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Ethylacetoacetate tagged basic imidazolium salt: multi-task in CuI nanoparticle catalyzed amination of aryl halides

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ABSTRACT

Copper catalyzed reactions suffer from harsh conditions of high temperature, high pressure, over-stoichiometric amount of copper reagents and use of expensive ligands. In an attempt to develop a mild, efficient and reusable system for copper catalyzed reactions, ethylacetoacetate was doped into ionic liquid (IL) by tagging it with imidazolium cation stabilized by a counter hydroxide or acetate anion (**4a** and **4b**). The novel ligand-anchored ILs demonstrated high efficiency in generation and stabilization of uniformly dispersed Cu(I)I nanoparticles with particle size in range 9–12 nm. Further, the catalytic system provided an efficient route to amination of aryl iodides, bromides and the less reactive chlorides under mild conditions with very low catalyst loading of only 2 mol % to yield primary aryl amines selectively. Furthermore, the reaction allowed easy isolation of products with recovery of ionic liquid containing an intact built-in ligand and base combination for further reuse.

1. Introduction

Primary aromatic amines traditionally were prepared by direct coupling of aryl halides with ammonia under harsh conditions of high temperature, high pressure and long reaction times.[1] The method due to its inherent shortcomings remained quite unpopular and was replaced by palladium[2] and copper[3] catalyzed reaction of aryl halides with ammonia or ammonia surrogates. Most of the palladium catalyzed methods offer broad substrate scope and excellent functional group tolerance. However using ammonia directly in palladium catalyzed reactions is complicated by issues, such as (a) binding of ammonia to metal centre in preference to the ligands needed to form active catalyst system, and (b) coupling of primary amines formed as a reaction product with aryl halides to yield di- and tri-aryl amines.[2c,4] The application of copper catalyzed amination reaction is also relatively limited as it has to go through the harsh reaction conditions involving elevated temperatures, highly polar solvents and most of the time use of over-stoichiometric amount of copper reagents.[5] Recently, it has been found that the use of copper chelating ligands, such as β-diketones,[3e,6,12] L-proline,[7] pyridine β-ketones,[8] vicinal diamines,[9] BINOL,[10] ascorbic acid[11] etc. accelerates the reaction rates and substantially lowers the reaction temperatures; yet these methodologies are restricted in their practical applicability sometimes due to the high expense, unavailability, or specificity of ligands. Hence the development of a mild system using catalytic amounts of copper would still represent a major advance. To address the same, we tried to design a system that could promote the amination of aryl halides with aqueous ammonia as a direct nitrogen source under mild conditions with low catalyst loading in the absence of external base and ligand. Moreover, the intention was to make the system work for less reactive aryl chlorides as they are the cheapest precursors for aryl amines.

Inspired by the β-keto ester type ligands as stabilizers for copper catalyzed reactions,[12] we envisaged the synthesis of an ethylacetoacetate (EAA) linked basic imidazolium salt, which could be utilized as (a) a solvent for generation and stabilization of copper iodide nanoparticles (NPs), (b) as a ligand that can coordinate with Cu(I) to form six membered ring structure, (c) as a base, (d) facilitate reaction under mild conditions and (e) could be reused after isolation of products. Imidazolium ion based ILs have recently been shown as promising media for generation and stabilization of transition metal nanoparticles, and have found application in nanoparticle catalyzed hydrogenation and Heck reaction.[13] Since the nanoparticles exhibit a high surface to bulk metal ratio, large enhancements in the activity and selectivity are expected when they are used as catalysts. Further, ionic liquids stabilize these nanoparticles thereby showing a positive effect on the reaction rates.

2. Results and discussion

1-Ethylacetoacetate-3-methyl imidazolium hydroxide (**4a**) and 1-ethylacetoacetate-3-methyl imidazolium acetate (**4b**) were

