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Brønsted Acid Ionic Liquid as a Solvent-Conserving Catalyst for Organic Reactions

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A sulfonyl-containing ammonium-based Brønsted acid ionic liquid was prepared and used as a liquid heterogeneous catalyst for organic reactions. The unique macroscopic phase heterogeneity of the IL in the reaction system not only ensures an excellent catalytic activity of the IL catalyst but also avoids the use of organic reaction solvents. The catalyst system is applicable for a wide range of reactions.

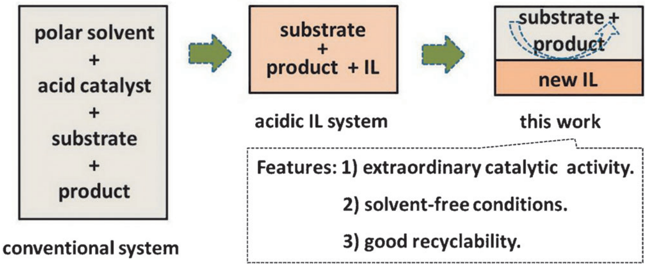

Figure 1. Schematic representation of acid catalyst systems.

Nearly 20 million tons of volatile organic compounds (VOCs) are released into the atmosphere each year through the activities of chemical industry[1] and are linked to global climate change and human illness. In order to reduce the emissions of VOCs, a lot of research has been devoted to the development of green solvents in the past two decades.[2] From the viewpoint of conserving materials, lessening energy consumption, and reducing reaction volume, solvent-free conditions are preferred to facilitate reactions of industrial significance. Although some reactions have been successfully performed under solvent-free conditions,[3] the use of organic solvents is still mandatory for most of the organic reactions. The main obstacles of eliminating solvents from these reactions stem from some pivotal functions of solvents, which cannot be fully attained without their use. Of all these functions, stabilization of the reaction intermediate ranks among the most important.

The use of Brønsted acid ionic liquids (ILs) as catalysts in organic reactions has gained considerable attention in the past decade.[4] When conventional ILs are used as catalysts, primarily to facilitate catalyst recycling, reactions often proceeded under solvent-free conditions (Figure 1, center).[5] In these cases, a mixture composed of substrate, product, and IL played the role of solvent. However, because the carbocation intermediate that was generated during the reaction may not be stabilized sufficiently in this mixture,[6] the full catalytic activity of the IL was, sometimes, not achieved.[7] We envisaged that this problem might be solved by a judicious structural design that enables the IL catalyst to show a macroscopic phase heterogeneity in the reaction system. This idea, if realized, might allow many reactions to be performed under solvent-free conditions. In this paper, a sulfonyl-containing ammonium-based Brønsted acid IL was synthesized that displayed an outstanding catalytic activity under solvent-free conditions for many organic reactions. Intriguingly, both substrate and product were immiscible with the IL, and the reaction proceeded under biphasic conditions, in which the Brønsted acid IL worked as a liquid heterogeneous catalyst (Figure 1, right).

The Brønsted acid ILs were prepared through a procedure depicted in Figure 2. Initially, divinyl sulfone was treated with an aliphatic amine in methanol at 60 °C, and a double Michael addition reaction provided sulfonyl-containing tertiary amines, **3a** and **3b**. The following quaternization of these amines with 1,3-propanesulfonate formed **4a** and **4b**. The structure of **4a** was confirmed by single crystal X-ray diffraction.[8] Finally, treatment of these zwitterionic salts with triflic acid (TfOH) at 80 °C produced the desired ILs, **1a** and **1b**. Both **1a** and **1b** are viscous liquids at room temperature. With these ILs in hand, we then started to examine their catalytic activity in organic reactions. In order to compare the efficiency of these ILs with that of non-sulfonyl ILs, two other Brønsted acid ILs, **1c** and **1d**, were also prepared (Figure 2).

