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Rapid synthesis of 1-amidoalkyl-2-naphthols over sulfonic acid functionalized imidazolium salts

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ABSTRACT

Novel sulfonic acid functionalized imidazolium salts including 3-methyl-1-sulfonic acid imidazolium chloride {[Msim]Cl} (an ionic liquid), 1,3-disulfonic acid imidazolium chloride {[Dsim]Cl} (an ionic liquid) and 3-methyl-1-sulfonic acid imidazolium tetrachloroaluminate {[Msim]$AlCl_4$} (a solid) efficiently catalyze one-pot multi-component condensation of β-naphthol with aromatic aldehydes and amide derivatives under solvent-free conditions to afford 1-amidoalkyl-2-naphthols in excellent yields (81–96%) and in very short reaction times (1–40 min).

1. Introduction

Ionic liquids (based imidazolium or other organic cations) have received considerable interest as eco-friendly solvents, catalysts and reagents in green synthesis because of their unique properties, such as low volatility, nonflammability, high thermal stability, negligible vapor pressure and ability to dissolve a wide range of materials [1–9]. Among them, Brønsted acidic ionic liquids have designed to replace solid acids and traditional mineral liquid acids like sulfuric acid and hydrochloric acid in chemical procedures [10–14].

As mentioned imidazolium salts having a Brønsted acidic group are of importance, and they have been successfully utilized as catalyst in organic synthesis. These subjects encouraged us to synthesize some functionalized imidazolium salts, with Brønsted acidic property, including ionic liquid 3-methyl-1-sulfonic acid imidazolium chloride {[Msim]Cl} [10–12], ionic liquid 1,3-disulfonic acid imidazolium chloride {[Dsim]Cl} and 3-methyl-1-sulfonic acid imidazolium tetrachloroaluminate {[Msim]$AlCl_4$} (as a solid) (Fig. 1). We wish to use them as catalysts for different organic transformations. Herein, we have found that the synthesis of 1-amidoalkyl-2-naphthols from β-naphthol, aromatic aldehydes and amide derivatives can be efficiently performed in the presence of these imidazolium salts.

1-Amidoalkyl-2-naphthol derivatives are of importance as they can be easily converted to biologically active compounds, 1-aminoalkyl-2-naphthols, by amide hydrolysis reaction. Hypotensive and bradycardiac properties have been reported for this class of compounds [15–17]. 1-Amidoalkyl-2-naphthols can be also converted to 1,3-oxazine derivatives [18]. 1,3-Oxazines have potentially different biological activities including antibiotic [19], antitumor [20], analgesic [21], anticonvulsant [22], antipsychotic [23], antimalarial [24], antianginal [25], antihypertensive [26], and antirheumatic properties [27]. One-pot multi-component condensation of β-naphthol with aromatic aldehydes and amide derivatives or acetonitrile has been used as a practical synthetic route toward 1-amidoalkyl-2-naphthols [28–43]. Several Lewis and Brønsted acids have been applied to catalyze this transformation, such as $Ce(SO_4)_2$ [28], *p*-toluenesulfonic acid [29], iodine [30], cation-exchanged resins [31], $Fe(HSO_4)_3$ [32], sulfamic acid/ultrasound [33], $HClO_4/SiO_2$ [34], wet cyanuric chloride [35], trityl chloride [36], $H_3PW_{12}O_{40}$ [37], P_2O_5 [38], 4-(1-imidazolium)butane sulfonate [39], *N*-(4-sulfonic acid)butyl triethylammonium hydrogensulfate [40], 1-butyl-3-methylimidazolium hydrogen sulphate [41], $Cu_{1.5}PW_{12}O_{40}$ [42], and silica sulfuric acid [43]. Nevertheless, many of the reported methods are associated with one or more of the following draw-

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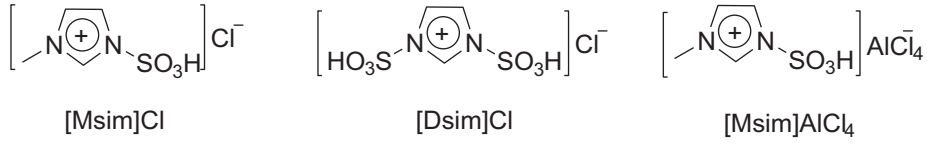


Fig. 1. Structures of 3-methyl-1-sulfonic acid imidazolium chloride {[Msim]Cl}, 1,3-disulfonic acid imidazolium chloride {[Dsim]Cl} and 3-methyl-1-sulfonic acid imidazolium tetrachloroaluminate {[Msim]$AlCl_4$}.

backs: (i) low yields, (ii) long reaction times, (iii) the use of large amount of catalyst, (iv) the use of toxic or expensive catalysts, (v) inefficiency of method when aromatic amides or urea are used in the reaction, and (vi) no agreement with the green chemistry protocols. Thus, search for finding an efficient, general and nonpolluting method for the synthesis of 1-aminoalkyl-2-naphthols is still of practical importance.

In this paper, we report our results on the efficient and rapid synthesis of 1-amidoalkyl-2-naphthols from β-naphthol, aryl aldehydes and amides/urea in the presence of catalytic amounts of the functionalized imidazolium salts, [Msim]Cl, [Dsim]Cl or [Msim]$AlCl_4$, under solvent-free conditions (Scheme 1). Interestingly, this method for the preparation of 1-amidoalkyl-2-naphthol derivatives has none of the above-mentioned drawbacks at all.

2. Experimental

All chemicals were purchased from Merck or Fluka Chemical Companies. The known products were identified by comparison of their melting points and spectral data with those reported in the literature. Progress of the reactions was monitored by TLC using silica gel SIL G/UV 254 plates. The reaction conversions were measured by GC on a Shimadzu model GC-16A instrument using a 25 m CBPI-S25 (0.32 mm ID, 0.5 μm coating) capillary column. The ^{1}H NMR (250 or 300 MHz) and ^{13}C NMR (62.5 or 75 MHz) were run on a Bruker Avance DPX-250 FT-NMR spectrometer (δ in ppm). Microanalyses were performed on a Perkin-Elmer 240-B microanalyzer. Melting points were recorded on a Büchi B-545 apparatus in open capillary tubes.

2.1. General procedure for the preparation of ionic liquid [Msim]Cl (Fig. 1)

A round-bottomed flask (100 mL) was charged with 1-methylimidazole (0.410 g, 5 mmol) in dry CH_2Cl_2 (50 mL), and then chlorosulfonic acid (0.605 g, 5.2 mmol) was added dropwise over a period of 5 min at room temperature. After the addition was completed, the reaction mixture was stirred for 20 min, stand for 5 min, and the CH_2Cl_2 was decanted. The residue was washed with dry CH_2Cl_2 (3 × 50 mL) and dried under vacuum to give [Msim]Cl as a viscous colorless oil in 92% yield, 0.912 g [10–12].

2.1.1. Spectral data of [Msim]Cl

Viscous colorless oil (lit. [10–12] viscous colorless oil); ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) 3.77 (s, 3H, CH_3), 7.46 (s, 1H), 7.51 (s, 1H), 8.84 (s, 1H), 13.96 (s, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ (ppm) 36.5, 120.6, 124.2, 136.6; MS: *m/z* = 199 (M^++1), 198 (M^+), 183 (M^+–CH_3), 163 (M^+–Cl), 82 (M^+–$ClSO_3H$), 67 (M^+–CH_4ClSO_3).

