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Sulfonic Acid-Functionalized Ionic Liquids as Metal-Free, Efficient and Reusable Catalysts for Direct Amination of Alcohols

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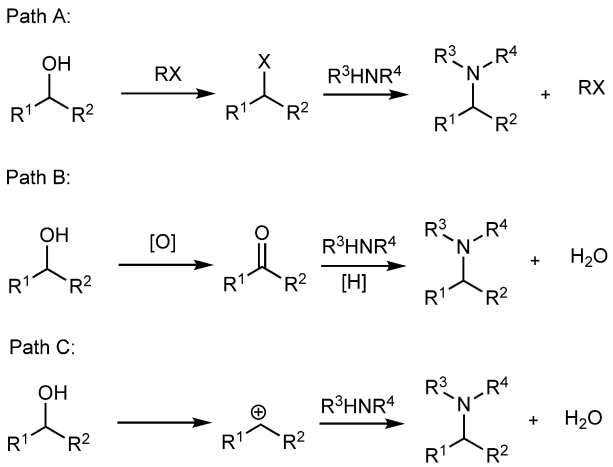
Abstract: A series of sulfonic acid-functionalized (SO_3H-functionalized) ionic liquids was synthesized and used as metal-free, highly selective and efficient catalysts for the direct amination of alcohols. Notably, the activities of the series of SO_3H-functionalized ionic liquids were compared and a 92% isolated yield was obtained using 3-tetradecyl-1-(butyl-4-sulfonyl)imidazolium trifluoromethanesulfonate ([BsTdIM][OTf]) as the catalyst. Importantly, the catalytic system has wide substrate scope including benzylic, allyl, propargylic, aliphatic alcohols with sulfonamide, amide, carbamate, aromatic amine and N-heterocyclic compounds. Interestingly, the system was also suitable for a multi-gram scale direct amination of alcohols. Additionally, the reusable nature of [BsTdIM][OTf] makes this protocol more attractive and avoids the disposal and neutralization of acidic catalysts. Moreover, preliminary experiments indicated that this reaction should proceed *via* an S_N1 pathway.

Keywords: alcohols; amination; ionic liquids; sulfonic acid-functionalized ionic liquids