The newly synthesized Brønsted acidic ILs were then utilized in some acid-catalyzed reactions that are associated with a carbocation intermediate. Firstly, arylmethylation of phenylacetylene **6a** with benzhydrol **5a** was examined, which has been realized by means of two catalytic systems, TfOH/Fe(OTf)$_3$[9] and Cu(OTf)$_2$.[10] However, the reactions have to be performed in organic solvents. We found that, under solvent-free conditions, TfOH is ineffective for this reaction (Table 1, entry 1). A moderate yield could be obtained in dichloroethane (DCE) (entry 2). Previously, 77% of yield was obtained by adding a catalytic amount of Fe(OTf)$_3$ into the TfOH/DCE system (entry 3).[9] With the hope of developing a solvent-free system, **1a** was then used as catalyst. To our delight, the yield of **7a** reached 95%

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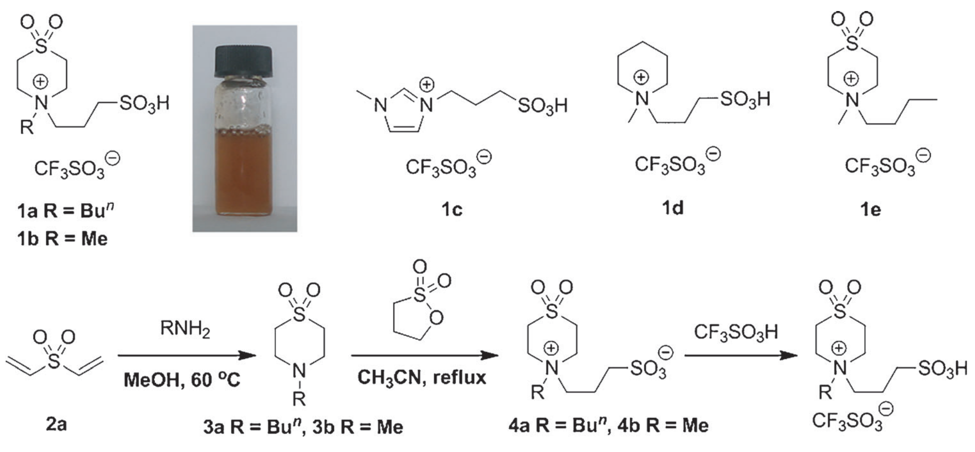
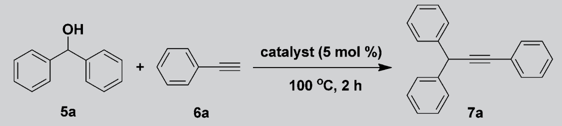


Figure 2. Sulfonyl-containing Brønsted acid ILs used in this work.

Table 1. Arylmethylation of phenylacetylene with benzhydrol.[a]



Entry	Catalyst and some specified conditions	Yield [%]
1	TfOH, 24 h	trace
2	TfOH in DCE, reflux, 24 h	52
3	TfOH/Fe(OTf)$_3$ in DCE, reflux, 24 h	77[b]
4	**1 a**	95, 89[g]
5	**1 b**	90
6	**1 c**	25
7	**1 d**	37
8	**1 d**/**1 e**	71
9	**1 e**	0
10	**1 a** with water	79,[c] 63,[d] 8[e]
11[f]	**1 a**	94

[a] **5 a**, 2.5 mmol, **6 a**, 2.5 mmol, catalyst, 0.125 mmol, 100 °C, 2 h. [b] Literature result in Ref. [9]. [c] 0.5 mmol water. [d] 1.0 mmol water. [e] 2.0 mmol water. [f] **1 a** was reused for the seventh time. [g] The reaction was performed at a scale of 30 mmol.

within 2 h at 100 °C (entry 4). IL **1 b** also exhibited excellent performance, and **7 a** could be obtained in 90 % yield (entry 5). In a sharp contrast to these good results, only 25 % of yield was obtained with the conventional Forbes's IL **1 c** under the identical conditions (entry 6). When **1 d**, the sulfonyl-free congener of **1 b**, was used as catalyst, only 37 % of **7 a** was obtained (entry 7). On the basis of these results, we can conclude that the existence of sulfonyl groups in the ILs **1 a** and **1 b** significantly influences their catalytic activities.

