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Synthesis and applications of novel imidazole and benzimidazole based sulfonic acid group functionalized Brönsted acidic ionic liquid catalysts

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ABSTRACT

In this study, a variety of imidazole/benzimidazole based sulfonic acid group functionalized Brönsted acidic ionic liquids (BAILs) were synthesized. Catalytic activities of BAILs were assessed using multi-component coupling reactions. Catalytic activities of BAILs were high when compared with those of solid acid catalysts such as H-ZSM-5, H-BETA, and sulfonic acid functionalized SBA-15 catalysts. The Hammett acidity order determined from UV–visible spectroscopy of BAILs is consistent with their activity order observed in acid-catalyzed reactions. Theoretical studies demonstrate that the hydrogen bonding plays a key role in tuning the acidity of BAILs. Recycling experiments suggest that these novel BAILs can be reused without significant loss in catalytic activity. Novel BAILs offer several attractive features such as low cost, high catalytic activity, and recyclability.

1. Introduction

The chemical industry routinely uses strong Brönsted acid catalysts for fine chemical synthesis [1]. In this context, solid acid catalysts are being most widely used as nonvolatile materials, as they are deemed less noxious than traditional liquid acids [2,3]. However, solid acids have several disadvantages as well. Among the more troublesome of these are restricted accessibility of the matrix-bound acidic sites, high molecular weight/active-site ratios, and rapid deactivation from coking [3,4]. Bearing in mind both the advantages and disadvantages of solid acids, the identification of systems that are Brönsted acids with solid-like non-volatility but that manifest the motility, greater effective surface area, and potential activity of a liquid phase continues to be useful.

Ionic liquids (ILs) have potential to substitute solid acid catalysts in liquid phase catalytic reactions. ILs have been described as one of the most promising new reaction mediums [5,6]. ILs have the ability to dissolve many organic and inorganic substrates. They can be readily recycled and are tunable to specific chemical tasks [6–9]. A new class of reagents designed as task-specific ILs (TSILs) has been developed: such derivatives combine an IL-type part with an attached extra function designed for the specific property [10]. Functionalization ability of the TSILs gives us more opportunity to manipulate their structures (with respect to the organic cation, inorganic anion and the length of the side chain attached to the organic cation) to achieve special properties according to the given reactions. The vast majority of TSIL chemistry is based on nitrogen-containing heterocyclic compounds [11].

Imidazoles and benzimidazoles have received significant attention because of their biological activities such as antihistaminic, antiparasitic, antiulcer, antihypertensive, antiviral, antifungal and anticancer activities [12,13]. They are used in diverse areas of chemistry and are very important intermediates in organic reactions. The use of imidazole in the IL synthesis has been widely investigated [6]. However, only a few reports are available where benzimidazole has been used as organic cations in ILs [14]. Recently, some significant research findings have been reported for Lewis acidic ILs and Brönsted acidic ILs [15–18]. Compared to conventional homogeneous and heterogeneous acid catalysts, acidic ILs demonstrate several advantages that include the following: reactions can be carried out under solvent-free condition, the product can be separated by easy decantation, and ILs can be recycled. Brönsted acidic ILs can be prepared by functionalizing SO_3H (IL-SO_3H) group on heterocyclic ring or replacing Cl^- with HSO_4^- (IL.HSO_4^-). Such functionalized ILs have been reported as novel eco-benign catalysts for some acid catalyzed reactions [15–18].

To the best of our knowledge, there is no report in literature which clearly state whether (IL-SO_3H) or (IL.HSO_4^-) is highly active. Enhancement in catalytic activity by increasing the number of $-SO_3H$ in functionalized ILs is not known very precisely.

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The objective of this study is to prepare a variety of imidazole and benzimidazole based (one/two/three/four) sulfonic acid group functionalized Brönsted acidic ionic liquids (BAILs) and investigate their applications in suitable catalytic reactions. In this study, catalytic activities of BAILs were assessed using multi-component coupling reactions. The catalytic activities of BAILs were compared with several solid acid catalysts such as H-ZSM-5, H-BETA, and SO_3H functionalized SBA-15 catalysts. Structure–activity relationship was established using theoretical modeling and UV–visible spectroscopic methods.

2. Experimental

2.1. Catalyst preparation

2.1.1. Synthesis of imidazole based BAILs

BAIL-1 was synthesized according to the reported procedure [19]. BAIL-2 was synthesized according to the reported procedure [18], except the sulfonation step, in which only two equivalents of H_2SO_4 was taken.

For the synthesis of BAIL-3, first compound c (Scheme 1) was synthesized using the reported procedure [20]. It was then sulfonated using three equivalents of H_2SO_4 (yield = 77.4%).

BAIL-3: IR (KBr, υ, cm^{-1}) = 3393, 3368, 3145, 3024, 2914, 1700, 1560, 1454, 1142, 1023, 875, 709, 611. ^{1}H NMR (D_2O) δ = 8.91 (s, 1H), 7.32–7.45 (m, 10H), 5.29 (s, 4H). ^{13}C NMR δ = 136.61, 135.02, 129.76, 129.49, 126.97, 123.32, 53.18. Elemental analysis for $C_{17}H_{18}N_2O_{10}S_3$: Theoretical (%): C 40.32, H 3.56, N 5.53; Experimental (%): C 39.93, H 3.84, N 5.81.

For the synthesis of BAIL-4, first compound d (Scheme 1) was synthesized from compound b (two equivalents) and 1,6-dibromohexane (one equivalent) using the reported procedure [20]. Compound d was then sulfonated using four equivalents of H_2SO_4 (yield = 75.2%).

BAIL-4: IR (KBr, υ, cm^{-1}) = 3395, 3149, 3084, 2943, 2867, 2525, 1702, 1563, 1498, 1455, 1146, 1022, 875, 708. ^{1}H NMR (D_2O) δ = 8.59 (s, 2H), 7.23–7.27 (m, 12H), 5.19 (s, 4H), 3.94 (t, 4H), 1.61 (quint, 4H), 1.05 (quint, 4H). ^{13}C NMR δ = 134.64, 133.37, 131.52, 128.86, 128.09, 122.15, 121.96, 52.36, 48.96, 28.34, 24.1. Elemental analysis for $C_{26}H_{34}N_4O_{14}S_4$: Theoretical (%): C 41.38, H 4.51, N 7.43; Experimental (%): C 41.58, H 4.24, N 7.55.

2.1.2. Synthesis of benzimidazole based BAILs

1-Benzyl-benzimidazole is the precursor of benzimidazole based BAILs. Synthesis of 1-benzyl-benzimidazole is as follows: In a two necked round-bottomed flask, K_2CO_3 (75 mmol), 40 ml acetonitrile and benzimidazole (50 mmol) were taken and refluxed for 30 min. Benzyl chloride (50 mmol) was subsequently added drop wise over a period of 30 min and the mixture was refluxed for 24 h. After the reaction, the reaction mixture was cooled to room temperature, and the solvent was removed under reduced pressure. Water was added in the reaction mixture. The aqueous layer was then separated and extracted three times with dichloromethane. Organic phases were combined and the dried over sodium sulfate and solvent was removed by Rota-evaporator (yield = 92%).

