Catalysis Science & Technology

PAPER

View Article Online
View Journal

Cite this: DOI: 10.1039/c5cy02159f

Magnetic nanoparticle-supported phosphine gold(I) complex: a highly efficient and recyclable catalyst for the direct reductive amination of aldehydes and ketones†

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Received 13th December 2015,
Accepted 6th February 2016

DOI: 10.1039/c5cy02159f

www.rsc.org/catalysis

The direct reductive amination of aldehydes and ketones has been achieved in dichloromethane at room temperature by using a magnetic nanoparticle-supported phosphine gold(I) complex [Fe_3O_4@SiO_2-P–AuCl] as the catalyst and ethyl Hantzsch ester as the hydrogen source, yielding a variety of secondary amines in excellent yields under neutral conditions. The new heterogeneous gold catalyst can be prepared by a simple procedure from commercially readily available reagents and can easily be separated from the reaction mixture by applying an external magnet and recycled at least 10 times without any loss of activity.

Introduction

Amine functionality plays a vital role in organic chemistry due to its prominence in natural products, pharmaceuticals and agrochemicals.[1] Direct reductive amination of carbonyl compounds, mostly aldehydes or ketones, with primary or secondary amines is one of the most attractive methods for the synthesis of substituted amines.[2] This is particularly advantageous because the carbonyl compound and the amine with a suitable chemoselective reducing agent are treated in a one-pot fashion such that the isolation of the intermediary imine or iminium is avoided. So far, there have been many reagents developed to effect the direct reductive amination of carbonyl compounds, including active borane,[3] tin,[4] indium[5] and iridium[6] compounds. Recently, direct one-pot reductive amination of aldehydes with anilines or nitroarenes promoted by heterogeneous palladium catalysts has also been reported.[7] Although these methods are encouraging, most of them have some drawbacks in one or another respect, such as acidic conditions, limited substrate scope, excess amount of reagents, poor stability and toxic by-products. Therefore, the development of an alternative method that employs simple and mild as well as environmentally benign conditions is highly desirable.

The past decade has witnessed a dramatic growth in reports on organic transformations catalyzed by gold complexes owing to their unique reactivity as soft and carbophilic Lewis acids.[8] Reactions catalyzed by gold generally proceed under facile conditions with high yields and chemoselectivity without the exclusion of water and oxygen. To date, gold-catalyzed carbon–carbon[9] and carbon–heteroatom[10] bond formation reactions and oxidation[11] and reduction[12] reactions have successfully been applied in organic synthesis. However, the industrial applications of these homogeneous gold catalysts remain a challenge because they are quite expensive, cannot be recycled, and are difficult to separate from the product mixture, which is a particularly significant drawback for their application in the pharmaceutical industry. In contrast, heterogeneous catalysts have received more and more attention because of the advantages of high catalytic efficiency and easy recycling, which are important for precious metal catalyst and flow chemistry processes.[13] Although gold nanoparticles supported on different matrices have been widely used as heterogeneous catalysts in recent years,[14] little progress has been made on the supported gold complex-catalyzed reactions so far.[15] Recently, magnetic nanoparticles have emerged as smart and promising supports with great industrial potential for immobilization because the magnetic nanoparticle-supported catalysts can easily be separated from the reaction mixture by using an external magnet, which prevents loss of catalyst and improves the reusability.[16] During recent years, magnetic nanoparticle-supported palladium,[17] ruthenium,[18] rhodium,[19] and copper[20] complexes have been prepared and successfully used in some organic reactions. However, to the

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c5cy02159f

best of our knowledge, no example of a magnetic nanoparticle-supported gold complex has been reported until now.

Cao *et al.* have reported that supported gold nanoclusters are efficient heterogeneous catalysts for transfer hydrogenation.[21] Bao and co-workers have described a chemoselective reduction of imines in the coexistence of aldehydes using the nanoporous gold skeleton (AuNPore) catalyst.[12a] In addition, Hantzsch ester 1,4-dihydropyridine (HEH), which is a safe, easy-to-handle and commercially available reagent, has been widely used as a reducing agent in organic synthesis.[22] In continuing our efforts to develop economical and eco-friendly synthetic pathways for organic transformations,[23] we here report the first synthesis of magnetic nanoparticle-supported phosphine gold(I) complex and its successful application to the direct reductive amination of aldehydes or ketones with amines using inexpensive ethyl Hantzsch ester as the hydrogen source. The new heterogeneous gold catalyst exhibits excellent catalytic activity in the reaction under mild reaction conditions and can easily be separated from the reaction mixture with the simple application of an external magnetic field, and its catalytic efficiency remains unaltered even after recycling ten times.

Results and discussion

The magnetic nanoparticle-supported phosphine gold(I) complex was synthesized according to the procedure summarized in Scheme 1. Firstly, Fe_3O_4 nanoparticles were coated with a thin layer of silica through a sol–gel process using $Si(OEt)_4$ as the silica source and aqueous NH_3 as the hydrolyzing agent to give silica-coated Fe_3O_4 (Fe_3O_4@SiO_2). The latter was treated with commercially available 2-(diphenylphosphino)-ethyltriethoxysilane in toluene under reflux for 24 h to afford the phosphino-functionalized magnetic nanoparticles (Fe_3O_4@SiO_2-P); the phosphine content was determined to be 0.44 mmol g^{-1} by elemental analysis. The supported gold(I) complex (Fe_3O_4@SiO_2-P–AuCl) was obtained by the reaction of AuCl with Fe_3O_4@SiO_2-P in methanol at 65 °C with a loading of 0.39 mmol of gold per gram as determined by ICP-AES.

The transmission electron microscopy (TEM) image showed that the diameter of the complex was approximately

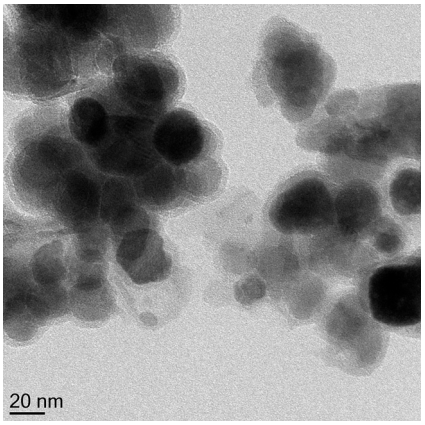
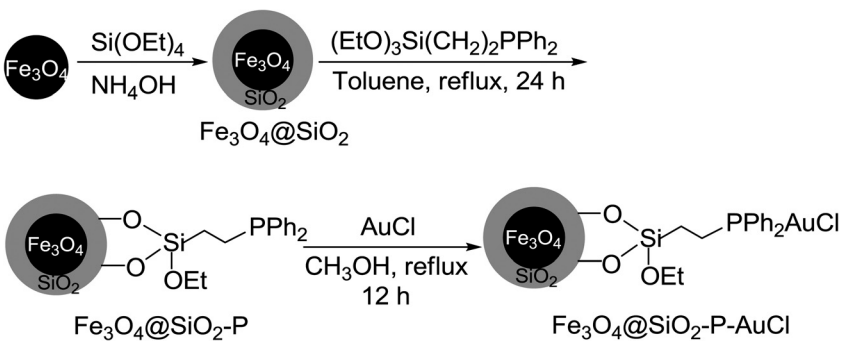


Fig. 1 TEM image of Fe_3O_4@SiO_2-P–AuCl catalyst.