In order to shed light on the intensification effect of the sulfonyl group on the catalytic activity of **1 a**, we scrutinized the acid strength of the catalysts by Hammett method.[11] It was found that the acid strength of TfOH is greater than that of the others. However, no significant difference on their acid strength was observed between **1 a** and Forbes's IL **1 c**, which ruled out the effect of acid strength on the catalytic activity.[8] Quite recently, some ILs were proved to be labile under harsh conditions.[12] In particular, after a long time of irradiation with ultrasound or microwave, acidic species, such as SO_2 and SO_3, could be detected in the pyrolysis products of sulfur-containing ILs; these acidic species can, if produced, potentially influence the reaction outcome. To this end, the reaction was stopped after 1 hour, and **1 a** was neutralized with an aqueous solution of sodium hydroxide (1.0 N). No precipitate was observed after adding $AgNO_3$ (aq.) into the system, indicating that sulfur oxides were not formed in our system.

Interestingly, when **1 a** was used as catalyst, two phases could be observed clearly even at high temperature (100 °C, Figure 3 a).[13] The upper phase was composed mainly of organic compounds, and only tiny amount of **1 a** could be detected by ^{1}H NMR. In order to check where the reaction takes place, the upper organic phase was separated after being heated for 30 min of reaction. Half of the solution was directly subjected to isolation. The remainder was stirred at 100 °C for 2 h. Finally, almost the same yield was obtained (34 % *vs* 35 %). This implies that **1 a** dissolved in the organic phase is not responsible for the progress of the reaction. We have also measured the volume of the ionic phase at 100 °C. It was found that it by increased approximately 6 % after adding organic substrates.[8] All these results imply that, during the reaction, the IL phase absorbs organic substrates without itself becoming significantly dissolved into the organic phase.[14] For this reason, we speculated that the reaction might take place either in the IL phase or at the interface between the ionic and organic phases. The sulfonyl fragments in the ionic phase might play a key role in enhancing the catalytic activity of **1 a**. In order to verify this, a neutral salt, **1 e**, which also contains a sulfonyl group, was added to the **1 d**-catalysed reaction (5 mol %). In this case, yield of **7 a** increased to 71 % from 37 % (entry 8). Because **1 e** alone cannot initiate the reaction (entry 9), a synergistic effect between sulfonic and sulfonyl groups in the ionic phase could be responsible for the improvement in yield.

As water was produced during the reaction, we were interested in (i) where was the generated water? and (ii) how the water affected the reaction? By means of analysis with Karl-

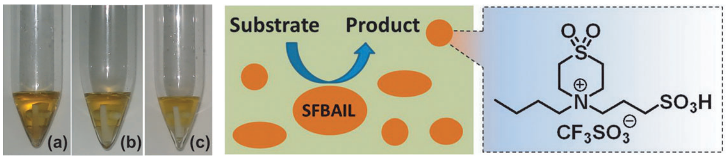
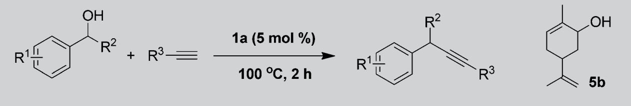


Figure 3. Photos of different IL systems and a schematic representation of the catalytic reaction. Photos are taken at the end of the reaction, 100 °C: (a) **1 a**; (b) **1 c**; (c) **1 d**.

Fischer titration, it was found that the generated water exists predominantly in the IL phase during the reaction. Fortunately, in the model reaction, the **1a** catalyst is quite robust in the presence of a small amount of water. This can be verified by the control experiments in Table 1 (entry 11).

