Science Advances

Supplementary Materials for

Acceptorless dehydrogenation and hydrogenation of N- and O-containing compounds on Pd₃Au₁(111) facets

Xinjiang Cui, Zhangjun Huang, Antoine P. van Muyden, Zhaofu Fei, Tao Wang*, Paul J. Dyson*

*Corresponding author. Email: paul.dyson@epfl.ch (P.J.D.); twang86@stanford.edu (T.W.)

This PDF file includes:

Supplementary Materials and Methods
Scheme S1 and S2
Figs. S1 to S6
Tables S1 to S4
NMR data

Materials and Methods

Catalyst characterization

Transmission electron microscopy (TEM) was performed on an FEI Talos instrument operated at 200 kV high tension. Energy-dispersive X-ray spectroscopy (EDS) mapping was used for elemental characterization. For atomic resolution spherical aberration corrected imaging, measurements were performed on an FEI Titan Themis 60-300 operated at 200 kV with an aberration-corrected electron probe in high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) mode.

X-ray diffraction (XRD) patterns were recorded on a Bruker Nonius Apex II Advance X-ray diffractometer equipped with a Mo-Kα radiation.

X-ray photoelectron spectroscopy (XPS) was recorded on a PHI Versa Probe II scanning X-ray electron spectrometer with an Al Kα X-ray source and the curve fitting was performed using PHI Multipak software.

ICP-OES analysis was performed on a NexIon 350 (Perkin Elmer) instrument. The catalyst was placed in muffle oven to remove the carbon support and ensure all of the metal ions were exposed by heated at 600 °C for 6 h in air. After dropwise addition of nitric acid (mixture of 0.25 mL ultrapure nitric acid (65%, Merck KGaA) and 5 mL H_2O), the metal is dissolved and filtered. The solid was washed with distilled water (3 x 1 mL). All the filtrate and washings are collected and combined in one volumetric flask and the total volume was adjusted to 10 mL by addition of water.

## Catalyst Recycling Experiments

Using a similar procedure general procedure for dehydrogenation and hydrogenation reactions described in the article, the catalyst was separated by centrifugation, washed with xylene and toluene and used without further reactivation or purification for the next run.

Preparation of D-indoline
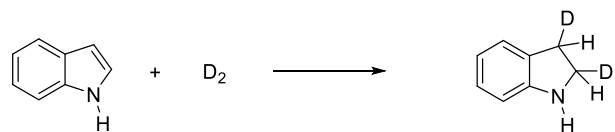
Prepared using the general hydrogenation procedure, except under D_2 gas (2 bar) instead of H_2. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.11 (d, 1H), 7.09 – 6.95 (m, 1H), 6.95 – 6.59 (m, 2H), 3.61 (s, 1H), 3.59 – 3.43 (m, 1H), 3.02 (d, 1H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 171.22, 127.32, 124.76, 118.86, 109.66, 77.48, 77.16, 76.85, 47.31, 29.82.

General procedure for the dehydrogenation of D-indoline
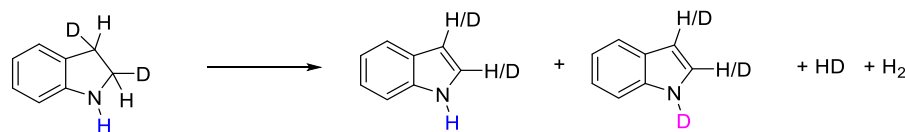
Pd$_3$Au$_1$/CNT (5mg), indoline (0.2 mmol) and xylene (0.4 mL) were placed in a sapphire NMR tube and charged with nitrogen. The sealed NMR tube was heated to reflux and the formation of HD and H_2 gas were analyzed in-situ by NMR spectroscopy. After 24h, the flask was cooled to room temperature and the product was isolated by column chromatography and characterized by NMR spectroscopy. ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.04 (s, 1H), 7.68 – 7.48 (m, 1H), 7.32 (m, .0 Hz, 1H), 7.16 – 7.01 (m, 3H), 6.49 (q, 1H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 135.89, 127.96, 124.25, 122.10, 120.85, 119.93, 111.15, 102.73
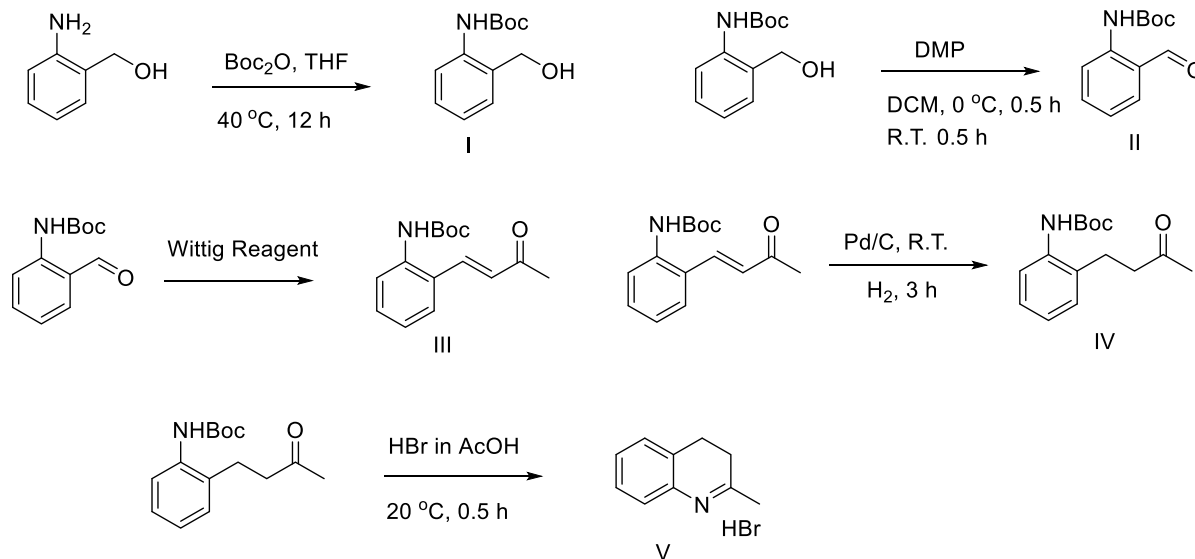
Preparation of 1,2-dihydroquinoline
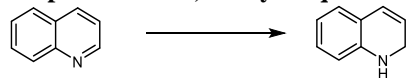
The synthesis of 1,2-dihydroquinoline was conducted using a literature procedure. A solution of quinoline (500 mg, 3.87 mmol) in dry THF (2.5 mL) was added slowly to an ice-cold suspension of lithium aluminum hydride (172 mg, 4.645 mmol) in dry THF (10 mL). The solution was stirred for 2 h at 0 °C until the conversion was complete (reaction was monitored by TLC). The reaction was then carefully quenched with ice and filtered. The filtrate was extracted with ethyl acetate (20 ml). The crude reaction product was purified by column chromatography. The product was analyzed by NMR spectroscopy. ^{1}H NMR (400 MHz, CDCl$_3$) δ 6.85 (m, 1H), 6.73 (m, 1H), 6.49 (m, 1H), 6.28 (d, 1H), 6.21 (m, 1H), 5.64 – 5.52 (m, 1H), 4.10 (m, 2H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 144.80, 128.62, 126.78, 126.32, 121.97, 121.08, 117.84, 112.60, 77.36, 77.04, 76.72, 43.15.

Preparation of 2-methyl-3,4-dihydroquinoline

The intermediate 2-methyl-3,4-dihydroquinoline (V in Scheme S1) was prepared according to a literature method (*Chem. Eur. J.* **23**, 14167-14172 (2017)).

Scheme S1. Preparation of 2-methyl-3,4-dihydroquinoline.

Tert-butyl (2-(hydroxymethyl)phenyl)carbamate (I): ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.86 – 7.76 (m, 1H), 7.58 (s, 1H), 7.30 – 7.17 (m, 1H), 7.08 (m, 1H), 7.00 – 6.89 (m, 1H), 4.59 (d, *J* = 4.1 Hz, 2H), 1.44 (s, 9H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 153.58, 138.06, 129.25, 129.19, 129.08, 123.29, 121.26, 80.58, 64.34, 28.48.

