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A green approach for the synthesis of 2-amino-4H-chromene derivatives using Polystyrene-Supported 1-Methylimidazolium tetrachloroferrate as an efficient heterogeneous catalyst in water

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Abstract
In this study, we reported facile and efficient synthesis of 2-amino-4H-chromenes that catalyzed by polystyrene-supported 1-methylimidazolium tetrachloroferrateas. The synthesis proceeds with various aldehydes under mild conditions and afford the target products with good to high yields.

Key words: Green chemistry; Polymer-supported ionic liquid; 2-amino-4H-chromene derivatives; Multi component reactions

Introduction
Ionic liquids (ILs) have offered great potential (such as low vapor pressure, wide liquid range, low flammability, high conductivity, excellent stability and large electrochemical

window) for developing clean catalytic technologies due to their unique properties and have been studied widely in catalytic reactions. ILs can be designed for specific catalytic processes and using them usually presents the ad-vantages of high catalytic activity and good selectivity [1, 2]. Recently, the term "magnetic ionic liquid" (MIL) was proposed by Hamaguchi and co-workers to introduce ILs with paramagnetic like temperature dependence of susceptibility[3, 4]. The MILs are primarily based on high-spin d5 Fe (III) in the form of tetrachloro- or tetrabromoferrate(III) with various counter cations. Owing to the high single-ion magnetic moments, these MILs exhibited a strong response to magnetic fields[5]. Since then, much attention has been paid to the design and synthesis of this new class of ILs[6-10]. Moreover, the catalytic activities of MILs have been studied in Friedel Crafts acylation[11], aryl grignard cross coupling of alkyl halides[12], preparation of 1,2-azidoalcohols[13], glycolysis of poly(ethylene terephthalate)[14], "liquid fixed-bed" catalysts in flow application[15] , oxidative desulfurization of fuels[16], multi-component synthesis of 1- and 5-substituted 1H-tetrazoles[17], quinazoline derivatives[18] and 1-amidoalkyl-2-naphtols[19].

The chromene moiety, including that of 2H-chromene and 4H-chromene, belongs to a major class of natural oxygen-containing heterocycliccompounds, which are widely found in edible fruits and vegetables. These compounds have occupied an important place in drug research because of their various biological and pharmacological activities such as antioxidant, antileishmanial, antibacterial, antifungal, hypotensive, anticoagulant, antiviral, diuretic, antiallergenic, and antitumor activities. Generally, the biological and pharmacological activities of chromenes depend on the nature of substituents being either on the 4H-pyran or the adjacent rings. Especially, among various chromene derivatives, 2-amino-4Hchromene with cyano-functionality has potential applications in the treatment of rheumatoid, psoriasis, and cancer. Other properties such as laser dyes, optical brighteners, fluorescence markers, pigments, cosmetics, and potent biodegradable agrochemicals are well known for decades [20].

Experimental

1- Materials and Instruments

All Infra-red spectrometry (FT-IR) experiments were performed on an AnalystDate PerkinElmer that were registered in solid KBr. Melting points of the products were measured by an Amstead ElectroThermal 9200 instrument using the capillary tubes.

Progress of the reactions was observed on Merck DC-Alufolien plates pre-coated 67 with silica gel F_{254}. In table 2-1 the properties of the used Merrifild resin are observed.

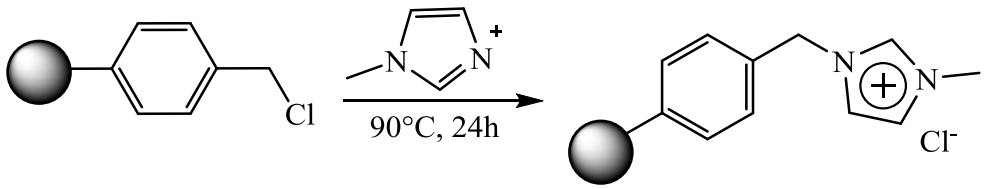
Table 1 The properties of Merrifild resin

	Company	**Mesh**	**Cross Linked**	**Ca**
Merrifild resin	Alfa Asear	200-400	2%	**2-4mol/ca**

