

Convenient synthesis of cobalt nanoparticles for the hydrogenation of quinolines in water

J. Hervochon, V. Dorcet, K. Junge, M. Beller, C. Fischmeister

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1. General information

All reagents were obtained from commercial sources and used as received. Were used as received. Toluene was dried on a MBraun Solvent Purification System apparatus and degassed prior to use. NaBH_4 , 98% was purchased from Sigma-Aldrich, CoCl_2 99% was purchased from Strem $(\text{NH}_4)_2\text{Co}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ 98% was purchased from Alfa. Distilled-deionised water was used. NMR spectra were recorded on Bruker Avance I 300 MHz or Avance III 400 MHz spectrometers. Chemical shifts are given in ppm and referenced vs TMS using the residual solvent signal.

2. General procedure for the catalytic hydrogenation of quinoline

A high-pressure reactor was charged sequentially with CoCl_2 (5 mol%), Sodium borohydride (10 mol%), 1 mL of H_2O and quinoline (100 mg, 0.78 mmol). The reactor was then charged with H_2 (30 bar) and stirred at the appropriate temperature (oil bath) for 17 h. The reactor was cooled down to r.t. and carefully depressurized. The reaction mixture was extracted three times with ethyl-acetate and the grouped organic fraction dried with sodium sulfate and the solvent evaporated under vacuum. The crude product was analyzed by ^1H NMR. This crude product was then purified by flash column chromatography on silica gel using a mixture of heptane and ethyl acetate as the eluent.

3. Recycling test

2 different tests were performed following reactions performed as described in the general information.

3.1 After 17h, the reactor was slowly depressurized. The reaction medium was washed 3 times with ethyl acetate and the organic phase was analyzed by ^1H NMR. The reaction medium was loaded with quinoline and 30 bar of hydrogen. After 17 h at 130 °C, the reaction medium was analyzed by ^1H NMR showing no conversion of quinoline.

3.2 After 17h, the reactor was slowly depressurized. The reaction medium was washed 3 times with ethyl acetate and the organic phase was analyzed by ^1H NMR. The reaction medium was loaded with quinoline, NaBH_4 and 30 bar of hydrogen. After 17 h at 130 °C, the reaction media was analyzed by ^1H NMR showing complete disappearance of quinoline.