Tert-butyl (2-formylphenyl)carbamate (II): ^{1}H NMR (400 MHz, CDCl$_3$) δ 10.39 (s, 1H), 9.89 (m, 1H), 8.45 (m, 1H), 7.74 – 7.49 (m, 2H), 7.12 (m, 1H), 1.53 (s, 9H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 195.13, 152.99, 141.91, 136.18, 136.05, 121.60, 121.32, 118.34, 81.06, 28.40.

Tert-butyl (E)-(2-(3-oxobut-1-en-1-yl)phenyl)carbamate (III): ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.78 – 7.63 (m, 2H), 7.54 (m, 1H), 7.37 (m, 1H), 7.14 (m, 1H), 6.68 (m, 1H), 6.54 (s, 1H), 2.54 – 2.24 (m, 3H), 1.75 – 1.40 (m, 9H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 198.13, 153.24, 138.11, 136.94, 131.10, 128.62, 127.29, 124.95, 123.69, 81.23, 77.48, 77.16, 76.84, 28.40.

Tert-butyl (2-(3-oxobutyl)phenyl)carbamate (IV): ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.15 – 6.81 (m, 5H), 3.08 – 2.68 (m, 4H), 2.06 (s, 3H), 1.46 (s, 9H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 209.08, 131.83, 129.42, 126.96, 124.19, 123.27, 80.05, 44.60, 29.98, 28.43, 24.08.

2-Methyl-3,4-dihydroquinolinehydrobromide (V): ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.58 – 7.32 (m, 5H), 3.08 (m, 4H), 2.73 – 2.63 (m, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 190.13, 134.45, 133.26, 131.48, 130.60, 129.40, 122.60, 26.49, 22.64, 22.55.
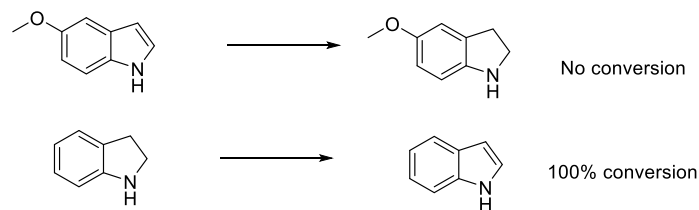
Scheme S2. Conversion of indoline using 5-methoxylindole as a hydrogen acceptor. Full conversion of indoline without any hydrogenated 5-methoxylindoline was achieved, indicating that the released hydrogen does not re-reduce the product and implying that the N-D bond shown in Figure **3c** is formed by tautomerization rather than the hydrogenation of the C=N in the presence of released HD.
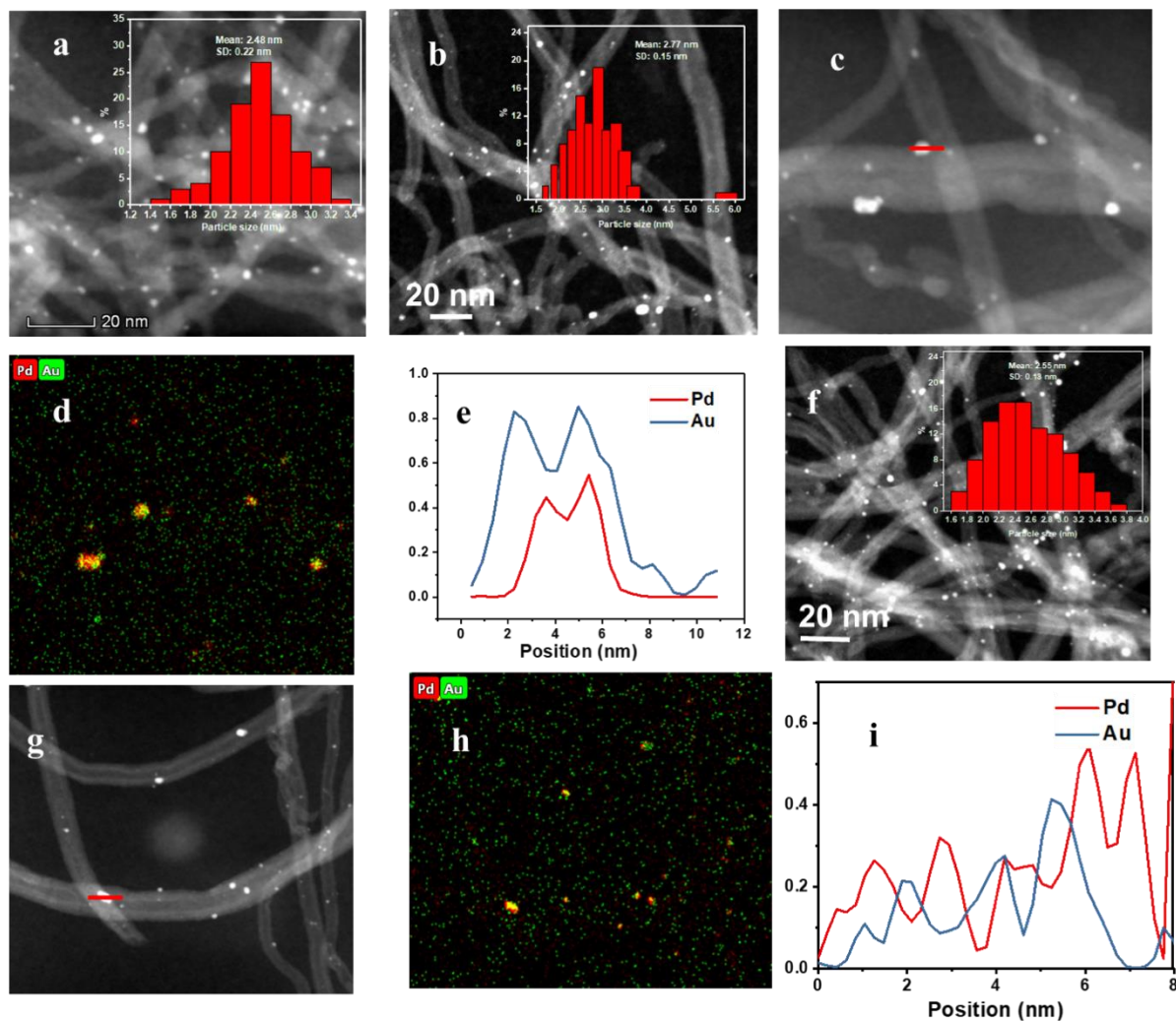

