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Highly efficient heterogeneous aerobic oxidative C–C coupling from C_{sp3}–H bonds by a magnetic nanoparticles-immobilized bipy-gold(III) catalyst

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A highly efficient heterogeneous cross-dehydrogenative coupling (CDC) of tertiary amines with nitroalkanes and various unmodified ketones was achieved by using a magnetic nanoparticles-immobilized bipy-gold(III) complex as catalyst and air as the sole oxidant to afford the corresponding C–C coupling products in good to excellent yields under mild reaction conditions. The new heterogeneous gold catalyst can easily be separated from the reaction mixture by applying an external magnet and can be recycled for at least ten times without a significant loss of activity.

Introduction

The construction of C–C bond is a central part of many chemical syntheses, and the development of new methods for forming C–C bonds will profoundly improve overall synthetic efficiency. Transition metal-catalyzed C–H bond activations and subsequent C–C bond formations[1] and cross-coupling reactions of various reactive functional groups[2] have become powerful tools for constructing C–C bonds. From a practical point of view, the cross-dehydrogenative coupling (CDC) reaction of two different

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C–H bonds of pronucleophiles and proelectrophiles will avoid the use of previously functionalized substrates and thus make synthetic schemes shorter and more efficient. Since the pioneering works on the cross-dehydrogenative coupling (CDC) reactions demonstrated by Li and Murahashi through the activation of the α-C_{sp3}–H bond of tertiary amines,[3] a tremendous progress has been achieved on this subject mostly employing high-valent transition-metal catalysts combined with oxidants.[4] A wide range of transition-metals including copper,[5] ruthenium,[6] platinum,[7] palladium,[8] and vanadium[9] have been utilized as the catalysts for oxidative CDC reactions between tertiary amines and sp^3 C–H compounds in the presence of a stoichiometric amount of oxidants or pure oxygen. However, from the viewpoint of green and sustainable chemistry, the development of recyclable supported catalysts having a high catalytic activity for sp^3 C–H functionalizations would be highly desirable.[10] In spite of the significant progress made in the homogeneous transition-metal catalysis, very few reports on heterogeneous catalytic CDC reactions of tertiary amines have been described thus far[11] and, in most cases, these heterogeneous catalysts such as Fe_3O_4 nanoparticles, SBA-15-supported Fe(II) terpyridine complex, and RuO_2 nanoparticles on grapheme, did not exhibit satisfactory high recyclability and high temperatures were required for these heterogeneous reactions.

The past two decades have witnessed dramatic growth in reports on reactions catalyzed by gold complexes owing to their unique reactivity as soft and carbophilic Lewis acids.[12] To date, the gold-catalyzed carbon-carbon[13] and carbon-heteroatom[14] bond formation reactions have successfully been used in organic synthesis. However,

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the gold-catalyzed oxidative C–C coupling of sp^3 C–H bonds under aerobic oxidative conditions remains a challenge.[15] In addition, the use of homogeneous gold catalysts has seriously limited the utility of these reactions because they are quite expensive, cannot be recovered and recycled. Although gold nanoparticles supported on different matrices have been used as heterogeneous catalysts for some organic transformations in recent years,[16] little progress has been made on the supported gold complexes-catalyzed reactions so far.[17] Recently, magnetic nanoparticles-supported catalysts have received more and more attention because their magnetic separation is an alternative to filtration or centrifugation as it prevents loss of catalyst and increases the reusability.[18] It is well known that air is a sustainable and favorable oxidant and has received much attention in modern oxidation chemistry because of water as the only waste product.[19] To the best of our knowledge, there is no successful example of a heterogeneous gold-catalyzed α-C_{sp3}–H functionalization of tertiary amines with air as the sole oxidant. As a part of our continuing interest in the development of efficient heterogeneous catalysts for organic synthesis,[20] herein we wish to report an efficient magnetically recoverable and reusable Fe_3O_4 nanoparticles-immobilized bipy-gold(III) complex and its successful application to the oxidative cross-dehydrogenative coupling (CDC) of tertiary amines with nitroalkanes and various unmodified ketones with air as the sole oxidant. The new catalyst could be easily recovered by decantation of the reaction mixture in the presence of an external magnet and reused at least 10 times without significant loss of its catalytic activity.

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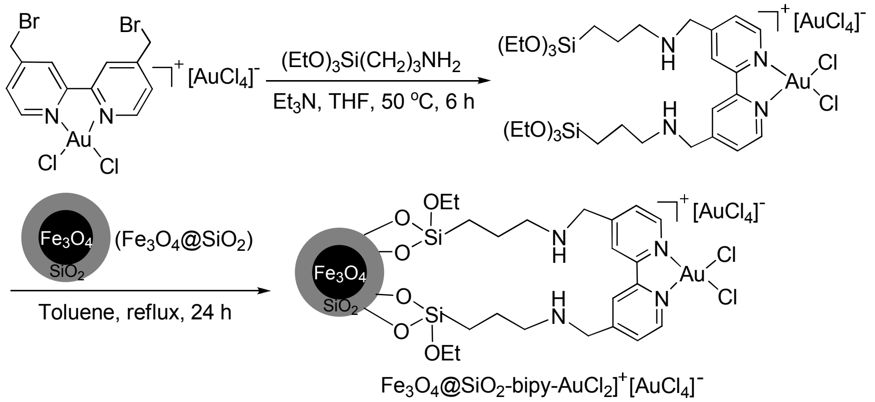
Results and discussion

The magnetic nanoparticles-immobilized bipy-gold(III) complex (Fe_3O_4@SiO_2-bipy-$AuCl_2]^+[AuCl_4]^-$) was synthesized according to the procedure summarized in Scheme 1. Firstly, the treatment of bis(bromomethyl)-functionalized bipy-gold(III) complex $[(BrCH_2)_2$bipy-$AuCl_2][AuCl_4]$[21] with 3-aminopropyltriethoxysilane in THF in the presence of Et_3N gave the triethoxysilyl-functionalized $[(bipy)AuCl_2][AuCl_4]$ complex. The latter was then reacted with the silica-coated Fe_3O_4 (Fe_3O_4@SiO_2)[22] in toluene under reflux for 24 h to afford the magnetic nanoparticles-immobilized bipy-gold(III) complex (Fe_3O_4@SiO_2-bipy-$AuCl_2]^+[AuCl_4]^-$), the gold content was determined to be 0.23 mmol g^{-1} by ICP-AES.



Scheme 1 Synthesis of magnetic nanoparticles-immobilized bipy-gold(III) complex.

The TEM image of the Fe_3O_4@SiO_2-bipy-$AuCl_2]^+[AuCl_4]^-$complex shows slight aggregation and the size of the particles were between 30 and 40 nm (Fig. 1a). The XRD spectra of Fe_3O_4@SiO_2 and Fe_3O_4@SiO_2-bipy-$AuCl_2]^+[AuCl_4]^-$ complex are presented in Fig. 2. XRD measurements of Fe_3O_4@SiO_2 exhibit diffraction peaks

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corresponding to the typical spinel maghemite structure whereas the diffraction peak of the layered amorphous silica was not obvious. XRD measurements of the Fe_3O_4 @SiO_2-bipy-$AuCl_2]^+[AuCl_4]^-$obviously show two sets of diffraction peaks, the new peaks that appeared are attributed to the Au species. The energy dispersive X-ray spectroscopy (EDS) shows the elements present in the material. EDS analysis of the fresh Fe_3O_4@SiO_2-bipy-$AuCl_2]^+[AuCl_4]^-$complex shows the presence of Si, O, C, N, Cl, Fe, and Au elements (Fig. 3).

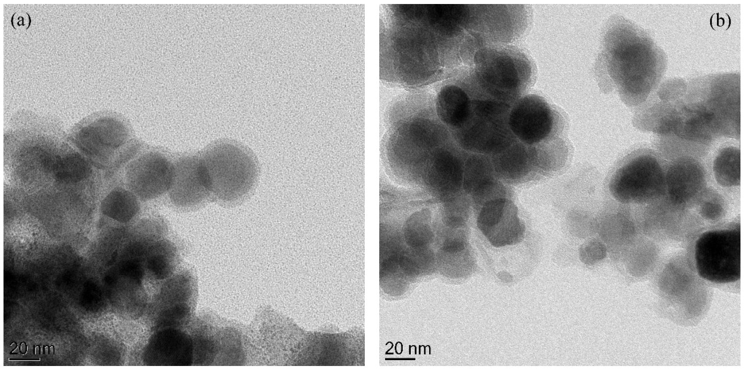

Fig. 1 TEM images of Fe_3O_4@SiO_2-bipy-$AuCl_2]^+[AuCl_4]^-$(a) and recycled Fe_3O_4@ SiO_2-bipy-$AuCl_2]^+[AuCl_4]^-$(b).