Because **1a** is not soluble in non-polar organic solvent, it can be easily recovered at the end of the reaction. A reuse experiment demonstrated that **1a** can be used at least 8 times without significant loss of its activity (Table 1, entry 12).[15] The reaction can also be effectively scaled up with similar efficiency. For example, the reaction of **5a** (30 mmol) with **6a** (30 mmol) gave the corresponding arylmethylation product **7a** in 89% yield (7.15 g, Table 1, entry 4). We also probed the scope of **1a**-catalyzed arylmethylation reaction with respect to both the alcohol and the alkyne components. As shown in Table 2, benzhydrols with different substituents smoothly reacted with phenylacetylene, producing the corresponding products in generally excellent yields (entries 1–7). Carveol can also be used as substrate to react with **6a** over **1a** catalyst (entry 14). The scope of the reaction with respect to alkyne was also found to be excellent (entries 8–13).

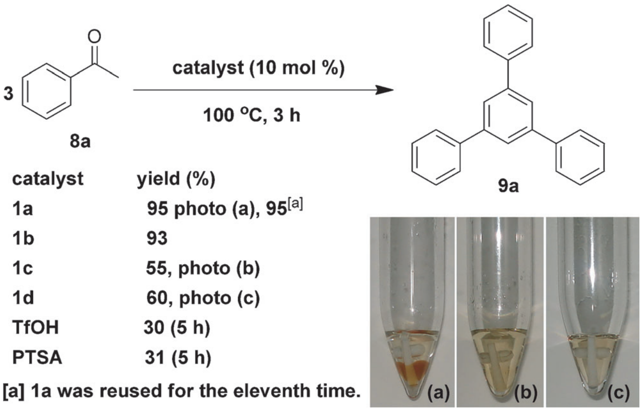
Table 2. Arylmethylation of terminal alkynes catalyzed by **1a**.[a]



Entry	R^1	R^2	R^3	Product	Yield [%]
1	p-OMe	C_6H_5	C_6H_5	**7b**	86
2	p-OMe	o-FC_6H_4	C_6H_5	**7c**	93
3	p-OMe	o-ClC_6H_4	C_6H_5	**7d**	88
4	p-Cl	p-ClC_6H_4	C_6H_5	**7e**	87
5	m-Br	o-MeC_6H_4	C_6H_5	**7f**	86
6	H	2-thienyl	C_6H_5	**7g**	85
7	p-OMe	$(CH_2)_2CH$	C_6H_5	**7h**	84
8	H	C_6H_5	p-EtC_6H_4	**7i**	95
9	H	C_6H_5	p-$Pr^nC_6H_4$	**7j**	95
10	H	C_6H_5	p-$Bu^nC_6H_4$	**7k**	96
11	H	C_6H_5	p-$Pn^nC_6H_4$	**7l**	94
12	H	C_6H_5	p-FC_6H_4	**7m**	89
13	H	C_6H_5	p-$MeOC_6H_4$	**7n**	92
14	**5b**+**6a**			**7o**	93

[a] Alcohol: 2.5 mmol, alkyne: 2.5 mmol, **1a**: 0.125 mmol, 100 °C, 2 h.

In the above-mentioned reactions, a macroscopic phase heterogeneity of the sulfonyl-containing Brønsted acid IL is the key to ensuring an excellent activity of **1a**. However, a limitation may appear in utilizing these ILs for a reaction with polar substrates, which tended to dissolve the catalyst, and consequently diminished the catalytic activity. To this end, these ILs were then applied in the cyclotrimerization of acetophenone,[16] which is a moderately polar substance. As shown in Figure 4, more than 90% yields were obtained within 3 h when **1a** and **1b** were used as catalysts. In these cases, the reaction also proceeded under biphasic conditions, whereas the use of **1c** and **1d** as catalysts resulted in homogenization of the reaction mixture, and **9a** was obtained only in moderate yields under identical conditions. These results indicated that sulfonyl group in **1a** indeed played a key role in limiting the dissolution of acetophenone into the IL phase, ensuring thus a macroscopic phase heterogeneity of the reaction system. TfOH and toluenesulfonic acid (PTSA) are also ineffective for this reaction. In literature, when PTSA was used as catalyst, a reaction time of 10 h and a temperature of 130 °C were needed in order to obtain a comparable yield with that of **1a**.[16b] Many acetophenone derivatives were applicable in this system.[8] Furthermore, in this reaction, **1a** can be reused at least 11 times without appreciable loss of its activity.