30 nm (Fig. 1). X-ray diffraction (XRD) and energy dispersive spectroscopy (EDS) were also used to characterize the supported phosphine gold(I) complex. Fig. 2 shows the XRD spectra of Fe_3O_4@SiO_2 and Fe_3O_4@SiO_2-P–AuCl complex. The XRD pattern of Fe_3O_4@SiO_2 exhibits diffraction peaks corresponding to a typical spinel maghemite structure, whereas the diffraction peak of the layered amorphous silica was not obvious. The XRD pattern of Fe_3O_4@SiO_2-P–AuCl complex obviously shows two sets of diffraction peaks; the new peaks that appeared at 2θ = 38.3°, 44.4° and 64.5° are attributed to the (111), (200) and (220) reflections of the Au species, respectively. The results from XRD imply that the Au complex has been successfully immobilized on the surface of MNPs. Energy dispersive X-ray spectroscopy (EDS) shows the elements present in the material. EDS analysis of fresh Fe_3O_4@SiO_2-P–AuCl complex shows the presence of Si, O, C, P, Cl, Fe, and Au elements (Fig. 3).

The magnetically separable nanocomposite Fe_3O_4@SiO_2-P–AuCl was then used as the catalyst for the direct reductive amination of aldehydes and ketones with amines using ethyl Hantzsch ester as the hydrogen source. Initial experiments with benzaldehyde (**1a**) and benzenamine (**2a**) were performed to optimize the reaction conditions, and the results are summarized in Table 1. At first, the solvent effect was examined in the presence of 3 mol% Fe_3O_4@SiO_2-P–AuCl at room temperature and a significant solvent effect was



Scheme 1 Synthesis of magnetic nanoparticle-supported phosphine gold(I) complex.

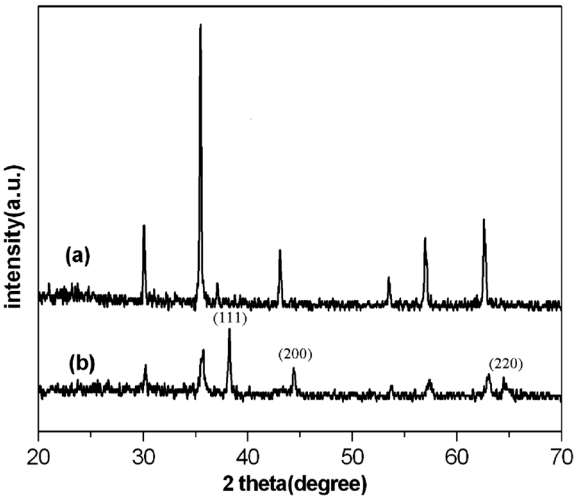


Fig. 2 XRD patterns of Fe_3O_4@SiO_2 (a) and Fe_3O_4@SiO_2-P–AuCl (b).

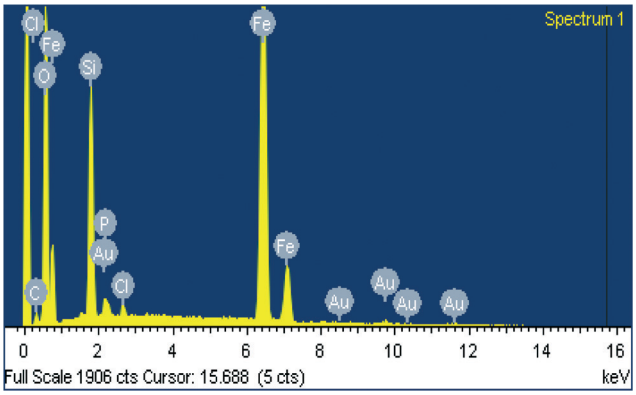
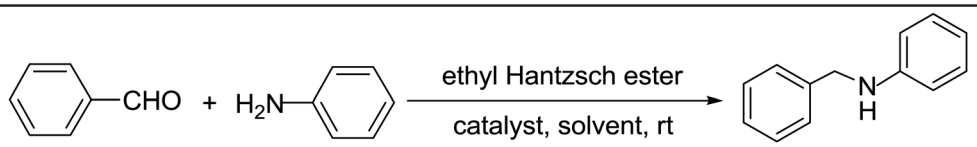


Fig. 3 Energy dispersive spectra (EDS) of Fe_3O_4@SiO_2-P–AuCl.

observed. DCM gave better conversions than other solvents, such as toluene, THF, dioxane, MeCN and MeOH; the desired product **3a** was isolated in 67% yield (Table 1, entries 1–6). To our delight, the reaction was promoted effectively by the addition of AgOTf and the yield of **3a** was increased to 95% (entry 7), whilst the use of AgOTf alone as catalyst resulted in a low yield (entry 8). Thus, Fe_3O_4@SiO_2-P–AuOTf, generated *in situ* from Fe_3O_4@SiO_2-P–AuCl and AgOTf, was found to be the most efficient for this reaction. The role of AgOTf is to convert Fe_3O_4@SiO_2-P–AuCl into Fe_3O_4@SiO_2-P–AuOTf. We next screened the amount of the supported gold catalyst and were pleased to find that there was no change in yield when the amount of catalyst was decreased to 1 mol% (entry 9). The reaction still proceeded smoothly even with only 0.5 mol% catalyst (entry 10). No reaction was observed in the absence of any catalyst (entry 11). In order to characterize the Fe_3O_4@SiO_2-P–AuOTf, we prepared the true catalyst by reaction of Fe_3O_4@SiO_2-P–AuCl with AgOTf in DCM. The TEM image revealed that the diameter of the Fe_3O_4@SiO_2-P–AuOTf complex was approximately 30 nm (Fig. 4a). Fig. 5 shows the XRD spectra of Fe_3O_4@SiO_2, Fe_3O_4@SiO_2-P–AuOTf and the recycled Fe_3O_4@SiO_2-P–AuOTf. XRD patterns of both Fe_3O_4@SiO_2-P–AuOTf and the recycled Fe_3O_4@SiO_2-P–AuOTf obviously show two sets of diffraction peaks compared with the XRD pattern of Fe_3O_4@SiO_2. The three peaks that appeared at 2θ = 38.0°, 44.3° and 64.6° should be attributed to the (111), (200) and (220) reflections of the Au species, respectively. EDS analysis of the fresh Fe_3O_4@SiO_2-P–AuOTf complex shows the presence of Si, O, C, P, S, F, Fe, and Au elements (Fig. 6). The structure of the supported gold catalyst was also verified by X-ray photoelectron spectroscopy (XPS). The XPS spectra of the fresh Fe_3O_4@SiO_2-P–AuOTf (Fig. 7a) displayed a spin–orbit pair at 85.0 and 88.7 eV that can

