

Imidazole-functionalized magnetic Fe₃O₄ nanoparticles: an efficient, green, recyclable catalyst for one-pot Friedländer quinoline synthesis

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Abstract An efficient and cost-effective procedure for preparation of Fe_3O_4 nanoparticles and supported Brønsted acidic ionic liquid 1-methyl-3-(3-trimethoxysilylpropyl)imidazolium hydrogen sulfate (Fe_3O_4 -IL-HSO_4) as a Brønsted acidic ionic liquid and efficient magnetic catalyst is described, together with its use for one-pot synthesis of polysubstituted quinolines through Friedländer condensation of 2-aminoaryl ketones with 1,3-dicarbonyl compounds under solvent-free conditions. The most noteworthy aspects of this methodology are its environmental friendliness, simplicity of operation, excellent yield within short reaction time, easy product isolation, and excellent reusability potential of the catalyst.

Keywords Friedländer quinoline synthesis \cdot Magnetic nanoparticles \cdot Fe₃O₄-IL-HSO₄ \cdot Solvent-free \cdot Brønsted acid ionic liquid

Introduction

Quinolines and their derivatives are an important class of nitrogen-containing heterocycles and have recently received great attention because of their wide range of therapeutic and biological properties such as antiasthmatic (chloroquine and

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mefloquine), tyrosine kinase inhibitory [luotonin A and 20(S)-camptothecin], cytotoxic (e.g., benzo[5,6]pyrrolizino[1,2-*b*]quinolines), antiinflammatory, antimalarial, antihypertensive, and antibacterial activities (Fig. 1) [1–5]. In addition to medicinal properties, the quinoline nucleus is frequently found in various natural products [6]; for example, aminoquinolines are found to inhibit acetylcholinesterase [7] and the butyrylcholinesterase family of enzymes [8] (Fig. 1). Also, quinoline derivatives are utilized for synthesis of nano- and mesostructures having enhanced electronic and photonic properties [9–11].

Various procedures for preparation of quinoline derivatives have been developed, such as the Skraup [12], Pfitzinger [13, 14], Conrad-Limpach-Knorr [15, 16], Friedländer [17, 18], and Combes methods [19, 20]. However, among the various methods for quinoline synthesis, Friedländer condensation is the most simple, versatile, and useful method for synthesis of polysubstituted quinolines. Friedländer condensation involves base- or acid-catalyzed or thermal condensation between a 2-aminoaryl ketone and a carbonyl compound having a reactive a-methylene group followed by cyclodehydration. Therefore, it is important to develop more convenient methods for preparation of quinoline derivatives. Several catalysts (Brønsted acids and Lewis acids) have been used to promote this reaction, such as hydrochloric acid [21], sulfamic acid [22], magnetic-nanoparticle-supported organocatalysts [23], oxalic acid [24], CeCl₃·7H₂O [25], Y(OTf)₃ [26], SnCl₂ and ZnCl₂ [27], organocatalysts [28], 1-butylimidazolium tetrafluoroborate [Hbim]BF₄ [29], sulfonic-acid-functionalized ionic liquid [30], phosphotungstic acid [31], silver phosphotungstate [32], and neodymium(III) nitrate hexahydrate [33], and an important review in the Friedländer reaction field has been published [34]. However, many of these methods suffer from one or more disadvantages, such as low product yield, long reaction time, harsh reaction conditions, difficulties in



IV: 20-(S)-Camptothecin

Fig. 1 Examples of biologically active quinoline derivatives

workup, tedious workup procedures, need for excess reagents and catalysts, and/or relatively expensive reagents, with no agreement regarding green chemistry protocols, high temperatures, and use of toxic organic solvents. Moreover, the main disadvantage of almost all existing methods is that the catalysts are destroyed in the workup procedure and cannot be recovered or reused. Therefore, introduction of a new and inexpensive catalyst that can be easily separated and reused, and does not become contaminated by the products is of prime importance. Recently, use of nanoparticles (NPs) in organic synthesis and industrial manufacture of materials has become of increasing importance because of their high surface area and unique magnetic properties. Also, magnetic nanoparticles have been investigated due to their potential biomedical applications in various fields, such as bioseparation [35, 36], magnetothermal therapy [37, 38], magnetic resonance imaging [39], drug delivery [40, 41], data storage [42], environmental remediation [43], and biomolecular sensing [44, 45]. In continuation of our studies toward development of new and cleaner methods for organic transformations [46–54], in this work we prepared Fe₃O₄ nanoparticles and supported Brønsted acidic ionic liquid 1-methyl-3-(3-trimethoxysilylpropyl)imidazolium hydrogen sulfate (Fe₃O₄-IL-HSO₄) for one-pot synthesis of polysubstituted quinolines through Friedländer condensation of 2-aminoaryl ketones with 1,3-dicarbonyl compounds in absence of solvent (Scheme 1). The mean size and surface morphology of the nanoparticles were characterized by transmission electron microscopy (TEM), scanning electron microscopy (SEM), vibrating-sample magnetometry (VSM), X-ray diffraction (XRD), and Fourier-transform infrared (FTIR) techniques.

