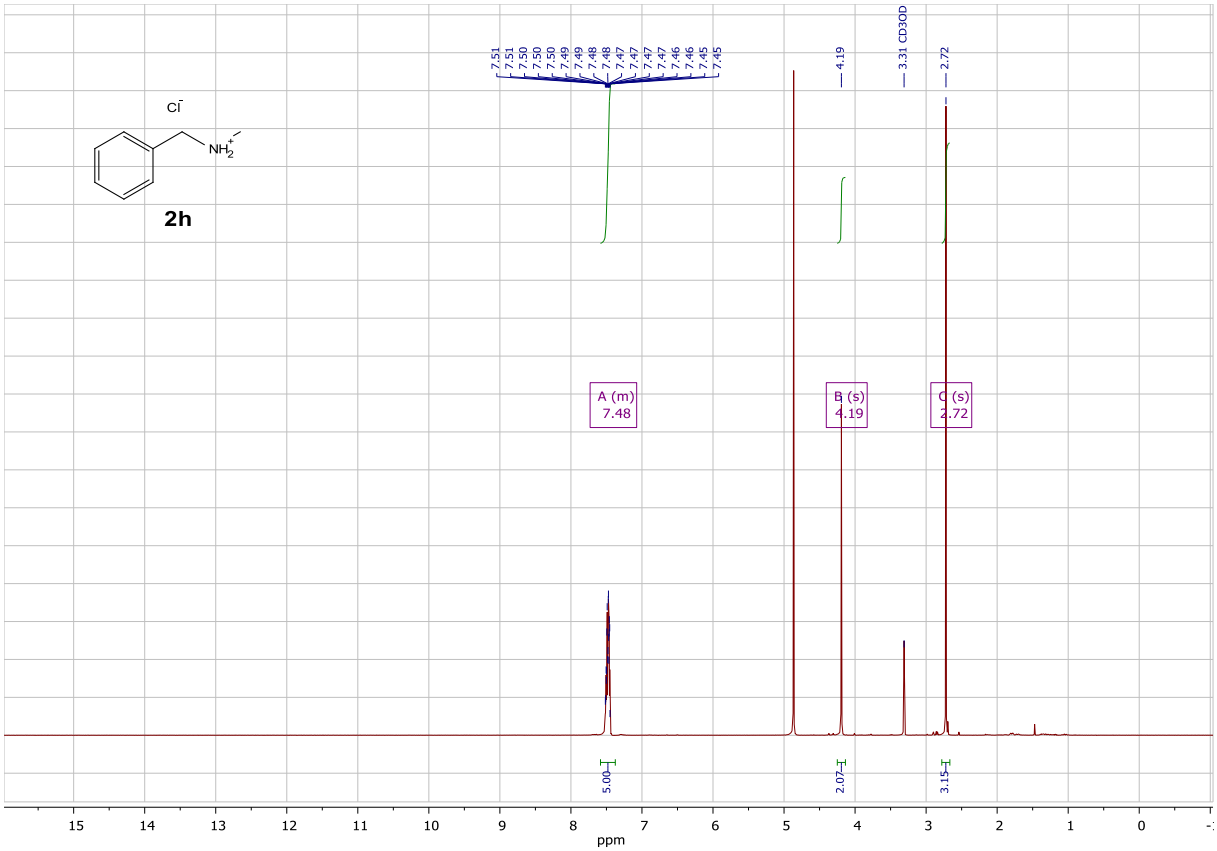

2f
ppm

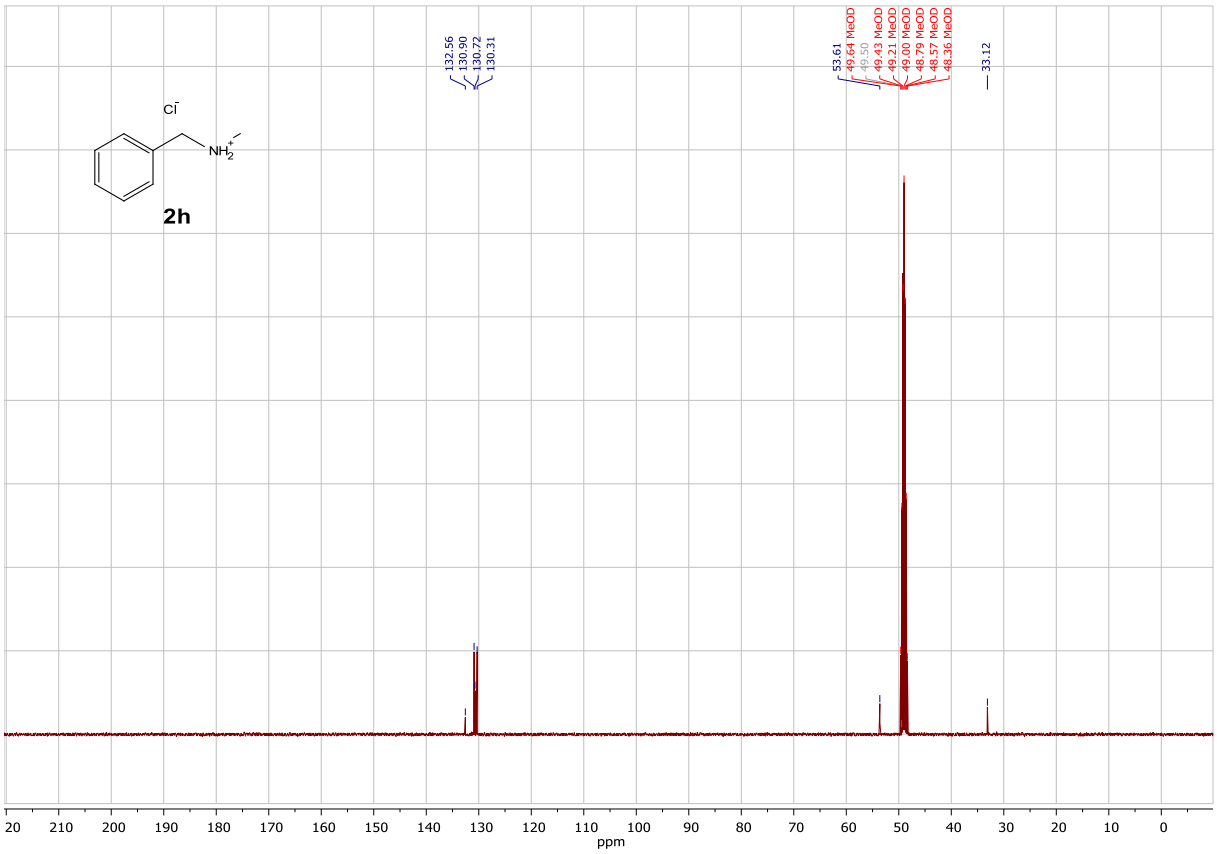

2D/11
Reyes, ree187_7, CDCl3
rau_sHSQCEDETGPSW CDCl3 {C:\Bruker\TopSpin3.0} AK_Jacobi 29
NH
NH
f2 (ppm)
f1 (ppm)

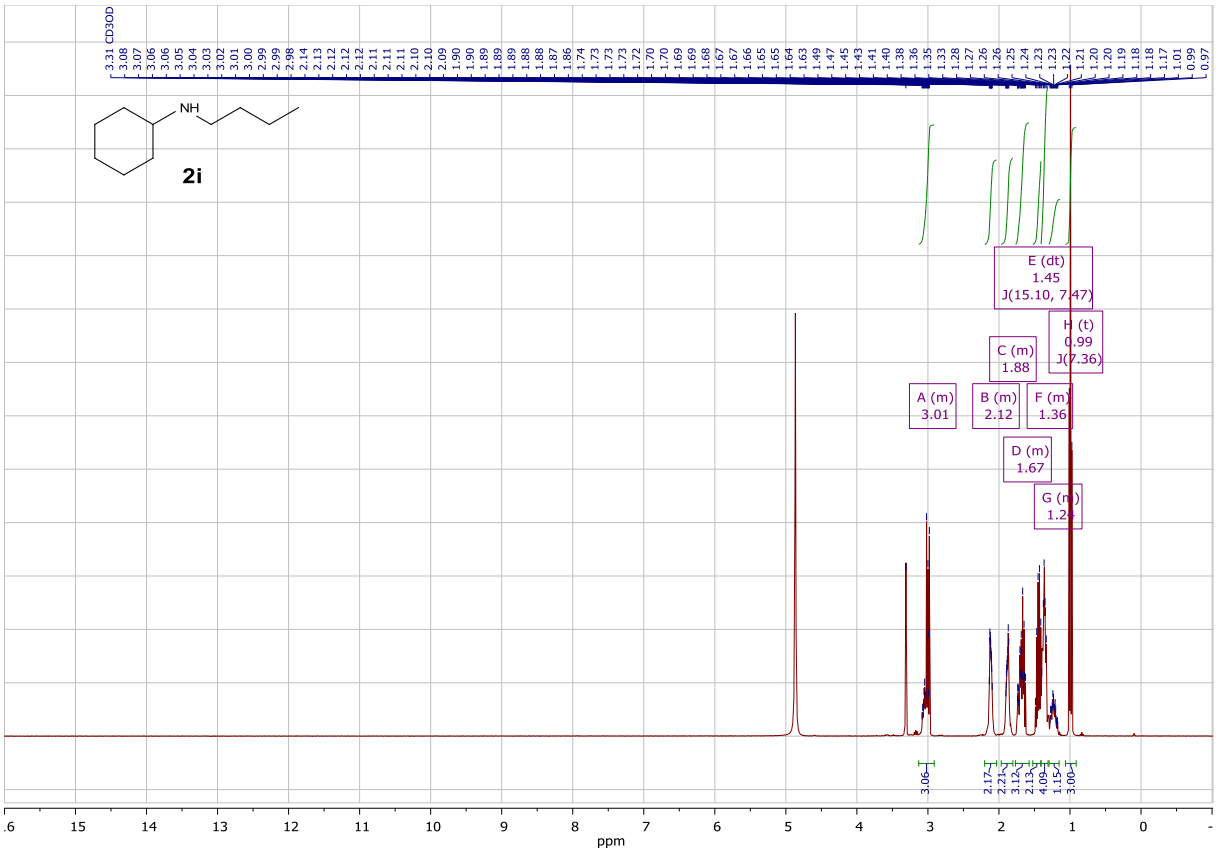

2D/13
Reyes, ree187_7, CDCl3
rau_sCOSYGPSW CDCl3 {C:\Bruker\TopSpin3.0} AK_Jacobi 29
NH
NH
f2 (ppm)
f1 (ppm)

