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# POLYSTYRENE-SUPPORTED 1-METHYLIMIDAZOLIUM TETRACHLORO FERRATE: SYNTHESIS, CHARACTERIZATION, AND APPLICATION AS AN EFFICIENT AND REUSABLE HETEROGENEOUS CATALYST FOR ONE-POT SYNTHESIS OF 4*H*-CHROMENE DERIVATIVES IN AQUEOUS MEDIA

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**ABSTRACT**. Polystyrene-supported 1-methylimidazolium tetrachloroferrate (PS[mim][$FeCl_4$]) was prepared and characterized by Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX). The catalytic activity of the heterogeneous catalyst was evaluated through one-pot synthesis of 2-amino-4*H*-chromene-3-carbonitriles *via* the three-component condensation reaction of aromatic aldehydes, malononitrile and dimedone or 2-naphthol in water. The heterogeneous catalyst could be recovered easily and reused five times without significant loss of its catalytic activity.

**KEY WORDS**: Green chemistry, Heterogeneous catalyst, 4*H*-chromene derivatives, Multi-component reactions, One-pot synthesis

## INTRODUCTION

The use of water as solvent for organic reactions is one of the best solutions to the problem of flammability, volatility, toxicity and disposal of organic solvents [1]. Since most organic reactants do not dissolve in water, the use of phase-transfer catalysts can overcome this problem. Both homogeneous and heterogeneous phase-transfer catalysts improve the intimate contact between inorganic reagents and organic substrates, but one of the major problems associated with the use of homogeneous catalysts is the recovery of the catalyst from the reaction medium. Immobilization of the phase-transfer catalysts on an insoluble matrix can provide a simple solution to this problem [2–5].

In this regard, polymer-supported reagents have become state-of-the-art tools, since the pioneering work by Merrifield in the field of solid-phase chemistry. They offer advantages such as reaction monitoring as well as increased safety, especially when the non-supported reagents are toxic or hazardous as they can be easily removed from reaction media and recycled [6].

Among various 4H-chromenes derivatives, especially, 2-amino-4*H*-chromenes have a potential applications in the treatment of rheumatoid, psoriasis, and cancer [7]. These compounds have received considerable attention due to their various biological and pharmacological activities such as antimicrobial [8], antibacterial [9], antitumoral [10], antioxidant [11] and antibiotical [12].

Due to the important above-mentioned properties of 2-amino-4*H*-chromenes, remarkable attention has been focused on the development of environmentally friendly methodologies to the synthesis of this heterocyclic compounds by three-component tandem reaction of aromatic/aliphatic aldehydes, malononitrile and diverse enolizable C-H activated acidic compounds [13–23]. However, many reported methods for the synthesis of these compounds suffer from disadvantages including relying on multi-step conditions, need for excessive amounts of the reagents, the use of toxic organic solvents or catalysts, harsh reaction conditions, tedious work-up procedure, long reaction times, low yields of products and non-recyclability of the catalyst.

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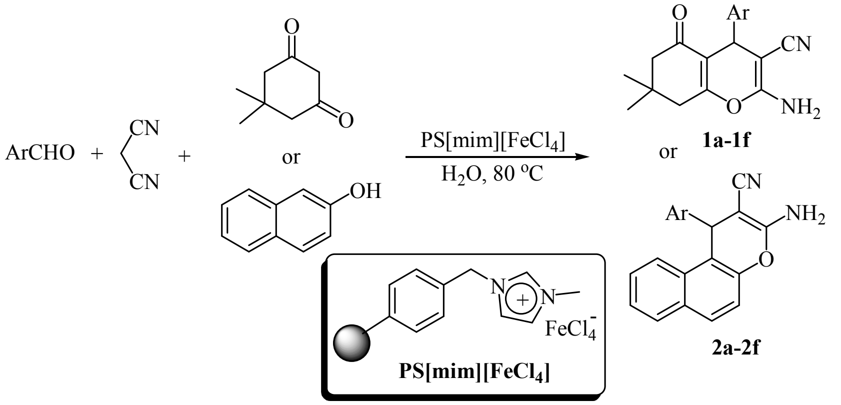
Owing to the widespread applications of the described compounds, and in continuation of our efforts on the synthesis of new heterogeneous catalysts [24–28], in this paper, we report our study on synthesis, characterization, and catalytic properties of polystyrene-supported 1-methylimidazolium tetrachloroferrate (PS[mim][$FeCl_4$]). The catalyst was characterized with several techniques, and its catalytic activity was investigated in the synthesis of 2-amino-4*H*-chromene-3-carbonitrile derivatives through the one-pot condensation reaction of various aryl aldehydes, malononitrile and dimedone or 2-naphthol under aqueous media (Scheme 1).



