Electronic Supplementary Information (ESI)

Water-soluble and reusable Ru–NHC catalyst for aqueous-phase transfer hydrogenation of quinolines with formic acid

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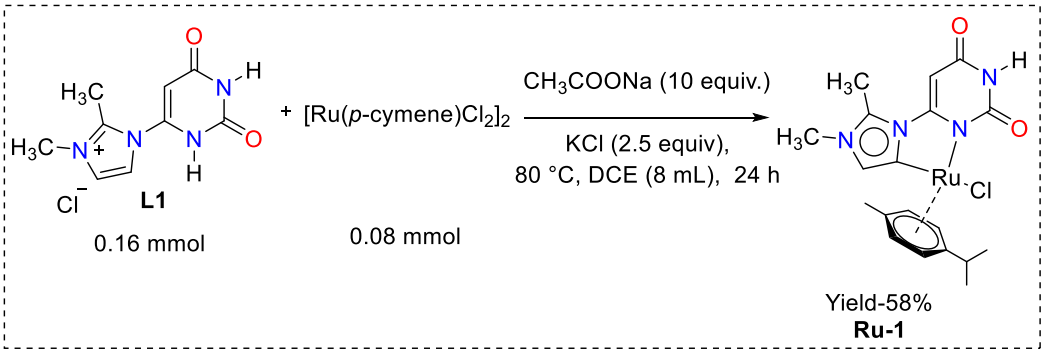
S1. General information

^{1}H and ^{13}C NMR spectra were recorded on Bruker AVANCE III 400 and 500 MHz NMR spectrometers at 25 °C unless mentioned otherwise. Chemical shifts (δ) are expressed in ppm using the residual proton resonance of the solvent as an internal reference as applicable $CDCl_3$: δ = 7.26 ppm for ^{1}H spectra; CD_3CN: 1.94 ppm for ^{1}H spectra. All coupling constants (J) are expressed in hertz (Hz) and only given for $^{1}H–^{1}H$ couplings unless mentioned otherwise. The following abbreviations were used to indicate multiplicity: s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), m (multiplet), bs (broad singlet). Single crystal X-ray diffraction measurements were performed with the Bruker APEX-II CCD instrument. Dry solvents and reagents were obtained from commercial suppliers and used without further purification. Deuterated solvents were purchased from CIL (Cambridge Isotope Laboratory). N_2 (purity 99.99%) and argon gases were purchased from INOX Air Products Pvt. Ltd. Dry MeOH, CH_3CN, and distilled H_2O were used in this work.

Synthesis of ligand **L1** and **L2** were done according to the reported literature.[S1]

S2. Synthesis of Ru-1

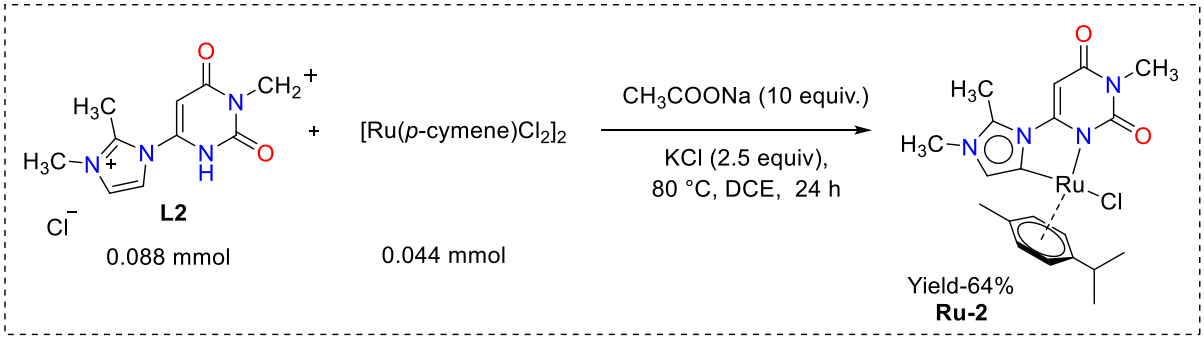
A mixture of ligand **L1** (38.8 mg, 0.16 mmol), [Ru (*p*-cymene) Cl_2]$_2$ (53.8 mg, 0.088 mmol) CH_3COONa (144 mg, 1.76 mmol), and KCl (32.8 mg, 0.44 mmol) were refluxed in 1,2-dichloroethane (DCE) (8 mL) for 14 h. After cooling to room temperature, the solvent was evaporated under reduced pressure. After that the residue was dissolved in CH_2Cl_2 and filtered through a G4 bed. The remaining solution was concentrated under vacuum. Addition of diethyl ether to this concentrated solution resulted into a large amount of precipitate. This precipitate was filtered and washed with diethyl ether to afford the desired product as a light-yellow solid. After that the powder complex was purified by neutral alumina column chromatography with 5% CH_3OH in CH_2Cl_2. Yield 44 mg (58%). ^{1}H NMR (400 MHz, CD_3CN) δ 7.21 (s, 1H), 5.97 (d, *J* = 6.0 Hz, 1H), 5.85 (d, *J* = 6.0 Hz, 1H), 5.79 (d, *J* = 5.8 Hz, 1H), 5.73 (s, 1H), 5.59 (d, *J* = 5.9 Hz, 1H), 3.75 (s, 4H), 2.72 (s, 3H), 2.50 (p, *J* = 6.9 Hz, 1H), 2.01 (s, 3H), 1.10 (d, *J* = 6.9 Hz, 3H), 1.01 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (176 MHz, DMSO-d_6, 294 K) 165.8, 157.0, 148.8, 145.0, 129.2, 126.5, 116.4,108.4, 95.9, 91.7, 90.8, 89.7, 88.0, 30.8, 24.4, 22.5, 21.8, 18.5, 12.9, HRMS (ESI, positive ion) *m/z*= 441.0890 (calculated= 441.0864 for $[C_{19}H_{23}N_4O_2Ru]^{+}$).



Scheme S1. Synthesis of **Ru-1**

S3. Synthesis of complex Ru-2

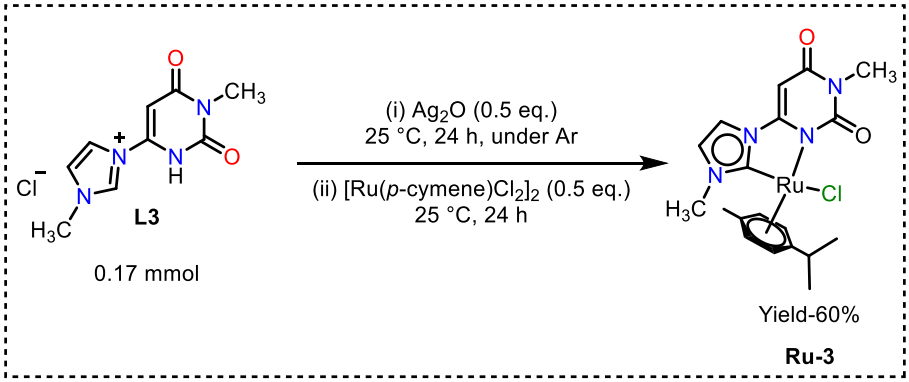
A mixture of ligand **L2** (22.58 mg, 0.088 mmol), [Ru (*p*-cymene) Cl_2]$_2$ (26.94 mg, 0.044 mmol) CH_3COONa (72 mg, 0.8 mmol), and KCl (16.4 mg, 0.22 mmol) was refluxed in DCE (8 mL) for 24 h. After cooling to room temperature, the reaction mixture was filtered through *Celite* and all volatiles were removed under reduced pressure. The complex was obtained as a light-yellow solid by precipitation from CH_2Cl_2/Et_2O. After that the powdered complex as obtained was kept for recrystallization in CH_2Cl_2/Et_2O, which provided the pure complex. Yield (31 mg, 64%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.00 (s, 1H), 6.13 (d, *J* = 4.9 Hz, 1H), 5.85 (s, 1H), 5.73 (d, *J* = 5.4 Hz, 1H), 5.51 (d, *J* = 4.9 Hz, 1H), 5.17 (d, *J* = 6.8 Hz, 1H), 3.79 (s, 3H), 3.46 (s, 3H), 2.80 (s, 3H), 2.55 – 2.40 (m, 1H), 2.50 (s, 3H), 2.10 (s, 3H), 1.13 (d, *J* = 7.0 Hz, 3H), 0.95 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (176 MHz, CD_3CN, 294 K) 165.7, 157.7, 156.5, 152.6, 144.0, 125.9, 105.4, 103.2, 92.3, 91.7, 87.7, 87.1, 86.4, 35.5, 31.7, 28.6, 22.9, 21.9, 18.9, 13.3, HRMS (ESI, positive ion) *m/z*= 456.1056 (calculated= 456.1126 for [$C_{20}H_{25}N_4O_2Ru$] $^+$).



Scheme S2. Synthesis of **Ru-2**

S4. Synthesis of complex Ru-3

For the synthesis of complex **Ru-3**, two steps were followed. In the first step, a mixture of ligand **L3** (41.2 mg, 0.17 mmol) and silver(I)-oxide (20 mg, 0.088 mmol) were taken in a Schlenk tube with dichloromethane (2 mL) as the solvent. Under nitrogen atmosphere, the reaction mixture was stirred at room temperature (25 °C) for 24 h. After that in the same Schlenk tube, [Ru(*p*-cymene)$_2$ Cl_2]$_2$ (53.9 mg, 0.088 mmol) was added and stirred at 25 °C under nitrogen environment for another 24 h. After completion of the reaction, it was filtered using *celite* and then the solvent was evaporated in a rotary evaporator. The remaining solid was dissolved in CH_2Cl_2 and precipitated using Et_2O. At last, the obtained yellow color solid was left out for recrystallization using CH_2Cl_2/Et_2O. Yield 49 mg, (60%). ^{1}H NMR (400 MHz, $CDCl_3$, 294 K) δ 7.27 (d, *J* = 1.7 Hz, 1H), 7.07 (d, *J* = 1.8 Hz, 1H), 6.27 (d, *J* = 6.1 Hz, 1H), 6.02 (d, *J* = 5.7 Hz, 1H), 5.76 (d, *J* = 5.8 Hz, 1H), 5.63 (s, 1H), 5.13 (d, *J* = 5.7 Hz, 1H), 4.07 (s, 3H), 3.42 (s, 3H), 2.35 (s, 1H), 2.25 (s, 3H), 0.97 (dd, *J* = 6.9, 3.5 Hz, 6H). HRMS (ESI, positive ion) *m/z*= 441.0901 (calculated = 441.0860 for [$C_{25}H_{25}N_4O_2Ru$] $^+$).^{13}C NMR (176 MHz, $CDCl_3$, 294 K) 185.6, 165.7, 157.2, 155.2, 136.6, 116.4, 91.3, 84.8, 83.9, 38.3, 31.2 28.5, 22.7, 22.6,19.4. Elemental analysis C 48.2480, H 4.8316, N 11.4198 (calculated = C 51.6905, H 5.2552, N 12.698).



Scheme S3. Synthesis of **Ru-3**

S5. ^{1}H NMR, ^{13}C{^{1}H} NMR, and ESI-MS spectra of Ru-1, Ru-2 and Ru-3

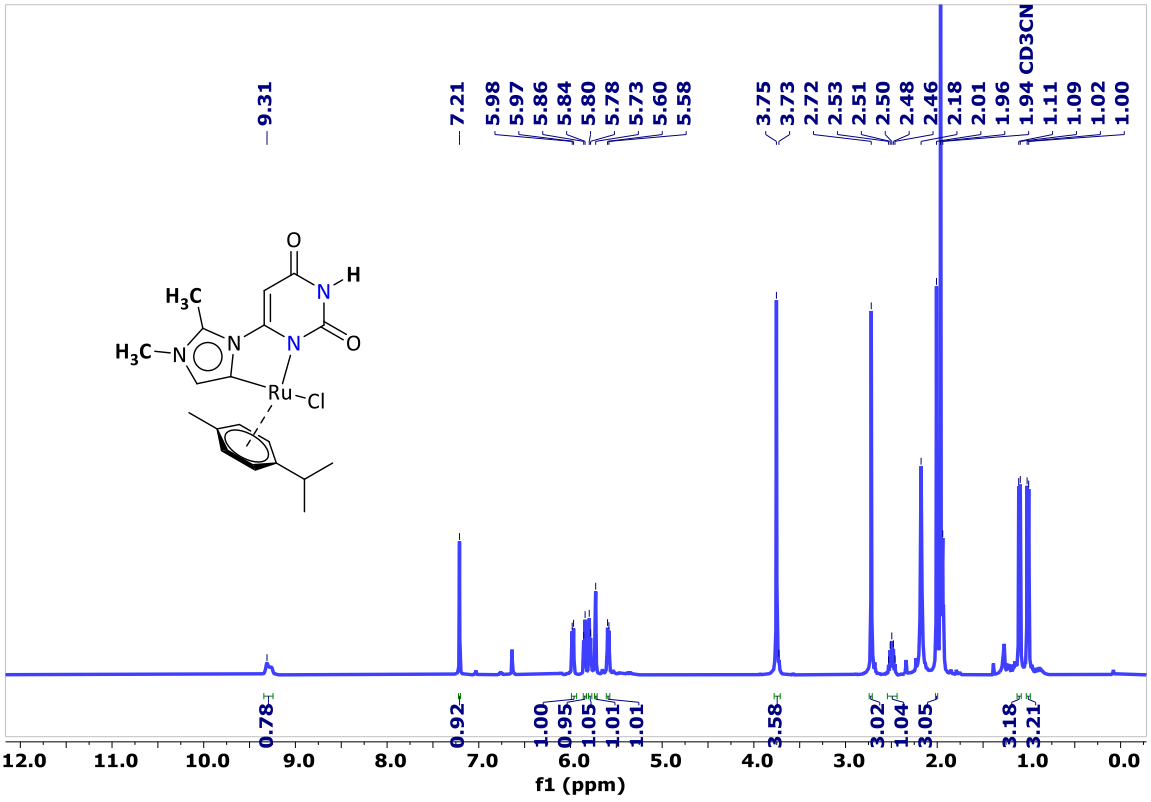


Fig. S1. ^{1}H NMR spectrum of **Ru-1** (500 MHz, CD_3CN)

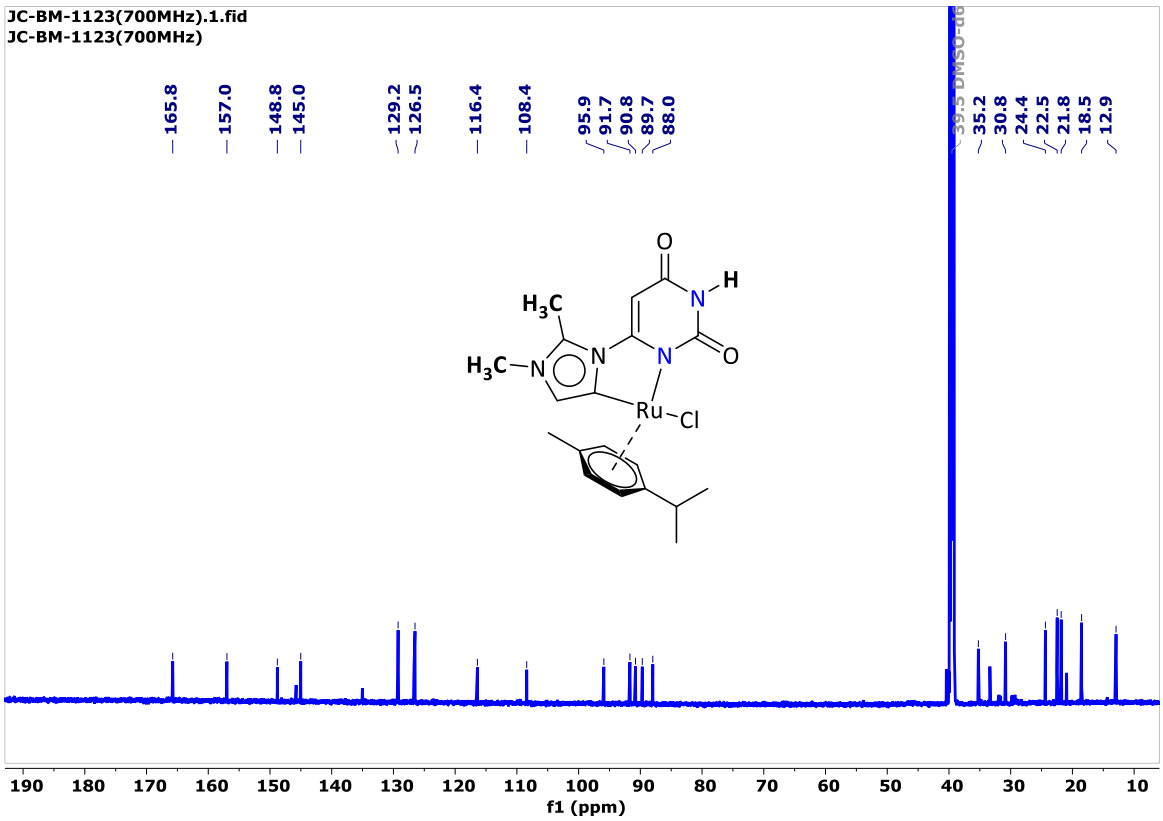


Fig. S2. ^{13}C{^{1}H} NMR spectrum of **Ru-1** in DMSO-d_6, (176 MHz)