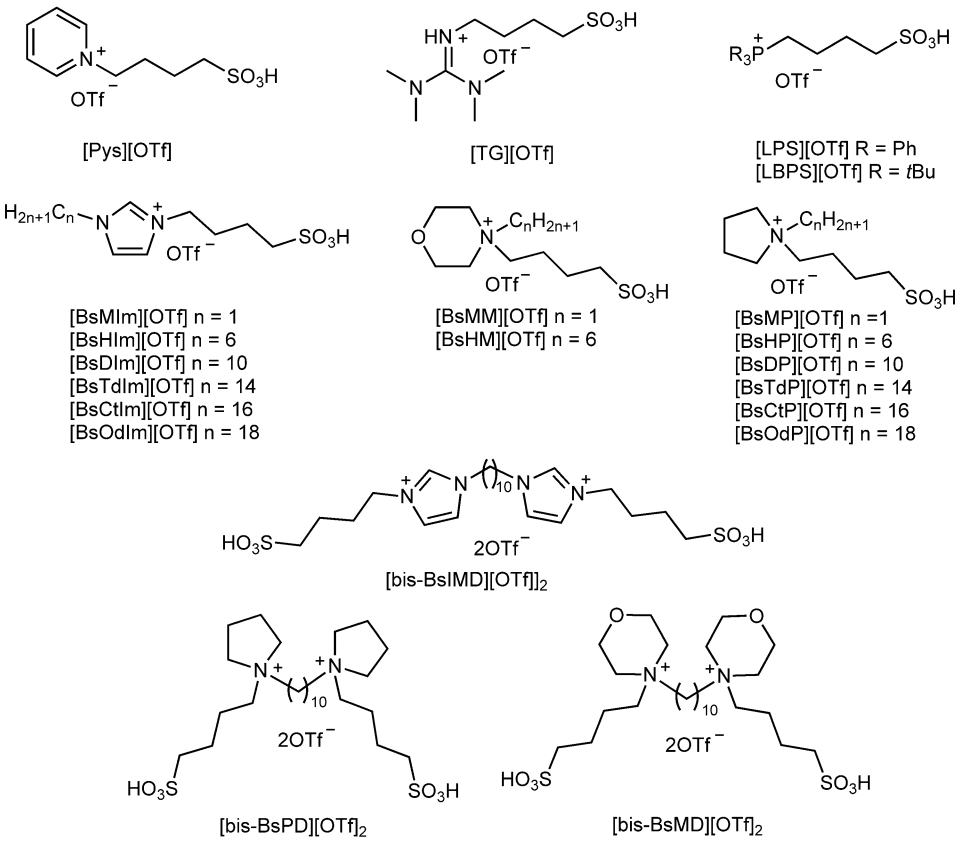
Introduction

Amination is a powerful method for the synthesis of amine derivatives, which are highly important intermediates because of their relevance for the synthesis of various pharmaceuticals and fine chemicals.[1] Nowadays, there are several methods to fulfil the transformation.[2] At present, a good alternative approach is to use alcohols as the alkylating agents to react with various amines as listed in Scheme 1. Obviously, the direct amination of alcohols (Scheme 1, paths B and C) is more competitive than the protocol of pre-activating alcohols (Scheme 1, path A) from the viewpoints of atom economy, green chemistry and sustainable development, since water is the only reaction by-product therein. In path B, transition metals with additives or ligands are essential, appropriate complexes are needed to realize the high performance of the late transition metals, and 3–5 equivalents of nucleophiles should be added, all of which make this protocol complicated.[4]

On the other hand, the carbocation process shown in path C seems to be more attractive. Various Lewis acids, such as triflate salts,[5] $BiCl_3$,[6] $FeCl_3$,[7] $InBr_3$,[8] $NaAuCl_4$,[9] $MoCl_5$,[10] $MoO_2(acac)_2$,[11] $Ca(NTf_2)_2$,[12]



Scheme 1. Methods for the amination of alcohols.



Scheme 2. SO_3H-functionalized ionic liquids used in the direct amination of alcohols.

iridium pincer catalyst,[13] Pd catalyst,[14] AuCl/$AgSbF_6$,[15] as well as Brønsted acids, such as *p*-toluenesulfonic acid or polymer-bound *p*-toluenesulfonic acid,[16] proton-exchanged montmorillonite,[17] dodecylbenzenesulfonic acid[18], $HClO_4{\cdot}SiO_2$,[19] and calix[4]resorcinarenesulfonic acid[20] have been employed to achieve this transformation. Unfortunately, the reported catalytic systems working through carbocation mechanism often suffered from one or more disadvangtages, including poor reactivity (low catalytic activity and selectivity, and relatively narrow substrate scope), and insufficient environmental friendliness (difficult catalyst reusability, excessive nucleophile utilization, and disposal and neutralization of strong acidic catalysts).

To overcome the above defects, novel efficient and environmentally-friendly acidic catalysts need to be developed for the direct amination of alcohols. Ionic liquids naturally come into view due to their excellent properties, such as very low or practically no vapor pressure and remarkable solubility behavior, as well as designability by varying their structure to manipulate parameters like density, solubility etc. and to achieve a specific purpose.[21,22] Recently, Zhu and coworkers developed the zinc-based ionic liquid ($[CHCl][ZnCl_2]_2$) bearing dual roles as an efficient catalyst for the direct nucleophilic substitution of alcohols with aniline, amide, sulfonamide, and 1,3-dicarbonyl compounds.[23] Although significant progress has been made, metal zinc was still used in the catalytic system and substrate scope also needed to be further expanded. In addition, using Amberlyst-15 immobilized in $[BMIM][BF_4]$ ionic liquid as an recyclable reagent for the direct substitution of alcohols with various nitrogen nucleophiles was also described by Bhanage and co-workers.[24] However, the use of an ionic liquid as a solvent was required in order to obtain higher yields of the products. Except for that, the direct amination of alcohols catalyzed by ionic liquids is still relatively rare. Therefore, it is significant and innovative to develop a metal-free, efficient and reusable ionic liquid catalyst system, which is applicable to a wide scope of alkylating agents and nucleophile classes for direct N-alkylation with alcohols.

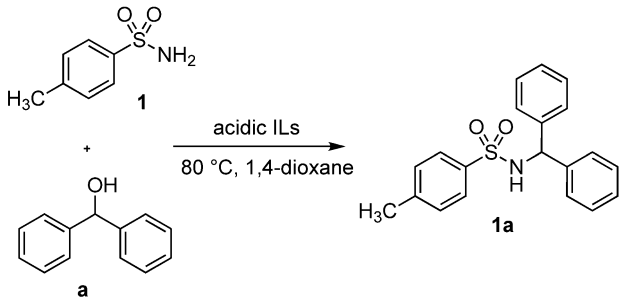
An alkanesulfonic acid group-functionalized ionic liquid, which was recently developed with the combined advantages of liquid acids and solid acids, for example, uniform acid sites, stability in water and air, easy separation and reusability,[25] seems to be an ideal option. In our continuing effort for developing acidic ionic liquid-catalyzed reactions,[26] a series of SO_3H-functionalized ionic liquids derived from pyri-

dine, phosphonium, guanidine, imidazole, pyrrolidine and morpholine (Scheme 2) was synthesized and applied to the direct amination of alcohols as metal-free, recyclable, selective and efficient catalysts. To our delight, the catalytic system has wide substrate scope including benzylic, allyl, propargylic, aliphatic alcohols with sulfonamide, amide, carbamate, aromatic amine and N-heterocyclic compounds with moderate to quantitative isolated yields. Moreover, [BsTdIM][OTf] exhibited the best activity and could be reused at least six times without significant loss of activity, which effectively avoided the disposal and neutralization of the acidic catalysts after reaction.

