

# Highly Selective Catalytic Reduction of Nitro- to Azoarenes under Ambient Conditions

Carlos G. Morales-Guio · Igor Yuranov ·  
Liubov Kiwi-Minsker

Published online: 3 September 2014  
© Springer Science+Business Media New York 2014

**Abstract** Catalytic system of Au nanoparticles supported on metal oxides has been developed to produce azoarenes in *one-step* directly from nitroarenes under mild conditions (30 °C, 1 bar of N<sub>2</sub>) using 2-propanol as solvent and reducing agent. Close to 100 % chemoselectivity to substituted azoarenes with different functional groups left intact and close to quantitative yields make this procedure promising for the production of azoarenes.

**Keywords** Nitroarenes · Azoarenes · Au supported catalyst · Chemoselectivity · H<sub>2</sub>-free reduction

## 1 Introduction

New processes that provide quantitative transformation of raw materials to products and minimize the use of energy are the main objectives of today research efforts.

Azoarenes are high value chemicals with wide applications as dyes and pigments, food additives, radical reaction initiators, pharmaceuticals and light-responsive functional materials [1–7]. Among industrial colorants, azo-dyes are by far the most important class, accounting for over 50 % of all commercial dyes [2–4]. A variety of methods have been developed for their production as summarized in recent reviews [1, 5]. The majority of existing protocols are not catalytic, like the classical diazo-coupling reaction that involves stoichiometric amounts of

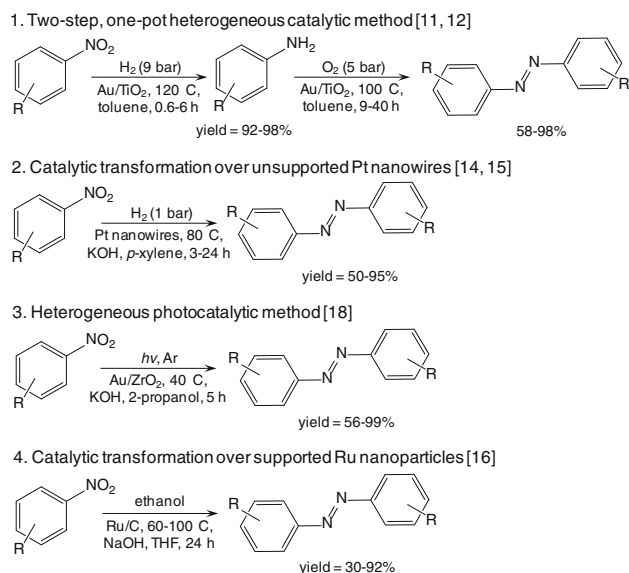
toxic nitrous acid and generates equivalent amounts of inorganic salt waste [7–10].

Recent developments in catalysis have opened a door to the more sustainable production of azoarenes through the catalytic oxidation of anilines [11–13] and reduction of nitroarenes [14–16]. Grirrane et al. first reported a novel two-step, one-pot catalytic method for the production of symmetric azoarenes [11, 12] (Fig. 1, reaction 1). The authors oxidized by molecular oxygen expensive aniline derivatives, which in turn could be produced by catalytic hydrogenation of nitroarenes using the same supported Au catalyst [17]. Hu et al. [14] synthesized azoarenes from nitroaromatics by H<sub>2</sub> reduction ( $P_{H_2} = 1$  bar,  $T = 80$ – $120$  °C) over unsupported Pt and Pd [15] catalysts (Fig. 1, reaction 2). Zhu et al. [18] reported that azo-compounds can be produced with a high yield (up to 99 %) directly from nitroarenes by photo-catalytic reduction under visible or ultraviolet light using Au nanoparticles (NPs) supported on ZrO<sub>2</sub> at ambient temperature and pressure (Fig. 1, reaction 3).

Despite such remarkable achievements in catalytic synthesis of azoarenes, the stepwise processing, elevated temperatures, or use of light irradiation present practical limitations.

