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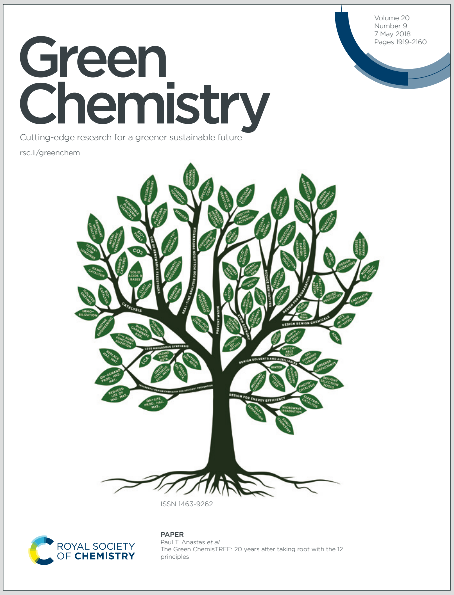

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ARTICLE

Tandem Selective Reduction of Nitroarenes Catalyzed by Palladium Nanoclusters

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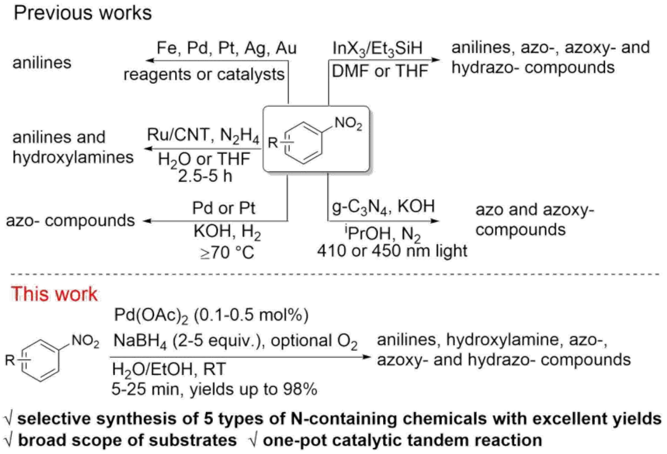
We report a catalytic tandem reduction of nitroarenes by sodium borohydride ($NaBH_4$) in aqueous solution at ambient conditions, which can selectively produce five categories of nitrogen-containing compounds: anilines, N-aryl hydroxylamines, azoxy-, azo- and hydrazo- compounds. The catalyst is the *in situ*-generated ultrasmall palladium nanoclusters (Pd NCs, diameter of 1.3±0.3 nm) from the reduction of $Pd(OAc)_2$ by $NaBH_4$. These highly active Pd NCs are stabilized by the surface-coordinated nitroarenes, which inhibit the further growth and aggregation of Pd NCs. By controlling the concentration of $Pd(OAc)_2$ (0.1-0.5 mol% of nitroarene) and $NaBH_4$, the water/ethanol solvent ratio and the tandem reaction sequence, each of the five categories of N-containing compounds can be obtained with excellent yields (up to 98%) in less than 30 min at room temperature. This tunable catalytic tandem reaction works efficiently with a broad range of nitroarene substrates, which offers a green and sustainable method for rapid and large-scale production of valuable N-containing chemicals.

Introduction

The selective reduction of nitroarenes can produce different N-containing compounds, such as anilines, hydroxylamines, nitroso-, azoxy-, azo- and hydrazo- compounds.[1] Many of these N-containing compounds are vital intermediates for the synthesis of organic dyes, food additives, agrochemicals, pharmaceuticals and functional materials[2-11]. Conventional reduction of nitroarenes are achieved by metal reduction at acidic conditions, which generates large amounts of by-products and waste acids. To overcome these issues, catalytic reduction of nitroarenes has been developed with transition metal catalysts in various hydrogenation systems[12-19]. Many efficient catalysts based on Fe[20], Co[21], Ni[22-24], Pd[25-27], Pt[28-30], Ru[31-33], Ag[34, 35] or Au[36-40] have been developed for selective reduction of nitroarenes to desired N-containing compounds. However, the applications of these catalytic reactions are limited because of 1) the usage of large amounts of expensive noble-metal catalysts; 2) the employment of toxic and/or hazardous reagents; 3) the request of harsh reaction conditions and tedious work-up process. Therefore, the development of green and sustainable catalytic reduction of nitroarenes represents a challenging task for both catalysis and organic synthesis.

