Article

JOURNAL OF THE CHINESE CHEMICAL SOCIETY

Fe_3O_4@SiO_2-imid-PMA^n Magnetic Porous Nanosphere as Reusable Catalyst for Synthesis of Polysubstituted Quinolines under Solvent-free Conditions

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(Received: Sept. 9, 2014; Accepted: Dec. 26, 2014; Published Online: Apr. 16, 2015; DOI: 10.1002/jccs.201400380)

In this research, a facile one-pot synthesis of poly-substituted quinoline derivatives has been demonstrated by using 2-aminobenzophenones and ethylacetoacetate or ketones in the presence of Fe_3O_4@SiO_2-imid-PMA^n and Fe_3O_4@SiO_2-imid-PMA^b nanoparticles as green and reusable catalysts under solvent-free conditions. The reaction proceeds efficiently in excellent yields and in a state of excellent purity. The nanocatalysts can be recycled and reused for at least four times without noticeably decreasing in catalytic activity.

Keywords: Polysubstituted quinolines; Heteropolyacides; Solvent-free; Magnetic nanocatalyst.

INTRODUCTION

Quinolines and their derivatives are very important compounds because wide applications in medicinal chemistry, includes antibacterial, antimalarial, anti-inflammatory, antiasthmatic, antihypertensive and tyrosine kinase inhibiting agents.[1-3] Also, quinoline derivatives have been employed in the study of bioorgano-metallic and bioorganic processes.[4,5] In addition, quinolines have been used for the preparation of nanostructures and polymers with enhanced electronic and photonic properties.[6,7]

For the synthesis of these various procedures such as Doebner-Von Miller, Skraup, Combes, Knorr methods and Friedlander have been developed.[8-11] Among various methodologies reported for the preparation of quinolines, Friedlander annulation is one of the simplest and straightforward methods for the synthesis of polysubstituted quinolines. The Friedlander quinoline synthesis consists of a condensation and cyclization between an aromatic 2-aminoaldehyde or ketone and a second carbonyl compound containing a reactive α-methylene group in the presence of base or acid catalysts. The Friedlander reaction can occur in the presence of Brønsted acid catalysts such as hydrochloric acid, sulfuric acid, oxalic acid, *p*-toluenesulfonic acid, sulfamic acid and polyphosphoric acids,[12-17] bases,[18,19] lewis acids such as $Y(OTf)_3$,[20] $Zr(DS)_4$,[21] $Bi(OTf)_3$,[22] silver phosphotungstate,[23] sodium fluoride,[24] ionic liquids,[25] ultrasound irradiation,[26] inorganic salt catalysts[27] and microwave conditions.[28,29] However, many of these procedures have significant drawbacks such as long reactions times, harsh reaction conditions, use of toxic and corrosive reagents, low yields and tedious work-up. In addition, the main disadvantage of almost all existing methods is that the catalysts cannot be recovered during the work-up procedure. Thus, the development of simple, convenient, and environmentally benign methods for the synthesis of quinolines is still required.

In the past decades, magnetic nanoparticles are used extensively in a broad range of applications, such as cell labeling and sorting,[30] drug delivery,[31] magnetic resonance imaging,[32-34] sensing as well as therapeutic applications[35] such as AC magnetic field-assisted cancer therapy, i.e. hyperthermia, and PDT,[36] wastewater treatment[37,38] and catalyst.[39] All these technological and medical applications require that the nanoparticles are superparamagnetic with sizes smaller than 20 nm, with a narrow size distribution to have uniform physical and chemical properties.[40]

Recently, more attention has been paid to the magnetic core–shell structure due to their unique magnetic properties. If core–shell structure composites use magnetic catalysts with the Fe_3O_4 core and the SiO_2 shell, the recycle use of the catalysts can be carried out under the magnetic field. Hence, the magnetic core–shell structure was a good support for the catalysts.[41,42]

