

**[Fe₃O₄@SiO₂@(C₃H₆)₂-(IMIDAZOLIUM)₂-BUTYL][MnCl₄²⁻] AS A NOVEL
NANOMAGNETIC CATALYST FOR THE ONE-POT SYNTHESIS OF
TETRAHYDROBENZO[b]PYRAN DERIVATIVES**

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ABSTRACT. In this article a convenient method for the synthesis of tetrahydrobenzo[b]pyran derivatives using imidazolium-based ionic liquid-stabilized on magnetic nanoparticles [Fe₃O₄@SiO₂@(C₃H₆)₂-(Imidazolium)₂-Butyl][MnCl₄²⁻] as a new heterogeneous catalyst has been described. These compounds were synthesized *via* one-pot three component condensation reaction between several aromatic aldehydes, malononitrile, and dimedone in water under reflux condition. The magnetic nanoparticle catalyst was fully characterized by Fourier transform infrared, scanning electron microscopy, energy dispersive X-ray spectroscopy, and vibrating sample magnetometer. Furthermore, the solid catalyst could be recovered and reused conveniently several times with satisfactory yields.

KEY WORDS: Chromene derivatives, Magnetic nanoparticles, Dicationic ionic liquid, Reusability, One-pot synthesis

INTRODUCTION

Tetrahydrobenzo[b]pyrans known as 4*H*-chromenes are present in many pharmaceuticals and exhibit remarkable biological activities such as anticoagulant, anti-tumor, antibacterial, anticoagulant and antiallergic [1, 2]. Also, 4*H*-chromenes have been widely used as cosmetics, pigments, and importantly biodegradable agrochemicals [3]. Thus, the attractive biological profiles of this group of compounds stimulate chemists to explore efficient methods for the synthesis of 4*H*-chromenes and their structural analogues [4-10].

In recent years, ionic liquids (ILs) have attracted a considerable attention in catalytic systems because they can dissolve a wide variety of organic, organometallic, and inorganic compounds [11, 12]. Also, they have low vapor pressure, low melting point and are relatively thermal stable [13]. Although ILs possess some advantages but the properties of high viscosity, some difficulties in recovery and homogeneity of ILs limit their practical applications in chemical processes [14]. These problems can be overcome by immobilization of ILs onto solid supports and functional groups to obtain heterogeneous catalysts [15, 16]. One of the most attractive alternatives to stabilize ILs is the magnetic nanoparticles support [17, 18].

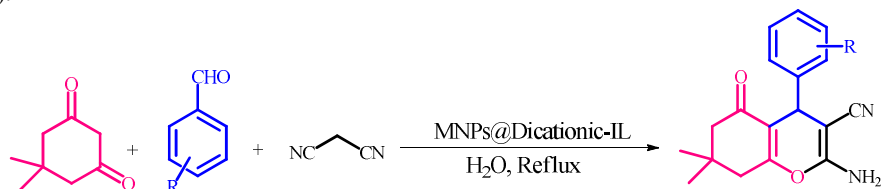
Magnetite nanoparticles (MNPs) are inorganic materials with metal-based configuration. These nanoparticles have received increasing consideration because they can be easily manipulated using alternating current magnetic field and subsequently employed in various fields including environmental science, analytical, medicine and importantly, catalysis [19-22]. MNPs exhibit inherent and unique properties, such as high surface area, less toxicity, high saturation magnetization, and catalyst loading capacity [23-25].

In view of the advantages of magnetic nanoparticles and ILs, some magnetic ILs composites have been developed [26, 27]. Following our ongoing efforts for the development of more benign and efficient nanocatalysts [28-31], herein, we present the design and preparation and use of [Fe₃O₄@SiO₂@(C₃H₆)₂-(Imidazolium)₂-Butyl][MnCl₄²⁻] or MNPs@Dicationic-IL as a

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nanosized ionic liquid catalyst for the synthesis of tetrahydrobenzo[b]pyran derivatives (Scheme 1).