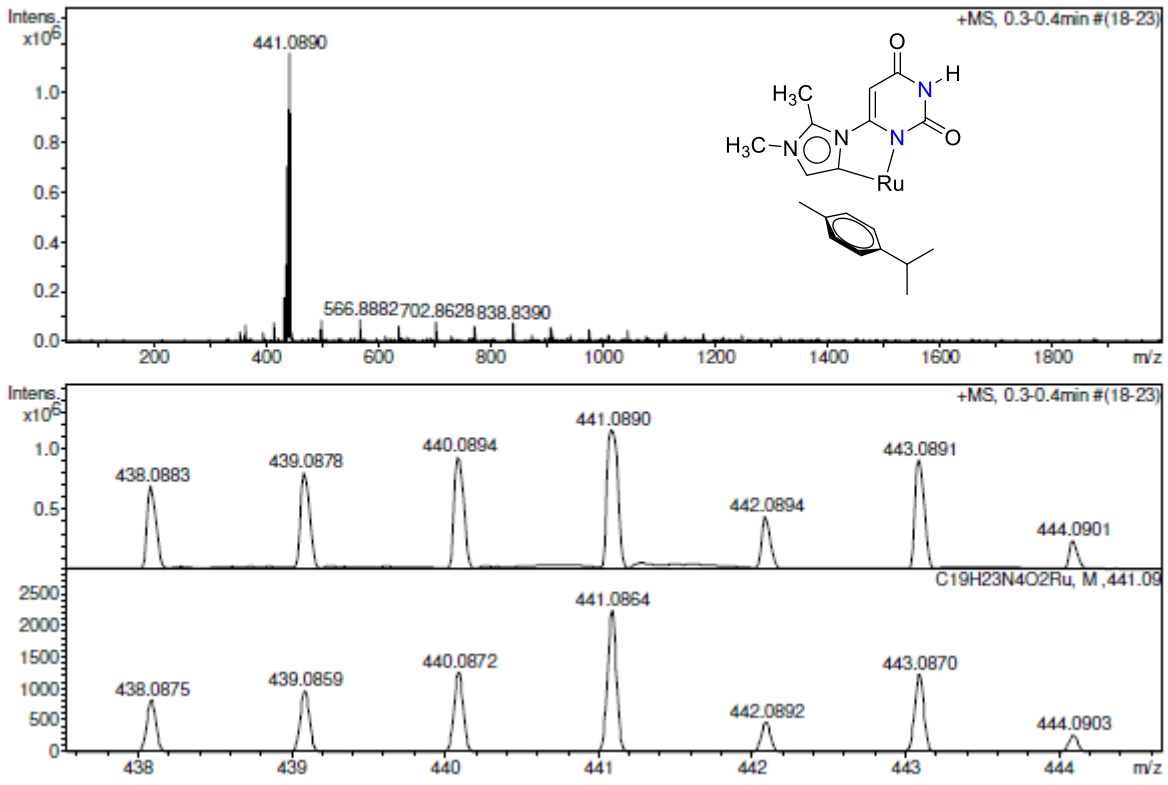


Fig. S3. ESI-MS (positive ion mode) of **Ru-1**

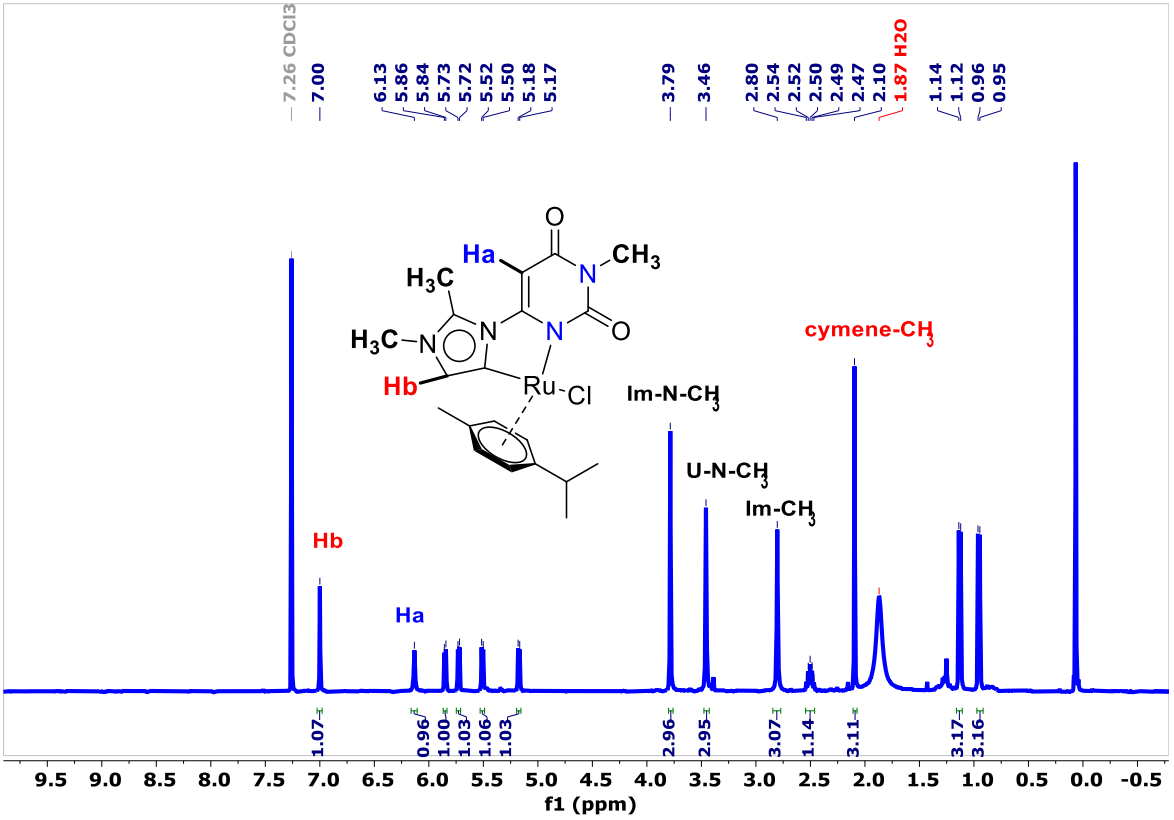


Fig. S4. ^{1}H NMR spectrum (500 MHz) of **Ru-2** in $CDCl_3$

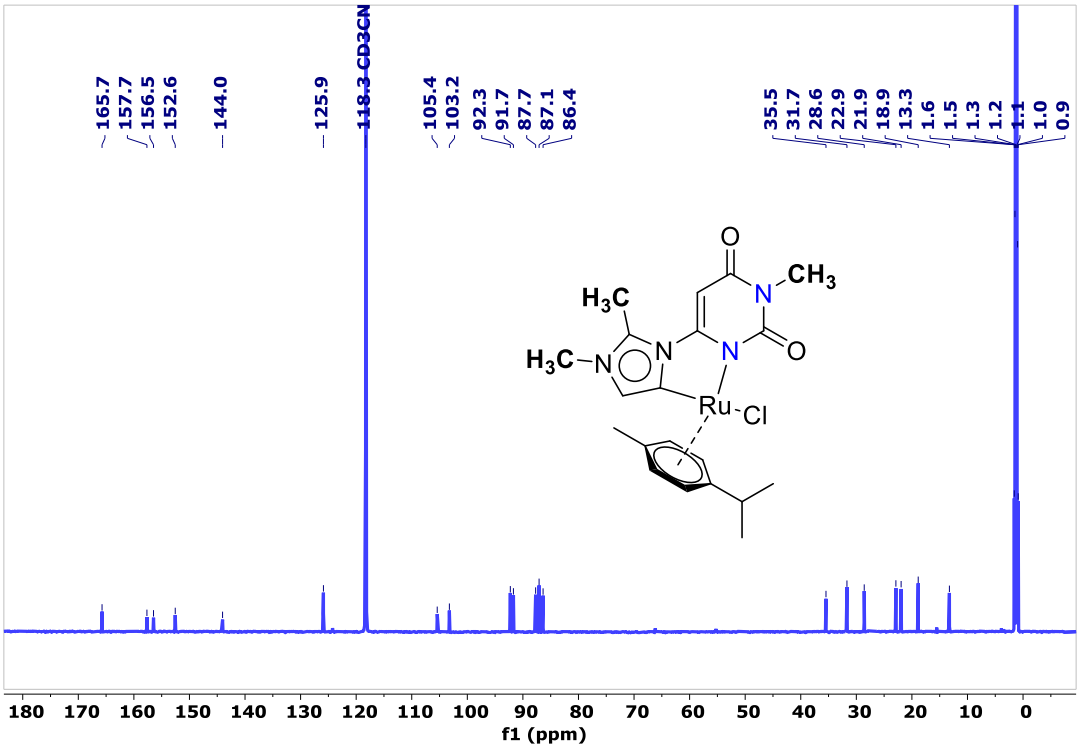


Fig. S5. $^{13}C\{^{1}H\}$ NMR spectrum (175 MHz) of **Ru-2** in CD_3CN

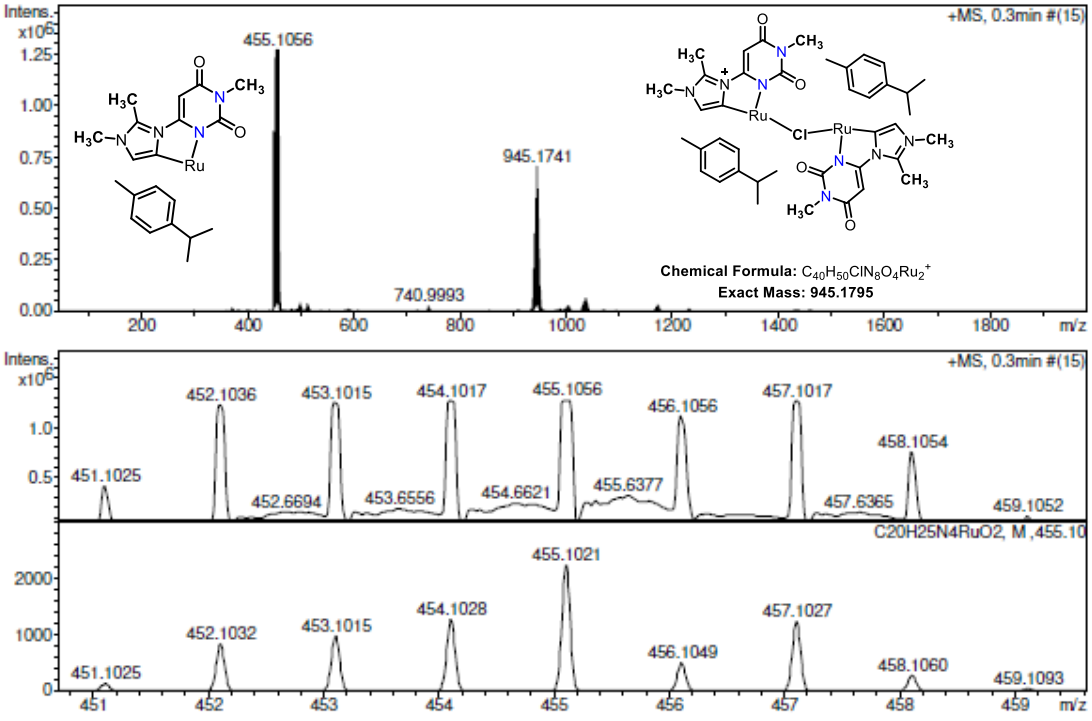


Fig. S6. ESI-MS (positive ion mode) of **Ru--2**

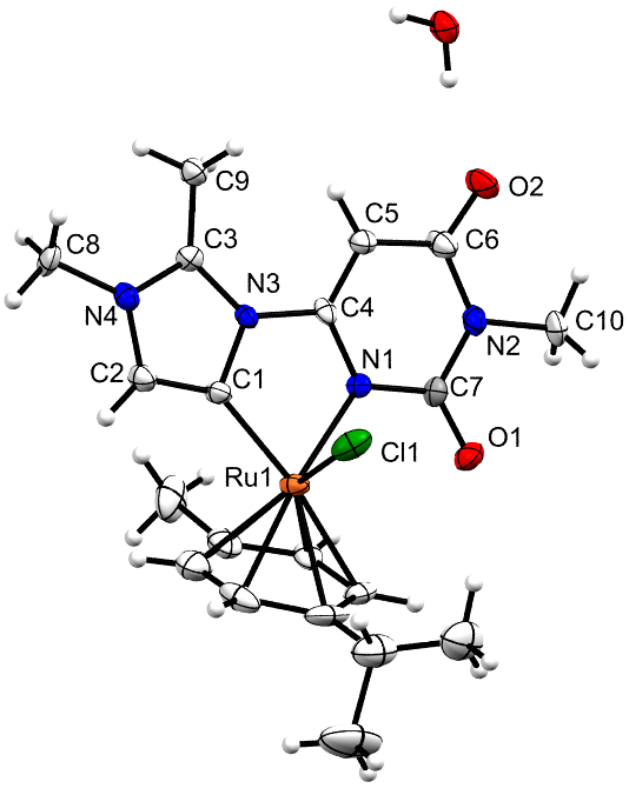


Fig. S7. X-ray crystal structure of **Ru–2** (CCDC 2143830) (50% ellipsoids probability level). Hydrogen atoms are removed for clarity.

Selected bond lengths (Å) and angles (deg) for complex **Ru–2** Ru1-Cl1 = 2.4224(18), Ru1-N1 = 2.118(5), Ru1-C1 = 2.004(6), O1-C7 = 1.219(7), O2-C6 = 1.240(7), N3-C1 = 1.405(7), N3-C4 = 1.406(7), N1-C4 = 1.355(7), N1-C7 = 1.375(7) C1-Ru1-N1 = 76.3(2), C1-Ru1-Cl1 = 86.05(18), N1-Ru1-Cl1 = 85.10(14), C4-N3-C1 = 117.7(5), N1-C7-O1 = 122.8(5), N1-C4-N3 = 111.1(5),

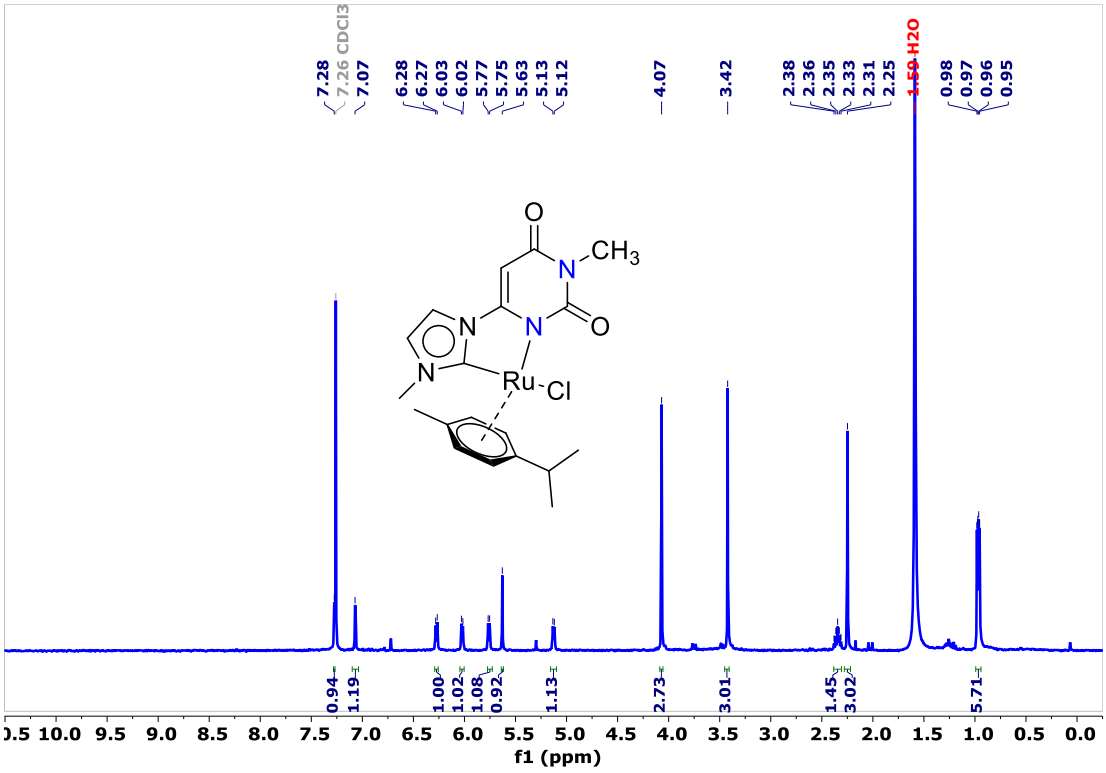


Fig. S8. ^{1}H NMR spectrum of **Ru–3** (500MHz) in $CDCl_3$

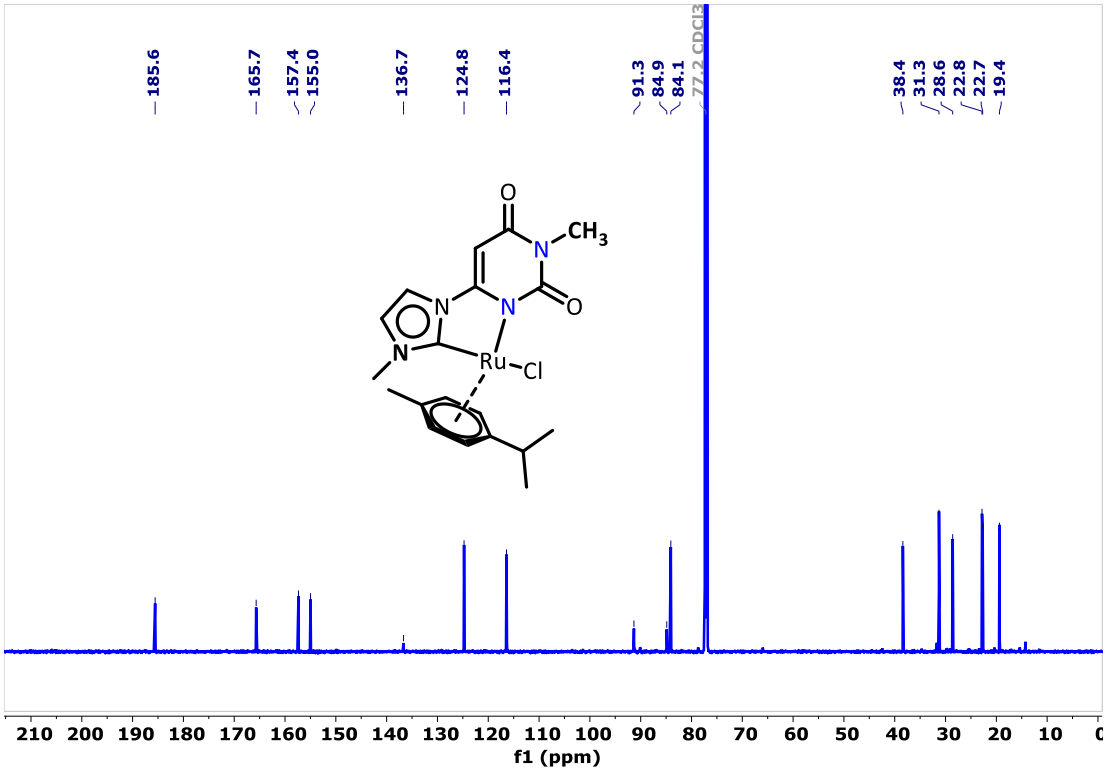


Fig. S9. $^{13}C\{^{1}H\}$ NMR spectrum (176 MHz) of **Ru–3** in $CDCl_3$

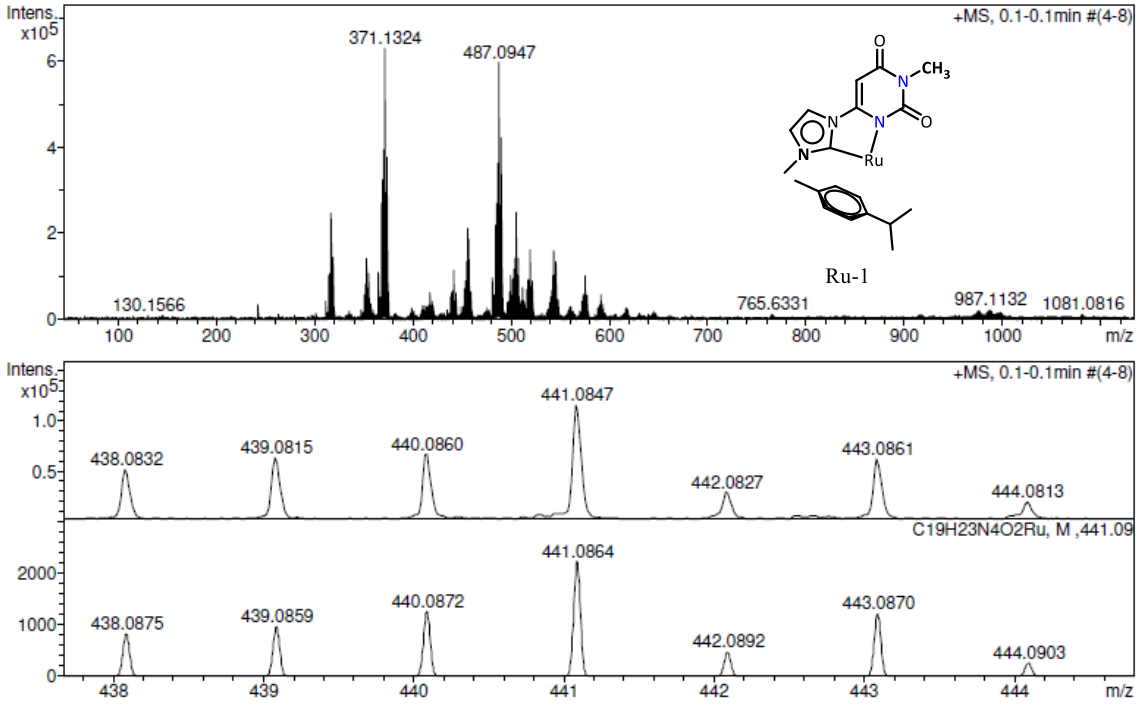


Fig. S10. ESI-MS (positive ion mode) of **Ru--3**

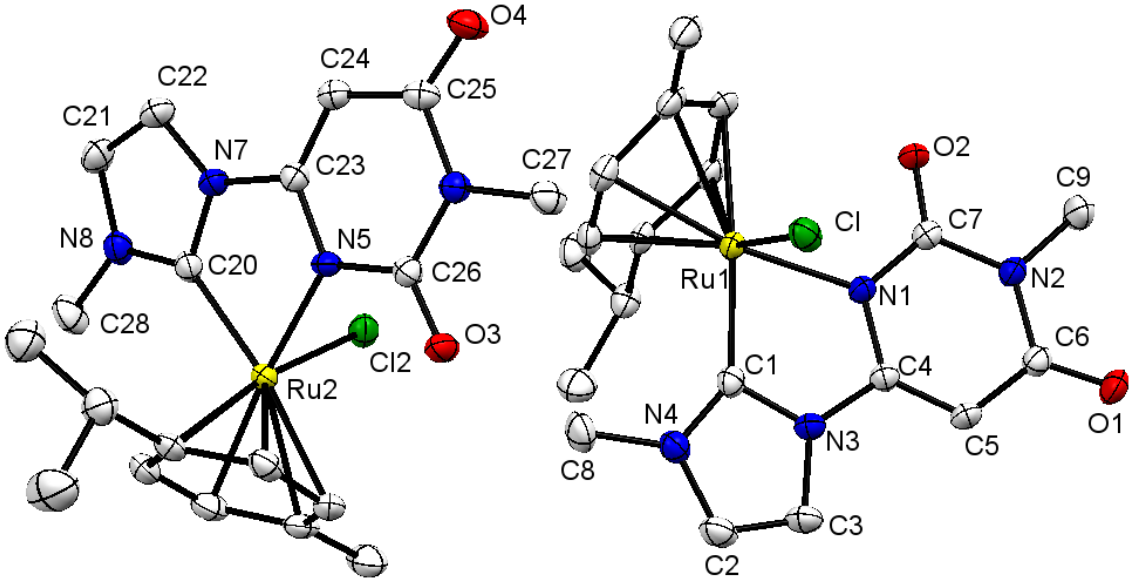
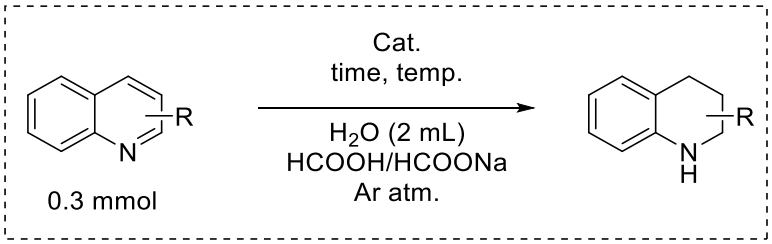


Fig. S11. X-ray crystal structure of **Ru--3** (CCDC 2143831) (50% ellipsoids probability level). Hydrogen atoms are removed for clarity. Selected bond lengths (Å) and angles (deg) for complex **Ru—3** Ru1-Cl1 = 2.4189(10), Ru1-N1 = 2.128(3), Ru1-C1 = 2.017(4), O1-C6 = 1.233(4), O2-C7 = 1.229(5), N3-C1 = 1.362(5), N3-C4 = 1.398(5), N1-C4 = 1.357(5), N1-C7 = 1.370(5), C1-Ru1-N1 = 84.52(9), N1-Ru1-C1 = 76.06(13), C4-N3-C1 = 119.4(3), N1-C7-O2 = 123.2(3), N1-C4-N3 = 104.6(3)

S6. Table S1 Data collection and structure refinement parameters for the complexes **Ru-2** and **Ru-3**.

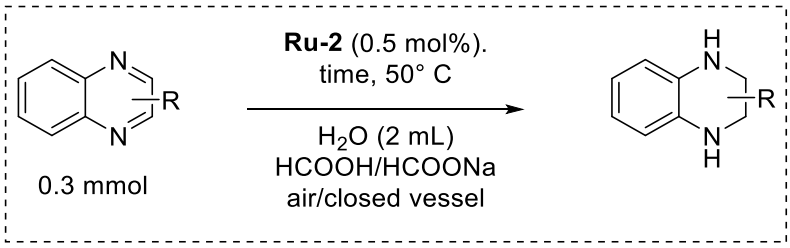
Identification code	**Ru--2**	**Ru--3**
CCDC No.	2143830	2143831
Empirical formula	$C_{20}H_{27}ClN_4O_3Ru$	$C_{19}H_{23}ClN_4O_2Ru$
Formula weight	507.97	475.93
Temperature/K	140.0	140.0
Crystal system	monoclinic	orthorhombic
Space group	$P2_1/c$	$Pna2_1$
a/Å	15.3310(12)	14.6419(12)
b/Å	11.0698(9)	13.5577(9)
c/Å	13.6313(10)	19.6678(16)
α/°	90	90
β/°	115.519(3)	90
γ/°	90	90
Volume/Å^3	2087.7(3)	3904.3(5)
Z	4	8
ρ_{calc}g/cm^3	1.616	1.619
μ/mm^{-1}	0.908	0.962
F(000)	1040.0	1936.0
Crystal size/mm^3	0.165 × 0.13 × 0.11	0.165 × 0.13 × 0.11
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.712 to 55.866	4.094 to 54.272
Index ranges	$-20 \le h \le 19$, $-14 \le k \le 14$, $-17 \le l \le 17$	$-18 \le h \le 18$, $-17 \le k \le 17$, $-25 \le l \le 25$
Reflections collected	27219	86372
Independent reflections	4979 [R_{int} = 0.1002, R_{sigma} = 0.0943]	8602 [R_{int} = 0.0468, R_{sigma} = 0.0231]
Data/restraints/parameters	4979/0/271	8602/1/498
Goodness-of-fit on F^2	1.061	1.037
Final R indexes [I>=2σ (I)]	R_1 = 0.0719, wR_2 = 0.1222	R_1 = 0.0219, wR_2 = 0.0507
Final R indexes [all data]	R_1 = 0.1274, wR_2 = 0.1399	R_1 = 0.0242, wR_2 = 0.0523
Largest diff. peak/hole / e Å^{-3}	2.08/-1.66	0.42/-0.26

S7. General procedure for transfer hydrogenation of N-heterocycles in HCOOH/HCOONa buffer solution



To a 25 mL Schlenk tube, the mixture of quinoline (0.3 mmol), catalyst (0.5 mol%, 0.0015 mmol, 100 µL stock solution in H_2O) and HCOOH/HCOONa (3 mmol HCOOH and 1.68 mmol HCOONa) buffer solution (with the corresponding pH) in water (2.0 mL) was added. The mixture was stirred at the desired temperature for the desired time under Ar. After the reaction was completed, the mixture was neutralized with a saturated solution of sodium bicarbonate whereupon an effervescence of carbon dioxide was observed. Then the reaction mixture was diluted with H_2O (15.0 mL), and extracted with EtOAc (5.0 mL × 3). The organic extract was washed with brine (5.0 mL × 3) and dried over anhydrous Na_2SO_4. After evaporation of EtOAc under vacuum, the yield of the product was determined by ^1H NMR spectroscopy using mesitylene (10 µL) as an internal standard. Further purification of the compound was done by column chromatography on silica gel with hexanes/ethyl acetate (5:1 to 50:1) to furnish the pure product.

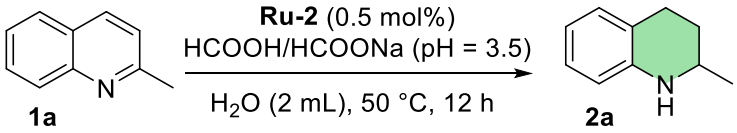
S8. General procedure for transfer hydrogenation of quinoxalines in HCOOH/HCOONa buffer solution

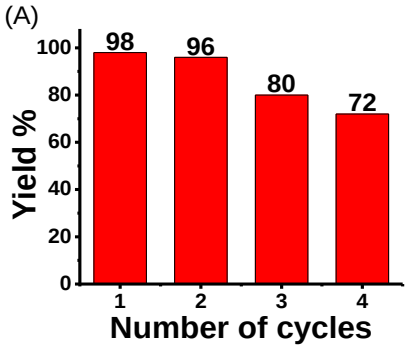


To a 25 mL Schlenk flask, the mixture of quinoxaline (0.3 mmol) and HCOOH/HCOONa buffer (pH = 3.5) in water (2.0 mL) was added. The reaction mixture was stirred for 15 min. After completion of 15 min, catalyst (0.5 mol%, 0.0015 mmol, 100 µL stock solution in H_2O) solution was added, and the reaction mixture was stirred at 50 °C for the desired time. After the reaction was completed, the mixture was neutralized with a saturated solution of sodium bicarbonate whereupon effervescence of carbon dioxide was observed. Then the reaction mixture was diluted with H_2O (5.0 mL), and extracted with EtOAc (10.0 mL × 3). The organic extract was washed with brine (5.0 mL × 3) and dried over anhydrous Na_2SO_4. After removal of EtOAc under vacuum, the yield of the product was determined by ^1H NMR spectroscopy using mesitylene (10 µL) as an internal standard. Further purification of the compound was done by column chromatography on silica gel with hexanes/ethyl acetate (5:1 to 50:1) to furnish the desired product.

