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Efficient Thiolation of Alcohols Catalyzed by Long Chained Acid-functionalized Ionic Liquids under Mild Conditions

Chengxia Miao,[a,b] Hongfeng Zhuang,[a] Yating Wen,[a] Feng Han,* [a,b] Qing-Feng Yang,[c] Lei Yang,[b] Zhen Li,[b] and Chungu Xia*[b]

Abstract: Thioethers as important building blocks have been usually found in organic synthesis. Herein, a series of long chained acid-functionalized ionic liquids derived from pyrrolidine were applied for the thiolation of alcohols to synthesize different compounds containing thioether structures. This kind of ionic liquids exhibited higher efficiency than general ionic liquids based on imidazole, providing up to 99% yield with [BsCtP][OTf] as the catalyst at room temperature for 0.25 h. The results indicated that the activities of the ionic liquids have relationship with the side chain length of ionic liquids based on pyrrolidine, anions and cations. The catalytic system had wide substrate scope and was applicable for the reaction of aromatic primary and secondary alcohols and thiols including aliphatic and aromatic thiols, benzothiazole-2-thiols and benzooxazole-2-thiols. Besides, there was no obvious change in activity of the catalyst after six runs. Thus, the catalytic system exhibited good recyclability. Additionally, carbocations should be the key intermediate and several functionalized groups of the ionic liquids have synergetic effect for the thiolation.

Introduction

Sulfur-containing compounds serve important functions in organic synthesis, such as substrates, photosensitizers or hydrogen-atom-transfer (HAT) reagents and so on.[1] Thioethers as important building blocks in some important drugs or some biologically active compounds (shown in Figure 1) have led to an increased awareness of researchers.[2-4] At present, a variety of methods for the corresponding synthesis of thioethers are available in the literatures.[5-8] The reaction of aryl halides and thiols is the typical method to construct C-S bonds.[9-11] Researchers also built other important methods for the formation of thioethers, such as the addition of thiols to carbonyl compounds followed by the in-situ reduction of the generated intermediate thionium ion,[12] deoxygenation of sulfoxides,[13] cross-coupling of aryl boronic acids and alkyl thiols or *N*-thio(alkyl, aryl, heteroaryl)imides,[14,15,16] metal catalyzed hydrothiolation of alkynes and so on.[17] During the development of the system for synthesis of thioethers, significant progress has been made.

With the development of Green Chemistry, easily available and cheap alcohols are attractive sources of electrophiles and the only byproduct formed in the reaction of alcohols and thiols is water. Thus, direct nucleophilic substitution reactions of alcohols have gained much attention.[18-22] Previously, we realized direct synthesis of polysubstituted olefins via construction of C-C bonds from alcohols or alkenes with alcohols and also developed system for direct amination of alcohols.[23,24] Generally, carbocations from alcohols were proposed as the active intermediates during the systems. As for the direct displacement of alcohols with sulfur nucleophiles, there are also some reported systems at present. Sanz achieved the direct nucleophilic substitution of the hydroxy group of allylic and benzylic alcohols with a large variety of carbon- and heteroatom-centered nucleophiles catalyzed by simple Brønsted acids such as *p*-toluenesulfonic acid monohydrate or polymer-bound *p*-toluenesulfonic acid.[25] Aluminum dodecatungstophosphate or $ZrCl_2$ was also beneficial for the thiolation of alcohols, providing excellent yields.[26,27] Bandgar employed silica supported perchloric acid as the catalyst for synthesis of thioethers from alcohols and thiols.[28] Wu group also successfully realized the direct displacement of alcohols with sulfur nucleophiles catalyzed by $Ga(OTf)_3$.[29] Based on the systems, we found thiolation of alcohols could be carried out well with simple Lewis or Brønsted acids as the catalysts. However, these catalysts could not be recycled and separated easily with the product. On the other hand, some developed supported catalysts exhibited good recyclability but relatively poor activity. Therefore, it is significant and innovative to develop catalytic systems having both high activity and recyclability for thiolation of alcohols.