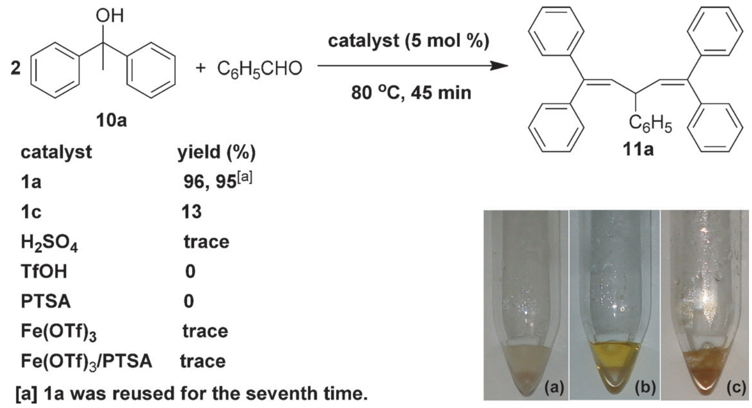
catalyst	yield (%)
1a	95 photo (a), 95[a]
1b	93
1c	55, photo (b)
1d	60, photo (c)
TfOH	30 (5 h)
PTSA	31 (5 h)

[a] 1a was reused for the eleventh time.

Figure 4. Cyclotrimerization of acetophenone.

Electrophilic reaction of aldehyde with 1,1-diphenylethylene has been sporadically investigated by using acid as catalyst.[17] However, the reported yields are rather low (< 50%) except on using some unusual substrates that have high reactivity, such as *para*-vinylanilines. Quite recently, Huang et al reported an efficient catalyst, $Fe(OTf)_3$/PTSA; however, the reaction was performed in a mixed solvent composed of toluene and methanol.[18] Because the catalytic activity of the sulfonyl-containing Brønsted acid IL was not significantly affected by the presence of a small amount of water, we then investigated the reaction of benzaldehyde and 1,1-diphenylethanol **10a**, which was considered as an alternative to 1,1-diphenylethylene (less expensive), with these ILs. A biphasic system can be visually observed (see Figure 5, picture a) during the reaction. The desired product, **11a**, could be obtained in 96% of yield after 45 min of reaction with **1a**. Interestingly, because **11a** is a solid and insoluble in the ionic phase, at the end of the reaction, the crude product solidified on top of the catalyst (picture (c)). This avoids the use of silica column chromatography for the product isolation. With Forbes's IL **1c** and some other commonly used acid catalysts, the reaction barely proceeded under the identical conditions. Compared with Huang's catalyst (12 h reaction time is needed),[18] our IL catalyst not only avoids the use of solvent, but also permits the reaction finishing within a very short time. Substrate scope of this system also proved to be excellent.[8]

Inspired by the reaction in Figure 5, we envisioned that a tandem dehydration/Michael addition reaction of **10a** and methyl vinyl ketone **12a** might be possible. Although the nucleophilicity of styrene has been well explored before, the use



catalyst	yield (%)
1a	96, 95[a]
1c	13
H_2SO_4	trace
TfOH	0
PTSA	0
$Fe(OTf)_3$	trace
$Fe(OTf)_3$/PTSA	trace

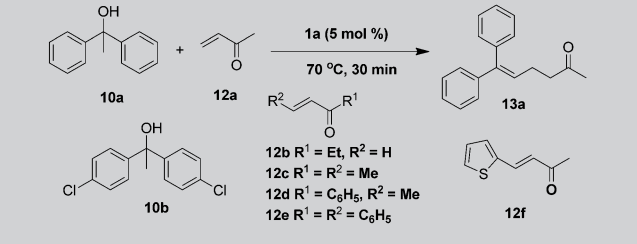
[a] 1a was reused for the seventh time.

