Supplementary Information (SI) for Catalysis Science & Technology.

Supporting Information

Selective and sustainable quinoline hydrogenation with a robust hierarchical catalyst framework

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Chemicals, Materials and Characterization

All materials were handled under an ambient lab atmosphere. Nickel foam (MTI Corporation as 1.6 mm thick roll and 1000 mm × 300 mm), ultrahigh purity H_2 and Argon (Airgas), absolute ethanol and hexanes (Honeywell Research Chemicals), hydrochloric acid (Fisher Chemical), $CDCl_3$, trimethyl aluminum (TMA, CAS 75-24-1, ≥97% purity), dopamine hydrochloride (Thermo Scientific Chemicals), palladium acetate (Acros Organics) were purchased and used as received. Water used in all the experiments was deionized water (DIW). Substrates: Quinoline (Acros Organics), 8-methylquinoline (Thermo Scientific Chemicals), 8-hyroxyquinoline (Thermo Scientific Chemicals), 8-methoxyquinoline (TCI), 6-chloroquinoline (TCI), 2,4-dimethylquinoline (Thermo Scientific Chemicals), 9-methylacridine (TCI), 2-quinolinecarbaldehyde (Thermo Scientific Chemicals), 6-ethynylquinoxaline (Thermo Scientific Chemicals), benzo[h]quinoline (TCI), 4-aminoisoquinoline (TCI) were used as received.

^1H NMR spectroscopy measurements were performed on a Bruker Avance III HD 400 MHz spectrometer, and all data were analyzed using Mestrelab Research MestReNova software. In situ XPS sample characterization was completed using ScientaOmicron's HippLab apparatus. The system uses a focused monochromatic Al Ka light source arranged to create a 55° source-sample-detector geometry when illuminating a sub-mm region at the surface of a given analyte positioned 400 mm from the entrance of a 400 mm, differentially-pumped, orifice through which ejected electrons are collected and analyzed. The system retains surface sensitivity at pressures ranging from UHV to mbar when used in this configuration.

Materials Synthesis

The catalyst, **Al_2O_3-Pd-D/Ni**, was prepared following our previously reported.[1] In brief, commercial Ni foams (1.7 g, precut to 24 mm × 12 mm × 1.6 mm, ~0.1 g) were ultrasonically cleaned in 0.15 M hydrochloric acid for 5 min at room temperature, extensively rinsed with DIW, and dried in an oven at 150 °C overnight. Next, the cleaned Ni foams were immersed in an aqueous solution of dopamine hydrochloride (1 g in 100 mL DIW) in a sealed 250 mL heavy-wall high-pressure flask at 150 °C under stirring. After 4 hours, the foams were removed, rinsed with DIW, and subsequently reacted with palladium acetate (0.3 g in 25 mL ethanol and 75 mL DIW) at 150 °C under stirring to facilitate solvothermal Pd deposition. After 70 hours, the foams were cleaned with DIW and dried in an oven at 150 °C overnight.

The foams were then coated with a 2 nm Al_2O_3 layer via thermal atomic layer deposition (ALD) using DIW and TMA as co-reactants. ALD was performed on a Fiji Gen2 ALD System (Veeco®) at 120 °C, following a standardized recipe with cycle adjustments based on in situ spectroscopic ellipsometry data. Each Al_2O_3 cycle consisted of a 60 ms TMA pulse, a 60 ms DIW pulse (purified by a Direct-Q Millipore system), and a 10 s Ar purge at 75 sccm between pulses. The Al_2O_3 overlayer thickness was measured using a J.A. Woollam M2000 spectroscopic ellipsometer (280–1690 nm range) with optical models constructed in CompleteEase software. A total of 30 ALD cycles resulted in a 2.17 nm Al_2O_3 thickness on a planar silicon substrate.

Finally, the materials underwent annealing at 400 °C for 1 hour in the laboratory atmosphere with a heating rate of 5 °C/min. The resulting material is labeled Al_2O_3-Pd-D/Ni.

Catalysis Experiments

The catalytic hydrogenation of quinoline was initially tested using an optimized protocol previously established by one of our groups.[1] Briefly, hydrogenations were conducted in a 25 mL Büchiglasuster Tinyclave glass reactor. Typically, the reactor was loaded with the substrate, catalyst, and solvent, followed by evacuation and rapid pressurization with ultrahigh-purity H_2. The reaction mixture was then heated in an oil bath to the desired temperature. Upon completion, the reactor was cooled to room temperature, and any remaining H_2 was vented. The catalyst was separated using tweezers and washed with DIW. Recovered catalysts for recycling trials were dried in an oven at 150 °C overnight.

For the product analysis, the solvent in the reaction mixture was removed under reduced pressure via rotary evaporation, yielding the product mixture. This mixture was dissolved in $CDCl_3$ and analyzed using ^1H NMR.

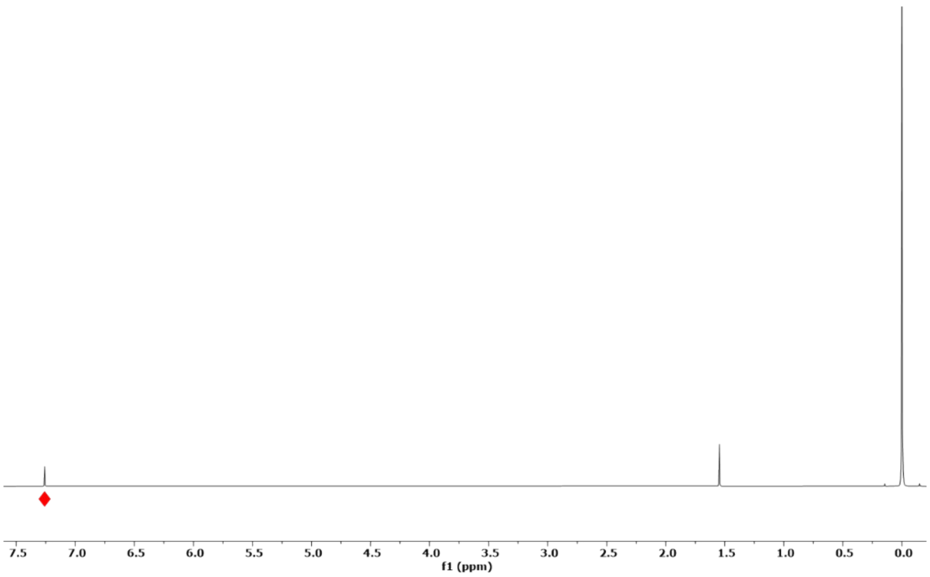

Figure S1. ^{1}H NMR spectrum (400 MHz) of $CDCl_3$ that was used in all the hydrogenation product analysis as an NMR solvent. *TMS gives a signal at 0 ppm and the absorbed water at 1.5 ppm.*[1]