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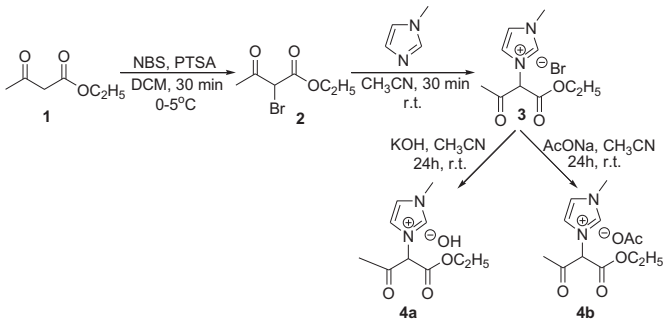
synthesized in a three step procedure starting from ethyl-acetoacetate (1) (Scheme 1). On bromination with NBS, **1** yielded ethyl-2-bromoacetoacetate (**2**), which readily reacted with *N*-methylimidazole at rt in less than 30 min to yield 1-ethylacetoacetate-3-methyl imidazolium bromide (**3**). Anion exchange with potassium hydroxide and sodium acetate yielded **4a** and **4b**, respectively. The ILs **4a** and **4b** were obtained in more than 99% purity and co-existed as a keto–enol mixture (Fig. 1) as was established by LC–MS and H NMR analysis (Supplementary, Fig. S1). The HPLC chromatogram showed two peaks at retention time 0.34 (73%), and 1.67 (27%) min for the keto and enol forms, respectively, giving the same molecular ion peak at 211 in mass spectra. This quantification was in accordance with the H NMR integration of protons for both keto and enol forms, which appeared as distinct signals (Supplementary). The imidazolium proton sandwiched between the two nitrogen atoms appeared most downfield at δ 9.11 ppm in **4a** (keto) and at δ 8.93 in **4a** (enol). One methylene proton for **4a** (keto) appeared at δ 5.50 ppm as expected and was absent for **4a** (enol). The carbon atoms for the keto and enol forms of **4a** were assigned on the basis of HSQC spectral interpretation (Supplementary).



Scheme 1. Synthesis of ethylacetoacetate tagged imidazolium IL **4a** and **4b**.

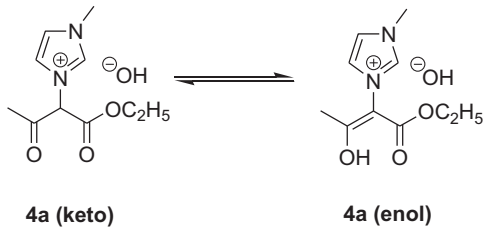
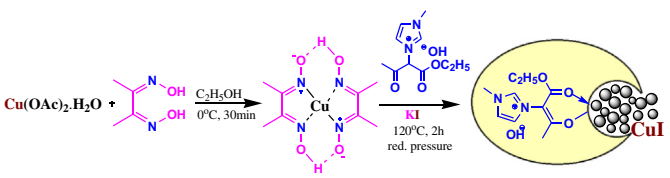


Fig. 1. The coexistence of keto and enol forms of ethylacetoacetate tagged imidazolium hydroxide **4a**.

CuI NPs were prepared by solvothermal method in the presence of **4a** as a stabilizing agent (Scheme 2), and characterized by XRD and EDAX. The XRD pattern of CuI NPs showed four peaks, which could be readily indexed to crystalline γ-CuI both in peak position and relative intensity (Fig. 2a) with no traces of any impurity in agreement with the reported data on JCPDS, 06-0246.[14] EDAX



Scheme 2. Synthesis of CuI nanoparticles in **4a**.