Scheme 1. Synthesis of 4*H*-chromene derivatives in the presence of PS[mim][$FeCl_4$].

## EXPERIMENTAL

### *Materials and apparatus*

Chemical reagents in high purity were purchased from Merck and Aldrich and were used without further purification. Merrifield resin (Mesh 200-400, 2% cross-linked with divinylbenzene, 2-4 mol capacity) was purchased from Alfa Aesar chemical company. 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 in open capillary tubes. Scanning electron microscopy (SEM) and energy dispersive X-ray (EDAX) analyses were carried out using a Philips XL30 instrument. FT-IR spectra of synthesized compounds were recorded on KBr pellets on a Bomem MB-1998 spectrophotometer. Raman measurements were performed on an Almega Thermo Nicolet Dispersive Raman spectrometer at a wavelength of 532 nm of a Nd:YLF laser. Progress of the reactions was observed by TLC on silica gel PolyGram SILG/UV 254 plates.

### *Synthesis of polystyrene-supported 1-methylimidazolium chloride (PS[mim][Cl])*

Merrifield resin (2 g; 200-400 mesh, 2% cross-linked) and 1-methylimidazole (10 mL) were placed in a round flask and stirred for 24 h at 90 ºC in an oil bath. The obtained yellow polymer-support (PS[mim][Cl]) was filtered and washed with ethanol and acetone, and dried at room temperature.

### *Synthesis of polystyrene-supported 1-methylimidazolium tetrachloroferrate (PS[mim][$FeCl_4$])*

The mixture of PS[mim][Cl] (2 g) and $FeCl_3.6H_2O$ (0.54 g, 2 mmol) in methanol (5 mL) were stirred for 15 min at room temperature. Afterwards, the resulted brown resins (PS[mim][$FeCl_4$]) were filtered and washed with distilled water and dried under vacuum.

*General procedure for the synthesis of 2-amino-4H-chromenes catalyzed by PS[mim][FeCl$_4$]*

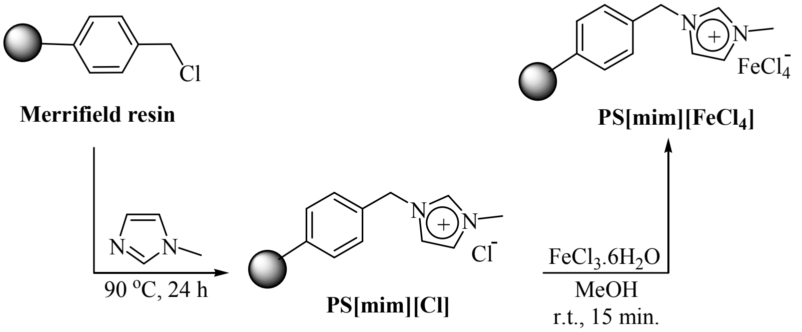
The heterogeneous catalyst, PS[mim][FeCl$_4$], (0.1 g) was added to a mixture of aromatic aldehydes (1 mmol), malononitrile (1 mmol), dimedone or 2-naphthol (1 mmol) in water (5 mL). The reaction mixture was stirred at 80 °C for the appropriate time shown in Table 2. After completion of the reaction according to TLC analysis (*n*-hexane:ethyl acetate; 4:1), the reaction mixture was filtered off and the filtrate was washed with cool ethanol to remove the excess malononitrile. Eventually, separation of the catalyst from the obtained 2-amino-4*H*-chromenes, and further purification of products were applied using methanol as solvent.