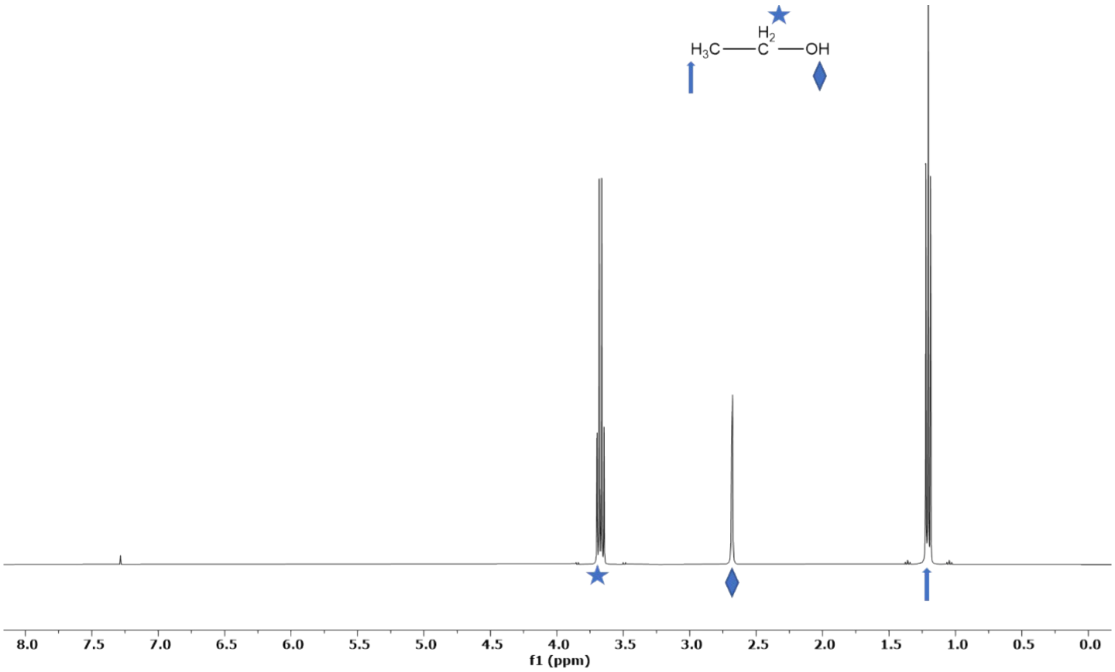

Figure S2. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of ethanol that was used as a solvent in all the catalytic systems.[1]

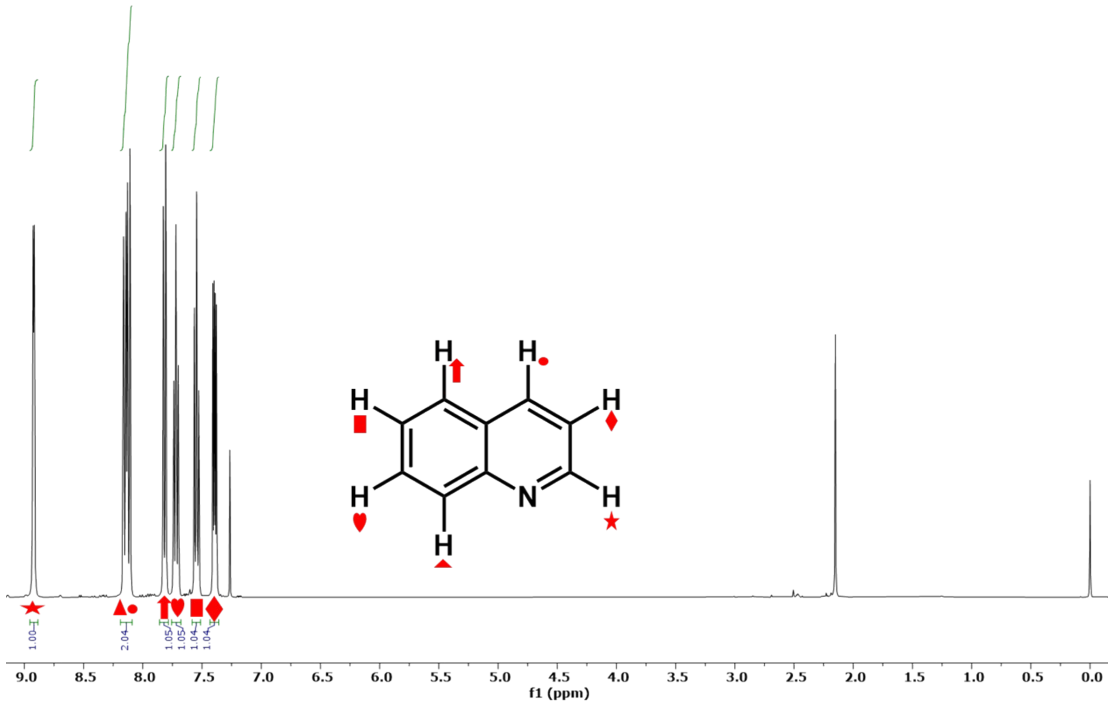

Figure S3. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of quinoline that was used as a model substrate to evaluate the catalytic system.

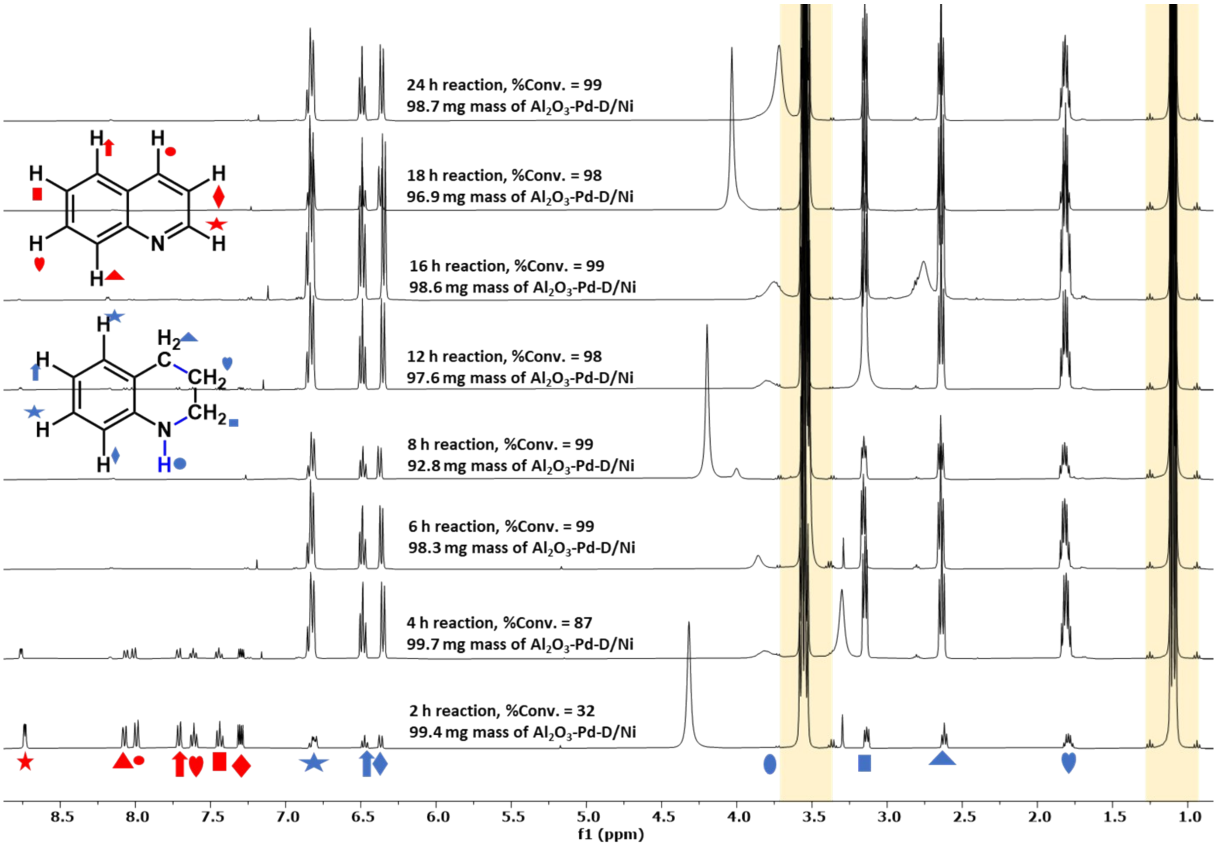

Figure S4. ^{1}H NMR spectra (400 MHz, $CDCl_3$) of isolated products for quinoline hydrogenation as a function of time utilizing 97.75 ± 2.05 mg Al_2O_3-Pd-D/Ni catalyst with 0.5 mmol quinoline, 5 mL ethanol, 6 bar H_2 gas, 100 °C.

