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Magnetic Ionic Liquid Functionalized Sulfonic Acid: a Green and Efficient Catalyst for the One-pot Synthesis of 1-Amidoalkyl-2-Naphthols

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Abstract

In this study, a novel acidic magnetic dicationic ionic liquid was prepared in three steps to serve as a green catalyst in organic synthesis. The newly synthesized catalyst was characterized by FT-IR, UV- VIS, and VSM analysis. Additionally, the decomposition steps and thermal stability of the catalyst were investigated by thermal analysis techniques (TGA/DSC). The synthesized acidic magnetic dicationic ion liquid has a magnetization of about 0.3 emu/g, which is less than $FeCl_3$ (o.7 emu.g- 1). Moreover, the catalytic activity of this acidic ionic liquid was successfully tested in the straight forward one-pot synthesis of 1-amidoalkyl-2-naphthol derivatives via three-component reaction between β-naphthol, aldehyde, and acetamide or Benzamide under solvent-free conditions. The pure products were determined by analyzing their physical data (melting points, IR).This method has several advantages such as easy work-up, not using a volatile organic solvent, high yield, and high atom economy. The catalyst can be reused and recovered without losing activity.

Keywords: 1-amidoalkyl-2-naphthols, Multicomponent reaction, acidic dicationic ionic liquid, solvent-free.

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Introduction

Recently, organic chemical reactions have been considered in green chemistry and the reduction of environmental impacts. Green chemistry methodology has progressed various factors such as increased manufacturing efficiency, lowered production energy requirement, recycling of reagents, reduced solvent utilization, less waste generation, and lowered the production cost. Along with this line, we've recently found that the oxidation reaction with air, performing the reaction in ionic liquid as a catalyst or solvent, and the use of water as a reaction medium [1]. Also, ionic liquids (IL) have been considered for organic synthesis as a solvent or catalyst due to their unique properties, including low vapor pressure, high thermal stability, low viscosity, and high ionic conductivity. Ionic fluids are defined as salts that are liquid at room temperature. They are generally composed of mineral anions and organic cations[2-4].

The dicationic ionic liquids include two asymmetric or symmetric cationic head groups which might be joined to each other by a tight or flexible alkyl bridge chain. Geminal dicationic ionic liquids (ILs) often show higher thermal stability, density, and viscosity compared to traditional mono-cationic ILs [5-7]. Among them, Bronsted acidic ionic liquids have applications in several reactions such as esterification of carboxylic acids, oxidation of alcohols, Munich reaction, polymerization, and multicomponent reactions. These compounds are designed to replace solid acids and traditional mineral acids such as sulfuric acid and hydrochloric acid. In these compounds, the alkylated group of sulfonic acid is linked to the ionic liquid cation and acts as a strong acid. These ionic liquids, which have a functional group (SO_3H), have the highest potential for using instead of the corrosive mineral acid catalyst and other homogeneous and heterogeneous catalysts. This class of catalysts has several benefits, such as flexible, non-corrosiveness, non- volatile, and immiscible with organic solvents[8-13].

Multi-component reaction (MCR) is a reaction in which two or more reactants react in one step and produce a new product. This method has several advantages, such as reducing the processes of purification, extraction, crystallization, reducing time, and increasing efficiency. It is also associated with reducing environmental damage and increasing the health of humans [14].The derivatives of 1-amidoalkyl, 2-naphthols are useful compounds in organic synthesis. This is due to their conversion into bioactive compounds, which display the number of pharmacological properties including improvement of heart disease and blood pressure. These compositions can be prepared by the presence of small amounts of aldehydes, β-naphthols, and acetonitrile or amides in the presence of Lewis or Brønstead acids such as iodine. As mentioned above, although the methods used to synthesize these compounds are useful, some of them have limitations such as a long time, the use of toxic solvents such as chloroform anddichloromethane, the use of toxic and expensive catalysts, low yields of products. Given these limitations, it is important to provide new methods for the synthesis of these compounds [15-.26]

According to our studies, and in continuation of our work on the catalytic properties of magnetic ionic liquids [27], for the first time, we decided to investigate the synthesis a novel acidic magnetic dicationic ionic liquid, AMDIL, which contained two acidic functional groups as well as a magnetic group. This catalyst has all the benefits of acidic ionic liquids and magnetic ion liquids. In continue,we investigated the catalytic effects of this catalyst in the one pot, multicomponent synthesis of 1-amidoalkyl-2-naphtholderivatives.