*2-Amino-7,7-dimethyl-5-oxo-4-phenyl-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile* ***(5a)***. White solid; m.p. = 229-231 °C; IR (KBr, cm$^{-1}$): $\nu_{\max}$ = 3394, 3325, 3209, 2962, 2199, 1678, 1661, 1600, 1369, 1250, 1215, 1161, 1138, 1033, 694; $^1$H NMR (400 MHz, DMSO-$d_6$, ppm): $\delta_H$ = 7.29 (t, $J$ = 7.2 Hz, 2H), 7.11–7.22 (m, 3H), 6.99 (s, 2H), 4.15 (s, 1H), 2.48 (s, 2H), 2.28 (d, $J$ = 16.1 Hz, 1H), 2.11 (d, $J$ = 16.1 Hz, 1H), 1.01 (s, 3H), 0.98 (s, 3H); $^{13}$C NMR (100 MHz, DMSO-$d_6$, ppm): $\delta_C$ = 195.45, 161.98, 159.12, 144.73, 128.18, 127.47, 126.50, 119.89, 111.96, 59.04, 50.03, 39.12, 34.86, 32.09, 29.63, 25.93.

## RESULTS AND DISCUSSION

*Synthesis and characterization of PS[mim][FeCl$_4$]*

Polystyrene-supported 1-methylimidazolium tetrachloroferrate was synthesized by the concise route outlined in Scheme 2. First, the Merrifield resin was treated with 1-methylimidazole at 90 °C for 24 h to afford the polystyrene-supported 1-methylimidazolium chloride as a yellow solid. Then, the stirring of the mixture of PS[mim][Cl] and ferric chloride in methanol at room temperature lead to the brown PS[mim][FeCl$_4$] resin.



Scheme 2. Synthesis of PS[mim][FeCl$_4$] as a new heterogeneous catalyst.

The catalyst PS[mim][FeCl$_4$] was characterized by the various techniques. The FT-IR spectrum (Figure 1) showed a band vibration at 3200-3600 cm$^{-1}$, which is probably related to the absorbed water. The CH stretching and bending bands appeared at 2830-2950 cm$^{-1}$ and 1400-1500 cm$^{-1}$, respectively. Two peaks at 1641 cm$^{-1}$ and 1560 cm$^{-1}$ assigned to C=C and C=N band vibrations, respectively. Raman spectroscopy is a useful technique for the identification of different types of ammonium tetrachloroferrate salts. The expanded Raman spectrum shows a strong peak at approximately 330 cm$^{-1}$ that is assigned to the totally symmetric Fe-Cl bond stretch vibration (Figure 2). The SEM images of unsupported resin (PS), PS[mim]Cl and PS[mim][FeCl$_4$] clearly indicated that the PS has a smooth surface while the polymer-supports have a rough surface and the changes in the morphology of polymers are remarkable (Figure 3).

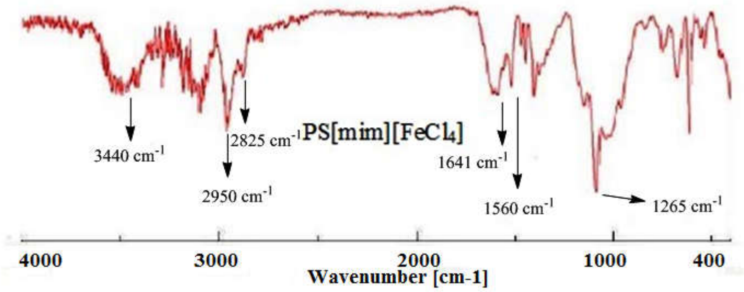


Figure 1. The FT-IR of PS[mim][$FeCl_4$].