Materials and methods

General

FeCl₂·4H₂O (99 %), FeCl₃·6H₂O (98 %), 2-aminoaryl ketones, 1,3-diketones or ketones, and other chemical materials were purchased from Fluka and Merck and used without further purification. All compounds are known, and their structures were identified by comparing their melting points and ¹H and ¹³C nuclear magnetic resonance (NMR) data with those reported in literature. ¹H and ¹³C NMR spectra were obtained in CDCl₃ at 500 and 125 MHz, respectively. Chemical shifts are given in ppm with respect to internal tetramethylsilane (TMS), and *J* values are



Scheme 1 Modified Friedländer reaction

quoted in Hz. IR spectra of the compounds were obtained on a PerkinElmer spectrometer version 10.03.06 using a KBr disk. Melting points were taken on an Electrothermal capillary melting point apparatus and are uncorrected. The phases present in the magnetic materials were analyzed using powder XRD (X'Pert model, Philips, The Netherlands), with Cu K_{α 1} radiation ($\lambda = 1.5401$ Å) generated at 40 kV and 30 mA. Diffraction patterns were collected from $2\theta = 20^{\circ}$ to 80° . Substrate purity assessment and reaction monitoring were carried out by TLC on Polygram SILG/UV254 silica gel plates.

Preparation of Fe₃O₄-IL-HSO₄

Magnetite nanoparticles were prepared by the conventional coprecipitation method [55]. A schematic representation of the synthesis of magnetic nanoparticles supporting ionic liquid is shown in Scheme 1. 1-Methyl-3-(3-trimethoxysilyl-propyl)imidazolium chloride (IL) prepared from reaction of imidazole with (3-chloropropyl)trimethoxysilane was heated at 110 °C for 17 h with continuous stirring under N₂ atmosphere [56]. Then, excess amount of KHSO₄ was added into deionized water and stirred for 24 h at room temperature. KCl was prepared by exchange of chloride anions with HSO₄ [57], and MNP-IL-HSO₄ was separated by magnetic decantation, washed with acetonitrile and dichloromethane, and left to dry in a desiccator.

General procedure for one-pot synthesis of quinoline derivatives 3a-n

A mixture of 2-aminoaryl ketone (1 mmol), carbonyl compounds (1 mmol), and Fe_3O_4 -IL-HSO_4 (20 mg) was stirred at 90 °C for the specified time (see Table 4). The reaction was monitored by TLC. After completion of the reaction, as monitored by TLC, the reaction mixture was cooled to room temperature, and extracted by EtOAc (10 mL) to separate the catalyst (the product is soluble in EtOAc). EtOAc was removed, and the crude product was recrystallized from aqueous ethanol (90 %) to afford pure product which required no further purification. The recovered catalyst was washed with EtOAc (2 × 10 mL), dried, and reused for the next run. The catalyst was reused for four times without any significant change in yield or reaction time. All products were identified by melting point determination and ¹H NMR and ¹³C NMR spectroscopy.

Table 4, entry 1: M.p.: 103–105 °C (lit. 102–103 °C) [31]; ¹H NMR (CDCl₃, 500 MHz) δ : 0.97 (t, J = 7.2 Hz, 3H), 2.82 (s, 3H), 4.10 (q, J = 7.2 Hz, 2H), 7.37–7.42 (m, 2H), 7.45–7.54 (m, 4H), 7.62 (dd, J = 8.4, 1.0 Hz, 1H), 7.75 (td, J = 8.3, 1.5 Hz, 1H), 8.11 (d, J = 8.5 Hz, 1H); ¹³C NMR (CDCl₃, 125 MHz) δ : 14.1, 24.3, 61.8, 125.5, 126.8, 126.9, 127.8, 128.7, 128.9, 129.3, 129.8, 130.7, 136.1, 146.7, 148.1, 155.0, 168.9.

Table 4, entry 2: M.p.: 102–104 °C (lit. 99–100 °C) [31]; ¹H NMR (CDCl₃, 500 MHz) δ : 2.78 (s, 3H), 3.55 (s, 3H), 7.41–8.03 (m, 9H); ¹³C NMR (CDCl₃, 125 MHz) δ : 24.19, 52.59, 126.92, 126.97, 127.72, 128.71,128.94, 129.66, 130.81, 136.08, 154.97.