Figure 5. Reaction of benzaldehyde with **10a** (Photos are taken at 80 °C, (a) 5 min; (b) 15 min; (c) at the end of the reaction).

of styrene as Michael donor has not been reported yet. We found that in the presence of 5 mol% of **1a**, the expected product **13a** was obtained in 95% yield under solvent-free biphasic conditions.[8] (Table 3, entry 1). In a sharp contrast to this good result, poor yields were obtained with **1c**, triflic acid, H_2SO_4, and $Sc(OTf)_3$ under the identical conditions (entries 2–7). A tertiary alcohol, **10b**, also participated readily in this reaction (entry 8). Other α,β-unsaturated ketones, such as **12b** to **12f**, can also be used as Michael acceptors (entries 9–14).

In summary, sulfonyl-containing ammonium-based Brønsted acid ILs were prepared and used as liquid heterogeneous catalysts for organic reactions under solvent-free conditions. The sulfonyl group endowed these ILs a unique macroscopic phase heterogeneity in the reaction system, thus ensuring outstanding catalytic activities of the ILs. These catalytic systems are applicable in a wide range of acid-catalyzed reactions. In particular, a hitherto unreported reaction of 1,1-diphenylethanol and α,β-unsaturated ketone was realized by using these IL catalysts.

Table 3. Tandem dehydration/Michael reaction of tertiary alcohols.[a]



Entry	Catalyst	Substrate	Product	Yield [%]
1	**1a**	**10a**+**12a**	**13a**	94, 93[b]
2	**1c**	**10a**+**12a**	**13a**	26
3	TfOH	**10a**+**12a**	**13a**	24
4	H_2SO_4	**10a**+**12a**	**13a**	15
5	PTSA	**10a**+**12a**	**13a**	17
6	$Sc(OTf)_3$	**10a**+**12a**	**13a**	13
7	**1a**	**10b**+**12a**	**13b**	96
8	**1a**	**10a**+**12b**	**13c**	94
9	**1a**	**10a**+**12c**	**13d**	96
10	**1a**	**10a**+**12d**	**13e**	94
11	**1a**	**10b**+**12d**	**13f**	91
12	**1a**	**10a**+**12e**	**13g**	93
13	**1a**	**10a**+**12f**	**13h**	80

[a] **10a**: 2.5 mmol, α,β-unsaturated ketone: 2.5 mmol, catalyst, 0.125 mmol, 70 °C, 0.5 h. [b] **1a** was reused for the fifth time.

Acknowledgements

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Keywords: acid catalysis · biphasic catalysis · green chemistry · ionic liquid

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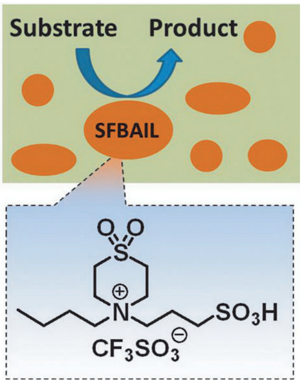
Brønsted Acid Ionic Liquid as a Solvent-Conserving Catalyst for Organic Reactions



Brains not Brønsted: Sulfonyl-containing ammonium-based Brønsted acid ionic liquids (ILs) are prepared and used as liquid heterogeneous catalysts for organic reactions under solvent-free conditions. The sulfonyl group endowed these ILs with unique macroscopic phase heterogeneity in the reaction system, ensuring outstanding catalytic activities of the ILs. These catalytic systems are applicable in a wide range of acid-catalyzed reactions.