Scheme 1

EXPERIMENTAL

Materials and apparatus

Chemical reagents in high purity were purchased from Merck and Aldrich and were used without further purification. Fe_3O_4 and $\text{Fe}_3\text{O}_4@\text{SiO}_2$ were prepared according to reported methods [29-30]. Purity of the synthesized compounds was monitored by TLC, visualizing with ultraviolet light and all yields refer to isolated products. Melting points were determined using a Stuart scientific apparatus. SEM images were obtained from a Zeiss-Vp-500 instrument. IR spectra of synthesized compounds were recorded on KBr pellets on a Bomem MB-1998 spectrophotometer. Magnetism analysis was performed on a vibrating sample magnetometer (4 in., Daghigh Meghnatis Kashan Company, Kashan, Iran) at room temperature. SEM-EDX analyses were carried out using a Philips XL30 instrument.

Preparation of $[\text{Fe}_3\text{O}_4@\text{SiO}_2@(\text{C}_3\text{H}_6)_2\text{-(Imidazolium)}_2\text{-Butyl}][\text{MnCl}_4^{2-}]$ as a heterogeneous catalyst

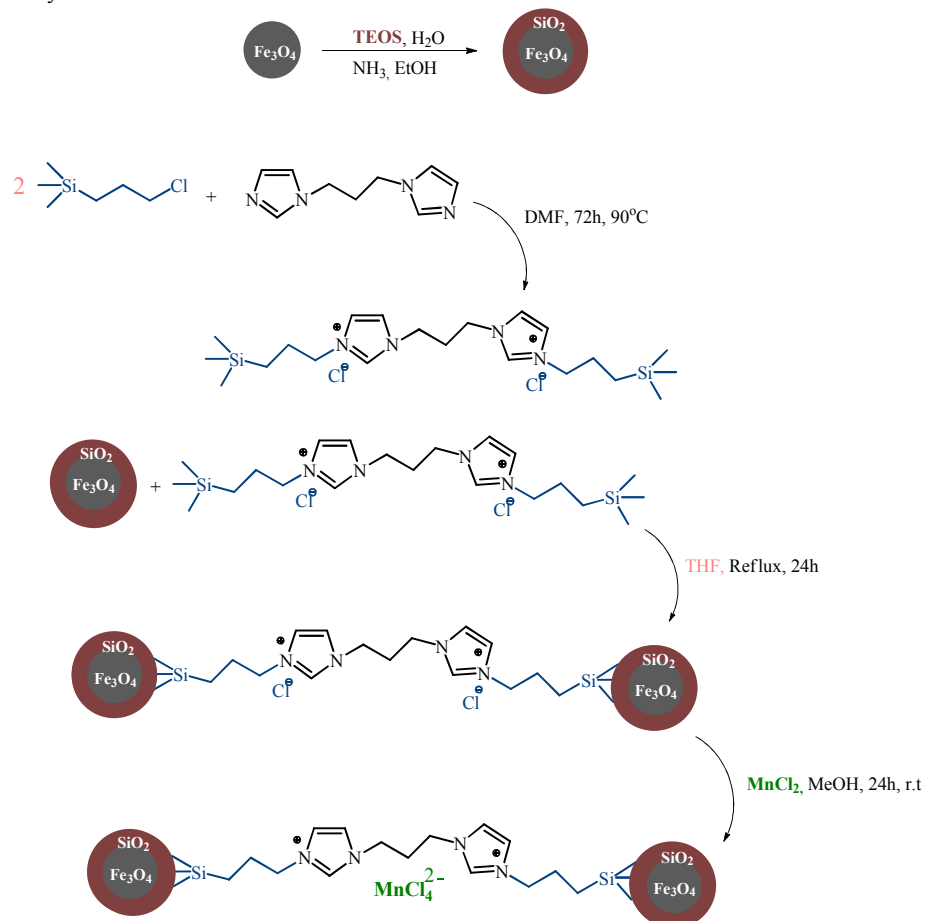
At first, dicationic-IL $[(\text{C}_3\text{H}_6)_2\text{-(Imidazolium)}_2\text{-Butyl}][\text{Cl}]_2$ was produced by adding 1,4-bis(imidazol-1-yl)-butane (0.237 g, 1.25 mmol), 3-chloropropyl-trimethoxysilane (0.497 g, 2.5 mmol) and DMF (5 mL) into a 50 mL round-bottom flask. The mixture was refluxed for 72 h. The obtained white solid material was filtered, washed with methanol and dried under reduced pressure. Next, $\text{SiO}_2@\text{Fe}_3\text{O}_4$ (0.5 g) was dispersed in 10 mL of dry toluene and, sonicated for 15 min using an ultrasonic bath. Then, dicationic-IL (1.0 g) was added to the mixture. The mixture was stirred and refluxed for 24 h. The treated $[\text{Fe}_3\text{O}_4@\text{SiO}_2@(\text{C}_3\text{H}_6)_2\text{-(Imidazolium)}_2\text{-Butyl}][\text{Cl}]_2$ was removed by using an external magnet and washed twice with ethanol, and dried. Finally, a solution of MnCl_2 (0.25 g) in methanol (5 mL) was added to the suspension of $\text{Fe}_3\text{O}_4@\text{SiO}_2@(\text{C}_3\text{H}_6)_2\text{-(Imidazolium)}_2\text{-Butyl}][\text{Cl}]_2$ (0.5 g) and the reaction mixture was stirred for 24 h. The imidazolium-based ionic liquid-stabilized on silica coated Fe_3O_4 magnetic nanoparticles $[\text{Fe}_3\text{O}_4@\text{SiO}_2@(\text{C}_3\text{H}_6)_2\text{-(Imidazolium)}_2\text{-Butyl}][\text{MnCl}_4^{2-}]$ was obtained after filtering, washing and drying.

