

Supporting Information

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69451 Weinheim, Germany

**Gold-Catalyzed Direct Hydrogenative Coupling of Nitroarenes To
Synthesize Aromatic Azo Compounds****

*Xiang Liu, Hai-Qian Li, Sen Ye, Yong-Mei Liu, He-Yong He, and Yong Cao**

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1. Materials and Methods

1.1 Catalytic materials

Gold catalysts including 1 wt% Au/Al₂O₃ (Strem catalogue number: 79-0160), 1 wt% Au/TiO₂ (Strem catalogue number: 79-0165), and 1 wt% Au/ZnO (Strem catalogue number: 79-0170) were supplied by Mintek. The TEM images and Au particle size distributions can be seen in Figure S2. Palladium chloride (PdCl₂), rhodium chloride hydrate (RhCl₃·xH₂O), ruthenium chloride hydrate (RuCl₃·xH₂O), hexachloroplatinic acid hexahydrate (H₂PtCl₆·6H₂O) and chloroauric acid tetrahydrate (HAuCl₄·4H₂O), were supplied by Aldrich and used without further purification.

1.2 Catalyst preparation

Preparation of Hydrotalcite (HT)

Mg-Al hydrotalcites (Mg_xAl-HT, x= 2, 3, 4, and 5) were prepared by a routine co-precipitation method as follows.^[S1] A salt solution (A) contained Mg(NO₃)₂·6H₂O (40-100 mmol) and Al(NO₃)₃·9H₂O (20 mmol) dissolved in 100 mL deionized water at various Mg/Al molar ratios (x = 2-5). The solution A was added dropwise into an equal volume of a second solution (B) containing Na₂CO₃ (40 mmol) and NaOH (OH⁻/(Al + Mg)=2) in around 1 h under vigorous stirring at room temperature. The formed suspension was stirred and aged for 18 h at 65 °C, filtered and washed extensively with water. The obtained solid was dried in oven overnight at 100 °C. XRD measurements confirmed the formation of the HTs structure (See Figure S1). The BET surface areas of the resultant Mg-Al HTs were 118, 110, 87, 51 m²·g⁻¹ for Mg₂Al-HT, Mg₃Al-HT, Mg₄Al-HT, and Mg₅Al-HT, respectively.

Preparation of Au/HT catalysts

A modified deposition-precipitation (DP) procedure has been employed to prepare the 1 wt% Au/Mg_xAl-HT (X= 2, 3, 4, 5) catalysts.^[S2] Briefly, the obtained Mg_xAl-HT (1.0 g) was dispersed in an aqueous solution of appropriate concentration of HAuCl₄·4H₂O (100 mL, 1.02 × 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 AgNO₃. The resulting compound was dried for 12 h in *vacuo* at room temperature, and finally reduced by 5% H₂/Ar at 300 °C for 2 h. The BET surface area of the resultant Au/Mg_xAl-HT catalysts can be seen in Table S2. The concentration of gold was 0.89, 1.02, 1.08, and 0.85 wt% for Au/Mg₂Al-HT, Au/Mg₃Al-HT, Au/Mg₄Al-HT, and Au/Mg₅Al-HT, respectively (ICP-AES). A large fraction of the Au particles in these catalysts were within 1-3 nm in diameter (TEM in Figure S2). 0.11 wt% Au/Mg₄Al-HT, 0.26 wt% Au/Mg₄Al-HT, 0.53 wt% Au/Mg₄Al-HT and 2.10 wt% Au/Mg₄Al-HT were prepared by the similar procedures.

Preparation of Au/CeO₂ catalyst

The 0.5 wt% Au/CeO₂ catalyst was prepared by a routine DP method.^[S3] An appropriate amount of aqueous solutions of HAuCl₄ was heated to 80 °C under vigorous stirring. The pH was adjusted to 10.0 by dropwise addition of NaOH (0.2 M), and then suitable amount of CeO₂ (Evonik, Ad Nano 50, specific surface area: 50 m²·g⁻¹) 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 subsequently reduced in 5 vol% H₂/Ar stream at 300 °C for 2 h.

Preparation of Au/ZrO₂ catalyst

The 0.8 wt% Au/ZrO₂ catalyst was prepared according to our previously reported procedure^[S4]: An appropriate amount of ZrO₂ was added to the aqueous solution of HAuCl₄ (0.25 mM), the pH of which was adjusted to 9 with 0.25 M NH₄OH under stirring. 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 chloride ions. The sample was dried under vacuum at room temperature for 12 h, and subsequently reduced in 5 vol% H₂/Ar stream at 300 °C for 2 h.

Preparation of Au/MgO catalyst

MgO powders were prepared following the reported procedure.^[S5] The 1.0 wt% Au/MgO sample was prepared by the homogeneous deposition-precipitation (HDP) method using urea.^[S6] Typically, 1 g of MgO was added to an aqueous solution with the 7.61×10^{-2} mmol HAuCl₄ and 0.914 g urea (urea/Au = 200, molar ratio). The suspension was then heated to 90 °C and stirred for 4 h, followed by filtering and washing for several times with distilled water. The resulting solid product was dried under vacuum at room temperature for 12 h before reduced in 5 vol% H₂/Ar at 300 °C for 2 h.

Preparation of Pd/Mg₄Al-HT, Pt/Mg₄Al-HT, Ru/Mg₄Al-HT, Rh/Mg₄Al-HT catalysts

0.1 wt% Pd/Mg₄Al-HT, 0.1 wt% Pt/Mg₄Al-HT, 0.1 wt% Ru/Mg₄Al-HT and 0.1 wt% Rh/Mg₄Al-HT catalysts were prepared by incipient-wetness impregnation of the support, with aqueous solution of PdCl₂, H₂PtCl₆·6H₂O, RuCl₃·xH₂O, RhCl₃·xH₂O precursors of appropriate concentrations (typically 1.0 mL/g support). After a perfect mixing of the corresponding slurries, samples were dried under vacuum at room temperature for 12 h and then reduced in 5 vol% H₂/Ar at 400 °C for 2 h. The corresponding TEM images and metal particle size distributions can be seen in Figure S2.

1.3 Catalyst characterization

Elemental analysis: The Au 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.

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) analysis: The crystal structures of HTs 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 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 K α , hv = 1253.6 eV) was used. The C 1s line (284.6 eV) was used as the reference to calibrate the binding energies (BE).

Transmission electron microscopy (TEM): A JEOL 2011 microscope operating at 200 kV equipped with an EDX unit (Si(Li) detector) was used for the TEM investigations. 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.

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.

CO₂/NH₃-Temperature-programmed desorption (CO₂/NH₃-TPD): Typically, the sample (100 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, CO₂ adsorption was performed by switching the Ar flow to a CO₂ gas until adsorption saturation. The gas-phase (and/or weakly adsorbed) NH₃, was purged by Ar at the same temperature for about 1h. CO₂-TPD was then performed in the Ar flow by raising the temperature to 800 °C at a rate of 10 °C·min⁻¹. The desorbed CO₂ molecules were monitored by an OmniStar mass spectrometer (QMS-200) with the signal of m/e = 44. NH₃-TPD was performed by using a similar procedure.

Diffuse Reflectance Infrared Fourier Transform (DRIFT) measurements: The diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) experiment was carried out on a Nicolet Magna-IR 760 Fourier transform spectrometer (ThermoNicolet, Madison, WI) using a MCT detector. Prior to chemisorptions, the sample (typically 20 mg) was pretreated in a flow of He (35 mL·min⁻¹) at 250 °C for 2 h and then cooled under He to 25 °C. Unless stated otherwise, infrared (IR) spectra were recorded against a background of the sample at the reaction temperature under flowing He. IR spectra were

recorded with co-addition 64 scans in single-beam spectra or absorbance spectra, by applying a resolution of 4 cm^{-1} .

2. Catalytic activity measurements

2.1 General Procedure A for the synthesis of symmetrical aromatic azo compounds

A mixture of nitroaromatics (1 mmol), toluene (5 mL), and catalyst (metal: 0.5 mol %) was charged into an autoclave (25 mL capacity). The resulting mixture was vigorously stirred (1000 rpm with a magnetic stir bar) at $50\text{ }^{\circ}\text{C}$ under H_2 atmosphere (2 MPa) for given reaction time. 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 ^1H NMR, and ^{13}C NMR and the spectra obtained were compared with the standard spectra. The conversion and yields were measured by high performance liquid chromatography (HPLC) using a C18 reverse-phase column [ZORBAX Eclipse Plus C18 (4.6×100 mm)] and a diode array UV/Vis detector. A mixture of water-acetonitrile was used as an eluent. HPLC retention times were in agreement with those of authentic samples.

2.2 General Procedure B for the hydrogenation of asymmetrical aromatic azo compounds

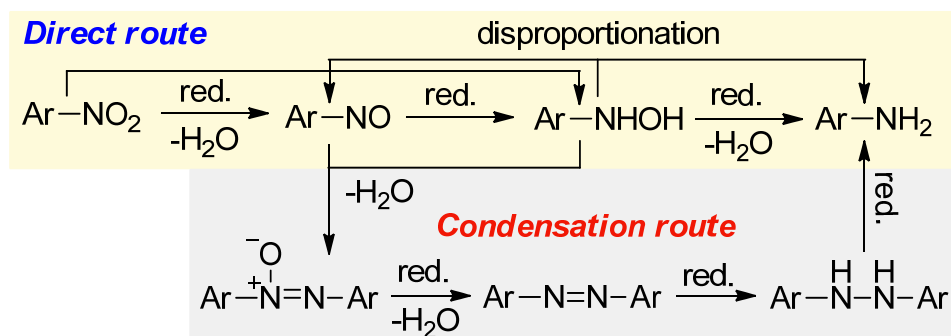
A mixture of $\text{R}^1\text{-PhNO}_2$ (0.5 mmol), $\text{R}^2\text{-PhNO}_2$ (1.5 mmol), and catalyst (1 mol% Au based on $\text{R}^1\text{-PhNO}_2$), H_2 (2 MPa), toluene (5 mL), $50\text{ }^{\circ}\text{C}$. The resulting mixture was vigorously stirred (1000 rpm with a magnetic stir bar) at $50\text{ }^{\circ}\text{C}$ under H_2 atmosphere (2 MPa) for given reaction time. 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 ^1H NMR, and ^{13}C NMR and the spectra obtained were compared with the standard spectra. The conversion and yields were measured by high performance liquid chromatography (HPLC) using a C18 reverse-phase column [ZORBAX Eclipse Plus C18 (4.6×100 mm)] and a diode array UV/Vis detector. A mixture of water-acetonitrile was used as an eluent. HPLC retention times were in agreement with those of authentic samples.

2.3 Procedure for 100-mmol scale and recycling experiments

A mixture of nitrobenzene (100 mmol) and 0.11 wt% Au/Mg₄Al-HT (metal: 0.005 mol% Au) was charged into an autoclave (100 mL capacity). The resulting mixture was vigorously stirred (1000 rpm with a magnetic stir bar) at $90\text{ }^{\circ}\text{C}$ under H_2 atmosphere (2 MPa) for given reaction time. After the completion of the reaction, the reaction mixture was extracted with EtOH for 3 times and the catalyst was filtered and washed thoroughly with ethanol. The catalyst was then dried under vacuum at room temperature for 12 h. In the five successive cycles, the yields of azobenzene were 94%, 94%, 92%, 90% and 90% (HPLC analysis), respectively.

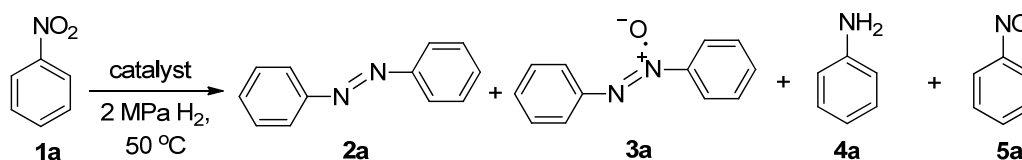
3. Results

A.



Scheme S1. Plausible pathways for the reduction of nitroarenes.