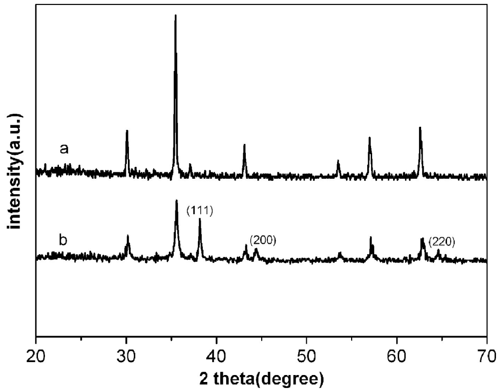

Fig. 2 XRD patterns of Fe_3O_4@SiO_2 (a) and Fe_3O_4@SiO_2-bipy-$AuCl_2]^+[AuCl_4]^-$(b).

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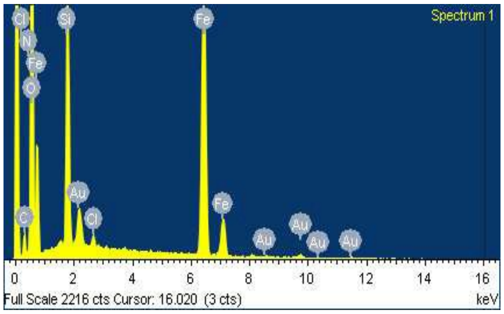

Fig. 3 EDS analysis of Fe_3O_4@SiO_2-bipy-$AuCl_2]^+[AuCl_4]^-$.

The presence of magnetic iron oxide inside Fe_3O_4@SiO_2-bipy-$AuCl_2]^+[AuCl_4]^-$ prevents the analysis of organic functional groups by solid state NMR spectroscopy. Therefore, these hybrid materials were further analyzed by FT-IR spectroscopy (Fig. 4) and elemental analysis. The FT-IR spectrum (Fig. 4a) of Fe_3O_4@SiO_2 shows the Fe–O stretching absorption at 580 cm^{-1} and a sharp band for the Si–O vibration at 1089 cm^{-1}. In the FT-IR spectrum (Fig. 4b) of Fe_3O_4@SiO_2-bipy-$AuCl_2]^+[AuCl_4]^-$absorptions at 3355 cm^{-1} (N–H), 2970 and 2884 cm^{-1} (CH_3), 2928 cm^{-1} (CH_2), and typical bipyridine bands at 1599, 1560 and 1443 cm^{-1} were observed indicating the presence of silylated bipy-gold(III) groups. The results from FT-IR imply that the bipy-gold(III) complex has been successfully grafted on the surface of MNPs. By determination of the nitrogen content (C, H, N elemental analysis), a bipy-gold(III) complex loading of approximately 0.12 mmol g^{-1} was calculated for the Fe_3O_4@SiO_2-bipy-$AuCl_2]^+[AuCl_4]^-$ complex, which is in well accordance with the Au content determined by ICP-AES analysis. The N_2 adsorption-desorption isotherms for Fe_3O_4@SiO_2 and Fe_3O_4@SiO_2-bipy-$AuCl_2]^+[AuCl_4]^-$are illustrated in Fig. 5. The isotherms in Fig. 5 have remarkable changes before and after grafting, but both samples exhibited type II isotherms, characteristic of non-porous materials according to the IUPAC classification. After the

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grafting the bipy-gold(III) complex onto $Fe_3O_4@SiO_2$, the surface area and pore volume decreased from 27.9 $m^2\ g^{-1}$ and 0.044 $cm^3\ g^{-1}$ to 11.4 $m^2\ g^{-1}$ and 0.025 $cm^3\ g^{-1}$, respectively.

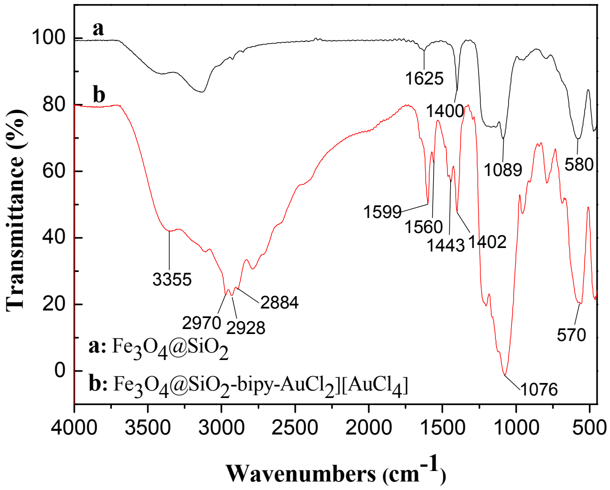

Fig. 4 FT-IR spectra of $Fe_3O_4@SiO_2$ (a) and $Fe_3O_4@SiO_2$-bipy-$AuCl_2]^+[AuCl_4]^-$(b).

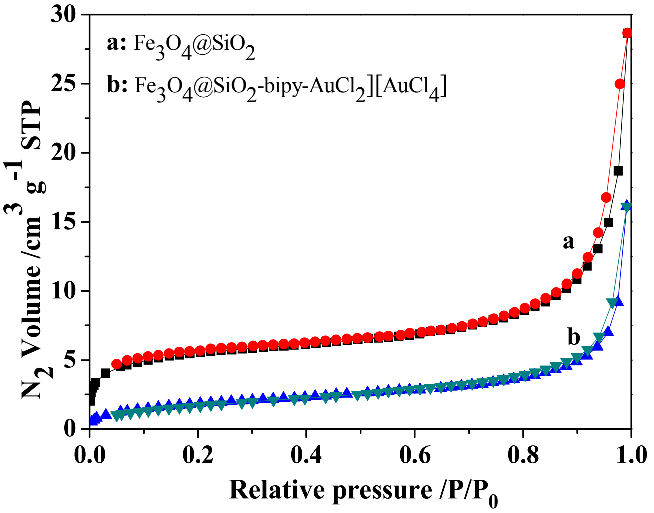

Fig. 5 N_2 adsorption/desorption isotherms of $Fe_3O_4@SiO_2$ (a) and $Fe_3O_4@SiO_2$-bipy-$AuCl_2]^+[AuCl_4]^-$(b).

In our initial screens, the aerobic oxidative C–C coupling of *N*-phenyl tetrahydroisoquinoline **1a** with nitromethane **2a** was selected as the model reaction to optimize

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the reaction conditions and the results are summarized in Table 1. Firstly, catalyst effect was examined by using various heterogeneous gold complexes as catalyst in MeOH as solvent at 60 ºC under air (Table 1, entries 1-3). When a magnetic nano-particles-supported phosphine-Au(I) complex[17f] (Fe_3O_4@SiO_2-P-AuCl) was used as catalyst, only a trace amount of the desired product **3a** was formed. To our delight, the aerobic oxidative C–C coupling reaction could proceed smoothly under the catalysis of Fe_3O_4@SiO_2-bipy-$AuCl_2]^+[AuCl_4]^-$to afford **3a** in 69% yield (entry 2). Whilst another magnetic nanoparticles-immobilized bipy-gold(III) complex[17e] (Fe_3O_4@SiO_2-bipy-$AuCl_2$][Cl]) was substantially less effective and gave a moderate yield (entry 3). A control experiment demonstrated that a trace amount of the desired product **3a** was obtained in the absence of any catalyst (entry 4). When the aerobic oxidative C–C coupling reaction was carried out in $MeNO_2$ as the solvent at 60 ºC under air, the desired product **3a** was obtained in 80% yield after 12 h (entry 5). We were pleased to find that the yield could be further increased to 83% within 6 h by addition of a small amount of MeOH (entry 6). Even if the amount of the catalyst was reduced to 3 mol%, the reaction also proceeded smoothly to afford **3a** in 82% yield after 8 h (entry 7). When the homogeneous unsupported bipy-gold(III) complex was used as the catalyst, the desired product **3a** was also isolated in 84% yield after 5 h (entry 8), indicating that the catalytic activity of Fe_3O_4@SiO_2-bipy-$AuCl_2]^+[AuCl_4]^-$was comparable to that of the homogeneous [(bipy)$AuCl_2$][$AuCl_4$] complex. It is noteworthy that, when the oxidative C–C coupling reaction was performed in an argon atmosphere instead of air, the reaction proceeded very slowly and a much lower yield was obtained (entry 9).

