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Synthesis and characterization of a novel paramagnetic functionalized ionic liquid as a highly efficient catalyst in one-pot synthesis of 1-amidoalkyl-2-naphtols

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ABSTRACT

A novel paramagnetic ionic liquid, 3-(2-hydroxyethyl)-1-methyl imidazolium bromotrichloro ferrate (III), was synthesized and exhibited high catalytic performance in the synthesis of 1-amidoalkyl-2-naphthols via one-pot three-component condensation reaction of aromatic aldehydes, 2-naphthol and acetamide at 85 °C under solvent-free conditions. The catalyst showed response to an external magnet and was characterized by Fourier transform infrared spectroscopy (FT-IR), UV–Visible spectroscopy, Thermal gravimetric analysis (TGA) and Raman spectroscopy.

1. Introduction

Due to their unique properties (such as low vapor pressure, wide liquid range, low flammability, high conductivity, excellent stability and large electrochemical window), ionic liquids (ILs) have offered great potential for developing clean catalytic technologies and have been studied widely in catalytic reactions. ILs can be designed for specific catalytic processes and using them usually presents the advantages 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 d^5 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] and multi-component synthesis of 1- and 5-substituted 1H-tetrazoles [17] and quinazoline derivatives [18].

1-Amidoalkyl-2-naphthol derivatives containing 1,3-amino-oxygenated functional groups are an important class of heterocyclic compounds. This is mainly due to the fact that they possess a broad range of biological, medicinal, and pharmacological activities [19–21]. Although many catalytic systems have been developed for the synthesis of amidoalkyl naphthols, some of them suffer from drawbacks such as prolonged reaction times, low yields, using carcinogenic solvents, toxicity and reusability of highly acidic and expensive catalysts, higher reaction temperature, harsh conditions, large waste production and undesirable byproducts [22–29].

In this paper, we report on the preparation of 3-(2-hydroxyethyl)-1-methyl imidazolium bromotrichloro ferrate (III) ([$C_2OHmim]FeCl_3Br^-$) as a novel paramagnetic ionic liquid. The catalytic activity of the MIL was investigated for the one-pot synthesis of 1-amidoalkyl-2-naphtols.

2. Experimental

All compounds were purchased from Aldrich and Merck companies and used as received without further purification. Progress of the reaction was monitored by TLC on Merck DC-Alufolien plates pre-coated with silica gel F_{254}.

2.1. Synthesis of MIL [$C_2OHmim]FeCl_3Br^-$

3-(2-Hydroxyethyl)-1-methyl imidazolium bromide (2.0 g) [30] and iron (III) chloride hexahydrate (2.7 g) were dissolved in dry methanol (10 mL). The resulting mixture was stirred at room temperature for 24 h. After the solution was filtered, methanol was removed under vacuum. The obtained ionic liquid was redissolved in ethyl acetate (10 mL) and the solution was centrifuged to separate possible residue of the inorganic salts. Then, ethyl acetate was evaporated and the resulting dark brown liquid, 3-(2-hydroxyethyl)-1-

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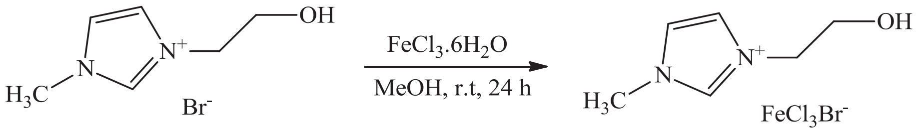

Scheme 1. Synthesis of the magnetic ionic liquid.

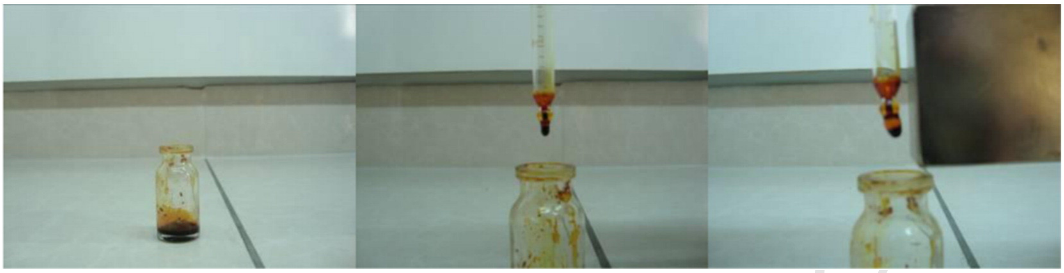

Fig. 1. Image of the [C_2OHmim]$FeCl_3Br^-$ ionic liquid droplet attracted toward a NbFeB magnet.

