

Supporting Information

Gold-Catalyzed Reductive Transformation of Nitro Compounds Using Formic Acid: Mild, Efficient, and Versatile

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1. Materials and Methods

1.1 Catalytic materials

ZrOCl₂ · 8H₂O and NH₄OH were supplied by Aladdin. Metal oxides including SiO₂, CeO₂, Al₂O₃, TiO₂ were supplied from the Degussa. Palladium chloride (PdCl₂), ruthenium chloride hydrate (RuCl₃ · xH₂O), chloroplatinic acid hexahydrate (H₂PtCl₆ · 6H₂O), chloroiridic acid hexahydrate (H₂IrCl₆ · 6H₂O) and chloroauric acid tetrahydrate (HAuCl₄ · 4H₂O), were supplied by Aldrich and used without further purification. 1 wt% Au/Al₂O₃ (catalogue number 79-0160) was supplied by Mintek.

1.2 Catalyst preparation

Preparation of zirconia (ZrO₂), Au/ZrO₂, Au/ZrO₂-NCs, Au/TiO₂, Au/CeO₂ and Au/SiO₂ : All the support and catalysts were prepared by previously reported methods (see ref S1-S6).

Preparation of anatase TiO₂: To prepare anatase TiO₂,^[S5] 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 m² g⁻¹.

Preparation of rutile TiO₂ support: Rutile TiO₂ was prepared according to previous literature.^[S7] Under stirring, TiCl₄ was added dropwise in ethanol. Then the formed transparent yellow sol was slowly added into deionized water under vigorously stirring. The molar ratio of ethanol, TiCl₄, and deionized water was 10:1:140. Subsequently, the solution was further stirred for 30 min. Finally, the solution was maintained in an oven at 50 °C for 24 h. After that, the formed white precipitate was separated by centrifugation, washed with deionized water for several times and dried at 50 °C. After that the sample was calcined at 400 °C for 3 h with the heating rate of 2 °C min⁻¹. The BET surface area of the rutile support was 65 m² g⁻¹.

Preparation of Au/rutile and Au/anatase catalyst: Au/rutile catalyst was prepared by a modified deposition-precipitation (DP) method.^[S5] Briefly, an appropriate amount of aqueous solutions of chloroauric acid (HAuCl₄) 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 1.0 g rutile TiO₂ 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 TiO₂ as the support, similar Au/anatase catalyst was prepared by the same method as Au/rutile. Elemental analysis (ICP-AES) results revealed that the real gold loading was 0.52 wt % and 0.49 wt % for Au/rutile and Au/anatase, respectively. The BET surface area of the resultant Au/rutile and Au/anatase catalyst was 61 m² g⁻¹ and 153 m² g⁻¹, respectively.

Preparation of Ir/rutile, Pd/rutile, Pt/rutile, Ru/rutile catalysts: 1 wt% Ir/rutile, 1 wt% Pd/rutile, 1 wt% Pt/rutile, 1 wt% Ru/rutile catalysts were prepared by incipient-wetness impregnation (IWI) of the support (rutile TiO₂), with aqueous solution of H₂IrCl₆ · 6H₂O, PdCl₂, H₂PtCl₆ · 6H₂O or RuCl₃ precursors of appropriate concentrations (typically 1.0 mL g⁻¹ support), respectively. 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 25 °C for 12 h and then reduced in 5 vol% H₂/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 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 K α radiation source at 40 kV and 40 mA.

X-ray absorption fine structure (XAFS): The X-ray absorption data at the Au L₃-edge of the samples were recorded at room temperature in transmission mode using ion chambers or in the fluorescent mode with silicon drift fluorescence detector at beam line BL14W1 of the Shanghai Synchrotron Radiation Facility (SSRF), China. The station was operated with a Si (311) double crystal monochromator. During the measurement, the synchrotron was operated at energy of 3.5 GeV and a current between 150-210 mA. The photon energy was calibrated with standard Pt metal foil. Data processing was performed using the program ATHENA.^[S8]

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 K α 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 \times 10⁻⁹ Torr. The binding energies scale was calibrated taking, as a reference, the adventitious C 1s peak at 284.6 eV.

Diffuse Reflectance Infrared Fourier Transform (DRIFT) measurements: The nitrobenzene and FA adsorption experiments were carried out on a Bruker Vector 22 FTIR spectrometer equipped with a MCT detector and Harrick diffuse reflectance accessory. Spectra were obtained on the apparatus loaded with 50 mg of catalyst. Prior to the saturated adsorption of nitrobenzene and FA at 30 °C, sample was subjected to the pretreatment with Helium flow at 200 °C for removing any other gases and moisture. Each spectrum was obtained after the 10 min evacuation treatment with Helium flow at 30 °C and by subtracting the background (base spectrum) of the unloaded sample.

2. Catalytic activity measurements

2.1 Unproductive FA decomposition during Au/ZrO₂-catalyzed nitrobenzene reduction

A mixture of nitrobenzene (1 mmol), FA (3 mmol), Au/ZrO₂ catalyst (Au: 1 mol %), toluene (5 mL) and *n*-decane (1 mmol, as the internal standard) were charged into a 50 mL Hastelloy-C high pressure Parr reactor. The resulting mixture was vigorously stirred (1000 rpm) at 60 °C under N₂ atmosphere (5 atm) for 40 min. While the conversion and selectivity of the liquid products were determined by the method described above, the gaseous composition was analyzed on an Agilent 6820 gas chromatograph equipped with a TDX-01 column and TCD. Typically, at a complete conversion of FA the specific amount of CO₂ and H₂ is measured as 2.81 and 1.53 mmol, respectively. These values mean that ca. 51% of the consumed FA was unproductively decomposed to hydrogen gas ($1.53/3 \times 100\% = 51\%$).

2.2 Procedure for a gram-scale reduction of nitrobenzene to aniline

Nitrobenzene (10 mmol), FA (30 mmol, was added by peristaltic pump over the course of 4.5 h), toluene (10 mL) and *n*-decane (5 mmol, as the internal standard) were placed into a three-necked round-bottom flask (150 mL capacity) fitted with a reflux condenser. The mixture was stirred for 15 min at room temperature before adding the Au/rutile catalyst (Au: 0.01 mol %). The resulting mixture was vigorously stirred (1000 rpm) at 120 °C under N₂ atmosphere (1 atm) for 5 h. The products were confirmed by using GC-MS spectrometer. The conversion and selectivity were determined by a Shimadzu GC-17A gas chromatograph equipped with a capillary column HP-FFAP (30 m × 0.25 mm) and a FID.

2.3 Recovery and reuse of Au/rutile under a gram-scale reaction

The reused catalyst was recovered by filtering the solid Au/rutile from liquid phase after the reaction. The recovered catalyst was washed with acetone for three times and then with distilled water for several times. The catalyst was then dried under vacuum at room temperature for 12 h. In the five successive cycles, the conversion of nitrobenzene (10 mmol) was >99 %, 99 %, 98%, 96% and 95%, respectively.

2.4 Procedure for the reduction of nitrobenzene to aniline at a lower loading of 0.001 mol% of Au

Nitrobenzene (10 mmol), FA (30 mmol, was added by peristaltic pump over the course of 24 h), toluene (10 mL) and *n*-decane (5 mmol, as the internal standard) were placed into a three-necked round-bottom flask (150 mL capacity) fitted with a reflux condenser. The mixture was stirred for 15 min at room temperature before adding the Au/rutile catalyst (Au: 0.001 mol %). The resulting mixture was vigorously stirred (1000 rpm) at 120 °C under N₂ atmosphere (1 atm) for 25 h. The products were confirmed by using GC-MS spectrometer. The conversion and selectivity were determined by a Shimadzu GC-17A gas chromatograph equipped with a capillary column HP-FFAP (30 m × 0.25 mm) and a FID.

3. Results

A. The effect of reaction time and temperature on nitrobenzene reduction over Au/ZrO₂ catalyst

Table S1. Reduction of nitrobenzene to aniline over Au/ZrO₂ catalyst.^[a]

Entry	T [°C]	t [min]	Conv. [%]	Sel. [%]
1	60	80	43	72
2	70	40	40	73

[a] Reaction conditions: nitrobenzene (1 mmol), FA (3 mmol), Au/ZrO₂ (1 mol% Au), toluene (5 mL), N₂ (1 atm). GC analysis using *n*-decane as an internal standard.

