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ARTICLE

Brønsted acidic ionic liquids of *aza*-crown ether complex cations: Preparation and applications in organic reactions

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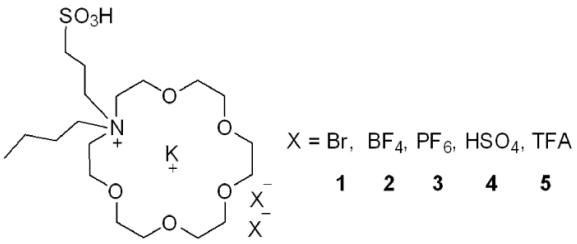
A series of novel Brønsted acidic ionic liquids composed of an *aza*-crown ether chelated potassium cation and various anions, were designed, synthesized and characterised by FTIR, NMR and mass spectra, thermogravimetric differential thermalanalysis (TG-DTA) and elemental analysis. These new Brønsted acidic ionic liquids of *aza*-crown ether complex cations (aCBAILs) were applied as catalyst to Biginelli reaction, Mannich reaction and synthesis of bis-(4-hydroxycoumarin-3-yl)methanes. These organic reactions were achieved in good yields under mild reaction conditions. Moreover, these new IL catalysts can be recycled several times.

Introduction

In decades, ionic liquids (ILs) have attracted great interests and been applied successfully in a variety of organic reactions in terms of their environmentally benign features, such as lower vapour pressure, remarkable solubility, recyclability, and excellent thermal and chemical stability.[1-4] Currently, many task-specific ionic liquids were designed and fabricated according to the requests of different reactions.[5-11] Since Cole first reported a new approach for esterification using acidic Brønsted functionalized ILs as solvent and catalyst,[12] the introduction of acidic Brønsted functional groups, especially -SO_3H, into cations of the ILs, has obviously enhanced the acidity and water solubility of the ILs.[13,14] It also gives great promise for using ILs as green catalysts with good catalytic activities in many organic reactions.[15]

Although many ionic liquids have been developed, the cations of them are almost limited in quaternary ammonium, *N*,*N'*-dialkylimidazolium and *N*-alkylpyridinium cations etc.. Differing with these traditional ionic liquids, we discovered a novel type of ionic liquid containing crown ether complex cations and various anions, which could greatly extend the IL family.[16] These new ILs were used to various organic reactions, such as Michael addition, Henry reaction, Heck reaction, oxidation reaction of aromatic alcohols, and asymmetric addition of CO_2 and epoxides.[16,17] To functionalized these ILs, an alkanesulfonic acid was successfully introduced into the *aza*-crown ether to produce the desired Brønsted acidic ionic liquids of *aza*-crown ether complex cations (Scheme 1) that can be applied to several organic reactions.



Scheme 1 Structure of Brønsted acidic ionic liquids of *aza*-crown ether complex cations

The Biginelli reaction is a useful multicomponent reaction for the synthesis of dihydropyrimidinones (DHPMs) that have displayed good bioactivities and pharmaceutical activities.[18] Many catalysts for Biginelli reaction have been documented[19-21] including some functionalized ionic liquids.[22,23] Herein, 1-butyl-1-*aza*-[18-C-6KSO_3H][BF_4]$_2$ was used to Biginelli reaction as an efficient IL catalyst, and recycled at least five times without evident loss of catalytic activity.

Mannich reaction is a wide avenue to approach β-amino carbonyl compounds catalysed by Lewis acids,[24,25] Brønsted acids,[26,27] heteropolyacids,[28] and organic acids etc..[29,30] The products are a type of synthetic intermediates in the manufacture of various pharmaceuticals and natural products.[31]

In this paper, 1-butyl-1-*aza*-[18-C-6KSO_3H]X_2 were utilized successfully in Biginelli and Mannich reactions respectively. Moreover, biscoumarins[32,33] were also synthesized using these ILs as catalysts.