2.2. Procedure for the preparation of ionic liquid [Dsim]Cl (Fig. 1)

To a round-bottomed flask (100 mL) containing imidazole (0.340 g, 5 mmol) in dry CH_2Cl_2 (50 mL), was added chlorosulfonic acid (1.1885 g, 10.2 mmol) dropwise over a period of 20 min at room temperature. After the addition was completed, the reaction mixture was stirred for 12 h under pressure of nitrogen (to remove the produced HCl), stand for 5 min, and the CH_2Cl_2 was decanted. The residue was washed with dry CH_2Cl_2 (3 × 50 mL) and dried under vacuum to give [Dsim]Cl as a viscous pale yellow oil in 95% yield, 1.257 g.

2.2.1. Spectral data of [Dsim]Cl

Pale yellow oil; ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) 7.34 (s, 2H), 8.67 (s, 1H), 13.34 (s, 2H); ^{13}C NMR (75 MHz, DMSO-d_6): δ (ppm) 119.5, 134.3; MS: *m/z* = 265 (M^++1), 264 (M^+), 229 (M^+–Cl), 148 (M^+–$ClSO_3H$), 67 (M^+–$2ClSO_3H$).

2.3. Procedure for the preparation of [Msim]$AlCl_4$ (Fig. 1)

A round-bottomed flask (50 mL) was charged with 3-methyl-1-sulfonic acid imidazolium chloride (0.9931 g, 5 mmol), and then $AlCl_3$ (0.6667 g, 5 mmol) was added over a period of 5 min at 50 °C. Afterward, the reaction mixture was stirred for 30 min at 50 °C to give [Msim]$AlCl_4$ as a white powder in 98% yield, 1.623 g.

2.3.1. Spectral data of [Msim]$AlCl_4$

White powder, mp 391 °C (dec.); ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) 3.83 (s, 3H, CH_3), 7.57 (s, 1H), 7.63 (s, 1H), 9.02 (s, 1H), 12.24 (s, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ (ppm) 35.8, 120.1, 123.5, 136.3; MS: *m/z* = 332 (M^++1), 331 (M^+), 316 (M^+–CH_3), 168 (M^+–$C_4H_7N_2O_3S$), 163 (M^+–$AlCl_4$), 82 (M^+–SO_3HAlCl_4).

2.4. General procedure for the synthesis of 1-amidoalkyl-2-naphthols ***1a–t***

To a well-ground mixture of β-naphthol (0.288 g, 2 mmol), aldehyde (2 mmol) and amide derivative (2.4 mmol) in a 10 mL round-bottomed flask connected to a reflux condenser, was added the catalyst (0.2 mmol), and the resulting mixture was stirred in an oil-bath (120 °C). After completion of the reaction, as monitored with TLC, the reaction mixture was cooled to room temperature, and was added to a column chromatography on silica gel, and eluted with EtOAc/*n*-hexane (1/1) to give the pure product.

Note: When liquid aldehydes were applied in the reaction, at first, β-naphthol and amide derivative were ground, and subsequently aldehyde and the catalyst were added.

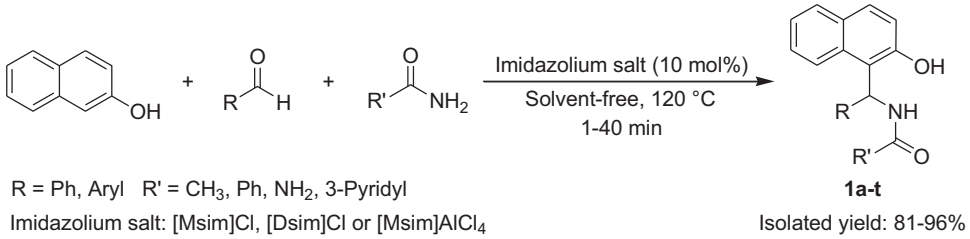
2.5. Selected spectral data of the products ***1a–t***

2.5.1. *N*-[(2-hydroxynaphthalen-1-yl)(phenyl)methyl)]acetamide (***1a***)

White solid; mp 238–240 °C (lit. [28] mp 241–243 °C); ^{1}H NMR (250 MHz, DMSO-d_6): δ (ppm) 2.06 (s, 3H), 7.01–7.20 (m, 9H), 7.65–7.73 (m, 3H), 8.11 (d, *J* = 7.7 Hz, 1H), 9.69 (s, 1H); ^{13}C NMR (62.5 MHz, DMSO-d_6): δ (ppm) 23.5, 41.3, 118.8, 120.2, 122.0, 123.9, 124.9, 125.7, 127.6, 128.1, 128.3, 128.5, 128.6, 134.2, 144.0, 152.6, 169.6.

2.5.2. *N*-[(2-hydroxynaphthalen-1-yl)(3-nitrophenyl)methyl)]acetamide (***1g***)

Pale yellow solid; mp 238–240 °C (lit. [33] mp 236–237 °C); ^{1}H NMR (250 MHz, DMSO-d_6): δ (ppm) 2.06 (s, 3H), 7.15–7.49 (m, 6H), 7.78–8.04 (m, 5H), 8.54 (d, *J* = 8.1 Hz, 1H), 10.12 (s, 1H); ^{13}C NMR



Scheme 1. The synthesis of 1-amidoalkyl-2-naphthols from β-naphthol, aromatic aldehydes and amide derivatives.

(62.5 MHz, DMSO-d_6): δ (ppm) 23.3, 48.1, 118.1, 118.7, 120.5, 122.3, 123.8, 125.7, 127.3, 128.4, 129.1, 129.6, 130.8, 133.1, 134.1, 144.5, 148.7, 152.9, 169.8.

2.5.3. N-[(2-hydroxynaphthalen-1-yl)(4-chlorophenyl)methyl)]acetamide (**1h**)

Pale yellow solid; mp 220–222 °C (lit. [28] mp 224–227 °C); ^{1}H NMR (250 MHz, DMSO-d_6): δ (ppm) 2.07 (s, 3H), 7.06 (m, 2H), 7.14–7.24 (m, 5H), 7.68–7.77 (m, 3H), 7.98 (d, J = 7.4 Hz, 1H), 8.16 (d, J = 7.1 Hz, 1H), 9.90 (s, 1H); ^{13}C NMR (62.5 MHz, DMSO-d_6): δ (ppm) 23.2, 47.6, 118.8, 119.8, 122.1, 123.7, 125.8, 126.9, 127.4, 128.3, 128.6, 129.3, 129.9, 134.0, 143.4, 152.5, 169.8.

2.5.4. N-[(4-chloro-phenyl)-(2-hydroxy-naphthalen-1-yl)-methyl]nicotinamide (**1t**)

White solid; mp 206–209 °C; IR (KBr): 3408, 3234, 3065, 1645, 1581, 1514, 1273 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) 7.27–7.50 (m, 9H), 7.83 (d, J = 8.7 Hz, 2H), 8.10 (d, J = 8.4 Hz, 1H), 8.27 (d, J = 7.8 Hz, 1H), 8.71 (d, J = 4.4 Hz, 1H), 9.12 (s, 1H), 9.35 (d, J = 7.6 Hz, 1H), 10.38 (s, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ (ppm) 49.4, 118.2, 119.1, 123.1, 123.5, 123.9, 127.2, 128.6, 128.9, 129.2, 130.1, 130.4, 131.7, 132.8, 135.8, 141.2, 149.1, 152.4, 153.9, 165.4; MS: m/z = 388.3 (M^+); Anal. Calcd. for $C_{23}H_{17}ClN_2O_2$: C, 71.04; H, 4.41; N, 7.20. Found: C, 70.78; H, 4.30; N, 7.35.