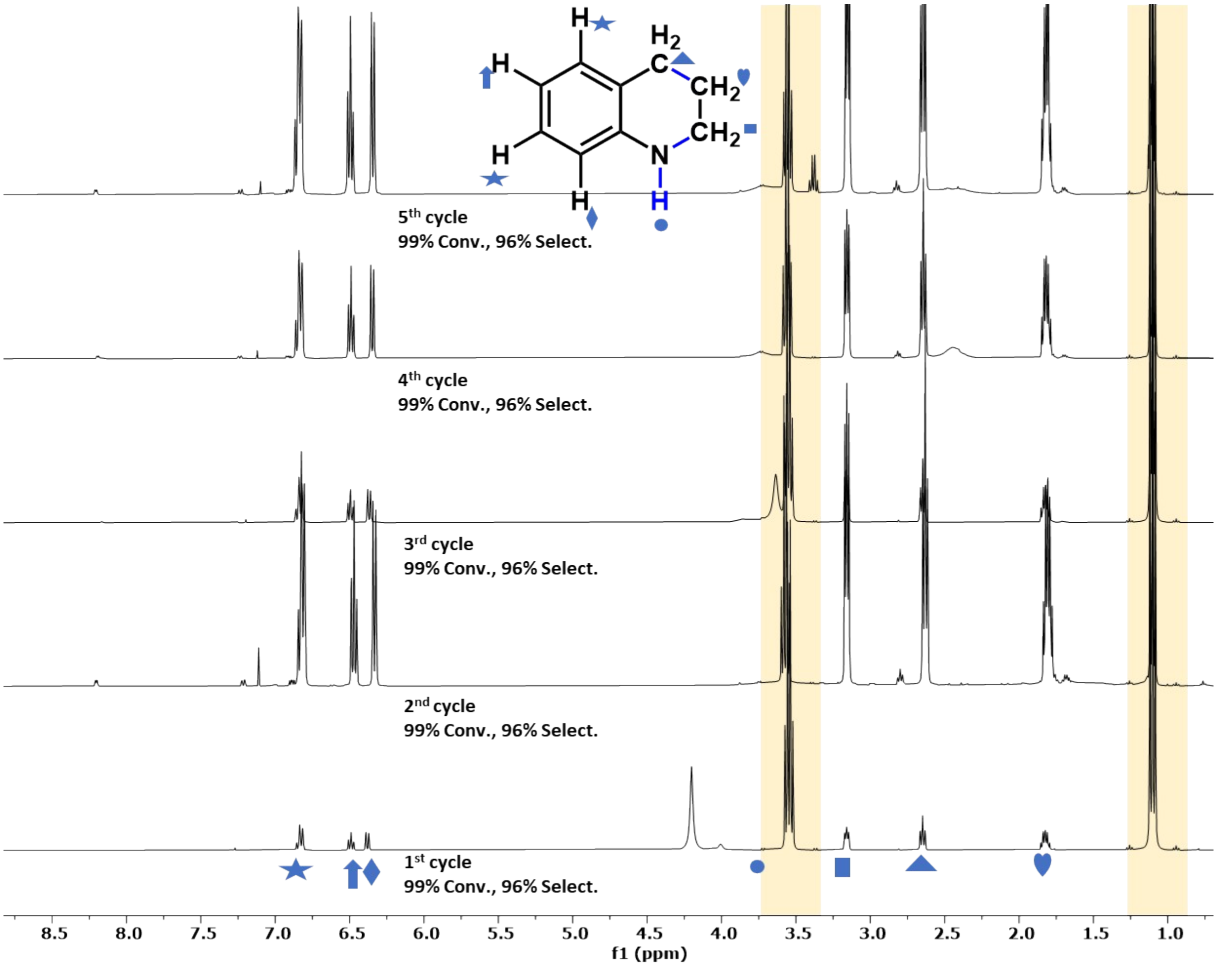

Figure S5. ^1H NMR spectra (400 MHz, $CDCl_3$) of isolated products after 24 hours for quinoline hydrogenation recycling trials utilizing 92.00 mg Al_2O_3-Pd-D/Ni with 0.5 mmol quinoline, 5 mL ethanol, 6 bar H_2 gas, 100 °C.

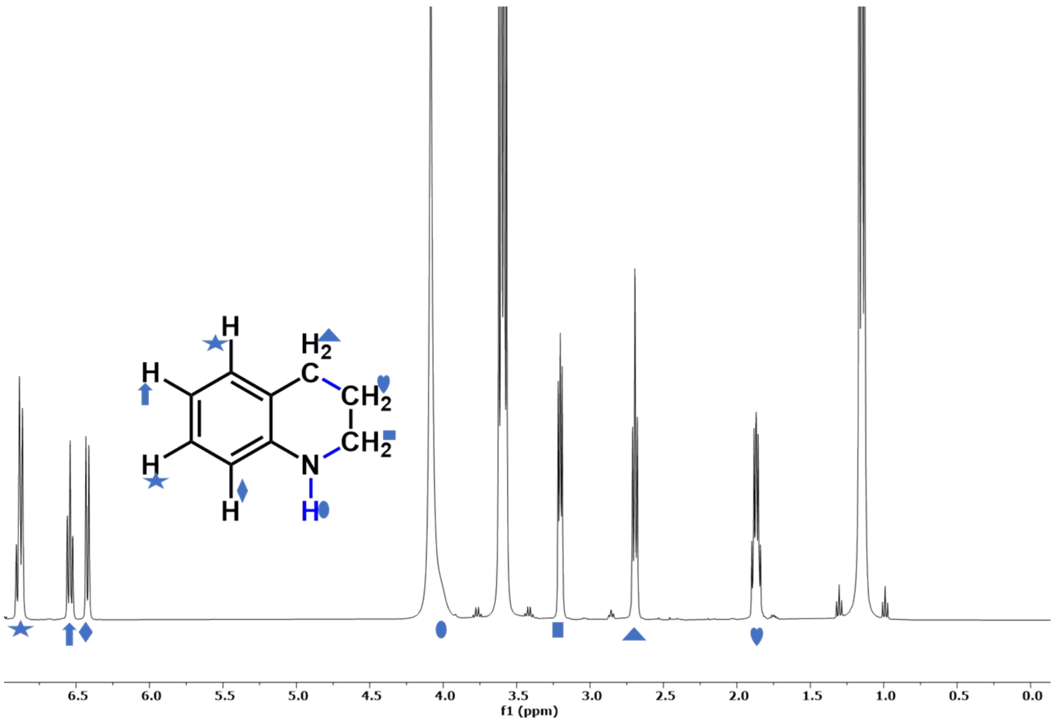

Figure S6. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of isolated products of reaction a, Figure 3. Al_2O_3-Pd-D/Ni= 96.9 mg

