Direct Reductive Amination of Aldehydes with Nitroarenes Using Bio-renewable Formic Acid as a Hydrogen Source

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1. Materials and Methods

1.1 Catalytic materials

$ZrOCl_2 \cdot 8H_2O$ and $NH_3 \cdot H_2O$ were supplied by Aladdin. Metal oxide CeO_2, TiO_2 were supplied from the Degussa. Palladium chloride ($PdCl_2$), ruthenium chloride hydrate ($RuCl_3 \cdot xH_2O$), chloroplatonic acid hexahydrate ($H_2PtCl_6 \cdot 6H_2O$), chloroiridic acid hexahydrate ($H_2IrCl_6 \cdot 6H_2O$) and chloroauric acid tetrahydrate ($HAuCl_4 \cdot 4H_2O$), were supplied by Aldrich and used without further purification. 1 wt% Au/Al_2O_3 (catalogue number 79-0160) was supplied by Mintek.

1.2 Catalyst preparation

Preparation of rutile TiO_2

TiO_2-A was prepared according to previous literature.[S1] To synthesize rutile TiO_2, titanium tetrachloride ($TiCl_4$) was added dropwise into ethanol under stirring. A transparent yellowish solution was formed, and then slowly added to distilled water under stirring. The molar ratio of $TiCl_4$, ethanol, and water was 2:20:280. After the addition was finished, the solution was further stirred for 30 min, and then was maintained in a closed system at 50 °C in an oven for 24 h. The white precipitate was harvested by centrifugation, and washed with distilled water and dried in an oven at 50 °C. After that the sample was calcined at 400 °C for 3 h at a heating rate of 2 °C·min^{-1}. The BET surface area of the resultant material was 65 m^2 g^{-1}.

Preparation of anatase TiO_2

TiO_2-A was prepared according to previous literature.[S1] To synthesize anatase TiO_2, 10 mL of titanium bis (ammonium lactate) dihydroxide (TALH) aqueous solution (50%) and a desired amount of 0.1 M urea were mixed followed by the addition of distilled water to reach a final volume of 100 mL. The resulting solution was transferred into a Teflon-lined autoclave, which was sealed and placed in an electric oven held at 160 °C for 24 h. Then, the autoclave was naturally cooled in air. The precipitates were separated by centrifugation, washed with distilled water until pH 7, and dried overnight at 60 °C in an oven. After that the sample was calcined at 400 °C for 3 h at a heating rate of 2 °C·min^{-1}. The BET surface area of the resultant material was 156 m^2 g^{-1}.

Preparation of Au/TiO_2-R、Au/TiO_2-A and Au/TiO_2-P25 catalysts

The 1 wt % Au/TiO_2-R catalyst was prepared by a modified deposition-precipitation (DP) method. [S1] Briefly, an appropriate amount of aqueous solutions of $HAuCl_4$ (100 mL,1.02×10^{-3} M) was heated to 80 °C under vigorous stirring. The pH was adjusted to 7.0 by dropwise addition of NaOH (0.2 M), and then rutile TiO_2 (1.0 g) was dispersed in the solution. After that, the pH was readjusted to 7.0 by dropwise addition of NaOH (0.2 M). The mixture was stirred for 2 h at 80 °C, after which the suspension was cooled to room temperature. Extensive washing with deionized water was then followed until it was free of chloride ions. The samples were dried under vacuum at room temperature for 12 h and then calcined in air at 350 °C for 2 h. By using anatase TiO_2 or TiO_2 (Evonik P25, specific surface area: 45 $m^2 \cdot g^{-1}$ nonporous, 70% anatase and 30% rutile) as the support, similar Au/TiO_2-A and Au/TiO_2-P25 catalysts were prepared by the same method as Au/TiO_2-R. Elemental analysis (ICP-AES) results revealed that the real gold loading was 0.87 wt %, 0.75 wt %, and 0.53 wt% for Au/TiO_2-R, Au/TiO_2-A and Au/TiO_2-P25, respectively.

Preparation of Au/ZrO_2 catalyst

ZrO_2 powders were prepared by a conventional precipitation method following the reported procedure.[S2] A modified deposition-precipitation (DP) method was employed to prepared the Au/ZrO_2 catalysts as follows: [S3] Initially, by mixing ZrO_2 powders (2 g) with appropriate amounts of aqueous solutions of chloroauric acid (100 mL, 1 mM), the pH was adjusted to 9.0 by dropwise addition of 0.25 M $NH_3 \cdot H_2O$. After 6 h continuous stirring at 25 °C the catalyst was washed five times with deionized water and separated by filtration. The samples were dried at 110 °C in air for 1 h, followed by reduction with a stream of 5 vol% H_2/Ar at 350 °C for 2 h. Safety note: The mixing of gold chloride and ammonia solutions may lead to the formation of explosive gold compounds (fulminating gold). Based on our experimental observations, mixing of ammonia solution (not concentrated, 0.25 M) with gold chloride solution with very low concentration (1 mM) at RT does not result in explosive and friction-sensitive gold compounds.

Preparation of Au/CeO_2 catalyst

The Au/CeO_2 sample was prepared according to a routine DP procedure described previously.[S4] An appropriate amount of aqueous solutions of $HAuCl_4$ was heated to 80 °C under vigorous stirring. The pH was adjusted to 10 by dropwise addition of NaOH (0.2 M), and then suitable amount of CeO_2 (Evonic, Adnano 90, specific surface area: 90 m^2/g) was dispersed in the solution. The mixture was aged for 2 h at 80 °C, after which the suspension was cooled to room temperature. Extensive washing with deionized water was then followed until it was free of chloride ions. The samples were dried under vacuum at room temperature for 12 h, and reduced in 5 vol% H_2/Ar at 300 °C for 2 h.

Preparation of Au/C catalyst

0.5 wt% Au/C catalyst was prepared by the procedure as described elsewhere.[S5] Typically, the poly vinyl alcohol (PVA) was added (Au/PVA = 1.5:1, wt/wt) to an aqueous solution containing appropriate amount of aqueous solutions of $HAuCl_4$ at 25 °C under vigorous stirring. The obtained solution was then left under stirring for 10 min. A following rapid injection of an aqueous solution of 0.1 M $NaBH_4$ (Au/$NaBH_4$ = 1:5, mol/mol), led to formation of a dark orange-brown solution, indicating the formation of the gold sol. Activated carbon (refluxed with 2.5 wt% HNO_3 solution for 6 h) was then added to the colloidal gold solution under stirring and kept in

contact until total adsorption (0.5 wt% of gold on the support) occurred. After 2 h stirring, the slurry was filtered and the resulting sample was dried at room temperature for 12 h.

Preparation of Pd/TiO$_2$-R, Pt/TiO$_2$-R, Ru/TiO$_2$-R catalysts

1 wt% Pd/TiO$_2$-R, 1 wt% Pt/TiO$_2$-R, 1 wt% Ru/TiO$_2$-R catalysts were prepared by incipient-wetness impregnation (IWI) of the support (rutile TiO$_2$), with aqueous solution of PdCl$_2$, H$_2$PtCl$_6$·6H$_2$O or RuCl$_3$ precursors of appropriate concentrations (typically 1.0 mL g^{-1} support). After a perfect mixing of the corresponding slurries, the resulting mixture was vigorously stirred at 80 °C for 4 h. Then samples were dried under vacuum at room temperature for 12 h and then reduced in 5 vol% H$_2$/Ar (80 mL min^{-1}) at 400 °C for 2 h.

1.3 Catalyst characterization

Elemental analysis: The metal loading of the catalysts was measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES) using a Thermo Electron IRIS Intrepid II XSP spectrometer.