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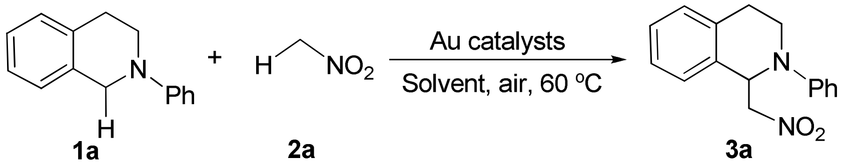
Thus, the optimized reaction conditions for this transformation are the $Fe_3O_4@SiO_2$-bipy-$AuCl_2]^+[AuCl_4]^-$(3 mol%) in $MeNO_2$ as solvent in the presence of a small amount of MeOH at 60 °C under air for 8 h (Table 1, entry 7).

Table 1 Optimization of the heterogeneous gold-catalyzed aerobic oxidative C–C coupling of *N*-phenyl tetrahydroisoquinoline **1a** with nitromethane **2a**.[a]



Entry	Au catalyst (mol%)	Solvent	Time (h)	Yield(%)[b]
1	$Fe_3O_4@SiO_2$-P-AuCl (5)	MeOH	12	trace
2	$Fe_3O_4@SiO_2$-bipy-$AuCl_2$][$AuCl_4$] (5)	MeOH	12	69
3	$Fe_3O_4@SiO_2$-bipy-$AuCl_2$][Cl] (5)	MeOH	12	45
4	–	MeOH	12	trace
5	$Fe_3O_4@SiO_2$-bipy-$AuCl_2$][$AuCl_4$] (5)	$MeNO_2$	12	80
6[c]	$Fe_3O_4@SiO_2$-bipy-$AuCl_2$][$AuCl_4$] (5)	$MeNO_2$	6	83
7[c]	$Fe_3O_4@SiO_2$-bipy-$AuCl_2$][$AuCl_4$] (3)	$MeNO_2$	8	82
8[c]	[(bipy)$AuCl_2$][$AuCl_4$] (3)	$MeNO_2$	5	84
9[c,d]	$Fe_3O_4@SiO_2$-bipy-$AuCl_2$][$AuCl_4$] (3)	$MeNO_2$	24	13

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.2 mL), heterogeneous Au catalyst (3-5 mol%), solvent (0.8 mL) at 60 ºC under air. [b] Isolated yield. [c] MeOH (0.1 mL) was used as co-solvent. [d] The reaction was performed under Ar.

With this promising result in hand, we started to investigate the scope of this heterogeneous gold(III)-catalyzed aerobic oxidative C–C coupling reaction under the optimized conditions. Initially, a variety of *N*-aryltetrahydroisoquinolines **1a-h** were investigated as substrates to explore the functional group tolerance and the results are listed in Table 2. To our delight, both electron-donating and electron-withdrawing

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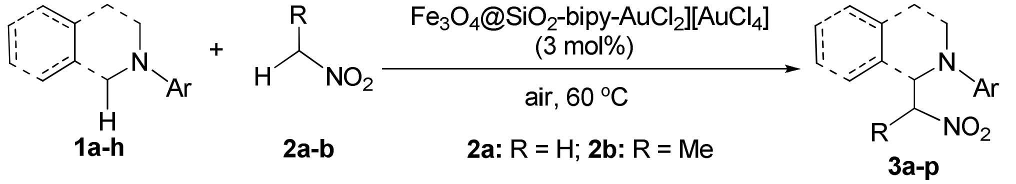
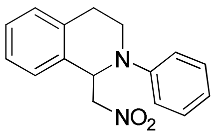
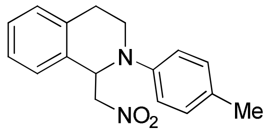
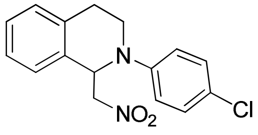
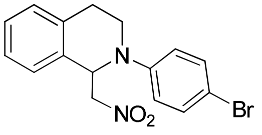
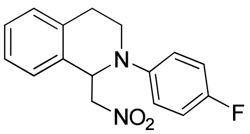
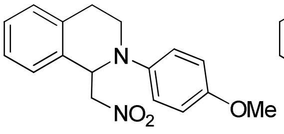
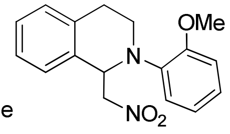
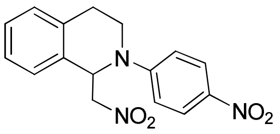
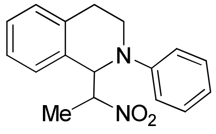
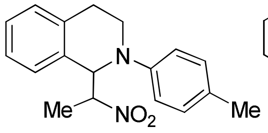
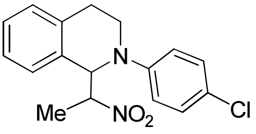
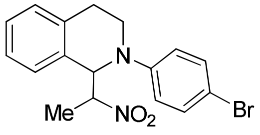
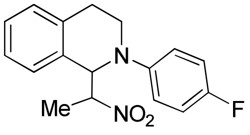
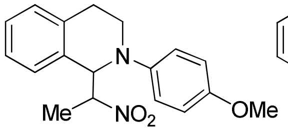
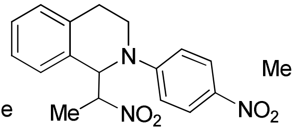
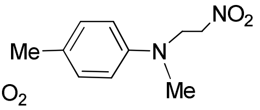
groups on the aromatic rings were compatible under the optimized reaction conditions. The reactions of all the substrates with nitromethane proceeded smoothly to afford the corresponding 1-nitromethyl-substituted *N*-aryltetrahydroisoquinolines **3a-h** in good to high yields. Interestingly, the less active nitroethane **2b** can also be used as the nucleophile under the optimized conditions to give the corresponding C–C coupling products **3i-o** in good yields. When a nonbenzylic tertiary amine such as *N,N*-dimethyl-4-methylaniline was employed as substrate, the desired product **3p** was also obtained in satisfactory yield after 36 h.

Table 2 Heterogeneous gold(III)-catalyzed aerobic oxidative C–C coupling reaction of tertiary amines with nitroalkanes.[a,b]



 **3a,** 82% yield	 **3b,** 85% yield	 **3c,** 87% yield	 **3d,** 84% yield
 **3e,** 86% yield	 **3f,** 90% yield	 **3g,** 74% yield	 **3h,** 91% yield
 **3i,** 81% yield	 **3j,** 83% yield	 **3k,** 82% yield	 **3l,** 80% yield
 **3m,** 76% yield	 **3n,** 85% yield	 **3o,** 88% yield	 **3p,** 48% yield[c]

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[a] Reaction conditions: tertiary aniline **1** (0.1 mmol), nitroalkane **2**/MeOH (v/v = 9:1, 1.0 mL), Fe_3O_4@SiO_2-bipy-$AuCl_2$][$AuCl_4$] (3 mol%) at 60 ºC for 8 h under air. [b] Isolated yield. [c] For 36 h.

Encouraged by the above results, we then applied the heterogeneous gold-catalyzed strategy to the aerobic oxidative C–C coupling reaction of *N*-aryltetrahydroisoquinolines with three unmodified ketones to further illustrate the generality of our protocol and the results are listed in Table 3. Initially, treatment of **1b** with acetone **2c** in the presence of 3 mol% of Fe_3O_4@SiO_2-bipy-$AuCl_2]^+[AuCl_4]^-$in acetone as solvent gave the desired product **3q** in only 27% yield. We were pleased to find that addition of molecular sieves (4 Å) and an acid were beneficial to the aerobic oxidative C–C coupling reaction and the yield of **3q** could be improved to 73%. Under the optimized reaction conditions, a wide range of *N*-aryltetrahydroisoquinolines could undergo the oxidative C–C coupling reaction with acetone smoothly to furnish the corresponding C–C coupling products **3q-v** in good yields (73-86%). The results indicated that the electronic effect of substituents on the aromatic rings has limited influence on this heterogeneous gold-catalyzed C–C coupling reaction. The bulky acetophenone **2d** was proved to be an active nucleophile and coupled with different *N*-aryltetrahydroisoquinolines effectively to afford the desired products **3w-z** in good yields. Notably, besides methyl ketones, cyclohexanone **2e** was also a suitable substrate and could undergo the aerobic oxidative C–C coupling reaction with *N*-aryltetrahydroisoquinolines smoothly to give the desired products **3a'** and **3b'** in useful synthetic yields.