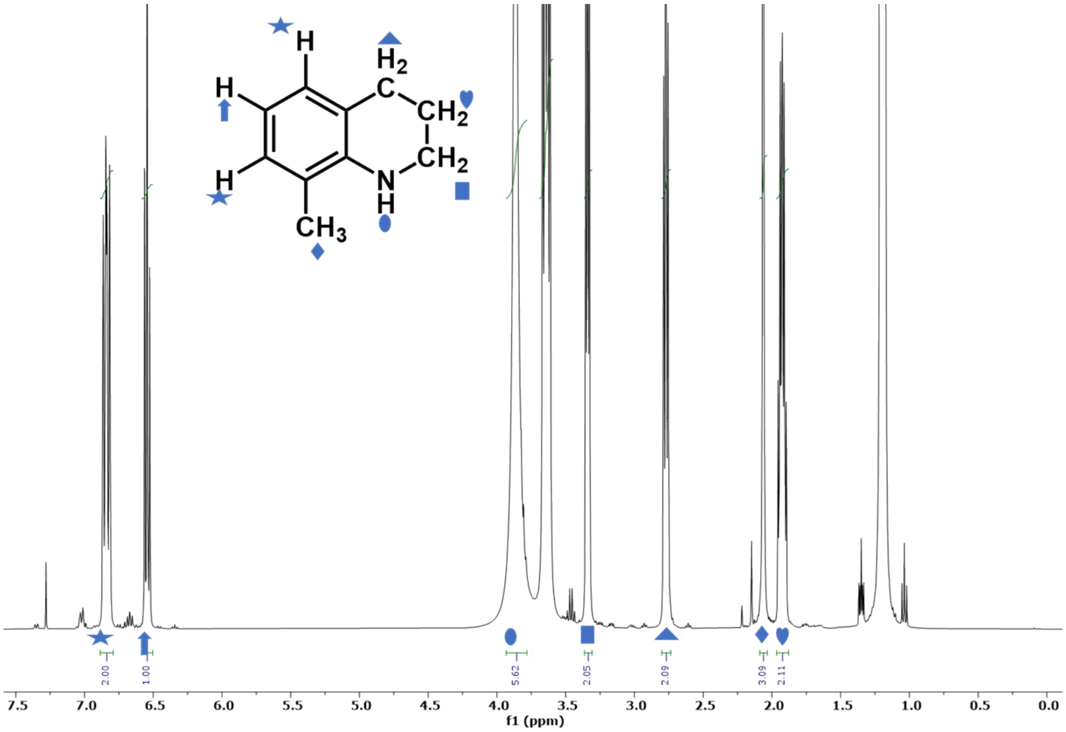

Figure S7. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of isolated products of reaction b, Figure 3. Al_2O_3-Pd-D/Ni= 94.8 mg

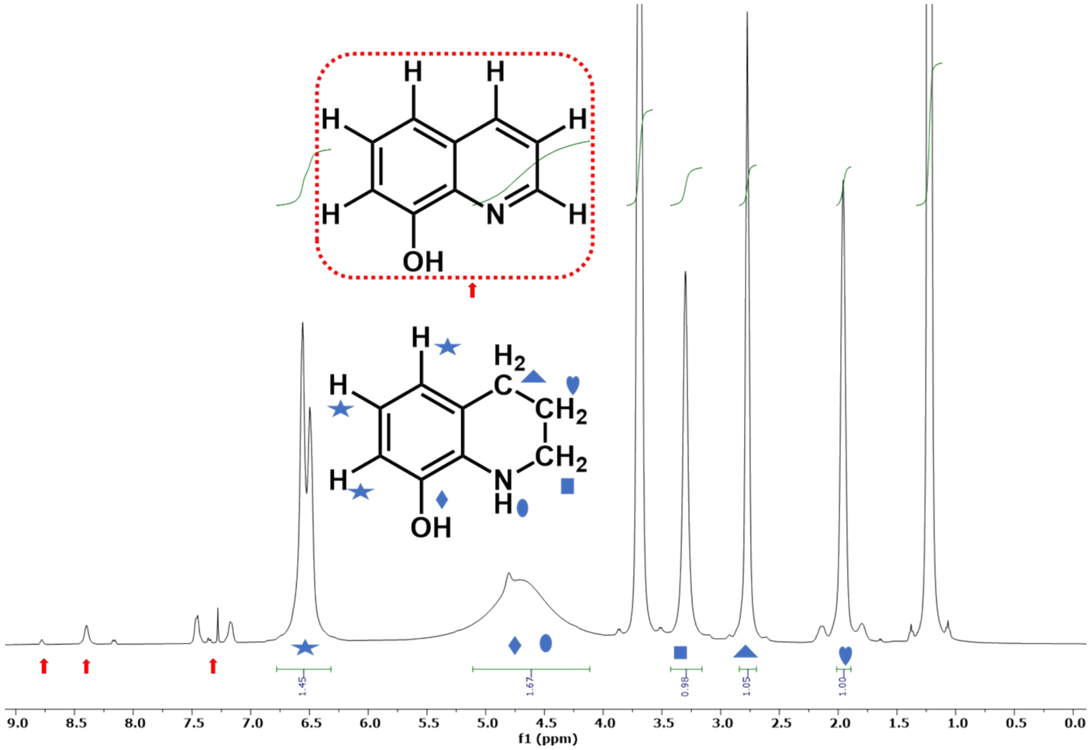

Figure S8. ^1H NMR spectrum (400 MHz, $CDCl_3$) of isolated products of reaction c, Figure 3. Al_2O_3-Pd-D/Ni= 97.5 mg

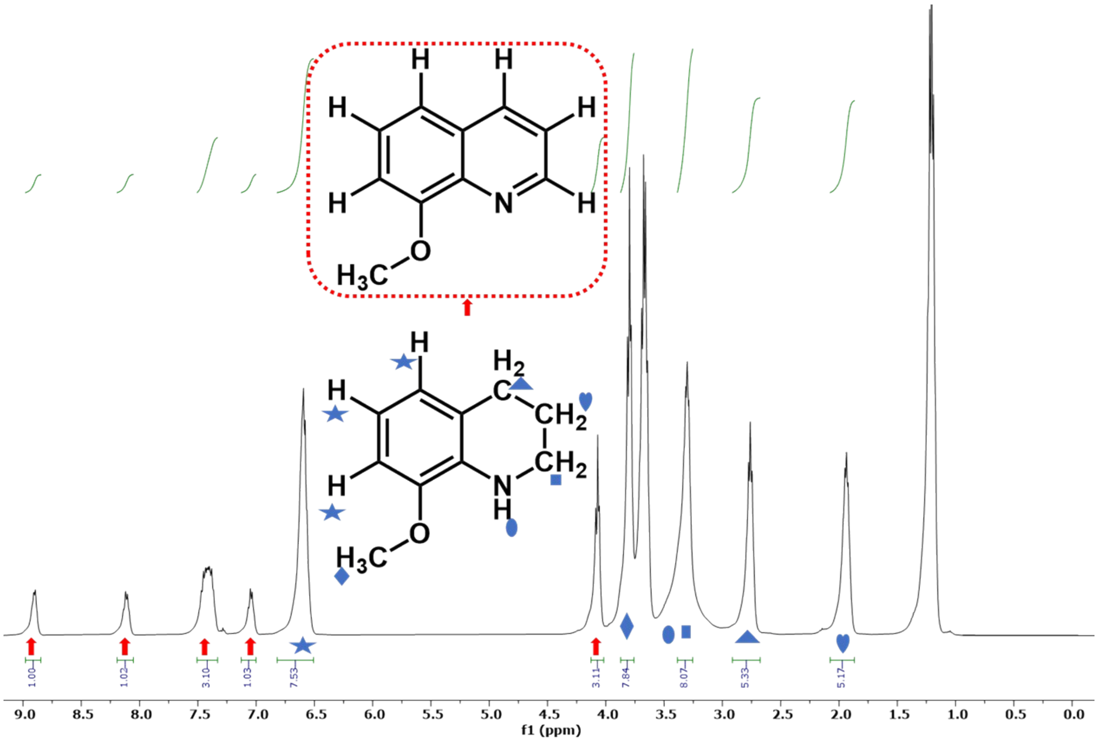

Figure S9. ^1H NMR spectrum (400 MHz, $CDCl_3$) of isolated products of reaction d, Figure 3. Al_2O_3-Pd-D/Ni= 94.2 mg