BET analysis: The BET specific surface areas of the prepared catalysts were determined by adsorption-desorption of nitrogen at liquid nitrogen temperature, using a Micromeritics TriStar 3000 equipment. Sample degassing was carried out at 300 °C prior to acquiring the adsorption isotherm.

X-ray diffraction (XRD): The crystal structures of various catalysts were characterized with powder X-ray diffraction (XRD) on a Bruker D8 Advance X-ray diffractometer using the Ni-filtered Cu Kα radiation source at 40 kV and 40 mA.

Transmission electron microscopy (TEM): TEM images for various noble metal catalysts were taken with a JEOL 2011 electron microscope operating at 200 kV. Before being transferred into the TEM chamber, the samples dispersed with ethanol were deposited onto a carbon-coated copper grid and then quickly moved into the vacuum evaporator. The size distribution of the metal nanoclusters was determined by measuring about 200 random particles on the images.

X-ray photoelectron spectroscopy (XPS): The XPS measurements were performed with a Perkin Elmer PHI 5000C spectrophotometer with Mg Kα radiation (1253.6 eV). The samples were pressed into a pellet and transferred to a test chamber. The spectra were collected with an analyzer pass energy of 23.5 eV and an electron takeoff angle of 45°. The vacuum in the test chamber was maintained below 1×10$^{−9}$ Torr. The binding energies scale was calibrated taking, as a reference, the adventitious C 1s peak at 284.6 eV.

CO$_2$/NH$_3$-Temperature-programmed desorption (CO$_2$/NH$_3$-TPD): Typically, the sample (50 mg) loaded in a quartz reactor was pretreated with high-purity Ar at 300 °C for 1 h. After cooling the sample to 100 °C, CO$_2$ adsorption was performed by switching the Ar flow to a CO$_2$ gas until adsorption saturation. The gas-phase (and/or weakly adsorbed) NH$_3$, was purged by Ar at the same temperature for about 1h. CO$_2$-TPD was then performed in the Ar flow by raising the temperature to 700 °C at a rate of 10 °C·min^{-1} . The desorbed CO$_2$ molecules were monitored by a OmniStar mass spectrometer (QMS-200) with the signal of m/e = 44. NH$_3$-TPD was performed by using a similar procedure.

2. Results

Table S1. DRA of benzaldehyde with nitrobenzene catalyzed by various Au supported catalysts ,TiO$_2$ supports or unsupported Au NPs. [a]

Entry	Catalyst	t [h]	Conv. [%]	Yield [%]			
				3	4	5	6
1	Au/TiO$_2$-R	3	>99	97	2	1	0
2	Au/TiO$_2$-P25	2/3/4.5	>99/>99/>99	59/76/95	11/6/2	30/18/3	0/0/0
3	Au/TiO$_2$-A	2/3/4.5	>99/>99/>99	60/78/96	13/9/3	27/13/1	0/0/0
4	Au/ZrO$_2$	2/3/4.5	>99/>99/>99	53/70/71	8/4/20	39/26/9	0/0/0
5	TiO$_2$-R	3	n.r.	-	-	-	0
6	TiO$_2$-A	3	n.r.	-	-	-	0
7	TiO$_2$-P25	3	n.r.	-	-	-	0
8	Au NPs [b]	3	2	1	1	0	0

[a] Reaction conditions: nitrobenzene (1 mmol), benzaldehyde (1 mmol), FA (4 mmol), catalyst (1 mol% Au), solvent (5 mL), N$_2$ (1 atm), 80 °C, n.r. = no reaction. Conversions (Conv.) based on nitrobenzene, Conv. and yields determined by GC using *n*-dodecane as the internal standard. [b] Au NPs were prepared according to previous literature.[S5] The average particle size is 3.5 nm.

Table S2. Au/TiO$_2$-R-catalyzed DRA of benzaldehyde with nitrobenzene in different solvents. [a]

Entry	Solvent	Conv. [%]	Yield [%]			
			3	4	5	6
1	Water	>99	97	1	2	0
2	DMF	>99	88	1	7	4
3	Ethanol	10	0	10	0	0
4	Triethylamine	97	16	60	21	0

5	THF	>99	33	33	15	19
6	Toluene	66	10	23	4	29

[a] Reaction conditions: nitrobenzene (1 mmol), benzaldehyde (1 mmol), FA (4 mmol), Au/TiO$_2$-R (1 mol% Au), solvent (5 mL), N$_2$ (1 atm), 80 °C, 3h. Conversions (Conv.) based on nitrobenzene, Conv. and yields determined by GC using *n*-dodecane as the internal standard.

Table S3. Control experiments clarifying the role of FA in the Au/TiO$_2$-R-catalyzed DRA reaction. [a]

Entry	Hydrogen source	Nitrobenzene [mmol]	Benzaldehyde [mmol]	Conversion of nitrobenzene [%]	Conversion of FA [%]
1	HCOOH	1	1	>99	>99
2[b]	H$_2$	1	1	7	-
3	HCOOH	0	0	-	n.r.

[a] Reaction conditions: FA (4 mmol), Au/TiO$_2$-R (1 mol% Au), water (5 mL), N$_2$ (1 atm), 80 °C, 3 h, n.r. = no reaction. Conversion of nitrobenzene determined by GC using *n*-dodecane as the internal standard. Conversion of FA was determined by HPLC. [b] H$_2$ (2 atm).
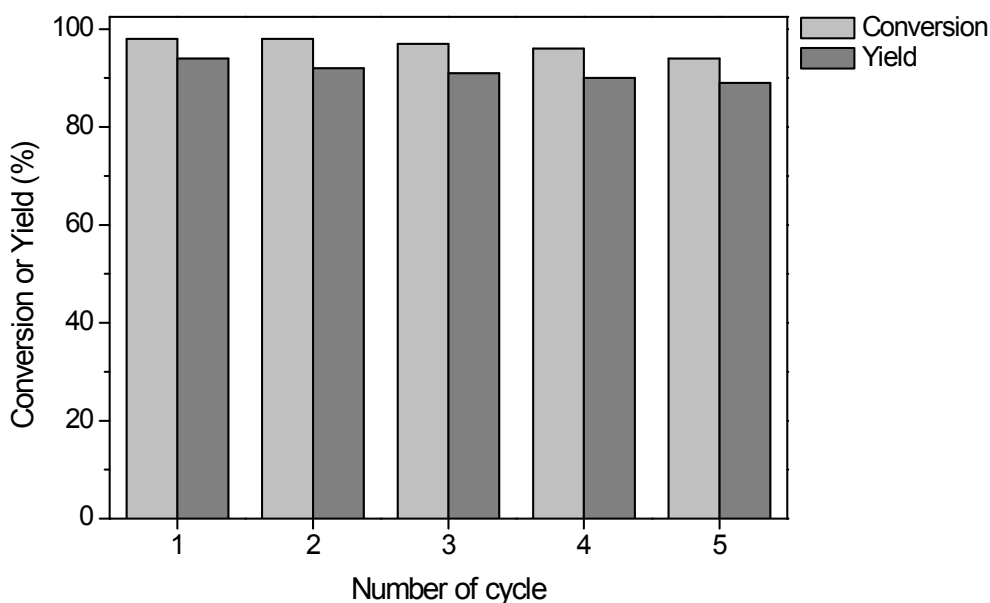

Figure S1. Reuse of the Au/TiO$_2$-R catalyst in the DRA of benzaldehyde with nitrobenzene.