Results and Discussion

The exploratory experiments were started by screening the activities of SO_3H-functionalized ionic liquids with *p*-toluenesulfonamide and diphenylcarbinol as the model substrates. Initially, a series of ILs based on phosphonium, imidazolium, guanidinium and morpholinium cations and Br^-, BF_4^-, OTs^-, $CH_3SO_3^-$, HSO_4^-, camphorsulphonate anions was tested and no reaction occurred (see the Supporting Information, Table S1). Fortunately, the reaction could be successfully carried out using OTf^- as the anion and pyridinium, phosphonium, guanidinium, imidazolium, pyrrolidinium and morpholinium as cations (Table 1). And only trace of the unwanted by-product ether could be found in some cases. Higher than 50% yields of the desired product could be obtained when [TG][OTf], [LPS][OTf], [LBPS][OTf] and [PyS][OTf] were used as the catalyst (entries 1–4). Subsequently, the results indicated that the length of the side chain of the imidazolium and pyrrolidinium cations has a great effect on the yield (entries 5–16). The yield increased sharply with the carbon number of the side chain increasing from one to fourteen and dramatically decreased or kept the same when further increasing the carbon number. And 92% yield could be obtained by employing [BsTdIM][OTf] as the catalyst. However, the length of the side chain seems to have little influence on the yield for ionic liquids derived from morpholine (entries 17 and 18). Besides, the activities of SO_3H-functionalized imidazole, pyrrolidine and morpholine-based dicationic ionic liquids were also investigated and only moderate yields could be obtained. Additionally, a control experiment was performed to compare the catalytic activities between TfOH (trifluoromethanesulfonic acid) and SO_3H-functionalized ionic liquids. Otherwise, only 56% yield could be obtained using TfOH as the catalyst (entry 22), and 42% of bis(diphenylmethyl) ether as an unwanted by-product could be isolated. The acidities of above imidazole-based SO_3H-functionalized ionic liquids were evaluated from the Hammett acidity function using UV-visible spectroscopy with 2-nitroanline as the indicator in dichloromethane[27] (see the Supporting Information, Figure S1 and Table S4). Interestingly, it was found that the acidities of the SO_3H-functionalized ionic liquids decreased along with the increase of the carbon atom number in the side chain of the imidazole ring of the ionic liquids, while on the contrary, the catalyst activities increased until a maximum was reached.

Table 1. Screening the activities of SO_3H-functionalized ionic liquids.[a]



Entry	Catalyst	Yield [%][b]
1	[TG][OTf]	79
2	[LPS][OTf]	62
3	[LBPS][OTf]	77
4	[PyS][OTf]	66
5	[BsMIM][OTf]	56
6	[BsHIM][OTf]	67
7	[BsDIM][OTf]	86
8	[BsTdIM][OTf]	92
9	[BsCtIM][OTf]	77
10	[BsOdIM][OTf]	82
11	[BsMP][OTf]	62
12	[BsHP][OTf]	79
13	[BsDP][OTf]	82
14	[BsTdP][OTf]	84
15	[BsCtP][OTf]	84
16	[BsOdP][OTf]	85
17	[BsMM][OTf]	54
18	[BsHM][OTf]	57
19	[Bis-BsIMD][$OTf]_2$	67
20	[Bis-BsPD][$OTf]_2$	62
21	[Bis-BsMD][$OTf]_2$	60
22	TfOH	56

[a] *Reaction conditions:* *p*-toluenesulfonamide: 0.75 mmol, diphenylcarbinol: 0.5 mmol, catalyst: 20 mol% (referred to diphenylcarbinol), reaction temperature: 80 °C, solvent: 1,4-dioxane, 2 mL, reaction time: 3 h.

[b] Isolated yield.