Fig. S1. TEM characterization of the Pd₃Au₁/CNT, Pd₁Au₁/CNT and Pd₁Au₃/CNT catalysts. (a) HAADF-STEM image of the PdAu/CNT catalyst. For Pd₁Au₁/CNT, (b) and (c) HAADF-STEM image; (d) HAADF-TEM-EDS mapping images of Au and Pd and (e) crossline profiles of elemental composition of the AuPd NP. For Pd₁Au₃/CNT, (f) and (g) HAADF-STEM image; (h) HAADF-TEM-EDS mapping images of Au and Pd, (i) crossline profiles of elemental composition of the AuPd NP and (I) XRD analysis.
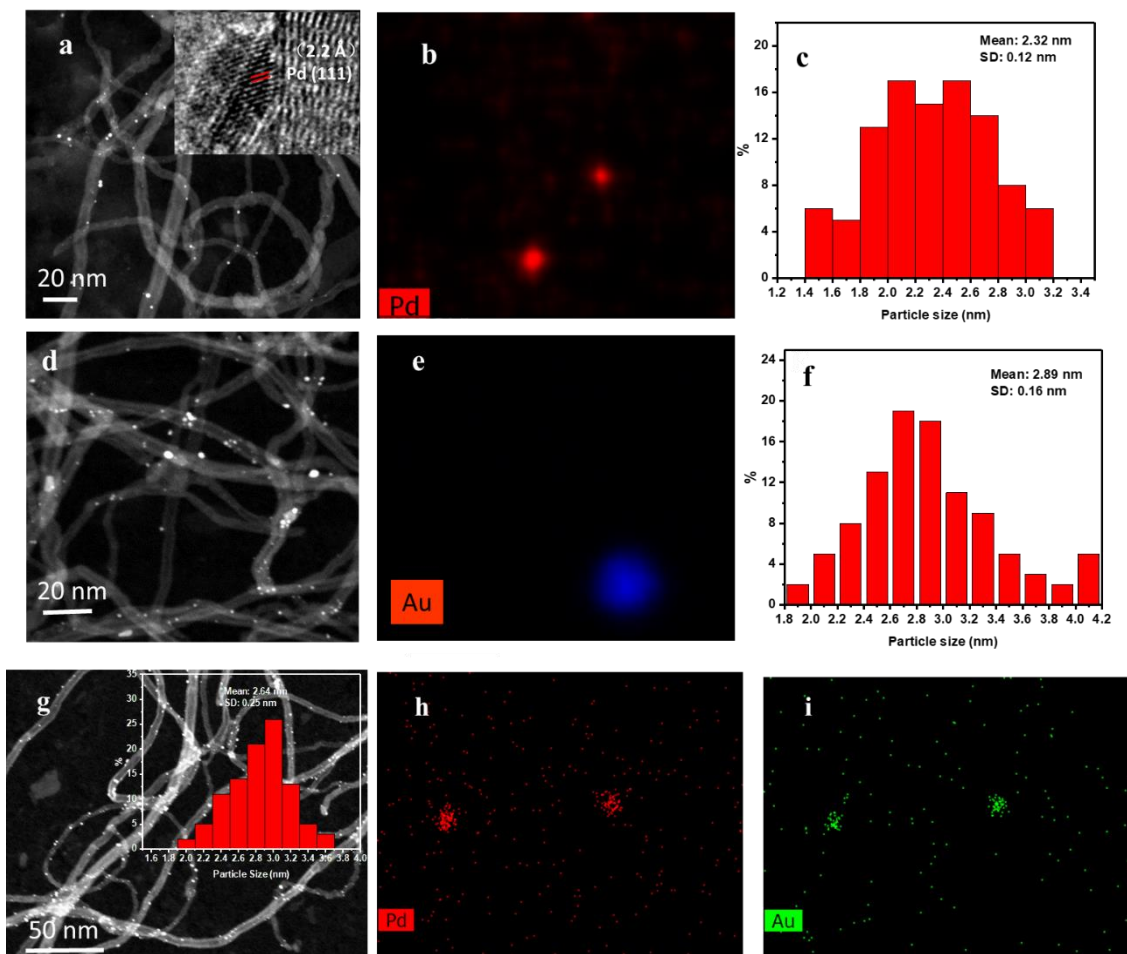
Fig. S2. TEM characterization of the Pd/CNT, Au/CNT and used Pd₃Au₁/CNT catalysts. For Pd/CNT, (a) HAADF-STEM image; (b) TEM-EDS mapping images of Pd and (c) size distribution. And characterization of the Au/CNT catalyst: (d) HAADF-STEM image; (e) HAADF-TEM-EDS mapping images of Au and (f) size distribution. Characterization Pd₃Au₁/CNT catalyst after use: (g) HAADF-STEM images; HAADF-TEM-EDS mapping images of Pd (h) and Au (i).
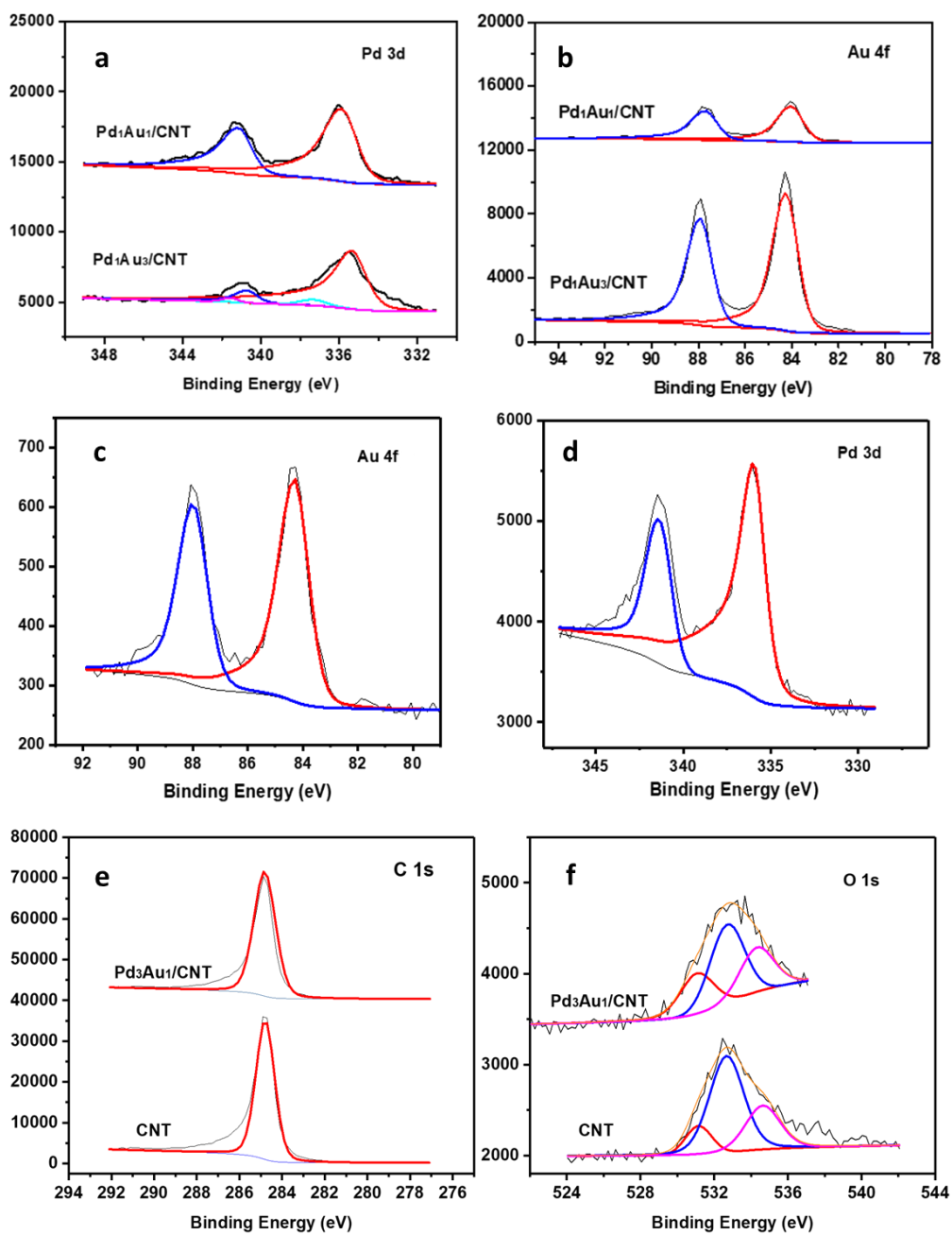
Fig. S3. **XPS characterization of the catalysts.** Pd 3d (a) spectra and Au 4f (b) spectra of the Pd_1Au_3/CNT and Pd_1Au_1/CNT catalysts. XPS of Au 4f spectra (c) and Pd 3d (d) spectra of the Pd_3Au_1/CNT after use. XPS of C 1s (e) and O 1s (f) spectra of Pd_3Au_1/CNT and CNT.
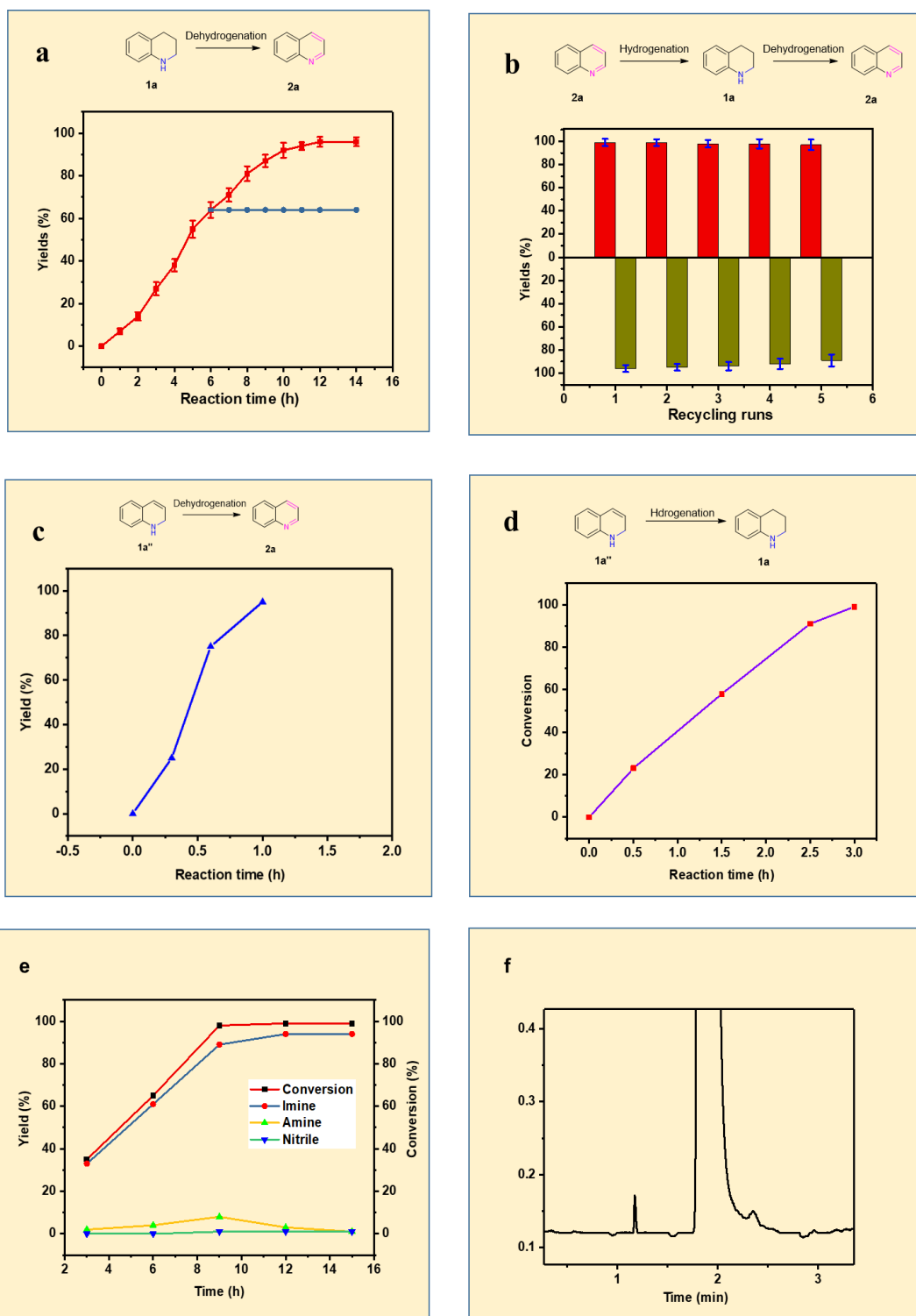
