Deoxygenative coupling of nitroarenes to synthesize aromatic azo compounds with CO using supported gold nanoparticles

Hai-Qian Li, Xiang Liu, Qi Zhang, Shu-Shuang Li, Yong-Mei Liu, He-Yong He and Yong Cao*

Department of Chemistry, Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Fudan University, Shanghai 200433, P. R. China.

Electronic Supplementary Information

1. Chemicals and materials

Gold catalysts including 1 wt% Au/Al_2O_3 (catalogue number: 79-0160), 1 wt% Au/TiO_2 (catalogue number 79-0165) and 1 wt% Au/ZnO (catalogue number: 79-0170) were supplied by Mintek. 4.5 wt% Au/Fe_2O_3 (type C, lot no. Au/Fe_2O_3 no. 02-5) was supplied by the World Gold Council (WGC). Palladium chloride ($PdCl_2$), rhodium chloride hydrate ($RhCl_3 \cdot xH_2O$), ruthenium chloride hydrate ($RuCl_3 \cdot xH_2O$), hexachloro-platonic acid hexahydrate ($H_2PtCl_6 \cdot 6H_2O$) and chloroauric acid tetrahydrate ($HAuCl_4 \cdot 4H_2O$), were supplied by Aldrich and used without further purification. Hexadecyl trimethyl ammonium bromide (CTAB) was supplied by Aladdin Reagent Company Limited (Shanghai, China).

2. Catalyst preparation

2.1 Preparation of CeO_2 support: meso-CeO_2 was prepared by a template-assisted precipitation method.[S1] Typically, a NaOH solution (2 g in 300 mL of distilled H_2O) was added to a stirred solution of $Ce(NO_3)_3 \cdot 6H_2O$ (4.34g) and CTAB (2.19 g) in 200 mL distilled water at 25 °C. The mixture was then maintained in a sealed glass vessel under stirring for 24 h. After thermal aging at 90 °C for 3 h, the pale yellow precipitate was filtered and washed with hot water (80 °C) to remove the residual CTAB. The resultant powder was dried at 100 °C for 6 h and then calcined at 450 °C for 4 h. The BET surface area of the as-synthesized meso-CeO_2 was 139 $m^2 \cdot g^{-1}$. Conventional CeO_2 having a surface area of 31 $m^2 \cdot g^{-1}$ was synthesized by a sol-gel method.[S2] An aqueous solution (100 mL) of $Ce(NO_3)_3 \cdot 6H_2O$ (4.342 g, 10 mmol) and citrate (1.82 g, 20 mmol) was heated at 90 °C under stirring until it became a viscous gel. Then the gel was dried at 120 °C overnight, and then calcined at 550 °C for 4 h to obtain the final material.

2.2 Preparation of 0.8 wt% Au/CeO_2: The Au/CeO_2 catalysts were prepared by a routine deposition-precipitation (DP) method. An appropriate amount of aqueous solutions of $HAuCl_4$ was heated to 75 °C under vigorous stirring. The pH was adjusted to 8 by dropwise addition of NaOH (0.2 M), and then 1.0 g of CeO_2 powders was dispersed in the solution. The mixture was aged for 2 h, after which the suspension was cooled

to 25 °C. Following extensive washing with deionized water, the samples was dried under vacuum at 25 °C overnight and then calcined in air at 400 °C for 4 h. Similarly prepared gold catalysts supported on commercial CeO_2 samples (Degussa Adnano 50, 50 $m^2 \cdot g^{-1}$ and Degussa Adnano 90, 90 $m^2 \cdot g^{-1}$) and meso-CeO_2 were denoted as Au/CeO_2-50, Au/CeO_2-90 and $Au/meso$-CeO_2, respectively.

2.3 Preparation of 0.8 wt% Au/ZrO_2: The ZrO_2 support was prepared by a conventional precipitation method following the reported procedure.[S3] The Au/ZrO_2 catalysts were prepared according to our previously reported procedure:[S4] An appropriate amount of ZrO_2 was added to the aqueous solution of $HAuCl_4$ (100 mL, 1 mM), the pH of which was adjusted to 9.0 by the dropwise addition of 0.25 M $NH_3 \cdot H_2O$. The aqueous dispersion was stirred for 8 h at 25 °C while the pH was maintained constantly at 9.0, and then filtered. Extensive washing with deionized water was then followed until it was free of Cl^- ions. The sample was dried under vacuum at 25 °C for 12 h before reduction at 300 °C for 2 h in 5 vol% H_2/Ar stream.

2.4 Preparation of 1.0 wt% Au/HT: Hydrotalcite (HT, $Mg_6Al_2(OH)_{16}CO_3$) was synthesized according to literature procedures.[S5] A modified deposition-precipitation (DP) procedure has been employed to prepare the Au/HT catalyst.[S6] Briefly, the obtained HT (1.0 g) was dispersed in an aqueous solution of appropriate concentration of $HAuCl_4 \cdot 4H_2O$ (100 mL, 1.02 $\times 10^{-3}$ M) with vigorously stirring. After agitation for 4 h at 25 °C, the mixtures were filtrated and washed thoroughly with deionized water until no Cl^- was detected in the filtrate by using $AgNO_3$. The resulting compound was dried under vacuum at room temperature for 12 h, and finally reduced by 5 vol% H_2/Ar at 300 °C for 2 h.

2.5 Preparation of 1.0 wt% Pt/meso-CeO_2, 1.0 wt% Pd/meso-CeO_2, 1.0 wt% Ru/meso-CeO_2 and 1.0 wt% Rh/meso-CeO_2: All these catalysts were prepared by impregnation technique. Meso-CeO_2 (1.0 g) was added to an appropriate amount of aqueous solution containing $H_2PtCl_6 \cdot 6H_2O$, $PdCl_2$, $RuCl_3 \cdot xH_2O$ or $RhCl_3 \cdot xH_2O$. After a perfect mixing of the corresponding slurries, the samples were dried in flowing air at 80 °C for 12 h and then reduced in 5 vol% H_2/Ar stream at 400 °C for 2 h.

3. Catalyst characterization

3.1 Elemental analysis: The gold loading of the catalysts was measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES) using a Thermo Electron IRIS Intrepid II XSP spectrometer. The detection limit for Au is 7 ppb.

3.2 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.

3.3 X-ray diffraction (XRD) analysis: The XRD information of the samples was carried out on a German Bruker D8 Avance X-ray diffractometer using the Ni-filtered Cu Kα radiation source at 40 kV and 40 mA.

3.4 X-ray photoelectron spectroscopy (XPS): XPS data were recorded with a Perkin Elmer PHI 5000C system equipped with a hemispherical electron energy analyzer. The spectrometer was operated at 15 kV and 20 mA, and a magnesium anode (Mg Kα, hν = 1253.6 eV) was used. The C 1s line (284.6 eV) was used as

the reference to calibrate the binding energies (BE).