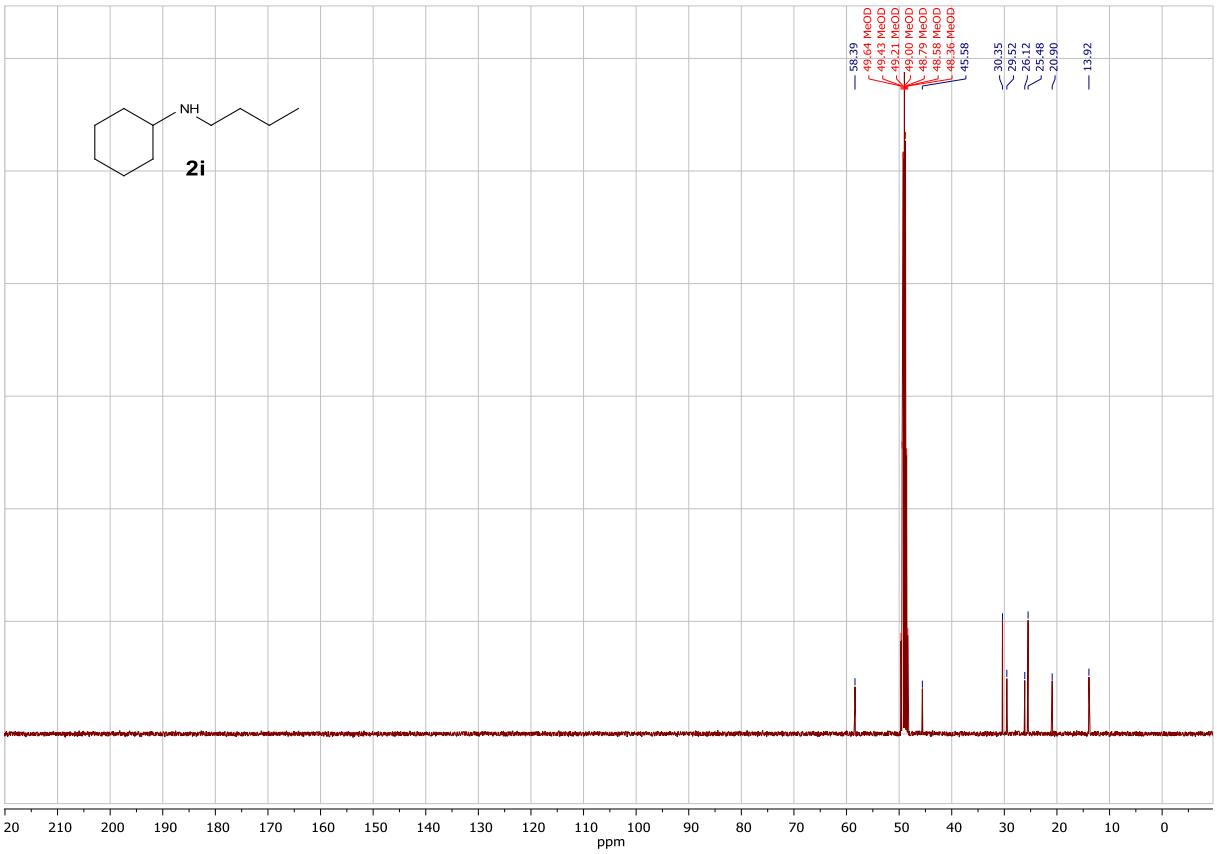

Cl⁻
NH2+
2g
7.53
7.53
7.52
7.52
7.51
7.50
7.50
7.49
7.48
7.48
7.48
7.47
7.47
7.47
7.46
7.45
7.45
7.45
4.25
3.31 CD3OD
B (m)
7.47
A (m)
7.52
C (s)
4.25
4.01
6.03
4.00
ppm

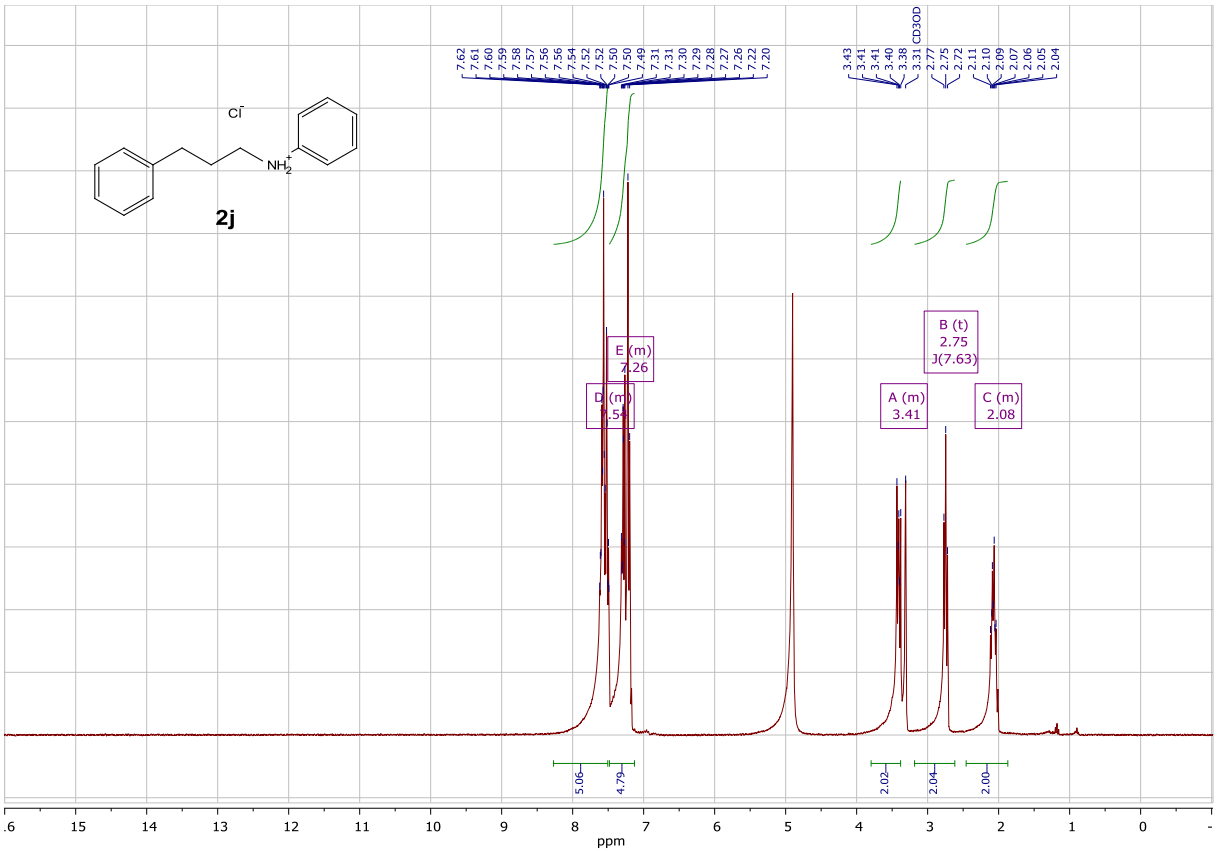

Cl⁻
NH2+
2g
132.40
131.11
130.70
130.30
52.04
49.64
49.43
49.21
49.00 CD3OD
48.79
48.57
48.36
ppm

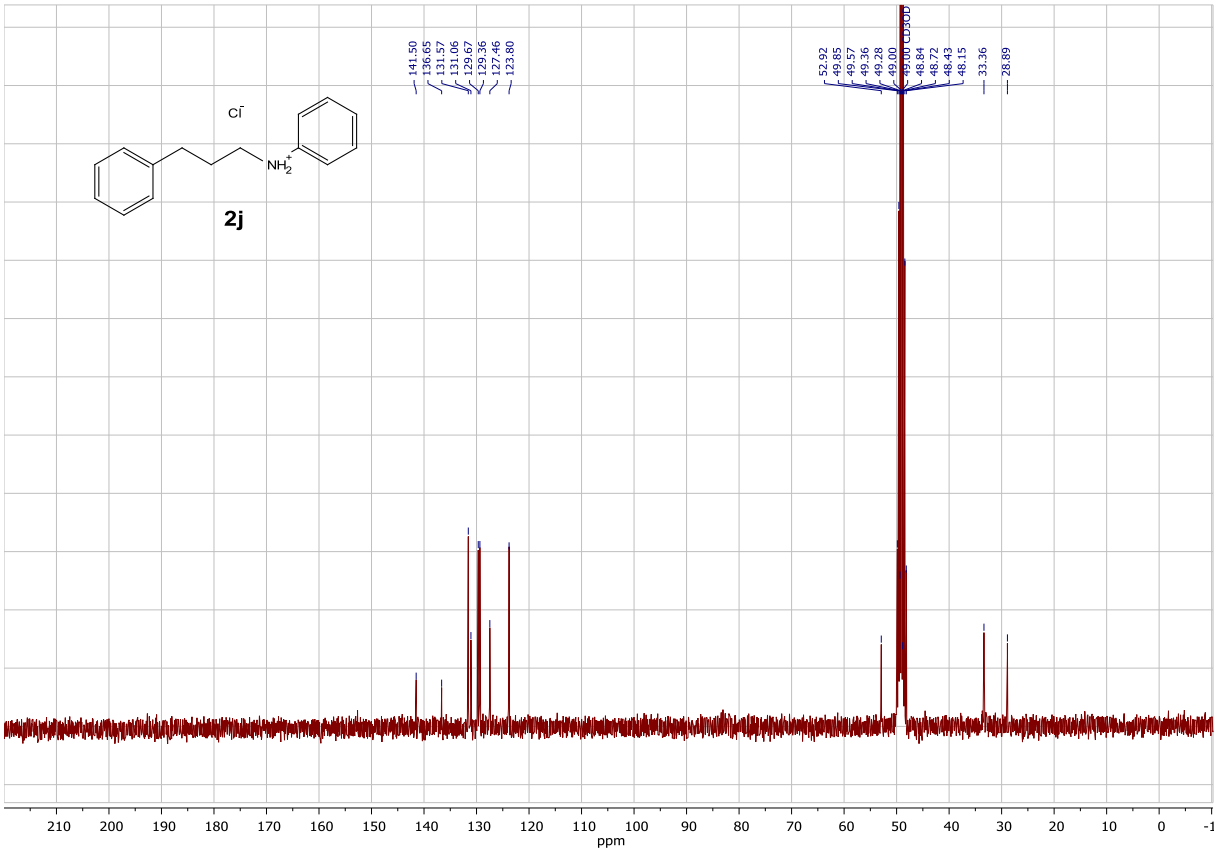

Cl⁻
NH2+
2h
7.51
7.51
7.50
7.50
7.50
7.49
7.49
7.48
7.47
7.47
7.47
7.46
7.46
7.45
7.45
4.19
3.31 CD3OD
2.72
A (m)
7.48
B (s)
4.19
C (s)
2.72
5.00
2.07
3.15
ppm