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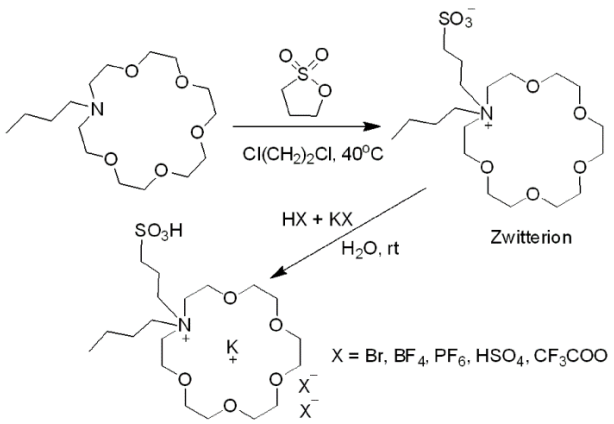
Results and discussion

Understanding the weak electrostatic interactions among the cations and anions decrease the melting point of the ILs and enhance the basicity and nucleophilicity of the anions,[16] we attempted to develop a new type of Brønsted acidic ionic liquids via a protocol of functionalization of *aza*-crown ether cation. Fortunately, five ionic liquids of *aza*-crown ether complex cations functionalized by alkanesulfonic acid were successfully synthesized (Scheme 2). Firstly, a zwitterionic-type *aza*-crown ether was prepared by using a direct sulfonation reaction of butyl-*aza*-crown ether and 1,3-propanesulfone in dichloroethane; then equimolar of the functionalized *aza*-crown ether, potassium salt and relevant acid were mixed together in water at room temperature leading to the pure Brønsted acidic *aza*-crown ether complex cation ionic liquid in quantity.



Scheme 2 Synthetic route to Brønsted acidic ionic liquids of *aza*-crown ether complex cations

All of the aCBAILs made up of dication and dianion are very viscous, yellow and colloidal complexes. They are very soluble in water, readily soluble in polar solvents such as methanol, ethanol, and acetone, insoluble in nonpolar solvents such as alkanes, ethers and aromatic hydrocarbons. The new ionic liquids show melting points lower than 25 degree (–4~12°C) and good thermodynamic stabilities up to 197-261 °C measured by TG-DTA (Table 1).

Table 1 The properties of Brønsted acidic ionic liquids of *aza*-crown ether complex cations

Entry	Catalyst/anion	m.p./°C	T_d/°C[a]
1	**1**/Br	2	207
2	**2**/BF_4	12	260
3	**3**/PF_6	-4	261
4	**4**/HSO_4	-1	201
5	**5**/CF_3CO_2	8	197

[a] Decomposition temperatures (T_d) were determined by TG-DTA heating at 10 °C min^{-1} under nitrogen.

Acidic Brønsted ionic liquids are of great value because they possess simultaneously the advantages of liquid acids and solid acids, such as uniform acid site, stability in water, easy separation and reusability.[34] Additionally, they have also excellent catalytic activity owing to their plentiful hydrogen bonds with substrates, which can accelerate the product formation by lowering the activation barrier.[35] Similarly, our new Brønsted acidic ionic liquids of *aza*-crown ether complex cations can provide both hydrogen bond donors and hydrogen bond acceptors. The alkanesulfonic acid attached to *aza*-crown ether complex cation directly activated aldehyde carbonyl via hydrogen bond to undergo nucleophilic addition.[36,37] So our new ionic liquids catalysts can increase effectively the electrophilicity of the carbonyl that is easy to perform the nucleophilic addition.

Biginelli reaction

The synthesis of 3,4-dihydropyrimidinones was firstly reported by Biginelli in 1893, involving a one-pot condensation reaction under strongly acidic conditions.[38] Since then, several modifications have been developed for the classical Biginelli approach.[39-44] Searching for a more efficient and recyclable IL catalyst, the Biginelli reaction of benzaldehyde, ethyl acetoacetate, and urea in ethanol was investigated in the presence of a *aza*-crown ether cation IL. After screening various aCBAILs, they can promote this reaction except 1-butyl-1-*aza*-[18-C-6KSO_3H][HSO_4]$_2$ (Table 2, entries 2-6). It can be seen that the reaction was difficult to take place in the absence of IL catalyst (Table 2, entry 1). The best IL catalyst of 1-butyl-1-*aza*-[18-C-6KSO_3H][BF_4]$_2$ (**2**) gave the hightest yield (92%) of DHPM (Table 2, entry 3). The concentration of catalyst **2** also affected the yield of product (Table 2, entries 7-10). Compared with the most traditional ILs that must initiated this reaction with large amount of catalyst under extra ultrasound (Table 2, entry 17) or microwave (Table 2, entry 18) assistance, our new aCBAIL catalysts have significant advantages of less amount of catalyst usage under very mild reaction conditions.