2-Methods

2-1- Synthesis of polystyrene-supported 1-methyl imidazolium chloride

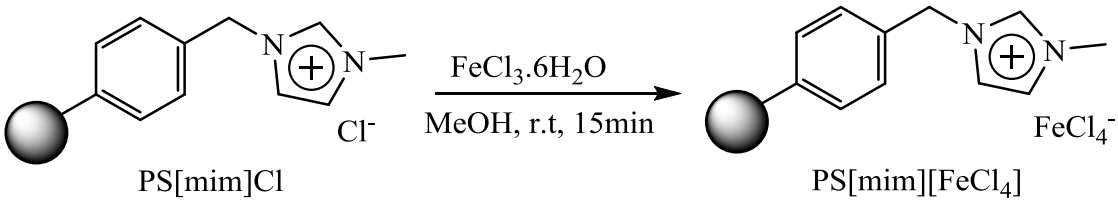
1-methyl imidazole (12 ml) and merrifild resin(2 gr) were placed in a round flask. The mixture was placed in an oil bath and was stirred for 24hr in 90ºC. Then the residue was filtered and washed with 10 ml of ethanol and acetone. Eventually the yellow polymer support PS[mim][Cl] was synthesized (scheme 1).



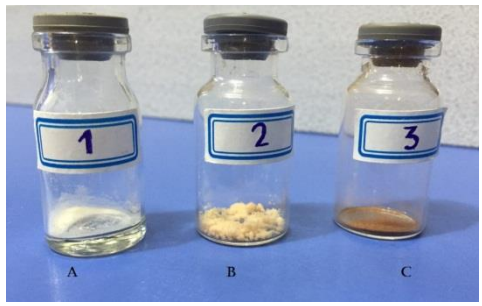
Scheme 1 PS[mim][Cl] synthesis

2-2- Synthesis of polystyrene-supported 1-methyl imidazolium tetrachloroferrat(III)

PS[mim][Cl] (2 gr), $FeCl_3.6H_2O$ (0.55 gr) and methanol (5 ml) were put in a round flask and magnetically stirred for 15 minutes. Afterwards the resulted resin was filtered and washed throughout with distilled water. The resulting brown resin PS[mim][$FeCl_4$] was acquired.



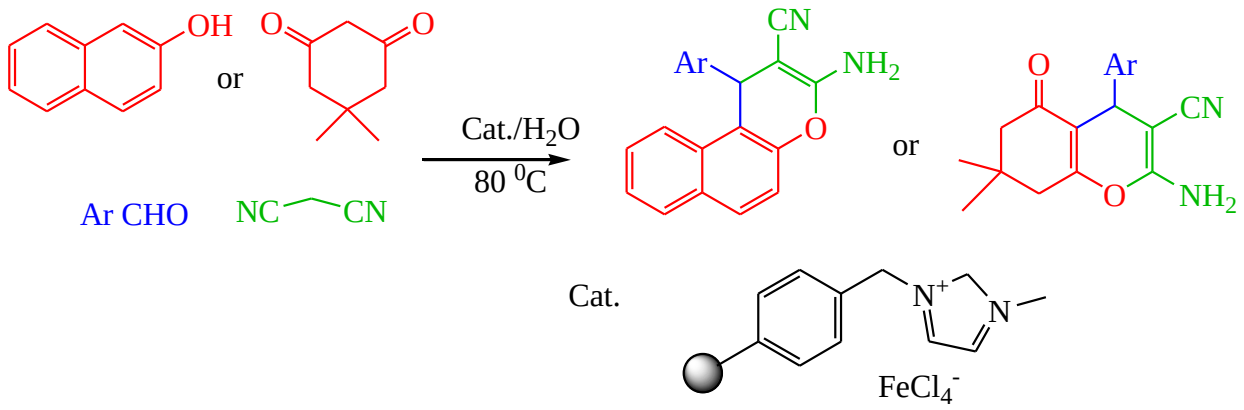
Scheme 2 PS[mim][$FeCl_4$] synthesis



Scheme 3 1: Merrifild resin; 2: PS[mim][Cl]; 3: PS[mim][$FeCl_4$]

2-3- General procedure for the synthesis of 2-benzylidene malononitriles catalized by PS[mim][$FeCl_4$]