In recent years, brønsted acids such as Keggin-type heteropolyacids (HPAs) have been used as efficient catalysts for a variety of organic reactions because of their

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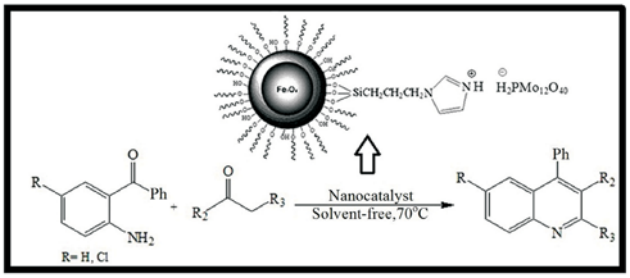
superacidic and redox properties, low in toxicity, highly stable towards humidity, air stable, high proton mobility, stronger acids than homogeneous acid catalysts and development of clean technologies.[43] Although HPAs in their acidic form are versatile compounds, their main disadvantages are high solubility in polar solvents and low surface area (<10 m^2/g). Therefore, in a homogeneous reaction the isolation of the products and the reuse of the catalyst after reaction become difficult.[43] Therefore, in order to overcome this problem, these materials disperse on supports (such as silica, acidic ion-exchange resins, active carbon and etc.) which possess large surface area. The use of support allows the heteropolyacids to be dispersed over a large surface area and increases theirs catalytic activity.[44]

Therefore in this work, we wish to report a simple and milder protocol for the synthesis of quinoline derivatives in the presence of Fe_3O_4@SiO_2-imid-PMA^n and Fe_3O_4@SiO_2-imid-PMA^b nanoparticles as effective catalysts via the Friedlander method (Scheme 1).

Scheme 1 Synthesize poly-substituted quinoline derivatives with using Fe_3O_4@SiO_2-imid-PMA^n nanocatalyst



EXPERIMENTAL

General methods: Chemicals were purchased from the Fluka and Merck chemical companies. The NMR spectra were recorded on a Bruker avance DPX 250 MHz spectrometer in chloroform ($CDCl_3$) using tetramethylsilane (TMS) as an internal reference. Fourier transform infrared (FT-IR) spectra were recorded on a Shimadzu FT-IR 8300 spectrophotometer. Elemental analysis was done on a 2400 series Perkin-Elmer analyzer. Melting points were determined on a Mel-Temp apparatus and are Uncorrected. Therefore, all of the products were characterized by FT-IR, ^{1}H NMR and ^{13}C NMR, and also by comparison with authentic samples.

General procedure

Preparation of Fe_3O_4@SiO_2 Core-Shell: The core–shell Fe_3O_4@SiO_2 nanospheres were prepared by a modified Stober method in our previous work.[45] In a typical procedure, the mixture of $FeCl_3.6H_2O$ (1.3 g, 4.8 mmol) in water (15 mL) was added to the solution of polyvinyl alcohol (PVA 15000), as a surfactant, and $FeCl_2.4H_2O$ (0.9 g, 4.5 mmol) in water (15 mL), which was prepared by completely dissolving PVA in water followed by addition of $FeCl_2.4H_2O$. The resultant solution was left to be stirred for 30 min in 80 °C. Then, hexamethylentetraamine (HMTA) (1.0 mol/l) was added drop by drop with vigorous stirring to produce a black solid product when the reaction media reaches pH 10. The resultant mixture was heated on water bath for 2 h at 60 °C and the black magnetite solid product was filtered and washed with ethanol three times and was then dried at 80 °C for 10 h.Then Fe_3O_4 nanoparticle (0.50 g, 2.1 mmol) was dispersed in the mixture of ethanol (50 mL), deionized water (5 mL) and tetraethoxysilane (TEOS) (0.20 mL), followed by the addition of 5.0 mL of NaOH (10 wt%). This solution was stirred mechanically for 30 min at room temperature. Then the product, Fe_3O_4@SiO_2, was separated by an external magnet, and was washed with deionized water and ethanol three times and dried at 80 °C for 10 h.