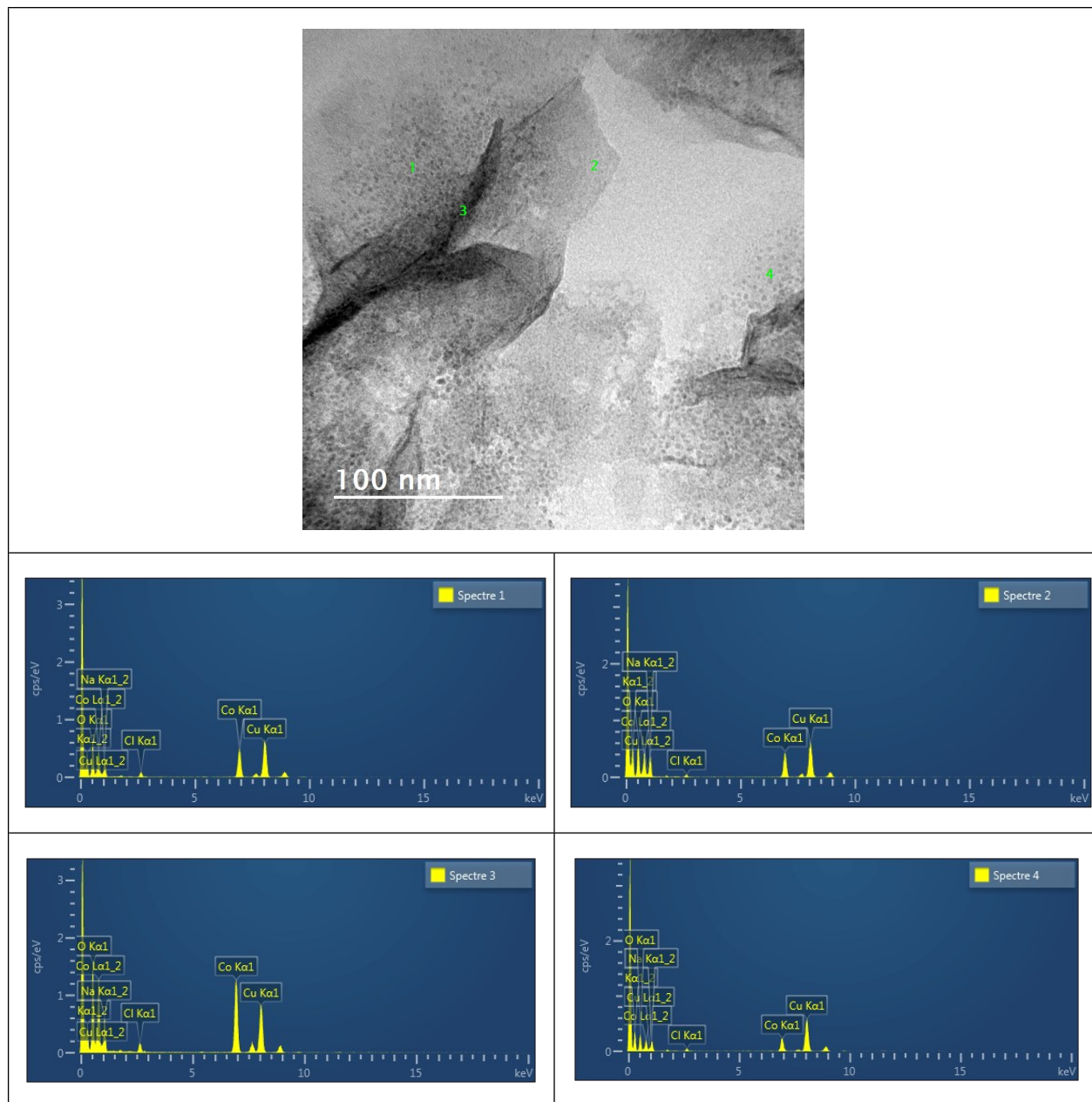
4. Scale-up reaction.

The reaction was conducted in a Hastelloy-C 100 mL Parr autoclave using 2 g (15.5 mmol) of quinoline, 100.4 mg (5 mol%) of CoCl_2 , 58.2 mg (10 mol%) of NaBH_4 and 20 mL of water. The analysis protocol was the one adopted for 0.5 mmol scale reactions. ^1H NMR showed full conversion of quinoline with selective formation of 1,2,3,4,-tetrahydroquinoline.