For the synthesis of BAIL-5, first, 1-benzyl-3-dodecyl-benzimidazolium bromide was prepared. In a typical synthesis, 1-benzyl-benzimidazole (10 mmol) was dissolved in toluene (20 ml) and dodecylbromide (10 mmol) was added drop-wise and the mixture was refluxed for 24 h. Upon completion of the reaction, the solvent was evaporated under vacuum. The residue was washed 3–4 times with ethyl acetate and then dried under vacuum at 343 K for 4 h to afford 1-benzyl-3-dodecyl-benzimidazolium bromide (yield = 93%). 1-Benzyl-3-dodecyl-benzimidazolium bromide was sulfonated using three equivalents of H_2SO_4 to obtain BAIL-5 (yield = 86%).

BAIL-5: IR (KBr, υ, cm^{-1}) = 3392, 2892, 1699, 1635, 1309, 1145, 1025, 875, 751, 697. ^{1}H NMR (D_2O + DMSO-d_6) δ = 9.97 (s, 1H), 8.26–7.67 (m, 7H), 5.98 (s, 2H), 4.16 (m, 2H), 1.37 (m, 20H), 1.06 (t, 3H). ^{13}C NMR δ = 144.09, 142.80, 140.50, 134.17, 132.18, 129.54, 128.75, 127.39, 123.12, 114.46, 113.75, 50.88, 47.71, 32.62, 31.97, 31.28, 29.38, 29.16, 26.53, 22.18, 14.54. Elemental analysis for $C_{26}H_{38}N_2S_3O_7$: Theoretical (%): C 53.24, H 6.48, N 4.78; Experimental (%): C 53.21, H 6.51, N 4.83.

For the synthesis of BAIL-6, first, 1,3-dibenzyl-benzimidazolium chloride was prepared using a similar procedure that was adopted for the synthesis of 1-benzyl-3-dodecyl-benzimidazolium bromide. For this, 1-benzyl-benzimidazol (10 mmol) and benzyl chloride (10 mmol) was reacted to obtain 1,3-dibenzyl-benzimidazolium chloride (yield = 94%). 1,3-dibenzyl-benzimidazolium chloride was sulfonated using four equivalents of H_2SO_4 to obtain BAIL-6 (yield = 87%).

BAIL-6: IR (KBr, υ, cm^{-1}) = 3405, 3144, 3072, 2922, 2854, 2480, 1696, 1563, 1455, 1136, 1024, 877, 743, 703. ^{1}H NMR (D_2O + DMSO-d_6) δ = 9.76 (s, 1H), 7.82 (d, 4H), 7.64 (d, 4H), 7.48–7.42 (m, 3H), 5.78 (s, 4H). ^{13}C NMR δ = 146.30, 142.93, 139.79, 135.20, 134.25, 130.48, 129.20, 128.26, 122.98, 116.83, 113.17, 50.50, 50.20. Elemental analysis for $C_{21}H_{20}N_2S_4O_{13}$: Theoretical (%): C 39.62, H 3.14, N 4.40; Experimental (%): C 39.47, H 3.36, N 4.49.

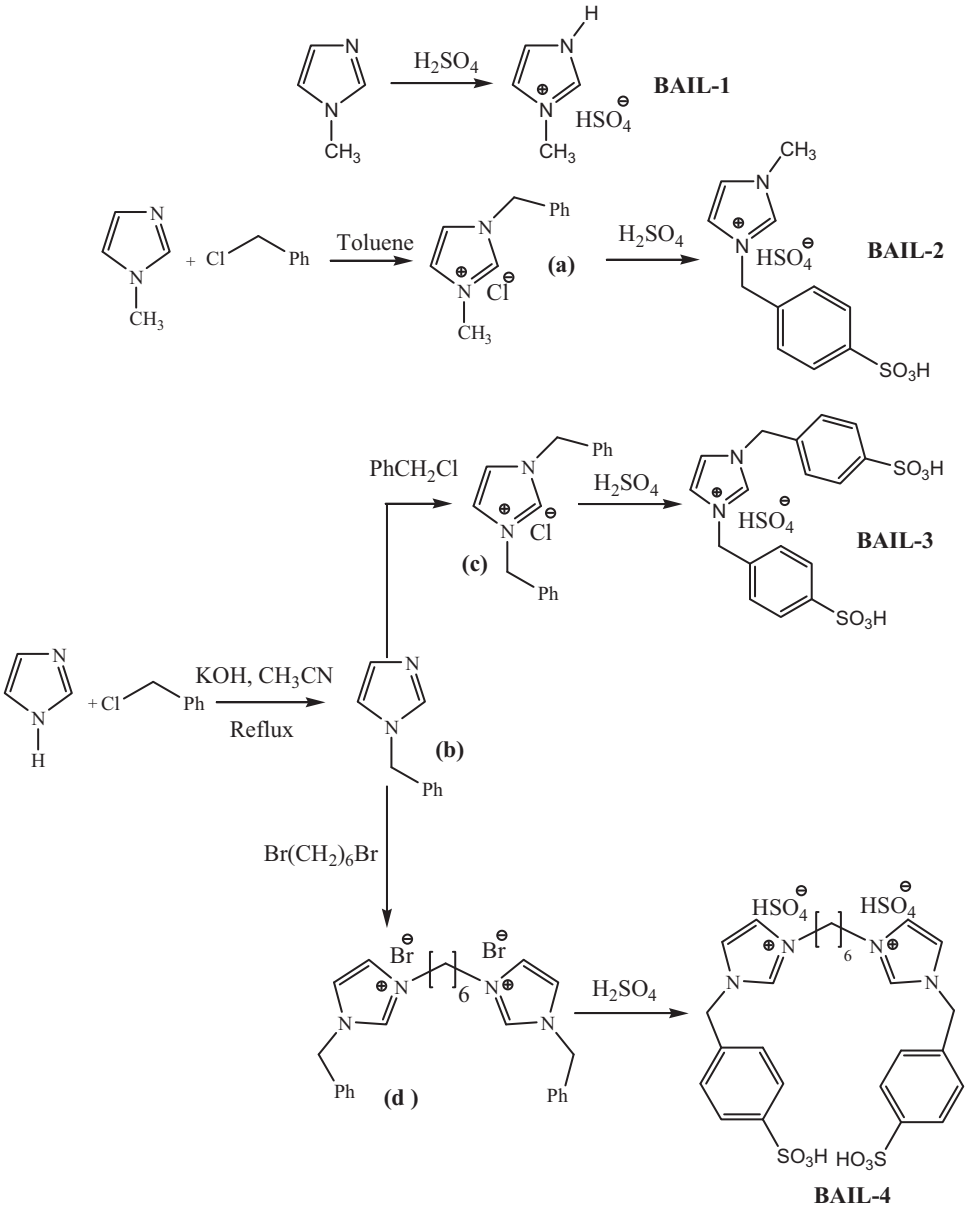
For the synthesis BAIL-7, first, 3,3′-(hexane-1,6-diyl)bis(1-benzyl-benzimidazolium)bromide was prepared using a similar procedure that was adopted for the synthesis of 1-benzyl-3-dodecyl-benzimidazolium bromide. For this, 1-benzyl-benzimidazol (20 mmol) and 1,6-dibromohexane (10 mmol) was reacted to obtain 3,3′-(hexane-1,6-diyl)bis(1-benzyl-benzimidazolium)bromide (yield = 91%) [14]. 3,3′-(Hexane-1,6-diyl)bis(1-benzyl-benzimidazolium)bromide was sulfonated using six equivalents of H_2SO_4 to obtain BIL-7 (yield = 78.4%).