S9. Reusable transfer hydrogenation using liquid/liquid extraction methodology

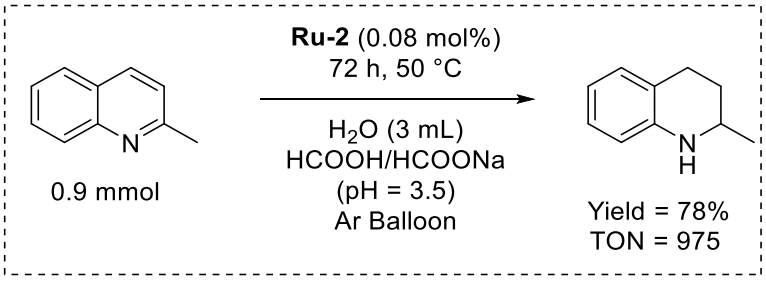
In a 25 mL Schlenk flask, the substrate **1a** (0.3 mmol, 43 µL) and catalyst **Ru–2** (0.5 mol%, 90 µL, and stock solution in H_2O) were taken. After that, the reaction vessel was evacuated by applying vacuum, and then the flask was refilled with N_2. This process was repeated three times. After that 2 mL of aqueous HCOOH/HCOONa buffer solution (pH = 3.5) was added to this reaction vessel. The resulting mixture was stirred at 50 °C for 12 h. After completing one round of the TH reaction, 2-Me-THF (3 mL × 2) was added to extract the organic compound. Then in the aqueous layer, 0.3 mmol of **1a** and hydride source was added and run for the next round of TH reaction. The same procedure was repeated four times. The yield of the product was calculated by ^{1}H NMR spectroscopy using mesitylene as an internal standard.





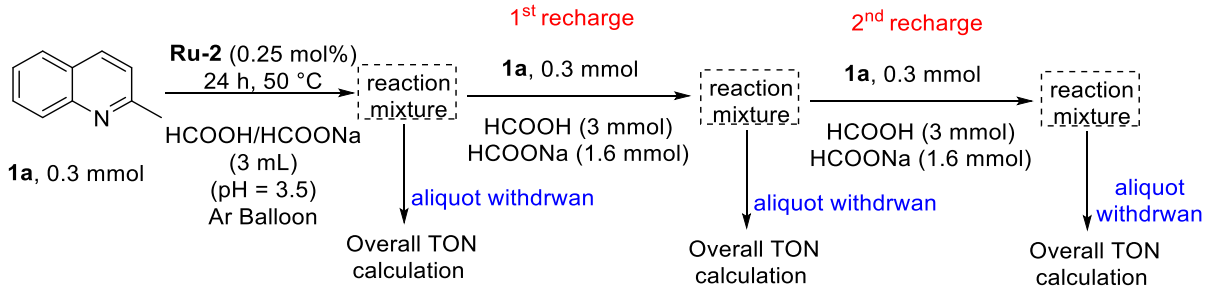
S10a. Long term TH reaction with Ru-2

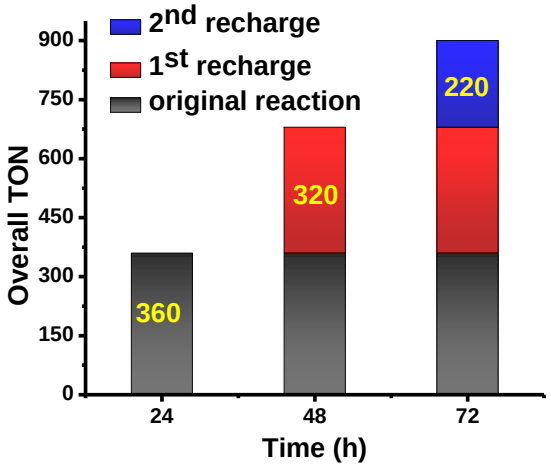
In a 25 mL Schlenk flask, the substrate **1a** (0.9 mmol, 130 µL) and catalyst **Ru–2** (0.08 mol%, 100 µL, and stock solution in H_2O) were taken. After that, the reaction vessel was evacuated by applying vacuum, and then the flask was refilled with N_2. This process was repeated three times. After that 3 mL of aqueous HCOOH/HCOONa buffer solution (pH = 3.5) was added to this reaction vessel. The resulting mixture was stirred at 50 °C for desired time. After completion of 72 h of reaction time, the mixture was neutralized with a saturated solution of sodium bicarbonate whereupon effervescence of carbon dioxide was observed. Then the reaction mixture was diluted with H_2O (5.0 mL), and extracted with EtOAc (10.0 mL × 3). The organic extract was washed with brine (5.0 mL × 2) and dried over anhydrous Na_2SO_4. After removal of EtOAc under vacuum, the yield of the product was determined by ^{1}H NMR spectroscopy using mesitylene (20 µL) as an internal standard.



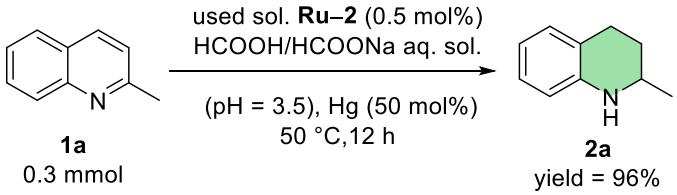
S10b. Long term recharging TH reaction with Ru-2

In a 25 mL Schlenk flask, the substrate **1a** (0.3 mmol, 43 µL) and catalyst **Ru–2** (0.25 mol%, 100 µL, and stock solution in H_2O) were taken. After that, the reaction vessel was evacuated by applying vacuum, and then the flask was refilled with N_2. This process was repeated three times. After that 3 mL of aqueous HCOOH/HCOONa buffer solution (pH = 3.5) was added to this reaction vessel. The resulting mixture was stirred at 50 °C for desired time (24 h). After the completion of 24 h of reaction, 100 µL of aliquot was withdrawn from the reaction mixture and the yield of the product was calculated by ^{1}H NMR spectroscopy using mesitylene as an internal standard. In the meantime, to the original reaction flask, 0.3 mmol of **1a** and HCOOH (3 mmol)/HCOONa (1.6 mmol), but no additional catalyst, were added and the reaction was continued under the same conditions for the next 24 h. The same procedure was repeated in the next cycle (2nd recharge). Finally, the overall TON values were plotted against each 24 h reaction cycle.





S11. Hg drop experiment



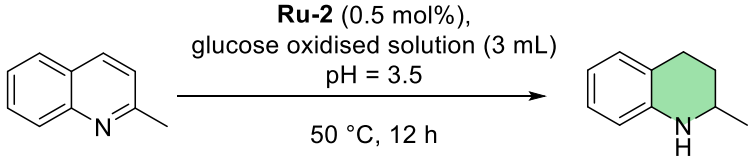
1a
0.3 mmol

2a
yield = 96%

In a 25.0 mL Schlenk tube containing a stirring bar, substrate (0.3 mmol, 43 µL), Hg (50 mol%), and **Ru-2** (0.5 mol%, stock solution in H_2O) were taken. After that, the reaction vessel was evacuated by applying vacuum and then was refilled with N_2. After that 2 mL of aqueous HCOOH/HCOONa buffer solution (pH = 3.5) was added to this reaction vessel. The resulting mixture was stirred at 50 °C for 12 h. After completion of the reaction, EtOAc was added (3 mL x 2) and stirred for 5 minutes to remove the organic products. The yield of the organic products was calculated by ^{1}H NMR spectroscopy using mesitylene as an internal standard.

S12. Transfer hydrogenation of 1a using glucose oxidation solution as the HCOOH source

To a 25 mL Schlenk tube, the mixture of quinoline (0.3 mmol), catalyst **Ru-2** (0.5 mol %, 0.0015 mmol, 100 µL stock solution in H_2O), and glucose-oxidised solution (pH = 3.5) was added. The mixture was stirred at 50 °C for 24 h. After that, the mixture was neutralized with a saturated sodium bicarbonate solution whereupon the effervescence of carbon dioxide was observed. Then the reaction mixture was diluted with H_2O (15.0 mL, and extracted with EtOAc (10.0 mL × 3). The yield of the product was determined according to the same procedure described above. The oxidation of glucose was done according to the reported literature procedure. [S3] In a typical procedure, glucose (2 mmol, 360 mg), Ag_2O (100%, 462 mg) and 6.25 mL of 1.5 M NaOH solution were first loaded into a pressure tube. Then, this reaction vessel was closed and heated to 135 °C for 30 min. After that, the reactor was cooled to room temperature. Then the pH of the solution was adjusted to 3.5 by dropwise addition of 1 M H_2SO_4 solution. The pH of the solution was monitored by a pH meter.



1a

2a
yield, 52%

S13. Control experiment I: Generation and detection of Ru-(OOCH) intermediate

In an NMR tube, **Ru—2** (0.003 mmol, 100 µL stock solution) was taken and to it 10 equivalents of HCOONa (100 µL stock solution in H_2O, 0.3 M) were added. After that 0.5 mL of CD_3CN was added to the mixture. Then the solution in the NMR tube was stirred at 50 °C for 10 min and afterward ^1H NMR spectrum was recorded. The peak at 7.66 ppm indicated the coordinated formato proton of the intermediate **Ru-OOCH**. The peak at 4.56 ppm showed the presence of the dissolved hydrogen gas which might have evolved through protonation of the subsequent Ru–H intermediate. Previously the formate adduct of similar ruthenium(II) complex was reported in the literature. [S2] The corresponding ^1H NMR spectra are shown in Fig. S13 and Fig. S14.

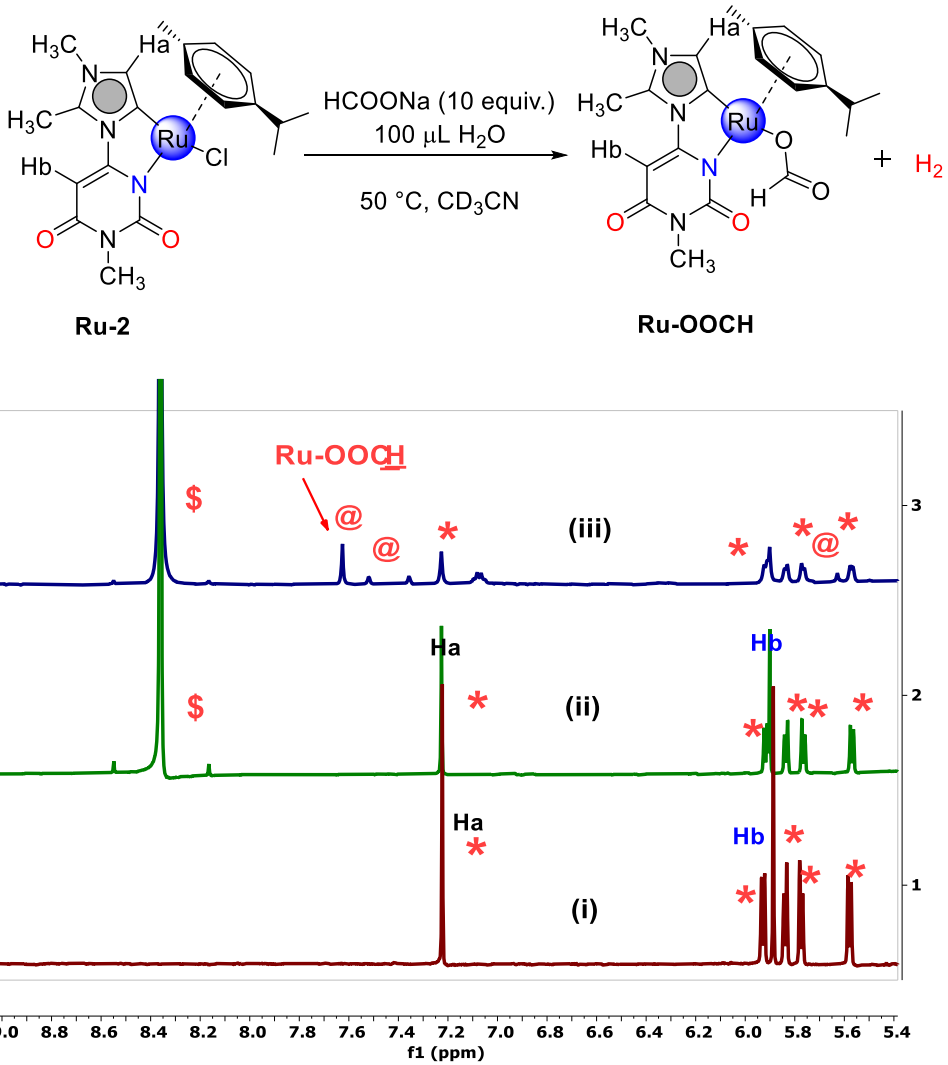


Fig. S12. ^1H NMR spectra (**downfield region**) of a control reaction of catalyst **Ru–2** in CD_3CN with HCOONa. (i) free catalyst; (ii) catalyst + HCOONa, at r.t; (iii) catalyst + HCOONa. 50 °C (10 min). $: for sodium formate peak. @: for **Ru-OOCH** species, *: for **Ru-2** species.

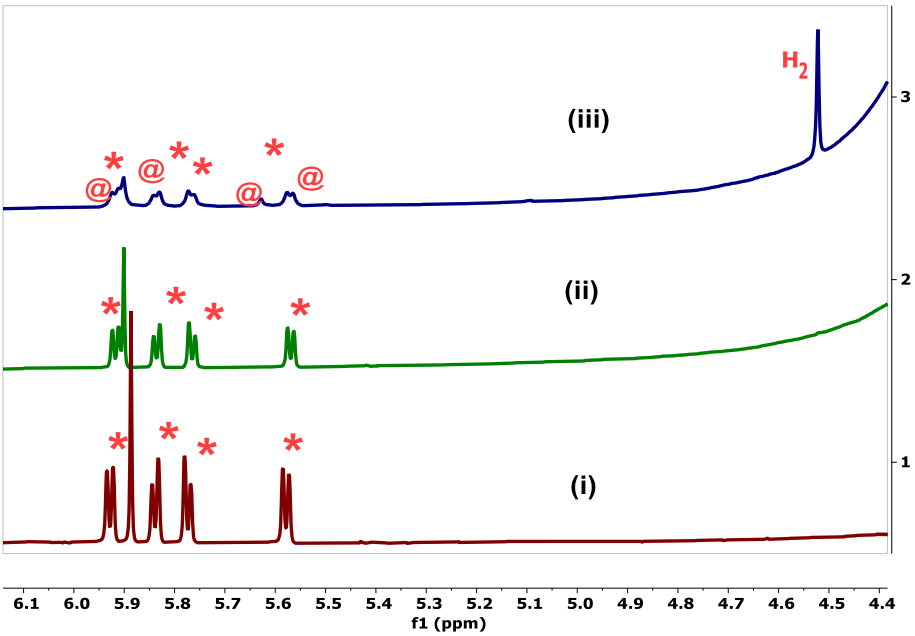
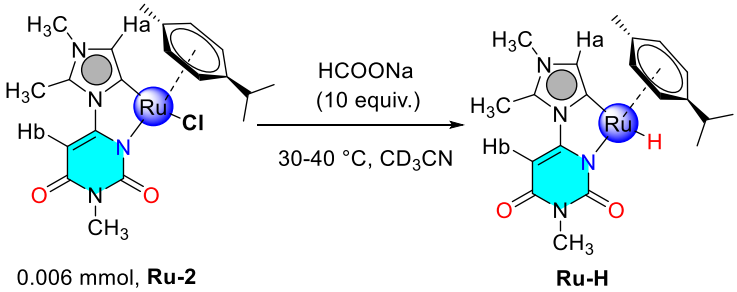


Fig. S13. ^{1}H NMR spectra (4.4-6.2 ppm region) of a control reaction of catalyst **Ru–2** in CD_3CN with HCOONa. (i) free catalyst; (ii) catalyst + HCOONa, at r.t; (iii) catalyst + HCOONa. 50 °C (10 min). $: for sodium formate peak. @: for **Ru-OOCH** species, *: for **Ru-2** species.

S14. Control experiments II and III: Generation, detection and reaction of Ru-H intermediate with Ru-2

In a dried NMR tube (Wilmad, 5 mm), **Ru–2** (3 mg, 0.006 mmol) was dissolved in CD_3CN (500 µL). To this solution was added a solution of HCOONa (0.06 mmol, 50 µL stock solution in H_2O). Then, the NMR tube was quickly subjected to ^{1}H NMR spectroscopic analysis. Data were recorded first at 303 K, and then at elevated temperatures by following 10 K increment in temperature up to 313 K. After the generation and detection of the **Ru-H** intermediate (within 10 min), **1a** (2 eq.) and HCOOH (2 eq.) were added in the same NMR tube. Keeping the NMR tube for 15 min at 40 °C, again the spectrum was recorded. The corresponding ^{1}H NMR spectra are shown in Fig. S18, to Fig. S20.



0.006 mmol, **Ru-2** **Ru-H**

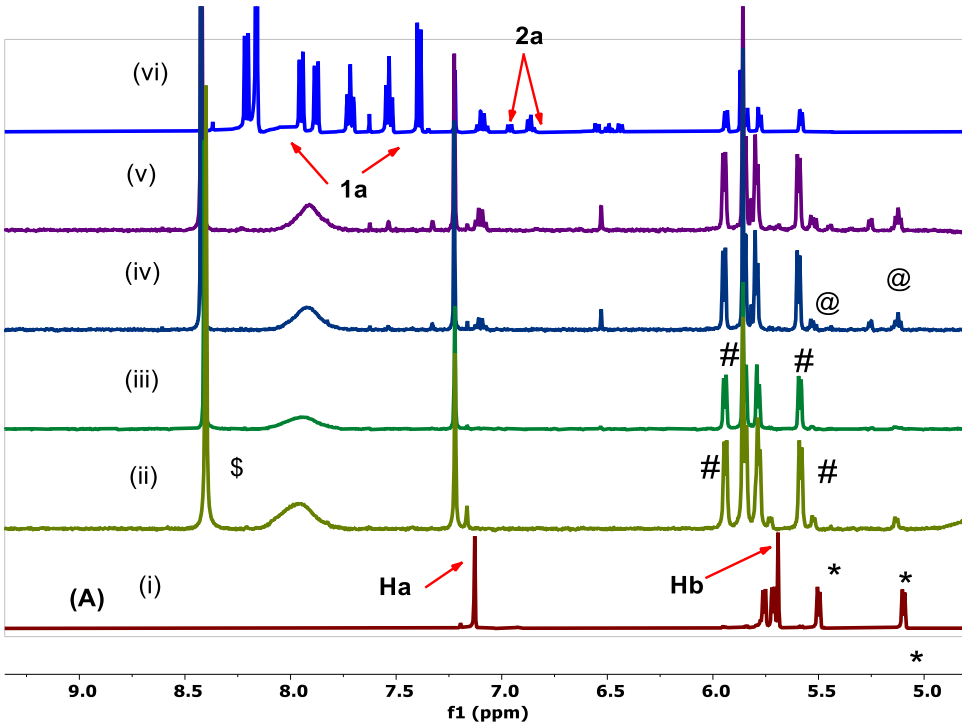


Fig. S14. (A) ^{1}H NMR spectra of a control reaction of **Ru–2** in CD_3CN with HCOONa. (i) only catalayst (ii) catalyst + HCOONa, at r.t; (iii) catalyst + HCOONa, 30 °C (iv) catalyst + HCOONa, 40 °C (v) catalyst + HCOONa, 40 °C, 10 min. (vi) after addition of 1a (0.01 mmol) and formic acid (0.01 mmol), 40 °C, 10 min here $: for formate peak. @: for **Ru-H** species, *: for **Ru–2** and # is for Ru-sol species

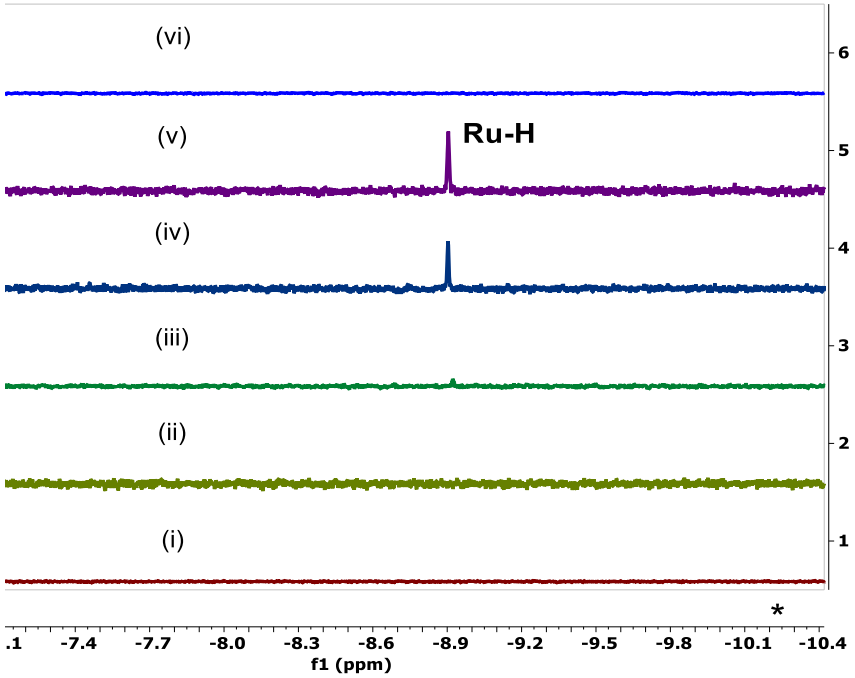
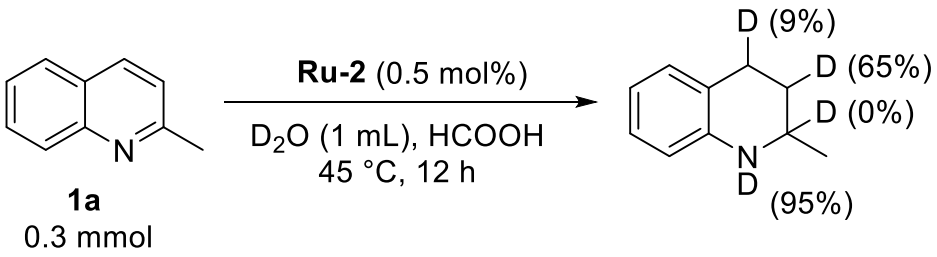


Fig.15. (A) ^{1}H NMR spectra of a control reaction of **Ru–2** in CD_3CN with HCOONa. (i) only catalayst (ii) catalyst + HCOONa, at r.t; (iii) catalyst + HCOONa, 30 °C (iv) catalyst + HCOONa, 40 °C (v) catalyst + HCOONa, 40 °C, 10 min. (vi) after addition of 1a (0.01 mmol) and formic acid (0.01 mmol), 40 °C, 10 min.