3.5 High resolution transmission electron microscopy (HRTEM): HRTEM images for catalysts were taken with a JEM-2100F electron microscope operating at 200 kV. The samples for electron microscopy were prepared by grinding and subsequent dispersing the powder in ethanol and applying a drop of very dilute suspension on carbon-coated grids.

3.6 CO Temperature-programmed reduction (CO-TPR): TPR profiles were obtained on a homemade apparatus loaded with 50 mg of catalyst. Prior to TPR test, the sample was pretreated in a 10 vol% O_2/N_2 stream at 250°C for 60 min, then cooled down to room temperature and purged with pure He for 60 min. A 4 vol% CO/He gas mixture was passed over the sample, which was heated at 10 °C per min to 600 °C. The effluent gas was analyzed by an on-line mass spectrometry (OmniStar[TM], QMS 200).

3.7 Oxygen storage capacity (OSC) measurements: Oxygen storage capacity (OSC) data were collected at 150°C under atmospheric pressure using a fixed bed quartz reactor (i.d. 3 mm) equipped with 20 mg Au/CeO_2 diluted with quartz powder (60-80 mesh). After the samples were treated in a 10 vol% O_2/N_2 stream at 250°C for 60 min, and purged with pure He for 60 min, CO (4% CO, 1 % Ar as internal standard, and 95% balance He) pulses (1.0 mL per each pulse) were introduced into the reactor at intervals of 5 min until complete reduction of the samples at 150°C. The OSC data were determined by the amount of CO consumed during CO pulses analyzed by an on-line mass spectrometry (OmniStar[TM], QMS 200).

4. Catalytic activity measurement

