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ARTICLE

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Solvent-free synthesis of compounds containing chromene core catalyzed by novel Brønsted acidic ionic liquids-ClO_4

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Abstract

A series of novel sulfonic acid-functionalized Brønsted acidic ionic liquids (BAILs) with perchlorate counter anion are introduced. These ionic liquid catalysts were prepared through simple and eco-friendly procedures in high yields. Various analytical techniques such as Fourier transform infrared, ^{1}H and ^{13}C NMR, electro-spray ionization mass spectrometry, elemental analysis (CHNS), and thermogravimetric techniques were used for well characterization of these catalysts. Next, the prepared BAILs were applied as efficient catalysts with high yields under solvent-free conditions for the synthesis of chromenes. The proposed method offers several superiorities, such as high yields, decreased reaction times, cleaner reactions, and the lack of laborious workup or purification procedures. The simplicity in operation, applicability, and feasibility of this protocol for diverse substrates makes it an efficient alternative to conventional methods.

KEYWORDS

$[PhBs_1]$-ClO_4, $[PipBs_1]$-ClO_4, $[PipBs_2]$-$(ClO_4)_2$, BAILs, chromenes, IL catalysts

1 | INTRODUCTION

Nowadays, ionic liquids (ILs) constitute one of the most widely used materials that have been exploited in many different applications including reaction media, catalysts, and reagents in organic reactions. Their great usefulness is rooted in unique properties of these materials comprising negligible vapor pressure, good thermal stability, high ion conductivity, simple functionality, and ease of recovery/reuse processes.[1,2] It should be noted that there is now a greater tendency toward non-solvent applications of ILs since their use as the solvent requires large amounts of ILs that are not cost-effective. On the other hand, the occurrence of difficulties in the purification phase for stripping the reaction wastes has caused their use as the reaction media not to be satisfactory in all aspects.[3–7] Therefore, non-solvent applications of ILs emerging in the statue of "task-specific ILs" are of particular importance.[8–11] Among them, Brønsted acidic ionic liquids (BAILs) due to numerous abundant advantages such as high thermal stability, high acidity, and simultaneously negligible release of hazardous gases, easy separation, and the ability to recycle and reuse for several times render the most important subset of task-specific ILs.[12]

Recently, alkane sulfonic acid group functionalized ILs have been introduced, proposing a new opportunity for developing green acidic catalysts due to the combination of the advantages of mineral liquid acids and solid acids, such as uniform acid sites, water and air resistant, simple and fast separation, and reusability. In 2002, Cole et al. first published an article about sulfonic acid group functionalized ILs with strong Brønsted acidity.[13] The prepared BAILs were reused at least five times without significant loss of activity for the synthesis of ethyl acetate. The fifth type of BAILs can have two or more H^+ on the acidic functional groups and on the anion or cation (Scheme 1).

There are a number of routes to synthesize this type of BAILs with multiple acidic sites as shown in Scheme 1. The research and application of various —SO_3H functionalized strong BAILs have received much attention for their potential application in replacing conventional homogeneous/heterogeneous acidic catalysts because they are flexible, nonvolatile, noncorrosive, and immiscible with many organic solvents and could be used as dual solvents and catalysts.[14–20]

Recently, we have prepared some new BAILs with acidic hydrogen-containing functional groups attached to the cation based on 1,4-dimethyl piperazinium and 1,10-phenantrolinium cations with phosphotungstate anion counterparts as powerful acidic catalysts for the synthesis of 3,3′-diaryloxindoles,[21] 2H-indazolo[2,1-b] phthalazine-triones,[22] esterification reaction[23], and selective oxidation of alcohols.[24]

The "chromene" heterocyclic scaffolds represent a "privileged" structural motif that is extensively found in nature, as they constitute structural components of diverse natural compounds with a broad spectrum of potent biological activities that include antimicrobial,[25] antiviral,[26] antimalarial,[27] antitumor,[28] and anticancer.[29]

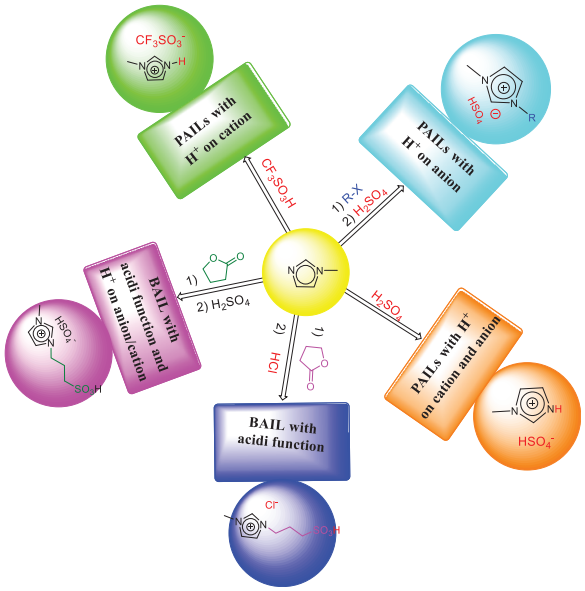
The extensive biological and medicinal activities of chromene have attracted great interest in developing new synthetic routes for their preparation. Due to the importance of the functionalized 4*H*-chromenes, especially in medicinal chemistry, several synthetic protocols have been reported in the literature; that most of them suffer from some disadvantages such as multiple synthetic steps, boring reaction conditions, and expensive reagents.[30–38]