Therefore, we aimed at the development of a *catalytic* system to produce *selectively* azo-compounds in *one-step* under mild conditions. Although the use of alcohols for hydrogen transfer reactions was reported several decades ago [19], their use for the reduction of nitroarenes is still rare. Recently, Ru-NPs supported on non-activated charcoal (Fig. 1, reaction 4) [16] and Au-NPs supported on mesoporous ceria [20] were reported as novel catalytic systems to produce azo-, azoxy- and/or aminoarenes from the corresponding nitroarenes using alcohols as reducing agents. However, low selectivity and slow kinetics even at

C. G. Morales-Guio · I. Yuranov · L. Kiwi-Minsker (✉)  
Institut des sciences et ingénierie chimiques, Ecole  
polytechnique fédérale de Lausanne (EPFL), CH H3 594,  
Station 6, 1015 Lausanne, Switzerland  
e-mail: liubov.kiwi-minsker@epfl.ch



**Fig. 1** State-of-the-art catalytic methods of azoarenes synthesis

high temperatures are still important issues that need to be addressed. Thus, the development of valuable alternatives for the one-step production of azoarenes remains of fundamental and industrial importance.

Herein we report a direct and highly chemoselective catalytic transformation of a wide range of substituted nitroarenes to azoarenes using 2-propanol as solvent and the reducing agent at the same time. A typical reaction was carried out at 30 °C in a 2-propanol solution of KOH and nitroarene in the presence of Au-based catalyst under N<sub>2</sub> flow. Such a simple procedure under ambient pressure and low temperature renders *selectively* the azoarenes, tolerating a large number of substituents in the aromatic ring such as -halo, -OCH<sub>3</sub> and vinyl groups. The catalysts have been characterized via atomic absorption spectroscopy (AAS), high resolution transmission electron microscopy (HRTEM), powder X-ray diffraction (XRD), and X-ray photo-electron spectroscopy (XPS).

## 2 Experimental Section

### 2.1 Reagents

Commercial 1.0 % gold on titanium dioxide extrudates (Au/TiO<sub>2</sub>, AUROLite™), 1.0 % gold on aluminum oxide extrudates (Au/Al<sub>2</sub>O<sub>3</sub>, AUROLite™), 1.0 % gold on zinc oxide granulate (Au/ZnO, AUROLite™) were bought from STREM Chemical Inc., whereas 1.0 % platinum on gamma alumina powder reduced (1.0 % Pt/Al<sub>2</sub>O<sub>3</sub>) was bought from ABCR GmbH & Co. 5.0 % palladium on aluminum oxide (5.0 % Pd/Al<sub>2</sub>O<sub>3</sub>) was acquired from STREM

Chemical Inc. 5.0 % copper on aluminum oxide (5.0 % Cu/Al<sub>2</sub>O<sub>3</sub>) was home made by impregnation of Al<sub>2</sub>O<sub>3</sub> by an aqueous solution of Cu(II) nitrate followed by drying and reduction by H<sub>2</sub>.

All the reactants used in this study are commercially available from Aldrich, Alfa Aesar, Acros Organic.

### 2.2 Au/HT Catalyst Preparation

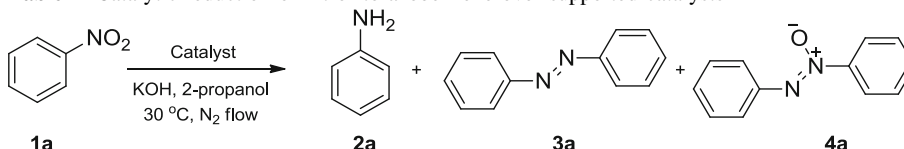
The Mg–Al hydrotalcite (HT, Mg<sub>6</sub>Al<sub>2</sub>(OH)<sub>16</sub>CO<sub>3</sub>) support synthesis was carried out by a well-known co-precipitation procedure [21]. The 1.3 % Au/HT catalyst was synthesized by deposition of gold precursor HAuCl<sub>4</sub> (ABCR GmbH & Co., 49 % Au) on the synthesized HT support. The yellow slurry obtained after stirring (8 h) of the support (2 g) in an aqueous HAuCl<sub>4</sub> solution (1.3 M, 50 ml) was filtered, washed with deionized water, and dried at 30 °C under vacuum. Subsequent Au<sup>3+</sup> reduction was performed in 2-propanol (50 mL) at 80 °C (2 h) under nitrogen flow (100 mL min<sup>-1</sup>). The resulting solid Au/HT was filtered, washed thoroughly by water and dried at 30 °C under vacuum.