Table 3 Heterogeneous gold(III)-catalyzed aerobic oxidative C–C coupling reaction of *N*-aryltetrahydroisoquinolines with ketones.[a,b]

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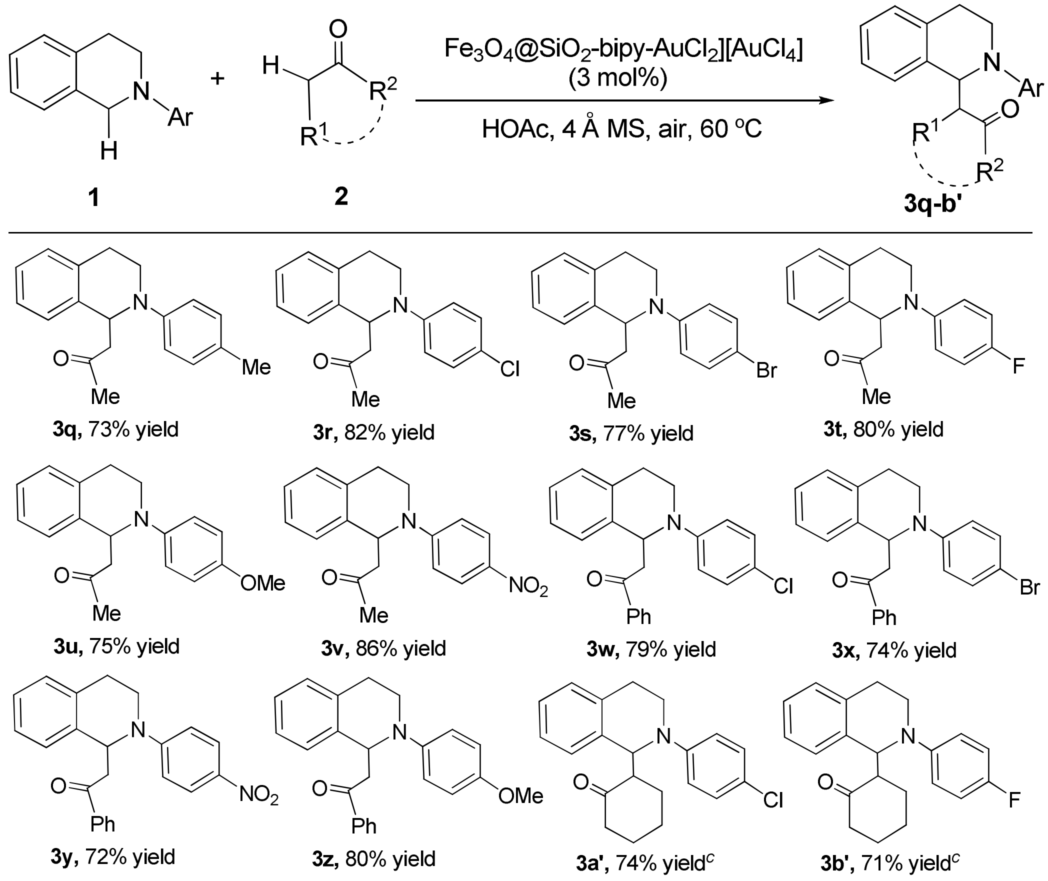

3q, 73% yield
3r, 82% yield
3s, 77% yield
3t, 80% yield
3u, 75% yield
3v, 86% yield
3w, 79% yield
3x, 74% yield
3y, 72% yield
3z, 80% yield
3a', 74% yield[c]
3b', 71% yield[c]

[a] Reaction conditions: *N*-aryltetrahydroisoquinoline **1** (0.1 mmol), ketone **2** (0.5 mL), 4 Å MS (60 mg), HOAc (0.1 mL), Fe_3O_4@SiO_2-bipy-$AuCl_2$][$AuCl_4$] (3 mol%) at 60 ºC for 12 h under air. [b] Isolated yield. [c] MsOH (5 μL) was used.

To determine whether the observed catalysis was due to the heterogeneous catalyst Fe_3O_4@SiO_2-bipy-$AuCl_2]^+[AuCl_4]^-$ or to a leached gold species in solution, the aerobic oxidative C–C coupling reaction of *N*-phenyl tetrahydroisoquinoline **1a** with nitromethane **2a** was carried out until an approximately 50% conversion of **1a** was reached. The Fe_3O_4@SiO_2-bipy-$AuCl_2]^+[AuCl_4]^-$catalyst was then separated magnetically from the solution and the reaction solution was transferred to another reaction tube and stirred again at 60 ºC for 6 h. If gold was leaching from the solid surface during the reaction, the solution should contain gold. In this case, no signi-

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ficant increase in conversion of **1a** was observed, indicating that leached Au species from the catalyst (if any) are not responsible for the observed activity. It was confirmed by ICP-AES analysis that indicated that no gold species could be detected in the reaction solution after the separation of $Fe_3O_4@SiO_2$-bipy-$AuCl_2]^+[AuCl_4]^-$. These results rule out any contribution to the observed catalysis from a homogeneous gold species demonstrating that the catalytic oxidative C–C coupling reaction was intrinsically heterogeneous.

Although the exact mechanism of the gold-catalyzed C–C coupling reaction is not clear at this stage, a plausible mechanism for this heterogeneous gold-catalyzed reaction is showed in Scheme 2. Initially, the $Fe_3O_4@SiO_2$-bipy-$AuCl_2]^+[AuCl_4]^-$complex may be reduced by the solvent or substrates to a magnetic nanoparticles-supported gold(I) species (**A**),[13e] which would coordinate to tertiary amine (**1a**) to produce an intermediate (**B**). An electron transfer and subsequent hydrogen transfer from tertiary amine (**1a**) to gold gives a magnetic nanoparticles-supported iminium gold hydride complex (**C**). The AuH species (**C**) could form the iminium ion/AuOOH complex (**D**) in the presence of air (O_2) in a similar way to PdH and RuH.[23] The supported iminium ion/AuOOH complex (**D**) can be trapped with nitromethane (**2a**) quickly to afford the desired product (**3a**), H_2O and the supported gold(III) oxo complex (**E**). Subsequently, the latter reacts with another tertiary amine (**1a**) to produce the supported iminium intermediate (**F**) by electron and hydrogen transfer.[24] Finally, the supported iminium intermediate (**F**) could react with nitromethane (**2a**) to give the product (**3a**) and regenerate the magnetic nanoparticles-supported gold(I) species (**A**) to complete the

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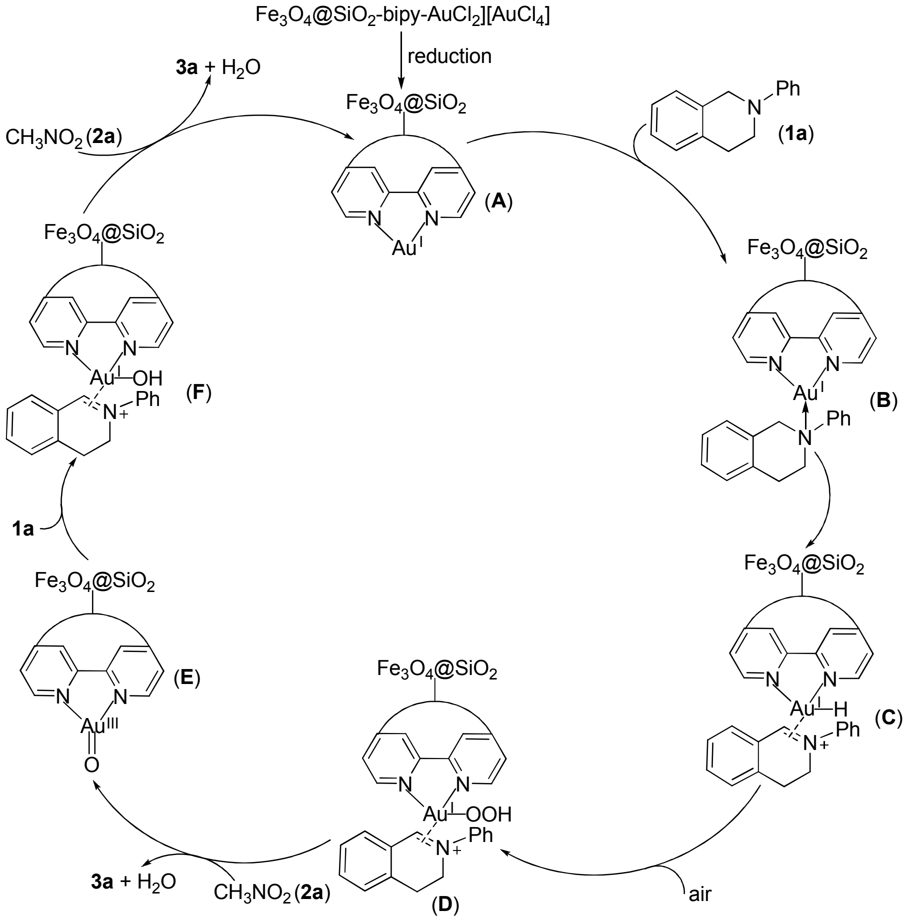
catalytic cycle.