4.1 General procedure for the deoxygenative coupling of nitroarenes by CO: A mixture of substrate, supported metal catalysts, and solvent (5 mL) was put into a batch autoclave reactor (75 mL). After sealing the reactor, CO was fed to the reactor through a gas inlet tube to the arranged pressure. The reaction mixture was stirred (800 rpm with a magnetic stir bar) at 150 °C. After the completion of the reaction, the reaction mixture was filtered and the catalyst was washed thoroughly with ethanol. Then the filtrate was concentrated and dried under reduced pressure using a rotary evaporator. The crude product was purified by column chromatography [silica 200-300; dichloromethane/petroleum ether mixture] to afford the product. All the products were confirmed by ^{1}H NMR, and ^{13}C NMR and the spectra obtained were compared with the standard spectra. The conversion and product selectivity were periodically determined by a GC-17A gas chromatograph equipped with a HP-5 column (30 m × 0.25 mm) and a flame ionization detector (FID) using *tert*-butylbenzene as an internal standard.
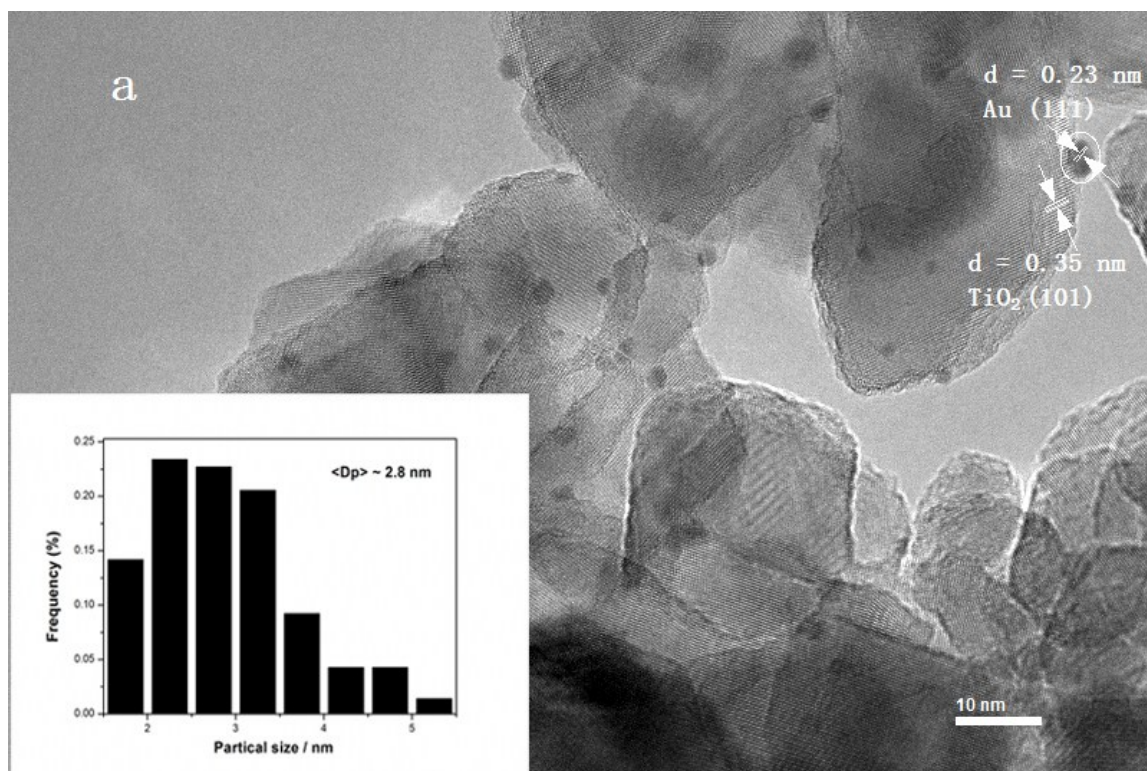
4.2 Recovery and reuse of Au/meso-CeO2: After the completion of the reaction, the reaction mixture was filtered and the catalyst was washed with acetone for at least three times and then with distilled water for several times. The catalyst was then dried under vacuum at 25 °C for 12 h to obtain the reused catalyst. In the five successive cycles, the yield of azobenzene was 96 %, 94 %, 94%, 93% and 88 %.
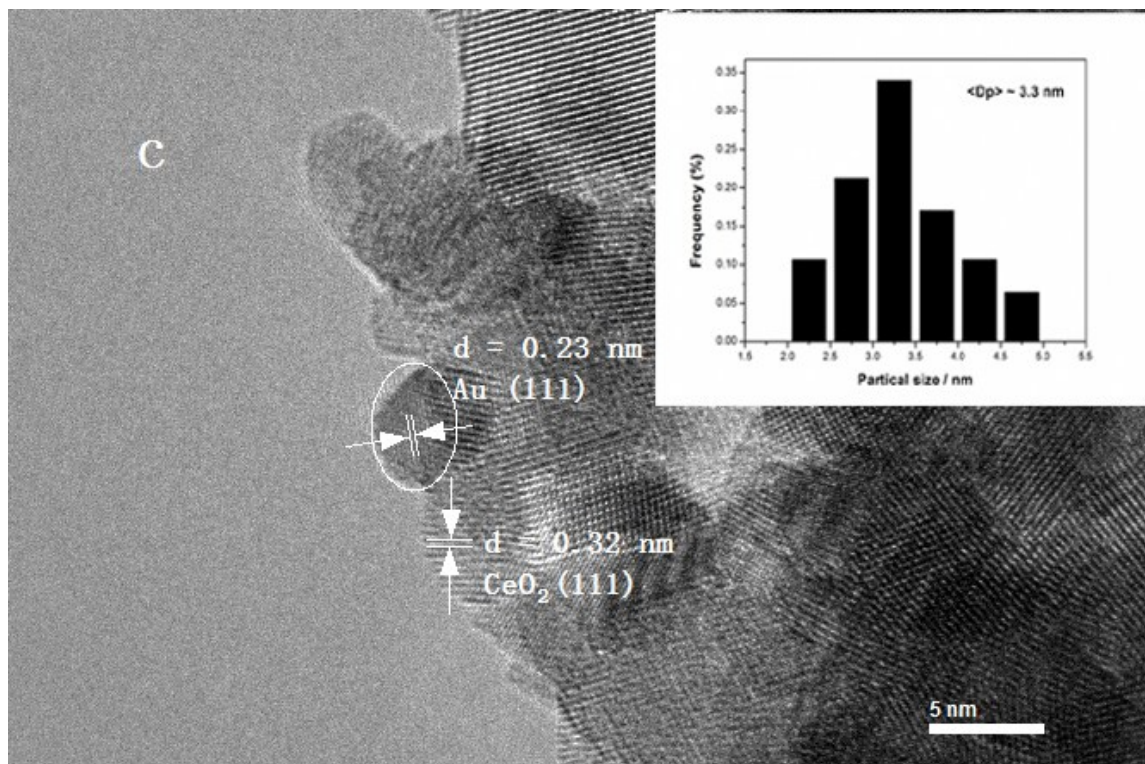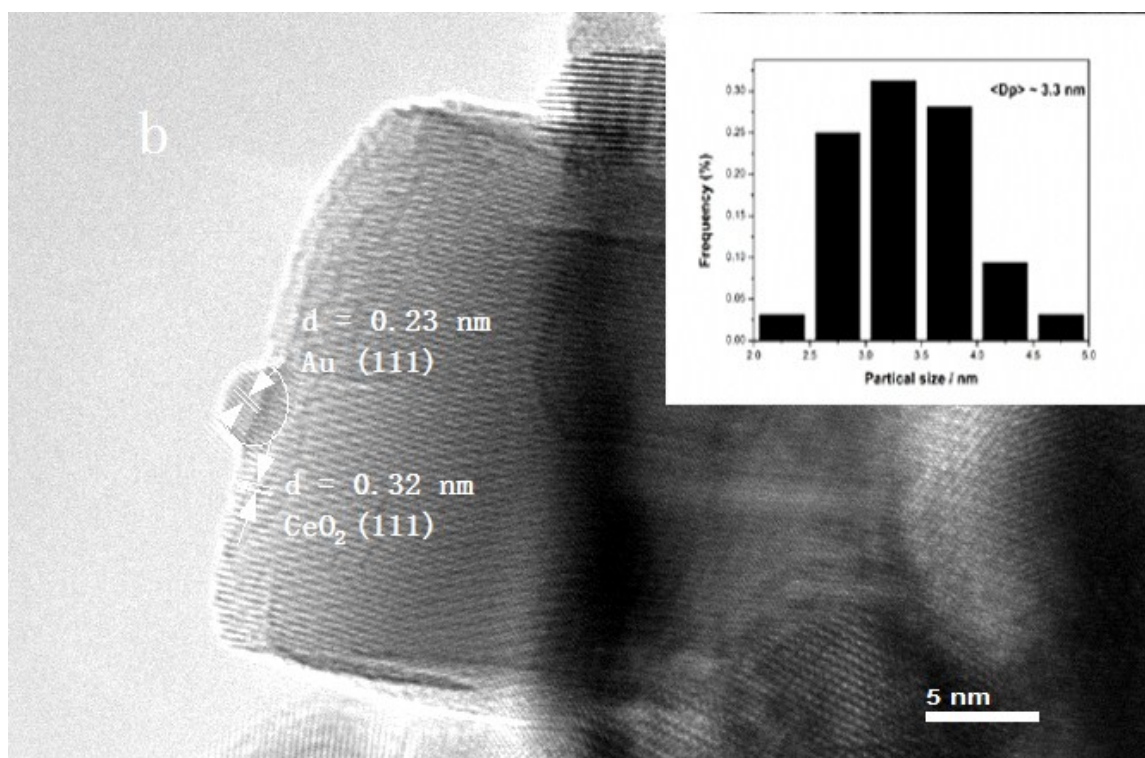
4.3 Procedure for 20-mmol scale CO-mediated deoxygenative coupling of nitrobenzene: A mixture of nitrobenzene (20 mmol), Au/meso-CeO2 (Au: 0.05 mol%) and anhydrous toluene (20ml) was charged into