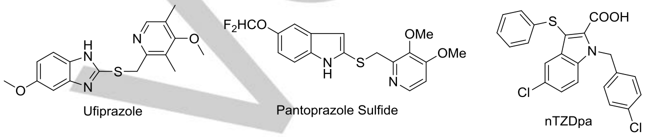

Figure 1. Some important compounds containing thioethers structure.

Ionic Liquids (ILs) are organic salts, generally composed of an organic cation and a wide range of different anions.[30] Ionic liquids were often used as a class of environmentally friendly solvents because of their extraordinary properties such as nonvolatility, nonflammability, high stability, high ionic conductivity, and easy recyclability.[31] Recently, task-specific ionic liquids have received more and more attention and were

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Supporting information for this article is given via a link at the end of the document.((Please delete this text if not appropriate)) employed as the catalyst and so on.[32] Among them, acidic ionic liquids have been widely used in alkylation, oxidation, esterification and so on and long chained ionic liquids would exhibit surface activity and have certain promoted effect on reactions.[33]

In our continuing effort on developing acidic ionic liquids catalyzed reactions,[23,24,34-37] we synthesized a series of muti-functionalized ionic liquids derived from pyrrolidine and applied them for the thiolation of alcohols (Figure 2). Delightedly, the ionic liquids based on pyrrolidine exhibited more efficiency than general ionic liquids based on imidazole, providing up to 99% yield with [BsCtP][OTf] as the catalyst at room temperature for 0.25 h (Scheme 1). The results indicated that the activities of the ionic liquids have relationship with anions, cations and the side chain length of ionic liquids based on pyrrolidine. Moreover, the catalytic system exhibited good recyclability.

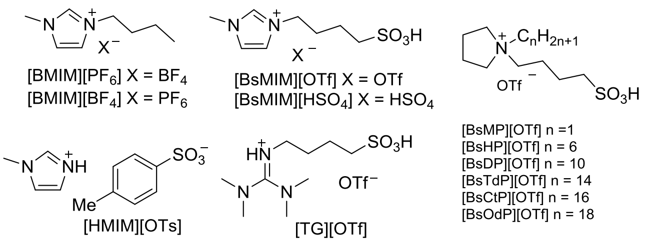
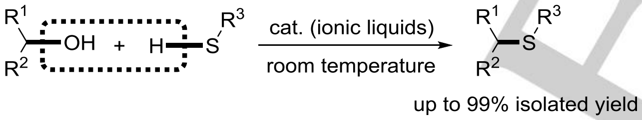


Figure 2. A series of ionic liquids used in the work. (OTf = trifluoromethanesulfonyl, OTs = *p*-toluenesulfonyl).



Scheme 1. Thiolation of alcohols at room temperature.

Results and Discussion

We commenced our studies with diphenylcarbinol and benzooxazole-2-thiol as the substrates and the results were summarized in Table 1. Initially, simple neutral ionic liquids such as [BMIM][BF$_4$] and [BMIM][PF$_6$] were tested and no reaction occurred (Table 1, entries 1-2). The reaction was also inert using [HMIM][OTs] as the catalyst (Table 1, entry 3). Fortunately, the reaction could work smoothly when ILs based on imidazolium have acidic anions and the side chain introduced by acidic group (Table 1, entries 4 and 5). Moreover, OTf$^-$ as the anion gave better result. Guanidinium ionic liquids ([TG][OTf]) provided up to 79% yield (Table 1, entry 6). The results indicated that the activities of the reactions have relationship with anions and cations of the ionic liquids. Inspired by this, a series of pyrrolidinium ionic liquids were synthesized and applied for the reaction (Table 1, entries 7-12). And the results demonstrated that the length of the side chain would affect the yields of the products. [BsCtP][OTf] with sixteen carbons on the side chain provided 87% yield, however, the yield would reduce by further increasing the chain length (Table 1, entries 11 vs 12). Subsequently, other reaction conditions such as solvents and the loading of catalyst were also investigated (Table S1 and S2). Then, [BsCtP][OTf] (10 mol%) as the catalyst, 1,2-dichloroethane (DCE) as the solvent and room temperature were the optimized reaction conditions.