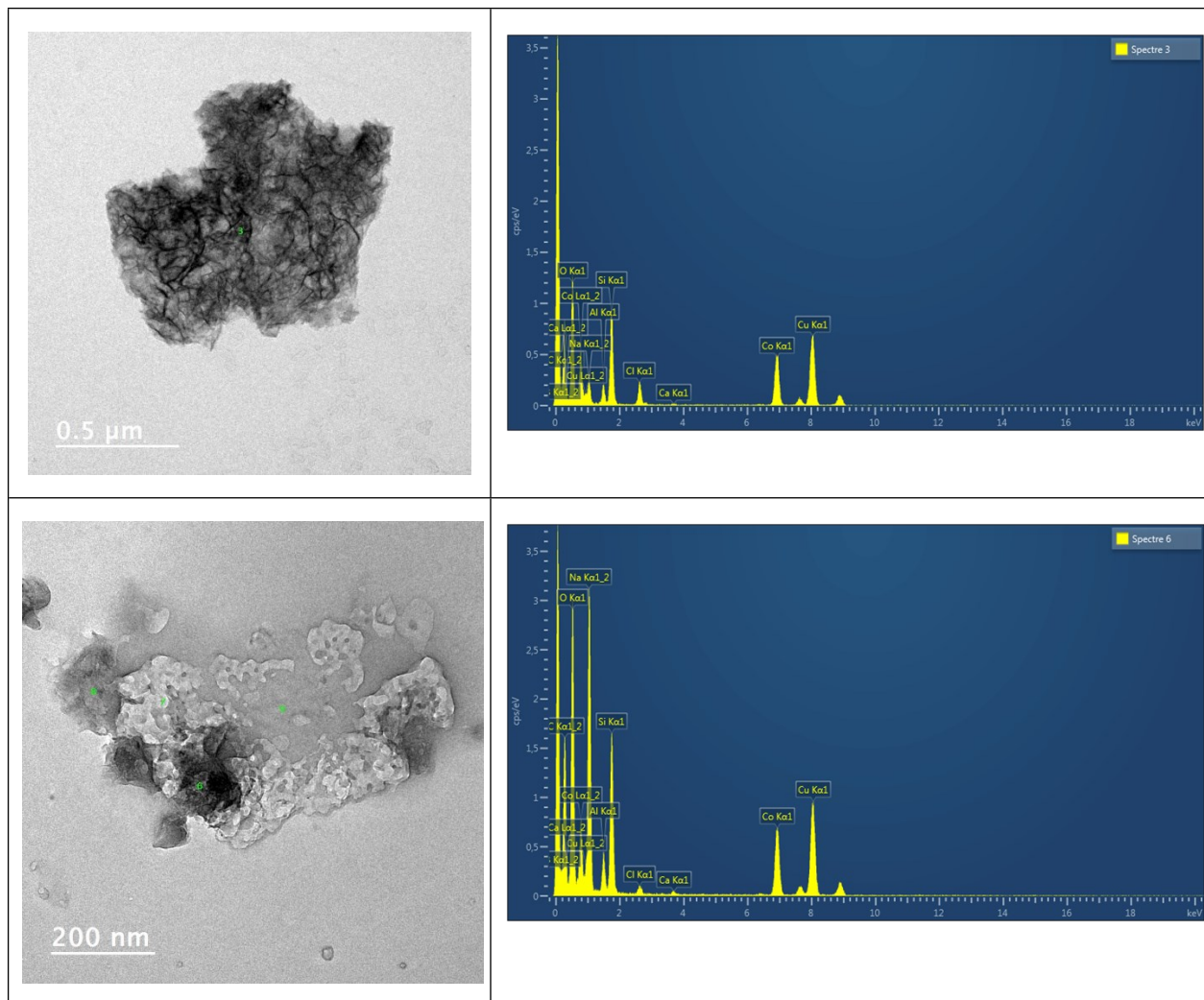
5. TEM/EDS Analyses

2 samples were analyzed by TEM/EDS (JEOL 2100 LAB6 operating at 200 kV coupled with an energy-dispersive X-ray spectroscopy detector SDD X-Oxford 80 mm²).

A first sample was prepared by hydrolysis of NaBH₄ in the presence of CoCl₂ in a 2/1 ratio. After decantation of the reaction media, drops of the supernatant were deposited onto holey carbon grids. Representative TEM pictures and EDS analyses are presented hereafter.

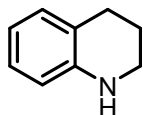


A second sample was analyzed after a catalytic run as described in the general method. Representative TEM pictures and EDS analyses are presented hereafter.



6. Product characterization

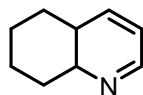
1,2,3,4-tetrahydroquinoline [1]



colorless oil, 100% conversion, 99% yield

^1H NMR (400 MHz, CDCl_3): δ = 6.97 (t, J = 8.5 Hz, 2H), 6.62 (t, J = 7.2 Hz, 1H), 6.48 (d, J = 7.8 Hz, 1H), 3.69 (bs, 1H), 3.31 (t, J = 6.4 Hz, 2H), 2.78 (t, J = 6.4 Hz, 2H), 1.96 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3): δ = 144.8, 129.5, 126.7, 121.5, 117.0, 114.2, 42.0, 27.0, 22.2.