B. Table S1. Hydrogenation of nitrobenzene to azobenzene over Au-based catalysts at 50 °C.



Entry	Catalyst	Conv.(%)*	Sel.(%)*			
			2a	3a	4a	5a
1	Au/Mg ₂ Al-HT	99	34	<1	64	1
2	Au/TiO ₂	100	0	0	100	0
3	Au/Al ₂ O ₃	100	<1	0	>99	0
4	Au/ZrO ₂	100	1	0	99	0
5	Au/CeO ₂	100	9	7	84	0
6	Au/ZnO	100	6	0	94	0
7	Au/MgO	100	8	3	89	0
8	Au/TiO ₂ + Mg ₂ Al-HT [†]	100	0	0	100	0
9	Mg ₂ Al-HT [†]	0	0	0	0	0

Reaction conditions: nitrobenzene (1 mmol), catalyst (0.5 mol% Au), H₂ (2 MPa), toluene (5 mL), 50 °C, 3.5 h. *Conversion and selectivity measured by HPLC analysis. [†]Mg₂Al-HT (100 mg).

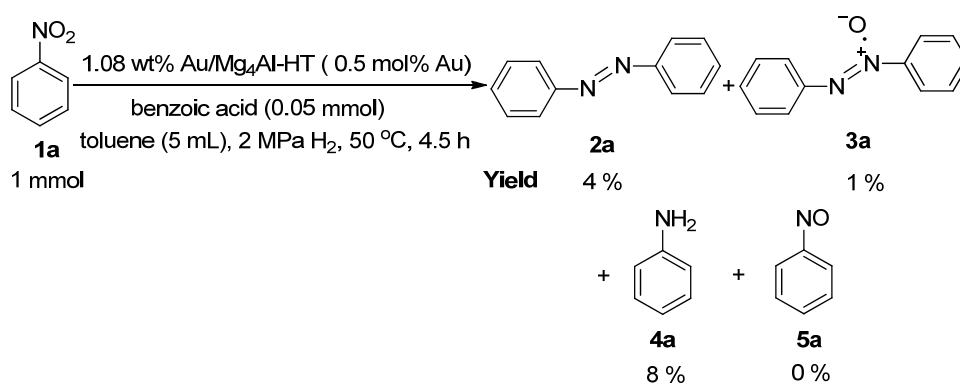
C. Table S2. Characterization results of Au/MgAl-HT catalysts.

Entry	Metal loading (wt%)	Mg/Al (mol/mol)	Base density (mmol·g ⁻¹)*	Acid density (mmol·g ⁻¹)*	BET surface area (m ² ·g ⁻¹) [†]
1	0.89	2	0.32	0.18	99
2	1.02	3	0.49	0.15	95
3	1.08	4	0.53	0.13	71
4	0.85	5	0.45	0.09	40
5	2.10	4	0.48	0.11	59
6	0.53	4	0.55	0.13	73
7	0.26	4	0.56	0.14	74
8	0.11	4	0.56	0.14	76

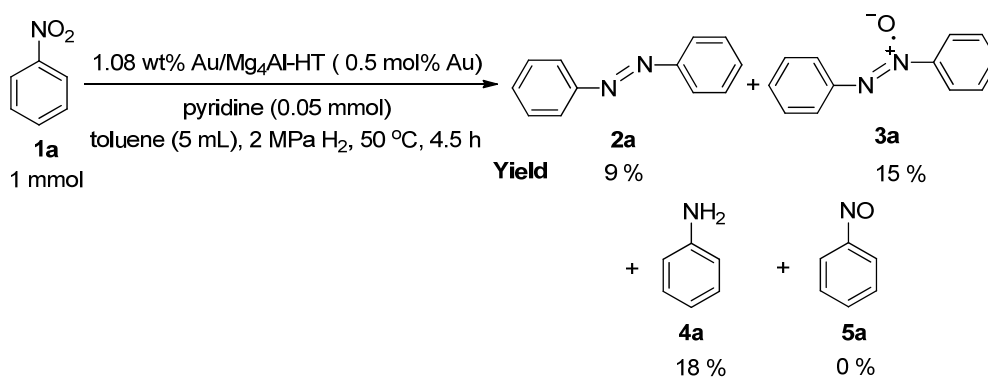
*Determined by TPD of CO₂ or NH₃. [†]Determined by adsorption-desorption of nitrogen.

D. Poisoning experiments

(a) benzoic acid poisoning experiment

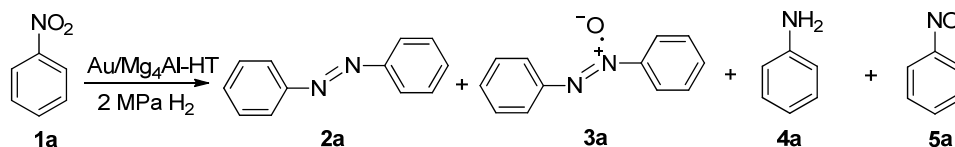


(b) pyridine poisoning experiment



Scheme S2. Benzoic acid or pyridine poisoning experiments for hydrogenation of nitrobenzene using 1.08 wt% Au/Mg₄Al-HT catalyst.

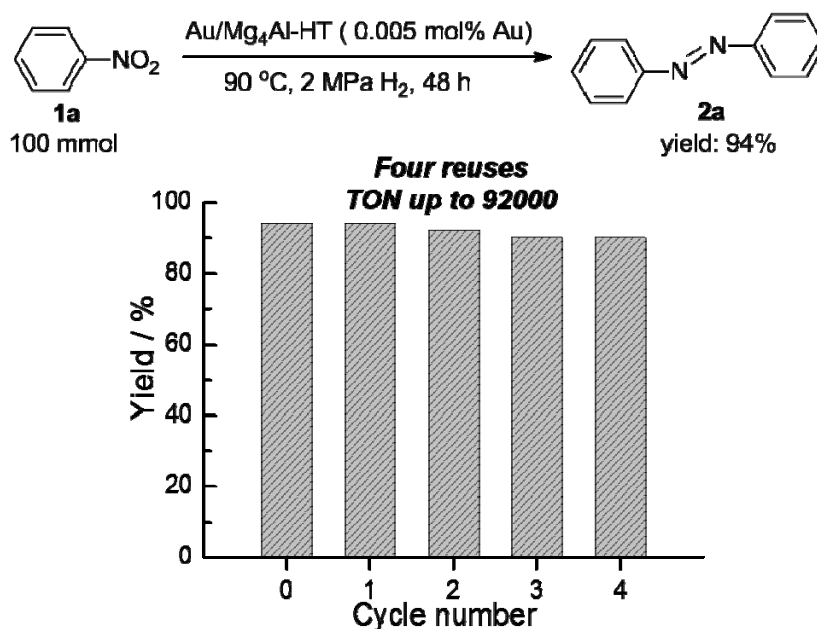
E. Table S3. Hydrogenation of nitrobenzene over 0.11 wt% Au/Mg₄Al-HT under various conditions.



Entry	Solvent	T (°C)	P(H ₂) (MPa)	t (h)	Conv. (%) [*]	Sel. (%) [*]			
						2a	3a	4a	5a
1	Toluene	50	2	4.5	>99	98	1	1	0
2	DMF	50	2	7	14	7	64	29	0
3	DMSO	50	2	4.5	1	0	0	100	0
4	Ethanol	50	2	4.5	40	0	0	100	0
5	THF	50	2	4.5	43	0	0	41	0
6	Toluene	50	1	10	90	87	<1	11	<1
7	Toluene	50	3	2.5	>99	94	0	6	0
8	Toluene	25	2	24	>99	99	0	<1	0

Reaction conditions: nitrobenzene (1 mmol), 0.11 wt% Au/Mg₄Al-HT (0.5 mol% Au), solvent (5 mL).
^{*}Conversion and selectivity measured by HPLC analysis.

F.



Scheme S3. Au-catalyzed 100 mmol scale of hydrogenative coupling of 1a.

G.

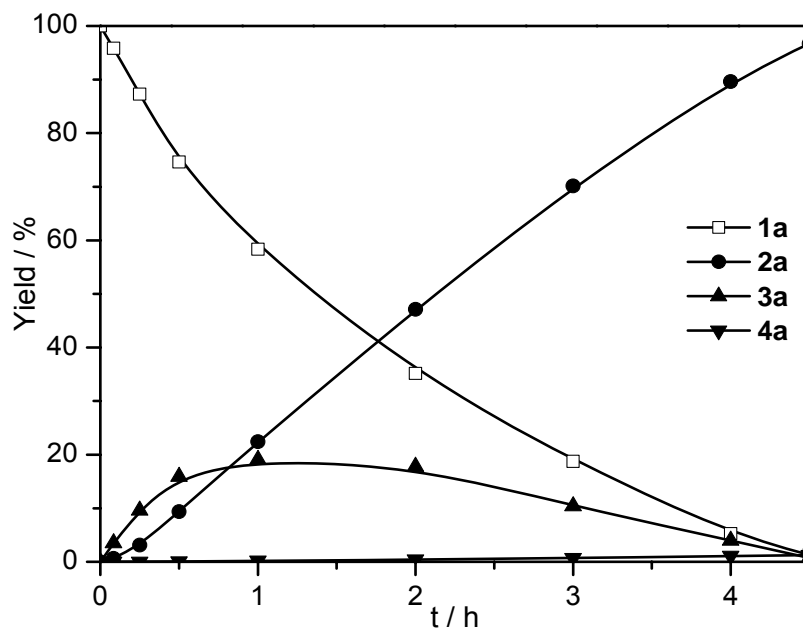


Figure S1. Reaction profiles for the 2a synthesis from 1a over 0.11 wt% Au/ Mg₄Al-HT. Reaction conditions: nitrobenzene (1 mmol), catalyst (0.5 mol% Au), H₂ (2 MPa), toluene (5 mL), 50 °C.

H. Kinetic experiments of sequential transformation for hydrogenation of nitrobenzene

Hydrogenation of nitrobenzene (1a)

A mixture of **1a** (1 mmol), 0.11 wt% Au/Mg₄Al-HT (1 g), and toluene (5 mL) was charged into an autoclave (25 mL capacity). The resulting mixture was vigorously stirred at 50 °C under H₂ atmosphere (2 MPa) for 15 min to give **2a**, **3a**, and **4a** in 3%, 10%, 0% yield, respectively (Scheme S2a).

Hydrogenation of nitrosobenzene (5a)

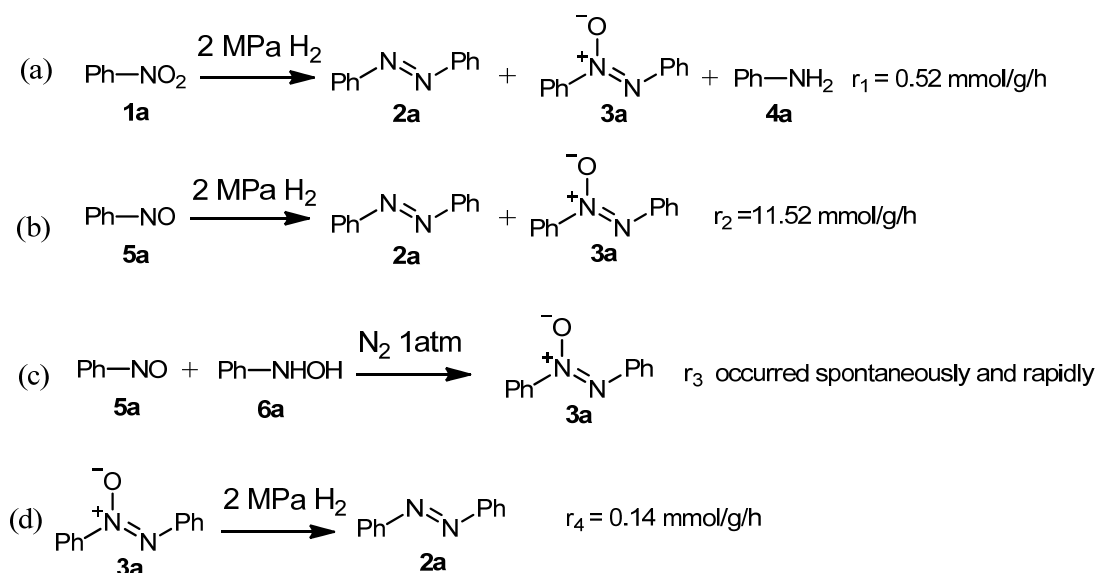
A mixture of **5a** (1 mmol), 0.11 wt% Au/Mg₄Al-HT (1 g), and toluene (5 mL) was charged into an autoclave (25 mL capacity). The resulting mixture was vigorously stirred at 50 °C under H₂ atmosphere (2 MPa) for 5 min to give **2a** and **3a** in 2%, 94% yield, respectively (Scheme S2b).