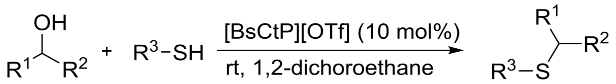
Table 1. Screening of ionic liquids for thiolation of diphenylcarbinol with benzooxazole-2-thiol.[a]

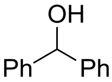
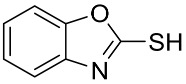
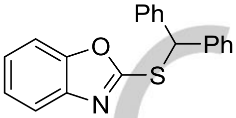
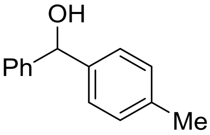
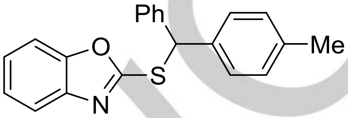
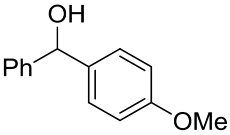
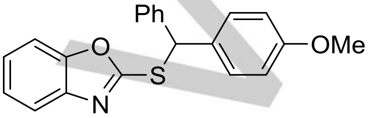
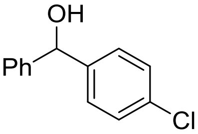
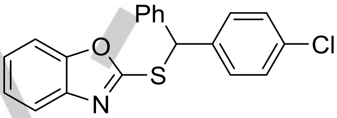
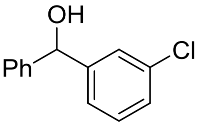
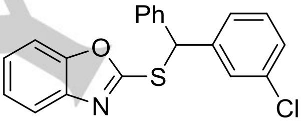
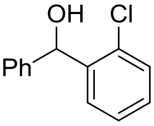
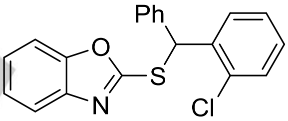
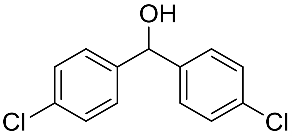
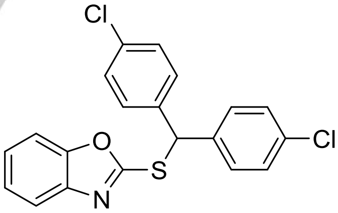
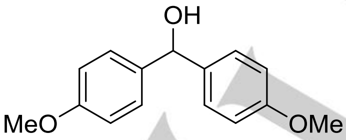
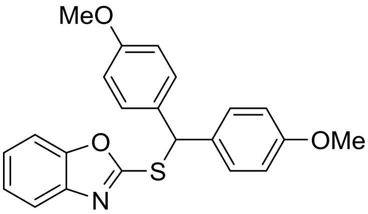
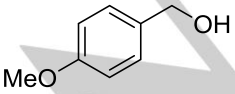
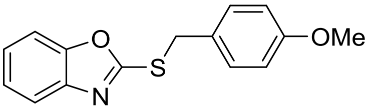
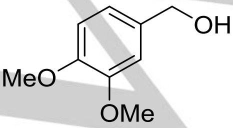
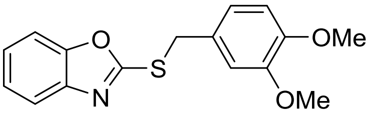
Entry	Catalyst	Yield (%)[b]
1	[BMIM][BF$_4$]	NR[c]
2	[BMIM][PF$_6$]	NR[c]
3	[HMIM][OTs]	NR[c]
4	[BsMIM][HSO$_4$]	28
5	[BsMIM][OTf]	59
6	[TG][OTf]	79
7	[BsMP][OTf]	34
8	[BsHP][OTf]	68
9	[BsDP][OTf]	80
10	[BsTdP][OTf]	83
11	[BsCtP][OTf]	87
12	[BsOdP][OTf]	81