Preparation of $H_3PW_{12}O_{40}$ nanoparticles (PMA^n): PMA^n nanoparticles were prepared in our previous work.[46] In a typical procedure, 5 mmol of bulk $H_3PMo_{12}O_{40}$ (PMA^b) was dispersed in 50 mL n-Octane and the resulting dispersion was stirred vigorously for 30 min at room temperature to form a homogeneous dispersion. This dispersion was transferred into a Teflon-lined stainless autoclave filling 80% of the total volume. The autoclave was sealed and maintained at 150 °C for 12 h. The autoclave was then cooled to room temperature. Finally, the resulted powder was filtered and washed for several times by Octane, and dried in a vacuum at 80 °C for 12 h.

Preparation of Fe_3O_4@SiO_2-imid-PMA^n: Fe_3O_4@SiO_2 (1 g) was added to the solution of 3-chlorotriethoxypropylsilane (1 mmol, 0.241 g) and imidazole (1 mmol, 0.0680 g) in *p*-xylene (20 mL) and the resultant mixture was under reflux for 24 h under nitrogen atmosphere. After refluxing for about 24 h, the mixture was cooled to room temperature, filtered by an external magnet and the product was washed with xylene to remove no reacted species and dried at 70 °C for 6 h. Fe_3O_4@SiO_2-imid (1.0 g) was added to an acetonitrile solution of PMA^n (1.0 mmol) in 20 mL was taken in a round-bottom flask. The mixture was refluxed for 24 h under nitrogen atmosphere. After 24 h, the mixture was filtered by an external magnet, washed with acetonitrile and dichloromethane, and dried at 70 °C for 6 h. Also, the same method was used for the synthesis of Fe_3O_4@SiO_2-imid-PMA^b (PMA^n = nano $H_3PMo_{12}O_{40}$, PMA^b = $H_3PMo_{12}O_{40}$).[47]

General Procedure for the Synthesis of quinoline derivatives in the presence of magnetic nanocatalysts: A mixture of

2-aminobenzophenone (1 mmol), ethyl acetoacetate (1.2 mmol) and Fe_3O_4@SiO_2-imid-PMA^n (0.02 g) or Fe_3O_4@SiO_2-imid-PMA^b (0.03 g) in solvent-free conditions was stirred at 70 ºC. The progress of the reaction was monitored by TLC. The reaction was followed by TLC. After completion of the reaction, ethyl acetate was added to the solidified mixture and the insoluble catalyst was separated by magnetic field. The filtrate was dried and organic medium was removed with a rotary evaporator under reduced pressure. Then, the resulting solid product was recrystallized from ethanol to give pure product.

RESULTS AND DISCUSSION

In pursuit of our continued interest in the development of solvent-free and environmentally friendly synthetic protocols, we decided to explore the use of Fe_3O_4@SiO_2-imid-PMA^n and Fe_3O_4@SiO_2-imid-PMA^b catalysts for the synthesis of quinoline derivatives via Friedlander condensation in good to excellent yields under solvent-free conditions at 70 ºC.

Initially the reaction between 2-aminobenzophenone (1 mmol) and ethyl acetoacetate (1.2 mmol), as the model reaction was examined in the presence varying amount of the catalysts and the results are presented in Table 1. The best result was achieved by carrying out the reaction with (0.02 or 0.03:1:1.2) ratio of Fe_3O_4@SiO_2-imid-PMA^n or Fe_3O_4@SiO_2-imid-PMA^b catalysts, 2-aminobenzo-phenone and ethyl acetoacetate at 70 ^{o}C (Table 1, entry 12^c, 13^d). Use of a higher amount of catalysts did not improve the yield while a decrease in the amount of catalysts decreases the yield (Table 1). In the absence of Fe_3O_4@SiO_2-imid-PMA^n or Fe_3O_4@SiO_2-imid-PMA^b the reaction did not proceed even after a long reaction time (12 h) (Table 1, entry 15).