Since the reduction of nitroarenes is typically a tandem reaction, selectivity has also become an urgent issue. Most of nitro-reduction methods are developed to produce aniline, the fully reduced product. As shown in Scheme 1, only a few reports are available for the selective synthesis of partially reduced products by nitroarene reduction, such as hydroxylamine, azoxy- and azo- aromatic compounds. For instance, Garcia and Cao used Au catalysts to reduce nitroarenes into azo- compounds[36, 39], which requires high reaction temperature, and pressured hydrogen as the reducing agent. Konakahara used InX_3/Et_3SiH reduction system to selectively produce four partially reduced products from nitroarene[41]. Su presented a photocatalytic strategy for the synthesis of azoxy- and azo- compounds under visible light irradiation[42]. Gu used Pd[26, 27] and Pt[29] nanoparticles to



Scheme 1. Synthetic methods for partial reduction of nitroarenes.

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Electronic Supplementary Information (ESI) available: details of reaction conditions and characterization data. See DOI: 10.1039/x0xx00000x catalytically reduce nitroarenes to azo- compounds, which needs high reaction temperature, pressured hydrogen and corrosive strong base. Although significant progress has been made toward the selective catalytic reduction of nitroarenes, these reactions usually need harsh reaction conditions (such as high pressure, high temperature, corrosive or toxic reagents) and long reaction time.

Recently, Pd nanoclusters (Pd NCs) with diameter less than 2 nm have attracted much attentions.[43-46] Owing to the quantum size effect, these ultrasmall Pd NCs show distinct catalytic properties as compared to larger Pd nanoparticles.[43] However, these ultrasmall Pd NCs are quite unstable, which have to be stabilized by either thiolate ligands[45, 46] or being caged in a porous structure, such as metal-organic frameworks.[43, 44] Since sulfur is generally a poison to many noble-metal catalysts, the thiolate ligands would significantly reduce the catalytic activity of ultrasmall Pd NCs.

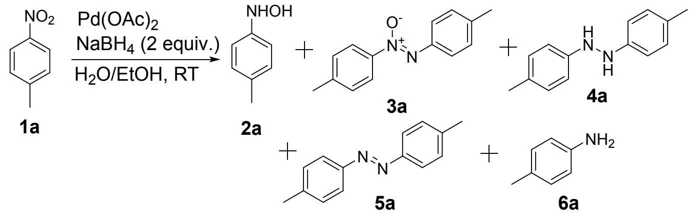
Herein, we report a catalytic tandem reduction approach to conveniently and selectively convert nitroarenes into five categories of products: anilines, hydroxylamines, azoxy-, azo- and hydrazo- compounds. With $NaBH_4$ as the reducing agent, the selective reduction of nitroarene is catalyzed by *in situ* generated ultrasmall Pd NCs from $Pd(OAc)_2$. Without using any additional ligands, these ultrasmall Pd NCs (diameter of 1.3±0.3 nm) are stabilized by surface-coordinating nitroarenes and well-dispersed in the reaction solution. By controlling the concentration of $Pd(OAc)_2$ (0.1 or 0.5 mol% of nitroarene) and $NaBH_4$, water/ethanol solvent ratio and reaction sequence, each of the five reduction products can be acquired with excellent yields (up to 98%) in less than 30 min at room temperature.

Results and discussion

The catalytic reduction of nitroarenes was studied using *p*-nitrotoluene (**1a**) as the model substrate. Briefly, 1 mmol nitrotoluene was dissolved in 10 mL water/EtOH mixture. $NaBH_4$ solid was added to the mixture as reducing agent. Then, $Pd(OAc)_2$ was dissolved in a minimum amount of CH_2Cl_2 and added to the mixture. The reaction conditions were optimized by changing the concentration of $Pd(OAc)_2$ and $NaBH_4$, the ratio of water and ethanol as the solvent, and the reaction time and sequence. Table 1 shows the yield of the corresponding hydroxylamine, aniline, azoxy-, azo-, and hydrazo- compounds at different reaction conditions. According to the result, the reduction reaction is significantly solvent-directed: the reduction of **1a** to hydroxylamine (**2a**) gave almost no conversion in EtOH (entry 1); whereas, 60% conversion was achieved in a $V_{water} : V_{EtOH} = 1:3$ mixture (entry 2), which indicates that the ratio of water and EtOH exerts crucial impact on the reaction. To improve the conversion of **1a** to **2a**, the ratio of water was further increased. When the volume ratio of water and EtOH was 2:3, **1a** was completely converted and afforded **2a** in a yield of 85% in 10 min (entry 3). Surprisingly, when the reaction time was shortened to 5 min, **2a** was obtained with a higher yield of 97% (entry 4), which could be because of the minimized oxidation of **2a**. Further increasing the percentage of water ($V_{water} : V_{EtOH} = 1:1$) decrease the yield of **2a**, and a small amount of 4,4'-dimethylazoxybenzene (**3a**) was discovered (entry 5). When **2a** in solution is exposed to air, **2a** can be slowly oxidized to **3a** (entry 6). To speed up the oxidation, we use O_2 to oxidize **2a**. When the **2a** solution is stirred under O_2 atmosphere for 3 min, pure **3a** was conveniently obtained with 92% yield (entry 7) as a precipitate by filtration and washing.