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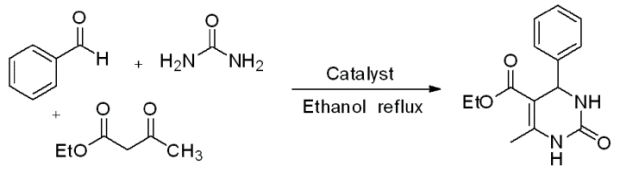
Table 2 Biginelli reaction catalysed by different catalysts[a]



Entry	Catalyst	Amount (mol %)	Yield[b] (%)
1	none	0	trace
2	**1**/1-butyl-1-*aza*-[18-C-6KSO$_3$H][Br]$_2$	7	46
3	**2**/1-butyl-1-*aza*-[18-C-6KSO$_3$H][BF$_4$]$_2$	7	92
4	**3**/1-butyl-1-*aza*-[18-C-6KSO$_3$H][PF$_6$]$_2$	7	87
5	**4**/1-butyl-1-*aza*-[18-C-6KSO$_3$H][HSO$_4$]$_2$	7	trace
6	**5**/1-butyl-1-*aza*-[18-C-6KSO$_3$H][TFA]$_2$	7	53
7	**2**/1-butyl-1-*aza*-[18-C-6KSO$_3$H][BF$_4$]$_2$	5	71
8	**2**/1-butyl-1-*aza*-[18-C-6KSO$_3$H][BF$_4$]$_2$	6	86
9	**2**/1-butyl-1-*aza*-[18-C-6KSO$_3$H][BF$_4$]$_2$	8	90
10	**2**/1-butyl-1-*aza*-[18-C-6KSO$_3$H][BF$_4$]$_2$	10	88
11	1-butyl-1-*aza*-[18-C-6SO$_3$H][BF$_4$][c]	7	86
12	$NaHSO_4$	7	trace
13	$KHSO_4$	7	trace
14	NH_4HSO_4	7	trace
15	CH_3SO_3H	7	58
16	*p*-TsOH	7	75
17	[Hbim]BF$_4$	60	97[d]
18	$GlyNO_3$	40	92[e]
19	[Bmim]MeSO$_4$	1	90[f]

[a] Reaction conditions: aldehyde 1.0 mmol, ethyl acetoacetate 3.0 mmol, urea 1.5 mmol, ethanol 2 mL, reflux, 5 hours. [b] Isolated yield. [c] The IL catalyst without adding KBF_4. [d] See ref. 39. [e] See ref .42. [f] See ref .44.

Compared with traditional acid catalysts, easy recycling is an attractive property of this type of acidic ionic liquids. Consequently, we investigated the recovery and reuse of best catalyst of 1-butyl-1-*aza*-[18-C-6KSO$_3$H][BF$_4$]$_2$ in the multicomponent reaction of benzaldehyde, ethyl acetoacetate, and urea. As shown in Table 3, the catalyst can be reused at least four times without significant loss of activity.

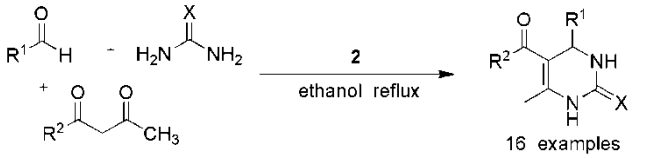
Table 3 Recycling of 1-butyl-1-aza-[18-C-6KSO$_3$H][BF$_4$]$_2$ in Biginelli reaction[a]

Entry	Yield[b] (%)
1	92
2	90
3	90
4	89
5	85

[a] Reaction conditions: aldehyde 1.0 mmol, ethyl acetoacetate 3.0 mmol, urea 1.5 mmol, catalyst **2** 0.07 mmol, ethanol 2 mL, reflux, 5 hours. [b] Isolated yield.

