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PAPER

Sulfonic acid supported on hydroxyapatite-encapsulated-γ-Fe_2O_3 nanocrystallites as a magnetically separable catalyst for one-pot reductive amination of carbonyl compounds†

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A novel, environmentally friendly procedure has been developed for the preparation of secondary or tertiary amines by one-pot reductive amination of carbonyl compounds using sodium borohydride in the presence of a magnetically recoverable sulfonic acid supported on hydroxyapatite-encapsulated-γ-Fe_2O_3 [γ-Fe_2O_3@HAP-SO_3H] at room temperature. The catalyst was easily separated from the reaction mixture by applying an external magnet and reused for six cycles without significant loss of catalytic activity.

Introduction

Currently, the development of novel, non-toxic, low cost, eco-friendly, recyclable catalytic systems with high efficiency has received a great deal of research attention in organic synthesis for environmental and economic reasons. In this regard, nanoparticles (NPs) have emerged as viable and appealing candidates and are considered to be a bridge between homogeneous and heterogeneous catalysts.[1] NPs-supported catalysts mimic their homogeneous counterparts and can be employed in a quasi-homogeneous phase or serve as precursors for heterogeneous catalysts since they readily disperse in reaction medium through forming stable suspensions, thus display highly accessible surface catalytic sites. Despite their distinct catalytic activities, difficulties in recovering the catalyst from the reaction mixture, due to their small diameter, severely limit their wide applications. To further address the issues of recyclability and reusability, magnetic nanoparticles (MNPs) are particularly attractive since their paramagnetic nature enables trouble-free separation of the catalyst from the reaction mixture using an external magnet. Thus eliminating the necessity for tedious centrifugation, filtration, or membrane separation.[2] Meanwhile, tandem catalysis that enables multi-step reactions in one-pot has the great advantage over multiple-step synthesis, of eliminating isolation of unstable intermediates and reducing the number of chemical steps and waste production.[3] Design of a recyclable catalytic system that promotes efficient one-pot synthesis has become an important research area in organic chemistry.

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† Electronic supplementary information (ESI) available: XRD, IR and TEM data of the catalyst, and ^1H NMR and ^{13}C NMR spectra of all new compounds. See DOI: 10.1039/c1gc15470b

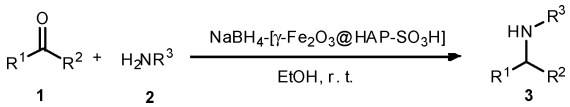
Amine formation is one of most important transformations in organic synthesis. Amides are also found in numerous natural products and also serve as building blocks for pharmaceuticals, agrochemicals, dyes, resins, fine chemicals, solvents, textile additives, disinfectants, rubber stabilizers, corrosion inhibitors, in the manufacture of detergents and plastics, bases for many synthetic transformations, and ligands in coordination chemistry.[4] As a consequence, various methods for the efficient formation of C–N bond have been widely investigated. Among all the available methods, direct reductive amination (DRA) is one of the oldest, but the most powerful and widely used synthetic transformations, which allows creation of a new C–N bond by coupling diverse carbonyl compounds with amine-containing fragments in one vessel without isolation of the intermediary imines or hydroxyamines.[5]

A variety of methods have been reported to accomplished this transformation including hydrogenation in the presence of Pd/C, iridium complex or Fe^{II}/EDTA complex,[6] transfer hydrogenation,[7] or using a reducing agent such as sodium cyanoborohydride,[8] sodium triacetoxyborohydride,[9] zinc borohydride,[10] *N*-methyl piperidine zinc borohydride,[11] pyridine-BH_3,[12] zirconium borohydride-piperazine complexes,[13] organosilane,[14] poly(methylhydrosiloxane (PMHS),[15] tin hydride complex[16] 1,2,3-triazole-borane complexes,[17] aminoboranes,[18] and Al.[19] However, consideration of functional group tolerance, and side reactions, most of these reagents may have one or more drawbacks. For example, catalytic hydrogenation methods, are efficient for DRAs, but are not compatible with compounds containing other reducible functional groups such as carbon–carbon double or triple bonds, cyano, and nitro groups, and require expensive metals as catalysts. Cyanoborohydride and organotin are highly toxic and resulted in contamination of the product with toxic by-products such as HCN, NaCN or organotin compounds. Pyridine-BH_3 is

quite unstable to heat and must be handled with extreme care. Triacetoxyborohydride is flammable, water-reactive, and poorly soluble in most organic solvents.

Sodium borohydride is a relatively inexpensive, mild, safe, water tolerant agent for applications in a wide range of reduction processes.[20] Although sodium borohydride has been used in combination with some catalysts such as $Ti(O\text{-}i\text{-}Pr)_4$,[21] $ZrCl_4$,[22] $NiCl_2$,[23] H_3BO_3,[24] $H_3PW_{12}O_{40}$,[25] guanidine hydrochloride,[26] silica phosphoric acid,[27] Amberlyst-15,[28] silica chloride,[29] wet clay,[30] and cellulose sulfric acid[31] or in 2,2,2-trifluoroethanol[32] for DRAs, in some cases catalyst can not be recovered or high temperature was required. Therefore, the search continues for better methods for reductive amination of carbonyl compounds with mild reaction conditions, economic viability and environmentally benignity.

