Supporting Information

One-pot dual catalysis for the hydrogenation of heteroarenes and arenes

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General experimental procedure: Chemicals were purchased from Acros, Sigma-Aldrich, Alfa-aesar and were used without further purification. Dry solvents were prepared according to standard procedures. ^{1}H, ^{13}C spectra were recorded at Bruker AV-400 (^{1}H: 400 MHz, ^{13}C: 100.6 MHz). ^{1}H, $^{13}C\{^{1}H\}$ NMR chemical shifts were reported in ppm downfield from tetramethyl silane. Multiplicity is abbreviated as: s, singlet; d, doublet; t, triplet; q, quartet; br, broad; m, multiplate. Assignment of spectra was done based on one-dimensional (dept-135) NMR technique. IR spectra were recorded on Bruker FTIR spectrometer. Mass spectra were recorded on Bruker micrOTOF-Q II Spectrometer. GC spectra were recorded on Shimadzu GC-2010 Plus spectrometer [HP-Molesieve column (TCD) 30 meter from Agilent]. Program: Initial Column temperature 50 ºC (hold time 1 min). Then 12 ºC min^{-1} upto 260 ºC (Hold time 2 min). Total run time = 20.50 min.

Safety Warning: This protocol involves High-pressure experiments with compressed H_2 (g). Thus, experiments must be carried out only with appropriate reaction set-up behind the blast shield and under rigorous safety precautions.

Preparation of [{(η^6-*p*-cymene)RuCl}$_2$(μ-H-μ-Cl)] 1: Complex **1** is prepared by following our previous reports from [Ru(*p*-cymene)Cl_2]$_2$.[1] The stock solution of **1** is prepared by dissolving [{(η^6-*p*-cymene)RuCl}$_2$(μ-H-μ-Cl)] **1** (289 mg) in 2 mL of 1,4-dioxane. The prepared stock solution was then stored inside glove-box freezer and further used as catalyst solution of standard concentration (5.77 mg/40 µl = 0.01 mmol = 1 mol% of **1** for 1 mmol scale reactions).

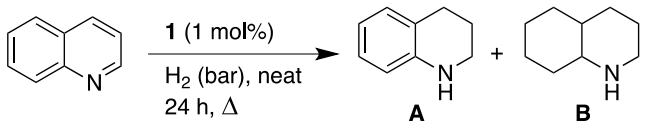
General procedure for the hydrogenation of heteroarenes: To a scintillation glass vial containing a small stirrer bar, heteroarene (1 mmol), and catalyst **1** (0.01 mmol in 40 µl stock solution) were charged under nitrogen atmosphere [1,4-dioxane (0.3 mL) was used as a solvent for solid substrates]. The glass vial then placed inside a high-pressure Parr reactor, evacuated and pressurized with H_2 (30-50 bar) gas. After completion of the reaction, the reactor was cooled to room temperature and the pressurized gas (H_2) was slowly released. The reaction mixture was analysed by gas chromatography and ^{1}H NMR spectroscopy. The selected crude reaction mixtures were extracted with dichloromethane (3 x 10 mL). The

combined organic phase was dried over sodium sulphate and the solvent was evaporated under reduced pressure. The crude product was purified by flash column chromatography.

Optimization of the reaction conditions:

At the outset hydrogenation of quinoline was carried out using **1** as a catalyst (1 mol%) with 30 bar H_2 at 75 °C. After 24 h, quantitative conversion of quinoline was observed, with a good selectivity toward the formation of THQ (Tetrahydroquinoline) (entry 1, Table S1). Increasing the H_2 pressure to 50 bar leads to the quantitative conversion of quinoline to DHQ (entry 3, Table S1). The control experiment without catalyst provided no hydrogenation reaction and unreacted quinoline was recovered, revealing the necessity of catalyst for this transformation (entry 4, Table S1). Interestingly, this catalytic hydrogenation occurs under solvent free condition and generates no waste, exhibiting green catalysis.

Table S1. Optimization of the reaction conditions[a]



Entry	Cat (1 mol%)	H_2 (bar)	Temp. (°C)	Conv.[b]	A:B[b]
1	**1**	30	75	>99	95:5
2	**1**	50	75	>99	1:99
3	-	50	75	-	-

[a]Conditions: Quinoline (1 mmol), and catalyst (0.01 mmol) were added to a scintillation glass vial under nitrogen atmosphere and placed inside high pressure (Parr) reactor. The reactor was charged with H_2 and heated at the indicated temperature and stirred for 24 h. [b]Conversions and product distributions determined by GC-FID using tetradecane as internal standard.

Spectral data of heterocycles obtained from hydrogenation of heteroarenes:

1,2,3,4-Tetrahydroquinoline (3b):[2] Yellow liquid. Yield: 121 mg (91%). IR(DCM): 3370, 2900, 2876, 2210, 1514, 1416, 1290, 1157, 734, 654 cm^{-1}. ^1H NMR ($CDCl_3$): δ 6.97 (m, 2H, ArC*H*), 6.64 (t, *J* = 8 Hz, 1H, ArC*H*), 6.50 (d, *J* = 4 Hz, 1H, ArC*H*). 3.60 (s, 1H, N*H*), 3.32 (t, *J* = 6 Hz, 2H, CH_2), 2.80 (t, *J* = 6 Hz, 2H, CH_2), 1.97 (t, *J* = 6 Hz, 2H, CH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 144.82 (quat-*C*), 129.55 (Ar*C*H), 126.76 (Ar*C*H), 121.47 (quat-*C*), 116.96 (Ar*C*H), 114.22 (Ar*C*H), 42.02 (*C*H_2), 27.02 (*C*H_2), 22.22 (*C*H_2). MS (EI) m/z calcd for $C_9H_{11}N$: $(M)^+$ 133, found: 133.

Decahydroquinoline (3c):[3] IR(DCM): 3337, 2986, 2874, 2217, 1549, 1497, 1210, 1168, 827, 654 cm^{-1}. ^1H NMR ($CDCl_3$): δ 3.02-2.99 (m, 1H, C*H*), 2.83 (d, *J* = 4 Hz, 1H), 2.66-2.60 (m, 1H, CH_2), 2.07 (br. s, N*H*, 1H), 1.63-1.49 (m, 13H, CH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 62.05 (*C*H), 47.23 (*C*H_2), 43.16 (*C*H), 33.85 (*C*H_2), 32.65 (*C*H_2), 32.37 (*C*H_2), 27.11 (*C*H_2), 26.25 (*C*H_2), 25.61 (*C*H_2). MS (EI) m/z calcd for $C_9H_{17}N$: $(M)^+$ 139, found: 139.

6-Methyl-1,2,3,4-tetrahydroquinoline (4b):[2] Yellow liquid. Yield: 127 mg (87%). IR(DCM): 3355, 2947, 2854, 2230, 1578, 1419, 1216, 1119, 826, 725 cm^{-1}. ^1H NMR ($CDCl_3$): δ 6.84 (d, *J* = 4 Hz, 2H, ArC*H*), 6.46 (d, *J* = 8 Hz, 1H, ArC*H*), 3.60 (s, 1H, N*H*), 3.59-3.30 (m, 2H, CH_2), 2.78 (d, *J* = 8 Hz, 2H, CH_2), 2.26 (s, 3H, CH_3), 2.01-1.95 (m, 2H, CH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 142.47 (quat-*C*), 130.11 (Ar*C*H), 127.28 (Ar*C*H), 126.25 (quat-*C*), 121.62 (quat-*C*), 114.49 (Ar*C*H), 42.22 (*C*H_2), 26.96 (*C*H_2), 22.48 (*C*H_3), 20.45 (*C*H_2). MS (EI) m/z calcd for $C_{10}H_{13}N$: $(M)^+$ 147, found: 147.

6-Methyldecahydroquinoline (4c):[4] IR(DCM): 3319, 2987, 2815, 2240, 1516, 1471, 1210, 1146, 713, 610 cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.34 (s, 1H, N*H*), 1.61-1.58 (m, 8*H*, CH_2 and C*H*), 1.57-1.51 (m, 4*H*, CH_2 and C*H*), 1.38-1.16 (m, 4*H*, CH_2), 0.89 (d, *J* = 8Hz, 3H, CH_3). MS (EI) m/z calcd for $C_{10}H_{19}N$: $(M)^+$ 153, found: 153.

6-Methoxy-1,2,3,4-tetrahydroquinoline (5b):[2] Yellow liquid. Yield: 146 mg (90%). IR(DCM): 3389, 2915, 2879, 2215, 1574, 1443, 1219, 1167, 1050, 625 cm^{-1}. ^1H NMR ($CDCl_3$): δ 6.63-6.59 (m, 2H, ArC*H*), 6.47 (d, *J* = 8 Hz, 1H, ArC*H*), 3.75 (s, 3H, OCH_3), 3.50 (s, 1H, N*H*), 3.27 (t, *J* = 8 Hz, 2H, CH_2), 2.78 (t, *J* = 8 Hz, 2H, CH_2), 1.98-1.92 (m, 2H, CH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 151.84 (quat-*C*), 138.90 (quat-*C*), 122.89 (quat-*C*), 115.57 (Ar*C*H), 114.91 (Ar*C*H), 112.92 (Ar*C*H), 55.83 (O*C*H_3), 42.36 (*C*H_2), 27.18 (*C*H_2), 22.47 (*C*H_2). MS (EI) m/z calcd for $C_{10}H_{13}NO$: $(M)^+$ 163, found: 163.

6-Methoxydecahydroquinoline (5c):[5] IR(DCM): 3394, 2910, 2818, 2217, 1516, 1487, 1278, 1169, 928, 767, 616 cm^{-1}. ^1H NMR ($CDCl_3$): δ 3.27 (s, 3H, CH_3), 3.12-3.02 (m, 2H, C*H* and CH_2), 2.78- 2.77 (br. m, 2H, overlapped N*H* and C*H*), 1.72-1.39 (m, 11H, CH_2). MS (EI) m/z calcd for $C_{10}H_{19}NO$: $(M)^+$ 169, found: 169.

Piperazine (6b):[6] White solid. Yield: 75 mg (87%). IR(DCM): 3387, 2918, 2867, 2233, 1557, 1416, 1219, 1176, 829, 654 cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.75 (s, 8H, CH_2), 1.81 (br. s, 1H, N*H*). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 47.14. MS (EI) m/z calcd for $C_4H_{10}N_2$: $(M)^+$ 86, found: 86.

2-Methyl-1,2,3,4-tetrahydroquinoxaline (7b):[7] Brown liquid. Yield: 118 mg (80%). IR(DCM): 3383, 2917, 2871, 2216, 1547, 1419, 1291, 1156, 816, 723, 616 cm^{-1}. ^1H NMR ($CDCl_3$): δ 6.60-6.56 (m, 2H, ArC*H*), 6.51-6.48 (m, 2H, ArC*H*), 3.59 (s, 2H, N*H*), 3.53-3.46 (m, 1H, C*H*), 3.29 (d, *J* = 8 Hz, 1H, CH_2), 3.01 (t, *J* = 8 Hz, 1H, CH_2), 1.17 (d, *J* = 4 Hz, 3H, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 133.58 (quat-*C*),

133.23 (quat-*C*), 118.60 (Overlapped 2Ar*C*H), 114.43 (Ar*C*H), 114.37 (Ar*C*H), 48.22 (*C*H_2), 45.66 (*C*H_2), 19.87 (*C*H_3). MS (EI) m/z calcd for $C_9H_{12}N_2$: $(M)^+$ 148, found: 148.

Decahydroquinoxaline (8b):[8] IR(DCM): 3372, 2918, 2874, 2219, 1554, 1433, 1216, 1149, 826, 677 cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.84 (d, *J* = 4Hz, 2H, C*H*$_2$), 2.74 (br. s, 2H, C*H*$_2$), 2.57 (t, *J* = 4 Hz, 2H, C*H*$_2$), 2.15 (br. s, 1H, N*H*), 1.76 (br. s, 2H, C*H*$_2$), 1.46- 1.03 (m, 6H, C*H*$_2$). MS (EI) m/z calcd for $C_8H_{16}N_2$: $(M)^+$ 140, found: 140.

Tetradecahydroacridine (9b):[9] Yellow liquid. Yield: 145 mg (75%). IR(DCM): 3373, 3018, 2910, 2879, 2215, 1564, 1417, 1219, 1177, 728, 671 cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.85-2.80 (m, 2H, C*H*), 2.66 (br. m, 1H, N*H*), 1.74-1.10 (m, 20H, C*H*$_2$ and C*H*). MS (EI) m/z calcd for $C_{13}H_{23}N$: $(M)^+$ 193, found: 193.

Piperidine (10b):[5] Light yellow liquid. Yield: 63 mg (89%). IR(DCM): 3410, 3018, 2917, 2210, 1516, 1417, 1210, 1164, 827, 717 cm^{-1}. ^1H NMR ($CDCl_3$): δ 3.13 (br. s, 1H, N*H*), 2.84 (m, 4H, C*H*$_2$), 1.80 (m, 4H, C*H*$_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 46.87 (*C*H_2), 25.47 (*C*H_2). MS (EI) m/z calcd for C_4H_9N: $(M)^+$ 71, found: 71.

Octahydro-1*H*-indole (11b):[10] IR(DCM): 3390, 2987, 2856, 2233, 1543, 1418, 1291, 1165, 731, 659 cm^{-1}. ^1H NMR ($CDCl_3$): δ 3.04-2.90 (m, 3H, C*H*$_2$ and C*H*), 2.68 (br. s, 1H, N*H*), 1.94-1.58 (m, 3H, C*H*$_2$ and C*H*), 1.57-1.46 (m, 5H, C*H*$_2$), 1.36-1.15 (m, 3H, C*H*$_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 57.56 (*C*H), 44.07 (*C*H_2), 38.14 (*C*H_2), 30.66 (*C*H), 27.65 (*C*H_2), 27.19 (*C*H_2), 23.52 (*C*H_2), 21.63 (*C*H_2). MS (EI) m/z calcd for $C_8H_{15}N$: $(M)^+$ 125, found: 125.

Octahydrobenzofuran (12b):[11] IR(DCM): 3010, 2978, 2817, 1557, 1312, 1157, 1060, 721, 627 cm^{-1}. ^1H NMR ($CDCl_3$): δ 3.92-3.57 (m, 2H, C*H*$_2$), 1.93-0.79 (m, 12H, C*H*$_2$). MS (EI) m/z calcd for $C_8H_{14}O$: $(M)^+$ 126, found: 126.

2,5-Dicyclohexyloxazolidine (14b): White solid. Yield: 201 mg (85%). IR(DCM): 3407, 3019, 2956, 2871, 2211, 1533, 1417, 1219, 1165, 825, 661 cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.38 (s, 1H, N*H*), 3.24 (m, 2H, C*H*$_2$), 2.04-2.00 (m, 11H, C*H*$_2$ and C*H*), 1.40-0.91(m, 13H, C*H*$_2$ and C*H*). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 45.88 (*C*H_2), 37.37 (*C*H), 35.68 (CH), 33.40 (*C*H_2), 29.98 (*C*H_2), 26.73(*C*H_2), 26.46 (Overlapped *C*H_2), 26.01 (Overlapped *C*H_2). HRMS (EI) m/z calcd for $C_{15}H_{28}NO$: 238.2171 $(M+H)^+$, found: 238.2170.

General procedure for the hydrogenation of arenes: To a scintillation glass vial containing a small stirrer bar, arenes (1 mmol), and catalyst **1** (0.01 mmol in 40 µl stock solution) were charged under nitrogen atmosphere [1,4-dioxane (0.3 mL) was used as a solvent for solid substrates]. The glass vial then placed inside a high-pressure Parr reactor or finger tube pressure reactor, evacuated and pressurized with H_2 (30-50 bar) gas. After completion of the reaction, the reactor was cooled to room temperature and the

pressurized gas (H_2) was slowly released. The reaction mixture was analysed by gas chromatography and ^{1}H NMR spectroscopy. The selected crude reaction mixtures were extracted with dichloromethane (3 x 10 mL). The combined organic phase was dried over sodium sulphate and the solvent was evaporated under reduced pressure. The crude product was purified by flash column chromatography.

Recycling experiments, toluene hydrogenation: After a first catalytic reaction, the reaction mixture was decanted, the supernatant was removed and the catalyst was separated. The solution was analyzed by GC and the catalyst was washed with acetone (1 mL) before a fresh batch of toluene was introduced and the reaction was performed again under the same conditions.

Table S2. Hydrogenation of toluene, recycling experiments[a]

Entry	Cycle	Yield methylcyclohexane[b]
1	1	>99
2	2	>99
3	3	>99

[a]Conditions: Toluene (1 mmol), and catalyst (0.01 mmol) were added to a scintillation glass vial under nitrogen atmosphere and placed inside high pressure (Parr) reactor. The reactor was charged with H_2 and heated at 90°C and stirred for 40 h. [b]Yield determined by GC-FID using tetradecane as internal standard.

Spectral data of carbocycles obtained from hydrogenation of arenes:

Cyclohexane (15b):[12] Colorless liquid. IR(DCM): 2987, 2887, 1487 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.32 (s, 12H, CH_2). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 27.06 (*C*H_2). MS (EI) m/z calcd for C_6H_{12}: $(M)^+$ 84, found: 84.

Methylcyclohexane (16b):[13] Colorless liquid. IR(DCM): 2991, 2888, 1490, 1310, 921, 728 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.70-1.62 (m, 5H, CH_2 and C*H*), 1.38-1.09 (m, 4H, CH_2), 0.87-0.85 (m, 5H, CH_2 and CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 35.60 (*C*H_2), 32.90 (*C*H), 26.61 (*C*H_2), 26.50 (*C*H_2), 23.06 (*C*H_3). MS (EI) m/z calcd for C_7H_{14}: $(M)^+$ 98, found: 98.

1,2-Dimethylcyclohexane (17b):[14] IR(DCM): 2981, 2895, 1486, 1319, 879, 776 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.71-1.62 (m, 4H, CH_2), 1.47-1.32 (m, 4H, CH_2), 0.88 (d, J = 4 Hz, 6H, CH_3), 0.77 (q, J = 6 Hz, 1H, C*H*), 0.55 (q, J = 6 Hz, 1H, C*H*). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 34.28 (*C*H_2), 31.39 (*C*H_2), 23.65 (*C*H), 19.87 (*C*H_2), 16.10 (*C*H_3). MS (EI) m/z calcd for C_8H_{16}: $(M)^+$ 112, found: 112.

1,3-Dimethylcyclohexane (18b):[15] Colorless liquid. IR(DCM): 2995, 2897, 1419, 1216, 971, 829 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.68-1.33 (m, 6H, CH_2 and CH_3), 0.84 (CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 44.63 (*C*H_2), 35.18 (*C*H_2), 32.93 (*C*H), 26.59 (*C*H_2), 23.09 (*C*H_3). MS (EI) m/z calcd for C_8H_{16}: $(M)^+$ 112, found: 112.

1,4-Dimethylcyclohexane (19b):[15] Colorless liquid. IR(DCM): 2916, 2878, 1434, 1319, 971, 771 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.46-1.43 (m, 2H, C*H*), 1.31-1.25 (m, 8H, CH_2), 0.91 (d, J = 8 Hz, 6H, CH_3). MS (EI) m/z calcd for C_8H_{16}: $(M)^+$ 112, found: 112.

1,2,3,4-Tetrahydronaphthalene (20b):[16] Colorless liquid. IR(DCM): 2987, 2878, 1489, 1316, 871, 716 cm^{-1}. ^1H NMR ($CDCl_3$, Data recorded from reaction mixture spectrum): δ 7.07-7.02 (m, 4H, ArC*H*), 2.75 (m, 4H, CH_2), 1.78 (m, 4H, CH_2). MS (EI) m/z calcd for $C_{10}H_{12}$: $(M)^+$ 132, found: 132.

Decahydronaphthalene (20c):[17] Colorless liquid. Yield: 127 mg (92%). Colorless liquid. IR(DCM): 3010, 2957, 2881, 1477, 1315, 1216, 821, 757 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.71-1.23 (m, 15H, CH_2), 1.02-0.86 (m, 3H, C*H* and CH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 43.75 (*C*H), 36.53 (*C*H), 34.43 (*C*H_2), 26.96 (*C*H_2). MS (EI) m/z calcd for $C_{10}H_{18}$: $(M)^+$ 138, found: 138.

(Tetradecahydroanthracen-9-yl)methanol (22b) (Data inferred from reaction mixture)**:** IR (DCM): 3340, 3112, 2985, 2785, 1491, 1311, 827, 739, 625 cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.10 (s, 2H, CH_2O), 3.09-2.94 (m, 6H, CH_2), 2.53 (broad m, 4H, CH), 1.90-1.80 (broad m, 10H, CH_2).

Cyclohexylmethanol (24b):[13] IR(DCM): 3315, 3016, 2918, 2877, 1519, 1397, 971, 811, 697 cm^{-1}. ^1H NMR ($CDCl_3$): δ 3.36 (d, J = 4 Hz, 2H, OCH_2), 1.69-1.61 (m, 6H, CH_2), 1.43-1.12 (m, 5H, CH_2 and C*H*). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 68.59 (O*C*H_2), 40.53 (*C*H), 29.65 (*C*H_2), 26.64 (*C*H_2), 25.89 (*C*H_2). MS (EI) m/z calcd for $C_7H_{14}O$: $(M)^+$ 114, found: 114.

Cyclohexylamine (25b):[18] Yellow liquid. Yield: 77 mg (78%). IR (DCM): 3401, 3016, 2988, 2811, 1510, 1361, 921, 815 cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.58-2.51 (m, 1H, C*H*), 1.76-1.62 (m, 5H, CH_2), 1.17-0.95 (m, 7H, Overlapped CH_2 and 2 N*H*). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 50.50 (*C*H), 36.96 (*C*H_2), 25.72 (*C*H_2), 25.18 (*C*H_2). MS (EI) m/z calcd for $C_6H_{13}N$: $(M)^+$ 99, found: 99.

3,5-dimethylcyclohexanamine (26b):[19] IR (DCM): 3395, 3021, 2976, 2779, 1487, 1399, 815, 726 cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.55 (m, 1H, NH_2C*H*), 2.07 (Br S, 2H, N*H*), 1.65 (m, 3H, Overlapped CH_2 and C*H*), 1.29-1.27 (m, 5H, CH_2 and C*H*), 0.75 (d, 6H, J = 8 Hz, CH_3). MS (EI) m/z calcd for $C_6H_{13}N$: $(M)^+$ 127, found: 127.

***N*-Methylcyclohexanamine (27b):[20]** Yellow liquid. Yield: 90 mg (80%). IR(DCM): 3299, 3021, 2905, 2871, 1489, 1312, 871, 775 cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.40 (s, 3H, CH_3), 2.15 (br. S, 1H, NH), 1.87 (m, 2H, CH_2), 1.70 (m, 2H, CH_2), 1.25-1.03 (m, 7H, C*H* and CH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 58.49 (*C*H),

33.25 (*C*H_3), 32.84 (*C*H_2), 26.06 (*C*H_2), 24.94 (*C*H_2). MS (EI) m/z calcd for $C_7H_{15}N$: $(M)^+$ 113, found: 113.

Dicyclohexylamine (28b):[21] Colorless liquid. Yield: 148 mg (82%). IR(DCM): 3310, 2997, 2899, 2806, 1489, 1315, 861, 725, 673 cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.47-2.40 (m, 2H, C*H*), 1.72-1.57 (m, 9H, CH_2), 1.14-0.89 (m, 11H, Overlapped CH_2 and N*H*). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 52.88 (*C*H), 34.08 (*C*H_2), 26.04 (*C*H_2), 25.15 (*C*H_2). MS (EI) m/z calcd for $C_{12}H_{23}N$: $(M)^+$ 181, found: 181.

Cyclohexanecarboxamide (29b):[13] Colorless liquid. Yield: 108 mg (85%). IR(DCM): 3278, 3016, 2995, 2816, 1690, 1417, 1233, 921, 756 cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.55 (br, 2H, N*H*), 2.16-2.10 (m, 1H, C*H*), 1.90-1.64 (m, 5H, CH_2), 1.44-1.18 (m, 5H, CH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 179.03 (Amide *C*O), 67.19 (*C*H), 44.90 (*C*H_2), 29.79 (*C*H_2), 25.82 (*C*H_2). MS (EI) m/z calcd for $C_7H_{13}NO$: $(M)^+$ 127, found: 127.

9,10-Dihydroacridine:[26] ^1H NMR ($CDCl_3$): δ 7.13-7.09 (m, 4H, ArC*H*), 6.88 (t, 2H, *J* = 6 Hz, ArC*H*), 6.68 (d, 2H, *J* = 4 Hz, ArC*H*), 5.97 (br. S, 1H, N*H*), 4.07 (s, 2H, CH_2).

Kinetic study: Time profile for arene (toluene) and heteroarene (quinoline) hydrogenation

(a) Time profile for the conversion of quinoline to THQ and DHQ at 30 bar of H_2 pressure

To a scintillation glass vial containing a small stirrer bar, quinoline (1.0 mmol, 129.16 mg), catalyst **1** (0.01 mmol, 5.77 mg) were charged under nitrogen atmosphere in the glove box. The glass vial then placed inside a high-pressure Parr reactor, evacuated and pressurized with H_2 (30 bar) gas and heated to 75 °C for 2 h. The reaction was repeated at 4 h, 6 h, 8 h, 12 h, 16 h, 20 h, and 24 h of time intervals. After completion of the reaction, the reactor was cooled to room temperature and the pressurized gas (H_2) was slowly released. The reaction mixture was analyzed by gas chromatography. At 20 bar of H_2 pressure, formation of THQ as a product from the quinoline was observed with an linear progression in the rate of reaction with the time whereas not even traces of DHQ as product was observed at such low pressure.