Condensation of nitrosobenzene (5a) and phenylhydroxylamine (6a)

6a (1 mmol) was added into a solution contained **5a** (1 mmol) dissolved in toluene (5 mL) under vigorous stirring in a flask (25 mL) at 50 °C under N₂ atmosphere (1 atm). The reaction occurred spontaneously and rapidly (too fast to permit the measurement of the conversion rate) even in the absence of the 0.11 wt% Au/Mg₄Al-HT sample to give **3a** in 98% yield (Scheme S2c).

Hydrogenation of azoxybenzene (3a)

A mixture of **3a** (0.5 mmol), 0.11 wt% Au/Mg₄Al-HT (1 g), and toluene (5 mL) was charged into an autoclave (25 mL capacity). The resulting mixture was vigorously stirred at 50 °C under H₂ atmosphere (2 MPa) for 15 min to give **2a** in 7% yield (Scheme S2d).

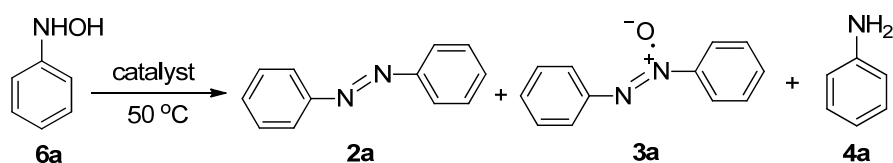


Scheme S4. Initial reaction rates (r) calculated for the sequential transformation of hydrogenative coupling of **1a** by 0.11 wt% Au/Mg₄Al-HT at 50 °C.

Hydrogenation of phenylhydroxylamine (6a)

A mixture of **6a** (1 mmol), catalyst (0.5 mol% Au), and toluene (5 mL) was charged into an autoclave (25 mL capacity). The resulting mixture was vigorously stirred at 50 °C under H₂ atmosphere (2 MPa) for 30 min (Table S4).

Table S4. Hydrogenation of phenylhydroxylamine over Au-based catalysts at 50 °C.

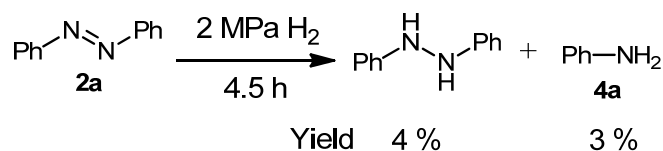


Entry	Catalyst	Conv.(%)*	Sel.(%)*		
			2a	3a	4a
1	Au/Mg ₄ Al-HT(H ₂) [†]	94	10	39	51
2	Au/Mg ₄ Al-HT(N ₂) [†]	93	0	50	50
3	Au/TiO ₂	73	0	11	89
4	Au/Al ₂ O ₃	82	0	14	86
5	Au/ZrO ₂	52	<1	15	84
6	Au/CeO ₂	90	1	26	73
7	Au/ZnO	45	<1	17	82
8	Au/MgO	49	1	20	79

Reaction conditions: phenylhydroxylamine (1 mmol), catalyst (0.5 mol% Au), H₂ (2 MPa), toluene (5 mL), 50 °C, 30 min. *Conversion and selectivity measured by HPLC. [†]Au loading: 0.11 wt%.

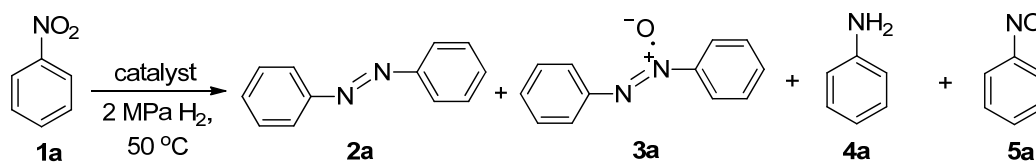
Hydrogenation of azobenzene (2a)

A mixture of **2a** (0.5 mmol), 0.11 wt% Au/Mg₄Al-HT (1 g), and toluene (5 mL) was charged into an autoclave (25 mL capacity). The resulting mixture was vigorously stirred at 50 °C under H₂ atmosphere (2 MPa) for 4.5 h to give hydrazobenzene and **4a** in 4% and 3% yield, respectively (Scheme S3).



Scheme S5. Hydrogenation of **2a** using 0.11 wt% Au/Mg₄Al-HT at 50 °C.

I. Table S5. Hydrogenation of nitrobenzene over various Mg₄Al-HT-supported noble metal catalysts at 50 °C.



Entry	Catalyst	Conv.(%)*	Sel.(%)*			
			2a	3a	4a	5a
1	0.1 wt% Pt/Mg ₄ Al-HT	100	0	0	100	0
2	0.1 wt% Pd/Mg ₄ Al-HT	100	0	0	100	0
3	0.1 wt% Ru/Mg ₄ Al-HT	100	0	0	>99	0
4	0.1 wt% Rh/Mg ₄ Al-HT	>99	0	0	>99	0

Reaction conditions: nitrobenzene (1 mmol), catalyst (0.5 mol% metal), H₂ (2 MPa), toluene (5 mL), 50 °C, 4.5 h. *Conversion and selectivity measured by HPLC analysis.