In the mixture of **3a** product and Pd NCs catalyst, additional reducing agent $NaBH_4$ (3 mmol.) and solvent MeOH was added. **3a** can be dissolved with the help of MeOH and rapidly reduced to give 4,4'-dimethylhydrazobenzene (**4a**) (entry 8). Since hydrazobenzene is easily oxidized to form azobenzene under air during the work-up process, **4a** was obtained in a slightly lower isolate yield (85%) and the corresponding azobenzene **5a** was

Table 1. Optimization of reaction conditions[a].



Entry	H$_2$O/EtOH (ml/ml)	Pd(OAc)$_2$ (mol %)	Total time (min)	Conv. (%)	Selectivity[%][b]				
					2a	3a	4a	5a	6a
1	0/10.0	0.1	20	10	trace	-	-	-	-
2	2.5/7.5	0.1	20	60	50	trace	-	-	-
3	4.0/6.0	0.1	10	100	85	10	-	-	-
4	4.0/6.0	0.1	5	100	97	-	-	-	-
5	5.0/5.0	0.1	5	100	85	trace	-	-	-
6[c]	4.0/6.0	0.1	8	100	50	40	-	trace	-
7[d]	4.0/6.0	0.1	8	100	-	92	-	trace	-
8[e]	4.0/6.0	0.1	20	100	-	-	85	14	-
9[f]	4.0/6.0	0.1	25	100	-	-	-	97	-

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10	7.5/2.5	0.1	5	100	50	10	-	-	37
11	7.5/2.5	0.5	5	100	-	-	-	-	98

[a] Condition: **1a** (1.0 mmol), $Pd(OAc)_2$ (0.1 or 0.5 mol%), $NaBH_4$ (2.0 mmol) in solvent(10 ml), RT. [b] all the yields are isolation yields. [c] Under air. [d] O_2 is bubbled into solution for 3 min. [e] $NaBH_4$ (3.0 mmol) and MeOH (10 ml) were added and reacted for 12 min. **4a** is easily oxidized to **5a** during purification. [f] O_2 is bubbled into solution to oxidize **4a** to **5a**.

obtained in 14% yield. Inspired by this rapid oxidation process, **5a** was conveniently obtained in 97% yield by the oxidation of **4a** in the reaction system by using O_2 (entry 9).

When the percentage of water was further increased to V_{water} : V_{EtOH} = 3:1, the Pd-catalytic reduction of **1a** is faster, with 100% conversion achieved in 5 min, but the selectivity is poor (entry 10). **2a**, **3a** and **6a** (p-methylaniline) were obtained with 50%, 10% and 37% yield, respectively. However, when the amount of $Pd(OAc)_2$ was increased to 0.5 mol% of **1a**, the fully reduced product **6a** can be obtained with excellent yield (98%) in 5 min (entry11).

After the optimization of reduction conditions, we have achieved the selective reduction **1a** to N-aryl hydroxylamine with solvent ratio of V_{water} : V_{EtOH} = 2:3. Then N-aryl hydroxylamine can be oxidized by O_2 to form azoxy compound, followed for the Pd-catalyzed reduction of azoxy compound to hydrazo compound, and finally oxidized by O_2 to form azo compound. The conversion from nitroarenes to the final azo compound can be achieved in 25 min with 97% yield at the presence of only 0.1 mol% of in-situ generated Pd NCs as the catalyst. Surprisingly, the activity of Pd NCs is well preserved during the two oxidation steps using O_2 as the oxidant. To prepare the fully reduced product: aniline, we just need to change the solvent ratio to V_{water} : V_{EtOH} = 3:1 and increase the usage of $Pd(OAc)_2$ to 0.5 mol% of nitroarene. With this more polar solvent mixture and higher concentration of Pd NCs, the nitroarene would be quickly and completely reduced to aniline.