Very recently, we have discovered that magnetic Fe_3O_4 nanoparticles are excellent catalysts for the synthesis of quinoxalines[33] and 2,3-dihydroquinazolin-4(1*H*)-ones.[34] As a continuation of our interest in developing efficient and environmental benign synthetic methodologies,[35] we report here a new, green, and practical method for one-pot reductive amination of carbonyl compounds using $NaBH_4$ in the presence of γ-Fe_2O_3@HAP-SO_3H as an highly efficient, inexpensive, and reusable catalyst (Scheme 1).



Scheme 1 Reductive amination of carbonyl compounds by $NaBH_4$-[γ-Fe_2O_3@HAP-SO_3H].

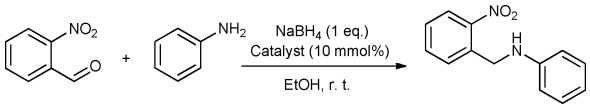
Results and discussion

Initially, 2-nitrobenzaldehyde and aniline were used as model substrates to study the activity of various catalysts, including protic acids such as toluenesulfonic acid, Lewis acids such as LiCl, solid acid such as $HClO_4/SiO_2$, heteropoly acids such as silicotungstic acid, and nanocrystalline metal oxides such as nano Fe_3O_4 and γ-Fe_2O_3 (Table 1).

In a typical reaction, 2-nitrobenzaldehyde and aniline were mixeded in EtOH and catalyst was then added. After completion of the imine formation, $NaBH_4$ was added. The mixture was stirred at room temperature. It was observed that all of the investigated catalysts were able to catalyze this DRA and furnished the corresponding product in moderate to high yields, while the reaction performed in the absence of catalyst, only resulted in the formation of trace amount of the desired product. In order to further improve this procedure and recover the heterogeneous catalyst, we decided to prepare the sulfonic acid supported on hydroxyapatite-encapsulated-γ-Fe_2O_3 [γ-Fe_2O_3@HAP-SO_3H] according to a previously reported procedure with some modifications.[36] The prepared catalyst was characterized by XRD, SEM, TEM, and FT-IR (ESI†, Fig. S1–4). We examined the use of γ-Fe_2O_3@HAP-SO_3H as a catalyst and observed that this reaction proceeded well and afforded the alkylated aniline in 95% yield.

In the following studies, the above reaction was conducted in the presence of γ-Fe_2O_3@HAP-SO_3H with various solvents. The

Table 1 Influence of different catalysts on the reductive condensation of 2-nitrobenzaldehyde with aniline[a]



Entry	Catalyst	Time (min)	Isolated yield (%)
1	No	180	Trace
2	*p*-TSA	60	77
3	Chlorosulfonic acid	40	39
4	LiCl	60	61
5	$HClO_4/SiO_2$	60	80
6	Silicotungstic acid	60	62
7	Nano Fe_3O_4	60	42
8	Nano γ- Fe_2O_3	180	25
9	γ-Fe_2O_3@HAP-SO_3H	45	95

[a] Reaction conditions: 2-nitrobenzaldehyde (1 mmol), aniline (1 mmol), $NaBH_4$ (1 mmol), catalyst (10 mmol%), EtOH (5 ml).

Table 2 Optimisation of reaction conditions[a]

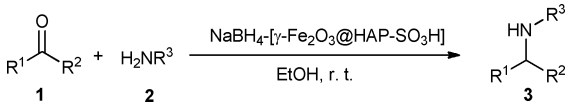
Entry	Catalyst (mol%)	Solvent	Time (min)	Isolated yield (%)
1	10	No	60	78
2	10	CH_2Cl_2	60	65
3	10	CH_3CN	60	73
4	10	AcOEt	60	61
5	10	H_2O	45	90
6	10	MeOH	45	94
7	5	EtOH	60	81
8	10	EtOH	45	95
9	15	EtOH	45	96

[a] Reaction conditions: 2-nitrobenzaldehyde (1 mmol), aniline (1 mmol), $NaBH_4$ (1 mmol), solvent (5 ml).

results indicated that different solvents affected the efficiency of the reaction (Table 2). Based on the reaction yields and environmental consideration, ethanol was proved to be superior to others such as dichloromethane, acetonitrile, ethyl acetate, methanol, and water. Moreover, we found that the yields were obviously affected by the loading of γ-Fe_2O_3@HAP-SO_3H. When 5 mol%, 10 mol% and 15 mol% of γ-Fe_2O_3@HAP-SO_3H were used, the yields were 81%, 95%, and 96%, respectively (Table 2, entries 7–9). Therefore, 10 mol% of γ-Fe_2O_3@HAP-SO_3H was sufficient for this DRA.