Experimental

Material

Melting points were measured on an Electro thermal 9100 apparatus and were uncorrected.^{1}H &^{13}C-NMR spectra were recorded on a Bruker Advanced DPX 400 MHz instrument spectrometers using TMS as the internal standard in $CDCl_3$. IR spectra have been recorded on a BOMEM MB-Series 1988 FT-IR spectrometer. Chemical substances employed in this study such as ß-Naphthol, aromatic aldehydes, acetamide, and imidazole were bought from Merck Company in high purity. Products were characterized by comparison of their physical and spectroscopic data with those of known samples. The purity of products and reaction monitoring was accomplished by TLC on silica gel PolyGram SILG/UV 254 plates.

Synthesis of 1,6-di(1H-imidazole-1-yl)hexane (C_6BIM)

Imidazole (8.2 g, 0.12 mol) was melted at around 100 °C and NaOH (4 g, 0.1 mol) was added. After the solid NaOH thawed, toluene (50 mL) was added and heated to remove water by an azeotropefor 3 h. Toluene was evaporated under reduced pressure. 'Subsequently' the solution of 1, 6-dibromohexane (14 g, 0.06 mol) in CH_3CN (80 mL) was added. The mixture was stirred at70 °C for 12 h. The solvent was removed by distillation, the residue dissolved in CH_2Cl_2 and washed with waterseveraltimestoremoveinorganicsaltsandexcessimidazole.Aftereliminationofsolvent,
20.5 g of the desired compound (C_6BIM) was obtained (yield 89 %).

Procedure for preparation of 1,6-di(1H-imidazole-yl)hexane bis N-sulphonic acid 1,6-hexyl (1,6-diyl) bis imidazole-bis sulfonic acid (([C_6BIM]$(HSO_3)_2Cl_2$))

A round-bottomed flask (50 mL) was taken with C_6BIM (0.492 g, 6.0 mmol) in dry CH_2Cl_2 (10 mL), and then chlorosulfonic acid (0.700 g, 6.0 mmol) was added dropwise over 10 min and the solution was left for cooling in ice-bath. After cooling, 6.0 mmol of sulfuric acid (0.588 g) was added slowly over 40 min at the temperature less than 10 °C. The resulting mixture was put on stirring for 8h under pressure of nitrogen (to remove the produced HCl), and increase the temperature up to 45 °C. Furthermore, after a gap of 60 min, dichloromethane (CH_2Cl_2) was decanted. The residue was washed with dry CH_2Cl_2 (3 × 20 mL) and vacuum drying that resulted in a 95% yield.