Pd-based nanomaterials have been utilized as catalysts for the reduction of nitroarenes.[26, 27] In the pioneer works by Gu, worm-like aggregates of Pd nanoparticles were prepared separately and then added to the reaction mixture. These large aggregates would form black precipitate, which hinders their catalytic activity. In our case, when the $Pd(OAc)_2/CH_2Cl_2$ solution was added into the mixture containing nitroarene and $NaBH_4$, the colour of the solution quickly turned into brown, indicating the formation of Pd NCs.[45, 46] However, during the whole reaction process, there was no formation of Pd black precipitate. We hypothesize that the nitro group of nitroarenes can coordinate to the surface of new-born Pd NCs and inhibit their further growth (Figure 1a). To probe this hypothesis, we took the high-resolution transmission electron microscopy (HR-TEM) image of the brown colour reaction mixture (Figure 1b), which showed crystalline nanoclusters with the diameter around 1-2 nm. The well-resolved lattice fringe of 0.21 nm corresponds to the Pd (111) fringe.[47] In another TEM image, a large number of well-separated Pd NCs were observed (Figure 1c). The statistical analysis result of these Pd NCs shows the average diameter is 1.3±0.3 nm (Figure 1d), which indicates a quite uniform size distribution. When we used 4-nitrobenzoic acid as the reactant, the in-situ generated Pd NCs with 4-nitrobenzoic acid as surface ligands can be easily precipitated by adjusting the solution to acidic (pH≈2). These dark brown color solid could be washed by water to remove excess 4-nitrobenzoic acid, then dissolved in ethanol to give a brown-color clear solution (Figure 1e, insert picture). This solution was studied by using dynamic light scattering (DLS, Figure 1e), which also confirmed the uniform size distribution of Pd NCs in solution. The measured average hydrodynamic diameter of Pd NCs was 6.5 nm, which is bigger than the diameter measured by TEM. This is because the diameter on TEM shows only the palladium core of Pd NCs. The hydrodynamic diameter is the size of palladium core plus the 4-nitrobenzoic acid ligand layer and also the solvating layer, which should be significantly bigger. We also measured the UV-vis spectrum of the Pd NCs solution and compared with that of the

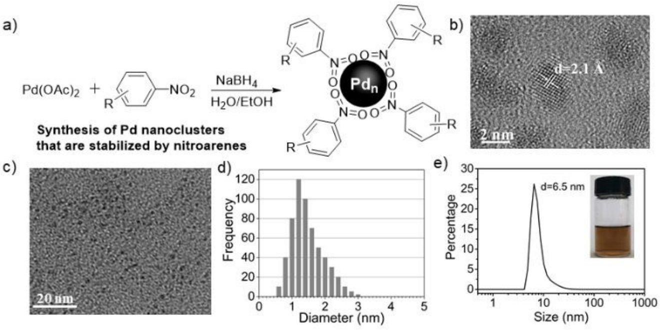
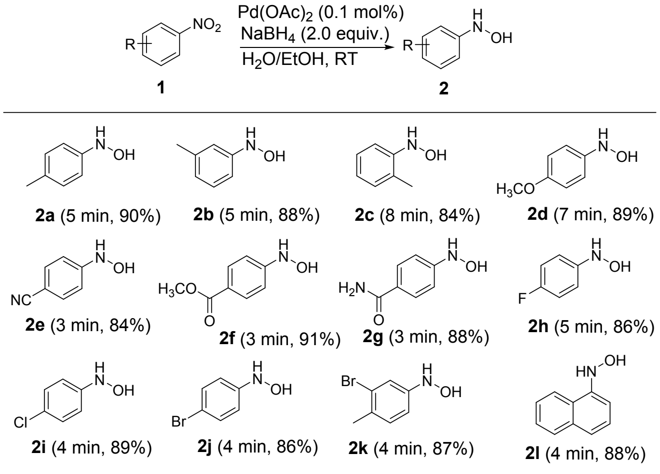


Figure 1. Characterization of Pd NCs. a) In-situ formation of Pd NCs. b) High-resolution TEM image of Pd NCs showing the crystalline structure of Pd NCs. c) A typical TEM image and d) size distribution of Pd NCs. e) Picture (insert) and the hydrodynamic diameter of Pd NCs in an ethanol solution.



Scheme 2. Synthesis of hydroxylamines **2**. Reaction condition: nitroarene (1.0 mmol), $Pd(OAc)_2$ (0.1 mol%), $NaBH_4$ (2.0 mmol), water/EtOH (4 ml/6 ml), stirring at RT for indicated time in the parentheses. all the yields are isolation yields.