General procedure for the synthesis of 4H-chromene derivatives

In a round bottom flask, to a mixture of aromatic aldehyde (1 mmol), dimedone (1 mmol), malononitrile (1.2 mmol), and H_2O (5 mL), $[\text{Fe}_3\text{O}_4@\text{SiO}_2@(\text{C}_3\text{H}_6)_2\text{-(Imidazolium)}_2\text{-Butyl}][\text{MnCl}_4^{2-}]$ (0.05 g) was added. Then, the reaction mixture was refluxed at 80 °C for the corresponding time, as indexed in Table 2. After completion of the reaction as monitored by TLC (*n*-hexane/ethyl acetate, 4:1), the reaction mixture was diluted with ethyl acetate and stirred for 5 min. Then, the catalyst was separated by using an external magnet and the

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remaining supernatant was diluted with water and stirred for 5 min. The precipitated product was filtered, washed with water, and dried in an oven. The residue was purified by recrystallization in ethanol.



Scheme 2. Synthesis of imidazolium-based ionic liquid-stabilized on silica coated Fe₃O₄ magnetic nano particles.

RESULTS AND DISCUSSION

Synthesis and characterization of [Fe₃O₄@SiO₂@(C₃H₆)₂-(Imidazolium)₂-Butyl][MnCl₄²⁻] as a heterogeneous catalyst

We report the synthesis of imidazolium-based ionic liquid-stabilized on silica coated Fe₃O₄ magnetic nano particles and discuss its performance as a novel strong and recyclable catalyst (Scheme 2). The structure of catalyst was studied and characterized by FT-IR, EDX, SEM and VSM analysis.

The FT-IR spectrum of the bare Fe_3O_4 MNPs (Figure 1) presents a characteristic absorption peak of Fe–O bond at about 623 cm^{-1} . The absorption peaks of the silica shell in MNPs around 1104 and 801 cm^{-1} are attributed to the asymmetric and symmetric stretching vibrations of Si–O–Si, respectively. The absorption peak at 2923 cm^{-1} is related to the stretching vibration of C–H groups. Also, the absorption peaks at 3200 and 1618 cm^{-1} are associated with the stretching vibrations of aromatic C–H groups and C=N bond on imidazolium ring. Moreover, the absorption band at 3412 cm^{-1} is attributed to the stretching vibration of O–H in the Si–OH group.