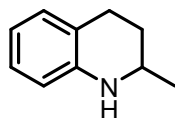
5,6,7,8-tetrahydroquinoline [2]



colorless oil

^1H NMR (400 MHz, CDCl_3): δ = 8.32 (dd, J = 5.0, 1.0 Hz, 1H), 7.32 (d, J = 8.0 Hz, 1H), 6.99 (m, 1H), 2.91 (t, J = 8.0 Hz, 2H), 2.75 (t, J = 8.0 Hz, 2H), 1.85-1.78 (m, 2H), 1.76-1.69 (m, 2H); ^{13}C NMR (CDCl_3 , 101 MHz) δ 158.6, 147.4, 138.9, 132.8, 122.1, 33.5, 30.03, 23.2, 22.7.

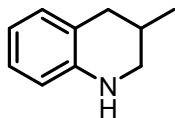
2-methyl-1,2,3,4-tetrahydroquinoline [1]



colorless oil, 100% conversion, 83% yield

^1H NMR (400 MHz, CDCl_3): δ = 6.97 (m, 2H), 6.62 (t, J = 7.3 Hz, 1H), 6.48 (d, J = 8.3 Hz, 1H), 3.70 (bs, 1H), 3.45 – 3.38 (m, 1H), 2.91-2.81 (m, 1H), 2.77 – 2.71 (m, 1H), 1.99-1.91 (m, 1H), 1.67-1.56 (m, 1H), 1.23 (d, J = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3): δ = 144.9, 129.4, 126.8, 121.2, 117.1, 114.1, 47.3, 30.3, 26.7, 22.8.

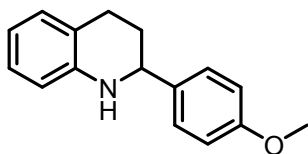
3-methyl-1,2,3,4-tetrahydroquinoline [1]



Colorless oil, 77% conversion, 23% yield

^1H NMR (400 MHz, CDCl_3): δ = 6.95 (m, 2H), 6.61 (t, J = 8.1 Hz, 1H), 6.49 (d, J = 7.3 Hz, 1H), 3.84 (bs, 1H), 3.28 (ddd, J = 9.3, 3.7, 1.9 Hz, 1H), 2.90 (t, J = 9.8 Hz, 1H), 2.78 (m, 1H), 2.44 (m, 1H), 2.11 – 2.03 (m, 1H), 1.05 (d, J = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3): δ = 144.3, 129.5, 126.7, 121.1, 116.9, 113.9, 48.9, 35.5, 27.3, 19.0.

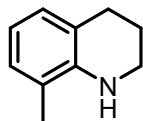
2-(4-methoxyphenyl)-1,2,3,4-tetrahydroquinoline [3]



yellow solid, 85% conversion, 57% yield,

^1H NMR (400 MHz, CDCl_3) δ 7.31 (d, J = 8.6 Hz, 2H), 7.01 (m, 2H), 6.89 (d, J = 8.6 Hz, 2H), 6.64 (t, J = 8.6 Hz, 1H), 6.53 (d, J = 8.6 Hz, 1H), 4.38 (dd, J = 9.5, 3.2 Hz, 1H), 3.97 (bs, 1H), 3.81 (s, 3H), 2.93 (ddd, J = 16.4, 10.9, 5.5 Hz, 1H), 2.74 (dt, J = 16.3, 4.7 Hz, 1H), 2.12-2.05 (m, 1H), 2.01-1.91 (m, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 156.7, 144.8, 136.9, 129.3, 127.6, 126.8, 120.9, 117.1, 114.0, 56.7, 55.3, 31.1, 26.6.