Scheme 2 Plausible mechanism for heterogeneous gold-catalyzed aerobic oxidative C–C coupling reaction.

For the practical application of a heterogeneous precious metal catalyst system, its stability and reusability are important factors. We next investigated the recycling of $Fe_3O_4@SiO_2$-bipy-$AuCl_2]^+[AuCl_4]^-$complex by using the coupling of *N*-(4-methoxy-phenyl)tetrahydroisoquinoline **1f** with nitromethane **2a** as a model reaction. Each time, after the reaction was finished, more than 99% of the gold catalyst could simply be recovered by fixing a magnet near to the reaction vessel. The recovered catalyst was washed with MeOH, air-dried and used directly in the next run without further puri-

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fication. The recovered gold catalyst was used for ten consecutive cycles using fresh substrates and solvent under identical conditions and the results are presented in Fig. 6. As shown in Fig. 6, the yield of the desired product **3f** in all cases was found to be almost similar which confirmed that the developed catalyst can be recycled efficiently for at least ten times without significant loss of activity. In addition, from the TEM images of the recovered catalyst (Fig. 1b) and the fresh one (Fig. 1a), no obvious differences in the morphology and dispersion of nanoparticles could be observed. The excellent reusability of the catalyst should result from the chelating action of bidentate bipyridine ligand on gold and the magnetic separation. The result is important from industrial and environmental points of view.

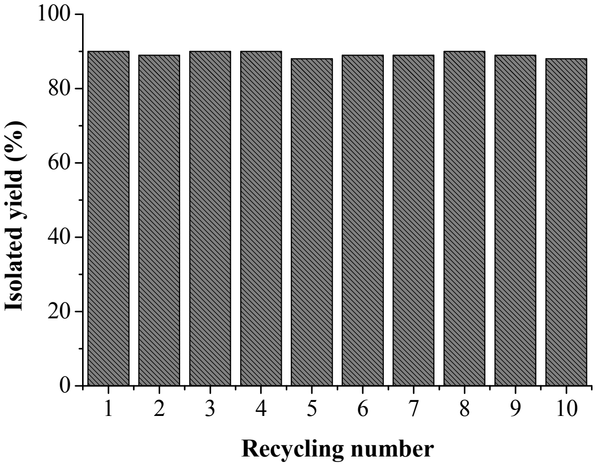

Fig. 6 Recycle of the $Fe_3O_4@SiO_2$-bipy-$AuCl_2]^+[AuCl_4]^-$catalyst.

Conclusions

In conclusion, we have developed a highly efficient heterogeneous aerobic oxidative C–C coupling reaction of tertiary amines with nitroalkanes and various unmodified ketones by using a magnetic nanoparticles-immobilized bipy-gold(III) complex (Fe_3O_4@SiO_2-bipy-$AuCl_2]^+[AuCl_4]^-$) as catalyst and air as the sole oxidant. The reaction proceeds with high efficiency under mild conditions, generating the corresponding C–C coupling products in good to high yields. More importantly, this heterogeneous gold catalyst can simply be recovered by applying an external magnet and recycled at least ten times without significant loss of activity. The advantageous features such as safe, convenient, and environmentally benign process, the broad substrate scope, good yields, as well as easy recovery and recyclability of the catalyst make the present protocol very practical.

Experimental

All reagents were obtained from commercial sources without further purification, and commercially available solvents were purified before use. Bis(bromomethyl)-functionalized bipy-gold complex $[(BrCH_2)_2$bipy-$AuCl_2][AuCl_4]$,[21] [(bipy)$AuCl_2][AuCl_4]$,[21] 4,4'-bis[3-(triethoxysilyl)propylaminomethyl]-2,2'-bipyridine[17e] and the silica-coated Fe_3O_4 (Fe_3O_4@SiO_2)[22] were prepared according to literature procedures. All products were fully characterized. ^{1}H 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 in a transmission electron microscope

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operated at an accelerated voltage of 200 kV. X-ray diffraction (XRD) measurements were carried out at room temperature using an X-ray powder diffractmeter. X-ray energy dispersive spectroscopy (EDS) was performed using a microscope.

Preparation of Fe_3O_4@SiO_2-P-AuCl complex

To a suspension of 0.75 g of Fe_3O_4@SiO_2 in 30 mL of dry toluene was added a solution of $(EtO)_3SiCH_2CH_2PPh_2$ (0.57 g) in 10 mL of dry toluene. The mixture was stirred at 110 ºC 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 ºC 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.

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 Fe_3O_4@SiO_2-P was added. The mixture was stirred at 65 ºC for 12 h, then the solid catalyst was magnetically separated, washed thoroughly with MeOH, and dried under vacuum at 100 ºC 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} by ICP-AES.

Preparation of Fe_3O_4@SiO_2-bipy-$AuCl_2$][$AuCl_4$] complex

Et_3N (0.202 g, 2 mmol) and 3-aminopropyltriethoxysilane (0.442 g, 2 mmol) were

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added to a solution of [$(BrCH_2)_2$bipy-$AuCl_2$][$AuCl_4$] (0.190 g, 0.2 mmol) in THF (10 mL), and the mixture was stirred at 50 ºC under Ar for 6 h. After cooling the solution to room temperature, hexane (20 mL) was added and the mixture was filtered through a short $MgSO_4$ column to remove the ammonium salt. The clear solution was then concentrated and dried under vacuum at 100 ºC for 24 h to give the triethoxysilyl-functionalized [(bipy)$AuCl_2$][$AuCl_4$] complex. The latter was added to a suspension of Fe_3O_4@SiO_2 (0.5 g) in 40 mL of dry toluene. The reaction mixture was stirred at 110 ºC under Ar 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 80 ºC under vacuum for 3 h to afford 0.621 g of the Fe_3O_4@SiO_2-bipy-$AuCl_2$] [$AuCl_4$] complex as brown nanoparticles. The nitrogen content was found to be 0.51 mmol g^{-1} by elemental analysis and the gold content was determined to be 0.23 mmol g^{-1} by ICP-AES.

Preparation of Fe_3O_4@SiO_2-bipy-$AuCl_2$][Cl] complex

To a suspension of 0.75 g of Fe_3O_4@SiO_2 in 20 mL of dry toluene was added a solution of 4,4'-bis[3-(triethoxysilyl)propylaminomethyl]-2,2'-bipyridine (0.872 g, 1.4 mmol) in 40 mL of dry toluene. The mixture was stirred at 110 ºC under argon atmosphere for 24 h. Then the solid material was magnetically separated, washed repeatedly with toluene and CH_2Cl_2 to remove any unanchored species and dried at 100 ºC under vacuum for 5 h to afford 0.86 g of the bipyridine-functionalized Fe_3O_4@SiO_2 (Fe_3O_4@SiO_2-bipy) as brown nanoparticles. The nitrogen content was

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found to be 2.85 mmol g^{-1} by elemental analysis.

To a three-necked bottom flask, $AuCl_3$ (98 mg, 0.32 mmol) and MeOH (50 mL) were added. The solution was stirred at room temperature under argon atmosphere for 10 min, and then 0.421 g of Fe_3O_4@SiO_2-bipy was added. The mixture was stirred at 65 ºC for 24 h, then the solid catalyst was magnetically separated, washed thoroughly with MeOH, and dried under vacuum at 60 ºC for 3 h to give 0.456 g of Fe_3O_4@SiO_2-bipy-$AuCl_2$][Cl] as brown nanoparticles. The gold content was determined to be 0.63 mmol g^{-1} by ICP-AES.

General procedure for heterogeneous gold-catalyzed aerobic oxidative C–C coupling reaction of tertiary amines with nitroalkanes

To the mixture of *N*-aryl-1,2,3,4-tetrahydroisoquinoline (0.1 mmol) and Fe_3O_4@ SiO_2-bipy-$AuCl_2$][$AuCl_4$] (26 mg, 3 mol%) in nitroalkanes (0.9 mL) was added a small amount of methanol (0.1 mL). Then the reaction mixture was stirred at 60 ºC under air for 8 h. The reaction was monitored by TLC on silica-gel plates (GF 254). After completion of the reaction, the reaction mixture was cooled to room temperature and the supported catalyst was magnetically separated and washed with methanol (2 × 2 mL), air-dried and used directly for the next run. The reaction solution was concentrated under reduced pressure and the residue was purified by flash chromatography (petroleum ether : ethyl acetate = 15:1) to afford the desired product.