Reaction conditions: nitrobenzene (20 mmol), benzaldehyde (20 mmol), FA (80 mmol, was added by peristaltic pump over the course of 15 h), Au/TiO$_2$-R (0.05 mol% Au), *n*-dodecane (5 mmol, as the internal standard), water (10 mL), N$_2$ (1 atm), 90 °C, 20 h.
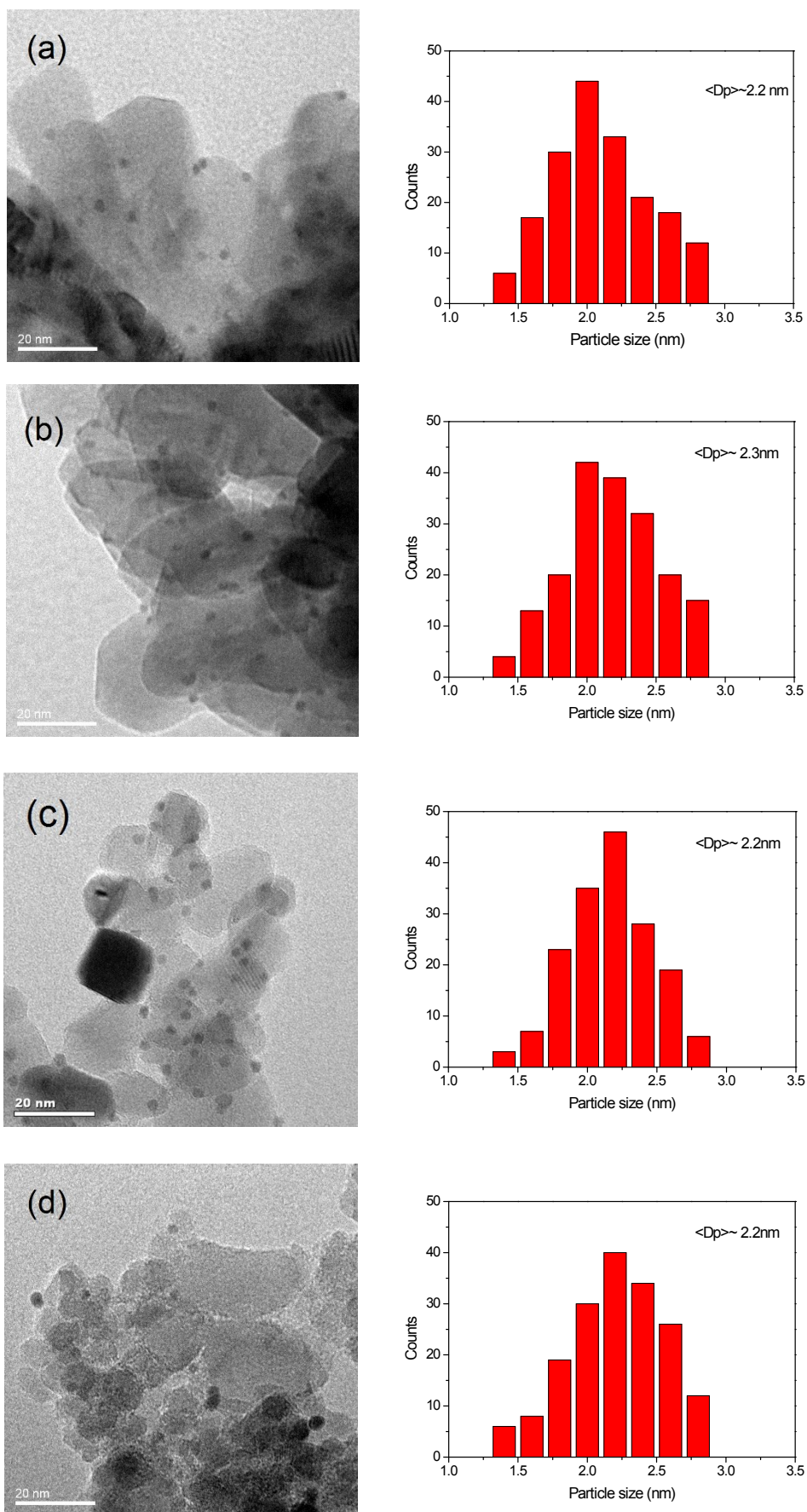
Figure S2. TEM images and metal particle size distributions of various catalysts a) Au/TiO$_2$-R before reaction; b) Au/TiO$_2$-R after five runs; c) Au/TiO$_2$-P25 before reaction; d) Au/TiO$_2$-A before reaction.
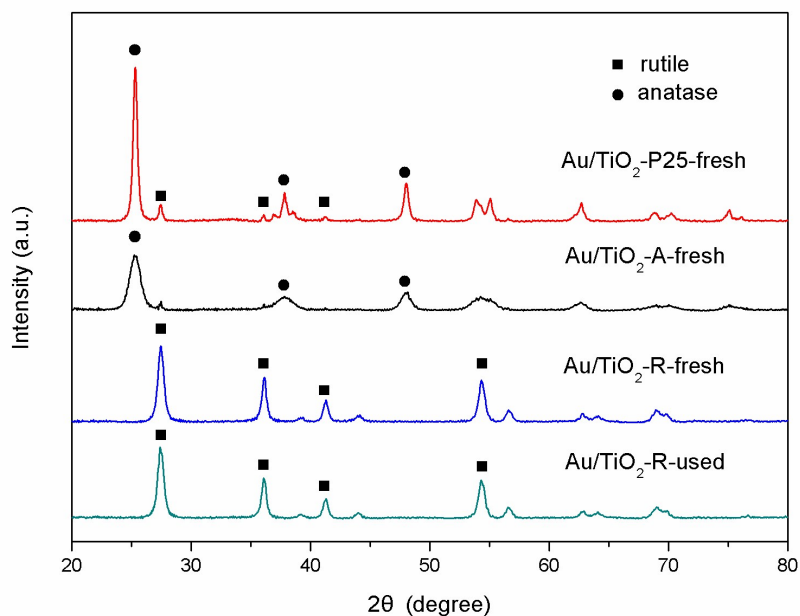
Figure S3. X-ray diffraction (XRD) patterns for various TiO_2 supported gold catalysts. It is clear from this figure that XRD patterns of samples Au/TiO_2-A and Au/TiO_2-R show the characteristic diffraction peaks of anatase phase (JCPDS No. 21-1272) and rutile phase (JCPDS No. 21-1276) TiO_2, respectively. For sample Au/TiO_2-P25, the characteristic diffraction peaks of anatase and rutile composites are observed. In addition, no distinct Au reflections are visible in the XRD patterns of any samples, confirming the formation of very small gold particles on the different allotropic forms of titania support.
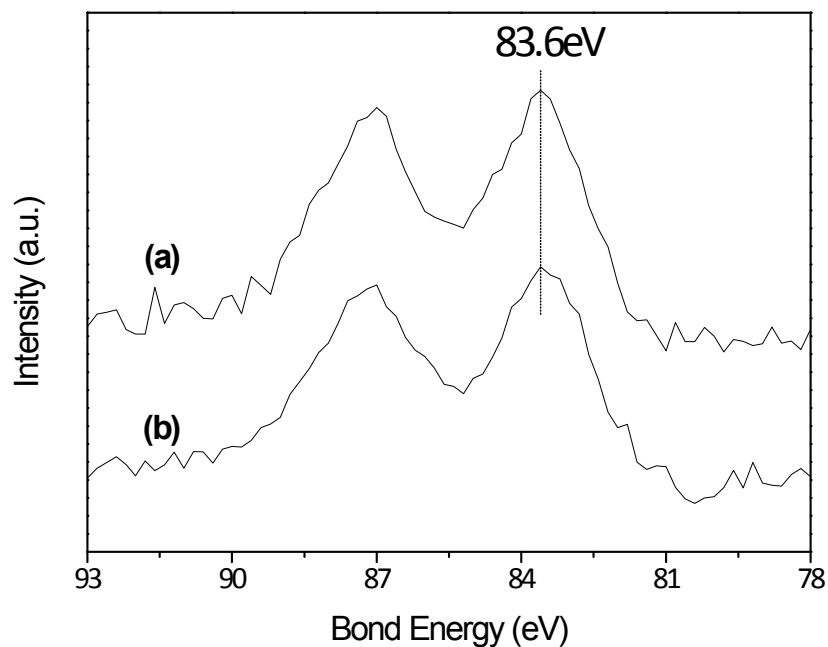