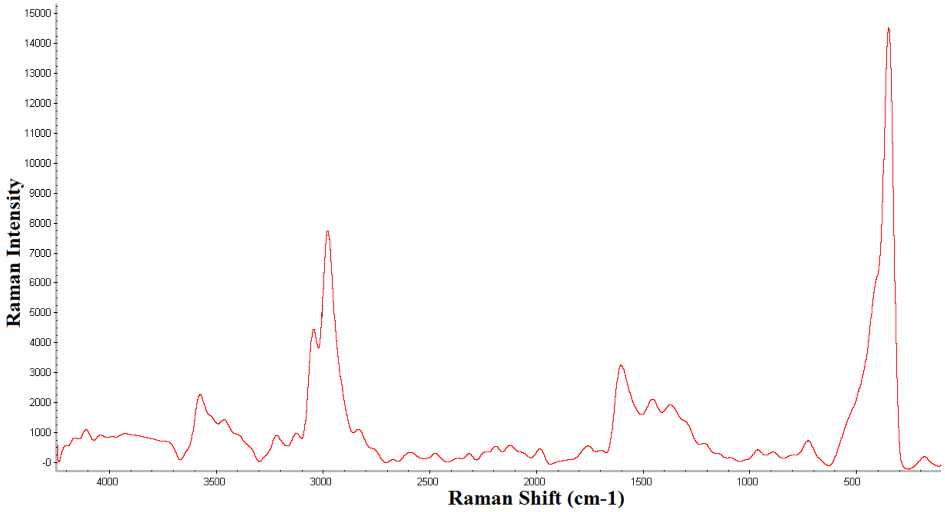
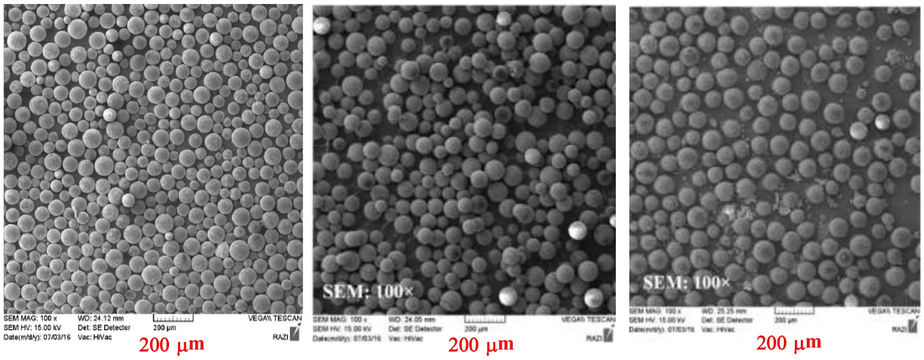


Figure 2. The Raman spectrum of PS[mim][$FeCl_4$].



a b c

Figure 3. The SEM images of PS (a), PS[mim][Cl] (b) and PS[mim][$FeCl_4$] (c).

The data from EDX analysis are consistent with our expectations and confirms the presence of carbon, nitrogen, iron and chlorine elements in PS[mim][$FeCl_4$] (Figure 4).