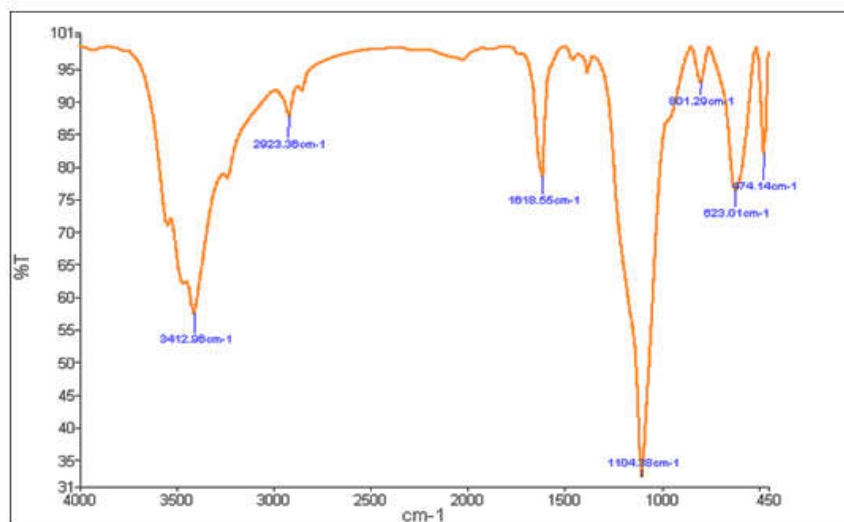


Figure 1. FT-IR spectrum of the bare Fe_3O_4 MNPs.

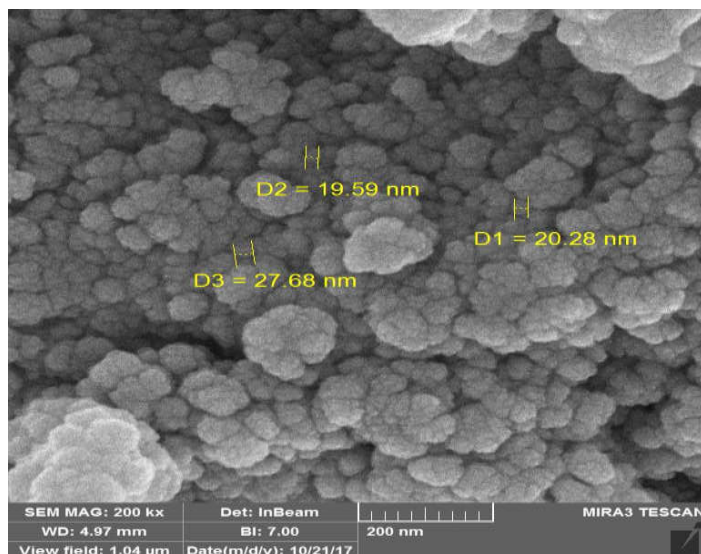


Figure 2. SEM image of the MNP catalyst.

To determine the morphology and the size of the MNP catalyst, SEM was used. The image of the MNP catalyst shows that these particles have nearly spherical shape with sizes of between about 19-28 nm.

The magnetic properties of Fe₃O₄ and MNPs@Dicationic-IL were evaluated by vibrating sample magnetometry (VSM) at room temperature. The magnetic saturation values were 60 emu/g and 32 emu/g for Fe₃O₄ and [Fe₃O₄@SiO₂@(C₃H₆)₂-(Imidazolium)₂-Butyl][MnCl₄²⁻], respectively. Compared with the uncoated Fe₃O₄ particles, the saturation magnetization of the [Fe₃O₄@SiO₂@(C₃H₆)₂-(Imidazolium)₂-Butyl][MnCl₄²⁻] obviously decreased because the contribution of the thick SiO₂ and organic matter resulted in a low mass fraction of the Fe₃O₄ magnetic substance. The results show that even with the lower magnetic saturation, catalyst can still be effectively separated from the solution by an external magnet.