(b) Time profile for the conversion of quinoline to THQ and DHQ at 50 bar H_2 Pressure

To a scintillation glass vial containing a small stirrer bar, quinoline (1.0 mmol, 129.16 mg), catalyst **1** (0.01 mmol, 5.77 mg) were charged under nitrogen atmosphere in the glove box. The glass vial then placed inside a high-pressure Parr reactor, evacuated and pressurized with H_2 (50 bar) gas and heated to 75 °C for 2 h. The reaction was repeated at 4 h, 6 h, 8 h, 12 h, 16 h, 20 h, and 24 h of time intervals. After completion of the reaction, the reactor was cooled to room temperature and the pressurized gas (H_2) was slowly released. The reaction mixture was analyzed by gas chromatography. The conversion of quinoline to THQ and DHQ at different time intervals was plotted in graph. The rate of reaction for the conversion of quinoline to DHQ gives a sigmoidal shape curve with an induction period of 12 h for a DHQ whereas for the THQ exponential increase in the rate of reaction was observed with time.

(c) Time profile for the conversion of toluene to methylcyclohexane

To a scintillation glass vial containing a small stirrer bar, toluene (1.0 mmol, 92. mg), catalyst **1** (0.015 mmol, 8.66 mg) were charged under nitrogen atmosphere in the glove box. The glass vial then placed inside a high-pressure Parr reactor, evacuated and pressurized with H_2 (50 bar) gas and heated to 90 °C for 2 h. The reaction was repeated at 4 h, 8 h, 12 h, 16 h, 24 h, and 40 h of time intervals. After completion of the reaction, the reactor was cooled to room temperature and the pressurized gas (H_2) was slowly released. The reaction mixture was analyzed by gas chromatography. The monitoring of reaction and then plot of conversion of toluene to methyl cyclohexane at different time intervals gives a sigmoidal shape curve with an induction period of 16 hrs.

Quantitative poisoning experiments with 1,10-phenanthroline as a poison:

(a) 1,10-phenanthroline poisoning experiments with evolved catalytic system for arenes:

To a scintillation glass vial containing a small stirrer bar, toluene (3.0 mmol, 272.46 mg), catalyst **1** (0.03 mmol, 17.3 mg) were charged under nitrogen atmosphere in the glove box. The glass vial then placed inside a high-pressure Parr reactor, evacuated and pressurized with H_2 (50 bar) gas and heated to 90 °C for 40 h. After completion of reaction, it was cooled down and supernatant was removed. The remaining black color precipitate of Ru(0) was washed, dried and again charged with fresh substrate i.e. toluene (3.0 mmol, 272.46 mg). Different concentration of poison 1,10-phenanthroline (0.0 equiv. |(no poison added), 0.25 equiv. (1.34 mg), 0.50 equiv. (2.69 mg), 1.0 equiv. (5.39 mg) was added to this evolved catalytic system. The reaction was repeated at 2 h, 4 h, 6 h, and 8 h of time intervals. After completion of the reaction, the reactor was cooled to room temperature and the pressurized gas (H_2) was slowly released. The reaction mixture was analyzed by gas chromatography to check the effect of poison (Figure S1).

(b) 1,10-phenanthroline poisoning experiments with fresh catalytic system for arenes:

To a scintillation glass vial containing a small stirrer bar, toluene (3.0 mmol, 272.46 mg), catalyst **1** (0.03 mmol, 17.3 mg) were charged under nitrogen atmosphere in the glove box. Different concentration of poison 1,10-phenanthroline (0.0 equiv. |(no poison added), 0.25 equiv. (1.34 mg), 0.50 equiv. (2.69 mg), 1.0 equiv. (5.39 mg) was added to the reaction mixture. The glass vial then placed inside a high-pressure Parr reactor, evacuated and pressurized with H_2 (50 bar) gas and heated to 90 °C for 24 h. The reaction was repeated at 2 h, 4 h, 8 h, 12 h, 16 h, 20 h, 24 h, 40 h of time intervals. After completion of the reaction, the reactor was cooled to room temperature and the pressurized gas (H_2) was slowly released. The reaction mixture was analyzed by gas chromatography (Figure S2).

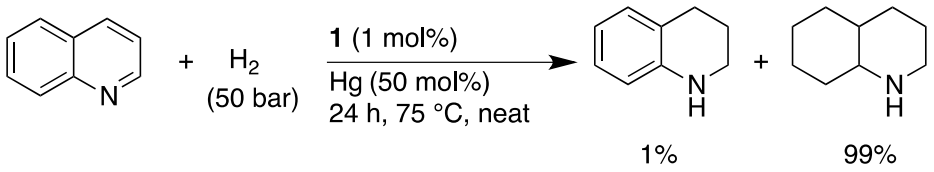
(c) 1,10-phenathroline poisoning experiments with evolved catalytic system for heteroarenes:

To a scintillation glass vial containing a small stirrer bar, quinoline (1.0 mmol, 129.16 mg), catalyst **1** (0.01 mmol, 5.77 mg) were charged under nitrogen atmosphere in the glove box. The glass vial then placed inside a high-pressure Parr reactor, evacuated and pressurized with H_2 (50 bar) gas and heated to 75 °C for 24 h. After completion of reaction, it was cooled down. The formed black color precipitate of Ru(0) was again charged with fresh substrate i.e. quinoline (1.0 mmol, 129.16 mg) and different concentration of poison 1,10-phenanthroline (0.0 equiv. |(no poison added), 0.50 equiv. (0.901 mg), 1.0 equiv. (1.80 mg), 2.0 (3.60 mg) was added to this evolved catalytic system. The reaction was done for 24 h. After completion of the reaction, the reactor was cooled to room temperature and the pressurized gas (H_2) was slowly released. The reaction mixture was analyzed by gas chromatography to check the effect of poison (Figure S3).

Monitoring of reaction progress for conversion of quinoline to tetrahydroquinoline (THQ): in presence and absence of Hg (study of the kinetic competence):

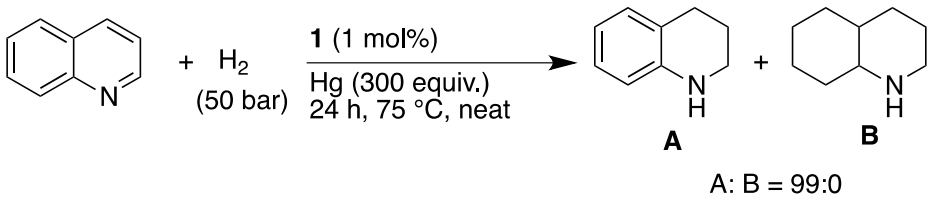
To a scintillation glass vial containing a small stirrer bar, quinoline (1 mmol, 118 µl), catalyst **1** (0.01 mmol in 40 µl stock solution) were charged under nitrogen atmosphere. The glass vial then placed inside a high-pressure Parr reactor, evacuated and pressurized with H_2 (30 bar) gas and heated to 75 °C. The reaction was intervened at 2 h interval, cooled to room temperature and the pressurized gas (H_2) was slowly released. Small amount (0.5 µl) of reaction mixture were taken out and after dilution with acetone the reaction mixture was analyzed by gas chromatography. The reactor then again pressurized and continued for further reaction progress. Similar experiment is carried out with quinoline (1 mmol, 118 µl), catalyst 1 (0.01 mmol in 40 µl stock solution) in presence of Hg (300 equiv. Vs Ru, 600 mg) and analyzed by gas chromatography after 2 h interval. Concentration of THQ is determined by relative peak intensities (area of the signal) with respect to the quinoline peak intensity. Kinetic competence (Figure S3) revealed comparable rates of hydrogenation in presence of Hg with respect to the standard reaction condition, revealing homogeneous catalysis operative for hydrogenation of heteroarenes.

Hydrogenation of quinoline to DHQ with 50 mol% Hg(0):



To a scintillation glass vial containing a small stirrer bar, quinoline (1 mmol, 118 µl), catalyst **1** (0.01 mmol in 40 µl stock solution), and Hg (50 mol%, 100 mg) were charged under nitrogen atmosphere. The glass vial then placed inside a high-pressure Parr reactor, evacuated and pressurized with H_2 (50 bar) gas and heated to 75 °C. After completion of the reaction, the reactor was cooled to room temperature and the pressurized gas (H_2) was slowly released. The reaction mixture was analyzed by gas chromatography. GC analysis revealed no alteration of reaction efficiency.

Hydrogenation of quinoline to DHQ with excess Hg(0):



To a scintillation glass vial containing a small stirrer bar, quinoline (0.1 mmol, 12 µl), catalyst **1** (0.001 mmol in 4 µl stock solution), Hg (300 equiv., 6 g) and 1,4-dioxane (1 mL) were charged under nitrogen

atmosphere. The glass vial then placed inside a high-pressure Parr reactor, evacuated and pressurized with H_2 (50 bar) gas and heated to 75 °C. After completion of the reaction, the reactor was cooled to room temperature and the pressurized gas (H_2) was slowly released. The reaction mixture was analyzed by gas chromatography. GC analysis revealed complete alteration of reaction efficiency, indicating heterogeneous pathway for complete hydrogenation of quinoline. However, hydrogenation of quinoline to tetrahydroquinoline remains unaffected by the presence of Hg(0). The catalyst efficiency was further verified by adding Hg(0) at 50% hydrogenation of quinoline to tetrahydroquinoline, which revealed that the catalyst remains active until complete hydrogenation of quinoline to tetrahydroquinoline demonstrating efficient homogeneous hydrogenation of heteroarene motif.

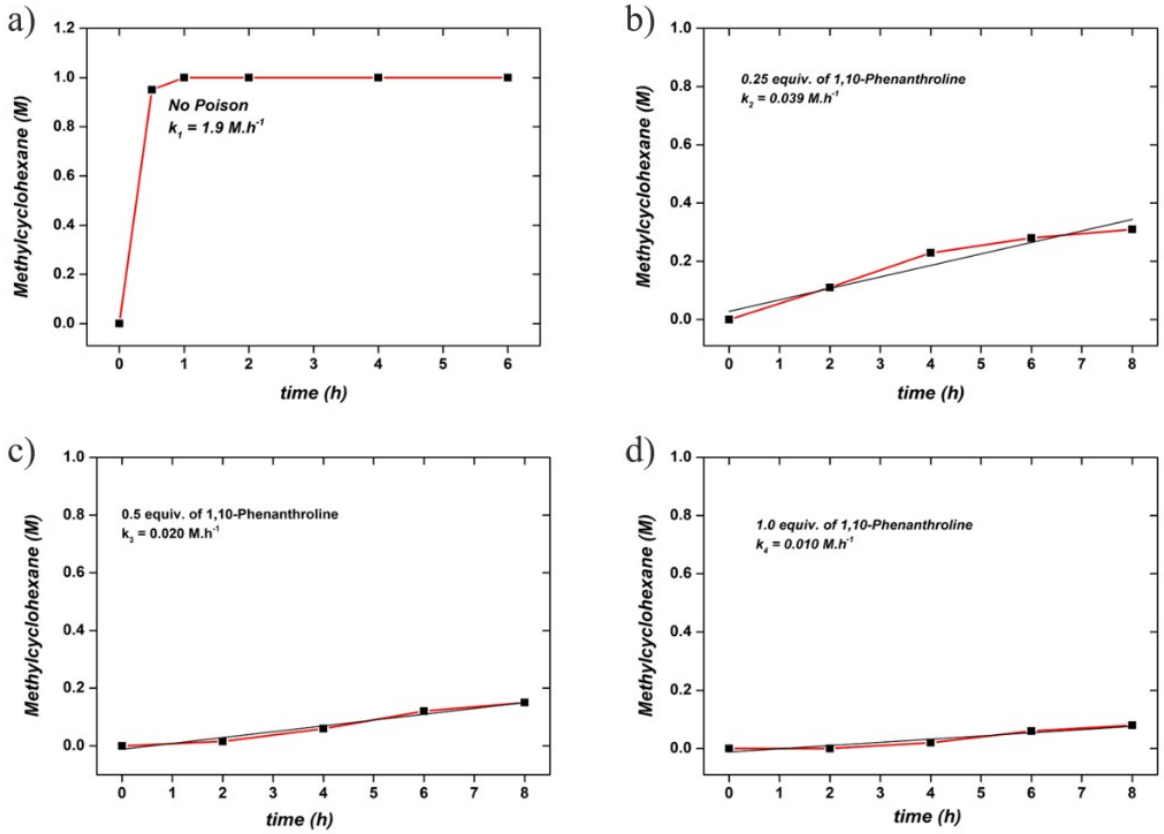


Figure S1: Effect of poison (0.0, 0.25, 5.0, 1.0 equiv.) in the rate of reaction with time for the evolved catalytic system for conversion of toluene to methylcyclohexane.

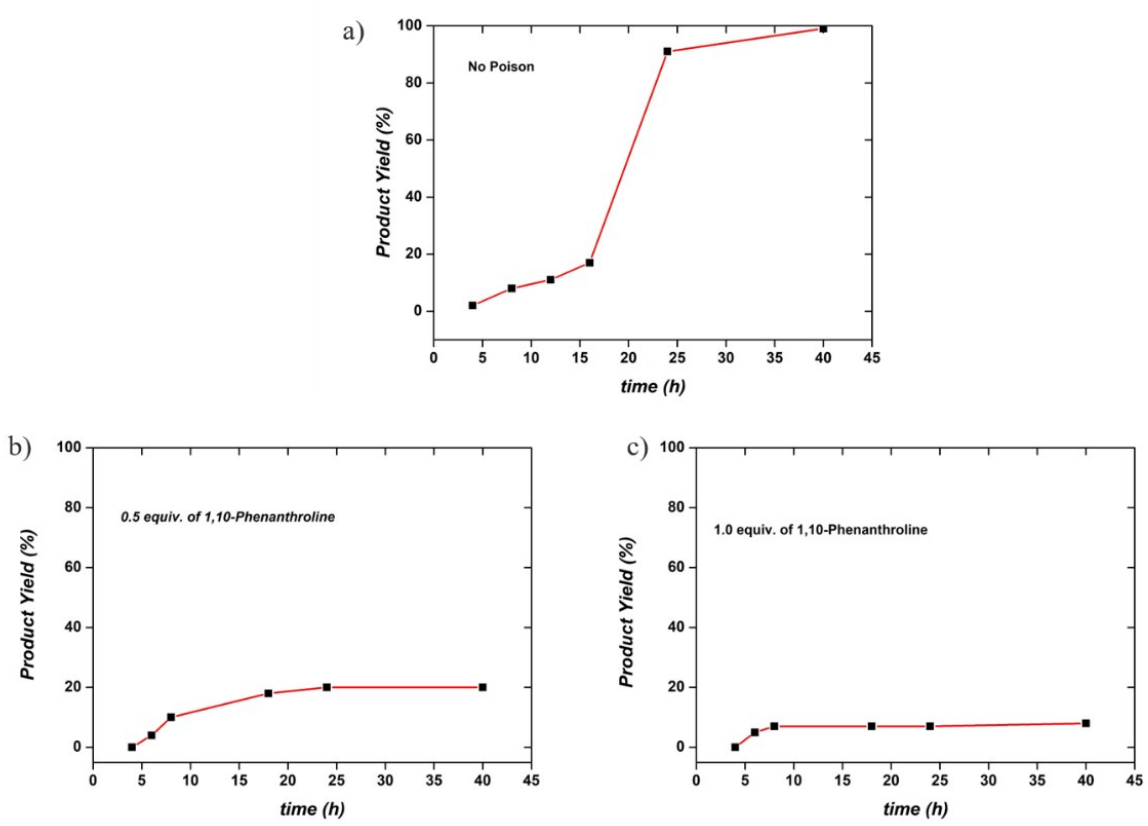


Figure S2: Effect of poison (0.0, 0.25, 5.0, 1.0 equiv.) in the rate of reaction with time for the fresh catalytic system for conversion of toluene to methylcyclohexane.

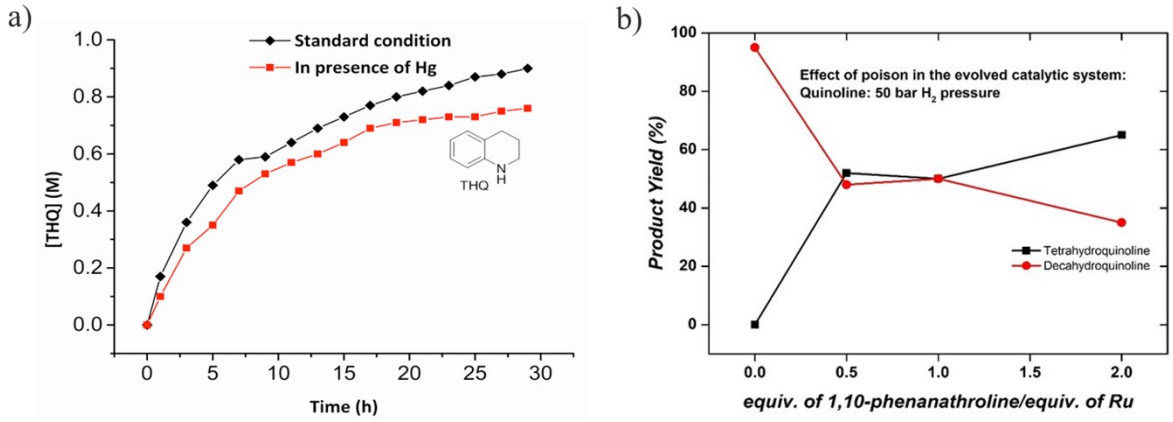


Figure S3: a) Monitoring of reaction progress of quinoline hydrogenation in presence and absence of Hg. b) Effect of poison (0.0, 5.0, 1.0, 2.0 equiv.) in the rate of reaction with time for the evolved catalytic system for conversion of quinoline to tetrahydroquinoline and decahydroquinoline respectively.

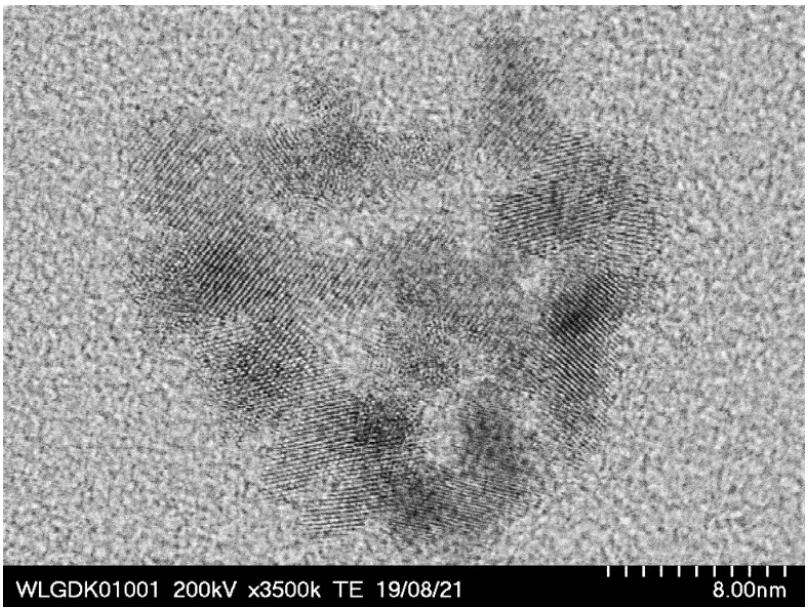


Figure S4: Characterization of the formed nanoparticles by transmission electron microscopy (d = 6.2 ± 0.7 nm).

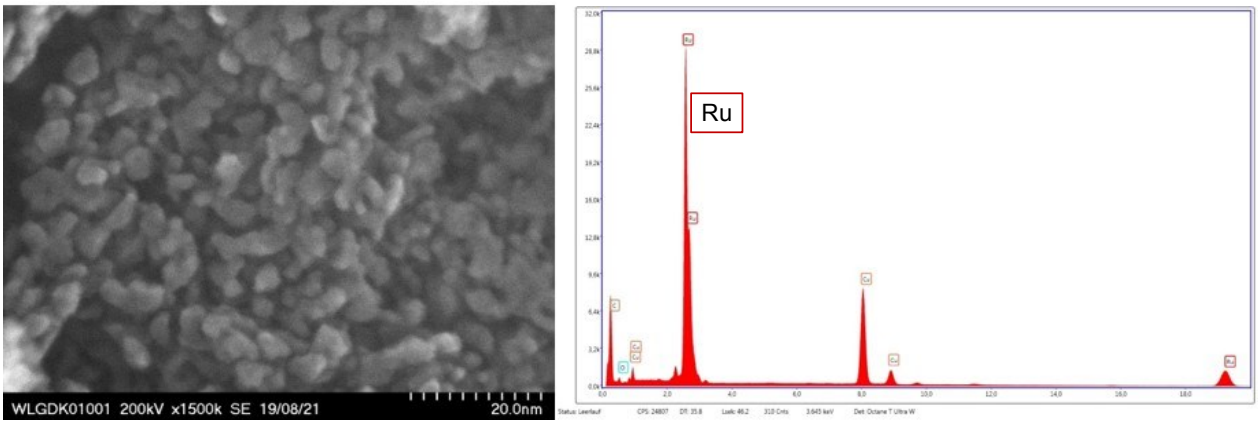
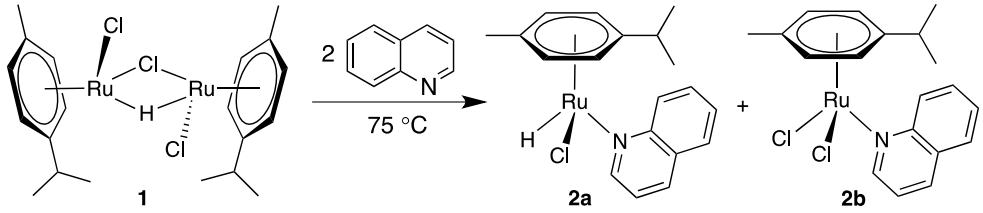


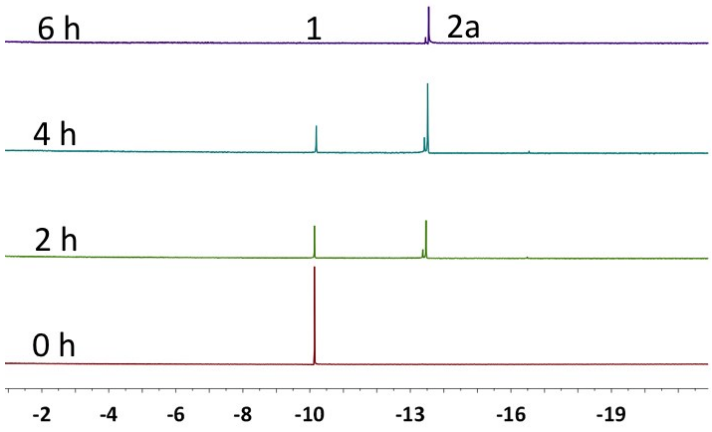
Figure S5: Characterization of the formed nanoparticles by scanning electron microscopy with energy dispersive X-ray (EDX).

Synthesis and isolation of complex 2b from 1:

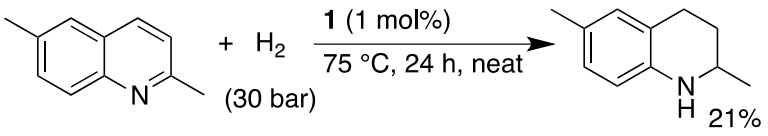


To a screw cap NMR tube complex **1** (20 mg, 0.034 mmol), quinoline (8.3 µl, 0.07 mmol) and C_6D_6 were added under nitrogen atmosphere. The reaction mixture then heated to 75 ºC for 6 h and the progress of the reaction was monitored by ^{1}H NMR spectroscopy. After complete disappearance of complex **1**, the reaction mixture was cooled to room temperature, filtered and allowed for crystallization, which provided the suitable crystals of **2b** for single crystal X-ray analyses. IR (C_6D_6): 2944, 2892, 2091, 2014 (Ru–*H*), 1556, 1431, 1312, 1187, 823, 677 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 9.30 (m, 2H, ArC*H*), 8.18 (d, *J* = 8 Hz, 1H, ArC*H*), 7.80 (d, *J* = 8 Hz, 2H, ArC*H*), 7.56 (t, *J* = 8 Hz, 1H, ArC*H*), 7.37 (s, 1H, ArC*H*), 5.56 (m, 2H, ArC*H*), 5.32 (m, 2H, ArC*H*), 2.91(m, 1H, ^{i}PrC*H*), 1.93 (s, 3H, CH_3), 1.26 (d, *J* = 4Hz, 6H, ^{i}PrCH_3). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 157.92 (quat-*C*), 139.25 (quat-*C*), 121.17 (Ar*C*H), 103.24 (Ar*C*H), 101.30 (quat-*C*), 97.76 (Ar*C*H), 96.83 (quat-*C*), 83.33 (Ar*C*H), 82.17 (Ar*C*H), 81.39 (Ar*C*H), 80.62 (Ar*C*H), 30.58 (*C*H), 22.37 (*C*H_3), 22.23 (*C*H_3), 18.20 (*C*H_3).