### 2.3 Characterization

The Au content in the synthesized catalyst was measured by AAS using a Shimadzu AA-6650 spectrometer with an air-acetylene flame from the diluted solutions in “aqua regia” (1/3 v/v HNO<sub>3</sub>/HCl). Powder X-ray diffractograms were recorded on a Bruker/Siemens D500 incident X-ray diffractometer (Cu Kα radiation). HR-TEM was performed using a JEOL JEM-3011 high-resolution transmission electron microscope operated at an accelerating voltage of 300 kV. The detailed analysis of particle morphology was done using Gatan Digital Micrograph 3.6.5. The specimens were prepared by droplet coating of MeOH suspensions on carbon coated Ni grids (Agar Scientific, 300 mesh). NMR spectra were recorded on a Bruker Avance III 400 MHz spectrometer at room temperature using CDCl<sub>3</sub> as solvent. Chemical shifts are reported relative to the residual proton or carbon signal of the solvent. XPS spectra were measured on a Kratos Axis Ultra DLD XPS System using a dual Al–Mg X-ray anode with a circular spatial resolution of 15 μm. Samples were prepared by droplet coating of the methanol dispersed catalyst particles on Si wafers.

### 2.4 Hydrogenation Reaction

All catalytic experiments were carried out in a stirred round-bottom flask heated at 30 °C containing a solution of KOH (0.5 mmol) in 2-propanol (25 mL), aromatic nitroarene (1.5 mmol) and *n*-dodecane as an internal standard. The amount of the base was previously optimized in order

**Table 1** Catalytic reduction of nitro- to azobenzene over supported catalysts


Entry	Catalyst	<i>t</i> (h)	Yield (%) <sup>a</sup>			Conv. (%) <sup>a</sup>	Sel. <b>3a</b> (%) <sup>a</sup>
			<b>2a</b>	<b>3a</b>	<b>4a</b>		
1	–	8.0	2	2	10	14	14
2	1.3 % Au/HT	2.5	0	>99	0	100	>99
3 <sup>b</sup>	1.3 % Au/HT	3.1	0	>99	0	100	>99
4 <sup>c</sup>	1.3 % Au/HT	0.5	3	95	2	100	95
5	1.0 % Au/TiO <sub>2</sub>	3.0	1	99	0	100	99
6	1.0 % Au/Al <sub>2</sub> O <sub>3</sub>	3.5	1	95	1	99	96
7	1.0 % Au/ZnO	7.5	0	>99	0	100	>99
8 <sup>c</sup>	1.0 % Pt/Al <sub>2</sub> O <sub>3</sub>	3.5	0	0	0	<1	0
9 <sup>c</sup>	5.0 % Pd/Al <sub>2</sub> O <sub>3</sub>	8.0	14	8	44	75	12
10 <sup>c</sup>	5.0 % Cu/Al <sub>2</sub> O <sub>3</sub>	3.0	0	0	2	2	0

Reaction conditions: catalyst (M: 1.0 mol %), **1a** (1.5 mmol), KOH (0.5 mmol), 2-propanol (25 mL), N<sub>2</sub> flow (100 mL/min, STP) at 30 °C

<sup>a</sup> Determined by GC using *n*-dodecane as internal standard

<sup>b</sup> 2nd Catalyst reuse

<sup>c</sup> 65°

to increase selectivity towards the desired azoarenes. After 15 min of stirring under N<sub>2</sub> flow, the catalyst containing 1 mol% of metal in respect to a nitroarene was quickly added to the solution. The flask was closed and kept under a N<sub>2</sub> flow until the end of the reaction. Small samples (<0.2 mL) were taken periodically during the reaction and analyzed using a gas chromatography (Perkin-Elmer Auto System XL equipped with a programmed split/splitless injector and a flame ionization detector, employing a DB-1 capillary column (i.d. = 0.33 mm, length = 30 m, film thickness = 0.20 μm) or TLC.