J. XRD patterns of HT-based catalysts

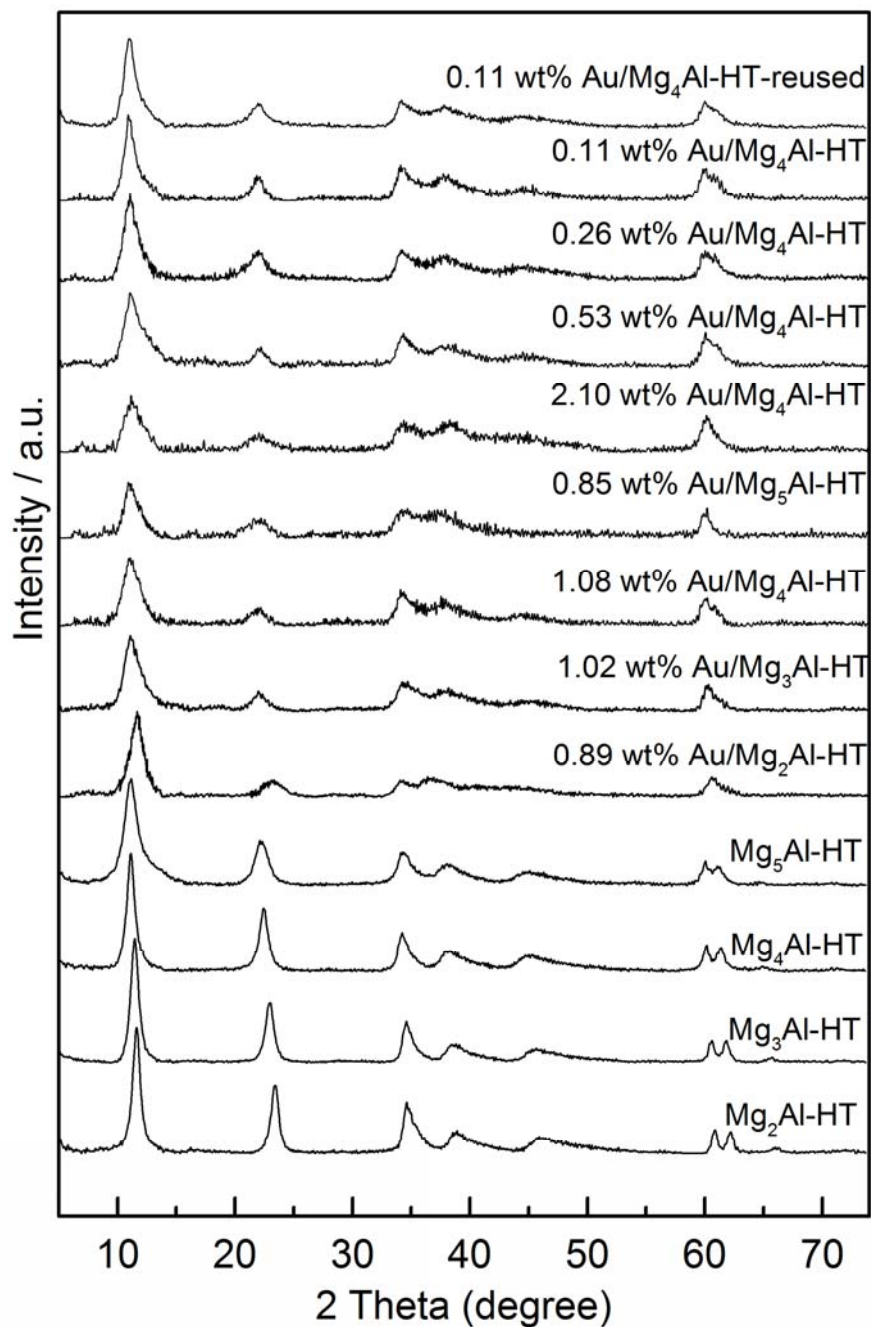
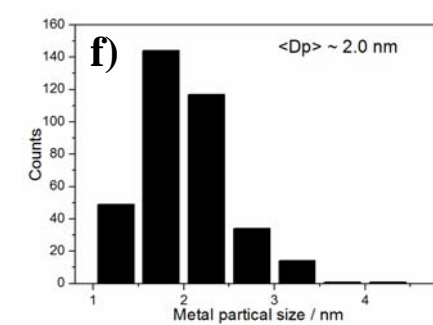
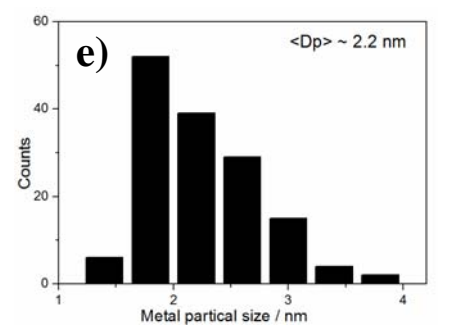
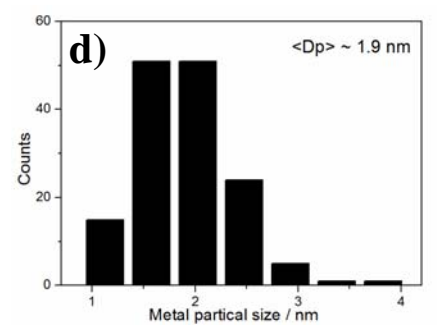
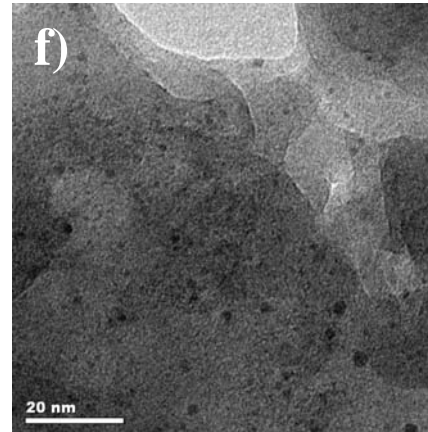
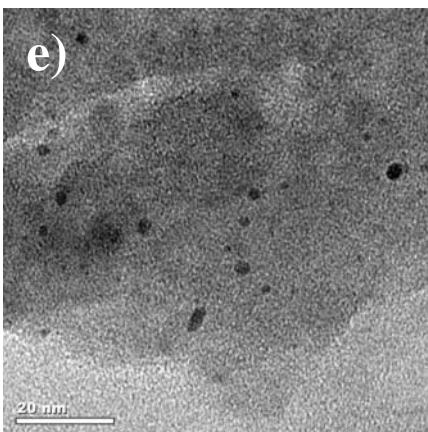
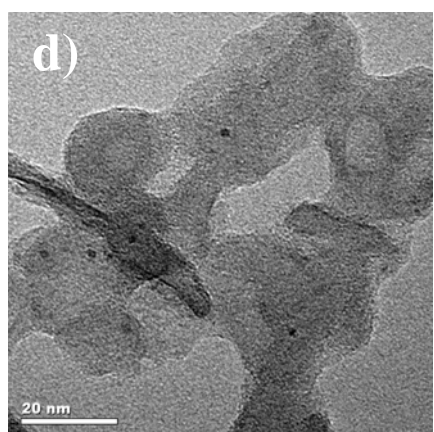
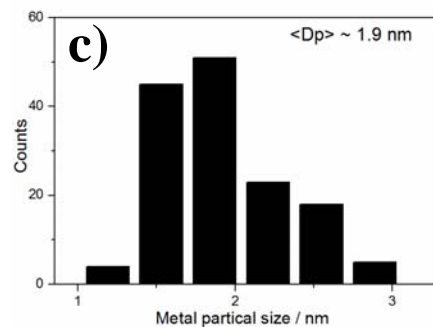
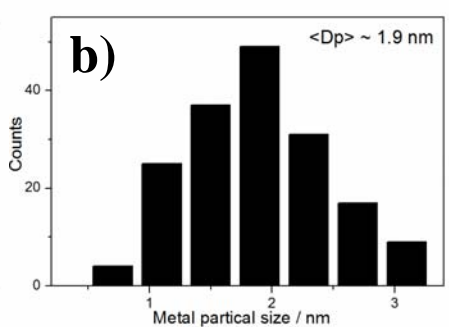
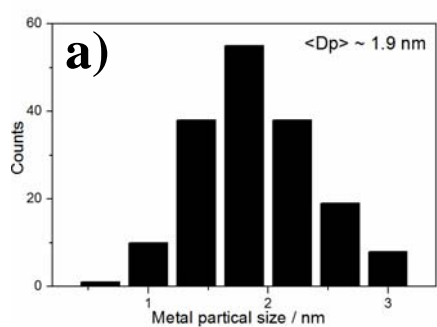
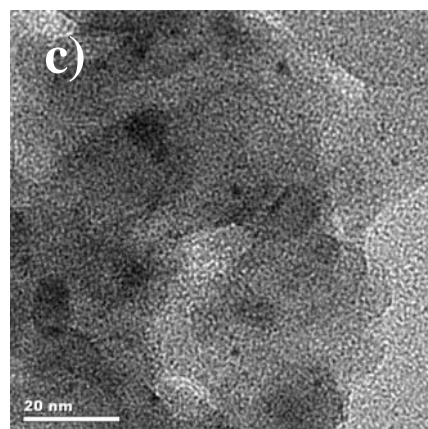
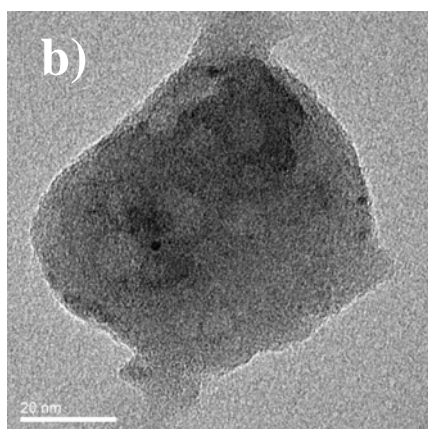
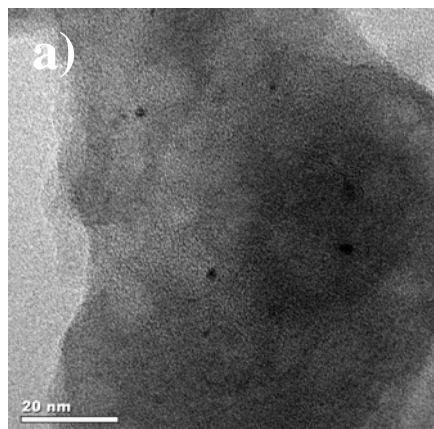
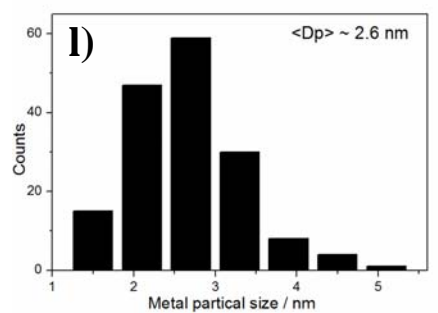
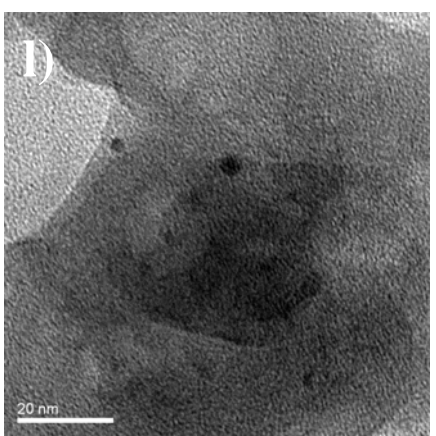
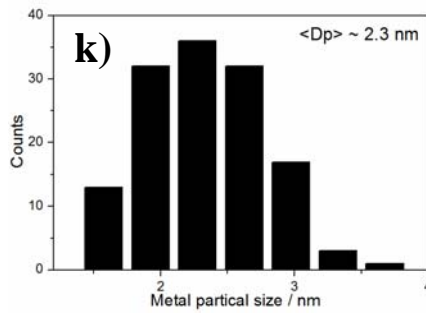
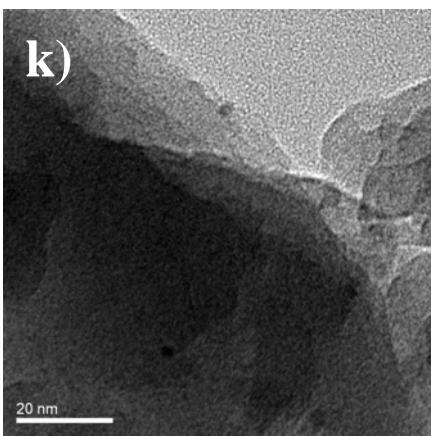
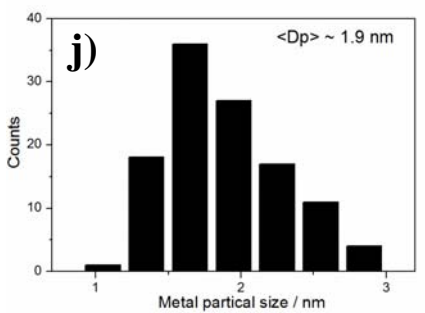
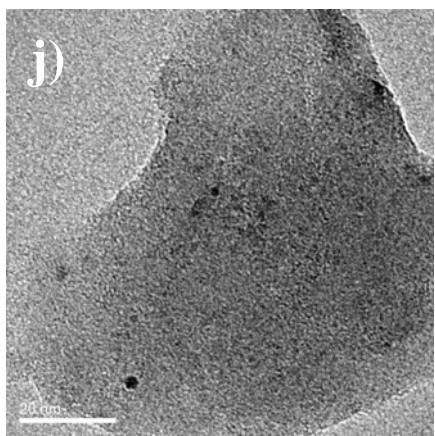
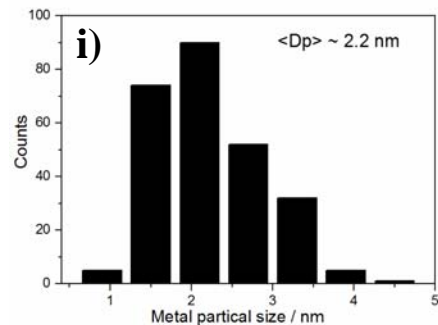
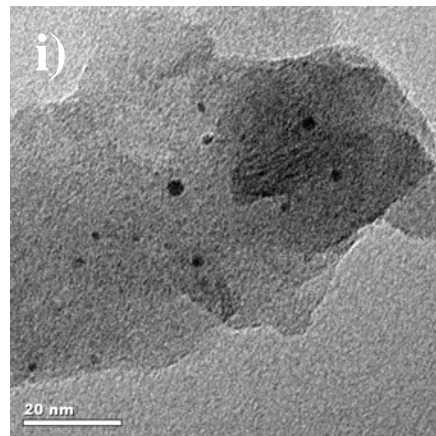
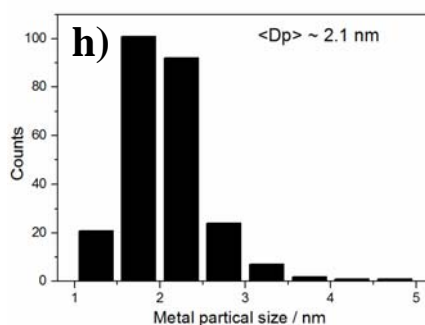
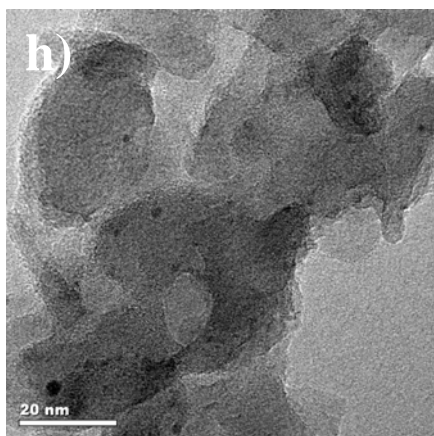
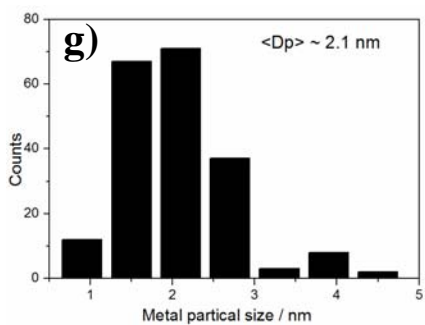
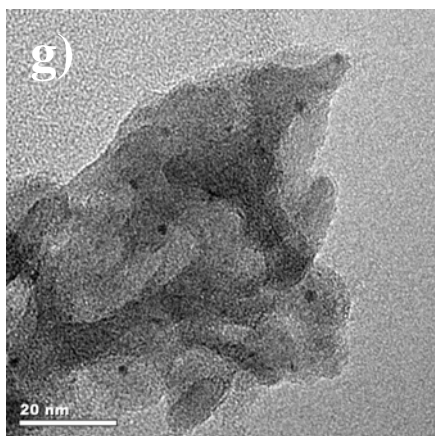
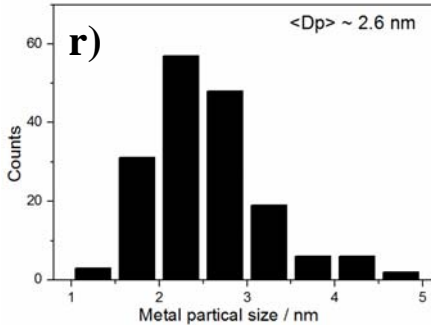
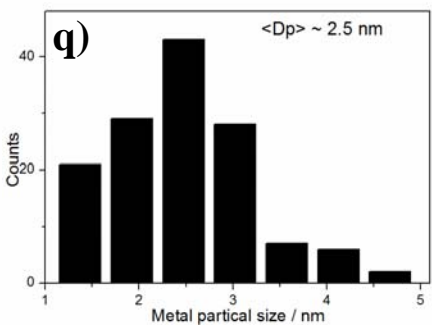
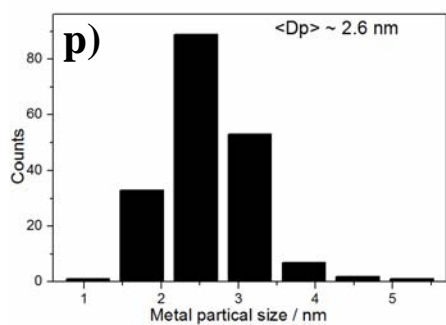
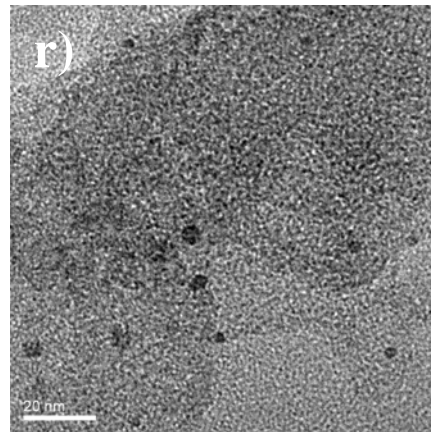
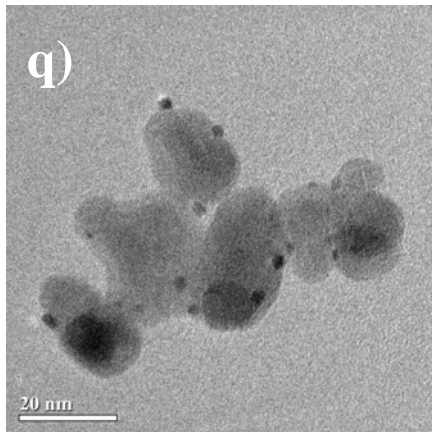
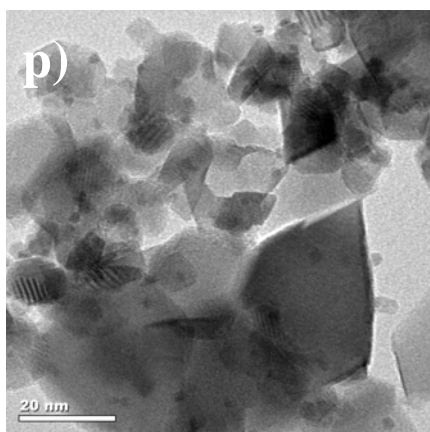
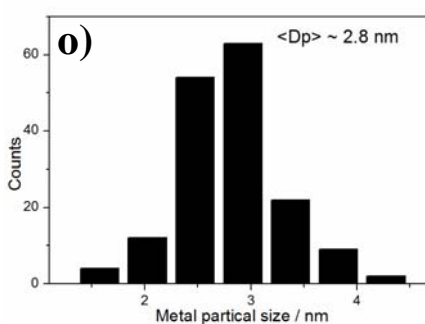
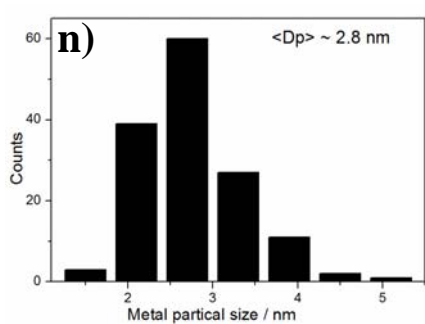
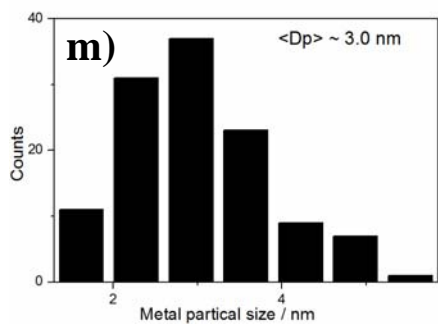
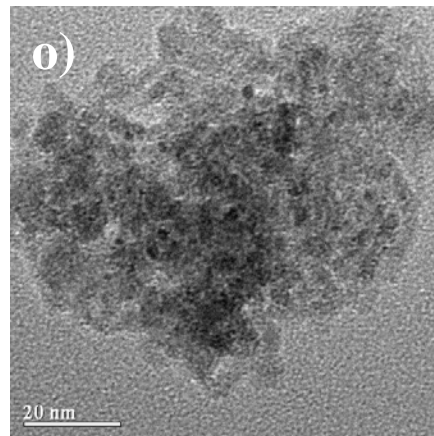
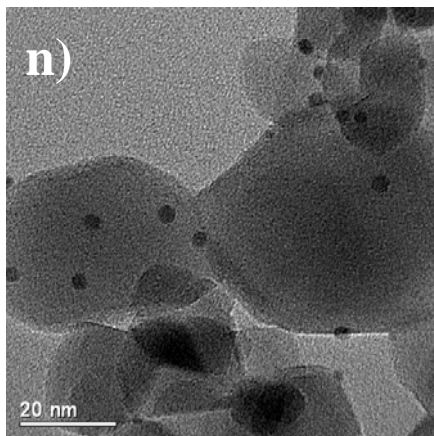
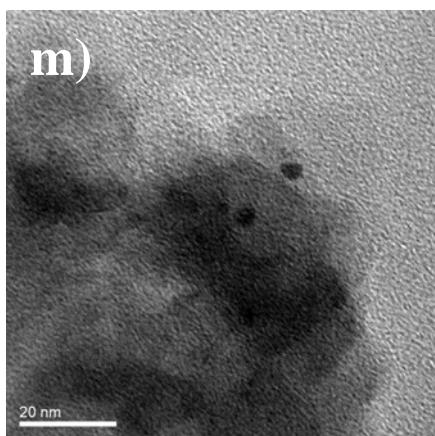