A mixture of aryl aldehyde (1 mmol), malononitrile (1.2 mmol), 5,5-dimethylcyclohexane-1,3-dione (1 mmol) or 2-naphthol (1 mmol), PS[mim][$FeCl_4$] (0.1 gr) and distilled water (5 ml) was placed in a round glass flask and heated to 80ºC while being magnetically stirred for the time shown in table(4). The progress of the reaction was monitored by TLC (using n-hexane/ethylacetate (4:1) as eluent). After the completion of the reaction the mixture was allowed to cool in to room temperature afterwards was filtered and the remained solvent was evaporated by being dried in the oven. Subsequently in order to remove the excess malononitrile the residue was washed with mixed distilled water and ethanol (50:50). Eventually the recrystallization method was applied using methanol as solvent for further purification.

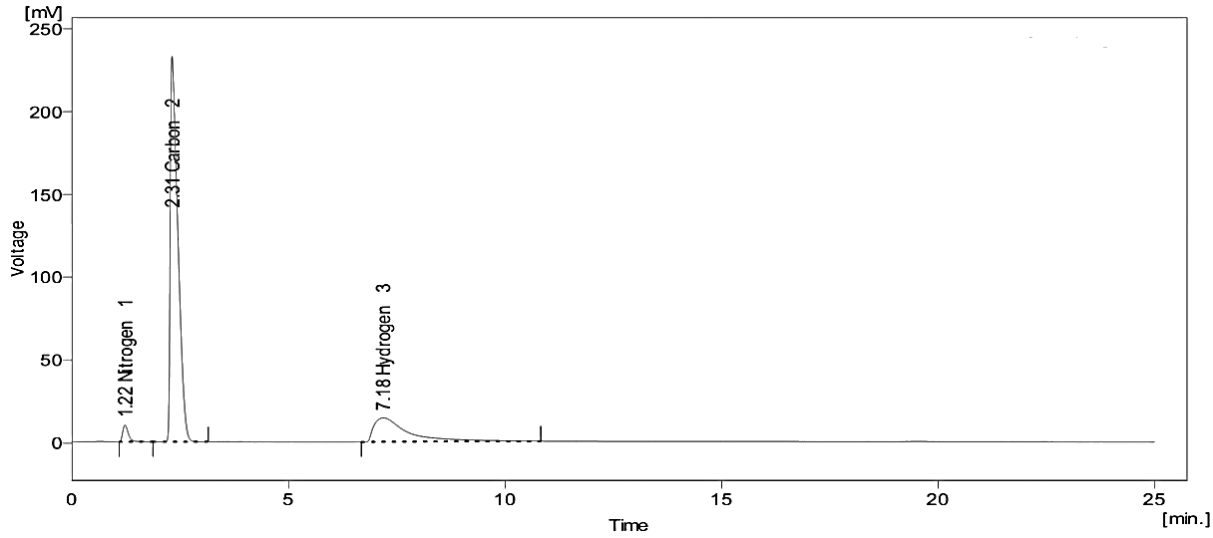


Scheme 4 PS [mim][$FeCl_4$] catalyzed synthesis of 2-amino-4H-chromene derivatives by knoevenagel condensation

Results and discussions

1- Characterization of PS[mim]Cl

Apparently for notifying the amount of nitrogen on the polymer a CHN test was done. According to the analysis 2.04 mmol ionic liquid per each gram was obtained (scheme 5).



Scheme 5 CHN spectroscopy of PS[mim]Cl

Table2 CHN data

	Reten. Time (min)	Respose	Weight (mg)	Weight (%)	Peak type	Element Name
1	1.217	92.046	0.033	5.72	refer	**nitrogen**
2	2.307	2785.337	0.401	69.30	refer	**carbon**
3	7.183	789.897	0.038	6.51	refer	**hydrogen**
	Total		0.0578	81.53		

