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$Fe_3O_4@SiO_2-SO_3H$ as a recyclable heterogeneous nanomagnetic catalyst for the one-pot synthesis of substituted quinolines *via* Friedländer heteroannulation under solvent-free conditions

Monire Beyki[a], Mehdi Fallah-Mehrjardi[a,b,*]

[a]*Department of Chemistry, Payame Noor University, Tehran, P.O. BOX 19395-4697, Iran*

[b]*Research Center of Environmental Chemistry, Payame Noor University, Ardakan, Yazd, Iran*

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Abstract

An efficient method has been developed for the Friedländer synthesis of substituted quinolines through a condensation reaction of 2-aminoaryl ketones with α-methylene ketones in the presence of a catalytic amount of nano $Fe_3O_4@SiO_2-SO_3H$ under solvent-free conditions at 110 °C. The reactions are completed in short times, and the products are obtained in good to excellent yields. The results revealed several advantages to our procedure, including high product yields, short reaction time, facile work-up procedure, simplicity in operation, eco-friendly reaction conditions, reusability of the catalyst and green aspects by avoiding toxic catalysts and solvents. The catalyst could simply be separated and recovered from the reaction mixture by an external magnet and reused in subsequent reactions without significant loss in activity.

Keywords: $Fe_3O_4@SiO_2-SO_3H$; quinolines; Friedländer reaction; solvent-free; recyclable nanomagnetic catalyst; green chemistry.

Introduction

Quinolines and their derivatives are an important class of heterocyclic compounds that occur widely in natural products [1,2], drugs [3,4] and biologically active compounds [5,6]. A large variety of quinolines have displayed interesting physiological activities and found attractive applications as pharmaceuticals and agrochemicals [7]. Furthermore, poly-substituted quinolines have been found to undergo hierarchical self-assembly into a variety of nano- and meso-structures with enhanced electronic and photonic functions [8,9].

In accordance with these useful properties and related applications as above-mentioned, a number of methods have been reported for the synthesis of quinolines. Although other methods such as the Skraup [10], Doebner-von Miller [11] and Combes [12] procedures have been reported, the Friedländer heteroannulation is still one of the most simple and straightforward methods used to produce poly-substituted quinolines. The Friedländer synthesis involves a condensation reaction followed by a cyclodehydration reaction between a 2-aminoaryl aldehyde or ketone and an aldehyde or ketone containing an

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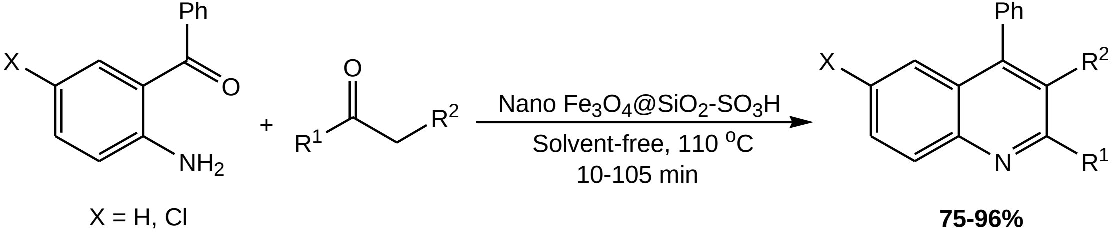
*Corresponding author: Mehdi Fallah-Mehrjardi
Tel: +98 (35) 32220011, Fax: +98 (35) 32220011
E-mail: fallah.mehrjerdi@pnu.ac.ir

α-methylene group [13]. This procedure has been catalyzed by several homogeneous and heterogeneous catalysts, such as Brønsted acids [14-25], Lewis acids [26-30], ionic liquids [31], *etc.* Although these catalytic methods have their own advantages, many of them suffer from one or more drawbacks such as prolonged reaction times, low product yields, difficulty in work-up and lack of reusability of the catalyst. Therefore, the development of mild, effective and environmentally friendly processes suitable for the synthesis of poly-substituted quinolines is highly desirable.

The recent tendency of green chemistry has contributed to a recent increase in research attention directed toward the synthesis of magnetic nanoparticles and their application in catalysis [32-37]. Due to their magnetic properties, the catalyst could be quickly and easily recovered by means of an external magnet. On the other hand, for the stringent and growing environmental regulations, organic chemists are requested to develop environmentally benign synthetic methodologies. One of the most promising approaches is the performance of organic reactions under solvent-free conditions, including using microwave irradiation and conventional heating techniques [38].