The effect of solvent was studied by carrying out the model reaction at different solvents under reflux condition (Table 1, entry 1-7). The reactions were conducted in refluxing toluene, $CHCl_3$, CH_2Cl_2, n-Hexane, H_2O, EtOH and CH_3CN as solvents and under solvent-less condition at 70 ^{o}C. As shown in Table 1, with no solvent, gave the best results in reaction time and conversion. This observation confirms that the solvent-free condition plays an important role in the synthesis of quinoline derivatives and the best rate was observed when the reaction was carried out without solvent (Table 1, entry 12^c, 13^d). Also, the effect of temperature was studied by carrying out the model reaction at different temperatures under solvent-free condition (room temperature, 50 ^{o}C and 70 ^{o}C) and the best results were obtained at 70 ^{o}C (Table 1, entries 10^c-12^c, 11^d-13^d).

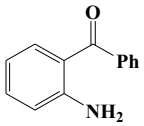
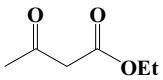
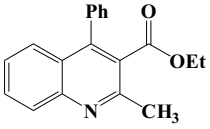
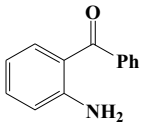
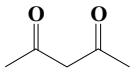
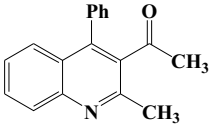
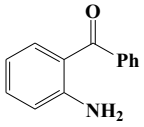
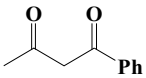
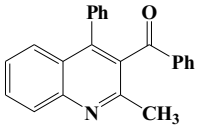
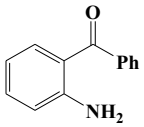
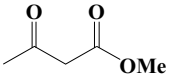
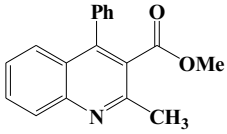
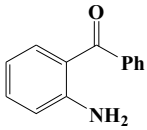
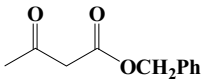
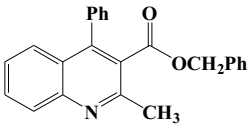
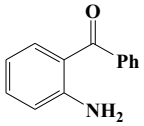
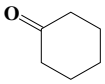
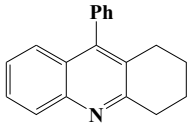
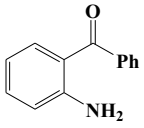
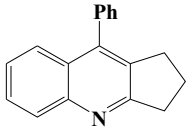
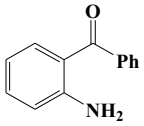
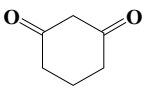
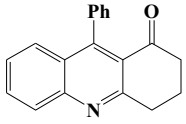
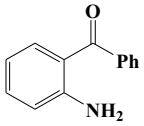
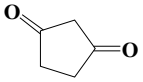
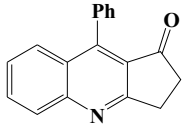
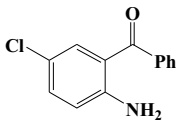
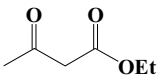
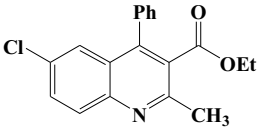
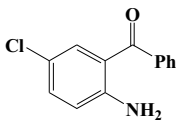
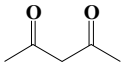
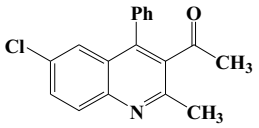
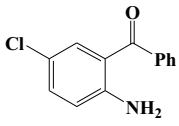
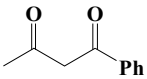
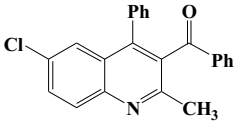
To study the generality of this process, a good range of *o*-aminoaryl ketones and 1,3-diketones were condensed to the corresponding quinoline derivatives in the presence of catalytic amounts of Fe_3O_4@SiO_2-imid-PMA^n or