an autoclave (100 mL). After sealing the reactor, CO (4 MPa) was fed to the reactor via a gas inlet tube. The reaction mixture was stirred (800 rpm) at 170 °C for 72 h. The conversion and product selectivity were periodically determined by GC using *tert*-butylbenzene as an internal standard.

4.4 Procedure for the deoxygenative coupling of nitrosobenzene: A mixture of nitrosobenzene (2 mmol), Au/meso-CeO$_2$ (Au: 0.5 mol%), and anhydrous toluene (5 mL) was charged into an autoclave (75 mL capacity). The resulting mixture was vigorously stirred at 150 °C under CO atmosphere (5 atm) for 5 h to give **2a**, **3a** and **4a** in 18%, 81% and 1% yield, respectively.

5. Results

d = 0.23 nm
Au (111)

d = 0.32 nm
CeO₂ (111)

<Dp> ~ 3.3 nm

5 nm

d = 0.23 nm
Au (111)

d = 0.32 nm
CeO₂ (111)

<Dp> ~ 3.3 nm

5 nm
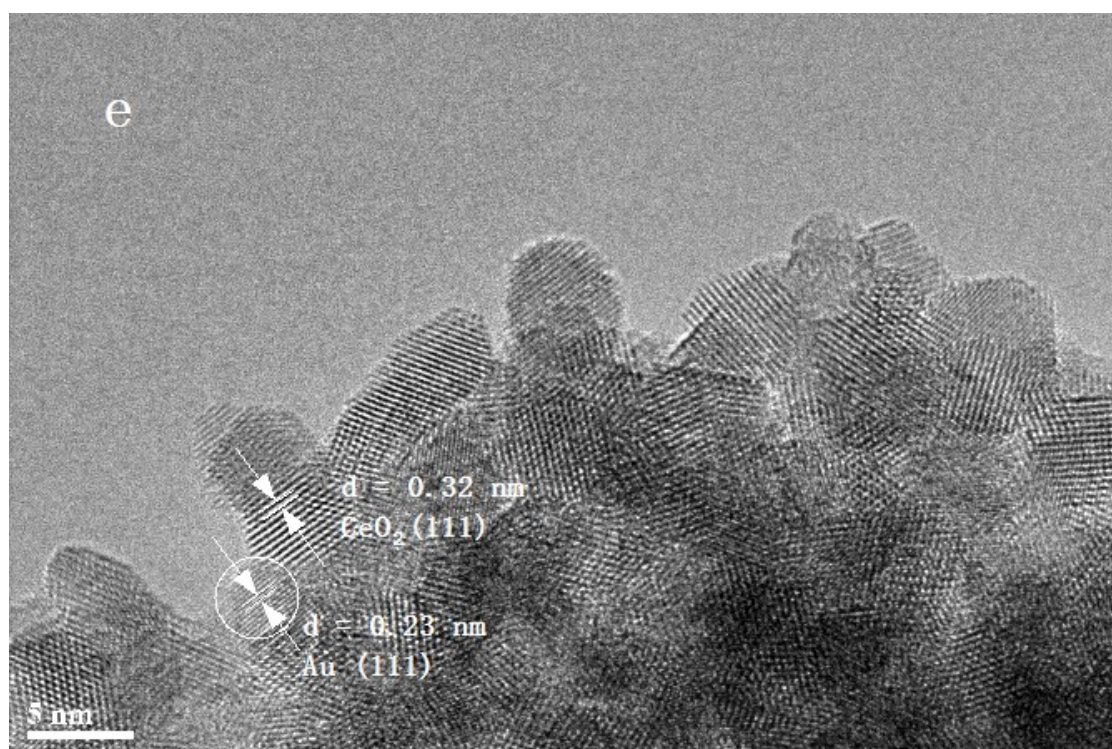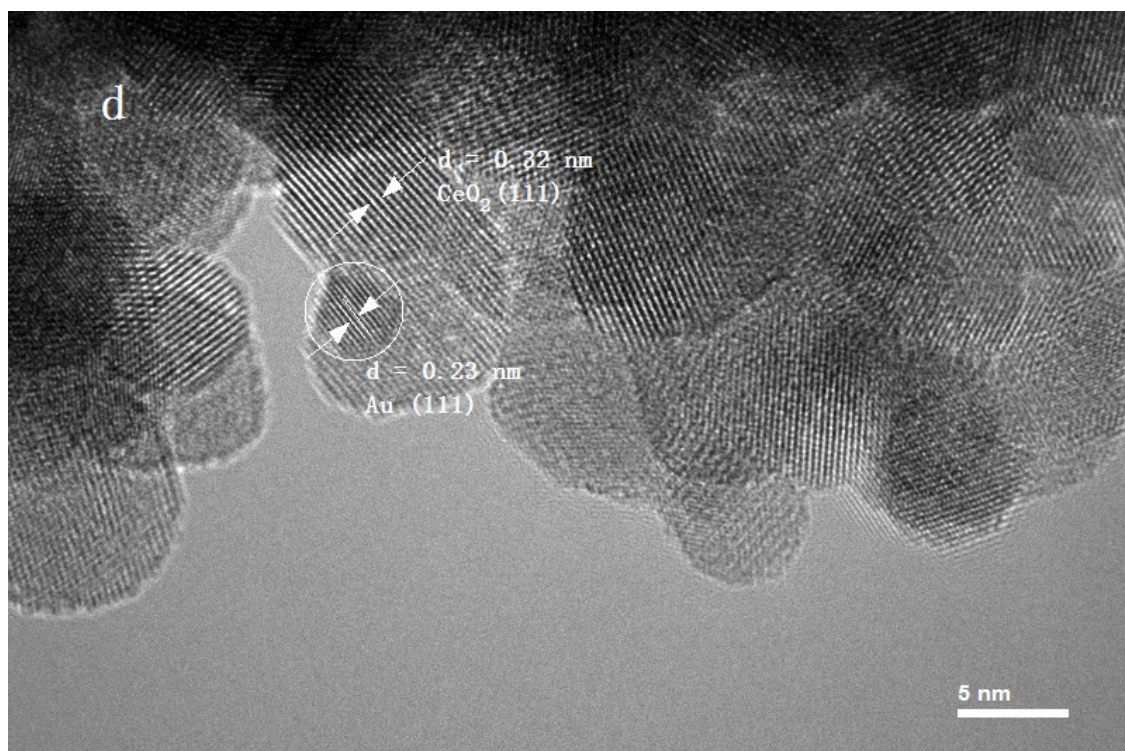
Fig. S1 HRTEM images and size distribution of (a) Au/TiO$_2$, (b) Au/CeO$_2$-50, (c) Au/CeO$_2$-90 (d) Au/meso-CeO$_2$, (e) Au/meso-CeO$_2$-reused. According to the image, the average size of the meso-CeO$_2$ NPs was 4.8 nm. However, the poor contrast between Au and mesostructured ceria support prevented obtaining the gold particle size distributions, but the existence of small Au particles can be confirmed by a careful lattice fringe analysis of the observed images.[S1]
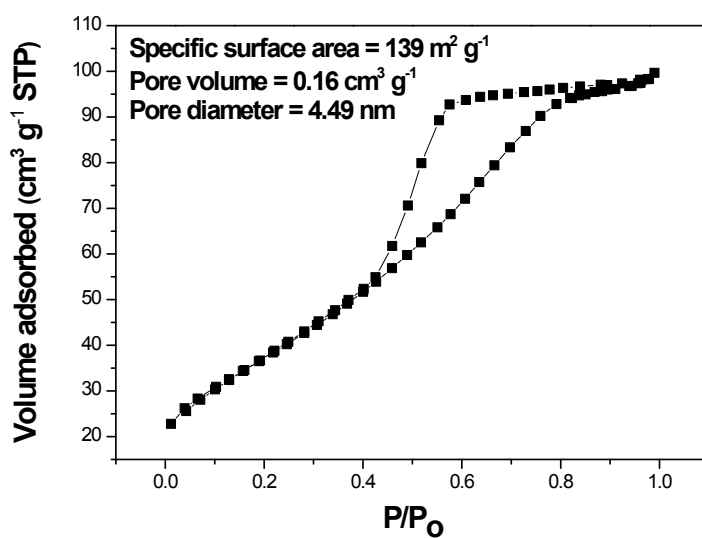
Fig. S2 N_2 adsorption-desorption data of meso-CeO_2.
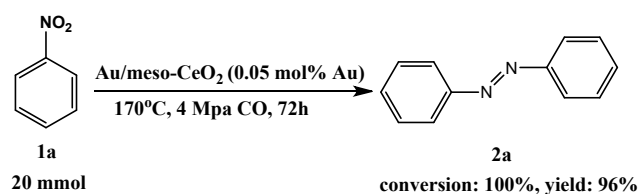
Scheme S1. Au-catalyzed 20 mmol scale of deoxygenative coupling of **1a**.
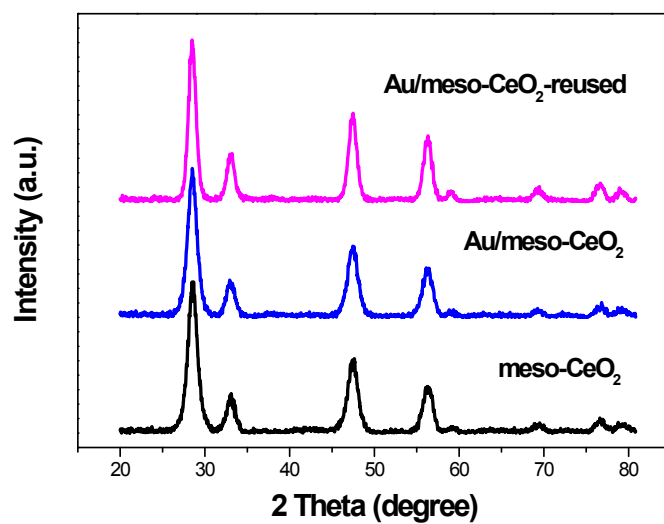
Fig. S3 XRD patterns of meso-CeO_2, Au/meso-CeO_2, and Au/meso-CeO_2-reused.

