

Assessment of the Catalytic Activities of Novel Brönsted Acidic Ionic Liquid Catalysts

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Abstract Brönsted acidic ionic liquids (BILs) were synthesized by a two step synthetic protocol. Catalytic activities of BILs were assessed by means of suitable catalytic reactions such as acylation of 2-methoxynaphthalene with acetic anhydride, Biginelli reaction to synthesize 3,4-dihydropyrimidin-2(1H)-one, stereoselective synthesis of β -amino ketone via direct Mannich-type reaction and esterification of hexanoic acid with benzyl alcohol. Catalytic activities of BILs were high when compared with those of solid acid catalysts such as ZSM-5, beta, dealuminated beta and Al-SBA-15. BILs catalysts were found to be highly stereo/regio-selective for above mentioned reactions. Novel BILs catalyst offers several attractive features such as low cost, high catalytic activity/selectivity and recyclability.

Keywords Brönsted acidic ionic liquids · Acylation · Biginelli reaction · β -Amino ketone · Esterification

1 Introduction

The development of eco-friendly catalytic routes for organic transformations such as isomerisation, alkylation, oxidation, reduction, etc. is among the ongoing interests of catalytic researchers [1–4]. From laboratory scale to chemical manufacturing plants, the use of strong Brönsted acid is essential [5]. In this context, solid acids are being more widely used because they are less toxic compared to traditional liquid acids and they are also nonvolatile materials [6, 7]. However, solid acids too have several

disadvantages [8, 9]. Among the more troublesome of these are restricted accessibility of the matrix-bound acidic sites [8, 9]. Bearing in mind both the advantages and disadvantages of solid acids, it becomes imperative to identify such systems that are Brönsted acids with solid like nonvolatility. Ionic liquid is one of the good candidates.

Ionic liquids (ILs) have been described as one of the most promising reaction medium [10–17]. Some of the simple physical properties of the ILs that make them interesting as potential solvents for synthesis are the following: (1) they are good solvents for a wide range of both inorganic and organic materials, and unusual combinations of reagents can be brought into the same phase; (2) they are often composed of poorly coordinating ions, so they have the potential to be highly polar yet noncoordinating solvents; (3) they are immiscible with a number of organic solvents and provide a nonaqueous, polar alternative for two-phase systems. Hydrophobic ILs can also be used as immiscible polar phases with water; (4) ILs are nonvolatile, hence they can be used in high-vacuum systems and eliminate many containment problems. In recent times, room temperature ILs have attracted increasing attention in the area of green chemistry. Although ionic liquid was initially introduced as an alternative green reaction medium [8], today it has marched far beyond showing its significant role in controlling the reaction as catalyst [10, 11]. Since the first successful use of ionic liquid, dialkylimidazolium chloroaluminate, as a catalyst in Friedel–Crafts acylations [12], a number of ILs with unique properties have been developed and applied to catalyze many types of reactions [10]. Some significant research findings have been reported for Lewis acidic ionic liquid [12–14] but only a few reports are available for Brönsted acidic ionic liquids (BILs) [15–17]. Compared to conventional homogeneous and heterogeneous acid catalysts, acidic ILs demonstrate

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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. However, these reports [10–17] have not been entirely satisfactory and suffer from drawbacks such as the higher amount of ILs (20–300 mol%), relatively long reaction time (2.5–48 h), etc.

The objective of this study is to obtain acidic Ionic liquid catalysts that offers stereo/regio-selective product which is rather difficult to obtain even with heterogeneous catalyst. Herein, we wish to report the study on the application of two novel BILs, based on sulfonic acid group, which serve as a catalyst for the synthesis of several important synthetic intermediates. These catalysts are able to provide highly stereo/regio-selective products in many catalytic reactions. However, in this study, their catalytic activities were shown for acylation of 2-methoxynaphthalene with acetic anhydride, Biginelli reaction to synthesize 3,4-dihydropyrimidin-2(1H)-one, stereoselective synthesis of β -amino ketone via direct Mannich-type reaction and esterification of hexanoic acid with benzyl alcohol. The catalytic activities of BILs were compared with several solid acid catalysts such as ZSM-5, beta, dealuminated beta, and Al-SBA-15.

2 Experimental

2.1 Catalyst Preparation

2.1.1 Synthesis of Brønsted Acidic Ionic Liquids Catalyst

N-methylimidazole/pyridine (40 mmol) was dissolved in toluene (25 mL) and the resultant solution was cooled to 273 K. Benzyl chloride (40 mmol) was added drop wise over a period of 30 min at 273 K. Reaction mixture was stirred for 8 h at this temperature, then was heated to 343 K for 24 h. Upon completion of the reaction, the solvent was evaporated under vacuum. The residue was washed with ethyl acetate (3 \times 50 mL) and then dried under vacuum at 343 K for 8 h to afford (a)/(b) as off-white viscous oily liquid (Yield = 95%).