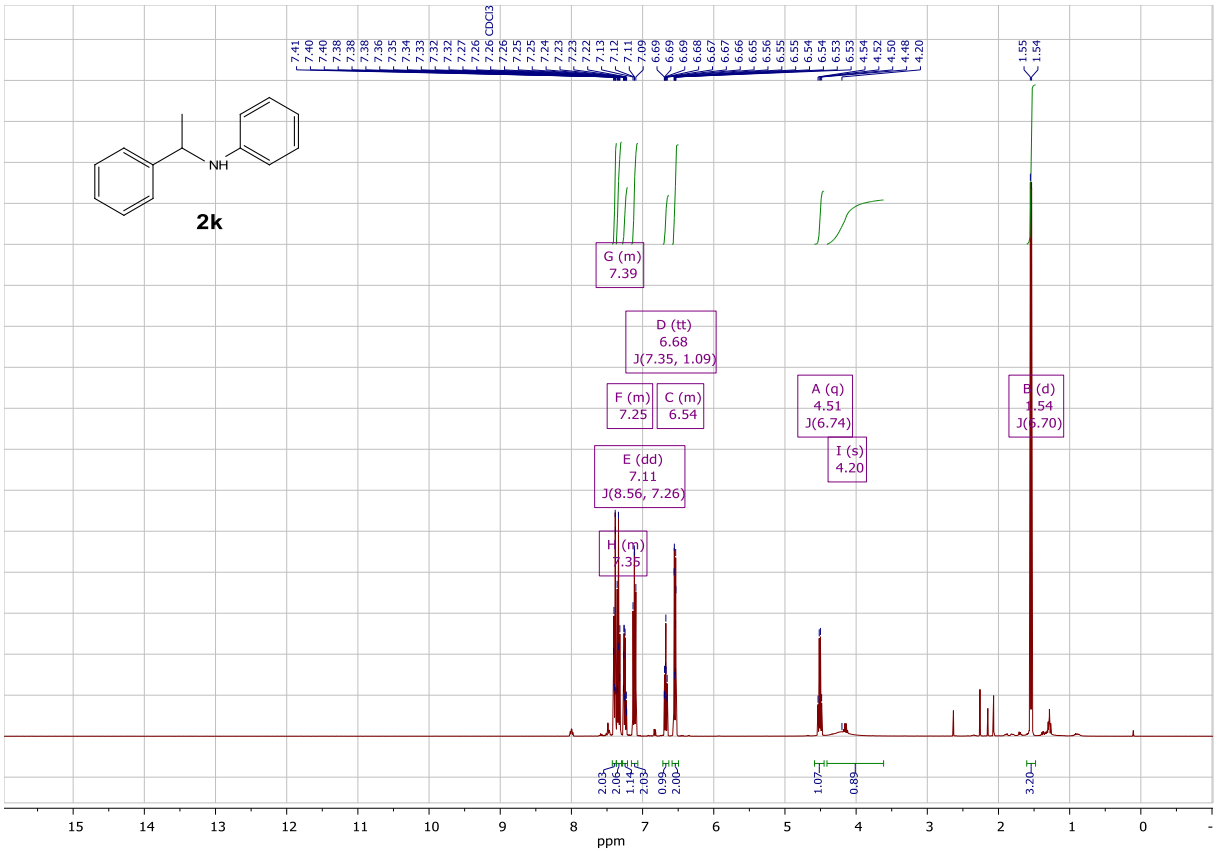

Cl⁻
NH2+
2h
132.56
130.90
130.72
130.31
53.61
49.64 MeOD
49.43 MeOD
49.21 MeOD
49.00 MeOD
48.79 MeOD
48.57 MeOD
48.36 MeOD
33.12
ppm

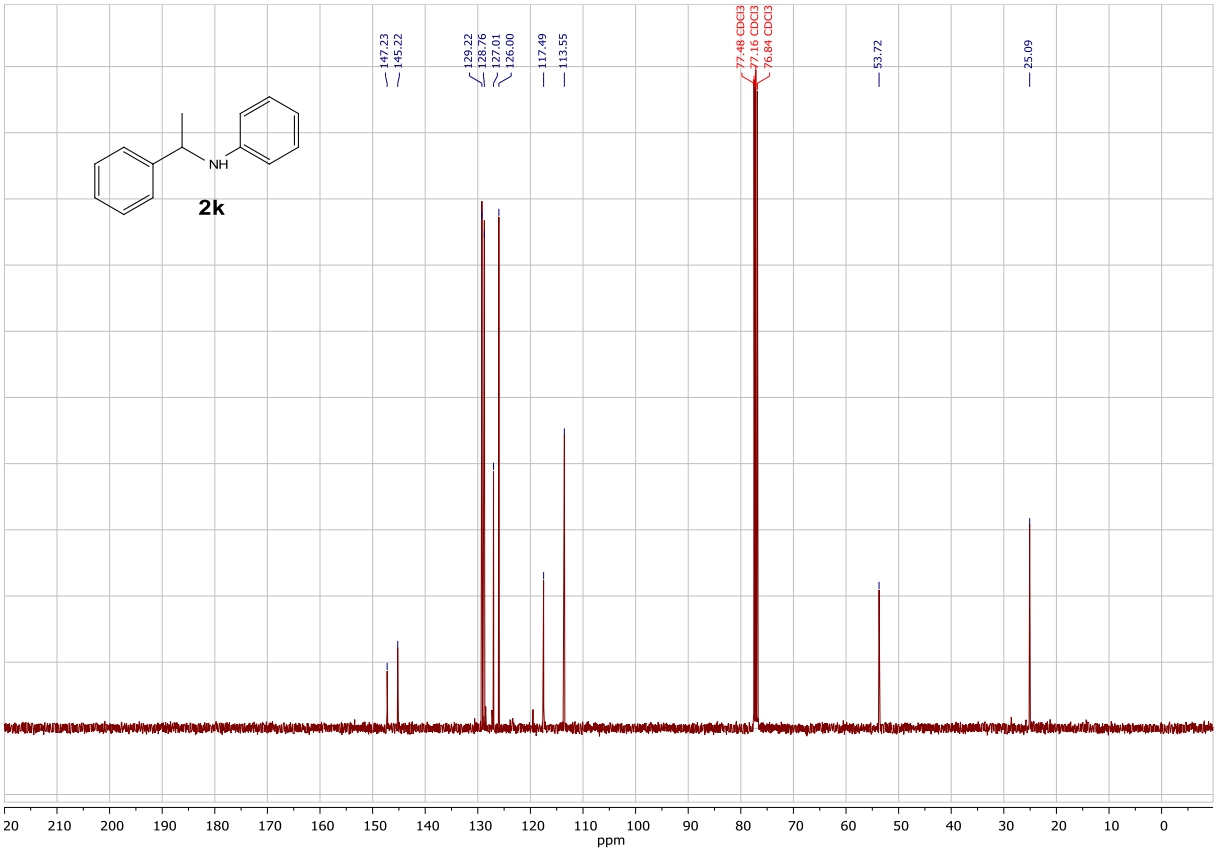

NH
2i
E (dt)
1.45
J(15.10, 7.47)
H (t)
0.99
J(7.36)
C (m)
1.88
A (m)
3.01
B (m)
2.12
F (m)
1.36
D (m)
1.67
ppm