In this paper, we wish to explore a straightforward and convenient method for the one-pot synthesis of quinoline derivatives using $Fe_3O_4@SiO_2$-SO_3H nanoparticles as an efficient, mild, and harmless catalyst to the environment, and also as a recyclable, non-toxic and powerful magnetic solid acid catalyst with good stability toward humidity, under solvent-free conditions at 110 °C (Scheme 1). This green procedure has many obvious advantages compared to those reported in the previous literatures, including avoiding the use of harmful catalysts, easy work-up of the reaction, increasing the yields, decreasing the reaction time, simplicity of the methodology, and recyclability of the catalyst.



Scheme 1. Friedländer reaction of 2-aminoaryl ketones with carbonyl compounds containing α-methylene groups

Experimental

General

All of the commercially available chemicals were purchased from Fluka, Aldrich and Merck and used without further purification. Fe_3O_4, $Fe_3O_4@SiO_2$ and $Fe_3O_4@SiO_2$-SO_3H were prepared according to the reported method [39]. The products were characterized by comparison of their physical properties and spectroscopic data with authentic samples. The reactions were monitored by TLC on silica gel polygram SILG/UV 254 plates. Infrared (IR) spectra were recorded on KBr Pellets on a Shimadzu IRPresting-21 spectrophotometer in the range of 4000–400 cm^{-1}. NMR spectra were recorded in $CDCl_3$ on a Bruker Advanced DPX 400 MHz spectrometer using TMS as an internal reference. Melting points were obtained in open capillary tubes and were measured on an electrothermal 9200 apparatus.

Preparation of the catalyst

The nano $Fe_3O_4@SiO_2$–SO_3H was prepared according to the reported method [39].

Determination of the acidity of the catalyst

To determine the acidity of the catalyst, $Fe_3O_4@SiO_2$-SO_3H (100 mg) was added to a 25 mL aqueous solution of NaCl (1 M, pH = 6.24), and the resulting mixture was stirred for 24 h. The pH of the solution was reduced to 2.11, indicating the presence of 1.94 mmol/g of H^+.

Typical procedure for the synthesis of quinoline derivatives

A mixture of 2-aminobenzophenone (1 mmol), dimedone (1.2 mmol) and $Fe_3O_4@SiO_2$–SO_3H (0.05 g) was heated in an oil bath at 110 °C under solvent-free conditions. After completion of the reaction as indicated by TLC (ethyl acetate/*n*-hexane 2/5) and cooling, hot ethanol (5 mL) was added to the mixture and stirred for 10 min. In the presence of an external magnet, the nanocatalyst was removed and the desired product was isolated and purified by recrystallization in hot EtOH.

Characterization data

*1-(2-Methyl-4-phenylquinolin-3-yl)ethanone (**3a**)*

M.p. = 113-115 °C; IR (KBr): ῡ (cm^{-1}) 3069, 2921, 1698, 1612, 1563, 1491, 1212, 761; ^{1}HNMR ($CDCl_3$, 400 MHz): δ (ppm) 2.34 (s, 3H), 2.64 (s, 3H), 7.29–7.31 (m, 2H), 7.44 (m, 1H), 7.52–7.55 (m, 3H), 7.83 (m, 1H), 8.08 (m, 1H), 8.36 (m, 1H); ^{13}CNMR ($CDCl_3$, 100 MHz): δ (ppm) 21.3, 29.6, 123.4, 124.5, 125.7, 127.2, 128.0, 130.1, 130.3, 132.3, 132.9, 136.1, 145.4, 147.8, 152.1, 155.6, 204.8.

1-(6-Chloro-2-methyl-4-phenylquinolin-3-yl)ethanone (3b)

M.p. = 151-154 °C; IR (KBr): ῡ (cm^{-1}) 3054, 2962, 1703, 1602, 1569, 1484, 906, 708; ^{1}HNMR ($CDCl_3$, 400 MHz): δ (ppm) 1.94 (s, 3H), 2.61 (s, 3H), 7.34–7.41 (m, 2H), 7.51–7.52 (m, 3H), 7.59 (m, 1H), 7.58–7.62 (m, 1H), 7.96 (m, 1H); ^{13}CNMR ($CDCl_3$, 100 MHz): δ (ppm) 23.8, 32.8, 124.9, 125.2, 126.0, 128.9, 129.2, 129.6, 130.1, 131.9, 135.1, 135.4, 143.1, 145.8, 154.0, 204.4.