Figure S2. Powder XRD patterns of MgAl-HTs and MgAl-HT-supported gold catalysts. Note that the crystalline structure of HT was largely maintained in the Au-containing samples. No diffraction lines of metallic gold were observed in all of the metal-loaded samples, which indicated that the gold particles were highly dispersed and the sizes were very small (< 5 nm).

K. TEM images







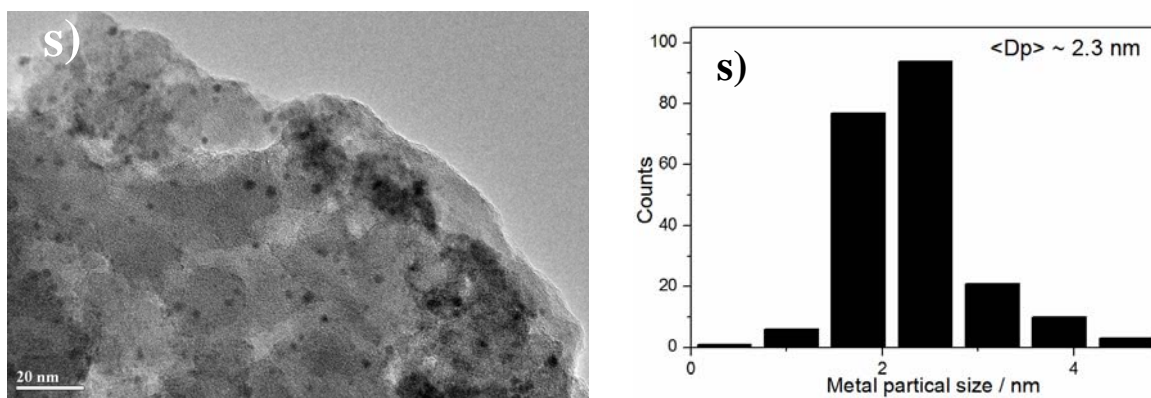


Figure S3. TEM images and metal particle size distributions of the catalysts: a) 0.11 wt% Au/Mg₄Al-HT before and b) after five reaction cycles; c) 0.26 wt% Au/Mg₄Al-HT; d) 0.53 wt% Au/Mg₄Al-HT; e) 1.08 wt% Au/Mg₄Al-HT; f) 2.10 wt% Au/Mg₄Al-HT; g) 0.89 wt% Au/Mg₂Al-HT; h) 1.02 wt% Au/Mg₃Al-HT; i) 0.85 wt% Au/Mg₅Al-HT; j) 0.1 wt% Pd/Mg₄Al-HT; k) 0.1 wt% Pt/Mg₄Al-HT; l) 0.1 wt% Ru/Mg₄Al-HT; m) 0.1 wt% Rh/Mg₄Al-HT; n) Au/TiO₂; o) Au/Al₂O₃; p) Au/CeO₂; q) Au/ZnO; r) Au/MgO and s) Au/ZrO₂.

L. XP spectra

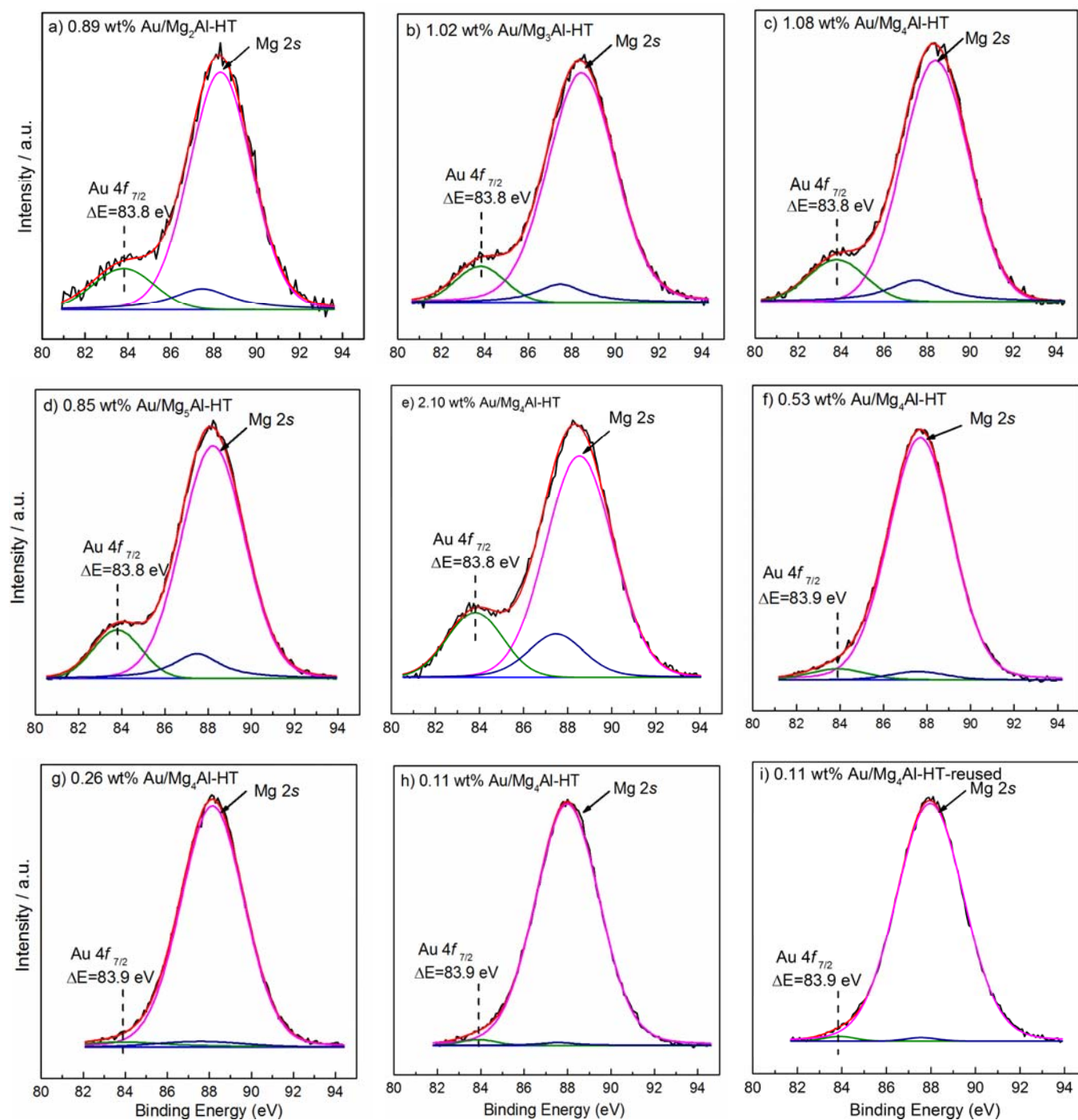


Figure S4. XPS of the Au/HT catalysts: a) 0.89 wt% Au/Mg₂Al-HT; b) 1.02 wt% Au/Mg₃Al-HT; c) 1.08 wt% Au/Mg₄Al-HT; d) 0.85 wt% Au/Mg₅Al-HT; e) 2.10 wt% Au/Mg₄Al-HT; f) 0.53 wt% Au/Mg₄Al-HT; g) 0.26 wt% Au/Mg₄Al-HT; h) 0.11 wt% Au/Mg₄Al-HT before and i) after five reaction cycles. The metallic state of Au practically undergoes no change after the five successive runs.