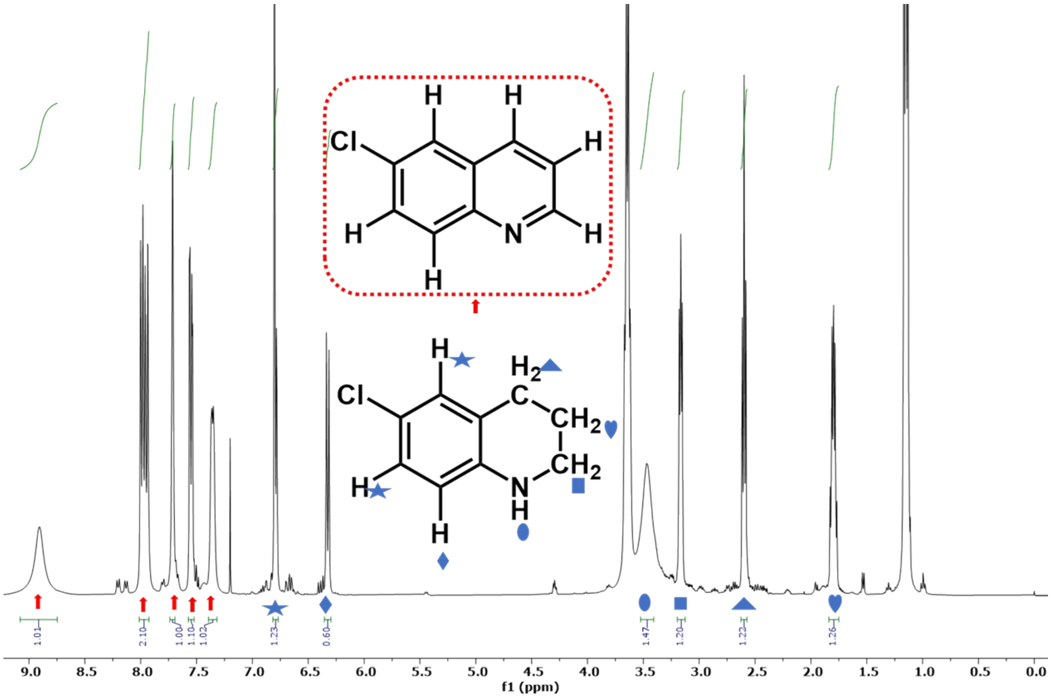

Figure S10. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of isolated products of reaction e, Figure 3. Al_2O_3-Pd-D/Ni= 86.1 mg

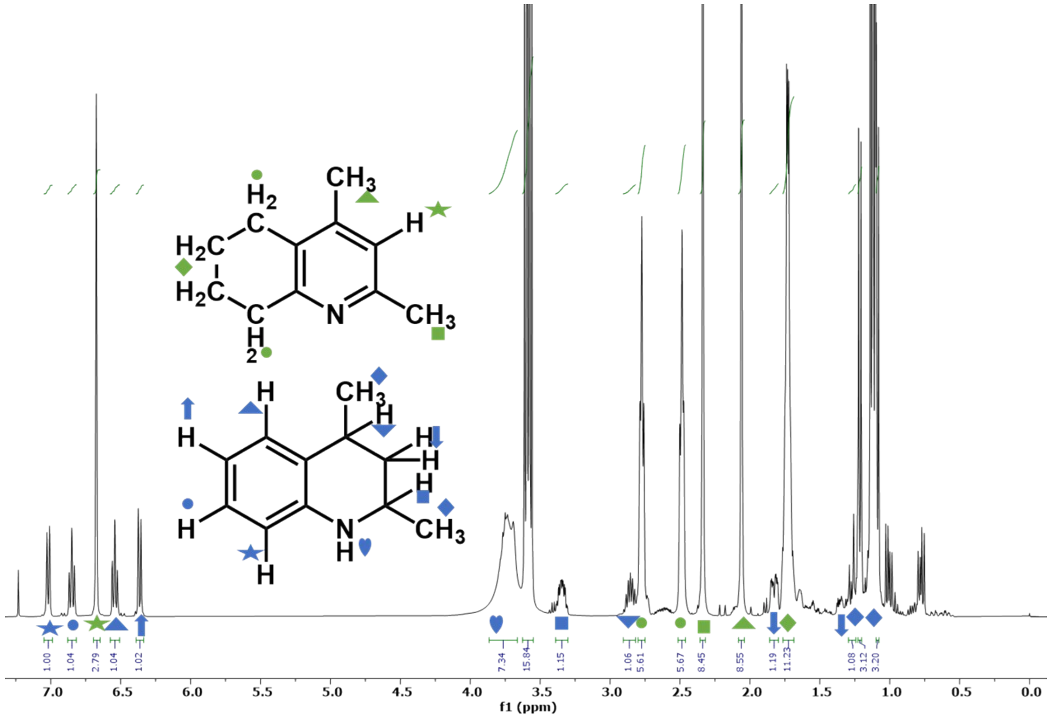

Figure S11. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of isolated products of reaction f, Figure 3. Al_2O_3-Pd-D/Ni= 94.8 mg

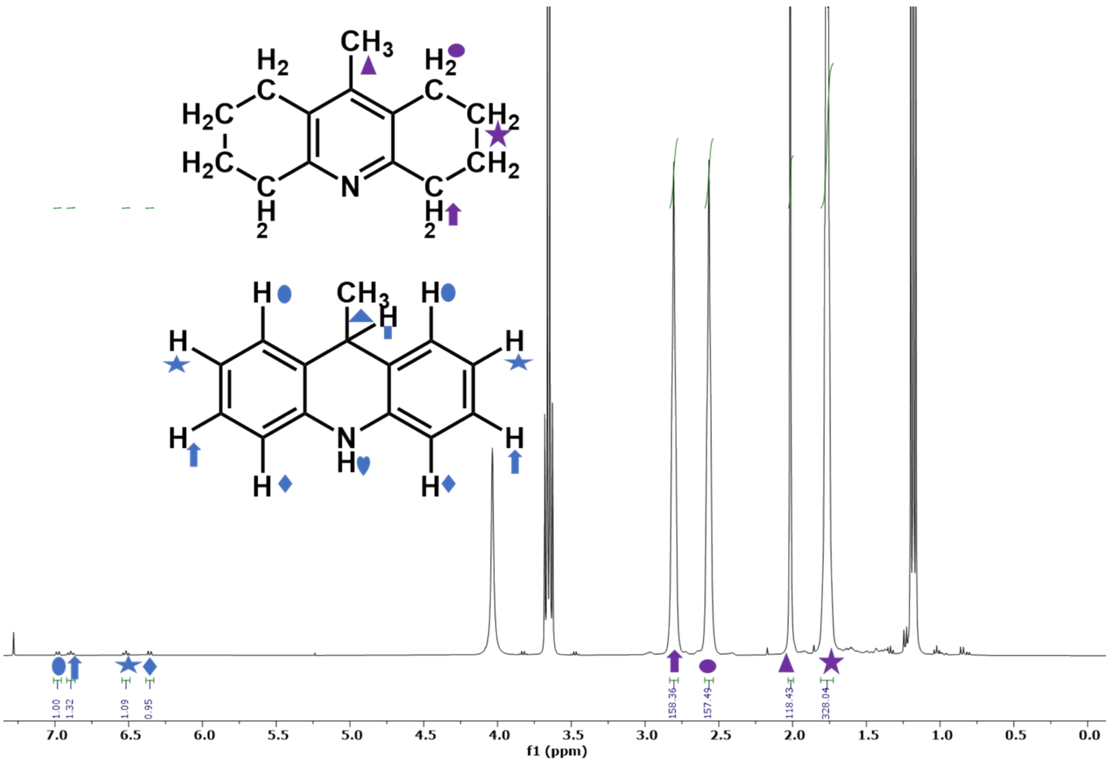

Figure S12. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of isolated products of reaction g, Figure 3. Al_2O_3-Pd-D/Ni= 110 mg