B. Reuse of Au/rutile catalyst in a gram-scale reaction

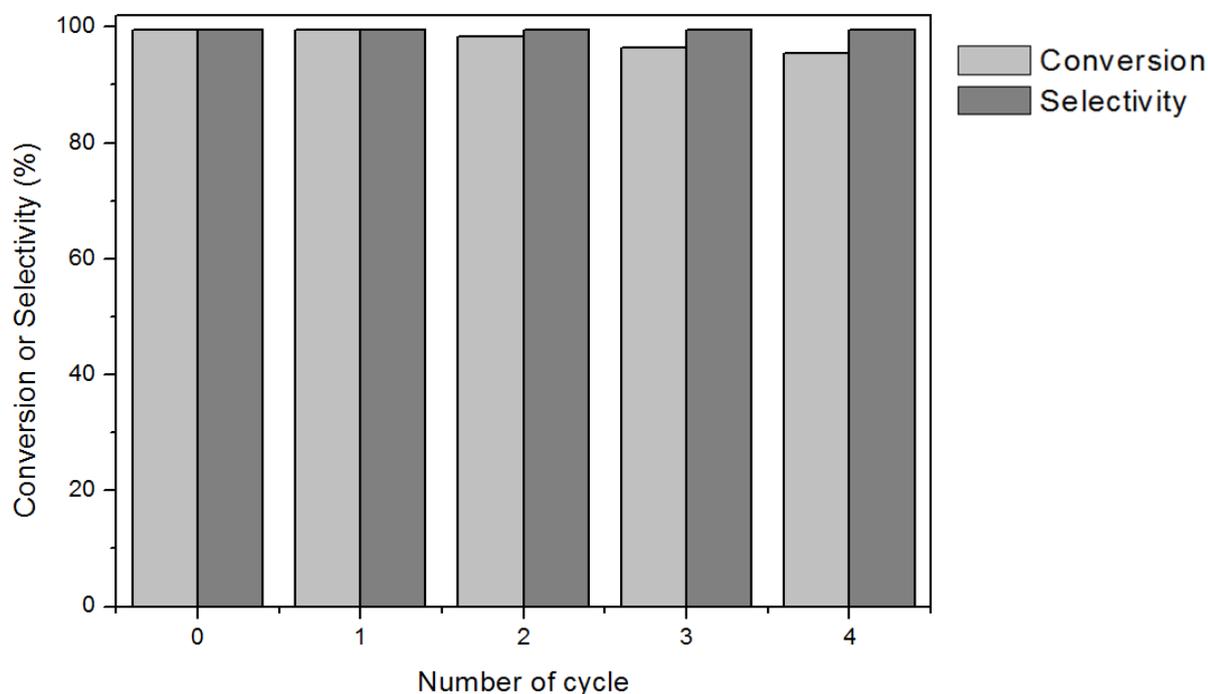
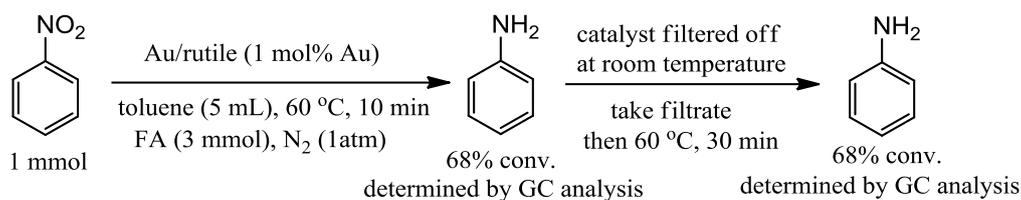


Figure S1. Reuse of the Au/rutile catalyst in the reduction of nitrobenzene to aniline. Reaction conditions: nitrobenzene (10 mmol), FA (30 mmol, was added by peristaltic pump over the course of 4.5 h), Au/rutile (0.01 mol% Au), toluene (10 mL), N₂ (1 atm), 120 °C, 5 h.

C. Catalyst filtration experiment



Scheme S1. Catalyst filtration experiment.

D. The effect of the amounts of FA on nitrobenzene reduction over Au/rutile catalyst

Table S2. Reduction of nitrobenzene to aniline with different amounts of FA over the Au/rutile catalyst.^[a]

Entry	FA [mmol]	Conv. [%]	Sel. to aniline [%]
1	3	>99	>99
2	2	66	>99
3	1	33	>99

[a] Reaction conditions: nitrobenzene (1 mmol), Au/rutile (1 mol% Au), toluene (5 mL), N₂ (1 atm), 60 °C, 40 min. GC analysis using *n*-decane as an internal standard.

E. Intermolecular competitive reaction between nitrobenzene and other unsaturated substrates

Table S3. Reduction of nitrobenzene and other unsaturated substrates by FA.^[a]

Entry	Competitive substrate	Conversion of nitrobenzene [%]	Conversion of others [%]
1	nitrobenzene & styrene	>99	0
2	nitrobenzene & acetophenone	>99	0
3	nitrobenzene & benzonitrile	>99	0

[a] Reaction conditions: nitrobenzene (1 mmol), other unsaturated substrate (1 mmol), FA (3 mmol), Au/rutile (1 mol% Au based on nitrobenzene), toluene (5 mL), N₂ (1 atm), 60 °C, 40 min. GC analysis using *n*-decane as an internal standard.

F. XANES analysis of Au/rutile catalyst

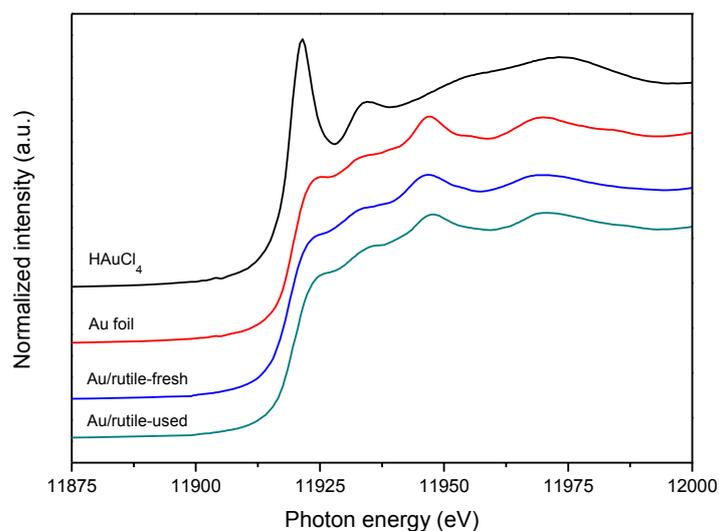


Figure S2. XANES for fresh Au/rutile catalyst before reaction and used Au/rutile catalyst after five runs. Note that Au L_3 -edge XANES data of the fresh and used Au/rutile catalyst were clearly different from that of HAuCl₄ (as a reference compound for ionic Au³⁺ species) but rather similar to that of Au foil, which indicated that Au species in the fresh and used Au/rutile catalysts exist in metallic state.

G. XRD analysis of various TiO₂ supported gold catalysts

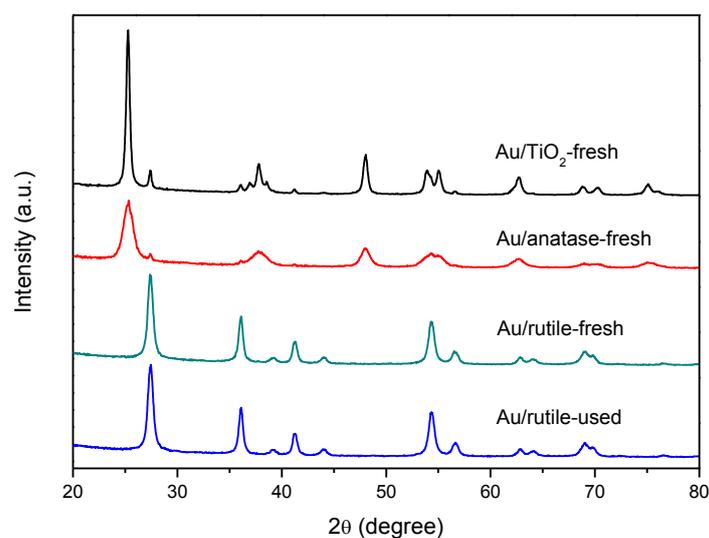


Figure S3. X-ray diffraction (XRD) patterns for various TiO₂ supported gold catalysts.

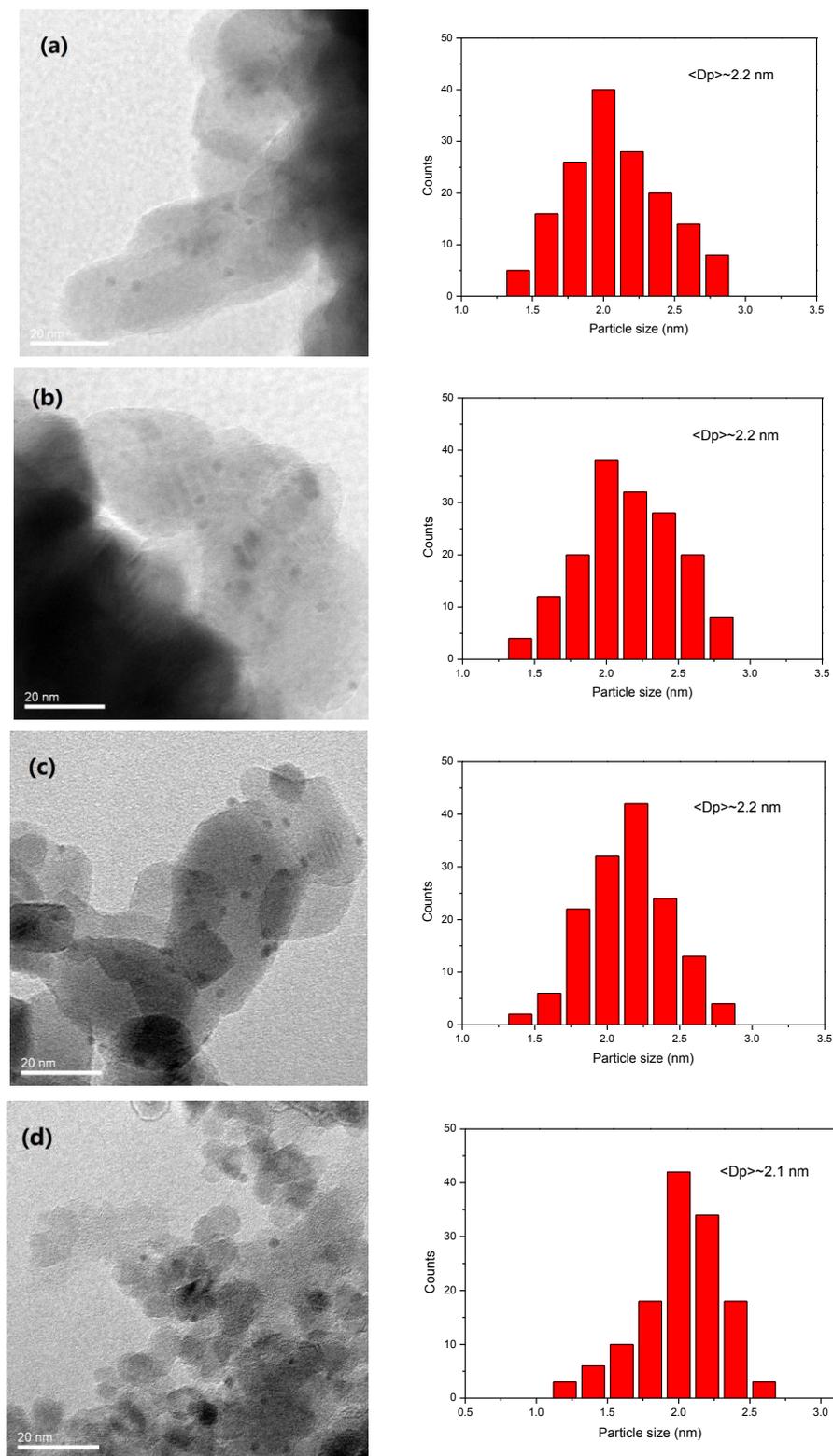
H. TEM analysis of various TiO₂ supported gold catalyst