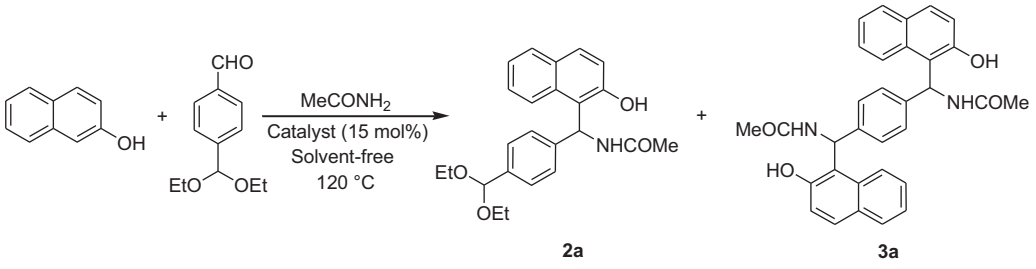
2.6. General procedure for the preparation of 1-amidoalkyl-2-naphthol derivatives **2a**, **3a** and **3b**

To a well-ground mixture of β-naphthol (0.576 g, 4 mmol), terephthalaldehyde (0.268 g, 2 mmol) and acetamide (0.284 g, 4.8 mmol) in a 10 mL round-bottomed flask connected to a reflux condenser, was added the catalyst (0.3 mmol, 15 mol%), and the resulting mixture was stirred in an oil-bath (120 °C) for the appropriate time (Schemes 2 and 3). Afterward, the reaction mixture was cooled to room temperature, and warm aqueous ethanol (15%, 30 mL) containing triethylamine (0.2 mL) were added to it, and stirred for 5 min (1-amidoalkyl-2-naphthol is soluble in warm aqueous ethanol, however, bis-1-amidoalkyl-2-naphthol is insoluble in this solvent). During this time, the crude 1-amidoalkyl-2-naphthol was dissolved in the ethanol, and pure bis-1-amidoalkyl-2-naphthol was remained; thus, two products were easily separated by filtration. Then, the solvent of the filtrate was evaporated and the crude 1-amidoalkyl-2-naphthol was purified by column chromatography on silica gel eluted with EtOAc/*n*-hexane (1/1).

2.7. Selected spectral data of the products **2a**, **3a** and **3b**

2.7.1. N-[(4-diethoxymethyl-phenyl)-(2-hydroxy-naphthalen-1-yl)-methyl]acetamide (**2a**)

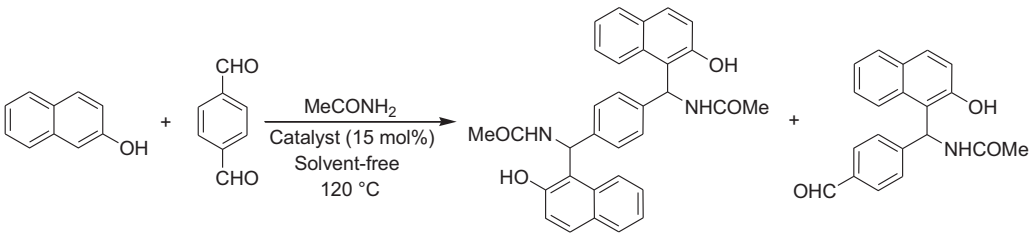
Pale yellow solid; mp 173–175 °C (lit. [36] mp 173–175 °C); ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.17 (t, J = 6.9 Hz, 6H), 2.02 (s, 3H),



Catalyst	Molar ratio of β-naphthol/aldehyde/amide	Time (min)	Yield[a] (%)	
			2a	**3a**
[Msim]Cl	1/1/1.2	5	25	31
[Msim]Cl	2/1/2.4	6	6	78
[Dsim]Cl	1/1/1.2	4	27	34
[Dsim]Cl	2/1/2.4	6	8	81
[Msim]$AlCl_4$	1/1/1.2	7	22	30
[Msim]$AlCl_4$	2/1/2.4	9	5	73

[a]Isolated yield.

Scheme 2. The condensation of β-naphthol with 4-(diethoxymethyl)benzaldehyde and acetamide.



3a **3b**

Catalyst	Molar ratio of β-naphthol/aldehyde/amide	Time (min)	Yield[a] (%)	
			3a	**3b**
[Msim]Cl	1/1/1.2	5	29	34
[Msim]Cl	2/1/2.4	6	82	14
[Dsim]Cl	1/1/1.2	4	38	32
[Dsim]Cl	2/1/2.4	5	84	12
$[Msim]AlCl_4$	1/1/1.2	6	27	33
$[Msim]AlCl_4$	2/1/2.4	9	78	12

[a]Isolated yield.

Scheme 3. The condensation of β-naphthol with terephthaldehyde and acetamide.

3.58 (q, J = 6.9 Hz, 4H), 6.96–7.46 (m, 9H), 7.73–7.85 (m, 3H), 8.26 (d, J = 8.5 Hz, 1H), 10.22 (s, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ (ppm) 19.1, 23.2, 48.5, 56.7, 111.8, 119.1, 119.6, 120.9, 122.7, 124.5, 126.2, 128.5, 129.1, 129.7, 132.9, 134.8, 139.7, 142.4, 153.3, 169.9.

*2.7.2. N-[{4-[acetylamino-(2-hydroxy-naphthalen-1-yl)-methyl]-phenyl}-(2-hydroxy-naphthalen-1-yl)-methyl]acetamide (**3a**)*

White solid; mp 277–279 °C (lit. [36] mp 277–279 °C); ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) 2.01 (s, 6H), 7.17–7.39 (m, 12H), 7.77–7.93 (m, 6H), 8.53 (d, J = 8.2 Hz, 2H), 10.09 (s, 2H); ^{13}C NMR (75 MHz, DMSO-d_6): δ (ppm) 23.1, 48.2, 118.9, 119.2, 122.8, 126.3, 126.8, 128.9, 129.0, 129.6, 132.7, 140.8, 140.9, 153.6, 169.7.

*2.7.3. N-[(4-formylphenyl)(2-hydroxynaphthalen-1-yl)methyl]acetamide (**3b**)*

Pale yellow solid; mp 237–240 °C (lit. [36] mp 237–240 °C); ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) 2.02 (s, 3H), 6.91–7.39 (m, 6H), 7.79–7.82 (m, 4H), 8.41 (d, J = 6.6 Hz, 1H), 8.56 (d, J = 7.6 Hz, 1H), 9.93 (s, 1H), 10.10 (s, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ (ppm) 23.0, 48.4, 118.6, 118.8, 122.9, 123.5, 126.3, 127.1, 128.9, 129.1, 129.9, 130.1, 132.7, 134.9, 150.6, 153.7, 170.1, 193.1.

3. Results and discussion

3.1. Studies to confirm the structures of the imidazolium salts

The structures of the sulfonic acid functionalized imidazolium salts were identified by ^{1}H and ^{13}C NMR as well as mass spectra. The corresponding spectral data have been reported in Section 2. Moreover, the graphical ^{1}H and ^{13}C NMR spectra of the imidazolium salts are presented in Figs. 2 and 3. Here, we study ^{1}H NMR data of ionic liquid 3-methyl-1-sulfonic acid imidazolium chloride {[Msim]Cl}. The important peak of ^{1}H NMR spectra of [Msim]Cl is related to the acidic hydrogen (SO_3H) which observed in 13.96 ppm. To confirm that this peak (13.96 ppm) is really related to the hydrogen of SO_3H in the compound, not hydrogen of $ClSO_3H$ (its unreacted starting material) or another possible product formed from the reaction of 1-methylimidazole with $ClSO_3H$ (i.e. 1-methylimidazolium chlorosulfonate), we also run the ^{1}H NMR spectra of $ClSO_3H$ and 1-methylimidazolium chloride in DMSO-d_6 (the acidic hydrogens of 1-methylimidazolium chlorosulfonate and 1-methylimidazolium chloride are same). In these spectra, the peaks of the acidic hydrogens of [Msim]Cl, $ClSO_3H$ and 1-methylimidazolium chloride were observed in 13.96, 13.45 and 8.46 ppm, respectively. The difference between the peaks of the acidic hydrogens in [Msim]Cl, $ClSO_3H$ and 1-methylimidazolium chloride confirmed that the peak observed in 13.96 ppm of the ^{1}H NMR spectra of [Msim]Cl is correctly related to the SO_3H group of this compound.