BAIL-7: IR (KBr, υ, cm^{-1}) = 3372, 3131, 3069, 2939, 2869, 2484, 1694, 1619, 1557, 1486, 1451, 1373, 1312, 1230, 1143, 1016, 861, 754, 703. ^{1}H NMR (D_2O + DMSO-d_6) δ = 9.63 (s, 2H), 7.88–7.36 (m, 14H), 5.69 (s, 4H), 4.48 (t, 4H), 1.92 (m, 4H), 1.34 (m, 4H). ^{13}C NMR δ = 144.96, 143.02, 141.85, 135.34, 133.39, 129.34, 128.61, 125.51, 124.60, 116.37, 114.23, 51.10, 47.93, 27.61, 23.38. Elemental analysis for $C_{34}H_{38}N_4S_6O_{14}$: Theoretical (%): C 44.44, H 4.14, N 6.10; Experimental (%): C 44.31, H 4.29, N 6.18.

H-ZSM-5 [4], H-BETA [21], and SBA-15-pr-SO_3H [22] were synthesized following the reported procedures.

2.2. Catalyst characterizations

FT-IR was recorded on Bruker Tensor-27 spectrometer in the range of 400–4000 cm^{-1} (spectral resolution = 4 cm^{-1}; number of scans = 100). UV–visible spectra were recorded on Analytikjena Specord 250 PLUS spectrophotometer. ^{1}H and ^{13}C NMR was recorded on Bruker AM-400 MHz NMR. X-ray diffraction (XRD) patterns of solid samples were recorded in the 2θ range of 5–50° with a scan speed of 2°/min on PANalytical X'PERT PRO diffractometer using Cu Kα radiation (λ = 0.1542 nm, 40 kV, 20 mA) and a proportional counter detector. Nitrogen adsorption measurement at 77 K of solid samples was performed by Autosorb IQ volumetric adsorption analyzer of Quantachrome Instruments. Samples were out-gassed at 150–300 °C for 4 h in the degas port of the adsorption apparatus. The specific surface area was determined by BET method using the data points of P/P_0 in the range of about 0.05–0.3. The pore diameter was estimated using the Barret–Joyner–Halenda (BJH) model. Si and Al contents in the solid catalysts were estimated using a Rigaku 3070 E wavelength-dispersive X-ray



Scheme 1. Synthesis of imidazole based BAILs.

fluorescence (XRF) spectrometer with Rh target energized at 50 kV and 40 mA.

2.3. Catalytic reactions

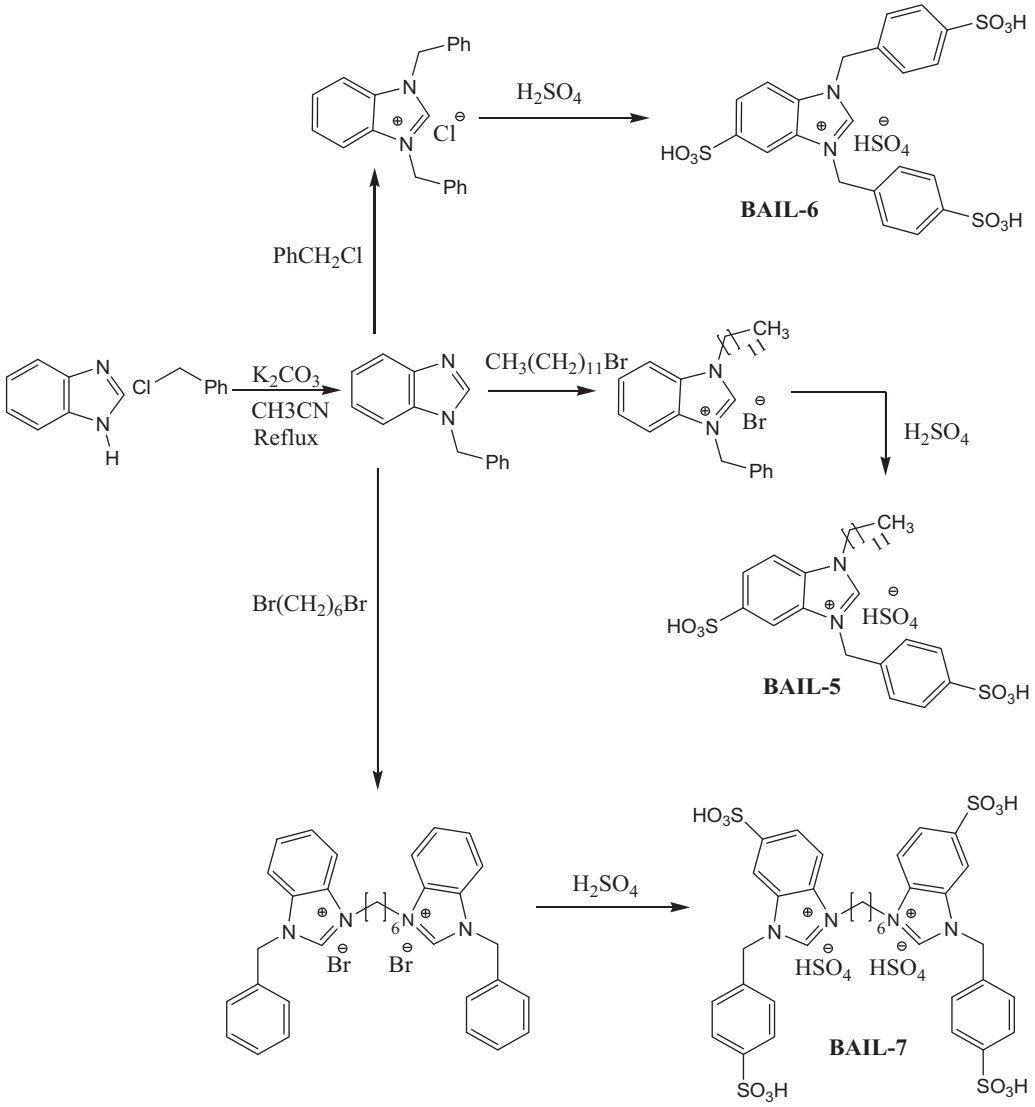
2.3.1. Synthesis of dihydropyrimidinones

In a typical synthesis, benzaldehyde (5 mmol), urea (7.5 mmol), ethylacetoacetate (5 mmol) and catalyst (0.1 mmol) were mixed in a 100 ml flask. Reaction was conducted at 313 K for 3 h. After the reaction, ethyl acetate was added in the reaction mixture to dissolve the product and the catalyst was removed by simple decantation/filtration. Products were isolated via column chromatography (hexane/ethyl acetate, 3:1) and characterized by using FT-IR, NMR and elemental analysis, which matches well with the reported value in literature [23].

Table 1
Textural properties of various solid acid catalysts investigated in this work.

Catalyst	S_{BET}[a] (m^2/g)	Ext. surface area (m^2/g)	Total pore volume (ml/g)	Concentration of active species
H-ZSM-5	350	67	0.2	Si/Al = 18[b]
H-BETA	595	212	0.44	Si/Al = 14[b]
SBA-15-pr-SO_3H	690	618	0.95	Organic functional group (0.64 mmol/g)[c]

[a] S_{BET} is the surface area which was calculated using the Brunauer–Emmett–Teller equation.
[b] Obtained from ICP.
[c] Determined from the elemental analysis.



Scheme 2. Synthesis of benzimidazole based BAILs.