Figure. S4 XPS for Au/TiO_2-R a) before reaction; b) after five runs. The binding energy of Au $4f_{7/2}$ for Au/TiO_2-R is ca. 83.6 eV. Note that the metallic state of Au practically undergoes no change after the five successive runs.
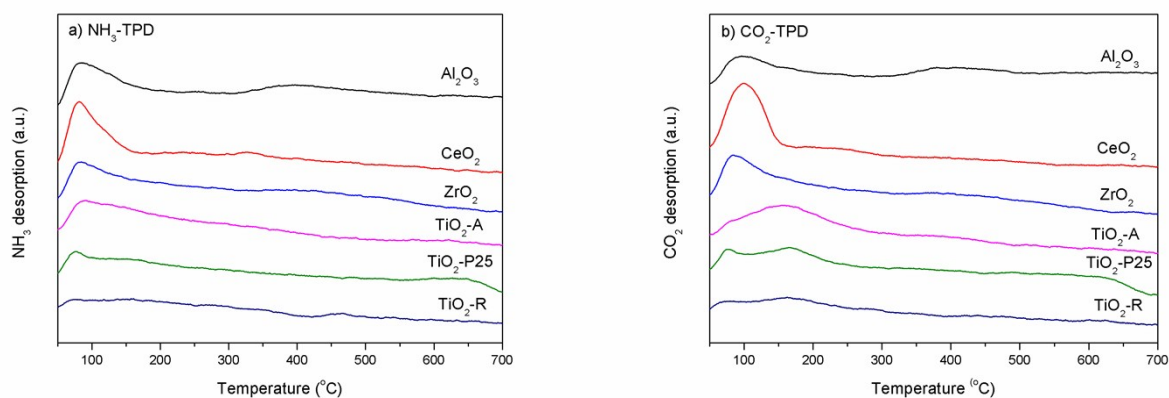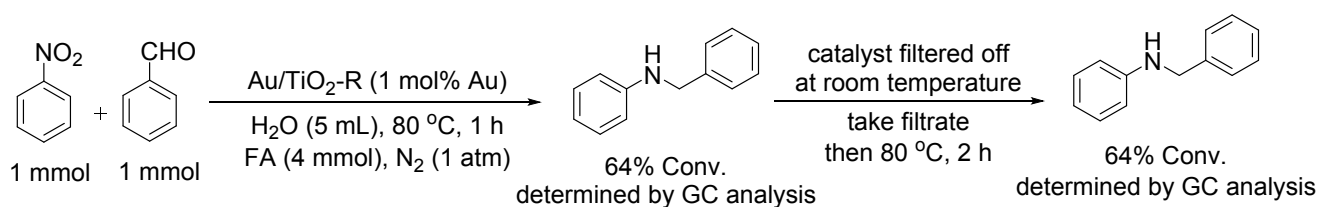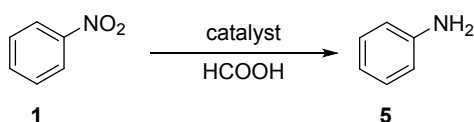
Figure. S5 NH$_3$- and CO$_2$-TPD for various supports.

Table S4. Direct reduction of nitrobenzene in the absence of benzaldehyde with FA over various catalysts. [a]

Entry	Catalyst	Conv. [%]	Sel. [%]
1	Au/TiO$_2$-R	>99	>99
2	Au/TiO$_2$-A	73	>99
3	Au/TiO$_2$-P25	81	>99
4	Au/ZrO$_2$	55	>99
5	Au/CeO$_2$	9	>99
6	Au/Al$_2$O$_3$	12	>99

[a] Reaction conditions: nitrobenzene (5 mmol), FA (15 mmol), Au (0.1 mol%), water (5 mL), N$_2$ (1 atm), 80 °C, 15 min. Conversion (Conv.) and selectivity (Sel.) determined by GC using *n*-dodecane as an internal standard.

Table S5. Direct condensation of benzaldehyde with aniline to N-benzylidenebenzylamine over various catalysts. [a]
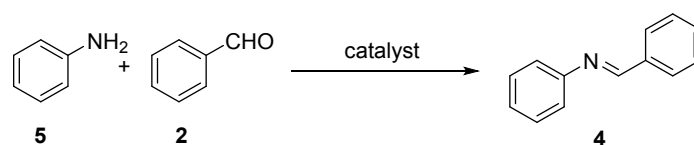
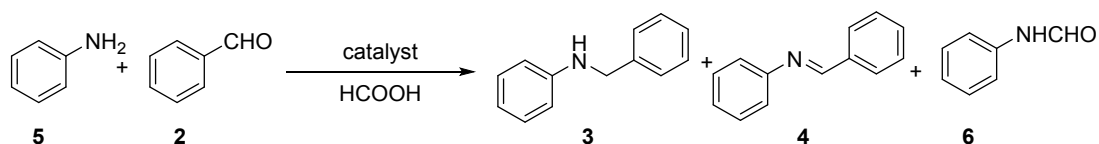| Entry	Catalyst	Conv. [%]	Sel. [%]
1	-	33	>99
2	Au/TiO$_2$-R	99	>99
3	TiO$_2$-R	99	>99
4	Au/TiO$_2$-A	77	>99
5	Au/TiO$_2$-P25	65	>99
6	Au/ZrO$_2$	58	>99
7	Au/CeO$_2$	55	>99
8	Au/Al$_2$O$_3$	59	>99

[a] Reaction conditions: aniline (1 mmol), benzaldehyde (1 mmol), Au (1 mol%), water (5 mL), N$_2$ (1 atm), 80 °C, 3 h. Conversion (Conv.) and selectivity (Sel.) determined by GC using *n*-dodecane as an internal standard.

Table S6. Reduction of N-benzylidenebenzylamine to N-benzylaniline with FA over Au catalysts. [a]
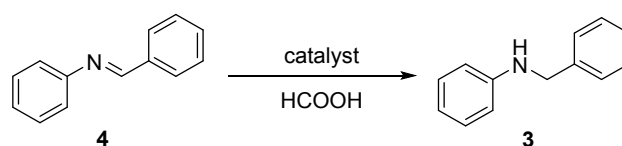
| Entry	Catalyst	Conv. [%]	Sel. [%]
1	Au/TiO$_2$-R	98	>99
2	Au/TiO$_2$-A	92	>99
3	Au/TiO$_2$-P25	92	>99
4	Au/ZrO$_2$	84	>99
5	Au/CeO$_2$	62	>99
6	Au/Al$_2$O$_3$	82	>99

[a] Reaction conditions: N-benzylidenebenzylamine (1 mmol), FA (1 mmol), Au (1 mol%), water (5 mL), N$_2$ (1 atm), 80 °C, 3 h. Conversion (Conv.) and selectivity (Sel.) determined by GC using *n*-dodecane as an internal standard.