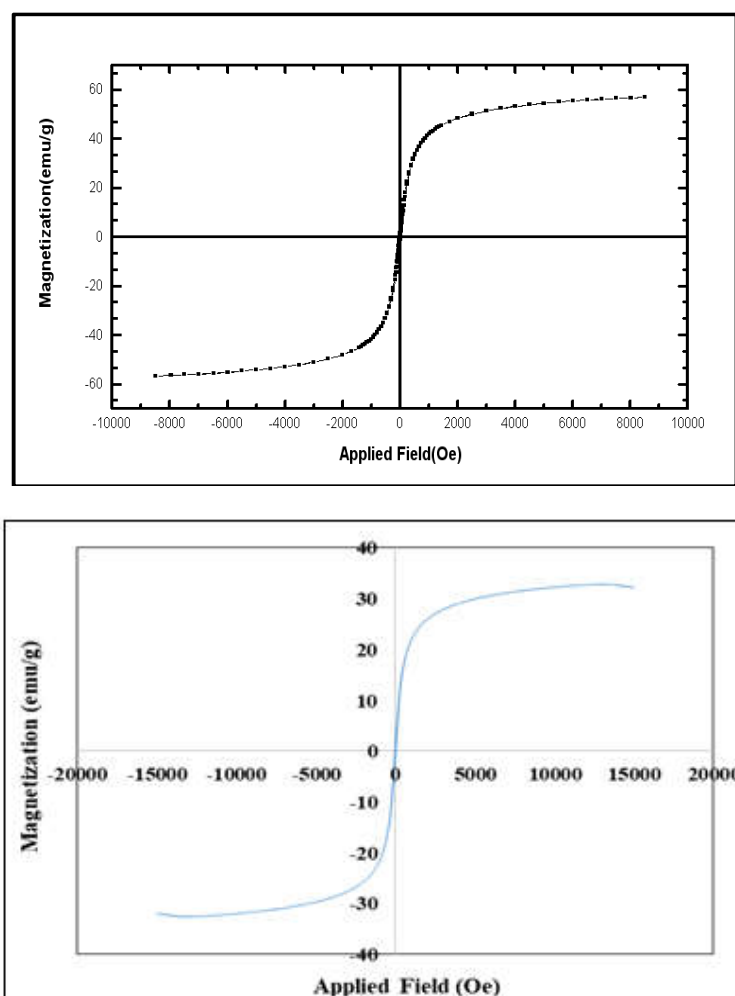


Figure 3. Results of vibrating sample magnetometry of Fe₃O₄ and [Fe₃O₄@SiO₂@(C₃H₆)₂-(Imidazolium)₂-Butyl][MnCl₄²⁻], respectively.

The elemental composition of $[\text{Fe}_3\text{O}_4@\text{SiO}_2@(\text{C}_3\text{H}_6)_2\text{-(Imidazolium)}_2\text{-Butyl}][\text{MnCl}_4^{2-}]$ was analyzed by energy dispersive X-ray (EDX) spectroscopy and the result (Figure 4) clearly indicates the expected elemental composition (N, O, Si, Cl, Mn, Fe).

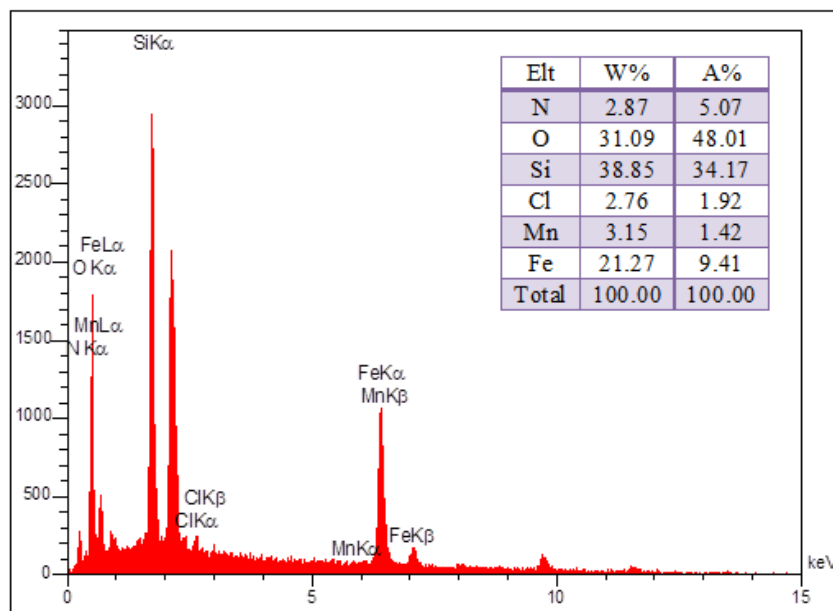


Figure 4. Energy dispersive X-ray spectrum of $[\text{Fe}_3\text{O}_4@\text{SiO}_2@(\text{C}_3\text{H}_6)_2\text{-(Imidazolium)}_2\text{-Butyl}][\text{MnCl}_4^{2-}]$