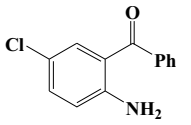
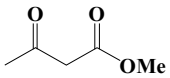
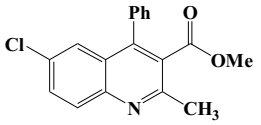
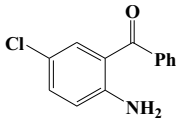
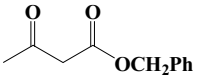
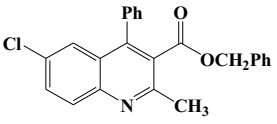
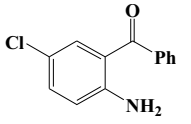
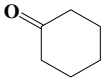
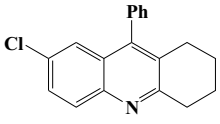
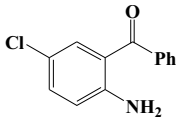
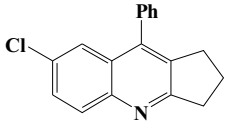
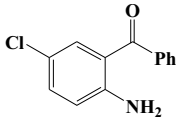
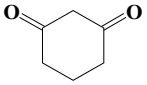
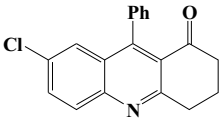
Table 1. Optimization of different proportions of Fe_3O_4@SiO_2-imid-PMA^n and Fe_3O_4@SiO_2-imid PMA^b catalysts and also effect of solvents in the synthesis of ethyl 2-methyl-4-phenyl quinoline-3-carboxylate[a]

Entry	Solvent	Catalyst[c] (gr)	Condition	Time[c]	Yield (%)[b,c]	Catalyst[d] (gr)	Condition	Time[d]	Yield (%)[b,d]
1	CH_3CN	0.02	reflux	1.5 h	58	0.03	reflux	1.5 h	42
2	Ethanol	0.02	reflux	1.5 h	64	0.03	reflux	1.5 h	43
3	H_2O	0.02	reflux	1.5 h	24	0.03	reflux	1.5 h	17
4	n-Hexane	0.02	reflux	1.5 h	78	0.03	reflux	1.5 h	64
5	CH_2Cl_2	0.02	reflux	1.5 h	54	0.03	reflux	1.5 h	49
6	$CHCl_3$	0.02	reflux	1.5 h	56	0.03	reflux	1.5 h	46
7	Toluene	0.02	reflux	1.5 h	73	0.03	reflux	1.5 h	76
8	Solvent-free	0.005	70 ^{o}C	1.5 h	45	0.005	70 ^{o}C	1.5 h	51
9	Solvent-free	0.01	70 ^{o}C	1.5 h	59	0.01	70 ^{o}C	1.5 h	67
10	Solvent-free	0.02	r.t	1.5 h	Trace	0.02	70 ^{o}C	1 h	85
11	Solvent-free	0.02	50 ^{o}C	1 h	67	0.03	r.t	1.5 h	Trace
12	Solvent-free	0.02	70 ^{o}C	50 min	95	0.03	50 ^{o}C	1 h	69
13	Solvent-free	0.03	70 ^{o}C	50 min	94	0.03	70 ^{o}C	55 min	91
14	Solvent-free	0.04	70 ^{o}C	50 min	91	0.04	70 ^{o}C	55 min	91
15	Solvent-free	None	70 ^{o}C	12 h	Trace	None	70 ^{o}C	12 h	Trace

[a] Reaction condition: 2-aminobenzophenone (1 mmol), ethylacetoacetate (1.2 mmol).
[b] Isolated yield.
[c] Fe_3O_4@SiO_2-imid-PMA^n.
[d] Fe_3O_4@SiO_2-imid-PMA^b.