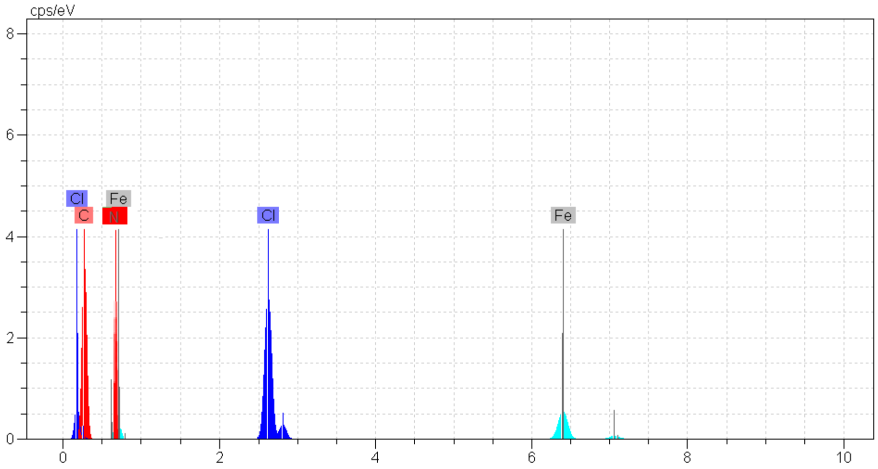


Figure 4. The EDX spectroscopy of PS[mim][$FeCl_4$].

### *Application of PS[mim][$FeCl_4$] as heterogeneous catalyst for the synthesis of 4H-chromene derivatives in water*

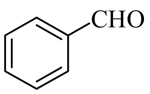
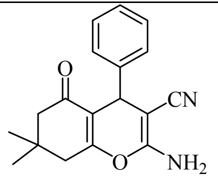
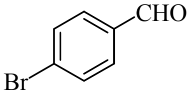
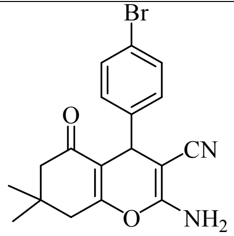
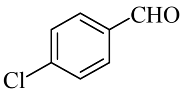
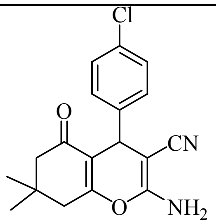
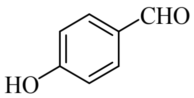
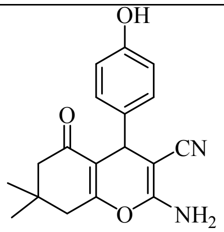
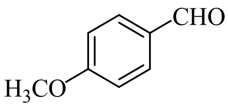
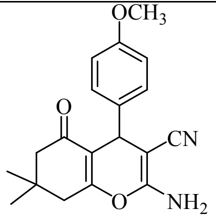
After successful characterization of PS[mim][$FeCl_4$], it was decided to evaluate its catalytic activity as a heterogeneous phase-transfer catalyst in the synthesis of 2-amino-4*H*-chromene-3-carbonitriles. In order to optimize conditions the reaction of benzaldehyde with malononitrile and dimedone was selected as a model reaction. After preliminary experiments, it was found that the condensation reaction was efficiently carried out in the presence of 0.1 g of PS[mim][$FeCl_4$] in water at 80 °C and produced 2-amino-3-cyano-7,7-dimethyl-4-(4-methylphenyl)-5-oxo-4*H*-5,6,7,8-tetrahydrobenzo-pyran (**1a**) in excellent yield and in short reaction time (Table 1, entry 5). After optimizing the reaction conditions, we applied this catalyst for the synthesis of 2-amino-4*H*-chromene-3-carbonitrile derivatives using different aryl aldehydes, malononitrile and dimedone or 2-naphthol in water to establish the catalytic activity of PS[mim][$FeCl_4$] for this transformation (Table 2).