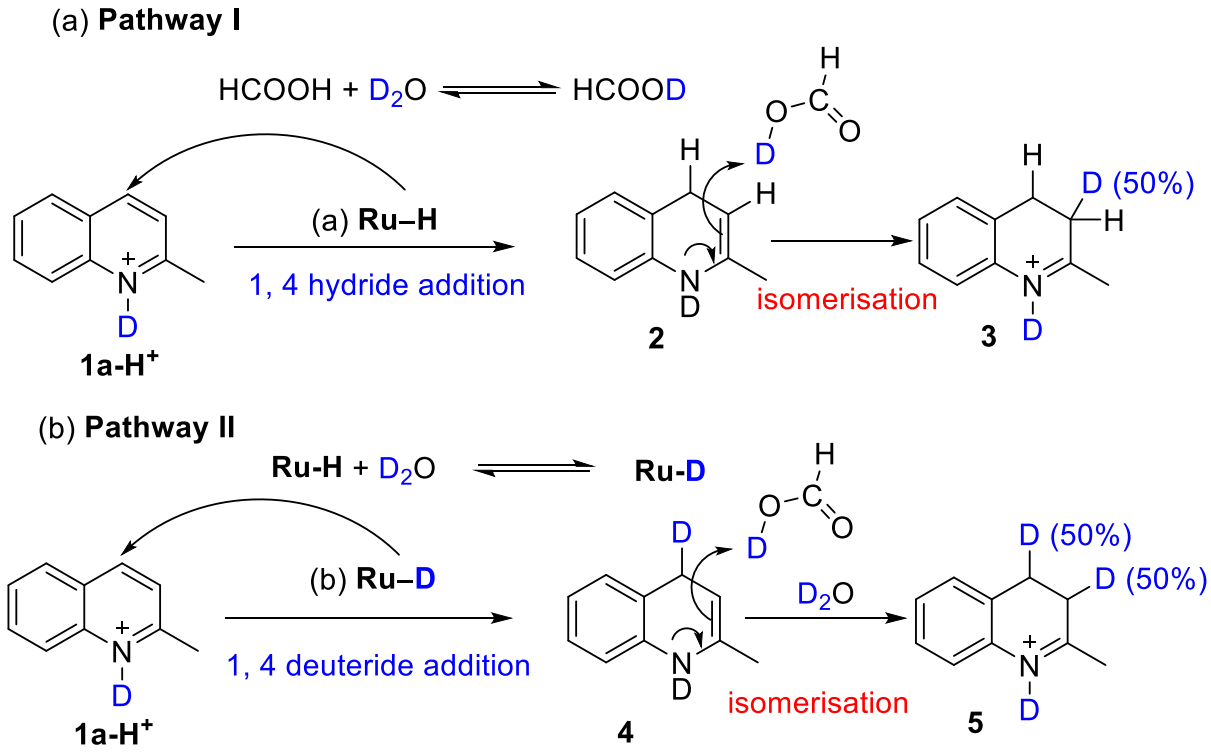
S15. Control experiment IV



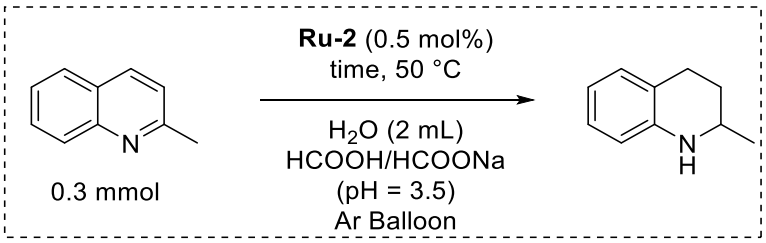
To a 25.0 mL Schlenk tube containing a stirring bar, substrate (0.3 mmol) and catalyst (0.5 mol%, stock solution in D_2O) were taken. After that, the reaction vessel was evacuated by applying vacuum and refilled from a balloon attached at the top of the condenser. The same procedure was repeated three times. After that 1 mL D_2O having HCO_2H (10 eq.), was added in to this reaction vessel. The mixture was stirred at 50 °C for desired 12 h. After the reaction was completed, the solution was neutralized with a saturated sodium bicarbonate solution. The aqueous layer was extracted with ethyl acetate (5 mL × 2). The organic layer was collected and dried over anhydrous sodium sulfate. Filtration, followed by solvent evaporation under reduced pressure, obtained the crude mixture. The yield of the crude product was calculated by ^{1}H NMR spectroscopy using mesitylene as an internal standard.

Explanation for the deuterium incorporation

Transfer hydrogenation of the protonated 2-methyl quinoline can be possible by the two competitive pathways. In pathway I, formic acid undergoes deuterium exchange with the solvent (D_2O) molecule to form HCOOD. Now after the first hydride transfer (by **Ru-H**, 1, 4 hydride addition pathway), it can undergo protonation at C3 position to form **3** with 50% D level at C3. Whereas in pathway II, **Ru-H** can undergo deuterium exchange to form **Ru-D**. Now this **Ru-D** can undergo deuteride transfer (by **Ru-D**, 1, 4 hydride addition pathway) to form **4** with 50% D level at C4. Finally, the protonation at C3 position to form **5** with 50% D level at C3. In our case, we have found only exclusive deuterium incorporation at C3 not in C4 , which indicates that there is no exchange between ruthenium hydride and D_2O.



S16 Time-dependent progress of Transfer hydrogenation of 1a



To a 25 mL Schlenk tube, the mixture of quinoline (0.3 mmol), catalyst (0.5 mol%, 0.0015 mmol, 100 µL stock solution in H_2O) and HCOOH/HCOONa buffer solution (pH = 3.5, 2 mL) was added. The mixture was stirred at the desired temperature for the desired time under Ar. After the reaction was completed, the mixture was neutralized with a saturated solution of sodium bicarbonate whereupon an effervescence of carbon dioxide was observed. Then the reaction mixture was diluted with H_2O (5.0 mL), and extracted with EtOAc (5.0 mL × 3). The organic extract was washed with brine (5.0 mL × 2) and dried over anhydrous Na_2SO_4. After evaporation of EtOAc under vacuum, the yield of the product was determined by ^1H NMR spectroscopy using mesitylene (10 µL) as an internal standard.

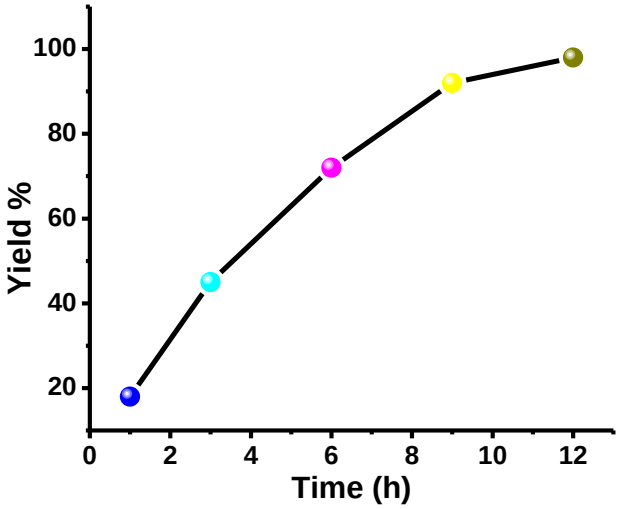


Fig. S16. The five-time points were calculated from five separated reactions that were stopped at the corresponding time. The same catalyst stock solution was used for the different time-dependent studies.

S17. Initial rate method for the reaction with Ru–2

(a) Order with respect to the substrate

A two-neck round bottom flask was charged with **1a** (in different concentrations) and catalyst **Ru–2** (0.0015 mmol, from stock solution). Then 2 mL of aqueous buffer solution (HCOOH/HCOONa, pH = 3.5) and 0.5 mL of methanol were added to the flask under the Ar balloon. After stirring for a specific time, a known volume of aliquot was withdrawn and analyzed with GC to calculate the yield of the product. The following plots were used to calculate the order.

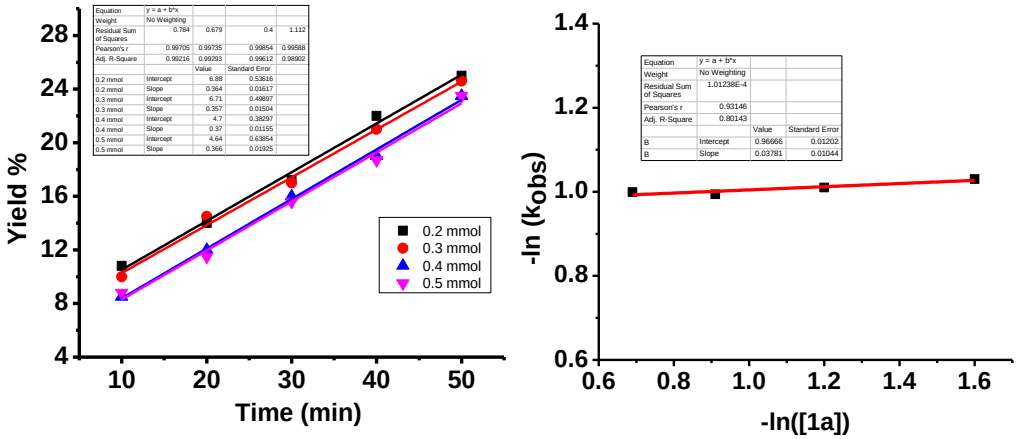


Fig. S17. (left) Plot of %yield vs time at different **1a** concentrations. (right) Plot of $-\ln(k_{obs})$ vs $-\ln(\mathbf{1a})$.

b) Order with respect to the Ru–2

A two-neck round bottom flask was charged with **Ru–2** (in different concentrations) and catalyst **1a** (0.3 mmol). Then 2 mL of aqueous buffer solution (HCOOH/HCOONa, pH = 3.5) and 0.5 mL of methanol were added to the flask under the Ar balloon. After stirring for a

specific time, a known volume of aliquot was withdrawn and analyzed with GC to calculate the yield of the product. The following plots were used to calculate the order.

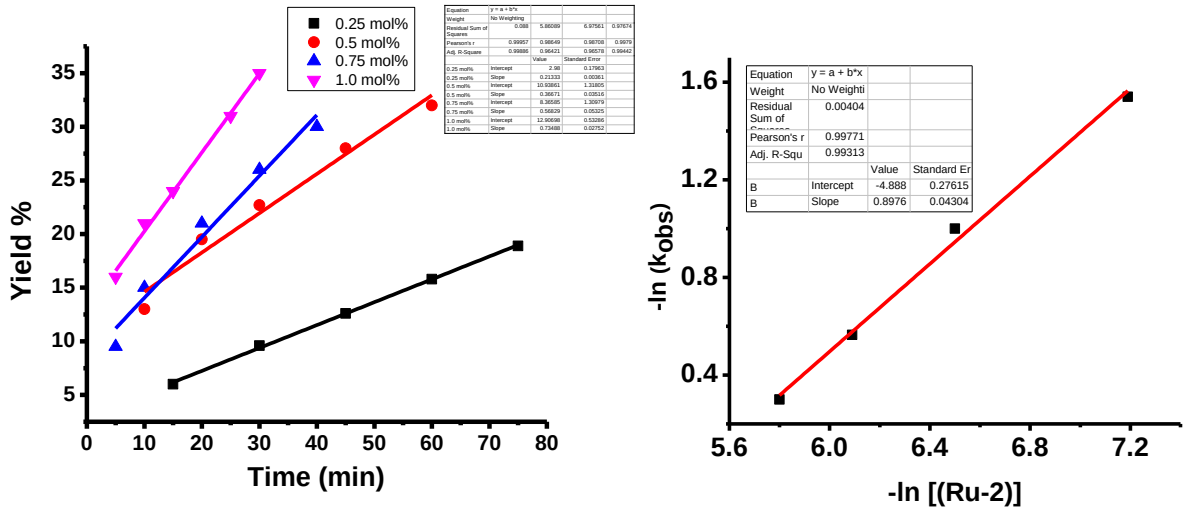


Fig. S18. (left) Plot of %yield vs time at different **Ru–2** concentrations. (right) Plot of −ln(k_{obs}) vs −ln(**Ru–2**).

Rate = k_{obs} [**Ru-2**]^1 [**1a**]^0 [HCOOH + HCOONa], k' = k_{obs} [HCOOH+HCOONa]

Rate = k' [**Ru-2**] [**1a**]

S18 Investigating the presence of the *p*-cymene ligand bound to ruthenium centre in Ru-2 during the catalytic reaction

A standard transfer hydrogenation reaction was carried out with **Ru-2**. After completion of the reaction, all the organic compounds were separated out using ethyl acetate (5 mL x 2). Then the aqueous part was extracted with CH_2Cl_2 (5 x 2 mL). The CH_2Cl_2 extract was collected and dried over anhydrous sodium sulfate. Filtration, followed by solvent evaporation under reduced pressure provided a solid residue. The residue was subjected to ^{1}H NMR spectroscopy and mass spectrometry analysis. Finally, the identity of the compound has been confirmed by ^{1}H NMR spectroscopy. The comparison of the spectra of the catalyst before and after the reaction is provided below. Further confirmation of **Ru-2** was done by ESI-HRMS of the solution after catalysis. In addition, the initially separated organic layer was also examined for the presence or absence of free *para*-cymene.

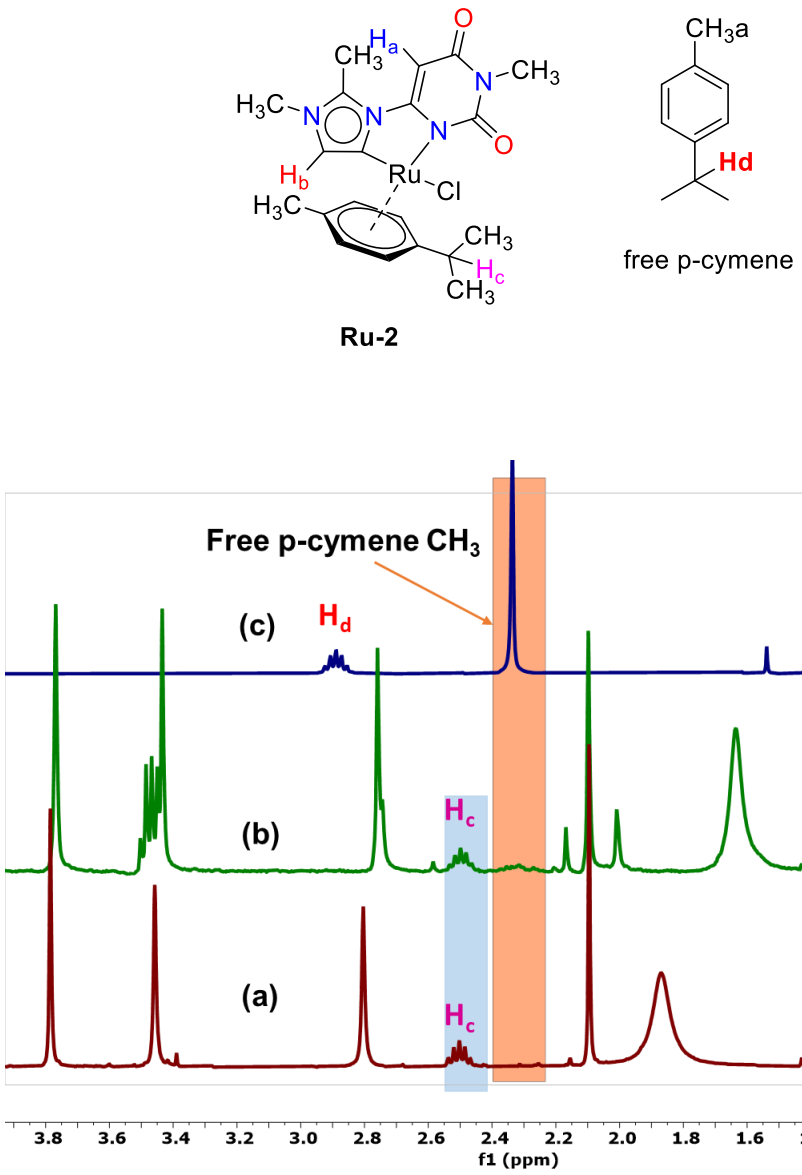


Fig. S19 ^{1}H NMR stacked plot up field region of (a) pure **Ru-2** (b) species after catalysis (c) pure free *p*-cymene ($CDCl_3$, 400 MHz).

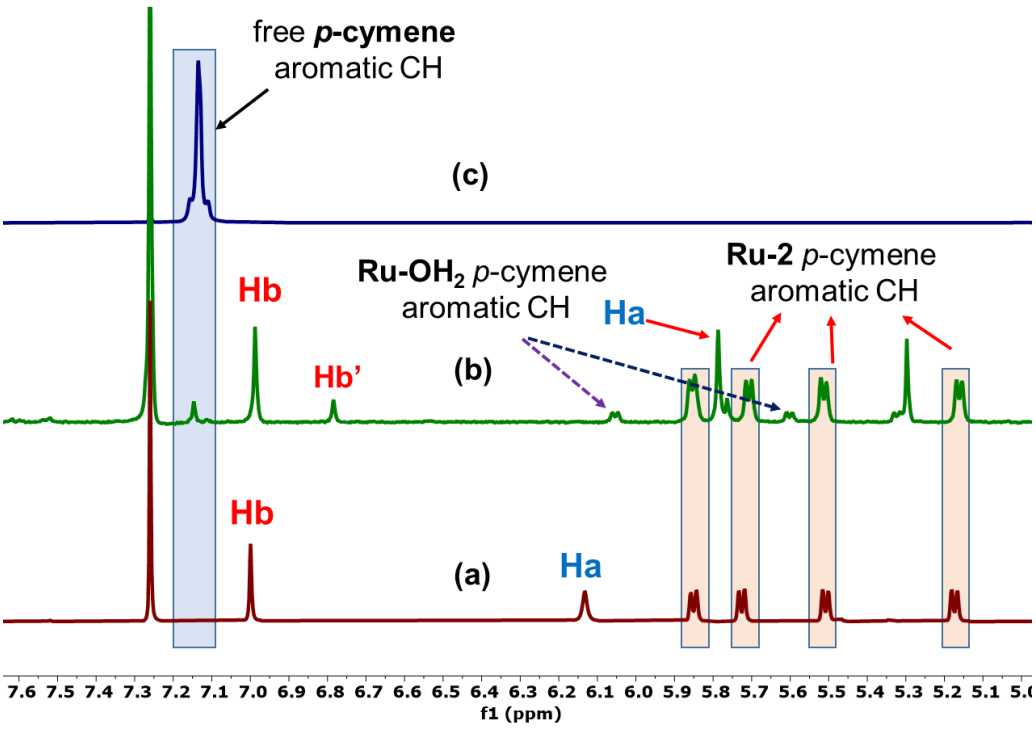


Fig. S20 ^{1}H NMR stacked plot down field region of (a) pure **Ru-2** (b) species after catalysis (c) pure free *p*-cymene ($CDCl_3$, 400 MHz).

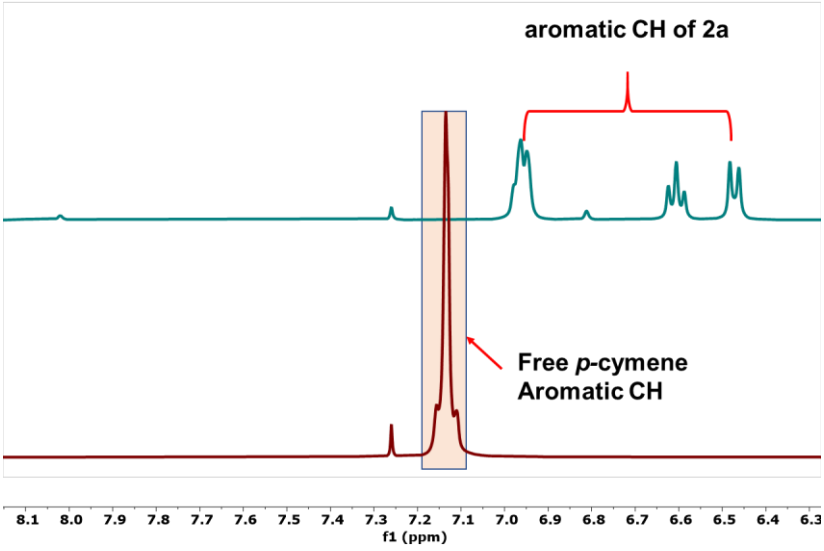


Fig. S21 ^{1}H NMR stacked plot in the downfield region of (a) pure free *p*-cymene (b) organic layer after catalysis ($CDCl_3$, 400 MHz).

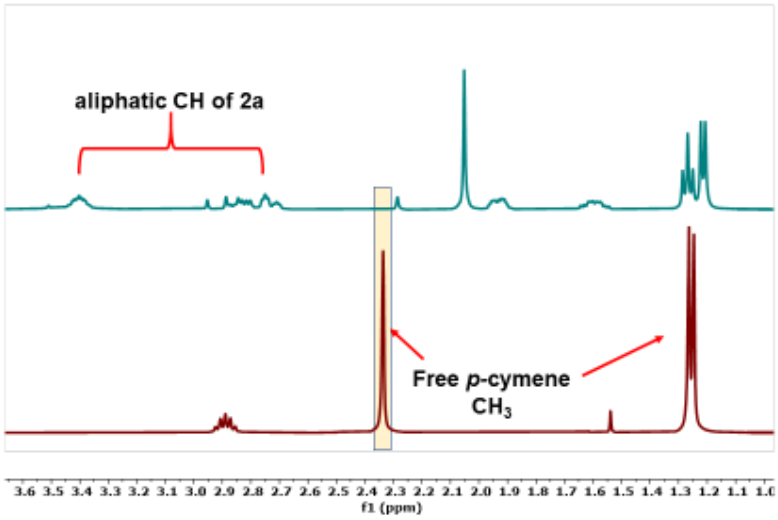


Fig. S22 ^{1}H NMR stacked plot in the upfield region of (a) pure free *p*-cymene in (b) organic layer after catalysis ($CDCl_3$, 400 MHz).

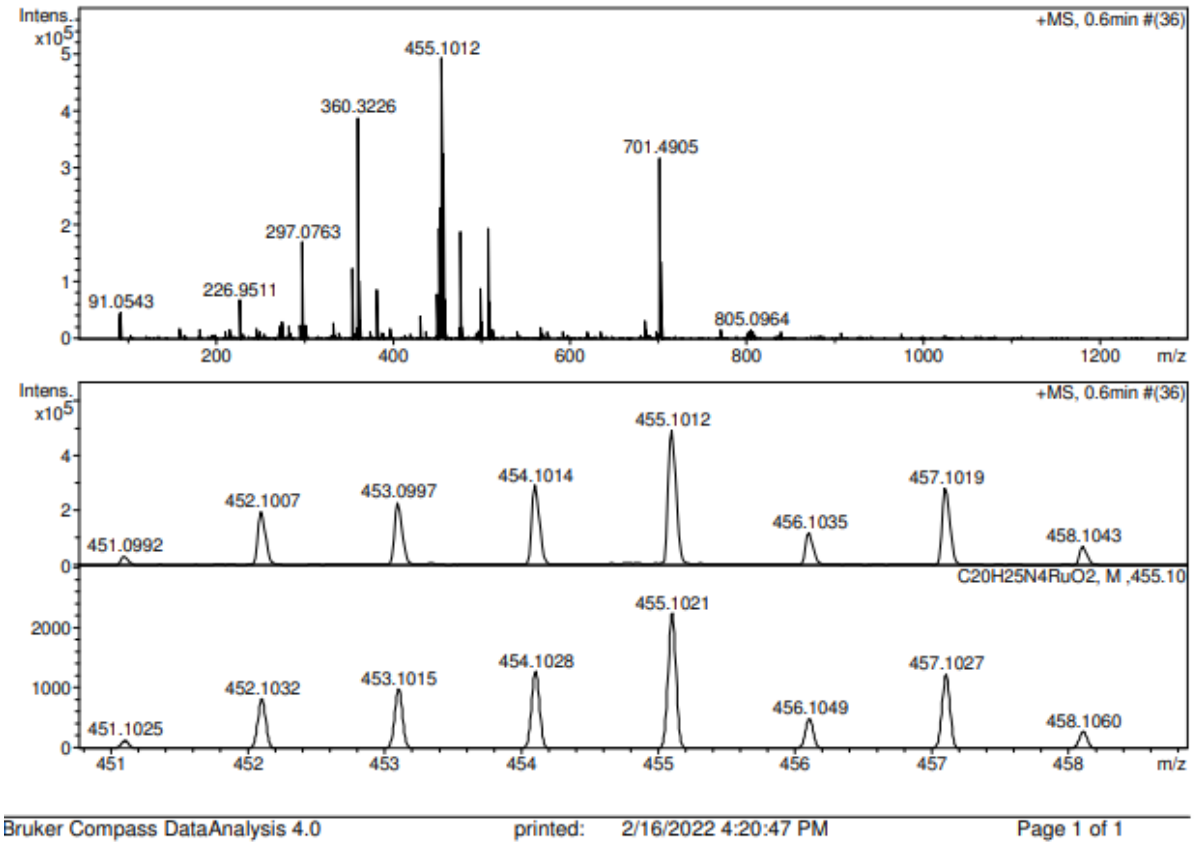


Fig. S23 HRMS of the residue (ESI, positive ion) in CH_3CN after catalysis *m/z*= 455.1012 (calculated= 455.1053) for $[C_{20}H_{25}N_4O_2Ru]^+$).

fragment	*m/z* value	present
L-Ru-(*p*-cymene)	455.1053	Yes
L-Ru-(*p*-cymene)(CH_3CN)	496.1318	No
L-Ru (CH_3CN)$_3$	444.07544	No
L-Ru-Cl (CH_3CN)$_3$	479.0442	No
L-Ru-(CH_3CN)$_2$Cl	438.0177	No
L-Ru-(CH_3CN)$_2$	403.0488	No

In summary, from the above mass spectrometry and ^{1}H NMR spectroscopic results, it was clear that the decomposition of the catalyst during the catalysis was not going on. Possible decomposition products in the mass condition were not obtained which again indicates the robustness of the ligand backbone.