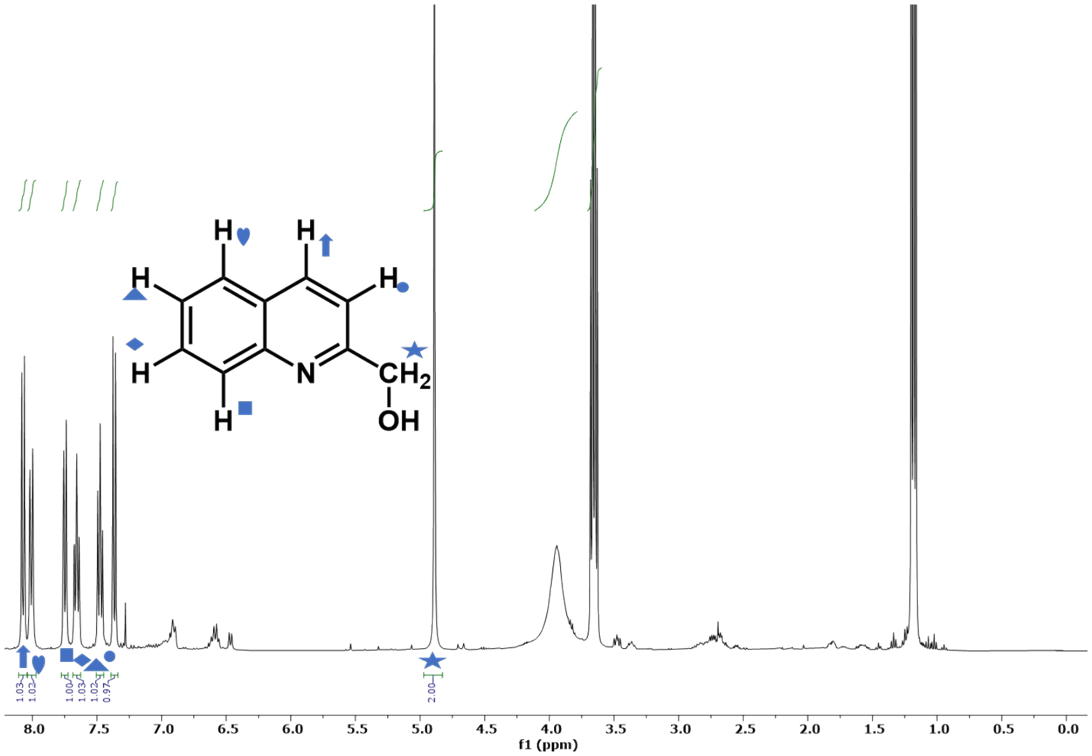

Figure S13. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of isolated products of reaction h, Figure 3. Al_2O_3-Pd-D/Ni= 89.7 mg

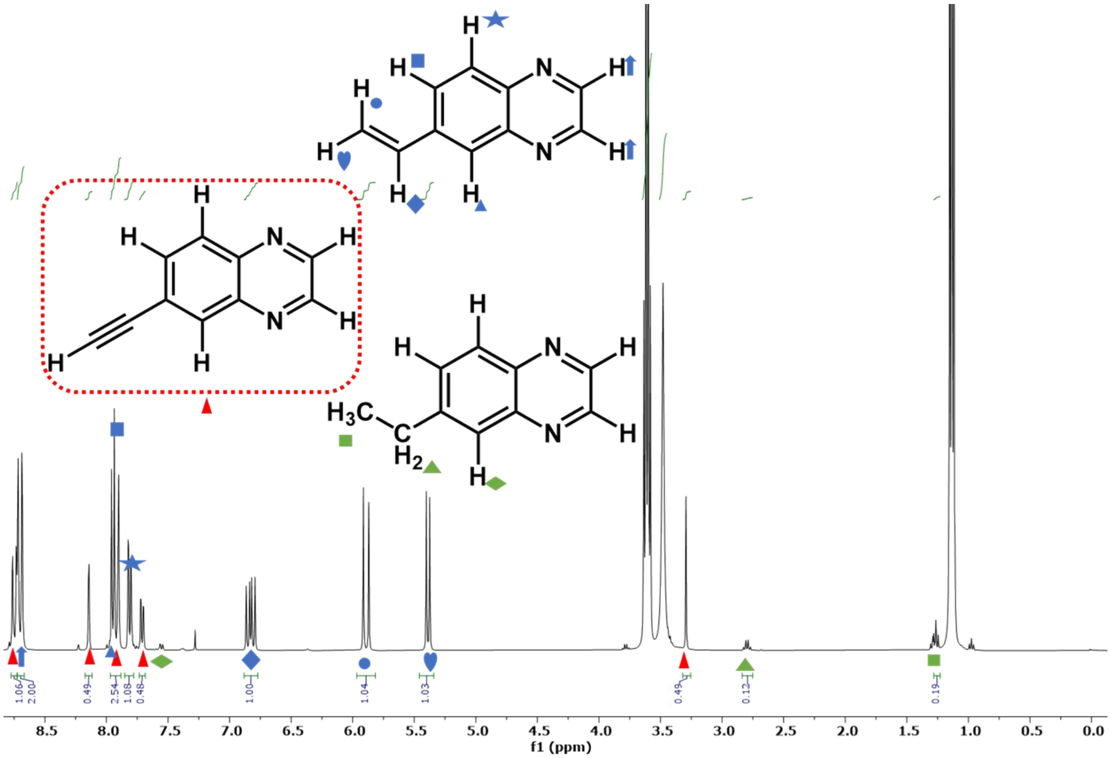

Figure S14. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of isolated products of reaction i, Figure 3. Al_2O_3-Pd-D/Ni= 110.5 mg

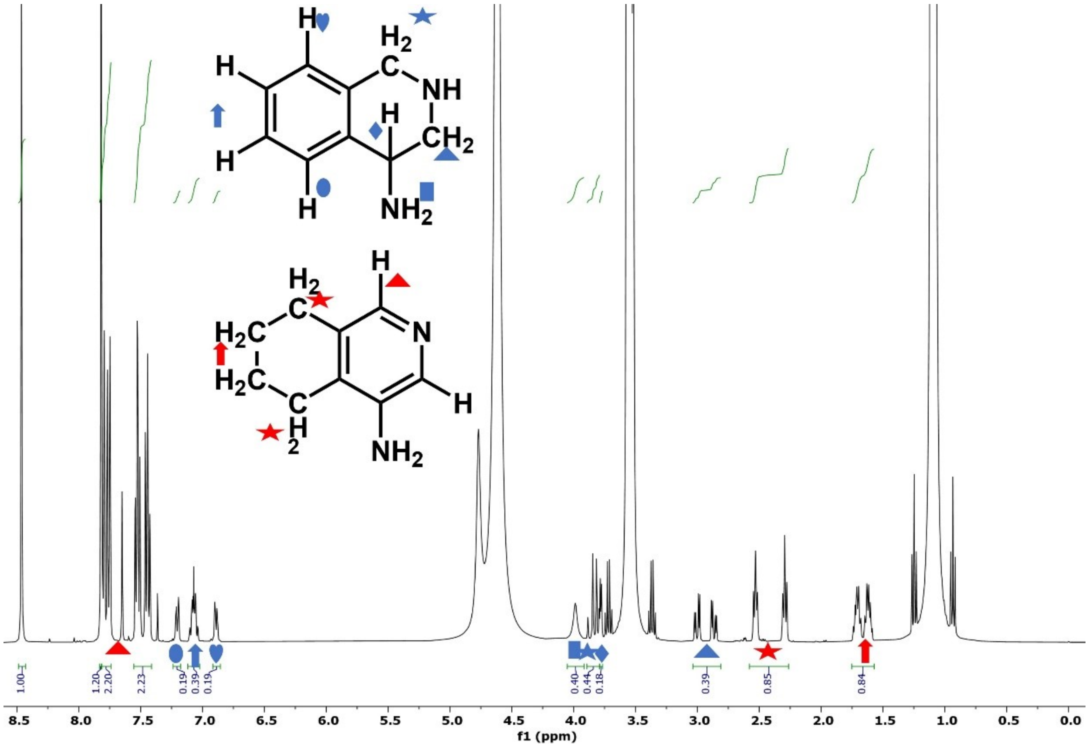

Figure S15. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of isolated products of reaction j, Figure 3 at 100 °C. Al_2O_3-Pd-D/Ni= 92.2 mg