(a)/(b) (30 mmol) was added slowly into concentrated H₂SO₄ (15 g, 97%) at 270–273 K under stirring. Stirring continued at this temperature for 8 h and then the temperature was increased to 343 K for 4 h. Upon completion, the reaction mixture was dried under high vacuum at 343 K for 5–6 h. The residue was purified by flash column chromatography using silica gel (methanol:ethyl acetate = 95:5). BIL-1/BIL-2 was obtained as light yellow oily liquid (Yield = 85%).

BIL-1: IR (KBr, ν , cm⁻¹) = 3415, 3154, 2960, 1696, 1455, 1252, 1055, 880, 673, 585. ¹H NMR δ = 8.64

(s, 1H), 7.20–7.50 (m, 6H), 5.26 (s, 2H), 3.73 (s, 3H), Elemental analysis for C₁₁H₁₄N₂O₇S₂: Theoretical (%): C 37.71, H 4.03, N 8.00; Experimental (%): C 38.11, H 3.98, N 7.89.

BIL-2: IR (KBr, ν , cm⁻¹) = 3400, 3154, 1698, 1645, 1228, 1055, 1000, 880, 660 cm⁻¹. ¹H NMR δ = 8.90 (d, 2H), 8.6 (m, 2H), 8.1 (m, 1H), 7.5–7.54 (d, 4H), 5.81 (s, 2H). Elemental analysis for C₁₂H₁₃NO₇S₂: Theoretical (%): C 41.49, H 3.77, N 4.03; Experimental (%): C 41.75, H 3.70, N 3.89.

H-ZSM-5 [9], H-BEA, H-BEA-pH2 [18] and Al-SBA-15 [19] were prepared as per the reported procedures.

2.2 Catalysts Characterizations

X-ray diffraction (XRD) patterns of solid samples investigated in this study were recorded in the 2θ range of 5–50° with a scan speed of 2°/min on a Rigaku X-ray diffractometer using Cu K _{α} radiation (λ = 0.1542 nm, 40 kV, 20 mA) and a proportional counter detector. Nitrogen adsorption measurement at 77 K of solid samples investigated in this study was performed by NOVA 1000 series Quantachrome Instruments volumetric adsorption analyzer. Samples were out-gassed at 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/P₀ 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 fluorescence (XRF) spectrometer with Rh target energized at 50 kV and 40 mA. The C, H and N composition was estimated by a Carlo-Erba 1106 analyzer. FT-IR was recorded on Shimadzu 8201 PC spectrophotometer in the region 400–4,000 cm⁻¹. ¹H NMR was recorded on Bruker AM-400 MHz NMR.

2.3 Catalytic Reactions

2.3.1 Acylation Reaction of 2-Methoxynaphthalene

For acylation reaction, 10 mmol of 2-methoxynaphthalene, 10–50 mmol acetic anhydride, 5 g of 1, 2-dichloroethane, and catalyst (0.5 mmol BILs or 100 mg solid acid catalysts) were added to the reactor and the reaction was conducted at 373 K for 4 h. After the reaction, the autoclave was cooled to room temperature with cold water immediately. After completion of the reaction, the catalyst was removed by simple filtration/decantation. The products were analyzed using GC, Shimadzu GC-14B equipped with ZB-50 capillary column (30 m length \times 0.25 mm inner diameter) and confirmed with GC-MS, Shimadzu GCMS-QP5050 and authentic samples.

2.3.2 One Pot Three Component Reaction of Benzaldehyde, Urea and Ethylacetoacetate

In a typical synthesis benzaldehyde (20 mmol), urea (30 mmol), ethylacetoacetate (20 mmol) and catalyst (0.1 mmol BILs or 50 mg solid catalysts) were mixed in a 100 mL flask. Reaction was conducted at 353 K for 2–4 h. After the completion of the reaction, the catalyst was removed by simple filtration/decantation. Products were isolated via flash column chromatography (petroleum ether/ethyl acetate, 3:1).

2.3.2.1 5-Ethoxycarbonyl-4-phenyl-6-methyl-3,4-dihydropyrimidin-2(1H)-one (3,4-dihydropyrimidinones—[A]) IR (KBr, ν , cm^{-1}): 1090, 1221, 1645, 1700, 1723, 3115, 3245. $^1\text{H NMR } \delta$: 9.17 (s, 1H), 7.75 (s, 1H), 7.20–7.30 (m, 5H), 5.10 (d, 1H), 3.95 (q, 2H), 2.20 (s, 3H), 1.07 (t, 3H). Elemental analysis for $\text{C}_{14}\text{H}_{16}\text{N}_2\text{O}_3$: Theoretical (%): C, 64.60; H, 6.20; N, 10.76. Experimental (%): C, 64.8; H, 6.08; N, 10.60.