Figure S4. TEM images and metal particle size distributions of a) Au/rutile before reaction; b) Au/rutile after five runs; c) Au/TiO₂ before reaction; d) Au/anatase before reaction.

I. XPS analysis of Au/rutile catalyst

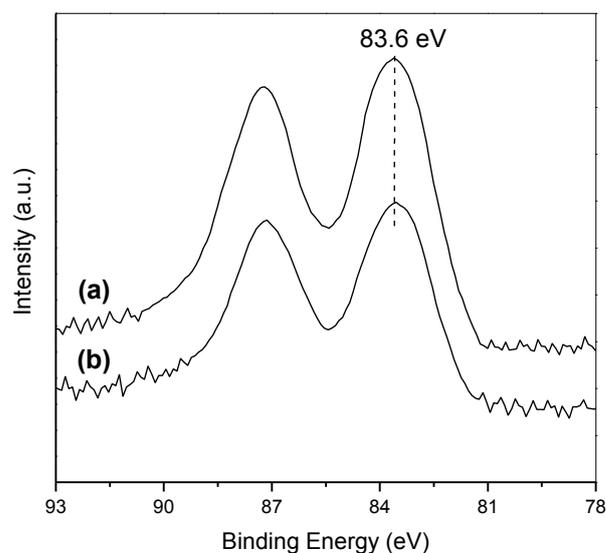


Figure S5. XPS for Au/rutile a) before reaction; b) after five runs. The binding energy of Au $4f_{7/2}$ for Au/rutile is ca. 83.6 eV. Note that the metallic state of Au practically undergoes no change after the five successive runs.

J. Reaction profiles for the reduction of nitrobenzene to aniline with Au/rutile

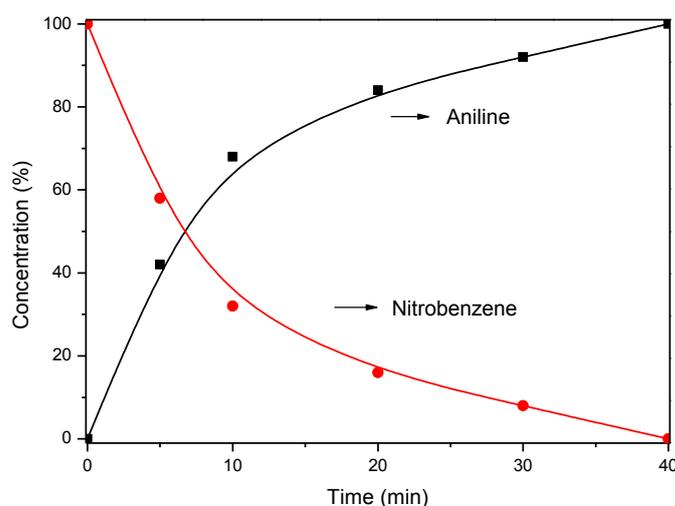


Figure S6. Time-course plot for the reduction of nitrobenzene with Au/rutile. Reaction conditions: Au/rutile (1 mol% Au), nitrobenzene (1 mmol), FA (3 mmol), toluene (5 mL), 60 °C, N_2 (1 atm). GC analysis using *n*-decane as an internal standard.

K. Determining the Au/rutile-mediated nitro reduction catalysis is a transfer hydrogenation process**Table S4.** Control experiments for determining FA was a transfer hydrogen reagent.^[a]

Entry	Hydrogen source	Nitrobenzene [mmol]	Conversion of nitrobenzene [%]	Conversion of FA [%]
1	HCOOH	1	>99	>99
2 ^[b]	H ₂	1	4	-
3	HCOOH	0	-	n.r.

[a] Reaction conditions: FA (3 mmol), Au/rutile (1 mol% Au), toluene (5 mL), N₂ (1 atm), 60 °C, 40 min, n.r.=no reaction. GC analysis using *n*-decane as an internal standard. Conversion of FA was determined by HPLC. [b] H₂ (2 atm).

L. The effect of hydrogen source on nitrobenzene reduction over Au/rutile catalyst**Table S5.** Reduction of nitrobenzene to aniline with different hydrogen source over Au/rutile catalyst.^[a]

Entry	Hydrogen source	Conv. [%]	Sel. [%]
1	HCOONH ₄	59	85
2	HCOOK	12	>99
3	HCOONa	11	>99

[a] Reaction conditions: nitrobenzene (1 mmol), formate (3 mmol), Au/rutile (1 mol% Au), toluene (5 mL), N₂ (1 atm), 60 °C, 40 min. GC analysis using *n*-decane as an internal standard.

M. The dependency of reaction rates in the FA-mediated reduction of nitrobenzene

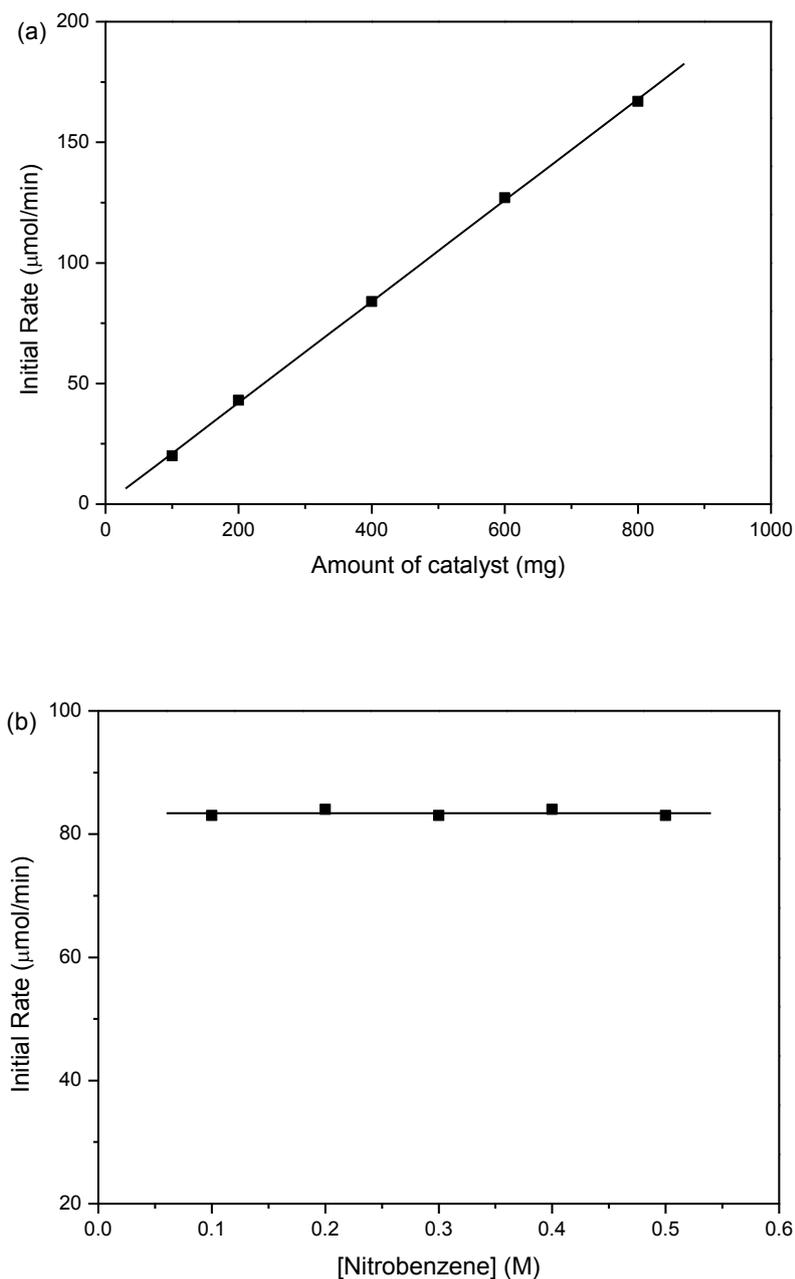


Figure S7. (a) Dependence of the initial reaction rates on the amounts of catalyst for the reduction of nitrobenzene. Reaction conditions: nitrobenzene (1 mmol), FA (3 mmol), toluene (5 mL), N₂ (1 atm), 60 °C. (b) Dependence of the initial reaction rates on the amounts of substrate for the reduction of nitrobenzene by FA. Reaction conditions: Au/rutile (0.01 mmol Au), FA (4.5 mmol), toluene (5 mL), N₂ (1 atm), 60 °C. GC analysis using *n*-decane as an internal standard.