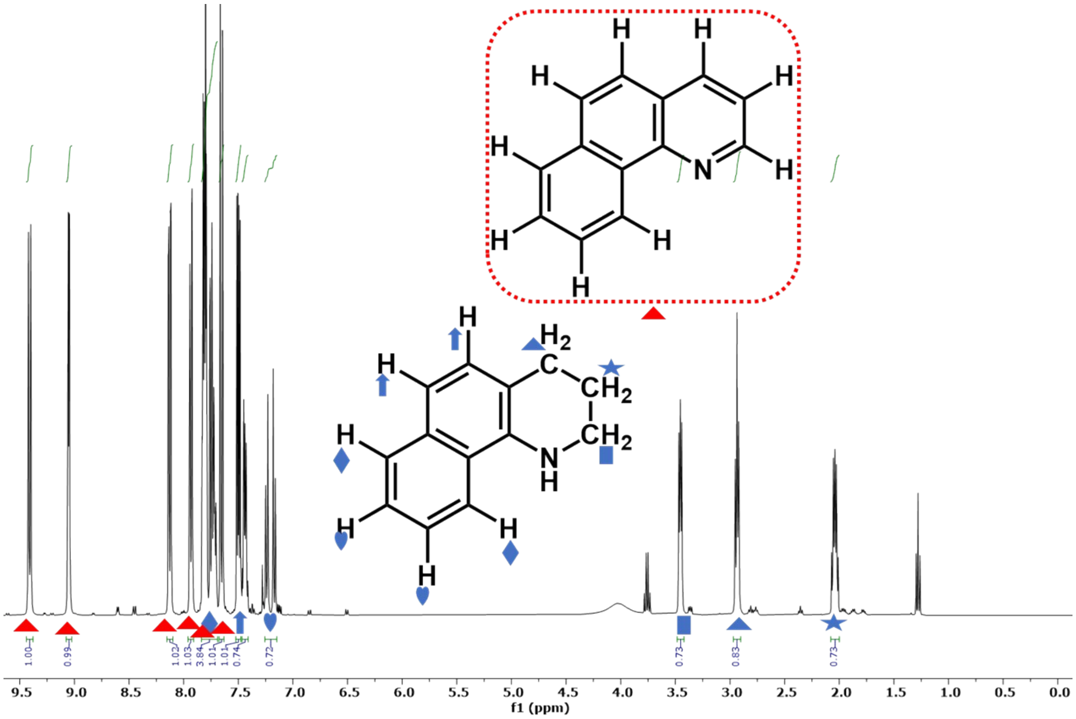

Figure S16. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of isolated products of reaction k, Figure 3 at 50 °C. Al_2O_3-Pd-D/Ni= 88.2 mg

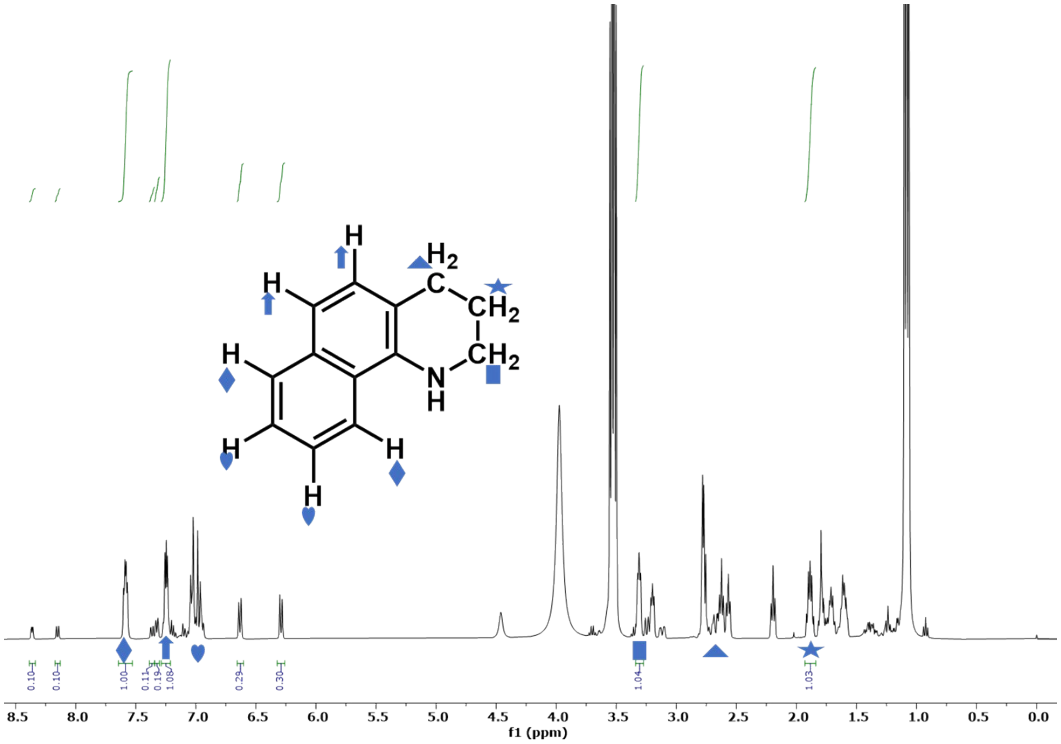

Figure S17. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of isolated products of reaction k, Figure 3. Al_2O_3-Pd-D/Ni= 91.3 mg

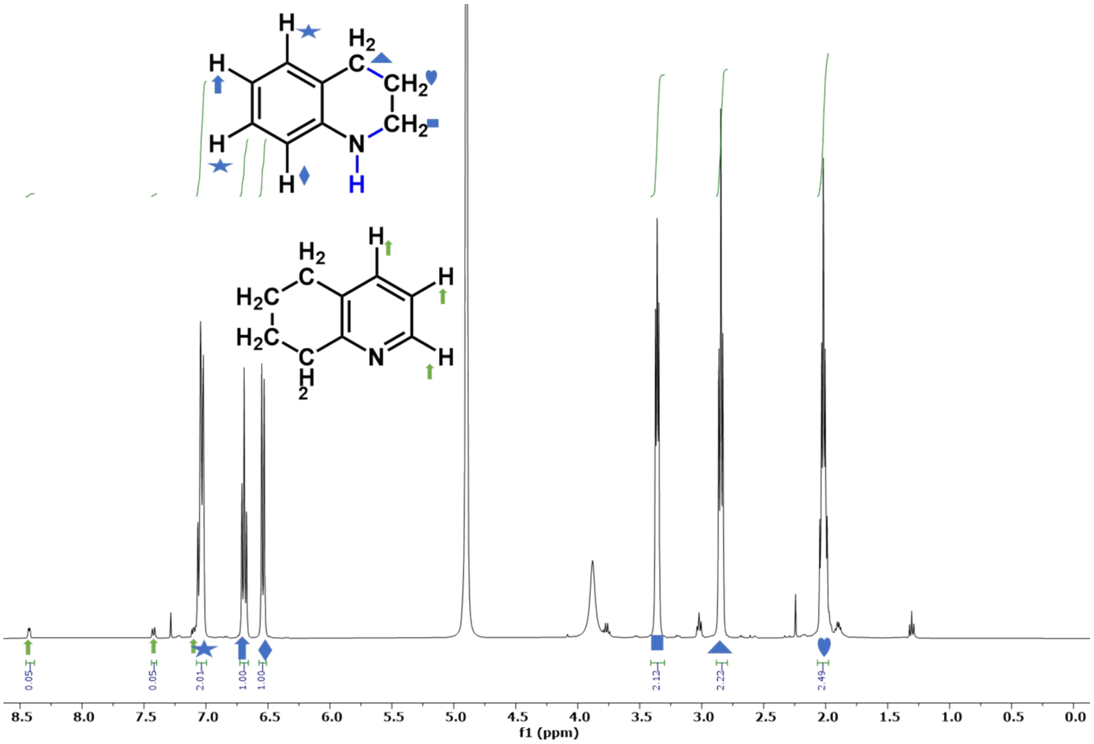

Figure S18. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of isolated products of reaction k, Figure 3. Al_2O_3-Pd-D/Ni= 99.8 mg