Table 1 Optimization of the reaction conditions of the direct reductive amination reaction catalyzed by Fe_3O_4@SiO_2-P–AuCl[a]



1a **2a** **3a**

Entry	Catalyst (mol%)	Solvent	t (h)	Yield[b] (%)
1	Fe_3O_4@SiO_2-P–AuCl (3)	Toluene	2	45
2	Fe_3O_4@SiO_2-P–AuCl (3)	THF	2	41
3	Fe_3O_4@SiO_2-P–AuCl (3)	DCM	2	67
4	Fe_3O_4@SiO_2-P–AuCl (3)	MeCN	2	31
5	Fe_3O_4@SiO_2-P–AuCl (3)	Dioxane	2	39
6	Fe_3O_4@SiO_2-P–AuCl (3)	MeOH	2	36
7	Fe_3O_4@SiO_2-P–AuCl (3) + AgOTf (3)	DCM	1	95
8	AgOTf (3)	DCM	2	32
9	Fe_3O_4@SiO_2-P–AuCl (1) + AgOTf (1)	DCM	1	95
10	Fe_3O_4@SiO_2-P–AuCl (0.5) + AgOTf (0.5)	DCM	2	91
11	None	DCM	24	0
12	Fe_3O_4@SiO_2-P–AuOTf (1)	DCM	1	94
13	AuCl (1) + AgOTf (1)	DCM	2	41

[a] Reaction conditions: **1a** (1 mmol), **2a** (1 mmol), ethyl Hantzsch ester (1.3 mmol) in solvent (3 mL), rt. [b] Isolated yields.

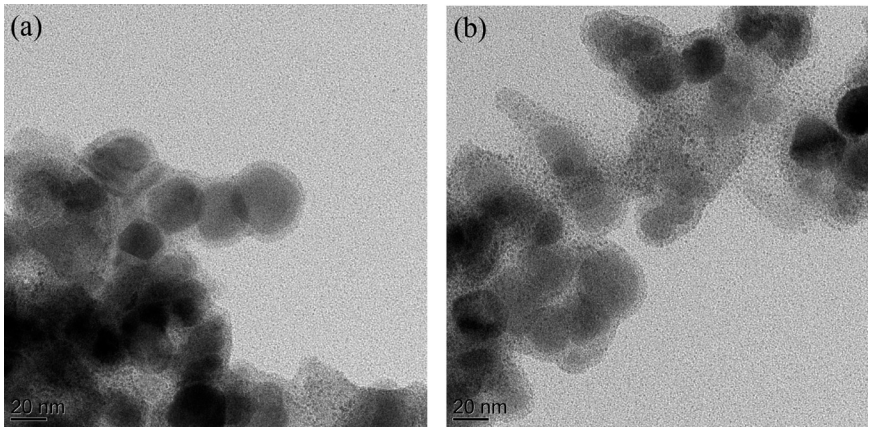


Fig. 4 TEM images of the fresh Fe_3O_4@SiO_2-P–AuOTf (a) and recycled Fe_3O_4@ SiO_2-P-AuOTf after the 10th run (b).

be assigned to Au(I).[24] The binding energies of Au $4f^{7/2}$ and Au $4f^{5/2}$ of the recycled Fe_3O_4@SiO_2-P–AuOTf (after the 10th run) are 84.9 and 88.5 eV, respectively (Fig. 7b), indicating that the oxidation state of gold in the used catalyst is still Au(I). In order to further confirm that the supported AuOTf is the real catalyst, freshly prepared Fe_3O_4@SiO_2-P–AuOTf (1 mol%) was used as the catalyst; the desired product **3a** was isolated in 94% yield after 1 h (entry 12). However, when AuCl/AgOTf (1 mol%) was used as the catalyst, only 41% yield of **3a** was obtained (entry 13). These results indicated that the Fe_3O_4@SiO_2-P–AuOTf complex is the real catalyst.

With the optimized conditions established (1 mol% Fe_3O_4@SiO_2-P–AuCl/AgOTf, DCM, rt), we tried to investigate the scope of this heterogeneous gold-catalyzed direct reductive amination reaction. Firstly, reactions of benzaldehyde with various amines were examined and the results are summarized in Table 2. The reactions of a variety of substituted anilines bearing both electron-donating and electron-withdrawing groups with benzaldehyde (**1a**) proceeded smoothly, leading to the desired products **3b**–**3o** in high yields (89–95%) within 1–3 h. The results indicated that the electronic effect of substituents on the benzene ring has limited influence on this heterogeneous gold-catalyzed direct reductive amination reaction. It is noteworthy that, for 4-nitrobenzenamine with a strong electron-withdrawing group, the reaction required a longer time (3 h) to obtain a high yield of **3h** due to lower reactivity. The *o*-substituted anilines such as 2-chlorobenzenamine, 2-hydroxybenzenamine, 2,4-dichlorobenzenamine, and 2,4-difluorobenzenamine also displayed lower reactivity and the reactions afforded the desired products **3l**–**3o** in 89–93% yields after 3 h. In addition to substituted anilines, bulky naphthalidine and a heterocyclic amine were also applicable under the optimized reaction conditions to afford the corresponding products **3p** and **3q** in 87% and 93% yields, respectively.

Encouraged by the above results, reactions of different aldehydes or ketones with benzenamine were then examined and the results are listed in Table 3. Substituted benzaldehydes with various substituents, regardless of their electronic properties and substitution positions, all afforded the expected products **3r**–**3y** in good to excellent yields (88–96%). Compared to the *p*-substituted benzaldehydes, the *o*-substituted benzaldehydes such as 2-bromobenzaldehyde also gave the desired product **3x** in 93% yield within 1 h, but electron-deficient 2-nitrobenzaldehyde was an exception. The phenomenon observed here was quite different from that of the *o*-substituted anilines in Table 2. Heteroaromatic aldehydes

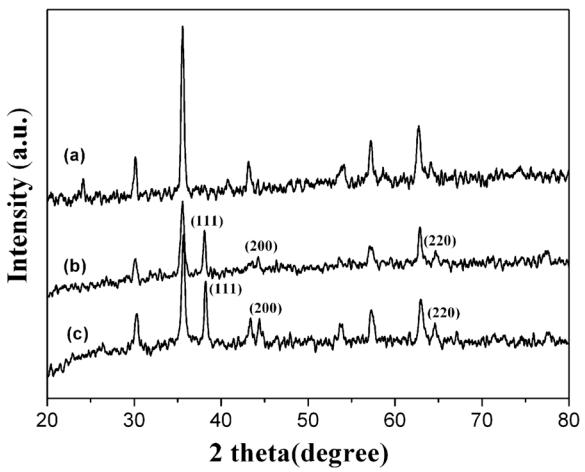


Fig. 5 XRD patterns of Fe_3O_4@SiO_2 (a), Fe_3O_4@SiO_2-P–AuOTf (b) and recycled Fe_3O_4@SiO_2-P–AuOTf (c).