In order to prove that the sulfonic acid functionalized with imidazolium salts was correctly synthesized, and this is responsible of the catalytic results, as a model, the solvent-free condensation of β-naphthol with 4-chlorobenzaldehyde and acetamide was examined in the presence of 10 mol% of the starting materials used for the preparation of the catalysts (i.e. 1-methylimidazole and $ClSO_3H$) as well as a possible product formed from the reaction of 1-methylimidazole with $ClSO_3H$ (this possible product is 1-methylimidazolium chlorosulfonate; however, there was not this compound in the Chemical Companies catalogs. Moreover, the acidic hydrogen of 1-methylimidazolium chlorosulfonate catalyzes the reaction. Thus, we used 1-methylimidazolim chloride instead of it). The reaction was carried out at 120 °C and the catalytic results are presented in Table 1. It can be seen that 1-methylimidazole and 1-methylimidazolium chloride afforded lower yield of reaction products to those achieved over the catalysts. Only in the case of $ClSO_3H$, it has been observed a relatively moderate yield. The reaction was also performed in the presence of imidazole as well as imidazolium chloride in which the product was obtained in low or moderate yields after long reaction times (Table 1, entries 8 and 9). However, when the reaction was carried out in the presence of [Msim]Cl, [Dsim]Cl or $[Msim]AlCl_4$, we observed high yields at very short reaction times. These results also confirmed that the functionalized sulfonic acid imidazolium salts have been correctly synthesized.

The other case for the mixing of 1-methylimidazole with $ClSO_3H$ in CH_2Cl_2, is formation of a separate phase, "$ClSO_3H$ dissolved in

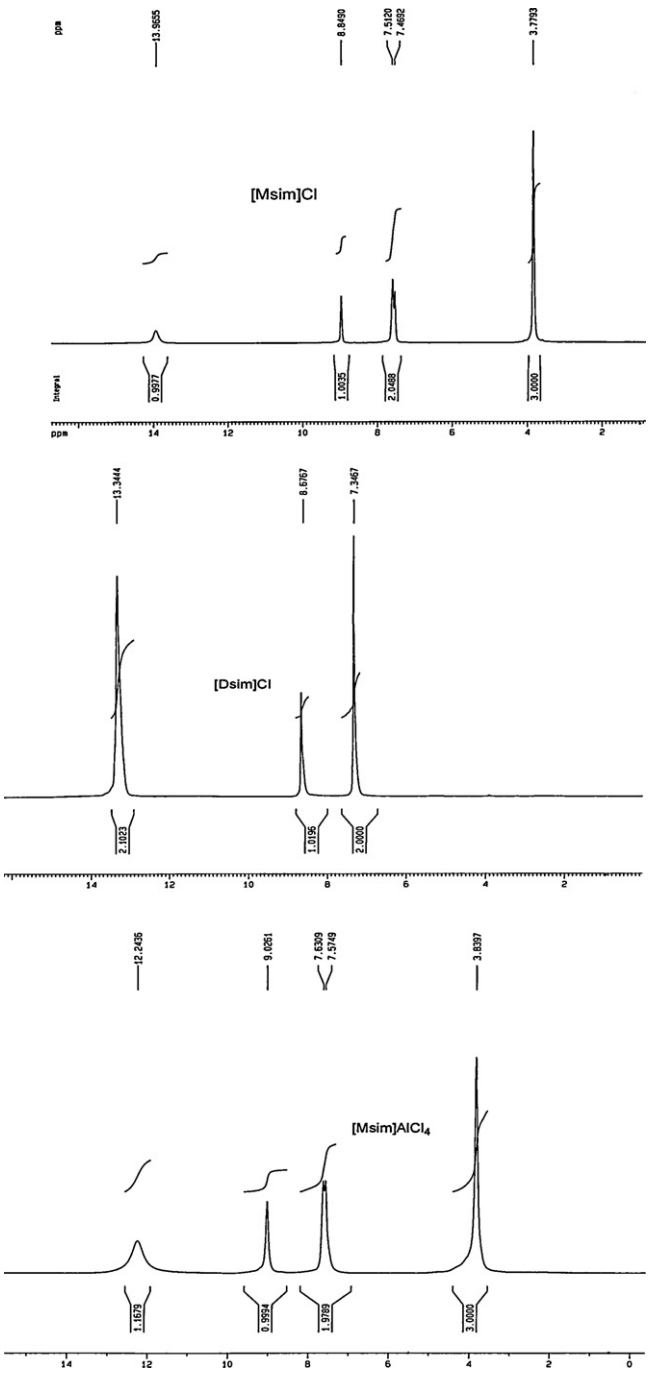


Fig. 2. ^{1}H NMR of 3-methyl-1-sulfonic acid imidazolium chloride {[Msim]Cl}, 1,3-disulfonic acid imidazolium chloride {[Dsim]Cl} and 3-methyl-1-sulfonic acid imidazolium tetrachloroaluminate {[Msim]$AlCl_4$}.

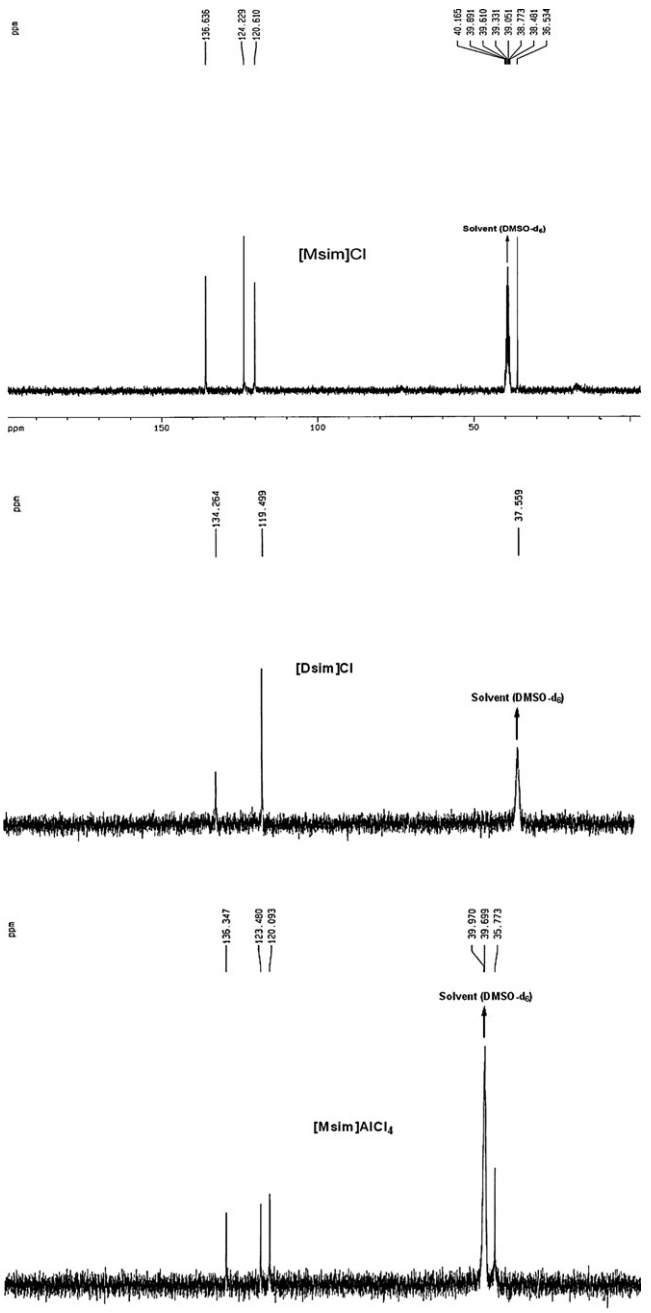


Fig. 3. ^{13}C NMR of 3-methyl-1-sulfonic acid imidazolium chloride {[Msim]Cl}, 1,3-disulfonic acid imidazolium chloride {[Dsim]Cl} and 3-methyl-1-sulfonic acid imidazolium tetrachloroaluminate {[Msim]$AlCl_4$}.