2.3.2. Synthesis of amidoalkylnaphthols

A mixture of 2-naphthol (1.0 mmol), benzaldehyde (1.0 mmol), benzamide (1.1 mmol), catalyst (0.05 mmol) and 1,2-dicholoethane (3 ml) was stirred at 298 K. The progress of the reaction was monitored by TLC. After the reaction, crude product was washed with water and purified by column chromatography using silica gel (100–200) and hexane/ethyl acetate (95/5) as eluent to obtain the desired compound in pure form. Product was characterized by using FT-IR, NMR and elemental analysis, which matches well with the reported value in the literature [24]. Water fraction having ILs was evaporated under reduced pressure to remove the water and BAILs were recycled.

Table 2
Calculation and comparison of H_0 values of BAIL-1 to BAIL-4 in water at 298 K.

E. no.	ILs	A_{max}	[I] (%)	[IH$^+$] (%)	H_0
1	No BAIL	1.696	100	0	–
2	BAIL-1	1.588	93.6	06.4	2.155
3	BAIL-2	1.260	74.3	25.7	1.451
4	BAIL-3	1.041	61.4	38.6	1.192
5	BAIL-4	1.001	59.0	41.0	1.148

Indicator: 4-nitroanline.

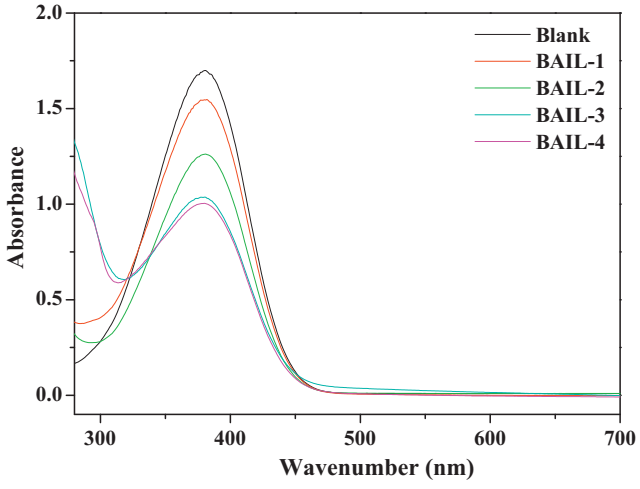
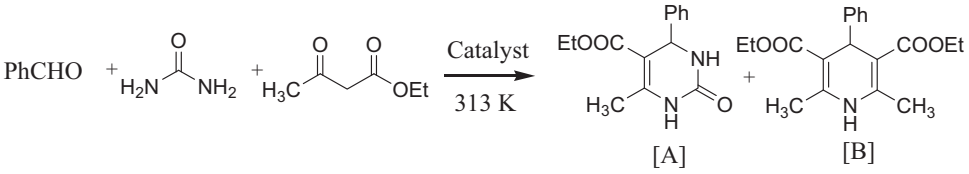


Fig. 1. Absorbance spectra of 4-nitroaniline after addition of BAIL-1 to BAIL-4 in water.



Scheme 3. Three component coupling reaction of benzaldehyde, urea and ethylacetoacetate.

Table 3
Reaction of benzaldehyde, urea and ethylacetoacetate under different reaction condition.

E. no.	Catalyst	Reactant ratio[a]	Solvent	Yield (%)		TON[c]
				A	B	
1	BAIL-2	1:1:1.5	Ethanol	48.6	0	24.3
2	BAIL-2	1:1:1.5	Water	16.6	10	13.3
3	BAIL-2	1:1:1.5	Ethanol/water (1:1)	21.1	8.9	15.0
4	BAIL-2	1:1.25:1.5	Ethanol	43.7	6.3	25.0
5	BAIL-2	1:1.25:1.5	None	45	5	25.0
6	BAIL-2	1:1:1.5	None	50.2	0	25.1
7	BAIL-2[b]	1:1:1.5	None	48.4	0	24.2
8	BAIL-1	1:1:1.5	None	29.4	0	14.7
9	BAIL-3	1:1:1.5	None	68.1	0	34.0
10	BAIL-4	1:1:1.5	None	72.2	0	36.1
11	BAIL-5	1:1:1.5	None	47.1	0	23.5
12	BAIL-6	1:1:1.5	None	81.5	0	40.8
13	BAIL-6[b]	1:1:1.5	None	78.7	0	39.4
14	BAIL-7	1:1:1.5	None	78.4	0	39.2
15	HZSM-5	1:1:1.5	None	0	0	–
16	HBEA	1:1:1.5	None	3.4	0	1.7
17	SBA-15-pr-SO_3H	1:1:1.5	None	7.3	0	3.6

Reaction conditions: reactant ratio as shown in the table (5 mmol = 1); solvent (5.0 g); catalyst (0.1 mmol); reaction time (3 h); reaction temperature (313 K).
[a] Reactant ratio = benzaldehyde:ethylacetoacetate:urea.
[b] Catalytic activity data of BAIL-2 and BAIL-6 in third cycle.
[c] TON = moles of reactant converted per mole of catalyst.

2.3.3. Synthesis of 1-(phenyl (piperidin-1-yl) methyl) naphthalene-2-ol (Betti base)

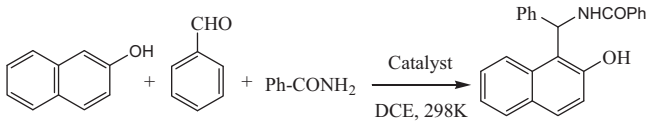
A mixture of benzaldehyde (1 mmol), 2-naphthol (1 mmol), piperidine (1 mmol), catalyst (0.05 mmol) and water (3 ml) was stirred at 298 K. After the reaction, the reaction mixture was extracted with ethyl acetate. The aqueous-phase was extracted with ethyl acetate. The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure to get the crude product as a white solid, which was purified by column chromatography with hexane/ethyl acetate (95/5). Product was characterized by using FT-IR, NMR and elemental analysis, which matches well with the reported value in the literature [25]. Water fraction having ILs was evaporated under reduced pressure to remove the water and BAILs were recycled.

3. Results and discussion

3.1. Synthesis and characterizations of BAILs

Except BAIL-1, all other BAILs were synthesized by multistep synthetic route. First 1-benzyl imidazole and 1-benzylbenzimidazole were synthesized and then they were used as precursors to synthesize all kinds of imidazole and benzimidazole based BAILs (Schemes 1 and 2). Samples were characterized by using FT-IR, NMR and elemental analysis. For comparative study, solid acid catalysts such as H-ZSM-5, H-BETA, and SBA-15-pr-SO_3H were prepared. Phase purity of H-ZSM-5, H-BETA, and SBA-15-pr-SO_3H samples was confirmed using wide angle and low angle XRD patterns. Solid acids were characterized by using N_2-adsorption, XRF and elemental analysis (Table 1).

Acidity of BAILs was measured using UV–visible spectrophotometer with a basic indicator by following the concept reported in literature [26–28]. In this manuscript, acidity of imidazole based BAILs (BAIL-1 to BAIL-4) was investigated using 4-nitroanline as indicator. With the increase of acidity of the BAILs, the absorbance of the unprotonated form of the basic indicator decreased, whereas

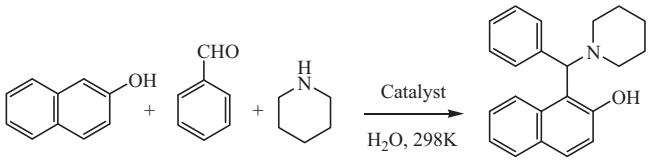


Scheme 4. Three component coupling reaction of 2-naphthol, benzaldehyde and benzamide.