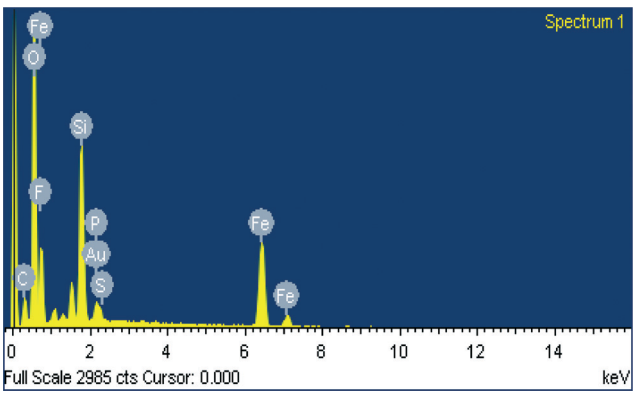


Fig. 6 Energy dispersive spectra (EDS) of Fe_3O_4@SiO_2-P–AuOTf.

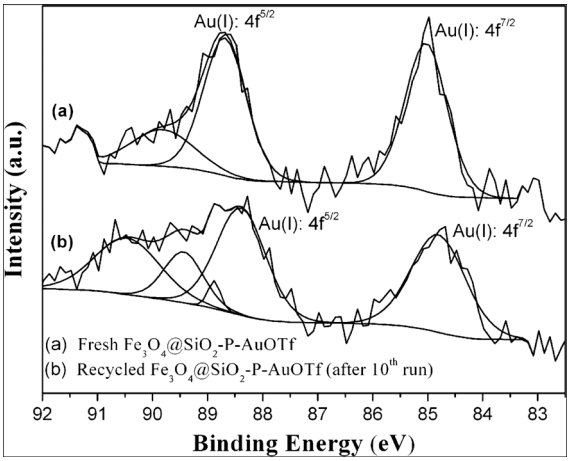


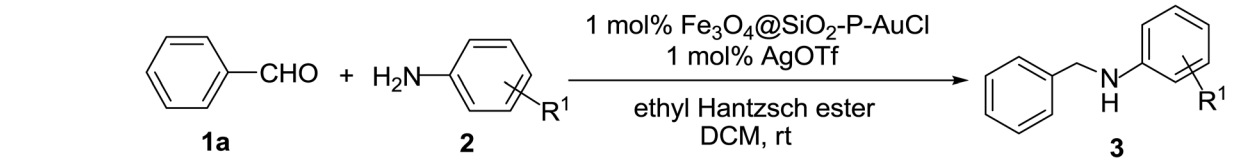
Fig. 7 XPS of the supported Au catalysts.

such as 4-pyridinealdehyde and 2-furaldehyde could also react with benzenamine effectively to give the corresponding products **3z** and **3a′** in 92% and 94% yields, respectively. Aliphatic ketones such as butanone, cyclopentanone and cyclohexanone are also good substrates under the optimized conditions and the reactions with benzenamine proceeded smoothly at higher reaction temperature (50 °C), affording the desired products **3b′**–**3d′** in high yields in longer times.

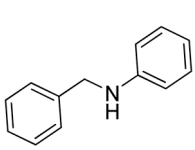
To verify whether the observed catalysis was due to the heterogeneous catalyst Fe_3O_4@SiO_2-P–AuOTf or to a leached gold species in solution, the reaction of benzaldehyde (**1a**) with benzenamine (**2a**) was carried out until an approximately 50% conversion of **1a** was reached. Then the Fe_3O_4@SiO_2-P–AuOTf catalyst was separated magnetically from the solution and the solution was transferred to another reaction tube and stirred again at room temperature for 2 h. In this case, no significant increase in conversion was observed, indicating that leached gold species from the catalyst (if any) are not responsible for the observed activity. It was confirmed by ICP-AES analysis that no gold species could be detected in the solution (below the detection limit). These results rule out any contribution to the observed catalysis from a homogeneous gold species, demonstrating that the observed catalysis was intrinsically heterogeneous.

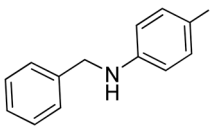
It is well documented that some homogeneous gold-catalyzed reactions might in fact be proton catalyzed.[25] The mechanism for this heterogeneous gold-catalyzed reductive amination reaction may be through a proton-promoted hydride transfer process (Scheme 2). The catalyst Fe_3O_4@SiO_2-P–AuOTf

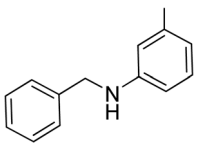
Table 2 One-pot reductive amination of benzaldehyde with various aromatic amines catalyzed by Fe_3O_4@SiO_2-P–AuCl/AgOTf[a,b]