4f$_{7/2}$ 83.8 eV (Au^0) **4f$_{5/2}$ 87.5 eV (Au^0)** **(a)**

Intensity (a.u.)

80 82 84 86 88 90 92
Binding energy (eV)

4f$_{7/2}$ 83.8 eV (Au^0) **4f$_{5/2}$ 87.5 eV (Au^0)** **(b)**

Intensity (a.u.)

80 82 84 86 88 90 92
Binding energy (eV)
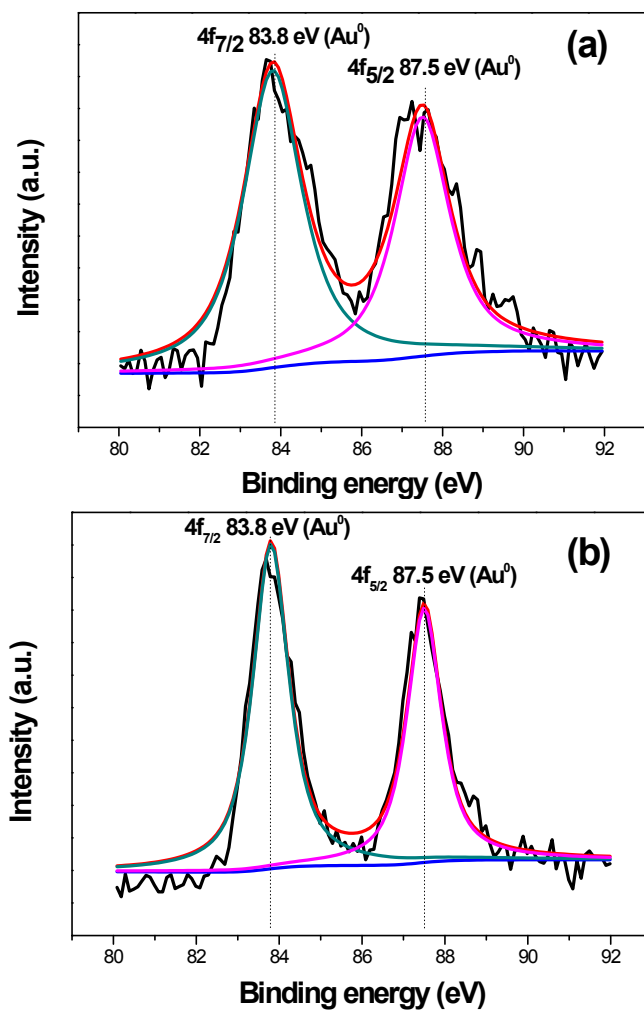
Fig. S4 XPS data of (a) Au/meso-CeO$_2$ and (b) Au/meso-CeO$_2$-reused.

Table S1 Deoxygenative coupling of nitrobenzene to azobenzene with CO over various catalysts.[a]
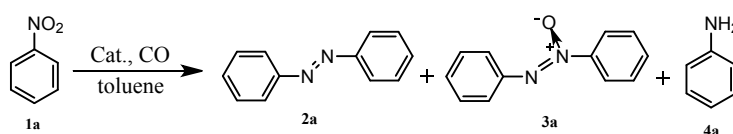
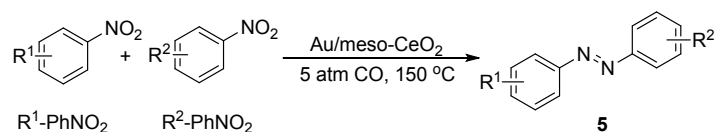| Entry	Catalyst	Conv. (%)[b]	Sel. (%)[b]		
			2a	**3a**	**4a**
1	Au/meso-CeO$_2$	100	99	0	1
2	Rh/meso-CeO$_2$	100	49	50	1
3	Ru/meso-CeO$_2$	64	27	72	1
4	Pd/meso-CeO$_2$	78	7	92	1
5	Pt/meso-CeO$_2$	100	65	33	2
6	HAuCl$_4$	no reaction	-	-	-
7	Au$_2$O$_3$	no reaction	-	-	-
8	Au^0 powder	no reaction	-	-	-

[a] Reaction conditions: 2 mmol nitrobenzene, catalyst (0.5 mol% metal), anhydrous toluene (5 mL), CO (5 atm), 150 °C, 5 h. [b] GC analysis using *tert*-butylbenzene as an internal standard.
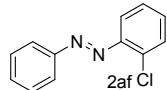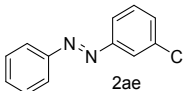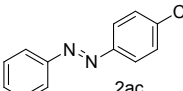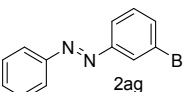
Table S2 Deoxygenative coupling of nitrobenzene to azobenzene with CO in various solvents.[a]

Entry	Solvent	Conv. (%)[b]	Sel. (%)[b]		
			2a	3a	4a
1	toluene	100	99	0	1
2	*n*-heptane	100	85	14	1
3	*p*-xylene	100	61	37	2
4	1,4-dioxane	100	38	59	3
5	acetonitrile	28	8	89	3

[a] Reaction conditions: 2 mmol nitrobenzene, Au/meso-CeO$_2$ (Au: 0.5 mol%), solvent (5 mL), freshly distilled before used, CO (5 atm), 150 °C, 5 h. [b] GC analysis using *tert*-butylbenzene as an internal standard.