After the reaction, the mixture was immediately filtered. Toluene was used to wash the solid catalyst and to extract the products. The filtrate was neutralized with an aqueous solution of HCl. Subsequently, after phase separation the solvent was evaporated and an orange powder was re-dissolved in toluene. The organic phase was washed three times with distilled water. The final solvent evaporation gave an aromatic azo-compound as orange crystals.

### 3 Results and Discussion

Selective transformation of nitrobenzene **1a** to azobenzene **3a** (Table 1, entries 2–7) was achieved using both the commercially available Au<sup>0</sup>-NPs (*d*<sub>av.</sub> ~ 3 nm) heterogeneous catalysts (Au/TiO<sub>2</sub>, Au/Al<sub>2</sub>O<sub>3</sub>, Au/ZnO) [22–24] and home-made Au<sup>0</sup>-NPs supported on Mg–Al hydrotalcite (Au/HT). It is worth to note that without catalyst and/or

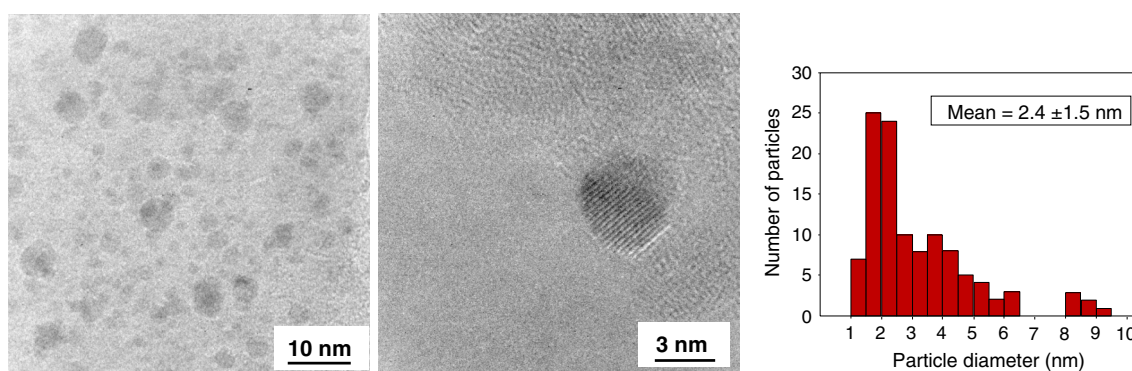
base only a negligible conversion of **1a** was detected (Table 1, entry 1). The smallest Au<sup>0</sup>-NPs (*d*<sub>av.</sub> ~ 2.4 nm) supported on basic HT (Fig. 2) demonstrated the shortest time to attain a full conversion of nitrobenzene indicating the highest activity (Table 1, entry 2). The catalyst reuse (2 times) after its filtration and washing showed some decrease in catalytic activity without noticeable change in chemoselectivity (Table 1, entry 3). TEM measurements (not shown) confirmed that the Au<sup>0</sup>-NP size distribution did not change after the recycling. No gold was found in the resulting liquid phase (Atomic Absorption Spectroscopy analysis) confirming the absence of Au leaching.

The reaction time over Au/HT can be reduced from 2.5 to 0.5 h maintaining high selectivity towards **3a** (~95 %) by increasing the reaction temperature up to 65 °C (Table 1, entry 4).

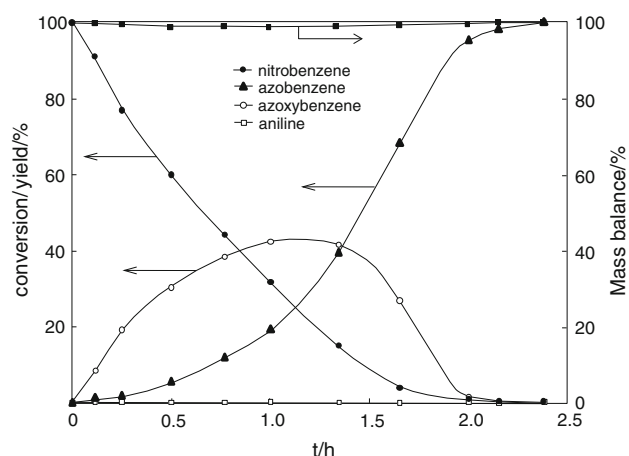
At higher temperatures, **3a** undergoes over-hydrogenation to aniline **2a**. The transformation of nitro- to azobenzene was followed by GC analysis over the reaction time. It was found that nitrobenzene was first reduced to azoxybenzene and then to azobenzene (Fig. 3). The mass balance was consistently above 98 % indicating that azoxybenzene was the only detectable reaction intermediate.