1-methylimidazole". To recognize that this physical phenomenon cannot be achieved in these conditions, we noticed to the ^{1}H NMR spectral data of the product obtained from the mixing, with those in 1-methylimidazole and $ClSO_3H$ separately. The ^{1}H NMR spectral data include:

The product: ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) 3.77 (s, 3H, CH_3), 7.46 (s, 1H), 7.51 (s, 1H), 8.84 (s, 1H), 13.96 (s, 1H).
1-Methylimidazole: ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) 3.61 (s, 3H, CH_3), 7.02 (s, 1H), 7.11 (s, 1H), 7.64 (s, 1H).
$ClSO_3H$: ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) 13.45 (s, 1H).

As it can be seen, the ^{1}H NMR data of the product are different with those in 1-methylimidazole and $ClSO_3H$. Thus, the treatment of 1-methylimidazole with $ClSO_3H$ did not afford the separate phase, "$ClSO_3H$ dissolved in 1-methylimidazole", and really gave [Msim]Cl. Moreover, 1-methylimidazole and $ClSO_3H$ were easily dissolved in CH_2Cl_2; however, the product obtained from the mixing of these compounds {[Msim]Cl} was insoluble in CH_2Cl_2. This subject also confirmed that the separate phase, "$ClSO_3H$ dissolved in 1-methylimidazole" was not formed.

The above explanations are also applicable for the synthesis of [Dsim]Cl from imidazole and $ClSO_3H$.

In another study, to prove that the reaction of [Msim]Cl with $AlCl_3$ leads to [Msim]$AlCl_4$, not [Msim]Cl/$AlCl_3$ mixture, we achieved carefully the reaction of β-naphthol with 4-

Table 1
The condensation of β-naphthol with 4-chlorobenzaldehyde and acetamide using 1-methylimidazole, chlorosulfonic acid, 1-methylimidazolium chloride, imidazole and imidazolium chloride.

Entry[a]	Catalyst[b]	Time (min)	Yield[c]/Conv.[d] (%)
1	–	12 h	No reaction
2	[Msim]Cl	2	96/99
3	[Dsim]Cl	2	96/99
4	[Msim]$AlCl_4$	2	95/98
5	1-Methylimidazole	150	29/34
6	Chlorosulfonic acid	5	73/77
7	1-Methylimidazolium chloride	120	51/56
8	Imidazole	150	34/39
9	Imidazolium chloride	120	57/61

[a] All reactions were carried out at 120 °C.
[b] The amount of the catalysts was 10 mol%.
[c] Isolated yield.
[d] Conversion.

chlorobenzaldehyde and acetamide, as well as with benzaldehyde and urea in the presence of 10 mol% of [Msim]Cl/$AlCl_3$ mixture (1/0.5 to 1/1 molar ratio) as well as $AlCl_3$ at 120 °C (Table 2). As Table 2 shows, when the reactions were carried out using [Msim]Cl/$AlCl_3$ mixture, the yields were similar to those obtained using [Msim]Cl, not [Msim]$AlCl_4$. In these cases, the reaction times were not sufficient to produce [Msim]$AlCl_4$ (the time needed for the synthesis of this catalyst is 35 min); thus, the results were not similar to [Msim]$AlCl_4$. $AlCl_3$ also afforded moderate yields of the products in longer reaction times. Moreover, in the mass spectra of [Msim]$AlCl_4$, there was a peak in 168 which related to $AlCl_4$. [Msim]Cl and [Msim]$AlCl_4$ have also different ^1H and ^{13}C NMR spectra (please see Figs. 2 and 3). These observations confirmed the structure of [Msim]$AlCl_4$.

Study on thermal gravimetric analysis (TGA) of [Msim]Cl and [Msim]$AlCl_4$ was also confirmed that [Msim]$AlCl_4$ has been synthesized. The corresponding diagrams are shown in Fig. 4. As it can be seen in Fig. 4, the thermogravimetry (TG) and derivative thermogravimetry (DTG) of the catalysts showed weight losses in one step; [Msim]Cl and [Msim]$AlCl_4$ were decomposed after 330 and 390 °C in one step. This subject confirmed that the catalysts are one-system, not binary systems. In binary systems, the thermogravimetry (TG) diagrams must be showed weight losses in two or more steps. Moreover, the TG and DTG diagrams of [Msim]Cl and [Msim]$AlCl_4$ are different. These results are important to prove that the reaction of [Msim]Cl with $AlCl_3$ leads to [Msim]$AlCl_4$, not [Msim]Cl/$AlCl_3$ binary system.

3.2. The synthesis of 1-amidoalkyl-2-naphthols **1a–t**

To optimize the reaction conditions, the condensation of β-naphthol (2 mmol) with 4-chlorobenzaldehyde (2 mmol) and acetamide (2.4 mmol) was examined in the presence of different quantities of the functionalized imidazolium salts, [Msim]Cl, [Dsim]Cl or [Msim]$AlCl_4$, at range of 90–130 °C under solvent-free conditions (Scheme 1). The results are summarized in Table 3. Interestingly, the three imidazolium salts were highly efficient and 10 mol% of them was sufficient to afford the product in excellent yields and in very short reaction times at 120 °C (Table 3, entry 3). No improvement in the reaction results was observed by increasing the amount of the catalysts and the temperature. The solvent-free condensation was also tested at 120 °C without catalyst in which the reaction was not progressed even after long reaction time (12 h).

In another study, the solvent-free reaction of β-naphthol with 4-chlorobenzaldehyde and acetamide was checked using the catalysts at 120 °C, and conversion percents as well as yields of the reactions were measured in different reaction times (each 15 s). The corresponding curves (variation of conversion or yield with time) are presented in Fig. 5. As it can be seen in Fig. 5, the catalytic activity of [Dsim]Cl was higher than [Msim]Cl and [Msim]$AlCl_4$. This can be attributed to more number of SO_3H groups in [Dsim]Cl; this catalyst has two SO_3H groups, but [Msim]Cl and [Msim]$AlCl_4$ have one SO_3H group. Moreover, [Msim]Cl and [Msim]$AlCl_4$ showed almost similar catalytic activity in this reaction.

After optimization of the reaction conditions, the condensation of β-naphthol with various aryl aldehydes and amides/urea was examined in the presence of [Msim]Cl, [Dsim]Cl or [Msim]$AlCl_4$ at 120 °C in the absence of solvent, in order to assess the scope and the generality of the catalysts. The results are displayed in Table 4 . As it is shown in Table 4, aryl aldehydes possessing electron-releasing substituents, electron-withdrawing substituents and halogens on their aromatic rings were utilized successfully in the reaction, and gave the desired products in high yields and in very short reaction times. Moreover, the imidazolium salts efficiently catalyzed the reaction when benzamide, urea or nicotinamide were used instead of acetamide. Thus, all catalysts were general and highly efficient.

3.3. The synthesis of 1-amidoalkyl-2-naphthols **2a**, **3a** and **3b**

It must be mentioned that the condensation of β-naphthol with 4-(diethoxymethyl)benzaldehyde and acetamide in the presence of [Msim]Cl, [Dsim]Cl or [Msim]$AlCl_4$ afforded two products **2a** and **3a** (Scheme 3). When 1 equiv. of β-naphthol and 1 equiv. of the aldehyde were reacted with 1.2 equiv. of acetamide, both 1-amidoalkyl-2-naphthol **2a** and bis-1-amidoalkyl-2-naphthol **3a** were obtained in moderate yields. However, the use of 2 equiv. of β-naphthol, 1 equiv. of 4-(diethoxymethyl)benzaldehyde and 2.4 equiv. of acetamide afforded mainly compound **3a**.