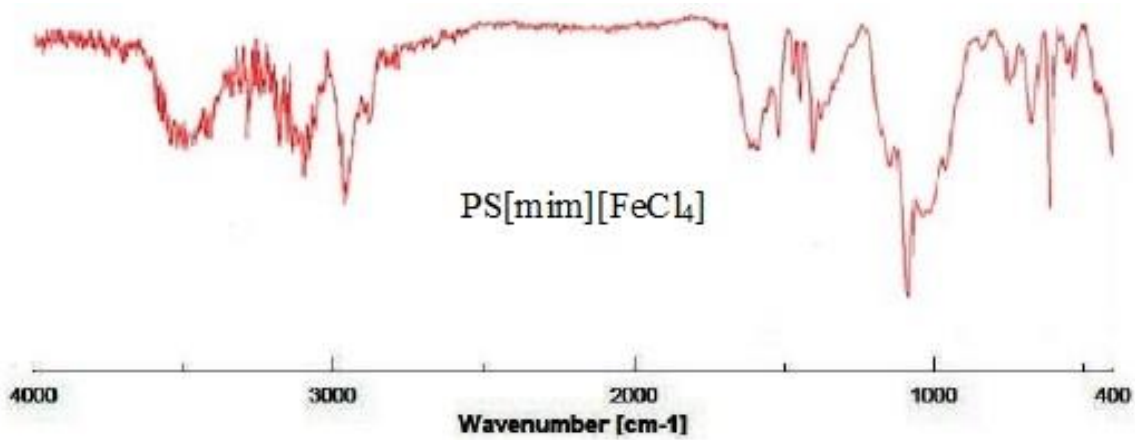
Table3 CHN analysis of Merrifild resin and stabilized ionic liquid

Materials	C (W%)	H (W%)	N (W%)
1% DVB Merrifield resin	83.35	7.2	**0.1**
PS[mim][Cl]	77.7	6.51	**5.72**

2- Characterization of PS[mim][FeCl4]

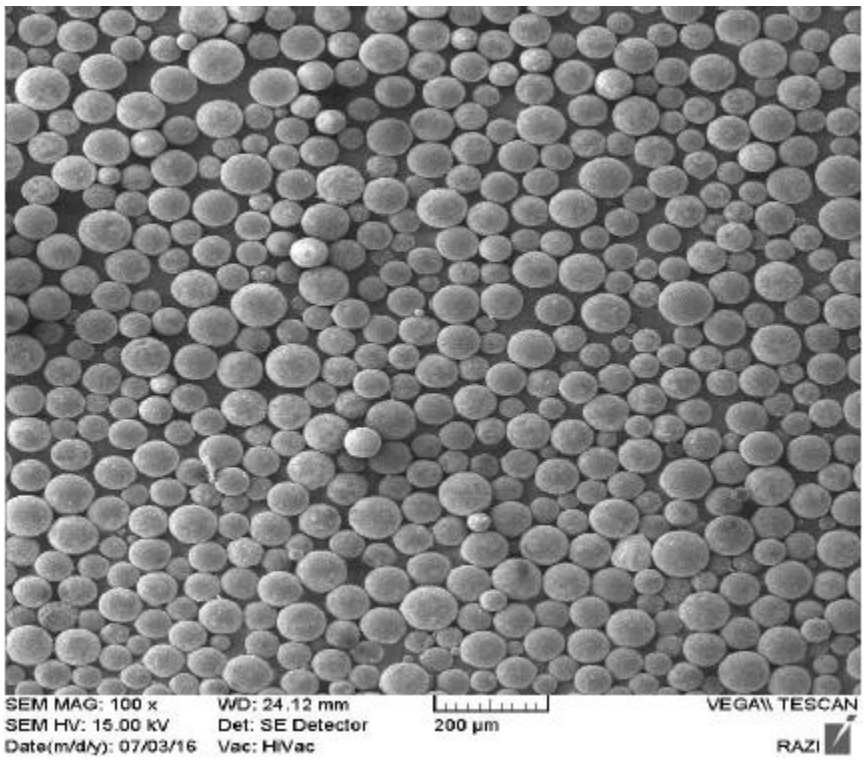
The FT-IR spectra was obtained in the range of 450-4000 cm^{-1} by creating disks of the samples with KBr. The weak peak at 2830-2950 cm^{-1} is due to symmetric and asymmetric stretch vibrations of C-H. The strong peak at 1630 cm^{-1} is probably related to

the absorbed water and also the two peaks at 1560 and 1641 cm^{-1} are coherent with C=C and C=N band vibrations.