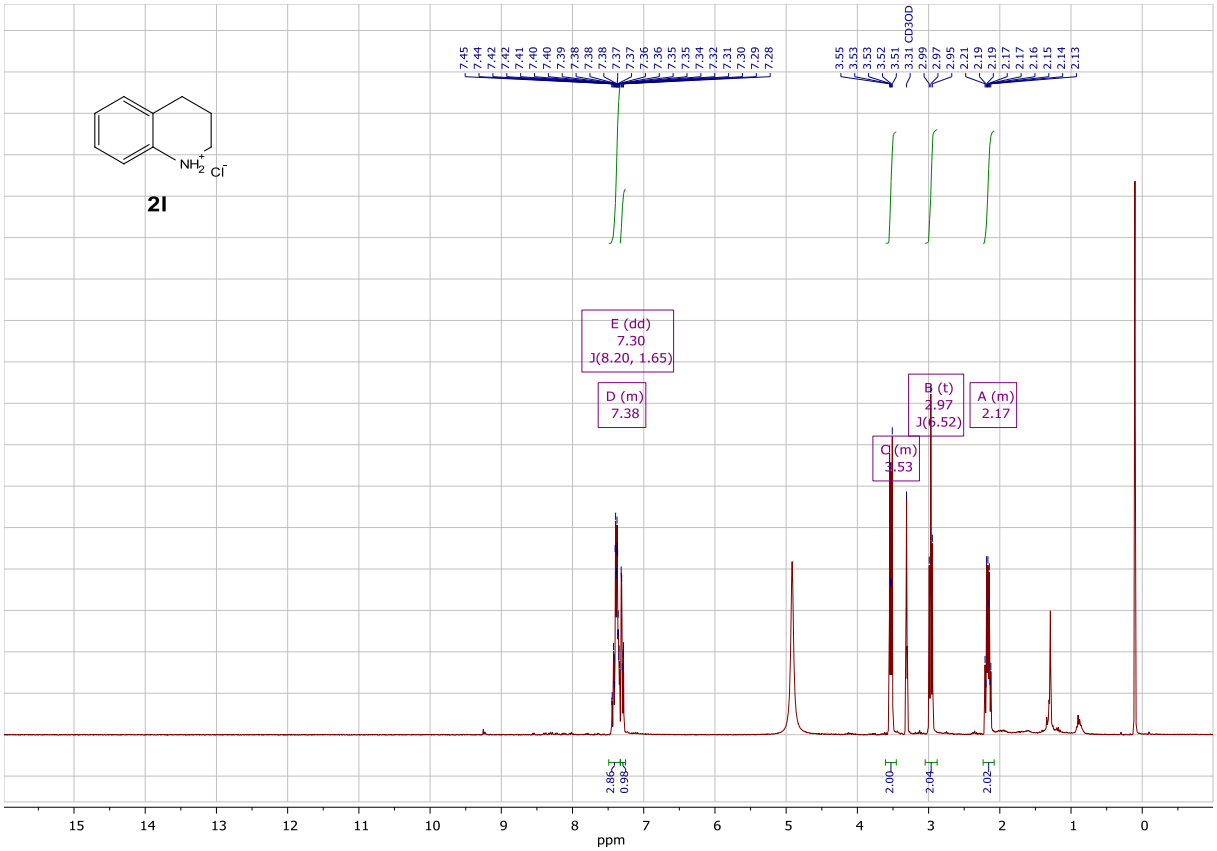

NH
2i
ppm

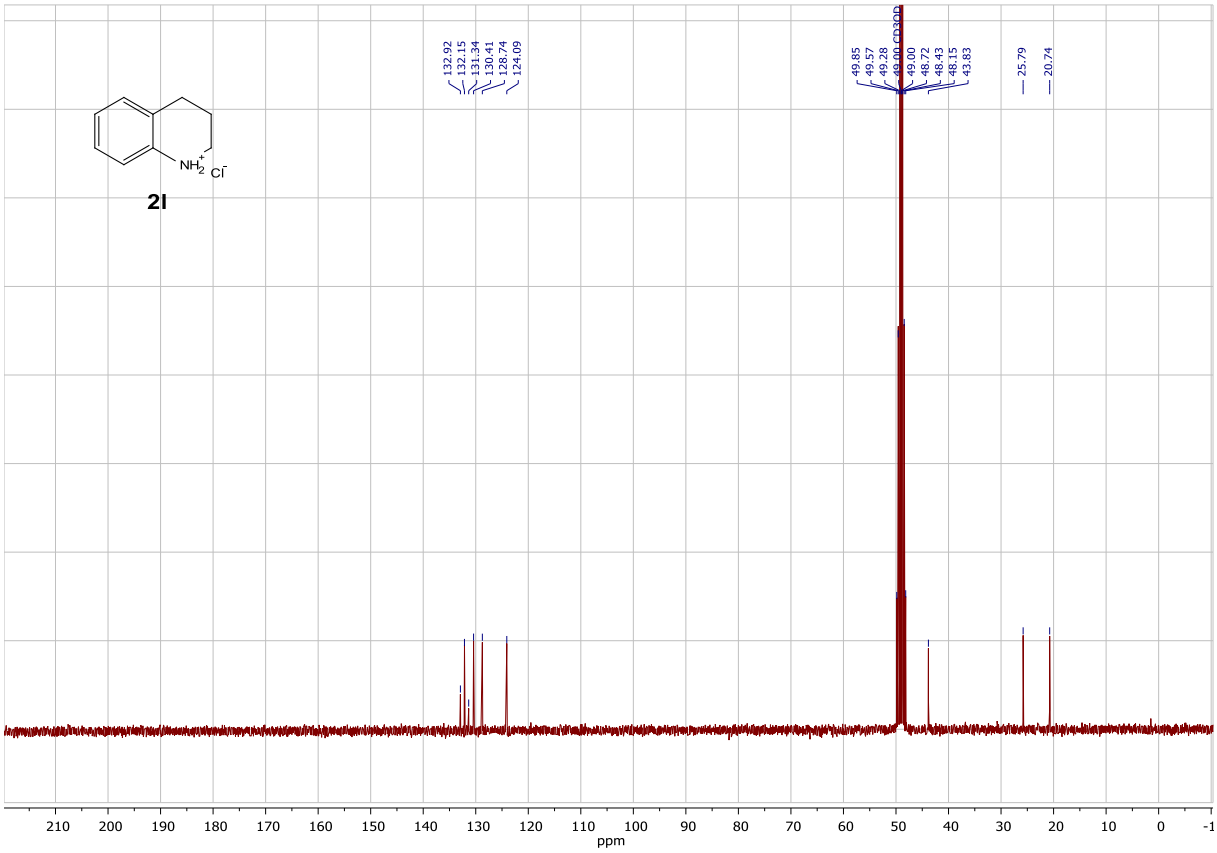

Cl⁻
NH2+
2j
7.62 7.61 7.60 7.59 7.58 7.57 7.56 7.56 7.54 7.52 7.52 7.50 7.50 7.50 7.49 7.31 7.31 7.30 7.29 7.28 7.27 7.26 7.22 7.20
3.43 3.41 3.41 3.40 3.38 3.31 CD3OD 2.77 2.75 2.72 2.11 2.10 2.09 2.07 2.06 2.05 2.04
E (m) 7.26
D (m) 7.54
B (t) 2.75 J(7.63)
A (m) 3.41
C (m) 2.08
5.06 4.79 2.02 2.04 2.00
ppm

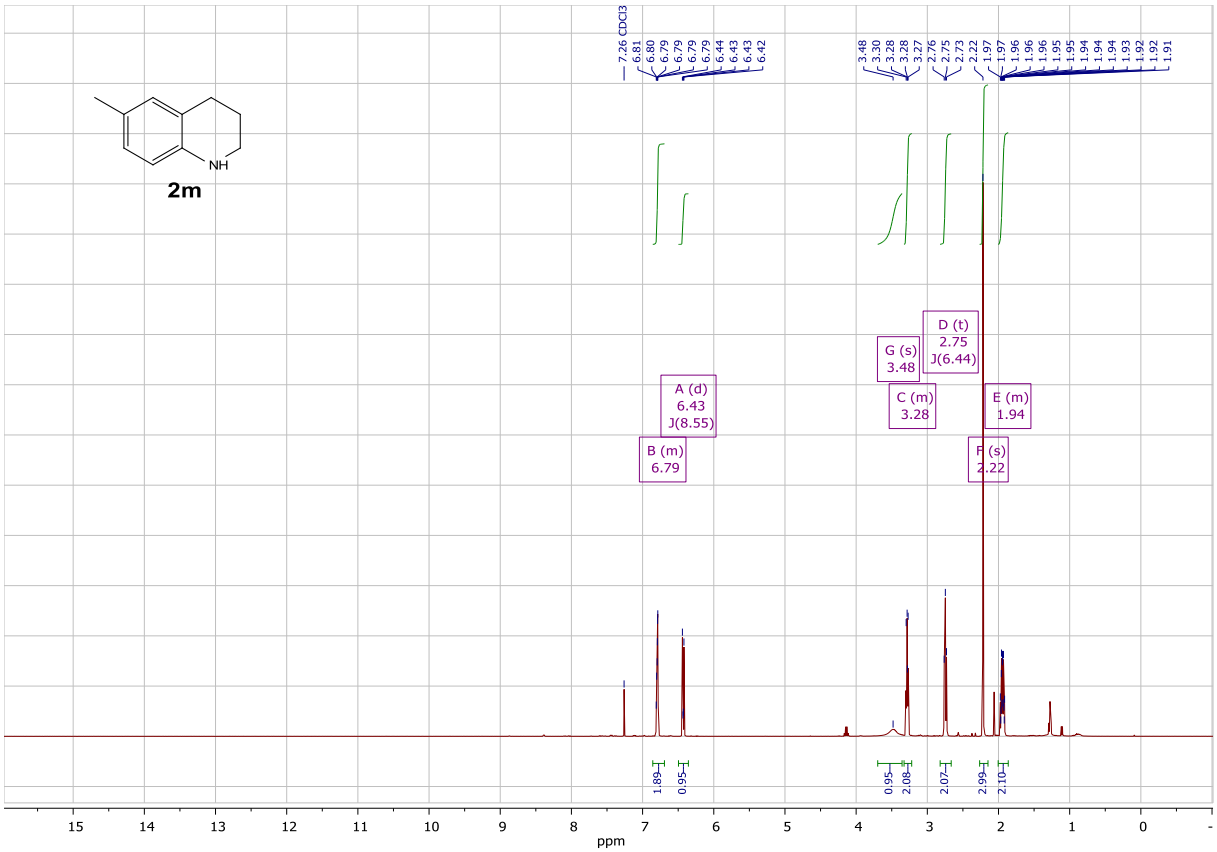

Cl⁻
NH2+
2j
141.50 136.65 131.57 131.06 129.67 129.36 127.46 123.80
52.92 49.85 49.57 49.36 49.28 49.00 CD3OD 48.84 48.72 48.43 48.15 33.36 28.89
ppm

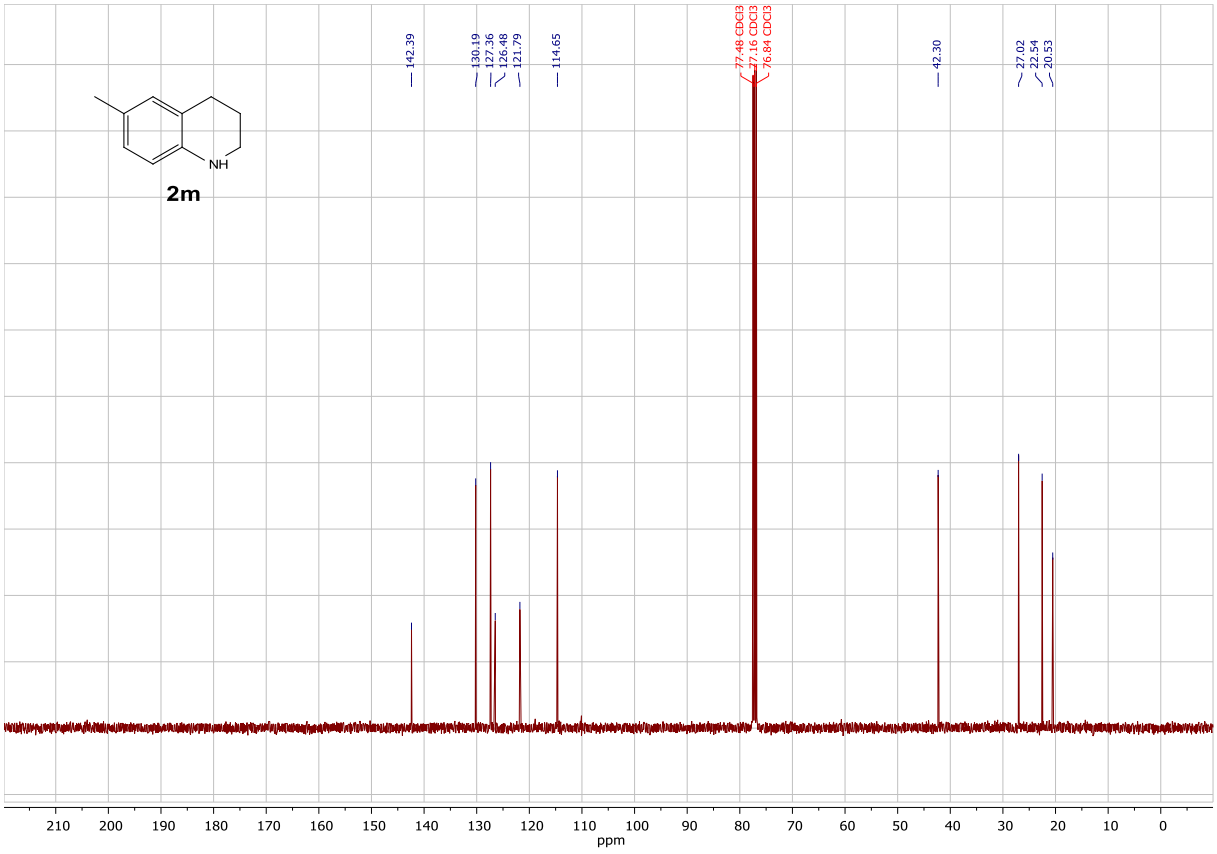

NH
2k
G (m)
7.39
D (tt)
6.68
J(7.35, 1.09)
F (m)
7.25
C (m)
6.54
A (q)
4.51
J(6.74)
I (s)
4.20
B (d)
1.54
J(6.70)
E (dd)
7.11
J(8.56, 7.26)
H (m)
7.35
ppm