Table 4
Synthesis of 1-amidoalkyl 2-naphthol using different catalysts investigated in this study.

E. no.	Catalyst	Yield (%)	TON[b]
1	BAIL-1	41.6	8.3
2	BAIL-2	68.8	13.8
3	BAIL-2[a]	64.5	12.9
4	BAIL-3	81.2	16.2
5	BAIL-4	83.3	16.7
6	BAIL-5	57.2	11.4
9	BAIL-6	93.8	18.8
10	BAIL-6[a]	91.2	18.2
11	BAIL-7	90.7	18.1
12	H-ZSM-5	0	–
13	H-BETA	5.2	1.0
14	SBA-15-pr-SO_3H	14.5	2.9

Reaction condition: 2-naphthol (1.0 mmol), benzaldehyde (1.0 mmol), benzamide (1.1 mmol), catalyst (0.05 mmol), DCE (3 ml), temperature (298 K), reaction time (4 h).
[a] Catalytic activity data of BAIL-2 and BAIL-6 in third cycle.
[b] TON = moles of reactant converted per mole of catalyst.



Scheme 5. Three component coupling reaction of 2-naphthol, benzaldehyde and piperidine.

the protonated form of the indicator could not be observed because of its small molar absorptivity and its location, so the $[I]/[IH^+]$ (I represents indicator) ratio can be determined from the differences of measured absorbance after the addition of BAILs and Hammett function, H_0, can be calculated using Eq. (1). This value can be regarded as the relative acidity of the BAILs:

$$H_0 = pK(I)_{aq} + \log\left[\frac{I}{IH^+}\right] \quad (1)$$

Under the same concentration of 4-nitroanline (5 mg/L, $pK(I)_{aq} = pK_a = 0.99$) and BAILs (25 mmol/L) in water, H_0 values of all BAILs were determined. The maximal absorbance of the unprotonated form of the indicator was observed at 380 nm in water. When the BAIL was added, the absorbance of the unprotonated form of the basic indicator decreased. As shown in Fig. 1, the absorbance of the unprotonated form of the indicator on addition of BAILs decreased as follows: BAIL-1 > BAIL-2 > BAIL-3 > BAIL-4. Calculations suggest that the Hammett acidity (H_0) of these ILs follows the order: BAIL-4 > BAIL-3 > BAIL-2 > BAIL-1 (Table 2). It may be noted that when similar UV–visible spectroscopy was used to investigate the acidity of benzimidazole based BAILs (BAIL-5 to BAIL-7), the absorbance of basic indicator increased, rather than decreased, upon addition of BAILs. This is due to the fact that the absorbance of BAIL-5 to BAIL-7 was overlapping with the 4-nitroanline absorbance. Further study is underway to develop a suitable probe molecule to evaluate the acidity of BAIL-5 to BAIL-7 using UV–visible spectroscopic method. However, the catalytic investigations and theoretical calculations described in the following sections are able to assess and explain the difference in activity observed in these BAILs.

3.2. Catalytic activities

Catalytic activities of BAILs were assessed using multi-component coupling reactions. Dihydropyrimidinones are an important class of organic compounds, which show prominent biological activity and are normally prepared using Biginelli reaction (Scheme 3) [29]. A large number of reports are available in literature for this protocol, including a few examples of Biginelli reaction in water [30,31]. The reaction is purely catalytic. No product was obtained in the absence of catalyst. First the reaction condition was optimized using BAIL-2. Using BAIL-2 catalyst, approximately 50% yield of Biginelli product was obtained in the ethanolic medium (Table 3, entry 1). When the reaction was conducted in water or ethanol/water mixture, in addition to Biginelli product (A), Hantzsch product (B) was also observed (entries 2 and 3) (Scheme 3). It was also observed that a mixture of products was found in ethanolic medium when the ratio of ethylacetoacetate to benzaldehyde was greater than one (entries 4 and 5). It is interesting to note that, when the reaction was carried out in the absence of any solvent, only Biginelli product was observed (Entry 6). However, this was possible only when the ethylacetoacetate to benzaldehyde ratio was one (compare entries 5 and 6). A principle of green chemistry says that no solvent condition is

Table 5
Synthesis of 1-(phenyl(piperidin-1-yl) methyl) naphthalene-2-ol over different catalysts investigated in this study.

E. no.	Catalyst	Yield (%)	TON[b]
1	BAIL-1	37.5	7.5
2	BAIL-2	56.3	11.3
3	BAIL-2[a]	55.2	11.0
4	BAIL-3	73.4	14.7
5	BAIL-4	74.2	14.8
6	BAIL-5	51.2	10.2
7	BAIL-6	90.8	18.2
8	BAIL-6[a]	88.4	17.7
9	BAIL-7	88.1	17.6
10	H-ZSM-5	0	–
13	H-BETA	0	–
14	SBA-15-pr-SO_3H	<1	–

Reaction condition: 2-naphthol (1.0 mmol), benzaldehyde (1.0 mmol), piperidine (1.0 mmol), catalyst (0.05 mmol), water (3 ml), temperature (298 K), reaction time (4 h).

[a] Catalytic activity data of BAIL-2 and BAIL-6 in third cycle.

[b] TON = moles of reactant converted per mole of catalyst.

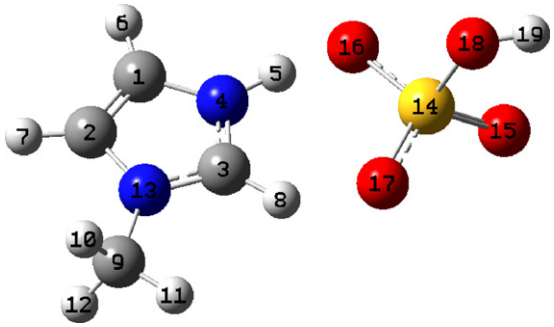


Fig. 2. Optimized molecular structure of BAIL-1 using RHF/6-31G.

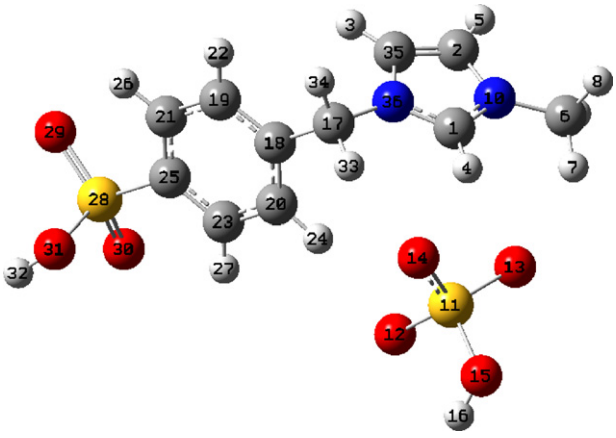


Fig. 3. Optimized molecular structure of BAIL-2 using RHF/6-31G.

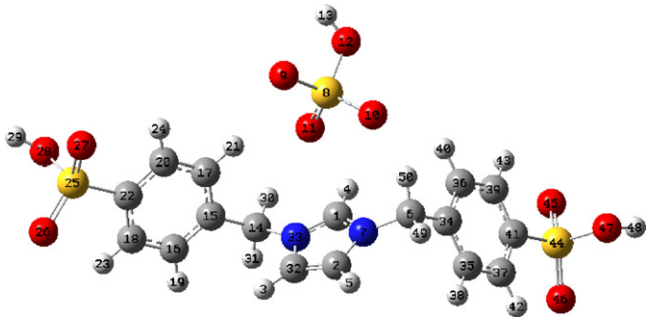


Fig. 4. Optimized molecular structure of BAIL-3 using RHF/6-31G.