Application of MNPs@Dicationic-IL as heterogeneous catalyst for the synthesis of chromene derivatives in water

In order to optimize the reaction conditions, the reaction between benzaldehyde, malononitrile, and dimedone was chosen as a simple model reaction and different reaction parameters such as solvent, catalyst amount and reaction temperature were investigated (Table 1). As can be seen from the results, 50 mg of MNPs catalyst was found to be the optimum amount of the catalyst (Table 1, entries 1-5). Increasing the amount of MNPs catalyst did not change significantly the yield and the reaction time (Table 1, entries 4 and 5). To examine the effect of the solvent on the catalytic reaction, the model reaction in the presence of 50 mg of nano magnetic catalyst was performed in various solvents and under solvent-free condition (Table 1, entries 6-9). According to the experimental results, the best results in terms of the reaction rates and yields were achieved in MeOH and H_2O for 10 min and 15 min respectively (Table 1, entries 3 and 8). However, with regard to environmental considerations, H_2O was chosen as the solvent for the reaction. Additionally, at room temperature, only 55% yield was obtained after 120 min (Table 1, entry 10). The slight increase in malononitrile was favorable, and therefore, the molar ratio of benzaldehyde and dimedone to malononitrile was obtained at 1:1:1.2. To compare the effect of the supported catalyst in comparison with non-supported catalyst, the model reaction was studied in the presence of 50 mg pure dicationic-IL $[(\text{C}_3\text{H}_6)_2\text{-(Imidazolium)}_2\text{-Butyl}][\text{Cl}]_2$ under reflux condition. The result showed that the reaction did not give the desired product (Table 1, entry 11). It is worth mentioning that in the absence of catalyst, the product was produced in trace amount after 120 min (Table 1, entry 12).

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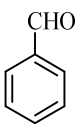
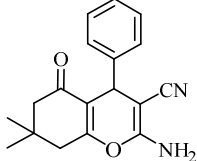
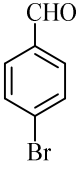
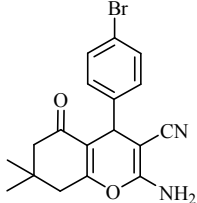
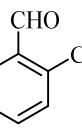
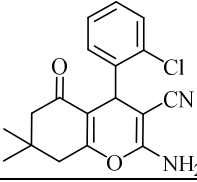
Table 1. Optimization of reaction conditions.

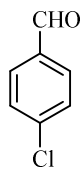
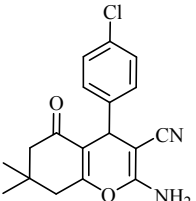
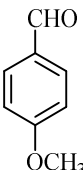
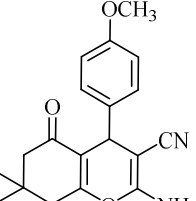
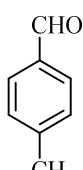
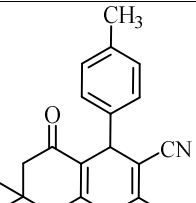
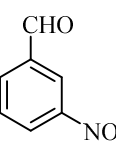
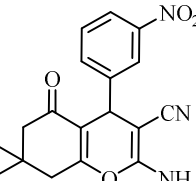
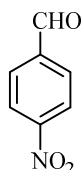
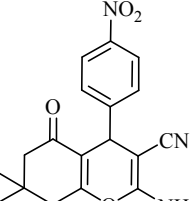
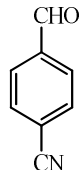
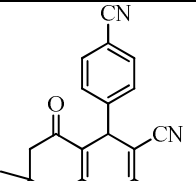
No	Catalyst	Catalyst amount (mg)	Solvent	Condition	Time (min)	Yield ^a (%)
1	MNPs@Dicationic-IL	30	H ₂ O	reflux	60	45
2	MNPs@Dicationic-IL	40	H ₂ O	reflux	60	70
3	MNPs@Dicationic-IL	50	H ₂ O	reflux	15	90
4	MNPs@Dicationic-IL	60	H ₂ O	reflux	15	90
5	MNPs@Dicationic-IL	70	H ₂ O	reflux	15	92
6	MNPs@Dicationic-IL	50	CHCl ₃	reflux	15	75
7	MNPs@Dicationic-IL	50	CH ₃ CN	reflux	15	85
8	MNPs@Dicationic-IL	50	MeOH	reflux	10	92
9	MNPs@Dicationic-IL	50	-	reflux	15	65
10	MNPs@Dicationic-IL	50	H ₂ O	r.t.	120	55
11	Dicationic-IL	50	H ₂ O	reflux	15	75
12	None	-	H ₂ O	reflux	120	Trace