The condensation of β-naphthol with bis-aldehydes (terephthaldehyde) and acetamide, using the imidazolium salts, was also rapidly performed (Scheme 4). The use 1 equiv. of β-naphthol, 1 equiv. of terephthalaldehyde and 1.2 equiv. of acetamide in the reaction afforded both bis-1-amidoalkyl-2-naphthol **3a** and 1-

Table 2
The reaction of β-naphthol with 4-chlorobenzaldehyde and acetamide (A) as well as with benzaldehyde and urea (B) using [Msim]Cl/$AlCl_3$ mixture and also $AlCl_3$ (1/0.5 to 1/1, mol/mol).

Entry[a]	Catalyst[b]	Reaction A		Reaction B	
		Time (min)	Yield[c]/Conv.[d] (%)	Time (min)	Yield[c]/Conv.[d] (%)
1	[Msim]Cl	2	96/99	5	81/86
2	[Msim]$AlCl_4$	2	95/98	6	85/89
3	$AlCl_3$	10	82/85	20	70/74
4	[Msim]Cl/$AlCl_3$ (1/0.5)	2	96/99	6	82/86
5	[Msim]Cl/$AlCl_3$ (1/0.75)	2	96/99	6	83/87
6	[Msim]Cl/$AlCl_3$ (1/1)	2	96/99	6	83/87

[a] The reaction temperature was 120 °C.
[b] The amount of the catalysts was 10 mol%.
[c] Isolated yield.
[d] Conversion.

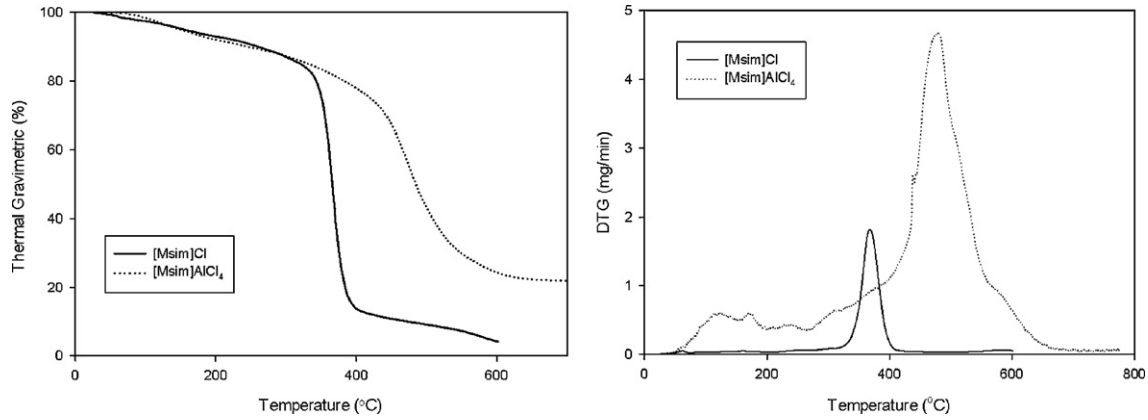


Fig. 4. The TG and DTG diagrams of [Msim]Cl and [Msim]$AlCl_4$.

Table 3
Effect of amounts of the catalysts and temperature on the condensation of β-naphthol with 4-chlorobenzaldehyde and acetamide.

Entry	Catalyst amount[a] (mol%)	Temp. (°C)	[Msim]Cl		[Dsim]Cl		[Msim]$AlCl_4$	
			Time (min)	Yield[b]/Conv.[c] (%)	Time (min)	Yield[b]/Conv.[c] (%)	Time (min)	Yield[b]/Conv.[c] (%)
1	5	120	5	87/90	4	89/91	6	84/88
2	7.5	120	3	92/95	2	93/95	3	90/93
3	10	120	2	96/99	2	96/99	2	95/98
4	15	120	2	96/99	2	96/99	2	94/98
5	10	90	15	68/73	11	72/76	20	59/64
6	10	100	10	79/83	8	84/87	12	73/78
7	10	110	5	86/89	4	89/93	6	82/86
8	10	130	2	92/99	2	91/99	2	90/99

[a] The reaction was not proceeded in the absence of catalyst.
[b] Isolated yield.
[c] Conversion.

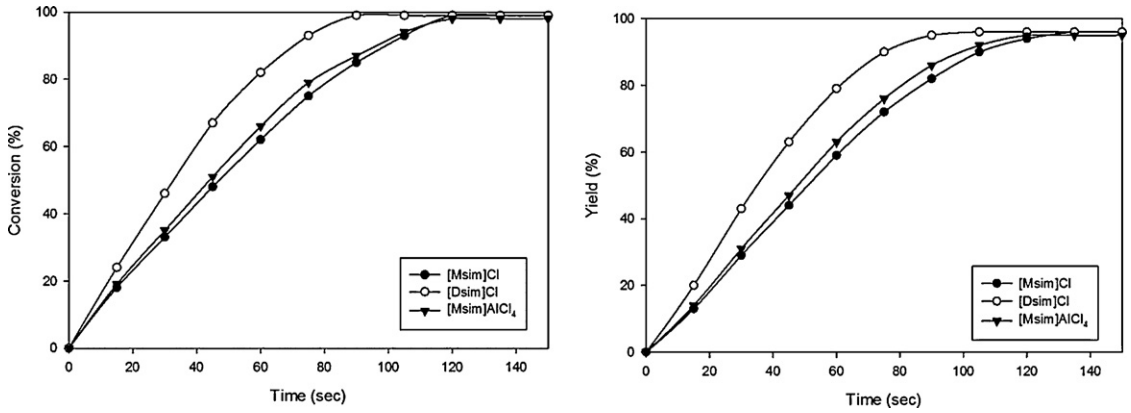


Fig. 5. Variation of the reaction conversion and yield with time on the solvent-free condensation of β-naphthol with 4-chlorobenzaldehyde and acetamide using the imidazolium salts at 120 °C.

amidoalkyl-2-naphthol **3b** in moderate yields. Nevertheless, the condensation of 2 equiv. of β-naphthol with 1 equiv. of the aldehyde and 2.4 equiv. of acetamide gave compounds **3b** as a main product.

3.4. Comparison of the efficiency of the catalysts with the recently reported catalysts for the synthesis of 1-amidoalkyl-2-naphthols

To compare the applicability and the efficiency of our catalysts with the reported catalysts for the synthesis of 1-amidoalkyl-2-naphthols, we have tabulated the results of these catalysts to perform the condensation of β-naphthol with 4-chlorobenzaldehyde and acetamide in Table 5. As it is shown in Table 5, [Msim]Cl, [Dsim]Cl and [Msim]$AlCl_4$ remarkably improved the synthesis of 1-amidoalkyl-2-naphthols in different terms, for example in terms of reaction time, yield and turn-over frequency (TOF). The reaction times were shorter, and the yields and TOFs were higher when our catalysts were utilized.

3.5. Proposed mechanism

In a plausible mechanism (Scheme 5) which is supported by the literature [29,31,38]; at first, aromatic aldehyde is activated by acidic group of [Msim]Cl to produce **I**. Then, β-naphthol attacks to the carbonyl group of the activated aldehyde, and affords intermediate **II**. Next, by removing H_2O from **II**, orthoquinone methide (*o*-QM, **III**) is prepared. [Msim]Cl again activates intermediate **III** to give **IV** as a Michael acceptor. Afterward, Michael addition

Table 4
The solvent-free synthesis of 1-aminoalkyl-2-naphthols from β-naphthol, aromatic aldehydes and amides/urea using the sulfonic acid functionalized imidazolium salts.