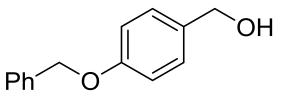
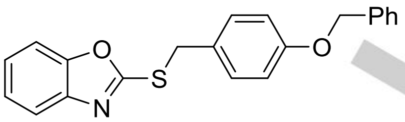
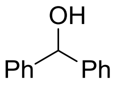
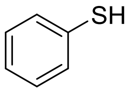
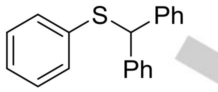
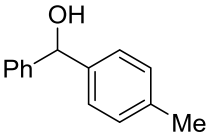
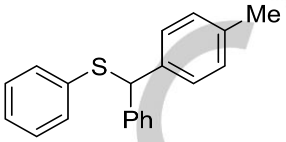
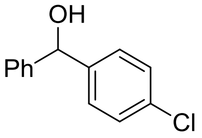
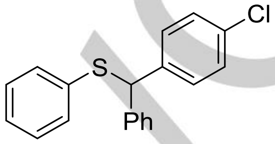
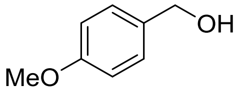
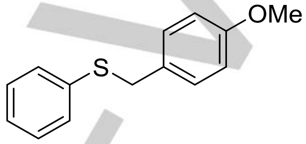
[a] Reaction conditions: diphenylcarbinol (0.5 mmol), benzooxazole-2-thiol (0.6 mmol) and catalyst (10 mol%, according to diphenylcarbinol) dissolved in 2 mL of 1,2-dichloroethane were stirred at room temperature for 1 h. [b] GC yield, biphenyl as internal standard. [c] NR = no reaction.

With optimized reaction conditions in hand, we first investigated the reactivities of a series of aromatic secondary and primary alcohols with benzooxazole-2-thiol or benzenethiols shown in Table 2. Obviously, the activities of benzohydrol derivatives had certain relationship with the electron properties and steric hindrance of substituent groups on the phenyl ring (Table 2, entries 1-6). Benzohydrol derivatives with electron-donating groups (such as OMe, Me) on one side of the phenyl ring gave better activities (Table 2, entries 2, 3 vs 1). On the other hand, benzohydrol derivatives with electron-withdrawing groups (Cl) as the substrate could give 90% yield when the reaction time was 4 h (Table 2, entry 4). (3- or 2-Chlorophenyl)(phenyl)methanol provided 89% or 84% yield respectively after prolonging the reaction time to 20 hours (Table 2, entries 5 and 6). And there is no significant influence of the electron properties on the activities by using diphenylcarbinol derivatives with two substituent groups on two phenyl rings as the substrates (Table 2, entries 7 and 8). Additionally, a series of benzyl alcohols were also examined. The electron properties and steric hindrance of substituent groups on the phenyl ring also affected the activities of the benzyl alcohols (Table 2, entries 9-11). Then the reactivities of aromatic secondary and primary alcohols with benzenethiol were studied (Table 2, entries 12-15). Interestingly, benzohydrol with 4-substituted groups exhibited better reactivities than simple diphenylcarbinol, providing more than 90% yields within 0.25 h (Table 2, entries 13, 14 vs 12). Additionally, 83% yield could be obtained by employing 4-methoxybenzyl alcohol as the substrate (Table 2, entry 15).