Table S3 Au-catalyzed deoxygenative coupling of **1a** with H$_2$.[a]

Entry	Time (min)	Conv. (%)[b]	Yield (%)[b]		
			2a	3a	4a
1	30	57	6	14	37
2	70	96	11	12	73
3	90	100	1	2	97

[a] Reaction conditions: 2 mmol nitrobenzene, Au/meso-CeO$_2$ (0.05 mol% Au), anhydrous toluene (5 mL), H$_2$ (5 atm), 150 °C. [b] GC anaylsis using *tert*-butylbenzene as an internal standard.
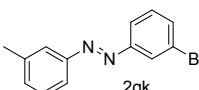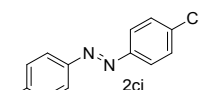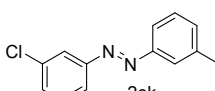

Table S4 Cross-coupling reaction between nitrobenzene (**1a**) and 2-chloronitrobenzene (**1f**).[a]
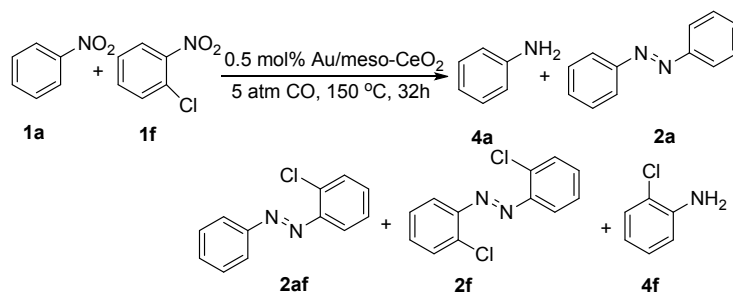
Entry	Substrates (2 mmol)	Conv. (%)	Yield (%)				
	1a/1f		4a	2a	2af	2f	4f
1	1/1	100	1	60	39	59	2
2	1/2	100	1	42	57	71	1
3	1/3	100	0	37	63	77	2
4	1/4	100	0	36	64	83	1

[a] The conversion and yields of **4a**, **2a** and **2af** were calculated based on **1a** consumption by GC. The yields of **2f**, **4f** were calculated based on **1f**. Note that the target cross-couping product of **2af** could be obtained in a good yield of 63% with the optimal molar ratio of **1a/1g** = 1/3.

Table S5 Au/meso-CeO$_2$ catalyzed deoxygenative coupling of nitroarenes to give unsymmetrical azo compounds.[a]

Entry	Substrates		Product	Time (h)	Yield (%)[b]
	R^1	R^2			
1	o-Cl	H	2af	32	63 (58)
2	m-Cl	H	2ae	8	60 (54)
3	p-Cl	H	2ac	19	65 (60)
4	m-Br	H	2ag	30	68 (61)
5	m-Br	m-CH$_3$	2gk	27	70 (63)
6	p-CH$_3$	p-Cl	2cj	29	65 (58)
7	m-CH$_3$	m-Cl	2ek	9	68 (59)

[a] Reaction conditions: R$_1$-C$_6$H$_4$-NO$_2$ (1.5mmol), R$_2$-C$_6$H$_4$-NO$_2$ (0.5mmol), anhydrous toluene (5ml) and Au/meso-CeO$_2$ (Au 0.5 mol%) at 150 °C under 5 atm of CO. [b] GC yield based on R$_2$-C$_6$H$_4$-NO$_2$ consumption. Numbers within parentheses refer to yields of isolated products.
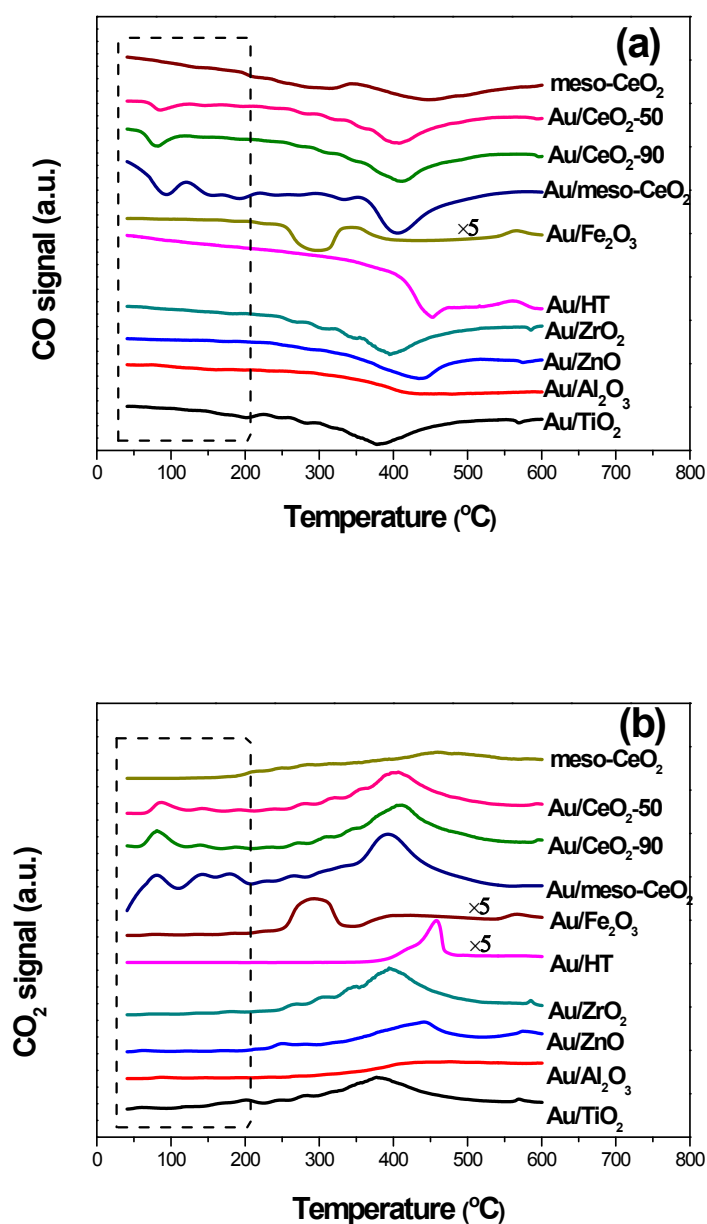
Fig. S5 Mass spectrometry of evolved gases during CO-TPR characterization of various catalysts; measuring:
(a) CO consumption; (b) CO_2 formation.
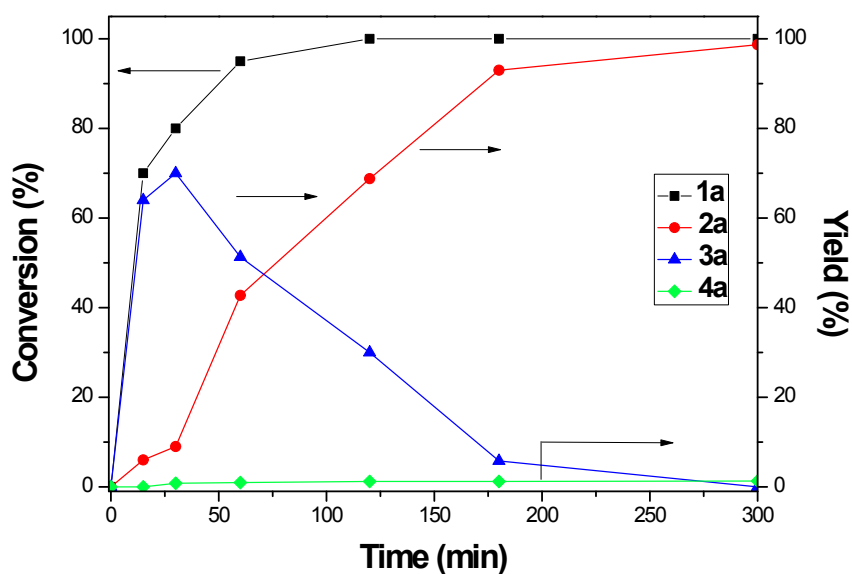
Fig. S6 Reaction profiles for the **2a** synthesis from **1a** over Au/meso-CeO$_2$. Reaction conditions: 2.0 mmol **1a**, anhydrous toluene (5 mL) and the gold catalyst (Au 0.5 mol%) at 150 °C under 5 atm of CO.
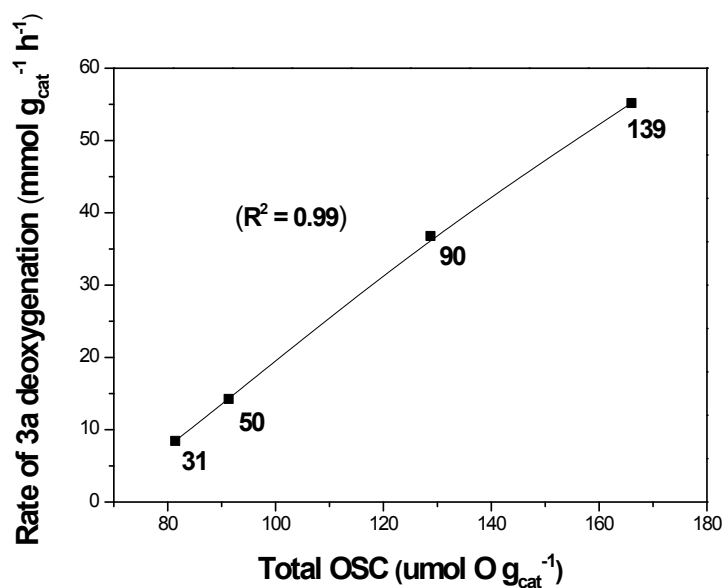