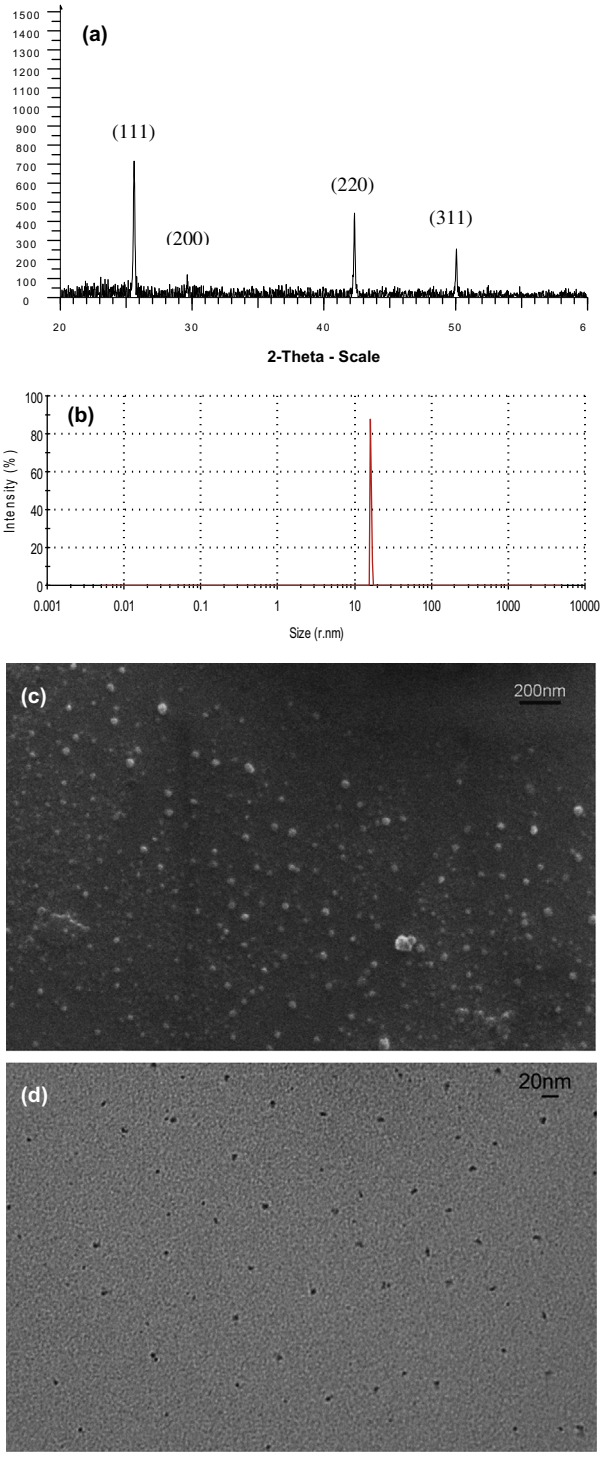


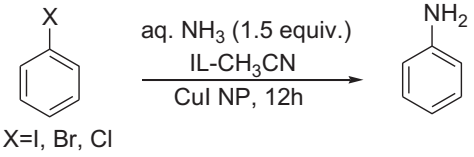
Fig. 2. Characterization of CuI nanoparticles (a) XRD image (b) DLS showing intensity distributed particle size (c) SEM image (d) TEM image.

showed the presence of both copper and iodine (Supplementary, Fig. S5).

Microscopic morphology was visualized by SEM and TEM analysis (Fig. 2c,d). TEM showed the nanoparticles to be spherical and well-dispersed in the size range 9–12 nm. This was almost in agreement with the size obtained from DLS measurements (14–16 nm). The slightly larger size of CuI NPs from DLS is not unusual as DLS measures the hydrodynamic radius (Fig. 2b) of the particles.

The optimization of reaction conditions for amination of iodo, bromo and chlorobenzene with aqueous ammonia was carried out by varying the ionic liquid, catalyst ratio and temperature (Table 1). The screening of ILs **4a** and **4b** showed that amination of aryl halides was more facile in **4a** than **4b** and gave a higher yield of product (Table 1, entries 1 and 2). This could be attributed to the greater basicity furnished by hydroxide anion based **4a** compared to acetate anion based **4b** ideal for amination. The amount of IL also played a major role in controlling the reaction yield. With 1 equiv of **4a** with respect to aryl iodide, the yield of aniline was only 21% (Table 1, entry 1). On increasing the amount to 3 equiv, yield of aminated product increased to 82% (Table 1, entry 2). Further increase in IL concentration did not alter the product yield. The reaction was very clean and no side reaction, such as biaryl formation, reduction of iodobenzene, or formation of monosubstituted and disubstituted aniline was observed. Test reactions with 1, 2 and 10 mol % of CuI NPs at rt gave aniline in 26%, 82% and 82% yields, respectively (Table 1, entries 3–5) while the same reaction required a 20 mol % of CuI bulk to get 80% yield of aniline indicating that a low catalyst loading of CuI as nanoparticles was sufficient to drive the reaction efficiently. The significant 10-fold reduction in catalyst loading was by virtue of using nanoparticles stabilized by ionic framework of **4a**. Further, use of 2 mol % and 10 mol % of CuI bulk instead of CuI NPs under same conditions yielded aniline in 0% and 28% yields, respectively (Table 1, entry 6).

Table 1
Amination of aryl halides: optimization of the catalytic conditions[a]



Entry	X	**4a** (equiv)	CuI NPs (mol %)	Temp (°C)	Yield[b] %
1	I	1	10.0	rt	21 (14)[c]
2	I	3	10.0	rt	82 (45)[c]
3	I	4	10.0	rt	82
4	I	3	1.0	rt	26
5	I	3	2.0	rt	82 (80)[d]
6	I	3	—	rt	0[e] (28)[f]
7	I	0	2.0	rt	15[g] (30)[h]
8	Br	3	2.0	rt	0
9	Br	3	2.0	80	79
10	Cl	3	2.0	80	23
11	Cl	3	2.0	120	77

[a] Reaction conditions: aryl halide (1.0 mmol), commercial 28% aqueous NH_3 (1.5 mmol), CuI NP, **4a**, CH_3CN (2.0 mL), 12 h.
[b] Isolated yield.
[c] Reaction carried out in **4b**.
[d] Reaction with 20 mol % of CuI bulk.
[e] Reaction with 2 mol % of CuI bulk.
[f] Reaction with 10 mol % of CuI bulk.
[g] Reaction carried out in DMSO (2 mL), ethylacetoacetate (40 mol %), K_2CO_3 (3 equiv).
[h] Reaction carried out in [bmim]OH (3 equiv), ethylacetoacetate (3 equiv).