Subsequently, the effects of various reaction parameters were examined. Preliminary results indicated that the solvent had a certain impact on the reaction (see the Supporting Information, Table S2). Either polar or non-polar solvents showed almost equal good performances and several solvents such as dimethyl sulfoxide, dimethylformamide and PEG-400 exhibited poor activity, especially no amination product was ob-

Table 2. Dependence of the yield on catalyst loading and reaction temperature.[a]

Entry	Catalyst [mol%]	Temperature [°C]	Yield [%][b]
1	20	40	31
2	20	60	73
3	20	100	93
4	20	120	95
5	1	80	trace
6	2.5	80	33
7	5	80	60
8	7.5	80	82
9	10	80	90
10	20	80	92
11	30	80	93

[a] *Reaction conditions: p*-toluenesulfonamide: 0.75 mmol, diphenylcarbinol: 0.5 mmol, solvent: 1,4-dioxane, 2 mL, reaction time: 3 h.
[b] Isolated yield.

tained employing PEG-400 as the solvent probably because of the existence of the hydroxy group inhibiting the reaction. Additionally, control experiments were carried out to test the influence of the reaction temperature and the results are summarized in Table 2. It was apparent that the yield remarkably increased when the temperature increased from 40 °C to 80 °C (entries 1, 2 and 10) and there was no significant change when further increasing the temperature (entries 3 and 4). Besides, the dependence of the yield on catalyst loading was also examined. Unfortunately,

Table 3. Catalytic *N*-alkylation of *p*-toluenesulfonamide and 4-nitroaniline with different alcohols.[a]

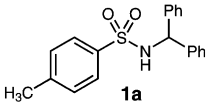
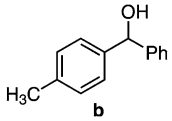
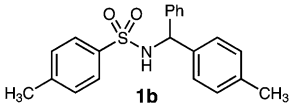
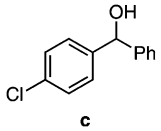
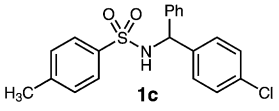
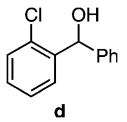
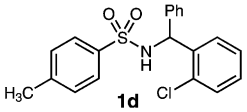
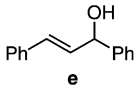
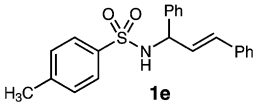
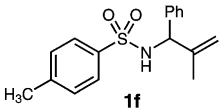
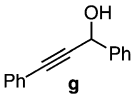
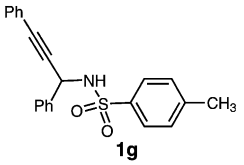
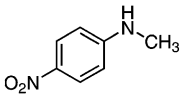
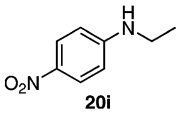
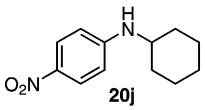
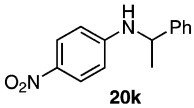
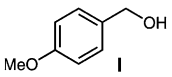
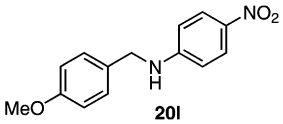
Entry	Alcohol	Product	Yield [%][b]
1	 **a**	 **1a**	90
2	 **b**	 **1b**	89
3	 **c**	 **1c**	84
4	 **d**	 **1d**	65
5	 **e**	 **1e**	87

Table 3. (Continued)

Entry	Alcohol	Product	Yield [%][b]
6	 **f**	 **1f**	71
7	 **g**	 **1g**	87
8[c]	CH_3OH **h**	 **20h**	19
9[c]	CH_3CH_2OH **i**	 **20i**	24
10[c]	 **j**	 **20j**	49
11[c]	 **k**	 **20k**	65
12[d]	 **l**	 **20l**	75

[a] *Reaction conditions: p*-toluenesulfonamide: 0.75 mmol, alcohol: 0.5 mmol, catalyst: [BsTdIM][OTf], 10 mol% (referred to alcohol), reaction temperature: 80 °C, solvent: 1,4-dioxane, 2 mL, reaction time: 3 h.
[b] Isolated yield.
[c] 4-Nitroaniline as N source, [TG][OTf] as catalyst, 10 mol%; reaction temperature: 140 °C, reaction time: 24 h.
[d] 4-Nitroaniline as N source, [BsTdIM][OTf] as catalyst, 10 mol%; reaction temperature: 120 °C, reaction time: 12 h.

only traces of product could be acquired with 1 mol% catalyst loading (entry 5). It could easily be seen that catalyst loading also had a great influence on yield with variation of loading from 2.5 to 10 mol% (entries 6–9); whereas the yield slightly changed with catalyst loadings in the range of 10–30 mol% (entries 9–11). As a whole, the optimized reaction conditions were 10 mol% [BsTdIM][OTf] as the catalyst, 80 °C and 2 mL of 1,4-dioxane.