To evaluate the scope and limitations of this methodology, we extended our studies to various structurally different carbonyl compounds and amines. Firstly, we examined the reactions of aniline with different aldehydes and the results are summarized in Table 3. It was found that there was no remarkable electron and position effects from the aromatic aldehydes for this DRA, since benzaldehydes with *o*-, *m*, and *p*-substituents (Table 3, entries 14–16) resulted in the corresponding alkylated anilines in excellent yields, while both 4-methoxybenzaldehyde (Table 3, entry 5) and 4-nitrobenzaldehyde (Table 3, entry 21) were competent substrates in this procedure. It is important to note that acid-sensitive aldehydes such as furan-2-carbaldehyde, thiophene-2-carbaldehyde, and nicotinaldehyde (Table 3, entries 26–28) were suitable substrates, affording the corresponding products in high yields without the formation of any side products. Furthermore, this procedure is applicable to reductive amination

Table 3 Direct reductive amination of carbonyl compounds using $NaBH_4$-[γ-Fe_2O_3@HAP-SO_3H]



1 2 3

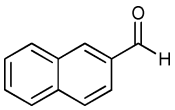
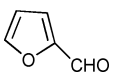
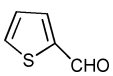
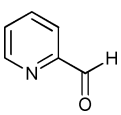
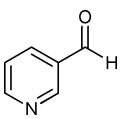
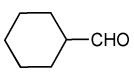
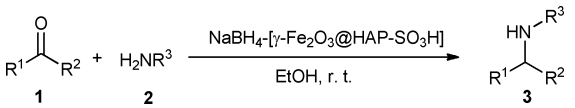
Entry	Carbonyl compound	Amine	Product	Time (min)	Yield (%)[a]	Ref.
1	PhCHO	$PhNH_2$	**3a**	40	94	14a
2	3-$CH_3C_6H_4CHO$	$PhNH_2$	**3b**	40	93	37
3	4-$CH_3C_6H_4CHO$	$PhNH_2$	**3c**	40	92	31
4	2-$OCH_3C_6H_4CHO$	$PhNH_2$	**3d**	35	93	37
5	4-$OCH_3C_6H_5CHO$	$PhNH_2$	**3e**	20	94	14a
6	2,3,4-$(OMe)_3C_6H_2CHO$	$PhNH_2$	**3f**	30	93	
7	2-OHC_6H_4CHO	$PhNH_2$	**3g**	30	93	30
8	3-OMe-2-OHC_6H_3CHO	$PhNH_2$	**3h**	30	91	
9	4-OMe-2-OHC_6H_3CHO	$PhNH_2$	**3i**	30	90	
10	5-F-2-OHC_6H_3CHO	$PhNH_2$	**3j**	45	92	
11	5-Br-2-OHC_6H_3CHO	$PhNH_2$	**3k**	35	93	
12	5-NO_2-2-OHC_6H_3CHO	$PhNH_2$	**3l**	45	92	38
13	4-FC_6H_4CHO	$PhNH_2$	**3m**	35	93	39
14	2-ClC_6H_4CHO	$PhNH_2$	**3n**	40	91	31
15	3-ClC_6H_4CHO	$PhNH_2$	**3o**	35	92	32
16	4-ClC_6H_4CHO	$PhNH_2$	**3p**	35	94	31
17	4-BrC_6H_4CHO	$PhNH_2$	**3q**	35	93	14a
18	4-IC_6H_4CHO	$PhNH_2$	**3r**	60	85	
19	2-$NO_2C_6H_4CHO$	$PhNH_2$	**3s**	45	95	31
20	3-$NO_2C_6H_4CHO$	$PhNH_2$	**3t**	40	93	15a
21	4-$NO_2C_6H_4CHO$	$PhNH_2$	**3u**	40	94	14a
22	3-$CF_3C_6H_4CHO$	$PhNH_2$	**3v**	80	91	14a
23	4-CNC_6H_4CHO	$PhNH_2$	**3w**	80	90	14a
24	PhCH=CHCHO	$PhNH_2$	**3x**	60	94	14a
25		$PhNH_2$	**3y**	100	85	39
26		$PhNH_2$	**3z**	40	95	15a
27		$PhNH_2$	**3aa**	60	95	15a
28		$PhNH_2$	**3ab**	40	90	15b
29		$PhNH_2$	**3ac**	60	81	36
30		$PhNH_2$	**3ad**	45	93	15b
31	CH_3CHO	$PhNH_2$	**3ae**	40	88	40
32	CH_3CH_2CHO	$PhNH_2$	**3af**	40	90	35e
33	$CH_3(CH_2)_2CHO$	$PhNH_2$	**3ag**	60	92	27
34	$CH_3(CH_2)_4CHO$	$PhNH_2$	**3ah**	50	91	15a
35	$CH_3(CH_2)_7CHO$	$PhNH_2$	**3ai**	60	94	24
36	$PhCH_2CHO$	$PhNH_2$	**3aj**	60	85	41
37	PhCHO	4-$OCH_3C_6H_5NH_2$	**3ak**	20	95	32
38	PhCHO	4-$OEtC_6H_5NH_2$	**3al**	25	94	31
39	PhCHO	4-$CH_3C_6H_4NH_2$	**3am**	30	93	31
40	PhCHO	4-$ClC_6H_4NH_2$	**3an**	75	90	37
41	PhCHO	4-$ClC_6H_4NH_2$	**3ao**	70	89	31
42	PhCHO	4-$BrC_6H_4NH_2$	**3ap**	100	91	15a
43	PhCHO	4-$NO_2C_6H_4NH_2$	**3aq**	180	89	31