To circumvent these constraints, the evolution of green and environmentally friendly methods by using effective and achievable catalysts with high catalytic activity and short reaction time for the preparation of chromene is still of interest. Consequently, by considering unique catalytic properties of BAILs and in the following of our previous study to introduce novel sultone based BAILs with phosphotungstate anion (BAILs-PW),[21–24] a series of new BAILs with perchlorate anion (BAIL-ClO_4) based on sulfonic acid functionalized 1,10-phennantroline and 1,4-dimethylpiperazine (Scheme 2) are synthesized, characterized, and their capability is investigated for the synthesis of structurally diverse chromenes under solvent-free conditions (Scheme 3).

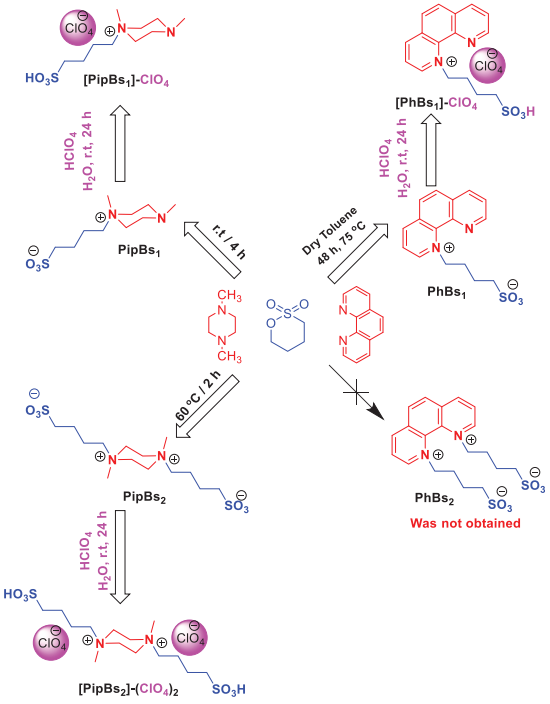
2 | RESULTS AND DISCUSSION

2.1 | Preparation of $[PhBs_1]ClO_4$, $[PipBs_1]ClO_4$ and $[PipBs_2](ClO_4)_2$ catalysts

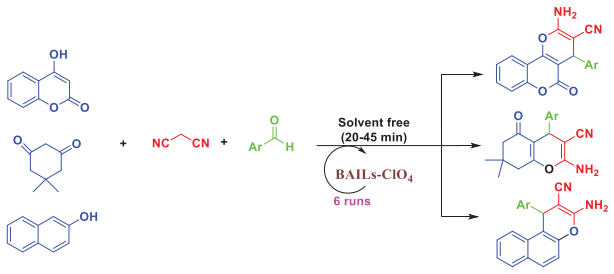
The BAILs-ClO_4 catalysts used in this study were prepared from the method shown in Scheme 2. As shown in Scheme 2, the synthetic pathway of these compounds is performed in two steps, which include preliminary quaternization of aliphatic and aromatic bis-amines through nucleophilic ring-opening reaction with 1,4-butanesultone followed by addition of the obtained



SCHEME 1 Preparation of BAILs



SCHEME 2 Preparation of BAILs-ClO_4 catalysts



SCHEME 3 BAILs-ClO_4 catalyzed synthesis of 2-amino-4*H*-chromenes

zwitterion salts to $HClO_4$ acid. As is clear, the alkylation of aromatic bis-amine requires higher temperature. Moreover, the synthesis of bis-alkylated salts proceeds at higher temperatures. Despite our effort, the synthesis of bis-alkylated ammonium salt was not successful in the case of 1,10-phenanthroline. This is probably due to increased steric hindrance as well as the decreased nucleophilicity of nitrogen after the first alkylation, which makes 1,10-phenanthroline resistant to second alkylation.

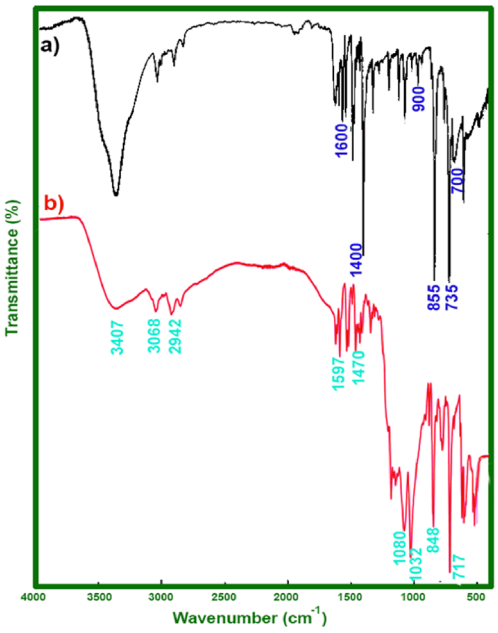


FIGURE 1 FT-IR spectrum of pristine 1,10-phenanthroline (a) and [$PhBs_1$]-ClO_4 catalyst (b)