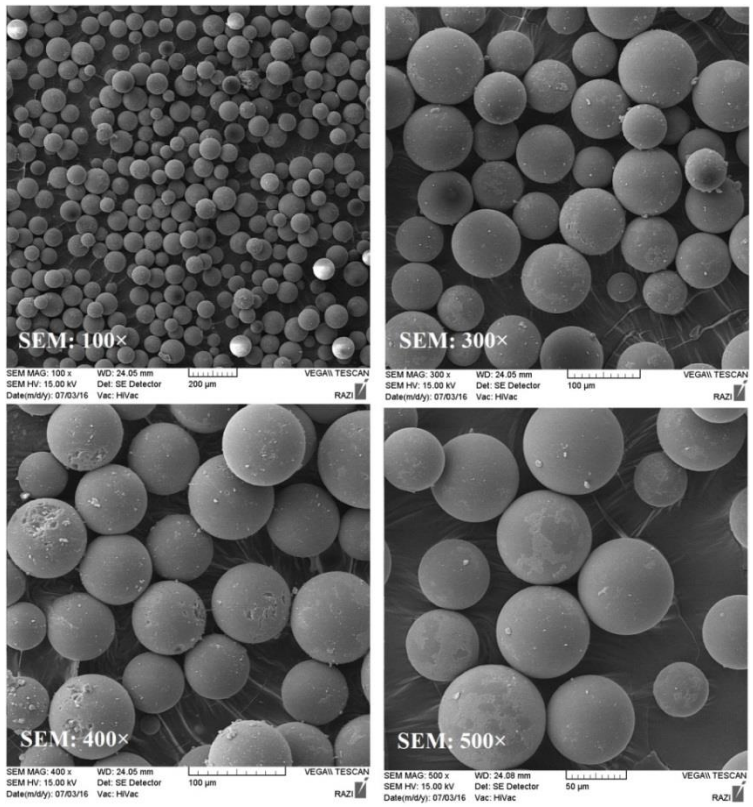


Scheme 6 The FT-IR of the PS[mim][$FeCl_4$] sample

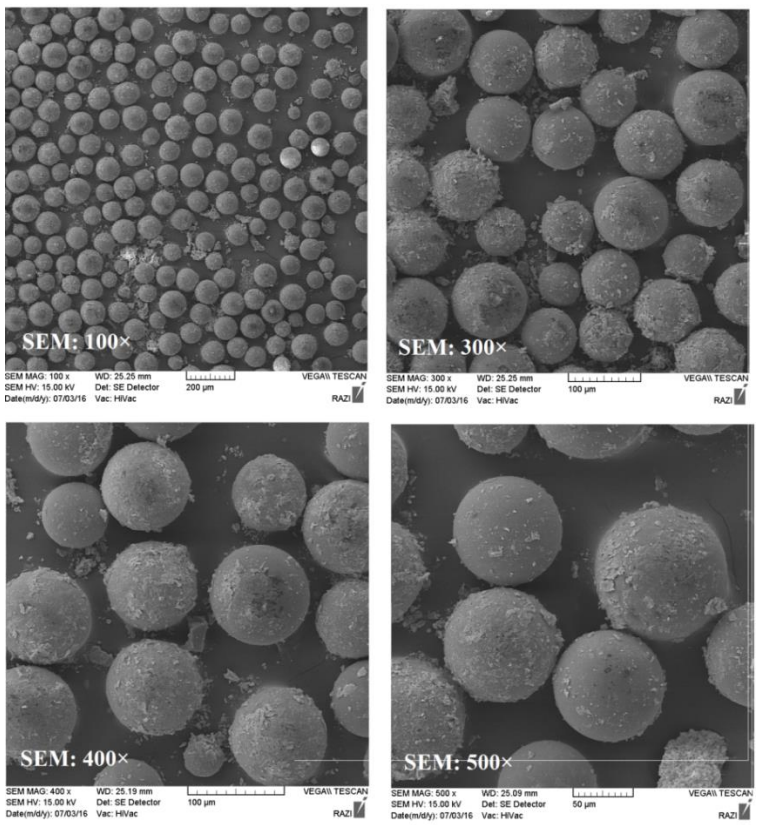
The morphological differences among each polymer support(PS), PS[mim]Cl and PS[mim][$FeCl_4$] surfaces are obvious in schemes 8, 9 and 10. The images clearly indicate that the polymer support has a smooth surface but the linked products have a rough surface. The changes in the morphology of products are remarkable.



