Supplementary Material (ESI) for Green Chemistry

On the quantitative recycling of Raney-Nickel catalysts on a lab-scale

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Supporting information

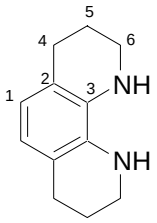
General

Toluene was freshly dried and distilled over sodium/benzophenone under an atmosphere of argon. [1,10]phenanthroline and 2,9-dimethyl[1,10]phenanthroline are comercially available from Lancaster and Acros. Synthesis of the 2,9-bisfunctionalized phenanthrolines was effected via sequential organolithium addition and MnO_2-mediated oxidation (R = *s*-Bu, *t*-Bu, Ph, *n*-Bu; publication in preparation). All reactions were performed under argon in flame dried glassware using syringe-septum techniques. NMR spectra were obtained on a Bruker DPX 300. High pressure hydrogenations were performed in a 300 mL Parr autoclave (Parr 4842) fitted with a temperature control, gas inlet, and stirrer. Nickel atom absorption spectroscopy was performed with a Varian Techtron AA6 at 232 nm and referenced vs. nickel(II) standard solutions. High resolution mass spectra (HRMS) were obtained on a Varian MAT 711 and Finnigan Incos 500. Silica gel chromatography was performed with 60 (0.040-0.063 mm; pH = 6.5-7.5) silica gel from KMF. Uncorrected melting points were measured on a Büchi Dr. Tottoli 510 apparatus. CHN analysis was performed with an Elementar Vario EL.

Representative procedure:

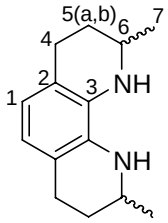
A 50 mL Parr® high pressure reactor was charged with 0.83 mmol of 2,9-bisfunctionalized phenanthroline and 6 ml abs. ethanol. A teflon-coated magnetic stir bar covered with Raney-Nickel (5 mg, 0.083 mmol, 10 mol%) was added, and the reactor was pressurized with hydrogen (20 bar). The reaction was stirred at 100 °C (25 bar). After 16 h, the reactor was cooled to rt and slowly depressurized. The catalyst-covered stir bar was retrieved with a pair of tweezers, washed with ethanol (2 × 1 mL), and the solution passed through a Celite pad (3 cm). The filtrate was concentrated in an oil pump vacuum to give the analytically pure octahydrophenanthroline derivative. The stir bar was stored in ethanol or used for a new reaction without further manipulation within 7 days.

1,2,3,4,7,8,9,10-Octahydro[1,10]phenanthroline (1)



^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.91 (m, 4H, H-5), 2.76 (t, 4H, 6.33 Hz, H-4), 3.32 (m, 4H, H-6), 6.47 (s, 2H, H-1) **^{13}C-NMR (75 MHz, $CDCl_3$):** δ = 22.53 (C-4), 26.93 (C-5), 42.63 (C-6), 119.14 (C-1), 120.47 (C-2), 132.84 (C-3) **Mp.** 70°C **IR ATR [cm^{-1}]:** 3334 (br,m), 3039 (w), 2920 (s), 2838 (s), 1614 (m), 1578 (s), 1491 (s), 1440 (s), 1328 (s), 1264 (m), 1177 (m), 1117 (m) **LR MS (EI, 70 eV, m/z):** 188 M^+, 170, 159, 154, 145, 130, 117, 104, 91, 86, 80, 72, 65, 58, 51

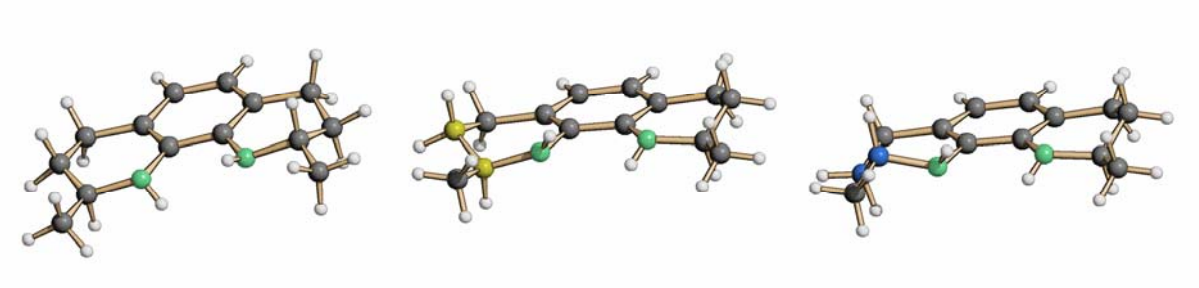
2.9-Dimethyl-1,2,3,4,7,8,9,10-octahydro[1,10]phenanthroline (2)