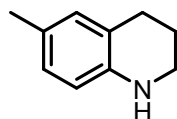
8-methyl-1,2,3,4-tetrahydroquinoline [1]



yellow oil, 100% conversion, 70% yield,

^1H NMR (400 MHz, CDCl_3): δ = 6.89 – 6.84 (m, 2H), 6.55 (t, J = 7.4 Hz, 1H), 3.65 (br, 1H), 3.38 (t, J = 5.3 Hz, 2H), 2.79 (t, J = 6.6 Hz, 2H), 2.08 (s, 3H), 1.97 – 1.91 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3): δ = 142.8, 128.0, 127.5, 121.3, 120.1, 116.5, 42.5, 27.4, 22.3, 17.3.

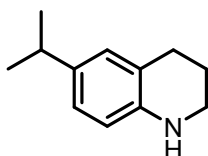
6-methyl-1,2,3,4-tetrahydroquinoline [4]



yellow oil, 100% conversion, 81% yield,

^1H NMR (400 MHz, CDCl_3) δ 6.82 (m, 2H), 6.44 (m, 1H), 3.55 (bs, 1H), 3.30 (m, 2H), 2.77 (t, $J=6,3$ Hz, 2H), 2.25 (s, 3H), 1.97 (m, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 142.5, 130.2, 127.3, 126.3, 121.7, 114.0, 42.3, 27.0, 25.5, 20.5.

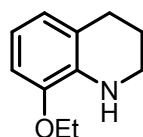
6-Isopropyl-1,2,3,4-tetrahydroquinoline [5]



yellow oil, 90% conversion, 87% yield

^1H NMR (300 MHz, CDCl_3): δ (ppm): 6.91 (m, 2H), 6.49 (d, $J = 8.2$ Hz, 1H), 3.68 (br, 1H), 3.32 (t, $J = 5,5$ Hz, 2H), 2.78-2.87z (m, 3H), 1.96-2.03 (m, 2H), 1.27 (d, $J = 6.9$ Hz, 6H); ^{13}C NMR (75 MHz, CDCl_3): δ (ppm): 144.1, 139.0, 127.9, 125.8, 121.8, 114.9, 44.9, 36.2, 27.5, 24.8, 22.9.

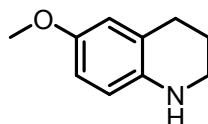
8-Ethoxy-1,2,3,4-tetrahydroquinoline [5]



yellow oil, 100% conversion, 99% yield,

^1H NMR (300 MHz, CDCl_3): δ (ppm): 6.59 – 6.63 (m, 3H), 4.05 (q, $J = 7.0$ Hz, 2H), 3.36 (m, 2H), 2.80 (t, $J = 6.4$ Hz, 2H), 1.99 (m, 2H), 1.44 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ (ppm): 145.7, 134.7, 121.7, 121.5, 115.8, 108.4, 63.7, 41.6, 26.9, 22.3, 15.2.

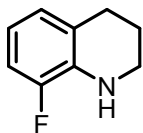
6-methoxy-1,2,3,4-tetrahydroquinoline [2]



yellow oil, 100% conversion, 97% yield,

^1H NMR (400.13 MHz, CDCl_3): δ 6.61 (m, 2H), 6.47 (d, J = 8.4 Hz, 1H), 3.74 (s, 1H), 3.58 (bs, 1H), 3.26 (m, 2H), 2.77 (t, J = 6.6 Hz, 2H), 1.99 (m, 2H); ^{13}C NMR (125.77 MHz, CDCl_3): δ 151.9, 138.8, 123.0, 115.7, 114.9, 113.0, 53.9, 42.4, 27.2, 22.5.