Notably, it was found that amination of aryl iodide in DMSO with CuI NPs (2 mol %) and EAA added externally (40 mol %) as a ligand gave aniline in 15% yield only along with an array of unidentified side products (Table 1, entry 7). This clearly demonstrated the role of **4a** in stabilizing Cu(I)I NPs, which tend to get aggregated in DMSO thereby losing their catalytic efficiency, which is seen in the form of a major drop in the reaction yield. Further the same reaction in 1-butyl-3-methyl imidazolium hydroxide [bmim]OH[15](3 equiv) with CuI NPs (2 mol %) and EAA (3 equiv) added externally gave the monoaminated product along with a side product in 30% yield (Table 1, entry 7).

All these results point out towards the fact that tagging of EAA to imidazolium core as in **4a** induces a unique favourable environment in terms of providing a higher concentration of the enol form of the ligand (27%) responsible for stabilizing the copper(I) species, which is not the case when EAA is added externally as a ligand in DMSO or [bmim]OH since it exists primarily in the keto form (92%). In previous studies Bao et al. demonstrated that compared to other β-keto ester ligands screened by them, EAA was quite ineffective in promoting copper catalyzed N-arylation of 2-pyrrolidinone with iodobenzene with Cs_2CO_3 base in DMF.[3e,6,12] However, tagging of EAA to imidazolium ion appears to enhance its binding ability to copper(I) making it a much more efficient ligand for copper catalyzed reactions. With bromo and chlorobenzene, amination at rt resulted in low conversion rates and therefore slightly higher temperatures were required to achieve full conversion (Table 1, entries 8–11). A blank experiment confirmed that in the absence of **4a** or metal catalyst, no aminated product was formed.

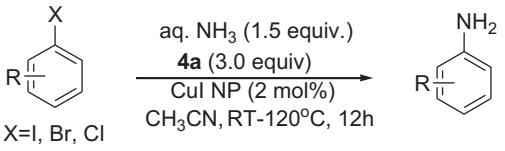
After the best reaction condition was set, the scope of amination was explored by screening different aryl and a few heterocyclic halides. Table 2 summarizes reactions conducted under our optimized conditions giving aminated product in yields ranging from 78% to 87% for aryl iodides at rt. Both electron rich and electron deficient aryl iodides were observed to display similar reactivities. Cu(I)-4a catalytic system displayed a great tolerance to multiple functional groups, such as methoxy, nitro, keto, cyano and fluoro (Table 2, entries 3, 4, 7–9). It is noteworthy to mention that amination of aryl chlorides, which is generally challenging owing to their low reactivity gave good yields with only 2 mol % of CuI NP catalyst when the temperature was raised to 120 °C (Table 2, entries 11 and 12). In contrast to this, previous reports using aqueous ammonia and CuI NPs in tetrabutyl ammonium hydroxide for amination of chlorobenzene and other aryl chlorides failed to yield any aminated product.[14c] In yet another study it was reported that use of 1 mol % ascorbic acid as a ligand for Cu(I) catalyzed amination using liquid ammonia gave less than 5% yield of aniline with inactivated chlorobenzne.[11] Furthermore, the heterocyclic bromides also reacted well with aqueous ammonia under our conditions to afford corresponding heterocyclic amines with satisfactory yields (Table 2, entries 13 and 14).

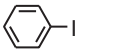
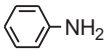
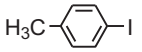
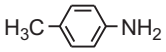
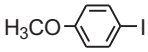
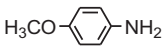
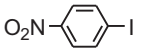
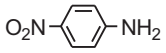
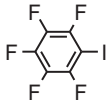
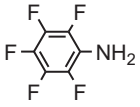
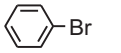
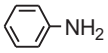
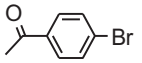
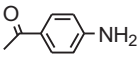
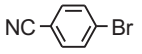
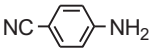
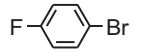
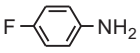
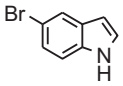
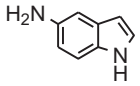
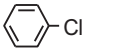
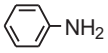
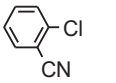
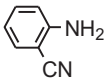
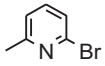
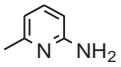
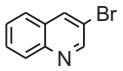
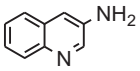
After completion of reaction, the products were extracted with diethyl ether leaving behind catalyst immobilized in **4a**. The reusability of recovered copper catalyst in **4a** for amination was tested by addition of a fresh lot of aryl halide and aqueous ammonia to it. The yield of amine after first and second recycle was found to be 74 and 70%, respectively (Table 2, entry 2). The TEM analysis of CuI NPs showed no significant change in shape and size after first recycle (Supplementary, Fig. S7(b)). Also the powder XRD analysis showed identical peaks for both the fresh and recovered catalyst. After second recycle, however, the catalyst was found to get agglomerated (Supplementary, Fig. S7(c)) and its activity dropped enormously as a negligible yield of only 10% aniline was obtained from amination of iodobenzene. Scheme 3 illustrates a possible mechanism for the reaction. We propose that the chelating CuI with enolate form of **4a** forms a six member reactive species (**5**), which on subsequent oxidative addition with aryl halide leads to the intermediate (**6**). Similar type of Cu(I) enolate complexes have been isolated and characterized.[16] In the presence of hydroxide ion furnished by **4a**, ammonia reacts with intermediate (**6**) readily to afford intermediate (**7**) followed by reductive elimination to provide the desired aminated product, and regenerating back the Cu(I) species.