Table 3 (*Contd.*)



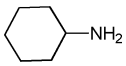
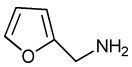
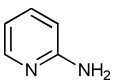
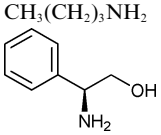
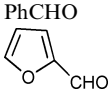
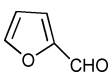
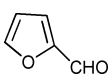
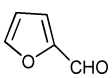
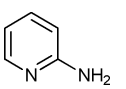
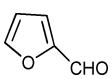
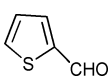
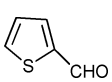
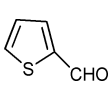
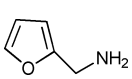
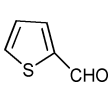
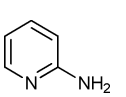
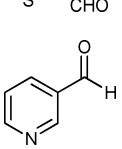
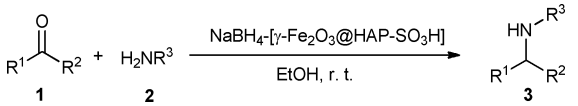
Entry	Carbonyl compound	Amine	Product	Time (min)	Yield (%)[a]	Ref.
44	PhCHO		**3ar**	2	90	15a
45	PhCHO		**3as**	1	93	42
46	PhCHO		**3at**	120	82	32
47	PhCHO	$PhCH_3NH_2$	**3au**	5	92	31
48	PHCHO	$MeNH_2$	**3av**	2	90	43
49	PHCHO	$EtNH_2$	**3aw**	2	88	44
50	PhCHO	$CH_3(CH_2)_3NH_2$	**3ax**	1	91	19
51	PhCHO		**3ay**	10	91	45
52	PhCHO	$CH_2{=}CHCH_2NH_2$	**3az**	1	90	27
53		$4\text{-}OCH_3C_6H_5NH_2$	**3ba**	30	92	26
54		$4\text{-}ClC_6H_4NH_2$	**3bb**	40	91	46
55		$4\text{-}BrC_6H_4NH_2$	**3bc**	60	88	44
56			**3bd**	180	81	37
57		$CH_3(CH_2)_3NH_2$	**3be**	1	94	47
58		$4\text{-}OCH_3C_6H_5NH_2$	**3bf**	45	92	
59		$4\text{-}ClC_6H_4NH_2$	**3bg**	45	90	46
60			**3bh**	1	95	
61			**3bi**	120	80	37
62		$CH_3(CH_2)_3NH_2$	**3bj**	1	96	47
63		$4\text{-}CH_3C_6H_5NH_2$	**3bk**	60	92	46

Table 3 (*Contd.*)



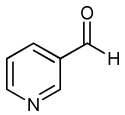
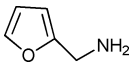
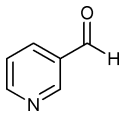
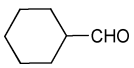
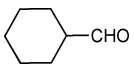
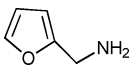
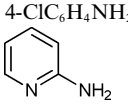
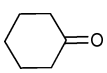
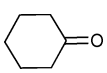
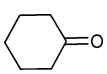
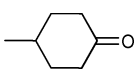
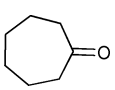
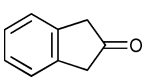
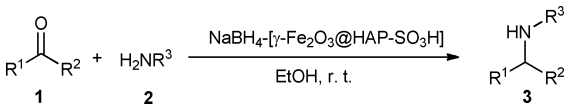
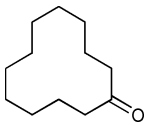
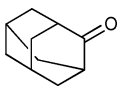
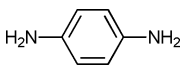
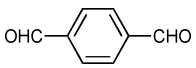
Entry	Carbonyl compound	Amine	Product	Time (min)	Yield (%)[a]	Ref.
64			**3bl**	1	93	48
65		$CH_3(CH_2)_3NH_2$	**3bm**	1	94	
66		$PhCH_2NH_2$	**3bn**	5	94	24
67			**3bo**	2	93	
68	PhCH=CHCHO	$4\text{-}CH_3C_6H_5NH_2$	**3bp**	40	90	49
69	PhCH=CHCHO	$4\text{-}OCH_3C_6H_5NH_2$	**3bq**	35	91	49
70	PhCH=CHCHO	$4\text{-}ClC_6H_4NH_2$	**3br**	45	88	49
71	PhCH=CHCHO		**3bs**	140	82	
72	PhCHO		**3bt**	7	89	31
73	PhCHO		**3bu**	5	90	31
74		$PhNH_2$	**3bv**	40	87	50
75		$PhNH_2$	**3bw**	40	87	31
76		$CH_3(CH_2)_3NH_2$	**3bx**	5	92	19
77		$CH_2=CHCH_2NH_2$	**3by**	5	93	19
78		$PhNH_2$	**3bz**	45	88	51
79		$PhNH_2$	**3ca**	45	89	50
80		$PhNH_2$	**3cb**	35	91	52
81		$PhNH_2$	**3cc**	45	87	53

Table 3 (*Contd.*)