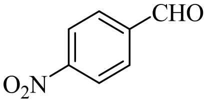
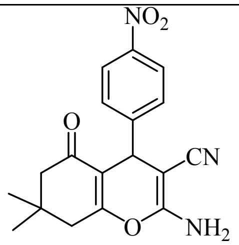
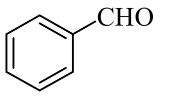
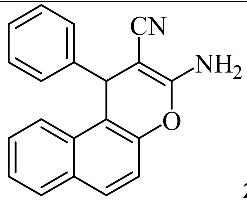
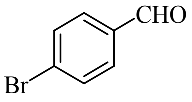
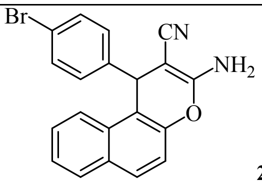
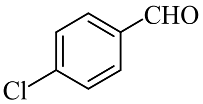
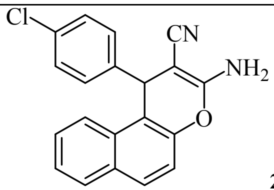
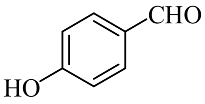
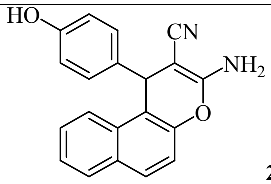
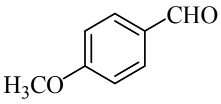
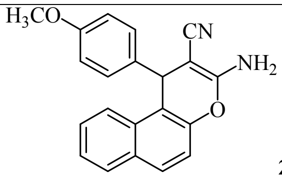
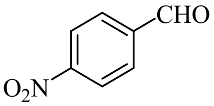
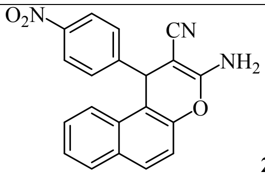
Table 1. Optimization of reaction conditions.

| Entry | Catalyst (g) | Solvent | Condition | Time (min) | Yield (%)[a] |
|---|---|---|---|---|---|
| 1 | PS[mim][$FeCl_4$] (0.2) | $H_2O$ | reflux | 18 | 91 |
| 2 | PS[mim][$FeCl_4$] (0.1) | $H_2O$ | reflux | 20 | 93 |
| 3 | PS[mim][$FeCl_4$] (0.1) | $H_2O$ | r.t. | 90 | 35 |
| 4 | PS[mim][$FeCl_4$] (0.1) | $H_2O$ | 50 °C | 90 | 65 |
| 5 | PS[mim][$FeCl_4$] (0.1) | $H_2O$ | 80 °C | 20 | 92 |
| 6 | PS[mim][$FeCl_4$] (0.05) | $H_2O$ | 80 °C | 90 | 88 |
| 7 | PS[mim][$FeCl_4$] (0.1) | Neat | 80 °C | 90 | 65 |
| 8 | PS[mim][$FeCl_4$] (0.1) | $CHCl_3$ | reflux | 90 | 35 |
| 9 | PS[mim][$FeCl_4$] (0.1) | $CH_3CN$ | reflux | 90 | 55 |
| 10 | PS[mim][$FeCl_4$] (0.1) | MeOH | reflux | 90 | 60 |
| 11 | PS[mim][Cl] (0.1) | $H_2O$ | reflux | 90 | 40 |
| 12 | - | $H_2O$ | reflux | 90 | trace |

[a]Isolated yields.

Table 2. Synthesis of 4*H*-chromene derivatives catalyzed by PS[mim][$FeCl_4$]$^a$.

| Entry | Aldehyde | Product | Time (h) | Yield (%)$^b$ | m.p. (°C) [Ref.] |
|---|---|---|---|---|---|
| 1 |  |  **1a** | 20 | 92 | 229-231 [18] |
| 2 |  |  **1b** | 15 | 90 | 198-200 [19] |
| 3 |  |  **1c** | 15 | 88 | 212-214 [20] |
| 4 |  |  **1d** | 90 | 91 | 202-204 [19] |
| 5 |  |  **1e** | 60 | 85 | 196-197 [18] |

| | | | | | |
|---|---|---|---|---|---|
| 6 |  |  **1f** | 20 | 90 | 175-177<br>[18] |
| 7 |  |  **2a** | 30 | 90 | 286-288<br>[29] |
| 8 |  |  **2b** | 25 | 88 | 239-241<br>[21] |
| 9 |  |  **2c** | 30 | 85 | 206-208<br>[21] |
| 10 |  |  **2d** | 35 | 87 | 261-263<br>[22] |
| 11 |  |  **2e** | 90 | 92 | 186-187<br>[21] |
| 12 |  |  **2f** | 30 | 88 | 187-188<br>[29] |