M. DRIFT measurements

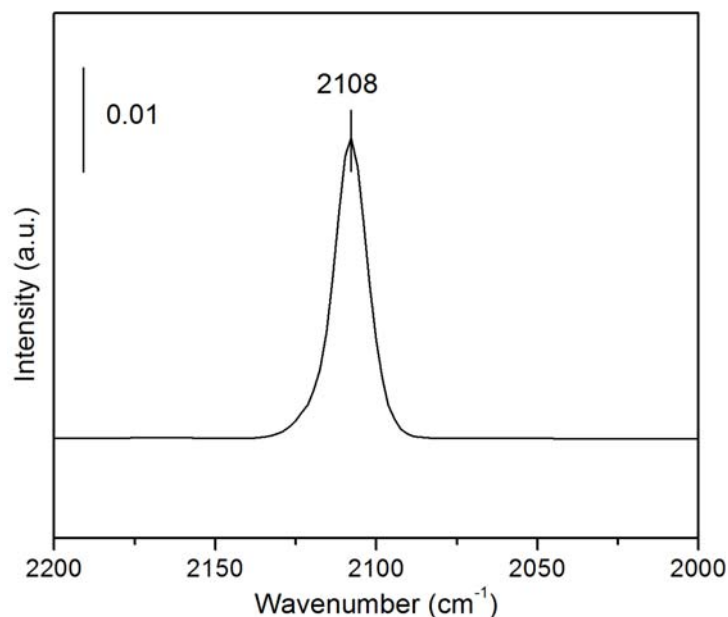
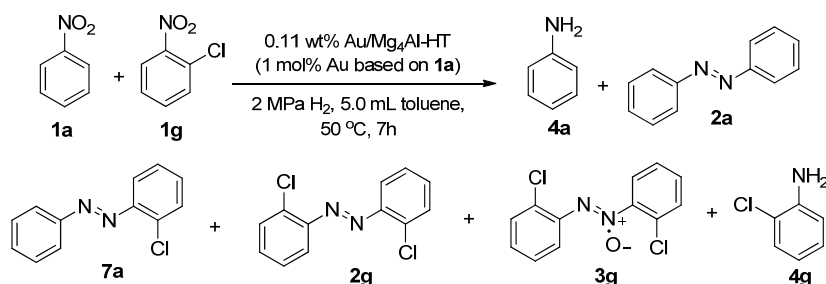


Figure S5. DRIFT spectrum of CO adsorption over 1.08 wt% Au/Mg₄Al-HT catalyst after CO adsorption for 20 min at 25 °C. Noted that there is only single peak of CO adsorption on gold catalysts at 2108 cm⁻¹ attributed to the vibration of CO adsorbed on Au⁰ species.^[S7]

N. Table S6 Cross-coupling reaction between nitrobenzene (**1a**) and 2-chloronitrobenzene (**1g**).

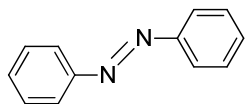


Entry	Substrates (mmol)		Conv. (%) [*]	Yield (%)					
	1a	1g		4a [*]	2a [*]	7a [*]	2g [†]	3g [†]	4g [†]
1	0.5	0.5	100	2	60	38	27	12	16
2	0.5	1	100	2	35	63	10	3	8
3	0.5	1.5	100	1	24	75	5	2	4
4	0.5	2	100	1	23	76	3	2	3

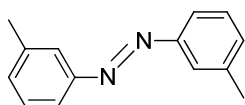
^{*}The conversion and yields of **4a**, **2a** and **7a** were calculated based on **1a** consumption by HPLC.

[†]The yields of **2g**, **3g** and **4g** were calculated based on **1g**. Note that the target cross-coupling product of **7a** could be obtained in a good yield of 75% with the optimal molar ratio of **1a/1g** = 1/3. Meanwhile, homocoupling azo compounds including azobenzene, and 2, 2'-dichloroazobenzene as well as aniline, 2-chloroaniline, 2, 2'-dichloroazoxybenzene were also detected as by-products in the resultant mixture.

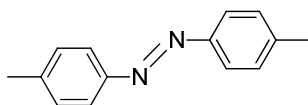
4. Characterization of aromatic azo compounds



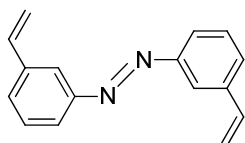
azobenzene (2a). Prepared according to the general procedure A and the reaction complete in 4.5 hrs. The crude reaction mixture was purified on silica gel (10% EtOAc/petroleum ether) to afford the product as a yellowish red solide (94% yield). **¹H NMR** (CDCl₃, 500 MHz): δ 7.96-7.95 (d, *J*=7.0 Hz, 4H), 7.57-7.49 (m, 6H); **¹³C NMR** (CDCl₃, 125 MHz): δ 152.7, 131.0, 129.1, 122.9. The physical data were identical in all respects to those previously reported.^[S8]



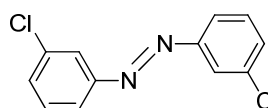
1,2-di-*m*-tolyldiazene (2b). Prepared according to the general procedure A and the reaction complete in 5 hrs. The crude reaction mixture was purified on silica gel (10% EtOAc/petroleum ether) to afford the product as a red solide (82% yield). **¹H NMR** (CDCl₃, 500 MHz): δ 7.72 (s, 4H), 7.42-7.39 (t, *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. The physical data were identical in all respects to those previously reported.^[S8]



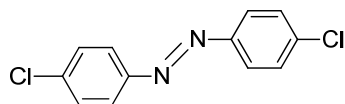
1,2-di-*p*-tolyldiazene (2c). Prepared according to the general procedure A and the reaction complete in 11 hrs. The crude reaction mixture was purified on silica gel (10% EtOAc/petroleum ether) to afford the product as a yellow solide (74% yield). **¹H NMR** (CDCl₃, 500 MHz): δ 7.82-7.80 (d, *J*=8.5 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, 122.7, 21.5. The physical data were identical in all respects to those previously reported.^[S8]



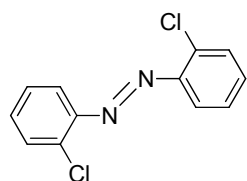
1,2-bis(3-vinylphenyl)diazene (2d).^[S9] Prepared according to the general procedure A and the reaction complete in 12 hrs. The crude reaction mixture was purified on silica gel (10% EtOAc/petroleum ether) to afford the product as a yellowish red solide (85% yield). **¹H NMR** (CDCl₃, 500 MHz): δ 7.97 (s, 2H), 7.82-7.80 (d, *J*=8.0 Hz, 2H), 7.52-7.45 (m, 4H), 6.84-6.78 (dd, *J*=10.5, 11.0 Hz, 2H), 5.89-5.86 (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, 115.0. The physical data were identical in all respects to those previously reported.^[S9]



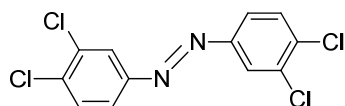
1,2-bis(3-chlorophenyl)diazene (2e). Prepared according to the general procedure A and the reaction complete in 7 hrs. The crude reaction mixture was purified on silica gel (10% dichloromethane/petroleum ether) to afford the product as a yellow solid (97% yield). **¹H NMR** (CDCl₃, 500 MHz): δ 7.90 (s, 2H), 7.85-7.83 (m, 2 H), 7.50-7.47 (m, 4H); **¹³C NMR** (CDCl₃, 125 MHz): δ 153.2, 135.3, 131.2, 130.2, 122.6, 122.0. The physical data were identical in all respects to those previously reported.^[S8]



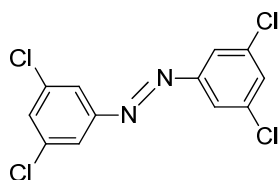
1,2-bis(4-chlorophenyl)diazene (2f). Prepared according to the general procedure A and the reaction complete in 9 hrs. The crude reaction mixture was purified on silica gel (10% dichloromethane/petroleum ether) to afford the product as a yellow solid (90% yield). **¹H NMR** (CDCl₃, 500 MHz): δ 7.90-7.88 (d, *J*=8.5 Hz, 4H), 7.53-7.51 (d, *J*=8.5 Hz, 4H). **¹³C NMR** (CDCl₃, 125 MHz): δ 150.9, 137.3, 129.4, 124.2. The physical data were identical in all respects to those previously reported.^[S8]



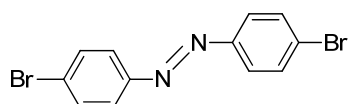
1,2-bis(2-chlorophenyl)diazene (2g). Prepared according to the general procedure A and the reaction complete in 15 hrs. The crude reaction mixture was purified on silica gel (10% dichloromethane/petroleum ether) to afford the product as a yellow solid (75% yield). **¹H NMR** (CDCl₃, 500 MHz): δ 7.78-7.76 (dd, *J*=1.5, 2.0 Hz, 2H), 7.57-7.55 (dd, *J*=1.5, 2.0 Hz, 2H), 7.43-7.40 (m, 2H), 7.37-7.34 (m, 2 H); **¹³C NMR** (CDCl₃, 125 MHz): δ 148.8, 135.8, 132.2, 130.7, 127.3, 118.1. The physical data were identical in all respects to those previously reported.^[S10]



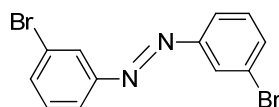
1,2-bis(3,4-dichlorophenyl)diazene (2h). Prepared according to the general procedure A and the reaction complete in 24 hrs. The crude reaction mixture was purified on silica gel (10% dichloromethane/petroleum ether) to afford the product as a yellow solid (93% yield). **¹H NMR** (CDCl₃, 500 MHz): δ 8.02-8.01 (d, *J*=2.5 Hz, 2H), 7.80-7.78 (dd, *J*=2.0, 2.0 Hz, 2H), 7.62-7.61 (d, *J*=7.5 Hz, 2H); **¹³C NMR** (CDCl₃, 125 MHz): δ 151.1, 135.7, 133.7, 131.0, 124.1, 123.0.



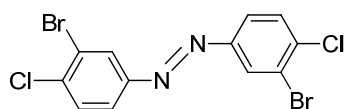
1,2-bis(3,5-dichlorophenyl)diazene (2i). Prepared according to the general procedure A and the reaction complete in 35 hrs. The crude reaction mixture was purified on silica gel (10% dichloromethane/petroleum ether) to afford the product as a yellow solide (91% yield). $^1\text{H NMR}$ (CDCl_3 , 500 MHz): δ 7.82-7.81 (d, $J=2.0$ Hz, 4H), 7.50 (t, $J=2.0$ Hz, 2H); $^{13}\text{C NMR}$ (CDCl_3 , 125 MHz): δ 153.1, 135.9, 131.3, 121.8.



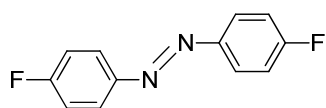
1,2-bis(4-bromophenyl)diazene (2j). Prepared according to the general procedure A and the reaction complete in 24 hrs. The crude reaction mixture was purified on silica gel (10% dichloromethane/petroleum ether) to afford the product as a yellow solide (82% yield). $^1\text{H NMR}$ (CDCl_3 , 500 MHz): δ 7.80-7.78 (d, $J=9.0$ Hz, 4H), 7.66-7.64 (d, $J=9.0$ Hz, 4H); $^{13}\text{C NMR}$ (CDCl_3 , 125 MHz): δ 151.2, 132.4, 125.7, 124.4. The physical data were identical in all respects to those previously reported.^[S8]



1,2-bis(3-bromophenyl)diazene (2k). Prepared according to the general procedure A and the reaction complete in 18 hrs. The crude reaction mixture was purified on silica gel (10% dichloromethane/petroleum ether) to afford the product as a yellow solide (93% yield). $^1\text{H NMR}$ (CDCl_3 , 500 MHz): δ 8.05 (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); $^{13}\text{C NMR}$ (CDCl_3 , 125 MHz): δ 153.2, 134.1, 130.5, 124.8, 123.2. The physical data were identical in all respects to those previously reported.^[S10]

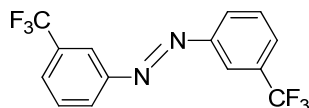


1,2-bis(3-bromo-4-chlorophenyl)diazene (2l). Prepared according to the general procedure A and the reaction complete in 36 hrs. The crude reaction mixture was purified on silica gel (10% dichloromethane/petroleum ether) to afford the product as a yellow solide (90% yield). $^1\text{H NMR}$ (CDCl_3 , 500 MHz): δ 7.82-7.81 (d, $J=2.0$ Hz, 4H), 7.51-7.50 (t, $J=2.0$ Hz, 2H); $^{13}\text{C NMR}$ (CDCl_3 , 125 MHz): δ 151.0, 137.7, 130.9, 127.4, 123.9, 119.4.