Table 4, entry 4: M.p.: 150–152 °C (lit. 153–154 °C) [31]; ¹H NMR (CDCl₃, 500 MHz) δ : 1.64–1.66 (m, 2H), 1.88–1.89 (m, 4H), 2.70–2.75 (m, 2H), 3.31–3.33 (m, 2H), 7.24–7.38 (m, 4H), 7.48–7.65 (m, 4H), 8.06 (d, J = 8.4 Hz, 1H); ¹³C NMR (CDCl₃, 125 MHz) δ : 27.5, 28.9, 31.1, 32.4, 40.6, 126.0, 126.8, 127.3, 128.0, 128.6, 128.9, 129.0, 129.9, 134.2, 138.1, 145.9, 146.2, 165.2.

Table 4, entry 11: M.p.: 151-154 °C (lit. 150-152 °C) [31]; ¹H NMR (CDCl₃, 500 MHz) δ : 2.00 (s, 3H), 2.68 (s, 3H), 7.35–7.95 (m, 8H); ¹³C NMR (CDCl₃, 125 MHz) δ : 23.6, 31.6, 124.7, 125.8, 128.8, 129.1, 129.8, 130.8, 132.3, 134.5, 135.4, 142.9, 145.8, 153.8, 204.9.

Results and discussion

Preparation and characterization of Fe₃O₄-IL-HSO₄

A schematic representation of the synthesis of magnetic nanoparticles supporting ionic liquid is shown in Scheme 2. Firstly, imidazole was reacted with (3chloropropyl)trimethoxysilane by heating at 110 °C for 17 h with continuous stirring under N₂ atmosphere to afford 1-methyl-3-(3-trimethoxysilylpropyl)imidazolium chloride. In the next step, excess amount of KHSO₄ was added into deionized water and stirred for 24 h at room temperature. Finally, KCl was prepared by exchange of chloride anions with HSO₄ [57], and MNP-IL-HSO₄ was separated by magnetic decantation, washed with acetonitrile and dichloromethane, and left to dry in a desiccator [55–57] (see Electronic Supplementary Information for experimental procedures for synthesis of Fe₃O₄-IL-HSO₄ as well as TEM, SEM, VSM, XRD, and FTIR results).

Optimization of reaction conditions

After preparation of Fe_3O_4 -IL-HSO₄, condensation of 2-aminoaryl ketones with 1,3dicarbonyl compounds in presence of Fe_3O_4 -IL-HSO₄ for preparation of polysubstituted quinolines was studied (Scheme 1). To standardize the conditions, a model reaction using 2-aminobenzophenone **1** (1 mmol) and ethyl acetoacetate **2** (1 mmol) was carried out using different amounts of Fe_3O_4 -IL-HSO₄ under solvent-free condition to provide ethyl 2-methyl-4-phenylquinoline-3-carboxylate; the results are presented in Table 1, from which it can be seen that this reaction was strongly influenced by the amount of catalyst. The best results were obtained using 20 mg Fe_3O_4 -IL-HSO₄, giving ethyl 2-methyl-4-phenylquinoline-3-carboxylate in excellent yield and short reaction time (Table 1, entry 6).

In the next part of the study, we carried out the reaction of 2-aminobenzophenone 1 (1 mmol) and ethyl acetoacetate 2 (1 mmol) in presence of 20 mg Fe₃O₄-IL-HSO₄ at various temperatures under solvent-free conditions (Table 2). As shown in Table 2, different temperatures resulted in different yields, with shorter reaction time and excellent yield being obtained when the reaction was carried out in presence of 20 mg Fe₃O₄-IL-HSO₄ at 90 °C.



Scheme 2 Synthesis of magnetic-nanoparticle-supported ionic liquid (MNP-IL-HSO₄)

Entry	Catalyst	Catalyst amount (mg)	Time (min)	Yield (%) ^a
1	Fe ₃ O ₄ -IL-HSO ₄	None	12 h	Trace
2	Fe ₃ O ₄ -IL-HSO ₄	1	120	41
3	Fe ₃ O ₄ -IL-HSO ₄	5	90	54
4	Fe ₃ O ₄ -IL-HSO ₄	10	80	65
5	Fe ₃ O ₄ -IL-HSO ₄	15	65	78
6	Fe ₃ O ₄ -IL-HSO ₄	20	40	85
7	Fe ₃ O ₄ -IL-HSO ₄	30	40	71