2.2 | Characterization of the catalysts

2.2.1 | Fourier transform infrared spectra

The Fourier transform infrared (FT-IR) technique is quite useful to identify or confirm the structural and bonding changes present in the prepared BAILs-ClO_4 compared to the nitrogen sources as starting materials. The FTIR spectra of [$PhBs_1$]ClO_4 and pure 1,10-phenanthroline are presented in Figure 1. The FTIR spectra of [$PipBs_1$]ClO_4 and [$PipBs_2$]$(ClO_4)_2$ with comparative depiction with 1,4-dimetylpiperazine are shown in Figure 2. In the FTIR spectrum of 1,10-phenanthroline, strong bands are observed in two frequency regions, namely from 700 to 900 cm^{-1} and from 1,400 to 1,650 cm^{-1}. The strong bands at 738 and 854 cm^{-1} have been assigned to the out of the plane motion of the hydrogen atoms on the heterocyclic rings, and to the hydrogen on the center ring, respectively. Most intense and characteristic bands in the vibrational spectrum of 1,10-phenanthroline appear in the region 1,400–1,600 cm^{-1}. All of these bands involve C—C and C—N stretching vibrations. Four other bands can be assigned to C—C and C—N vibrations, two of which give rise to symmetric, and two anti-symmetric in plane ring deformation frequencies (Figure 1a). The FTIR spectrum of [$PhBs_1$]ClO_4 (Figure 1b), compared with the FTIR spectrum of the pure 1,10-phenanthroline (Figure 1a), shows two characteristic absorption bands at 1,080 and

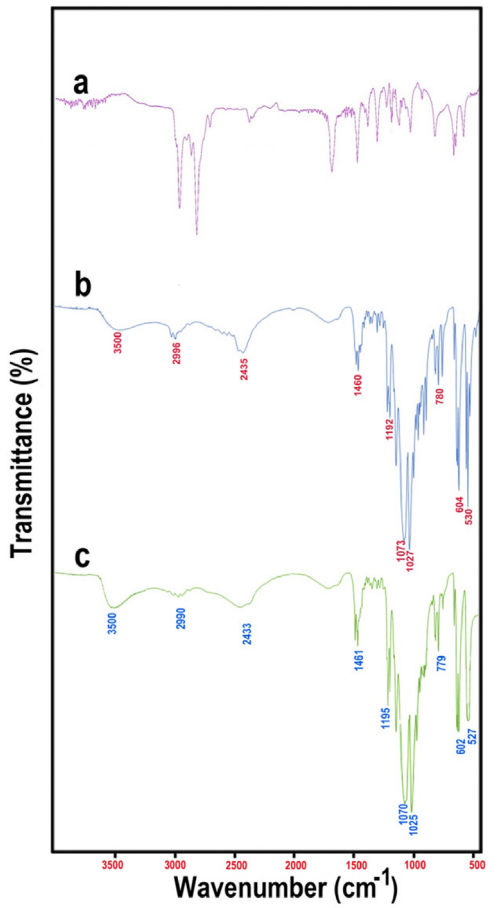


FIGURE 2 The FT-IR spectrum of 1,4-dimethylPiperazine (a), [$PipBs_2$]$(ClO_4)_2$ catalyst (b) and [$PipBs_1$]ClO_4 (c)

1,032 cm^{-1} as new peaks that are assigned to the asymmetric ClO_4^- stretching vibration. In the case of $[PipBs_1]ClO_4$, these absorption bands appear as new bands at 1,070 and 1,025 cm^{-1} (Figure 2c vs Figure 2a), and for $[PipBs_2](ClO_4)_2$, absorption bands appear at 1,073 and 1,027 cm^{-1}, respectively (Figure 2b vs Figure 2a). Furthermore, for all these three prepared BAILs, new bands at nearly 600 cm^{-1} are attributed to symmetric stretching vibration, and bands at 530–520 cm^{-1} are referred to bending vibration of ClO_4^- counterpart anion. The broad bands observed at 2,900–3,500 cm^{-1} in the FT-IR spectra of the BAILs catalysts are referred to OH groups. Finally, the SO_2 asymmetric vibrations of the BAILs are found at around 1,470 and 1,200 cm^{-1}.

2.2.2 | Study of thermal stability

The thermal stability of the prepared BAILs was investigated by thermogravimetric analysis (TGA). TGA curves of all these BAILs are illustrated in Figure 3. Thermal degradations are started before 200°C for $[PhBs_1]ClO_4$, 220°C for $[PipBs_2](ClO_4)_2$, and 240°C for $[PipBs_1]ClO_4$, which are acceptable thermal stability for experimental usage. The evaporation of adsorbed water lower than 150°C is the reason for the slight weight loss at this temperature range.