^aIsolated yields.

After optimizing the reaction conditions, the scope and generality for the developed protocol were explored by using different substituted aryl aldehydes. The reaction of malononitrile and dimedone with a variety of arylaldehydes bearing electron withdrawing as well as electron donating groups provided the corresponding 4*H*-chromenes in 85–92% yield in short reaction times (Table 2, entries 1-11). It should be mentioned that the present method is compatible with a wide range of functional groups such as methoxy, methyl, halogens and nitro at the *ortho*, *meta* or *para* position of arene moiety, and functional group nature does not significantly effect on the yield of the reaction.

Table 2. Formation of 4*H*-chromene derivatives catalyzed by MNPs@Dicationic-IL.

No.	Substrate	Product	Time (min)	Yield ^a (%)	M.P. (°C) [Ref.]
1			15	90	235-237 [32]
2			10	92	265-267 [33]
3			10	87	211-213 [34]

4			15	90	209-210 [35]
5			35	91	199-202 [36]
6			20	90	213-215 [36]
7			20	85	208-210 [8]
8			30	90	178-180 [8]
9			10	88	227-229 [37]

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10			20	85	223-225 [8]
11			20	88	221-223 [8]

^aIsolated yields.

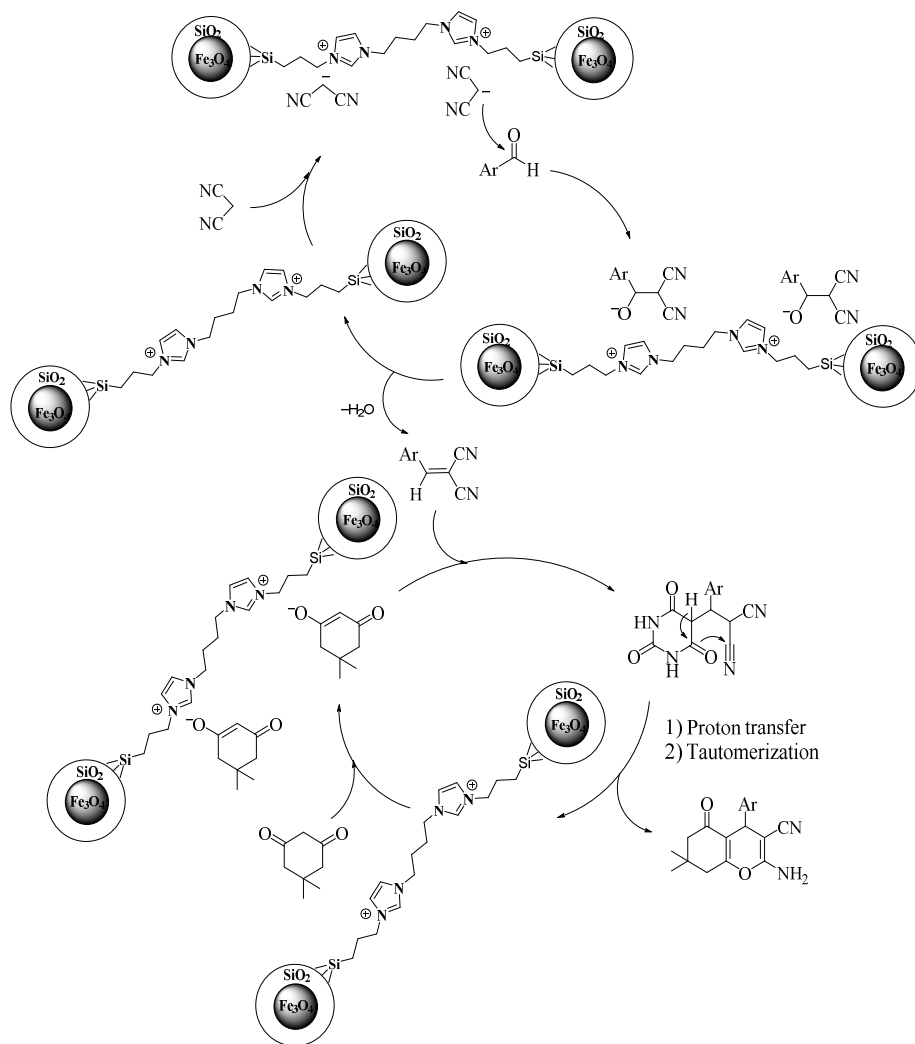
We proposed the plausible reaction mechanism on the basis of the literature reports [38] and the above mentioned results. Firstly, the MNP catalyst activates the carbonyl group of the aromatic aldehyde and tautomerizes malononitrile. The Knoevenagel condensation of aromatic aldehyde and malononitrile forms the arylidene malononitrile. Subsequently, dimedone is tautomerized and reacts with arylidene malononitrile to give Michael adduct. Finally, intramolecular cyclization and tautomerization of Michael adduct provided the corresponding 4*H*-chromene (Scheme 3).