dr: 2.2 / 1 (*meso/rac*) **^{1}H-NMR (300 MHz, $CDCl_3$):** δ = 1.31 (d, 6H, 5.9 Hz, H-7), 1.54 (m, 2H, H-5a), 1.94 (m, 2H, H-5b), 2.76 (m, 4H, H-4), 3.35 (br, 2H, H-6), 6.50 (s, 2H, H-7) **^{13}C-NMR (75 MHz, $CDCl_3$):** δ = 22.62 (C-7), 26.81 (C-4), 30.42 (C-5), 47.92 (C-6), 118.78 (C-1), 120.16 (C-2), 132.69 (C-3) **Mp.** 76°C (from EtOH) **IR ATR [cm^{-1}]:** 3348 (w,br), 3059 (w), 1951 (s), 2843 (s), 1615 (w), 1581 (s), 1447 (s), 1332 (s), 1256 (s), 1160 (m), 778 (m) **LR MS (EI, 70 eV, m/z):** 216 M^+, 201 (M-CH_3), 185 (M-C_2H_6), 173, 159, 144, 130, 117, 103, 93, 86, 77, 65, 51 **HR MS (m/z):** calc. 216.163 M^+ found 216.163 M^+

Crystal structure: The unit cell contains *meso* and *rac* isomers and exhibits some disorder with respect to C29 and C30 of the *R*,*R*-**2** and *meso*-**2** isomers (highlighted in yellow and blue atoms). *S*,*S*-**2** exhibited no disordering. Structure refinement resulted in a statistical 3/1 (*rac*/*meso*) mixture in the crystal.

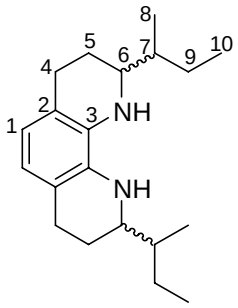
Crystal structures of the *S*,*S*- *meso*-, and *R*,*R*-isomers:



Crystal data: (CCDC# 647735)

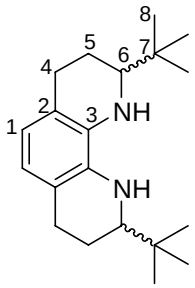
Temperature	100(2) K
Wavelength	0.71073 Å
Space-group	P -1 - triclinic
Cell	a=8.952(2), Å b=10.126(3) Å, c=14.757(4) Å
	α=70.511(10)°, β=79.526(10)° , γ=76.960(10)°
Volume	1220.2(5) $Å^3$
Z	4
Calculated density	1.178 g/m^3
Absorption coefficient	0.070 mm^{-1}
F(000)	472
Crystal size	0.2 x 0.1 x 0.05 mm
Theta range for data collection	1.47 to 25.00 deg.
Limiting indices	$-10 \leq h \leq 10$, $-11 \leq k \leq 12$, $-13 \leq l \leq 17$
Reflections collected / unique	4976 / 4031 [R(int) = 0.0556]
Reflection observed [I>2 σ (I)]	1380
Completeness to theta = 25.00	93.9 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4031 / 0 / 326
Goodness-of-fit on F^2	0.965
Final R indices [I>2 σ (I)]	R1 = 0.0821, wR2 = 0.1982
R indices (all data)	R1 = 0.2403, wR2 = 0.2672
Largest diff. peak and hole	0.293 and -0.230 e. $Å^{-3}$

2,9-Di-*sec*-butyl-1,2,3,4,7,8,9,10-octahydro[1,10]phenanthroline (3)