Other metals (Pt, Pd, Cu) known to be active in the reduction of nitroarenes were also tested showing very low activities with poor selectivity (Table 1, entries 8–10).

It was found that the **1a** conversion of less than 40 % could be attained if the reaction was conducted in a static N<sub>2</sub> atmosphere. Moreover, no reaction was observed if



**Fig. 2** 1.3 %Au/HT: TEM images and particle size distribution



**Fig. 3** Reduction of nitrobenzene at 30 °C over Au/HT catalyst in 2-propanol

acetone (10 vol%) was added to the initial reaction mixture. Therefore, it was suggested that acetone produced from *i*-PrOH during the reaction inhibits strongly the hydrogen transfer. In order to avoid the inhibition, the  $N_2$  flow was kept through the experiments.

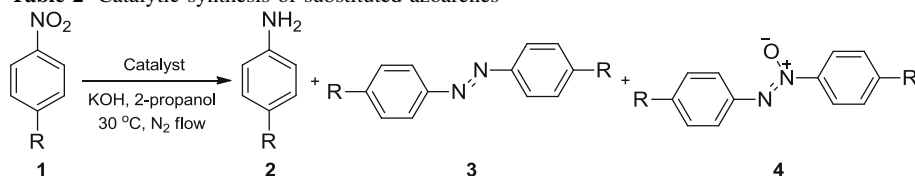
Although the detailed mechanism of transfer hydrogenation of nitrobenzene over Au-supported catalysts is unknown, the formation of intermediate hydride species [Au–H] on the  $Au^0$ -NP surface during the hydrogen transfer from 2-propanol (hydrogen source) to nitrobenzene has been proposed [18, 25]. A basic site of the support abstracts  $H^+$  from hydroxyl group of 2-propanol followed by  $\beta$ -hydride transfer to  $Au^0$ -NP thus forming [Au–H]<sup>−</sup> hydride species [26, 27]. The Au-hydride and  $H^+$  seem to be responsible for the nitrobenzene hydrogenation reaction. It is obvious that the smallest  $Au^0$ -NPs supported on a strongly basic HT can provide more active sites on the interface between  $Au^0$ -NPs and the support resulting in a higher catalytic activity. Due to a basic environment, the reaction is channeled preferentially into the condensation

route (formation of **3a** and **4a**, see Table 1) of the reaction network proposed by Haber for the reduction of nitroaromatics [28].

A special run was carried out in the dark using the Au/HT catalyst in order to verify a possible contribution of photocatalysis. The same catalyst activity was observed irrespectively of day-light irradiation. This finding contradicts the results reported by Zhu et al. [18] for the reductive coupling of nitroarenes over Au supported on  $ZrO_2$  under similar reaction conditions. The authors claimed that the reaction was driven exclusively by light and only a negligible reduction of nitrobenzene occurred over the Au/ $ZrO_2$  catalyst in the dark. Moreover, the catalytic effect was attributed to a surface plasmon resonance effect that requires Au nanoparticles of a 5–8 nm diameter. Our experiments showed that smaller Au nanoparticles (2–3 nm) are superior catalysts under both dark and day-light conditions.

Using optimum reaction conditions for the Au/HT and commercial Au/ $TiO_2$  catalysts, the synthesis of a range of substituted azoarenes was examined. The results presented in Table 2 demonstrate that the protocol can be successfully employed regardless of the presence of electron donating (**1d** and **e**) or withdrawing substituents (**1b**). In the latter case, the reaction of transfer hydrogenation was observed to be much slower. It is worth noting that, in contrast to nitro-substrates and azoxy-intermediates, most of azo-products are less soluble in 2-propanol. Once formed, they precipitate preventing further over-hydrogenation. Remarkably, the reductive coupling of nitrostyrene **1e** gives quantitatively 4,4'-divinylazobenzene **3e** which is of great industrial importance for the production of photo mobile polymer materials and azobenzene polymers [6, 7].