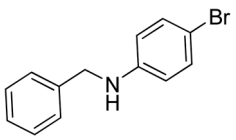


1a **2** **3**

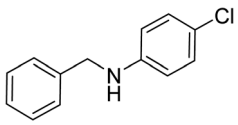

3a, 95% yield, 1 h


3b, 92% yield, 1 h

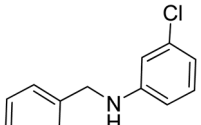

3c, 91% yield, 1 h



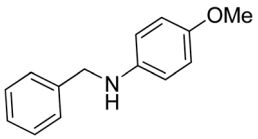
3d, 92% yield, 1h



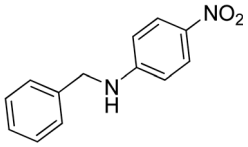
3e, 91% yield, 1.5h



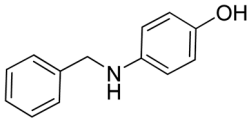
3f, 92% yield, 1.5 h



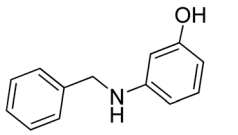
3g, 95% yield, 1 h



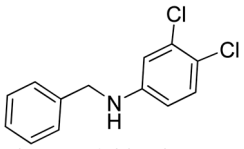
3h, 90% yield, 3 h



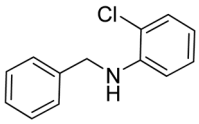
3i, 91% yield, 1 h



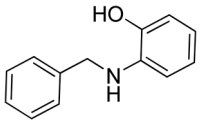
3j, 92% yield, 1 h



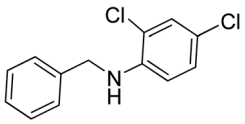
3k, 94% yield, 1 h



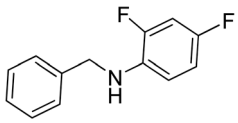
3l, 91% yield, 3 h



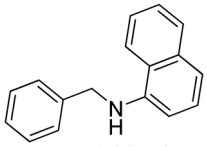
3m, 89% yield, 3 h

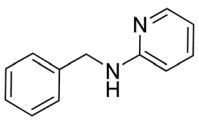


3n, 92% yield, 3 h



3o, 93% yield, 3 h

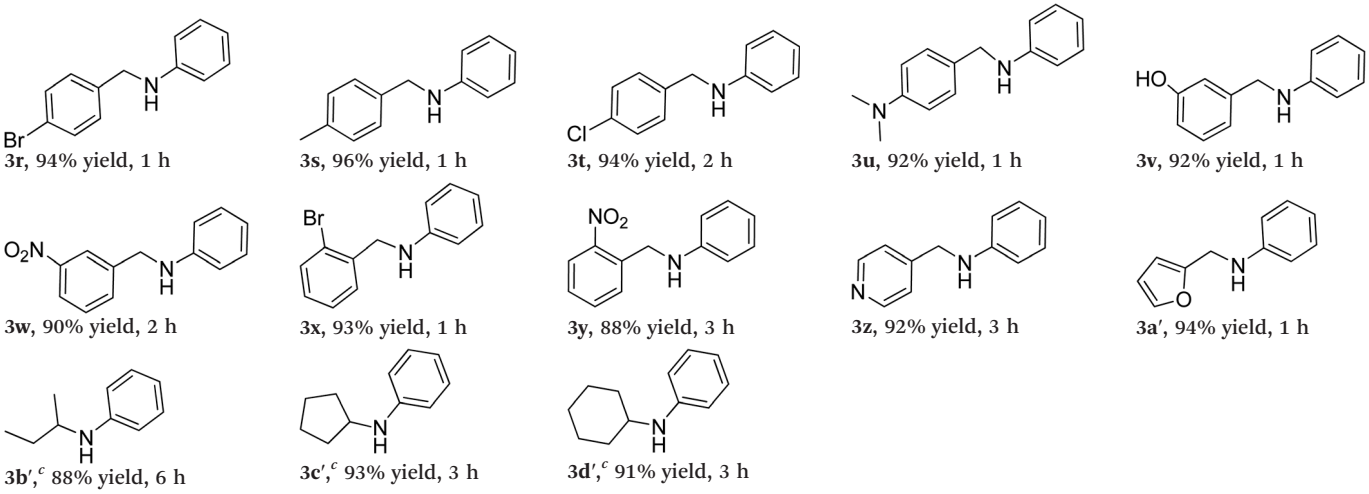

3p, 87% yield, 3 h



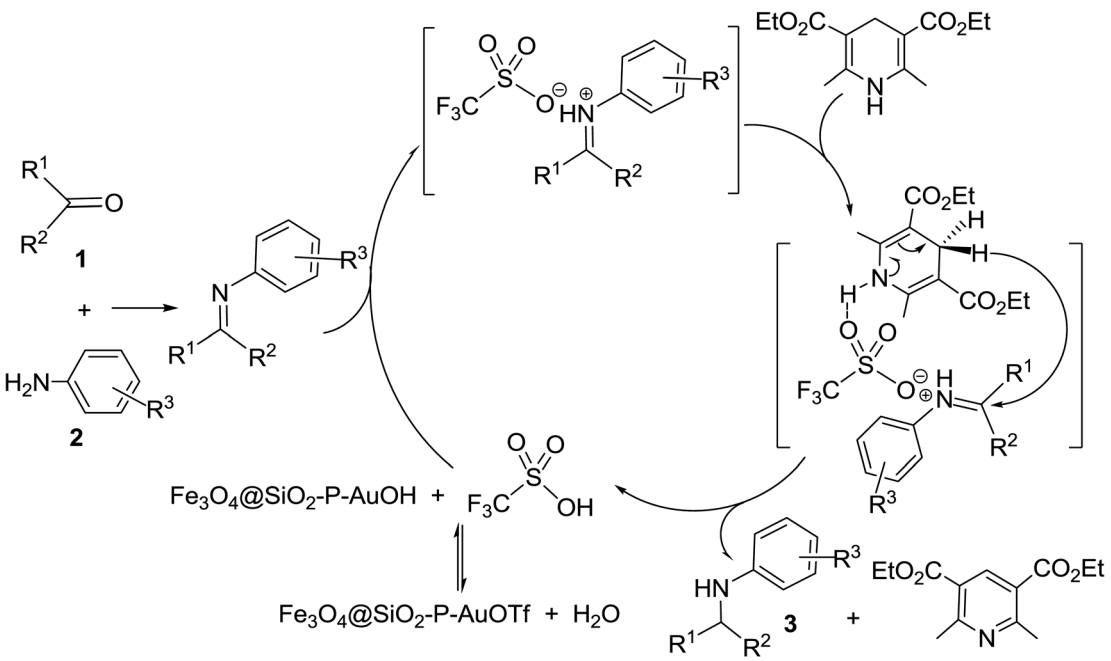
3q, 93% yield, 2 h

[a] Reaction conditions: **1a** (1 mmol), **2** (1 mmol), ethyl Hantzsch ester (1.3 mmol), Fe_3O_4@SiO_2-P–AuCl (1 mol%), AgOTf (1 mol%) in DCM (3 mL), rt. [b] Isolated yields.

Table 3 One-pot reductive amination of aromatic aldehydes and ketones with benzenamine catalyzed by Fe_3O_4@SiO_2-P–AuCl/AgOTf[a,b]



[a] Reaction conditions: **1** (1 mmol), **2a** (1 mmol), ethyl Hantzsch ester (1.3 mmol), Fe_3O_4@SiO_2-P–AuCl (1 mol%), AgOTf (1 mol%) in DCM (3 mL), rt. [b] Isolated yields. [c] 50 °C.



Scheme 2 A possible mechanism for this Au-catalyzed reductive amination reaction.

is partially hydrolyzed by traces of water, generating the proton, which can protonate the imine.[26] The resulting iminium can then be reduced by the ethyl Hantzsch ester as the hydride source.[27] For a supported precious metal catalyst, it is important to examine its ease of separation, good recoverability and reusability. The recyclability of the supported phosphine gold(I) catalyst was also investigated. More than 99% of the catalyst could simply be recovered by fixing a magnet near the reaction vessel (Fig. 8b and c). The recovered catalyst was washed with CH_2Cl_2, air-dried and used directly in the next run without further purification. As shown in Fig. 8a, the supported gold catalyst could be reused ten times without any loss of activity for

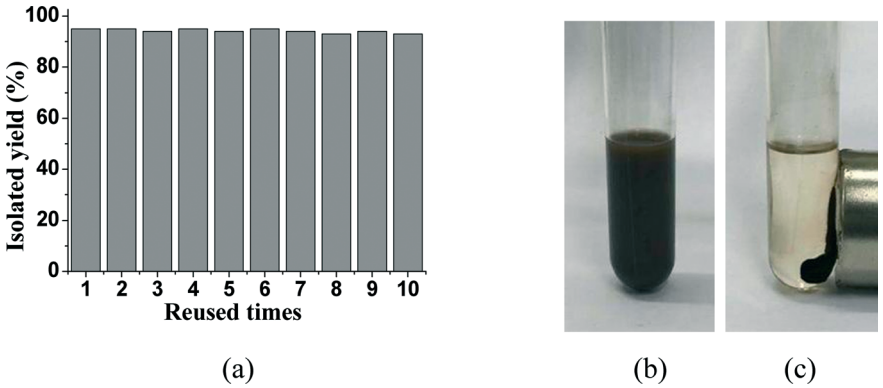


Fig. 8 Recycle of the Fe_3O_4@SiO_2-P–AuCl catalyst.

the direct reductive amination reaction of benzaldehyde (**1a**) with benzenamine (**2a**). In addition, from the TEM image of the recovered catalyst, no obvious change in the morphology and dispersion of particles was observed after ten reaction cycles (Fig. 4b). The observed excellent catalytic activity and reusability of the Fe_3O_4@SiO_2-P–AuCl should result from the properties of the catalyst, such as the nano size (about 30 nm), good dispersion and stability of particles. It was noteworthy that the reaction catalyzed by the recovered catalyst did not need the addition of AgOTf because the Fe_3O_4@SiO_2-P–AuCl had been changed to the Fe_3O_4@SiO_2-P–AuOTf after the first cycle.