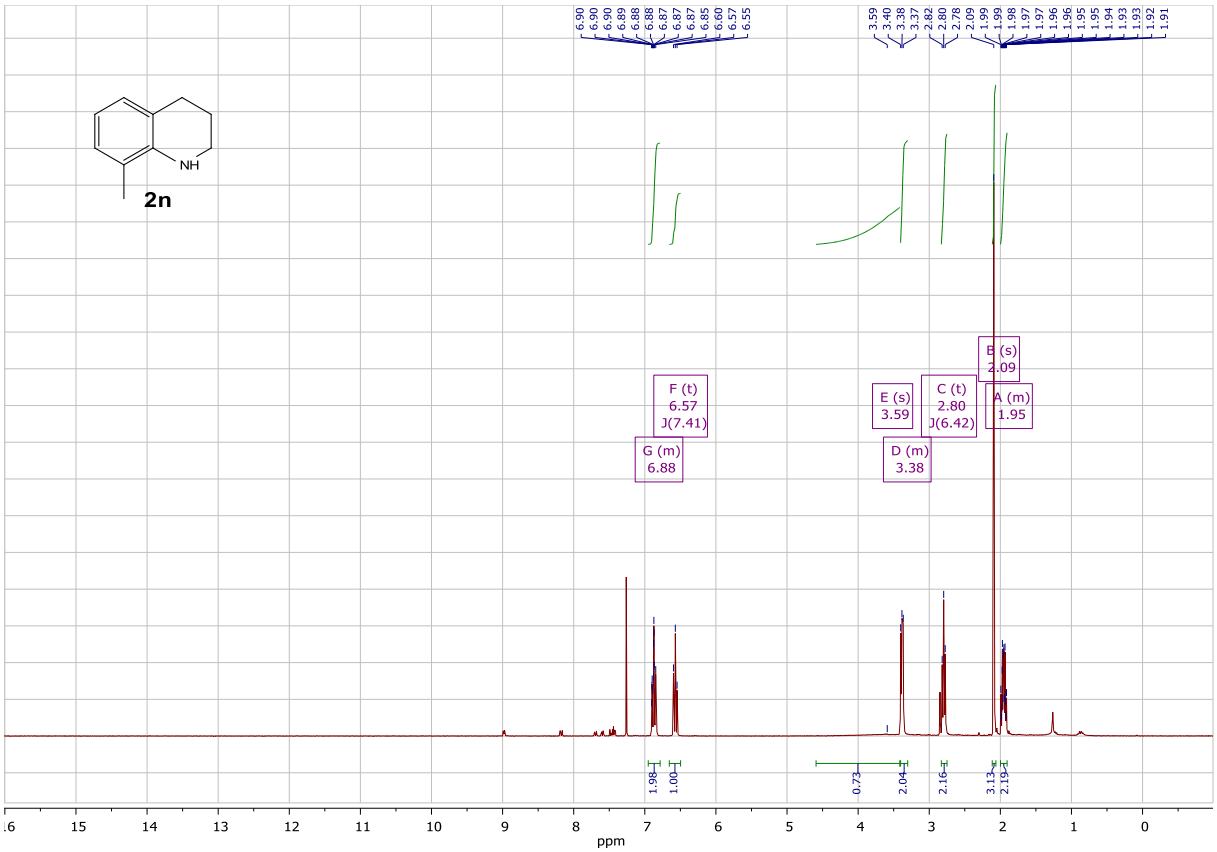

NH
2k
147.23
145.22
129.22
128.76
127.01
126.00
117.49
113.55
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
53.72
25.09
ppm

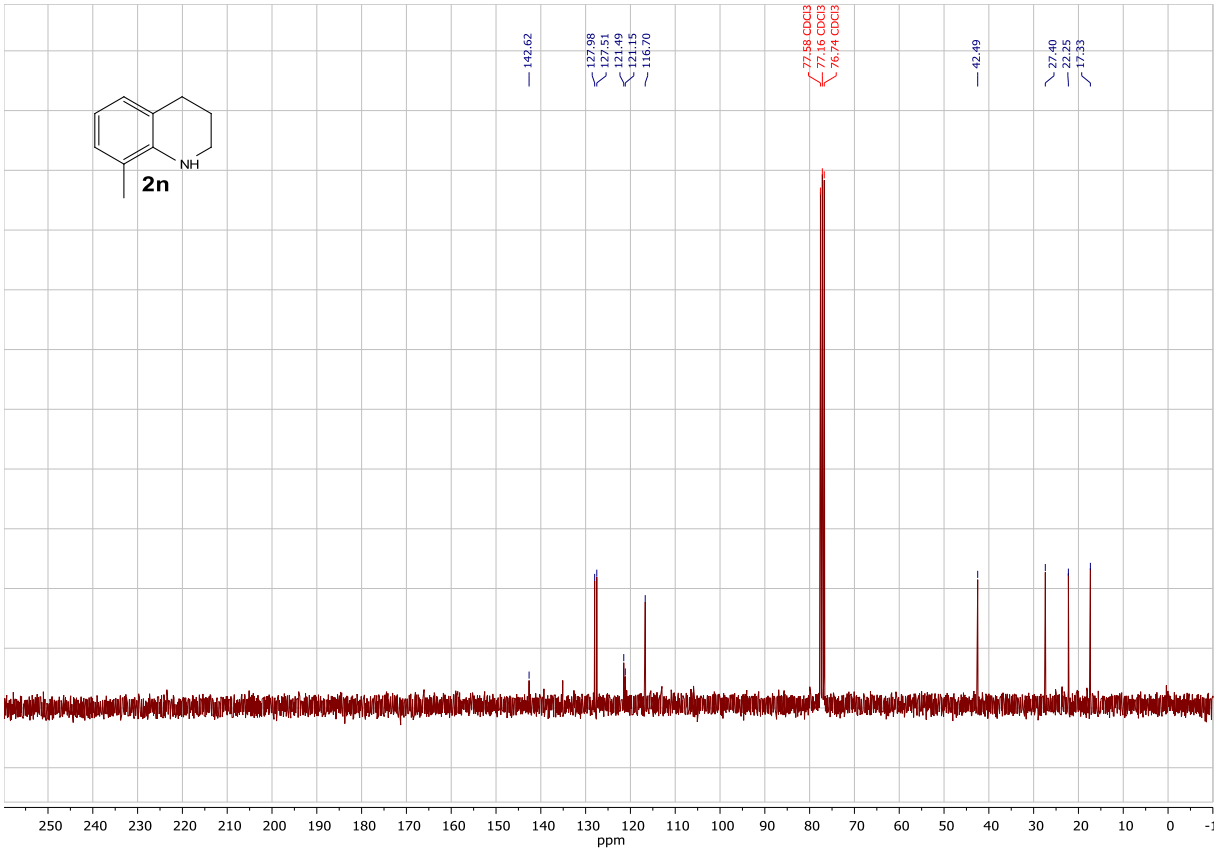

2l
E (dd)
7.30
J(8.20, 1.65)
D (m)
7.38
C (m)
3.53
B (t)
2.97
J(6.52)
A (m)
2.17
ppm