1 2 3

Entry	Carbonyl compound	Amine	Product	Time (min)	Yield (%)[a]	Ref.
82		$PhNH_2$	**3cd**	40	90	
83		$PhNH_2$	**3ce**	35	92	54
84	PhCHO		**3cf**	40	88[b]	55
85		$PhNH_2$	**3cg**	60	89[c]	56

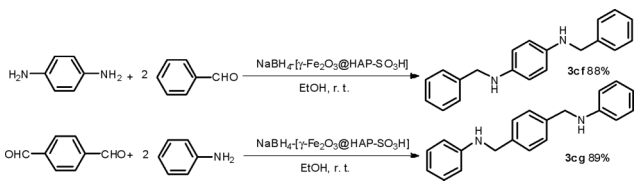
[a] Isolated yield. [b] Two equivalents of benzaldehyde were used. [c] Two equivalents of amines were used.

of aliphatic and α,β-unsaturated aldehydes. In addition to aldehydes, some ketones were also selected to carry out this DRA. For the aliphatic ketones like cyclohexanone, cyclododecanone, bicyclo[2.2.1]heptan-2-one, 1*H*-inden-2(3*H*)-one and adamantan-2-one, the desired products were smoothly obtained in high yield through this catalytic system. Unfortunately, only a trace amount of the target product was isolated, when less reactive aromatic ketones like acetophenone was aminated with the aromatic and aliphatic amines under the same reaction conditions.

The reactivities of amines in this DRA were then tested. Aromatic amines with electron-withdrawing groups such as a nitro group showed slightly weaker reactivity than those containing electron-neutral or electron-donating groups (Table 3, entry 43). Besides, heteroaromatic amines like pyridin-2-amine acted as a suitable candidate for this reaction. Aliphatic amines and allylic amine were reactive and underwent the title reaction in a shorter reaction time compared to aromatic amines. It is noteworthy that optically active plenylglycinol underwent reductive amination successfully to give the corresponding amine (**3ay**) without any racemization or inversion as determined by measurement of optical rotation. The reactions worked also well when secondary amines like piperidine and morpholine were utilized.

Encouraged by the above interesting results, we also attempted to prepare bis-alkylated amines to further broaden the scope. To our delight, the reaction of *p*-phenylenediamine with 2 equiv. of benzaldehyde resulted in the desired product (**3cf**) in high yield. Similarly, terephthaldicarboxaldehyde also underwent reductive amination smoothly to afford the target product **3cg** in 89% yield (Scheme 2). Moreover, the model reaction was carried out in a scale of 100 mmol. As expected, the reaction proceeded nicely to afford the desired product in 93% yield in 50 min.

An important feature of this procedure is the tolerance of a variety of function groups such as fluoro, chloro, iodine, nitro,



Scheme 2 Synthesis of bis-alkylated amines.

cyanide, ethers, carbon-carbon double bond under the reaction conditions. Furthermore, the reaction was clean and no side products were observed.

From the view point of green chemistry, good recovery and reusability of the catalyst are highly preferable. In this work, we examined the possibility of recovery and reuse of γ-Fe_2O_3@HAP-SO_3H. After completion of the reaction of nitrobenzaldehyde and amine, the catalyst was recovered from the reaction mixture simply by applying an external magnet. Then the recovered catalyst was first washed with water and then with diethyl ether, and dried at room temperature. The recovered catalyst was added to fresh reaction mixture under same conditions for six runs without significant drop in yield and its catalytic activity (Fig. 1). No quantifiable amount of leached Fe was detected in the filtrates as determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES). To determine of the percent leaching of the acid, the model reaction was carried out in the presence of γ-Fe_2O_3@HAP-SO_3H for 20 min and at that point the catalyst was removed by external magnet. The residual solution was then allowed to react, but no significant progress was observed after 1 h. Therefore, these experiments are a further testimony to the heterogeneous nature of the catalytic system.[57] Furthermore, the SEM images of the used catalyst showed that the shape and size of catalyst particles remained almost the same after six-run reuse, which proved its robustness (ESI†).

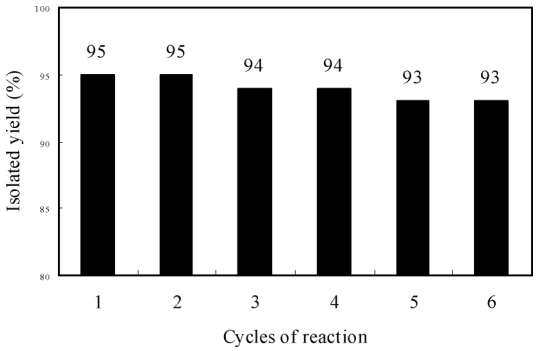


Fig. 1 The catalytic activity of γ-Fe_2O_3@HAP-SO_3H in six cycles for the model reaction.

Conclusions

In conclusion, we have developed a highly efficient and eco-friendly method for one-pot reductive amination of carbonyl compounds using magnetically separable sulfonic acid supported on hydroxyapatite-encapsulated-γ-Fe_2O_3 as the catalyst under mild conditions. This protocol can be used to generate a diverse range of secondary or tertiary amines in high to excellent yields. The catalyst is completely magnetically recoverable and the efficiency of the catalyst remains unaltered even after six cycles. These advantages make this methodology attractive for large-scale synthesis.