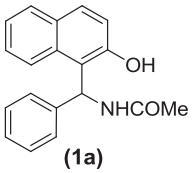
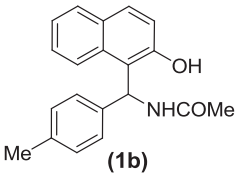
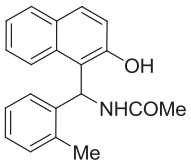
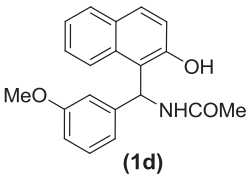
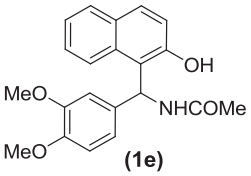
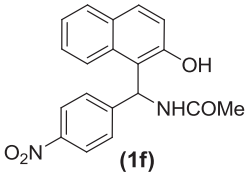
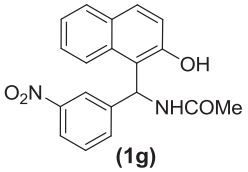
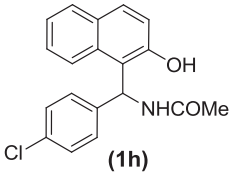
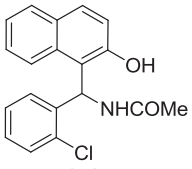
Product[a]	[Msim]Cl		[Dsim]Cl		[Msim]$AlCl_4$		Mp °C (Lit.)
	Time (min)	Yield[b]/Conv.[c] (%)	Time (min)	Yield[b]/Conv.[c] (%)	Time (min)	Yield[b]/Conv.[c] (%)	
 (1a)	5	94/97	1	95/98	5	95/98	238–240 (241–243) [28]
 (1b)	5	91/95	2	94/97	6	93/97	223–225 (220–230) [37]
 (1c)	5	88/91	3	90/94	5	89/93	197–199 (200–202) [31]
 (1d)	12	87/91	7	90/94	15	86/91	200–202 (203–205) [32]
 (1e)	15	85/88	16	95/97	25	89/92	230–232 (235–236) [32]
 (1f)	4	95/98	2	94/98	4	95/98	246–248 (248–250) [37]
 (1g)	3	96/99	2	95/99	3	93/97	238–240 (236–237) [33]
 (1h)	2	96/99	2	96/99	2	95/98	220–222 (224–227) [28]
 (1i)	3	93/97	2	93/97	3	92/95	197–199 (194–196) [33]

Table 4 (*Continued*)

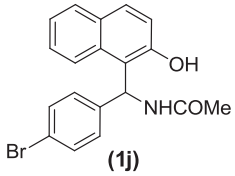
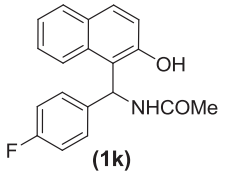
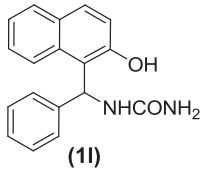
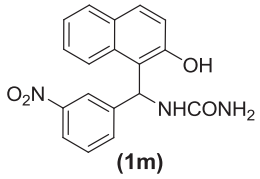
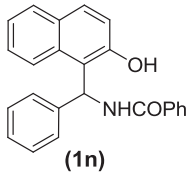
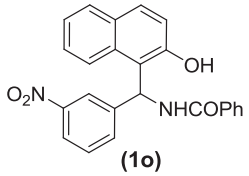
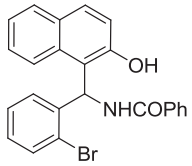
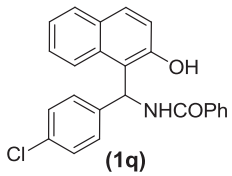
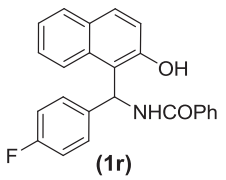
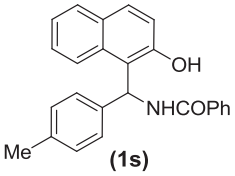
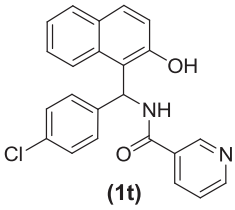
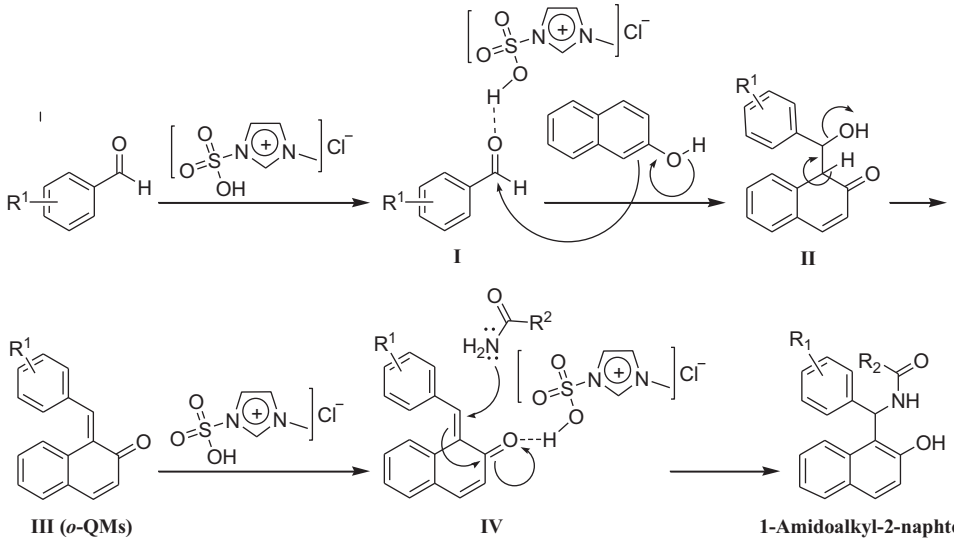
Product[a]	[Msim]Cl		[Dsim]Cl		[Msim]$AlCl_4$		Mp °C (Lit.)
	Time (min)	Yield[b]/Conv.[c] (%)	Time (min)	Yield[b]/Conv.[c] (%)	Time (min)	Yield[b]/Conv.[c] (%)	
 (1j)	3	91/93	2	94/97	3	93/96	226–228 (228–230) [32]
 (1k)	4	90/94	2	94/97	4	89/93	206–208 (203–205) [33]
 (1l)	5	81/86	4	92/96	6	85/89	174–176 (172–174) [33]
 (1m)	4	83/87	3	94/97	6	84/88	183–185 (184–186) [33]
 (1n)	6	86/90	4	93/96	7	85/88	237–239 (234–236) [33]
 (1o)	5	90/93	3	94/96	5	88/91	214–216 (216–217) [33]
 (1p)	4	87/90	3	89/93	5	86/90	225–227 (228–230) [31]
 (1q)	4	90/94	2	92/96	4	91/94	178–180 (177–178) [33]
 (1r)	5	87/90	3	90/94	6	89/93	191–193 (193–194) [33]

Table 4 (*Continued*)

Product[a]	[Msim]Cl		[Dsim]Cl		[Msim]$AlCl_4$		Mp °C (Lit.)
	Time (min)	Yield[b]/Conv.[c] (%)	Time (min)	Yield[b]/Conv.[c] (%)	Time (min)	Yield[b]/Conv.[c] (%)	
 (1s)	7	86/91	4	91/95	7	85/90	187–189 (192–193) [33]
 (1t)	35	83/87	20	89/94	40	85/89	206–209

[a] All products were synthesized at 120 °C.
[b] Isolated yield.
[c] Conversion.