Fig. S7 Reaction rate of **3a** deoxygenation as a function of the oxygen storage capacity (OSC) of different ceria-supported gold catalysts. The values in the graph are the ceria surface area. Reaction conditions: 1 mmol **3a**, anhydrous toluene (5 mL), Au/CeO$_2$ catalyst (Au 0.1 mol%, gold loading: 0.8 wt%), 5 atm CO, 150 °C.

6. Characterization of aromatic azo compounds

The products were characterized by GC, GC-MS, and NMR. The physical data were identical in all respects to those previously reported.[S6],[S7]
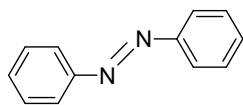
azobenzene (2a). **^{1}H NMR** (CDCl$_3$, 500 MHz): δ 7.95-7.93 (d, *J*=7.0 Hz, 4H), 7.56-7.49 (m, 6H); **^{13}C NMR** (CDCl$_3$, 125 MHz): δ 152.6, 131.0, 129.1, 122.8.
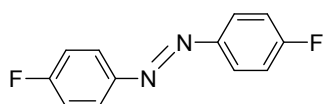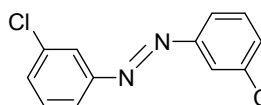

1,2-bis(4-fluorophenyl)diazene (2b). **^{1}H NMR** (CDCl$_3$, 500 MHz): δ 7.91-7.89 (m, 4H), 7.22-7.16 (m, 4H); **^{13}C NMR** (CDCl$_3$, 125 MHz): δ 165.3, 163.4, 149.0, 124.9, 124.8, 116.2, 116.0.
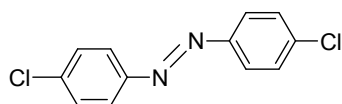
1,2-bis(4-chlorophenyl)diazene (2c). **^{1}H NMR** (CDCl$_3$, 500 MHz): δ 7.89-7.87 (d, *J*=8.5 Hz, 4H), 7.52-7.50 (d, *J*=8.5 Hz, 4H).**^{13}C NMR** (CDCl$_3$, 125 MHz): δ 150.9, 137.4, 129.5, 124.4.
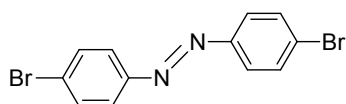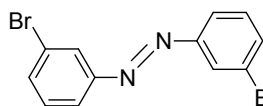

1,2-bis(4-bromophenyl)diazene (2d). **^{1}H NMR** (CDCl$_3$, 500 MHz): δ 7.81-7.78 (d, *J*=9.0 Hz, 4H), 7.66-7.64 (d, *J*=9.0 Hz, 4H); **^{13}C NMR** (CDCl$_3$, 125 MHz): δ 151.2, 132.4, 125.6, 124.4.
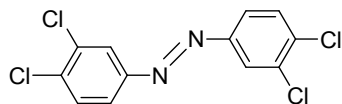

1,2-bis(3-chlorophenyl)diazene (2e). **^{1}H NMR** (CDCl$_3$, 500 MHz): δ 7.89 (s, 2H), 7.84-7.83 (m, 2 H), 7.50-7.47 (m, 4H); **^{13}C NMR** (CDCl$_3$, 125 MHz): δ 153.2, 135.5, 131.2, 130.2, 122.6, 122.1.
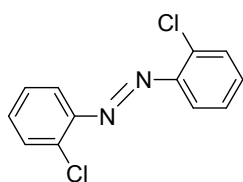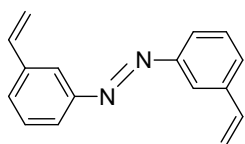

1,2-bis(2-chlorophenyl)diazene (2f). **^{1}H NMR** (CDCl$_3$, 500 MHz): δ 7.78-7.76 (d, *J*=1.5, 2.0 Hz, 2H), 7.58-7.56 (dd, *J*=1.5, 2.0 Hz, 2H), 7.43-7.40 (m, 2H), 7.38-7.34 (m, 2 H); **^{13}C NMR** (CDCl$_3$, 125 MHz): δ 148.8, 135.7, 132.2, 130.7, 127.3, 118.1.

1,2-bis(3-bromophenyl)diazene (2g). **¹H NMR** (CDCl₃, 500 MHz): δ 8.08 (s, 2H), 7.89-7.87 (d, *J*=3.0 Hz, 2H), 7.63-7.61 (d, *J*=2.0 Hz, 2H), 7.43-7.40 (t, *J*=8.0 Hz, 2H); **¹³C NMR** (CDCl₃, 125 MHz): δ 153.2, 134.1, 130.5, 124.8, 123.2.
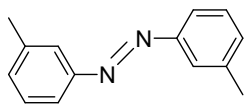
1,2-bis(3,4-dichlorophenyl)diazene (2h). **¹H NMR** (CDCl₃, 500 MHz): δ 8.02-8.00 (d, *J*=2.5 Hz, 2H), 7.80-7.78 (dd, *J*=2.0, 2.0 Hz, 2H), 7.63-7.61 (d, *J*=7.5 Hz, 2H); **¹³C NMR** (CDCl₃, 125 MHz): δ 151.1, 135.7, 133.7, 131.0, 124.1, 123.0.