To examine the utility and generality of the catalyst system for the direct amination, the scope of the reaction with respect to alcohols including benzylic, allyl, propargylic and aliphatic alcohols, and tertiary alcohols was first investigated and the results are listed in

Table 4. Catalytic *N*-alkylation of diphenylcarbinol (**a**) or (*E*)-1,3-diphenylprop-2-en-1-ol (**e**) with different N sources.[a]

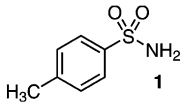
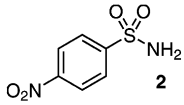
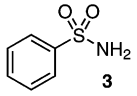
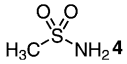
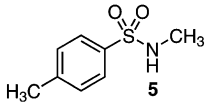
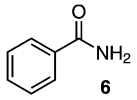
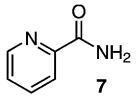
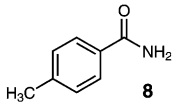
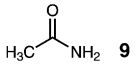
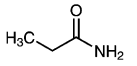
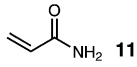
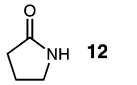
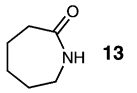
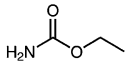
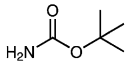
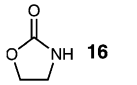
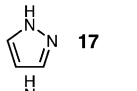
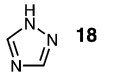
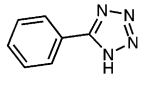
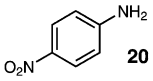
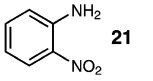
Entry	N Source	R^3OH	Time [h]	Product/Yield [%][b]
1	 **1**	**a**	3	**1a**/90
2		**e**	3	**1e**/87
3	 **2**	**a**	3	**2a**/85
4	 **3**	**a**	3	**3a**/83
5		**e**	3	**3e** 93
6[c]	 **4**	**a**	24	**4a**/76
7		**e**	2	**4e**/99
8	 **5**	**e**	3	**5e**/89
9	 **6**	**a**	3	**6a**/81
10		**e**	3	**6e**/79
11[d]		**k**	24	**6k**/63
12[c]	 **7**	**e**	3	**7e**/81
13	 **8**	**a**	3	**8a**/89
14	 **9**	**e**	3	**9e**/98
15	 **10**	**e**	3	**10e**/99
16	 **11**	**e**	3	**11e**/95
17	 **12**	**e**	1.5	**12e**/98
18	 **13**	**e**	3	**13e**/71
19	 **14**	**a**	3	**14a**/86
20		**e**	3	**14e**/85
21	 **15**	**e**	3	**15e**/93
22	 **16**	**a**	3	**16a**/75
23		**e**	0.3	**16e**/98
24	 **17**	**e**	3	**17e**/90
25	 **18**	**e**	1	**18e**/99
26	 **19**	**a**	3	**19a**/96
27[e]		**e**	0.25	**19e**/93

Table 4. (Continued)

Entry	N Source	R^3OH	Time [h]	Product/Yield [%][b]
28	 **20**	**a**	3	**20a**/87
29	 **21**	**a**	3	**21a**/89

[a] *Reaction conditions:* N source: 0.75 mmol, diphenylcarbinol or (*E*)-1,3-diphenylprop-2-en-1-ol: 0.5 mmol, catalyst: [BsTdIM][OTf], 10 mol% (referred to alcohol), reaction temperature: 80 °C, solvent: 1, 4-dioxane, 2 mL.
[b] Isolated yield.
[c] Reaction temperature: 120 °C, reaction time: 24 h.
[d] α-Phenylethanol (**k**) as alcohol, reaction temperature: 120 °C, reaction time: 24 h.
[e] Room temperature.

Table 3. Obviously, the electronic properties of the substituent group had no significant influence on the activities of diphenylcarbinol derivatives (entries 1–3). However, the yield sharply decreased due to the steric hindrance when employing (2-chlorophenyl)-(phenyl)methanol as the substrate (entry 4). Besides, allyl or propargylic alcohols also showed good activities with 71–87% yields (entries 5–7). Interestingly, aliphatic alcohols usually exhibiting poor activities still reacted smoothly with 4-nitroaniline when using [TG][OTf] as the catalyst and enhancing the temperature to 140 °C (entries 8–10). And α-phenylethanol also showed moderate activity with 4-nitroaniline as the N source (entry 11). However, the desired products cannot be obtained when using tertiary alcohols as the substrates (see the Supporting Information, Table S3). To our delight, benzylic primary alcohols with donating groups could make the reaction occur well, wherein 4-nitroaniline serves as the N source (entry 12).