Table S7. Reductive amination of benzaldehyde and aniline with FA over various catalysts. [a]


Entry	Catalyst	Conv. [%]	Yield [%]		
			3	**4**	**6**
1	-	42	0	36	6
2	Au/TiO$_2$-R	99	98	1	0
3	Au/TiO$_2$-A	82	77	5	0
4	Au/TiO$_2$-P25	81	75	6	0
5	Au/CeO$_2$	52	34	18	0
6	Au/ZrO$_2$	65	60	5	0
7	Au/Al$_2$O$_3$	56	45	11	0

[a] Reaction conditions: aniline (1 mmol), benzaldehyde (1 mmol), FA (1 mmol), Au (1 mol%), water (5 mL), N$_2$ (1 atm), 80 °C, 3h.

Conversion (Conv.) was based on aniline, Conv. and yield were determined by GC using *n*-dodecane as an internal standard.
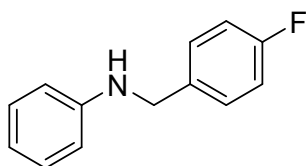
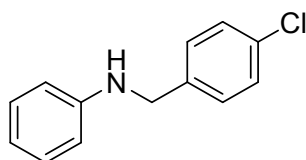## 3. Characterization of secondary amines and 2-phenylbenzimidazole
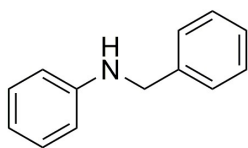
N-benzylaniline (Table 2, entry 1). The crude reaction mixture was purified on silica gel (EtOAc/petroleum ether = 1:10, v/v) to afford the product as colorless oil (94% yield). ^{1}H NMR (500 MHz, CDCl$_3$): δ = 4.22 (br s, 1H), 4.35 (s, 2H), 6.67 (d, 2H, J= 7.9 Hz), 6.75 (t, 1H, J= 7.3 Hz), 7.20 (t, 2H, J= 7.9 Hz), 7.26 - 7.47 (m, 5H). ^{13}C NMR (125 MHz, CDCl$_3$): δ = 48.4, 112.9, 117.7, 127.2, 127.5, 128.6, 129. 2, 139.3, 147.9. The physical data were identical in all respects to those previously reported.[S6]
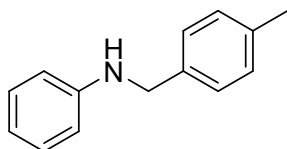
N-(4-methylbenzyl)aniline (Table 2, entry 2). The crude reaction mixture was purified on silica gel (EtOAc/petroleum ether = 1:10, v/v) to afford the product as yellow oil (95% yield). ^{1}H NMR (500 MHz, CDCl$_3$) δ = 2.29 (s, 3H), 4.09 (br s, 1H), 4.23 (s, 2H), 6.59 (d, *J* = 7.8 Hz, 2H), 6.66 (t, *J* = 7.3 Hz, 1H), 7.11 (dd, *J* = 15.0, 7.8 Hz, 4H), 7.21 (d, *J* = 7.7 Hz, 2H). ^{13}C NMR (125 MHz, CDCl$_3$) δ = 21.0, 48.1, 112.9, 117.6, 127.5, 129.2, 129.3, 136.2, 136.8, 148.0. The physical data were identical in all respects to those previously reported.[S6]

N-(4-fluorobenzyl)aniline (Table 2, entry 3). The crude reaction mixture was purified on silica gel (EtOAc/petroleum ether = 1:10, v/v) to afford the product as yellow oil (92% yield). ^{1}H NMR (500 MHz, CDCl$_3$) δ = 4.23 (br s, 1H), 4.32 (s, 2H), 6.66 (d, J = 7.9 Hz, 2H), 6.76 (t, J = 7.3 Hz, 1H), 7.05 (t, J = 8.6 Hz, 2H), 7.20 (t, J = 7.8 Hz, 2H), 7.36 (dd, J = 8.2, 5.5 Hz, 2H). ^{13}C NMR (125 MHz, CDCl$_3$) δ = 47.7, 113.0, 115.3, 115.5, 117.9, 128.98, 129.04, 129.2, 134.9, 147.7, 161.1, 163.0. The physical data were identical in all respects to those previously reported.[S6]
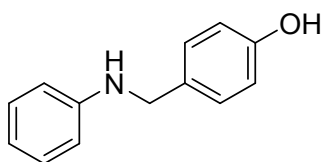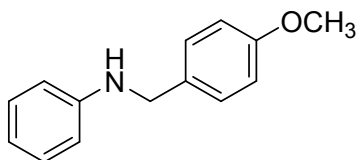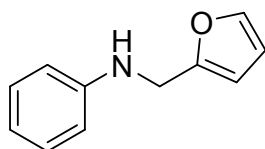

N-(4-chlorobenzyl)aniline (Table 2, entry 4). The crude reaction mixture was purified on silica gel (EtOAc/petroleum ether = 1:10, v/v) to afford the product as yellow oil (92% yield). ^{1}H NMR (500 MHz, CDCl$_3$) δ = 4.13 (br s, 1H), 4.34 (s, 2H), 6.64 (d, J = 7.7 Hz, 2H), 6.77 (t, J = 7.3 Hz, 1H), 7.21 (t, J = 7.9 Hz, 2H), 7.33 (s, 4H). ^{13}C NMR (125 MHz, CDCl$_3$) δ = 47.6, 112.9, 117.8, 128.68, 128.71, 129.3, 132.8, 138.0, 147.8. The physical data were identical in all respects to those previously reported.[S6]
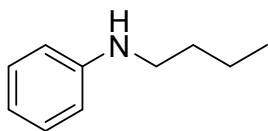

4-((phenylamino)methyl)phenol (Table 2, entry 5). The crude reaction mixture was purified on silica gel (EtOAc/petroleum ether = 1:2, v/v) to afford the product as yellow oil (90% yield).^{1}H NMR (500 MHz, CDCl$_3$) δ = 4.23 (s, 2H), 4.36 (br s, 1H), 4.51 (br s, 1H), 6.64 (d, J = 8.0 Hz, 2H), 6.73 (t, J = 7.3 Hz, 1H), 6.77 (d, J = 8.3 Hz, 2H), 7.17 (t, J = 7.7 Hz, 2H), 7.22 (d, J = 8.3 Hz, 2H). ^{13}C NMR (126 MHz, CDCl$_3$) δ = 47.9, 113.1, 115.4, 117.8, 129.0, 129.2, 131.4, 148.0, 154.8. The physical data were identical in all respects to those previously reported.[S7]

N-(4-methoxybenzyl)aniline (Table 2, entry 6). The crude reaction mixture was purified on silica gel (EtOAc/petroleum ether = 1:10, v/v) to afford the product as pale yellow oil (91% yield). ^{1}H NMR (500 MHz, CDCl$_3$) δ = 3.85 (s, 3H), 3.97 (br s, 1H), 4.30 (s, 2H), 6.70 (d, J = 7.6 Hz, 2H), 6.79 (t, J = 6.9 Hz, 1H), 6.94 (d, J = 7.9 Hz, 2H), 7.24 (t, J = 7.2 Hz, 2H), 7.35 (d, J = 7.8 Hz, 2H). ^{13}C NMR (125 MHz, CDCl$_3$) δ = 47.8, 55.3, 112.9, 114.0, 117.5, 128.8, 129.2, 131.4, 148.2, 158.9. The physical data were identical in all respects to those previously reported.[S6]