2.2.3 | Acidities of the prepared BAILs

Hammett equation was used to evaluate the acidity of the introduced BAILs. The Brønsted acidities of the BAILs were measured using the Hammett method and UV–Vis spectroscopy at 110°C. The Hammett function (H_0) is defined as follows:

$$H_0 = pK(I)_{aq} + \log([I]/[IH^+]).$$

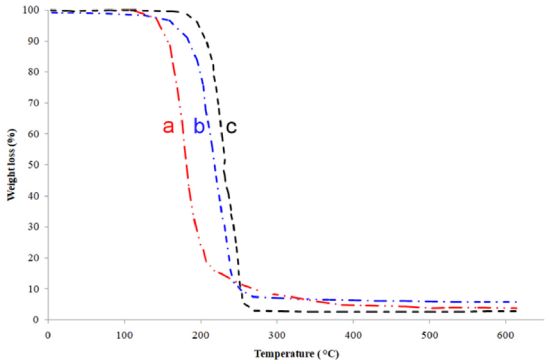


FIGURE 3 TGA of $[PhBs_1]ClO_4$ (a), $[PipBs_2](ClO_4)_2$ (b), and $[PipBs_1]ClO_4$ (c)

where $pK(I)_{aq}$ is the pK_a value of the indicator referred to an aqueous solution, IH^+ is the protonated form of indicator, and [I] and $[IH^+]$ are the molar concentrations of unprotonated and protonated forms of indicator in the BAILs, respectively (Figure 4). Moreover, 2,4-dichloro-6-nitroaniline ($pK(I)_{aq} = -3.31$) was chosen as the indicator base (I). The H_0 value of BAILs was calculated by determining the $[I]/[IH^+]$ ratio from the measured absorbance. Table 1 shows that $[PipBs_2](ClO_4)_2$ has slightly stronger acidity than $[PipBs_1]ClO_4$, and $[PhBs_1]ClO_4$ is the weakest acid among these BAILs.

2.3 | Optimization of the reaction condition catalyzed by $[PhBs_1]$-ClO_4, $[PipBs_1]$-ClO_4 and $[PipBs_2]$-$(ClO_4)_2$

As a model to optimize the reaction conditions, the condensation reaction of 4-hydroxychomarine, benzaldehyde, and malononitrile was selected as a model (Table 2). Originally, to determine the optimal conditions, we employed the solvent-less process started at 90°C in the presence of various amounts of each BAILs-ClO_4 ($[PhBs_1]$-ClO_4, $[PipBs_1]$-ClO_4, and $[PipBs_2]$-$(ClO_4)_2$) as the catalyst. As shown in Table 2, the highest yield (96%) was achieved using 3 mol% (0.020 g) of $[PipBs_2]$-$(ClO_4)_2$ catalyst in 20 min at 110°C (Table 2, entry 3).

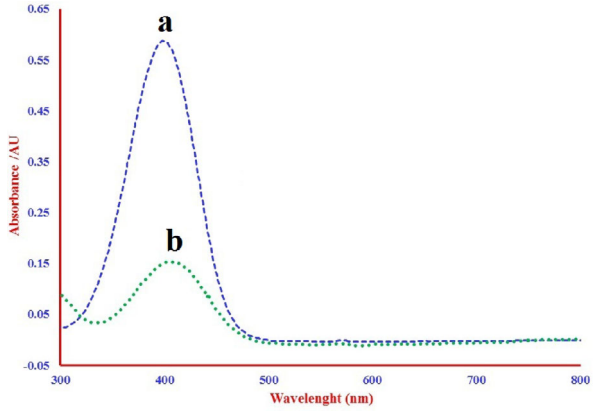
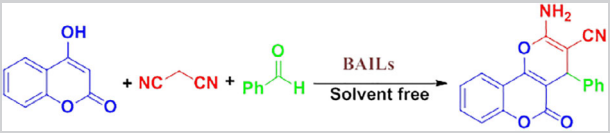


FIGURE 4 Absorption spectra of 0.025 mg/ml 2,4-dichloro-6-nitroaniline in ethanol (a) and in $[PipBs_2](ClO_4)_2$ (b)

TABLE 1 H_0 values of the BAILs at 110°C

BAILs	[I] (%)	$[HI^+]$ (%)	H_0
$[PipBs_2](ClO_4)_2$	32	68	−3.64
$[PipBs_1]ClO_4$	40	60	−3.47
$[PhBs_1]ClO_4$	45	55	−3.40

TABLE 2 Optimization study for the preparation of 2-amino-4*H*-chromenes using BAILs-ClO_4 under solvent-free condition at different temperatures