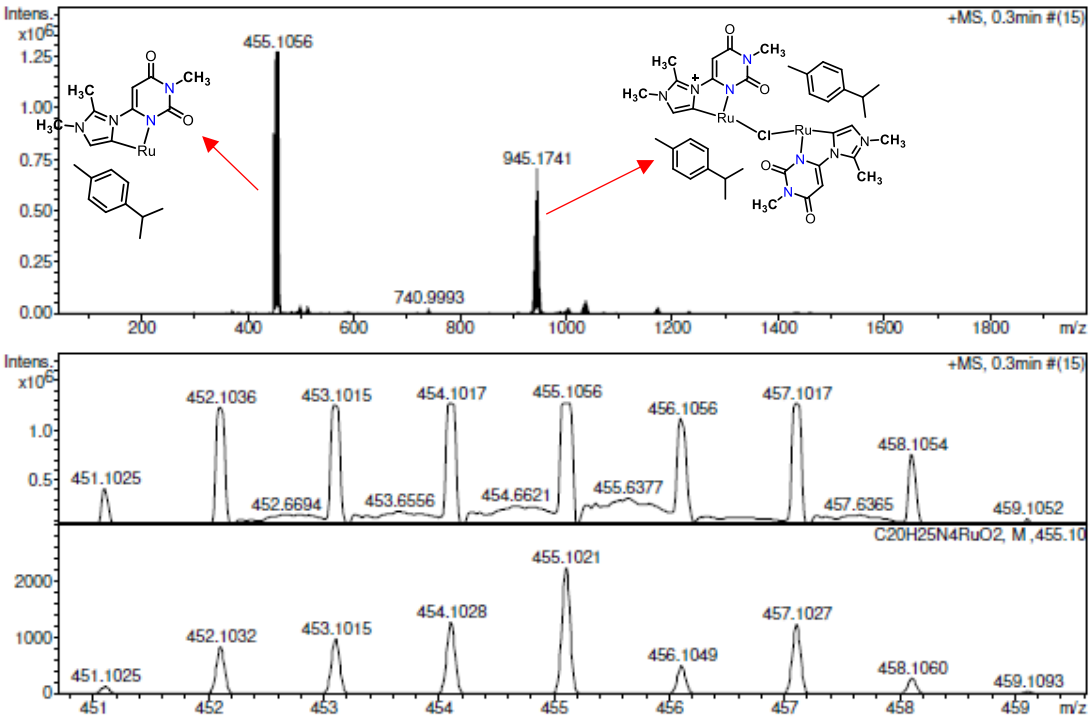


Fig. S24 HRMS of **Ru-2** (ESI, positive ion) in CH_3CN before catalysis *m/z*= 455.1012 (calculated= 455.1053) for $[C_{20}H_{25}N_4O_2Ru]^+$).

S19. Computational details

The density functional theory (DFT)[S4] calculations were carried out using the B3LYP functional. The Pople diffused basis set 6-31g(d,p) was used for non-metals [S5-S7](C, H, N, O, and Cl) and the LANL2DZ[S8-S9] with effective core potential (ECPs) was used for metal (Ru). Non-covalent interactions were considered utilizing Grimme's DFT-D3 potential. [S10] The SMD solvation model[S11] was used to optimise all of the structures in the presence of a water solvent. All of the transition states (TSs) were optimised and confirmed by the presence of only one imaginary vibrational frequency.

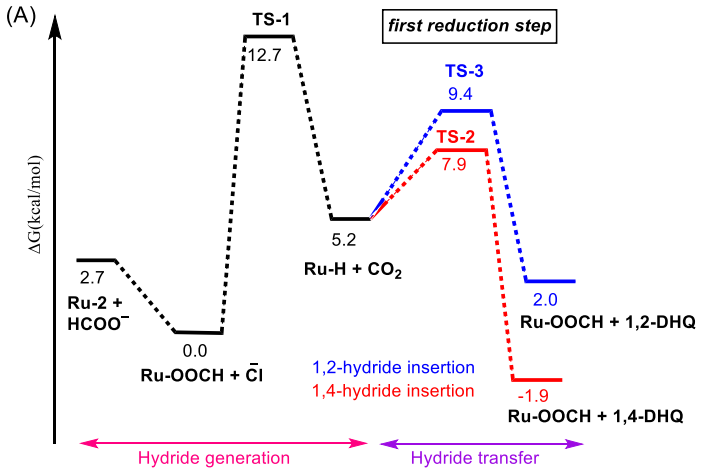
S20. References

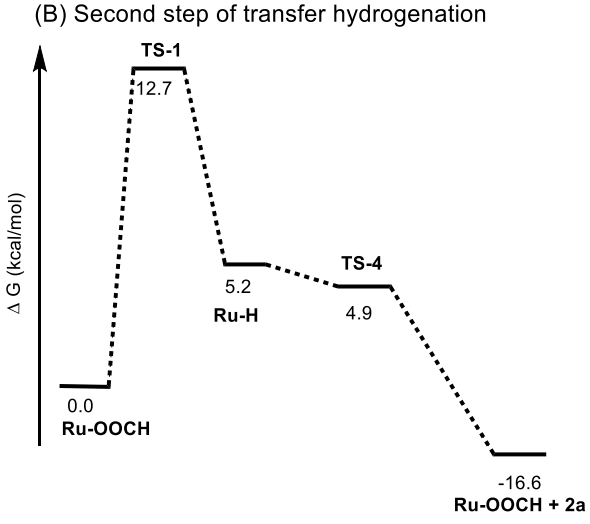
S1. B. Maji and J. Choudhury, *Chem. Commun*., 2019, **55**, 4574-4577.
S2. S. Betanzos-Lara, A. Habtemariam and P. J. Sadler, *J. Mex. Chem. Soc*., 2013, **57**, 160-168.
S3. R. He, T. Ma, J. Cheng, B. Jin and J. Xu, *ACS Omega*, 2021, **6**, 11260-11265.
S4. M. J. Frisch, et al., Gaussian Revision D.01, *Gaussian, Inc., Wallingford CT*, 2013.
S5. W. J. Hehre, R. Ditchfield and J. A. Pople, *J. Chem. Phys*., 1972, **56**, 2257–2261.
S6. P. C. Hariharan and J. A. Pople, *Theor. Chim. Acta*, 1973, **28**, 213–222.
S7. R. Krishnan, J. S. Binkley, R. Seeger and J. A. Pople, *J. Chem. Phys*., 1980, **72**, 650–654
S8 P. J. Hay and W. R. Wadt, *J. Chem. Phys*., 1985, **82,** 270–283.
S9. P. J. Hay and W. R. Wadt, *J. Chem. Phys*., 1985, **82**, 299–310.
S10. S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *J. Chem. Phys*.,2010, **132**, 154104–154123
S11. A. V. Marenich, C. J. Cramer and D. G. Truhlar, *J. Phys.Chem. B*, 2009, **113**, 6378–6396.

S21. Absolute Calculation Energies, Enthalpies, imaginary frequency and Free Energies

ENTRY	E	H	G	E+G	IF
1a-H$^+$	-441.744660	0.186996	0.143837	-441.600823	
1,4-DHQ	-442.467521	0.196145	0.152013	-442.315508	
1,2-Im$^+$	-442.945761	0.209962	0.166204	-442.779557	
2a	-443.693506	0.220370	0.175940	-443.517566	
4b	-441.741868	0.187186	0.144922	-441.596947	
4c	-442.462522	0.196535	0.152893	-442.309629	
4d	-442.463445	0.196647	0.153157	-442.310288	
CO_2	-188.573394	0.015002	-0.009322	-188.582716	
1c´	-442.462711	0.196658	0.153569	-442.309143	
Cl$^-$	-460.356440	0.002360	-0.015023	-460.371463	

$HCOO^-$	-189.291743	0.024569	-0.002513	-189.294256	
Ru-2	-1700.956746	0.458874	0.371533	-1700.585213	
Ru-OOCH	-1429.901906	0.482886	0.389655	-1429.512250	
TS-1	-1429.877214	0.477764	0.385264	-1429.491950	-453.13
Ru-H	-1241.299543	0.462971	0.378345	-1240.921198	
TS-2	-1683.064842	0.649163	0.547104	-1682.517738	-477.67
TS-3	-1683.062194	0.649964	0.546860	-1682.515334	-451.59
TS-4	-1684.269809	0.673405	0.568622	-1683.701187	-351.22
TS-6	-1683.057963	0.649518	0.546907	-1682.511056	-497.18
TS-5	-1683.062400	0.649923	0.546394	-1682.516006	-354.79





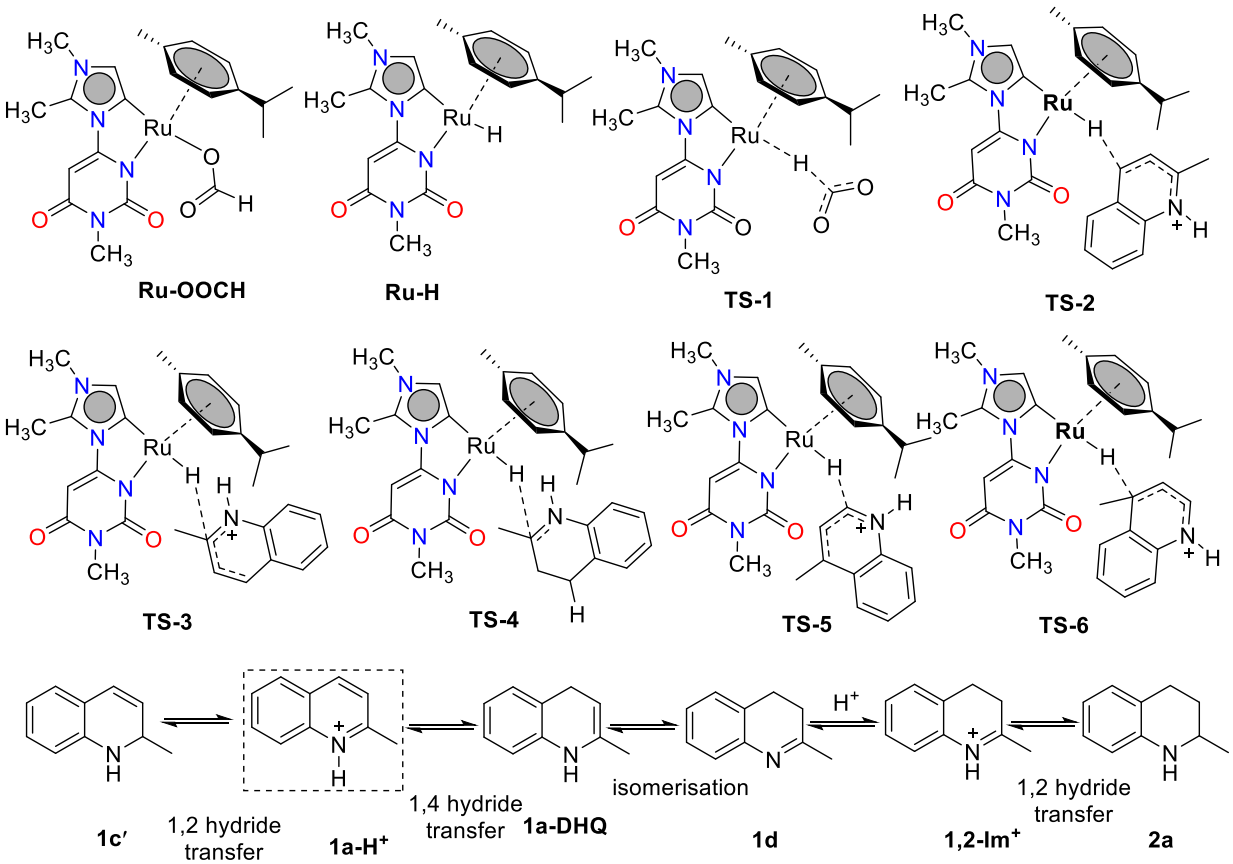


Fig. S25. Energy profile for the transfer hydrogenation of 2-methyl quinoline (A) first step of the transfer hydrogenation (B) second step of transfer hydrogenation reaction.

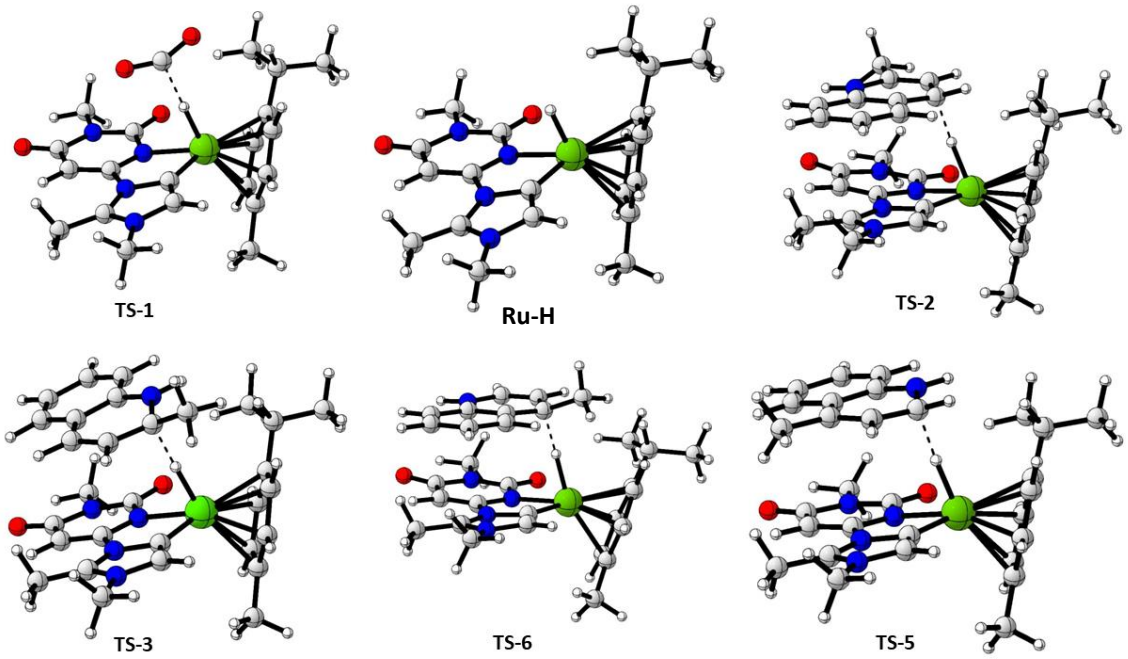


Fig. S26 Optimized structures and transition states in the catalytic cycles of the transfer hydrogenation reaction.

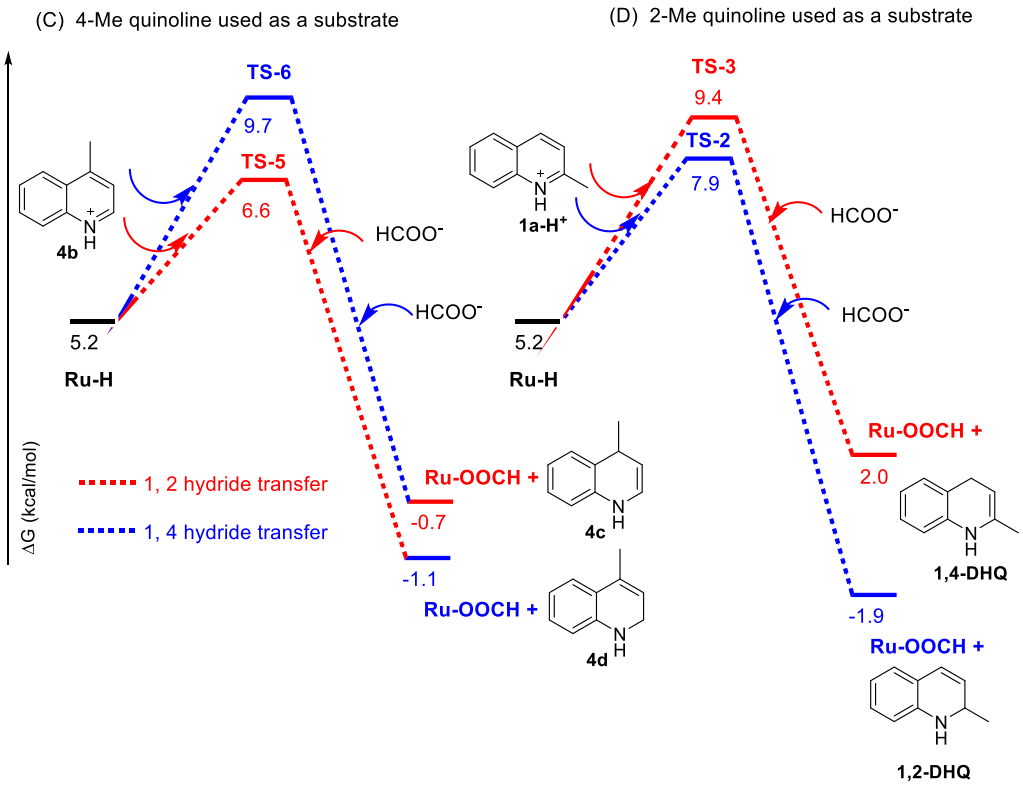


Fig. S27. Comparison energy profile for the transfer hydrogenation reaction (C) 4-methyl quinoline used as a substrate (D) 2-methyl quinoline used as a substrate.

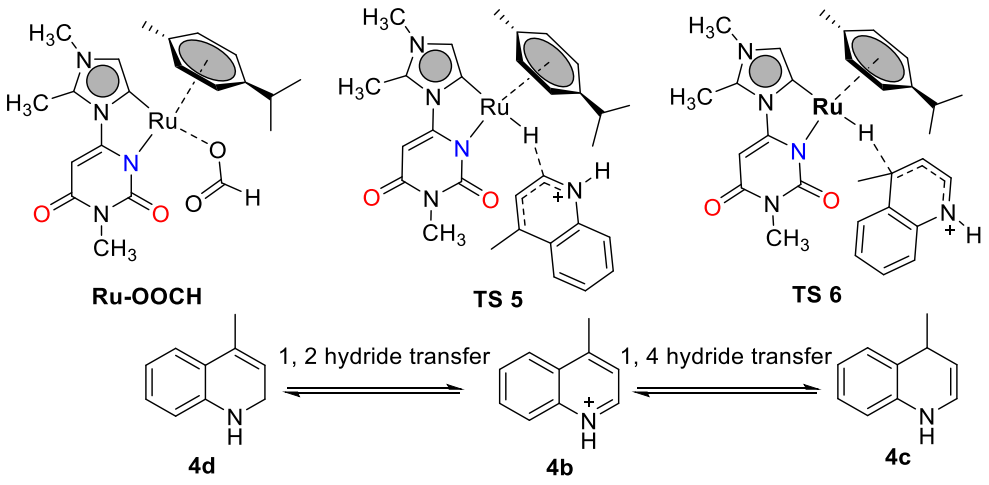


Fig. S28 Energy profile for the transfer hydrogenation of 4-methyl quinoline (red colour) 1,4-hydride transfer (blue colour) 1, 2-hydride transfer reaction.

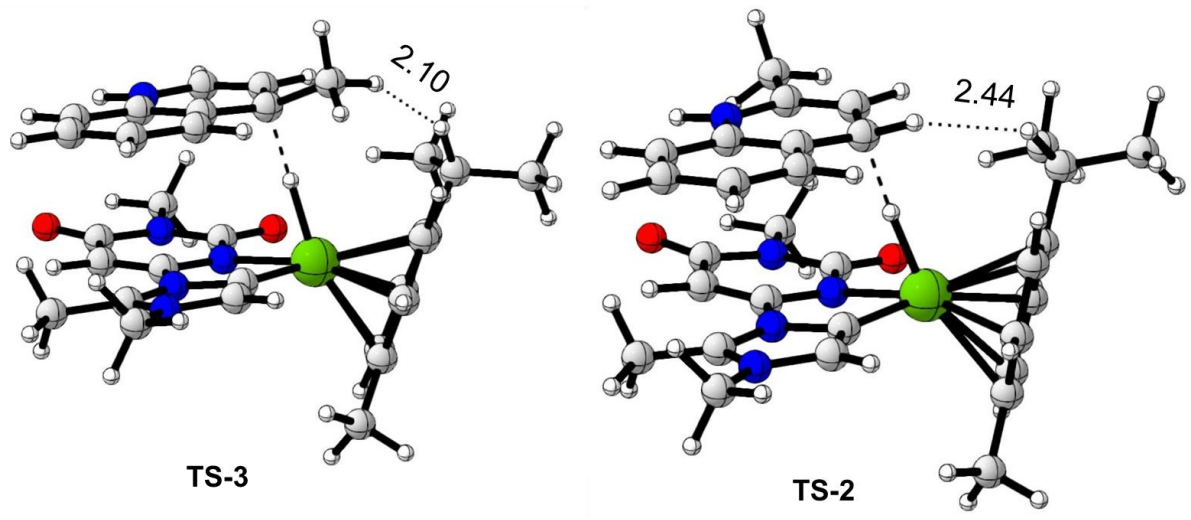


Fig. S29. Optmised structures for the 1, 4-hydride transfer. The distances are given in angstroms.

S22. ^{1}H NMR spectra of the products

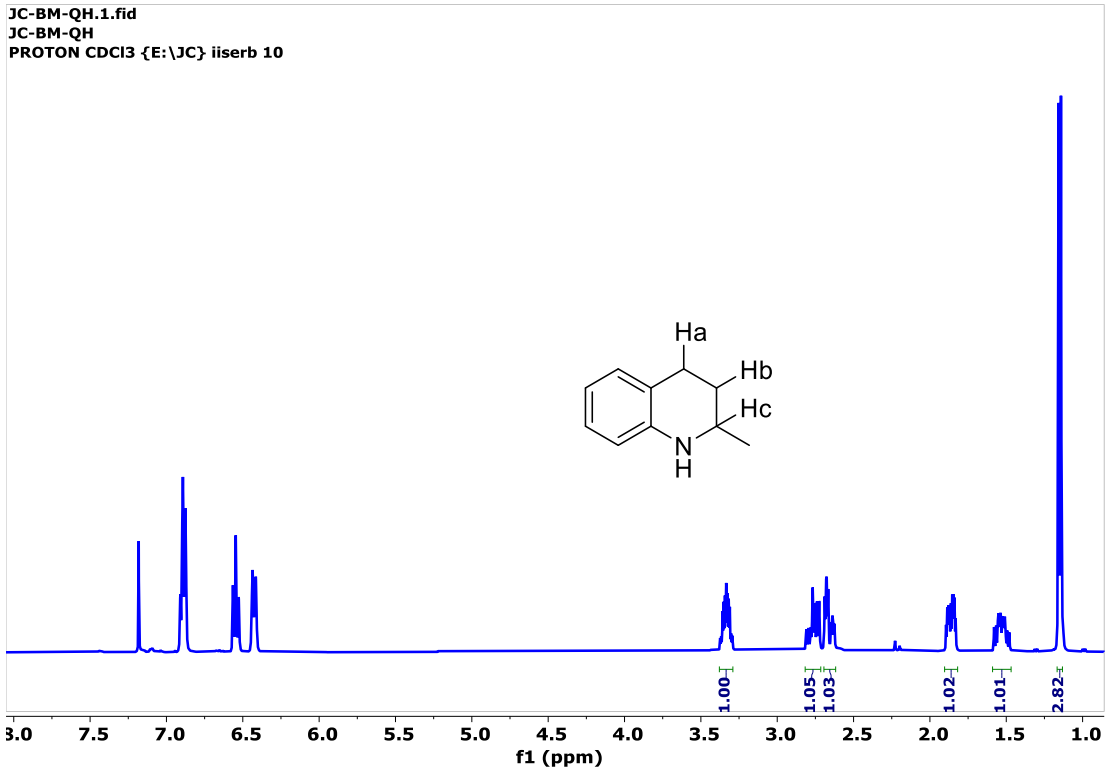


Fig. S30 ^{1}H NMR of 2-methyl-1, 2, 3, 4-tetrahydroquinoline $CDCl_3$, 400 MHz

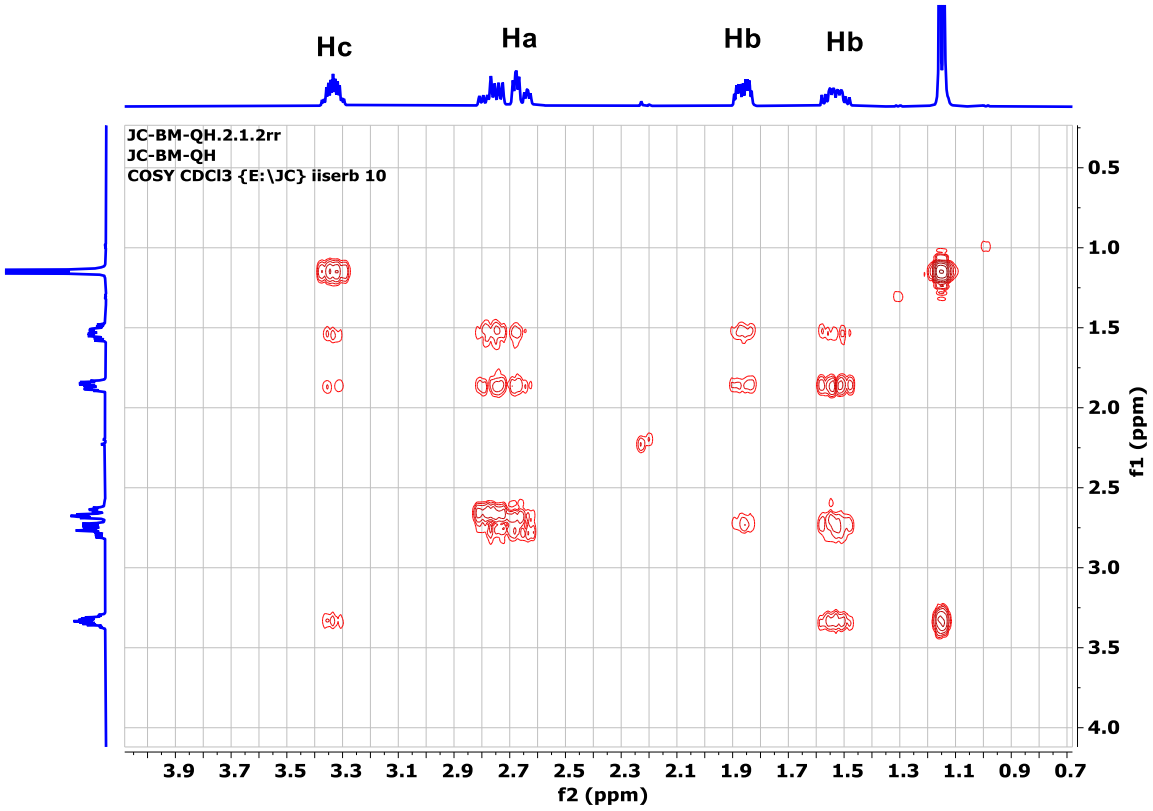


Fig. S31. ^{1}H-^{1}H COSY NMR spectrum of 2-methyl-1, 2, 3, 4-tetrahydroquinoline $CDCl_3$, 400 MHz