2.3.2.2 4-Phenyl-2,6-dimethyl-1,4-dihydro-3,5-ethoxycarbonyl pyridine (1,4-dihydropyridinones—[B]) IR (KBr, ν , cm^{-1}): 1090, 1210, 1485, 1650, 1685, 3340. $^1\text{H NMR } \delta$: 8.76 (s, 1H), 7.02–7.17 (m, 5H), 4.81 (s, 1H), 3.94 (q, 4H), 2.22 (s, 6H), 1.09 (t, 6H). Elemental analysis for $\text{C}_{19}\text{H}_{23}\text{NO}_4$: Theoretical (%): C, 69.28; H, 7.04; N, 4.25. Experimental (%): C, 69.48; H, 6.90; N, 4.16.

2.3.3 One Pot Three Component Reaction of Benzaldehyde, Aniline and Ketones

A mixture of benzaldehyde (20 mmol), aniline (20 mmol), cyclohexanone/acetophenone (20 mmol) and catalyst (0.1 mmol BILs or 50 mg solid catalysts) was stirred in ethanol (10 g) at room temperature for different time intervals. After completion of the reaction, catalyst was removed by simple filtration/decantation. The filtrate was washed with NaHCO_3 (aq) and brine, and the products were dried over MgSO_4 . The solvent was removed under reduced pressure. Pure β -amino ketone was recrystallized from ethanol.

2.3.3.1 2-((phenyl) (phenylamino) methyl)-cyclohexanone IR (KBr, ν , cm^{-1}): 3396, 1697, 1600, 1501, 810. $^1\text{H NMR } \delta$: 7.43 (d, 2H), 7.33 (m, 2H), 7.11 (t, 1H), 7.0 (d, 2H), 6.75 (m, 2H), 6.6 (t, 1H), 5.2 (br s, 1 H), 4.85(d, $J = 4.4$ Hz, 1H), 2.91–2.95 (m, 1 H), 2.20–2.31 (m, 2H), 1.86–2.04 (m 4H), 1.5–1.76 (m, 2H). Elemental analysis for $\text{C}_{19}\text{H}_{21}\text{NO}$: Theoretical (%): C, 81.72; H, 7.52; N, 5.01. Experimental (%): C, 81.95; H, 7.46; N, 4.87.

2.3.3.2 3-(phenylamino)-1,3-diphenyl-propan-1-one IR (KBr, ν , cm^{-1}): 3398, 1675, 1598, 1519, 872. $^1\text{H NMR } \delta$: 7.83 (d, 2H), 7.54 (m, 2H), 7.41 (t, 1H), 7.3 (d, 2H), 7.2 (m, 2H), 7.01 (t, 1H), 6.93 (d, 2H), 6.67 (m, 2H), 6.5 (t, 1H), 5.33 (br s, 1H), 4.9 (t, $J = 4$ Hz, 1H), 3.6 (dd, $J = 14.4$ Hz, 1H), 3.40 (dd, $J = 15.6$ Hz, 1 H). Elemental analysis for $\text{C}_{21}\text{H}_{19}\text{NO}$: Theoretical (%): C, 83.72; H, 6.31; N, 4.65. Experimental (%): C, 83.98; H, 6.20; N, 4.46.

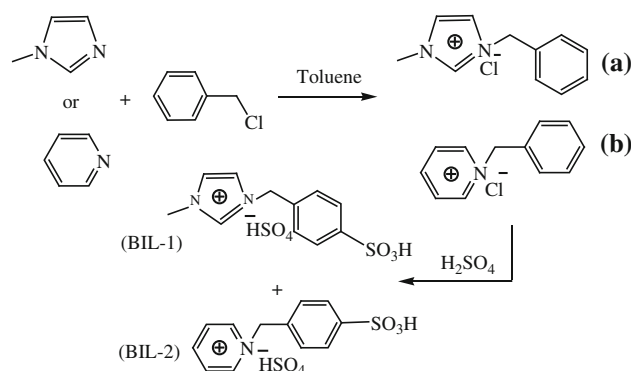
2.3.4 Esterification Reaction

The esterification reaction was conducted at 298–403 K for 2 h using benzyl alcohol (10 mmol), hexanoic acid (10 mmol), toluene (5 g) as solvent, and the catalyst (0.2 mmol BILs or 100 mg solid acid catalysts) in the autoclave. The post-reaction procedures were the same as that of the acylation reaction.