Fig. S4. Control experiments using the Pd₃Au₁/CNT catalyst. (a) Kinetic curves of the dehydrogenation reaction (red line) and the dehydrogenation reaction following the application of a hot filtration test (blue line). Reaction conditions: catalyst (0.3 mol% of metals to **1a**), **1a** (0.2 mmol), xylene (1 mL), N_2 atmosphere, 140 °C. (b) Interconversion between **2a** and **1a** via consecutive hydrogenation-dehydrogenation steps. Reaction conditions for the hydrogenation (red bars): catalyst (0.3 mol% of metals to **2a**), **2a** (0.2 mmol), xylene (1 mL), H_2 (1 bar), 80 °C, 12h. Reaction conditions for the dehydrogenation (brown bars): Pd₃Au₁/CNT (0.3 mol% of metals to **1a**), **1a** (0.2 mmol), xylene (1 mL), N_2 atmosphere, 140 °C, 12h. (c) Reaction profiles for the dehydrogenation of 1,2,-dihydroquinoline, (d) for the hydrogenation of 1,2,-diahydroquinoline by heating the mixture in xylene at 80 °C and 1 bar H_2, (e) for the dehydrogenative coupling of benzylamine to form imine, amine and nitrile products. (f) Released H_2 detected by GC-TCD.
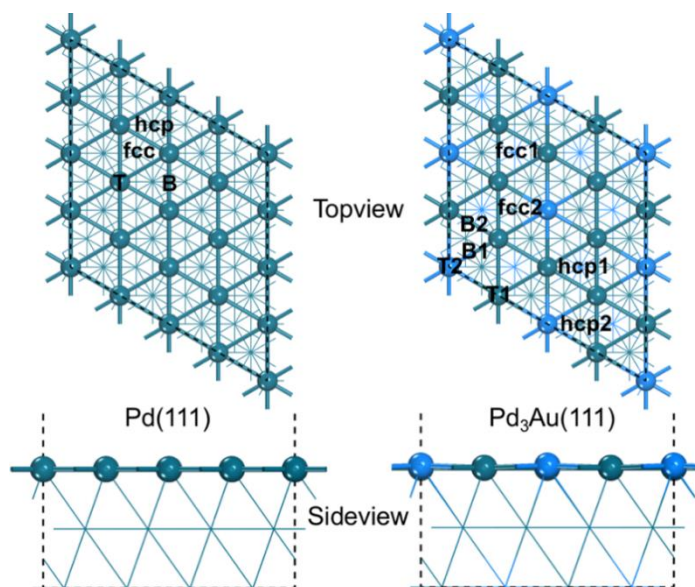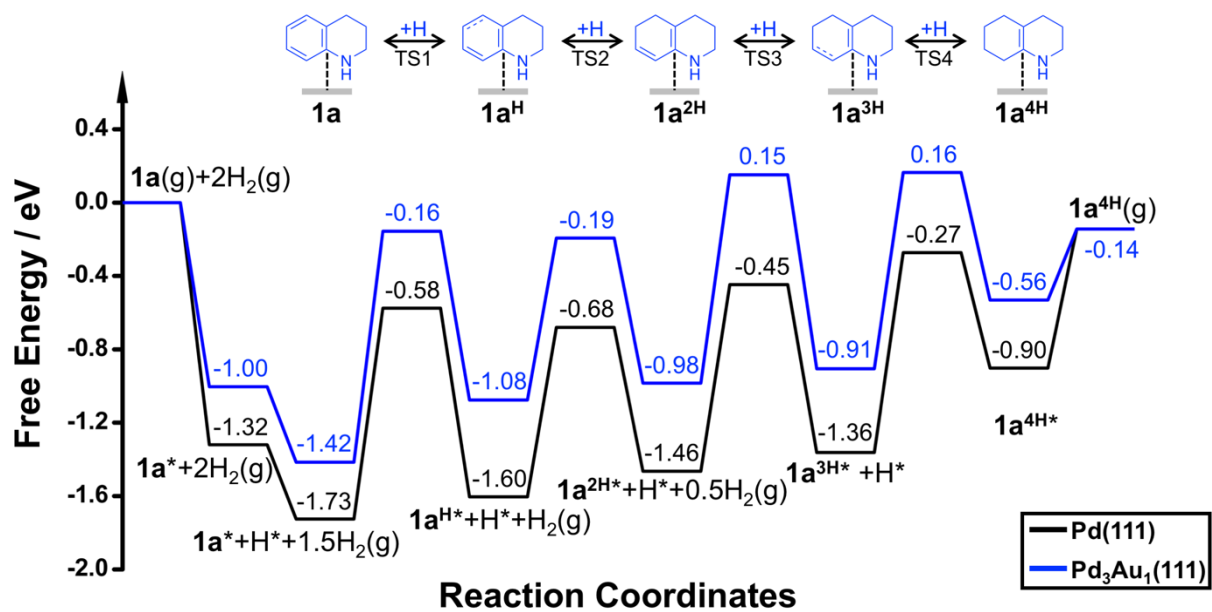
Fig. S5. Potential free energy diagrams for the deep hydrogenation and surface structure. (**top**) Hydrogenation of **1a** at 80 °C on the Pd(111) and Pd$_3$Au$_1$(111) surfaces. (**bottom**) Schematic top and side views of Pd(111) and Pd$_3$Au$_1$(111) surface structures.
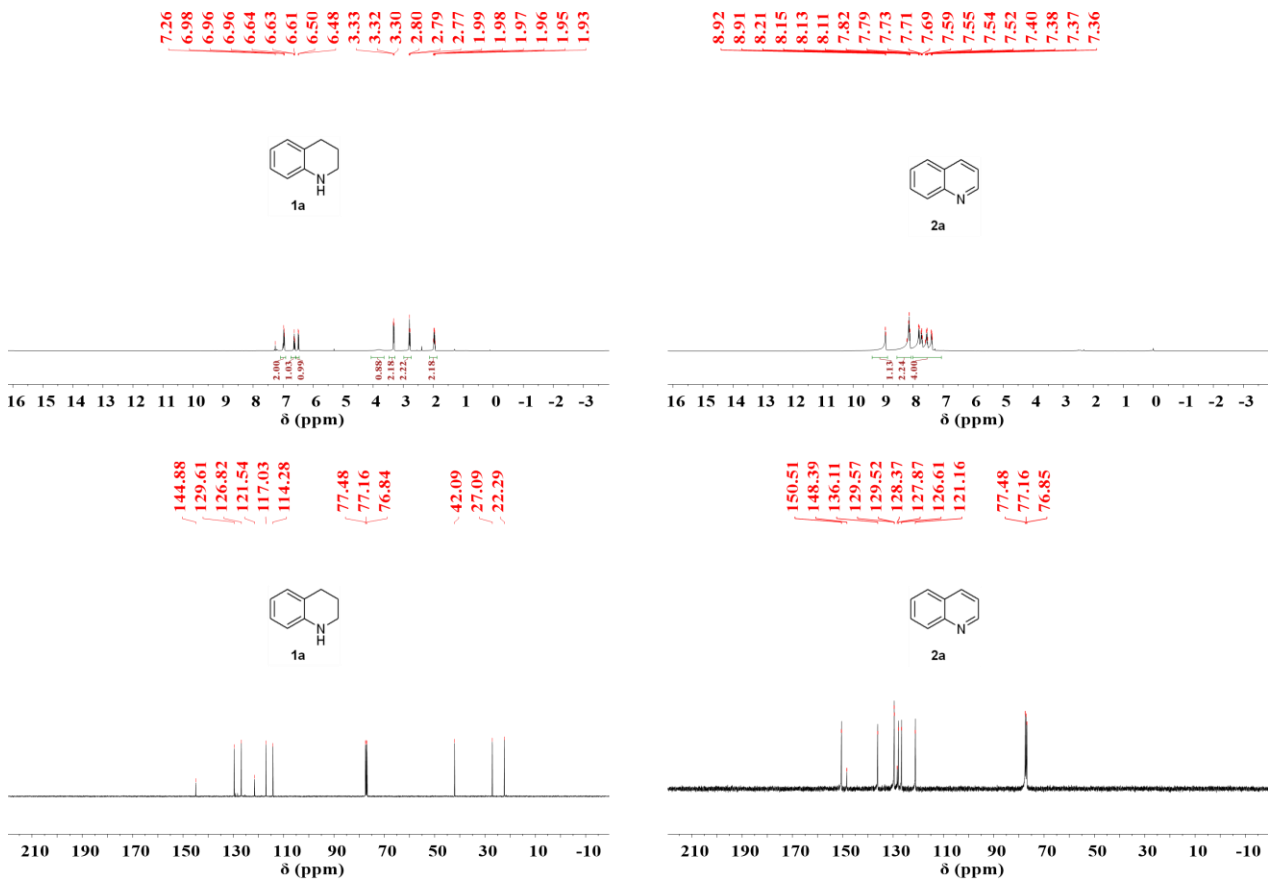
Fig. S6. ^{1}H and ^{13}C NMR of **1a** and **2a.**