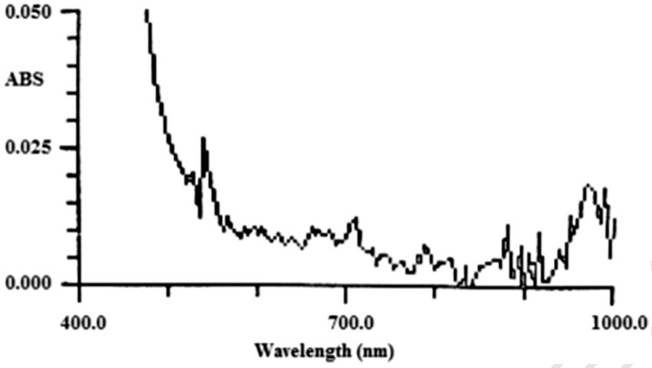

Fig. 2. Visible absorption spectrum of [C_2OHmim]$FeCl_3Br^-$ at a concentration of 0.1 M in acetonitrile.

methyl imidazolium bromotrichloro ferrate (III), was dried in a vacuum oven at 60 °C overnight.

2.2. General procedure for the synthesis of 1-amidoalkyl-2-naphthols by [C_2OHmim]$FeCl_3Br^-$

A mixture of 2-naphthol (1 mmol), aryl aldehyde (1 mmol), acetamide (1 mmol) and [C_2OHmim]$FeCl_3Br^-$ (0.05 mmol) was placed in a glass test tube and heated at 85 °C in an oil bath for the time shown in Table 2. After completion of the reaction as judged by TLC (using *n*-hexane/ethylacetate (4:1) as eluent), the mixture was allowed to cool to room temperature. Then, to separate the catalyst, diethyl ether (2 × 5 mL) was added to the reaction mixture and stirred for 5 min. The ethereal phase was decanted and evaporated to get the ionic liquid. The solid residue from previous step was isolated and purified by recrystallization in hot ethanol. The desired pure product was characterized by comparison of their physical data with those of known 1-amidoalkyl-2-naphthol derivatives.

3. Results and discussions

3.1. Synthesis and characterization of the paramagnetic ionic liquid [C_2OHmim]$FeCl_3Br^-$

The magnetic ionic liquid ([C_2OHmim]$FeCl_3Br^-$) was prepared following the straightforward synthesis procedure shown in Scheme 1. A dark brown liquid was obtained by mixing equimolar amount of [C_2OHmim]Br^- and $FeCl_3.6H_2O$ in dry methanol for 24 h.

[C_2OHmim]$FeCl_3Br^-$ exhibits paramagnetism response to an external neodymium iron boride (NeFeB) magnet. A droplet of the ionic liquid is distorted, as the magnet is approached (Fig. 1).

The visible absorption spectrum was recorded on a Jenway UV–Visible spectrometer model Genova Plus in acetonitrile (0.1 M,

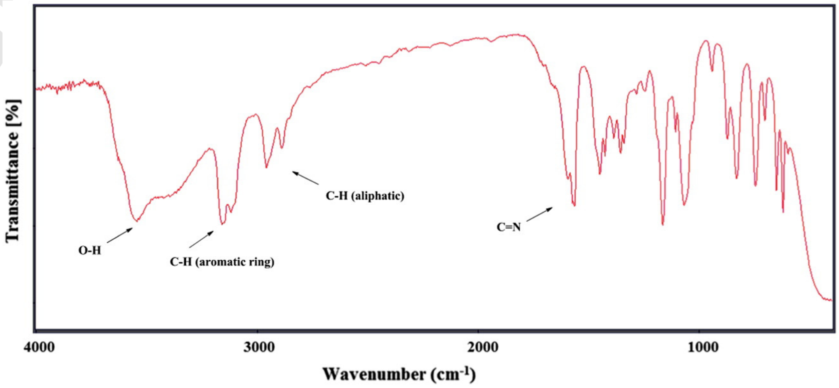

Fig. 3. FT-IR spectrum of [C_2OHmim]$FeCl_3Br^-$.