Next, a series of N sources including sulfonamide, amide, carbamate, aromatic amines and various N-heterocyclic compounds was investigated with diphenylcarbinol or (*E*)-1,3-diphenylprop-2-en-1-ol as the alkylating reagent. The reactions of sulfonamide compounds with diphenylcarbinol or (*E*)-1,3-diphenylprop-2-en-1-ol proceeded smoothly with above 80% yields within 3 h (Table 4, entries 1–5, 7 and 8). And the yield of the reaction of methanesulfonamide and diphenylcarbinol could reach up to 76% after prolonging the reaction time to 24 h (entry 6). As for an amide as the N sources for the reaction, aliphatic amides could be completely transformed (entries 14–16) and aromatic amides exhibited slightly poorer activities (entries 9, 10, 12, 13). Additionally, cyclic amides also showed good activities and nearly quantitative yields could be obtained using pyrrolidin-2-one

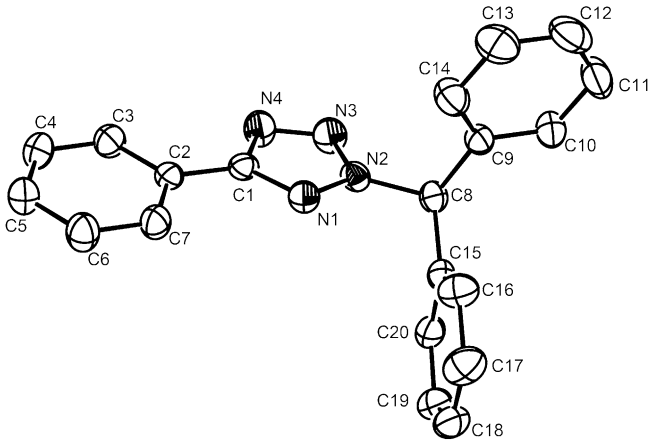
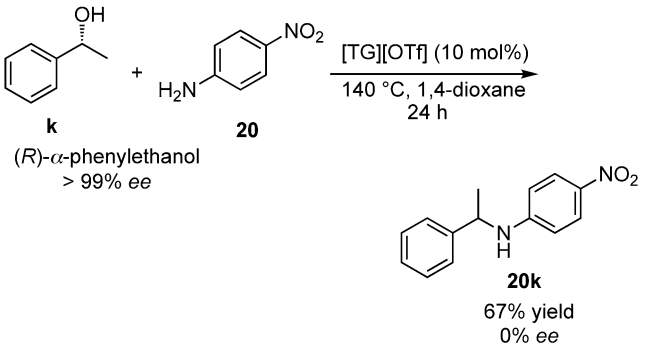


Figure 1. X-ray structure of 2-benzhydryl-5-phenyl-*2H*-tetrazole **19a** (hydrogen atoms are omitted for clarity, crystal data see the Supporting Information, **3**).



Scheme 3. [TG][OTf]-catalyzed direct amination of **k**.

as the substrate within 1.5 h (entry 17). However, extending the cycle of the cyclic amide would decrease the yield even after prolonging the reaction time to 3 h (entry 18). Besides, 75–98% yields are achieved for the amination of diphenylcarbinol or (*E*)-1,3-diphenylprop-2-en-1-ol with carbamate (entries 19–23). There is nearly no difference in activities using either diphenylcarbinol or (*E*)-1,3-diphenylprop-2-en-1-ol as the alkylating agent with ethyl carbamate as the N source (entries 19 and 20). However, significant differences existed on employing oxazolidin-2-one as the N source and quantitative yields could be afforded within 0.3 h (entries 22 *vs.* 23). On the other hand, the amination of diphenylcarbinol or (*E*)-1,3-diphenylprop-2-en-1-ol with azole compounds was also successfully with >90% yields (entries 24–27). Surprisingly, a 93% yield could be attained for the reaction of 5-phenyltetrazole and (*E*)-1,3-diphenylprop-2-en-1-ol even at room temperature for 0.25 h (entry 27). And the structure of the corresponding product **19a** has been elucidated by X-ray and is described in Figure 1, which indicates that the alkylation takes place at the N-2 position of tetrazole.[28] Finally, the activities of aromatic amines were also tested and about 90% yields could be obtained (entries 28 and 29).

In addition to an evaluation of the scope and limitations of the SO_3H-functionalized ionic liquid-catalyzed direct amination, some preliminary mechanistic investigations were performed. Optically active alcohol **k** with >99% *ee* was treated with **20** under the specified reaction conditions and racemic product **20k** was observed as anticipated (Scheme 3). Although the exact reaction mechanism is not quite clear at the moment, the amination under our catalytic system seems to proceed by a carbocation intermediate, which was attacked by the nucleophile (N source). The above chirality-transfer experiment supported that the nucleophilic attack was achieved through an S_N1 pathway and not an S_N2 pathway.