Table 1 Optimization of catalyst loading in model reaction

^a Isolated yields

In another study, the reaction was examined in presence of different catalysts (Lewis and Brønsted acids) such as Fe^{2+} supported on hydroxyapatite core–shell c-Fe₂O₃ nanoparticles (Table 3, entry 1), Ni²⁺ supported on hydroxyapatite core–

Table 2 Optimization oftemperature in presence of	Entry	Temperature (°C)	Time (min)	Yield (%) ^a
20 mg Fe ₃ O ₄ -IL-HSO ₄	1	80	30	88
	2	90	25	96
	3	100	25	91
	4	120	35	88
^a Isolated vields	5	130	40	84

 Table 3 Synthesis of compound 3a using different catalysts

Entry	Catalyst	Time (min)	Yield (%) ^f
1	γ-Fe ₂ O ₃ -HAp-Fe ^{2+a}	45	91
2	γ-Fe ₂ O ₃ -HAp-Ni ^{2+b}	45	89
3	Citric acid ^c	120	60
4	Cyanuric chloride ^d	150	55
5	SESA ^e	30	87
6	Fe ₃ O ₄ -IL-HSO ₄	25	96

 $^a~20~mg~\gamma\mbox{-}Fe_2O_3\mbox{-}HAp\mbox{-}Fe^{2+}$ was used

 $^{\rm b}~20~mg~\gamma\mbox{-}Fe_2O_3\mbox{-}HAp\mbox{-}Ni^{2+}$ was used

^c 7 mol % citric acid was used

^d 5 mol % cyanuric chloride was used

^e 10 mol % SESA was used

f Isolated yields

shell c-Fe₂O₃ nanoparticles (Table 3, entry 2), citric acid (Table 3, entry 3), cyanuric chloride (Table 3, entry 4), and silica-supported [2-(sulfooxy)ethyl]sulfamic acid (Table 3, entry 5). The results are summarized in Table 1. Excellent yield of ethyl 2-methyl-4-phenylquinoline-3-carboxylate was obtained in short reaction time when Fe₃O₄-IL-HSO₄ was utilized as catalyst (Table 3, entry 6). Subsequently, we used 20 mg Fe₃O₄-IL-HSO₄ for one-pot synthesis of polysubstituted quinolines by Friedländer condensation of 2-aminoaryl ketones with 1,3-dicarbonyl compounds under solvent-free conditions at 90 °C. The results are summarized in Table 3.

Scope of reaction

As can be seen from Table 4, to assess the efficiency and scope of Fe_3O_4 -IL-HSO₄ for one-pot synthesis of polysubstituted quinolines, various 1,3-dicarbonyl compounds (acyclic 1,3-diketone, cyclic 1,3-diketones, and β -ketoesters) were reacted with 2-aminoaryl ketones or 2-amino-5-chloroaryl ketones using the optimal reaction conditions to produce the desired products in good to high yield (85–96 %) and short reaction time (20–60 min). Carbonyl compounds including β -ketoesters (methyl and ethyl acetoacetate), cyclic ketones (cyclohexanone, cyclopentanone,

Entry	2-aminoaryl ketones 1	Ketone 2	Product 3	Time (min)	Yield (%) ^a
1	O Ph NH ₂	O O OEt	Ph CO ₂ Et	25	96
2	Ph NH ₂	O O OMe	Ph CO ₂ Me	20	94
3	O Ph NH ₂		Ph COMe	20	90
4	O Ph NH ₂		Ph N	15	95
5	O Ph NH ₂		Ph N	25	93
6	Ph NH ₂		Ph O N	40	88
7	Ph NH ₂	0,00	Ph O N	45	85
8	Ph NH ₂		Ph N	40	89
9	Ph NH ₂		Ph N Ph	25	91
10	Cl Ph NH2	O O OMe	Cl CO ₂ Me	45	95

Table 4 Synthesis of quinoline derivatives catalyzed by Fe₃O₄-IL-HSO₄

Entry	2-aminoaryl ketones 1	Ketone 2	Product 3	Time (min)	Yield (%) ^a
11	Cl Ph NH ₂		Cl COMe	35	93
12	Cl Ph NH ₂		Cl Ph	35	91
13	Cl Ph		Cl Ph	20	92
14	Cl Ph	0,000	Cl Ph O N	60	87
15	Cl Ph NH ₂		Cl Ph O N	60	86

Table 4 continued

Reaction conditions: 2-aminoaryl ketones (1 mmol), carbonyl compounds (1 mmol), catalyst Fe_3O_4 -IL-HSO₄ (20 mg); 90 °C, solvent-free

^a Isolated yields

and acetophenone), and pentane-2,4-dione were reacted with 2-aminoaryl ketones to afford excellent yields in short reaction times (Table 1, entries 1–5, 9). Also, cyclic 1,3-diketones (1,3-cyclohexanedione and 5,5-dimethylcyclohexanedione), cyclic ketones (cyclohexanone and cyclopentanone), β -ketoester (methyl acetoacetate), and 2,3-dihydroinden-1-one were reacted with 2-aminoaryl ketones or 2-amino-5-chloroaryl ketones, giving good yields in slightly longer reaction times (Table 4, entries 6–8, 10–15). All synthesized compounds were characterized by melting point and ¹H and ¹³C NMR spectral techniques.