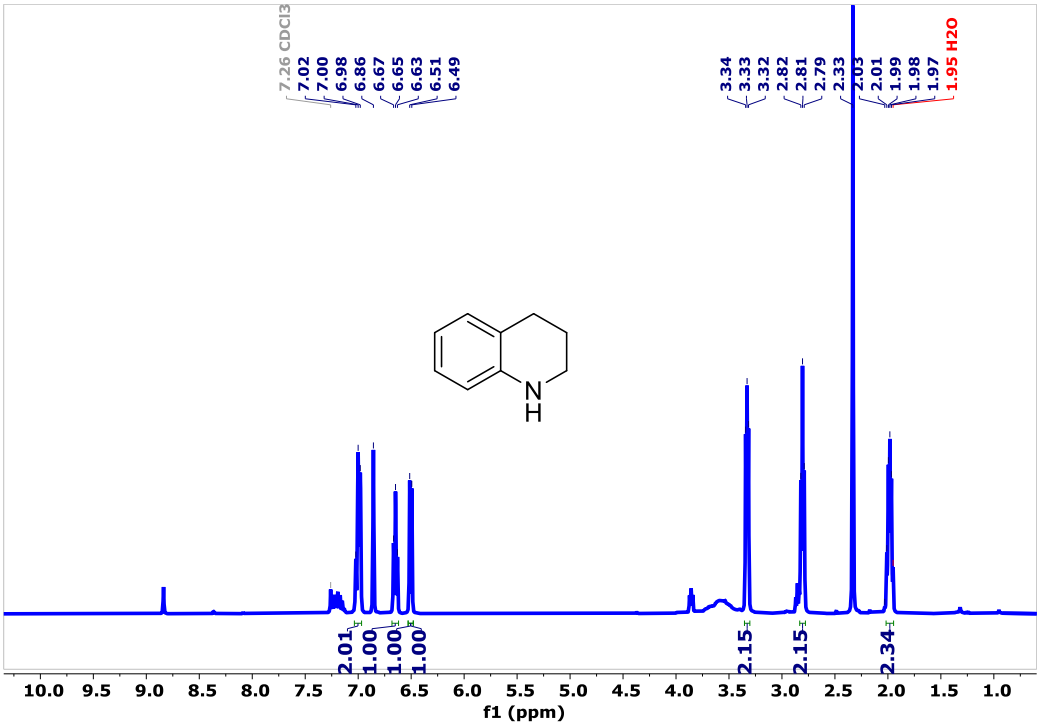


Fig. S32. ^{1}H NMR spectrum of 1, 2, 3, 4-tetrahydroquinoline $CDCl_3$, 400 MHz

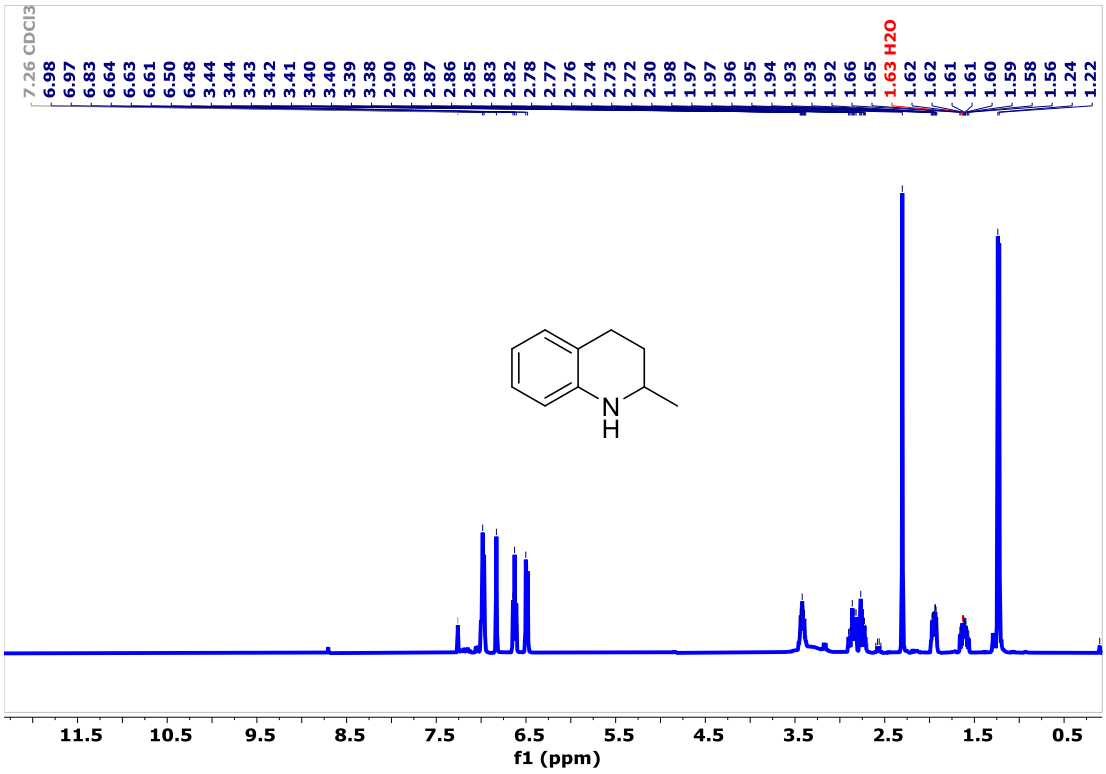


Fig. S33. ^{1}H NMR spectrum of 2-methyl-1, 2, 3, 4-tetrahydroquinoline $CDCl_3$, 400 MHz

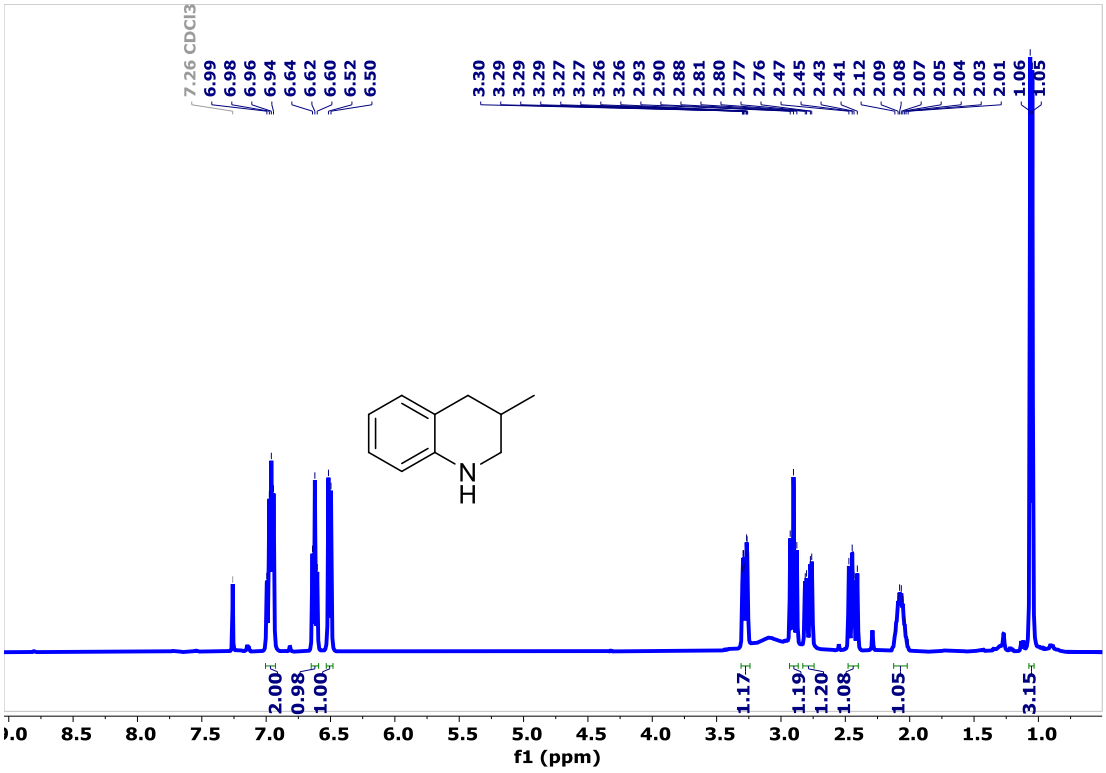


Fig. S34. [1]H NMR spectrum of 3-methyl-1, 2, 3, 4-tetrahydroquinoline $CDCl_3$, 400 MHz

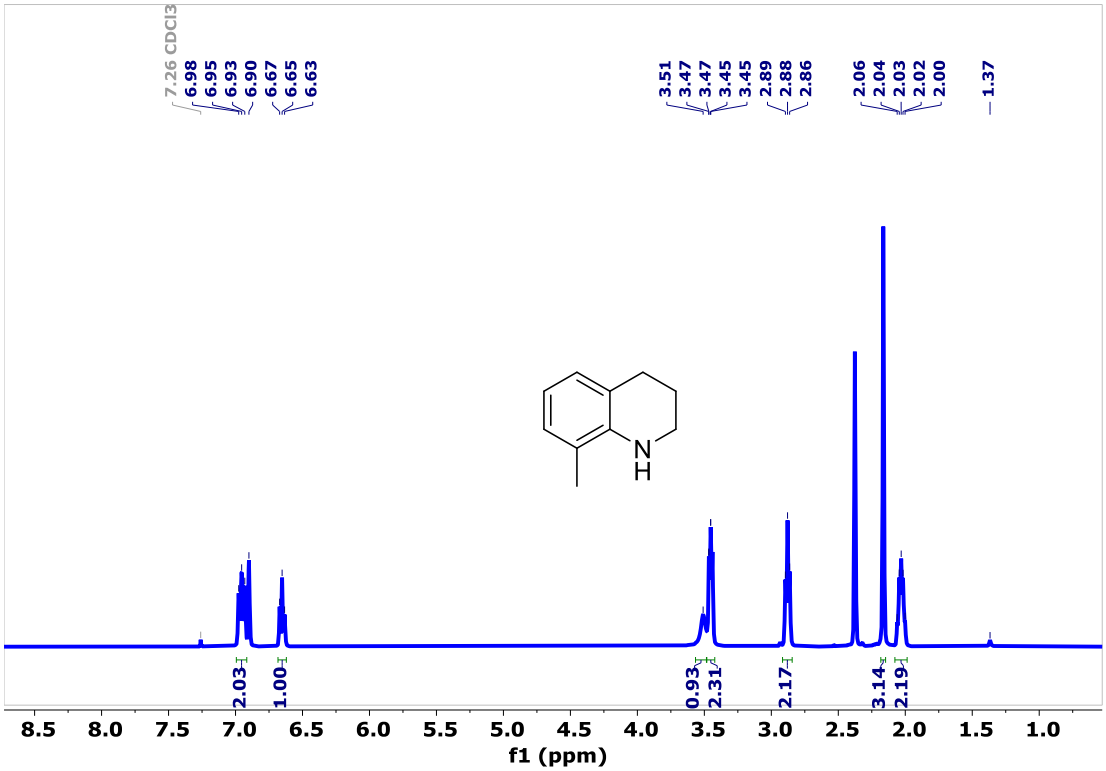


Fig. S35.[1]H NMR spectrum of 8-methyl-1, 2, 3, 4-tetrahydroquinoline $CDCl_3$, 400 MHz

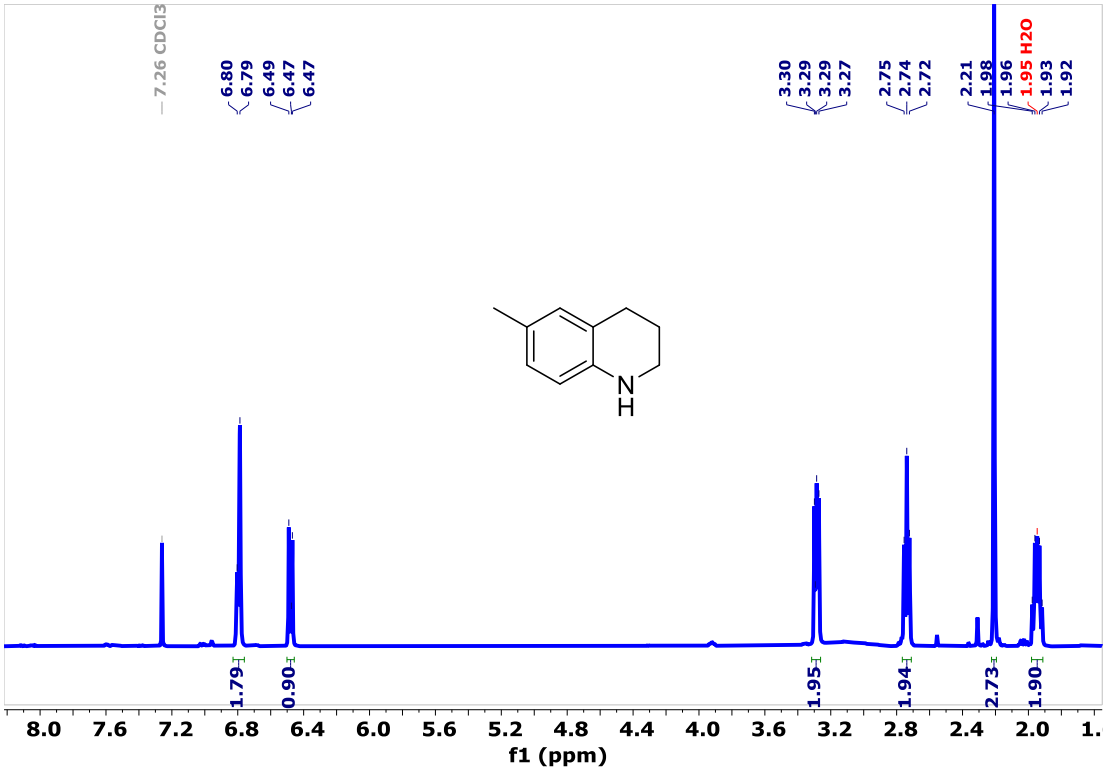


Fig. S36. [1]H NMR of 6-methyl 1, 2, 3, 4-tetrahydroquinoline $CDCl_3$, 400 MHz

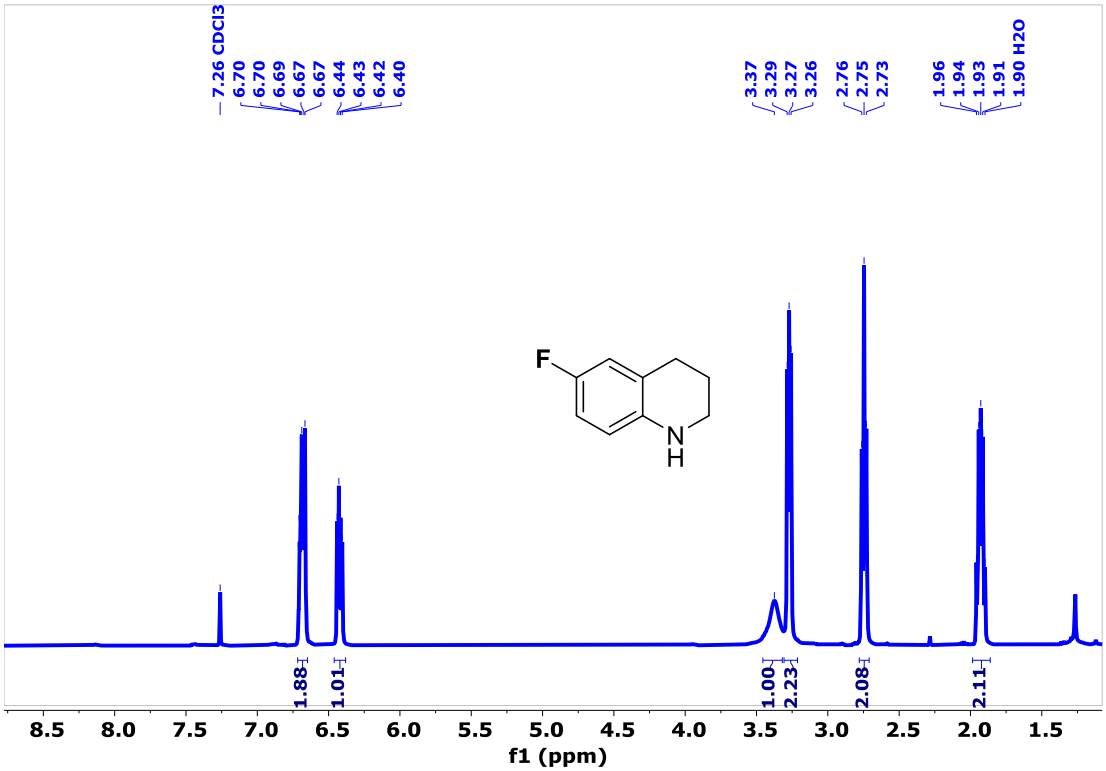


Fig. S37. [1]H NMR spectrum of NMR of 6-fluoro 1, 2, 3, 4-tetrahydroquinoline

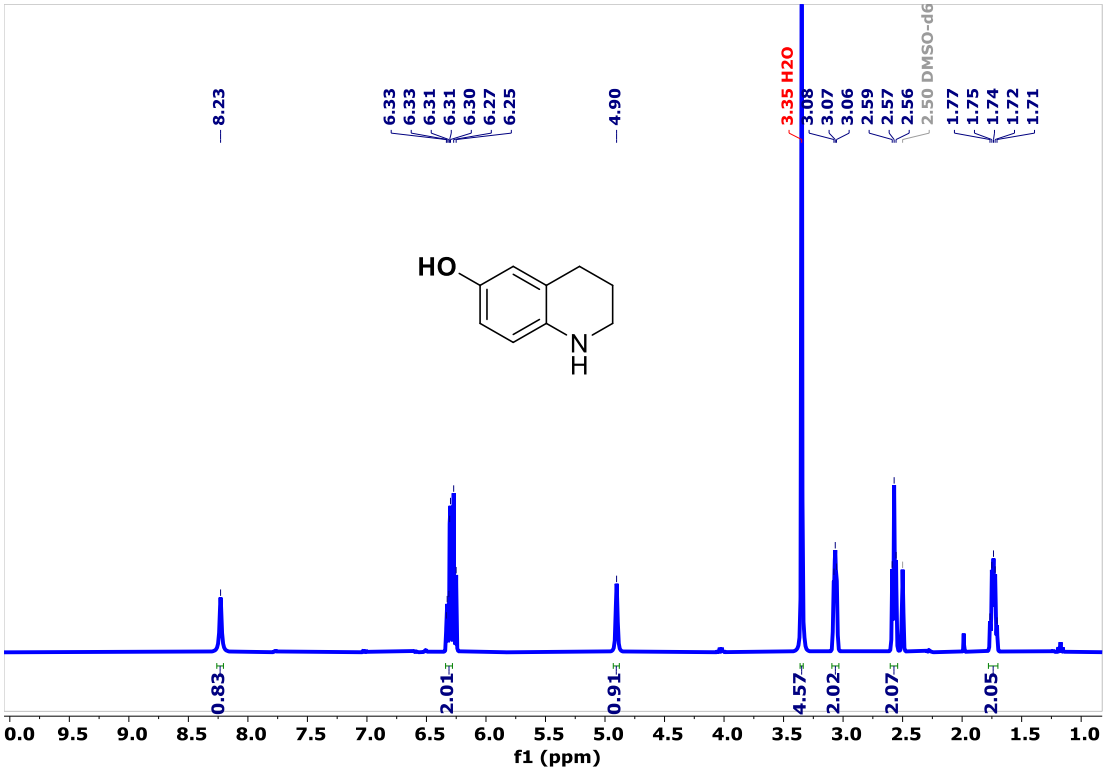


Fig. S38. ^{1}H NMR of 6-hydroxy 1, 2, 3, 4-tetrahydroquinoline DMSO-d_6, 400 MHz