Procedure for preparation of $[C_6BIM]\ (HSO_3)_2(FeBr_3Cl)_2$

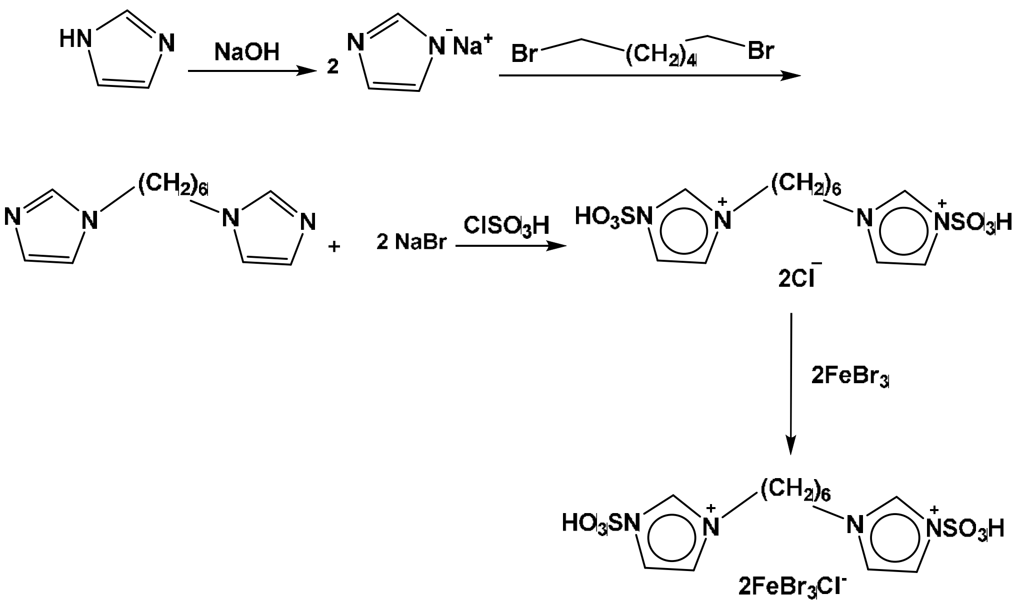
$[C_6BIM]\ (HSO_3)_2(FeBr_3Cl)_2$ was prepared by mixing $[C_6BIM](HSO_3)_2Cl_2$ (1 mmol) with anhydrous $FeBr_3$ (2 mmol) at room temperature for 3h, a brown liquid was obtained. The obtained product was extracted with a small amount of ethyl acetate. The solvent was evaporated and the resulting clear brown liquid was dried in a vacuum oven at 60 °C for 24 h. The catalyst was obtained in high yield (87 %).

Synthesis of 1-amidoalkyl-2-naphthol derivatives: General Procedure

In a typical synthesis reaction, a mixture of β-naphthol(1mmol), aldehyde (1 mmol), acetamide or benzamide (1.2mmol) and AMDIL (0.1 g) was heated at 100 °C for 30 min. The completion of the reaction was indicated by TLC. After completion of the reaction, it was cooled to room temperature. Then, 10mL of water was added to the mixture. The ionic liquid was dissolved in water, and filtered for separation of the crude product. The separated product was washed twice with water (2 × 5 mL). Finally, the crude productwas purified through recrystallization from hot ethanol. All of the desired products were characterized by a comparison of theirspectral data and melting points.

Results and Discussion

In recent years, ionic liquids have been considered as catalyst or solvent in organic reactions and separation approaches.Herein, we designed and synthesized a new acidic magnetic dicationic ionic liquid,as a catalyst, for facile synthesis of 1-amidoalkyl-2 naphthols. At first, the reaction of imidazole andsodium hydroxide was performed in toluene as a solvent to afford imidazolium salt. Secondly, reacting with 1, 6-dibromohexane to afforded1,6-hexyl bis imidazole (C_6BIM).Then adding chlorosulfonic acid and washing with CH_2Cl_2. HCl gas as a by- product can be removed from the environment and neutralized in a solution of ammonia. In the final stage, the Cl^- was exchanged with $FeBr_3Cl^-$anion by the reaction of $FeBr_3$. The AMDIL was obtained with high efficiency (Scheme1). Due to the paramagnetic nature of the AMDIL, nuclear magnetic resonance technique could not be used to confirm its structure. Instead, UV, FT-IR, TGA, and VSM were used to identify magnetic ion liquid.



$[C_6BIM](SO_3H)_2(FeBr_3Cl)_2$

AMDIL

Scheme 1. Synthesis of $[C_6BIM]\ (HSO_3)_2(FeBr_3Cl)_2$.