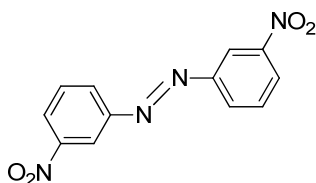


1,2-bis(4-fluorophenyl)diazene (2m). Prepared according to the general procedure A and the reaction complete in 25 hrs. The crude reaction mixture was

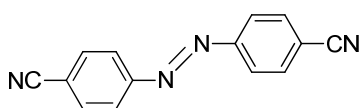
purified on silica gel (10% dichloromethane/petroleum ether) to afford the product as a yellow solide (58% yield). $^1\text{H NMR}$ (CDCl_3 , 500 MHz): δ 7.92-7.90 (m, 4H), 7.20-7.16 (m, 4H); $^{13}\text{C NMR}$ (CDCl_3 , 125 MHz): δ 165.4, 163.4, 149.0, 124.9, 124.8, 116.2, 116.0. The physical data were identical in all respects to those previously reported.^[S8]



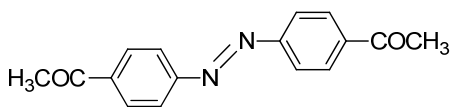
1,2-bis(3-(trifluoromethyl)phenyl)diazene (2n). Prepared according to the general procedure A and the reaction complete in 10 hrs. The crude reaction mixture was purified on silica gel (5% EtOAc/petroleum ether) to afford the product as a yellowish red solide (91% yield). $^1\text{H NMR}$ (CDCl_3 , 500 MHz): δ 8.22 (s, 2H), 8.14-8.12 (d, $J=9.0$ Hz, 2H), 7.78-7.76 (d, $J=2.5$ Hz, 2H), 7.69-7.65 (t, $J=9.0$ Hz, 2H); $^{13}\text{C NMR}$ (CDCl_3 , 125 MHz): δ 152.2, 129.8, 127.9, 126.5, 119.8.



1,2-bis(3-nitrophenyl)diazene (2o). Prepared according to the general procedure A and the reaction complete in 24 hrs. The crude reaction mixture was purified on silica gel (5% dichloromethane/petroleum ether) to afford the product as a yellow solide (92% yield). $^1\text{H NMR}$ (CDCl_3 , 500 MHz): δ 8.80-8.79 (t, $J=2.0$ Hz, 2H), 8.42-7.40 (m, 2H), 8.34-8.32 (m, 2H), 7.79-7.76 (t, $J=9.0$ Hz, 2H); $^{13}\text{C NMR}$ (CDCl_3 , 125 MHz): δ 152.4, 149.1, 130.3, 129.7, 125.9, 117.2. The physical data were identical in all respects to those previously reported.^[S11]

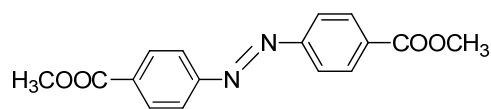


4,4'-(diazene-1,2-diyl)dibenzonitrile (2p). Prepared according to the general procedure A and the reaction complete in 30 hrs. The crude reaction mixture was purified on silica gel (5% EtOAc/petroleum ether) to afford the product as a red solide (81% yield). $^1\text{H NMR}$ (CDCl_3 , 500 MHz): δ 8.04-8.03 (d, $J=9.0$ Hz, 4H), 7.86-7.84 (d, $J=9.0$ Hz, 4H); $^{13}\text{C NMR}$ (CDCl_3 , 125 MHz): δ 154.0, 133.4, 123.8, 118.1, 115.2. The physical data were identical in all respects to those previously reported.^[S8]



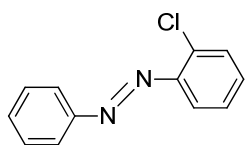
1,1'-(diazene-1,2-diylbis(4,1-phenylene))diethanone (2q). Prepared according to the general procedure A and the reaction complete in 33 hrs. The crude reaction mixture was purified on silica gel (5% EtOAc/petroleum ether) to afford the product as a yellow solide (79% yield). $^1\text{H NMR}$ (CDCl_3 , 500 MHz): δ 8.14-8.12 (d, $J=9.0$ Hz, 4H), 8.02-8.01 (d,

$J=9.0$ Hz, 4H), 2.68 (s, 6H); ^{13}C NMR (CDCl_3 , 125 MHz): δ 197.3, 154.9, 139.0, 129.4, 123.2, 26.9. The physical data were identical in all respects to those previously reported.^[S8]



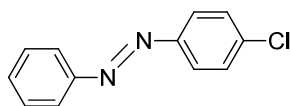
dimethyl 4,4'-(diazene-1,2-diyl)dibenzoate (2r). Prepared

according to the general procedure A and the reaction complete in 30 hrs. The crude reaction mixture was purified on silica gel (5% dichloromethane/petroleum ether) to afford the product as a yellow solid (75% yield). ^1H NMR (CDCl_3 , 500 MHz): δ 8.25-8.23 (d, $J=8.5$ Hz, 4H), 8.02-7.00 (d, $J=8.5$ Hz, 4H), 3.97 (s, 6H); ^{13}C NMR (CDCl_3 , 125 MHz): δ 166.4, 154.9, 132.4, 122.9, 52.4. The physical data were identical in all respects to those previously reported.^[S8]



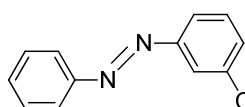
1-(2-chlorophenyl)-2-phenyldiazene (7a). Prepared according to the general

procedure B and the reaction complete in 7 hrs. The crude reaction mixture was purified on silica gel (5-10% dichloromethane/petroleum ether) to afford the product as a yellowish red oil (70% yield based on nitrobenzene). ^1H NMR (CDCl_3 , 500 MHz): δ 7.98-7.96 (dd, $J=1.5$, 1.0 Hz, 2H), 7.70-7.68 (dd, $J=1.5$, 1.5 Hz, 1H), 7.56-7.51 (m, 4H), 7.39-7.33 (m, 2H); ^{13}C NMR (CDCl_3 , 125 MHz): δ 152.8, 148.8, 131.6, 131.5, 130.7, 129.2, 127.3, 123.4, 117.6.



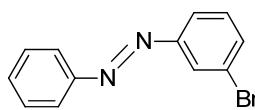
1-(4-chlorophenyl)-2-phenyldiazene (7b). Prepared according to the

general procedure B and the reaction complete in 6.5 hrs. The crude reaction mixture was purified on silica gel (5-10% dichloromethane/petroleum ether) to afford the product as a yellowish red solid (80% yield based on nitrobenzene). ^1H NMR (CDCl_3 , 500 MHz): δ 7.96-7.90 (m, 4H), 7.56-7.51 (m, 5H); ^{13}C NMR (CDCl_3 , 125 MHz): δ 152.5, 151.0, 136.9, 131.3, 129.3, 129.1, 124.1, 122.9. The physical data were identical in all respects to those previously reported.^[S8]

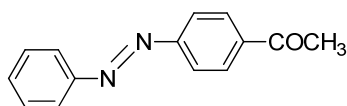


1-(3-chlorophenyl)-2-phenyldiazene (7c). Prepared according to the general

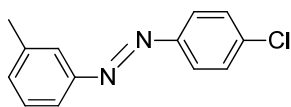
procedure B and the reaction complete in 5 hrs. The crude reaction mixture was purified on silica gel (5-10% EtOAc/hexanes) to afford the product as a yellowish red solid (87% yield based on nitrobenzene). ^1H NMR (CDCl_3 , 500 MHz): δ 7.94-7.92 (t, $J=7.0$ Hz, 3H), 7.86-7.85 (d, $J=7.0$ Hz, 1H), 7.55-7.50 (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.



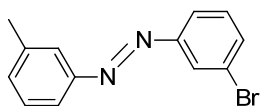
1-(3-bromophenyl)-2-phenyldiazene (7d). Prepared according to the general procedure B and the reaction complete in 6 hrs. The crude reaction mixture was purified on silica gel (5-10% dichloromethane/petroleum ether) to afford the product as a yellowish red solide (83% yield based on nitrobenzene). $^1\text{H NMR}$ (CDCl_3 , 500 MHz): δ 8.06-8.05 (t, $J=1.5$ Hz, 1H), 7.92-7.86 (m, 3H), 7.59-7.49 (m, 4H), 7.40-7.37 (t, $J=8.0$ Hz, 1H); $^{13}\text{C NMR}$ (CDCl_3 , 125 MHz): δ 153.6, 152.4, 133.6, 131.5, 130.4, 129.2, 124.7, 123.1, 122.9.



1-(4-(phenyldiazenyl)phenyl)ethanone (7e). Prepared according to the general procedure B and the reaction complete in 9 hrs. The crude reaction mixture was purified on silica gel (5% dichloromethane/petroleum ether) to afford the product as a yellowish red solide (71% yield based on nitrobenzene). $^1\text{H NMR}$ (CDCl_3 , 500 MHz): δ 8.12-8.10 (d, $J=1.5$ Hz, 2H), 7.98-7.94 (m, 4H), 7.54-7.52 (d, $J=8.0$ Hz, 3H), 2.67 (s, 3H); $^{13}\text{C NMR}$ (CDCl_3 , 125 MHz): δ 197.4, 152.6, 131.8, 131.4, 129.4, 129.2, 123.2, 122.9, 29.7. The physical data were identical in all respects to those previously reported.^[S8]



1-(4-chlorophenyl)-2-(*m*-tolyl)diazene (7f). Prepared according to the general procedure B and the reaction complete in 7 hrs. The crude reaction mixture was purified on silica gel (5% dichloromethane/hexanes) to afford the product as a yellowish red solide (83% yield based on 1-methyl-3-nitrobenzene). $^1\text{H NMR}$ (CDCl_3 , 500 MHz): δ 7.87-7.85 (d, $J=8.0$ Hz, 2H), 7.71 (s, 2H), 7.49-7.47 (d, $J=8.5$ Hz, 2H), 7.42-7.39 (t, $J=8.0$ Hz, 1H), 7.31-7.29 (d, $J=7.5$ Hz, 1H), 2.46 (s, 3H); $^{13}\text{C NMR}$ (CDCl_3 , 125 MHz): 152.6, 151.1, 139.1, 136.8, 132.1, 129.3, 129.0, 124.1, 123.0, 120.5, 21.4. The physical data were identical in all respects to those previously reported.^[S8]