Ethyl 2-methyl-4-phenylquinoline-3-carboxylate (3c)

M.p. = 93-95 °C; IR (KBr): ῡ (cm^{-1}) 3059, 2978, 1724, 1611, 1566, 1485, 1230, 1064, 702; ^{1}HNMR ($CDCl_3$, 400 MHz): δ (ppm) 1.03 (t, 3H, J = 6.3 Hz), 2.79 (s, 3H), 4.23–4.31 (q, 2H, J = 6.3 Hz), 7.40–7.45 (m, 2H), 7.48–7.51 (m, 1H), 7.55–7.59 (m, 3H), 7.65 (m, 1H), 7.82–7.87 (m, 1H), 8.27 (m, 1H); 12.6, 24.9, 44.3, 124.3, 125.3, 128.2, 128.9, 129.5, 131.0, 132.4, 133.7, 136.1, 145.2, 148.1, 153.7, 154.8, 167.2.

Ethyl-6-chloro-2-methyl-4-phenylquinoline-3-carboxylate (3d)

M.p. = 107-109 °C; IR (KBr): ῡ (cm^{-1}) 3063, 2979, 1722, 1601, 1225, 907, 736; ^{1}HNMR ($CDCl_3$, 400 MHz): δ (ppm) 0.93–0.96 (t, 3H, J = 6.9 Hz), 2.75 (s, 3H), 4.03–4.05 (q, 2H, J = 6.9 Hz), 7.32 (m, 2H), 7.48–7.55 (m, 4H), 7.54–7.61 (m, 1H), 8.02 (m, 1H); ^{13}CNMR ($CDCl_3$, 100 MHz): δ (ppm) 13.5, 23.5, 61.0, 125.2, 125.8, 129.1, 129.5, 129.8, 130.5, 131.2, 131.5, 131.9, 135.6, 145.7, 146.3, 154.7, 168.5.

3,3-Dimethyl-9-phenyl-3,4-dihydroacridin-1(2H)-one (3e)

M.p. = 188-191 °C; IR (KBr): ῡ (cm^{-1}) 3078, 2955, 2868, 1689, 1600, 1554, 1477, 1215, 698; ^{1}HNMR ($CDCl_3$, 400 MHz): δ (ppm) 1.61 (s, 6H), 2.58 (s, 2H), 3.29 (s, 2H), 7.17-7.24 (m, 2H), 7.38-7.42 (m, 1H), 7.47–7.50 (m, 4H), 7.73-7.78 (m, 1H), 8.06 (m, 1H); ^{13}CNMR ($CDCl_3$, 100 MHz): δ (ppm) 26.6, 31.4, 48.8, 52.9, 125.8, 127.3, 127.7, 128.1, 128.4, 128.9, 129.0, 129.3, 131.5, 132.6, 134.1, 138.3, 147.5, 150.0, 162.4, 201.7.

7-Chloro-3,3-dimethyl-9-phenyl-3,4-dihydro-2H-acridin-1-one (3f)

M.p. = 209-212 °C; IR (KBr): ῡ (cm^{-1}) 3075, 2954, 2870, 1693, 1600, 1554, 1481, 1215, 987, 698; ^{1}HNMR ($CDCl_3$, 400 MHz): δ (ppm) 1.12 (s, 6H), 2.58 (s, 2H), 3.22 (s, 2H), 7.14–7.17 (m, 2H), 7.44 (m, 1H), 7.50–7.52 (m, 3H), 7.66–7.68 (m, 1H), 7.99 -8.02 (m, 1H); ^{13}CNMR ($CDCl_3$, 100 MHz): δ (ppm) 28.3, 32.3, 48.3, 54.2, 123.3, 126.7, 127.9, 128.1, 128.4, 130.5, 132.3, 132.7, 136.7, 147.9, 150.1, 154.3, 161.5, 197.9.