[a]Reaction conditions: aryl aldehyde (1 mmol), malononitrile (1 mmol), dimedone or 2-naphthol (1 mmol), PS[mim][FeCl$_4$] (0.1 g), $H_2O$ (5 mL) at 80 °C. [b]Isolated yields.

Comparison of the catalytic efficiency of PS[mim][$FeCl_4$] in the one-pot condensation between benzaldehyde, malononitrile and dimedone to produce the corresponding tetrahydrobenzopyran with some of methods reported in the literature is presented in Tables 3. The results showed that our procedure provided higher yield of product in shorter reaction time and under milder reaction conditions.

Table 3. Comparative synthesis of compound **1a** using the reported methods versus the present method.

| Entry | Catalyst | Condition | Time (min) | Yield (%) | Ref. |
|---|---|---|---|---|---|
| 1 | TBAF | $H_2O$, reflux | 30 | 97 | [14] |
| 2 | MgO | Solvent-free, r.t. | 25 | 77 | [15] |
| 3 | [$H_3N^+CH_2CH_2OH$][$HCO_2^-$] | Solvent-free, r.t. | 5 | 70 | [16] |
| 4 | $SiO_2$ NPs | EtOH, r.t. | 25 | 94 | [17] |
| 5 | MNPs-Guanidine | PEG/$H_2O$, r.t. | 15 | 95 | [19] |
| 6 | [DiEG(mim)$_2$][OH]$_2$ | $H_2O$, r.t. | 20 | 92 | [22] |
| 7 | PS[mim][$FeCl_4$] | $H_2O$, 80 °C | 20 | 92 | This work |

To investigate the reusability of the catalyst, it was recovered from the reaction mixture and washed with acetone or methanol and dried in the air. It was then reused for subsequent experiments (up to five cycles) under similar reaction conditions. It was observed that the yields of the product remained comparable in these experiments (Figure 5, conversion decreases from 100% to 95%), established the recyclability and the reusability of the catalyst without any significant loss of its activity.

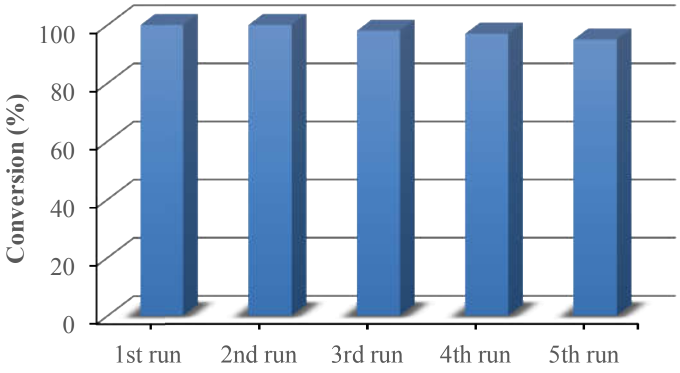


Figure 5. Recovery and reusability of the catalyst.

## CONCLUSION

In conclusion, a new heterogeneous catalyst (PS[mim][$FeCl_4$]) was successfully prepared, characterized and applied for the one-pot three-component synthesis of 2-amino-4H-chromenes under aqueous media. This novel catalytic method offers several advantages including environmental friendliness, high yield, involving a simple work-up procedure, ease of separation, and recyclability of the catalyst. So we think that this procedure could be considered a new and suitable addition to the present methodologies in this area.

## ACKNOWLEDGEMENT

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