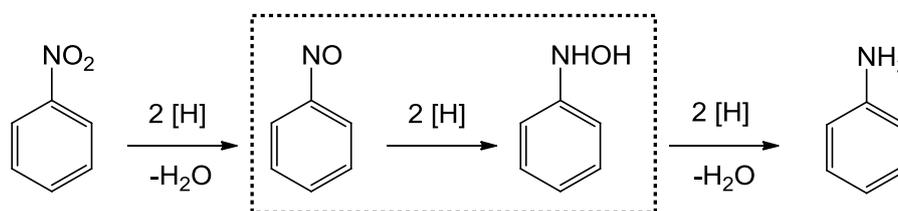
N. The reduction of possible intermediates

Table S6. Reduction of possible intermediates with FA over Au/rutile catalyst.^[a]

Entry	Substrate	t [min]	Conv. [%]	Sel. [%]		
				Aniline	Azoxybenzene	Azobenzen
1	Nitrobenzene	20	84	>99	-	-
2	Nitrobenzene	40	>99	>99	-	-
3 ^b	Nitrosobenzene	20	>99	51	14	35
4 ^b	Nitrosobenzene	40	>99	51	9	40
5 ^c	Phenyl hydroxylamine	20	>99	62	9	29
6 ^c	Phenyl hydroxylamine	40	>99	62	6	32
7 ^d	Azoxybenzene	40	89	9	-	91
8 ^e	Azobenzene	40	3	>99	-	-

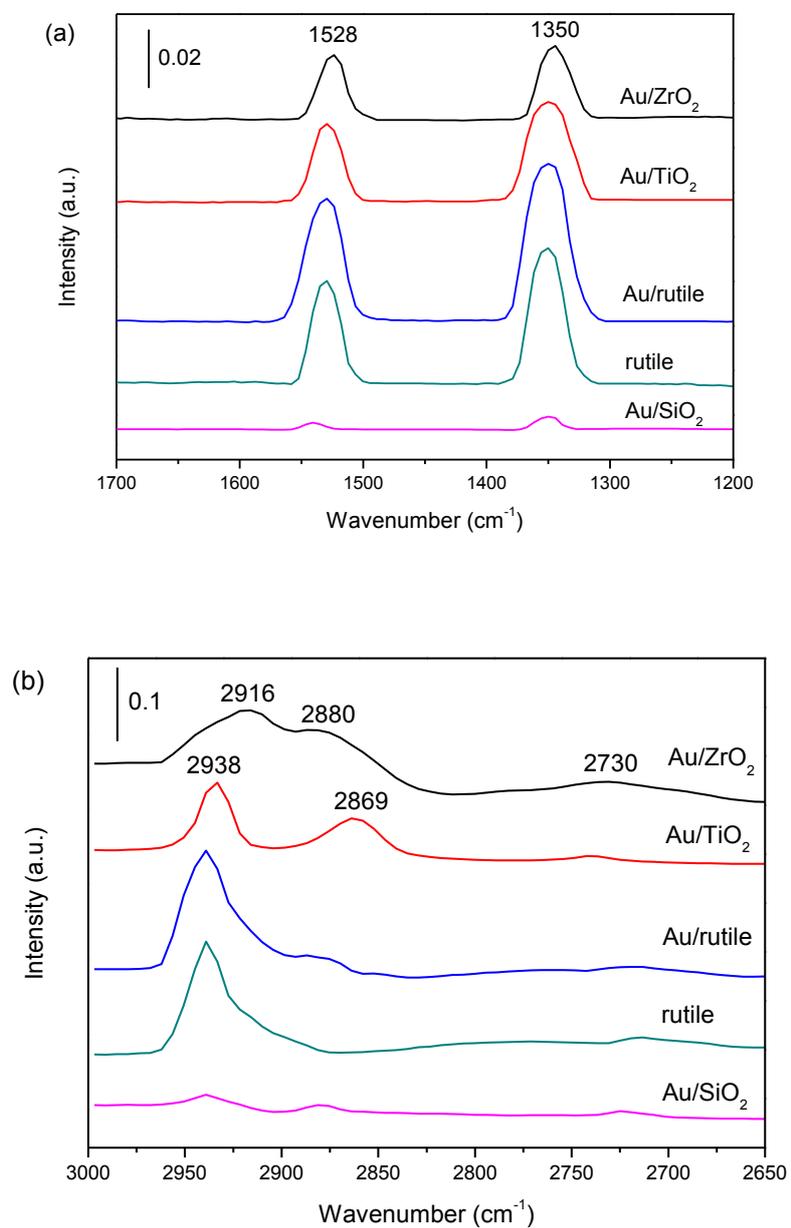
[a] Reaction conditions: substrate (1 mmol), FA (3 mmol), Au/rutile (1 mol% Au), toluene (5 mL), N₂ (1 atm), 60 °C. [b] FA (2 mmol). [c] FA (1 mmol). [d] FA (3 mmol). [e] FA (2 mmol).

O. The possible reaction pathway for reduction of nitrobenzene by FA-Au/rutile system



Scheme S2. Proposed reaction pathway for reduction of nitrobenzene by FA-Au/rutile system.

P. Fourier transform infrared (FTIR) studies of adsorption ability of various supports for nitrobenzene and FA



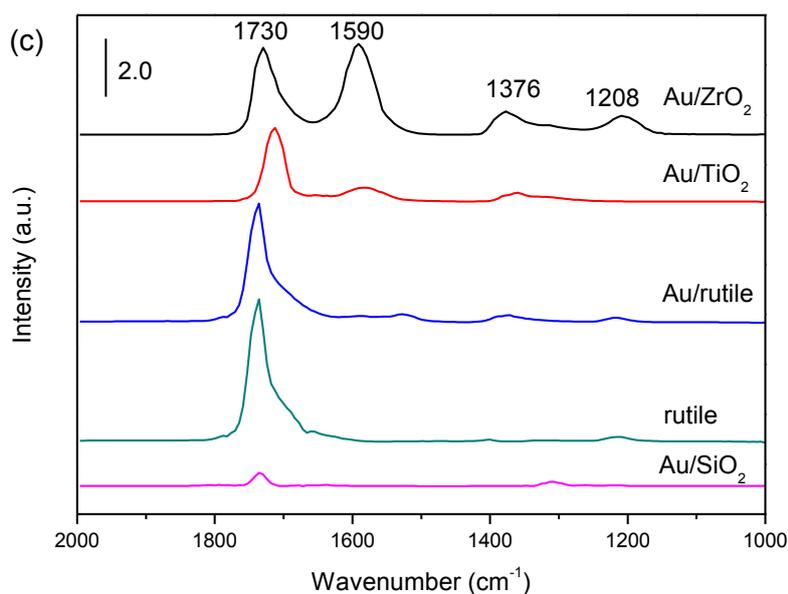


Figure S8. FTIR spectra of (a) nitrobenzene adsorption at 30 °C. (b) FA adsorption at 30 °C ranging from 3000-2650 cm^{-1} . (c) FA adsorption at 30 °C ranging from 2000-1000 cm^{-1} .

Q. Competitive reduction of nitrobenzene with H_2/DCOOD or D_2/HCOOH

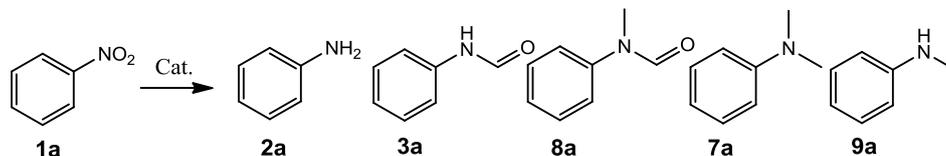
Table S7. Competitive reduction of nitrobenzene with H_2/DCOOD or D_2/HCOOH in a 50 mL Hastelloy-C high pressure Parr reactor.^[a]

Entry	Hydrogen source	Conv. [%]	Sel. [%]	
				
1	H_2/DCOOD	17	-	>99
2	D_2/HCOOH	>99	>99	-

[a] Reaction conditions: nitrobenzene (1 mmol), H_2 (1 atm)/ DCOOD (3 mmol) or D_2 (1 atm)/ HCOOH (3 mmol), Au/rutile (1 mol% Au), toluene (5 mL), 60 °C, 40 min.

R. Synthesis of dimethylated amines from nitrobenzene with FA and H₂

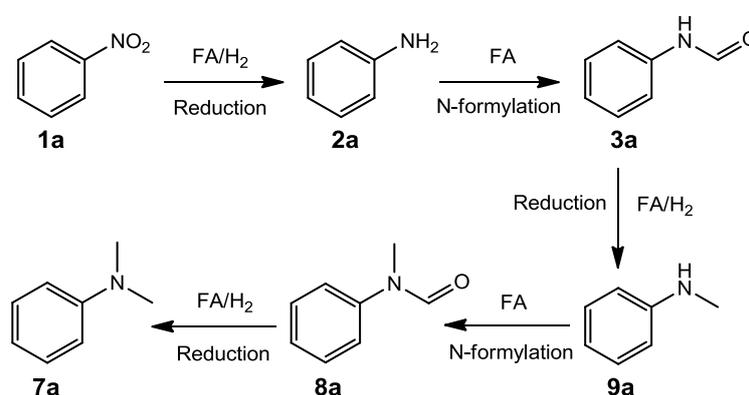
Table S8. Synthesis of dimethylated amines from nitrobenzene with FA and H₂ over Au/rutile catalyst.^[a]



Entry	FA [mmol]	H ₂ [MPa]	Con. [%]	Sel. [%]				
				2a	3a	8a	7a	9a
1	5	0	>99	33	26	18	7	16
2	7.5	0	>99	16	27	21	16	20
3	10	0	>99	12	21	15	25	27
4	10	2	>99	3	9	7	70	11
5	10	3	>99	-	3	2	91	4
6	10	4	>99	-	-	-	>99	-

[a] Reaction conditions: nitrobenzene (0.25 mmol), Au/rutile (4 mol% Au), toluene (5 mL), N₂ (1 atm), 140 °C, 3 h. GC analysis using *n*-decane as an internal standard.