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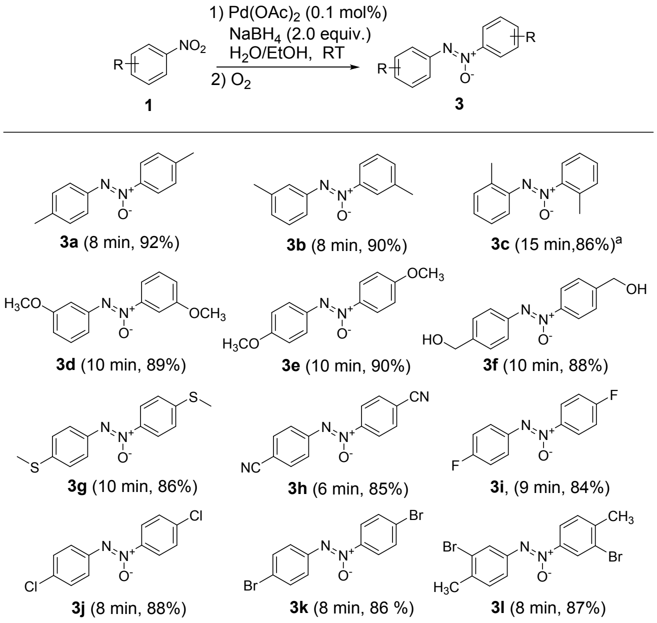
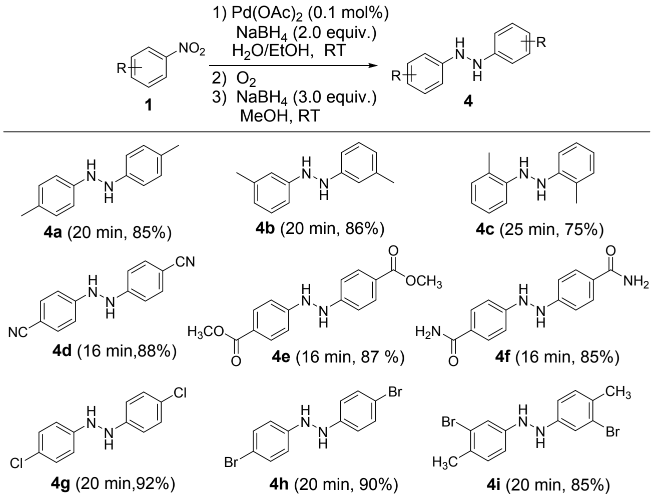
4-nitrobenzoic acid ligand (Figure S1). By adjusting the concentrations, the two spectra coincide with each other in the <300 nm wavelength range. However, in the 300-500 nm range, the absorption of Pd NCs solution is much higher than that of 4-nitrobenzoic acid solution, which agrees well with the reported absorption spectrum of ultrasmall Pd NCs.[44] With these characterization data, we have demonstrated the *in situ* formation of uniform Pd NCs in the reaction solution, which are stabilized by the surface coordinated nitroarenes.

With these optimized reaction conditions in hand, we have explored the substrate scope of this one-pot reduction method. We firstly examined the synthesis of N-aryl hydroxylamine derivatives from nitroaromatic compounds (Scheme 2). We found that the substituted position (*para*-, *meta*- and *ortho*-) of alkyl group had little effect on the reaction (**2a**-**2c**). Both electron-donating groups (such as methoxy group, **2d**) and electron-withdrawing groups (cyano, ester and amide groups, **2e**-**2g**) are also well-tolerated in the reduction reaction, and provide expected products with high yield (84-91%). In addition, F-, Cl- and Br- substituents are also adequately tolerated, which were efficiently converted to the corresponding products (**2h**, **2i**, **2j** and **2k**) in high yields (86-89%), with no dehalogenation products. However, I- substituent on aromatic ring would be reduced to H. We have also tried 1-nitro-naphthalene, which can also be rapidly reduced to the corresponding hydroxylamine with a high yield of 88% (**2l**). It is worthy noted that the hydroxylamine products with electro-withdrawing groups on the aromatic ring (**2e-2g**) are more resistant to air oxidation than those with electro-donating groups (**2a-2d**). The dimeric azoxy- compounds can slowly formed from the oxidation of **2a-2d** by air, which slowly turned from white solid to yellow color.