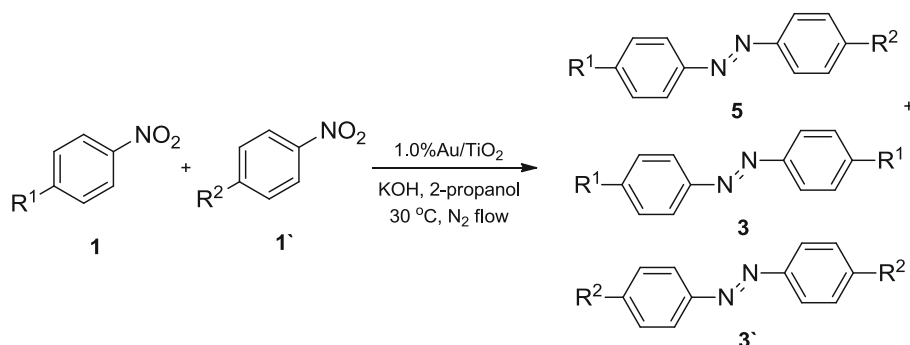
Asymmetric azoarenes are of great importance as fine chemicals. Conventionally, the synthesis of asymmetric azoarenes proceeds through the azo coupling, Mills or Wallach reactions [1]. In the case of the azo coupling, the diazonium salts used are unstable and thus strict control over the reaction temperature is necessary. In the Mills and

**Table 2** Catalytic synthesis of substituted azoarenes

Entry	<b>1</b>	–R	Catalyst	<i>t</i> (h)	Conv. (%)	Yield of <b>3</b> (%) <sup>a</sup>
1	<b>1a</b>	–H	1.3 % Au/HT	2.5	>99	>99
2			1.0 % Au/TiO <sub>2</sub>	3.0	>99	99
3	<b>1b</b>	–Cl	1.3 % Au/HT	8.5	>99	99
4			1.0 % Au/TiO <sub>2</sub>	24	>99	96
5	<b>1c</b>	–CH <sub>3</sub>	1.3 % Au/HT	3.0	99	97
6			1.0 % Au/TiO <sub>2</sub>	5.0	>99	97
7	<b>1d</b>	–OCH <sub>3</sub>	1.0 % Au/TiO <sub>2</sub>	5.0	>99	97
8	<b>1e</b>	<i>m</i> -CH=CH <sub>2</sub>	1.0 % Au/TiO <sub>2</sub>	6.0	>99	99

Reaction conditions: catalyst (Au: 1.0 mol %), nitroarene (1.5 mmol), KOH (0.5 mmol), 2-propanol (25 mL), N<sub>2</sub> flow (100 mL/min, STP) at 30 °C

<sup>a</sup> Yield of isolated product

**Table 3** Direct synthesis of asymmetrical azoarenes over Au/TiO<sub>2</sub>

Entry	Substrates	Ratio <b>1:1'</b>	<i>t</i> [h]	Yield (%) <sup>a</sup>			Conv. (%) <sup>a</sup>
				<b>5</b>	<b>3</b>	<b>3'</b>	
1		1:1	8.5	17	42	40	>99
2	R <sup>1</sup> = –H	2:1	6.0	19	56	22	98
3	R <sup>2</sup> = <i>p</i> -Cl	1:2	16.0	20	22	56	99
4 <sup>b</sup>		1:1	3.5	46	27	26	99
5	R <sup>1</sup> = –H	1:1	6.0	46	27	26	>99
6	R <sup>2</sup> = <i>p</i> -CH <sub>3</sub>	1.5:1	5.0	45	37	17	>99

Reaction conditions: catalyst (Au: 1.0 mol %), **1** (1.5 mmol), KOH (0.5 mmol), 2-propanol (25 mL), N<sub>2</sub> flow (100 mL/min, STP) at 30 °C

<sup>a</sup> Determined by GC using *n*-dodecane as internal standard

<sup>b</sup> Reaction at 50 °C with **1'** dosed drop-wise over 1.5 h

Wallach reactions, the synthesis of nitroso- and azoxybenzenes requires the use of oxidants or reducing reagents in stoichiometric or excess amounts and generates undesirable amounts of waste. Only a few attempts to synthesize catalytically asymmetric azoarenes directly from a mixture

of two nitroarenes have been reported in the open literature until now [14, 20].