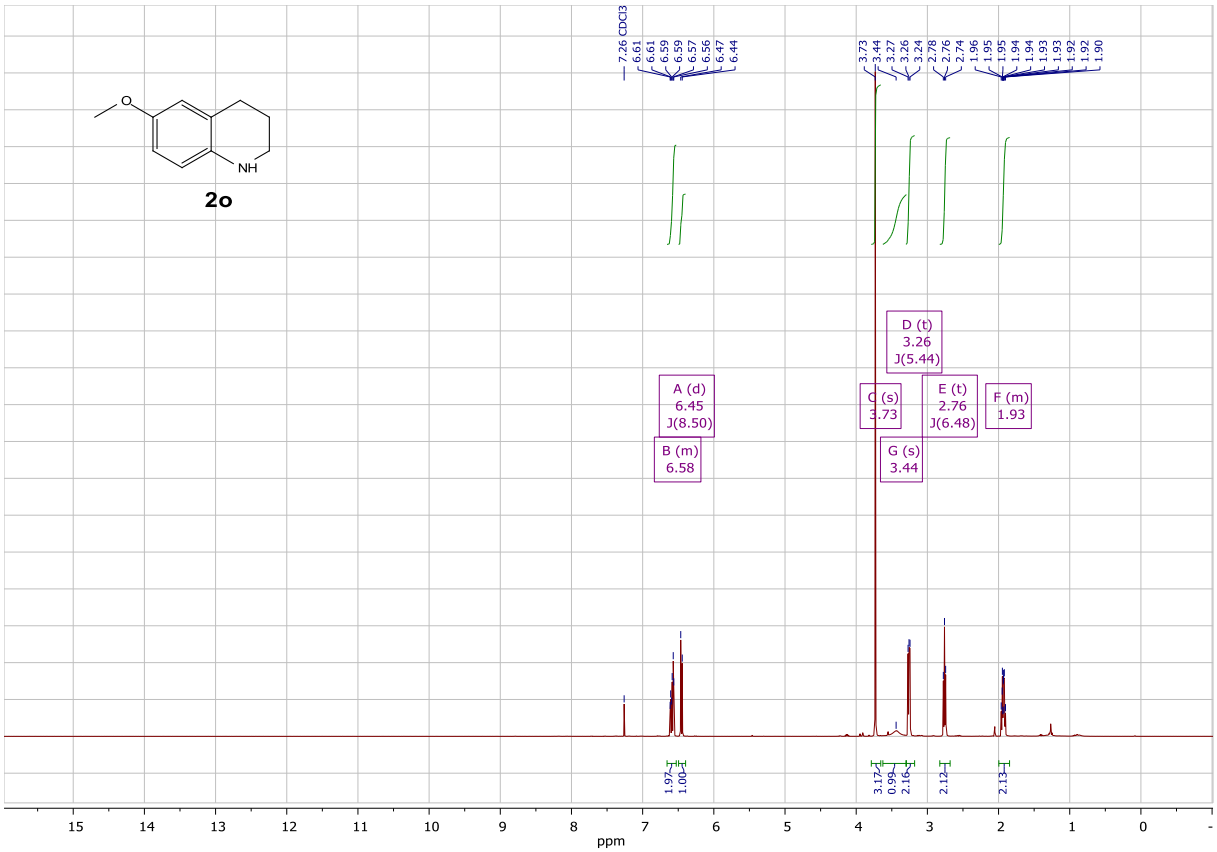

2l
ppm

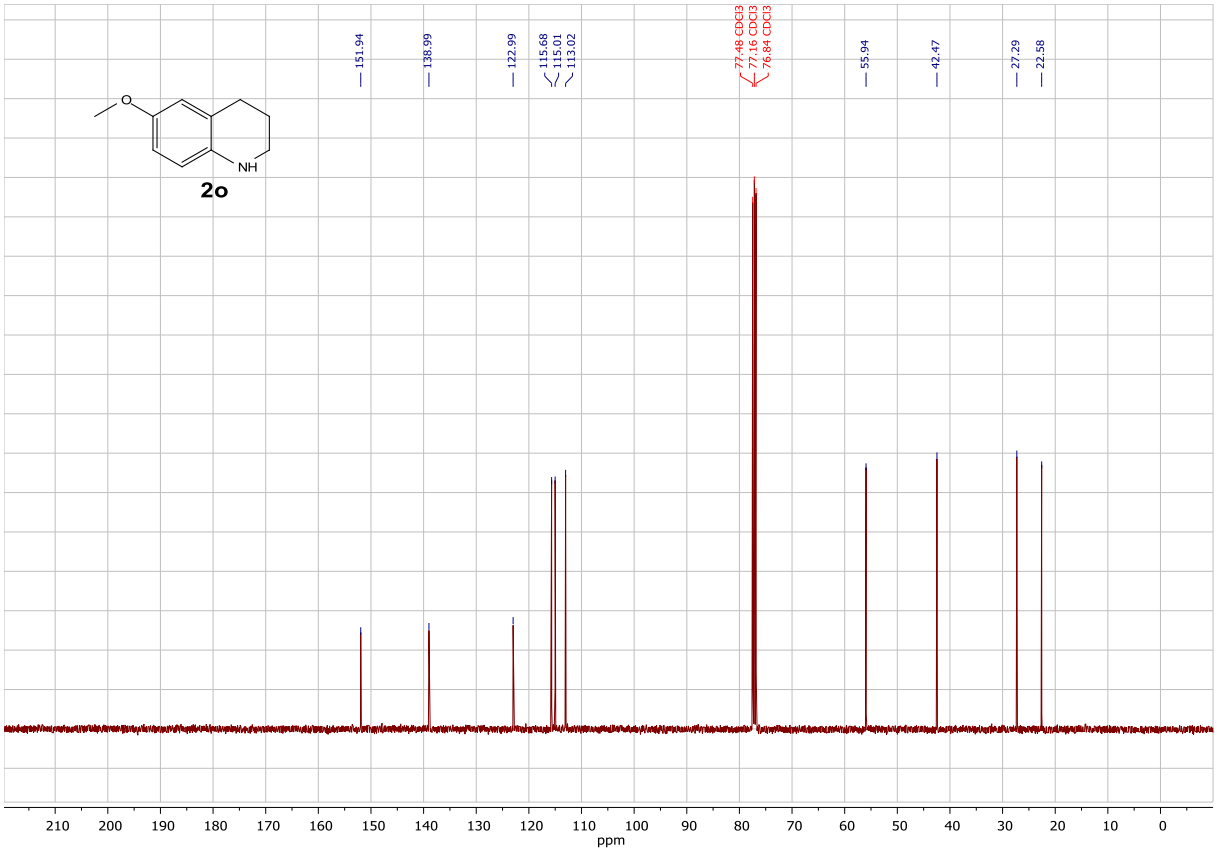

NH
2m
7.26 CDCl3
6.81
6.80
6.79
6.79
6.79
6.79
6.44
6.43
6.43
6.42
3.48
3.30
3.28
3.28
3.27
2.76
2.75
2.73
2.22
1.97
1.97
1.96
1.96
1.96
1.95
1.95
1.94
1.94
1.94
1.93
1.92
1.92
1.91
A (d)
6.43
J(8.55)
B (m)
6.79
G (s)
3.48
D (t)
2.75
J(6.44)
C (m)
3.28
E (m)
1.94
F (s)
2.22
1.89
0.95
0.95
2.08
2.07
2.99
2.10
ppm

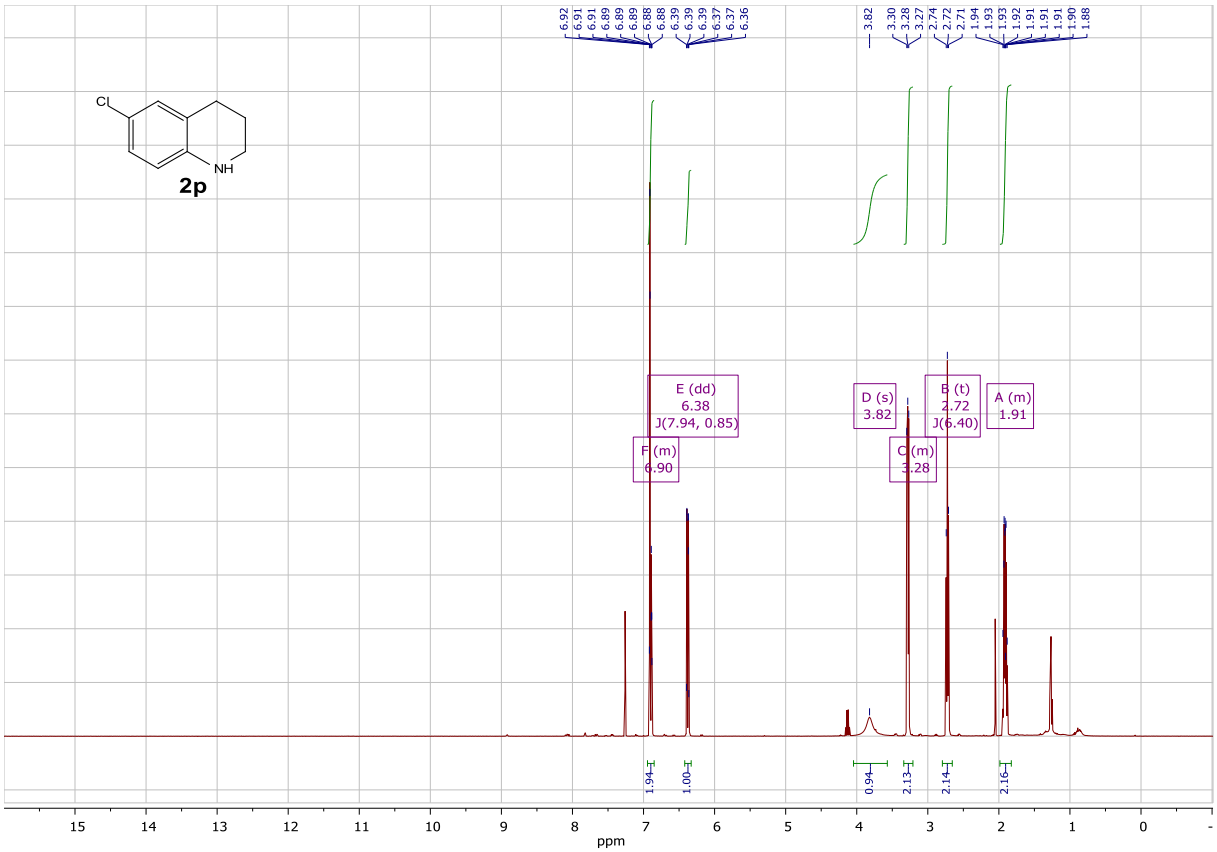

NH
2m
142.39
130.19
127.36
126.48
121.79
114.65
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
42.30
27.02
22.54
20.53
ppm

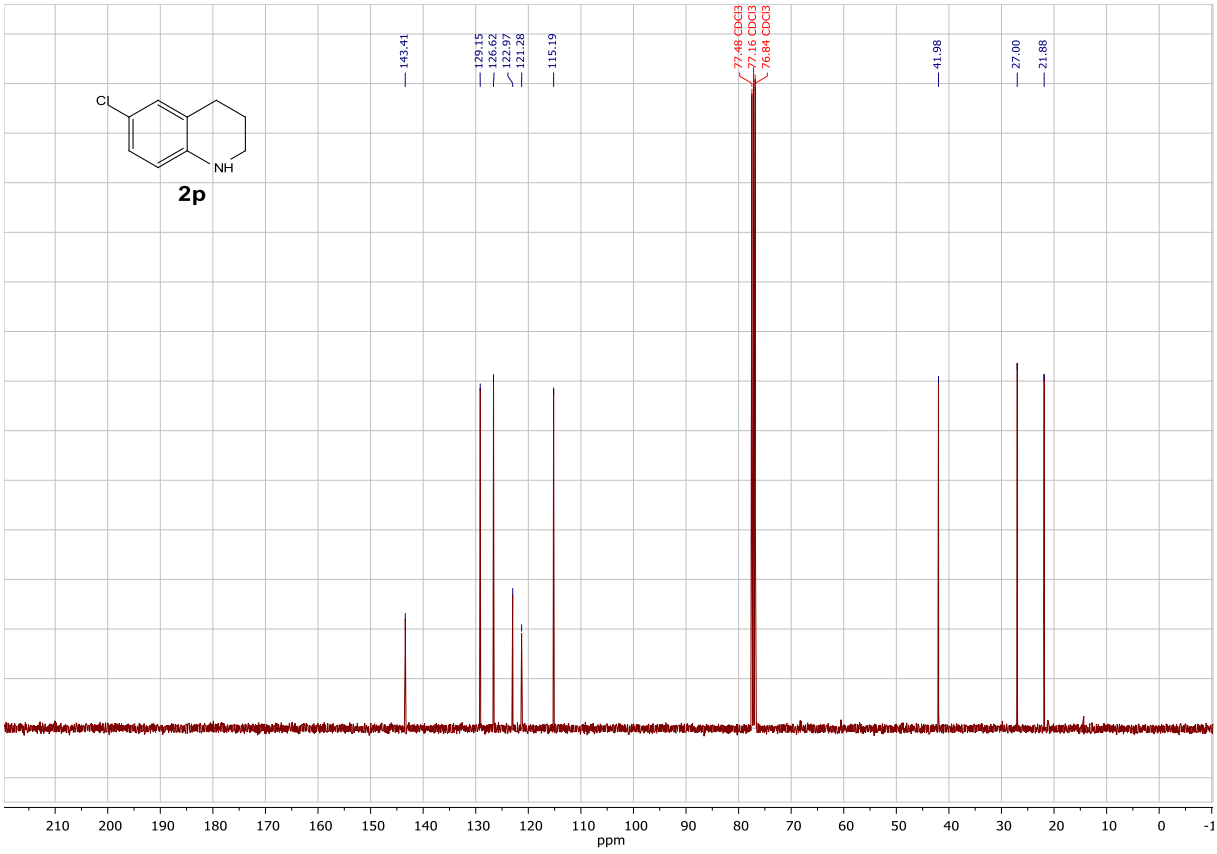

NH
2n
F (t)
6.57
J(7.41)
G (m)
6.88
E (s)
3.59
C (t)
2.80
J(6.42)
D (m)
3.38
B (s)
2.09
A (m)
1.95
ppm