S. The possible reaction pathway for N-methylation of nitrobenzene by FA-H₂-Au/rutile system



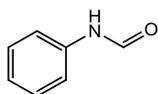
Scheme S3. Proposed reaction pathway for direct N-methylation of nitrobenzene by the FA-H₂-Au/rutile system.

T. The N-methylation of possible intermediates with FA and H₂ over Au/rutile**Table S9.** N-methylation of possible intermediates with FA and H₂ over Au/rutile.^[a]

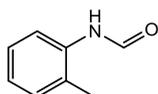
Entry	Substrate	t [h]	Conv. [%]	Sel. [%]				
				2a	3a	9a	8a	7a
1	1a	0.25	>99	9	47	5	35	4
2	1a	1	>99	<1	28	8	23	40
3	2a	0.25	93	-	52	6	37	5
4	3a	0.25	46	-	-	11	78	11
5	9a	0.25	91	-	-	-	87	13
6	8a	0.25	14	-	-	-	-	>99

[a] Reaction conditions: substrate (0.25 mmol), Au/rutile (4 mol% Au), FA (10mmol), H₂ (4 MPa), toluene (5 mL), 140 °C. GC analysis using *n*-decane as an internal standard.

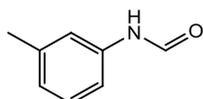
4. Characterization of formamides, benzimidazoles and dimethylated amines



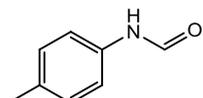
N-phenylformamide (3a). The crude reaction mixture was purified on silica gel (30% EtOAc/petroleum ether) to afford the product as a white solid (96% yield). $^1\text{H NMR}$ (CDCl_3 , 500 MHz): (*trans/cis*=50/50), δ 8.70 (d, $J = 11.4$ Hz, 1H, *trans*), 8.44 (br s, 1H, *trans*), 8.38 (d, $J = 1.2$ Hz, 1H, *cis*), 7.55 (d, $J = 7.9$ Hz, 2H), 7.49 (br s, 1H, *cis*), 7.35 (dt, $J = 13.3, 8.0$ Hz, 4H), 7.19 (t, $J = 7.5$ Hz, 1H), 7.14 (t, $J = 7.4$ Hz, 1H), 7.10 (d, $J = 7.7$ Hz, 2H); $^{13}\text{C NMR}$ (CDCl_3 , 125 MHz): δ 162.7, 159.0, 136.9, 136.7, 129.8, 129.1, 125.3, 124.9, 120.0, 118.8. The physical data were identical in all respects to those previously reported.^[S9]



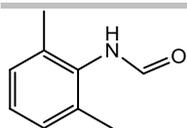
N-o-tolylformamide (3b). The crude reaction mixture was purified on silica gel (30% EtOAc/petroleum ether) to afford the product as a white solid (95% yield). $^1\text{H NMR}$ (CDCl_3 , 500 MHz): (*trans/cis*=65/35), δ 8.76 (br s, 1H, *trans*), 8.50 (d, $J = 11.1$ Hz, 1H, *trans*), 8.36 (s, 1H, *cis*), 7.80 (d, $J = 7.8$ Hz, 1H, *trans*), 7.22-7.05 (m, 3H, *trans*, 4H, *cis*), 2.30 (s, 3H, *trans*), 2.23 (s, 3H, *cis*); $^{13}\text{C NMR}$ (CDCl_3 , 125 MHz): δ 164.0, 159.8, 135.2, 134.8, 131.2, 130.6, 130.2, 129.3, 127.1, 126.7, 126.1, 125.6, 123.4, 121.0, 17.79, 17.76. The physical data were identical in all respects to those previously reported.^[S10]



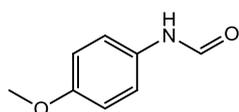
N-m-tolylformamide (3c). The crude reaction mixture was purified on silica gel (30% EtOAc/petroleum ether) to afford the product as a white solid (95% yield). $^1\text{H NMR}$ (CDCl_3 , 500 MHz): (*trans/cis*=60/40), δ 8.77 (br s, 1H, *trans*), 8.70 (d, $J = 9.8$ Hz, 1H, *trans*), 8.34 (s, 1H, *cis*), 7.80 (br s, 1H, *cis*), 7.40 (s, 1H, *cis*), 7.32 (d, $J = 8.0$ Hz, 1H, *cis*), 7.21 (m, 1H, *trans*, 1H, *cis*), 6.99 (d, $J = 7.5$ Hz, 1H, *cis*), 6.94 (d, $J = 7.5$ Hz, 1H, *cis*), 6.91 (s, 2H, *trans*), 2.34 (s, 3H, *trans*), 2.32 (s, 3H, *cis*); $^{13}\text{C NMR}$ (CDCl_3 , 125 MHz): δ 163.0, 159.3, 139.8, 139.0, 136.9, 136.7, 130.8, 129.5, 128.9, 126.0, 125.6, 120.7, 119.5, 117.1, 115.8, 21.44, 21.37. The physical data were identical in all respects to those previously reported.^[S9]



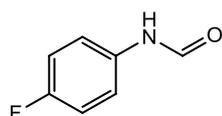
N-p-tolylformamide (3d). The crude reaction mixture was purified on silica gel (30% EtOAc/petroleum ether) to afford the product as a white solid (96% yield). $^1\text{H NMR}$ (CDCl_3 , 500 MHz): (*trans/cis*=50/50), δ 9.02 (br s, 1H, *trans*), 8.62 (d, $J = 11.4$ Hz, 1H, *trans*), 8.31 (br s, 1H, *cis*), 8.28 (d, $J = 1.6$ Hz, 1H, *cis*), 7.42 (d, $J = 8.3$ Hz, 2H, *cis*), 7.12 (d, $J = 8.1$ Hz, 2H, *trans*), 7.09 (d, $J = 8.2$ Hz, 2H, *cis*), 6.98 (d, $J = 8.3$ Hz, 2H, *trans*), 2.31 (s, 3H, *trans*), 2.28 (s, 3H, *cis*); $^{13}\text{C NMR}$ (CDCl_3 , 125 MHz): δ 162.8, 159.0, 135.1, 134.5, 134.3, 134.1, 130.2, 129.6, 120.1, 119.12, 20.9, 20.8. The physical data were identical in all respects to those previously reported.^[S11]



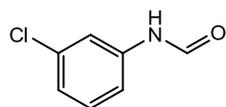
N-(2,6-dimethylphenyl)formamide (3e). The crude reaction mixture was purified on silica gel (30% EtOAc/petroleum ether) to afford the product as a white solid (94% yield). $^1\text{H NMR}$ (CDCl_3 , 500 MHz): (*trans/cis*=50/50), δ 8.34 (s, 1H, *cis*), 8.09 (d, $J = 11.9$ Hz, 1H, *trans*), 7.36 (br s, 1H, *trans*), 7.14 – 7.07 (m, 3H, *trans*, 3H, *cis*), 2.31 (s, 6H, *trans*), 2.24 (s, 6H, *cis*); $^{13}\text{C NMR}$ (CDCl_3 , 125 MHz): δ 165.0, 159.5, 135.3, 133.2, 132.4, 128.7, 128.3, 127.7, 18.73, 18.56. The physical data were identical in all respects to those previously reported.^[S12]



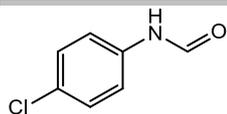
N-(4-methoxyphenyl)formamide (3f). The crude reaction mixture was purified on silica gel (30% EtOAc/petroleum ether) to afford the product as a white solid (93% yield). $^1\text{H NMR}$ (CDCl_3 , 500 MHz): (*trans/cis*=45/55), δ 8.57 (br s, 1H, *trans*), 8.52 (d, $J = 9.8$ Hz, 1H, *trans*), 8.28 (s, 1H, *cis*), 7.90 (br s, 1H, *cis*), 7.44 (d, $J = 8.9$ Hz, 2H, *cis*), 7.03 (d, $J = 8.8$ Hz, 2H, *trans*), 6.87 (d, $J = 8.9$ Hz, 2H, *trans*), 6.84 (d, $J = 8.9$ Hz, 2H, *cis*), 3.79 (s, 3H, *trans*), 3.77 (s, 3H, *cis*); $^{13}\text{C NMR}$ (CDCl_3 , 125 MHz): δ 163.4, 159.3, 157.6, 156.7, 130.1, 129.7, 121.9, 121.5, 114.9, 114.2, 55.56, 55.48. The physical data were identical in all respects to those previously reported.^[S9]



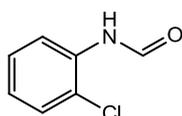
N-(4-fluorophenyl)formamide (3g). The crude reaction mixture was purified on silica gel (30% EtOAc/petroleum ether) to afford the product as a white solid (96% yield). $^1\text{H NMR}$ (CDCl_3 , 500 MHz): (*trans/cis*=40/60), δ 8.58 (d, $J = 11.3$ Hz, 1H, *trans*), 8.36 (s, 1H, *cis*), 8.13 (br s, 1H, *trans*), 7.51 (dd, $J = 9.0, 4.7$ Hz, 2H, *cis*), 7.36 (br s, 1H, *cis*), 7.07 (d, $J = 6.1$ Hz, 4H, *trans*), 7.03 (t, $J = 8.6$ Hz, 2H, *cis*); $^{13}\text{C NMR}$ (CDCl_3 , 125 MHz): δ 162.7, 161.4, 160.6, 159.5, 158.8, 158.6, 132.8, 132.6, 121.8, 121.8, 121.3, 121.2, 116.7, 116.5, 115.9, 115.7. The physical data were identical in all respects to those previously reported.^[S9]