Herein, we report an Au-based heterogeneous catalytic system for H<sub>2</sub>-free synthesis of asymmetrical aromatic azo-compounds directly from a mixture of corresponding

nitroarenes. Two asymmetrical azoarenes were synthesized with fair yields (Table 3). The cross coupling of nitroarenes with similar substituents (*i.e.* nitrobenzene and *p*-nitrotoluene, Table 3, entries 5–6) proceeds easily under the standard reaction conditions. In this case, the rates of consumption of the two substrates were observed to be close and the yield of an asymmetrical product does not depend on the initial molar ratio of the substrates.

In the case of nitroarenes with substituents of different nature (*i.e.* nitrobenzene and *p*-chloronitrobenzene), the substrates were observed to be consumed in succession. Nitrobenzene started to react only after the complete consumption of *p*-chloronitrobenzene, suggesting a much stronger adsorption of the latter on Au active sites. As a consequence, the yield of the asymmetrical azo-product was found to be low ~20 %, independently of the initial molar ratio of the substrates (Table 3, entries 1–3). In order to increase the yield of the target product, the reaction procedure was modified. In this case, at the beginning of the experiment only nitrobenzene was in the reaction mixture. *p*-Chloronitrobenzene was added to the mixture drop-wise during the first 1.5 h of the reaction maintaining its low instantaneous concentration. As a result, the yield of the asymmetrical azoarene increased more than 2.5-fold (Table 3, entries 4). These promising results open a new catalytic pathway for the catalytic production of asymmetric azo-compounds that circumvents the necessity to prepare anilines, diazonium salts, nitroso-derivatives or azoxy-compounds.

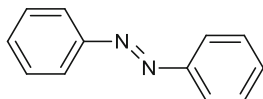
## 4 Conclusions

We have developed Au<sup>0</sup>-NPs based catalytic system to produce azoarenes in one-step directly from nitroarenes under mild, H<sub>2</sub>-free conditions using 2-propanol as solvent and reducing agent. The unique chemoselectivity over a range of functional groups (substituents), which did not undergo any transformation under reaction conditions and close to *quantitative* yields make this procedure promising for the production of symmetrical azoarenes.

The possibility to synthesize asymmetrical azoarenes directly from a mixture of corresponding nitroarenes was also demonstrated.

### 4.1 Analytical <sup>1</sup>H and <sup>13</sup>C NMR data

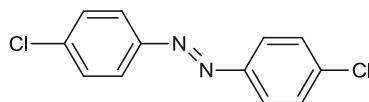
azobenzene (Table 1, entry 2):



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.96–7.94 (d, 4H), 7.56–7.47 (m, 6H);

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 122.98, 129.22, 131.11, 152.79.

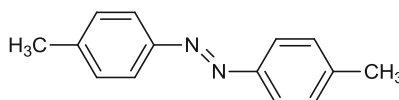
#### 4.1.1 1,2-bis(4-chlorophenyl)diazene (Table 2, entry 4)



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.88–7.85 (d, 4H), 7.50–7.48 (d, 4H);

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 124.34, 129.56, 137.39, 150.96.

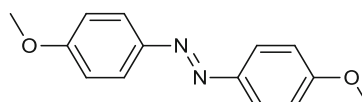
#### 4.1.2 1,2-dip-tolyldiazene (Table 2, entry 6)



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.84–7.82 (d, 4H), 7.33–7.31 (d, 4H), 2.44 (s, 6H);

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 21.63, 122.86, 129.85, 141.34, 150.98.

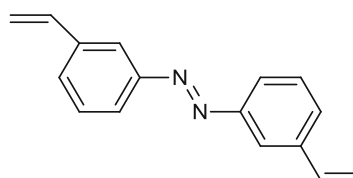
#### 4.1.3 1,2-bis(4-methoxyphenyl)diazene (Table 2, entry 7)



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.90–7.88 (d, 4H), 7.02–6.99 (d, 4H), 3.88 (s, 6H);

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 55.68, 114.29, 124.47, 147.21, 161.69.