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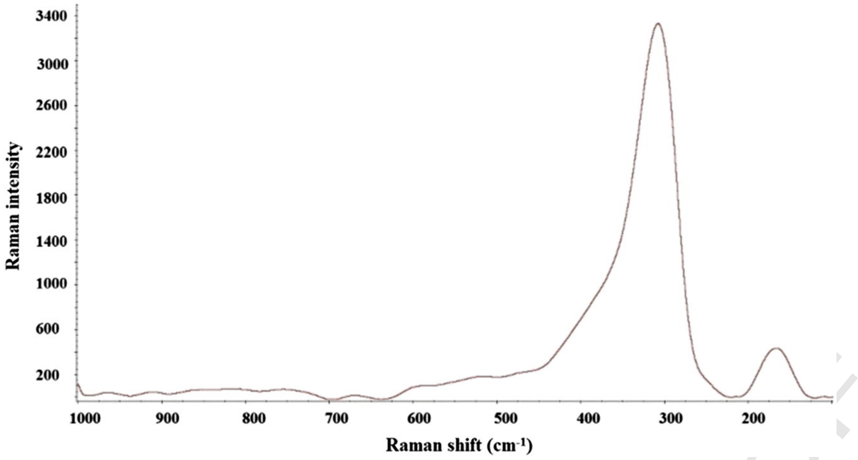


Fig. 4. Raman spectrum of [C_2OHmim]$FeCl_3Br^-$.

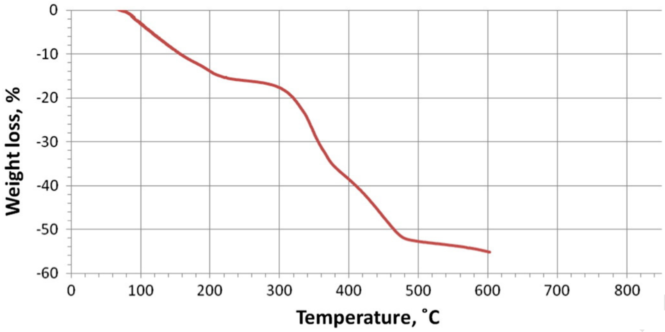


Fig. 5. TGA of [C_2OHmim]$FeCl_3Br^-$.

Table 1
Optimization of reaction condition.[a]

Entry	Catalyst (mmol)	Temperature (ºC)	Time (min)	Yield[b] (%)
1	0	85	140	34
2	1	r.t.	150	26
3	1	65	35	65
4	0.5	80	15	90
5	0.2	70	20	80
6	0.05	70	30	73
7	0.05	85	15	94

[a] Solvent-free.
[b] Isolated yield.

500–1000 nm). The MIL showed bands for the $[FeCl_3Br]^-$ ion similar to those for the $[FeBr_4]^-$ ion (Fig. 2.) [10].

The FT-IR spectrum of [C_2OHmim]$FeCl_3Br^-$ in the range of 400–4000 cm^{-1} was obtained on a BOMEM MB-Series 1998 FT-IR spectrometer. The broad peak at 3547 cm^{-1} is due to the hydroxyl group stretching vibration. The peaks at 3157 cm^{-1} and 2955 cm^{-1} are related to the stretching vibration of aromatic and aliphatic C–H bonds, respectively. Also, a relatively strong peak at 1563 cm^{-1} is assigned to C═N stretching vibration of imidazole ring (Fig. 3.).

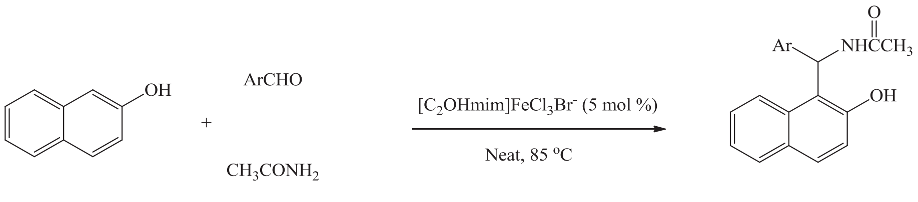
Raman measurements were carried out on an Almega Thermo Nicolet Dispersive Raman spectrometer at a wavelength of 532 nm of a Nd:YLF laser. Vibrational Raman spectrum of the MIL shows a peak at 307 cm^{1} and a shorter one at 166 cm^{-1}, which is most likely due to the formation of $FeCl_3Br^-$ anion (Fig. 4.).