3 Results and Discussion

3.1 Catalyst Characterizations

BIL-1 and BIL-2 (Scheme 1) were synthesized by a two step synthetic protocol. First, *N*-methylimidazole/pyridine was alkylated with benzyl chloride and the resulting quaternary chloride (a/b) was transformed into BIL-1/BIL-2 by using concentrated sulfuric acid as anion exchange and sulphonating reagents, respectively. Samples were characterized using FT-IR, NMR and elemental analysis. For comparative study, solid acid catalysts such as H-ZSM-5, H-BEA and Al-SBA-15 were prepared. Recently, it has been reported that the catalytic activity of zeolite beta can be significantly improved if it is dealuminated using oxalic acid at pH 2 [18]. Hence, in this study, H-BEA was dealuminated with oxalic acid at pH 2 (sample designated as H-BEA-pH2) and investigated in catalytic reactions. Solid acids were characterized using XRD, N_2 -adsorption and XRF. The details of their textural properties are given in



Scheme 1 Synthetic protocol for BILs

Table 1 Textural properties of various solid acid samples investigated in this study

Sample	Si/Al	Surface area (m ² /g)			Pore volume (cm ³ /g)	
		Total	Micropore	External	Total	Micropore
H-ZSM-5	19.8	325	287	38	0.18	0.16
H-BEA	17.5	600	381	251	0.48	0.20
H-BEA-pH2	24.5	660	391	269	0.64	0.19
Al-SBA-15	20.2	820	60	760	1.24	0.06

Table 1. Phase purity of H-ZSM-5, H-BEA, H-BEA-pH2, Al-SBA-15 samples was confirmed using wide angle and low angle XRD pattern (Figure not shown).

3.2 Catalytic Activities

The reaction condition for the acylation of 2-methoxynaphthalene (2-MON) with acetic anhydride was first optimized using BIL-1. 1-acetyl, 2-methoxy naphthalene (1-Ac,2-MON) was formed as a major product and 2-methoxy, 6-acetyl naphthalene (6-Ac,2-MON) was formed as a minor product in the acylation reaction of 2-MON using acetic anhydride (Scheme 2). Influence of molar ratio of 2-MON to acetic anhydride is shown in Fig. 1. A large difference in total conversion was observed when the molar ratio was changed from 1:1 to 1:2 but only a marginal increase in conversion was observed on further change of molar ratio up to 1:5. 1,2-dichloroethane was found to be the best solvent for this reaction [18]. After 2 h at 333 K, only 12.5% conversion of 2-MON and 99.3% selectivity for 1-Ac,2-MON was observed. After 12 h at 333 K, the conversion of 2-MON increased to 33.7% but the selectivity was slightly decreased (97.6%). However, it may be noted that when the reaction was performed at 373 K, 96% conversion for 2-MON with 96% selectivity for 1-Ac,2-MON was observed in 4 h. Thus, the following reactions were conducted in 1, 2-dichloroethane at a ratio of 2-MON to acetic anhydride of 1:2 at 373 K for 4 h.

Table 2 summarizes the results of acylation reactions of 2-MON with acetic anhydride over different catalysts investigated in this study. Among them, BILs were found to be the best. The activity of H-BEA for this reaction can be enhanced if the H-BEA was dealuminated with oxalic acid at pH2. However, the reaction with H-BEA had to carry out at 423 K. As shown in Table 2 (compare entries

Scheme 2 Acylation of 2-methoxynaphthalene with acetic anhydride

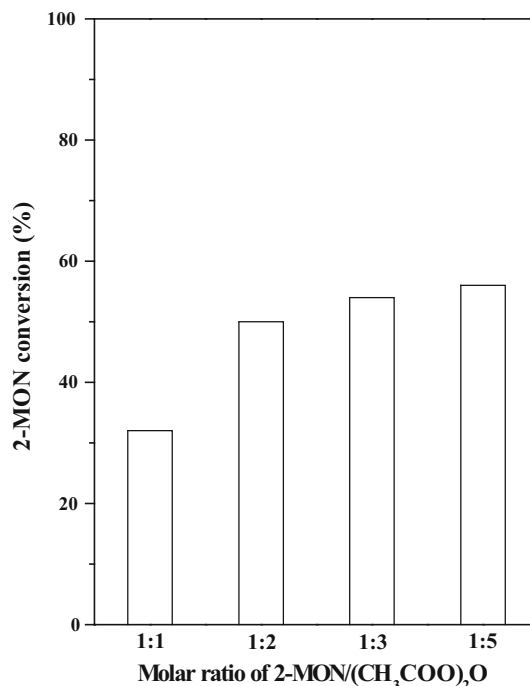
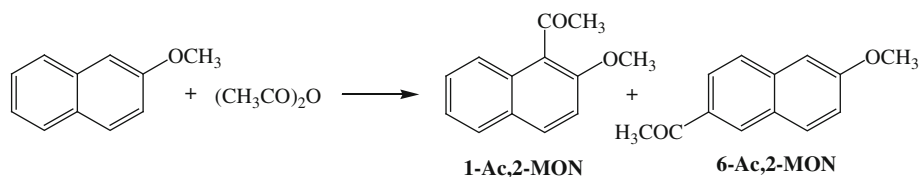