To extend the scope of this reaction, a variety of substituted aldehydes were investigated under the optimal conditions. The results are listed in Table 4. It can be seen that the aromatic aldehydes with both the electron-withdrawing and the electron-donating groups can generate the target products readily (Table 4, entries 1-10). Aromatic aldehydes with *ortho*-substituted groups led to lower reaction yield due to the steric effect (Table 4, entry 1, 4). The acetylacetone (Table 4, entry 11-13) and thiourea (Table 4, entries 14-16) can also be used to yield corresponding products in the presence of new IL.

Table 4 Biginelli reaction of various substrates catalysed by 1-*aza*-[18-C-6KSO$_3$H][BF$_4$]$_2$[a]



Entry	R^1	R^2	X	Yield[b] (%)
1	2-$CH_3OC_6H_4$	OCH_2CH_3	O	37
2	3-$CH_3OC_6H_4$	OCH_2CH_3	O	79
3	4-$CH_3OC_6H_4$	OCH_2CH_3	O	82
4	2-$NO_2C_6H_4$	OCH_2CH_3	O	48
5	3-$NO_2C_6H_4$	OCH_2CH_3	O	77
6	4-$NO_2C_6H_4$	OCH_2CH_3	O	84
7	4-ClC_6H_4	OCH_2CH_3	O	86
8	4-HOC_6H_4	OCH_2CH_3	O	71
9	4-$CH_3C_6H_4$	OCH_2CH_3	O	83
10	2,5-$(CH_3O)_2C_6H_3$	OCH_2CH_3	O	74
11	Ph	CH_3	O	80
12	4-$CH_3OC_6H_4$	CH_3	O	81
13	4-$NO_2C_6H_4$	CH_3	O	77
14	Ph	OCH_2CH_3	S	56
15	4-$CH_3OC_6H_4$	OCH_2CH_3	S	51
16	4-$NO_2C_6H_4$	OCH_2CH_3	S	47

[a] Reaction conditions: aCBAIL catalyst **2** 0.07 mmol, aldehyde 1.0 mmol, dicarbonyl compound 3.0 mmol, urea or thiourea 1.5 mmol, ethanol 2 mL, reflux, 5 hours. [b] Isolate yield.

Mannich reaction

Mannich reaction is one of the most important carbon–carbon bond formations in organic synthesis[45] and can be realized in ionic liquids.[46-48] With these new aCBAILs in hand, we try to used it as catalyst in Mannich reaction of benzaldehyde, aniline and acetophenone. Fortunately, this three-component reaction can be performed at room temperature (Table 5). 1-Butyl-1-*aza*-[18-C-6KSO$_3$H][TFA]$_2$ demonstrated good catalytic activity in ethanol (83%) (Table 5, entry 5). Furthermore, various substituted benzaldehydes and anilines were reacted with acetophenone to generate the corresponding products (Table 6).

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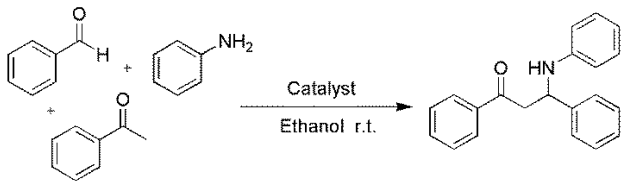
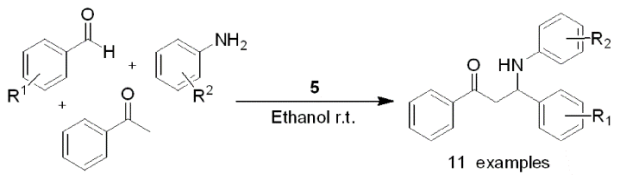
Table 5 Mannich reaction catalysed by different catalysts[a]



Entry	Catalyst	Amount (mol %)	Yield [b] (%)
1	**1**/1-butyl-1-*aza*-[18-C-6KSO$_3$H][Br]$_2$	10	57
2	**2**/1-butyl-1-*aza*-[18-C-6KSO$_3$H][BF$_4$]$_2$	10	27
3	**3**/1-butyl-1-*aza*-[18-C-6KSO$_3$H][PF$_6$]$_2$	10	48
4	**4**/1-butyl-1-*aza*-[18-C-6KSO$_3$H][HSO$_4$]$_2$	10	trace
5	**5**/1-butyl-1-*aza*-[18-C-6KSO$_3$H][TFA]$_2$	10	83
7	1-butyl-1-*aza*-[18-C-6SO$_3$H][TFA][c]	10	82
8	KHSO$_4$	10	trace
9	CH$_3$SO$_3$H	10	31
10	*p*-TsOH	10	77
11	[Hmim]TFA	16	85[d]
12	[DDPA]HSO$_4$	10	87[e]