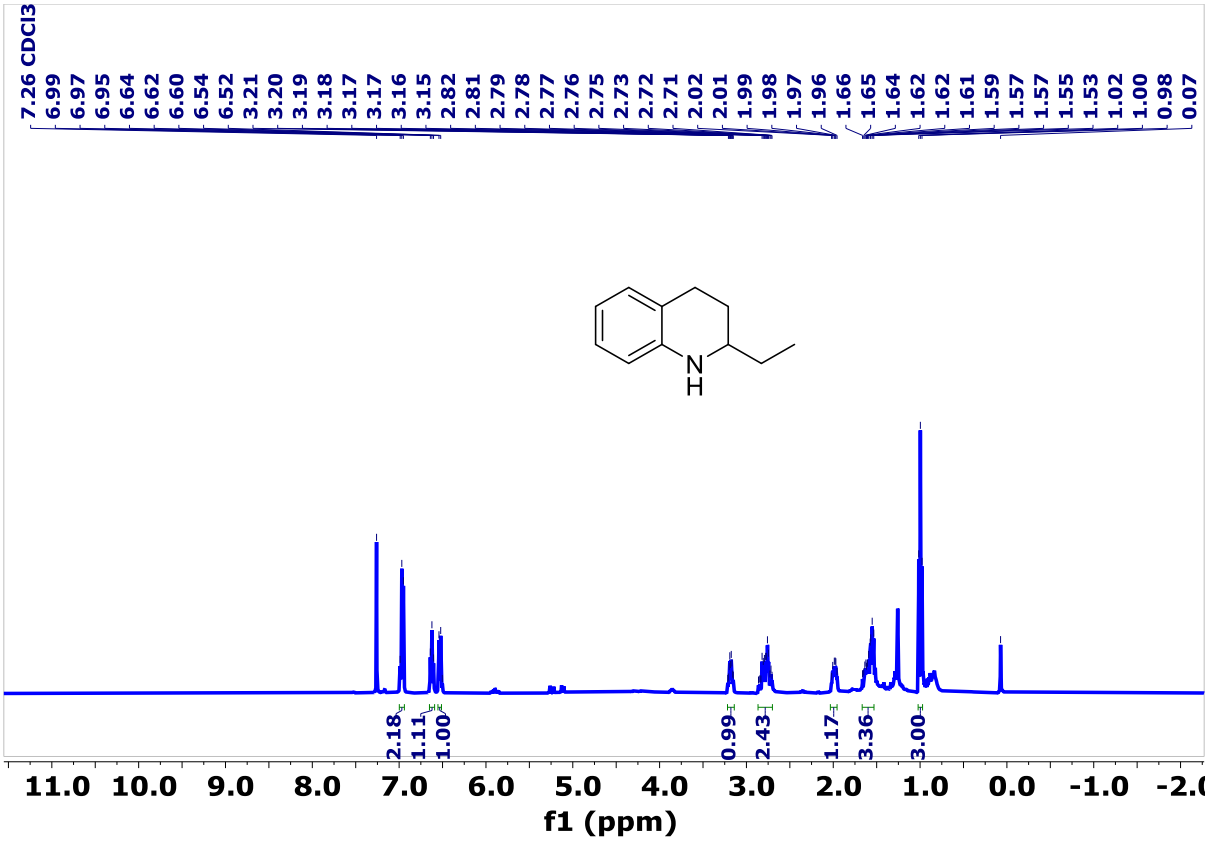


Fig. S39. ^{1}H NMR of 2-ethyl 1, 2, 3, 4-tetrahydroquinoline $CDCl_3$, 400 MHz

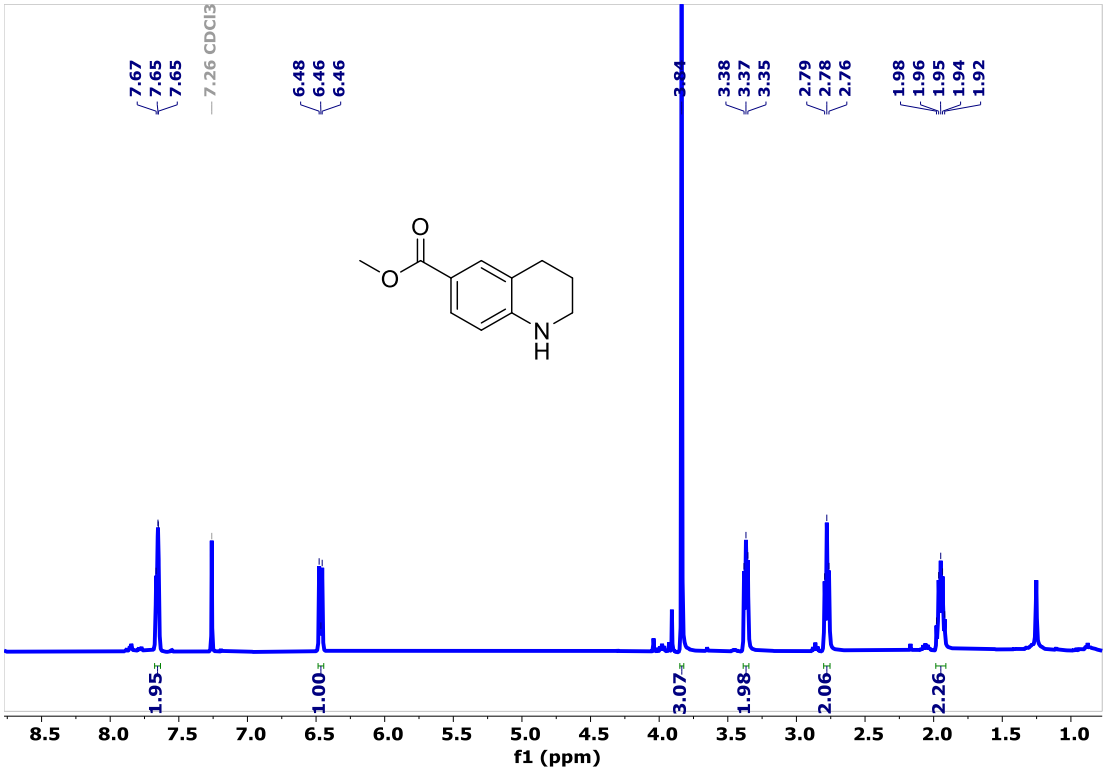


Fig. S40. [1]H NMR of 6-carboxylate 1, 2, 3, 4-tetrahydroquinoline

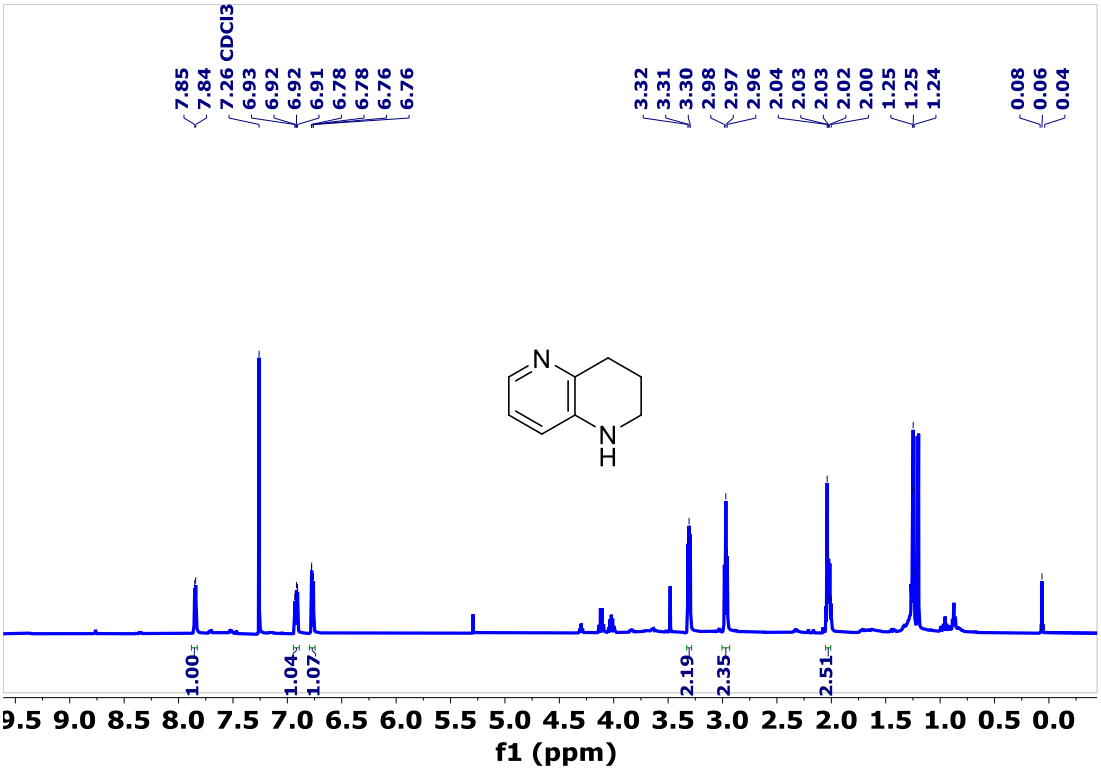


Fig. S41. [1]H NMR of 1,2,3,4-tetrahydro-1,5-naphthyridine (DMSO-d_6)

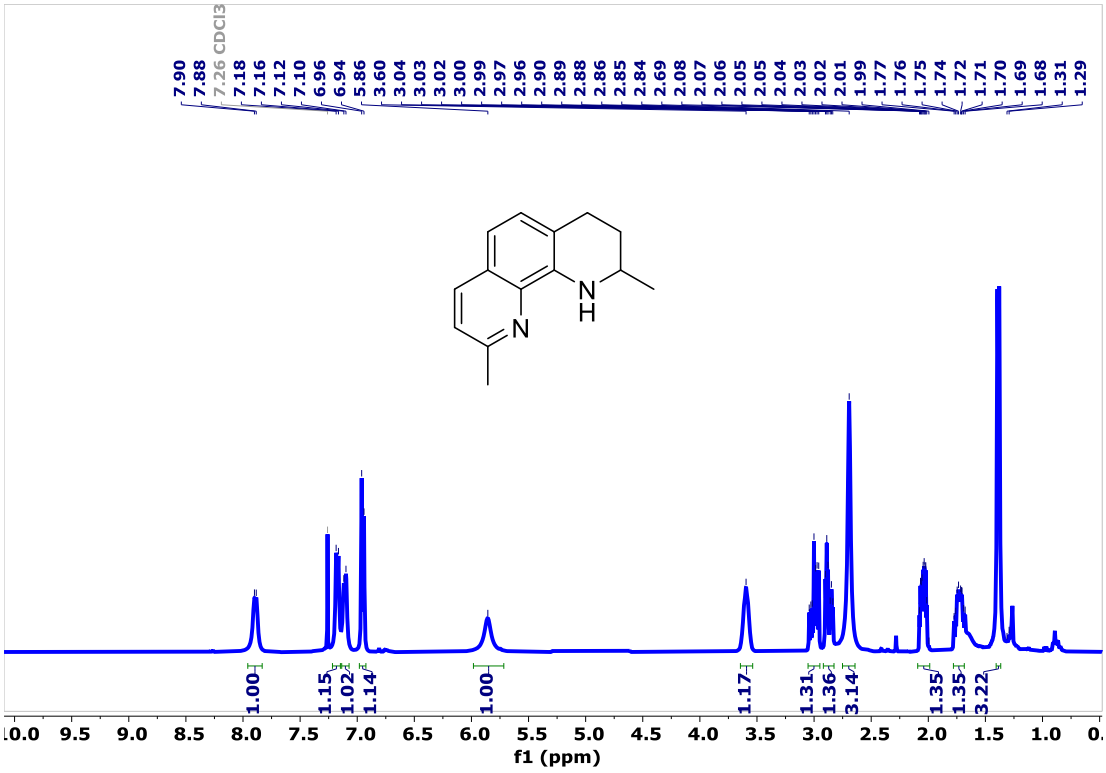


Fig. S42. [1]H NMR spectrum 2,9-dimethyl-1,2,3,4-tetrahydro-1,10-phenanthroline

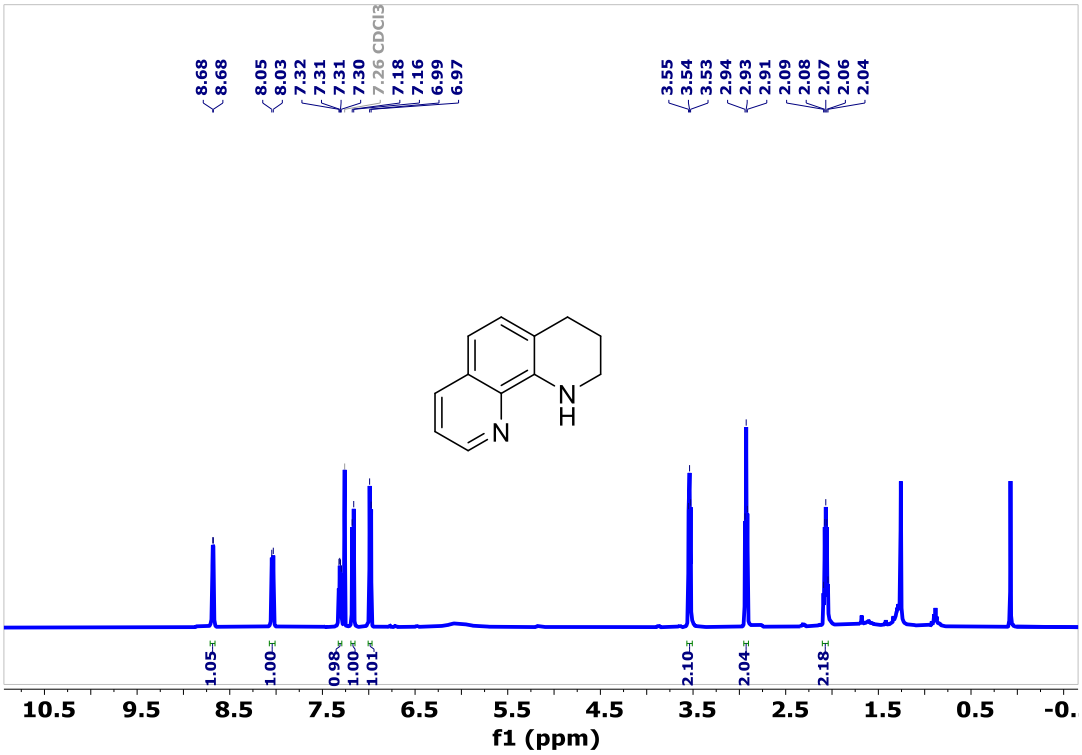


Fig. S43. [1]H NMR 1, 2, 3, 4-tetrahydrophenanthroline (DMSO-d_6)

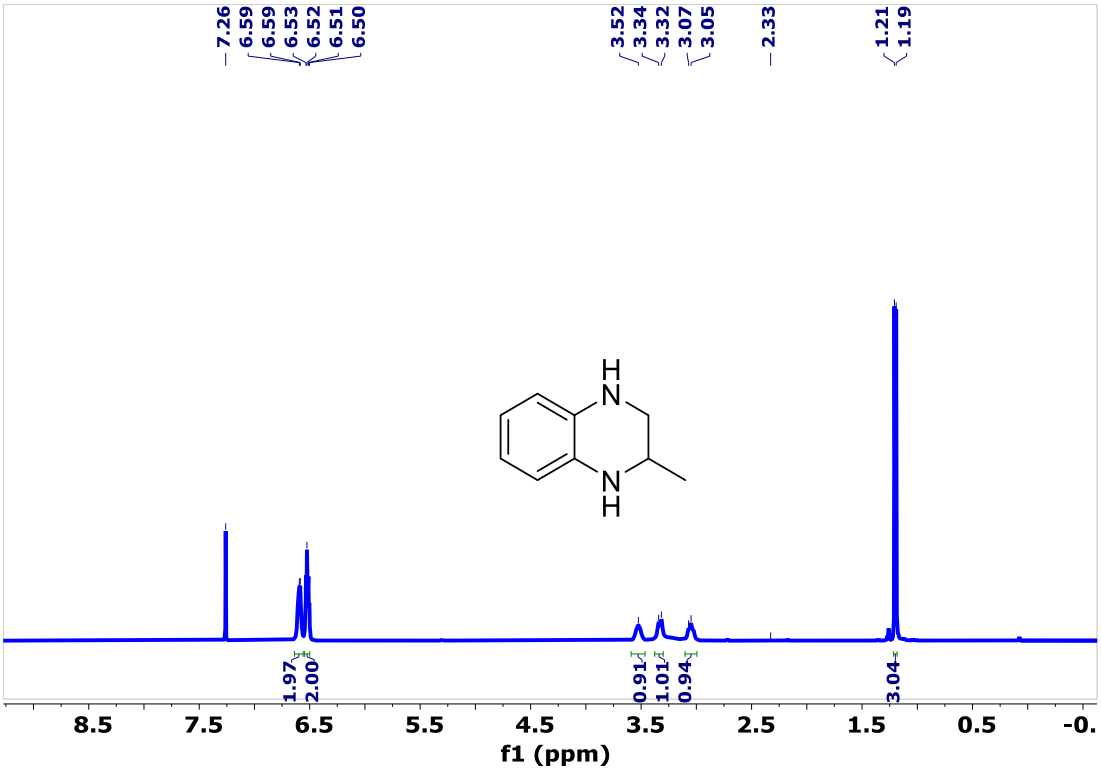


Fig. S44. ^{1}H NMR of 2-methyl 1,2,3,4-tetrahydroquinoxaline ($CDCl_3$, 400 MHz)

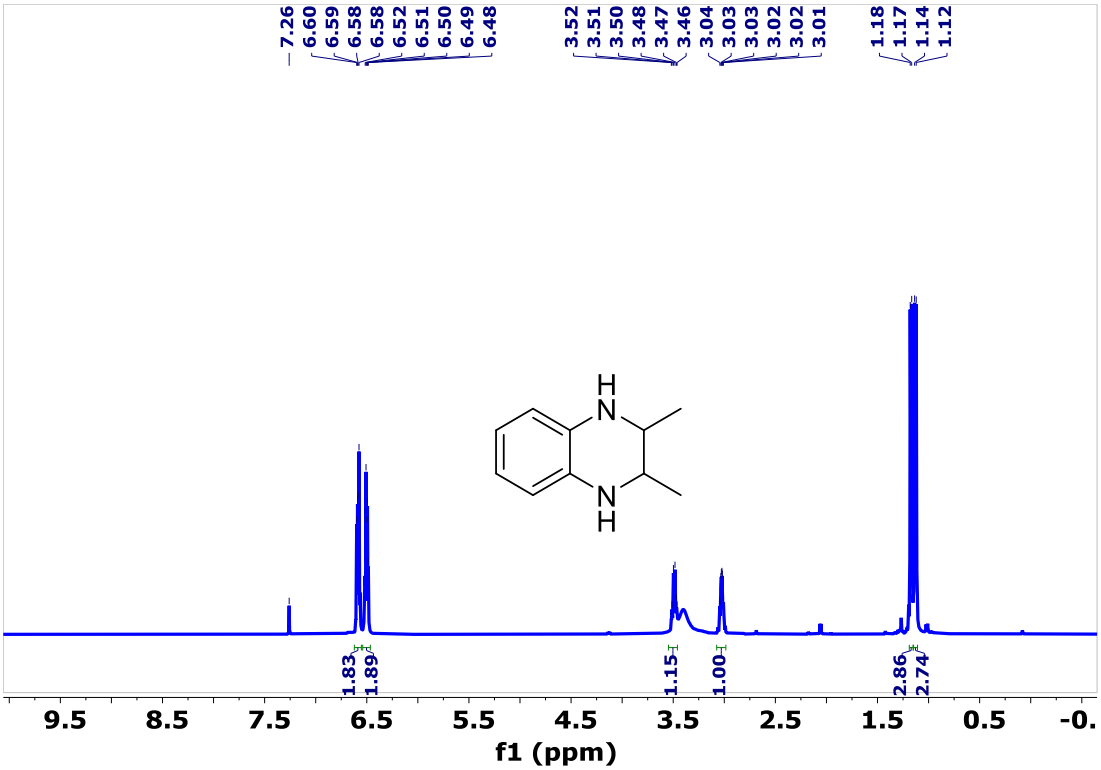


Fig. S45. ^{1}H NMR of 2, 3-dimethyl 1,2,3,4-tetrahydroquinoxaline ($CDCl_3$, 400 MHz)

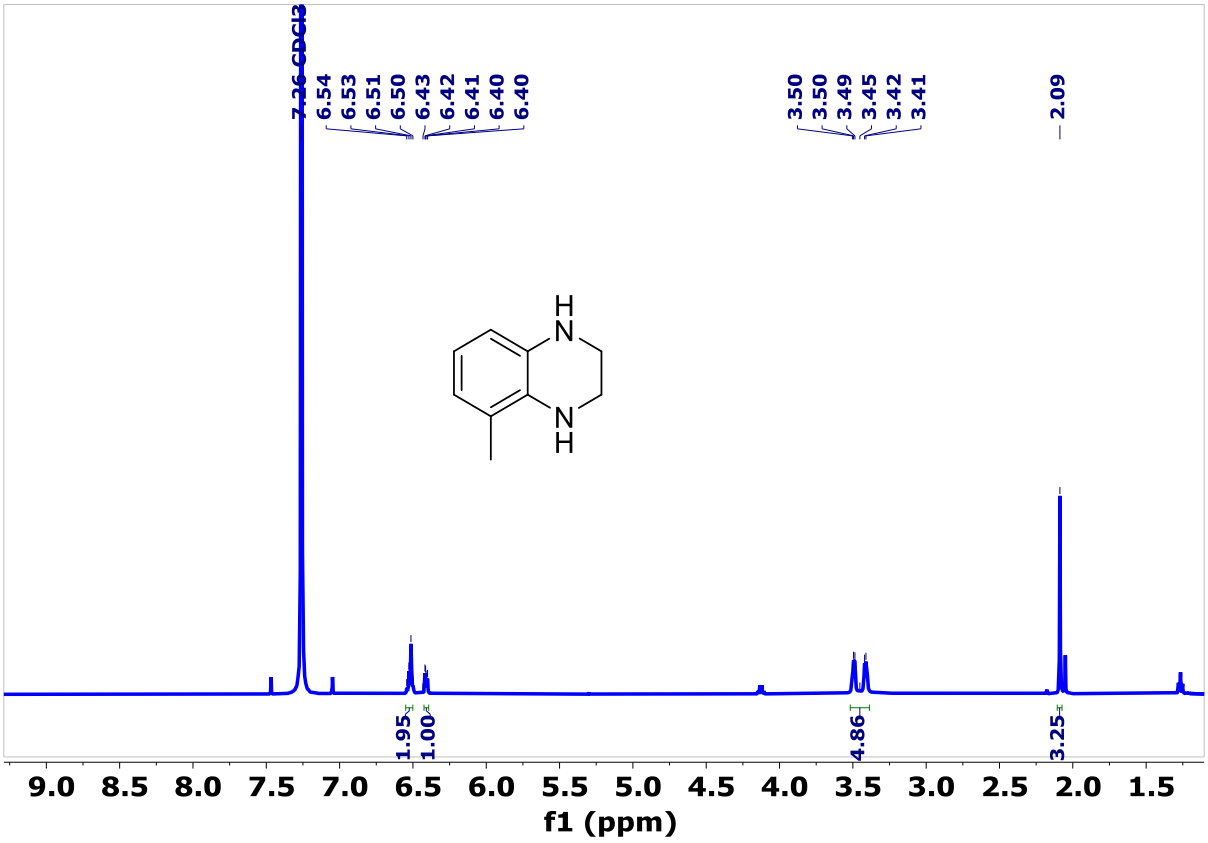


Fig. S46. ^{1}H NMR of 5-methyl 1,2,3,4-tetrahydroquinoxaline ($CDCl_3$, 400 MHz)

S23. Calculated cartesian coordinates of all the optimized molecules and transition states

Ru-2

Ru -0.72460500 -0.50957100 -0.00867700
O -0.77774200 2.71897400 0.62789600
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C -2.64721300 -1.59274600 -0.33741400
H -2.84041100 -2.05668400 -1.29907800
C 2.68278900 2.99687100 -0.31555500
C -1.96725800 -2.32448000 0.66138700
H -1.64089100 -3.33861700 0.45534300
C -3.11345600 -0.24957300 -0.09832300
C -1.66699500 -1.73440600 1.93437200
C -3.87431600 0.46360700 -1.20146400
H -3.37364800 0.19581700 -2.14148600
C -3.86448700 1.99051700 -1.07697800
H -4.44290200 2.32358500 -0.20787800
H -4.32038100 2.43788100 -1.96567800
H -2.84836200 2.38201400 -0.97719200
C -0.92992500 -2.52183900 2.98027600
H -0.52445200 -1.86730600 3.75601300
H -0.10672700 -3.08614900 2.53036600
H -1.60460800 -3.24252700 3.45707400
C -5.31534900 -0.07714200 -1.26816900
H -5.33015200 -1.16382200 -1.40146500
H -5.85337100 0.37548500 -2.10771100
H -5.85957100 0.16094400 -0.34718300
H -0.50568200 -0.22106600 -1.47862800
C 0.92978800 -0.40564900 -3.26691600
C 2.03564400 0.46487100 -3.41084900
H 0.30103800 -2.46282000 -3.23861400
C 1.14648900 -1.79454700 -3.36835800
C 3.32473100 -0.04313800 -3.65269500
C 3.50643400 -1.41377000 -3.74053900
C 2.41605300 -2.29561900 -3.60220400
H 4.15868000 0.64420600 -3.75676300
H 4.50163700 -1.81056500 -3.91417000
H 2.57720800 -3.36664900 -3.66562600
N 1.82561100 1.82685500 -3.31973500
C -0.50340400 1.57252100 -2.98735400
C 0.59988000 2.38611500 -3.13538700
H -1.47760300 2.02784000 -2.86238300
C -0.36593300 0.15657500 -2.92625100
H 2.63503500 2.43732300 -3.36720000
C 0.53358800 3.88149900 -3.17322400
H 1.37250400 4.32368000 -2.62770200
H 0.59110700 4.23269200 -4.21007000
H -0.40201400 4.23418000 -2.73762600
H -1.24142400 -0.45330000 -3.13434500

TS-3

Ru -0.81831700 -0.47192000 0.16746200
O -0.85840400 2.81413500 0.57971100
N 2.09921600 -0.65025000 0.06203900
N 0.64014400 1.09368700 0.34516300
N 2.78193600 -2.67492100 -0.26690900
N 1.35234200 3.34232200 0.65042500
O 3.57930300 3.91846400 0.48149600
C 0.92511100 -1.44726600 0.03281800
C 0.31720600 2.41566900 0.51845800
C 1.95114500 0.74494300 0.23420400
C 3.21272000 -1.41560400 -0.13714600