Table S1. Optimization of the dehydrogenation of 1,2,3,4-tetrahydro-quinoline. Reaction conditions: catalysts (5 mg, 0.3 mol% of Pd and Au to **2a** for entry 4), substrate (0.2 mmol), solvent (1.0 ml), N_2, 140 °C, 0.3 mol% of Pd to **1a** was used in entries 7-12. GC yield. TON = mol product/mol Pd and Au. TOF = TON/reaction time. TON and TOF in entries 2-6 and 13-17 were calculated according to the results by ICP-OES.

1a → **2a**
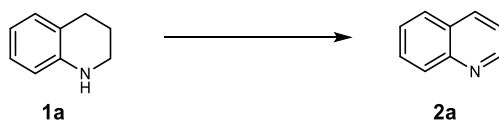
| Entry	Catalyst	Solvent	t (h)	Yield (%)	TON	TOF
1	CNT	Xylene	12	0	0	0
2	Au/CNT	Xylene	12	8	30	2.5
3	Pd/CNT	Xylene	12	30	66	5.5
4	Pd_3Au_1/CNT	Xylene	12	96	321	26.8
5	Pd_1Au_1/CNT	Xylene	12	91	309	25.7
6	Pd_1Au_3/CNT	Xylene	12	83	278	23.2
7	Pd/C	Xylene	12	26	65	5.4
8	PdO	Xylene	12	18	45	3.7
9	K_2PdCl_4	Xylene	12	5	12	1
10	$Pd(acac)_2$	Xylene	12	4	10	0.8
11	$Pd(NH_3)_4Cl_2$	Xylene	12	8	20	1.7
12	$PdCl_2$	Xylene	12	30	75	6.2
13	Pd_3Au_1/CNT	Toluene	12	67	224	18.7
14	Pd_3Au_1/CNT	DMF	12	35	117	9.8
15	Pd_3Au_1/CNT	Xylene	8	76	255	21.2
16	Pd_3Au_1/C	Xylene	12	29	89	7.4
17	Pd_3Au_1/Al_2O_3	Xylene	12	34	105	8.7

Table S2. Benchmark hydrogenation of quinoline: variation of the reaction conditions. Reaction conditions: catalysts (5 mg, 0.3 mol% of Pd and Au to **2a** for entry 3), substrate (0.2 mmol), xylene (0.5 ml), H_2 (1 bar). GC yield. TON = mol product/mol Pd and Au. TOF = TON/reaction time. TON and TOF were calculated according to the results by ICP-OES.
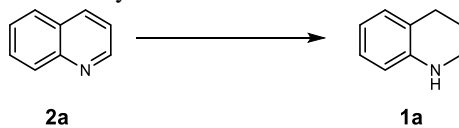
	2a			1a		
Entry	Catalyst	T (°C)	t (h)	Yield (%)	TON	TOF
1	Au/CNT	80	12	0	0	0
2	Pd/CNT	80	12	86[c]	192	15.9
3	Pd$_3$Au$_1$/CNT	80	12	99	351	29.3
4	Pd$_1$Au$_1$/CNT	80	12	90	306	25.5
5	Pd$_1$Au$_3$/CNT	80	12	82	330	27.5
6	Pd$_3$Au$_1$/CNT	60	12	81	287	23.9
7	Pd$_3$Au$_1$/CNT	80	8	89[†]	316	26.3
8	Pd$_3$Au$_1$/CNT	80	12	76[‡]	270	22.5
9	Pd$_3$Au$_1$/C	80	12	71	220	18.3
10	Pd$_3$Au$_1$/Al$_2$O$_3$	80	12	84	260	21.7

[†]Decahydroquinoline is the side product. [‡]DMF.

Table S3. **Dehydrogenation of amines and alcohols using the Pd$_3$Au$_1$/CNT catalyst.** Reaction conditions: Pd$_3$Au$_1$/CNT (0.3 mol% of metals to substrate), amines or alcohols (0.2 mmol), xylene (1 mL), N$_2$ atmosphere, 140 °C, 24 h.
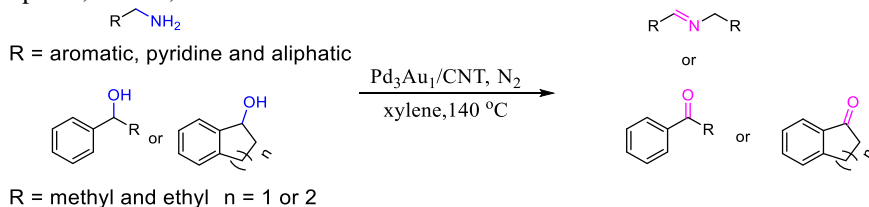
Entry	Substrate	Product	Yield (%)[†]
1	(5a)	(4a)	94
2	(5b)	(4f)	71[‡]
3	(5c)	(4g)	71[‡]
4	(5d)	(4h)	80[‡]
5	(5e)	(4i)	93[‡]
6	(5f)	(4j)	64[‡, §]
7	(5g)	(4k)	99
8	(5h)	(4l)	95
9	(5i)	(4m)	98
10	(5j)	(4n)	96[∥]
11	(5k)	(4o)	94[∥]

[†]Isolated yield. [‡]NMR yields with diphenylmethanol as standard. [§]Toluene used as solvent. [∥]12h

Table S4: Adsorption energies of quinoline vs TOF on different catalysts and TOFs for **1a** dehydrogenation.