[a].Reaction conditions: benaldehyde 1.0 mmol, aniline 1.0 mmol, acetophenone 1.0 mmol, ethanol 2 mL, room temperature, 5 hours. [b] Isolated yield. [c] The IL catalyst without adding CF$_3$COOK. [d] See ref. 46. [e] See ref. 48.

Table 6 Mannich reaction of various substrates catalysed by 1-*aza*-[18-C-6KSO$_3$H][TFA]$_2$[a]



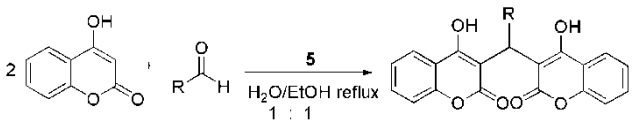
Entry	R^1	R^2	Yield[b] (%)
1	H	H	83
2	4-NO$_2$	H	64
3	4-OH	H	71
4	4-OCH$_3$	H	81
5	4-CH$_3$	H	80
6	3-NO$_2$	H	65
7	3-OCH$_3$	H	77
8	H	4-Cl	84
9	4-OCH$_3$	4-Cl	82
10	H	4-CH$_3$	87
11	4-OCH$_3$	4-CH$_3$	86

[a].Reaction conditions: aldehyde 1.0 mmol, aniline 1.0 mmol, ketone 1.0 mmol, aCBAIL catalyst **5** 0.10 mmol, ethanol 2 mL, room temperature, 5 hours. [b] Isolated yield.

Synthesis of bis-(4-hydroxycoumarin-3-yl)methanes

In the literatures,[49-51] the synthesis of biscoumarin derivatives was commonly approached via a condensation reaction of coumarin and aldehyde catalysed by acidic catalysts, such as sulfuric acid, trifluoroacetic acid, phosphorus pentoxide, and aluminum trichloride etc.. This reaction was carried out through the nucleophilic addition of 4-hydroxycoumarin to benzaldehyde followed by dehydration to form bis-(4-hydroxycoumarin-3-yl)methanes in the presence of aCBAIL. 1-Butyl-1-*aza*-[18-C-6KSO$_3$H][TFA]$_2$ showed the best activity to produce the target product up to 98% yield (Table 7, entry 5). It is clear to see that the mixed solvent of water-alcohol (1:1, v/v) exhibited more positive effect than water or alcohol (Table 7, entry 5 *vs* 6,7). Under the optimized reaction condition, various substrates (Table 7, entry 9-17) possessing the electron-donating group or electron-withdrawing group can give the target products in excellent yields.

Table 7 Synthesis of bis-(4-hydroxycoumarin-3-yl)methanes catalysed by 1-*aza*-[18-C-6KSO$_3$H][TFA]$_2$[a]:

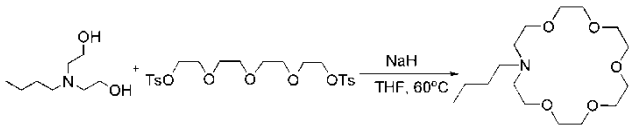


Entry	Cat.	R	Yield[b] (%)	Entry	Cat.	R	Yield (%)
1	**1**	Ph	72	9	**5**	3- NO$_2$C$_6$H$_5$	94
2	**2**	Ph	86	10	**5**	3-CH$_3$OC$_6$H$_5$	91
3	**3**	Ph	89	11	**5**	4-CH$_3$OC$_6$H$_5$	96
4	**4**	Ph	82	12	**5**	4-ClC$_6$H$_5$	87
5	**5**	Ph	98	13	**5**	4-CH$_3$C$_6$H$_5$	91
6	**5**	Ph	72[c]	14	**5**	4-OHC$_6$H$_5$	97
7	**5**	Ph	83[d]	15	**5**	4-NO$_2$C$_6$H$_5$	92
8	**5**	Ph	95[e]	16	**5**	Ph-CH=CH	94
				17	**5**	2,4-NO$_2$C$_6$H$_4$	77

[a] Reaction conditions: benzaldehyde 1.0 mmol, 4-hydroxycoumarin 2.0 mmol, aCBAIL catalyst **5** 0.05 mmol, EtOH 1 mL and H$_2$O 1 mL, reflux, 30 min. [b] Isolate yield. [c] Ethanol 2 mL as solvent. [d] Deionized water 2 mL as solvent. [e] See ref. 43.