The FT-IR spectra of acidic magnetic dicationic ionic liquid (AMDIL)/ $[C_6BIM]\ (HSO_3)_2\ (FeBr_3Cl)_2$ is presented in Figure 1. The peaks at 1171 and 1325.01cm^{-1} are related to the symmetric and asymmetric SO_2 stretching vibrations. The band in 28757 cm^{-1} reign may be attributed to the C-H aliphatic bending vibration, while the band at 1079 cm^{-1} is due to the S-OH group. The band at 1634 cm^{-1} is assigned to the stretching vibration of C=N. The symmetric S–N stretching vibration found at 744 cm^{-1}, while the broad peak at 3200–3550 cm^{-1} can be attributed to the hydroxyl groups in the acidic ionic liquid. These special peaks of the FT-IR confirmed that sulfonic groups were successfully introduced in the functional acidic ionic liquid.

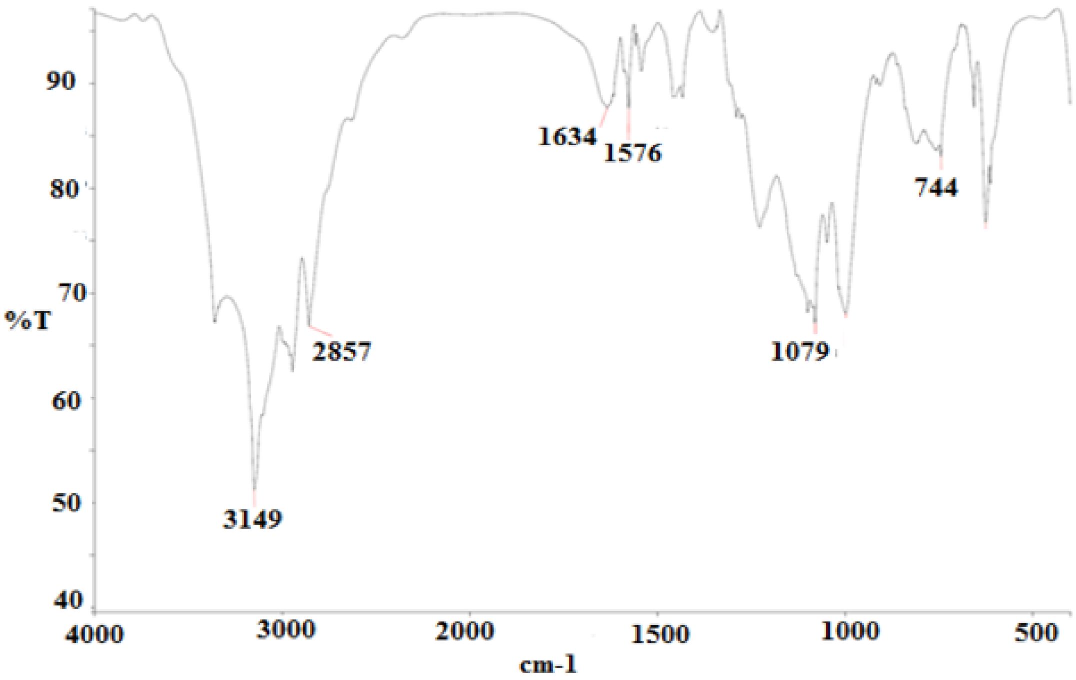


Figure 1. The FT-IR spectra of $[C_6BIM](HSO_3)_2(FeBr_3Cl)_2$.

The visible absorption spectrum was recorded on a Jenway UV–Visible spectrometer model Genova Plus in acetonitrile (0.1M, 300-800 nm). The AMDIL showed bands for the $[FeCl_3Br]$ ion similar to those for the $[FeCl_4^-]$ ion (Figure 2). The characteristic peak at 368 nm is due to the absorption band of $[FeCl_3Br]$ anion.