Experimental

IR spectra were recorded with a Shimadzu FTIR-8900 spectrometer. The ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra were recorded on a Bruker DRX-500 spectrometer using $CDCl_3$ as solvent and TMS as internal standard. Elemental analyses were carried out on a Vario EL III CHNOS elemental analyzer. Commercially available reagents were used without further purification.

Preparation of γ-Fe_2O_3@HAP-SO_3H[36]

To γ-Fe_2O_3@HAP (1 g), chlorosulfonic acid (1 g, 9 mmol) was added dropwise at room temperature during 15 min. After completion of the addition, the mixture was mechanically stirred for 6 h until HCl was removed from reaction vessel. Then the mixture was washed with CH_2Cl_2 (10 ml), resulted magnetic nanoparticles were separated by an external magnet device and washed with distilled water until neutral, then dried under vacuum at room temperature to obtain γ-Fe_2O_3@HAP-SO_3H as brown powder. The number of H^+ site (0.9 mmol SO_3H/g) of γ-Fe_2O_3@HAP-SO_3H was determined by acid–base titration.

General procedure for the reductive amination of carbonyl compounds

Carbonyl compound (1 mmol) and amine (1 mmol) were mixed in EtOH (5 ml) and then γ-Fe_2O_3@HAP-SO_3H (0.1 mmol) was added. After completion of the imine formation, $NaBH_4$ (1 mmol) was added. The progress of reaction was monitored by TLC or GC. After completion of the reaction, the catalyst was separated with the aid of an external magnet. Ethanol was evaporated and the crude product was purified by short column chromatography on silica gel using ethyl acetate/petroleum ether as the eluent.

***N*-(2,3,4-Trimethoxybenzyl)aniline (3f).** Viscous liquid; IR (neat): 3408, 2935, 1602, 1494, 1506, 1463, 1431, 1415, 1271, 1197, 1178, 1093, 1016, 904, 800, 750 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 3.82 (s, 3H), 3.87 (s, 3H), 3.91 (s, 3H), 3.98 (br s, 1H, NH), 4.25 (s, 2H), 6.60 (d, J = 8.0 Hz, 1H), 6.64 (d, J = 7.5 Hz, 2H), 6.68 (t, J = 7.5 Hz, 1H), 6.70 (d, J = 8.0 Hz, 1H), 7.15 (t, J = 7.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 43.3, 53.0, 60.9, 61.2, 107.2, 113.1, 117.4, 123.5, 125.1, 129.2, 142.3, 148.4, 151.3, 153.2; Anal. Calcd for $C_{16}H_{19}NO_3$: C, 70.31; H, 7.01; N, 5.12. Found: C, 70.12; H, 6.88; N, 4.98.

2-Methoxy-6-((phenylamino)methyl)phenol (3h). White solid, Mp: 62–64 °C; IR (KBr): 3311, 3012, 1601, 1500, 1477, 1440, 1429, 1356, 1269, 1247, 1224, 1168, 1083, 1051, 925 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 3.78 (s, 3H), 4.36 (s, 2H), 6.44 (dd, J = 8.5, 2.5 Hz, 1H), 6.48 (d, J = 2.5 Hz, 1H), 6.85 (d, J = 8.0 Hz, 2H), 6.92 (t, J = 7.5 Hz, 1H), 7.04 (d, J = 8.0 Hz, 1H), 7.23–7.26 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 44.2, 56.1, 110.0, 113.7, 118.2, 119.6, 121.2, 124.7, 129.2, 144.1, 146.8, 148.1; Anal. Calcd for $C_{14}H_{15}NO_2$: C, 73.34; H, 6.59; N, 6.11. Found: C, 73.15; H, 6.76; N, 5.98.

4-Methoxy-2-((phenylamino)methyl)phenol (3i). White solid, Mp: 137–139 °C; IR (KBr): 3254, 2960, 1614, 1593, 1516, 1445, 1437, 1421, 1325, 1282, 1232, 1107, 954 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 3.89 (s, 3H), 4.38 (s, 2H), 6.70–6.76 (m, 3H), 6.81 (d, J = 5.0 Hz, 2H), 6.89 (t, J = 5.0 Hz, 1H), 7.18 (t, J = 7.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 48.4, 55.3, 102.2, 106.0, 115.1, 116.0, 120.9, 129.3, 129.4, 147.2, 157.9, 160.7; Anal. Calcd for $C_{14}H_{15}NO_2$: C, 73.34; H, 6.59; N, 6.11. Found: C, 73.50; H, 6.41; N, 6.30.

4-Fluoro-2-((phenylamino)methyl)phenol (3j). White solid, Mp: 107–109 °C; IR (KBr): 3300, 1601,1498, 1438, 1252, 1230, 1201, 1078, 898, 825 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 4.39 (s, 2H), 6.80–6.84 (m, 3H), 6.87–6.95 (m, 3H), 7.23–7.26 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 48.6, 114.9 (d, $^2J_{FC}$ = 23.4 Hz), 115.3 (d, $^2J_{FC}$ = 22.6 Hz), 115.9, 117.4 (d, $^3J_{FC}$ = 7.6 Hz), 121.1, 123.9 (d, $^3J_{FC}$ = 6.9 Hz), 129.4, 146.9, 152.7, 156.5 (d, $^1J_{FC}$ = 236.1 Hz); Anal. Calcd for $C_{13}H_{12}FNO$: C, 71.87; H, 5.57; N, 6.45. Found: C, 71.92; H, 5.75; N, 6.28.