Catalyst reusability is of major importance in heterogeneous catalysis. The recovery and reusability of the catalyst were studied using the reaction of 2-aminobenzophenone **1** (1 mmol) and ethyl acetoacetate **2** (1 mmol) performed in presence of 20 mg Fe₃O₄-IL-HSO₄ at 90 °C. After completion of the reaction, as monitored by TLC, the reaction mixture was cooled to room temperature and extracted with warm EtOAc to separate the catalyst (the product is soluble in EtOAc). EtOAc was removed, and the recovered catalyst was washed with EtOAc, dried, and reused for synthesis of ethyl 2-methyl-4-phenylquinoline-3-carboxylate according to the mentioned procedure. The catalyst was consecutively reused six times without noticeable loss of catalytic activity (Fig. 2).



Fig. 2 Recyclability of Fe_3O_4 -IL-HSO₄ for synthesis of ethyl 2-methyl-4-phenylquinoline-3-carboxylate after 10 min

To show the merit of the present work in comparison with results reported in literature, we compare the results of Fe_3O_4 -IL-HSO₄ catalyst with reported catalysts for synthesis of quinoline derivatives in Table 5. As can be seen from this table, several of these methods suffer from one or more drawbacks such as long reaction time, harsh reaction conditions, use of hazardous catalyst, low product yield, or use

Reaction conditions	Catalyst loading (mol%)	Time (min)	Yield (%) ^a	Ref.
Hydrochloric acid, H ₂ O, 60 °C	0.1 ^b	30-360	85–96	[21]
Sulfamic acid, solvent-free, 70 °C	5	30–90	82–95	[22]
Oxalic acid, solvent-free, 80 °C	0.1 ^b	120	88–95	[24]
CeCl ₃ ·7H ₂ O, CH ₃ CN, room temperature	25	90-300	65–95	[25]
Yb(OTf) ₃ , CH ₂ Cl ₂ , room temperature	5	60-120	75–95	[26]
SnCl ₂ ·ZnCl ₂ , EtOH, 70 °C	16.55 ^b	180	70–98	[27]
CuO nanoparticles, solvent-free, 60 °C	5	60–480	85–98	[<mark>58</mark>]
PMA·SiO ₂ , EtOH, reflux	100 ^c	45-100	80–95	[<mark>59</mark>]
Chitosan-SO ₃ H, EtOH, reflux	100 ^c	20-40	79–92	[<mark>60</mark>]
γ -Fe ₂ O ₃ @HAp-Si-(CH ₂) ₃ -NHSO ₃ H, room temperature, neat	0.7	90–210	91–97	[<mark>61</mark>]
Fe ₃ O ₄ -IL-HSO ₄ , solvent-free, 80 °C	20 ^c	20-60	85–96	_ ^d

Table 5 Comparison of ${\rm Fe_3O_4\text{-}IL\text{-}HSO_4}$ with other acid catalysts for preparation of quinoline derivatives

^a Isolated yields

^d This work

^b In mmol

^c In mg

of nonrecyclable catalyst. So, Fe_3O_4 -IL-HSO₄ acts as an effective catalyst with respect to reaction time, yield, and products. In general, the reaction is very clean, rapid, efficient, and free from side-reactions, such as self-condensation of ketones as normally observed under basic conditions.

Conclusions

We have developed a simple, cost-effective, green methodology for one-pot synthesis of polysubstituted quinolines through Friedländer condensation of 2-aminoaryl ketones with 1,3-dicarbonyl compounds using Fe_3O_4 -IL-HSO₄ as Brønsted acidic ionic liquid and efficient magnetic catalyst under solvent-free conditions at 90 °C. The advantages of this method include experimental operational ease, avoidance of hazardous organic solvents and use of nontoxic reagents, short reaction time and high product yield in comparison with other procedures, inexpensive reagents, reusability of catalyst, and nonchromatographic purification of products, i.e., simple recrystallization from aqueous ethanol.

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