Experimental section

Materials and methods: All reagents were obtained from commercial resources and used without further purification. ^{1}H and ^{13}C NMR spectra were recorded respectively on Varian 300 spectrometer and Varian 400 spectrometer using TMS as the internal standard. Multiplicity is indicated by the following: s (singlet); d (doublet); t (triplet); q (quartet); m (multiplet); br (broad). Thermogravimetric differential thermal analysis (TG-DTA) was carried out on a STA 449-C (Netzsch, Germany). Elemental analyses were carried out on Carioel elemental analyzer. Infrared spectra were collected on a Nicolet NEXUS 670 FT-IR spectrometer using a KBr pallet.



Scheme 3 Synthesis of 1-butyl-1-*aza*-18-crown-6

Synthesis of 1-butyl-1-*aza*-18-crown-6: NaH (40 mmol, 80%) and dried THF (100 mL) were added to a 500 mL round-bottom flask and cooled down to around –5~0 ^{o}C in an ice-salt bath. N-butyldiethanolamine (10 mmol) were dissolved in 100 mL dried THF and added dropwise to the flask. The ice-bath was

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removed and the mixture was heated to reflux for 2 h. The flask was cooled again to 0 °C in the ice-bath and added dropwise the THF 100 mL dissolved tetraethylnene glycol ditosylate (10 mmol). Then the mixture was stirred for 48 h under refluxing. After completion of this reaction, it was quenched with 100 mL water. Most of THF was removed by rotary evaporator and the mixture was extracted with dichloromethane (3 × 30 mL) subsequently. The combined organic layer was washed with water (3×50 mL) and dried by anhydrous $MgSO_4$. After evaporating the volatiles under vaccum, a yellow oily product was collected in 65% yield.[52-54]

Preparation of Brønsted acidic ionic liquids of *aza*-crown ether complex cations: *aza*-crown ether (11 mmol) and 1,3-propanesultone (10 mmol) were dissolved in 1,2-dichloroethane (15 mL) and allowed to stir under Ar at 40 °C for 4 h. After completion of the reaction, the solvent was evaporated under reduced pressure, the residue was washed with hexane (3×10 mL) and dissolved in deionized water (20 mL). The excess of *aza*-crown ether can be extracted with CH_2Cl_2 (3×20 mL). After removing the water, a yellow viscous zwitterion product e was obtained in 95% yield. Then the equimolar potassium salt (9.5 mmol) and corresponding acid (9.5 mmol) were added to the water solution (20 mL) containing zwitterion product (9.5 mmol) that was stirred for 24 h at room temperature. The desired aCBAIL was obtained as a yellow viscous product after removing the water and stored in a desiccator (95%).

General procedure for the Biginelli reaction: A mixture of aldehyde (1 mmol), ethyl acetoacetate (3 mmol), urea (1.5 mmol,) and aCBAIL catalyst (0.07 mmol) was heated to reflux in ethanol (2 mL) for a proper time. After completion of the reaction monitored by TLC, the mixture was poured into ice water (10 mL). The resulting solid precipitate was filtered, washed with cooled ethanol, dried in *vacuo*, and characterised by ^{1}H NMR spectra that were consistent with the literature reports.[39]

To reuse the aCBAIL, the above filtrate was extracted with ether (3×10 mL) to remove the organic impurities. The treated water solution was then evaporated under vacuum to reproduce IL.

General procedure for the Mannich reaction: A round-bottom flask charged with aCBAIL (0.1 mmol) in 2 mL of ethanol was added aldehyde (1 mmol), aniline (1 mmol) and ketone (1 mmol). The mixture was stirred for a proper time at room temperature to precipitate a crude product that was collected by filtration and recrystallized from ethanol-acetone (1:1, v/v) to afford pure Mannich base.