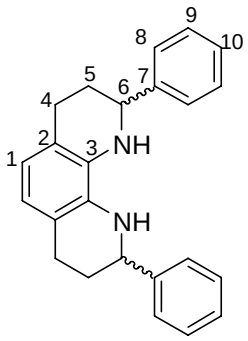
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 0.96 (br, H-5, 4H), 1.29 (s, br, H-5, 4H), 1.57 (m, H-7, H-9, 8H), 2.73 (m, H-4, 4H), 3.07 (m, H-6, 2H) **^{13}C-NMR (75 MHz, $CDCl_3$):** δ = 12.17 (C-10), 14.81 (C-8), 25.73 (C-9), 27.22 (C-4), 29.71 (C-5), 39.32 (C-7), 56.39 (C-6), 118.69 (C-1), 120.48 (C-2), 133.10 (C-3) **IR ATR [cm^{-1}]:** 3048 (w), 2920 (s), 2853 (s), 1583 (m), 1480 (s), 1462 (s), 1347 (m), 1260 (m), 804 (m), 728 (m) **LR MS (EI, 70 eV, m/z):** 300 M^+, 293, 243 (M-C_4H_9), 185, 171, 159, 144, 130, 117, 106, 93, 77, 67, 55 **HR MS (m/z):** calc. 300.257 M^+ found 300.257 M^+

2,9-Di-*tert*-butyl-1,2,3,4,7,8,9,10-octahydro[1,10]phenanthroline (4)



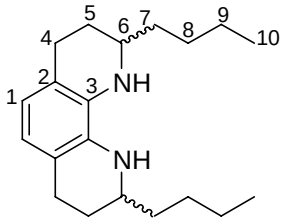
dr: 1.3 / 1 (*meso/rac*) **^{1}H-NMR (300 MHz, $CDCl_3$):** δ = 1.04 (s, 18H, H-8), 2.01 (m, 4H, H-5), 2.79 (m, 4H, H-4), 2.89 (m, 2H, H-6), 6.47 (s, 2H, H-1) **^{13}C-NMR (75 MHz, $CDCl_3$):** δ = 21.00 (C-4), 26.38 (C-8), 27.62 (C-7), 33.65 (C-5), 61.42 (C-6), 118.49 (C-1), 120.45 (C-2), 133.41 (C-3) **IR ATR [cm^{-1}]:** 3038 (w), 2950 (s), 2866 (s), 1586 (m), 1495 (s), 1362 (s), 1335 (m), 1120 (m), 781 (m), 768 (m) **LR MS (EI, 70 eV, m/z):** 300 M^+ , 243, 185, 159, 144, 130, 91, 79, 57 **HR MS (m/z):** calc. 300.257 M^+ found 300.257 M^+

2,9-Diphenyl-1,2,3,4,7,8,9,10-octahydro[1,10]phenanthroline (5)



dr: 1.25 / 1 (*meso/rac*) **^{1}H-NMR (300 MHz, $CDCl_3$):** δ = 2.13 (m, H-5, 4H), 2.81 (m, H-4, 4H), 4.42 (m, H-6, 2H), 6.58 (s, H-1, 2H), 7.13-7.59 (Ar, H-8, H-9, H-10, 10H) **^{13}C-NMR (75 MHz, $CDCl_3$):** δ = 27.07 (C-4), 31.38 (C-5), 57.07 (C-6), 119.09 (C-1), 119.96 (C-2), 126.81 (C-8), 127.44 (C-10), 128.61 (C-9), 132.67 (C-3), 144.96 (C-7) **IR ATR [cm^{-1}]:** 3050 (w), 2924 (w), 1489 , 1489 (m), 1253 (m), 1120 (s) **LR MS (EI, 70 eV, m/z):** 340 M^+, 311, 263, 249, 235, 219, 207, 159, 145, 132, 118, 104, 91, 78, 65, 51 **HR MS (m/z):** calc. 340.194 M^+ found 340.194 M^+

2,9-Dibutyl-1,2,3,4,7,8,9,10-octahydro[1,10]phenanthroline (6)