Fig. 1 Influence of 2-methoxynaphthalene/acetic anhydride ratio on acylation reaction over BIL-1

1, 2 and 7), H-BEA-pH2 and BILs exhibited similar catalytic activity (TON = 20). However, it may be noted that using BILs reactions were carried out at 373 K whereas using H-BEA-pH2, reaction had to carry out at 423 K. At 373 K, H-BEA-pH2 is less active (TON = 2). BILs exhibited much higher activity with very high selectivity for 1-Ac,2-MON at low temperature (373 K) compared to dealuminated H-BEA (423 K). To examine the feasibility of this reaction under eco-friendly conditions, reactions were performed in neat condition. BILs were found to be significantly active (TON = 18) under no solvent condition.

Dihydropyrimidinones are an important class of organic compounds, which show prominent biological activity and are normally prepared using Biginelli reaction [20] (Scheme 3). A large number of reports are available in literature for this protocol [21–23], including a few examples of Biginelli reaction in water [24, 25]. A summary of the optimized experiments with benzaldehyde, ethyl acetoacetate and urea is listed in Table 3. The reaction is purely catalytic. No product was obtained in the absence of catalyst. Using BIL-1 catalyst, 80% yield of

Table 2 Acylation of 2-methoxynaphthalene (2-MON) with acetic anhydride over different catalysts investigated in this study

E. No.	Catalyst	Temperature (K)	Conv. of 2-MON (%)	Product distribution (%)		TON
				1Ac,2-MON	6Ac,2-MON	
1	BIL-1	373	95.7	96	4	20
2	BIL-2	373	95.1	96.1	3.9	20
3	BIL-1 ^a	373	83.5	93	7	18
4	BIL-2 ^a	373	83.0	93.5	6.5	18
5	H-ZSM-5	423	<1	–	–	–
6	H-BEA	423	5.6	63	37	3
7	H-BEA-pH2	423	30.5	72	28	20
8	H-BEA-pH2	373	3.5	82	18	2
9	Al-SBA-15	423	10.7	75	25	5

Reaction conditions: 2-MON (10 mmol); acetic anhydride (20 mmol); 1,2-dichloroethane (5.0 g); catalyst (0.5 mmol BILs or 100 mg solid catalyst); reaction time (4 h)

^a Reactions were performed without solvent

TON moles of reactant converted per mole of catalyst

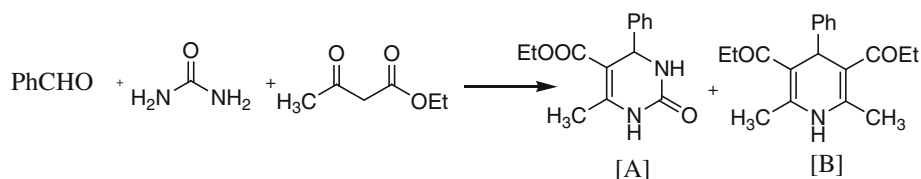
Biginelli product was obtained in the ethanol medium (entry 1, Table 3). When the reaction was conducted in water or ethanol/water mixture, in addition to Biginelli product (A), Hantzsch product (B) was also observed (entry 2–3) (Scheme 3). It was also observed that a mixture of products was found in ethanolic medium when the ratio of ethylacetoacetate to benzaldehyde was greater than one (entry 4). 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 is possible only when the ethylacetoacetate to benzaldehyde ratio is one (compare entry 5 and 6). Principles of green chemistry say that no solvent condition is the best medium. Hence, the catalytic activities of all other catalysts were compared in neat condition.

For comparative study, H-ZSM-5, H-BEA, H-BEA-pH2, and Al-SBA-15 were investigated. Using H-ZSM-5, very low yield of product was observed. But the yield was relatively high when H-BEA and mesoporous Al-SBA-15 were used. Low yield in the case of H-ZSM-5 can be ascribed due to pore diffusion limitation. Enhanced diffusion is possible in case of H-BEA and Al-SBA-15. However, the yield of product is low in case of Al-SBA-15. This is due to the low acidity of Al-SBA-15 compared to H-BEA. Among all the catalysts investigated here, BILs were found to be

the most appropriate (compare TON) for the selective formation of 3,4-dihydropyrimidinones. BIL-1 was found to be stable under the reaction condition and exhibited TON of 147 in third cycles.