Another practical feature of the designed catalyst system is the facile separation of the product and the recyclability of the catalyst. To test the catalyst reusability, the reaction was carried out in the presence of a catalytic amount of [BsTdIM][OTf] under the optimal reaction conditions with *p*-toluenesulfonamide and diphenylcarbinol as the substrates. After each cycle, the catalyst and the product were separated in deionized water and the crude product was washed three times with deionized water. Then the water layer containing the catalyst was concentrated and dried under reduced pressure at 80 °C for 24 h in order to be reused directly. The results shown in Figure 2 indicated that the isolated yield of the product **1a** was almost consistent after six runs and [BsTdIM][OTf] could be reused at least six times without significant loss of the activities. Likewise, good catalyst reusability could also be achieved with benzamide and diphenylcarbinol, *p*-toluenesulfon-

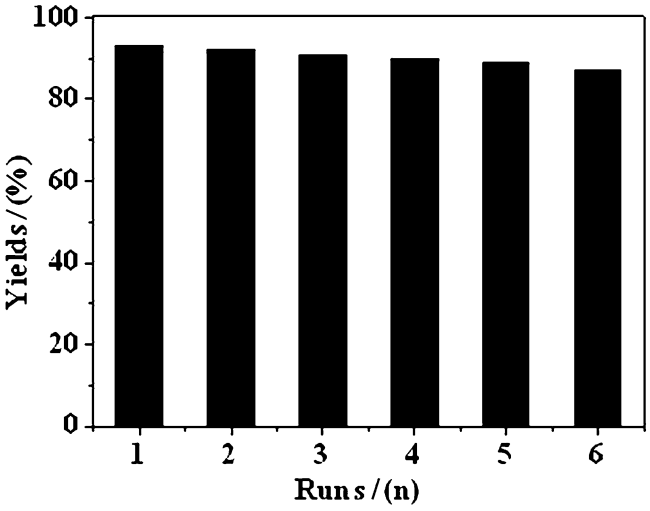
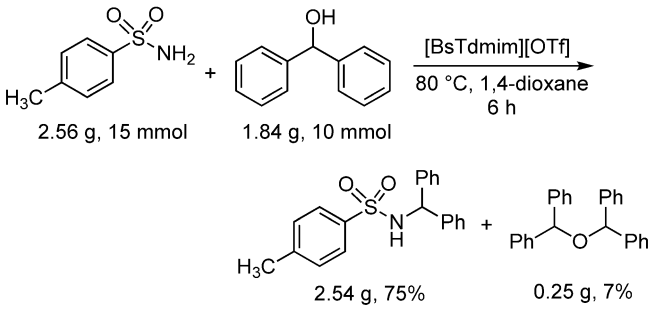


Figure 2. Recyclability of [BsTdIM][OTf] in direct amination of *p*-toluenesulfonamide and diphenylcarbinol.



Scheme 4. Large-scale direct amination of diphenylcarbinol.

amide and (*E*)-1,3-diphenylprop-2-en-1-ol, or 4-nitroaniline and diphenylcarbinol as the substrates (see the Supporting Information, Figure S2, Figure S3, and Figure S4.)

From the standpoint of practical applications, a large-scale direct amination of alcohols would be significant. As shown in Scheme 4, the present protocol could be carried out on a multigram scale. *N*-Benzhydryl-4-methylbenzenesulfonamide (2.54 g, 75%) could be obtained just by filtration and recrystallization. And the by-product ether (0.25 g, 7%) was isolated from the filtrate.

Conclusions

In summary, a series of SO_3H-functionalized ionic liquids derived from pyridine, phosphonium, guanidine, imidazole, pyrrolidine and morpholine was synthesized and applied to the direct amination of alcohols without adding any additives. Notably, [BsTdIM][OTf] exhibited the best activity and this catalytic system has a wide substrate scope including benzylic, allyl, propargylic, aliphatic alcohols with sulfonamide, amide, carbamate, aromatic amine and various N-heterocyclic compounds with moderate to quantitative isolated yields. Interestingly, the system was also suitable for the multigram scale direct amination of alcohols. Moreover, preliminary experiments indicated that the reaction should proceed by an S_N1 pathway. Studies on the developmont of the new catalytic system for this reaction and applying the catalytic system for new reactions are in progress in our laboratory.

Experimental Section

General

NMR spectra were recorded on Bruker DRX 400 spectrometers. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were obtained as solutions in either $CDCl_3$ or D_2O. Chemical shifts are reported in parts per million (ppm, δ) and referenced to $CHCl_3$ ($\delta = 7.26$) or D_2O ($\delta = 4.88$). GC-MS analyses were performed using an Agilent 6850 system (FID). Silica gel (200–300 microns) was used for all chromatographic separations. High resolution mass spectra (HR-MS) were recorded on a Bruker MicroTOF-QII mass instrument (ESI). Anhydrous organic solvents were dried and stored under nitrogen. All other chemicals used for synthetic procedures were reagent grade or better. Solutions were concentrated under vacuum with a rotary evaporator and the residue was purified using a silica gel column unless specified otherwise. All reactions were monitored by TLC with silica gel-coated plates and detection was conducted by UV absorption (254 nm). And the synthetic procedure for SO_3H-functionalized ionic liquid was in accordance with the references.[26b,29]