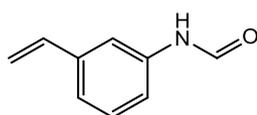
N-(3-chlorophenyl)formamide (3h). The crude reaction mixture was purified on silica gel (30% EtOAc/petroleum ether) to afford the product as a white solid (94% yield). $^1\text{H NMR}$ (CDCl_3 , 500 MHz): (*trans/cis*=40/60), δ 9.16 (br s, 1H, *trans*), 8.70 (d, $J = 11.2$ Hz, 1H, *trans*), 8.49 (br s, 1H, *cis*), 8.35 (s, 1H, *cis*), 7.67 (s, 1H, *cis*), 7.39 (d, $J = 7.4$ Hz, 1H, *cis*), 7.26 (t, $J = 8.0$ Hz, 1H, *trans*), 7.22 (t, $J = 8.1$ Hz, 1H, *trans*), 7.14 (d, $J = 8.8$ Hz, 1H, *cis*), 7.12 (s, 1H, *trans*), 7.11-7.04 (m, 1H, *cis*), 7.02-6.97 (m, 1H, *trans*); $^{13}\text{C NMR}$ (CDCl_3 , 125 MHz): δ 162.6, 159.3, 138.0, 137.9, 135.4, 134.7, 130.8, 130.1, 125.3, 124.9, 120.1, 118.7, 117.9, 116.6. The physical data were identical in all respects to those previously reported.^[S9]



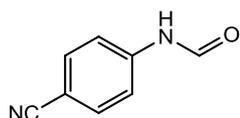
N-(4-chlorophenyl)formamide (3i). The crude reaction mixture was purified on silica gel (30% EtOAc/petroleum ether) to afford the product as a white solid (96% yield). $^1\text{H NMR}$ (CDCl_3 , 500 MHz): (*trans/cis*=40/60), δ 8.66 (d, $J = 10.6$ Hz, 1H, *trans*), 8.61 (br s, 1H, *trans*), 8.36 (s, 1H, *cis*), 7.66 (br s, 1H, *cis*), 7.50 (d, $J = 8.7$ Hz, 2H, *cis*), 7.33 (d, $J = 8.6$ Hz, 2H, *trans*), 7.29 (d, $J = 8.7$ Hz, 2H, *cis*), 7.04 (d, $J = 8.6$ Hz, 2H, *trans*); $^{13}\text{C NMR}$ (CDCl_3 , 125 MHz): δ 162.2, 158.8, 135.4, 129.9, 129.2, 121.2, 120.2, 92.1. δ 162.2, 158.8, 135.4, 129.9, 129.2, 121.2, 120.2, 92.1. The physical data were identical in all respects to those previously reported.^[S13]



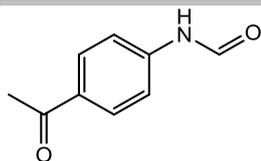
N-(2-chlorophenyl)formamide (3j). The crude reaction mixture was purified on silica gel (30% EtOAc/petroleum ether) to afford the product as a white solid (95% yield). $^1\text{H NMR}$ (CDCl_3 , 500 MHz): (*trans/cis*=30/70), δ 8.69 (d, $J = 11.0$ Hz, 1H, *trans*), 8.49 (s, 1H, *cis*), 8.37 (d, $J = 8.2$ Hz, 1H, *cis*), 8.05 (br s, 1H, *cis*), 7.41 (d, $J = 8.0$ Hz, 1H, *trans*), 7.36 (d, $J = 8.0$ Hz, 1H, *cis*), 7.29-7.22 (m, 2H, *trans*, 1H, *cis*), 7.15-7.09 (m, 1H, *trans*), 7.05 (t, $J = 7.7$ Hz, 1H, *cis*); $^{13}\text{C NMR}$ (CDCl_3 , 125 MHz): δ 161.4, 158.7, 133.7, 130.3, 129.1, 128.0, 127.8, 125.9, 125.1, 122.5, 122.0, 118.5. The physical data were identical in all respects to those previously reported.^[S9]



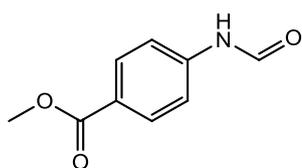
N-(3-vinylphenyl)formamide (3k). The crude reaction mixture was purified on silica gel (30% EtOAc/petroleum ether) to afford the product as colorless oil (92% yield). $^1\text{H NMR}$ (CDCl_3 , 500 MHz): (*trans/cis*=55/45), δ 8.71 (d, $J = 11.3$ Hz, 1H, *trans*), 8.54 (br s, 1H, *trans*), 8.38 (s, 1H, *cis*), 7.62 (s, 1H, *trans*), 7.58 (br s, 1H, *cis*), 7.43 (d, $J = 8.0$ Hz, 1H, *trans*), 7.34 – 7.22 (m, 2H, *trans*, 1H, *cis*), 7.19 (d, $J = 7.7$ Hz, 1H, *cis*), 7.11 (s, 1H, *cis*), 7.00 (d, $J = 7.8$ Hz, 1H, *cis*), 6.70 (dd, $J = 10.9, 3.9$ Hz, 1H, *trans*), 6.66 (dd, $J = 10.9, 3.9$ Hz, 1H, *cis*), 5.78 (d, $J = 10.2$ Hz, 1H, *trans*), 5.75 (d, $J = 10.2$ Hz, 1H, *cis*), 5.32 (d, $J = 10.9$ Hz, 1H, *trans*), 5.27 (d, $J = 10.9$ Hz, 1H, *cis*); $^{13}\text{C NMR}$ (CDCl_3 , 125 MHz): δ 162.7, 159.1, 139.3, 138.6, 137.2, 137.0, 136.3, 135.9, 129.9, 129.2, 123.2, 122.7, 119.4, 118.1, 117.8, 116.6, 115.4, 114.8.



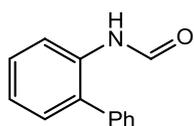
N-(4-cyanophenyl)formamide (3l). The crude reaction mixture was purified on silica gel (50% EtOAc/petroleum ether) to afford the product as a white solid (94% yield). $^1\text{H NMR}$ (DMSO, 500 MHz): (*trans/cis*=25/75), δ 10.59 (br s, 1H, *cis*), 10.47 (d, $J = 10.2$ Hz, 1H, *trans*), 8.93 (d, $J = 10.5$ Hz, 1H, *trans*), 8.31 (s, 1H, *cis*), 7.71 (q, $J = 8.6$ Hz, 2H, *trans*, 4H, *cis*), 7.32 (d, $J = 7.7$ Hz, 2H, *trans*); $^{13}\text{C NMR}$ (DMSO, 125 MHz): δ 163.2, 163.1, 161.2, 160.9, 160.8, 160.6, 143.4, 142.8, 134.3, 133.9, 119.8, 119.4, 117.6, 106.0, 105.8.



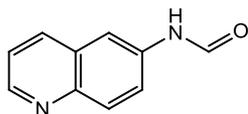
N-(4-acetylphenyl)formamide (3m). The crude reaction mixture was purified on silica gel (50% EtOAc/petroleum ether) to afford the product as a white solid (95% yield). $^1\text{H NMR}$ (CDCl_3 , 500 MHz): (*trans/cis*=35/65), δ 9.36 (d, $J = 10.7$ Hz, 1H, *trans*), 8.92 (d, $J = 3.9$ Hz, 1H, *cis*), 8.90 (br s, 1H, *trans*), 8.46 (d, $J = 0.9$ Hz, 1H, *cis*), 7.97 (d, $J = 8.5$ Hz, 2H, *trans*), 7.93 (d, $J = 8.6$ Hz, 2H, *cis*), 7.72 (d, $J = 8.6$ Hz, 2H, *cis*), 7.23 (d, $J = 8.5$ Hz, 2H, *trans*), 2.60 (s, 3H, *trans*), 2.59 (s, 3H, *cis*); $^{13}\text{C NMR}$ (CDCl_3 , 125 MHz): δ 197.4, 197.0, 162.2, 159.7, 141.6, 141.4, 133.4, 132.9, 130.3, 129.6, 119.2, 117.1, 26.4. The physical data were identical in all respects to those previously reported.^[S9]



methyl 4-formamidobenzoate (3n). The crude reaction mixture was purified on silica gel (50% EtOAc/petroleum ether) to afford the product as a white solid (95% yield). $^1\text{H NMR}$ (CDCl_3 , 500 MHz): (*trans/cis*=45/55), δ 9.00 (br s, 1H, *trans*), 8.82 (d, $J = 11.1$ Hz, 1H, *trans*), 8.38 (s, 1H, *cis*), 8.23 (br s, 1H, *cis*), 7.98 (d, $J = 8.5$ Hz, 2H, *trans*), 7.95 (d, $J = 8.6$ Hz, 2H, *cis*), 7.61 (d, $J = 8.6$ Hz, 2H, *cis*), 7.12 (d, $J = 8.6$ Hz, 2H, *trans*), 3.87 (s, 3H, *trans*), 3.85 (s, 3H, *cis*); $^{13}\text{C NMR}$ (CDCl_3 , 125 MHz): δ 166.5, 166.3, 162.1, 159.3, 141.1, 140.9, 131.4, 130.7, 126.4, 125.8, 119.0, 117.0, 52.05, 51.96.