N-(furan-2-ylmethyl)aniline (Table 2, entry 7). The crude reaction mixture was purified on silica gel (EtOAc/petroleum ether = 1:10, v/v) to afford the product as pale yellow oil (90% yield). ^{1}H NMR (500 MHz, CDCl$_3$) δ = 3.98 (br s, 1H), 4.27 (s, 2H), 6.19 (dd, J = 3.1, 0.7 Hz, 1H), 6.28 (dd, J = 3.0, 1.8 Hz, 1H), 6.63 (d, J = 7.7 Hz, 2H), 6.70 (t, J = 7.3 Hz, 1H), 7.15 (dd, J = 8.4, 7.4 Hz, 2H), 7.32 (d, J = 0.9 Hz, 1H). ^{13}C NMR (125 MHz, CDCl$_3$) δ = 41.4, 107.0, 110.3, 113.2, 118.0, 129.2, 141.9, 147.6, 152.7. The physical data were identical in all respects to those previously reported.[S8]

N-butylaniline (Table 2, entry 8). The crude reaction mixture was purified on silica gel (EtOAc/petroleum ether = 1:4, v/v) to afford the product as yellow oil (82% yield). ^{1}H NMR (500 MHz, CDCl$_3$) δ = 0.95 (t, J = 7.3 Hz, 3H), 1.41 (dt, J = 14.4, 7.4 Hz, 2H), 1.59 (dt, J = 14.7, 7.2 Hz, 2H), 3.10 (t, J = 7.1 Hz, 2H), 3.52 (br s, 1H), 6.59 (d, J = 8.4 Hz, 2H), 6.68 (t, J = 7.3 Hz, 1H),7.16 (t, J = 7.6 Hz, 2H). ^{13}C NMR (125 MHz, CDCl$_3$) δ = 13.9, 20.3, 31.6, 43.6, 112.7, 117.0, 129.2, 148.5. The physical data were identical in all respects to those previously reported.[S9]

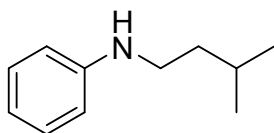**N-isopentylaniline (Table 2, entry 9).** The crude reaction mixture was purified on silica gel (EtOAc/petroleum ether = 1:8, v/v) to afford the product as yellow oil (85% yield). ^{1}H NMR (500 MHz, CDCl$_3$) δ = 0.95 (d, J = 6.6 Hz, 6H), 1.51 (dd, J = 14.6, 7.1 Hz, 2H), 1.71 (dp, J = 13.3, 6.7 Hz, 1H), 3.11 (t, J = 7.4 Hz, 2H), 3.58 (br s, 1H), 6.60 (d, J = 7.8 Hz, 2H), 6.68 (t, J = 7.3 Hz, 1H), 7.17 (t, J = 7.9 Hz, 2H). ^{13}C NMR (125 MHz, CDCl$_3$) δ = 22.6, 25.6, 38.6, 42.2, 112.7, 117.1, 129.2, 148.5. The physical data were identical in all respects to those previously reported.[S9]
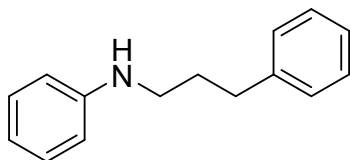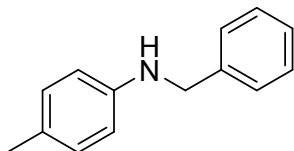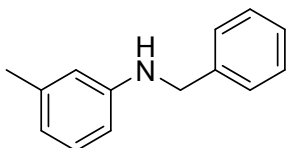

N-(3-phenylpropyl)aniline (Table 2, entry 10). The crude reaction mixture was purified on silica gel (EtOAc/petroleum ether = 1:10, v/v) to afford the product as pale yellow oil (80% yield). ^{1}H NMR (500 MHz, CDCl$_3$) δ = 1.89 (quintet, J = 7.3 Hz, 2H), 2.68 (t, J = 7.5 Hz, 2H), 3.09 (t, J = 7.1 Hz, 2H), 3.50 (br s, 1H), 6.54 (d, J = 8.4 Hz, 2H), 6.67 (t, J = 7.4 Hz, 1H), 7.09 - 7.18 (m, 5H), 7.26 (t, J = 6.8 Hz, 2H). ^{13}C NMR (125 MHz, CDCl$_3$) δ = 31.1, 33.5, 43.5, 112.9, 117.3, 128.5, 129.3, 141.8, 148.4. The physical data were identical in all respects to those previously reported.[S9]

N-benzyl-4-methylaniline (Table 3, entry 2). The crude reaction mixture was purified on silica gel (EtOAc/petroleum ether = 1:10, v/v) to afford the product as yellow oil (93% yield). ^{1}H NMR (500 MHz, CDCl$_3$) δ = 2.32 (s, 3H), 4.02 (br s, 1H), 4.36 (s, 2H) 6.47 - 6.57 (m, 2H), 6.60 (d, J = 6.9 Hz, 1H), 7.11 (t, J = 7.7 Hz, 1H), 7.28 - 7.45 (m, 5H). ^{13}C NMR (125 MHz, CDCl$_3$) δ = 21.6, 48.4, 110.0, 113.1, 113.7, 118.6, 127.2, 127.5, 128.6, 129.1, 129.7, 139.0, 139.5, 148.2. The physical data were identical in all respects to those previously reported.[S6]

N-benzyl-3-methylaniline (Table 3, entry 3). The crude reaction mixture was purified on silica gel (EtOAc/petroleum ether = 1:10, v/v) to afford the product as yellow oil (93% yield). ^{1}H NMR (500 MHz, CDCl$_3$) δ = 2.29 (s, 3H), 4.26 (br s, 1H), 4.34 (s, 2H), 6.52 - 6.47 (m, 2H), 6.58 (d, J = 7.4 Hz, 1H), 7.09 (t, J = 7.7 Hz, 1H), 7.31 - 7.27 (m, 1H), 7.37 (dt, J = 14.9, 7.4 Hz, 4H). ^{13}C NMR (125 MHz, CDCl$_3$) δ = 21.6, 48.6, 110.2, 113.9, 118.8, 127.2, 127.6, 128.6, 129.2, 139.1, 139.3, 147.9. The physical data were identical in all respects to those previously reported.[S11]

N-benzyl-2-methylaniline (Table 3, entry 4). The crude reaction mixture was purified on silica gel (EtOAc/petroleum ether = 1:10, v/v) to afford the product as yellow oil (91% yield). ^1H NMR (500 MHz, CDCl$_3$) δ = 2.16 (s, 3H), 3.96 (br s, 1H), 4.37 (s, 2H), 6.62 (d, J = 7.9 Hz, 1H), 6.68 (t, J = 7.3 Hz, 1H), 7.09 (dd, J = 15.1, 7.5 Hz, 2H), 7.28 (t, J = 7.0 Hz, 1H), 7.31 - 7.41 (m, 4H). ^{13}C NMR (125 MHz, CDCl$_3$) δ = 17.5, 48.4, 110.1, 117.3, 122.0, 127.2, 127.3, 127.6, 128.6, 130.1, 139.4, 145.9. The physical data were identical in all respects to those previously reported.[S6]
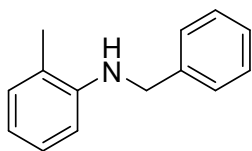

N-benzyl-4-fluoroaniline (Table 3, entry 5). The crude reaction mixture was purified on silica gel (EtOAc/petroleum ether = 1:10, v/v) to afford the product as yellow oil (92% yield). ^1H NMR (500 MHz, CDCl$_3$): δ = 3.92 (br s, 1H), 4.25 (s, 2H), 6.53 (dd, J = 9.0, 4.4 Hz, 2H), 6.86 (t, J = 8.7 Hz, 2H), 7.17 - 7.39 (m, 5H). ^{13}C NMR (125 MHz, CDCl$_3$) δ = 48.9, 113.7, 113.7, 115.6, 115.8, 127.3, 127.5, 128.7, 139.2, 144.4, 155.0, 156.8. The physical data were identical in all respects to those previously reported.[S6]
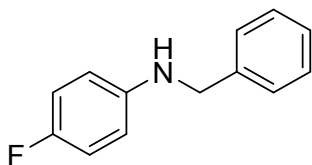