Scheme 3. Synthesis of azoxy- compounds **3**. Reaction condition: nitroarene (1.0 mmol), $Pd(OAc)_2$ (0.1 mol%), $NaBH_4$ (2.0 mmol), water/EtOH (4 ml/6 ml), stirring at RT for 5 min. Then O_2 is bubbled into the solution for 3-5 min. The total reaction time is indicated in the parentheses. All the yields are Isolation yields. [a] Stirring at RT for 10 min. Then O_2 is bubbled into the solution for 5 min.

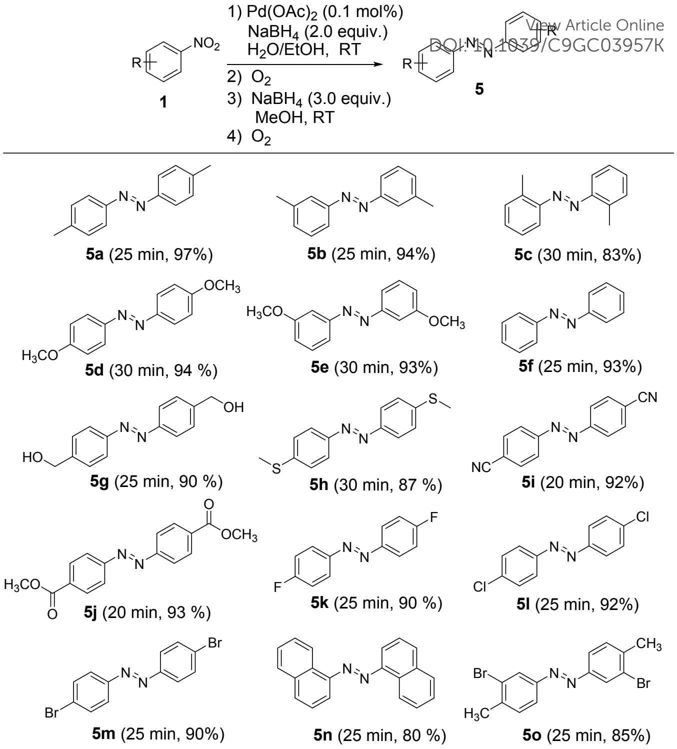


Scheme 4. Synthesis of hydrazo- compounds **4**. Reaction condition: nitroarene (1.0 mmol), $Pd(OAc)_2$ (0.1 mol%), $NaBH_4$ (2.0 mmol), water/EtOH (4 ml/6 ml), stirring at RT for 5-10 min, then input O_2 for 5 min, then $NaBH_4$ (3.0 mmol) and MeOH (10 ml) were added, stirring at RT for 5-15 min. The total reaction time is indicated in the parentheses. All the yields are isolation yields.

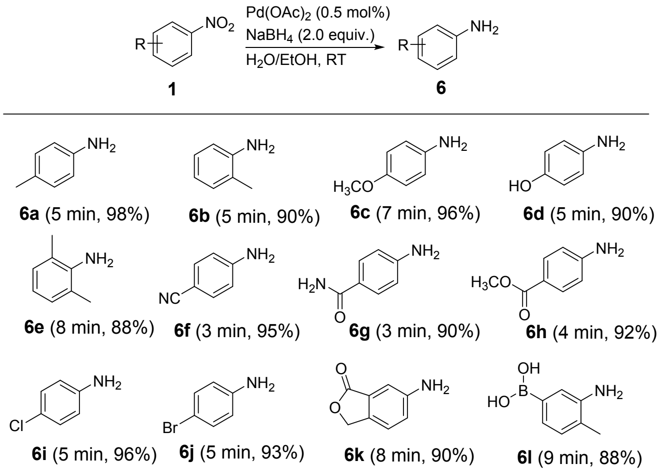
We next investigated the scope of controllable conversion of various nitroarenes into azoxy-compounds (Scheme 3). After the fast reduction of nitroarenes to N-aryl hydroxylamines, without isolation, the N-aryl hydroxylamines **2** are rapidly oxidized by O_2 to form corresponding azoxybenzenes **3,** which precipitate out as a solid after poured into a large amount of water. The alkyl group substituted position (*para*-, *meta*- and *ortho*-) has little effect on the reaction (**3a**-**3c**). Electron-donating groups (**3d**-**3f**), electron-withdrawing groups (**3h**) and halogen groups (**3i**-**3l**) are also well-tolerated in the reactions, and provide expected products with high yield (85-90%). Particularly, 4-nitrothioanisole is a highly challenging substrate for Pd-catalyst, since the thiolether may coordinate with Pd and inactivate the catalyst. However, the desired azoxy-compounds (**3g**) was successfully obtained in good yield (86%). It is likely that the coordinating affinity of thioether to Pd catalyst is reduced by the electro-withdrawing nitro and azoxy groups.