1-(Nitromethyl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3a).[5a] Yellow solid. Mp 89–90 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30-7.11 (m, 6H), 6.99-6.95 (m, 2H),

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6.86-6.82 (m, 1H), 5.54 (t, *J* = 7.2 Hz, 1H), 4.87-4.82 (m, 1H), 4.58-4.53 (m, 1H), 3.68-3.55 (m, 2H), 3.13-3.02 (m, 1H), 2.82-2.74 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 148.5, 135.3, 133.0, 129.5, 129.2, 128.1, 127.0, 126.7, 119.5, 115.2, 78.8, 58.2, 42.1, 26.5.

2-(4-Methylphenyl)-1-(nitromethyl)-1,2,3,4-tetrahydroisoquinoline (3b).[6] Yellow solid. Mp 95–96 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.25-7.10 (m, 4H), 7.06 (d, *J* = 8.6 Hz, 2H), 6.88 (d, *J* = 8.6 Hz, 2H), 5.51-5.45 (m, 1H), 4.87-4.80 (m, 1H), 4.58-4.53 (m, 1H), 3.68-3.51 (m, 2H), 3.11-2.99 (m, 1H), 2.77-2.70 (m, 1H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 146.4, 135.4, 133.0, 130.0, 129.3, 129.1, 128.0, 127.0, 126.7, 115.9, 78.9, 58.4, 42.3, 26.2, 20.4.

2-(4-Chlorophenyl)-1-(nitromethyl)-1,2,3,4-tetrahydroisoquinoline (3c).[6] Yellow solid. Mp 99–100 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.32-7.08 (m, 6H), 6.88 (d, *J* = 8.8 Hz, 2H), 5.48 (t, *J* = 7.4 Hz, 1H), 4.87-4.80 (m, 1H), 4.59-4.54 (m, 1H), 3.69-3.51 (m, 2H), 3.14-2.98 (m, 1H), 2.81-2.71 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 147.1, 135.1, 132.5, 129.3, 128.3, 127.0, 126.9, 124.4, 116.5, 78.7, 58.2, 42.2, 26.2.

2-(4-Bromophenyl)-1-(nitromethyl)-1,2,3,4-tetrahydroisoquinoline (3d).[15d] Yellow solid. Mp 105–106 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.36-7.27 (m, 2H), 7.26-7.10 (m, 4H), 6.84 (d, *J* = 8.8 Hz, 2H), 5.48 (t, *J* = 7.2 Hz, 1H), 4.86-4.80 (m, 1H), 4.59-4.53 (m, 1H), 3.71-3.51 (m, 2H), 3.11-2.98 (m, 1H), 2.83-2.73 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 147.5, 135.1, 132.5, 132.3, 129.3, 128.3, 127.0, 126.9, 116.8, 111.6, 78.7, 58.1, 42.2, 26.2.

2-(4-Fluorophenyl)-1-(nitromethyl)-1,2,3,4-tetrahydroisoquinoline (3e). Yellow

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oil. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.29-7.11 (m, 4H), 6.99-6.85 (m, 4H), 5.46-5.36 (m, 1H), 4.84-4.79 (m, 1H), 4.59-4.52 (m, 1H), 3.70-3.50 (m, 2H), 3.08-2.97 (m, 1H), 2.75-2.66 (m, 1H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 157.2 (d, *J* = 237.7 Hz), 145.34 (d, *J* = 2.2 Hz), 135.3, 132.6, 129.5, 128.1, 127.0, 126.8, 118.0 (d, *J* = 7.6 Hz), 115.9 (d, *J* = 22.2 Hz), 78.9, 58.8, 42.9, 25.8. HR-MS (ESI) *m/z* calcd for $C_{16}H_{15}FN_2O_2^+$ [M$^+$] 286.1118, found 286.1113.

2-(4-Methoxyphenyl)-1-(nitromethyl)-1,2,3,4-tetrahydroisoquinoline(3f).[5a] Yellow solid. Mp 103–104 ºC. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.21-7.02 (m, 4H), 6.84 (d, *J* = 8.8 Hz, 2H), 6.74 (d, *J* = 8.8 Hz, 2H), 5.34-5.28 (m, 1H), 4.78-4.71 (m, 1H), 4.52-4.44 (m, 1H), 3.67 (s, 3H), 3.48 (d, *J* = 4.4 Hz, 2H), 3.00-2.86 (m, 1H), 2.66-2.58 (m, 1H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 154.0, 143.1, 135.4, 132.9, 129.5, 127.9, 126.9, 126.6, 118.9, 114.7, 79.0, 58.9, 55.6, 43.2, 25.9.

2-(2-Methoxyphenyl)-1-(nitromethyl)-1,2,3,4-tetrahydroisoquinoline (3g).[5a] Yellow solid. Mp 101–102 ºC. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.27-7.13 (m, 4H), 7.02 (t, *J* = 7.6 Hz, 1H), 6.91-6.80 (m, 3H), 5.53-5.44 (m, 1H), 4.84-4.76 (m, 1H), 4.57-4.49 (m, 1H), 3.82 (s, 3H), 3.60-3.54 (m, 1H), 3.52-3.43 (m, 1H), 3.04-2.90 (m, 1H), 2.75-2.64 (m, 1H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 153.2, 139.0, 135.4, 133.7, 129.6, 127.6, 126.8, 126.4, 124.1, 122.0, 121.1, 112.6, 79.2, 58.2, 55.8, 43.0, 26.9.

1-(Nitromethyl)-2-(4-nitrophenyl)-1,2,3,4-tetrahydroisoquinoline (3h).[25] Yellow oil. ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.15 (d, *J* = 9.2 Hz, 2H), 7.32-7.14 (m, 4H), 6.96 (d, *J* = 9.2 Hz, 2H), 5.71 (t, *J* = 7.0 Hz, 1H), 4.89-4.84 (m, 1H), 4.66-4.60 (m, 1H), 3.74 (t, *J* = 6.0 Hz, 2H), 3.19-3.11 (m, 1H), 3.01-2.92 (m, 1H); ^{13}C NMR (100 MHz,

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$CDCl_3$): δ 152.6, 138.9, 134.5, 132.0, 129.1, 128.9, 127.3, 127.1, 126.3, 112.0, 78.1, 57.5, 42.3, 27.0.

1-(1-Nitroethyl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3i).[5a] Yellow oil. dr = 2:1. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31-7.07 (m, 6H), 7.02-6.96 (m, 2H), 6.85-6.78 (m, 1H), 5.27-5.20 (m, 1H), 5.08-4.85 (m, 1H), 3.87-3.50 (m, 2H), 3.10-2.85 (m, 2H), [1.70 (d, *J* = 6.6 Hz), 1.54 (d, *J* = 6.6 Hz), 3H]; ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.2, 148.9, 135.6, 134.8, 133.8, 132.1, 129.5, 129.3, 129.1, 128.9, 128.7, 128.4, 128.2, 127.3, 126.6, 126.2, 119.4, 118.8, 115.5, 114.5, 89.0, 85.5, 62.8, 61.2, 43.6, 42.7, 26.8, 26.4, 17.5, 16.4.

2-(4-Methylphenyl)-1-(1-nitroethyl)-1,2,3,4-tetrahydroisoquinoline (3j).[15d] Yellow oil. dr = 2:1. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26-6.99 (m, 6H), 6.89 (d, *J* = 8.4 Hz, 2H), 5.20-5.11 (m, 1H), 5.09-4.82 (m, 1H), 3.85-3.49 (m, 2H), 3.08-2.77 (m, 2H), [2.25 (s), 2.23 (s), 3H], [1.68 (d, *J* = 6.6 Hz), 1.53 (d, *J* = 6.6 Hz), 3H]; ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.2, 146.8, 135.8, 134.9, 133.8, 132.1, 130.9, 129.9, 129.8, 129.2, 128.9, 128.8, 128.4, 128.1, 127.3, 126.6, 126.1, 116.1, 115.2, 89.0, 85.6, 62.9, 61.5, 43.9, 43.1, 26.6, 26.3, 20.4, 20.3, 17.4, 16.5.

2-(4-Chlorophenyl)-1-(1-nitroethyl)-1,2,3,4-tetrahydroisoquinoline (3k). Yellow oil. dr = 2:1. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30-6.99 (m, 6H), 6.89 (d, *J* = 7.6 Hz, 2H), 5.21-5.11 (m, 1H), 5.05-4.81 (m, 1H), 3.86-3.44 (m, 2H), 3.09-2.83 (m, 2H), [1.67 (d, *J* = 6.6 Hz), 1.55 (d, *J* = 6.6 Hz), 3H]; ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.8, 147.5, 135.4, 134.6, 133.5, 131.8, 129.3, 129.2, 129.1, 128.8, 128.5, 128.4, 128.3, 127.3, 126.8, 126.3, 124.2, 123.7, 116.7, 115.7, 88.8, 85.5, 62.9, 61.2, 43.9, 42.9, 26.7,

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26.2, 17.4, 16.7. HR-MS (ESI) *m/z* calcd for $C_{17}H_{17}ClN_2O_2^+$ [M^+] 316.0979, found 316.0981.