3. Conclusions

Ethylacetoacetate-tagged basic IL **4a** is an all in one medium that effects the generation and stabilization of Cu(I)I NPs of small size

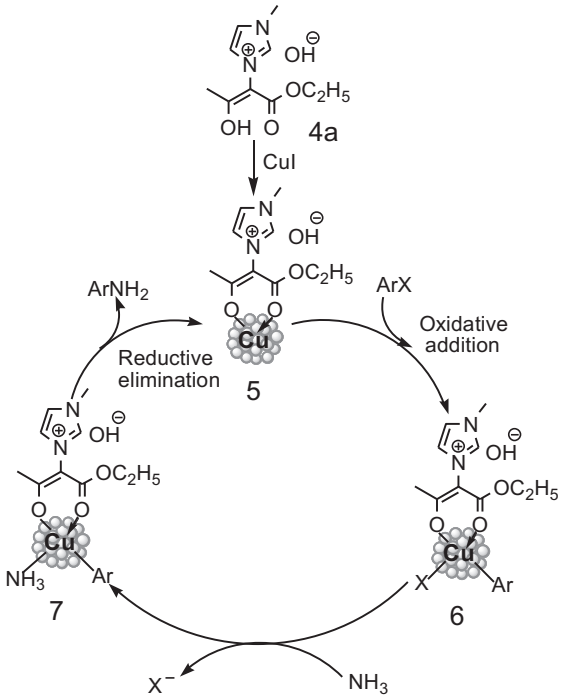
Table 2
Scope of the optimized CuI NP catalyzed amination of aryl and heterocyclic halides[a]



Entry	Aryl halide	Aryl amine	Yield[b] %
1			82
2			80 (74,[c] 70[d])
3			78
4			85
5			87
6			79[e]
7			72[e]
8			77[e]
9			71[e]
10			82[e]
11			77[f]
12			81[f]
13			75[e]
14			85[e]

[a] Reaction conditions: aryl halide (1.0 mmol), commercial 28% aqueous NH_3 (1.5 mmol), CuI NP (2 mol %), **4a** (3.0 mmol), CH_3CN (2.0 mL) stirred at rt for 12 h.
[b] Isolated yield.
[c] Yield after first recycle.
[d] Yield after second recycle.
[e] Reaction carried out at 80 °C.
[f] At 120 °C.

and uniform particle size distribution, functions as a ligand for active Cu(I) species and also serves as a base in promoting amination of aryl halides under mild conditions. The IL with built-in ligand and base enables a facile, clean and mild amination of aryl iodides, bromides as well as the less reactive chlorides with cheap aminating agent like aqueous ammonia at very low catalyst loading of 2 mol % CuI NP catalyst to yield primary aryl amines selectively. Further it allows easy isolation of products with the advantage of recovery and reuse of ionic liquid, and recyclability of catalyst up to two recycles thus making the overall process highly economical and cost-effectivlle.



Scheme 3. Proposed mechanism for amination.