Scheme 7 SEM image of PS

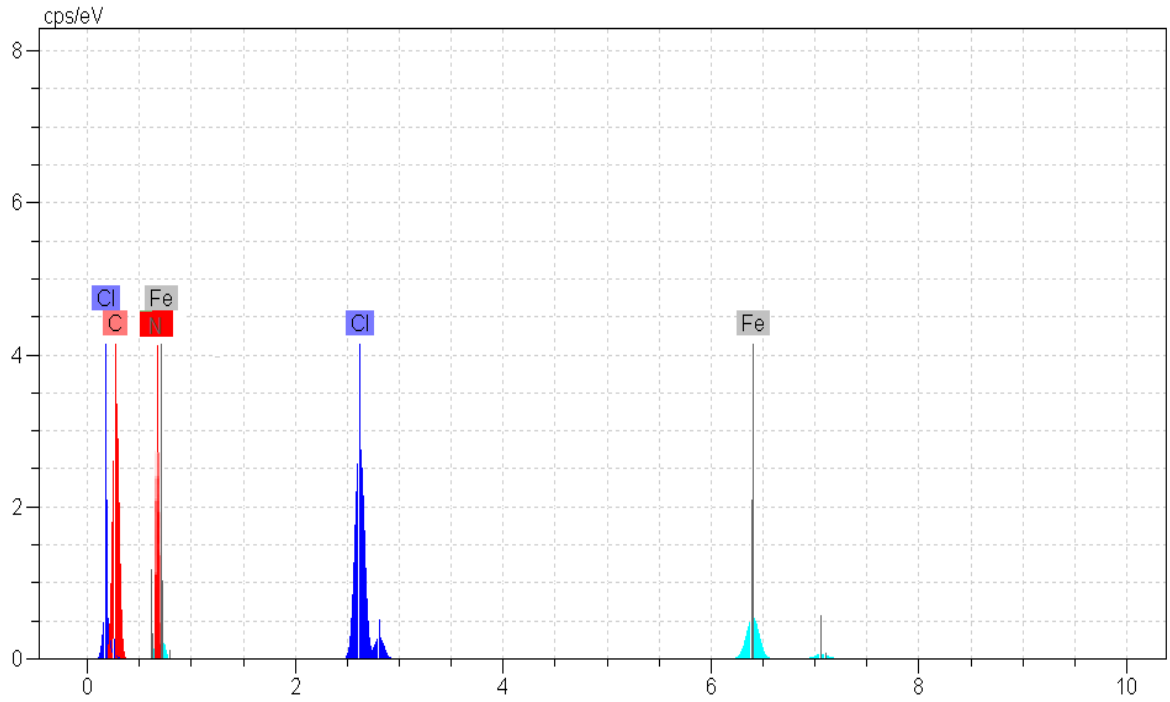


Scheme 8 SEM image of PS[mim] Cl



Scheme 9 SEM image of the catalyst PS[mim][$FeCl_4$]

More assuring direct evidence for the synthesis of PS[mim][$FeCl_4$] is the Energy dispersive X-ray spectroscopy (EDX or EDS) showed in scheme 10. Apparently it represents the presence of the carbon, nitrogen, chlorine and iron elements in the catalyst.