General procedure for synthesis of bis-(4-hydroxycoumarin-3-yl)methanes: A mixture of benzaldehyde (1 mmol), 4-hydroxycoumarin (2 mmol) and aCBAIL (0.05 mmol) in EtOH (1 mL) and H_2O (1 mL) was stirred under reflux condition for an appropriate time. After completion of the reaction monitored by TLC, the mixture was cooled down to room temperature. The solid product was collected by filtration, washed with water and cool ethanol.

Characterisation of catalysts: The NMR, IR and mass spectra, and the elemental analysis results of *aza*-crown ether complex cation ionic liquids are described as follows:

1-Butyl-1-*aza*-[18-C-6KSO$_3$H][Br]$_2$ ^{1}H NMR (300 MHz, D_2O) δ = 0.93 (t, J = 6.9 Hz, 3H), 1.36 (m, 2H), 1.69 (m, 2H), 2.16 (m, 2H), 2.93 (m, 2H), 3.39-3.68 (m, 24H), 3.90 (m, 4H) ppm; ^{13}C NMR (100 MHz, D_2O) δ = 12.53, 17.24, 18.61, 22.78, 46.84, 57.75, 58.07, 58.92, 59.64, 63.14, 63.38, 68.21, 68.69, 69.08, 69.08, 69.11, 69.12, 69.38, 69.89 ppm. IR (cm^{-1}) 3426.3 (m), 2911.4 (m), 2876.5 (m), 1718.4 (w), 1650.8 (w), 1469.3 (m), 1353.4 (m), 1249.8 (s), 1115.9 (vs), 1037.0 (s), 950.6 (m), 840.6 (w), 732.6 (w), 602.3 (m), 522.7 (m). Elemental analysis, calcd for $C_{19}H_{40}Br_2KNO_8S$ (%): C 35.57, H 6.28, N 2.18; found: C 35.21, H 6.24, N 1.83.

1-Butyl-1-*aza*-[18-C-6KSO$_3$H][BF$_4$]$_2$ ^{1}H NMR (300 MHz, D_2O) δ = 0.95 (t, J = 7.5 Hz, 3H), 1.38 (m, 2H), 1.70 (m, 2H), 2.17 (m, 2H), 2.95 (m, 2H), 3.40-3.71 (m, 24H), 3.92 (m, 4H) ppm; ^{13}C NMR (100 MHz, D_2O) δ = 12.58, 17.35, 18.81, 22.92, 46.95, 57.69, 59.03, 59.21, 59.66, 63.38, 63.57, 68.95, 69.22, 69.28, 69.35, 69.42, 69.48, 69.62, 69.65 ppm. IR (cm^{-1}) 3432.2 (m), 2924.3 (m), 2878.0 (m), 1718.7 (w), 1635.1 (w), 1465.2 (m), 1355.0 (m), 1295.5 (m), 1216.6 (m), 1119.0 (vs), 1040.0 (s), 947.8 (m), 839.1 (w), 733.4 (w), 601.7 (w), 526.4 (m). Elemental analysis calcd for $C_{19}H_{40}B_2F_8KNO_8S$ (%): C 34.82, H 6.15, N 2.14; found: C 34.52, H 6.38, N 2.01.

1-Butyl-1-*aza*-[18-C-6KSO$_3$H][PF$_6$]$_2$ ^{1}H NMR (300 MHz, D_2O) δ = 0.89 (t, J = 7.2 Hz, 3H), 1.31 (m, 2H), 1.64 (m, 2H), 2.11 (m, 2H), 2.87 (m, 2H), 3.33-3.64 (m, 24H), 3.85 (m, 4H) ppm; ^{13}C NMR (100 MHz, D_2O) δ = 12.63, 17.47, 18.86, 23.03, 47.10, 58.27, 59.07, 59.25, 59.68, 63.61, 63.70, 69.28, 69.32, 69.36, 69.38, 69.45, 69.48, 69.54, 69.68 ppm. IR (cm^{-1}) 3433.4 (m), 2921.7 (m), 2881.4 (m), 1717.3 (w), 1637.4 (w), 1469.2 (w), 1353.9 (w), 1248.2 (m), 1219.1 (m), 1114.2 (vs), 1035.4 (s), 845.3 (m), 743.0 (m), 604.6 (w), 556.3 (w), 525.3 (w), 485.2 (m). Elemental analysis calcd for $C_{19}H_{40}F_{12}KNO_8P_2S$ (%): C 29.57, H 5.23, N 1.82; found: C 29.32, H 5.41, N 1.57.