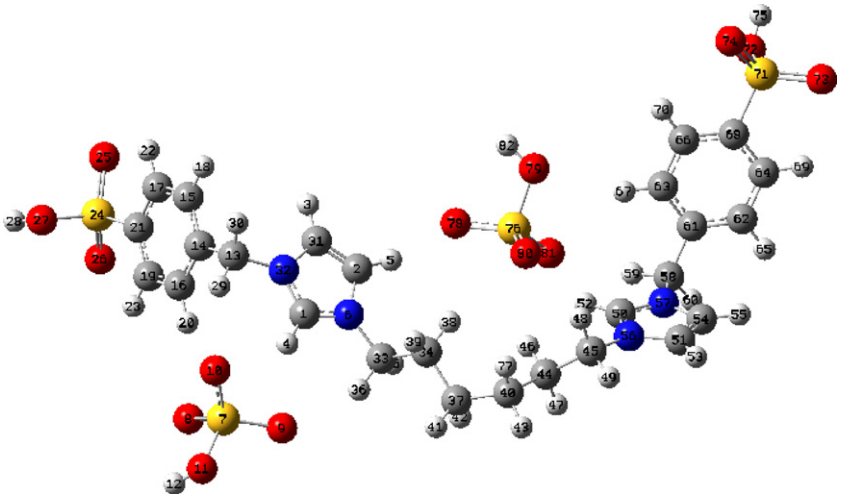


Fig. 5. Optimized molecular structure of BAIL-4 using RHF/6-31G.

the best medium. Hence, the catalytic activities of all other catalysts were compared in neat condition. The activity of Brönsted acidic ILs follows the order BAIL-6 > BAIL-7 > BAIL-4 > BAIL-3 > BAIL-2 > BAIL-5 > BAIL-1. For comparative study, H-ZSM-5, H-BETA, and SBA-15-pr-SO_3H were investigated. H-ZSM-5 was inactive whereas H-BETA and SBA-15-pr-SO_3H were weakly active. Among all catalysts investigated here, BAIL-6 was found to be the best (compare TON) for the selective formation of 3,4-dihydropyrimidinones. Recycling experiments confirm that the BAILs can be recycled without significant loss in catalytic activity (Table 3, entries 7 and 13).

Three component coupling reaction of 2-naphthol, benzaldehyde, and benzamide was investigated to synthesize amidoalkylnaphthols (Scheme 4). The reaction proceeds through the formation of o-quinone methide intermediates [32,33]. Further, nucleophilic conjugate addition of amide on o-quinone methide intermediate, leads to the formation of amidoalkylnaphthol as a product. BAIL-2 was chosen to optimize the synthetic protocol for this

Table 6
The geometry parameters of BAILs calculated at RHF/6-31G level.

Observed parameters	BAIL-1	BAIL-2	BAIL-3	BAIL-4
H–O bond distance of sulfonic acid (Å)		H_{32}–O_{31} = 0.960	H_{48}–O_{47} = 0.961 H_{29}–O_{28} = 0.960	H_{28}–O_{27} = 0.960 H_{75}–O_{72} = 0.961
H–O bond distance of HSO_4^- (Å)	H_{19}–O_{18} = 0.959	H_{16}–O_{15} = 0.959	H_{13}–O_{12} = 0.959	H_{12}–O_{11} = 0.959 H_{82}–O_{79} = 0.959
$(N)_2C$–H	C_3–H_8 = 1.070	C_1–H_4 = 1.066	C_1–H_4 = 1.065	C_2–H_5 = 1.065 C_{50}–H_{52} = 1.065
$(N)_2C$–H···O	H_8···O_{17} = 2.014	H_4···O_{14} = 2.099 H_4···O_{13} = 2.478	H_4···O_{11} = 2.131 H_4···O_{10} = 2.534	H_4···O_9 = 2.416 H_4···O_{10} = 2.115 H_{52}···O_{81} = 2.045 H_{52}···O_{80} = 2.535
Other hydrogen bonds in BAILs (Å)	H_5···O_{16} = 1.665	H_7···O_{13} = 2.280 H_{33}···O_{14} = 2.264 H_{24}···O_{12} = 2.429	H_{50}···O_{10} = 2.245 H_{21}···O_9 = 2.472 H_{40}···O_{10} = 2.402	H_{36}···O_9 = 2.327 H_{29}···O_{10} = 2.283 H_{20}···O_8 = 2.591 H_{46}···O_{81} = 2.508 H_5···O_{78} = 2.116 H_{59}···O_{81} = 2.416 H_{67}···O_{79} = 2.611
Energy (a.u.)	−961.454827	−1851.652966	−2702.543759	−3858.237388
Dipole moment (Debye)	13.4475	10.7362	8.0545	18.8607

Observed parameters	BAIL-5	BAIL-6	BAIL-7
H–O bond distance of sulfonic acid (Å)	H_{32}–O_{31} = 0.961 H_{33}–O_{26} = 0.983 H_{40}–O_{39} = 0.960	H_{33}–O_{26} = 0.974 H_{60}–O_{59} = 0.974 H_{32}–O_{31} = 0.975 H_{40}–O_{39} = 0.974	H_{32}–O_{31} = 0.961 H_{33}–O_{26} = 0.993 H_{95}–O_{87} = 0.979 H_{102}–O_{99} = 0.987 H_{84}–O_{83} = 0.960 H_{96}–O_{91} = 0.959
$(N)_2C$–H	C_7–H_{11} = 1.074	C_7–H_{11} = 1.069	C_7–H_{11} = 1.075 C_{62}–H_{64} = 1.066
$(N)_2C$–H···O	H_{11}···O_{42} = 1.936 H_{11}···O_{41} = 2.699	H_{11}···O_{41} = 2.030 H_{11}···O_{42} = 2.492	H_{11}···O_{88} = 1.821 H_{64}···O_{90} = 2.482
Other hydrogen bonds in BAILs (Å)	H_{45}···O_{42} = 2.523 H_{33}···O_{38} = 1.695	H_{44}···O_{42} = 2.166 H_{52}···O_{42} = 2.429 H_{18}···O_{38} = 2.546 H_{13}···O_{41} = 2.352	H_{95}···O_{29} = 1.767 H_{33}···O_{90} = 1.660 H_{76}···O_{92} = 2.566 H_{79}···O_{93} = 2.474
Energy (a.u.)	−3055.1889438	−3477.1618424	−5406.887302
Dipole moment (Debye)	16.1559	9.7614	42.1129

Table 7
Atomic charge analysis on the protons of $-SO_3H$ and HSO_4^- groups of BAILs.