1,2-bis(3-vinylphenyl)diazene (2i). **¹H NMR** (CDCl₃, 500 MHz): δ 7.97 (s, 2H), 7.82-7.80 (d, *J*=8.0 Hz, 2H), 7.52-7.44 (m, 4H), 6.84-6.78 (dd, *J*=10.5, 11.0 Hz, 2H), 5.9-5.86 (d, *J*=17.5 Hz, 2H), 5.36-5.34 (d, *J*=11.0 Hz, 2H); **¹³C NMR** (CDCl₃, 125 MHz): δ 152.9, 138.6, 136.2, 129.2, 128.7, 122.1, 120.6, 115.1.
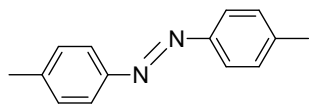
1,2-di-*p*-tolyldiazene (2j). **¹H NMR** (CDCl₃, 500 MHz): δ 7.83-7.81 (d, *J*=8.5 Hz, 4H), 7.31-7.29 (d, *J*=8.5 Hz, 4H), 2.43 (s, 6H); **¹³C NMR** (CDCl₃, 125 MHz): δ 150.9, 141.2, 129.7, 122.8, 21.5.

1,2-di-*m*-tolyldiazene (2k). **¹H NMR** (CDCl₃, 500 MHz): δ 7.72 (s, 4H), 7.42-7.38 (t, *J*=7.5 Hz, 2H), 7.29-7.28 (d, *J*=7.5 Hz, 2H), 2.46 (s, 6 H); **¹³C NMR** (CDCl₃, 125 MHz): δ 152.8, 139.0, 131.7, 128.9, 122.9, 120.4, 21.4.
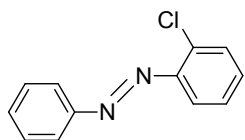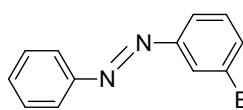
1-(2-chlorophenyl)-2-phenyldiazene (2af). **¹H NMR** (CDCl₃, 500 MHz): δ 7.98-7.96 (dd, *J*=1.5, 1.0 Hz, 2H), 7.70-7.67 (dd, *J*=1.5, 1.5 Hz, 1H), 7.56-7.51 (m, 4H), 7.39-7.32 (m, 2H); **¹³C NMR** (CDCl₃, 125 MHz): δ 152.8, 148.8, 131.6, 131.5, 130.7, 129.1, 127.3, 123.4, 117.6.
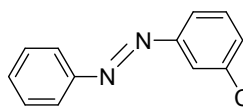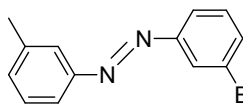
1-(3-chlorophenyl)-2-phenyldiazene (2ae). ^{1}**H NMR** (CDCl$_3$, 500 MHz): δ 7.94-7.91 (t, *J*=7.0 Hz, 3H), 7.86-7.85 (d, *J*=7.0 Hz, 1H), 7.55-7.49 (m, 3H), 7.48-7.44 (m, 2H); ^{13}**C NMR** (CDCl$_3$, 125 MHz): δ 153.5, 152.4, 131.5, 130.7, 130.1, 129.2, 123.1, 122.4, 121.8.
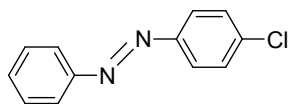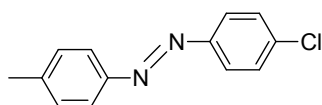
1-(4-chlorophenyl)-2-phenyldiazene (2ac). ^{1}**H NMR** (CDCl$_3$, 500 MHz): δ 7.96-7.90 (m, 4H), 7.56-7.52 (m, 5H); ^{13}**C NMR** (CDCl$_3$, 125 MHz): δ 152.5, 151.0, 136.9, 131.3, 129.3, 129.1, 124.1, 123.0.

1-(3-bromophenyl)-2-phenyldiazene (2ag). ^{1}**H NMR** (CDCl$_3$, 500 MHz): δ 8.06-8.05 (t, *J*=1.5 Hz, 1H), 7.92-7.86 (m, 3H), 7.59-7.50 (m, 4H), 7.40-7.37 (t, *J*=8.0 Hz, 1H); ^{13}**C NMR** (CDCl$_3$, 125 MHz): δ 153.6, 152.4, 133.6, 131.5, 130.4, 129.3, 124.7, 123.1, 122.9.

1-(3-bromophenyl)-2-(*m*-tolyl)diazene (2gk). ^{1}**H NMR** (CDCl$_3$, 500 MHz): δ 8.05 (s, 1H), 7.87-7.86 (d, *J*=7.0 Hz, 1H), 7.73-7.72 (d, *J*=5.0 Hz, 2H), 7.58-7.57 (d, *J*=8.0 Hz, 1H), 7.42-7.37 (m, 2H), 7.31-7.30 (d, *J*=7.5 Hz, 1H), 2.45 (s, 3H); ^{13}**C NMR** (CDCl$_3$, 125 MHz): 153.6, 152.5, 139.1, 133.5, 132.3, 130.4, 129.0, 124.6, 123.2, 122.9, 120.70, 21.4.

1-(4-chlorophenyl)-2-(*p*-tolyl)diazene (2cj). ^{1}**H NMR** (CDCl$_3$, 500 MHz): δ ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.88-7.83 (m, 2H), 7.82 (d, *J* = 8.3 Hz, 2H), 7.55-7.45 (m, 2H), 7.31 (d, *J* = 8.1 Hz, 2H), 2.44 (s, 3H). ^{13}**C NMR** (CDCl$_3$, 125 MHz): δ 151.1, 150.6, 141.9, 136.5, 129.8, 129.30, 124.0, 122.9, 21.5.
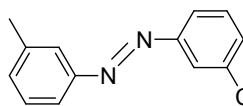
1-(3-chlorophenyl)-2-(*m*-tolyl)diazene (2ek). ^{1}**H NMR** (CDCl$_3$, 500 MHz): δ 7.88 (t, *J* = 1.9 Hz, 1H), 7.81 (dt, *J* = 6.9, 2.0 Hz, 1H), 7.73 (d, *J* = 5.9 Hz, 2H), 7.48-7.37 (m, 3H), 7.30 (d, *J* = 7.5 Hz, 1H), 2.45 (s, 3H). ^{13}**C NMR** (CDCl$_3$, 125 MHz): δ 153.4, 152.6, 139.0, 135.1, 132.3, 130.6, 130.1, 129.0, 123.2, 122.3, 121.8, 120.7, 21.4.

7. Reference

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8. ¹H and ¹³C NMR Spectra of New Compounds