Catalysts	Adsorption energy of **2a** (eV)	TOF (dehydrogenation) / h^{-1}
Pd(111)	-3.03	5.5
Pd$_3$Au$_1$(111)	-2.14	26.8
Pd$_1$Au$_1$ (111)	-1.45	25.7
Pd$_1$Au$_3$(111)	-1.13	23.2
Au(111)	-0.91	2.5

NMR data

(**2a**) ^{1}H NMR (400 MHz, CDCl$_3$) δ= 8.93-8.91(d, 1H), 8.54-8.06 (m, 2H), 8.01-7.06 (m, 4H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 150.51, 148.39, 136.11, 129.57, 129.52, 128.37, 127.87, 126.61, 121.16.

(**2b**) ^{1}H NMR (400 MHz, CDCl$_3$) δ= 7.95-7.92 (d, 2H), 7.75-7.53 (m, 2H), 7.41-7.36 (m, 1H), 7.20-7.16 (d, 1H), 2.66 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ= 159.06, 147.91, 136.30, 129.53, 128.68, 127.58, 126.57, 125.77, 122.09, 25.45.

(**2c**) ^{1}H NMR (400 MHz, CDCl$_3$) δ= 8.79-8.74 (d, 1H), 8.10-8.04 (m, 1H), 7.92-7.89 (d, 1H), 7.82-7.41 (m, 3H), 2.51 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ= 152.54, 146.69, 134.76, 130.57, 129.30, 128.53, 128.24, 127.24, 126.65, 18.87.

(**2d**) ^{1}H NMR (400 MHz, CDCl$_3$) δ= 8.79-8.75 (d, 1H), 8.13-8.09 (d, 1H), 8.01-7.96 (d, 1H), 7.73-7.69 (d, 1H), 7.58-7.54 (d, 1H), 7.39- 7.19 (m, 1H), 2.70 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ= 150.18, 147.96, 144.51, 130.04, 129.26, 128.38, 126.41, 123.92, 121.95, 18.77.

(**2e**) ^{1}H NMR (400 MHz, CDCl$_3$) δ= 10.00 (s, 1H), 8.67-8.63 (d, 1H), 8.15-8.12 (d, 1H), 7.87-7.84 (d, 1H), 7.38-7.33 (m, 2H), 7.17-7.12 (d, 1H). ^{13}C NMR (101 MHz, CDCl$_3$) δ= 155.43, 147.08, 143.00, 134.17, 130.38, 129.29, 121.94, 121.37, 108.30, 39.73, 39.52, 39.31.

(**2f**) ^{1}H NMR (400 MHz, CDCl$_3$) δ= 8.87-8.24 (m, 2H), 7.71-7.00 (m, 3H), 2.66 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ= 135.73, 131.13, 122.90, 119.77, 119.50, 110.76, 110.55, 25.32.

(**2g**) ^{1}H NMR (400 MHz, CDCl$_3$) δ= 8.59-8.55 (d, 1H), 7.85-7.81 (t, 2H), 7.49- 6.68 (m, 3H), 3.91 (s, 2H). ^{13}C NMR (101 MHz, CDCl$_3$) δ= 146.75, 144.81, 143.35, 134.03, 130.51, 129.93, 121.77, 121.50, 107.49.

(**2h**) ^{1}H NMR (400 MHz, CDCl$_3$) δ= 8.89-8.84 (m, 1H), 8.05-8.01 (m, 1H), 7.59-7.54 (m, 1H), 7.49-7.44 (d, 1H), 7.38-7.26 (m, 2H), 2.75 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ= 149.33, 147.43, 137.16, 136.46, 129.75, 128.38, 126.42, 125.98, 120.94, 18.28.

(**2i**) ^{1}H NMR (400 MHz, CDCl$_3$) δ= 8.77-8.72 (d, 1H), 8.26-8.22 (m, 2H), 8.06-7.95 (m, 2H), 7.79-7.76 (m, 2H), 7.55-7.51 (m, 2H). ^{13}C NMR (101 MHz, CDCl$_3$) δ= 149.20, 136.18, 130.42, 129.54, 128.33, 126.71, 125.81.

(**2j**) ^{1}H NMR (400 MHz, CDCl$_3$) δ= 9.17 (s, 1H), 8.66-8.54 (m, 2H), 8.26-8.18 (m, 1H), 8.12-8.01 (m, 1H), 7.89-7.83 (m, 1H), 7.82-7.61 (m, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ= 153.69, 144.60, 132.69, 131.14, 130.28, 128.90, 128.82, 127.62, 127.21, 122.35, 122.00.

(**2k**) ^{1}H NMR (400 MHz, CDCl$_3$) δ= 9.29-9.20 (d, 1H), 9.09-8.85 (m, 1H), 8.19-8.14 (m, 1H), 7.95-7.88 (d, 2H), 7.85-7.74 (m, 1H), 7.78-7.65 (m, 3H), 7.59-7.49 (m, 1H). ^{13}C NMR (101 MHz, CDCl$_3$) δ= 148.97, 146.73, 135.95, 133.75, 131.65, 128.33, 127.95, 127.90, 127.21, 126.54, 125.48, 124.50, 121.93.

(**2l**) ^{1}H NMR (400 MHz, CDCl$_3$) δ= 9.06-8.71 (m, 2H), 8.25-8.03 (m, 2H), 7.92-7.67 (m, 2H). ^{13}C NMR (101 MHz, CDCl$_3$) δ= 144.98, 143.05, 130.05, 129.53.

(**2m**) ^{1}H NMR (400 MHz, CDCl$_3$) δ= 9.29-9.18 (d, 1H), 8.58-8.47 (m, 1H), 7.99-7.85 (m, 1H), 7.76-7.89 (m, 1H), 7.74-7.50 (m, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ= 152.56, 143.05, 135.76, 130.31, 128.68, 127.61, 127.22, 126.46, 120.44.