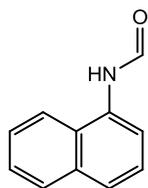


N-([1,1'-biphenyl]-2-yl)formamide (3o). The crude reaction mixture was purified on silica gel (30% EtOAc/petroleum ether) to afford the product as a white solid (96% yield). $^1\text{H NMR}$ (CDCl_3 , 500 MHz): (*trans/cis*=45/55), δ 8.72 (d, $J = 11.3$ Hz, 1H, *trans*), 8.49 (d, $J = 8.2$ Hz, 1H, *cis*), 8.36 (s, 1H, *cis*), 7.68-7.32 (m, 9H, *trans*, 9H, *cis*); $^{13}\text{C NMR}$ (CDCl_3 , 125 MHz): δ 162.0, 159.0, 137.7, 137.3, 133.7, 133.6, 133.0, 132.0, 131.0, 130.0, 129.2, 129.1, 129.0, 128.6, 128.3, 128.0, 127.9, 125.3, 124.5, 121.6, 118.5. The physical data were identical in all respects to those previously reported.^[S14]

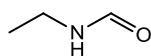


N-(quinolin-6-yl)formamide (3p). The crude reaction mixture was purified on silica gel (10% EtOAc/petroleum ether) to afford the product as a pale yellow solid (94% yield). $^1\text{H NMR}$ (CDCl_3 , 500 MHz): (*trans/cis*=35/65), δ 9.22 (br s, 1H, *trans*), 8.98 (d, $J = 25.8$ Hz, 1H, *cis*), 8.91 (d, $J = 11.2$ Hz, 1H, *trans*), 8.88 (d, $J = 3.9$ Hz, 1H, *trans*), 8.84 (d, $J = 4.0$ Hz, 1H, *cis*), 8.52 (d, $J = 1.1$ Hz, 1H, *cis*), 8.44 (d, $J = 2.1$ Hz, 1H, *cis*), 8.12 (d, $J = 7.4$ Hz, 2H, *cis*), 8.04 (d, $J = 9.0$ Hz, 2H, *trans*), 7.64 (dd, $J = 9.0, 2.3$ Hz, 1H, *cis*), 7.54-7.49 (m, 2H, *trans*), 7.43 (dd, $J = 8.3, 4.2$ Hz, 1H, *trans*), 7.39 (dd, $J = 8.3, 4.2$ Hz, 1H, *cis*); $^{13}\text{C NMR}$ (CDCl_3 , 125 MHz):

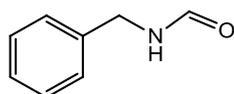
δ 162.7, 159.6, 149.7, 149.3, 145.8, 145.3, 136.2, 135.4, 135.2, 135.1, 131.2, 131.0, 129.9, 128.8, 123.2, 122.2, 122.1, 121.7, 116.7, 114.3.



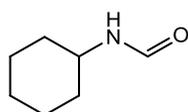
N-(naphthalen-1-yl)formamide (3q). The crude reaction mixture was purified on silica gel (30% EtOAc/petroleum ether) to afford the product as a pale yellow solid (95% yield). $^1\text{H NMR}$ (CDCl_3 , 500 MHz): (*trans/cis*=70/30), δ 9.06 (br s, 1H, *trans*), 8.62 (d, $J = 11.0$ Hz, 1H, *trans*), 8.58 (s, 1H, *cis*), 8.04 (d, $J = 8.2$ Hz, 1H, *trans*), 7.97 (d, $J = 7.4$ Hz, 1H, *cis*), 7.90-7.86 (m, 1H, *trans*), 7.86-7.83 (m, 1H, *cis*), 7.77 (d, $J = 8.3$ Hz, 1H, *trans*), 7.69 (d, $J = 8.2$ Hz, 1H, *cis*), 7.56 (ddt, $J = 7.7, 6.9, 3.3$ Hz, 2H, *trans*), 7.52-7.47 (m, 2H, *cis*), 7.47-7.40 (m, 1H, *trans*, 1H, *cis*), 7.29 (d, $J = 7.2$ Hz, 1H, *trans*); $^{13}\text{C NMR}$ (CDCl_3 , 125 MHz): δ 164.4, 159.9, 134.2, 134.0, 132.2, 131.1, 128.7, 128.4, 127.7, 126.9, 126.7, 126.4, 126.1, 126.0, 125.6, 125.4, 121.4, 120.9, 120.5, 118.9.



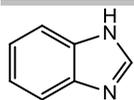
N-ethylformamide (3r). Colorless oil (94% yield). $^1\text{H NMR}$ (CDCl_3 , 500 MHz): (*trans/cis*=15/85), δ 8.11 (s, 1H, *cis*), 8.05 (d, $J = 12.1$ Hz, 1H, *trans*), 7.10 (br s, 1H, *cis*), 6.78 (br s, 1H, *trans*), 3.34-3.29 (m, 2H, *cis*), 3.27 (dd, $J = 9.4, 4.3$ Hz, 2H, *trans*), 1.21 (t, $J = 7.2$ Hz, 3H, *trans*), 1.17 (t, $J = 7.3$ Hz, 3H, *cis*); $^{13}\text{C NMR}$ (CDCl_3 , 125 MHz): δ 164.5, 161.3, 36.5, 32.7, 16.4, 14.3. The physical data were identical in all respects to those previously reported.^[S15]



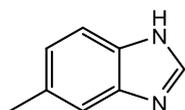
N-benzylformamide (3s). The crude reaction mixture was purified on silica gel (30% EtOAc/petroleum ether) to afford the product as a white solid (95% yield). $^1\text{H NMR}$ (CDCl_3 , 500 MHz): (*trans/cis*=85/15), δ 8.14 (d, $J = 6.6$ Hz, 1H, *trans*), 8.05 (dd, $J = 11.7, 8.3$ Hz, 1H, *cis*), 7.36-7.15 (m, 5H, *trans*, 5H, *cis*), 6.42 (br s, 1H, *trans*), 6.17 (br s, 1H, *cis*), 4.39 (t, $J = 5.4$ Hz, 2H, *trans*), 4.32 (t, $J = 5.6$ Hz, 1H, *cis*); $^{13}\text{C NMR}$ (CDCl_3 , 125 MHz): δ 164.7, 161.1, 137.6, 137.4, 128.8, 128.6, 127.8, 127.6, 127.5, 126.9, 45.6, 42.0. The physical data were identical in all respects to those previously reported.^[S11]



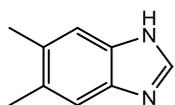
N-cyclohexylformamide (3t). Colorless oil (95% yield). $^1\text{H NMR}$ (CDCl_3 , 500 MHz): (*trans/cis*=15/85), δ 7.89 (d, $J = 12.0$ Hz, 1H, *trans*), 7.85 (s, 1H, *cis*), 6.84 (br s, 1H, *cis*), 6.67 (br s, 1H, *trans*), 3.67-3.51 (m, 1H, *cis*), 3.11-3.02 (m, 1H, *trans*), 1.71-0.92 (m, 10H, *trans*, 10H, *cis*); $^{13}\text{C NMR}$ (CDCl_3 , 125 MHz): δ 163.5, 160.3, 50.8, 46.7, 34.1, 32.4, 25.0, 24.6, 24.4. The physical data were identical in all respects to those previously reported.^[S16]



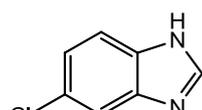
benzoimidazole (5a). The crude reaction mixture was purified on silica gel (5~15% MeOH/dichloromethane) to afford the product as a white solid (97% yield). $^1\text{H NMR}$ (CDCl_3 , 500 MHz): δ 8.31 (br s, 1H), 8.11 (s, 1H), 7.67-7.63 (m, 2H), 7.30-7.26 (m, 2H); $^{13}\text{C NMR}$ (CDCl_3 , 125 MHz): δ 140.4, 137.4, 123.1, 115.5. The physical data were identical in all respects to those previously reported.^[S17]



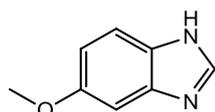
5-methylbenzoimidazole (5b). The crude reaction mixture was purified on silica gel (5~15% MeOH/dichloromethane) to afford the product as a white solid (96% yield). $^1\text{H NMR}$ (CDCl_3 , 500 MHz): δ 8.02 (s, 1H), 7.53 (d, $J = 8.2$ Hz, 1H), 7.41 (s, 1H), 7.09 (d, $J = 8.2$ Hz, 1H), 5.95 (br s, 1H), 2.45 (s, 3H); $^{13}\text{C NMR}$ (CDCl_3 , 125 MHz): δ 140.1, 137.2, 136.1, 133.0, 124.6, 115.5, 114.8, 21.6. The physical data were identical in all respects to those previously reported.^[S17]



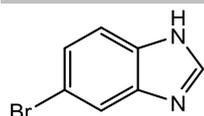
5,6-dimethylbenzoimidazole (5c). The crude reaction mixture was purified on silica gel (5~15% MeOH/dichloromethane) to afford the product as a pale yellow solid (95% yield). $^1\text{H NMR}$ (CDCl_3 , 500 MHz): δ 7.95 (s, 1H), 7.40 (s, 2H), 2.34 (s, 6H); $^{13}\text{C NMR}$ (CDCl_3 , 125 MHz): δ 139.6, 136.1, 132.0, 115.5, 20.4. The physical data were identical in all respects to those previously reported.^[S17]