β -Amino carbonyl compounds are important synthetic intermediates for various pharmaceutical and natural products. They can be prepared by C–C bond forming Mannich reactions [26–28]. One pot three component strategy can be adopted to prepare such compounds. A variety of catalysts, Zn(Otf)₂ [29, 30], H₃PW₁₂O₄₀ [31], ZrOCl₂·8H₂O [32], PS–SO₃H [33], L-Proline [34] and HClO₄–SiO₂ [35] have been reported for this reaction. However, these catalysts have several drawbacks, such as long reaction time, use of costly and non-recoverable catalysts, and requirement of special effort for catalyst preparation. The catalytic activity of BILs was investigated in the synthesis of β -amino carbonyl compounds (Scheme 4).

To optimize the reaction condition, three-component Mannich reaction of benzaldehyde, aniline, and cyclohexanone was examined in CH₃OH, C₂H₅OH, CH₂Cl₂, and H₂O (Table 4). Excellent anti-selectivity was observed in CH₃CN; however, the yield was found to be low in this case. Among all, C₂H₅OH showed high activity and good anti-selectivity. Therefore, C₂H₅OH was chosen as the



Scheme 3 Synthesis of: [A] 3,4-dihydropyrimidinones (Biginelli) and [B] 1,4-dihydropyridinones (Hantzsch) products from one pot reaction of benzaldehyde, urea and ethylacetoacetate

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

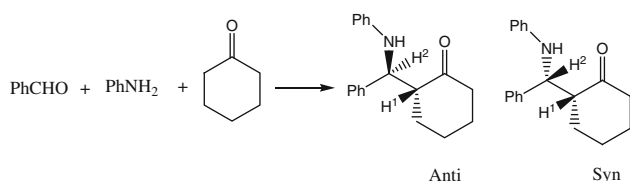
E. no.	Catalysts	Reactant ratio ^a	Solvent	Benzaldehyde conv. (%)	Product distribution (%)		TON
					A	B	
1	BIL-1	1:1:1.5	Ethanol	80	80	0	160
2	BIL-1	1:1:1.5	Water	40	25	15	80
3	BIL-1	1:1:1.5	Ethanol/water (1:1)	54	38	16	108
4	BIL-1	1:1.25:1.5	Ethanol	78	68	10	156
5	BIL-1	1:1.25:1.5	None	80	72	8	160
6	BIL-1	1:1:1.5	None	82	82	0	164
7	BIL-1 ^b	1:1:1.5	None	73.4	73.4	0	147
8	BIL-2	1:1:1.5	None	81.6	81.6	0	163
9	H-ZSM-5	1:1:1.5	None	2.2	2.2	0	1
10	H-BEA	1:1:1.5	None	10	8	0	5
11	H-BEA-pH2	1:1:1.5	None	20	20	0	13
12	Al-SBA-15	1:1:1.5	None	8	10	0	4

Reaction conditions: reactants ratio as shown in Table 1 (20 mmol = 1); solvent (15.0 g); catalyst (0.1 mmol BILs or 50 mg solid catalyst); reaction time (1 h); reaction temperature (353 K)

^a Reactant ratio = benzaldehyde:ethylacetoacetate:urea

^b Catalytic activity data of BIL-1 in third cycle

TON moles of reactant converted per mole of catalyst

**Scheme 4** Direct Mannich-type reactions of benzaldehydes, anilines and cyclohexanone

reaction medium to compare the catalytic activity. Anti and syn isomers were identified by the coupling constant (*J*) of the vicinal protons adjacent to CO and NH in their ¹H NMR spectra. *J* signal of anti isomer is higher than that of the syn one. The anti/syn ratio was determined by ¹H NMR judged by the intensity of the H² (Scheme 5). If hydrogen bonds are formed among BIL, the imine and the enol form of cyclohexanone, the aryl groups of aldimine would be anti to each other and there would be less steric repulsion between the methylene groups of cyclohexanone and phenyl group on the carbon atom, as well as BILs and H¹. So the most stable transition state would produce the anti isomer (Scheme 5).