(**2n**) ^{1}H NMR (400 MHz, CDCl$_3$) δ= 8.01 (s, 1H), 7.68-7.53 (m, 1H), 7.41-7.28 (m, 1H), 7.25- 7.08 (m, 2H), 7.08-7.00 (m, 1H), 6.58-6.39 (m, 1H). ^{13}C NMR (101 MHz, CDCl$_3$) δ= 135.90, 127.97, 124.24, 122.12, 120.86, 119.94, 111.14, 102.76.
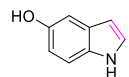
(**2o**) ¹H NMR (400 MHz, CDCl₃) δ= 8.01-7.89 (s, 1H), 7.23-7.08 (m, 2H), 7.08-6.83 (m, 1H), 6.78-6.57 (m, 1H), 6.36 (s, 1H), 4.46 (s, 1H). ¹³C NMR (101 MHz, CDCl₃) δ= 149.65, 131.31, 128.72, 125.39, 111.94, 111.76, 105.21, 102.20.
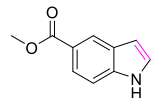
(**2p**) ¹H NMR (400 MHz, CDCl₃) δ= 8.47 (s, 1H), 8.35 (s, 1H), 7.93-7.71 (m, 1H), 7.54-7.09 (m, 2H), 6.57 (s, 1H), 3.86 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ= 138.55, 127.59, 125.69, 123.91, 123.47, 121.99, 110.89, 104.11, 52.02.
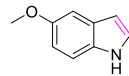
(**2q**) ¹H NMR (400 MHz, CDCl₃) δ= 8.00 (s, 1H), 7.58-6.61 (m, 4H), 6.57-6.08 (m, 1H), 3.77 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ= 154.29, 131.09, 128.41, 125.01, 112.44, 111.84, 102.45, 55.98.
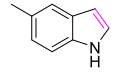
(**2r**) ¹H NMR (400 MHz, CDCl₃) δ= 7.73 (s, 1H), 7.63-7.31 (m, 1H), 7.33-7.11 (m, 1H), 7.11-6.94 (m, 2H), 6.01-6.29 (m, 1H), 2.35 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ= 136.16, 135.15, 129.19, 121.04, 119.74, 110.31, 100.51, 13.84.
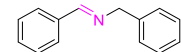
(**4a**) ¹H NMR (400 MHz, CDCl₃) δ= 8.33 (s, 1H), 7.77-7.62 (m, 2H), 7.43-7.24 (m, 8H), 4.65 (s, 2H). ¹³C NMR (101 MHz, CDCl₃) δ= 162.15, 139.41, 136.28, 130.91, 128.74, 128.63, 128.41, 128.12, 127.12, 65.19.
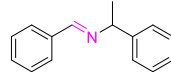
(**4b**) ¹H NMR (400 MHz, CDCl₃) δ= 8.37 (s, 1H), 7.87-7.74 (m, 2H), 7.49-7.37 (m, 5H), 7.53-7.23 (m, 2H), 7.28-7.19 (m, 1H), 4.64-4.35 (m, 1H), 1.69-1.45 (m, 3H). ¹³C NMR (101 MHz, CDCl₃) δ= 159.56, 145.34, 136.56, 130.69, 128.66, 128.55, 128.39, 126.95, 126.76, 69.87, 25.01.
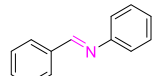
(**4c**) ¹H NMR (400 MHz, CDCl₃) δ= 8.39 (s, 1H), 7.98-7.71 (m, 2H), 7.46-7.24 (m, 5H), 7.20-7.00 (m, 3H). ¹³C NMR (101 MHz, CDCl₃) δ= 160.56, 152.22, 136.35, 131.52, 129.29, 128.95, 128.91, 126.07, 121.00.
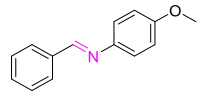
(**4d**) ¹H NMR (400 MHz, CDCl₃) δ= 8.39 (m, 1H), 8.14-7.78 (m, 2H), 7.58 -7.35 (m, 3H), 7.27-7.39 (d, 2H), 7.07-6.80 (m, 2H), 3.77 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ= 158.57, 131.20, 128.88, 128.75, 122.34, 114.53, 55.65.
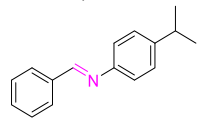
(**4e**) ¹H NMR (400 MHz, CDCl₃) δ= 8.39 (s, 1H), 7.95-7.68 (m, 2H), 7.49-7.24 (m, 3H), 7.24-7.05 (m, 4H), 2.96-2.71 (m, 1H), 1.29-1.02 (m, 6H). ¹³C NMR (101 MHz, CDCl₃) δ= 159.64, 149.75, 146.87, 136.40, 131.22, 128.76, 127.14, 120.88, 33.75, 24.11.
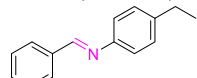
(**4f**) ¹H NMR (400 MHz, CDCl₃) δ= 8.40 (s, 1H), 7.92 (s, 2H), 7.83-7.11 (m, 5H), 7.09-6.84 (m, 1H), 3.11-2.64 (m, 2H), 1.59-0.85 (m, 3H). ¹³C NMR (101 MHz, CDCl₃) δ= 159.34, 131.20, 128.77, 128.66, 126.76, 125.90, 117.71, 24.84, 14.96.
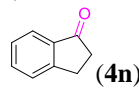
(**4k**) ¹H NMR (400 MHz, CDCl₃) δ 7.31-7.22 (m, 5H), 7.22-7.13 (m, 1H), 3.73 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 140.41, 128.53, 128.29, 127.08, 77.48, 77.16, 76.85, 53.29.
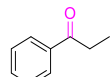
(**4l**) ¹H NMR (400 MHz, CDCl₃) δ= 7.94 -7.81 (m, 2H), 7.66-7.31 (m, 1H), 7.49-7.21 (m, 2H), 3.10-2.79 (m, 2H), 1.25-1.04 (m, 3H). ¹³C NMR (101 MHz, CDCl₃) δ= 200.94, 137.03, 132.98, 128.66, 128.08, 31.90, 8.36.
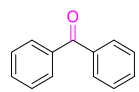
(**4m**) ¹H NMR (400 MHz, CDCl₃) δ= 7.92-7.68 (m, 4H), 7.56-7.48 (m, 2H), 7.48-7.32 (m, 4H). ¹³C NMR (101 MHz, CDCl₃) δ= 196.85, 137.71, 132.53, 130.17, 128.39.

(**4n**) ¹H NMR (400 MHz, CDCl₃) δ= 7.87-7.51 (m, 1H), 7.70-7.38 (m, 1H), 7.60-7.31 (m, 1H), 7.32-7.24 (m, 1H), 3.15-3.02 (m, 2H), 2.65-2.54 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ= 207.13, 155.24, 137.16, 134.67, 127.35, 126.79, 123.77, 36.30, 25.89.
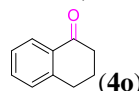
(**4o**) ¹H NMR (400 MHz, CDCl₃) δ= 8.10-7.81 (m, 1H), 7.58-7.21 (m, 1H), 7.32-7.03 (m, 2H), 2.99-2.81 (m, 2H), 2.76-2.50 (m, 2H), 2.26-1.95 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ= 198.50, 144.58, 133.47, 132.67, 128.85, 127.23, 126.69, 39.24, 29.79, 23.37.
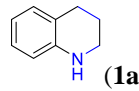
(**1a**) ¹H NMR (400 MHz, CDCl₃) δ= 7.09-6.91 (m, 2H), 6.83-6.51 (m, 1H), 6.69-6.37 (m, 1H), 3.81 (s, 1H), 3.47-3.28 (m, 2H), 2.99-2.67 (m, 2H), 2.12-1.87 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ= 144.88, 129.61, 126.82, 121.54, 117.03, 114.28, 42.09, 27.09, 22.29.
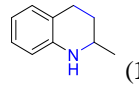
(**1b**) ¹H NMR (400 MHz, CDCl₃) δ= 7.14-6.87 (m, 2H), 6.76-6.39 (m, 2H), 3.67 (s, 1H), 3.61-3.21 (m, 1H), 3.13-2.61 (m, 3H), 2.05-1.84 (m, 1H), 1.75-1.53 (m, 1H), 1.42-1.17 (d, 3H). ¹³C NMR (101 MHz, CDCl₃) δ= 144.79, 129.28, 126.70, 121.11, 116.98, 114.00, 47.18, 30.15, 26.62, 22.64.
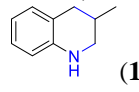
(**1c**) ¹H NMR (400 MHz, CDCl₃) δ= 7.07-6.92 (m, 2H), 6.83-6.67 (m, 1H), 6.60-6.38 (m, 1H), 3.85 (s, 1H), 3.48-3.08 (m, 1H), 3.10-2.91 (m, 1H), 2.87-2.73 (m, 1H), 2.55-2.36 (m, 1H), 2.21- 1.99 (m, 1H), 1.17-0.98 (d, 3H). ¹³C NMR (101 MHz, CDCl₃) δ= 144.40, 129.63, 126.80, 121.20, 117.01, 113.96, 48.96, 35.59, 27.30, 19.16.
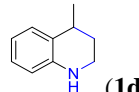
(**1d**) ¹H NMR (400 MHz, CDCl₃) δ= 7.13-6.91 (m, 2H), 6.72-6.43 (m, 2H), 3.90-3.59 (m, 1H), 3.52-3.19 (m, 2H), 2.99-2.79 (m, 1H), 2.14-1.94 (m, 1H), 1.80-1.64 (m, 1H), 1.41-1.28 (d, 3H). ¹³C NMR (101 MHz, CDCl₃) δ= 144.15, 128.58, 126.86, 117.25, 114.42, 39.16, 30.34, 29.97, 22.76.
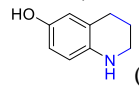
(**1e**) ¹H NMR (400 MHz, CDCl₃) δ= 6.66-6.29 (m, 3H), 3.91 (s, 1H), 3.31-3.13 (m, 2H), 2.91-2.64 (m, 2H), 2.01-1.87 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ= 123.67, 116.41, 116.15, 114.07, 42.53, 27.07, 22.51.
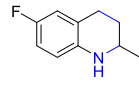
(**1f**) ¹H NMR (400 MHz, CDCl₃) δ= 6.88-6.57 (m, 2H), 6.50-6.29 (m, 1H), 3.55 (s, 1H), 3.45-3.28 (m, 1H), 2.92-2.63 (m, 2H), 1.98-1.87 (m, 1H), 1.68-1.49 (m, 1H), 1.35-1.11 (d, 3H). ¹³C NMR (101 MHz, CDCl₃) δ= 156.67, 154.33, 140.99, 140.97, 129.05, 122.51, 122.44, 115.50, 115.28, 114.74, 114.67, 113.27, 113.04, 47.32, 29.90, 26.73, 22.51.
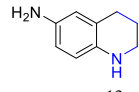
(**1g**) ¹H NMR (400 MHz, CDCl₃) δ= 6.74-6.11 (m, 3H), 3.67-2.85 (m, 5H), 2.84-2.65 (m, 2H), 2.01-1.84 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ= 117.03, 116.11, 114.81, 26.94, 22.64.
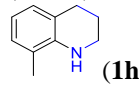
(**1h**) ¹H NMR (400 MHz, CDCl₃) δ= 7.06-6.72 (m, 2H), 6.72-6.39 (m, 1H), 3.63 (s, 1H), 3.51-3.29 (m, 2H), 2.91-2.74 (m, 2H), 2.10 (s, 3H), 2.08-1.88 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ= 142.72, 127.85, 127.38, 121.18, 120.87, 116.40, 42.37, 27.31, 22.19, 17.18.
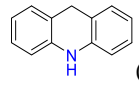
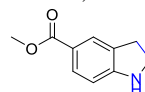(**1i**) ¹H NMR (400 MHz, CDCl₃) δ= 7.18-7.04 (m, 4H), 6.99-6.67 (m, 2H), 6.87-6.51 (m, 2H), 5.95 (s, 1H), 4.09 (s, 2H). ¹³C NMR (101 MHz, CDCl₃) δ= 140.25, 128.73, 127.12, 120.76, 120.17, 113.56, 31.52.
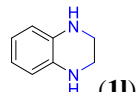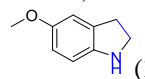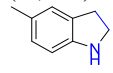
(**1l**) ¹H NMR (400 MHz, CDCl₃) δ= 6.81 – 6.44 (m, 4H), 3.63 (s, 2H), 3.41 (t, 4H). ¹³C NMR (101 MHz, CDCl₃) δ= 133.69, 118.76, 114.71, 41.41.
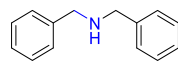
(**1m**) ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.14-6.84 (m, 4H), 3.93 (s, 2H), 3.06 (t, 2H), 2.72 (t, 2H), 1.79 (s, 1H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 136.07, 134.88, 129.42, 126.31, 126.11, 125.82, 48.44, 44.03, 29.30.
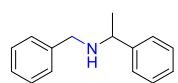
(**1n**) ^{1}H NMR (400 MHz, CDCl$_3$) δ= 7.23-7.01 (m, 1H), 7.13-6.94 (m, 1H), 6.77-6.62 (m, 2H), 3.84-3.60 (m, 1H), 3.71-3.48 (m, 2H), 3.24-2.91 (m, 2H). ^{13}C NMR (101 MHz, CDCl$_3$) δ= 151.46, 129.52, 127.34, 124.77, 118.95, 109.72, 47.42, 29.96.
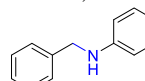
(**1p**) ^{1}H NMR (400 MHz, CDCl$_3$) δ= 7.88-7.51 (m, 2H), 6.80-6.34 (m, 1H), 4.11 (s, 1H), 3.77 (s, 3H), 3.68-3.42 (m, 2H), 3.08-2.84 (m, 2H). ^{13}C NMR (101 MHz, CDCl$_3$) δ= 167.47, 155.97, 130.70, 128.69, 126.13, 119.53, 107.37, 51.55, 47.28, 28.88.
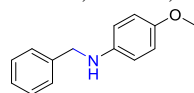
(**1q**) ^{1}H NMR (400 MHz, CDCl$_3$) δ= 7.03-6.47 (m, 3H), 3.90-3.78 (m, 4H), 3.65-3.47 (m, 2H), 3.15-2.89 (m, 2H). ^{13}C NMR (101 MHz, CDCl$_3$) δ= 153.80, 144.83, 131.36, 112.21, 111.57, 110.46, 56.00, 47.77, 30.46.
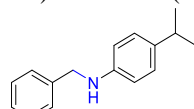
(**1r**) ^{1}H NMR (400 MHz, CDCl$_3$) δ= 7.19-6.79 (m, 2H), 6.69-6.49 (m, 1H), 3.76-3.46 (m, 3H), 3.12-2.97 (m, 2H), 2.28 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ= 149.14, 129.88, 128.29, 127.61, 125.54, 109.64, 47.66, 30.06, 20.90.
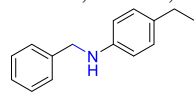
(**3a**) ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.32 – 7.12 (m, 10H), 3.74 (s, 4H), 1.67 (s, 1H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 128.54, 128.30, 127.10, 77.48, 77.16, 76.84, 53.28.