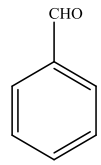
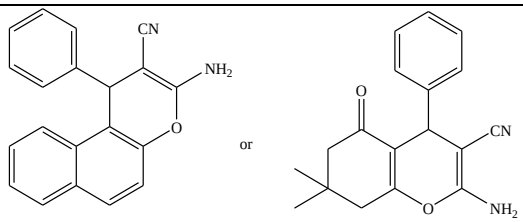
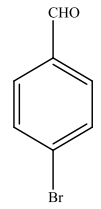
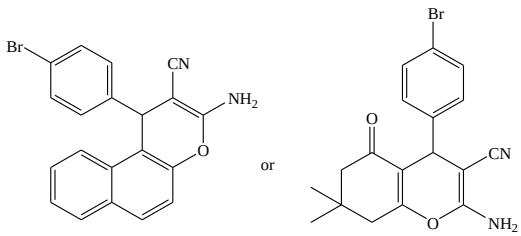
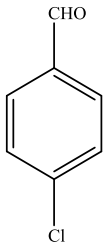
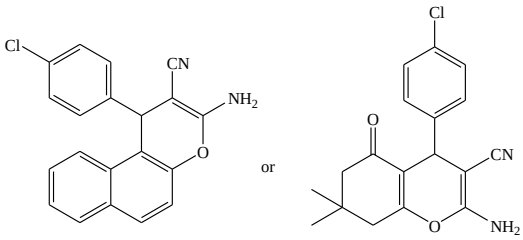
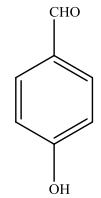
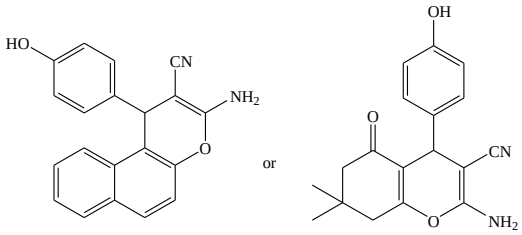
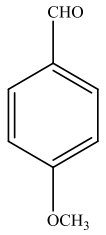
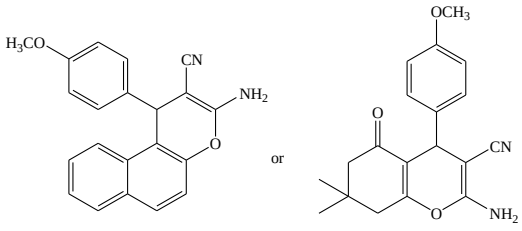
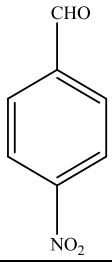
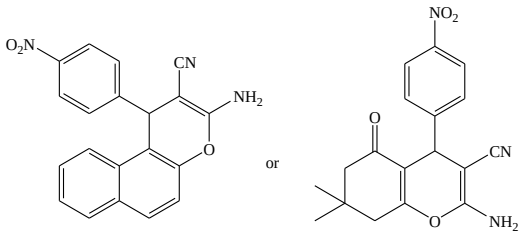
Scheme 10 PS[mim][$FeCl_4$] EDX spectroscopy

3- Application of PS[mim][FeCl4] for the synthesis of 2-amino-4H-chromene derivatives

The iron containing ionic liquid PS[mim][$FeCl_4$] was synthesized by mixing PS[mim][Cl] (2 gr), $FeCl_3.6H_2O$ (0.55 gr) and methanol (5 ml) following the procedure shown in scheme 3. A dark brown liquid was obtained and was characterized through the methods mentioned previously.

The catalyst showed a remarkable application in the synthesis of 2-amino-4H-chromene derivatives. These products were synthesized according to the procedure in scheme 4 that is, 1.2 mmol malononitrile, 1 mmol of different aldehydes, 5,5-dimethylcyclohexane-1,3-dione (1 mmol) or 2-naphthol(1 mmol) and 0.1 gr of PS[mim][$FeCl_4$] in the presence of H_2O as a solvent were mixed under reflux condition as seen in table 4.

Table 4 PS[mim][$FeCl_4$] catalized the knoevenagel condensation of benzylidene malononitriles from malononitrile and aryl aldehydes in the presence of ethanol as solvent

Entry	Aldehyde	Product	Time (h)	Yield (%)
1			2; 1/5	92; 90
2			1; 1/5	90;88
3			1/5; 2	88;85
4			5; 35	91; 87
5			4/5; 5	85; 92
6			2; 2/5	90;88

Conclusion

In this project a novel, easy and environmentally friendly procedure for the one-pot multicomponent synthesis of 2-amino-4H-chromene derivatives catalyzed by an iron containing ionic liquid (PS[mim][FeCl4]) was demonstrated. The synthesized catalyst was first characterized and then applied in the condensation reaction. Moreover the isolation of the resulting products was run through an easy way with high purity and yields.

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