Table 2. Fe_3O_4@SiO_2-imid-PMA^n and Fe_3O_4@SiO_2-imid-PMA^b catalyzed synthesis of quinolines under solvent-free conditions at 70 $^oC^a$

Entry	2-Amino ketone	Ketone	Product	Time (min)	Yield (%)[b,c]	Time (min)	Yield (%)[b,d]	m.p. (^oC)
1				50	95	55	91	98-99 (99^oC)[21]
2				55	96	60	91	113-114 (114-115)[48]
3				45	95	55	88	133-135
4				60	94	60	88	107-108 (107)[21]
5				50	90	60	86	90-92
6				40	94	50	90	141-143 (139-141)[48]
7				45	92	60	89	131-133 (130-132)[23]
8				35	95	45	91	157-159 (159)[21]
9				35	91	40	90	172-174
10				35	94	45	92	101-103 (101)[22]
11				30	96	50	89	155-157 (157)[21)]
12				45	96	55	90	216-218 (217)[21]

13				50	95	55	88	134-136 (135)[21]
14				40	92	50	86	121-123
15				60	96	80	91	163-165 (165)[21]
16				70	93	100	87	106-108 (106-107)[15]
17				50	95	100	89	184-185 (185)[21]

[a] Reaction condition 2-aminoarylketones (1 mmol), 1,3-diketones or ketones (1.2 mmol), Fe_3O_4@SiO_2-imid-PMA^n (0.02 g) or Fe_3O_4@SiO_2-imid-PMA^b (0.03 g), solvent-free, 70 °C.
[b] Isolated yield.
[c] Fe_3O_4@SiO_2-imid-PMA^n.
[d] Fe_3O_4@SiO_2-imid-PMA^b.

Fe_3O_4@SiO_2-imid-PMA^b and the related quinoline derivatives were obtained without observation of any by-product in good to excellent yields (Table 2). Also, cyclic ketones such as cyclopentanone and cyclohexanone underwent smooth condensation with 2-aminoarylketones to afford the respective tricyclicquinolines (Table 2, entry 6, 7, 15, 16). In addition, this method is approximately equal effective for both cyclic and acyclic ketones. Further, it is to be noted that highly pure products were obtained using this simple procedure and in most cases no further purification was needed.

A comparison among Fe_3O_4@SiO_2-imid-PMA^n and Fe_3O_4@SiO_2-imid-PMA^b and the other catalysts, which were reported in the literature, in the synthesis of ethyl 2-methyl-4-phenylquinoline-3-carboxylate revealed advantages of Fe_3O_4@SiO_2-imid-PMA^n and Fe_3O_4@SiO_2-imid-PMA^b over the most of them in term of higher yield and shorter reaction time (Table 3, entry 1,2).

According to these findings, it can be seen that Fe_3O_4@SiO_2-imid-PMA^n and Fe_3O_4@SiO_2-imid-PMA^b are a very efficient catalysts useful in the synthesis of quinoline derivatives (Table 3).

Fe_3O_4@SiO_2-imid-PMA^n magnetic catalyst dispersed in ethyl acetate can be easily separated by external magnetic field within several minutes without the need for a filtration step, and then can be readily redispersed with slightly shake, indicating directly that the nanoparticles possess magnetic properties (Fig. 1). Such magnetic separation performance makes the nanoparticles more effective and convenient in application.