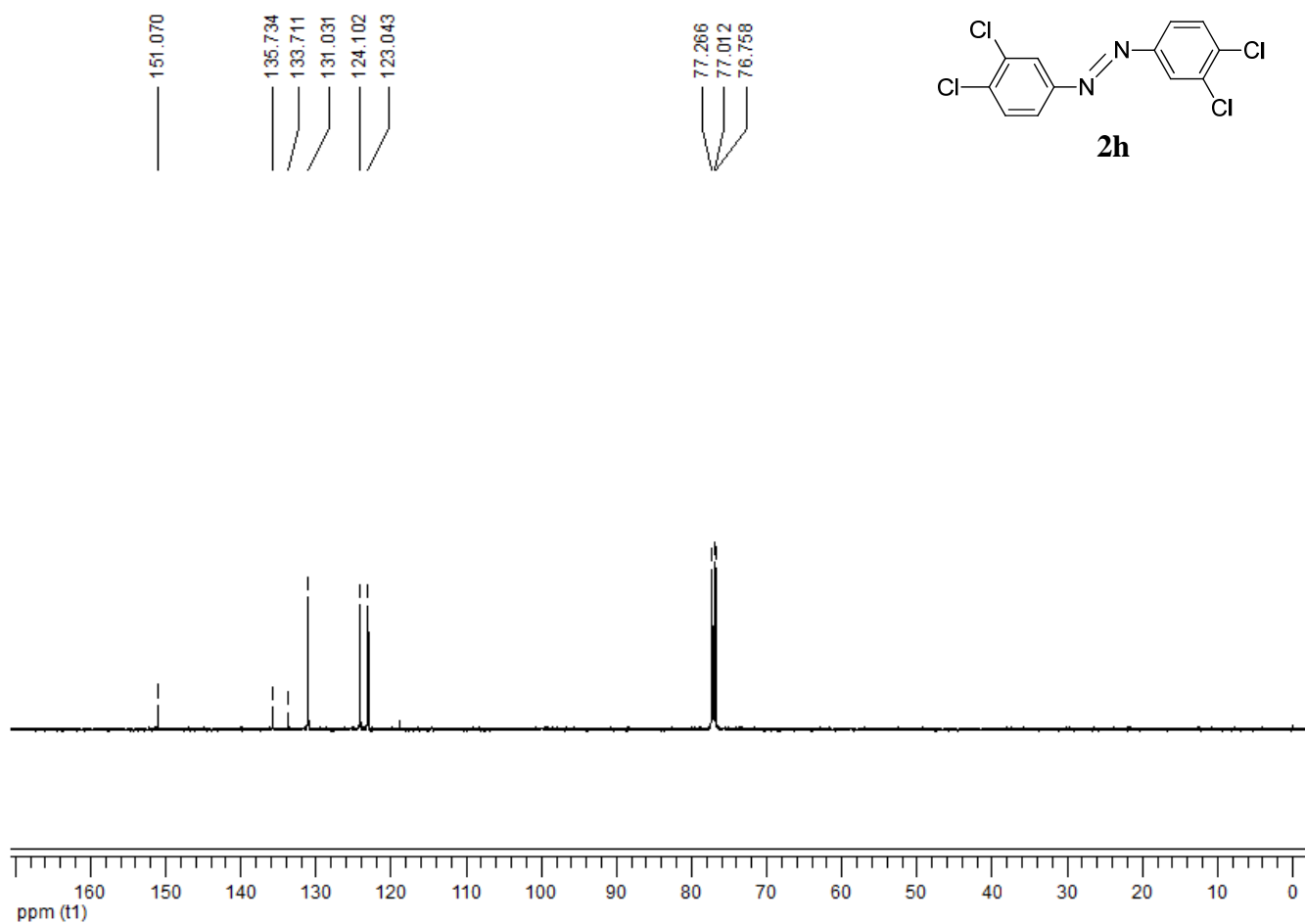
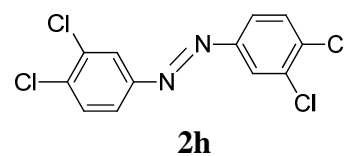
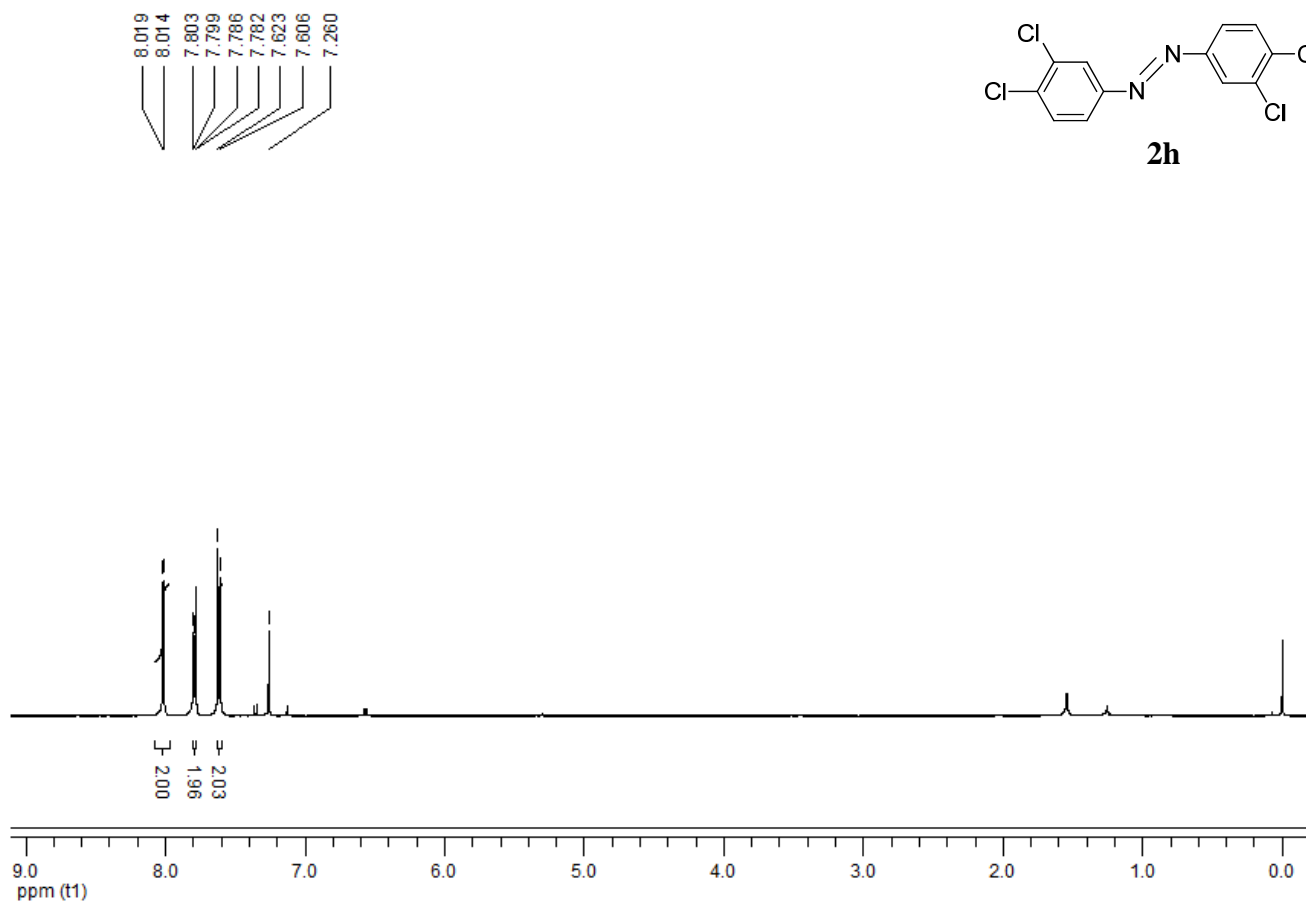
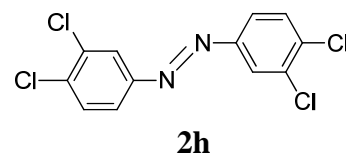


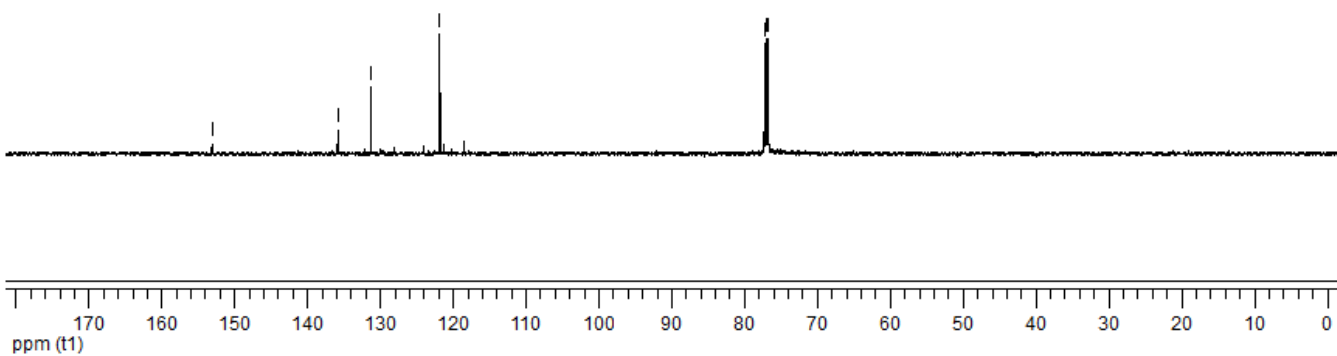
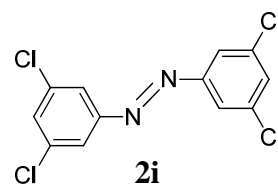
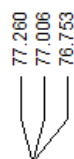
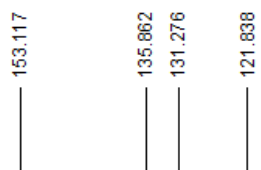
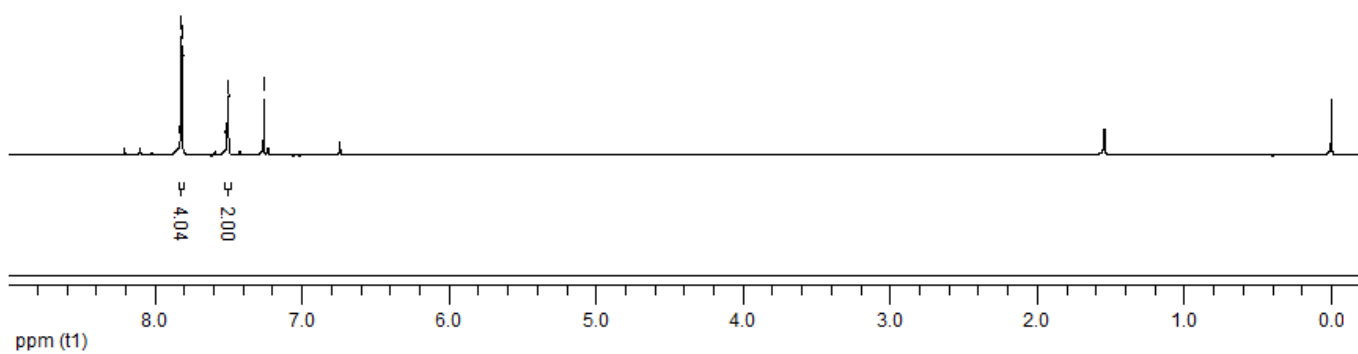
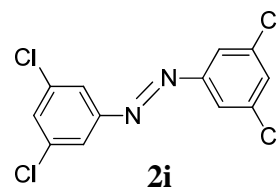
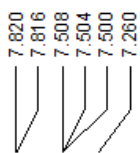
1-(3-bromophenyl)-2-(*m*-tolyl)diazene (7g). Prepared according to the general procedure B and the reaction complete in 8 hrs. The crude reaction mixture was purified on silica gel (5-10% dichloromethane/hexanes) to afford the product as a yellowish red solide (82% yield based on 1-methyl-3-nitrobenzene). $^1\text{H NMR}$ (CDCl_3 , 500 MHz): δ 8.041 (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); $^{13}\text{C NMR}$ (CDCl_3 , 125 MHz): 153.6, 152.5, 139.1, 133.5, 132.3, 130.4, 129.0, 124.6, 123.2, 122.9, 120.7, 21.4.

5. References

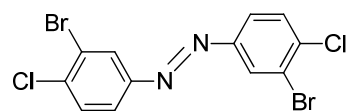
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6. ^1H and ^{13}C NMR Spectra of New Compounds.

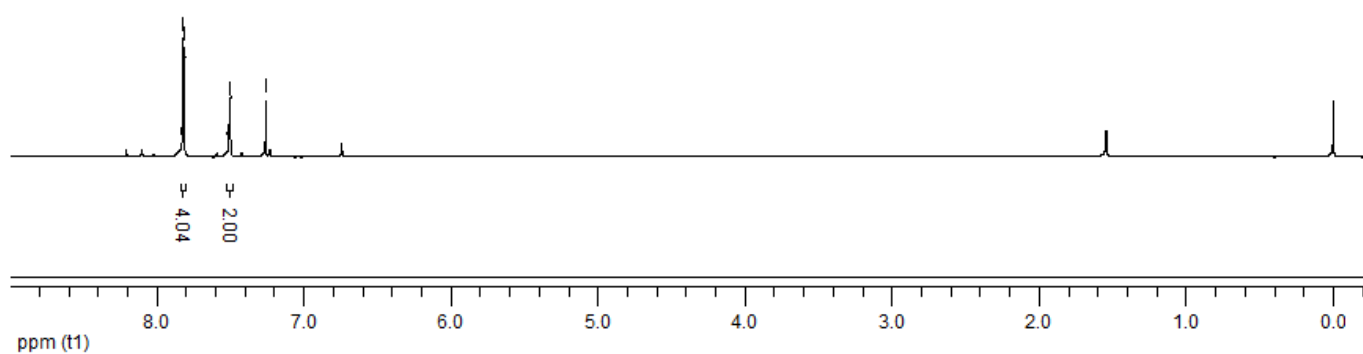




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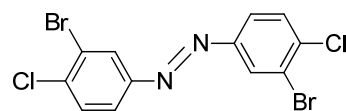


21



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21