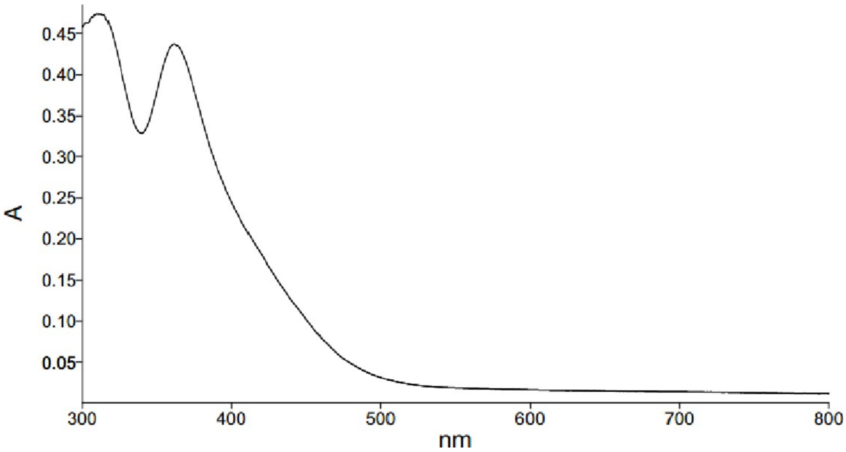


Figure 2. Visible spectrum of $[C_6BIM](HSO_3)_2(FeBr_3Cl)_2$

The magnetic property of a magnetic ionic liquid was measured by VSM. This technique is used to measure the magnetization of magnetic particles under an external field. For particles with a paramagnetic behavior, when the external magnetic field is eliminated, these particles do not show complete magnetization. The synthesized magnetic ion liquid has a magnetization of about 0.3 emu/g, which is less than $FeCl_3$ (o.7 emu.g^{-1}). Magnetic susceptibility of AMDIL is decreased due to the presence of non-magnetic fraction (alkyl groups) in the structure of AMDIL (Figure3).

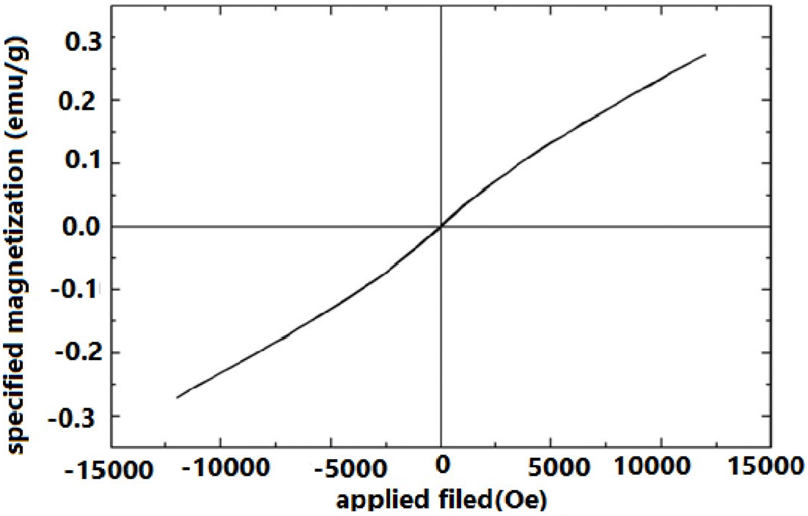


Figure 3. VSM of catalyst.

The thermal stability of the catalyst was achieved by thermal gravimetric analysis (TGA) and carried out on a BÄHR-Thermo analyze GmbH instrument from room temperature to 800 °C under a nitrogen atmosphere at a heating rate of 10 °C/min. The overall TGA loos profile can be divided into two sections: 30 to 300 °C; 300 to 800 °C. According to the TGA crave, the weight loss in the range of 30 to 300 °C is related to the evaporation of adsorbed water. The weight loss observed between 300-800 °C corresponds to the decomposition of the organic fraction of the AMDIL. According to the differential scanning calorimeter (DSC) result (data not shown), a major endothermic peak at 285 K was observed, which could be assigned to the melting point of AMDIL.