To dissolve the azoxy- products, additional 10 mL MeOH was added to the 10 mL water/EtOH (2:3) solution. Then, 3 mmol $NaBH_4$ solid was added. The azoxy products 3 are catalytically reduced to form hydrazo- products (Scheme 4). The alkyl substitution at the *para*-, *meta*- position (**4a**-**b**) shows little effect on the reaction. At ortho- position (**4c**), the yield (75%) was lower than the para- and meta- analog (~85%), which could be due to the steric hindering of the two ortho alkyl groups. Electron-withdrawing groups (**4d**), electron-donating groups (**4e**-**3f**), and halogen groups (**4g**-**4i**) are also well-tolerated in the reactions, and provide expected products with high yield (85-92%). Particularly, it is noteworthy that hydrazo-compounds with electro-withdrawing groups are quite stable under air at room temperature.

These results revealed above prompted us to test the selective preparation of azo-aromatic compounds by oxidizing the hydrazo- compounds using O_2, as summarized in Scheme 5. The azo-aromatic compounds are readily obtained after 10-min oxidation by O_2, which precipitate out as a solid after poured into a large amount of water. Again, the alkyl group substituted position (*para*-, *meta*- and *ortho*-) has little effect on the reaction (**5a**-**5c**). Both electron-donating, electron-withdrawing groups such as methoxy, hydroxymethyl, methanethiol, cyano, ester and halogen, are well tolerated, with good to excellent yields (83-97%). In addition, the azo-compound containing two naphthalene ring was also obtained in a good yield of 80% (**5n**), which was rarely reported in the literature. Previous reports use palladium[26, 27] and platinum[29] nanosticks to catalyze the reduction of nitroarene to azo-products, which request stoichiometric strong bases (KOH), high temperature (~100°C) and long reaction time (several hours). In contrast, we can achieve this conversion rapidly (less than 30 min) under very mild condition (room temperature, no need of acid or base as additives).



Scheme 5. Synthesis of azo- compounds **5**. Reaction condition: nitroarene (1.0 mmol), $Pd(OAc)_2$ (0.1 mol%), $NaBH_4$ (2.0 mmol), water/EtOH (4 ml/6 ml), stirring at RT for 5 min. Then O_2 is bubbled into the solution for 3-5 min. Then $NaBH_4$ (3.0 mmol) and MeOH (10 ml) were added, stirring at RT for 5-10 min. Finally, O_2 is bubbled into the solution for 5-10 min. The total reaction time is indicated in the parentheses. All the yields are isolation yields.

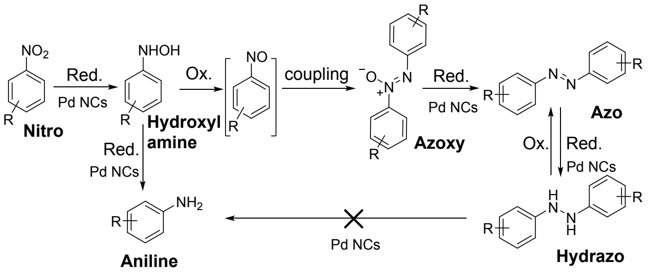


Scheme 6. Synthesis of anilines **6**. Reaction condition: nitroarene (1.0 mmol), $Pd(OAc)_2$ (0.5 mol%), $NaBH_4$ (2.0 mmol), water/EtOH (7.5 ml/2.5 ml), stirring at RT for indicated time in the parentheses. All the yields are isolation yields.

Finally, we have examined the scope of reduction of nitroarenes into anilines, as showed in Scheme 6. By increasing the solvent polarity (changing the V_{water} : V_{EtOH} ratio from 2:3 to 3:1) and increasing the usage of $Pd(OAc)_2$ from 0.1 mol% to 0.5 mol%, nitroarenes can be quickly and completely reduced to aniline in less than 10 min at room temperature. Hydroxyl-amines can be detected as the intermediate. In most of tested entries, the aniline products can be obtained as pure compound just by extraction with dichloromethane or ethyl acetate, without using column separation. This reaction condition is highly efficient for the synthesis of aniline derivatives, regardless of the presence of electronic-donating (**6a**-**6d**) or electron-withdrawing groups (**6f**-**6h**). From the sterically hindered 2,6-dimethylnitrobenzene substrate, 2,6-dimethylani-line (**6e**) was obtained with a good yield (88%). Halogen-substituted nitrobenzenes, which may undergo dehalogenation[25] during the reduction of nitro groups, were well preserved in the corresponding chloro- or bromoanilines (**6i**, **6j**) exmaples. Moreover, 4-chloroaniline is a crucial ingredient for the synthesis of an antimalarial drug, paludrine[48].