Table 3. Comparison results of different catalysts to the Fe_3O_4@SiO_2-imid-PMA^n and Fe_3O_4@SiO_2-imid-PMA^b in the synthesis of ethyl 2-methyl-4-phenylquinoline-3-carboxylate[a]

Entry	Catalyst	Time	Yield (%)	Literature reference
1	Fe_3O_4@SiO_2-imid-PMA^n	50 min	95	This work
2	Fe_3O_4@SiO_2-imid-PMA^b	55 min	91	This work
3	$H_3PMo_{12}O_{40}$	2 h	91	This work
4	$H_3PW_{12}O_{40}$	2 h	90	[49]
5	P-TSOH	12 h	50	[49]
6	SSA	5 h	60	[49]
7	$HClO_4$	12 h	40	[49]
8	$NaHSO_4$-SiO_2	240	80	[51]
9	Dodecylphosphonic acid	140 min	85	[52]
10	$Zr(DS)_4$	3 h	72	[21]
11	$CeCl_3$ -$7H_2O$	90	95	[53]
12	[bmim][HSO_4]	60 min	94	[50]

[a] Based on 2-aminobenzophenone and ethyl acetoacetate.

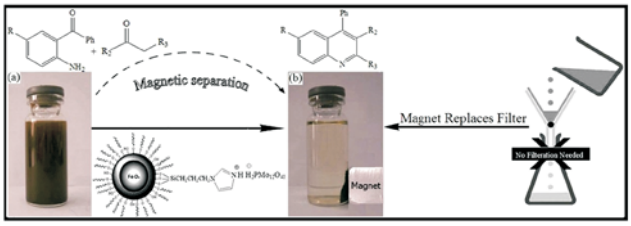
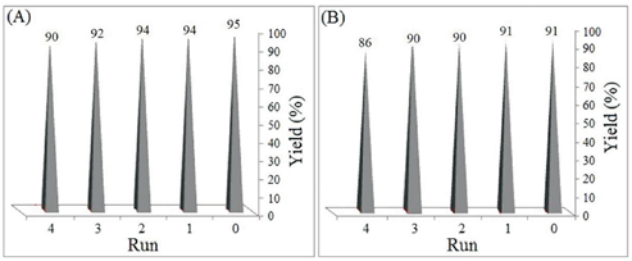


Fig. 1. Catalyst ability to effective recovery at the end of reactions by external magnetic field.



[a]Reaction conditions: (A) 2-aminobenzophenone (1mmol), ethyl acetoacetate (1.2mmol), Fe_3O_4@SiO_2-imid-PMA^n [a] (0.02g), solvent-free, 70°C. (B) 2-aminobenzophenone (1mmol), ethyl acetoacetate (1.2mmol), Fe_3O_4@SiO_2-imid-PMA^b (0.03g), solvent-free, 70°C.

Fig. 2. Recyclability of Fe_3O_4@SiO_2-imid-PMA^n (A) and Fe_3O_4@SiO_2-imid-PMA^b (B) in the synthesis of ethyl 2-methyl-4-phenyl quinoline-3-carboxylate under solvent-free condition.

The activity of the recycle catalysts were also examined under the optimized conditions and the desired products were obtained in high yields after 4 runs without distinct deterioration in catalytic activity (Fig. 2).

CONCLUSIONS

In conclusion, we have demonstrated a simple, efficient and straightforward synthesis of quinolines derivatives by Friedlander protocol using immobilization of phosphomolybdic acid nanoparticles on imidazole functionalized Fe_3O_4@SiO_2 as recyclable heterogeneous nanocatalyst. The protocol offers several advantages including easy preparation, heterogeneous nature and easy separation of the catalyst by external magnetic field, high yields of the products, short reaction times and operational simplicity. Also the nanocatalyst could be successfully recovered and recycled at least for four runs without significant loss in activity.