Procedure for 3-Tetradecyl-1-(butyl-4-sulfonyl)-imidazolium Trifluoromethanesulfonate ([BsTdIM][OTf])

1-Tetradecylimidazole (5.28 g, 0.020 mol) and 1,4-butanesultone (2.25 mL, 0.022 mol) were charged into a 100-mL round-bottom flask. Then the mixture was stirred at 40 °C for 10 h. After washing the salt with ether and toluene to remove any unreacted starting materials, the solid was dried under vacuum. Then, a stoichiometric amount of trifluoromethanesulfonic acid (1.80 mL, 0.020 mol) was added dropwise and the mixture stirred for 12 h at 80 °C, resulting in the formation of 3-tetradecyl-1-(butyl-4-sulfonyl)imidazolium trifluoromethanesulfonate ([BsTdIM][OTf]). The ionic liquid phase was then washed repeatedly with toluene and ether to remove non-ionic residues, and dried under vacuo. The product [yield: 10.8 g (98%)] was formed quantitatively and in high purity as assessed by NMR, IR and mass spectroscopy. ^{1}H NMR (400 MHz, D_2O): $\delta = 0.68$ (t, $J = 6.4$ Hz, 3H), 1.09–1.15 (m, 22H), 1.59–1.69 (m, 4H), 1.83–1.91 (m, 2H), 2.75 (t, $J = 7.6$ Hz, 2H), 4.04 (t, $J = 7.6$ Hz, 2H), 4.12 (t, $J = 7.6$ Hz, 2H), 7.37 (s, 1H), 7.47 (s, 1H), 8.78 (s, 1H); ^{13}C NMR (100 MHz, D_2O): $\delta = 13.7$, 21.2, 22.6, 26.2, 28.5, 29.2, 29.5, 29.6, 29.8, 29.9, 30.0, 32.0, 49.0, 49.5, 50.1, 118.2, 121.4, 122.2, 122.6, 135.4; IR: $\nu = 3159$, 3122, 3095, 2900, 2853, 1573, 1468, 1295, 1246, 1245, 1166, 1120, 1032, 915, 863, 776, 724, 639, 517 cm^{-1}; MS (ESI): $[m/z]^+ = 400.8$, $[m/z]^- = 148.9$.

Typical Procedure for Direct Amination of Alcohols and Reuse of [BsTdIM][OTf]

[BsTdIM][OTf] (27.5 mg, 10 mol%), alcohol **a** (92 mg, 0.5 mmol), *p*-toluenesulfonamide **1** (128.3 mg, 0.75 mmol), and dry 1,4-dioxane (2.0 mL) were added into the screw-cap vial. Then the mixture was stirred continuously at 80 °C for 3 h and monitored by TLC. At the end of the reaction, 10 mL of deionized water were added into the reaction mixture. When the mixture was cooled to room temperature, the crude product was isolated though simple filtration and the pure product – *N*-benzhydryl-4-methylbenzenesulfonamide (**1a**) – was obtained by recrystallization or flash column chromatography on silica gel as a white solid; yield: 92%; mp 159–160 °C. IR: $\nu = 3248$, 1560, 1495, 1452, 1316, 1161, 1092, 1057, 1028, 940, 812, 748, 702, 676, 571, 548, 491 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 2.37$ (s, 3H), 5.15

(d, $J=6.8$ Hz, 1H), 5.56 (d, $J=6.8$ Hz, 1H), 7.09–7.21 (m, 12H), 7.56 (d, $J=8.0$ Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=21.5$, 61.4, 127.2, 127.4, 127.6, 128.5, 129.4, 137.3, 140.5, 143.2; HR-MS (ESI): $m/z=360.1020$, calcd. for $C_{20}H_{19}NNaO_2S$ $[M+Na]^+$: 360.1029.

The ionic liquid ([BsTdIM][OTf]) obtained by drying the filtrate under vacuum for 24 h could be reused for another five runs without significant decrease in catalytic activity as shown in Figure 2.

Procedure for Large-Scale Direct Amination of Diphenylcarbinol

[BsTdIM]OTf (0.55 g, 10 mol%), diphenylcarbinol (1.84 g, 10 mmol), *p*-toluenesulfonamide (2.56 g, 15 mmol), and dry 1,4-dioxane (40 mL) were added into the screw-cap vial. Then the mixture was stirred at 80 °C for 6 h. After the reaction, 100 mL of deionized water were added into the reaction mixture. When the mixture was cooled to room temperature, the crude product was isolated though simple filtration. The pure product [yield: 2.54 g (75%)] was obtained by recrystallization three times and the by-product ether [yield: 0.25 g (7%)] was separated from the filtrate.

Acknowledgements

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[28] CCDC 838438 contains the supplementary crystallographic data for the compound **19a**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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