N-benzyl-4-chloroaniline (Table 3, entry 6). The crude reaction mixture was purified on silica gel (EtOAc/petroleum ether = 1:10, v/v) to afford the product as yellow oil (91% yield). ^1H NMR (500 MHz, CDCl$_3$) δ = 4.11 (br s, 1H), 4.25 (s, 2H), 6.50 (d, J = 8.8 Hz, 2H), 7.06 (d, J = 8.8 Hz, 2H), 7.24 (dd, J = 8.5, 4.3 Hz, 1H), 7.30 (d, J = 4.2 Hz, 4H). ^{13}C NMR (125 MHz, CDCl$_3$) δ = 48.4, 114.0, 122.2, 127.4, 128.7, 129.0, 138.3, 146.5. The physical data were identical in all respects to those previously reported.[S6]

N-benzyl-3,4-dichloroaniline (Table 3, entry 7) The crude reaction mixture was purified on silica gel (EtOAc/petroleum ether = 1:10, v/v) to afford the product as yellow oil (90% yield). ^1H NMR (500 MHz, CDCl$_3$) δ = 4.17 (br s, 1H), 4.31 (s, 2H), 6.47 (dd, J = 8.7, 2.6 Hz, 1H), 6.72 (d, J = 2.6 Hz, 1H), 7.20 (d, J = 8.7 Hz, 1H), 7.29 - 7.44 (m, 5H). ^{13}C NMR (125 MHz, CDCl$_3$) δ = 48.1, 112.5, 113.1, 113.9, 118.0, 119.9, 127.4, 127.5, 128.8, 129.3, 130.6, 132.8, 138.3, 147.5. The physical data were identical in all respects to those previously reported.[S10]

N-benzyl-[1,1'-biphenyl]-2-amine (Table 3, entry 8). The crude reaction mixture was purified on silica gel (EtOAc/petroleum ether = 1:10, v/v) to afford the product as white solid (82% yield). ^1H NMR (500 MHz, CDCl$_3$) δ = 4.30 (s, 2H), 4.41 (br s, 1H), 6.64 (d, J = 8.2 Hz, 1H), 6.76 (dd, J = 10.6, 4.2 Hz, 1H), 7.10 (dd, J = 7.4, 1.1 Hz, 1H), 7.11 - 7.40 (m, 7H), 7.38 - 7.49 (m, 4H). ^{13}C NMR (125 MHz, CDCl$_3$) δ = 48.2, 110.9, 117.3, 127.1, 127.4, 128.7, 128.8, 129.0, 129.5, 130.3, 139.6, 145.0. The physical data were identical in all respects to those previously reported.[S12]
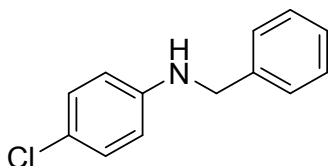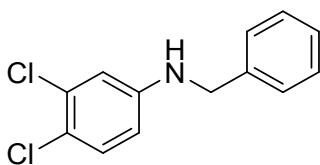
N-benzyl-4-methoxyaniline (Table 3, entry 9). The crude reaction mixture was purified on silica gel (EtOAc/petroleum ether = 1:10, v/v) to afford the product as yellow oil (90% yield). ^{1}H NMR (500 MHz, CDCl$_3$) δ = 3.69 (s, 3H), 3.78 (br s, 1H), 4.23 (s, 2H), 6.56 (d, J = 8.8 Hz, 2H), 6.73 (d, J = 8.8 Hz, 2H), 7.21 (dd, J = 13.3, 6.1 Hz, 1H), 7.25 - 7.36 (m, 4H). ^{13}C NMR (125 MHz, CDCl$_3$) δ = 49.3, 55.8, 114.2, 114.9, 127.2, 127.6, 128.6, 139.5, 142.2, 152.2. The physical data were identical in all respects to those previously reported.[S6]

1-(4-(benzylamino)phenyl)ethan-1-one (Table 3, entry 10). The crude reaction mixture was purified on silica gel (EtOAc/petroleum ether = 1:5, v/v) to afford the product as white solid (88% yield). ^{1}H NMR (500 MHz, CDCl$_3$) δ = 2.45 (s, 3H), 4.36 (s, 2H), 4.80 (br s, 1H), 6.57 (d, J = 8.7 Hz, 2H), 7.23 - 7.35 (m, 5H), 7.79 (d, J = 8.6 Hz, 2H). ^{13}C NMR (125 MHz, CDCl$_3$) δ = 25.9, 47.4, 111.6, 126.8, 127.2, 127.4, 128.7, 130.7, 138.2, 151.9, 196.3. The physical data were identical in all respects to those previously reported.[S6]
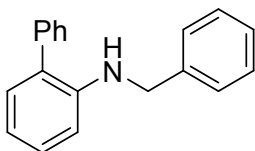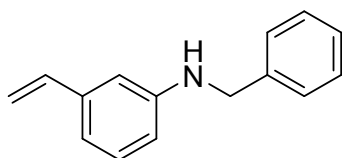

N-benzyl-3-vinylaniline (Table 3, entry 11). The crude reaction mixture was purified on silica gel (EtOAc/petroleum ether = 1:10, v/v) to afford the product as white solid (87% yield). ^{1}H NMR (500 MHz, CDCl$_3$) δ = 4.34 (s, 1H), 4.86 (br s, 1H), 5.19 (d, J = 10.8 Hz, 1H), 5.67 (d, J = 17.6 Hz, 1H), 6.60 (ddd, J = 12.8, 9.5, 6.2 Hz, 2H), 6.72 (s, 1H), 6.82 (d, J = 7.6 Hz, 1H), 7.13 (t, J = 7.8 Hz, 1H), 7.25 - 7.40 (m, 5H). ^{13}C NMR (125 MHz, CDCl$_3$) δ = 48.8, 111.2, 113.1, 113.6, 116.5, 127.7, 128.7, 129.4, 137.2, 138.6, 138.9, 147.7.
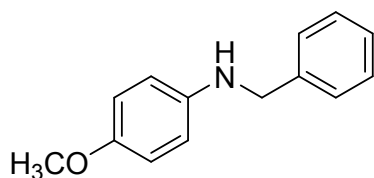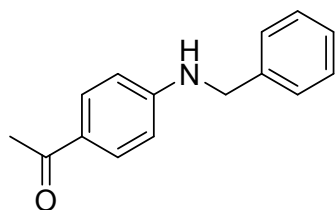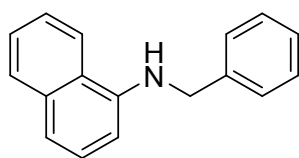