4. Experimental section

4.1. Materials and methods

Chemicals were either purchased or purified by standard techniques without special instructions. The products were purified by column chromatography on silica gel (60–120 mesh, SRL). ^1H NMR and ^{13}C NMR spectra were measured on a Bruker DPX-300 MHz spectrometer (^1H 300 MHz, ^{13}C 75 MHz) using $CDCl_3$ and CD_3OD as the solvent and tetramethylsilane (TMS) as the internal standard at rt. ^1H NMR and ^{13}C NMR spectra of **4a** were measured on a Bruker Advance-400 MHz spectrometer (^1H 400 MHz, ^{13}C 100 MHz). Chemical shifts are given in δ relative to TMS, the coupling constants J are given in hertz. The ESI-MS was performed on MICROTOF-II mass instrument. LC–MS was performed on Waters 2767 sample manager with waters ZQ mass detector. The sample dissolved in methanol was run on develosil (50×4.6, 5 μm) column with 0.1% formic acid in acetonitrile as the mobile phase. High resolution transmission electron microscope (HRTEM) experiments were conducted in JEM 2100 F. Scanning electron microscope image was captured by a Zeiss Evo series SEM model EVO 50. The size of nanoparticles was determined by Malvern DLS. UV–vis spectroscopy was recorded on Lambda Bio 20, Perkin–Elmer. Powder XRD was taken on powder X-ray diffractometer (Bruker).

4.2. Synthesis of ethyl-2-bromoacetoacetate (2)

To a stirred solution of *N*-bromosuccinimide (5 mmol, 1 equiv) and *p*-toluenesulfonic acid (5 mg) in dichloromethane (15 mL) ethylacetoacetate (5 mmol, 1 equiv) was added at ice-bath temperature, and the reaction mixture was stirred for half an hour. After completion of the reaction as monitored by TLC, dichloromethane was evaporated and the residual white solid was extracted with hexane. Finally, the hexane solution was concentrated under reduced pressure and was purified through silica gel column chromatography by eluting with a mixture of 2% ethyl acetate in hexane to obtain the pure product **2** in 88% yield; ^1H

NMR (300 MHz, $CDCl_3$) δ 4.83 (1H, s, CH), 4.28 (2H, q, *J* 7.2, 6.9 Hz, $-CH_2$), 2.45 (3H, s, $-C(O)CH_3$), 1.32 (3H, t, *J* 7.2 Hz, $-CH_3$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 196.13, 165.00, 63.02, 49.17, 26.31, 13.98; MS (ESI): ($M+Na^+$), found 230.9640. $C_6H_9O_3Br$ requires 230.969.

4.3. Synthesis of 1-ethylacetoacetate-3-methyl imidazolium hydroxide (4a) and 1-ethylacetoacetate-3-methyl imidazolium acetate (4b)

To a stirring solution of *N*-methylimidazole (2.5 mmol, 1 equiv) in acetonitrile, **2** was added (2.5 mmol, 1 equiv) and the contents were stirred for half an hour at rt. Completion of reaction was monitored by TLC. The product was purified by repeated washing with hexane and ether alternatively to remove any unreacted reactants. The pure product 1-ethylacetoacetate-3-methyl imidazolium bromide (**3**) was obtained in 85% yield after drying the sample for 24 h in vacuo. KOH (3.75 mmol, 1.5 equiv) was added to a solution of **3** (2.5 mmol, 1 equiv) in acetonitrile (5 mL) and the contents were stirred at rt for 24 h. The reaction mixture was filtered through Celite to remove precipitated KBr and the solvent evaporated in vacuo to give the title compound **4a** as a colourless oil in 82% yield. The synthesis of **4b** was carried out using a similar procedure as for **4a** with $NaOAc\cdot 3H_2O$ (3.75 mmol, 1.5 equiv) as the salt for anion exchange reaction; ^1H NMR (400 MHz, CD_3OD): **4a** (keto): δ 9.11 (1H, s, imidazolium C-2H), 7.67–7.63 (2H, m, imidazolium C-4H, C-5H), 5.50 (1H, s, $-CO-CH-CO-$), 4.28 (2H, q, *J* 7.0 Hz, $-CH_2$), 4.04 (3H, s, $N-CH_3$), 2.58 (3H, s, $-COCH_3$), 1.22 (3H, t, *J* 7 Hz, $-CH_2CH_3$), **4a** (enol): 8.93 (1H, s, imidazolium C-2H), 7.74 (1H, d, *J* 3.36 Hz, imidazolium C-5H), 7.49 (1H, s, imidazolium C-4H), 4.19 (2H, q, *J* 7 Hz, $-CH_2$), 3.99 (3H, s, $N-CH_3$), 2.01 (3H, s, $-C(OH)CH_3$), 1.37 (3H, t, *J* 7 Hz, $-CH_2CH_3$); ^{13}C NMR (100 MHz, CD_3OD): **4a** (keto): δ 195.69 ($-CO-$), 177.78 ($-COO-$), 140.41 (imidazolium C2), 125.44 (imidazolium C5), 124.08 (imidazolium C4), 65.11 ($-CH_2$), 54.90 ($-CO-CH-CO-$), 37.14 ($N-CH_3$), 28.65 ($-COCH_3$), 14.41($-CH_2CH_3$). Compound **4a** (enol): 168.73 ($-COO-$), 164.47 (C–OH), 139.29 (imidazolium C2), 126.82 (imidazolium C5), 124.92 (imidazolium C4), 101.42 ($-COH-C-CO-$), 63.49 ($-CH_2$), 36.67 ($N-CH_3$), 18.27 ($-COCH_3$), 14.59 ($-CH_2CH_3$); HRMS (ESI): ($M+Na^+$), found 211.1077. $C_{10}H_{15}O_3N_2$ requires 211.1077.