#### 4.1.4 4,4'-divinylazobenzene (Table 2, entry 8)



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.99 (pseudo-s, 2H), 7.85–7.83 (d, 2H), 7.55–7.47 (m, 4H), 6.86–6.84 (d, 1H), 6.82–6.79 (d, 1H), 5.92–5.88 (d, 2H), 5.38–5.35 (d, 2H);

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 115.20, 120.71, 122.30, 128.92, 129.36, 136.32, 138.77, 152.99.

**Acknowledgments** The authors thank P. Abdulkin (University of Cambridge) for the participation in catalyst characterization and I. Cornu (EPFL, Lausanne) for the participation in experimental work. The financial support from the Swiss national Science Foundation is highly appreciated.

## References

1. Merino E (2011) *Chem Soc Rev* 40:3835–3853
2. Hunger K (2003) *Industrial dyes: chemistry, properties applications*. Wiley-VCH, Weinheim
3. Zollinger H (2003) *Color chemistry: synthesis, properties and applications of organic dyes and pigments*. Wiley-VCH, Weinheim
4. Merino E, Ribagorda M (2012) *Beilstein J Org Chem* 8:1071–1090
5. Hamon F, Djedaini-Pilard F, Barbot F, Len C (2009) *Tetrahedron* 65:10105–10123
6. Emoto A, Uchida E, Fukuda T (2012) *Polymers* 4:150–186
7. Yamada M, Kondo M, Mamiya J, Yu Y, Kinoshita M, Barrett CJ, Ikeda T (2008) *Angew Chem Int Ed* 47:4986–4988
8. Baer E, Tosoni AL (1956) *J Am Chem Soc* 7:2857–2858
9. Firouzabadi H, Mostafavipoor Z (1983) *Bull Chem Soc Jpn* 56:914–917
10. Orito K, Hatakeyama T, Takeo M, Uchiito S, Tokuda M, Sugimoto H (1998) *Tetrahedron* 54:8403–8410
11. Gorrane A, Corma A, García H (2008) *Science* 322:1661–1664
12. Zhang C, Jiao N (2010) *Angew Chem Int Ed* 49:6174–6177
13. Cai S, Rong H, Yu X, Liu X, Wang D, He W, Li Y (2013) *ACS Catal* 3:478–486
14. Hu L, Cao X, Chen L, Zheng J, Lu J, Sun X, Gu H (2012) *Chem Commun* 48:3445–3447
15. Hu L, Cao X, Shi L, Qi F, Guo Z, Lu J, Gu H (2011) *Org Lett* 13:5640–5643
16. Kim JH, Park JH, Chung YK, Park KH (2012) *Adv Synth Catal* 354:2412–2418
17. Corma A, Serna P (2006) *Science* 313:332–334
18. Zhu H, Ke X, Yang X, Sarina S, Liu H (2010) *Angew Chem Int Ed* 49:9657–9661
19. Brieger G, Nestrick TJ (1974) *Chem Rev* 74:567–580
20. Liu X, Ye S, Li HQ, Liu YM, Cao Y, Fan KN (2013) *Catal Sci Technol* 3:3200–3206
21. Cavani F, Trifiro F, Vaccari A (1991) *Catal Today* 11:173–301
22. Gaur S, Wu H, Stanley GS, More K, Kumar CSSR, Spivey JJ (2013) *Catal Today* 208:72–81
23. Aghaei P, Berger RJ (2013) *Appl Catal B* 132–133:195–203
24. Walther G, Mowbray DJ, Jiang T, Jones G, Jensen S, Quaade UJ, Horch S (2008) *J Catal* 260:86–92
25. Abad A, Concepcion P, Corma A, Garcia H (2005) *Angew Chem Int Ed* 44:4046–4049
26. Nougima A, Mitsudome T, Mizugaki T, Jitsukawa K (2011) *Kaneda K Molecules* 16:8209–8227
27. Shang C, Liu ZP (2011) *J Am Chem Soc* 133:9938–9947
28. Haber F (1898) *Z Elektrochem* 4:506–514