Entry	Catalyst (BAILClO$_4$) (mol%/mg)		Conditions	Time (min)	Yield (%)[a]
1	None	None	Solvent-free 90°C	1 day	Trace
2	[PipBs$_2$]-(ClO$_4$)$_2$	3% (20 mg)	Solvent-free 100°C	20	89
3	[PipBs$_2$]-(ClO$_4$)$_2$	3% (20 mg)	Solvent-free 110°C	20	96
4	[PipBs$_2$]-(ClO$_4$)$_2$	5% (33 mg)	Solvent-free 110°C	20	93
5	[PipBs$_1$]-ClO$_4$	7% (25 mg)	Solvent-free 110°C	20	94
6	[PipBs$_1$]-ClO$_4$	5% (18 mg)	Solvent-free 110°C	30	90
7	[PipBs$_1$]-ClO$_4$	3% (11 mg)	Solvent-free 110°C	45	85
8	[PhBs$_1$]-ClO$_4$	7% (30 mg)	Solvent-free 110°C	20	94
9	[PhBs$_1$]-ClO$_4$	5% (21 mg)	Solvent-free 110°C	30	86
10	[PhBs$_1$]-ClO$_4$	9% (38 mg)	Solvent-free 110°C	30	87
11	[PipBs$_2$]-(ClO$_4$)$_2$	3% (20 mg)	Solvent-free 80°C	40	82
12	[PipBs$_2$]-(ClO$_4$)$_2$	3% (20 mg)	Solvent-free 120°C	40	89

[a]Isolated yield.

Descending the temperature reduced the yield of the product (82%) (Table 2, entry 11), while ascending the temperature reduces the product yield even more (Table 2, entries 12,13). The model reaction was also examined in the absence of catalyst under solvent-free conditions, and the reaction did not proceed even after 1 day at 90°C (Table 2, entry 1). As is clear, [PipBs$_2$]-(ClO$_4$)$_2$ is much more effective for this synthesis and affords higher yields of 2-amino-4*H*-chromene products in shorter reaction times.

2.4 | Studying the scope and efficiency of the catalyst

Thus, in the next step, we explored the scope and efficiency of the reaction. Therefore, different substituted 2-amino-4*H*-chromenes were synthesized by three BAILs-ClO_4 catalysts under the discovered optimal conditions. From Table 3 and Scheme 3, under these optimized conditions, the reaction of enol or enolizable ketones, malononitrile, and various aromatic aldehydes was explored using three BAILs-ClO_4 catalysts. The catalytic activities of [PhBs$_1$]-ClO$_4$, [PipBs$_1$]-ClO$_4$ and [PipBs$_2$]-(ClO$_4$)$_2$ for the synthesis of 2-amino-4*H*-chromene derivatives are presented comparatively in Table 3. All the products were cleanly isolated and recrystallized from hot ethanol. In all the cases, aromatic aldehydes substituted with either electron-donating or electron-withdrawing groups smoothly underwent the reaction and gave the target products in good to excellent yields. However, as is clear, [PipBs$_2$]-(ClO$_4$)$_2$ is much more effective for this synthesis and affords higher yields of 2-amino-4*H*-chromene products in shorter reaction times.

A proposed mechanism to demonstrate the role of the catalyst is shown in Scheme 4. A Knoevenagel reaction, Michael addition, and intra-molecular cyclization are involved simultaneously in the synthesis of 2-amino-4*H*-chromene derivatives. In the first step, the BAIL-ClO_4 catalyst activates the carbonyl group by protonation, and then the anionic form of BAIL-ClO_4 abstracts a proton from the active methylene group of malononitrile, leading to the formation of carbanion. The formed carbanion of malononitrile makes a nucleophilic attack on the activated carbonyl of aromatic aldehyde, followed by loss of a water molecule to form cyanocinnamonitrile intermediate. In the second step, BAIL-ClO_4 catalyst reacts with dimedone and makes an enol form. Michael addition of enol intermediate to Knoevenagel products, followed by ring-closing and deprotonation, furnish 2-amino-4*H*-chromene derivative.

Although most of the previously reported catalysts[30–38] have proper ability to advance the reactions with good yields, some of them require harsh conditions, such as high reaction temperatures or long times, and others suffer from a problem in separating the

TABLE 3 Solvent-free synthesis of 2-amino-4*H*-chromenes using BAILs-ClO_4 as catalyst under thermal conditions