ILs	Mullikan			NBO			CHELPG		
	$(N)_2C-\mathbf{H}$	$-SO_3\mathbf{H}$	$\mathbf{H}SO_4^-$	$(N)_2C-\mathbf{H}$	$-SO_3\mathbf{H}$	$\mathbf{H}SO_4^-$	$(N)_2C-\mathbf{H}$	$-SO_3\mathbf{H}$	$\mathbf{H}SO_4^-$
BAIL-1	0.407	–	0.456	0.317	–	0.528	0.285	–	0.529
BAIL-2	0.405	0.477	0.469	0.312	0.538	0.542	0.225	0.579	0.531
BAIL-3	0.389	0.470, 0.470	0.461	0.312	0.537, 0.537	0.532	0.190	0.573, 0.574	0.525
BAIL-4	0.393, 0.402	0.467, 0.471	0.455, 0.465	0.305, 0.307	0.535, 0.537	0.523, 0.534	0.204, 0.203	0.570, 0.570	0.515, 0.548
BAIL-5	0.450	0.476, 0.552	0.467	0.325	0.570, 0.542	0.538	0.275	0.568, 0.574	0.531
BAIL-6	0.409	0.471, 0.478, 0.469	0.465	0.322	0.530, 0.543, 0.536	0.535	0.195	0.573, 0.582, 0.578	0.528
BAIL-7	0.474, 0.353	0.480, 0.555, 0.565, 0.464	0.543, 0.457	0.331, 0.287	0.545, 0.577, 0.578, 0.533	0.568, 0.528	0.353, 0.214	0.580, 0.615, 0.578, 0.538	0.548, 0.659

reaction. First, the role of solvent was investigated. Activity of BAIL-2 in protic polar solvents, such as water, methanol, and ethanol, was found to be less than aprotic polar solvent such as 1,4-dioxane and 1,2-dicholoethane (DCE). The reaction can also be performed without a solvent, but only if carried out at high temperature (353 K). Activity of BAIL-2 was higher in DCE, hence DCE was chosen as the reaction medium for this reaction for further studies. Having found the optimized condition, all catalysts were assessed for their catalytic acidity. The activity of Brönsted acidic ILs follows the order BAIL-6 > BAIL-7 > BAIL-4 > BAIL-3 > BAIL-2 > BAIL-5 > BAIL-1. For comparative study, H-ZSM-5, H-BETA, and SBA-15-pr-SO_3H were investigated. H-ZSM-5 was inactive whereas H-BETA and SBA-15-pr-SO_3H were weakly active. Among all the catalysts investigated here, BAIL-6 was found to be the best for the synthesis of amidoalkylnaphthols. Recycling experiments confirmed that the BAILs can be recycled without significant loss in catalytic activity (Table 4, entries 3 and 10).

Further, multi-component Mannich type coupling reaction of 2-naphthol, benzaldehyde and piperidine was investigated for the synthesis of 1-(phenyl (piperidin-1-yl) methyl) naphthalene-2-ol (Betti base) in aqueous medium (Scheme 5) [25]. The reaction proceeds through the imine formation of the aldehyde and piperidine, followed by the attack of 2-naphthol. Under the optimized reaction condition the activity of Brönsted acidic ILs follows the order BAIL-6 > BAIL-7 > BAIL-4 > BAIL-3 > BAIL-2 > BAIL-5 > BAIL-1 (Table 5). All solid acid catalysts investigated in this study were found to be inactive for this reaction under the optimized reaction condition.

The activity of imidazole based Brönsted acidic ILs follows the order BAIL-1 < BAIL-BAIL-2 < BAIL-3 ≈ BAIL-4, which is consistent with the acidity measurement using UV–visible spectroscopy. As shown in Tables 3–5, the activity of imidazole/benzimidazole based multi-sulfonic acid group functionalized BAILs is comparatively higher than that of mono-sulfonic acid group functionalized BAIL-2. However, it may be noted that each BAIL have different numbers of acid sites (SO_3H and HSO_4^-), hence all of them have different TON per mol. If the number of acid sites (SO_3H and HSO_4^-) present in BAILs is taken into account for calculating TON, the activity of BAIL-2 is found to be higher than other BAILs investigated in this study. This may be due to the fact that the all $-SO_3H$ groups are not equivalent in all kinds of BAILs. Hydrogen bonding may exist in these BAILs, which influences their catalytic activity. To understand this phenomenon, structures of BAILs were optimized using theoretical modeling (Section 3.3).

3.3. The molecular geometries of BAILs

The minimum-energy geometries of BAILs were determined by performing ab initio geometry optimizations at the RHF/6-31G level [34]. The fully optimized geometries of these BAILs are presented in Figs. 2–8 and Table 6. In addition to this, atomic charge analysis on the protons of $-SO_3H$ and HSO_4^- groups of BAILs have also been performed and summarized in Table 7. All calculations were carried out using the Gaussian 09 series of programs. Theoretical study confirmed that a strong hydrogen bond network is presented in the BAILs. Molecular geometry

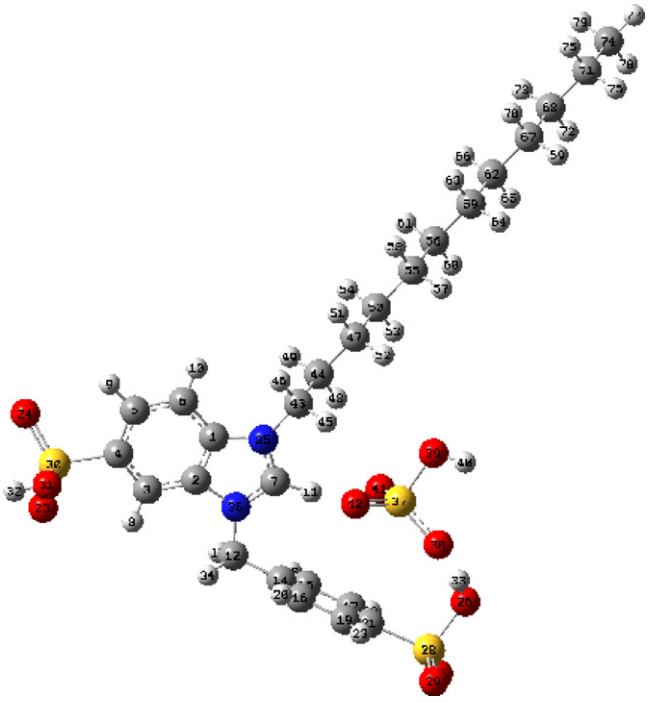


Fig. 6. Optimized molecular structure of BAIL-5 using RHF/6-31G.

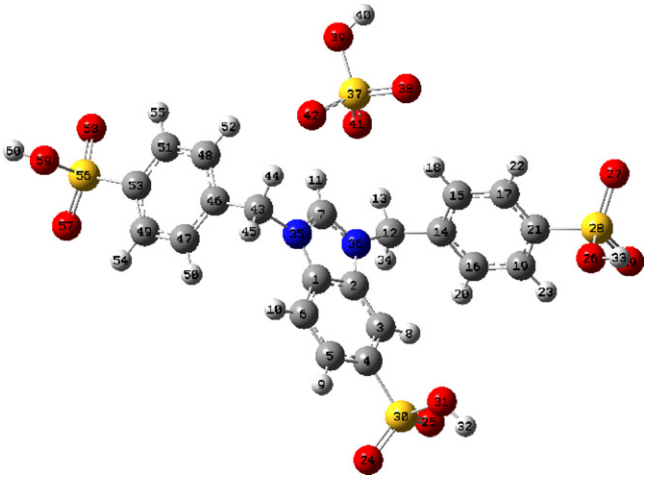


Fig. 7. Optimized molecular structure of BAIL-6 using RHF/6-31G.