To investigate the structure and property of different ketones, acetophenone (Scheme 6) was chosen. Acetophenone was less reactive than cyclohexanone; hence, long reaction time was required. For this reaction, BILs were found to be very active catalysts compared to solid acid catalysts. The results are shown in Table 5. H-ZSM-5 was found to be inactive, whereas H-BEA and Al-SBA-15 were weakly active. BIL-1 was found to be stable under the

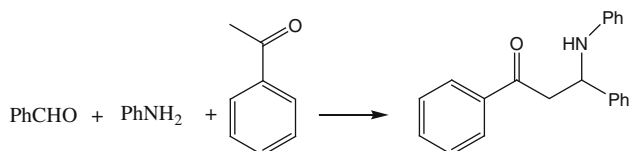
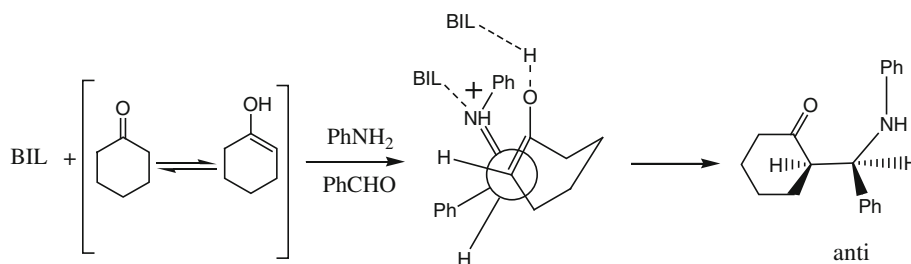
Table 4 Mannich reaction of benzaldehyde, aniline and cyclohexanone under different solvent medium

E. no.	Catalyst	Solvent	Time	% Yield	Anti/syn	TON
1	BIL-1	CH ₂ Cl ₂	5 min	40	80/20	80
2	BIL-1	CH ₃ CN	5 min	50	95/05	100
3	BIL-1	CH ₃ OH	5 min	76	82/18	152
4	BIL-1	H ₂ O	5 min	72	63/37	144
5	BIL-1	C ₂ H ₅ OH	5 min	85	88/12	170
6	BIL-2	C ₂ H ₅ OH	5 min	86	88/12	172
7	H-ZSM-5	C ₂ H ₅ OH	1 h	<1	–	–
8	H-BEA	C ₂ H ₅ OH	5 min	1.2	–	1
9	H-BEA	C ₂ H ₅ OH	1 h	5	75/25	3
10	H-BEA-pH2	C ₂ H ₅ OH	5 min	3.2	–	2
11	H-BEA-pH2	C ₂ H ₅ OH	1 h	15.8	80/20	10
12	Al-SBA-15	C ₂ H ₅ OH	5 min	2.5	–	2
13	Al-SBA-15	C ₂ H ₅ OH	1 h	10.0	70/30	8

Reaction conditions: benzaldehyde, aniline, cyclohexanone (20 mmol) each; solvent (10.0 g); catalyst (0.1 mmol BILs or 50 mg solid catalyst); reaction temperature (298 K)

reaction condition and exhibited TON of 140 in third cycles.

Next, the activity of these catalysts was investigated for esterification of benzyl alcohol with hexanoic acid. In this reaction, ester was formed as a major product while dibenzyl ether is formed as a by-product due to a dehydrative condensation between two alcohol molecules (Scheme 7). The result obtained is provided in Table 6. When the reaction was performed at 298 K, more than 50%

Scheme 5 Possible transition state leading to anti product**Scheme 6** Direct Mannich-type reactions of benzaldehydes, anilines and acetophenone**Table 5** Mannich reaction of benzaldehyde, aniline and acetophenone over various catalysts investigated in this study

E. no.	Catalyst	Time	% Yield	TON
1	BIL-1	30 min	80	160
2	BIL-1 ^a	30 min	70	140
3	BIL-2	30 min	78	156
4	H-ZSM-5	30 min	0	–
5	H-ZSM-5	6 h	<1	–
6	H-BEA	30 min	<1	–
7	H-BEA	6 h	5.2	3
8	H-BEA-pH2	30 min	4	2
9	H-BEA-pH2	6 h	17	11
10	Al-SBA-15	30 min	3	2
11	Al-SBA-15	6 h	11.5	9

Reaction conditions: benzaldehyde, aniline, acetophenone (20 mmol) each; ethanol (10.0 g); catalyst (0.1 mmol BILs or 50 mg solid catalyst); reaction temperature (298 K)

^a Catalytic activity data of BIL-1 in third cycle

benzyl alcohol conversion and 99.6% ester selectivity was observed within 2 h of the reaction. It is interesting to note that neither H-ZSM-5 nor H-BEA is active at this temperature. When the reaction temperature was raised to 323 K, BILs shows 85% benzyl alcohol conversion with 99% selectivity for ester. Under this condition, H-ZSM-5

was inactive while H-BEA was weakly active (TON = 2). H-BEA was moderately active (TON = 9) for this reaction at 403 K but with a very less ester selectivity (73%). Activity of H-BEA was improved (TON = 27) on dealumination with oxalic acid at pH 2, but the selectivity was still very poor (66%). BIL-1 is recyclable and stable under the reaction condition and exhibited TON of 40 in third cycles.