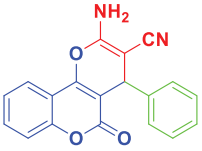
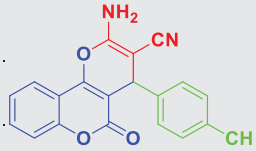
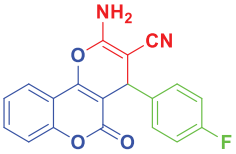
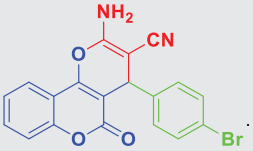
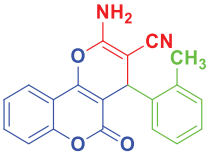
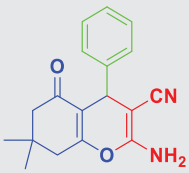
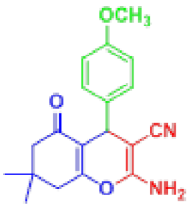
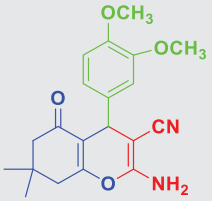
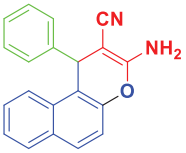
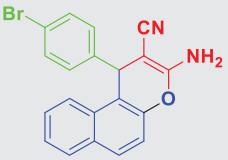
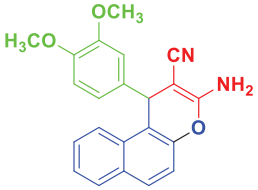
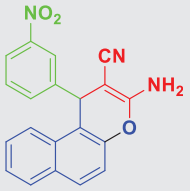
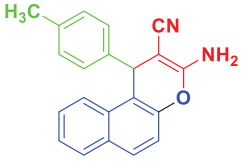
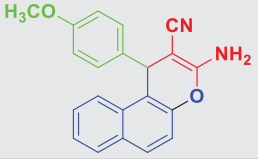
No.	Product	BAILs-ClO_4	Time (min)	Yield (%)[a]
1		$[PipBs_2]$-$(ClO_4)_2$	25	96
		$[PipBs_1]$-ClO_4	30	95
		$[PhBs_1]$-ClO_4	25	93
2		$[PipBs_2]$-$(ClO_4)_2$	21	90
		$[PipBs_1]$-ClO_4	28	86
		$[PhBs_1]$-ClO_4	22	83
3		$[PipBs_2]$-$(ClO_4)_2$	31	93
		$[PipBs_1]$-ClO_4	40	90
		$[PhBs_1]$-ClO_4	34	86
4		$[PipBs_2]$-$(ClO_4)_2$	19	98
		$[PipBs_1]$-ClO_4	38	94
		$[PhBs_1]$-ClO_4	32	90
5		$[PipBs_2]$-$(ClO_4)_2$	16	99
		$[PipBs_1]$-ClO_4	36	97
		$[PhBs_1]$-ClO_4	30	94
6		$[PipBs_2]$-$(ClO_4)_2$	16	97
		$[PipBs_1]$-ClO_4	34	95
		$[PhBs_1]$-ClO_4	28	91
7		$[PipBs_2]$-$(ClO_4)_2$	22	95
		$[PipBs_1]$-ClO_4	31	93
		$[PhBs_1]$-ClO_4	25	89
8		$[PipBs_2]$-$(ClO_4)_2$	20	93
		$[PipBs_1]$-ClO_4	25	90
		$[PhBs_1]$-ClO_4	22	86
9		$[PipBs_2]$-$(ClO_4)_2$	18	91
		$[PipBs_1]$-ClO_4	24	88
		$[PhBs_1]$-ClO_4	19	84
10		$[PipBs_2]$-$(ClO_4)_2$	21	89
		$[PipBs_1]$-ClO_4	33	85
		$[PhBs_1]$-ClO_4	28	81

TABLE 3 (Continued)

No.	Product	BAILs-ClO_4	Time (min)	Yield (%)[a]
11		$[PipBs_2]$-$(ClO_4)_2$	33	87
		$[PipBs_1]$-ClO_4	42	83
		$[PhBs_1]$-ClO_4	36	79
12		$[PipBs_2]$-$(ClO_4)_2$	31	84
		$[PipBs_1]$-ClO_4	35	80
		$[PhBs_1]$-ClO_4	29	77
13		$[PipBs_2]$-$(ClO_4)_2$	21	87
		$[PipBs_1]$-ClO_4	28	89
		$[PhBs_1]$-ClO_4	22	85
14		$[PipBs_2]$-$(ClO_4)_2$	28	93
		$[PipBs_1]$-ClO_4	27	91
		$[PhBs_1]$-ClO_4	22	88

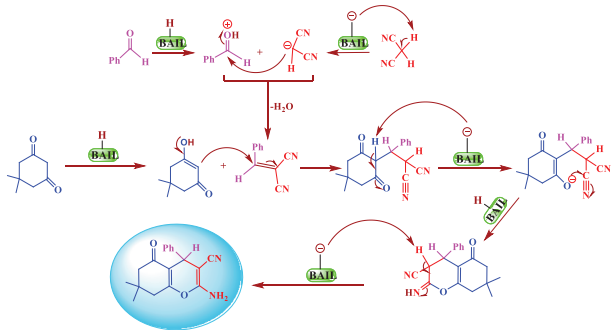
[a]Isolated yield.

catalyst from the reaction mixture and nonrecyclable catalyst. The features of this method, which makes it more preferable than other reported methods, are mild reaction conditions, environmentally benign, easy recovery of BAILs-ClO_4 catalyst, reuse of the catalyst for six consecutive times without loss of catalyst performance, high yields of 2-amino-4*H*-chromene derivative products, and short reaction times.

The BAILs-ClO_4 catalysts recoverability was investigated (Table 4). To investigate this property for the introduced novel BAILs, the preparation reaction catalyzed by $[PipBs_2](ClO_4)_2$ was selected as the model. After completion of the reaction, H_2O was added to the mixture and then stirred for 5 min, the reaction mixture was filtered. The H_2O solvent of the filtered mixture was evaporated under reduced pressure to give the recovered BAIL as precipitate, which was washed several times with ethyl acetate (5 ml) to remove the contaminants, dried in an oven at 80°C, and used for the new run under similar reaction conditions. The yield of the product was calculated after recrystallization of filtrate precipitation in hot EtOH. It was found that the catalyst could be reused for six consecutive reactions with high yields and negligible deterioration in catalytic activity.