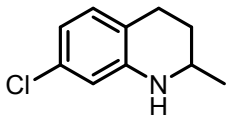
8-fluoro-1,2,3,4-tetrahydroquinoline [6]



yellow oil, 100% conversion, 75% yield,

^1H NMR (400.13 MHz, CDCl_3): δ 6.84-6.77 (m, 2H), 6.55 (m, 2H), 3.97 (br, 1H), 3.37 (t, J = 6.4 Hz, 2H), 2.82 (t, J = 6.4 Hz, 2H), 1.99 (m, 2H); ^{13}C NMR (101 MHz, CDCl_3): δ 151.0 (d, J = 238 Hz), 133.3 (d, J = 11.9 Hz), 124.6 (d, J = 2.6 Hz), 123.7 (d, J = 3.9 Hz), 115.6 (d, J = 7.2 Hz), 112.20 (d, J = 18.4 Hz), 41.3, 26.6, 21.9.

7-Chloro-2-methyl-1,2,3,4-tetrahydroquinoline [5]

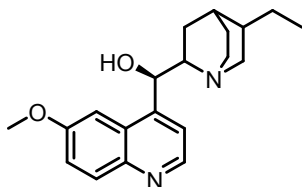


Colorless liquid, 100% conversion, 68% yield,

^1H NMR (300 MHz, CDCl_3): δ (ppm) 6.86 (d, J = 8.0 Hz, 1H), 6.54 (dd, J = 8.0, 2.1 Hz, 1H), 6.44 (d, J = 2.1 Hz, 1H), 3.38 (dtd, J = 12.6, 6.3, 3.0 Hz, 1H), 2.88–2.52 (m, 2H), 1.93 (dddd, J = 12.9, 5.4, 3.9, 3.0 Hz, 1H), 1.56 (dddd, J = 12.9, 11.0, 9.7, 5.7 Hz, 1H), 1.21 (d, J = 6.3 Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3): δ (ppm) 145.7, 131.9, 130.2, 119.3, 116.6, 113.3, 47.0, 29.8, 26.1, 22.5.

^{13}C NMR (75 MHz, CDCl_3): δ (ppm) 145.7, 131.9, 130.2, 119.3, 116.6, 113.3, 47.0, 29.8, 26.1, 22.5.

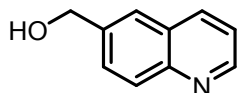
Hydroquinine [7]



White solid, 100% conversion 95% yield

^1H NMR (400 MHz, CDCl_3) δ : 8.57(1H, d, J = 4.5 Hz), 7.95 (1H, d, J = 9.2 Hz), 7.48 (1H, d, 4.6 Hz), 7.29(m, 2H), 5.49 (1H, d, J = 4.0 Hz), 4.32(br, 1H), 3.92 (3H, s), 3.47-3.39 (1H, m), 3.13-3.00 (2H, m), 2.70-2.57 (1H, m), 2.40-2.33 (1H, m), 1.78-1.68 (3H, m), 1.52-1.37 (3H, m), 1.30-1.19 (2H, m), 0.81 (3H, t, J = 7.3 Hz); ^{13}C NMR (101 MHz, CDCl_3) δ : 157.7, 148.0, 147.5, 144.2, 131.5, 126.7, 121.4, 118.5, 101.5, 72.18, 59.8, 58.7, 55.7, 43.3, 37.6, 28.4, 27.7, 25.5, 21.6, 12.10.

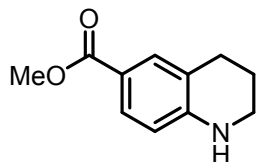
6-(Hydroxymethyl)quinoline [8]



Yellow oil, 100% conversion 80% yield

^1H NMR (400 MHz, CDCl_3) δ 8.89-8.87(dd, J = 4.5, 2.0 Hz, 1H), 8.16-8.07 (m, 2H), 7.81 (s, 1H), 7.70 (dd, J = 8.6, 2.0 Hz, 1H), 7.42-7.38 (dd, J = 8.2, 4.5 Hz, 1H); 4.91 (s, 2H), ^{13}C NMR (101 MHz, CDCl_3) δ 150.3, 147.8, 138.4, 136.1, 129.7, 128.7, 128.0, 125.0, 121.4, 64.9.