To further confirm the stability of BIL-1 under the reaction condition, leaching experiments were designed at partial conversions. Initially, reaction was performed for 30 min and then BIL-1 was removed from the reaction mixture and the reaction was continued. No significant increase in the conversion of benzyl alcohol was observed (Fig. 2) after removing the catalyst from the reaction mixture. Similar experiment was also performed after removing the catalyst from the reaction mixture after 60 min from the start of reaction. This clearly shows that BIL-1 is stable under the reaction condition.

4 Conclusions

An efficient and environmental friendly catalyst was developed for acylation of 2-methoxynaphthalene with acetic anhydride, Biginelli reaction to synthesize 3,4-dihydropyrimidin-2(1H)-one, stereoselective synthesis of β -amino ketone via direct Mannich-type reaction and esterification of hexanoic acid with benzyl alcohol. These reactions are easy to perform and the purification protocol is simple. BILs are inexpensive and easy to synthesize, and can be separated easily and reused for several cycles. Apart from the experimental simplicity, the advantage of this methodology is the use of milder and efficient catalysts for

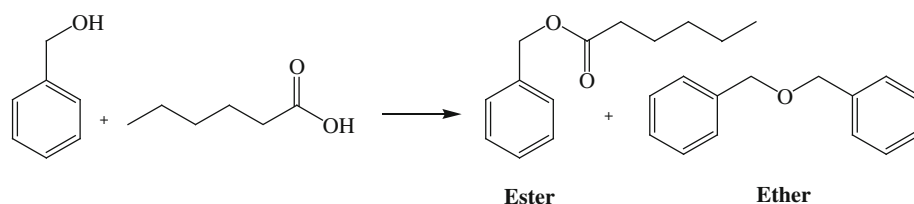
Scheme 7 Esterification reaction of benzyl alcohol with hexanoic acid

Table 6 Esterification of benzyl alcohol with hexanoic acid over various catalysts investigated in this study

E. no.	Catalyst	Temperature (K)	Conv. of benzyl alcohol (%)	Product distribution (%)		TON
				Ester	Ether	
1	BIL-1	298	57	99.6	0.4	27
2	BIL-1	323	85	99.1	0.9	42
3	BIL-1 ^a	323	80.5	99.2	0.8	40
4	BIL-2	323	87	99.0	1.0	45
5	H-ZSM-5	403	0	–	–	–
6	H-BEA	323	4.0	78	22	2
7	H-BEA	403	20.3	74	26	9
8	H-BEA-pH2	323	8.0	70	30	5
9	H-BEA-pH2	403	43.0	66	34	27
10	Al-SBA-15	323	4.5	80	20	2
11	Al-SBA-15	403	21.9	78	22	11

Reaction conditions: benzyl alcohol (10 mmol); hexanoic acid (10 mmol); toluene (5.0 g); catalyst (0.2 mmol BILs or 100 mg solid catalyst); reaction time (2 h)

^a Catalytic activity data of BIL-1 in third cycle

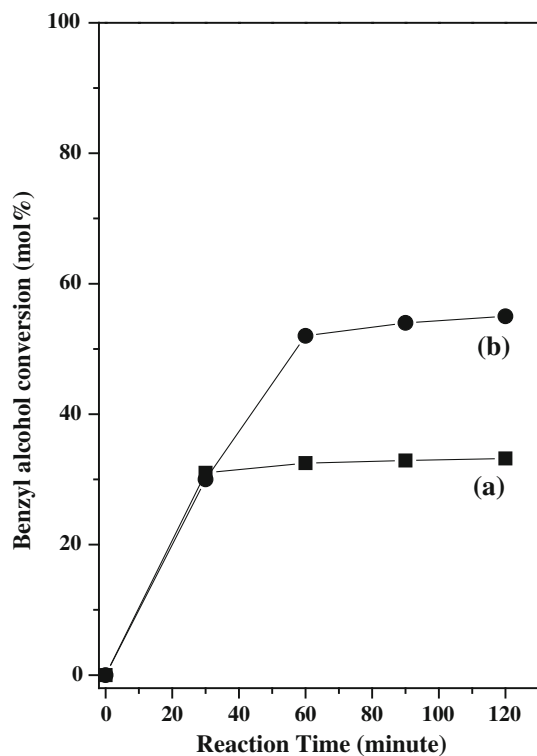


Fig. 2 BIL-1 catalyst was removed after (a) 30 min and (b) 60 min from the start of esterification reaction of benzyl alcohol with hexanoic acid in leaching experiment

various reactions that make them interesting candidates for commercial use.

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