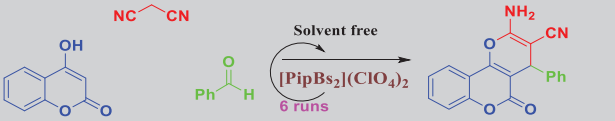
3 | EXPERIMENTAL

All necessary chemicals were provided commercially from Sigma-Aldrich and Merck companies and used without additional purification. Known products have been identified by comparing spectral and physical data with those reported in the papers. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance spectrometer in DMSO-d_6, $CDCl_3$ or D_2O solvents with tetramethylsilane (TMS) as the internal standard. UV–Vis spectra were recorded on Perkin-Elmer Lambda 365 UV–Vis spectrophotometer at room temperature. FT-IR spectra were obtained as potassium bromide pellets in the range of 400–4000 cm^{-1} using an AVATAR 370 Thermo Nicolet spectrophotometer. Elemental analyses (C, H, and N) were performed with a Heraeus CHN-O-Rapid analyzer. The TGA was performed on Netsch STA449c. The sample weight was ca. 10 mg and was heated from room temperature up to 600°C with 10°C/min using alumina sample holders. The melting points are measured in open capillary tubes in an electrothermal apparatus (Barnstead IA 8103) and are uncorrected. The reaction was monitored by TLC on PolyGram SILG/UV 254 silica gel sheets.



SCHEME 4 The proposed mechanism for BAILs-ClO_4 catalyzed formation of 2-amino-4*H*-chromenes

TABLE 4 Recyclability and reusability study of $[PipBs_2](ClO_4)_2$ BAIL catalyst for the solvent-free synthesis of 2-amino-4*H*-chromenes



Run	1	2	3	4	5	6
Time (min)	20	20	20	20	25	25
Yield (%)[a]	96	95	95	93	92	91

[a]Isolated yield.

3.1 | Preparation of 4-(1,10-phenanthrolin-1-ium-1-yl)butane-1-sulfonate ($PhBs_1$)

A mixture of 1,10-Phenanthroline (10 mmol) and 1,4-butane sultone (12 mmol) in anhydrous toluene (10 ml) was stirred for 24 hr at 75°C under inert atmosphere (N_2 flow). The yielding white precipitate ($PhBs_1$) was separated through filtration and rather purified by multiple washing with diethyl ether (3 × 20 ml) followed by drying under vacuum. White solid product of 97% yield was obtained.

3.1.1 | Characterization data for $PhBs_1$

^{1}H NMR (400 MHz, DMSO-d_6, TMS): δ 1.16 (quintet, 2H, J = 7.6 Hz), 2.16 (quintet, 2H, J = 7.6 Hz), 2.46 (t, 2H, J = 7.6 Hz), 5.96 (t, 2H, J = 7.6 Hz), 8.1 (m, 1H), 8.40–847 (m, 3H), 8.82 (m, 1H), 9.34 (m, 1H), 9.41 (m, 1H), 9.66 (m, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 22.4, 27.7, 50.7, 51.9, 56.8, 121.1, 121.3, 124.2, 128.1, 128.4, 128.8, 136.3, 138.2, 143.2, 146.9, 150.2, 199.1. (electro-spray ionization mass spectrometry—ESI-MS) m/z Calcd for $PhBs_1$: 316.37; Found: 316.08. Anal. Calcd for $C_{16}H_{16}N_2O_3S$: C, 60.74; H, 5.09; N, 8.86. Found: C, 60.79; H 5.1; N, 8.91%.

3.2 | Preparation of 4-(1,4-dimethylpiperazin-1-ium-1-yl) butane-1-sulfonate ($PipBs_1$)

A round bottom flask filled with 1,4-dimethylpiperazine (10 mmol) and 1,4-butane sultone (12 mmol) was allowed to stir for 4 hr at room temperature under inert atmosphere (N_2 flow). The yielding white precipitate ($PipBs_1$) was separated through filtration followed by washing with diethyl ether (3 × 20 ml) and then drying under vacuum. White solid product of 95% yield was obtained.

3.2.1 | Characterization data for $PipBs_1$

^{1}H NMR (400 MHz, D_2O, TMS): δ 1.65–1.80 (m, 2H), 1.81–1.97 (m, 2H), 2.28 (s, 3H), 2.66–2.86 (m, 4*H*), 2.88 (t, 3H, J = 6.8 Hz), 3.02 (s, 3H), 3.20–3.50 (m, 5 H). ^{13}CNMR (100 MHz, D_2O): δ 20.3, 22.1, 31.20, 46.7, 50.5, 54.0, 56.5, 58.1. Anal. Calcd for $C_{10}H_{22}N_2O_3S$: C, 47.98; H, 8.86; N, 11.19; S, 12.81. Found: 47.95; H, 8.90; N, 11.21; S, 12.83.