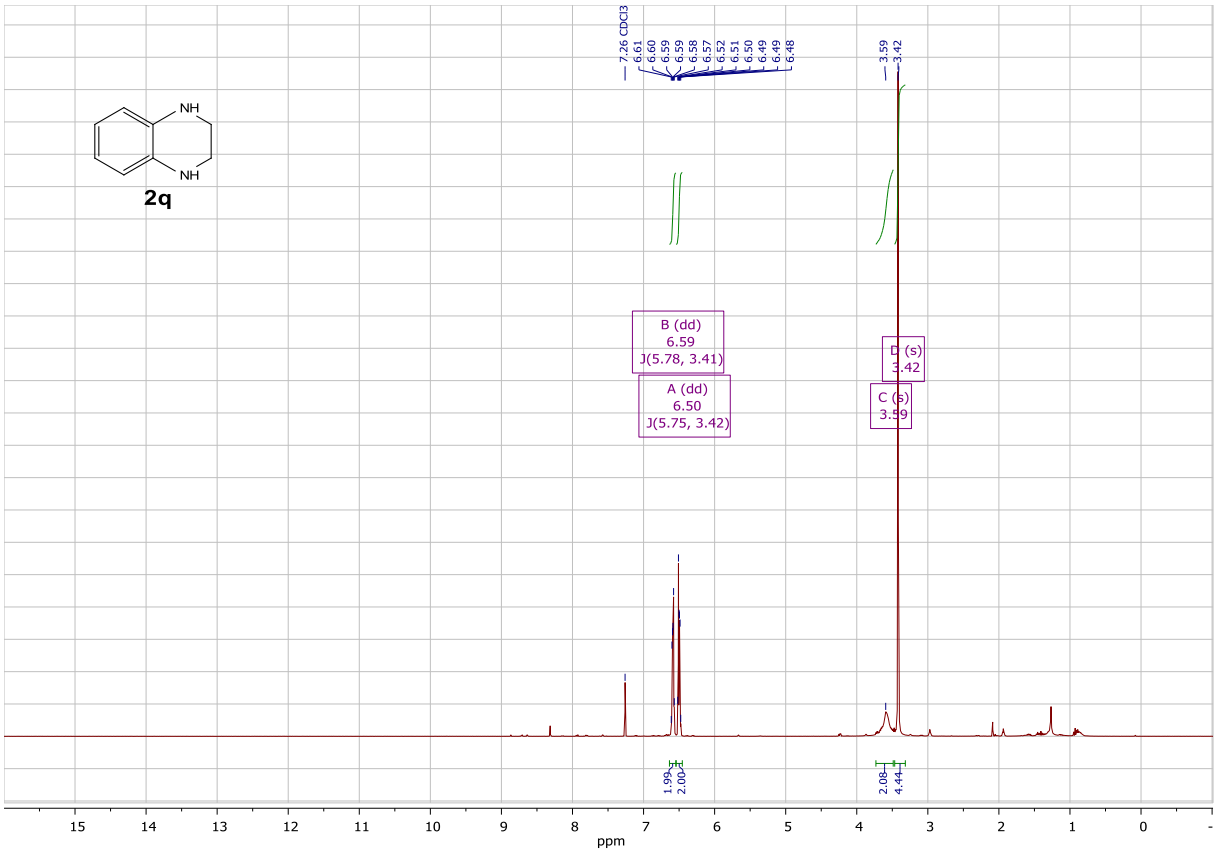

NH
2n
142.62
127.98
127.51
121.49
121.15
116.70
77.58 CDCl3
77.16 CDCl3
76.74 CDCl3
42.49
27.40
22.25
17.33
ppm

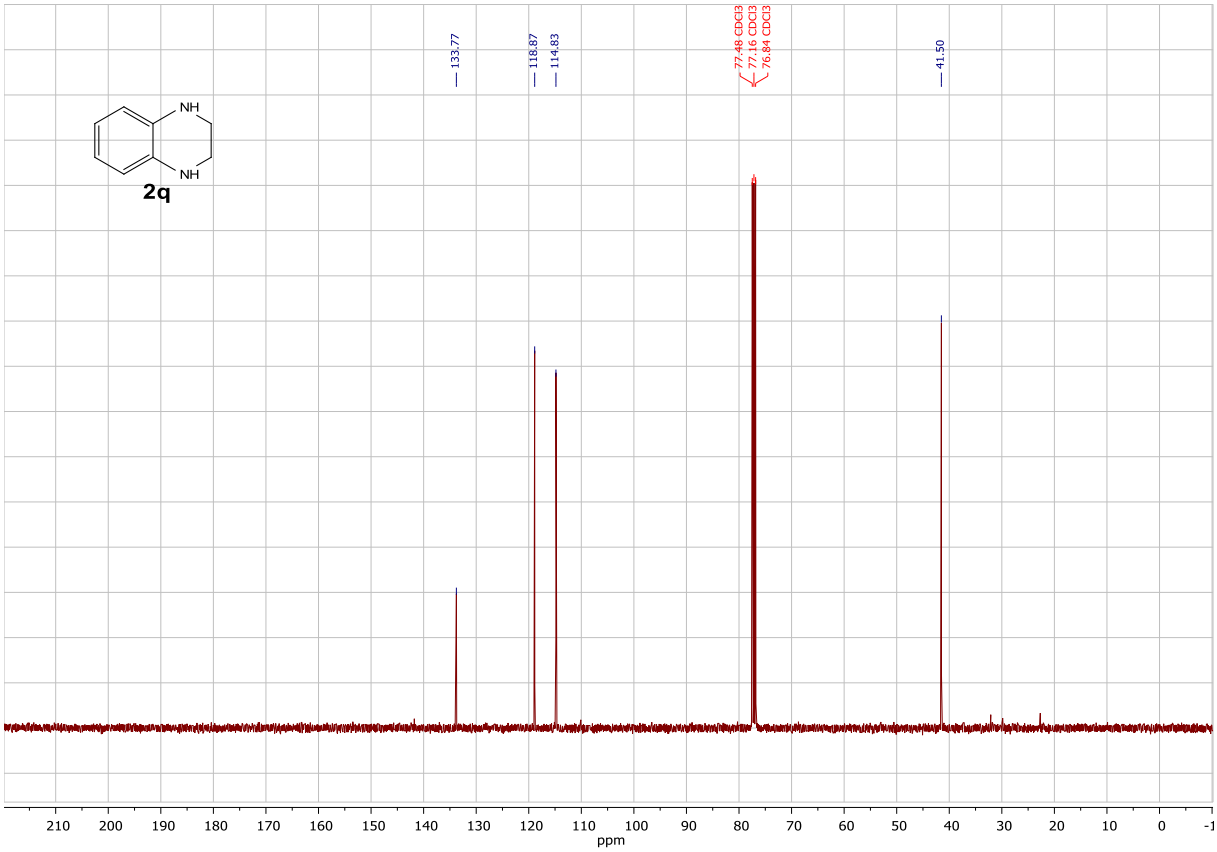

O
NH
2o
7.26 CDCl3
6.61
6.61
6.59
6.59
6.57
6.56
6.47
6.44
3.73
3.44
3.27
3.26
3.24
2.78
2.76
2.74
1.96
1.95
1.95
1.94
1.94
1.93
1.93
1.92
1.92
1.90
A (d)
6.45
J(8.50)
B (m)
6.58
C (s)
3.73
D (t)
3.26
J(5.44)
E (t)
2.76
J(6.48)
F (m)
1.93
G (s)
3.44
1.97
1.00
3.17
0.99
2.16
2.12
2.13
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm

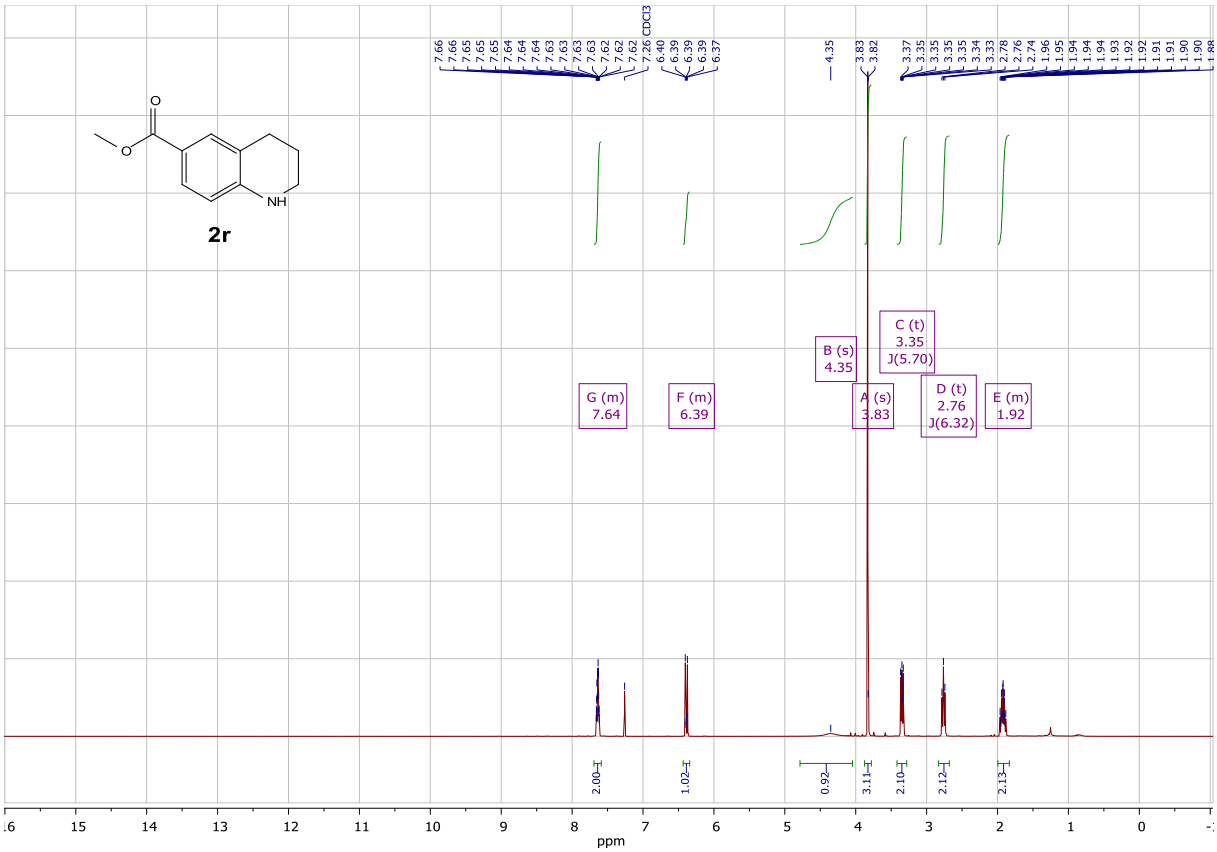

O
NH
2o
151.94
138.99
122.99
115.68
115.01
113.02
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
55.94
42.47
27.29
22.58
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