To compare the reactivity of the [Fe₃O₄@SiO₂-(C₃H₆)₂-(Imidazolium)₂-Butyl][MnCl₄²⁻] with previously reported catalysts a comparative chart is presented in Table 3. The reaction times and product yields showed that our novel catalyst is equal or more effective than those reported for other catalytic systems.

Table 3. Comparison of the efficiency of MNPs@Dicationic-IL with some of catalyst reported in the literature.

No	Catalyst	Solvent	Condition	Time (min)	Yield (%)	Ref.
1	Sodium selenate	EtOH/H ₂ O	Reflux	180	90	39
2	SO ₄ ²⁻ /MCM-41	EtOH	Reflux	60	80	40
3	TBAF	H ₂ O	Reflux	30	97	41
4	Phenylboronic acid	EtOH/H ₂ O	Reflux	30	84	42
5	Fe ₃ O ₄ @SiO ₂ @NH-NH ₂ PW	H ₂ O	Reflux	25	92	43
6	LiBr	H ₂ O	Reflux	15	95	44
7	Nano titania sulfuric acid	EtOH	Ultrasonic/40 °C	15	94	45
8	NH ₄ H ₂ PO ₄ /Al ₂ O ₃	Solvent free	80 °C	30	88	46
9	TBAB	H ₂ O	Reflux	30	95	47

We have examined the recyclability of [Fe₃O₄@SiO₂-(C₃H₆)₂-(Imidazolium)₂-Butyl][MnCl₄²⁻] catalyst for the model reaction, because it is crucial to approve that the highly active catalyst is recyclable. The study indicated that the catalyst can be reused up to the 5th cycle (Table 4) under optimized reaction conditions without important loss of its catalytic activity. At the end of each repeated reaction, the catalyst was separated by using a magnet and then washed with deionized water followed by ethyl acetate, dried at 100 °C and reused for the next cycle.



Scheme 3

Table 4. Reusability of MNPs@Dicationic-IL in the synthesis of 4H-chromenes.

Run	1	2	3	4	5
Time (min)	15	15	18	20	22
Yield (%)	90	88	88	85	82

CONCLUSION

In the present work, a novel imidazolium based dicationic ionic liquid was produced and successfully grafted on magnetite nanoparticles and its efficiency as heterogeneous and reusable catalyst for synthesis of 4H-chromenes in water was also investigated. The MNPs@Dicationic-

IL promotes both the reaction rate and simplify the work-up procedure. In addition, the catalyst was reused for five times with no considerable decrease in its catalytic activity. Simple operation, eco-friendly benign, high yields of products and short reaction times are other advantages of this new catalytic system.

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