9-Phenyl-3,4-dihydroacridin-1(2H)-one (3g)

M.p. = 151-154 °C; IR (KBr): ῡ (cm^{-1}) 3035, 2976, 1692, 1552, 1484, 776, 701; ^{1}HNMR ($CDCl_3$, 400 MHz): δ (ppm) 2.35 (m, 2H), 2.82 (t, 2H, J = 5.4 Hz), 3.44-3.51 (t, 2H, J = 5.6 Hz), 7.21-7.29 (m, 2H), 7.39-7.44 (m, 5H), 7.53 (m, 1H), 8.01 (m, 1H). ^{13}CNMR ($CDCl_3$, 100 MHz): δ (ppm) 21.4, 34.6, 40.6, 123.6, 126.2, 127.3, 127.9, 128.0, 128.7, 129.2, 129.4, 132.7, 138.2, 148.4, 151.1, 162.1, 197.7.

7-Chloro-9-phenyl-3,4-dihydroacridin-1(2H)-one (3h)

M.p. = 185-187 °C; IR (KBr): ῡ (cm^{-1}) 3022, 2959, 1692, 1553, 1459, 1217, 842, 699; ^{1}HNMR ($CDCl_3$, 400 MHz): δ (ppm) 2.21–2.24 (m, 2H), 2.65 (t, 2H, J = 6.4 Hz), 3.29 (t, 2H, J = 6.1 Hz), 7.11–7.15 (m, 2H), 7.43 (m, 1H), 7.51–7.54 (m, 3H), 7.65–7.69 (m, 1H), 8.02 (m, 1H); ^{13}CNMR ($CDCl_3$, 100 MHz): δ (ppm) 21.8, 32.2, 40.1, 123.7, 123.8, 124.5, 127.4, 127.9, 128.8, 129.9, 132.0, 134.1, 137.1, 144.6, 154.2, 161.1, 197.2.

9-Phenyl-1,2,3,4-tetrahydroacridine (3i)

M.p. = 137-141 °C; IR (KBr): ῡ (cm^{-1}) 3059, 2935, 2862, 1570, 1485, 759, 702; ^{1}HNMR ($CDCl_3$, 400 MHz): δ (ppm) 1.67-175 (m, 2H), 1.88-1.89 (m, 2H), 2.47 (t, 2H, J = 6.3 Hz), 3.23 (t, 2H, J = 6.6 Hz), 7.21 (m, 1H), 7.27 (m, 1H), 7.38-7.42 (m, 6H), 7.89 (m, 1H). ^{13}CNMR ($CDCl_3$, 100 MHz): δ (ppm) 22.6, 22.9, 28.1, 34.2, 125.4, 126.2, 127.1, 127.9, 128.4, 128.7, 128.9, 130.0, 130.2, 130.8, 137.1, 146.5, 158.8.

7-Chloro-9-phenyl-1,2,3,4-tetrahydroacridine (3j)

M.p. = 162-165 °C; IR (KBr): ῡ (cm^{-1}) 3055, 2935, 2858, 1600, 1570, 1477, 1215, 702; ^{1}HNMR ($CDCl_3$, 400 MHz): δ (ppm) 1.68 (m, 2H), 1.79-1.81 (m, 2H), 2.56-2.58 (m, 2H), 3.21-3.23 (m, 2H), 7.20 (m, 2H), 7.22–7.24 (m, 1H), 7.41–7.45 (m, 4H), 7.91 (m, 1H); ^{13}CNMR ($CDCl_3$, 100 MHz): δ (ppm) 23, 23.4, 28.5, 34.4, 124.5, 127.7, 128.5, 128.9, 129.3, 129.6, 129.9, 130.3, 131.6, 136.7, 144.1, 145.3, 159.9.

2-Chloro-11-phenyl-7,8,9,10-tetrahydro-6H-cyclohepta-[b]quinoline (3k)