C -2.06803300 -0.25816400 2.13530700
H -1.78099500 0.29022100 3.02655000
C 1.39020200 -2.71751600 -0.16759100
H 0.86219600 -3.65118800 -0.27316300
C -2.84888200 0.40707400 1.13200300
H -3.11035900 1.44448400 1.29090200
C 2.98858100 1.63830100 0.27945400
H 4.02191900 1.36360100 0.16404100
C 4.63132500 -0.99007400 -0.21493700
H 4.77554000 -0.28515900 -1.04005800
H 5.27325300 -1.85372000 -0.38517200
H 4.94606800 -0.50473400 0.71364800
C 0.95440300 4.73773600 0.84884000
H 0.36718200 4.82613100 1.76525800
H 0.35227700 5.08340500 0.00705000
H 1.85600800 5.33969100 0.92758900
C 3.63272500 -3.84524400 -0.49947000
H 4.20462500 -3.71774300 -1.41981800
H 2.98718500 -4.71675200 -0.59501000
H 4.31220900 -3.98927500 0.34229500
C -2.71791000 -1.58211400 -0.24952800
H -2.92944200 -2.09323700 -1.18228300
C 2.70698600 3.02745600 0.46520700
C -2.01173700 -2.26227900 0.76588200
H -1.68347100 -3.28326600 0.60045800
C -3.19041100 -0.23218400 -0.06465300
C -1.68700000 -1.60898600 2.00244900
C -3.99757600 0.42151700 -1.17033000
H -3.57890500 0.05720700 -2.11685900
C -3.91950800 1.95184200 -1.17740900
H -4.43774100 2.38319700 -0.31388400
H -4.40352000 2.34222900 -2.07809100
H -2.88421700 2.30258500 -1.16061100
C -0.91998900 -2.33765800 3.06879200
H -0.12712600 -2.94814300 2.62550600
H -1.58659500 -3.00827300 3.62373600
H -0.47091700 -1.63862000 3.77892200
C -5.45874800 -0.05995700 -1.09389500
H -5.52278000 -1.15238400 -1.13330800
H -6.03757300 0.34620200 -1.92998700
H -5.92526600 0.27573500 -0.16078900
H -0.49283800 -0.31288000 -1.47141800
C 1.27962800 2.33582800 -2.85403400
C -0.13447600 2.37466100 -2.96292600
H 3.06138200 3.51303100 -2.58420000
C 1.98155800 3.54659500 -2.69024800
C -0.82205200 3.59863200 -2.91815100
C -0.10222000 4.77388700 -2.75817200
C 1.30076100 4.75269200 -2.64015900
H -1.90431200 3.60853200 -3.00134800
H -0.63213900 5.72016700 -2.71424400
H 1.84547800 5.68063800 -2.50220300
N -0.81341100 1.18482500 -3.15130600
C 1.19638100 -0.08997300 -2.96187000
C -0.25415800 -0.04754800 -2.92809400
H 1.66549300 -1.06650600 -2.96172600
C 1.92508200 1.05360800 -2.91335100
H 3.01014100 1.01549600 -2.90648500
C -1.02460700 -1.23855600 -3.44589900
H -0.64048100 -2.15226800 -2.98909800
H -2.09027000 -1.14917200 -3.22785500
H -0.88982000 -1.29981400 -4.53139300
H -1.82708600 1.23207400 -3.18915100

TS-4

Ru -0.77721900 -0.47060900 0.03242500
O -0.97977500 2.81824200 0.46270600
N 2.14036800 -0.53477600 0.24001600
N 0.59342600 1.15018400 0.37863100
N 2.94530200 -2.51413700 -0.08564100
N 1.19337200 3.42823400 0.72729700
O 3.40395300 4.08996600 0.72744900
C 1.01589900 -1.36209700 -0.02441400
C 0.20934200 2.46110400 0.50938900
C 1.92008500 0.85285200 0.40408400
C 3.29987600 -1.25798400 0.20103800
C -2.02470000 -0.46825200 2.04172600
H -1.74363500 -0.00416200 2.98138200
C 1.55851800 -2.60182500 -0.22482400

H 1.09213100 -3.54304400 -0.46553100
C -2.79795900 0.28447800 1.09572000
H -3.06562300 1.30216800 1.34826800
C 2.91641800 1.78585100 0.52387900
H 3.96491500 1.55009200 0.48837700
C 4.69096700 -0.79811000 0.43459600
H 5.03029300 -0.14919700 -0.38008500
H 5.36478400 -1.65258800 0.49389300
H 4.76043900 -0.24164600 1.37298600
C 0.72368600 4.80590600 0.89174400
H 0.07741000 4.87347700 1.76964800
H 0.16114900 5.12239100 0.01241800
H 1.59110500 5.44740900 1.02287400
C 3.86286400 -3.64946700 -0.21446200
H 4.32426800 -3.87540300 0.74870800
H 4.63600400 -3.42366400 -0.95005300
H 3.28844600 -4.51135200 -0.55038000
C -2.67551300 -1.56886900 -0.45567100
H -2.90197000 -2.00125700 -1.42349100
C 2.56874700 3.16620000 0.65879700
C -1.94696400 -2.32998300 0.48457200
H -1.61676800 -3.33093300 0.22677900
C -3.16192000 -0.24837500 -0.14668600
C -1.62848300 -1.79186000 1.77800700
C -4.03797000 0.47989500 -1.14929800
H -3.75875700 0.10742400 -2.14155400
C -3.85289000 2.00180500 -1.15442800
H -4.21423300 2.45617600 -0.22516000
H -4.42677200 2.44063000 -1.97699200
H -2.80264200 2.27810000 -1.27571800
C -0.84894800 -2.61076100 2.76704600
H -0.02632500 -3.13522500 2.27010300
H -1.49584000 -3.36711800 3.22657000
H -0.43668700 -1.98339500 3.56154600
C -5.51137300 0.09880500 -0.90932900
H -5.65457100 -0.98609600 -0.95315700
H -6.15439000 0.55868600 -1.66730700
H -5.84340200 0.44548800 0.07602600
H -0.44234800 -0.26394800 -1.56161100
C 1.34140900 2.20328000 -2.93729500
C -0.03922500 2.38432400 -3.10615100
H 3.18270800 3.20644900 -2.49314500
C 2.11468300 3.33039100 -2.64747000
C -0.63449200 3.64556000 -2.99922200
C 0.16015200 4.75490400 -2.72021800
C 1.53735300 4.59678300 -2.53838300
H -1.70799100 3.74414600 -3.13111300
H -0.29623300 5.73563300 -2.63363400
H 2.15883600 5.45436700 -2.30160900
N -0.86737400 1.26622000 -3.35968300
C 1.01093500 -0.25589400 -3.53349300
C -0.45231600 0.00913000 -3.31978300
H 1.09686900 -0.34104800 -4.62696200
C 1.96255200 0.82699100 -3.00819700
H 2.85290000 0.86058300 -3.64299700
C -1.41406900 -1.07245900 -3.69417400
H -1.15035200 -2.00348100 -3.19206400
H -2.44557500 -0.80518900 -3.46362300
H -1.32705900 -1.23092600 -4.77668200
H -1.87067700 1.43449400 -3.34123900
H 2.31850200 0.55504300 -2.01368100
H 1.25779300 -1.23635200 -3.12140900

TS-5

Ru -0.85260600 -0.45152600 0.20148800
O -1.00731200 2.80446200 0.79235100
N 2.07388200 -0.50801100 0.05810200
N 0.55195900 1.16482200 0.42864400
N 2.83330400 -2.50257000 -0.28106800
N 1.17103800 3.45071200 0.66065000
O 3.36136300 4.12374300 0.38817500
C 0.92856100 -1.34515900 -0.00101900
C 0.17907000 2.46972000 0.62730500
C 1.86955900 0.87844100 0.24063000
C 3.21997400 -1.23360200 -0.11047100
C -2.14947500 -0.44131600 2.17395800
H -1.91517600 0.05162900 3.11184000
C 1.44240600 -2.59415300 -0.21776900
H 0.95015000 -3.54401900 -0.34823800
C -2.92818000 0.26249500 1.19491800

H -3.24148000 1.27295800 1.42015800
C 2.86453600 1.81923300 0.22252100
H 3.90001300 1.59116200 0.04226700
C 4.63213200 -0.77792600 -0.05916100
H 4.87186500 -0.12435400 -0.90253100
H 5.30357800 -1.63576900 -0.09321400
H 4.82249600 -0.23005400 0.86842400
C 0.71938700 4.82922300 0.86938700
H 0.33318200 4.95073000 1.88473200
H -0.07187500 5.07145000 0.16049100
H 1.56723400 5.49197100 0.71900400
C 3.72662500 -3.64363100 -0.49924400
H 3.10998600 -4.52656900 -0.65949300
H 4.36086400 -3.79979000 0.37517300
H 4.34676600 -3.47149900 -1.38005000
C -2.67918400 -1.61386600 -0.32113600
H -2.84709500 -2.06539600 -1.29342900
C 2.52940600 3.19534900 0.41597700
C -1.96072800 -2.33011600 0.66209800
H -1.58010600 -3.32033500 0.43357400
C -3.21738300 -0.30374300 -0.05206400
C -1.70154300 -1.75807400 1.95354600
C -4.02963400 0.38895500 -1.13085000
H -3.53676800 0.15769300 -2.08506000
C -4.09172700 1.91300100 -0.98202500
H -4.67393200 2.20527900 -0.10106300
H -4.57997400 2.35165000 -1.85779500
H -3.09485900 2.35295900 -0.88622200
C -0.92747300 -2.53160100 2.98280900
H -0.08417300 -3.05412100 2.51947500
H -1.56881700 -3.28730400 3.45148100
H -0.54464000 -1.87349500 3.76698600
C -5.44423800 -0.21925400 -1.18001300
H -5.40886200 -1.30198900 -1.33885300
H -6.02160000 0.22599700 -1.99691600
H -5.97796700 -0.02969200 -0.24180400
H -0.58435600 -0.15667300 -1.40896000
C 1.31780400 2.41992700 -2.90238900
C -0.08689700 2.61832200 -2.82904600
H 3.22612500 3.42922200 -2.83170700
C 2.15035200 3.55429800 -2.79483600
C -0.63285500 3.90187300 -2.66044600
C 0.21658500 4.99191600 -2.55911700
C 1.61159100 4.81923500 -2.62156700
H -1.71098600 4.01844300 -2.60572600
H -0.20035400 5.98415600 -2.41954500
H 2.26779300 5.67772300 -2.52576900
N -0.91822700 1.52420300 -2.96566700
C 0.94057000 0.02954000 -3.07589800
C -0.46288400 0.24625700 -2.86519000
H 1.28361200 -0.99588000 -3.14962500
C 1.82316900 1.07245600 -3.08341800
H -1.91812700 1.68092600 -2.89152300
C 3.29379800 0.83666400 -3.26320900
H 3.65764000 1.32541500 -4.17380400
H 3.85323200 1.26322100 -2.42514000
H 3.51617900 -0.23054100 -3.32412200
H -1.17811000 -0.51930500 -3.14429500

TS-6

Ru -0.78421900 -0.55555300 -0.04966000
O -0.77555000 2.73435100 0.12114500
N 2.12837800 -0.79853700 -0.11503800
N 0.70359000 0.98447200 0.05268100
N 2.77335100 -2.85110600 -0.31231400
N 1.43366400 3.24500500 -0.06690700
O 3.65937300 3.75777100 -0.39215700
C 0.93593000 -1.56574600 -0.18190900
C 0.39293100 2.31984000 0.03857800
C 2.00640100 0.60753700 -0.06223100
C 3.23166900 -1.59962600 -0.20007600
C -1.93685500 -0.46122900 1.99386400
H -1.58734600 -0.00984800 2.91648400
C 1.37983300 -2.85431400 -0.31250600
H 0.83444500 -3.77693400 -0.42500100
C -2.73516300 0.31935300 1.09401800
H -2.94999300 1.34665800 1.35884200
C 3.05291800 1.48514000 -0.16111200
H 4.07561600 1.18180700 -0.29822600
C 4.66219600 -1.21620400 -0.10871800

H 4.97076000 -0.63539000 -0.98256100
H 5.28731500 -2.10725000 -0.05436500
H 4.83746800 -0.61484600 0.78796200
C 1.04153100 4.65221100 -0.16955300
H 0.48695600 4.95252900 0.72154300
H 0.40597200 4.79983600 -1.04635500
H 1.94386100 5.25096900 -0.26233800
C 3.60322400 -4.03944600 -0.52066700
H 2.94095100 -4.88748500 -0.68753400
H 4.22160000 -4.23110800 0.35807300
H 4.23667600 -3.89731900 -1.39752900
C -2.75906700 -1.53930100 -0.45968000
H -3.03915000 -1.95499400 -1.42132600
C 2.78334000 2.88780300 -0.21593400
C -2.03946200 -2.33945100 0.45400800
H -1.77007100 -3.35528700 0.18491300
C -3.17871500 -0.20023200 -0.12737400
C -1.62597900 -1.81004900 1.72145300
C -4.08118100 0.54769000 -1.09055500
H -3.79529900 0.23147100 -2.10092500
C -3.95577200 2.07277000 -1.02174900
H -4.30100500 2.46312200 -0.05779100
H -4.57705200 2.52804500 -1.79952000
H -2.92290200 2.39788300 -1.16832400
C -0.85134400 -2.66344700 2.68453500
H -0.08036600 -3.23690900 2.16063400
H -1.52184000 -3.37798400 3.17594000
H -0.37378900 -2.05429600 3.45611800
C -5.53793700 0.10014400 -0.85944900
H -5.64107400 -0.98642400 -0.94846300
H -6.20211400 0.56671700 -1.59458500
H -5.87635700 0.39291500 0.14117100
H -0.50991800 -0.32636100 -1.69996900
C 1.13107600 -0.32767100 -3.32827000
C 2.12907200 0.67997900 -3.32160200
H 0.81265100 -2.46094200 -3.42734000
C 1.55292400 -1.67051300 -3.43927800
C 3.49319800 0.35146700 -3.43298300
C 3.86846400 -0.97542000 -3.53921900
C 2.89540400 -1.99364100 -3.53971200
H 4.23155200 1.14737200 -3.42201900
H 4.92039900 -1.23124000 -3.61520900
H 3.19910800 -3.03271200 -3.61141700
N 1.74966100 2.00346200 -3.21854800
C -0.55788200 1.44910900 -3.18085300
C 0.44773900 2.37552600 -3.16100500
H -1.58689900 1.78644500 -3.14914500
C -0.27821800 0.04146900 -3.15185700
H 2.47226500 2.71281000 -3.16250800
H 0.26247100 3.44217900 -3.12362000
C -1.35080100 -0.88929300 -3.68932700
H -1.24579400 -1.90802600 -3.31555800
H -2.34088000 -0.52144400 -3.41588800
H -1.27816700 -0.90933600 -4.78291400

1a-H$^+$

C -2.95324100 0.29588400 0.00004700
C -1.94643800 1.23619800 0.00002300
C -0.58913500 0.82360700 -0.00001000
C -0.30447100 -0.57000200 -0.00003900
C -1.33709800 -1.52705200 -0.00002200
C -2.64556100 -1.08685100 0.00002800
H 0.30116500 2.79309400 -0.00000700
H -3.99135500 0.61081700 0.00008000
H -2.16788000 2.29863500 0.00003800
C 0.50245500 1.72611400 -0.00001500
H -1.09210000 -2.58444000 -0.00003400
H -3.45277100 -1.81210700 0.00005500
C 2.06012600 -0.11753900 -0.00006700
C 1.80230400 1.26494200 -0.00003800
H 1.20906000 -1.95882800 -0.00011200
H 2.64291200 1.94759700 -0.00004200
N 1.01539500 -0.95794900 -0.00008600
C 3.43075600 -0.70931100 0.00009400
H 3.56948300 -1.33959900 0.88501100
H 3.56902400 -1.34153000 -0.88350300
H 4.18653100 0.07605700 -0.00089800

1,4-DHQ

C -2.97771300 0.26183000 -0.15601700
C -1.93753500 1.19288100 -0.09297300
C -0.60582300 0.79721500 0.06002300
C -0.31730700 -0.58156200 0.13114000
C -1.35782900 -1.52254900 0.06242600
C -2.67911600 -1.10158300 -0.07419300
H 0.48886400 2.27476100 1.18389300
H -4.00479500 0.59604800 -0.26719500
H -2.15950600 2.25583100 -0.15675400
C 0.51317400 1.81832600 0.17929400
H -1.11841600 -2.58187000 0.11292000
H -3.47366700 -1.84078400 -0.12423800
C 2.06700700 -0.13040200 -0.01481700
C 1.86338100 1.19617900 -0.08247200
H 1.17789100 -1.98808400 0.08942400
N 1.00716300 -1.00699800 0.27010300
C 3.39616700 -0.80007800 -0.20633500
H 3.68128900 -1.36349700 0.69075900
H 3.35975700 -1.51668900 -1.03661700
H 4.17792000 -0.06664800 -0.41483300
H 0.32883600 2.64998800 -0.51384400
H 2.70525800 1.84839700 -0.29069300

1,2 Im^+

C -2.99421100 0.27521300 -0.07159100
C -1.96115600 1.21244700 0.02458400
C -0.63038500 0.80157200 0.09817900
C -0.37073700 -0.57565200 0.06516500
C -1.38572700 -1.52766100 -0.02393300
C -2.70872900 -1.09262400 -0.09367200
H 0.71121600 1.90126800 1.34272400
H -4.02354800 0.61513100 -0.12879000
H -2.18658900 2.27459600 0.04687100
C 0.53086000 1.74967900 0.27053500
H -1.13854200 -2.58500300 -0.04426400
H -3.51096200 -1.81941800 -0.16700700
C 2.02407300 -0.25184700 -0.04625000
C 1.80001400 1.18646300 -0.38045100
H 1.13655500 -2.00642400 0.32087000
H 1.72025000 1.21870700 -1.47839900
N 0.98459700 -1.01392300 0.13849400
C 3.39044300 -0.81361300 0.03265900
H 3.91294500 -0.34137600 0.87307800
H 3.39412500 -1.89777000 0.15685700
H 3.93968100 -0.53532300 -0.87389300
H 0.29827700 2.72720900 -0.15731400
H 2.68774700 1.76200500 -0.11153500

2a

C 3.04312700 0.29403200 0.01588000
C 1.98217400 1.20201400 -0.02156400
C 0.64846700 0.78221400 -0.03694300
C 0.36918000 -0.60462300 0.00238400
C 1.44004200 -1.51983900 0.03738600
C 2.75979900 -1.07552800 0.04274700
H -0.58166100 2.13555700 -1.15719200
H 4.06961600 0.64794700 0.02518800
H 2.18701800 2.27050100 -0.04527900
C -0.48632500 1.78486800 -0.12014500
H 1.21977900 -2.58461700 0.06433000
H 3.56790500 -1.80169100 0.06923100
C -2.04278400 -0.18451400 -0.33440100
C -1.82185700 1.17832300 0.32669400
H -1.05458200 -2.02436700 -0.26260400
H -1.83080000 1.04170700 1.41544100
N -0.94445100 -1.07104800 0.06370200
C -3.37378100 -0.81506300 0.06156200
H -4.20599000 -0.18944500 -0.27612300
H -3.49191400 -1.80593000 -0.39195700
H -3.44242600 -0.92755900 1.14910100
H -0.24649200 2.67109700 0.47831400
H -2.64970700 1.84766000 0.07184000
H -2.03784400 -0.03482000 -1.42780000

1,2 DHQ

C 3.00071800 0.34156300 0.00298200
C 1.93574300 1.24564200 0.03348200
C 0.60838800 0.80226400 0.03815800
C 0.33934400 -0.59188500 0.02164300

C 1.41215600 -1.49658100 -0.00671200
C 2.72837700 -1.03005400 -0.01594200
H 4.02518500 0.70056700 -0.00366600
H 2.12688400 2.31605900 0.05233800
C -0.53531400 1.71083700 0.08323000
H 1.20688800 -2.56415900 -0.01844400
H 3.54494900 -1.74652700 -0.04134300
C -2.07806500 -0.19250500 -0.39187400
C -1.78626100 1.26110900 -0.09842500
H -1.10352900 -2.00960100 -0.08073200
N -0.97767000 -1.02393700 0.12045600
C -3.39564100 -0.65346100 0.23412800
H -4.23190800 -0.07851900 -0.17592200
H -3.57539400 -1.71280700 0.02074700
H -3.37542400 -0.51669000 1.32014000
H -2.63481100 1.94022700 -0.08856100
H -0.34214700 2.76706200 0.25710000
H -2.17367400 -0.30962500 -1.48886900

4b

C -2.31366000 1.19427000 0.00000700
C -0.96849700 1.49292800 0.00014900
C 0.00158500 0.45539800 0.00007900
C -0.47041900 -0.88855600 -0.00016500
C -1.84706200 -1.18860000 -0.00031400
C -2.75468100 -0.15050200 -0.00022400
H -3.04500300 1.99565700 0.00007200
H -0.64122500 2.52564600 0.00032900
C 1.41288300 0.69767600 0.00022900
H -2.16804700 -2.22523400 -0.00048900
H -3.81801700 -0.36604400 -0.00033300
C 1.77076600 -1.69206800 -0.00010600
C 2.27366700 -0.39319500 0.00014100
H 0.11531800 -2.86574800 -0.00043600
H 3.34756000 -0.25259100 0.00024300
N 0.45503000 -1.90557300 -0.00024800
H 2.40537300 -2.56963000 -0.00019800
C 1.95583800 2.09358600 0.00040600
H 1.60469300 2.64124800 -0.88081800
H 1.60463800 2.64106000 0.88172400
H 3.04699000 2.08902900 0.00043500

4c

C -2.48378900 0.98885900 0.22693000
C -1.15418600 1.38195000 0.39388900
C -0.09293200 0.48722200 0.22046600
C -0.39315100 -0.85103500 -0.11414700
C -1.72891900 -1.25264500 -0.28402600
C -2.76508500 -0.33681400 -0.12006900
H -3.28801000 1.70563200 0.36273500
H -0.92485500 2.41161700 0.65929700
C 1.35204000 0.96070500 0.33677800
H -1.94174300 -2.28833100 -0.53767200
H -3.79280400 -0.66209100 -0.25485600
C 1.91390600 -1.46648200 0.22403400
C 2.27683100 -0.21707000 0.54995700
H 0.37894400 -2.75192000 -0.27270700
N 0.64316800 -1.77611400 -0.26153400
H 3.28298900 -0.03047500 0.91126100
C 1.76823300 1.77215400 -0.91219700
H 1.69288800 1.15417600 -1.81349100
H 1.12316900 2.64851300 -1.04168700
H 2.80410000 2.11904000 -0.82197000
H 2.58332800 -2.31553900 0.31292200
H 1.42213000 1.64111400 1.19721500

4d

C -2.40833600 1.11593400 0.13280400
C -1.05080700 1.44761800 0.12186100
C -0.05666400 0.46606500 0.00894500
C -0.45262800 -0.89468000 -0.10840500
C -1.81707700 -1.22259000 -0.10020800
C -2.78520400 -0.22468400 0.01845900
H -3.15918400 1.89442200 0.22692900
H -0.75928700 2.48977800 0.20692900
C 1.38593900 0.77781100 -0.02806600
H -2.11013500 -2.26580600 -0.19054900
H -3.83622300 -0.50024900 0.02685300
C 1.83822000 -1.65393900 0.29275900
C 2.27232200 -0.22822800 0.08531900
H 0.17492400 -2.81235100 -0.18424200

N 0.52132800 -1.86854900 -0.31336800

H 3.34026200 -0.02588100 0.08137400

C 1.82522900 2.21085200 -0.17835300

H 1.39946000 2.66817500 -1.07950400

H 1.49260500 2.81999800 0.67105700

H 2.91457200 2.28264100 -0.23702100

H 2.54936200 -2.34332900 -0.17268800

H 1.83836500 -1.89251400 1.37375100

CO_2

C 0.00000000 0.00000000 0.00000000

O 0.00000000 0.00000000 1.16979700

O 0.00000000 0.00000000 -1.16979700

$HCOO^-$

C 0.00000000 0.00000000 0.33589300

O 0.00000000 1.13402600 -0.21719400

O 0.00000000 -1.13402600 -0.21719400

H 0.00000000 0.00000000 1.45974300

Cl^-

Cl 0.00000000 0.00000000 0.00000000