3.3 | Preparation of 4,4′-(1,4-dimethylpiperazine-1,4-diium-1,4-diyl) bis(butane-1-sulfonate) ($PipBs_2$)

A round bottom flask charged with 1,4-dimethylpiperazine (10 mmol) and 1,4-butane sultone (30 mmol) was magnetically stirred for 2 hr at 60°C under inert atmosphere (N_2 flow). The yielding white precipitate was separated through filtration and rather purified by multiple washing with diethyl ether (3 × 20 ml) followed by drying under vacuum.

3.3.1 | Characterization data for $PipBs_2$

^{1}H NMR (400 MHz, D_2O, TMS): δ 1.65–1.82 (m, 4*H*), 1.82–2.35 (m, 4*H*), 2.90 (t, 4*H*, J = 8 Hz), 3.22 (s, 3H), 2.24 (s, 3H), 3.30–4.50 (m, 12H). ^{13}CNMR (100 MHz, D_2O, TMS): δ 20.2, 20.9, 22.3, 22.8, 35.7, 35.8, 47.1, 47.9, 49.7, 53.9, 54.6, 58.2, 58.8. (ESI-MS) m/z Calcd for $PipBs_2$: 386.15; Found: 306.12. Anal. Calcd for $C_{14}H_{30}N_2O_6S_2$: C, 43.50; H, 7.82; N, 7.25; S, 16.59%. Found: C, 43.40; H, 7.88; N, 7.23; S, 16.63%.

3.4 | Preparation of the $[PhBs_1]ClO_4$, $[PipBs_1]ClO_4$ and $[PipBs_2](ClO_4)_2$ catalysts

A magnetically stirred aqueous solution of $PhBs_1$ or $PipBs_1$ prepared by dissolving the corresponding solid (18 mmol) into distilled water in a round bottom flask (25 ml) and 18 mmol of $HClO_4$ were added dropwise. The resulting mixture was then allowed to react for 24 hr at room temperature. Evaporation of water in reduced pressure afforded $[PhBs_1]ClO_4$ or $[PipBs_1]ClO_4$ as a solid product. The same procedure was used for the preparation of $[PipBs_2](ClO_4)_2$ using 36 mmol of $HClO_4$ instead. The remaining residues were dried at 50°C for 4 hr. At the end, $[PipBs_1]ClO_4$ $[PiPBs_2](ClO_4)_2$ and $[PhBs_1]ClO_4$ BAILs were collected with 100% yield.

3.5 | Determination of acidity using UV–Vis spectrophotometer

The UV spectra were recorded on a Perkin-Elmer Lambda 365 UV–Vis spectrophotometer at room temperature. The freshly prepared BAILs are viscous colorless liquids and then gradually solidify at room temperature. Since they melt at 90–95°C, the experiments were performed at 110°C in order to obtain comparable acidity results, temperature, indicator concentration, and water content of BAILs were chosen almost same in all runs. Consequently, BAILs were heated to 110°C to form liquid with good fluidity. Then, a solution of indicator dissolved in EtOH (indicator concentration: 0.025 mg/ml) was added into the BAIL, and the mixture was stirred for 20 min to form the solution at 110°C. The concentration of the indicator in the BAIL was located within the scale of the calibration curve. The UV spectra were recorded at room temperature and the calibration curves with linearity higher than 0.999 for the indicator in the unprotonated form were shaped by means of their ethanol solutions.

3.6 | General procedure for BAILs-ClO_4 accelerated synthesis of 2-amino-4*H*-chromenes

ß-naphthol or enolizable compound (1 mmol), aldehyde (1 mmol), and malononitrile (1 mmol) were placed together in a round-bottom flask containing BAILs-ClO_4 (7 mmol% for $[PhBs_1]$-ClO_4 and $[PipBs_1]$-ClO_4 and 3 mmol % for $[PipBs_2]$-$(ClO_4)_2$, and the mixture was heated in an oil bath at 110°C for suitable period of time indicated in Table 3. Following completion of the reaction as confirmed by TLC, the mixture was allowed to cool. Subsequently, the reaction mixture was suspended in water (5 ml), and the suspension was filtered to separate the crude product. The crude product was dissolved in EtOH (5 ml), and crystallized by dropwise addition of water (15 ml). The filtered was evaporated under vacuum to precipitate the BAIL catalyst. The recovered catalyst was washed several times with dietylether, dried, and stored for further similar consecutive runs. The products are known compounds and are characterized by IR and NMR spectroscopy. Their melting points are compared with the reported values.[30–38]

4 | CONCLUSIONS

In conclusion, a series of new recyclable BAILs-ClO_4 catalysts are reported to be green and efficient catalysts for the synthesis of 2-amino-4*H*-chromenes under solvent-free conditions. Moreover, this method is successfully extended to a wide variety of enol or enolizable ketones, malononitrile, and various aromatic aldehydes. Furthermore, the developed method has numerous benefits, comprising efficiency, generality, simple work-up procedure, mild reaction conditions, green and clean process, easy recycling, and reusability of BAILs up to six runs with simple extraction from the organic phase by dissolving in water, excellent yields of chromene derivatives, and short reaction times.

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