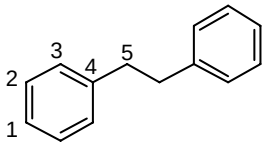


dr: 1.3 / 1 (*meso/rac*) **^{1}H-NMR (300 MHz, $CDCl_3$):** δ = 0.99 (t, 6H, H-10), 1.20-1.62 (12H, H-7, H8, H9), 2,77 (m, 4H, H-4), 3.21 (m, 4H, H-5), 3.34 (m, 2H, H-6), 6.49 (s, 2H, H-1) **^{13}C-NMR (75 MHz, $CDCl_3$):** δ = 14.17 (C-10), 22.94 (C-9), 26.65 (C-4), 28.43 (C-8), 36.68 (C-7), 42.74 (C-6), 52.33 (C-5), 118.93 (C-1), 120.42 (C-2), 132.74 (C-3) 2.62 (C-7), 26.81 (C-4), 30.42 (C-5), 47.92 (C-6), 118.78 (C-1), 120.16 (C-2), 132.69 (C-3) **IR ATR [cm^{-1}]:** 3048 (w), 2995 (s), 2925 (s), 2872 (m), 2854 (m), 1560 (m), 1521 (m), 1461 (m), 1377 (m), 796 (m) **LR MS (EI, 70 eV, m/z):** 300 M^+, 293, 243, 185, 159, 144, 93, 55 **HR MS (m/z):** calc. 300.257 M^+ found 300.257 M^+

1,2-Diphenylethane (7)

A round-bottomed flask was charged with 90 mg (0.5 mmol) *trans*-stilbene and 2 mL abs. methanol. A teflon-coated magnetic stir bar covered with Raney-Nickel (2 mg, 7 mol%) was added, and the reaction mixture was stirred at room temperature under an atmosphere of 1 bar hydrogen. After 12 h, the stir bar was retrieved with a pair of tweezers, washed with ethanol

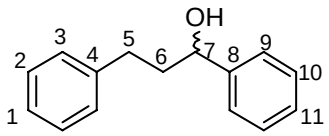
(2 × 1 mL), and the solution passed through a Celite pad (3 cm). The filtrate was concentrated in an oil pump vacuum to give analytically pure 1,2-diphenylethane (**7**, 98 % yield).



^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.95 (s, 4H, H5), 7.21-7.40 (10H, m, H-1,2,3) **^{13}C-NMR (75 MHz, $CDCl_3$):** δ = 38.1 (C-5) , 126.0 (C-1), 128.5, 128.6, 141.9 (C-4). **LR MS (EI, 70 eV, m/z):** 182 M^+, 165, 152, 104, 91, 77, 65, 51, 39.

1,3-Diphenyl-1-propanol (8)

A round-bottomed flask was charged with 105 mg (0.5 mmol) *trans*-1,3-diphenylprop-2-en-1-ol and 2 mL abs. methanol. A teflon-coated magnetic stir bar covered with Raney-Nickel (2 mg, 7 mol%) was added, and the reaction mixture was stirred at room temperature under an atmosphere of hydrogen. After 12 h, the catalyst-covered stir bar was retrieved with a pair of tweezers, washed with ethanol (2 × 1 mL), and the solution passed through a Celite pad (3 cm). The filtrate was concentrated in an oil pump vacuum to give analytically pure 1,3-diphenylpropan-1-ol (**8**, 99 % yield).

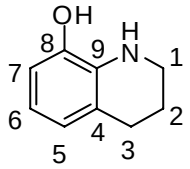


^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.08 (m, 2H, H-6), 2.70 (m, 2H, H-5), 4.67 (m, 1H, H-7), 7.14-7.38 (10H, m, H-1,2,3,9,10,11). **^{13}C-NMR (75 MHz, $CDCl_3$):** δ = 32.1, 40.5, 73.9, 125.9, 127.7, 128.5, 141.8, 144.6. **LR MS (EI, 70 eV, m/z):** 212 M^+, 194, 179, 165, 152, 139, 128, 115, 107, 91, 79, 77, 65, 51, 39.

8-Hydroxy-1,2,3,4-tetrahydroquinoline (9)

A 50 mL Parr® high pressure reactor was charged with 73 mg (0.5 mmol) of 8 hydroxyquinoline and 2 mL abs. ethanol. A teflon-coated magnetic stir bar covered with Raney-Nickel (2 mg, 7 mol%) was added, and the reactor was pressurized with hydrogen (30 bar). The reaction was stirred at 60 °C. After 12 h, the reactor was cooled to rt and slowly depressurized. The catalyst-covered stir bar was retrieved with a pair of tweezers, washed with ethanol (2 × 1 mL), and the solution passed through a Celite pad (3 cm). The filtrate was purified with flash chromatography (ethyl acetate/cyclohexane 1/3) and concentrated by oil pump vacuum to give analytically pure 8-hydroxytetrahydroquinoline **9** (88 % yield). The stir

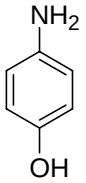
bar was stored in ethanol or used for a new reaction without further manipulation within 7 days.