2-(4-Bromophenyl)-1-(1-nitroethyl)-1,2,3,4-tetrahydroisoquinoline (3l).[15d] Yellow oil. dr = 2:1. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36-7.01 (m, 6H), 6.88-6.81 (m, 2H), 5.22-5.12 (m, 1H), 5.03-4.81 (m, 1H), 3.82-3.47 (m, 2H), 3.06-2.85 (m, 2H), [1.67 (d, *J* = 6.6 Hz), 1.54 (d, *J* = 6.6 Hz), 3H]; ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.2, 147.9, 135.3, 134.5, 133.5, 132.2, 132.0, 131.8, 129.2, 128.7, 128.5, 128.4, 128.3, 127.3, 126.8, 126.3, 117.0, 116.1, 111.5, 110.8, 88.8, 85.4, 62.8, 61.1, 43.8, 42.8, 26.7, 26.2, 17.4, 16.6.

2-(4-Fluorophenyl)-1-(1-nitroethyl)-1,2,3,4-tetrahydroisoquinoline (3m). Yellow oil. dr = 2:1. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27-7.06 (m, 4H), 7.04-6.84 (m, 4H), 5.15-4.80 (m, 2H), 3.87-3.76 (m, 1H), 3.61-3.42 (m, 1H), 3.14-2.76 (m, 2H), [1.67 (d, *J* = 6.6 Hz), 1.55 (d, *J* = 6.6 Hz), 3H]; ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.1 (d, *J* = 237.5 Hz), 156.8 (d, *J* = 237.2 Hz), 146.1 (d, *J* = 2.2 Hz), 145.7 (d, *J* = 2.2 Hz), 135.6, 134.8, 133.5, 131.9, 129.3, 129.0, 128.4, 128.3, 128.2, 127.2, 126.7, 126.2, 118.0 (d, *J* = 7.6 Hz), 117.2 (d, *J* = 7.6 Hz), 115.8 (d, *J* = 22.2 Hz), 115.7 (d, *J* = 22.2 Hz), 88.8, 85.7, 63.4, 61.9, 44.7, 43.6, 26.4, 26.0, 17.2, 16.8. HR-MS (ESI) *m/z* calcd for $C_{17}H_{17}FN_2O_2^+$ [M^+] 300.1274, found 300.1280.

2-(4-Methoxyphenyl)-1-(1-nitroethyl)-1,2,3,4-tetrahydroisoquinoline (3n).[5a] Yellow oil. dr = 1.3:1. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27-7.11 (m, 4H), 7.09-6.86 (m, 2H), 6.83-6.74 (m, 2H), 5.09-4.77 (m, 2H), 3.82-3.44 (m, 5H), 3.05-2.73 (m, 2H), [1.67 (d, *J* = 6.6 Hz), 1.53 (d, *J* = 6.6 Hz), 3H]; ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.8,

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153.6, 143.9, 143.5, 135.9, 135.1, 133.7, 132.1, 129.3, 129.0, 128.4, 128.1, 128.0, 127.2, 126.5, 126.1, 118.9, 118.3, 114.7, 114.6, 88.8, 85.8, 63.5, 62.2, 45.0, 44.0, 26.3, 26.1, 17.1, 16.6.

1-(1-Nitroethyl)-2-(4-nitrophenyl)-1,2,3,4-tetrahydroisoquinoline (3o). Yellow oil. dr = 4:1. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20-8.09 (m, 2H), 7.34-7.05 (m, 4H), 6.99-6.91 (m, 2H), 5.50-5.39 (m, 1H), 5.03-4.85 (m, 1H), 3.95-3.88 (m, 1H), 3.65-3.57 (m, 1H), 3.22-3.01 (m, 2H), [1.68 (d, J = 6.6 Hz), 1.58 (d, J = 6.6 Hz), 3H]; ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.3, 153.0, 138.8, 138.6, 134.7, 134.0, 133.0, 131.6, 129.1, 129.0, 128.8, 128.6, 128.2, 127.3, 127.2, 126.8, 126.2, 125.9, 112.1, 111.7, 88.4, 85.1, 62.2, 60.5, 44.0, 43.0, 27.3, 26.9, 17.4, 16.7. HR-MS (ESI) *m/z* calcd for $C_{17}H_{18}N_3O_4^+$ [M+H$^+$] 328.1297, found 328.1294.

N,4-Dimethyl-N-(2-nitroethyl)aniline (3p).[5a] Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.07 (d, J = 8.6 Hz, 2H), 6.66 (d, J = 8.6 Hz, 2H), 4.55 (t, J = 6.2 Hz, 2H), 3.96 (t, J = 6.2 Hz, 2H), 2.94 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.9, 130.0, 127.5, 113.2, 72.6, 51.0, 39.0, 20.2.

General procedure for heterogeneous gold-catalyzed aerobic oxidative C–C coupling reaction of tertiary amines with ketones

To the mixture of *N*-aryl-1,2,3,4-tetrahydroisoquinoline (0.1 mmol) and Fe_3O_4@ SiO_2-bipy-$AuCl_2$][$AuCl_4$] (26 mg, 3 mol%) and 4Å MS (60 mg) in ketone (0.5 mL) was injected a small amount of HOAc (0.1 mL). Subsequently, the reaction mixture was stirred at 60 ºC under air for 12 h. When the reaction was completed, the reaction mixture was cooled to room temperature and the supported catalyst was magnetically

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separated. The reaction mixture was poured into saturated Na_2CO_3 solution (5 mL) and extracted with ethyl acetate (3 × 10 mL). The combined organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by flash chromatography (petroleum ether : ethyl acetate = 15:1) to afford the desired product. The recovered catalyst was washed with methanol (2 × 2 mL), air-dried and used directly for the next run.

1-(2-(4-Methylphenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)propan-2-one (3q).[15d] Colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ 7.20-7.10 (m, 4H), 7.05 (d, J = 8.6 Hz, 2H), 6.86 (d, J = 8.6 Hz, 2H), 5.34 (t, J = 6.4 Hz, 1H), 3.67-3.45 (m, 2H), 3.11-2.98 (m, 2H), 2.85-2.74 (m, 2H), 2.25 (s, 3H), 2.07 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 207.3, 147.0, 138.3, 134.4, 129.8, 128.8, 128.0, 126.9, 126.7, 126.2, 115.8, 55.2, 50.1, 42.3, 31.0, 27.0, 20.3.

1-(2-(4-Chlorophenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)propan-2-one (3r).[15d] Yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ 7.23-7.08 (m, 6H), 6.85 (d, J = 8.8 Hz, 2H), 5.34 (t, J = 6.2 Hz, 1H), 3.68-3.43 (m, 2H), 3.05-2.97 (m, 2H), 2.86-2.80 (m, 2H), 2.08 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 207.1, 147.5, 137.9, 134.2, 129.2, 128.7, 127.0, 126.8, 126.4, 123.0, 115.8, 54.8, 50.2, 42.2, 31.2, 27.0.

1-(2-(4-Bromophenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)propan-2-one (3s).[15d] Colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ 7.30 (d, J = 8.8 Hz, 2H), 7.18-7.11 (m, 4H), 6.80 (d, J = 8.8 Hz, 2H), 5.33 (t, J = 6.0 Hz, 1H), 3.62-3.44 (m, 2H), 3.06-2.96 (m, 2H), 2.87-2.81 (m, 2H), 2.07 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 207.0, 147.9, 137.9, 134.2, 132.1, 128.7, 127.0, 126.8, 126.4, 116.2, 110.1, 54.7, 50.2, 42.2,

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31.1, 27.1.

1-(2-(4-Fluorophenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)propan-2-one (3t). Colorless oil. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.19-7.09 (m, 4H), 6.97-6.85 (m, 4H), 5.28 (t, J = 6.2 Hz, 1H), 3.64-3.44 (m, 2H), 3.10-2.94 (m, 2H), 2.85-2.73 (m, 2H), 2.07 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 207.3, 156.5 (d, J = 236.3 Hz), 145.8, 138.0, 134.2, 128.9, 126.9, 126.8, 126.4, 117.2 (d, J = 7.4 Hz), 115.7 (d, J = 21.9 Hz), 55.6, 50.1, 42.7, 31.1, 26.7. HR-MS (ESI) m/z calcd for $C_{18}H_{18}FNO^+$ [M$^+$] 283.1372, found 283.1365.