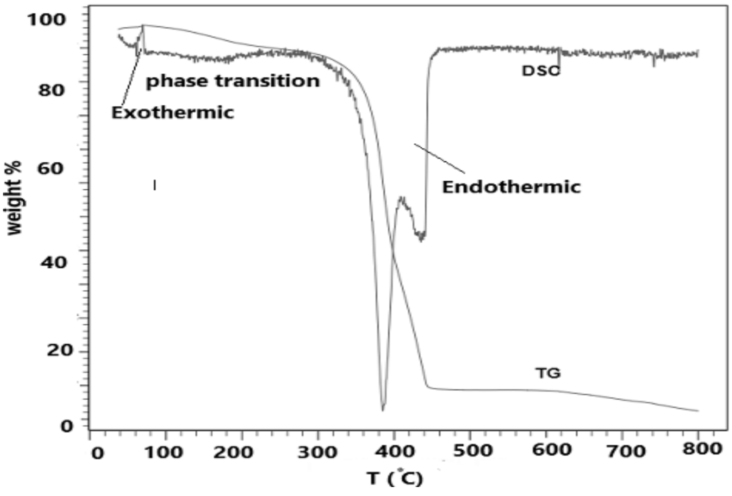


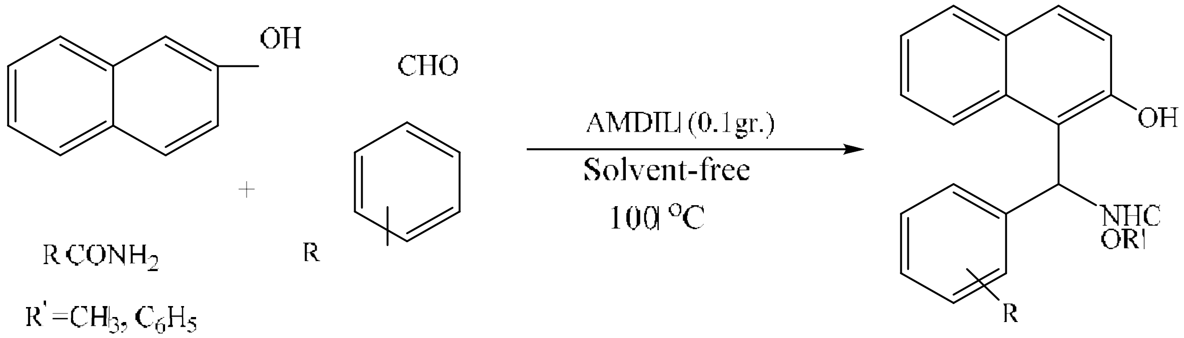
Figure 4. TGA of catalyst.

The catalytic activity of the AMDIL catalyst was studied by the reaction between 1 mmol ß-naphtol, 1mmol benzaldehyde and 1.2 mmol acetamide under solvent-free conditions. The reaction was carried out in the presence of different amounts of catalyst, and temperature. The results are presented in Table 1. Based on the results, 0.1 g of catalyst, 100 °C, and solvent-free conditions were selected as optimal conditions.

Table 1. Effect of the amount of catalyst, and temperature in the synthesis of 1-amidoalkyl-2 naphthol.

Temperature/°C	AMDIL (gr)	Time (min)	Yield (%)
25	0.1	120	0
60	0.1	100	40
80	0.1	80	66
100	0.1	15	90
120	0.1	15	90
100	0.1	120	0
100	0.05	100	65
100	0.15	15	90
100	0.2	15	90

As shown in Table 2, aromatic aldehydes containing electron-withdrawing and donating groups reacted successfully in the presence of AMDIL as catalyst, and uniformly converted to the same products with high yields within 15 to 20 minutes (Scheme 2). The substituent on the aromatic ring had no obvious effect on the yield or reaction time under the optimal conditions. Unlike some previously reported methods, the present method does not require toxic organic solvents to produce the 1-amidoalkyl-2-naphthol derivatives [32].All the products were characterized and identified by comparison of their spectral data (IR, ^{1}H NMR and, ^{13}CNMR) with those of authentic samples.



Scheme 2: Synthesis of 1-amidoalkyl-2-naphthols catalyzed by AMDIL.