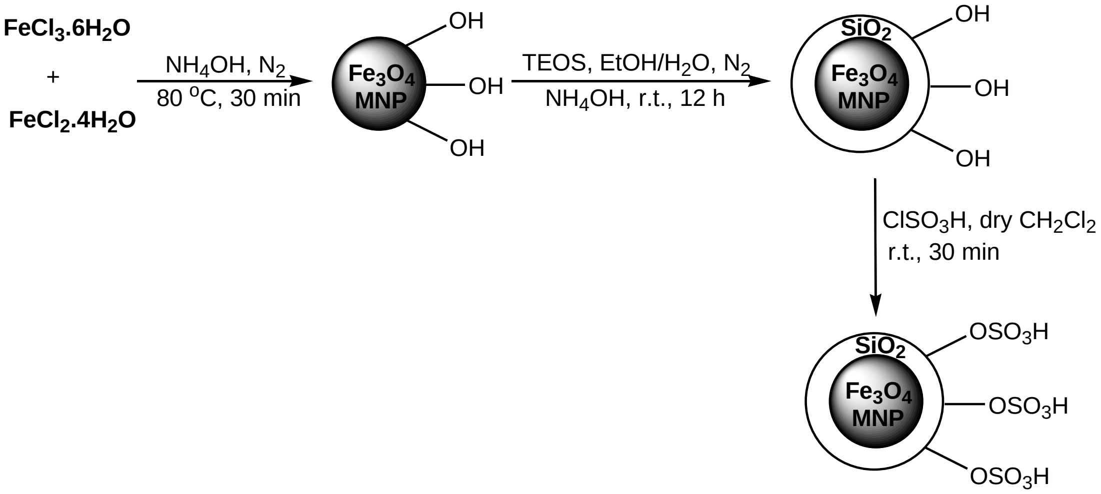
M.p. = 195-197 °C; IR (KBr): ῡ (cm^{-1}) 3067, 2949, 1602, 1564, 1485, 907, 705; ^{1}HNMR ($CDCl_3$, 400 MHz): δ (ppm) 1.02 (m, 2H), 1.29 (m, 2H), 1.61 (m, 2H), 2.58 (m, 2H), 3.31 (m, 2H), 7.19 (m, 2H), 7.25–7.27 (m, 1H), 7.47–7.49 (m, 4H), 7.93 (m, 1H); ^{13}CNMR ($CDCl_3$, 100 MHz): δ (ppm) 26.9, 28.1, 31.1, 31.7, 40.4, 125.2, 127.7, 127.9, 128.4, 128.7, 129.1, 130.0, 131.3, 132.1, 134.6, 136.9, 144.2, 144.7, 165.2.

Results and discussion

The Nano Fe_3O_4 encapsulated silica sulfuric acid ($Fe_3O_4@SiO_2$-SO_3H) has received considerable attention as an inexpensive, readily available, non-toxic and reusable catalyst for various organic transformations, affording the corresponding products in high yields [39-42]. However, to the best of our knowledge there has been no report on the use of this heterogeneous catalyst for Friedländer quinoline synthesis. We observed that $Fe_3O_4@SiO_2$-SO_3H is an efficient catalyst for the synthesis of poly-substituted quinolines through condensation/annulation reaction of 2-aminoaryl ketones and α-methylene ketones (Scheme 1).

The $Fe_3O_4@SiO_2$-SO_3H catalyst was prepared following the reported procedure in three steps [39]. Magnetite nanoparticles were synthesized by the co-precipitation of $FeCl_2$ and $FeCl_3$ in ammonia solution. To improve the chemical stability of magnetite nanoparticles, their surface engineering was successfully performed by the suitable deposition of silica onto nanoparticles surface by the ammonia-catalyzed hydrolysis of tetraethylorthosilicate (TEOS). Next, the SiO_2 spheres served as support for the immobilization of SO_3H groups by simple mixing of core–shell composite and chlorosulfonic acid in CH_2Cl_2 (Scheme 2).

Following the preparation of the catalyst, it was decided to consider the catalytic activity of the catalyst for the synthesis of quinoline derivatives. The reaction of 2-aminobenzophenone (1.0 mmol) with ethyl acetoacetate (1-1.5 mmol) was chosen as a model reaction, and the reaction was evaluated in various conditions (Table 1).



Scheme 2. Schematic diagram for the preparation of $Fe_3O_4@SiO_2$-SO_3H

Table 1. Optimization of the reaction conditions[a]

Entry	Ethyl acetoacetate (mmol)	Catalyst (g)	Solvent	Temp. (°C)	Time (h)	Yield (%)
1	1.5	-	Neat	110	3	Trace
2	1.5	0.025	Neat	110	3	75
3	1.5	0.05	Neat	110	1.5	93
4	1	0.05	Neat	110	3	50
5	1.1	0.05	Neat	110	3	72
6	1.2	0.05	Neat	110	1.75	94
7	1.2	0.05	Neat	100	3	77
8	1.5	0.05	MeCN	reflux	3	Trace
9	1.5	0.05	EtOAc	reflux	3	Trace
10	1.5	0.05	EtOH	reflux	3	Trace
11	1.5	0.05	Et_2O	reflux	3	Trace
12	1.5	0.05	CH_2Cl_2	reflux	3	Trace
13	1.5	0.05[b]	Neat	110	3	85