1-(2-(4-Methoxyphenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)propan-2-one (3u).[15d] Colorless oil. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.19-7.06 (m, 4H), 6.90 (d, J = 8.8 Hz, 2H), 6.81 (d, J = 8.8 Hz, 2H), 5.23 (t, J = 6.4 Hz, 1H), 3.74 (s, 3H), 3.58-3.41 (m, 2H), 3.06-2.93 (m, 2H), 2.81-2.70 (m, 2H), 2.05 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 207.3, 153.4, 143.7, 138.3, 134.3, 128.9, 126.8, 126.6, 126.2, 118.4, 114.7, 56.0, 55.6, 50.0, 43.0, 30.8, 26.8.

1-(2-(4-Nitrophenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)propan-2-one (3v). Yellow oil. ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.13 (d, J = 9.4 Hz, 2H), 7.24-7.15 (m, 4H), 6.85 (d, J = 9.4 Hz, 2H), 5.57-5.52 (m, 1H), 3.75-3.59 (m, 2H), 3.12-2.90 (m, 4H), 2.11 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 206.0, 152.7, 137.9, 137.3, 133.9, 128.4, 127.6, 126.9, 126.8, 126.2, 111.2, 54.0, 50.1, 43.0, 31.0, 27.8. HR-MS (ESI) m/z calcd for $C_{18}H_{19}N_2O_3^+$ [M+H$^+$] 311.1396, found 311.1394.

2-(2-(4-Chlorophenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)-1-phenylethanone (3w). White solid. Mp 67–68 ºC. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.85 (d, J = 7.6 Hz, 2H),

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7.53 (t, *J* = 7.2 Hz, 1H), 7.41 (t, *J* = 7.8 Hz, 2H), 7.24-7.08 (m, 6H), 6.88 (d, *J* = 9.2 Hz, 2H), 5.60 (t, *J* = 6.2 Hz, 1H), 3.65-3.49 (m, 3H), 3.42-3.34 (m, 1H), 3.14-3.04 (m, 1H), 2.95-2.85 (m, 1H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 198.5, 147.4, 138.2, 137.2, 134.3, 133.2, 129.1, 128.6, 128.5, 128.1, 127.1, 127.0, 126.4, 122.8, 115.6, 55.2, 45.3, 42.3, 27.3. HR-MS (ESI) *m/z* calcd for $C_{23}H_{21}ClNO^+$ [M+H$^+$] 362.1312, found 362.1317.

2-(2-(4-Bromophenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)-1-phenylethanone (3x). White solid. Mp 72–73 ºC. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.89-7.80 (m, 2H), 7.56-7.50 (m, 1H), 7.44-7.38 (m, 2H), 7.34-7.26 (m, 2H), 7.24-7.08 (m, 4H), 6.88-6.77 (m, 2H), 5.60 (t, *J* = 6.0 Hz, 1H), 3.64-3.51 (m, 3H), 3.42-3.34 (m, 1H), 3.13-3.04 (m, 1H), 2.96-2.87 (m, 1H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 198.4, 147.8, 138.2, 137.2, 134.3, 133.2, 132.0, 128.6, 128.5, 128.1, 127.1, 127.0, 126.4, 115.9, 109.9, 55.1, 45.3, 42.2, 27.3. HR-MS (ESI) *m/z* calcd for $C_{23}H_{21}BrNO^+$ [M+H$^+$] 406.0807, found 406.0804.

2-(2-(4-Nitrophenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)-1-phenylethanone (3y). Yellow solid. Mp 87–88 ºC. ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.12 (d, *J* = 9.6 Hz, 2H), 7.85 (d, *J* = 7.6 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.42 (t, *J* = 7.4 Hz, 2H), 7.29-7.13 (m, 4H), 6.89 (d, *J* = 9.6 Hz, 2H), 5.79 (t, *J* = 6.0 Hz, 1H), 3.82-3.63 (m, 2H), 3.52 (d, *J* = 6.0 Hz, 2H), 3.16-3.07 (m, 2H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 197.6, 152.7, 137.9, 137.4, 136.8, 133.9, 133.5, 128.7, 128.4, 128.1, 127.6, 127.1, 126.9, 126.2, 111.2, 54.6, 45.4, 43.0, 27.8. HR-MS (ESI) *m/z* calcd for $C_{23}H_{20}N_2O_3^+$ [M$^+$] 372.1474, found 372.1482.

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2-(2-(4-Methoxyphenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)-1-phenylethanone (3z).[15d] Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, J = 7.6 Hz, 2H), 7.50 (t, J = 7.4 Hz, 1H), 7.38 (t, J = 7.6 Hz, 2H), 7.20-7.06 (m, 4H), 6.95-6.88 (m, 2H), 6.83-6.74 (m, 2H), 5.51 (t, J = 6.0 Hz, 1H), 3.72 (s, 3H), 3.59-3.49 (m, 3H), 3.33-3.25 (m, 1H), 3.11-3.02 (m, 1H), 2.87-2.77 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.8, 153.1, 143.7, 138.6, 137.4, 134.3, 132.9, 128.8, 128.5, 128.1, 127.1, 126.7, 126.1, 117.9, 114.7, 56.3, 55.7, 45.0, 42.8, 27.3.

2-(2-(4-Chlorophenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)cyclohexanone (3a'). Yellow oil. dr = 1.2:1. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35-7.08 (m, 6H), 6.87-6.68 (m, 2H), [5.61 (d, J = 8.4 Hz), 5.54 (d, J = 4.8 Hz), 1H], 3.73-3.42 (m, 2H), 3.07-2.64 (m, 3H), 2.51-2.40 (m, 1H), 2.37-2.02 (m, 2H), 1.96-1.76 (m, 2H), 1.74-1.51 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.8, 147.9, 147.8, 140.1, 135.6, 134.8, 134.3, 129.1, 129.0, 128.7, 128.0, 127.9, 127.2, 126.9, 126.8, 126.5, 125.9, 122.9, 121.1, 116.1, 113.3, 59.3, 56.4, 55.2, 54.1, 43.8, 43.2, 42.7, 41.5, 32.9, 30.3, 28.7, 27.7, 27.3, 27.1, 25.7, 24.0. HR-MS (ESI) *m/z* calcd for $C_{21}H_{22}ClNO^+$ [M^+] 339.1390, found 339.1395.

2-(2-(4-Fluorophenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)cyclohexanone (3b'). Yellow oil. dr = 12:1. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23-7.08 (m, 4H), 6.97-6.79 (m, 4H), 5.42 (d, J = 5.6 Hz, 1H), 3.73-3.63 (m, 1H), 3.54-3.47 (m, 1H), 2.99-2.73 (m, 3H), 2.49-2.26 (m, 2H), 1.96-1.62 (m, 5H), 1.50-1.43 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.9, 156.4 (d, J = 237.1 Hz), 146.1 (d, J = 2.0 Hz), 135.8, 134.9, 128.9, 127.9, 126.8, 125.8, 117.3 (d, J = 7.3 Hz), 115.7 (d, J = 21.8 Hz), 56.4, 55.8, 43.5, 41.3, 30.4, 27.5, 26.7, 23.7. HR-MS (ESI) *m/z* calcd for $C_{21}H_{23}FNO^+$ [$M+H^+$]

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324.1764, found 324.1763.

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Graphical Abstract

Highly efficient heterogeneous aerobic oxidative C–C coupling from C_{sp^3}–H bonds by a magnetic nanoparticles-immobilized bipy-gold(III) catalyst

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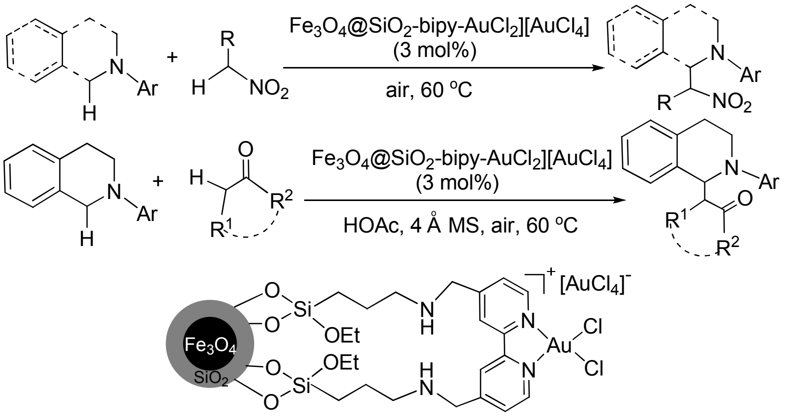

The cross-dehydrogenative coupling of tertiary amines with nitroalkanes and ketones has been achieved using a recyclable magnetic nanoparticles-immobilized bipy-gold(III) catalyst.