The thermal stability of the MIL was investigated by the thermal gravimetric analysis (TGA) and carried out on a BÄHR-Thermoanalyse GmbH instrument from room temperature to 600 °C under nitrogen atmosphere at a heating rate of 15 °C/min. According to the TGA curve, the weight loss (<200 °C) is most probably due to the evaporation of adsorbed water. Moreover, the weight loss observed between 300 °C and 460 °C is attributed to the decomposition of the organic cation of the MIL (Fig. 5.).

3.2. Application of [C_2OHmim]$FeCl_3Br^-$ for the synthesis of 1-aminoalkyl-2-naphthols

In view of ionic liquid catalysis, the combination of $FeCl_3Br^-$ as a magnetoactive metal complex anion [8] and alcohol-functionalized imidazolium base as counter-cation [31], may have unique catalytic potential applications.

Literature surveys indicate that, there is no report in MIL-catalyzed synthesis of 1-aminoalkyl-2-naphthols. In this regard, the performance of the MIL as catalyst was tested using condensation of benzaldehyde (1.0 mmol), 2-naphthol (1.0 mmol) with acetamide (1.0 mmol) as model substrates under solvent-free conditions. As seen from the data shown in Table 1, using 5 mol% of [C_2OHmim]$FeCl_3Br^-$ was sufficient to promote the multi-component reaction efficiently at 85 °C, to afford the product in excellent yields and in appropriate reaction time (Scheme 2), and also giving turn over number (TON) and turn over frequency (TOF) up to 18.8 and 75.2 h^{-1}, respectively.



Scheme 2. One-pot synthesis of 1-aminoalkyl-2-naphthols.

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Table 2

[C_2OHmim]$FeCl_3Br^-$ catalyzes synthesis of 1-aminoalkyl-2-naphthols from 2-naphthol, aryl aldehydes and acetamide.

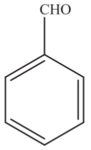
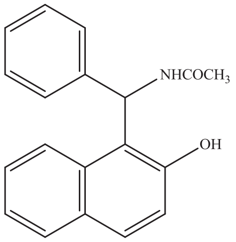
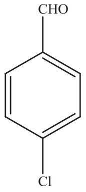
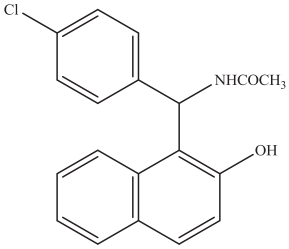
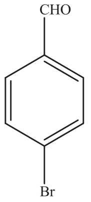
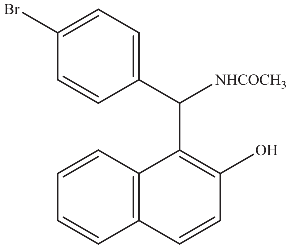
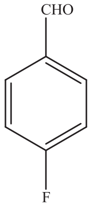
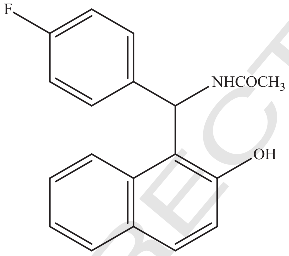
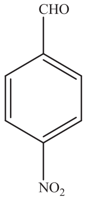
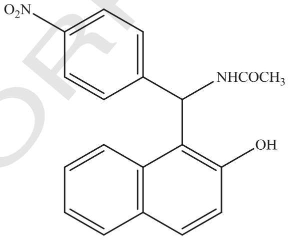
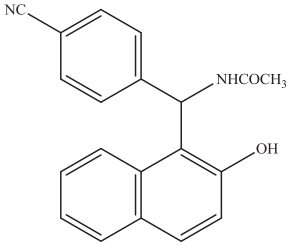
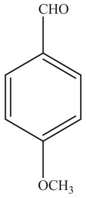
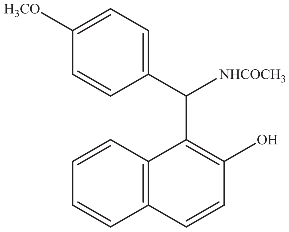
Entry	Aldehyde	Product[a]	Time (min)	Yield (%)[b]	M.p. (°C) (Lit.)
1			15	94	242–244 (238–240)
2			40	94	225–228 (220–222)
3			20	94	230–232 (228–230)
4			35	82	223–225 (226–228)
5			30	93	238–240 (246–248)
6			20	80	258–261 (260–262)
7			70	80	187–190 (183–185)