Spectral data

Table 2. entry 3. Yellow solid, m.p. 133-135 °C. ^{1}H-NMR (250 MHZ, $CDCl_3$): δ = 2.55 (3H, s, CH_3), 7.18 (m, 7H, CH), 7.36 (m, 2H, CH), 7.55 (m, 2H, CH), 7.68 (m, 1H, CH), 8.10 (d, 1H, CH). ^{13}C-NMR (63 MHz, $CDCl_3$): δ = 24.0, 125.1, 126.0, 126.30, 127.8, 128.0, 128.2, 128.7, 129.0, 129.8, 129.9, 132.2, 133.3, 134.6, 136.9, 145.3, 147.6, 154.4, 197.5. FT-IR (KBr pellets, cm^{-1}): 704, 769, 1575, 1675, 2911, 3060. $C_{23}H_{17}NO$: C, 85.4; H, 5.26; N, 4.33%, found: C, 85.12; H, 5.23; N, 4.21%. **Table 2. Entry 5.** White solid, m.p. 90-92 °C. ^{1}H-NMR (250 MHZ, $CDCl_3$): δ = 2.76 (s, 3 H, CH_3), 5.03 (s, 2H, CH_2), 7.08 (m, 2H, CH), 7.36 (m, 3H, CH), 7.41 (m, 2H, CH), 7.42 (m, 4H, CH), 7.44 (d, 1H), 7.71 (m, 1H, CH), 8.09 (d, 1H). ^{13}C-NMR (63 MHz, $CDCl_3$): δ = 23.8, 67.3, 124.8, 126.2, 126.2, 126.8, 128.1, 128.1, 128.2, 128.3, 128.39, 128.67, 129.1, 130.07, 134.6, 135.3, 146.0, 147.5, 154.3, 168.1. FT-IR (KBr pellets, cm^{-1}): 762, 889, 1490, 1565, 1720, 2915, 3070. Anal. calcd. for $C_{24}H_{19}NO_2$: C, 81.58; H, 5.38; N, 3.96%, found, C, 81.44; H, 5.28; N, 3.81%. **Table 2. Entry 9.** Yellow solid, m.p. 172-174 °C. ^{1}H-NMR (250 MHZ, $CDCl_3$): δ = 2.74 (m, 2H, CH_2), 3.36 (m, 2H, CH_2), 7.27 (m, 2H, CH), 7.44 (m, 4H, CH, CH), 7.73 (m, 2H, CH), 8.04 (d, 1H, CH). ^{13}C-NMR (63 MHz, $CDCl_3$): δ = 28.4, 36.5, 123.6, 126.3, 126.4, 127.8, 128.2, 128.6, 128.8, 129.1, 130.6, 131.9, 132.9, 148.7, 151.0, 170.7, 203.3. FT-IR (KBr pellets, cm^{-1}): 772, 835, 1565, 1710, 2931. Anal. calcd. for $C_{18}H_{13}NO$: C, 83.39; H, 5.02; N, 5.40%, found: C, 83.23; H, 5.12; N, 5.21%. **Table 2. Entry 14.** White solid, m.p. 121-123 °C. ^{1}H-NMR (250 MHZ, $CDCl_3$): δ = 2.66 (s, 3H, CH_3), 4.95 (s, 2H, CH_2), 7.00 (m, 2H), 7.20-7.26 (m, 5H, CH), 7.37 (m, 3H, CH), 7.46 (m, 1H, CH), 7.58 (m, 1H, CH), 7.94 (d, 1H, CH). ^{13}C-NMR (63 MHz, $CDCl_3$): δ = 23.7, 67.4, 125.0, 125.7, 126.9, 127.0, 127.6, 128.2, 128.3, 128.3, 128.4, 128.6, 129.0, 130.3, 130.9, 132.1, 134.4, 134.5, 145.9, 154.7, 167.7. FT-IR (KBr pellets, cm^{-1}): 710, 740, 834, 1225, 1481, 1580, 1720, 3042, 3080. Anal. calcd. for $C_{24}H_{18}ClNO_2$: C, 74.32; H, 4.64; N, 3.61. found, C, 74.67; H, 4.85; N, 3.53.

ACKNOWLEDGEMENTS

Authors are grateful to the council of Iran National Science Foundation and University of Shiraz for their unending effort to provide financial support to undertake this work.

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