^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.93 (m, 2H, H-2), 2.76 (m, 2H, H-3), 3.29 (m, 2H, H-1), 4.37 (2H, br, OH, NH), 6.28 - 6.79 (m, 3H, H-5,6,7). **^{13}C-NMR (75 MHz, $CDCl_3$):** δ = 22.22, 26.57, 41.82, 112.51, 117.25, 121.88, 133.41, 143.23. **LR MS (EI, 70 eV, m/z):** 149 M^+, 132, 103, 77, 54, 39

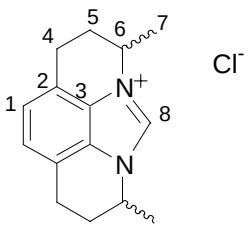
4-Aminophenol (10)

A 50 mL Parr® high pressure reactor was charged with 70 mg (0.5 mmol) of 4 nitrophenol and 2 mL abs. ethanol. A teflon-coated magnetic stir bar covered with Raney-Nickel (2 mg, 7 mol%) was added, and the reactor was pressurized with hydrogen (30 bar). The reaction was stirred at 60 °C. After 12 h, the reactor was cooled to rt and slowly depressurized. The catalyst-covered stir bar was retrieved with a pair of tweezers, washed with ethanol (2 × 1 mL), and the solution passed through a Celite pad (3 cm). The filtrate was concentrated in an oil pump vacuum to give analytically pure 4-aminophenol (**10**, 91% yield). The stir bar was stored in ethanol or used for a new reaction without further manipulation within 7 days.



^{1}H-NMR (300 MHz, DMSO): δ = 4.35 (br, NH_2), 6.23-6.60 (m, 2H), 8.34 (br, OH). **^{13}C-NMR (75 MHz, DMSO):** δ = 115.68, 115.94 (2C), 141.06, 148.61.

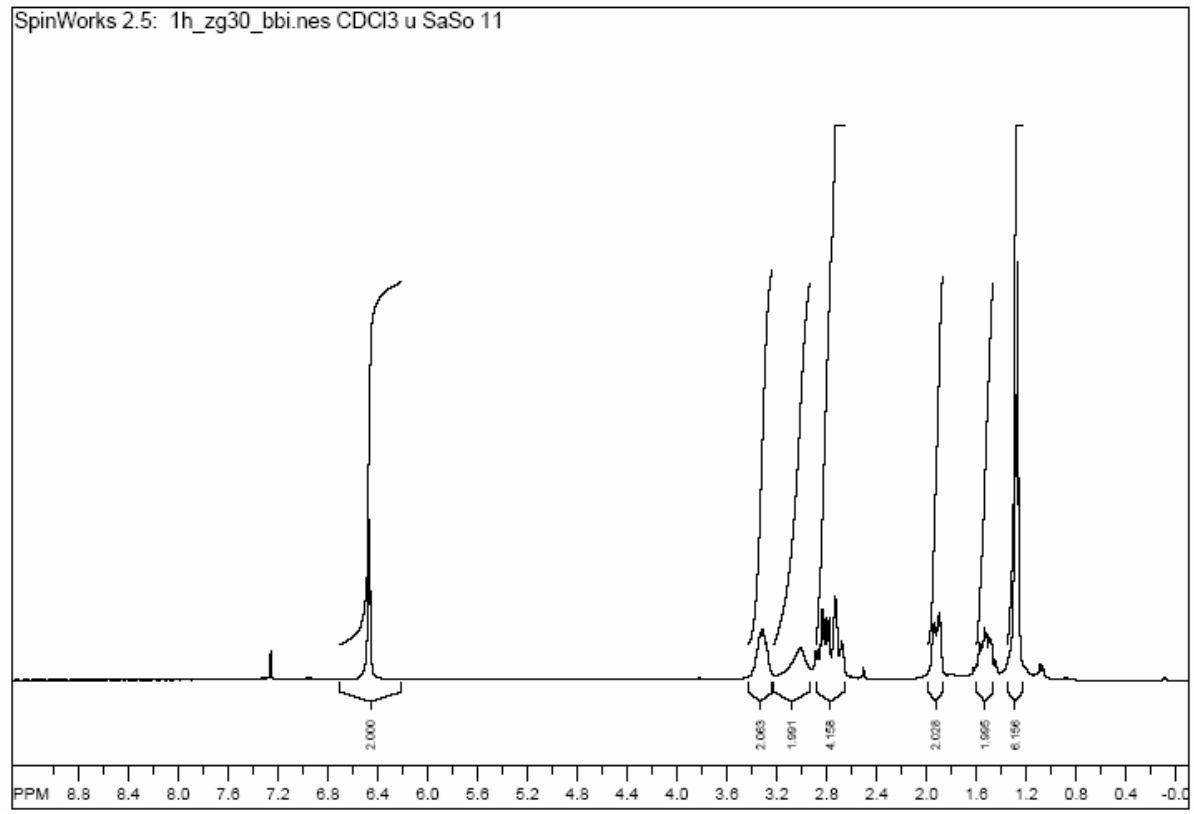
Benzimidazolium chloride (11)