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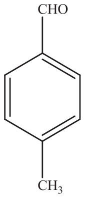
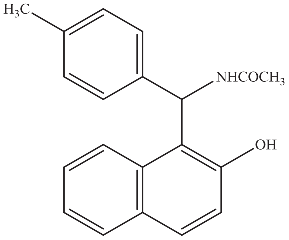
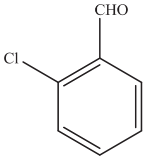
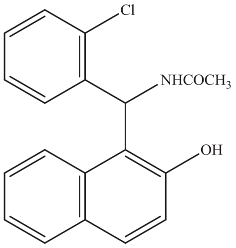
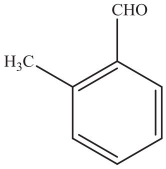
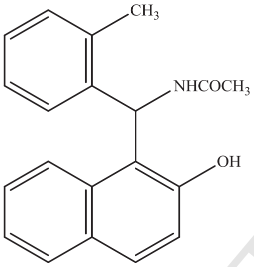
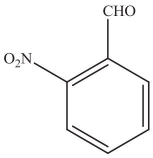
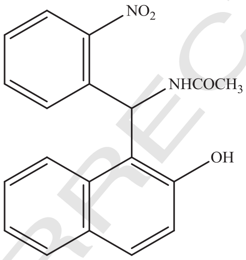
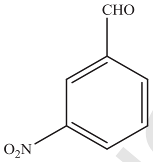
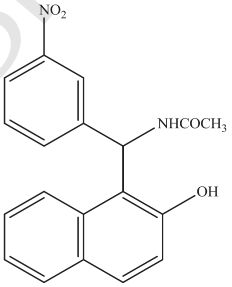
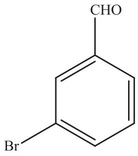
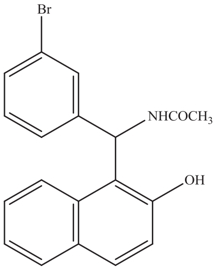
Table 2 *(continued)*

Entry	Aldehyde	Product[a]	Time (min)	Yield (%)[b]	M.p. (°C) (Lit.)
8			40	87	221–224 (223–225)
9			45	92	206–210 (197–199)
10			60	91	202–205 (197–199)
11			75	90	188–191 (177–179)
12			15	91	236–239 (238–240)
13			10	87	238–241 (245–247)

(continued on next page)

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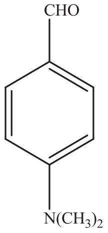
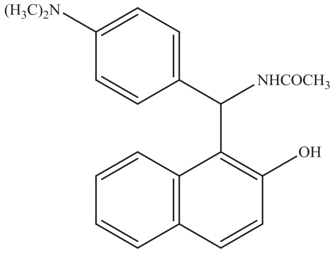
Table 2 *(continued)*

Entry	Aldehyde	Product[a]	Time (min)	Yield (%)[b]	M.p. (°C) (Lit.)
14			110	94	125–128 (119–121)

[a] All products are known and were identified by comparison of their physical and spectral data with those of authentic samples [25,27,32].
[b] Isolated yield.