N-benzylnaphthalen-1-amine (Table 3, entry 12). The crude reaction mixture was purified on silica gel (EtOAc/petroleum ether = 1:10, v/v) to afford the product as yellow oil (92% yield). ^{1}H NMR (500 MHz, CDCl$_3$) δ = 4.51 (s, 2H), 4.73 (br s, 1H), 6.66 (d, J = 7.4 Hz, 1H), 7.41 (dddd, J = 36.2, 28.5, 18.9, 8.2 Hz, 9H), 7.86 - 7.81 (m, 2H). ^{13}C NMR (126 MHz, CDCl$_3$) δ = 48.6, 104.8, 117.7, 119.9, 123.4, 124.8, 125.8, 126.6, 127.4, 127.8, 128.8, 134.4, 139.1, 143.2. The physical data were identical in all respects to those previously reported.[S6]
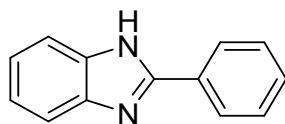
2-phenylbenzimidazole (8). The crude reaction mixture was purified on silica gel (EtOAc/petroleum ether = 1:1, v/v) to afford the product as white solid (87% yield).^{1}H NMR (500 MHz, CDCl$_3$) δ = 5.27 (s, 1H), 7.25 (dd, J = 6.0, 3.1 Hz, 2H), 7.45 (q, J = 5.8 Hz, 3H), 7.63 (dd, J = 5.6, 3.0 Hz, 2H), 8.03 (dd, J = 7.7, 1.6 Hz, 2H). 5.27 (s, 1H). ^{13}C NMR (126 MHz, CDCl$_3$) δ = 123.1, 126.6, 129.1, 129.6, 130.3, 151.4. The physical data were identical in all respects to those previously reported.[S13]

4. References

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5. ¹H and ¹³C NMR Spectra of secondary amines and 2-phenylbenzimidazole

^{1}H NMR (top) and ^{13}C NMR (bottom) spectra of N-(4-fluorobenzyl)aniline.

^{1}H NMR peaks: 7.37, 7.36, 7.35, 7.34, 7.27, 7.22, 7.20, 7.19, 7.06, 7.05, 7.03, 6.78, 6.76, 6.75, 6.67, 6.65, 4.32, 4.23

^{13}C NMR peaks: 163.01, 161.06, 147.71, 134.94, 129.25, 129.04, 128.98, 117.88, 115.48, 115.31, 113.00, 77.23, 76.97, 76.72, 47.69

1H NMR peaks: 7.33, 7.27, 7.23, 7.21, 7.19, 6.78, 6.77, 6.75, 6.65, 6.64, 4.34, 4.13

Integrations: 4.09, 2.08, 1.00, 2.00, 2.12, 0.99

f1 (ppm)

13C NMR peaks: 147.75, 137.95, 132.85, 129.27, 128.71, 128.68, 117.84, 112.92, 77.26, 77.01, 76.75, 47.62

f1 (ppm)

¹H NMR and ¹³C NMR spectra

7.23, 7.21, 7.19, 7.17, 7.16, 6.78, 6.76, 6.74, 6.73, 6.71, 6.65, 6.64

4.51, 4.36, 4.23

1.97, 2.04, 1.99, 1.06, 1.99

0.77, 0.97, 2.00

154.79, 147.95, 131.37, 129.25, 129.04, 117.78, 115.45, 113.09, 77.26, 77.00, 76.75, 47.94

1H NMR and 13C NMR spectra of N-(4-methoxybenzyl)aniline.

Peaks (^{1}H NMR): 7.36, 7.34, 7.26, 7.24, 7.23, 6.95, 6.94, 6.80, 6.79, 6.77, 6.70, 6.69, 4.30, 3.93, 3.85

Integrations: 2.02, 2.00, 2.01, 0.99, 2.00, 1.96, 0.93, 3.03

Peaks (^{13}C NMR): 158.88, 148.18, 131.41, 129.25, 128.81, 117.54, 114.04, 112.90, 77.33, 77.08, 76.82, 55.28, 47.81

¹H NMR peaks: 7.18, 7.16, 7.15, 6.69, 6.68, 6.66, 6.60, 6.58, 3.52, 3.11, 3.10, 3.08, 1.62, 1.61, 1.59, 1.58, 1.56, 1.46, 1.44, 1.43, 1.41, 1.40, 1.38, 0.97, 0.95, 0.94

Integrations: 1.96, 0.96, 2.00, 0.91, 2.02, 2.07, 2.06, 3.06

¹³C NMR peaks: 148.48, 129.17, 117.05, 112.67, 77.26, 77.01, 76.75, 43.65, 31.63, 20.27, 13.88

^{1}H NMR and ^{13}C NMR spectra of N-isopentylaniline.

^{1}H NMR spectrum

peaks: 7.28, 7.26, 7.25, 7.18, 7.17, 7.15, 7.14, 7.12, 7.11, 6.68, 6.67, 6.66, 6.54, 6.53, 3.50, 3.10, 3.09, 3.07, 2.70, 2.68, 2.67, 1.92, 1.91, 1.89, 1.88, 1.86

integrations: 2.04, 5.01, 0.99, 2.00, 0.96, 2.09, 2.11, 2.05

^{13}C NMR spectrum

peaks: 148.40, 141.77, 129.32, 128.53, 128.51, 126.05, 117.33, 112.88, 77.44, 77.19, 76.93, 43.51, 33.49, 31.13

1H NMR peaks: 7.34, 7.33, 7.32, 7.28, 7.27, 7.27, 7.26, 7.26, 7.25, 7.25, 7.24, 6.87, 6.86, 6.84, 6.54, 6.53, 6.52, 6.51, 4.25, 3.92

Integrals: 4.98, 1.93, 1.99, 2.00, 0.90

f1 (ppm): 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

13C NMR peaks: 156.83, 154.96, 144.45, 139.22, 128.67, 127.50, 127.32, 115.75, 115.58, 113.70, 113.65, 77.31, 77.05, 76.80, 48.92

f1 (ppm): 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1

NMR spectra for N-benzyl-3,4-dichloroaniline.

^{1}H NMR peaks: 7.41, 7.40, 7.38, 7.37, 7.36, 7.33, 7.27, 7.21, 7.19, 6.78, 6.77, 6.72, 6.72, 6.67, 6.65, 6.48, 6.47, 6.46, 6.46, 4.31, 4.17

Integrations: 5.14, 1.11, 0.98, 1.00, 1.99, 0.99

^{13}C NMR peaks: 147.52, 138.33, 130.58, 129.30, 128.77, 127.53, 127.34, 118.01, 113.90, 113.10, 112.54, 77.29, 77.04, 76.78, 48.12

7.79
7.78
7.33
7.31
7.30
7.27
7.27
6.58
6.56

4.80

4.36

2.45

2.11
5.00
2.10
0.95
2.00
3.03

f1 (ppm)

196.29

151.92

138.18
130.69
128.68
127.42
127.24
126.79

111.55

77.26
77.01
76.75

47.45

25.89

f1 (ppm)

¹H NMR spectrum (top) and ¹³C NMR spectrum (bottom) of N-benzyl-3-vinylaniline.

¹H NMR peaks: 7.38, 7.37, 7.35, 7.34, 7.32, 7.29, 7.27, 7.26, 7.15, 7.13, 7.12, 6.83, 6.81, 6.72, 6.64, 6.63, 6.60, 6.59, 5.69, 5.66, 5.20, 5.18, 4.80, 4.34

Integrations: 4.97, 1.00, 0.94, 0.98, 2.08, 0.99, 1.01, 0.96, 2.00

¹³C NMR peaks: 147.67, 138.88, 138.65, 137.18, 129.41, 128.66, 127.72, 116.46, 113.63, 113.08, 111.16, 77.28, 77.02, 76.77, 48.78

8.04 8.04 8.03 8.03 7.63 7.63 7.62 7.62 7.47 7.46 7.44 7.43 7.26 7.25 7.25 7.24

—5.27

2.00 2.03 3.05 2.04

1.07

f1 (ppm)
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5

—151.45

130.32 129.62 129.12 126.57 123.11

77.27 77.01 76.76

f1 (ppm)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10