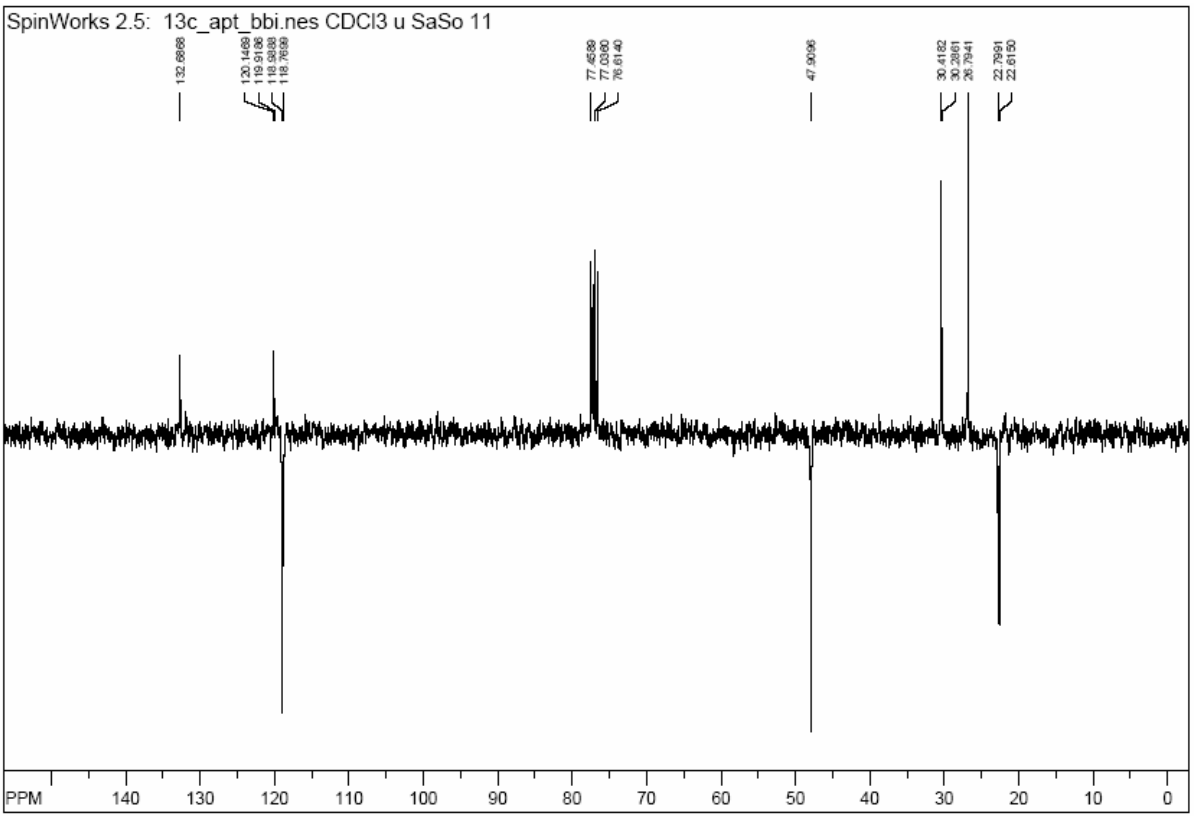


^{1}H-NMR (300 MHz, D^4-MeOD): δ = 1.82 (d, 6H, H-7), 2.13 (br, 2H, H-5), 2.51 (br, 2H- H-5), 3.15 (br, 4H, H-4), 4.84 (br, 2H, H-6), 7.37 (s, 2H, H-1), 9.77 (s, 2H, H-8) **^{13}C-NMR (75 MHz, D^4-MeOD):** δ = 18.53 (C-7), 21.97 (C-4), 30.85 (C-5), 52.81 (C-6), 122.92 (C-3),

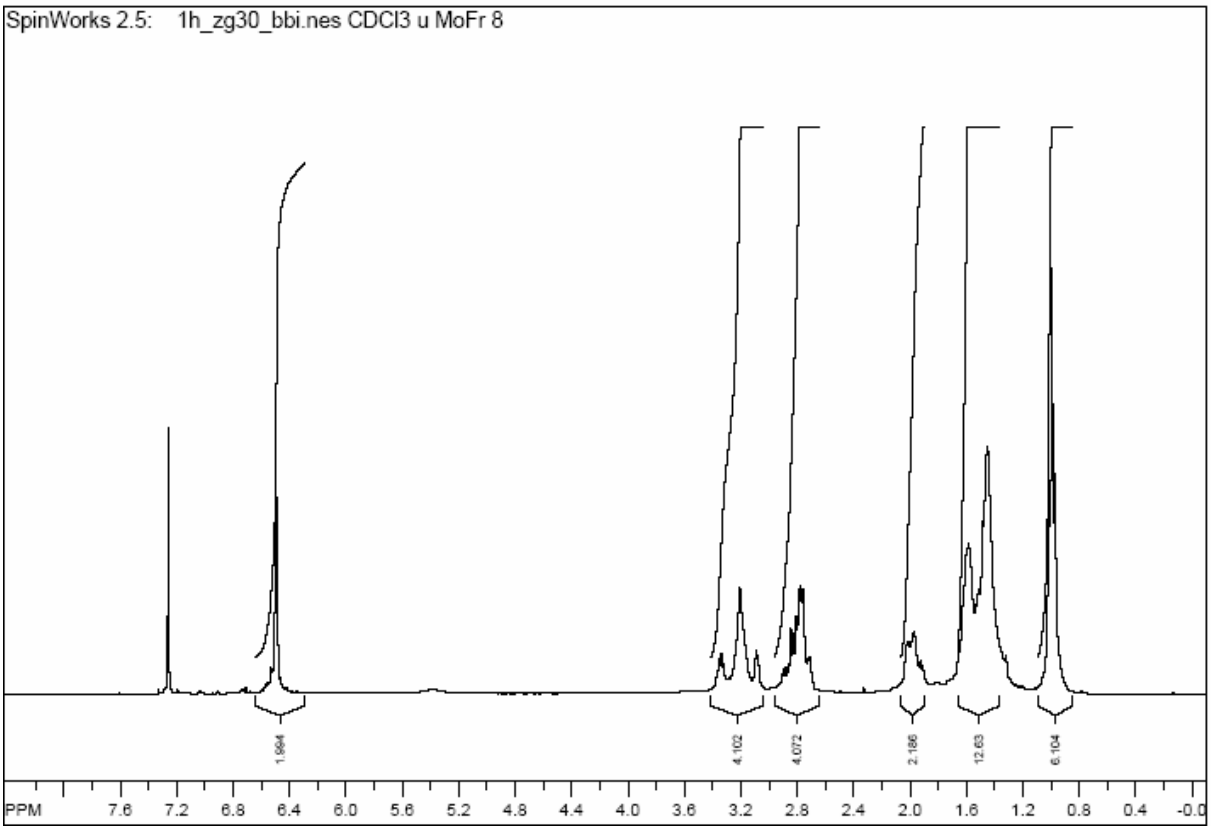
123.76 (C-1), 127.96 (C-2), 135.92 (C-8) **Mp.** 178-180°C (from EtOH) **IR ATR [cm^{-1}]:** 3457 (br,m), 2940 (m), 2845 (m), 2713 (w), 1539 (m), 1503 (s), 1314 (s), 1215 (s), 1103 (m), 1057 (m), 950 (m), 838 (m) **MS dip EI (70 eV +):** 262M^+, 254, 226, 211,185, 169, 144, 115, 91, 77 **HR MS ESI (m/z):** calc. 227.1548 M^+ found 227.155 M^+