4-Bromo-2-((phenylamino)methyl)phenol (3k). White solid, Mp: 114–116 °C; IR (KBr): 3267, 2974, 1602, 1489, 1456, 1355, 1290, 1251, 1218, 1182, 1126, 1089, 1055, 864, 827, 804 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 4.39 (s, 2H), 6.76 (d, J = 8.5 Hz, 1H), 6.84(d, J = 8.0 Hz, 2H), 6.95 (t, J = 7.5 Hz, 1H), 7.24–7.32 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 48.6, 111.8, 116.1, 118.5, 121.3, 124.9, 129.5, 131.1, 131.9, 146.7, 156.1; Anal. Calcd for $C_{13}H_{12}BrNO$: C, 56.14; H, 4.35; N, 5.04. Found: C, 55.98; H, 4.26; N, 4.88.

***N*-(4-Iodobenzyl)aniline (3r).** White solid, Mp: 53–55 °C; IR (KBr): 3429, 1593, 1504, 1492, 1436, 1448, 1398, 1375, 1325, 1292, 1271, 1153, 1124, 1058, 1028, 985, 806, 732 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 4.06 (br s, 1H, NH), 4.27 (s, 2H), 6.38 (d, J = 9.0 Hz, 2H), 7.25–7.28 (m, 1H) 7.32–7.33 (m, 4H), 7.38 (d, J = 9.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 47.92, 78.03, 115.0, 127.3, 128.6, 137.7, 138.7, 147.5; Anal. Calcd for

$C_{13}H_{12}IN$: C, 50.51; H, 3.91; N, 4.53. Found: C, 50.33; H, 7.05; N, 4.70.

(*S*)-2-(Benzylamino)-2-phenylethanol (3ay). White solid, Mp: 86–87 °C; $[\alpha]_D^{20} = +82.6$ (c 1.08 in $CHCl_3$), Lit.[45] $[\alpha]_D^{28} = +83.2$; IR (KBr): 3251, 2920, 1569, 1496, 1488, 1452, 1328, 1234, 1099, 1055, 1014, 920, 877, 756 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ: 3.64 (d, J = 13.5 Hz, 1H), 3.70–3.76 (m, 2H), 3.85 (d, J = 13.5 Hz, 1H), 3.88–3.91 (m, 1H), 7.28–7.40 (m, 10H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 51.1, 63.8, 66.7, 127.1, 127.3, 127.7, 128.2, 128.5, 128.7, 139.9, 140.3; Anal. Calcd for $C_{15}H_{17}NO$: C, 79.26; H, 7.54; N, 6.16. Found: C, 79.08; H, 7.70; N, 5.98.

4-Methoxy-*N*-(thiophen-2-ylmethyl)aniline (3bf). White solid, Mp: 64–66 °C; IR (KBr): 3393, 2831, 1512, 1460, 1440, 1406, 1311, 1298, 1267, 1236, 1178, 1116, 1035, 850 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ: 3.74 (s, 3H), 4.46 (s, 1H), 6.64 (d, J = 9.0 Hz, 2H), 6.78 (d, J = 9.0 Hz, 2H), 6.95 (t, J = 5.0 Hz, 1H), 6.99 (d, J = 3.0 HZ, 1H) 7.20 (dd, J = 5.0 HZ, 1.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 44.5, 55.8, 114.6, 114.9, 124.5, 124.9, 126.9, 141.9, 143.4, 152.6; Anal. Calcd for $C_{12}H_{13}NOS$: C, 65.72; H, 5.97; N, 6.39. Found: C, 65.90; H, 6.15; N, 6.58.

1-(Furan-2-yl)-*N*-(thiophen-2-ylmethyl)methanamine (3bh). Yellow oil; IR (neat): 3448, 1541, 1382, 1147, 1078, 1008, 734, 700 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ: 3.81 (s, 2H), 3.97 (s, 2H), 6.19 (d, J = 3.0 Hz, 1H), 6.32 (dd, J = 3.0, 1.0 Hz, 1H), 6.92–6.96 (m, 2H), 7.22 (dd, J = 5.0, 1.0 Hz, 1H, ArH), 7.37 (d, J = 1.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 44.9, 47.2, 107.3, 110.1, 124.6, 125.2, 126.7, 141.9, 143.6, 153.5; Anal. Calcd for $C_{10}H_{11}NOS$: C, 62.15; H, 5.74; N, 7.25. Found: C, 61.96; H, 5.92; N, 7.08.