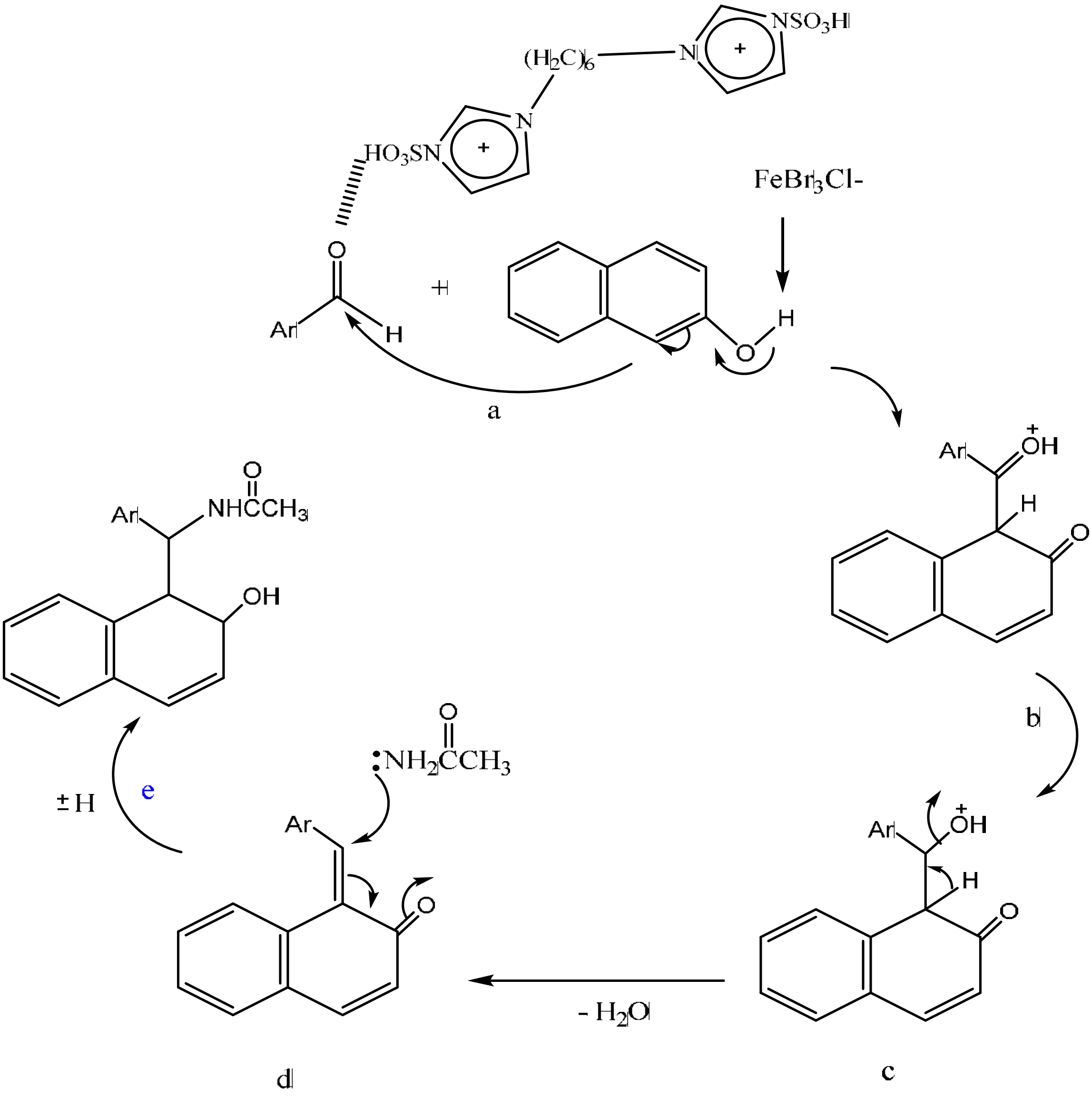
Table 2. One-pot synthesis of 1-amidoalkyl-2-naphthols with different aldehydes catalyzed by AMDIL under solvent free conditions