Conclusions

In conclusion, we have developed a highly efficient and easily recoverable magnetic nanoparticle-supported phosphine gold(I) catalyst for the direct reductive amination reaction of aldehydes or ketones with amines using commercially available, stable, and inexpensive ethyl Hantzsch ester as the hydrogen source. The reaction proceeds with high efficiency at room temperature under neutral conditions, generating a variety of secondary amines in excellent yields, which are extremely important synthetic intermediates in the construction of biologically active compounds. More importantly, this heterogeneous gold catalyst can simply be recovered by applying an external magnet and recycled at least ten times without any loss of activity. The Fe_3O_4@SiO_2-P–AuCl catalyst not only solves the basic problems of catalyst separation and recovery but also avoids the use of AgOTf in the recycling process. This makes our protocol facile, economical, and environmentally benign.

Experimental

All reagents were obtained from commercial sources without further purification, and commercially available solvents were purified before use. The reaction was carried out at room temperature without the exclusion of air or moisture from the reaction mixture. All compounds were fully characterized. ^1H and ^{13}C NMR spectra were recorded at 400 or 100 MHz with $CDCl_3$ as the solvent and TMS as an internal standard. Chemical shifts are reported in δ (ppm) relative to TMS. HRMS spectra were recorded on a Q-Tof spectrometer with micromass MS software using electrospray ionization (ESI). Gold content was determined with inductively coupled plasma atom emission spectrometry (ICP-AES). TEM images were recorded on a transmission electron microscope operated at an accelerated voltage of 200 kV. X-ray diffraction (XRD) measurements were carried out at room temperature using an X-ray powder diffractometer. X-ray energy dispersive spectroscopy (EDS) was performed using a microscope. X-ray photoelectron spectra (XPS) were recorded on an XSAM 800 spectrometer (Kratos).

Preparation of Fe_3O_4@SiO_2-P[17f]

Fe_3O_4 nanoparticles (0.50 g, with a diameter of approximately 20 nm, purchased from Aldrich) were diluted with 5.0 mL of deionized water and 50 mL of 2-propanol, and the mixture was sonicated for 40 min. To this well-dispersed nanoparticle solution, 2.0 mL of $NH_3{\cdot}H_2O$ followed by 1.65 g of $Si(OEt)_4$ were slowly added and stirred for 5 h at room temperature. The resulting product was washed repeatedly with water until the solution was neutral, then washed with ethanol and diethyl ether, respectively, and dried under vacuum to give 1.35 g of the silica-coated magnetic nanoparticles (Fe_3O_4@SiO_2).

To a suspension of 0.75 g of Fe_3O_4@SiO_2 in 30 mL of dry toluene was added a solution of 2-(diphenylphosphino)-ethyltriethoxysilane (0.57 g) in 10 mL of dry toluene. The mixture was stirred at 110 °C under argon atmosphere for 24 h. Then the resulting material was magnetically separated, washed repeatedly with toluene and CH_2Cl_2 to remove any unanchored species and dried at 100 °C under vacuum for 5 h to afford 0.85 g of the phosphino-functionalized Fe_3O_4@SiO_2 (Fe_3O_4@SiO_2-P) as brown nanoparticles. The phosphine content was found to be 0.44 mmol g^{-1} by elemental analysis.

Synthesis of Fe_3O_4@SiO_2-P–AuCl

To a three-necked round bottom flask, AuCl (80 mg, 0.34 mmol) and MeOH (50 mL) were added. The solution was stirred at room temperature under argon atmosphere for 10 min, and

then 0.82 g of the phosphino-functionalized magnetic nanoparticles (Fe_3O_4@SiO_2-P) was added. The mixture was stirred at 65 °C for 12 h, and then the solid catalyst was magnetically separated, washed thoroughly with methanol, and dried under vacuum at 100 °C for 3 h to afford 0.88 g of Fe_3O_4@SiO_2-P–AuCl as brown nanoparticles. The gold content was determined to be 0.39 mmol g^{-1} *via* inductively coupled plasma atomic emission spectrometry.

General procedure for the heterogeneous gold-catalyzed direct reductive amination of aldehydes or ketones with amines

A mixture of Fe_3O_4@SiO_2-P–AuCl (26 mg, 0.01 mmol) and AgOTf (2.6 mg, 0.01 mmol) in dichloromethane (3 mL) was stirred at room temperature. After 10 minutes, amine (1.0 mmol), aldehyde or ketone (1.0 mmol) and ethyl Hantzsch ester (1.3 mmol) were subsequently added into the stirred solution. The reaction was monitored by TLC on silica-gel plates (GF 254). After the reaction was completed, the supported catalyst was magnetically separated and the reaction mixture was concentrated under vacuum and then purified by flash chromatography (petroleum ether: ethyl acetate = 20 : 1) to afford the corresponding product. The recovered catalyst was washed with dichloromethane (2 × 2 mL), air-dried and used directly for the next run.

***N*-Benzylbenzenamine (3a)[28].** Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38–7.26 (m, 4H), 7.26 (t, J = 6.8 Hz, 1H), 7.16 (t, J = 8.0 Hz, 2H), 6.71 (t, J = 7.2 Hz, 1H), 6.63 (d, J = 7.6 Hz, 2H), 4.31 (s, 2H), 4.06 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.1, 139.4, 129.3, 128.7, 127.6, 127.3, 117.7, 113.0, 48.4.

***N*-Benzyl-4-methylbenzenamine (3b)[28].** Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36–7.23 (m, 5H), 6.97 (d, J = 8.0 Hz, 2H), 6.54 (d, J = 8.4 Hz, 2H), 4.28 (s, 2H), 3.89 (br, 1H), 2.22 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.0, 139.7, 129.8, 128.7, 127.6, 127.2, 126.9, 113.2, 48.8, 20.5.

***N*-Benzyl-3-methylbenzenamine (3c)[28].** Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37–7.24 (m, 5H), 7.05 (t, J = 7.6 Hz, 1H), 6.54 (d, J = 7.6 Hz, 1H), 6.47–6.41 (m, 2H), 4.29 (s, 2H), 3.98 (br, 1H), 2.26 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.1, 139.5, 139.1, 129.2, 128.7, 127.6, 127.3, 118.7, 113.8, 110.1, 48.5, 21.7.