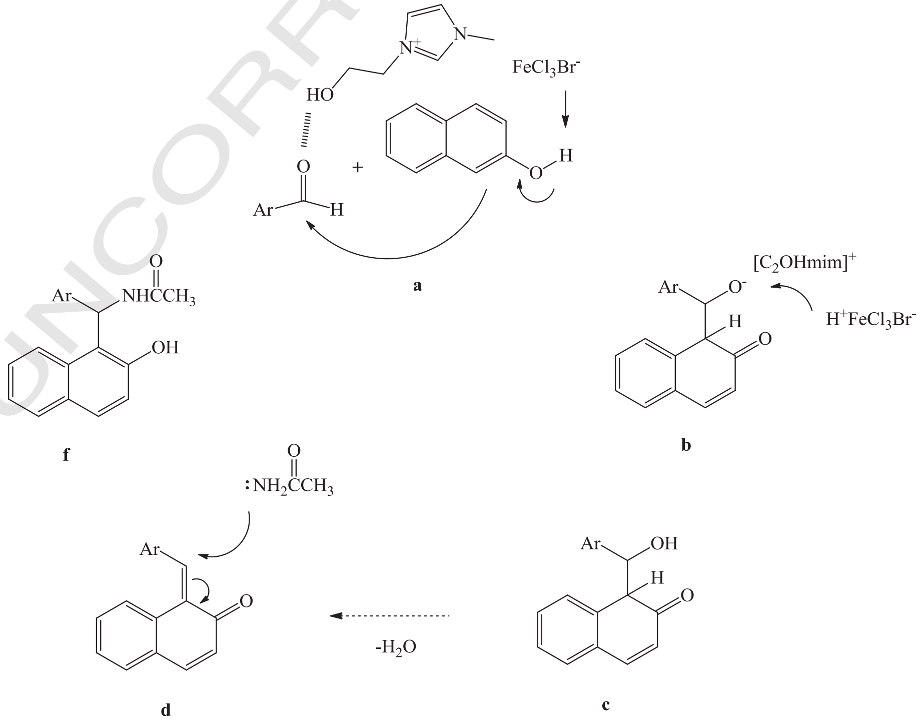
With these optimized conditions in hand, we decided to examine the scope and limitation of this MIL-catalyzed reaction. A wide variety of aryl benzaldehydes were applied and the results showed a highly effective performance of the catalyst in the preparation of 1-aminoalkyl-2-naphthols as shown in Table 2. According to Table 2, the electron-withdrawing groups enhance the reaction (entry 5, 6, 12) relative to electron-donating groups, which decrease the reaction rate (entry 7, 14). These effects can be explained in this way that, in the α,β-unsaturated intermediate (Scheme 3 (d)), the β-carbon is more electrophilic with electron-withdrawing groups thus the rate is increased. It is also noteworthy that the reaction time for the ortho-substituted-substrates are prolonged; due to the steric hindrance.

It has been assumed that, magnetic ionic liquids could act as efficient catalysts due to the synergic effect of the cation and anion [14]. A plausible mechanism to rationalize this catalytic condensation is illustrated (Scheme 3). Initially, the carbonyl group in aldehyde is activated by the [C2OHmim]$^+$ cation and meanwhile $FeCl_3Br^-$ anion interacts with the hydrogen in hydroxyl group of 2-naphthol. Hence, the nucleophilic attack becomes easier to obtain ortho-quinomethide (c). Finally, through condensation of (c) with acetamide after H^+ transferring by the catalyst, the desired 1-aminoalkyl-2-naphthol is generated.

To show the efficiency and superiority of using [C_2OHmim]$FeCl_3Br^-$ as catalyst for the synthesis of 1-amidoalkyl-2-naphthols, this procedure has been compared with that of the previously reported methods in Table 3.

4. Conclusion

In conclusion, we have prepared a novel paramagnetic ionic liquid, 3-(2-hydroxyethyl)-1-methyl imidazolium bromotrichloro ferrate (III) and characterized it by FT-IR, TGA, UV–Visible and Raman spectroscopy. The MIL shows remarkable catalytic activity in the preparation of 1-amidoalkyl-2-naphthol derivatives. In addition, the procedure provides some advantages like easy workup, short reaction time and high isolated yields.



Scheme 3. The proposed mechanism for [C_2OHmim]$FeCl_3Br^-$-catalyzed synthesis of 1-amidoalkyl-2-naphtols.

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Table 3
Comparison of various catalytic protocols with the MIL for the reaction of 2-naphthol with benzaldehyde and acetamide.

Entry	Catalyst, condition	Time (min)	Yield (%)
1	Graphite-$HClO_4$, solvent-free/125 °C [29]	120	81
2	MCM-41-*N*-propylsulfamic acid, solvent-free/130 °C [24]	120	97
3	[TEBSA][HSO_4], solvent-free/120 °C [33]	10	87
4	4-(1-Imidazolium) butane sulfonate, solvent-free/120 °C [34]	120	80
5	H_3BO_3, solvent-free/120 °C [35]	6	80
6	Silica sulfuric acid, solvent-free/r.t. [36]	270	30
7	[C_2OHmim]$FeCl_3Br^-$, solvent-free/85 °C [this work]	15	94

Acknowledgments

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