Entry	**R**	**R'**	**Time (min)**	**Yield (%)**^{b}	**M.P. (°C)**	
					Found	**Reported**
1	H	CH_3	15	90	228-230	227-229 [28]
2	4-Cl	CH_3	15	87	235-237	237-238 [29]
3	4-NO_2	CH_3	10	88	243-245	245-247 [30]
4	4-CH_3	CH_3	15	86	221-223	222-223 [29]
5	2, 4-Cl_2	CH_3	15	87	201-203	201-203 [28]
6	4-CH_3O	CH_3	20	87	180-182	181-183 [29]
7	H	C_6H_5	15	87	232-234	234-236 [30]
8	4-Cl	C_6H_5	10	89	233-235	235-238 [30]
9	4-NO_2	C_6H_5	15	87	238-240	238-240 [30]
10	4-CH_3	C_6H_5	15	86	216-218	215-216[30]
11	2, 4-Cl_2	C_6H_5	15	84	258-260	262-263 [30]
12	3-CH3O	C6H5	15	87	217-220	216 [30]

^{a}All reactions were carried out using β-naphthol (1mmol), aldehyde (1mmol), acetamide or Benzamide (1.2mmol) and AMDIL (0.1 g)

^{b}Isolated yields

It seems that magnetic acidic ionic liquids could act as efficient catalysts due to the synergic impact of the cation and anion. A plausible reaction mechanism to rationalize this catalytic MCR which is depicted in Scheme 3. Initially, the carbonyl group in aldehyde is activated by the [SO_3H] cation and 'meanwhile' $FeBr_3Cl^-$ anion interacts with the hydrogen in the hydroxyl group of 2-naphthol. Consequently, the nucleophilic attack becomes to achieve ortho-quinone methide (c). Finally through condensation of (c) with acetamide in a Michael-type style, is generated the desired product.



Scheme 3. Possible mechanism for promotion of reaction by AMDIL.

The achievement of the above reactions has led us to investigate the recyclability of catalyst. We have done our study using benzaldehyde, β-naphthol, and acetamide in optimal conditions as a model study. After completion of the reaction, water was added and the precipitated mixture was filtered to separate pure products. After washing the solid products, the ionic liquid-containing water (IL solution) evaporates under reduced pressure and ionic liquids are recovered (Table3). The catalyst could be reused for four times without considerably decrease in catalytic activity.

Table 3. Recycling studies of preparation N-(2-hydroxynaphtalen-1-yl)-phenyl-methyl]-acetamide.

Run	1	2	3	4
Yield (%)	90	86	83	79

The efficiency of AMDIL (time, yield reaction conditions) are compared with efficiency of othercatalysts in synthesis of 1-amidoalkyl-2-naphthols andthe results are presented in Table 4. Otherwise' other methods have disadvantages, and limitations, which including the long reaction time [32, 35], using of a relatively large amount of catalysts[34], expensive catalysts, high temperature [31, 33, 34], and toxic solvents [32], while the present method not only comparable in efficiency to the methods mentioned, but also has several advantages such as short reaction time,non-use of toxic solvents or volatile organic compounds, ease of product separation, and reducing environmental impacts.

Table 4. Comparison of efficiency of various catalysts in the synthesis of 1-amidoalkyl-2-naphthols.

Conditions	**Time (h)**	**Yield (%)**	**Ref.**
Ce $(SO_4)_2$, CH_3CN, reflux	36	72	[32]
Fe $(HSO_4)_3$, 85°C	20	56	[35]
I_2, 125°C	4.5	87	[33]
K-10 clay, 125°C	1.5	89	[31]
$K_5CoW_{12}O_{40}$. $3H_2O$ (1mol %)	2	90	[34]
AMDIL/Solvent-free/100 °C	15min	90	this work

Conclusion

In summary, we have provided a simple and green catalytic procedure for the efficient synthesis of 1-amidoalkyl-2-naphthol derivatives using acidic dicationic ionic liquid under solvent-free conditions. The acidic dicationic ionic liquid can be replace the corrosive mineral acid and other homogeneous or heterogeneous catalysts with reasonable recovery and reusability and therefore has great potential for use in green processes.

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