***N*-Benzyl-4-bromobenzenamine (3d)[28].** White solid. Mp 49–50 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35–7.31 (m, 4H), 7.30–7.26 (m, 1H), 7.22 (d, J = 8.8 Hz, 2H), 6.49 (d, J = 8.8 Hz, 2H), 4.28 (s, 2H), 4.13 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.0, 138.9, 132.0, 128.7, 127.5, 127.4, 114.5, 109.2, 48.3.

***N*-Benzyl-4-chlorobenzenamine (3e)[28].** White solid. Mp 42–43 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35–7.26 (m, 5H), 7.09 (d, J = 8.8 Hz, 2H), 6.53 (d, J = 8.4 Hz, 2H), 4.28 (s, 2H), 4.11 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.6, 138.9, 129.1, 128.7, 127.5, 127.4, 122.3, 114.1, 48.5.

***N*-Benzyl-3-chlorobenzenamine (3f)[28].** Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35–7.26 (m, 5H), 7.05 (t, J = 8.0 Hz, 1H), 6.66 (dd, J = 8.0, 1.2 Hz, 1H), 6.60 (t, J = 2.0 Hz, 1H), 6.47 (dd, J = 8.4, 1.6 Hz, 1H), 4.28 (s, 2H), 4.13 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.2, 138.8, 135.1, 130.2, 128.8, 127.5, 127.4, 117.5, 112.6, 111.2, 48.2.

***N*-Benzyl-4-methoxybenzenamine (3g)[28].** White solid. Mp 47–49 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39–7.23 (m, 5H), 6.77 (d, J = 8.8 Hz, 2H), 6.59 (d, J = 8.8 Hz, 2H), 4.27 (s, 2H), 4.10 (br, 1H), 3.72 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.4, 142.4, 139.7, 128.6, 127.6, 127.2, 115.0, 114.3, 55.9, 49.4.

***N*-Benzyl-4-nitrobenzenamine (3h)[28].** Yellow solid. Mp 145–146 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (d, J = 9.2 Hz, 2H), 7.40–7.30 (m, 5H), 6.56 (d, J = 9.2 Hz, 2H), 4.95 (br, 1H), 4.43 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.1, 138.5, 137.5, 128.9, 127.8, 127.3, 126.3, 111.4, 47.7.

***N*-Benzyl-4-hydroxybenzenamine (3i)[7b].** White solid. Mp 85–86 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37–7.22 (m, 5H), 6.67 (d, J = 8.8 Hz, 2H), 6.54 (d, J = 8.8 Hz, 2H), 4.25 (s, 2H), 4.14 (br, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.2, 139.6, 128.6, 127.6, 127.2, 123.4, 116.3, 114.6, 49.5.

***N*-Benzyl-3-hydroxybenzenamine (3j)[28].** Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33–7.22 (m, 5H), 6.98 (t, J = 8.0 Hz, 1H), 6.20 (d, J = 8.0 Hz, 1H), 6.16 (d, J = 8.0 Hz, 1H), 6.08 (s, 1H), 4.38 (br, 2H), 4.24 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.8, 149.7, 139.3, 130.3, 128.7, 127.6, 127.3, 106.1, 105.0, 100.2, 48.4.

***N*-Benzyl-3,4-dichlorobenzenamine (3k)[28].** Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.25 (m, 5H), 7.15 (d, J = 8.8 Hz, 1H), 6.68 (d, J = 2.4 Hz, 1H), 6.43 (dd, J = 8.8, 2.8 Hz, 1H), 4.27 (s, 2H), 4.13 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.5, 138.3, 132.8, 130.6, 128.8, 127.6, 127.5, 120.1, 114.0, 112.6, 48.2.

***N*-Benzyl-2-chlorobenzenamine (3l)[29].** Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37–7.25 (m, 6H), 7.10–7.05 (m, 1H), 6.65–6.60 (m, 2H), 4.77 (br, 1H), 4.39 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.9, 138.8, 129.1, 128.7, 127.8, 127.4, 127.3, 119.2, 117.5, 111.6, 47.9.

***N*-Benzyl-2-hydroxybenzenamine (3m)[30].** White solid. Mp 81–83 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39–7.23 (m, 5H), 6.83–6.75 (m, 1H), 6.73–6.58 (m, 3H), 4.50 (br, 2H), 4.32 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.7, 141.0, 137.2, 128.9 128.6, 127.5, 127.1, 117.8, 114.4, 112.5, 48.6.

***N*-Benzyl-2,4-dichlorobenzenamine (3n).** Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31–7.25 (m, 6H), 7.03 (d, J = 8.8 Hz, 1H), 6.51 (d, J = 8.8 Hz, 1H), 4.70 (br, 1H), 4.36 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.6, 138.3, 128.8, 128.7, 127.8, 127.5, 127.2, 112.1, 48.0. HRMS calcd for $C_{13}H_{12}Cl_2N^+$ [M^+ + H]: 252.0347, found 252.0344.

***N*-Benzyl-2,4-difluorobenzenamine (3o).** Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36–7.24 (m, 5H), 6.81–6.77 (m, 1H), 6.76–6.66 (m, 1H), 6.60–6.55 (m, 1H), 4.32 (s, 2H), 4.15 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.4 (dd, J = 247.2, 11.1 Hz), 150.9 (d, J = 228.8 Hz), 138.8, 133.1 (d, J = 11.5 Hz), 128.8, 127.5, 127.4, 112.3 (dd, J = 8.7, 4.6 Hz), 110.6 (dd, J = 21.4, 3.7 Hz), 103.4 (dd, J = 26.5, 22.6 Hz), 48.3. HRMS calcd for $C_{13}H_{12}F_2N^+$ [M^+ + H]: 220.0938, found 220.0932.

***N*-Benzylnaphthalidine (3p)[31].** White solid. Mp 68–69 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (d, J = 8.0 Hz, 2H), 7.51–

7.23 (m, 9H), 6.61 (d, J = 7.6 Hz, 1H), 4.70 (br, 1H), 4.46 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.2, 139.1, 134.4, 129.9, 128.8, 127.8, 127.4, 126.6, 125.8, 124.8, 123.5, 119.9, 117.8, 105.0, 48.7.

***N*-(2-Pyridyl)benzylamine (3q)[29]**. White solid. Mp 92–93 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (d, J = 3.6 Hz, 1H), 7.39–7.24 (m, 6H), 6.57 (t, J = 5.8 Hz, 1H), 6.36 (d, J = 8.0 Hz, 1H), 5.02 (br, 1H), 4.49 (d, J = 5.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.7, 148.1, 139.3, 137.5, 128.6, 127.4, 127.2, 113.1, 106.8, 46.3.

***N*-(4-Bromobenzyl)benzenamine (3r)[28]**. White solid. Mp 50–51 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (d, J = 8.4 Hz, 2H), 7.24–7.20 (m, 2H), 7.16 (t, J = 8.0 Hz, 2H), 6.72 (t, J = 7.4 Hz, 1H), 6.59 (d, J = 8.0 Hz, 2H), 4.27 (s, 2H), 4.10 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.8, 138.5, 131.7, 129.3, 129.1, 121.0, 118.0, 113.1, 47.8.