[a]Reaction conditions: 2-aminobenzophenone (1.0 mmol) and ethyl acetoacetate (1.0-1.5 mmol) were heated, with varying amount of catalyst (Fe_3O_4@SiO_2-SO_3H), either in solvent or under solvent-free conditions. [b]Catalyst: Fe_3O_4@SO_3H

The results showed that the reaction did not proceed in the absence of catalyst and gave the best results in 0.05 g of catalyst. A lower amount of catalyst, led to smaller yield and a higher amount, did not have a discernible impact on the yield or the rate of the reaction. Also, the results revealed that the reaction did not proceed in various polar and non-polar solvents under reflux conditions and gave the best results under solvent-free conditions at 110 °C.

With optimized conditions, consisting of a 1:1.2 molar ratios of 2-aminoaryl ketone and α-methylene ketone with a 0.05 g of Fe_3O_4@SiO_2-SO_3H at 110 °C under solvent-free conditions, the generality of this procedure was demonstrated through the synthesis of various substituted quinolines (Table 2). As shown in Table 2, various 1,3-dicarbonyl compounds including ethyl acetoacetate and acetylacetone, cyclic β-diketones such as 5,5-dimethyl-1,3-cyclohexanedione (dimedone) and 1,3-cyclohexanedione, reacted with 2-aminoaryl ketones to give the corresponding substituted quinolines without any side products (Table 2, Entries 1-8). Interestingly, cyclic ketones such as cyclohexanone and cycloheptanone reacted with 2-aminoaryl ketones to afford the respective tricyclic quinolines in good yields (Table 2, Entries 9-11).

This reaction which is very clean and free from side reactions such as self-condensation of ketones is normally observed under basic conditions. Moreover, the procedure gives the product in high yields and avoids problems associated with solvents and liquid acids' use (cost, handling, safety, pollution, corrosiveness, separation, and recovery).

Given the increasing levels of interest in green chemistry, the possibility of the magnetic recycling of catalyst was examined through the reaction of 2-amino-5-chlorobenzophenone and dimedone catalyzed by Fe_3O_4@SiO_2–SO_3H nanoparticles under optimized conditions. After completion of the reaction, hot ethanol was added and the catalyst was easily separated from the product by attaching an external magnet onto the reaction vessel (Figure 1), followed decantation of the reaction solution. The remaining catalyst was washed with ethanol to remove residual product and dried.

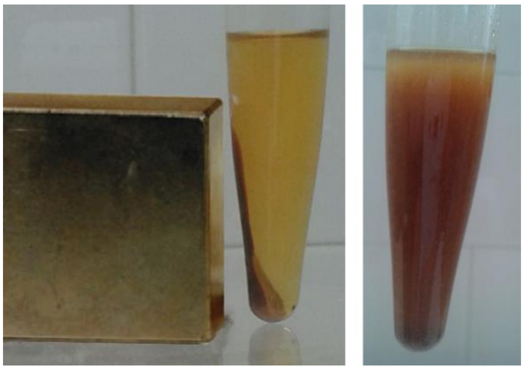
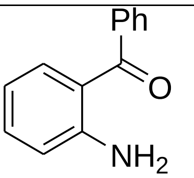
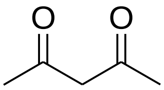
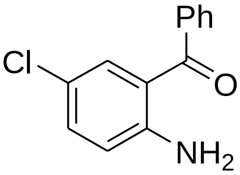
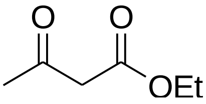
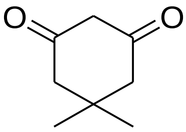
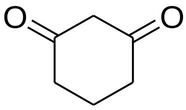
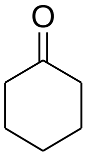
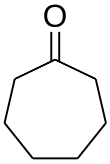


Figure 1. Image showing that the catalyst can be separated by applied magnetic field

Table 2. One-pot synthesis of substituted quinolines catalyzed by Fe_3O_4@SiO_2–SO_3H under solvent-free conditions at 110 °C