1-Butyl-1-*aza*-[18-C-6KSO$_3$H][HSO$_4$]$_2$ ^{1}H NMR (300 MHz, D_2O) δ = 0.92 (t, J = 7.2 Hz, 3H), 1.35 (m, 2H), 1.67 (m, 2H), 2.15 (m, 2H), 2.92 (m, 2H), 3.38-3.69 (m, 24H), 3.92 (m, 4H) ppm;^{13}C NMR (100 MHz, D_2O) δ = 12.58, 17.29, 18.67, 22.85, 46.92, 57.51, 58.06, 59.06, 59.78, 63.22, 63.42, 68.76, 69.10, 69.13, 69.16, 69.24, 69.26, 69.39, 69.46 ppm. IR (cm^{-1}) 3438.8 (m), 2920.1 (m), 2877.5 (m), 1722.3 (w), 1637.8 (w), 1468.1 (m), 1352.4 (m), 1235.0 (s), 1117.1 (vs), 1031.0 (s), 950.0 (m), 882.8 (m), 852.0 (m), 732.1 (w), 583.0 (vs), 523.8 (m). Elemental analysis calcd for $C_{19}H_{42}KNO_{16}S_3$ (%): C 33.77, H 6.26, N 2.07; found: C 33.41, H 6.44, N 1.92.

1-Butyl-1-*aza*-[18-C-6KSO$_3$H][TFA]$_2$ ^{1}H NMR (300 MHz, D_2O) δ = 0.91 (t, J = 7.2 Hz, 3H), 1.34 (m, 2H), 1.66 (m, 2H), 2.14 (m, 2H), 2.91 (m, 2H), 3.36-3.67 (m, 24H), 3.90 (m, 4H) ppm; ^{13}C NMR (100 MHz, D_2O) δ= 11.77, 16.53, 18.01, 22.20, 46.25, 57.38, 58.23, 58.36, 59.30, 62.58, 62.79, 68.42, 68.49, 68.53, 68.56, 68.60, 68.65, 68.82, 68.83, 115.25 (q, J = 291.3 Hz), 161.57, 161.93 ppm. IR (cm^{-1}) 3482.2 (m), 2965.8 (m), 2879.4 (m), 2529.6 (w), 2410.8 (w), 1958.1 (w), 1779.7 (m), 1745.3 (m), 1692.0 (m), 1417.2 (w), 1419.5 (w), 1354.5 (w), 1298.7 (w), 1180.7 (s), 1129.3 (s), 1042.3 (s), 949.2 (m), 798.3 (m), 706.5 (m), 608.7 (w), 525.1 (w). Elemental analysis calcd for $C_{23}H_{40}F_6KNO_{12}S$ (%): C 39.03, H 5.70, N 1.98; found: C 38.90, H 5.86, N 1.92.

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1-Butyl-1-*aza*-[18-C-6KSO$_3$H]][X]$_2$: MS (ESI) calcd. for $[M-H]^+$ 480.2, found 480.4; calcd. for $[M-K]^+$ 442. 2, found 442.5.

Conclusions

In summary, we designed and synthesized five new Brønsted acidic ionic liquids of *aza*-crown ether complex cations, in which, the cation bearing alkanesulfonic acid enables the aCBAIL possessing Brønsted acidity. Containing both hydrogen bond donors and acceptors, these new ILs can effectively increase the electrophilicity of the aldehydes. Thus, the organic reactions, such as Biginelli reactions, Mannich reaction and synthesis of bis-(4-hydroxycoumarin-3-yl)methanes can be achieved in good to excellent yields. To the best of our knowledge, it is the first report of synthesizing aCBAILs that can effectively catalyse different organic reactions. Further developments on their applications are underway in our laboratory.

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Notes and references

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