(**3b**) ^{1}H NMR (400 MHz, CDCl$_3$) δ= 7.62-7.33 (m, 5H), 7.52-7.21 (m, 5H), 4.85-4.67 (m, 2H), 3.78-3.58 (m, 1H), 1.59-1.38 (d, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ= 128.78, 128.69, 128.50, 127.82, 127.46, 127.38, 127.03, 126.30, 57.55, 51.68, 23.79.

(**3c**) ^{1}H NMR (400 MHz, CDCl$_3$) δ= 7.37-7.23 (m, 4H), 7.29-7.17 (m, 1H), 7.19-7.00 (s, 2H), 6.69-6.59 (m, 1H), 6.65-6.50 (m, 2H), 4.24 (s, 2H), 4.02 (s, 1H). ^{13}C NMR (101 MHz, CDCl$_3$) δ= 148.23, 139.53, 129.39, 128.76, 127.65, 127.36, 117.72, 113.00, 48.47.

(**3d**) ^{1}H NMR (400 MHz, CDCl$_3$) δ= 7.41-7.21 (m, 5H), 7.09-6.32 (m, 4H), 4.27 (s, 2H), 3.73 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ= 152.22, 142.50, 139.73, 128.62, 127.57, 127.20, 114.94, 114.13, 55.84, 49.27.

(**3e**) ^{1}H NMR (400 MHz, CDCl$_3$) δ= 7.47-7.29 (m, 5H), 7.15-7.01 (m, 2H), 6.69-6.58 (m, 2H), 4.32 (s, 2H), 4.12 (s, 1H), 2.94 – 2.74 (m, 1H), 1.29-1.14 (d, 6H). ^{13}C NMR (101 MHz, CDCl$_3$) δ= 146.20, 139.70, 138.40, 128.73, 127.74, 127.33, 127.26, 113.15, 48.92, 33.32, 24.39, 1.18.

(**3f**) ^{1}H NMR (400 MHz, CDCl$_3$) δ= 7.86-7.01 (m, 7H), 6.96-6.53 (m, 2H), 4.37 (s, 2H), 4.00 (s, 1H), 2.82-2.43 (m, 2H), 1.36-1.18 (m, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ= 145.50, 139.62, 128.70, 127.87, 127.59, 127.56, 127.27, 127.06, 117.39, 110.34, 48.40, 23.95, 12.92.

(**5g**) ^{1}H NMR (400 MHz, CDCl$_3$) δ= 7.49-7.21 (m, 4H), 7.35-7.28 (m, 1H), 4.94-4.81 (m, 1H), 1.59-1.41 (d, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ= 145.89, 128.43, 127.34, 125.44, 70.21, 25.13.

(**5h**) ^{1}H NMR (400 MHz, CDCl$_3$) δ= 7.40-7.05 (m, 5H), 4.61-4.48 (m, 1H), 1.79-1.61 (m, 2H), 0.93-1.74 (m, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ= 144.71, 128.50, 127.60, 127.58, 126.11, 126.09, 76.13, 31.99, 10.26.
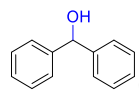
(5i) ^{1}H NMR (400 MHz, CDCl$_3$) δ= 7.82-7.19 (m, 10H), 5.81 (s, 1H), 2.28 (s, 1H). ^{13}C NMR (101 MHz, CDCl$_3$) δ= 143.92, 128.62, 127.69, 126.67, 76.38.
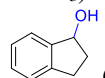
(5j) ^{1}H NMR (400 MHz, CDCl$_3$) δ= 7.56-7.18 (m, 4H), 5.41-5.19 (m, 1H), 3.19-2.98 (m, 1H), 2.93-2.72 (m, 1H), 2.66-2.34 (m, 1H), 2.00-1.81 (m, 1H). ^{13}C NMR (101 MHz, CDCl$_3$) δ= 145.10, 143.40, 128.39, 128.38, 126.79, 124.98, 124.30, 76.48, 36.01, 36.00, 29.89.