Lactone with nitro- group was also examined, providing the expected 6-aminophthalide in 90% yield (**6k**). **6K** is one key intermediate for the synthesis of inhibitors of B-RAF, a serine/threonine kinase[49]. In addition, the highly active boronate $–B(OH)_2$ group is also well preserved during the selective reduction of nitro group, which provides the corresponding amino-phenylboronic acid compound (**6l**). The successful preservation of halogen and $–B(OH)_2$ groups in these reduction reactions also suggests that the surface of Pd NCs is preferred coordinated by the nitro group, rather than the halogen and $–B(OH)_2$ groups.

To further verify the effectiveness of the present reduction system, a 50 mmol scale reduction of **1a** (6.85 gram) was carried out. The nitroarene **1a** could afford separately the corresponding N-aryl hydroxylamines, azoxy-, hydrazo-, azo-derivatives and anlines in 88%, 90%, 82%, 92%, 94% yield, respectively (Scheme S1-S5), implying the potential application for large scale synthesis of valuable N-containing chemicals. We also tested the recyclability of the Pd NC catalysts. The Pd NCs can be easily recycled by centrifuge and reused up to five cycles. To evaluate catalytic activity of the recycled Pd NCs, the hydrogenation reaction of **1a** converted toward **3a** was performed (see SI, Table S1). During the centrifuge of Pd NCs, the size of Pd NCs increased from 1-2 nm to 3-5 nm because of aggregation (Figure S2), and the catalytic activity of Pd NCs slightly decreased. However, we can still get good yields (~ 90%) by extend the reaction times (from 8 min to 15 min) and change the solvent ratios (from water/EtOH = 4:6 to water/EtOH = 5:5), as shown in Table S1.



Scheme 7. Proposed pathways for the reduction of nitroarenes to the corresponding fully and partially reduced N-containing products.

Based on previous mechanistic studies[39, 50, 51] for nitro group reduction, a plausible pathway of our Pd NCs catalytic system is described in Scheme 7. With a low catalyst concentration (0.1 mol% $Pd(OAc)_2$), hydroxylamine is formed by reduction of nitroarene, which can be readily oxidized under aerobic atmosphere to form nitroso intermediate and coupled to give azoxy-compound.[29] Azoxy-compound can be catalytically reduced to form azo- compound, and further reduced to hydrazo- compound. Hydrazo- compound are easily oxidized to azo- compound under air, especially for the hydrazo-compounds with electron-donating groups. We have also observed that hydrazo compounds cannot be reduced to aniline in our conditions. To produce aniline, a higher concentration of catalyst (0.5 mol% $Pd(OAc)_2$) and a more polar solvent mixture are required, which enable the quick reduction of nitroarene to aniline with hydroxylamine as the detectable intermediate. During the tandem reactions, Pd NCs are stabilized by either the nitroarenes or the formed azoxy- or azo- compounds.

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Conclusions

In conclusion, we have developed an efficient synthesis method to selectively produce five categories of N-containing compounds by the catalytic tandem reduction of nitroarenes with $NaBH_4$ as the convenient reducing agent, in aqueous solution at room temperature. These tandem reactions are catalyzed by the in-situ generated Pd NCs from the low-cost $Pd(OAc)_2$ precursor reduced by $NaBH_4$. The *in situ* generated Pd NCs are surface coordinated by nitroarenes, which prevent the further growth and aggregation of Pd NCs. Therefore, these separated ultrasmall Pd NCs show much higher catalytic activity than those aggregated or substrate-supported Pd nanomaterials. The latter catalysts usually require higher temperature, longer reaction period, and/or higher catalysts concentration to achieve the reduction of nitroarenes.[26, 27] Besides the high catalytic activity and broad scope of substrates, our Pd NCs catalysis system also exhibits many environment-friendly and energy-efficient features, including the usage of aqueous solvents, short reaction period at room temperature to reduce energy input, and simple separation process with minimum usage of column separation. The Pd NCs can also be reused for up to 5 times with well retained activity. These features enable this green and sustainable reaction attractive for large-scale preparation of valuable N-containing chemicals.

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements

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