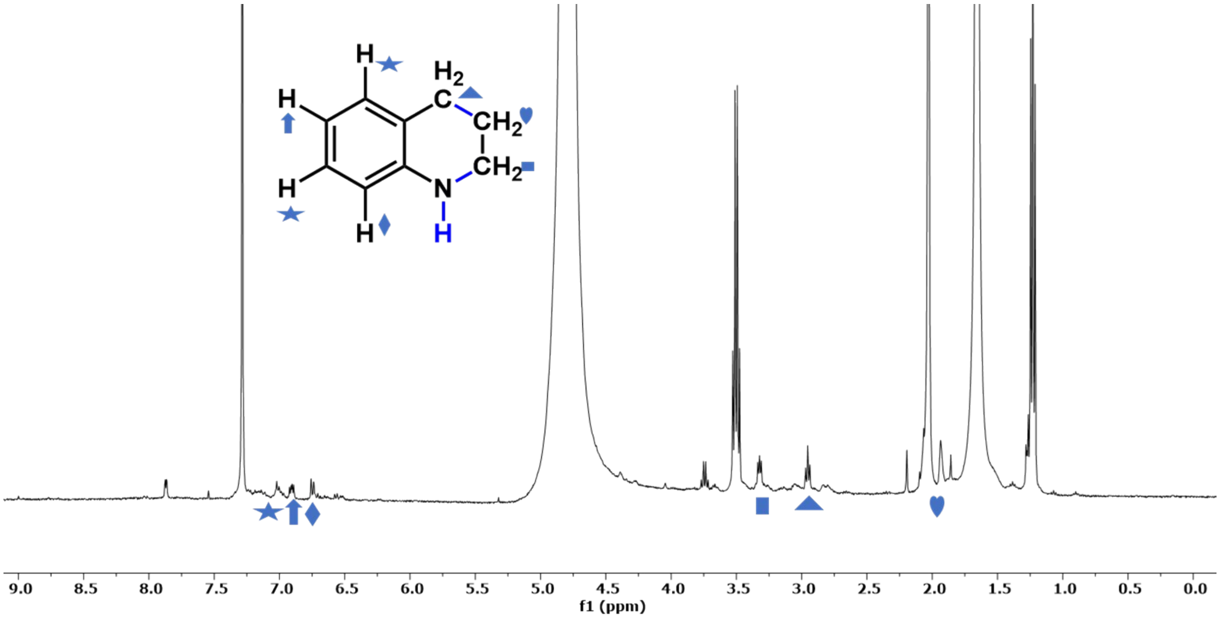

Figure S19. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of isolated products of reaction l, Figure 3. Al_2O_3-Pd-D/Ni= 101.8 mg and 5 mL H_2O as reaction solvent; reaction shows complete conversion of quinoline, but an unclear distribution of products, though predominantly the expected 1,2,3,4 product. *Trace EtOH signals are due to EtOH use to extract all products from reaction flask.*

Additional Computational Details

To analyze the bonding between the molecule and the surface in more detail, differential charge density distributions were calculated by $r_T - (r_s + r_m)$, where r_T, r_s, and r_m are charge density distribution of the molecule-adsorbed surface, surface slab model, and free-standing molecule, respectively. The results are shown in Fig. S20. Clear Shifts in the electron charge distributions can be seen in (A-C) for molecular adsorption on bare Pd surface forming bonds (chemisorption). On the other hand, there is almost no charge redistribution on PdO surface (physisorption) as shown in (D, E). The molecules are strongly bound in a flat adsorption compared to the tilted, which is consistent with the difference in the adsorption energies. Moreover, the shifts in the electron density took place across the entire 10-membered ring of the molecule Fig. S20(A,C). In the tilted adsorption, the shifted is localized near the binding N atom (Fig. S20B). This is clearer in the contour plots shown in Fig. S20(F-H) where electrons are accumulated near the C and N atoms when chemical bonds are formed between the molecules and the Pd atoms.

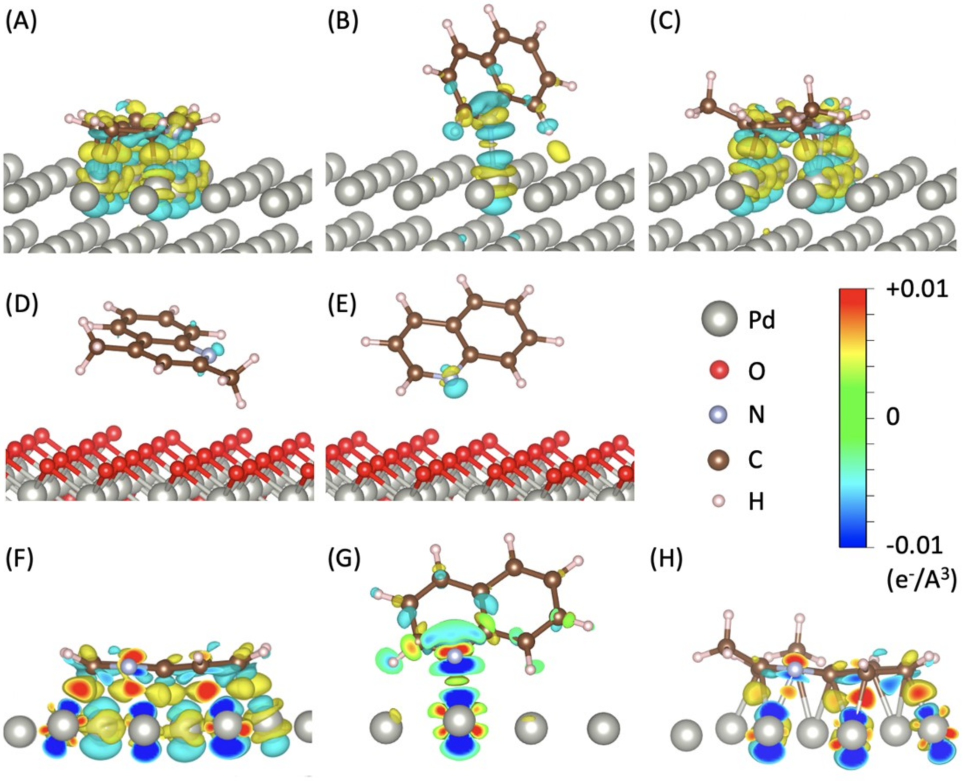

Figure S20. Differential charge density distribution of quinoline and 2,4-dimethylquinoline on Pd and PdO surface. Contour plots on planes near N atoms of the adsorbed molecules are also plotted. Isosurface of +/- 0.002 $e^-/\text{Å}^3$ is shown (+/- 0.005 for A and C). Yellow and blue surfaces correspond to positive and negative values, respectively.

References:

1. A. Rahmani, T. M. Currie, L. R. Shultz, J. T. Bryant, M. J. Beazley, F. J. Uribe-Romo, L. Tetard, N. G. Rudawski, S. Xie, F. Liu, T. H. Wang, T. G. Ong, L. Zhai and T. Jurca, *Catal. Sci. Technol.*, 2022, **12**, 6992-6997.