4.4. Synthesis of CuI nanoparticles

Dimethylglyoxime (dmgH) (0.464 g, 4 mmol) and $Cu(OAc)_2\cdot H_2O$ (0.4 g, 2 mmol) were taken in absolute ethanol (50 mL) and stirred at 0 °C for 30 min when a brown precipitate of $Cu(dmg)_2$ was formed. To this, **4a** (1 mL) and potassium iodide (0.664 g, 4 mmol) were added and the contents were heated at 120 °C for 2 h under reduced pressure. A black precipitate was obtained, which was collected by centrifugation and washed with ethanol and deionized water three times to ensure the removal of residual KI, and other impurities. The final product was then dried in a vacuum oven at rt for 12 h and 160 mg solid was obtained.

4.5. Characterization of CuI nanoparticles

Characterization of CuI nanoparticles was done by TEM, DLS, SEM/EDAX and UV analysis. To prepare the sample for SEM/EDAX, CuI NPs were redispersed in **4a**–acetonitrile mixture and sonicated for about 1 h. Sample was prepared on a glass slide with the help of spin coating to get a uniform distribution of particles. For TEM, sample was prepared by mounting the NPs dispersed in **4a**–acetonitrile mixture on a copper grid. DLS was recorded in acetonitrile at a sample concentration of 0.1 mg/mL.

4.6. General procedure for amination of aryl and heterocyclic halides

An oven-dried flask was charged with aryl halide (1.0 mmol), aqueous NH_3 (28%, 1.5 mmol), CuI nanoparticles (0.02 mmol), **4a** (3.0 mmol) and acetonitrile (2 mL). The contents were stirred under argon atmosphere at rt for 12 h. After completion of the reaction as monitored by TLC, the product was extracted with diethyl ether (5×5 mL). The organic layer was washed with brine, dried over $MgSO_4$ and concentrated in vacuo. Purification was done on silica gel column, and elution with ethyl acetate–hexane mixture afforded the aminated products. All products obtained herein are known compounds, and were confirmed by ^1H NMR, ^{13}C NMR and mass spectroscopic analysis, see Supplementary data for full details.

4.6.1. Aniline (Table 2, entries 1, 6, 11). Colourless liquid; ^1H NMR (300 MHz, $CDCl_3$) δ 7.34 (2H, t, *J* 7.5 Hz, H_1), 6.95 (1H, t, *J* 7.5 Hz, H_3), 6.79 (2H, d, *J* 7.8 Hz, H_2), 3.73 (2H, s, $-NH_2$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.76, 129.40, 118.46, 115.23; MS (ESI): ($M+H^+$), found 94.0715. C_6H_7N requires 94.0702.

4.6.2. 4-Aminotoluene (Table 2, entry 2). Yellow liquid; ^1H NMR (300 MHz, $CDCl_3$) δ 7.01 (2H, d, *J* 7.8 Hz, H_1), 6.64 (2H, d, *J* 7.8 Hz, H_2), 3.57 (2H, s, $-NH_2$), 2.29 (3H, s, $-CH_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.94, 129.80, 127.75, 115.34, 20.50; MS (ESI): ($M+H^+$), found 108.0802. C_7H_9N requires 108.0814.

4.6.3. 4-Methoxy-phenylamine (Table 2, entry 3). Dark brown solid; ^1H NMR (300 MHz, $CDCl_3$) δ 6.67 (2H, s, H_1), 6.58 (2H, s, H_2), 3.67 (3H, s, $-OCH_3$), 3.26 (2H, s, NH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.79, 139.96, 116.40, 114.81, 55.71; MS (ESI): ($M+H^+$), found 124.0767. C_7H_9ON requires 124.0850.

4.6.4. 4-Aminonitrobenzene (Table 2, entry 4). Yellow solid; ^1H NMR (300 MHz, $CDCl_3$) δ 8.04 (2H, d, *J* 8.4 Hz, H_2), 6.60 (2H, d, *J* 8.7 Hz, H_1), 4.36 (2H, s, $-NH_2$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.63, 128.98, 126.36, 113.38; MS (ESI): ($M+H^+$), found 139.0513. $C_6H_6O_2N_2$ requires 139.0673.