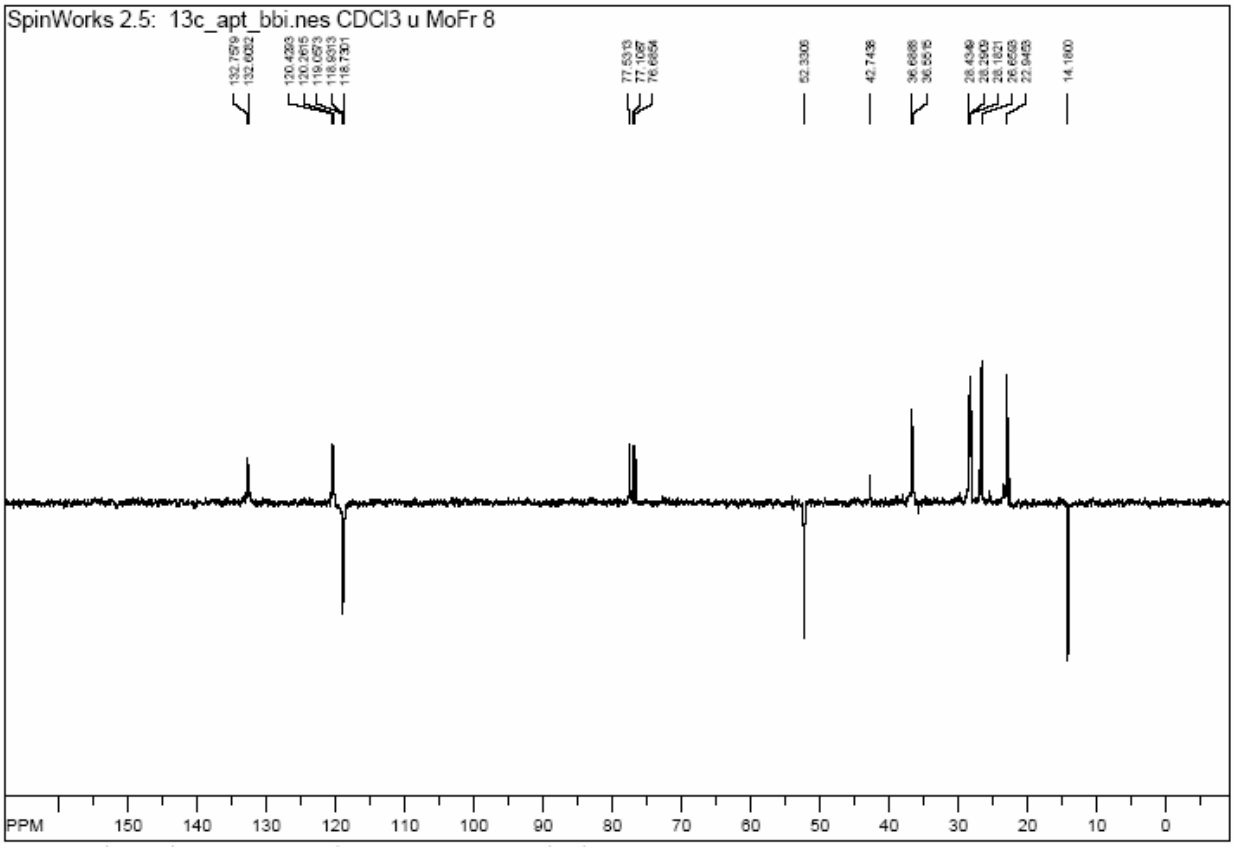
2,9-Dimethyloctahydro[1,10]phenanthroline (2)





2,9-Dibutyloctahydro[1,10]phenanthroline (6)





5,9-Dimethyl-3,4,5,9,10,11-hexahydroimidazo[1,5,4,3-lmn][1,10]phenanthrolin-6-ium chloride (11)