Reaction mixture ^{1}H NMR spectrum of **1** and quinoline (hydride region):

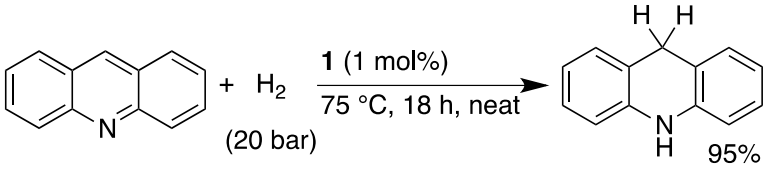


Experiment to understand influence of coordination on catalysis



To a scintillation glass vial containing a small stirrer bar, 2,6-dimethylquinoline (1 mmol, 157 mg), catalyst **1** (0.01 mmol in 40 µl stock solution) were charged under nitrogen atmosphere. The glass vial then placed inside a high-pressure Parr reactor, evacuated and pressurized with H_2 (30 bar) gas and heated to 75 °C. After 24 h the reactor was cooled to room temperature and the pressurized gas (H_2) was slowly released. The reaction mixture was analyzed by gas chromatography, which showed 21% hydrogenation. Inferior yield of 1,2,3,4-tetrahydro-2,6-dimethylquinoline revealed importance of coordination, which being affected by steric influence by a methyl group at 2-position.

Selective synthesis of 9,10-dihydroacridine: a product of facile 1,5-hydride transfer



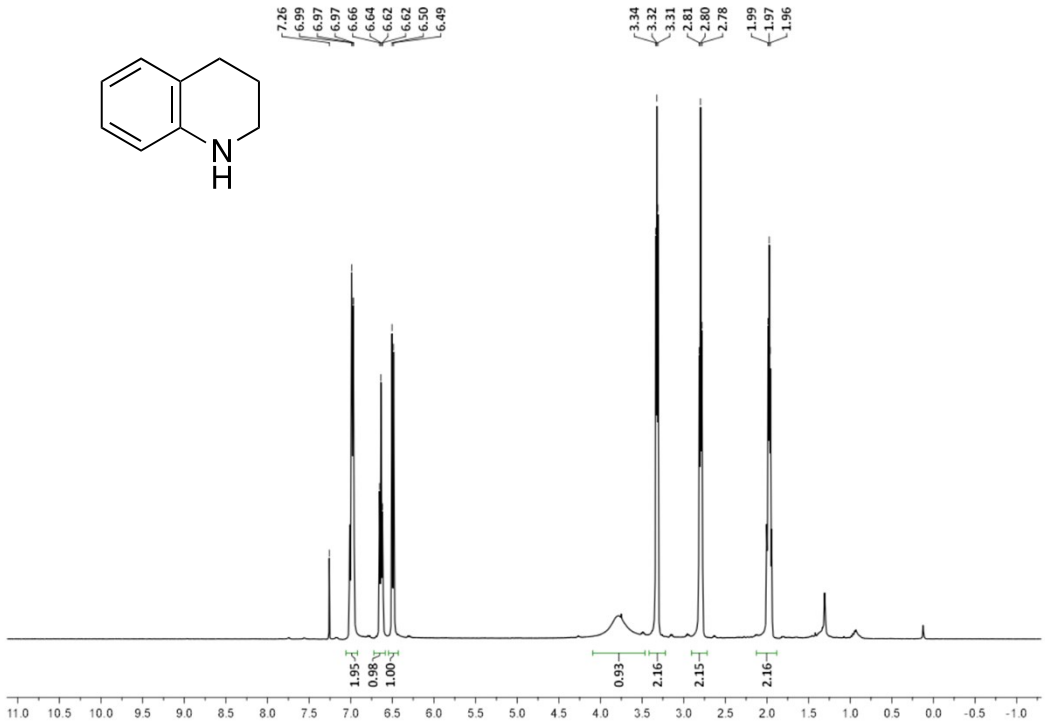
To a scintillation glass vial containing a small stirrer bar, acridine (1 mmol, 179 mg), catalyst **1** (0.01 mmol in 40 µl stock solution) were charged under nitrogen atmosphere. The glass vial then placed inside a high-pressure Parr reactor, evacuated and pressurized with H_2 (20 bar) gas and heated to 75 °C. After 18 h the reactor was cooled to room temperature and the pressurized gas (H_2) was slowly released. The reaction mixture was analyzed by NMR spectroscopy.

Determination of the molecular structure of 2b in the solid state by X-ray single crystal diffraction: A suitable single crystals of complex **2b** for X-ray analysis was obtained from reaction mixture of **1** and quinoline in C_6D_6. A suitable crystal was mounted on a glass fiber. Geometry and intensity data were collected with a Bruker SMART D8 goniometer equipped with an APEX CCD detector and with an Incoatec microsource (Mo-Kα radiation, λ = 0.71073 Å, multilayer optics). Temperature was controlled using an Oxford Cryostream 700 instrument. Intensities were integrated with SAINT+[22] and corrected for absorption with SADABS.[23] The structure was solved by direct methods and refined on F^2 with SHELXL-97.[24,25]

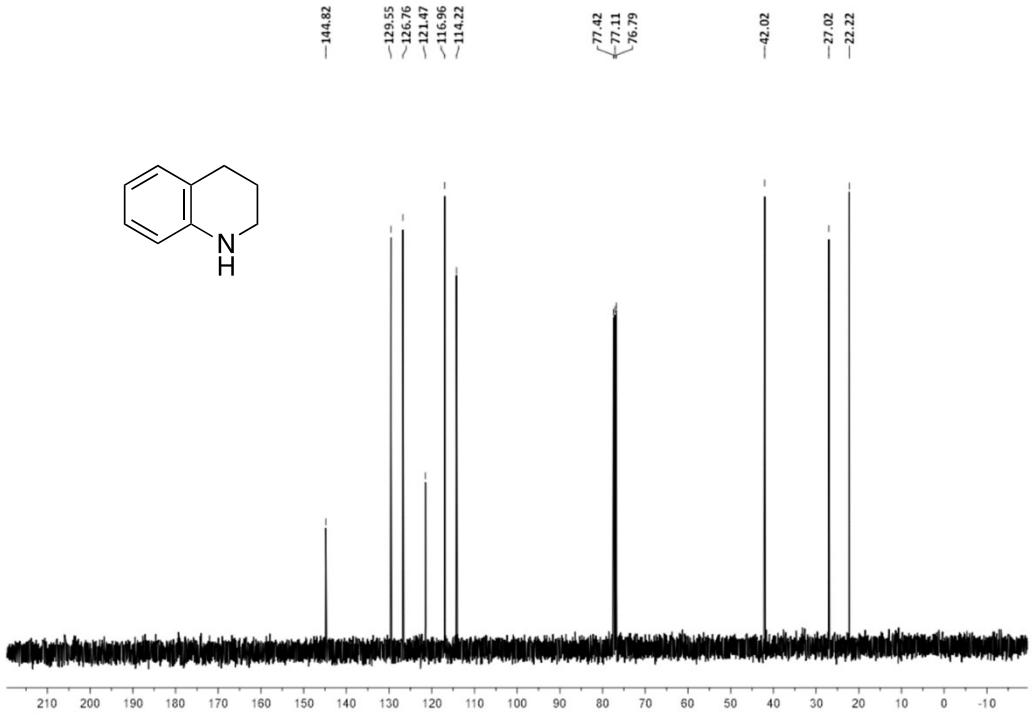
Crystal data of Ru-complex 2b: $C_{19}H_{21}Cl_2NRu$, crystal dimensions: 0.2 × 0.12 × 0.10, Orthorhombic with space group $Pca2_1$ a = 7.1672 (3) Å, b = 13.7037 (5) Å, c = 17.9697 (8) Å, α = 90°, β = 90°, γ = 90°, V = 1764.93 (13) Å^3, Z = 4, T = 100 K, $2\theta_{max}$ = 26.72, ρ_{calcd} = 1.638 g/cm^3, µ (MoKα) = 1.189 mm^{-1}. min/max transmission factors = 0.6332/0.7454, 3679 Reflections collected, 6483 unique ($R1$ = 0.0232), $WR2$ = 0.0426 (all data). The structure has been deposited at the CCDC data center and can be retrieved by using the number CCDC 1557989.

NMR spectra of hydrogenated heterocyles and carbocycles:

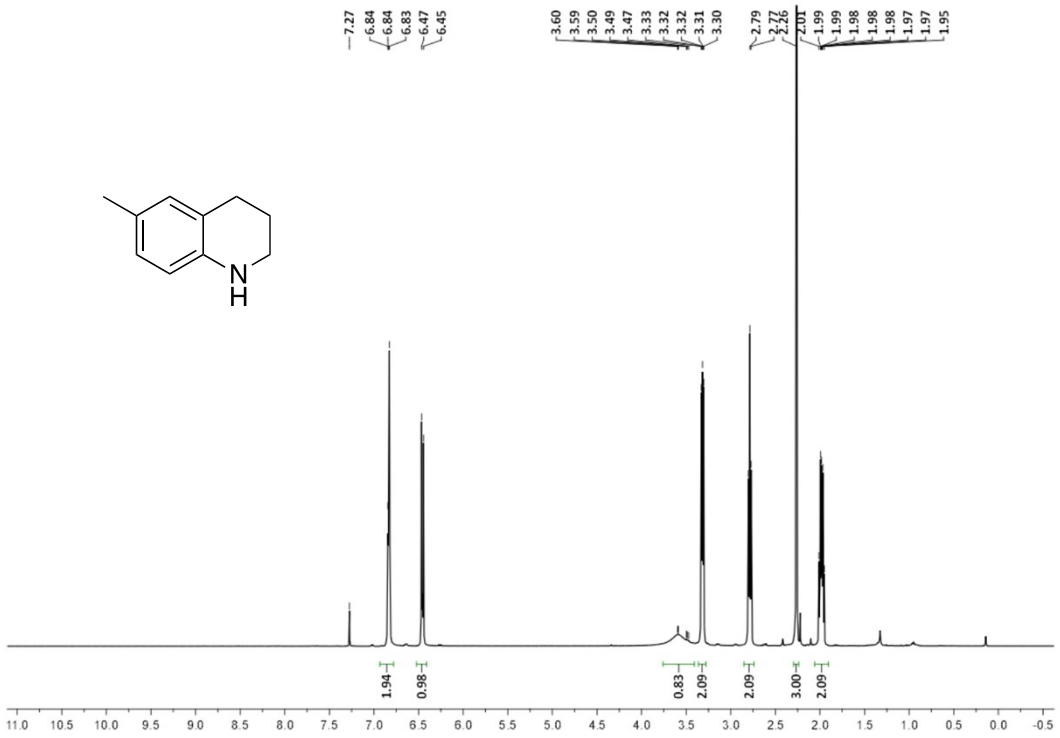
^{1}H NMR spectrum of 1,2,3,4-tetrahydroquinoline:



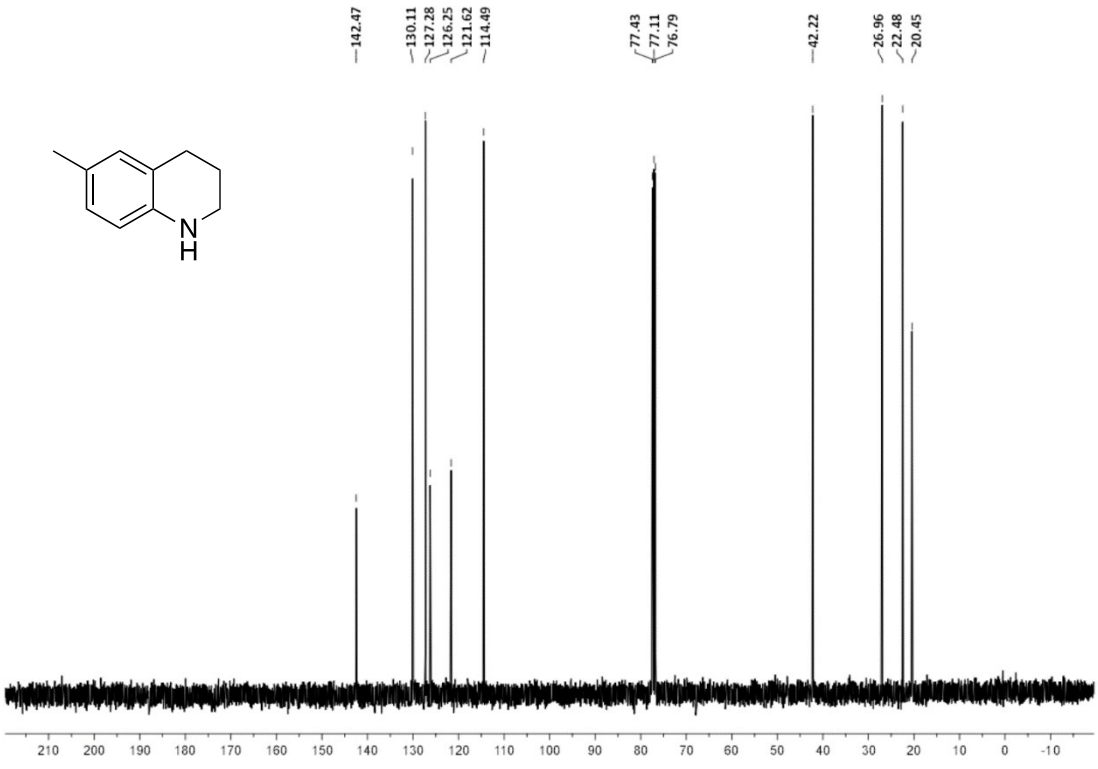
^{13}C NMR spectrum of 1,2,3,4-tetrahydroquinoline:



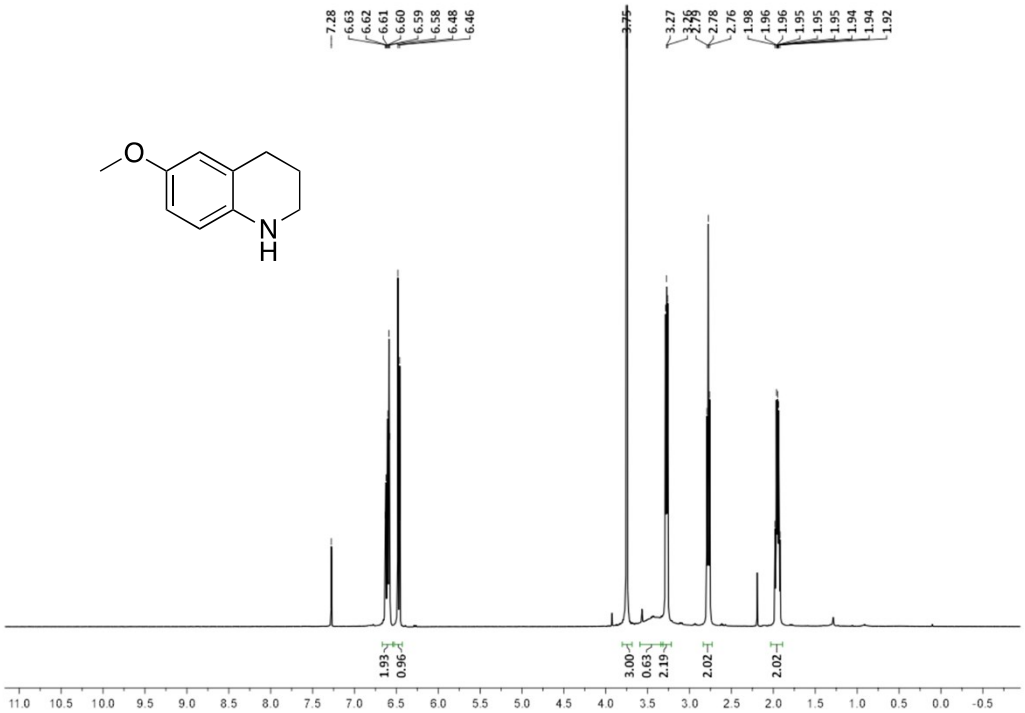
^{1}H NMR spectrum of 6-methyl-1,2,3,4-tetrahydroquinoline:



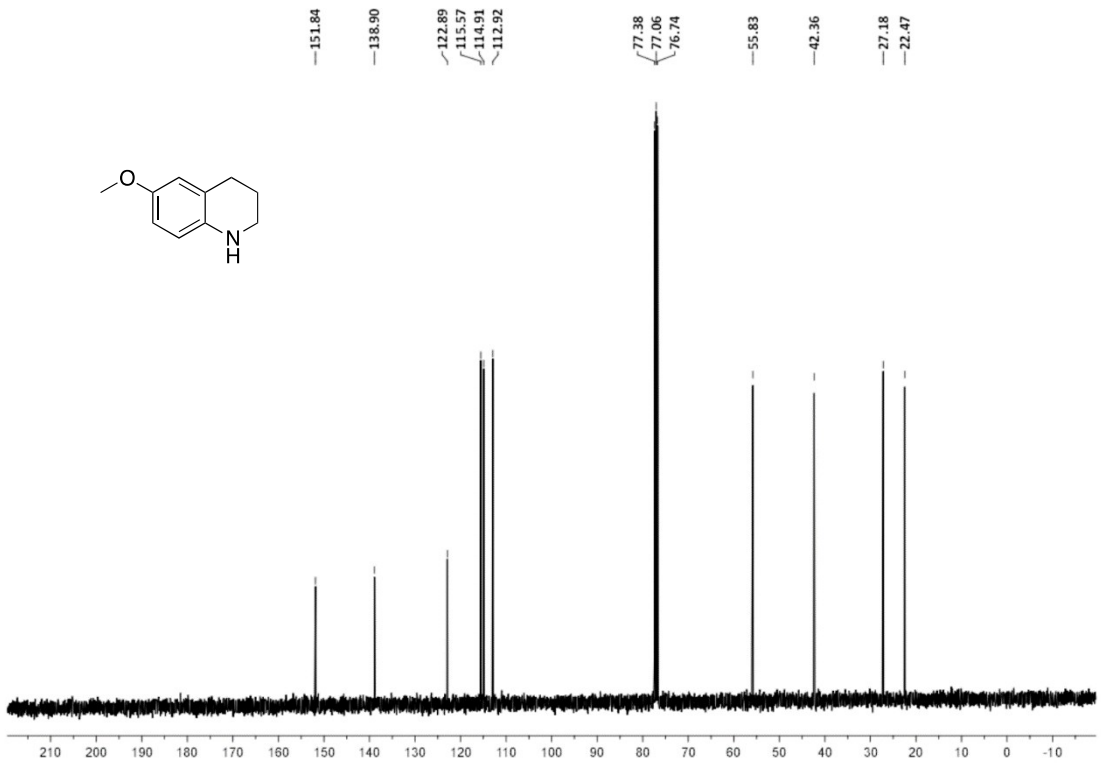
^{13}C NMR spectrum of 6-methyl-1,2,3,4-tetrahydroquinoline:



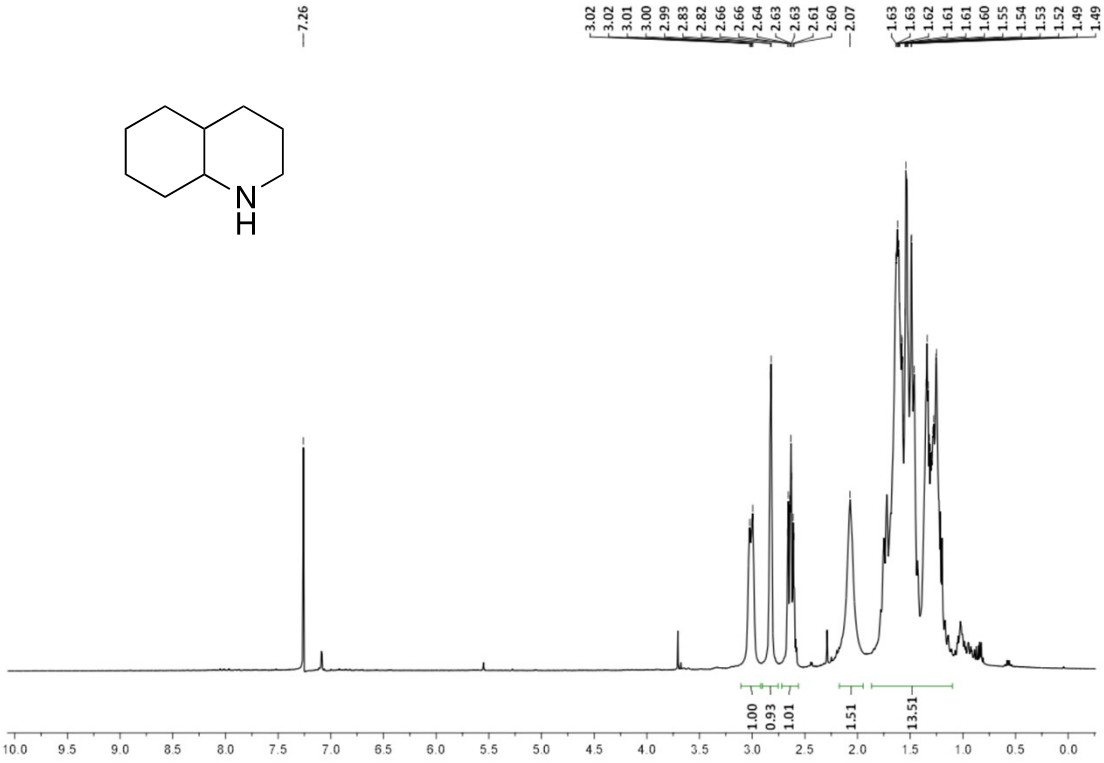
^{1}H NMR spectrum of 6-methoxy-1,2,3,4-tetrahydroquinoline:



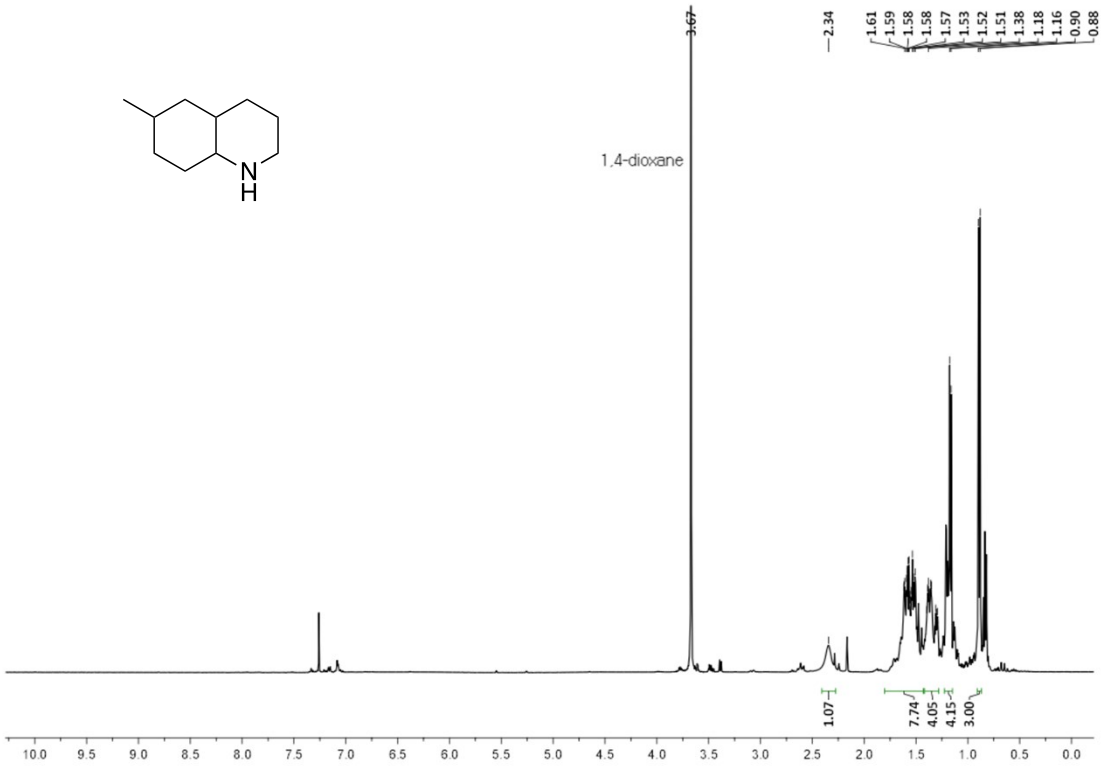
^{13}C NMR spectrum of 6-methoxy-1,2,3,4-tetrahydroquinoline:



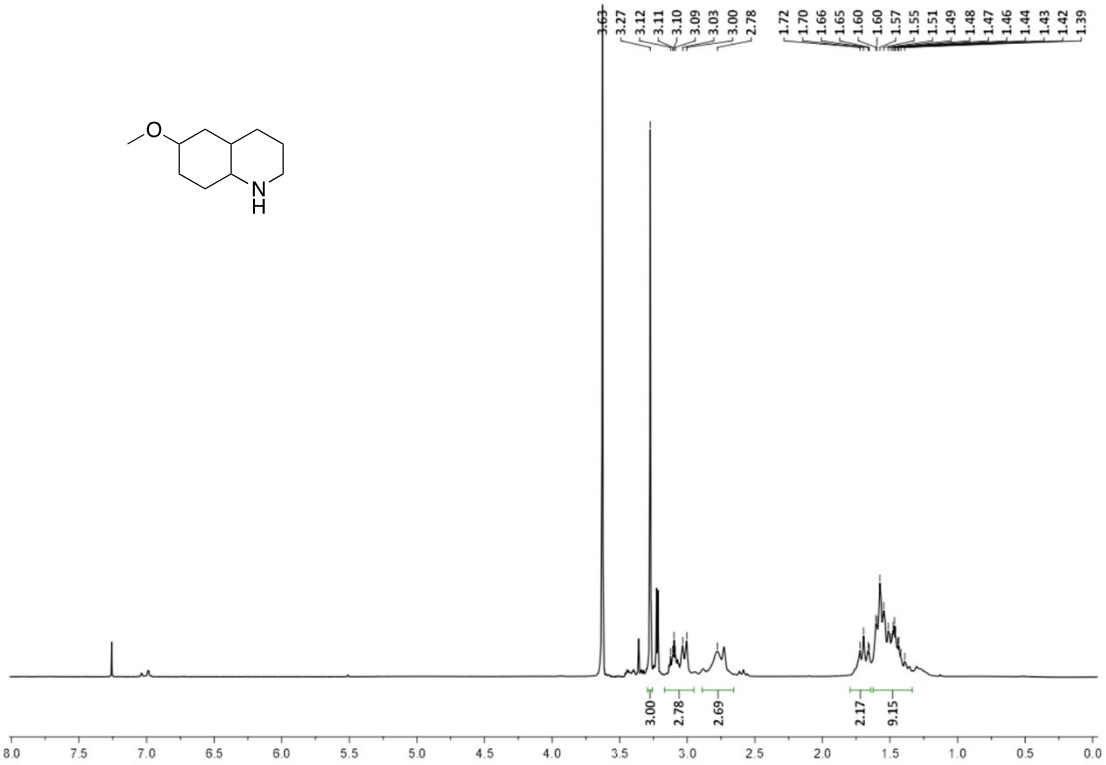
^{1}H NMR spectrum of decahydroquinoline:



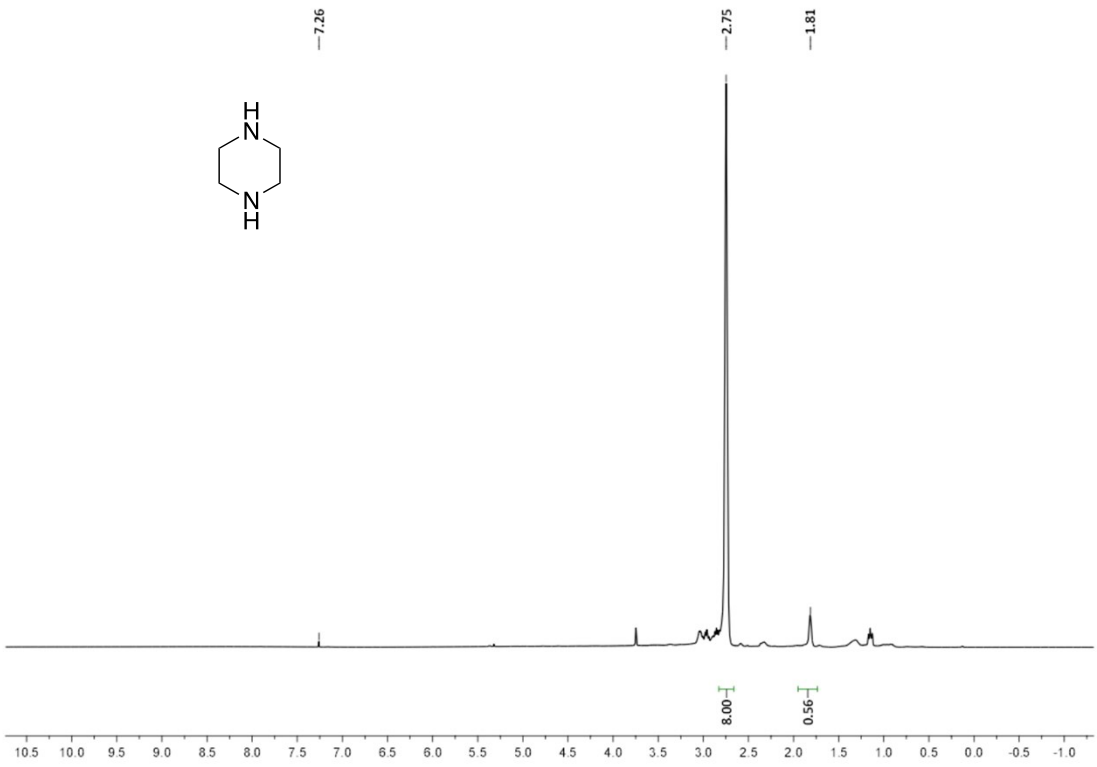
Reaction mixture ^{1}H NMR spectrum of 6-methyldecahydroquinoline:



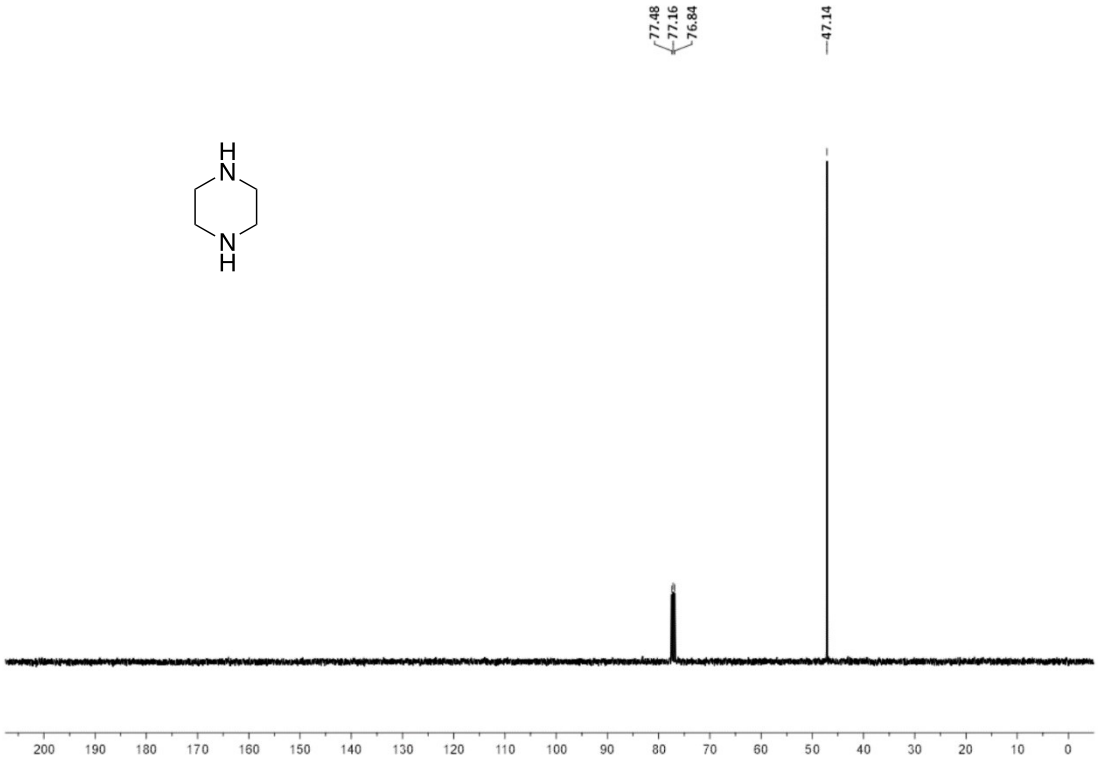
Reaction mixture ^{1}H NMR spectrum of 6-methoxydecahydroquinoline:



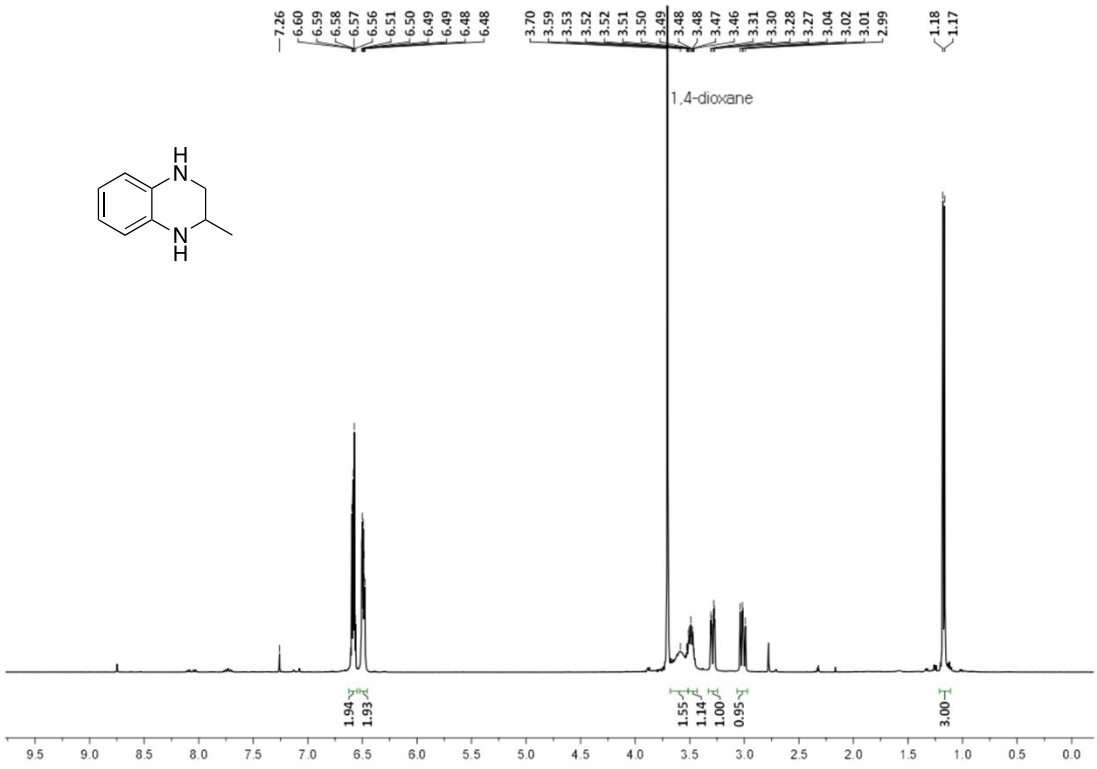
^{1}H NMR spectrum of piperazine:



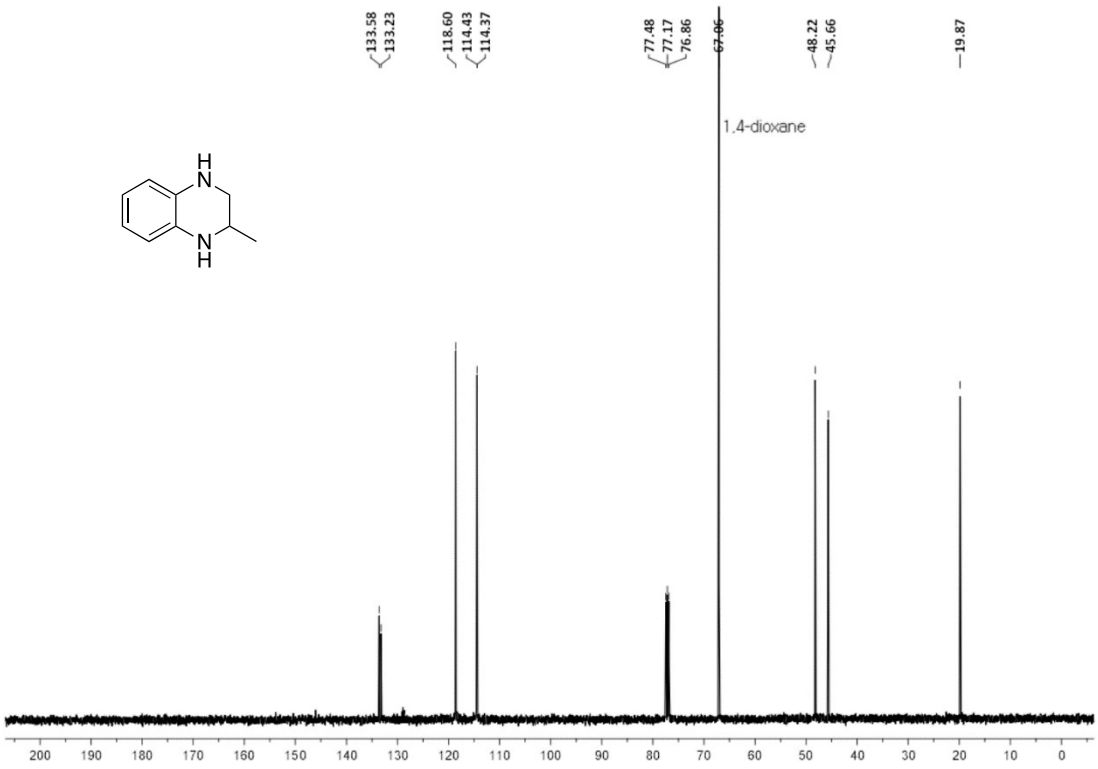
^{13}C NMR spectrum of piperazine:



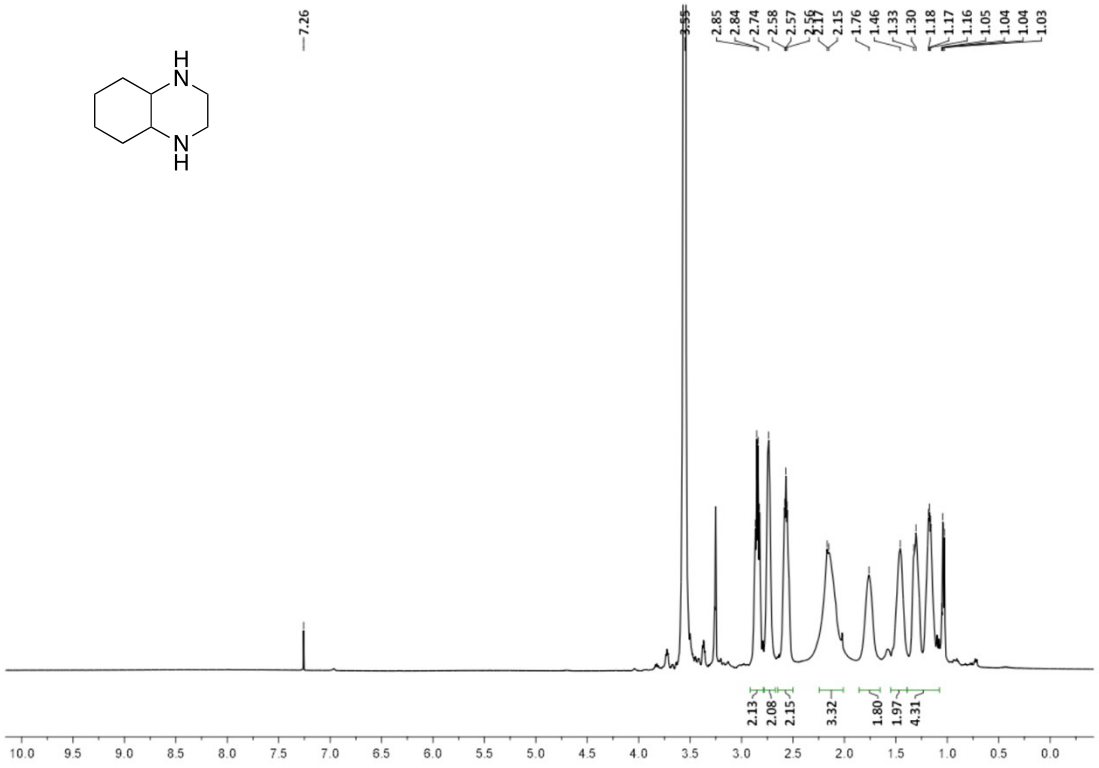
^{1}H NMR spectrum of 2-methyl-1,2,3,4-tetrahydroquinoxaline:



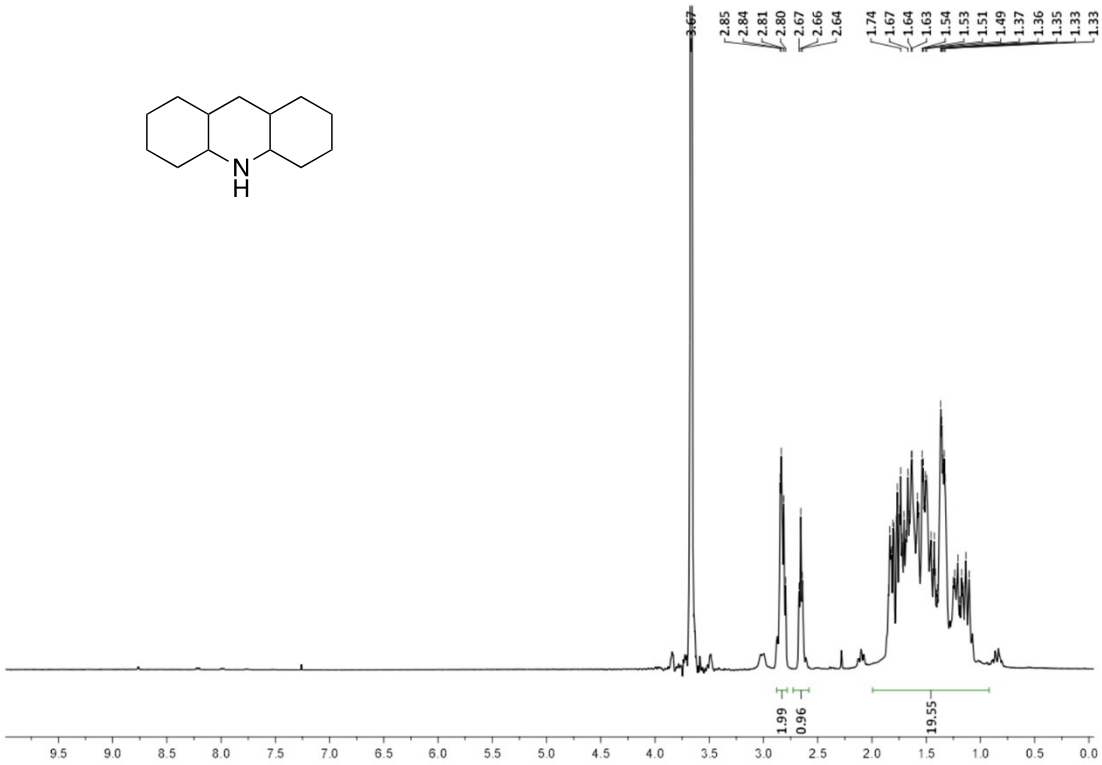
^{13}C NMR spectrum of 2-methyl-1,2,3,4-tetrahydroquinoxaline:



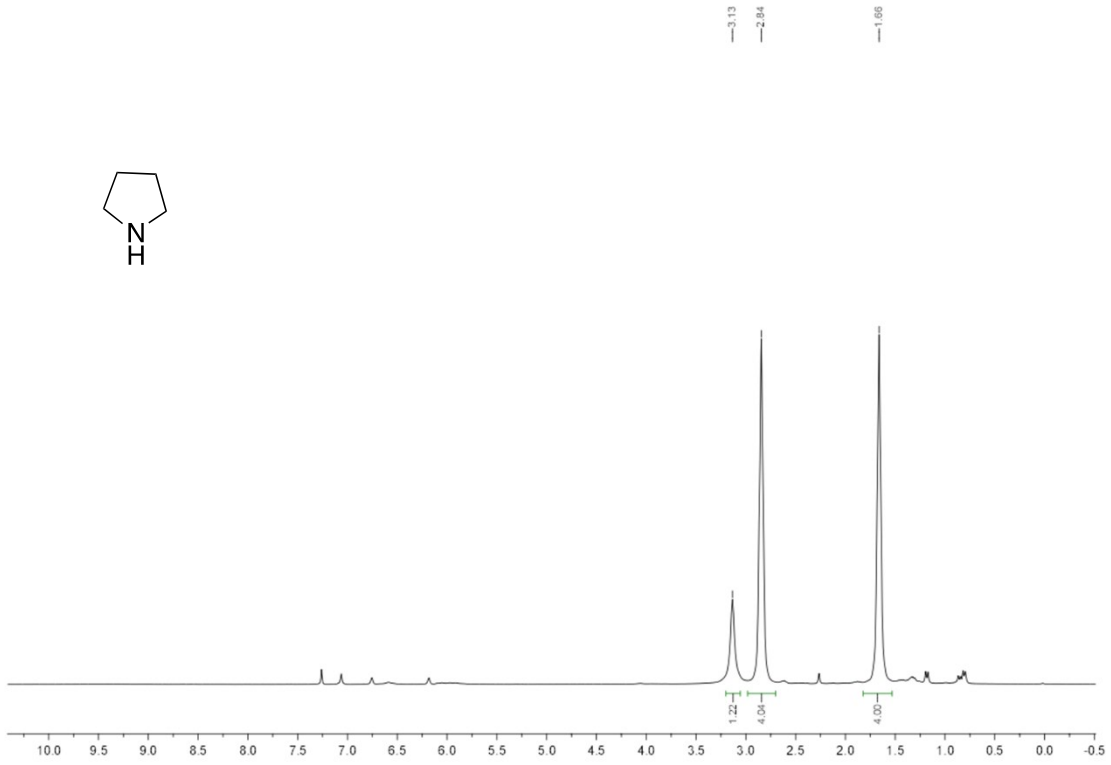
Reaction mixture ^{1}H NMR spectrum of quinoxaline:



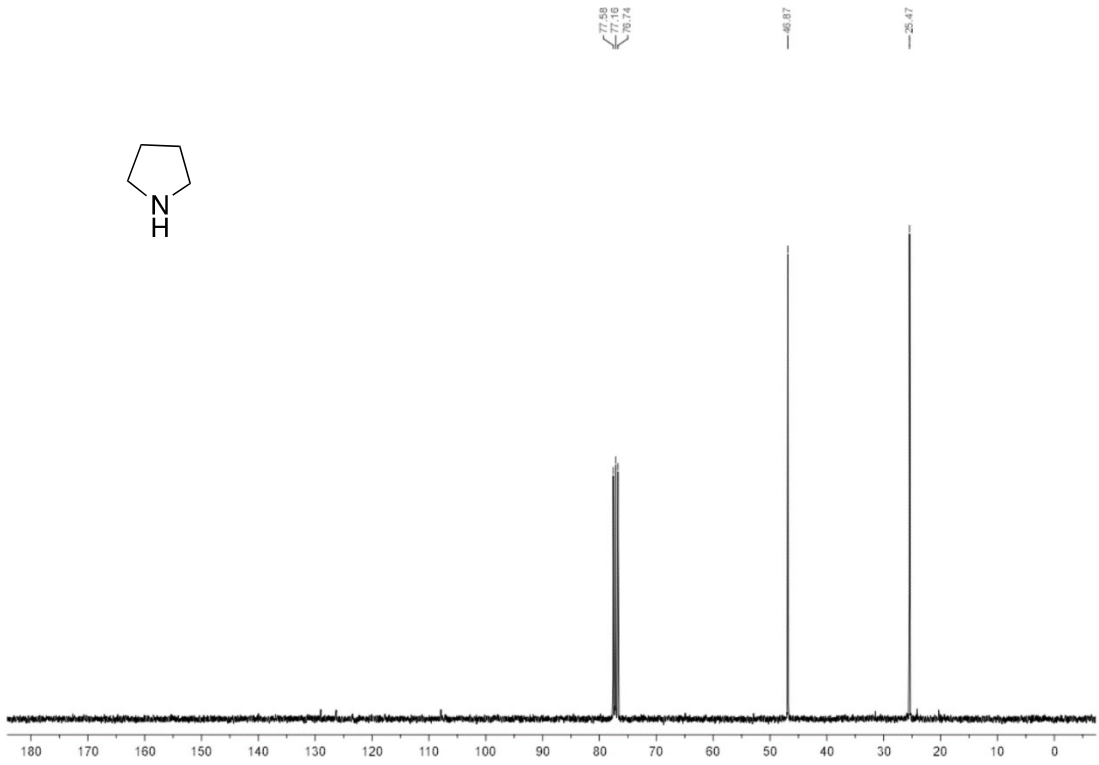
Reaction mixture ^{1}H NMR spectrum for hydrogenation of acridine:



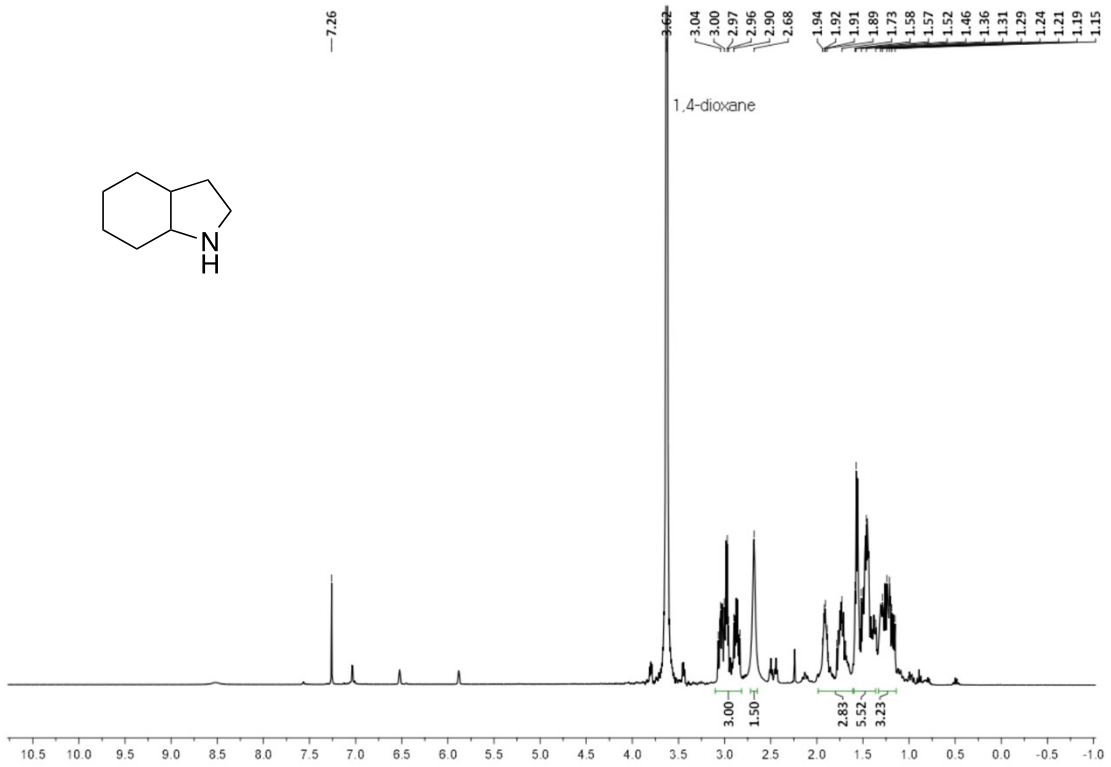
^{1}H NMR spectrum for piperidine:



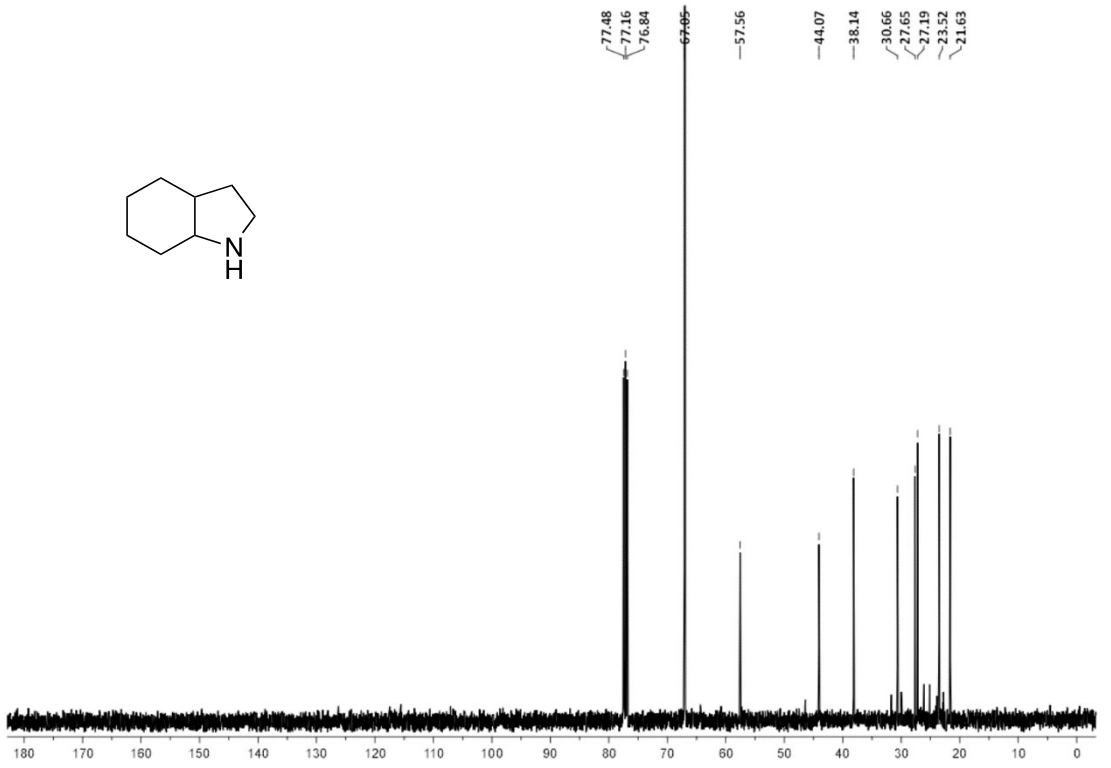
^{13}C NMR spectrum for piperidine:



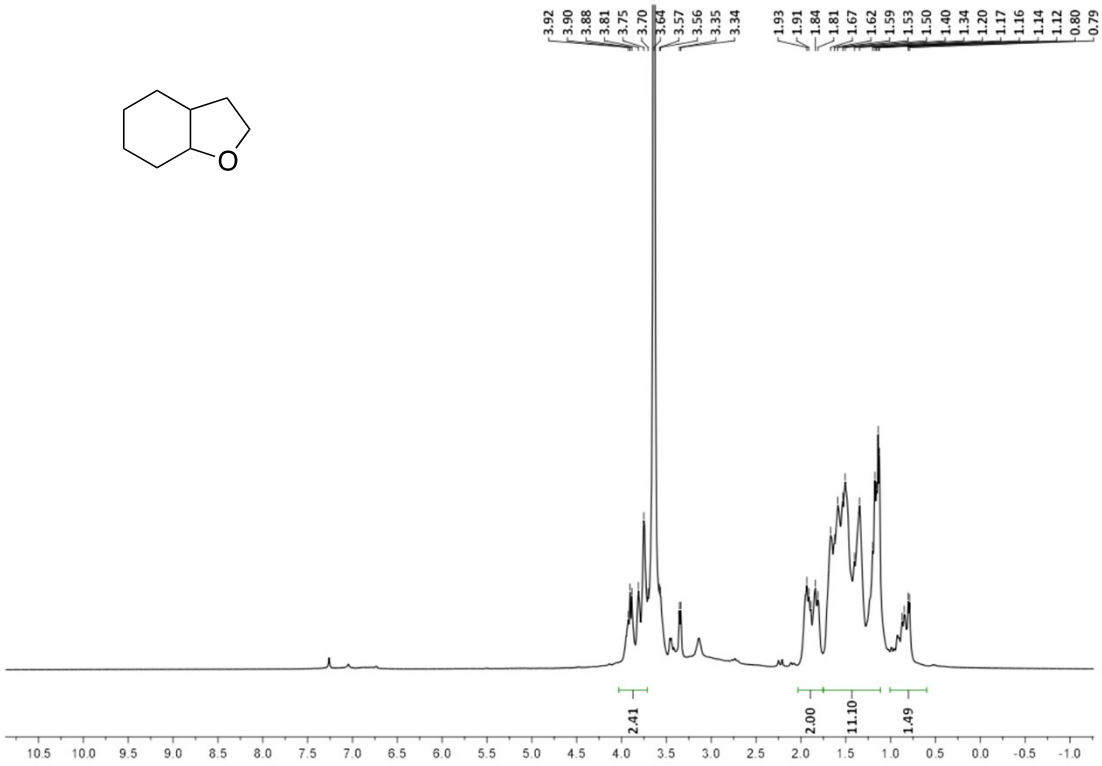
Reaction mixture ^{1}H NMR spectrum of octahydro-1*H*-indole:



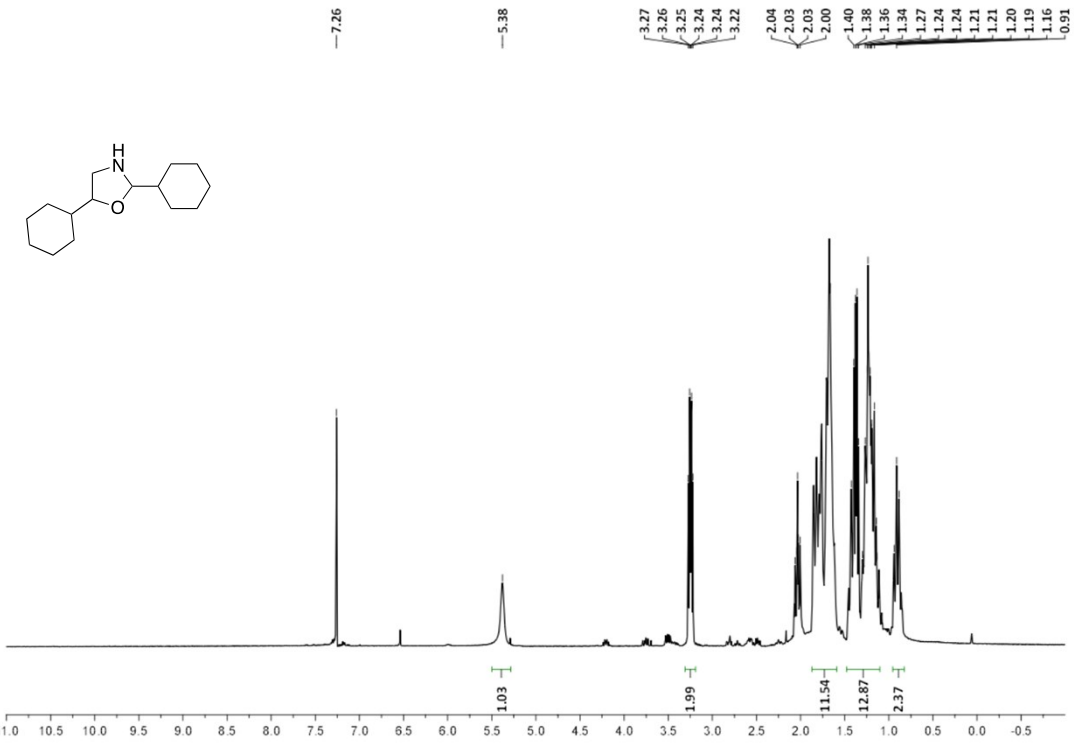
Reaction mixture ^{13}C NMR spectrum of octahydro-1*H*-indole:



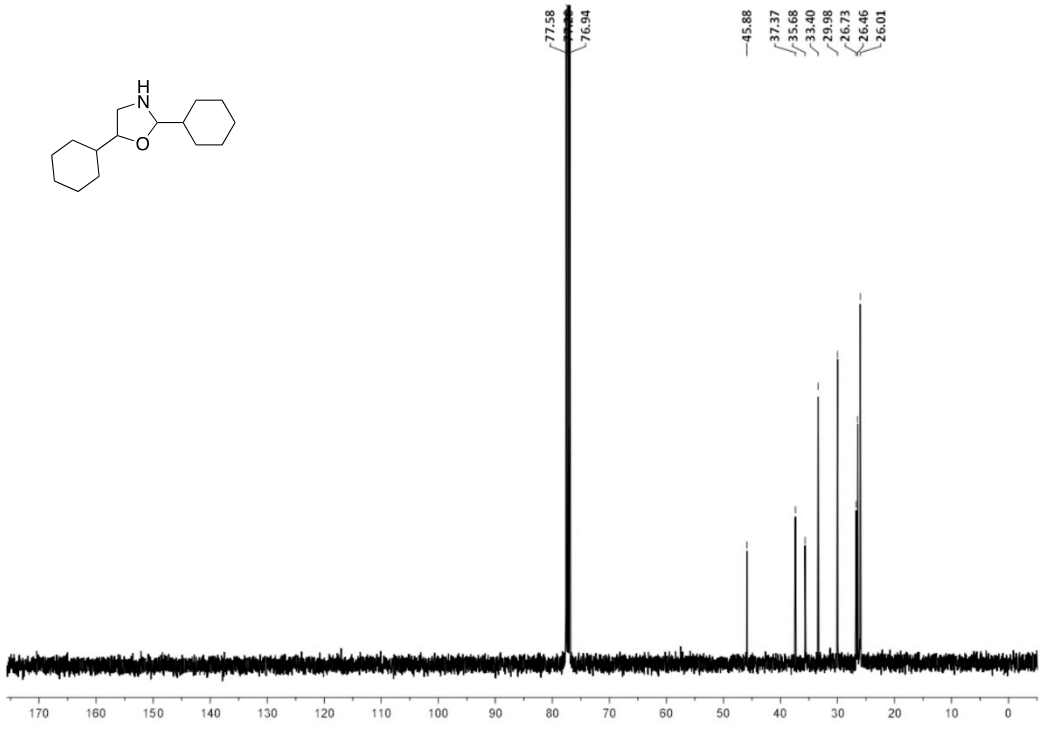
Reaction mixture ^{1}H NMR spectrum of octahydrobenzofuran:



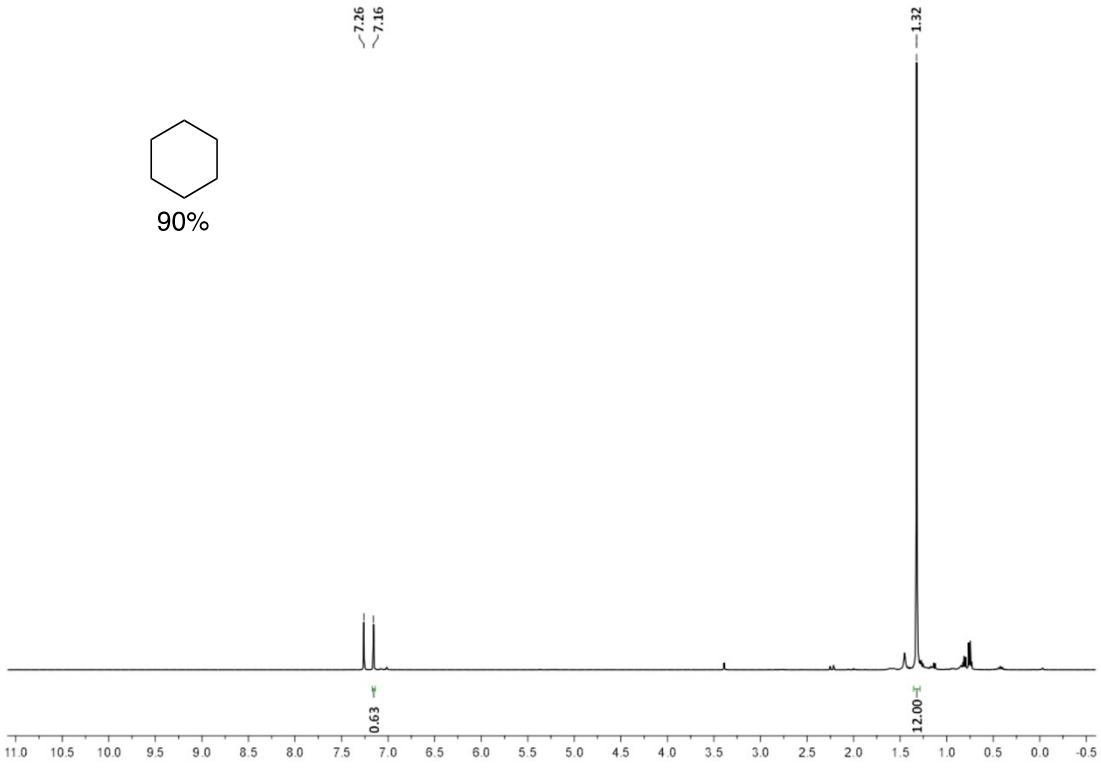
^{1}H NMR spectrum for hydrogenation of 2,5-dicyclohexyloxazolidine:



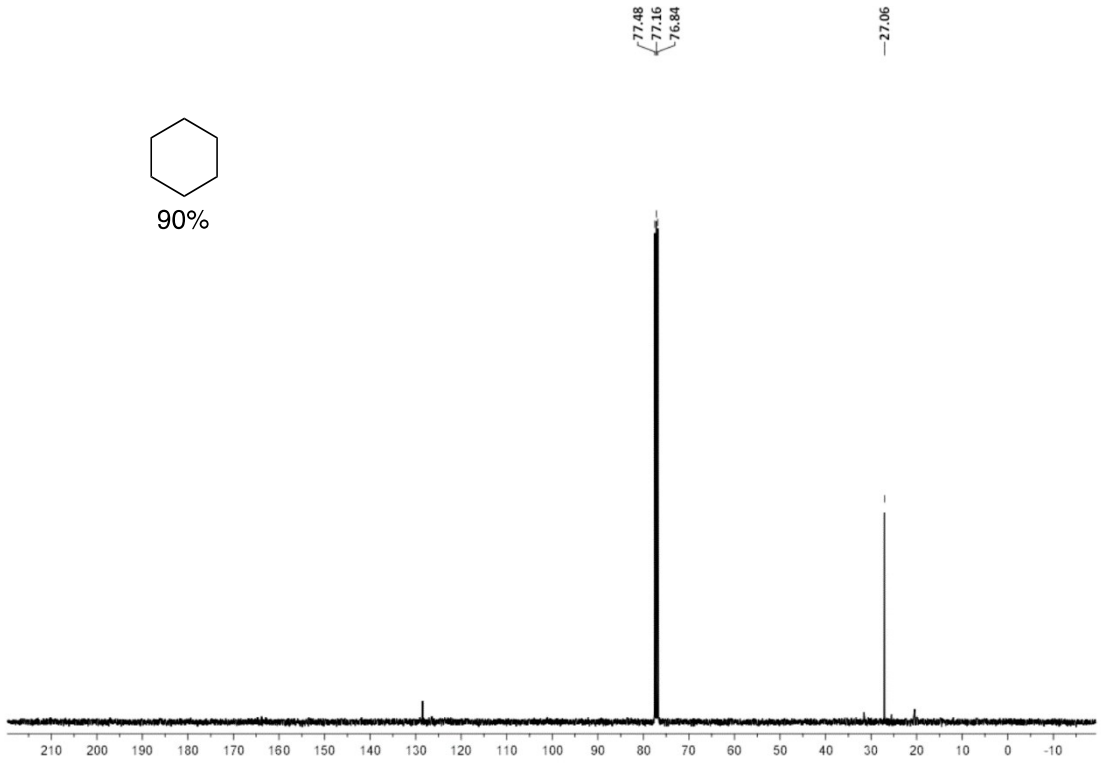
^{13}C NMR spectrum for hydrogenation of 2,5-dicyclohexyloxazolidine:



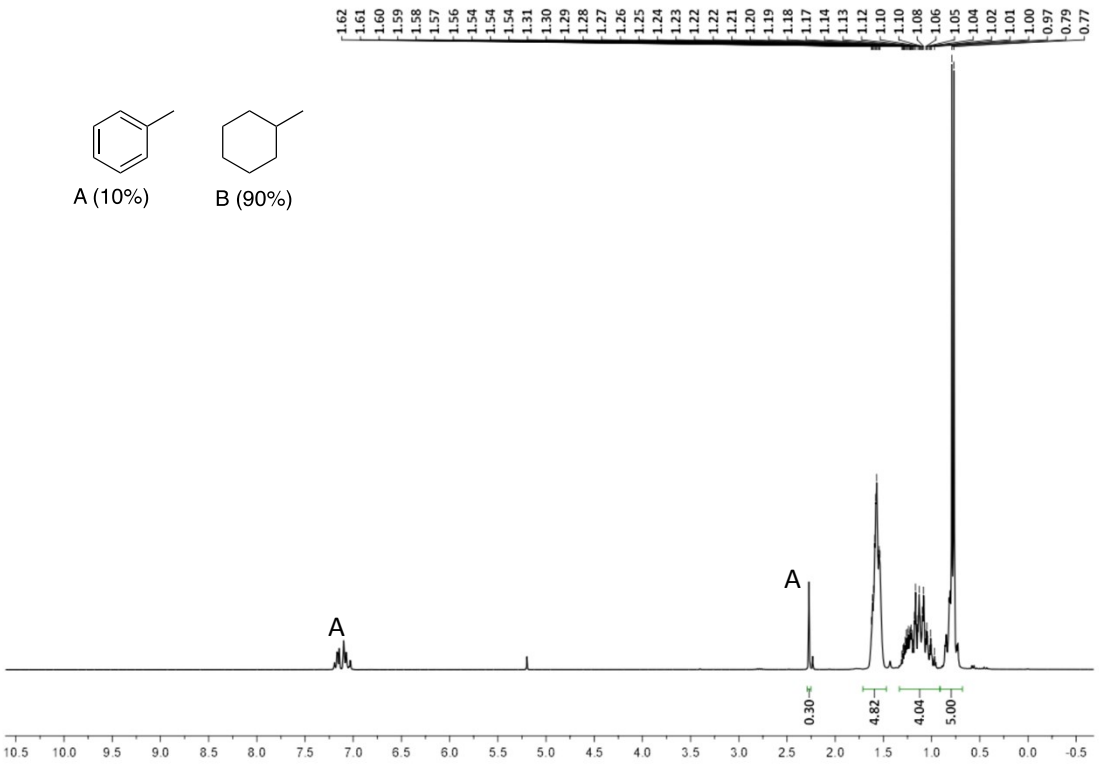
Reaction mixture ^{1}H NMR spectrum of hydrogenation of benzene:



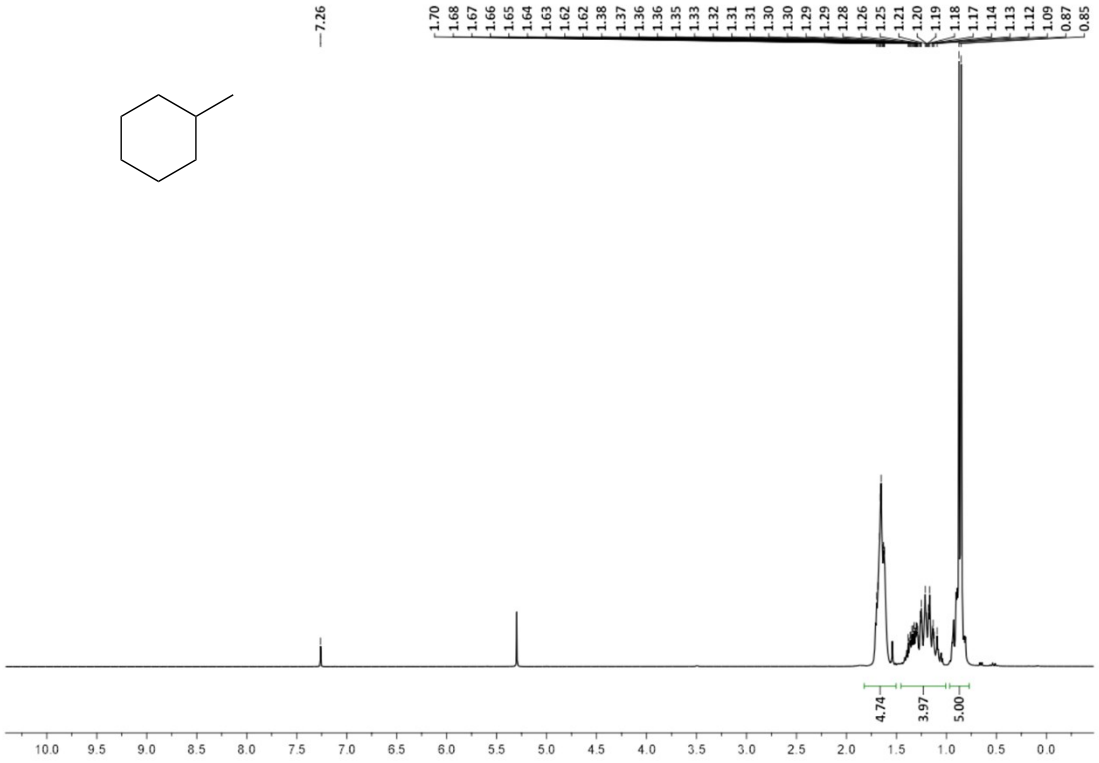
Reaction mixture ^{13}C NMR spectrum of hydrogenation of benzene:



Reaction mixture ^{1}H NMR spectrum of hydrogenation of toluene:

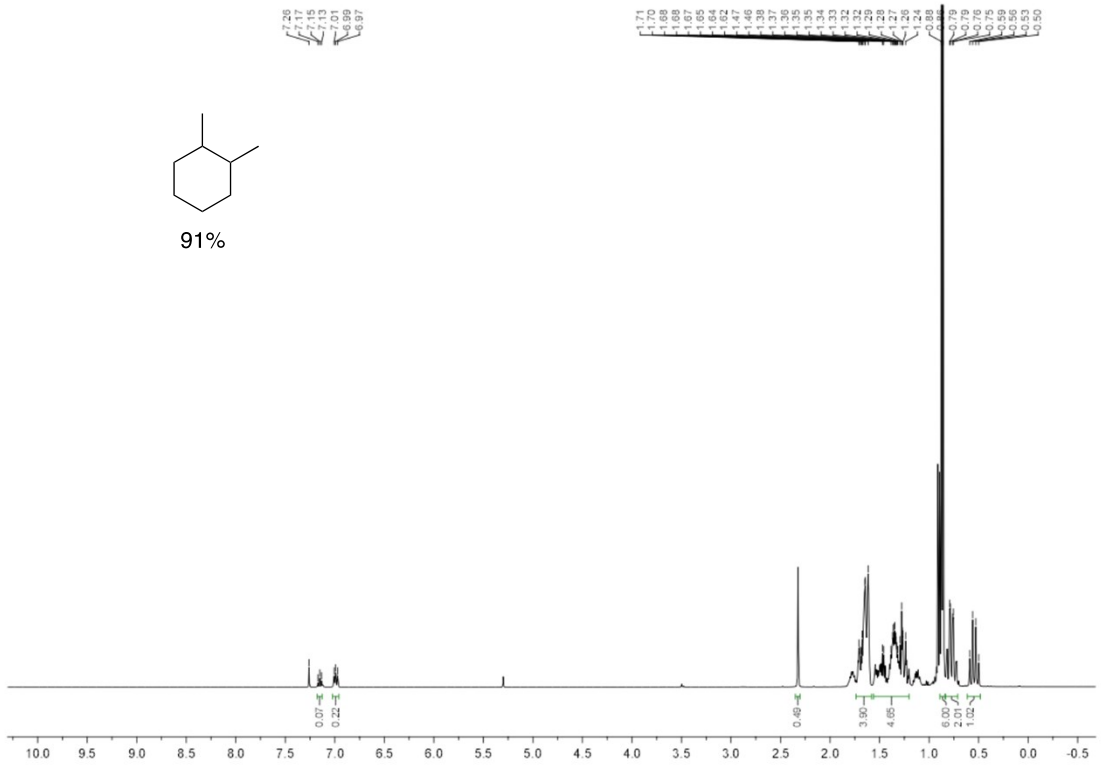


Reaction mixture ^{1}H NMR spectrum of hydrogenation of toluene:

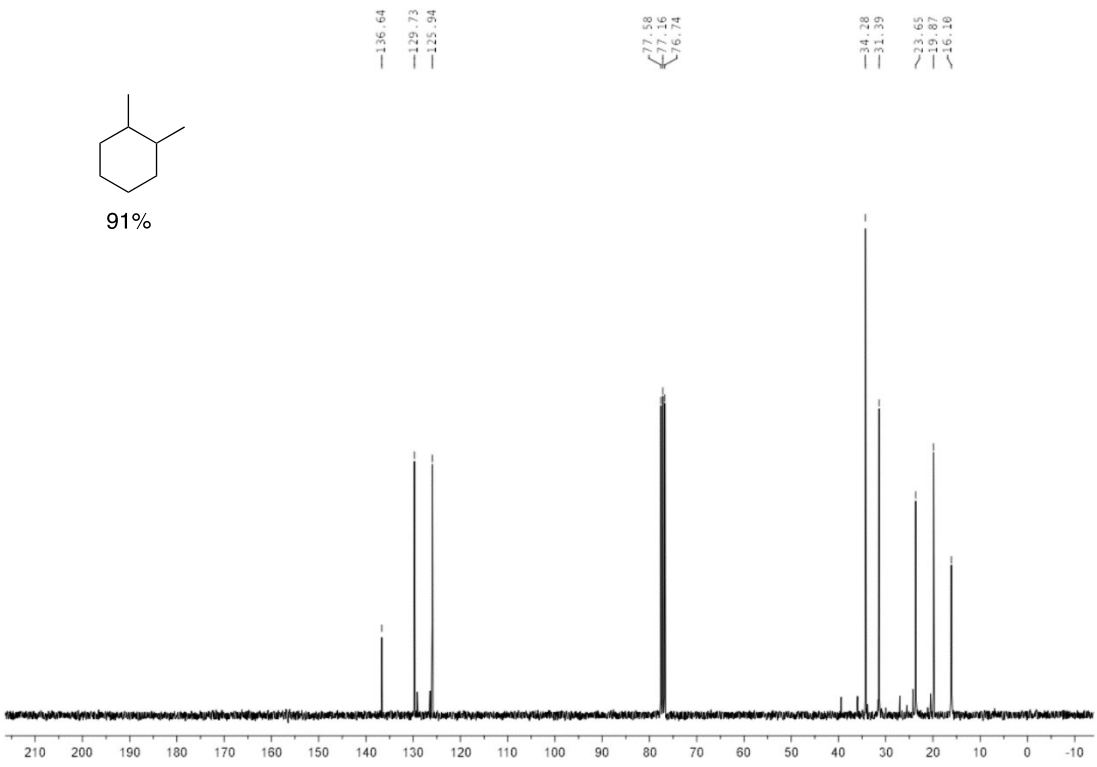


Reaction mixture ^{13}C NMR spectrum of hydrogenation of toluene:

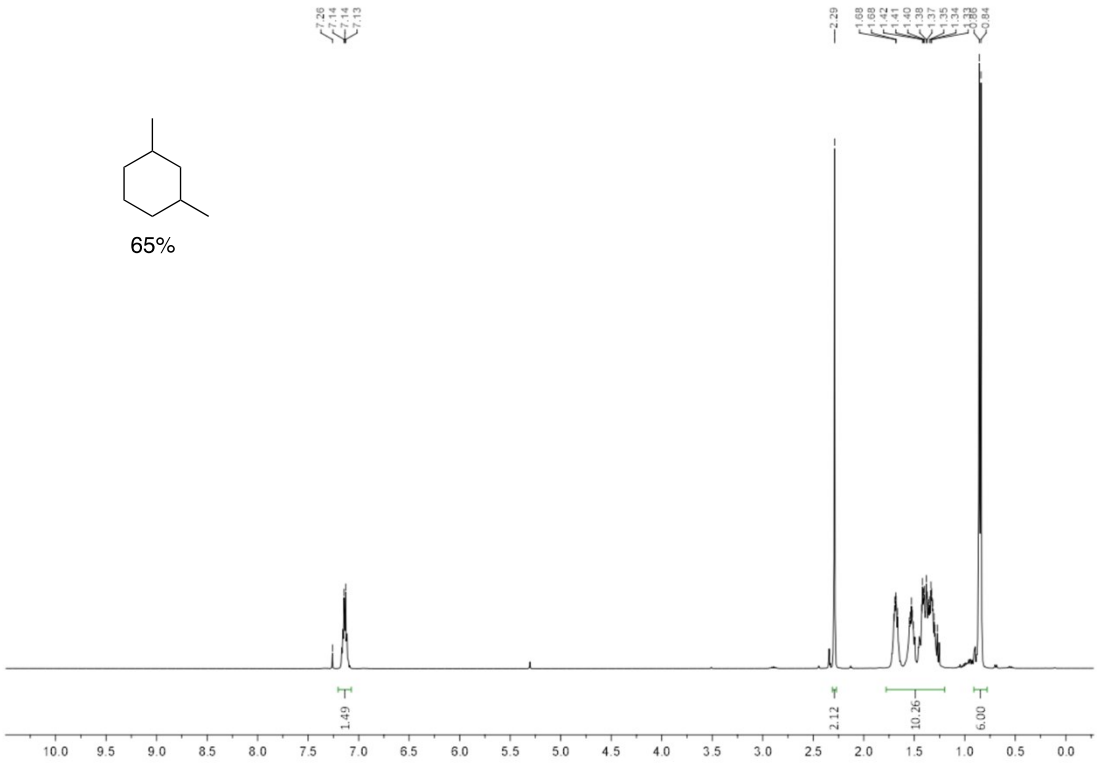
Reaction mixture ^{1}H NMR spectrum of hydrogenation of *o*-xylene:



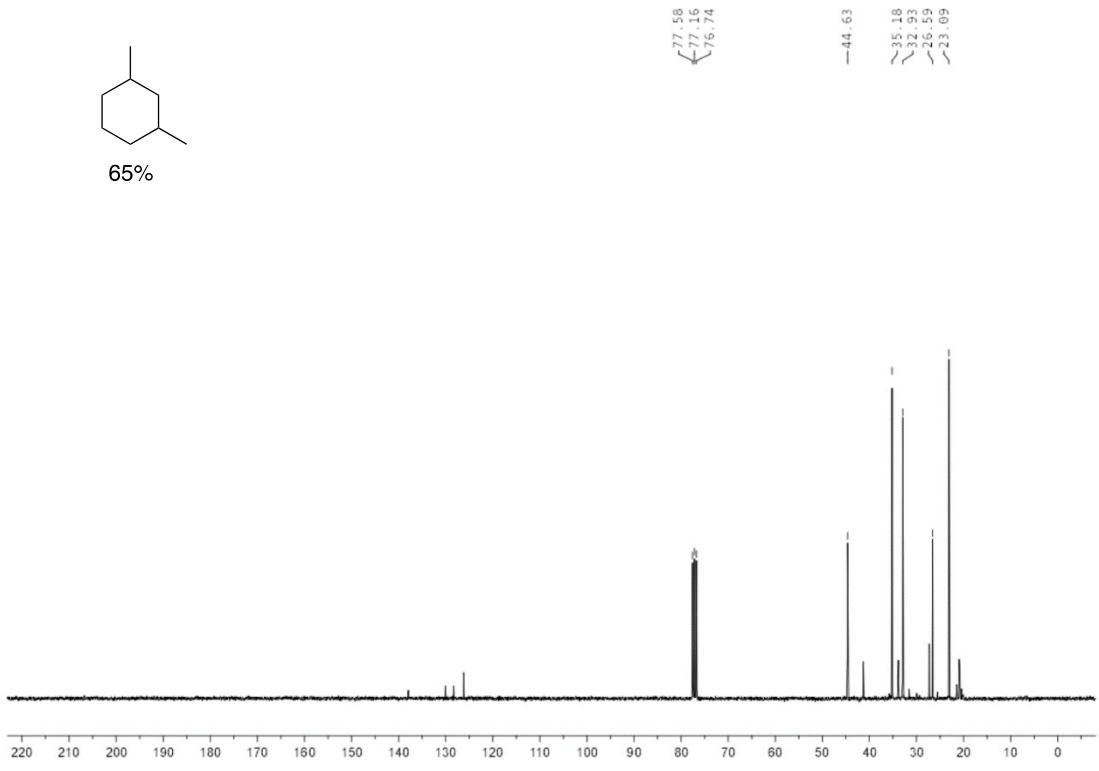
Reaction mixture ^{13}C NMR spectrum of hydrogenation of *o*-xylene:



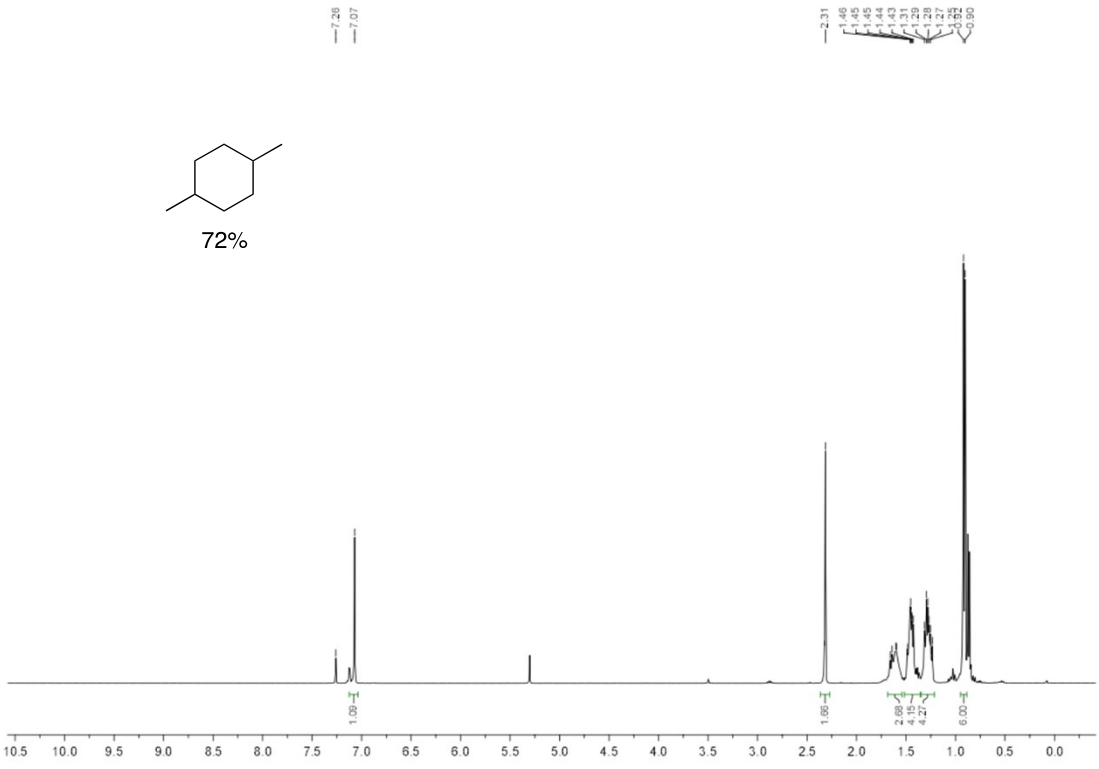
Reaction mixture ^{1}H NMR spectrum of hydrogenation of *m*-xylene:



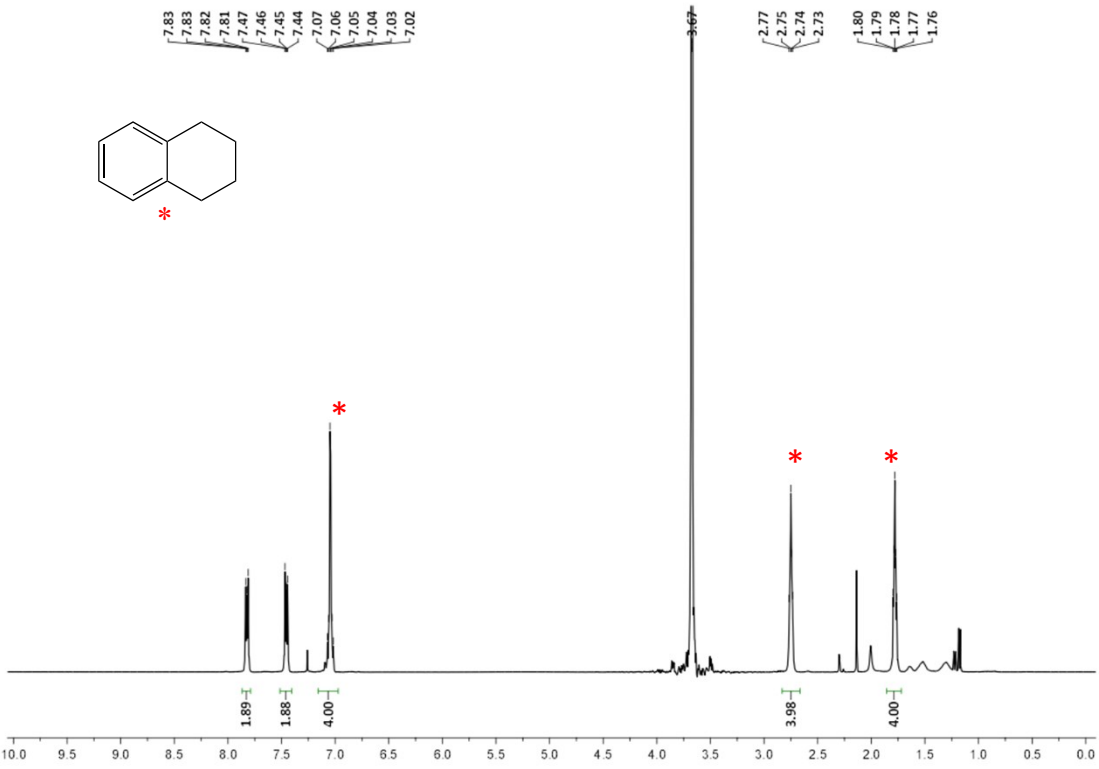
Reaction mixture ^{13}C NMR spectrum of hydrogenation of *m*-xylene:



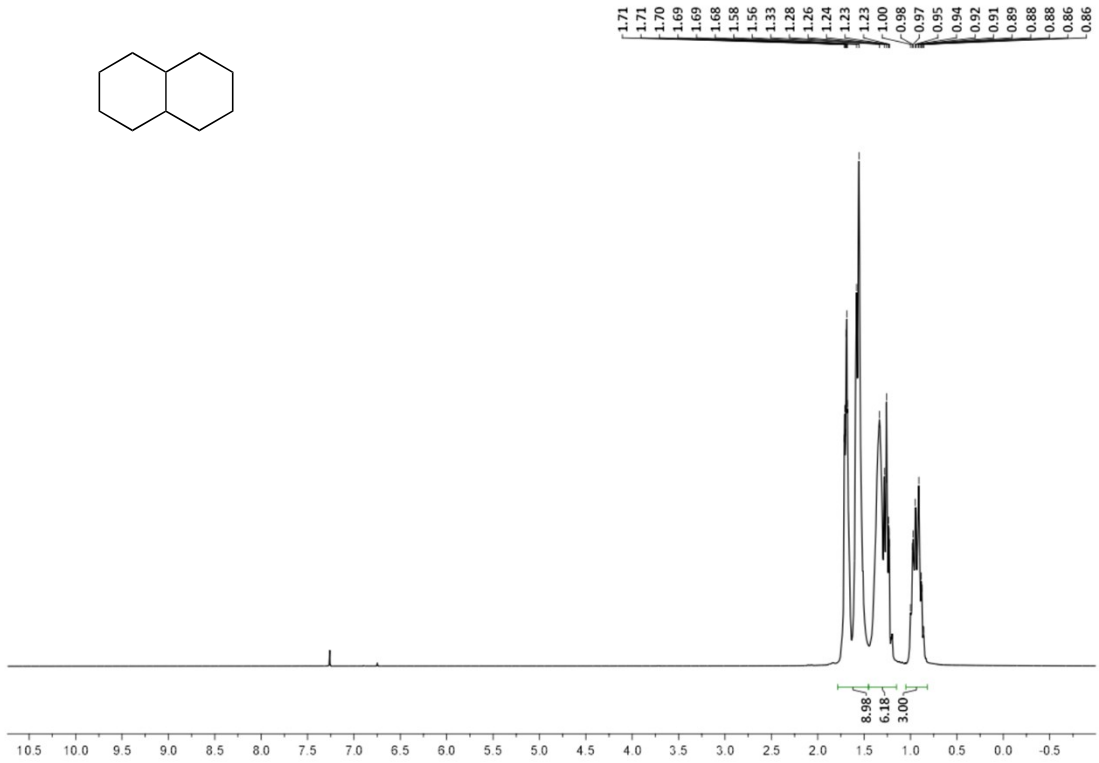
Reaction mixture ^{1}H NMR spectrum of hydrogenation of *p*-xylene:



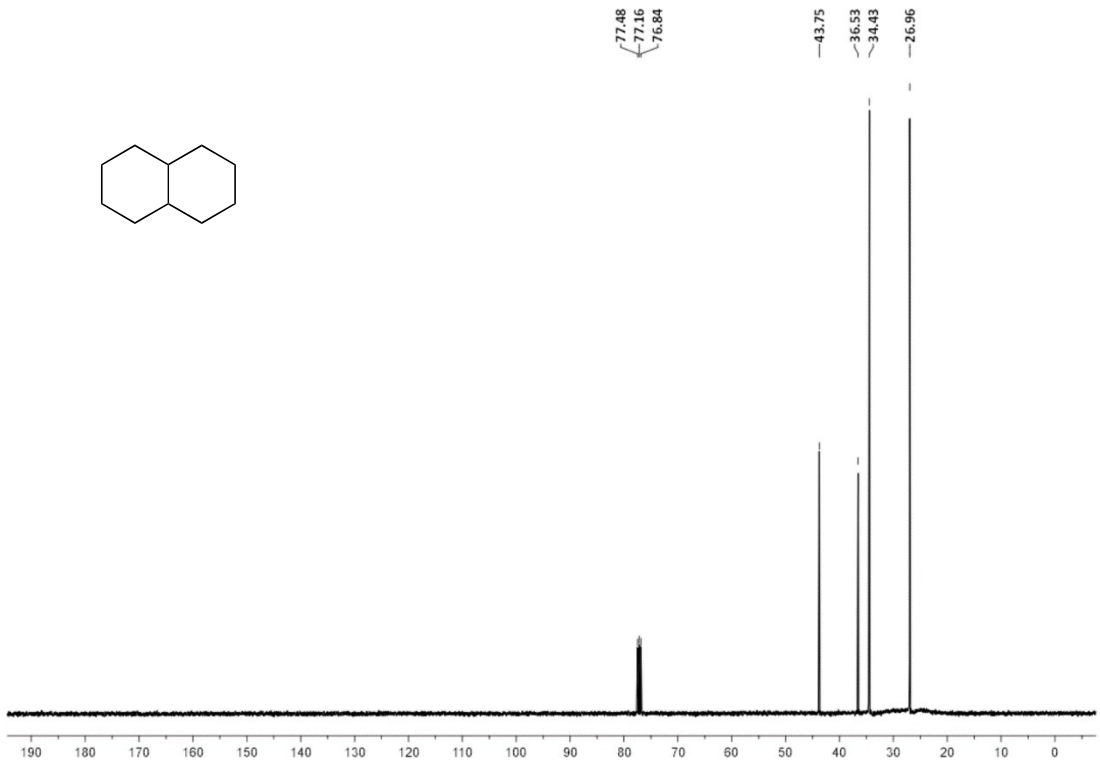
Reaction mixture ^{1}H NMR spectrum for hydrogenation of naphthalene:



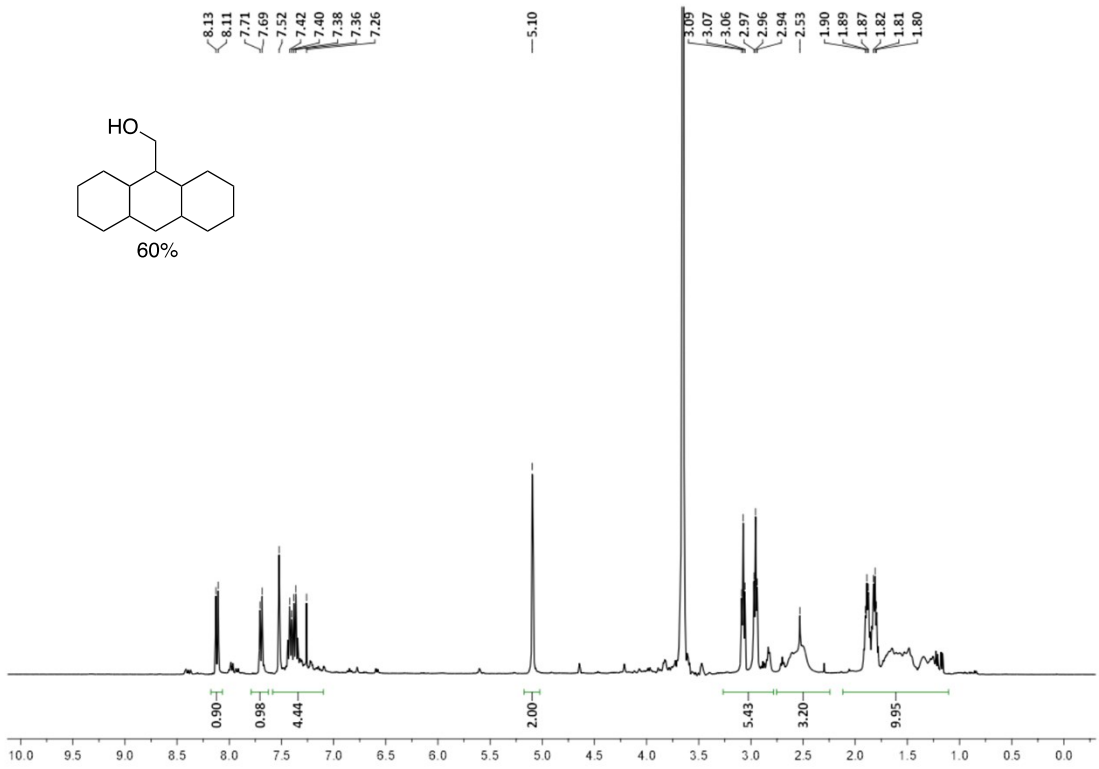
^{1}H NMR spectrum of decahydronaphthalene:



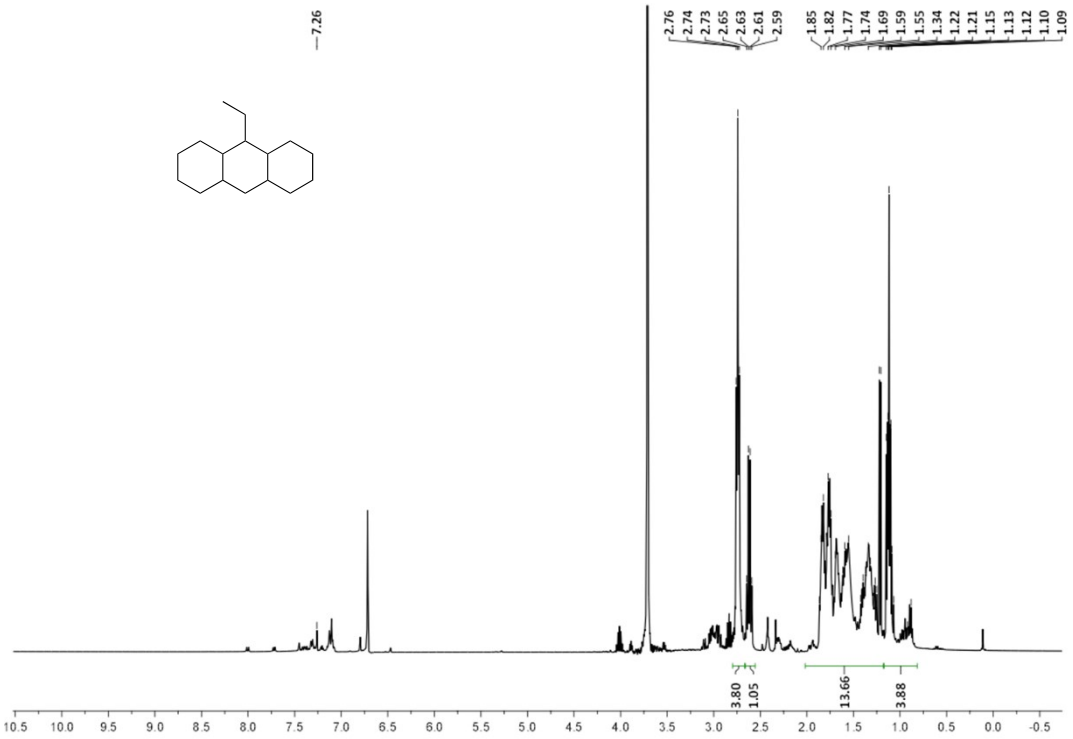
^{13}C NMR spectrum of decahydronaphthalene:



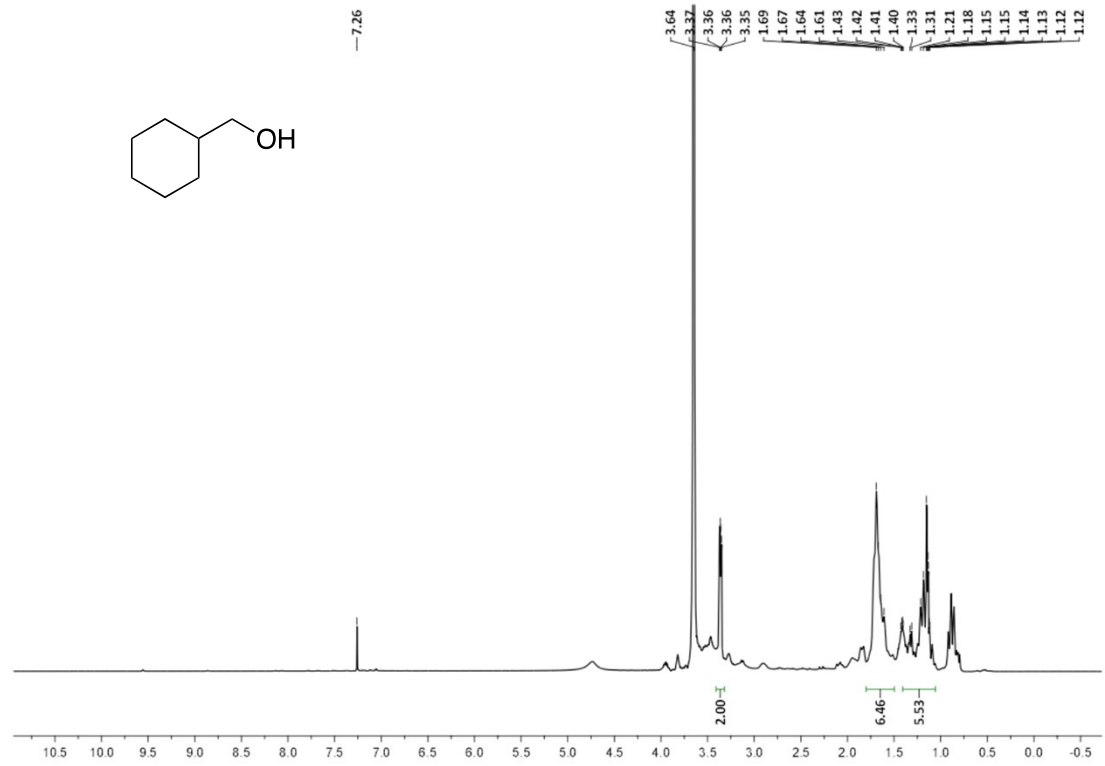
Reaction mixture ^{1}H NMR spectrum for hydrogenation of 9-anthracenecarboxaldehyde:



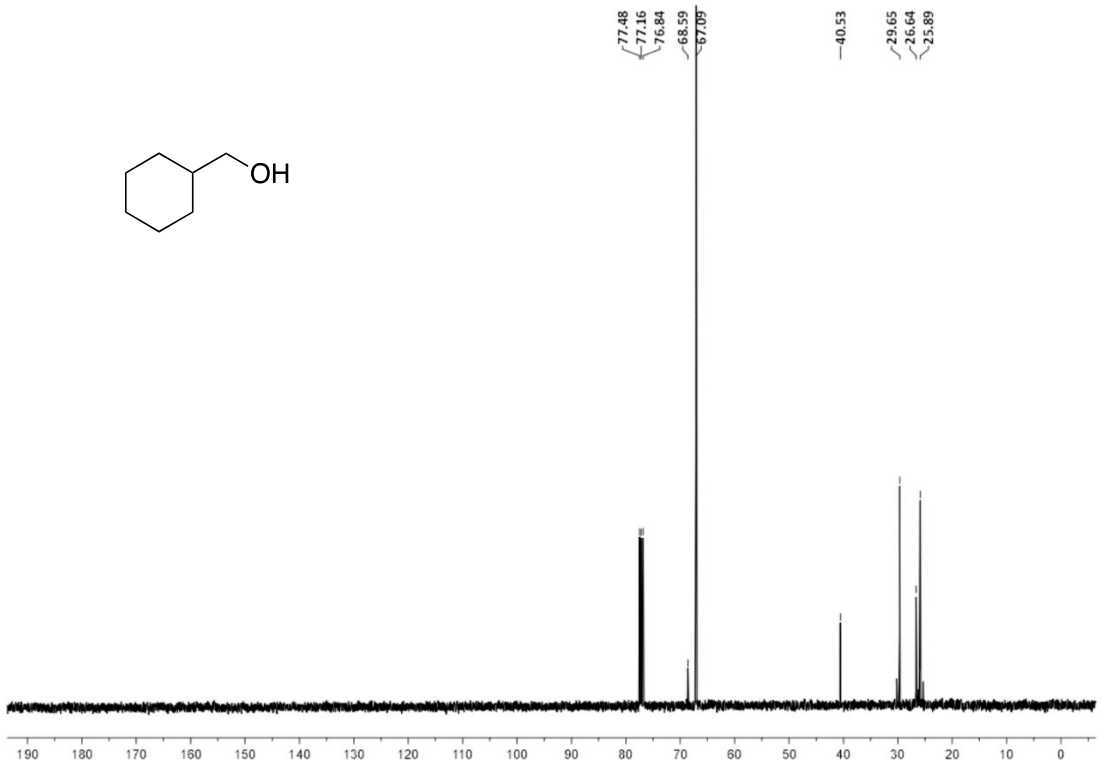
Reaction mixture ^{1}H NMR spectrum for hydrogenation of 9-vinylanthracene:



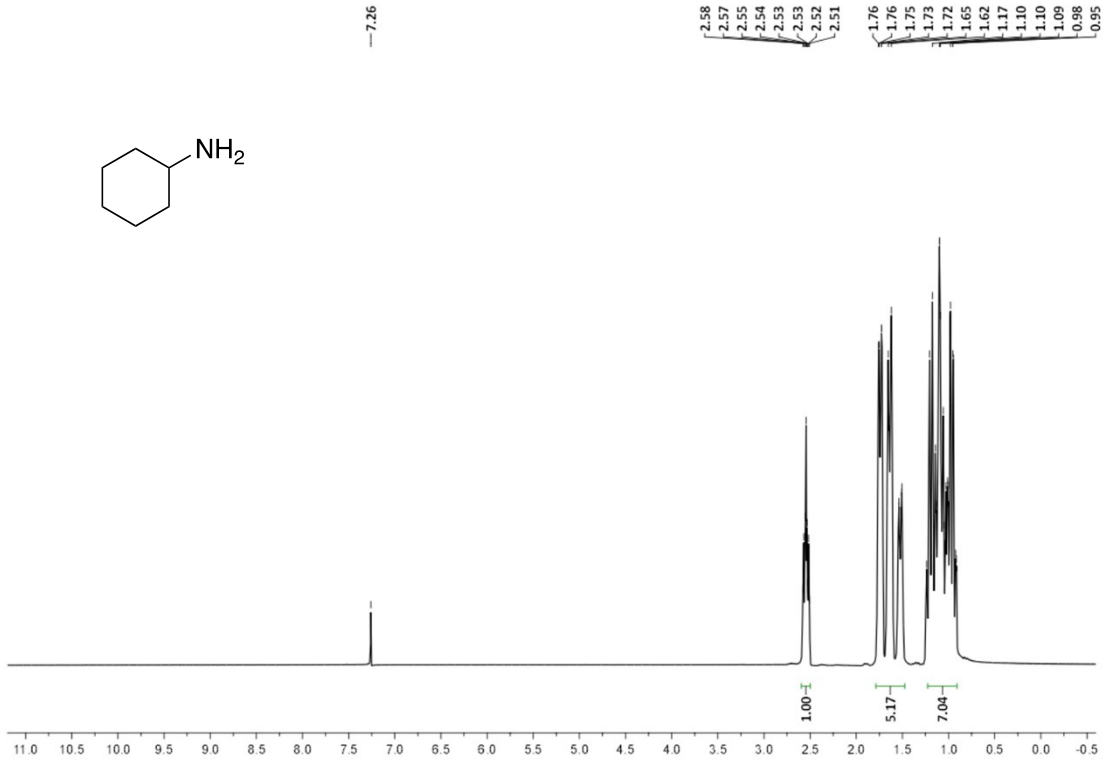
Reaction mixture ^{1}H NMR spectrum for hydrogenation of benzylalcohol:



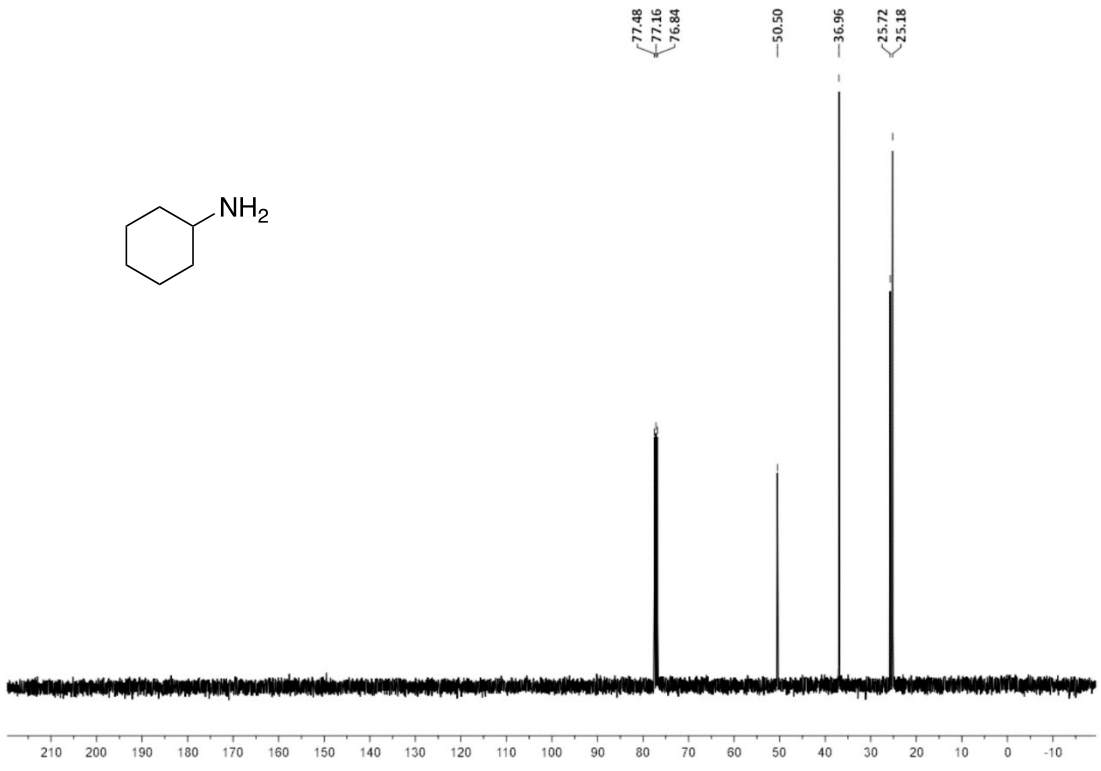
Reaction mixture ^{13}C NMR spectrum for hydrogenation of benzylalcohol:



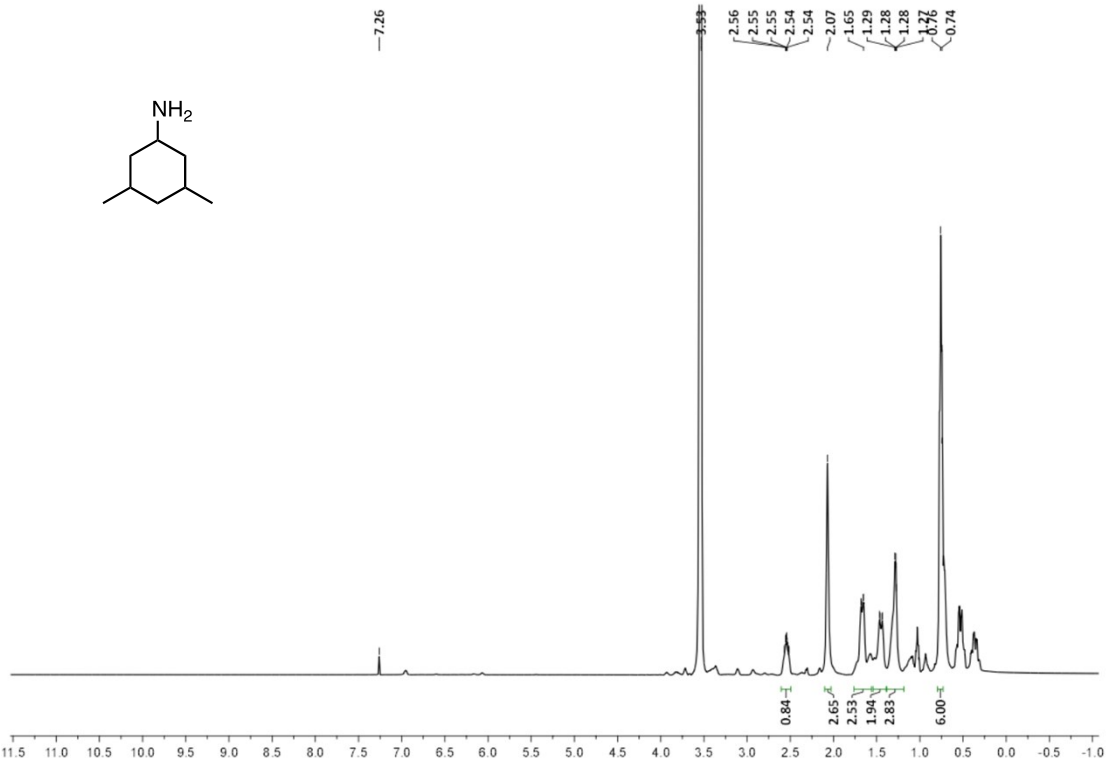
^{1}H NMR spectrum of cylohexylamine:



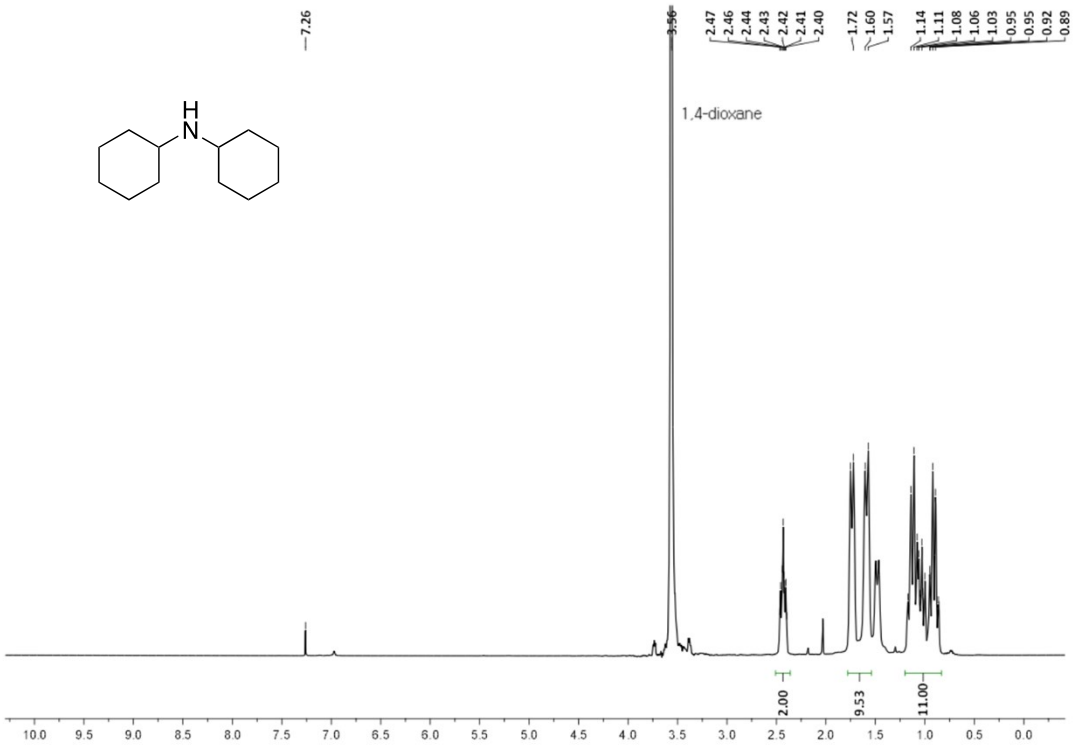
^{13}C NMR spectrum of cylohexylamine:



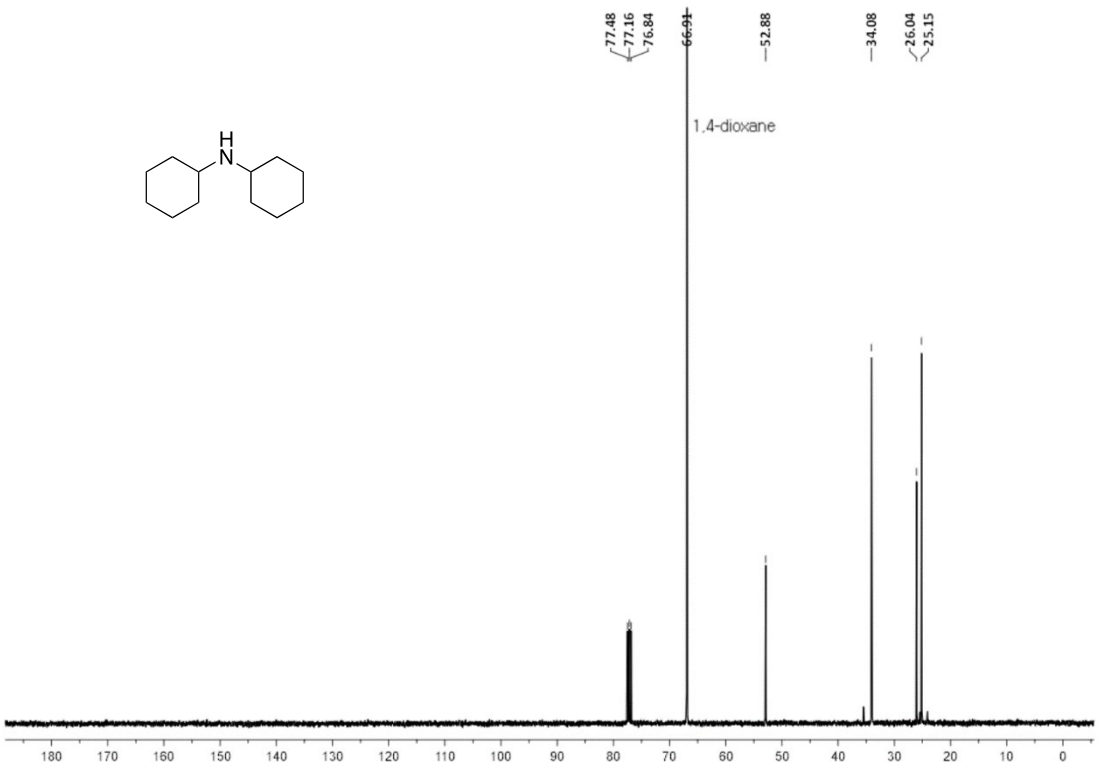
^{1}H NMR spectrum of 3,5-dimethylcyclohexanamine:



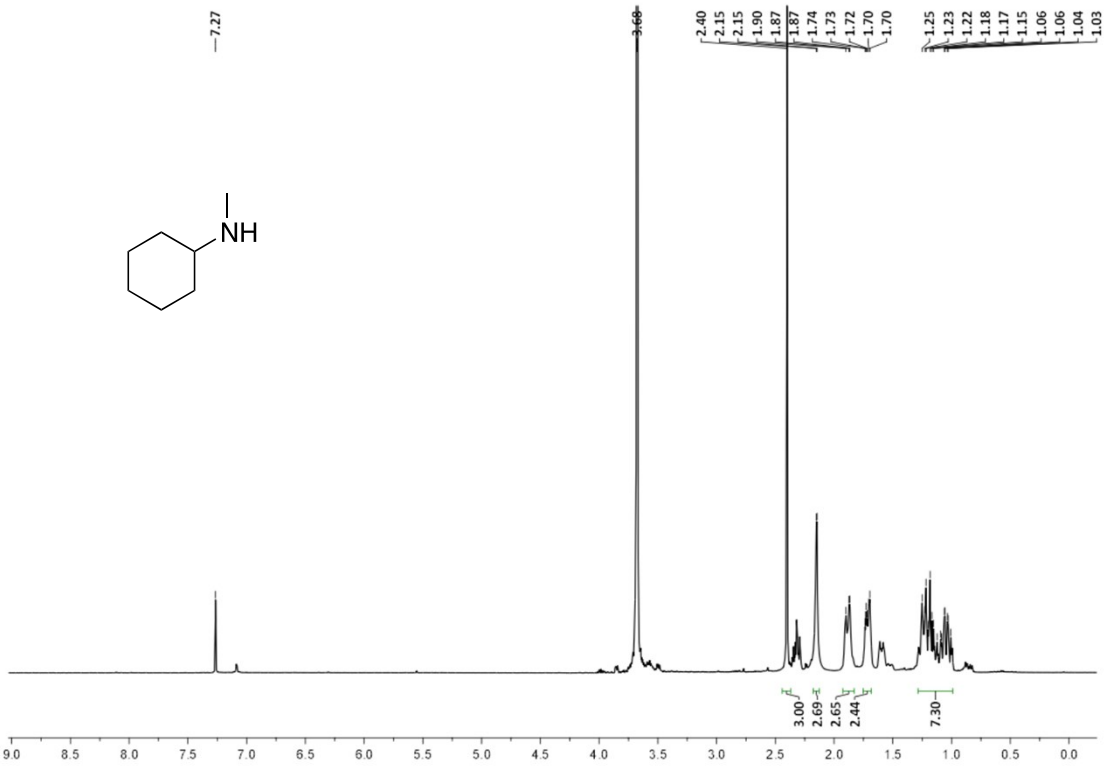
^{1}H NMR spectrum of dicylohexylamine:



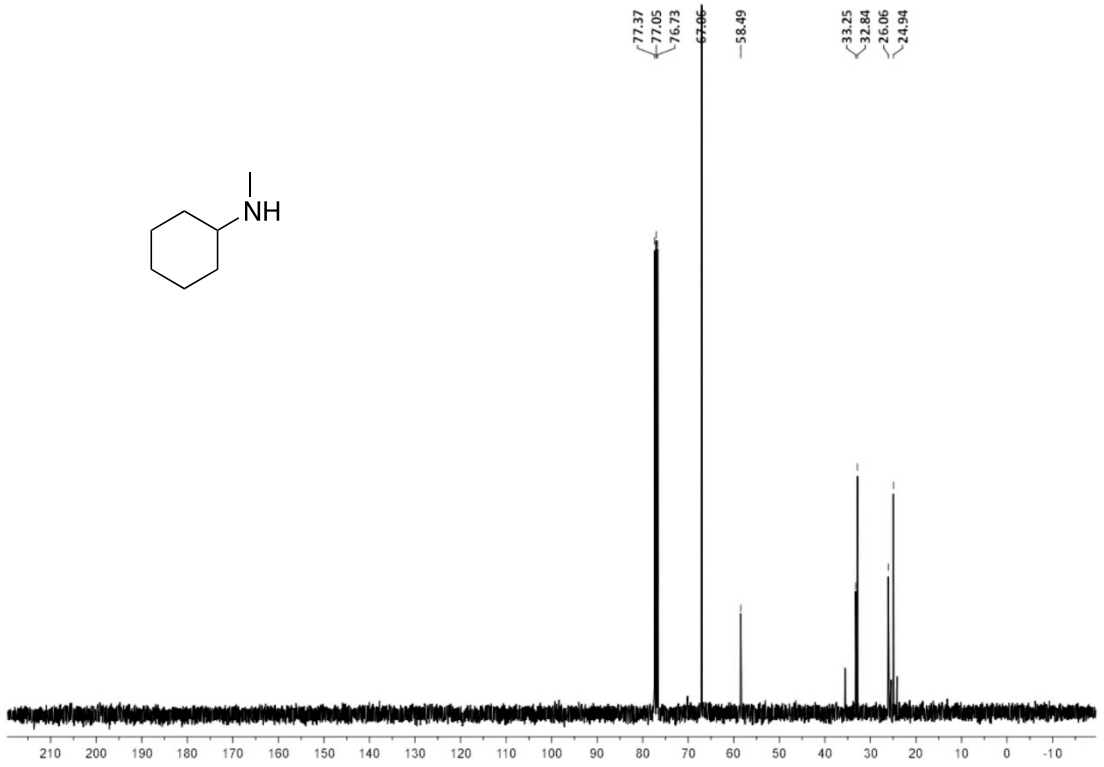
^{13}C NMR spectrum of dicylohexylamine:



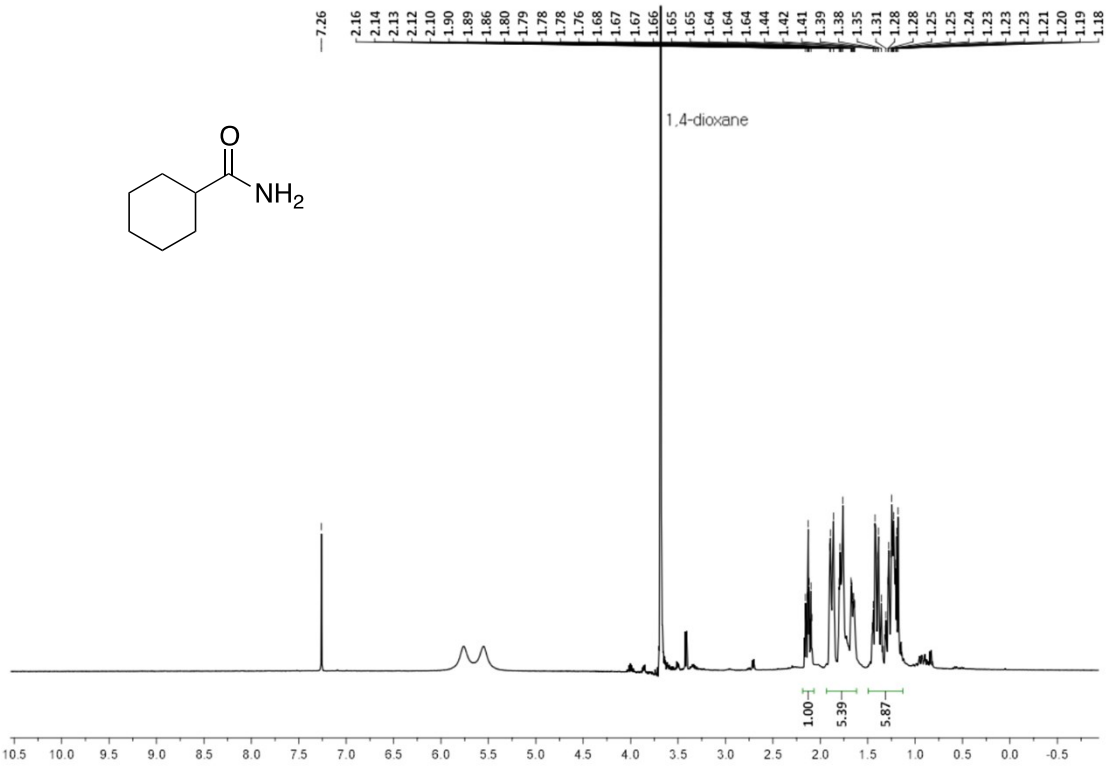
Reaction mixture ^{1}H NMR spectrum for hydrogenation of *N*-methylaniline:



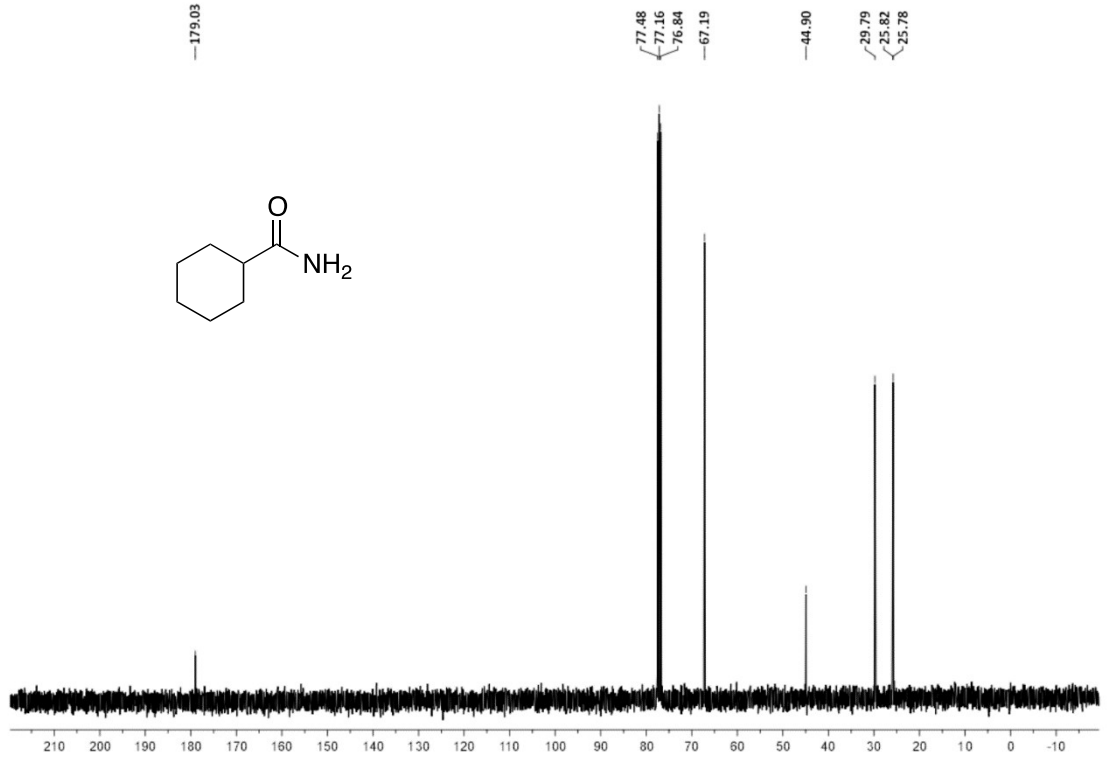
Reaction mixture ^{13}C NMR spectrum for hydrogenation of *N*-methylaniline:



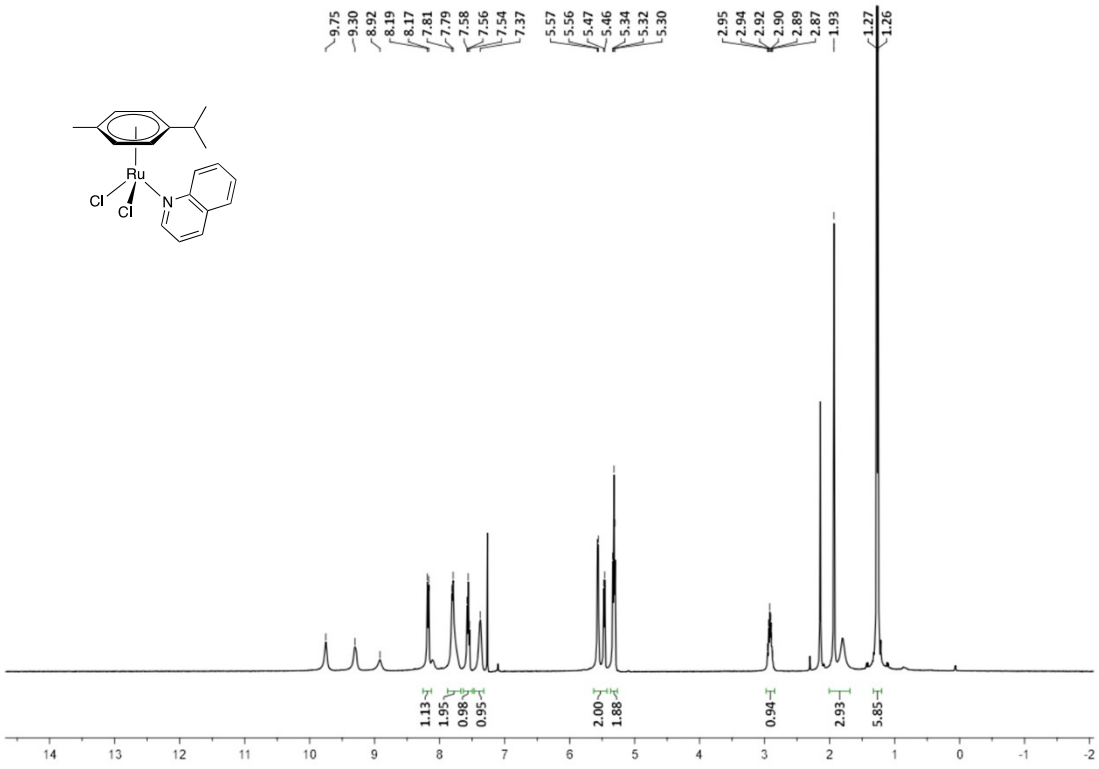
^{1}H NMR spectrum of cyclohexanecarboxamide:



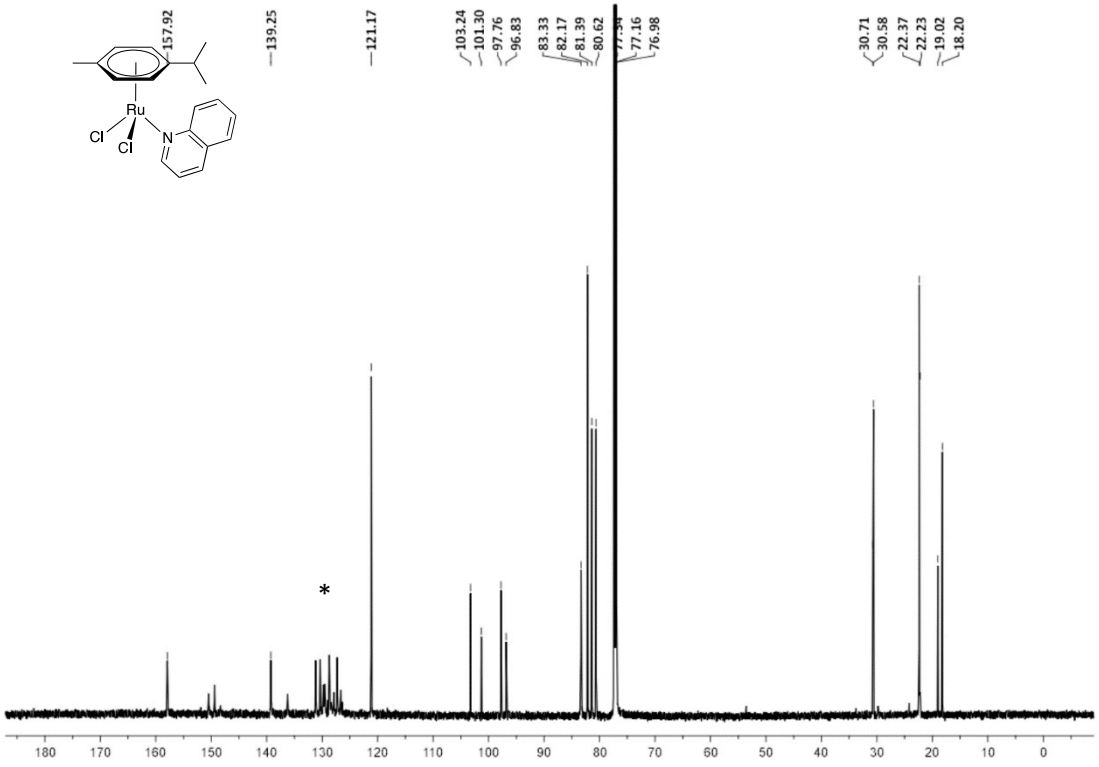
^{13}C NMR spectrum of cyclohexanecarboxamide:



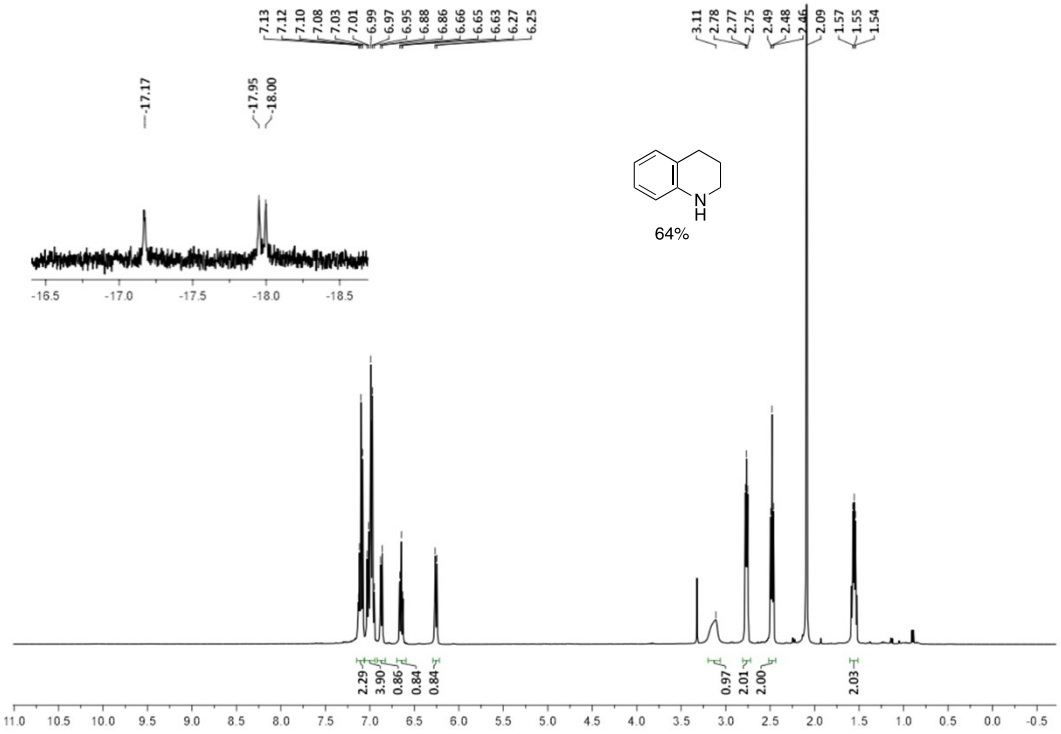
^{1}H NMR spectrum of isolated **2b** from the reaction mixture of **1** and quinoline:



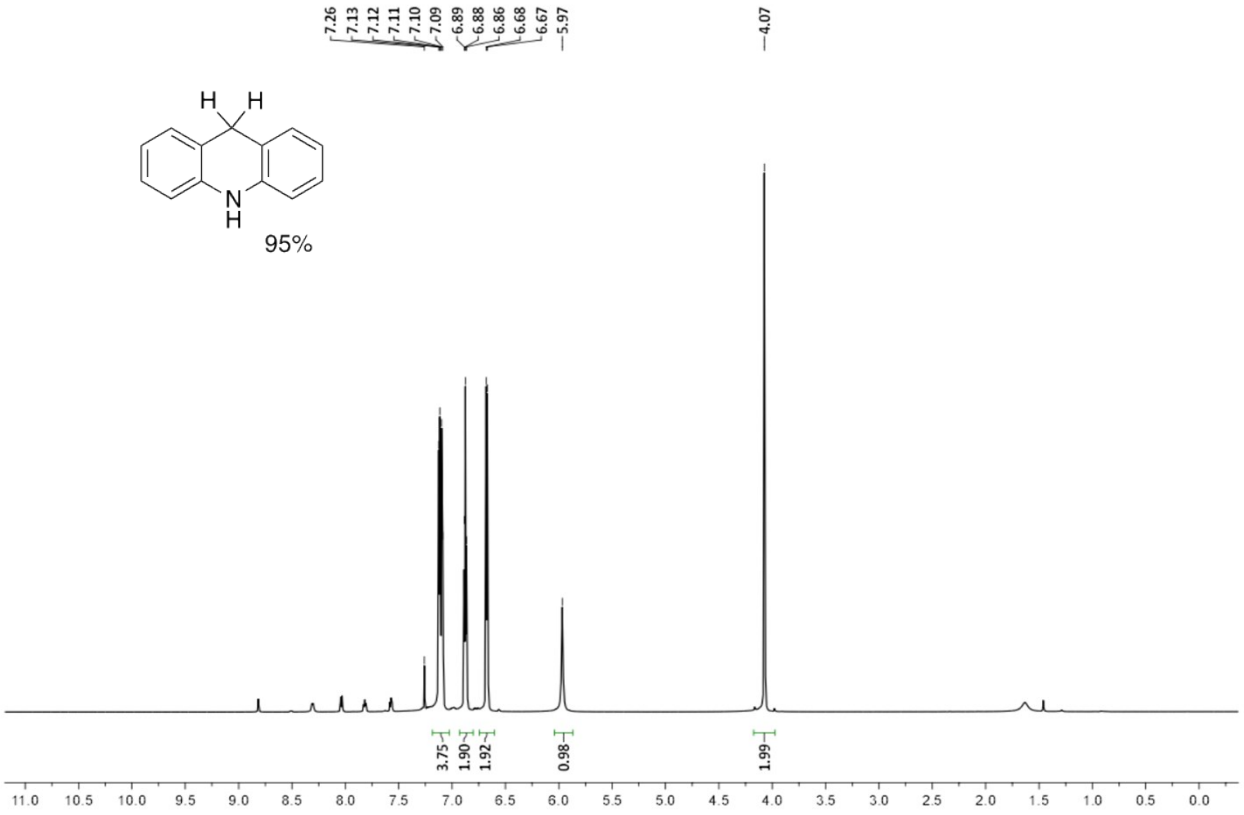
^{13}C NMR spectrum of isolated **2b** from the reaction mixture of **1** and quinoline: *Unknown peaks



Reaction mixture ^{1}H NMR spectrum of **2b** catalyzed quinoline hydrogenation: Evidence for molecular H_2 activation by monomeric-Ru intermediate.

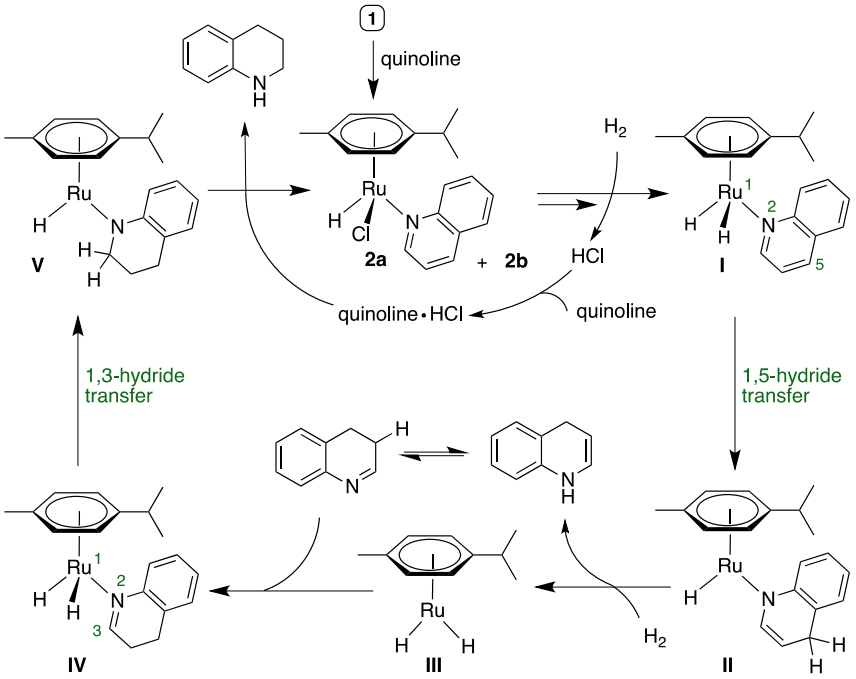


Reaction mixture ^{1}H NMR spectrum of 9,10-dihydroacridine:



An outline of plausible reaction mechanism for the hydrogenation of quinolone:

On the basis of the accumulated experimental observations, a plausible catalytic cycle is proposed for the hydrogenation of heteroarenes (Scheme S1). Upon coordination of quinoline, **2a** and **2b** are generated from **1**. Further heterolytic activation of H_2 by **2a** could lead to intermediate **I** and HCl. Alternatively, perhaps dissociation of quinoline and concomitant heterolytic activation of dihydrogen and further coordination of quinolone could also result in the formation of **I** and HCl. The liberated HCl should then react with quinoline to provide quinolinium hydrochloride salt. Intramolecular 1,5-hydride transfer to the coordinated quinoline ligand could then lead to the formation of intermediate **II,** which results in regioselective 1,4-hydride addition on quinoline motif (Scheme 2c).[17b] Further reaction with hydrogen could provide **III** and 1,4-dihydroquinoline, which is in equilibrium with 3,4-dihydroquinoline that coordinates to **III** to provide intermediate **IV**. Subsequent 1,3-hydride transfer could lead to **V** with coordinated tetrahydroquinolinyl ligand. Quinolinium hydrochloride salt can act as proton donor and it's reaction with **V** results in regeneration of **2a** upon liberation of hydrogenated product THQ to complete a catalytic cycle.



Scheme S1. Proposed mechanism for the catalytic hydrogenation of heteroarenes

References:

1. B. Chatterjee, C. Gunanathan, *Chem. Commun*. 2014, **50**, 888-890.
2. R. Adam, J. R. Cabrero-Antonino, A. Spannenberg, K. Junge, R. Jackstell, M. Beller, *Angew. Chem. Int. Ed.* 2017, **56**, 3216-3220.
3. M. Tang, J. Deng, M. Li, X. Li, H. Li, Z. Chen, Y. Wang, *Green Chem*. 2016, **18**, 6082-6090.
4. F. Fache, *Synlett* 2004, **15**, 2827-2829.
5. T. N. Ye, J. Li, M. Kitano, H. Hosono, *Green Chem*. 2017, **19**, 749-756.
6. M. Meuresch, S. Westhues, W. Leitner, J. Klankermayer, *Angew. Chem. Int. Ed.* 2016, **55**, 1392-1395.
7. Y. Zhang, J. Zhu, Y. T. Xia, X. T. Sun, L. Wu, *Adv. Synth. Catal*. 2016, **358**, 3039-3045.
8. D. Zhu, H. Jiang, L. Zhang, X. Zheng, H. Fu, M. Yuan, H. Chen, R. Li, *ChemCatChem*. 2014, **6**, 2954-2960.
9. P. Mignona, M. Tiano, P. Belmont, A. Favre-Réguillond, H. Chermettea, F. Fache, *J. Mol. Catal. A: Chem.* 2013, **371**, 63-69.
10. H. Y. Jiang, X. X. Zheng, *Appl. Catal. A: General* 2015, **499**, 118-123.
11. X. Cui, A. E. Surkus, K. Junge, C. Topf, J. Radnik, C. Kreyenschulte, M. Beller, *Nat. Commun*. 2016, **7**, 11326.
12. L. Luza, C. P. Rambor, A. Gual, J. A. Fernandes, D. Eberhardt, J. Dupont, *ACS Catal*. 2017, **7**, 2791-2799.
13. M. Ibrahim, R. Poreddy, K. Philippot, A. Riisager, E. Garcia-Suarez, J. *Dalton Trans.* 2016, **45**, 19368-19373.
14. X. Cui, H. Yuan, K. Junge, C. Topf, M. Beller, F. Shi, *Green Chem*. 2017, **19**, 305-310.
15. H. Bi, X. Tan, R. Dou, Y. Pei, M. Qiao, B. Sunb, B. Zong, *Green Chem*. 2016, **18**, 2216-2221.
16. S. Tian, X. Li, A. Wang, R. Prins, Y. Chen, Y. Hu, *Angew. Chem. Int. Ed*. 2016, **55**, 4030-4034.
17. M. M. Stalzer, C. P. Nicholas, A. Bhattacharyya, A. Motta, M. Delferro, T. J. Marks, *Angew. Chem. Int. Ed.* 2016, **55**, 5263-5267.
18. Y. Morioka, A. Matsuoka, K. Binder, B. R. Knappett, A. E. H. Wheatley, H. Naka, *Catal. Sci. Technol*. 2016, **6**, 5801-5805.

19. K. Ramalingam, M. Balasubramanian, V. Baliah, *Indian J. Chem.* 1972, **10**, 366-369.
20. M. Stein, B. Breit, *Angew. Chem. Int. Ed*. 2013, **52**, 2231-2234.
21. C. Schafer, C. J. Ellstrom, H. Cho, B. Torok, *Green Chem*. 2017, **19**, 1230-1234.
22. Bruker AXS, SAINT+, Program for Reduction of Data collected on Bruker CCD Area Detector Diffractometer *V. 6.02.* Bruker AXS Inc., (Madison, Wisconsin, USA, 1999).
23. Bruker AXS, SADABS, Program for Empirical Absorption Correction of Area Detector Data *V 2004/1,* Bruker AXS Inc., (Madison, Wisconsin, USA, 2004).
24. G. M. Sheldrick, *Acta Crystallogr.* 2008, **A64***,* 112-122.
25. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. J. Puschmann, *Appl. Crystallogr.* 2009, **42,** 339-341.
26. F. Ding, Y. Zhang, R. Zhao, Y. Jiang, R. L. Bao, K. Lina, L. Shi, *Chem. Commun*. 2017, **53**, 9262-9264.