4.6.5. Pentafluorophenylamine (Table 2, entry 5). Colourless liquid; ^1H NMR (300 MHz, $CDCl_3$) δ 4.13 (2H, s, $-NH_2$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.53–148.38, 145.50–145.24, 137.86–137.64, 134.66–134.43, 127.13–126.75.

4.6.6. 4-Aminoacetophenone (Table 2, entry 7). Brown solid; ^1H NMR (300 MHz, $CDCl_3$) δ 7.78 (2H, d, *J* 8.4 Hz, H_2), 6.62 (2H, d, *J* 8.1 Hz, H_1), 4.18 (2H, s, $-NH_2$), 2.57 (3H, s, $-CH_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.78, 151.80, 130.76, 127.11, 113.55, 25.95; MS (ESI): ($M+H^+$), found 136.0759. C_8H_9ON requires 136.0757.

4.6.7. 4-Aminobenzonitrile (Table 2, entry 8). Yellow liquid; ^1H NMR (300 MHz, $CDCl_3$) δ 7.34 (2H, d, *J* 8.4 Hz, H_2), 6.62 (2H, d, *J* 8.4 Hz, H_1), 4.40 (2H, s, $-NH_2$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.99, 133.70, 120.50, 114.40, 99.18; MS (ESI): ($M+H^+$), found 119.0608. $C_7H_6N_2$ requires 119.0693.

4.6.8. 4-Fluoro-phenylamine (Table 2, entry 9). Yellow liquid; ^1H NMR (300 MHz, $CDCl_3$) δ 6.85 (2H, t, *J* 8.4 Hz, H_2), 6.63 (1H, d, *J* 4.5 Hz, H_1), 6.60 (1H, d, *J* 4.5 Hz, H_1), 3.54 (2H, s, $-NH_2$); MS (ESI): (M), found 111.0460. C_6H_6NF requires 111.0524.

4.6.9. 1H-Indol-5-ylamine (Table 2, entry 10). Light brown solid; ^1H NMR (300 MHz, $CDCl_3$) δ 7.96 (1H, s, –NH), 7.20 (1H, d, *J* 8.1 Hz, H_1), 7.14 (1H, s, H_5), 6.96 (1H, s, H_3), 6.67 (1H, d, *J* 8.1 Hz, H_2), 6.38 (1H, s, H_4), 3.52 (2H, s, $-NH_2$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.49, 130.73,

128.80, 124.75, 112.98, 111.54, 105.59, 101.53; MS (ESI): ($M+H^+$), found 133.0753. $C_8H_8N_2$ requires 133.0851.

4.6.10. 2-Aminobenzonitrile (Table 2, entry 12). White solid; ^1H NMR (300 MHz, $CDCl_3$) δ 7.75 (1H, d, J 7.2 Hz, H_2), 7.42–7.30 (m, 3H, $H_{1,3,4}$), 6.65–6.43 (2H, br, $-NH_2$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.42, 133.90, 131.76, 130.83, 130.56, 130.38, 127.12; MS (ESI): ($M+K^+$), found 156.0190. $C_7H_6N_2$ requires 156.1432.

4.6.11. 6-Methyl-pyridin-2-ylamine (Table 2, entry 13). Yellow liquid; ^1H NMR (300 MHz, $CDCl_3$) δ 7.24 (1H, t, J 7.5 Hz, H_2), 6.41 (1H, d, J 7.2 Hz, H_1), 6.22 (1H, d, J 8.1 Hz, H_3), 4.71 (2H, s, $-NH_2$), 2.40 (3H, s, $-CH_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.21, 156.65, 138.05, 112.91, 105.43, 24.00; MS (ESI): ($M+H^+$), found 109.0772. $C_6H_8N_2$ requires 109.0851.

4.6.12. 3-Aminoquinoline (Table 2, entry 14). Brown solid; ^1H NMR (300 MHz, $CDCl_3$) δ 8.46 (1H, s, H_1), 7.95 (1H, s, H_6), 7.52 (1H, d, J 4.5 Hz, H_3), 7.39 (2H, d, J 1.2 Hz, $H_{4,5}$), 7.14 (1H, s, H_2), 3.95 (2H, s, $-NH_2$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.09, 142.46, 140.04, 129.18, 128.83, 126.87, 125.83, 125.44, 114.78; MS (ESI): ($M+H^+$), found 145.0893. $C_9H_8N_2$ requires 145.0851.

4.7. Recycling experiment

After completion of amination, the product was extracted with diethyl ether leaving behind the catalyst in **4a**. To it a fresh batch of aryl halide (1.0 mmol), aqueous NH_3 (28%, 1.5 mmol) and acetonitrile (2 mL) were added and the same procedure as above was followed.

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Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.tet.2013.04.088.

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