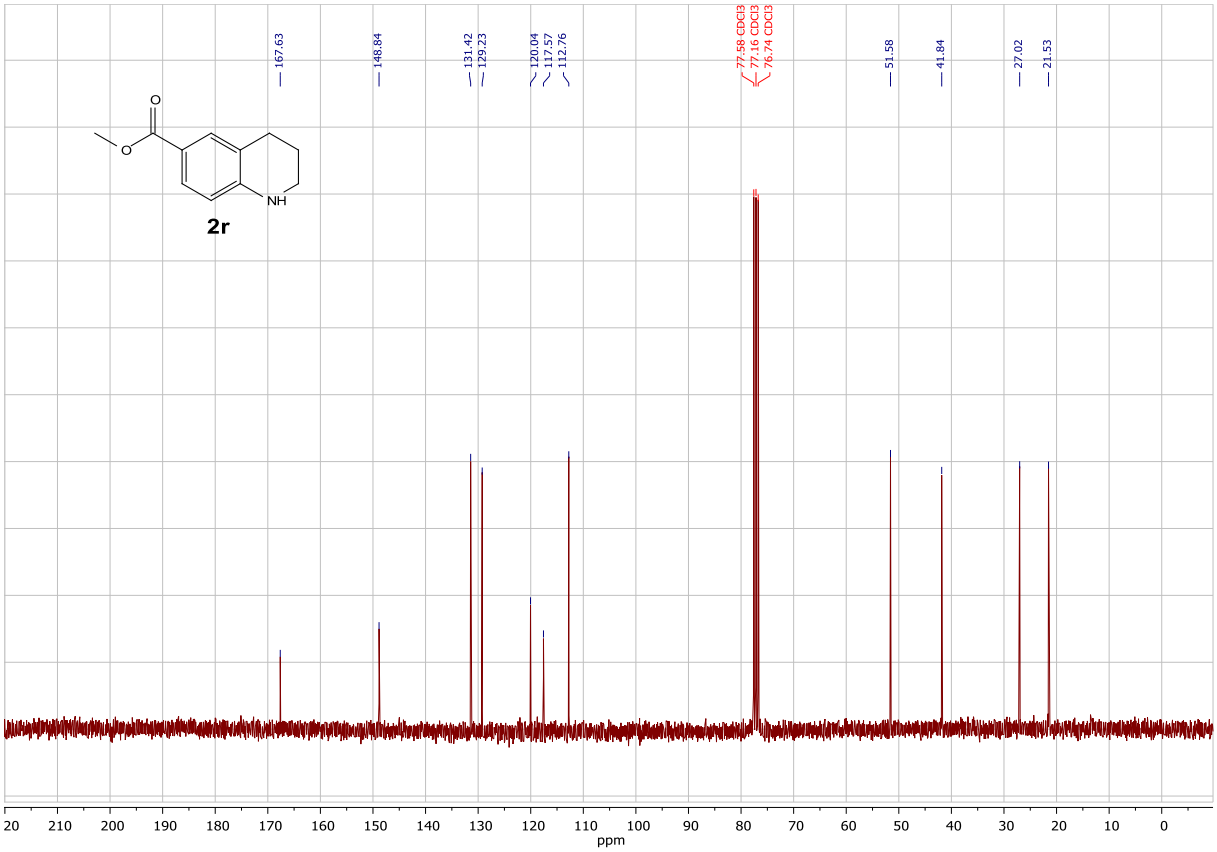

Cl
NH
2p
6.92
6.91
6.91
6.89
6.89
6.89
6.88
6.88
6.39
6.39
6.39
6.37
6.37
6.36
3.82
3.30
3.28
3.27
2.74
2.72
2.71
1.94
1.93
1.93
1.92
1.91
1.91
1.91
1.90
1.88
E (dd)
6.38
J(7.94, 0.85)
F (m)
6.90
D (s)
3.82
C (m)
3.28
B (t)
2.72
J(6.40)
A (m)
1.91
1.94
1.00
0.94
2.13
2.14
2.16
ppm

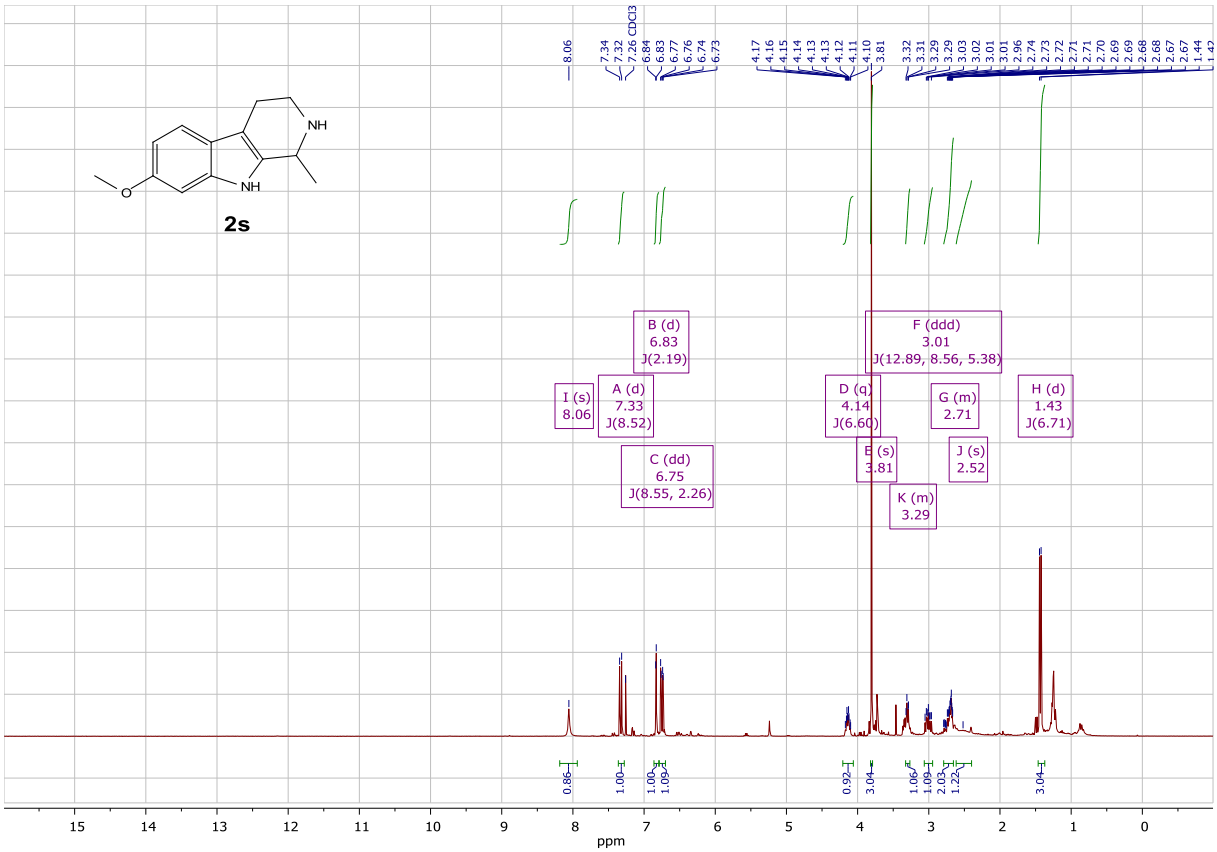

Cl
NH
2p
143.41
129.15
126.62
122.97
121.28
115.19
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
41.98
27.00
21.88
ppm

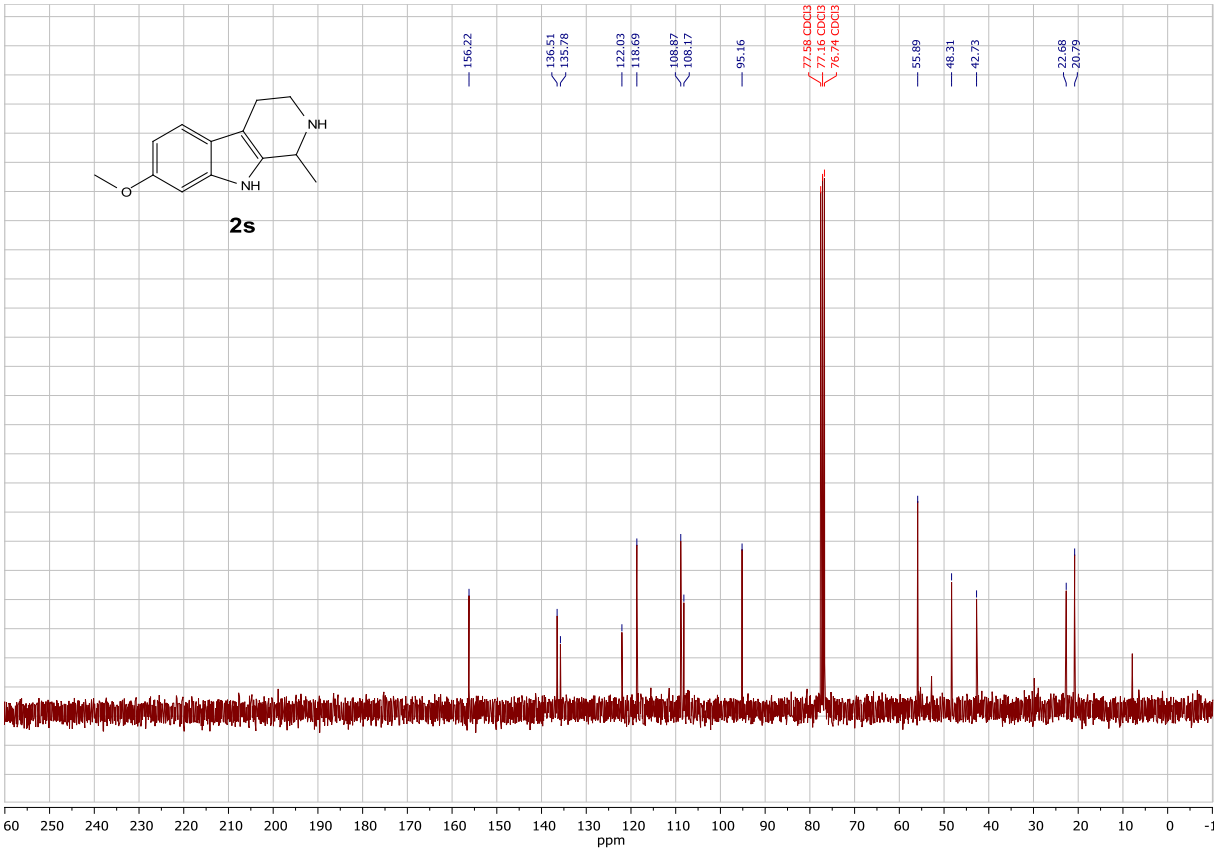

NH
NH
2q
7.26 CDCl3
6.61
6.60
6.59
6.59
6.59
6.58
6.57
6.52
6.51
6.50
6.49
6.49
6.48
3.59
3.42
B (dd)
6.59
J(5.78, 3.41)
A (dd)
6.50
J(5.75, 3.42)
D (s)
3.42
C (s)
3.59
1.99
2.00
2.08
4.44
ppm


NH
NH
2q
133.77
118.87
114.83
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
41.50
ppm


2r
G (m)
7.64
F (m)
6.39
B (s)
4.35
A (s)
3.83
C (t)
3.35
J(5.70)
D (t)
2.76
J(6.32)
E (m)
1.92
ppm


2r
167.63
148.84
131.42
129.23
120.04
117.57
112.76
77.58 CDCl3
77.16 CDCl3
76.74 CDCl3
51.58
41.84
27.02
21.53
ppm


NH
NH
O
2s
B (d)
6.83
J(2.19)
F (ddd)
3.01
J(12.89, 8.56, 5.38)
I (s)
8.06
A (d)
7.33
J(8.52)
D (q)
4.14
J(6.60)
G (m)
2.71
H (d)
1.43
J(6.71)
C (dd)
6.75
J(8.55, 2.26)
E (s)
3.81
J (s)
2.52
K (m)
3.29
ppm


NH
NH
O
2s
ppm