Entry	Compound 1	Compound 2	Product[a]	Time (min)	Yield[b] (%)
1	 **1a**	 **2a**	**3a**	60	87
2	 **1b**	2a	**3b**	45	91
3	**1a**	 2b	**3c**	105	94
4	**1b**	2b	**3d**	35	92
5	**1a**	 2c	**3e**	20	95
6	**1b**	2c	**3f**	10	95

7	**1a**	 2d	**3g**	30	93
8	**1b**	2d	**3h**	10	96
9	**1a**	 2e	**3i**	90	75
10	**1b**	2e	**3j**	60	85
11	**1b**	 2f	**3k**	30	87

[a]All of the products were characterized by IR, and ^{1}H and ^{13}C NMR, and their spectra were compared with those of the authentic samples. [b] Isolated yields

The recovered catalyst was reused at least five times in subsequent reactions without substantial loss of its catalytic activity (Figure 2). These results clearly show the practical reusability of the $Fe_3O_4@SiO_2–SO_3H$ catalyst under the described reaction conditions.

To demonstrate the capability and efficiency of $Fe_3O_4@SiO_2$-SO_3H nanoparticles over the reported catalysts in the literature for Friedländer synthesis of quinoline derivatives, the reaction of 2-aminobenzophenone with dimedone was considered as a representative example and conducted in the presence of different catalysts (Table 3). The results of this comparison study revealed that $Fe_3O_4@SiO_2$-SO_3H accelerated the rate of reaction considerably at the same time as providing a high yield of the desired product.

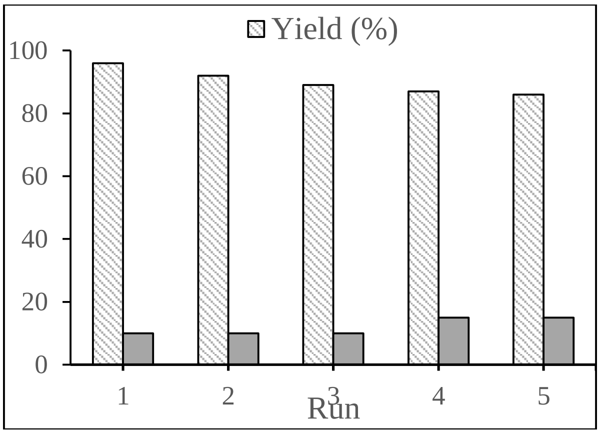


Figure 2. Reusability of the catalyst in the reaction of 2-amino-5-chlorobenzophenone (1.0 mmol) with dimedone (1.2 mmol) at 110 °C under solvent-free conditions

Table 3. Comparison of the efficiency of Fe_3O_4@SiO_2-SO_3H nanocatalyst with some other reported catalysts for the reaction of 2-aminobenzophenone with dimedone

Entry	Catalyst	Catalyst amount	Condition	Time (min)	Yield (%)	Ref.
1	Silica sulfuric acid	0.16 g	Solvent-free, 110 °C	120	86	[15]
2	$HClO_4$-SiO_2	0.2 g	CH_3CN, 60 °C	120	96	[18]
3	Oxalic acid	0.1 mmol	Solvent-free, 80 °C	120	89	[20]
4	Cellulose sulfuric acid	0.08 g	Solvent-free, 100 °C	35	70	[21]
5	P(4VPBSA)HSO_4	0.05 g	Solvent-free, 110 °C	30	95	[25]
6	$CeCl_3.7H_2O$	0.93 g	CH_3CN, r.t.	150	93	[26]
7	Nano Al_2O_3	0.03 mmol	$CHCl_3$, reflux	180	98	[29]
8[a]	Fe_3O_4@SiO_2-SO_3H	0.05 g	Solvent-free, 110 °C	20	95	-

[a]This procedure

Conclusion

In conclusion, we have demonstrated a simple, efficient and practical method for the synthesis of poly-substituted quinolines through a one-pot two component coupling of 2-aminoaryl ketones and α-methylene ketones by using Fe_3O_4@SiO_2-SO_3H as a nanomagnetically recyclable solid acid catalyst under solvent-free conditions. The simple experimental procedure, easy work-up, high yields of products, avoidance of the use of hazardous acids or bases, and easy recovery and reusability of the catalyst make this procedure simple and convenient for the synthesis of quinoline derivatives. So we think that this procedure could be considered a new and useful addition to the present methodologies in this area.

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