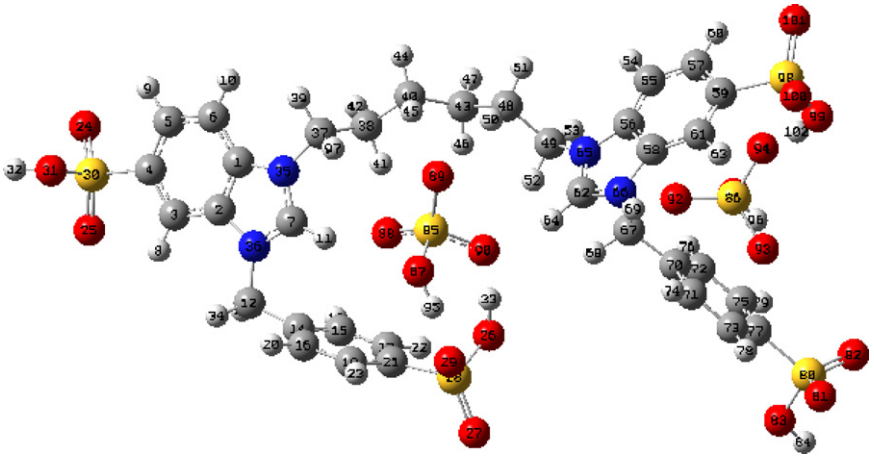


Fig. 8. Optimized molecular structure of BAIL-7 using RHF/6-31G.

study reveals that anion (HSO_4^-) interacts with the $-SO_3H$ and imidazole/benzimidazole ring through C–H···O or O–H···O type hydrogen bonding. In case of BAIL-1, there are two hydrogen bonds ($H_8\cdots O_{17}$ = 2.014 and $H_5\cdots O_{16}$ = 1.665) which are shorter than the Van der Waals distance of 2.67 Å (Fig. 2 and Table 6) [35]. The acidity in BAIL-1 is due to HSO_4^- and the acidic proton in imidazole ring. The activity of BAIL-2 should be high compared to BAIL-1 due to the presence of additional $-SO_3H$ group. Catalytic activity experiments reveal that the activity of BAIL-2 is approximately 1.5 times higher than BAIL-1. Optimized structure and hydrogen bonding revealed that imidazolium acid proton ($(N)_2C$–H bond distance of BAIL-2 < BAIL-1) and HSO_4^- of BAIL-2 is less acidic than BAIL-1(Fig. 3 and Table 6). In BAIL-2, benzene and imidazole ring hydrogen form weak hydrogen bonding with oxygen (O12, O13 and O14 of S=O) of HSO_4^- ($H_4\cdots O_{14}$ = 2.099, $H_4\cdots O_{13}$ = 2.478, $H_7\cdots O_{13}$ = 2.280, $H_{33}\cdots O_{14}$ = 2.264, $H_{24}\cdots O_{12}$ = 2.429). Whereas in BAIL-1, imidazolium ring hydrogens (H5 and H8) form comparatively strong hydrogen bonding with oxygen (O16 and O17 of S=O) of HSO_4^- ($H_5\cdots O_{16}$ = 1.665, $H_8\cdots O_{17}$ = 2.014) which makes proton of HSO_4^- in BAIL-1 more labile and acidic compared to the proton of HSO_4^- in BAIL-2. This is the reason why the activity of BAIL-2 is only 1.5 times higher than BAIL-1. Catalytic activity of BAIL-4 (having two imidazolium acid protons, two $-SO_3H$, and two HSO_4^- groups) was found to be only marginally more active than BAIL-3 (having one imidazolium acid proton, two $-SO_3H$ groups and one HSO_4^- group). Optimized structure and hydrogen bonding clearly show that in both cases, $-SO_3H$ groups and imidazolium acid protons are equally acidic ($(N)_2C$–H bond distance is same in both the cases, Table 6). Whereas HSO_4^- proton of BAIL-4 form comparatively strong hydrogen bonding ($H_{52}\cdots O_{81}$ = 2.045, $H_4\cdots O_{10}$ = 2.115, $H_5\cdots O_{78}$ = 2.116) than BAIL-3 ($H_4\cdots O_{11}$ = 2.131) (Table 6) that makes HSO_4^- protons of BAIL-4 less acidic as compared to the proton of HSO_4^- in BAIL-3. Hence, the overall activity of BAIL-4 is only marginally higher than BAIL-3 (Figs. 4 and 5 and Table 6). Based on the above observations, Tables 2–5 and Figs. 2–8, it can be concluded that, imidazolium acid proton, $-SO_3H$ and HSO_4^- groups contribute to the acidity of ionic liquids. It looks that both the catalytic activity and acidity increase with the number of $-SO_3H$ and HSO_4^- in BAIL-1 to BAIL-4.

As indicated by the catalytic activity data, the activity of benzimidazole based BAIL-5 is less than BAIL-3. This can be explained using the optimized structure obtained through theoretical modeling. In case of BAIL-3, none of the $-SO_3H$ group has any influence of HSO_4^-, whereas one $-SO_3H$ group in BAIL-5 is under the strong influence of HSO_4^- ($H_{33}\cdots O_{38}$ = 1.695) (Fig. 6). That makes proton of one of the $-SO_3H$ group in BAIL-5 less acidic (labile) than BAIL-3 and thus its activity is lower than the BAIL-3. As indicated by the catalytic activity data, the acidity of BAIL-6 (having three $-SO_3H$ groups and one HSO_4^- group) is more active than BAIL-7 (having four $-SO_3H$ and two HSO_4^- groups). This can also be explained using the optimized structure obtained through theoretical modeling. In case of BAIL-6, all three $-SO_3H$ groups have no influence of HSO_4^-, whereas two $-SO_3H$ groups in BAIL-7 are under strong influence of HSO_4^- ($H_{33}\cdots O_{90}$ = 1.660, $H_{95}\cdots O_{29}$ = 1.767, and $H_{11}\cdots O_{88}$ = 1.821) (Figs. 7 and 8). Optimized structure of BAIL-7 clearly shows that one of the HSO_4^- (S_{85}) and $-SO_3H$ (S_{28}) are so closely associated that they completely lose their activity, due to strong hydrogen bonding (Table 6). In addition, one of the $-SO_3H$ (S_{98}) group in BAIL-7 is under the influence of second HSO_4^- (S_{86}). Due to these interactions a close network structure is formed in which some of the acid protons are masked (except two terminal $-SO_3H$ groups acid protons) and inaccessible to the reactant molecules. Hence, the overall activity of BAIL-7 is less than the activity of BAIL-6. Theoretical modeling was able to correlate well with the activity–acidity order obtained using catalytic investigations.

4. Conclusions

In this study, the synthesis of several novel BAILs that contain one or multi-sulfonic acid group on imidazolium/benzimidazolium cation by simple and straight-forward procedures from cheap starting materials in good yields has been reported. BAILs served as efficient and reusable catalysts and realized the green synthesis of dihydropyrimidinones, amidoalkylnaphthols, and 1-(phenyl (piperidin-1-yl) methyl) naphthalene-2-ol. The activity of Brönsted acidic ILs follows the order BAIL-6 > BAIL-7 > BAIL-4 > BAIL-3 > BAIL-2 > BAIL-5 > BAIL-1, which is consistent with the acidity measurement using UV–visible spectroscopy and minimum-energy geometries determined by ab initio calculations. Based on the results obtained, one can also conclude that more numbers of $-SO_3H$ and HSO_4^- functionalization does not really improve the catalytic activity, when the catalytic activity is calculated per acid sites. Catalyst systems have several noteworthy features: (1) reactions can be carried out at relatively lower temperature with shorter reaction time; (2) products can be separated easily with high yields and purity; (3) BAILs can be reused several times (4) BAILs are cheap, environmentally benign and safe.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2011.06.003.

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