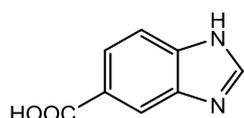
5-chlorobenzoimidazole (5d). The crude reaction mixture was purified on silica gel (5~15% MeOH/dichloromethane) to afford the product as a yellow solid (95% yield). $^1\text{H NMR}$ (CDCl_3 , 500 MHz): δ 8.11 (s, 1H), 7.66 (s, 1H), 7.59 (d, $J = 8.6$ Hz, 1H), 7.28 (d, $J = 8.6$ Hz, 1H), 5.94 (br s, 1H); $^{13}\text{C NMR}$ (CDCl_3 , 125 MHz): δ 141.3, 128.8, 123.8, 116.4, 115.4. The physical data were identical in all respects to those previously reported.^[S18]



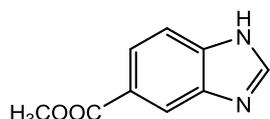
5-methoxybenzoimidazole (5e). The crude reaction mixture was purified on silica gel (5~15% MeOH/dichloromethane) to afford the product as a tan solid (94% yield). $^1\text{H NMR}$ (CDCl_3 , 500 MHz): δ 12.26 (br s, 1H), 8.10 (s, 1H), 7.55 (d, $J = 8.8$ Hz, 1H), 7.09 (s, 1H), 6.92 (dd, $J = 8.8, 2.1$ Hz, 1H), 3.78 (s, 3H); $^{13}\text{C NMR}$ (CDCl_3 , 125 MHz): δ 156.6, 140.6, 137.7, 133.1, 116.4, 112.6, 97.5, 55.8. The physical data were identical in all respects to those previously reported.^[S18]



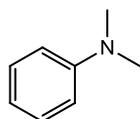
5-bromobenzimidazole (5f). The crude reaction mixture was purified on silica gel (5~15% MeOH/dichloromethane) to afford the product as a light yellow solid (96% yield). $^1\text{H NMR}$ ($(\text{CD}_3)_2\text{SO}$, 500 MHz): δ 12.61 (br s, 1H), 8.26 (d, $J = 1.2$ Hz, 1H), 7.80 (s, 1H), 7.56 (d, $J = 8.5$ Hz, 1H), 7.33 (dd, $J = 8.5, 1.9$ Hz, 1H); $^{13}\text{C NMR}$ ($(\text{CD}_3)_2\text{SO}$, 125 MHz): δ 143.2, 124.5, 113.9.



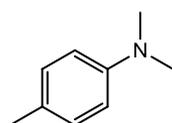
5-benzimidazolecarboxylic acid (5g). The crude reaction mixture was purified on silica gel (5~15% MeOH/dichloromethane) to afford the product as a yellow solid (93% yield). $^1\text{H NMR}$ ($(\text{CD}_3)_2\text{SO}$, 500 MHz): δ 12.71 (br s, 2H), 8.38 (s, 1H), 8.20 (s, 1H), 7.83 (dd, $J = 8.4, 1.5$ Hz, 1H), 7.65 (d, $J = 8.4$ Hz, 1H); $^{13}\text{C NMR}$ ($(\text{CD}_3)_2\text{SO}$, 125 MHz): δ 167.8, 144.2, 124.3, 123.0.



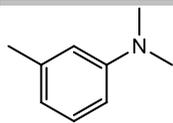
methyl 1H-benzimidazole-5-carboxylate (5h). The crude reaction mixture was purified on silica gel (5~15% MeOH/dichloromethane) to afford the product as a yellow solid (95% yield). $^1\text{H NMR}$ ($(\text{CD}_3)_2\text{SO}$, 500 MHz): δ 13.03 (br s, 1H), 8.52 (s, 1H), 8.30 (s, 1H), 7.88 (dd, $J = 8.5, 1.4$ Hz, 1H), 7.74 (d, $J = 8.5$ Hz, 1H), 3.88 (s, 3H); $^{13}\text{C NMR}$ ($(\text{CD}_3)_2\text{SO}$, 125 MHz): δ 166.1, 145.0, 131.7, 131.4, 128.6, 123.6, 123.2, 117.6, 114.9, 52.0.



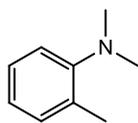
N,N-dimethylaniline (7a). The crude reaction mixture was purified on silica gel (5% EtOAc/petroleum ether) to afford the product as colorless oil (95% yield). $^1\text{H NMR}$ (CDCl_3 , 500 MHz): δ 7.28 (t, $J = 8.0$ Hz, 2H), 6.77 (dd, $J = 14.1, 7.6$ Hz, 3H), 2.97 (s, 6H); $^{13}\text{C NMR}$ (CDCl_3 , 125 MHz): δ 150.7, 129.1, 116.7, 112.8, 40.7. The physical data were identical in all respects to those previously reported.^[S19]



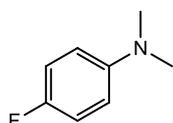
N,N-dimethyl-p-toluidine (7b). The crude reaction mixture was purified on silica gel (5% EtOAc/petroleum ether) to afford the product as colorless oil (95% yield). $^1\text{H NMR}$ (CDCl_3 , 500 MHz): δ 7.05 (d, $J = 8.2$ Hz, 2H), 6.69 (d, $J = 8.5$ Hz, 2H), 2.89 (s, 6H), 2.25 (s, 3H); $^{13}\text{C NMR}$ (CDCl_3 , 125 MHz): δ 148.8, 129.8, 129.6, 129.4, 126.2, 113.3, 41.1, 20.3. The physical data were identical in all respects to those previously reported.^[S19]



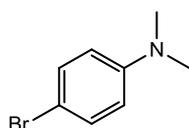
N,N-dimethyl-*m*-toluidine (7c). The crude reaction mixture was purified on silica gel (5% EtOAc/petroleum ether) to afford the product as colorless oil (95% yield). $^1\text{H NMR}$ (CDCl_3 , 500 MHz): δ 7.11 (dd, $J = 8.9, 7.4$ Hz, 1H), 6.54 (d, $J = 6.7$ Hz, 3H), 2.89 (s, 6H), 2.31 (s, 3H); $^{13}\text{C NMR}$ (CDCl_3 , 125 MHz): δ 150.8, 138.8, 129.0, 117.8, 113.6, 110.0, 40.8, 22.0. The physical data were identical in all respects to those previously reported.^[S19]



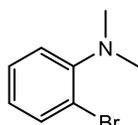
N,N-dimethyl-*o*-toluidine (7d). The crude reaction mixture was purified on silica gel (5% EtOAc/petroleum ether) to afford the product as colorless oil (94% yield). $^1\text{H NMR}$ (CDCl_3 , 500 MHz): δ 7.15 (t, $J = 6.9$ Hz, 2H), 7.03 (d, $J = 8.4$ Hz, 1H), 6.94 (t, $J = 7.4$ Hz, 1H), 2.69 (s, 7H), 2.32 (s, 3H); $^{13}\text{C NMR}$ (CDCl_3 , 125 MHz): δ 152.8, 132.2, 131.2, 126.5, 122.6, 118.4, 44.3, 18.4.



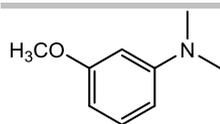
4-fluoro-N,N-dimethylaniline (7e). The crude reaction mixture was purified on silica gel (5% EtOAc/petroleum ether) to afford the product as a colorless solid (96% yield). $^1\text{H NMR}$ (CDCl_3 , 500 MHz): δ 6.94 (t, $J = 8.8$ Hz, 2H), 6.69 (dd, $J = 8.9, 4.3$ Hz, 2H), 2.90 (s, 6H); $^{13}\text{C NMR}$ (CDCl_3 , 125 MHz): δ 156.6, 154.8, 147.4, 115.5, 115.3, 114.1, 114.0, 41.4. The physical data were identical in all respects to those previously reported.^[S19]



4-bromo-N,N-dimethylaniline (7f). The crude reaction mixture was purified on silica gel (5% EtOAc/petroleum ether) to afford the product as a white solid (94% yield). $^1\text{H NMR}$ (CDCl_3 , 500 MHz): δ 7.27 (d, $J = 8.9$ Hz, 2H), 6.57 (d, $J = 7.7$ Hz, 2H), 2.89 (s, 6H); $^{13}\text{C NMR}$ (CDCl_3 , 125 MHz): δ 131.7, 114.2, 92.1, 40.6. The physical data were identical in all respects to those previously reported.^[S19]



2-bromo-N,N-dimethylaniline (7g). The crude reaction mixture was purified on silica gel (5% EtOAc/petroleum ether) to afford the product as colorless oil (95% yield). $^1\text{H NMR}$ (CDCl_3 , 500 MHz): δ 7.58 (dd, $J = 7.9, 1.6$ Hz, 1H), 7.31-7.27 (m, 1H), 7.13 (dd, $J = 8.0, 1.0$ Hz, 1H), 6.92 (m, 1H), 2.83 (s, 6H); $^{13}\text{C NMR}$ (CDCl_3 , 125 MHz): δ 151.8, 133.9, 128.1, 124.0, 120.6, 119.2, 44.3.



N,N-dimethyl-*m*-anisidine (7h). The crude reaction mixture was purified on silica gel (5%

EtOAc/petroleum ether) to afford the product as brown oil (94% yield). $^1\text{H NMR}$ (CDCl_3 , 500 MHz): δ 7.14 (t, $J = 8.1$ Hz, 1H), 6.36 (d, $J = 10.2$ Hz, 1H), 6.32–6.23 (m, 2H), 3.79 (s, 3H), 2.93 (s, 6H); $^{13}\text{C NMR}$ (CDCl_3 , 125 MHz): δ 160.7, 152.0, 129.8, 105.8, 101.5, 99.2, 55.11, 40.6.

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6. ^1H and ^{13}C NMR Spectra of formamides, benzimidazoles and dimethylated amines