Scheme 4. The proposed mechanism for the synthesis of 1-amidoalkyl-2-naphthols.

Table 5
Comparison of the results of the condensation of β-naphthol with 4-chlorobenzaldehyde and acetamide catalyzed by our new catalysts with those obtained by the recently reported catalysts.

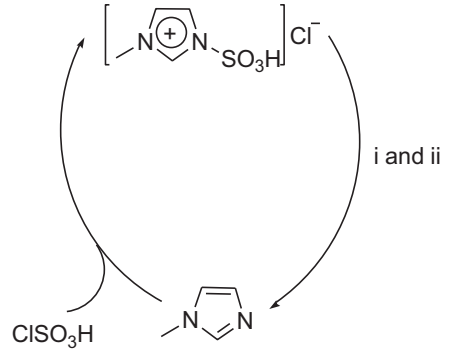
Catalyst	Catalyst amount (mol%)	Time (min)	Yield (%)	TOF[a] (min^{-1})	Ref.
[Msim]Cl, 120 °C	10	2	96[b]	4.8	–[c]
[Dsim]Cl, 120 °C	10	2	96[d]	6.4	–[c]
[Msim]$AlCl_4$, 120 °C	10	2	95[e]	4.75	–[c]
I_2, r.t.	5	690	90	0.026	[30]
Sulfamic acid, ultrasound, 28-30 °C	51.5	120	92	0.015	[33]
Cyanuric chloride, 100 °C	10	10	90	0.9	[35]
$H_3PW_{12}O_{40}$, 100 °C	2	80	88	0.55	[37]
$Fe(HSO_4)_3$, 85 °C	5	45	88	1.7	[32]
$HClO_4/SiO_2$, 90 °C	0.6	40	93	3.87	[34]
P_2O_5, 60 °C	10	5	96	1.92	[38]
4-(1-Imidazolium)butane sulfonate, 80 °C	10	120	85	0.07	[39]
N-(4-sulfonic acid)butyl triethylammonium hydrogensulfate, 120 °C	5	10	85	1.7	[40]
1-Butyl-3-methylimidazolium hydrogen sulphate, 60 °C	5	35	93	0.531	[41]
$Cu_{1.5}PW_{12}O_{40}$, 100 °C	2	90	78	0.433	[42]
Silica sulfuric acid, r.t.	0.02 g	96	89	–	[43]

[a] Turn-over frequency.
[b] In this reaction, the conversion was 99%.
[c] Our work.
[d] In this reaction, the conversion was 99%.
[e] In this reaction, the conversion was 98%.

Table 6
Effect of impurities of water on the condensation of β-naphthol with 4-chlorobenzaldehyde and acetamide.

Entry[a]	Water amount (mmol)	[Msim]Cl		[Dsim]Cl		[Msim]$AlCl_4$	
		Time (min)	Yield[b]/Conv.[c] (%)	Time (min)	Yield[b]/Conv.[c] (%)	Time (min)	Yield[b]/Conv.[c] (%)
1	–	2	96/99	2	96/99	2	95/98
2	2	2	96/99	2	96/99	2	95/98
3	4	4	96/99	2	96/99	3	95/98
4	8	6	93/96	2	96/99	5	94/97
5	16	15	89/92	3	96/99	10	93/96
6	24	25	83/86	7	94/97	20	90/93
7	30	35	78/82	15	91/94	30	86/89
8	50	60	71/74	40	84/87	50	78/81
9	80	120	65/69	110	79/82	120	70/74

[a] The amounts of β-naphthol, 4-chlorobenzaldehyde, acetamide and the catalyst in all reactions were 2, 2, 2.4 and 0.2 mmol, respectively, and the reaction temperature was 120 °C.
[b] Isolated yield.
[c] Conversion.



i) The synthesis of 1-amidoalkyl-2-naphthol
ii) Addition of NaOH solution

Scheme 5. The recovery and reuse cycle of [Msim]Cl.

of amide to intermediate **IV** affords the expected 1-amidoalkyl-2-naphthol. The reaction results, which have been presented in Table 4, confirm the mechanism. As Table 4 indicates, electron-releasing substituents slightly decreased the yields and increased the reaction times (Table 4, compounds **1b–e**), and electron-withdrawing substituents had no significant effects on the yields, but slightly decreased the reaction times (Table 4, compounds **1f**, **1g**, **1m** and **1o**). In fact, electron-releasing substituents deactivate aldehyde to accept nucleophilic attack of β-naphthol; however, electron-withdrawing groups activate aldehyde. These are in accordance with the proposed mechanism.

3.6. Recovering and reusing the catalysts (Scheme 5)

As previously showed, [Msim]Cl, [Dsim]Cl and [Msim]$AlCl_4$ were highly efficient and general for the synthesis of 1-amidoalkyl-2-naphthols. To raise the catalysts worth, recoverability and reusability of them were studied. For this purpose, the reaction of β-naphthol with 4-chlorobenzaldehyde and acetamide using [Msim]Cl was carried out several times, and the reaction mixtures were combined. Afterward, H_2O was added to the combined reaction mixtures, stirred for 5 min, and filtered {[Msim]Cl is soluble in H_2O; however, the reaction mixture is not soluble in H_2O}. In the aqueous media, a quantity of [Msim]Cl hydrolyzed to 1-methylimidazole (as monitored on TLC) and H_2SO_4. To complete hydrolysis of [Msim]Cl, and consequently formation of 1-methylimidazole, a solution of NaOH (10%) was added to the filtrate, and stirred for 5 min. The solution was extracted with EtOAc, washed with H_2O and dried. Evaporation of the solvent gave 1-methylimidazole. The recovered 1-methylimidazole was reacted with chlorosulfonic acid to give [Msim]Cl. The catalytic activity of the reproduced [Msim]Cl was as same as the first one. The recovery and reuse cycle of this catalysts are summarized in Scheme 5. [Dsim]Cl and [Msim]$AlCl_4$ were also reproduced accordingly.

3.7. Effect of impurity of water on the catalytic activity of the imidazolium salts

To study effect of impurity of water on the catalysts activity, the condensation of β-naphthol (2 mmol) with 4-chlorobenzaldehyde (2 mmol) and acetamide (2.4 mmol) using the imidazolium salts (0.2 mmol) was examined in the presence of different amounts of H_2O at 120 °C (Table 6). As Table 6 indicates, 16 mmol of H_2O did not affect significantly on the catalytic activity of [Msim]Cl and [Msim]$AlCl_4$; however, more increasing the amount of H_2O decreased their activity. This can be attributed to hydrolysis of these catalysts to 1-methylimidazole (as monitored on TLC) and H_2SO_4 in aqueous media. The catalytic activity of [Dsim]Cl retained in the presence of 30 mmol of H_2O. Moreover, the rate of decreasing the activity of [Dsim]Cl was slower than [Msim]Cl and [Msim]$AlCl_4$. These subjects are attributed to more number of SO_3H groups in [Dsim]Cl relative to [Msim]Cl and [Msim]$AlCl_4$.

4. Conclusions

In summary, we have introduced the novel sulfonic acid functionalized imidazolium salts, [Msim]Cl, [Dsim]Cl and [Msim]$AlCl_4$, as highly efficient and green catalysts for organic transformations. For example, in this work, the synthesis of 1-amidoalkyl-2-naphthols, *via* the one-pot three-component condensation of β-naphthol with various aryl aldehydes and amides/urea, was efficiently catalyzed by these imidazolium salts. The promising points for the presented methodology are efficiency, generality, high yields, very short reaction times, cleaner reaction profile, simplicity, ease of preparation of the catalyst, and compliance with the green chemistry protocols.

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