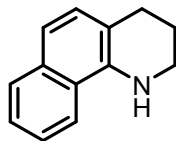
methyl 1,2,3,4-tetrahydroquinoline-6-carboxylate [5]



Colorless liquid, 100% conversion, 92% yield

^1H NMR (300 MHz, CDCl_3) δ 7.66 – 7.62 (m, 2H), 6.40 – 6.37 (m, 1H), 3.08 (s, 3H), 3.35 (m, 2H), 2.76 (t, J = 6.0 Hz, 2H), 1.97 – 1.83 (m, 2H). ^{13}C NMR (75 MHz, CDCl_3) δ 167.5, 149.8, 131.3, 129.1, 119.9, 117.5, 112.6, 51.5, 41.7, 26.9, 24.4.

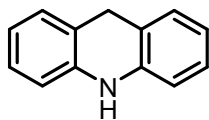
1,2,3,4-tetrahydrobenzo[h]quinoline [9]



Yellow oil, 100% conversion, 73% yield

^1H NMR (300 MHz, CDCl_3) δ 7.66-7.51 (m, 2H), 7.30-7.24 (m, 2H), 7.08-6.99 (m, 2H), 3.99 (br, 1H), 3.33 (t, J = 5.6 Hz, 2H), 2.79 (t, J = 5.6 Hz, 2H), 1.94-1.86 (m, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 139.1, 133.1, 128.7, 128.6, 125.0, 124.8, 123.3, 119.5, 117.0, 115.9, 42.5, 27.5, 22.2

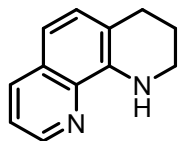
9,10-Dihydroacridine [9]



white solid, 100% conversion, 62% yield,

^1H NMR (400 MHz, CDCl_3) δ 7.11-7.06 (m, 4H), 6.85 (m, 2H), 6.67 (dd, J = 7.9, 0.8 Hz, 2H), 5.95 (br, 1H), 4.06 (s, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 140.3, 128.7, 127.1, 120.8, 120.2, 113.6, 31.5.

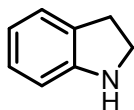
1-2,3,4-Tetrahydro-1,10-phenanthroline [9]



yellow oil, 100% conversion, 95% yield,

^1H NMR (400 MHz, CDCl_3) δ 8.68 (dd, J = 4.12, 1.53 Hz, 1H), 8.00 (dd, J = 8.30, 1.74 Hz, 1H), 7.30-7.27 (m, 1H), 7.16 (d, J = 8.3 Hz, 1H), 6.97 (d, J = 8.24 Hz, 1H), 5.97 (br, 1H), 3.53 (t, J = 5.36 Hz, 2H), 2.92 (t, J = 6.32 Hz, 2H), 2.10-2.04 (m, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 147.1, 140.8, 137.6, 136.0, 129.2, 127.5, 120.7, 116.7, 113.2, 41.4, 27.2, 22.0.

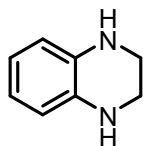
Indolin [9]



yellow oil, 100% conversion, 81% yield,

^1H NMR (400 MHz, CDCl_3) δ 7.12 (d, J = 7.2 Hz, 1H), 7.02 (t, J = 7.5, 1H), 6.71 (t, J = 7.5, 1H), 6.78-6.76 (d, J = 7.5 Hz, 1H), 3.75 (br, 1H), 3.55 (t, J = 8.4 Hz, 2H), 3.04 (t, J = 8.4 Hz, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 151.7, 129.4, 127.3, 124.7, 118.7, 109.5, 47.5, 15.72.

1,2,3,4-Tetrahydroquinoxaline [9]



yellow liquid, 100% conversion, 84% yield,

^1H NMR (400 MHz, CDCl_3): δ (ppm): 6.60-6.56 (m, 2H), 6.52-6.48 (m, 2H), 3.42 (s, 4H); ^{13}C NMR (101 MHz, CDCl_3) δ (ppm): 133.8, 118.9, 114.9, 41.5.

7 References

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8 NMR Spectra