***N*-(4-Methylbenzyl)benzenamine (3s)[28]**. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21 (d, J = 8.0 Hz, 2H), 7.16–7.08 (m, 4H), 6.68 (t, J = 7.4 Hz, 1H), 6.58 (d, J = 8.0 Hz, 2H), 4.21 (s, 2H), 3.85 (br, 1H), 2.31 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.4, 136.9, 136.6, 129.4, 129.3, 127.6, 117.6, 113.1, 48.2, 21.2.

***N*-(4-Chlorobenzyl)benzenamine (3t)[3c]**. White solid. Mp 48–49 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28 (s, 4H), 7.15 (t, J = 7.6 Hz, 2H), 6.71 (t, J = 7.4 Hz, 1H), 6.59 (d, J = 7.6 Hz, 2H), 4.28 (s, 2H), 3.98 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.9, 138.1, 132.9, 129.3, 128.8, 128.7, 117.9, 113.0, 47.7.

***N*-(4-Dimethylaminobenzyl)benzenamine (3u)[12a]**. White solid. Mp 58–60 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23 (d, J = 8.4 Hz, 2H), 7.16 (t, J = 7.8 Hz, 2H), 6.74–6.68 (m, 3H), 6.65–6.61 (m, 2H), 4.19 (s, 2H), 4.01 (br, 1H), 2.93 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.0, 148.4, 131.0, 129.3, 128.8, 117.4, 112.9, 112.8, 48.0, 40.8.

***N*-(3-Hydroxybenzyl)benzenamine (3v)[29]**. White solid. Mp 101–102 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.19–7.12 (m, 3H), 6.89 (d, J = 7.6 Hz, 1H), 6.77 (s, 1H), 6.74–6.66 (m, 2H), 6.61 (d, J = 8.0 Hz, 2H), 4.29 (br, 1H), 4.23 (s, 2H), 4.06 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.0, 148.0, 141.3, 129.9, 129.4, 119.7, 117.9, 114.4, 114.3, 113.2, 48.2.

***N*-(3-Nitrobenzyl)benzenamine (3w)[32]**. Yellow solid. Mp 82–83 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (s, 1H), 8.10 (d, J = 8.0 Hz, 1H), 7.70 (d, J = 7.6 Hz, 1H), 7.49 (t, J = 7.6 Hz, 1H), 7.16 (t, J = 7.8 Hz, 2H), 6.74 (t, J = 7.2 Hz, 1H), 6.60 (d, J = 8.0 Hz, 2H), 4.45 (s, 2H), 4.22 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.6, 147.4, 142.1, 133.3, 129.6, 129.4, 122.3, 122.1, 118.2, 113.0, 47.6.

***N*-(2-Bromobenzyl)benzenamine (3x)[28]**. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, J = 8.0 Hz, 1H), 7.39 (d, J = 7.2 Hz, 1H), 7.24 (t, J = 7.2 Hz, 1H), 7.16 (t, J = 8.0 Hz, 2H), 7.11 (t, J = 7.6 Hz, 1H), 6.72 (t, J = 7.4 Hz, 1H), 6.60 (d, J = 8.4 Hz, 2H), 4.39 (s, 2H), 4.22 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.7, 138.2, 132.8, 129.3, 129.2, 128.7, 127.6, 123.3, 117.9, 113.0, 48.5.

***N*-(2-Nitrobenzyl)benzenamine (3y)[30]**. Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (d, J = 8.0 Hz, 1H), 7.67 (d, J = 7.6 Hz, 1H), 7.56 (t, J = 7.6 Hz, 1H), 7.41 (t, J = 7.6 Hz, 1H), 7.15 (t, J = 7.4 Hz, 2H), 6.72 (t, J = 7.4 Hz, 1H), 6.57 (d, J = 7.6 Hz, 2H), 4.72 (s, 2H), 4.30 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 147.4, 135.6, 133.5, 129.9, 129.3, 128.8, 128.0, 125.1, 118.1, 113.0, 45.8.

***N*-((Pyridin-4-yl)methyl)benzenamine (3z)[3c]**. White solid. Mp 100–102 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.53 (d, J = 4.4 Hz, 2H), 7.29–7.24 (m, 2H), 7.16 (t, J = 7.8 Hz, 2H), 6.72 (t, J = 7.2 Hz, 1H), 6.57 (d, J = 7.6 Hz, 2H), 4.36 (s, 2H), 4.28 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.6, 147.4, 129.4, 129.3, 122.2, 118.1, 112.9, 47.1.

***N*-((Furan-2-yl)methyl)benzenamine (3a′)[4c]**. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (s, 1H), 7.18 (t, J = 7.8 Hz, 2H), 6.74 (t, J = 7.4 Hz, 1H), 6.67 (d, J = 7.6 Hz, 2H), 6.31 (s, 1H), 6.23 (s, 1H), 4.31 (s, 2H), 3.94 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.8, 147.6, 141.9, 129.2, 118.1, 113.3, 110.3, 107.0, 41.6.

***N*-sec-Butylbenzenamine (3b′)[32]**. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.08 (t, J = 8.0 Hz, 2H), 6.59 (t, J = 7.4 Hz, 1H), 6.51 (d, J = 8.4 Hz, 2H), 3.59 (br, 1H), 3.36–3.27 (m, 1H), 1.56–1.47 (m, 1H), 1.43–1.34 (m, 1H), 1.09 (d, J = 6.4 Hz, 3H), 0.88 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.1, 128.3, 116.3, 112.6, 49.2, 28.5, 19.0, 9.3.

***N*-Cyclopentylbenzenamine (3c′)[32]**. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.15 (dd, J = 8.4, 7.2 Hz, 2H), 6.66 (t, J = 7.2 Hz, 1H), 6.59 (d, J = 7.6 Hz, 2H), 3.81–3.74 (m, 1H), 3.59 (br, 1H), 2.05–1.95 (m, 2H), 1.76–1.66 (m, 2H), 1.64–1.57 (m, 2H), 1.49–1.41 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.1, 129.2, 117.0, 113.3, 54.7, 33.6, 24.1.

***N*-Cyclohexylbenzenamine (3d′)[33]**. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.17–7.12 (m, 2H), 6.65 (t, J = 7.4 Hz, 1H), 6.58 (d, J = 7.6 Hz, 2H), 3.44 (br, 1H), 3.28–3.20 (m, 1H), 2.06–2.01 (m, 2H), 1.77–1.71 (m, 2H), 1.38–1.26 (m, 2H), 1.25–1.14 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.4, 129.3, 116.9, 113.3, 51.8, 33.5, 26.0, 25.1.

Acknowledgements

We thank the National Natural Science Foundation of China (No. 21462021) and Key Laboratory of Functional Small Organic Molecule, Ministry of Education (No. KLFS-KF-201409) for financial support.

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