***N*-(Pyridin-3-ylmethyl)butan-1-amine (3bm).** Yellow oil; IR (neat): 3442, 2956, 2927, 1577, 1560, 1477, 1458, 1423, 1382, 1120, 1028, 785, 713 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ: 0.91 (t, J = 7.5 Hz, 3H), 1.35 (sext, J = 7.5 Hz, 2H), 1.49 (quin, J = 7.5 Hz, 2H), 2.63 (t, J = 7.5 Hz, 2H), 3.80 (s, 2H), 7.25 (dd, J = 7.5, 5.0 Hz, 1H), 7.67 (d, J = 7.5 Hz, 1H), 8.49 (dd, J = 5.0, 1.5 Hz, 1H), 8.56 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 14.0, 20.4, 32.2, 49.2, 51.3, 123.3, 135.7, 135.8, 148.4, 149.7; Anal. Calcd for $C_{10}H_{16}N_2$: C, 73.13; H, 9.82; N, 17.06. Found: C, 72.96; H, 10.01; N, 16.90.

1-Cyclohexyl-*N*-(furan-2-ylmethyl)methanamine (3bo). Colorless oil; IR (neat): 3421, 2922, 2850, 1506, 1448, 1332, 1147, 1120, 1074, 1006, 916, 731 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ: 0.86–0.93 (m, 2H), 1.13–1.27 (m, 2H), 1.42–1.48 (m, 1H), 1.64–1.74 (m, 6H), 2.44 (d, J = 7.0 Hz, 2H), 3.76 (s, 2H), 6.16 (d, J = 3.0 Hz, 1H), 6.30 (dd, J = 3.0, 1.5 Hz, 1H), 7.35 (d, J = 1.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 26.1, 26.7, 31.4, 37.94, 46.5, 56.0, 106.6, 110.0, 141.7, 154.8; Anal. Calcd for $C_{12}H_{19}NO$: C, 74.57; H, 9.91; N, 7.25. Found: C, 74.75; H, 10.09; N, 7.08.

***N*-Cinnamylpyridin-2-amine (3bs).** White solid, Mp: 74–76 °C; IR (KBr): 3232, 2923, 1598, 1573, 1529, 1440, 1328, 1290, 1157, 1147, 1124, 1080, 968, 767 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ: 4.11 (td, J = 6.0, 1.0 Hz, 2H), 4.68 (br s, 1H), 6.32 (dt, J = 16.0, 6.0 Hz, 1H), 6.43 (d, J = 7.5 Hz, 1H), 6.58–6.62 (m, 2H), 7.23 (t, J = 7.5 Hz, 1H), 7.31 (t, J = 7.5 Hz, 2H), 7.37 (d, J = 7.5 Hz, 2H), 7.43 (td, J = 7.5, 2.0 Hz, 1H), 8.11 (d, J = 5.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 44.3, 106.9, 113.2, 126.4, 126.7, 127.5, 128.6, 131.4, 136.8, 137.5, 148.2, 158.5; Anal. Calcd for $C_{14}H_{14}N_2$: C, 79.97; H, 6.71; N, 13.32. Found: C, 80.09; H, 6.88; N, 13.16.

***N*-Phenylcyclododecanamine (3cd).** Yellow solid, Mp: 75–77 °C; IR (KBr): 3401, 3043, 1601, 1503, 1440, 1435, 1316, 1260, 1185, 1145, 1110, 745, 690 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ: 1.28–1.72 (m, 22H), 2.47 (t, J = 6.0 Hz, 1H), 3.51 (br s, 1H), 6.58 (d, J = 7.5 Hz, 2H), 6.65 (t, J = 7.5 Hz, 1H), 7.15 (t, J = 7.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 21.3, 22.4, 22.6, 23.3, 24.0, 24.3, 24.4, 24.7, 24.8, 29.8, 40.4, 49.5, 113.1, 116.7, 129.3, 147.9; Anal. Calcd for $C_{18}H_{29}N$: C, 83.33; H, 11.27; N, 5.40. Found: C, 83.15; H, 11.08; N, 5.56.

***N*,*N*′-Dibenzyl-*p*-phenylenediamine (3cf).** White solid, Mp: 125–127 °C; IR (KBr): 3294, 1600, 1508, 1494, 1452, 1357, 1294, 1244, 1217, 1132, 1068, 1029, 817, 698 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ: 4.26 (s, 4H), 6.60 (s, 4H), 7.24–7.27 (m, 2H), 7.32 (t, J = 7.5 Hz, 4H), 7.36 (d, J = 7.5 Hz, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 49.6, 114.9, 127.1, 127.7, 128.5; Anal. Calcd for $C_{20}H_{20}N_2$: C, 83.30; H, 6.99; N, 9.71. Found: C, 83.45; H, 6.82; N, 9.90.

***N*-(4-((Phenylamino)methyl)benzyl)benzenamine (3cg).** White solid, Mp: 105–107 °C; IR (KBr): 3423, 1604, 1508, 1490, 1319, 1276, 1178, 1151, 1122, 1089, 1072, 983, 750 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ: 4.02 (br s, 2H), 4.32 (s, 4H), 6.63 (d, J = 7.5 Hz, 4H), 6.72 (t, J = 7.5 Hz, 2H), 7.17 (t, J = 7.5 Hz, 4H), 7.35 (s, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 48.0, 112.8, 117.6, 127.8, 129.3, 138.5, 148.1; Anal. Calcd for $C_{20}H_{20}N_2$: C, 83.30; H, 6.99; N, 9.71. Found: C, 83.16; H, 7.18; N, 9.53.

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