Table 2. Thiolation of a series of aromatic alcohols with benzooxazole-2-thiol or benzenethiol catalyzed by [BsCtP][OTf].[a]



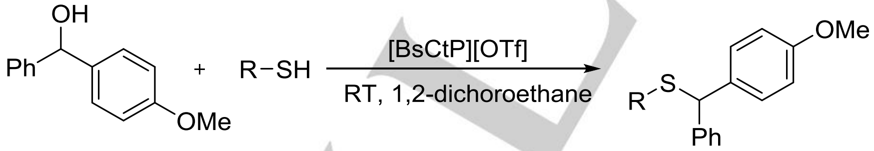
Entry	Alcohol	Thiol	Product	t (h)	Yield (%)
1				1	87[c]
2				1	96
3				1	97
4				4	90
5				20	89
6				20	84
7				2	92
8				2	97
9				2	95
10				2	81

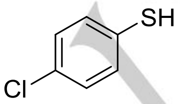
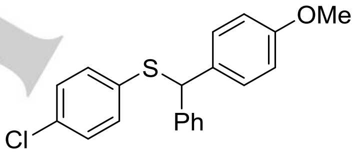
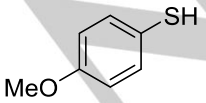
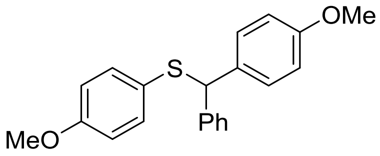
11				2	85
12				0.5	71
13				0.25	94
14				0.25	91
15				2	83

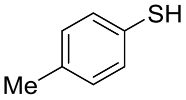
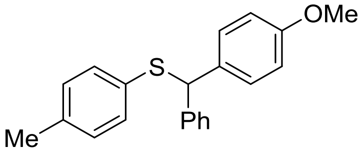
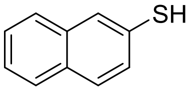
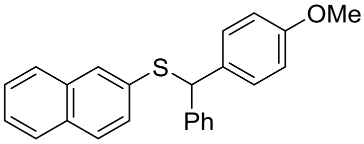
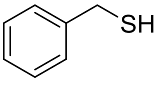
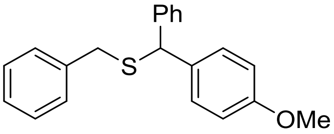
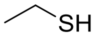
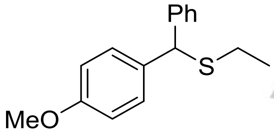
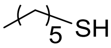
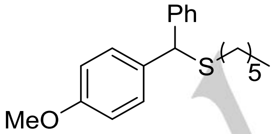
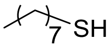
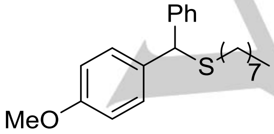
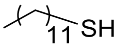
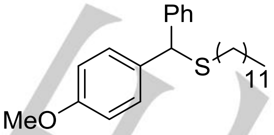
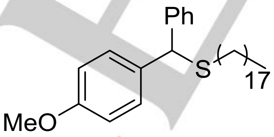
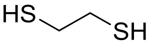
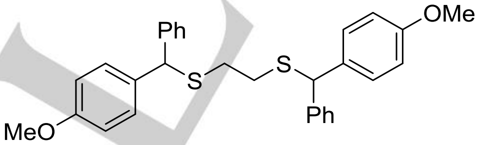
[a] Reaction conditions: alcohol (0.5 mmol), thiol (0.6 mmol) and [BsCtP][OTf] (10 mol%, according to alcohol) dissolved in 2 mL of 1,2-dichloroethane were stirred at room temperature for certain time. [b] Isolated yields. [c] GC yield, biphenyl as internal standard.

Subsequently, the reactions of (4-methoxyphenyl)(phenyl)methanol and a series of thiols were examined shown in Table 3. Interestingly, either aromatic or aliphatic thiols exhibited high activities, giving high yields within 0.5 h at room temperature. Firstly, several aromatic thiols were investigated. The results indicated that the electron properties and the steric hindrance of the substituted groups on the phenyl rings of benzohydrol derivatives have small influence on the reactivities (Table 3, entries 1-4). And 71% yield could be obtained even with phenylmethanethiol as the substrates just with 0.25 h (Table 3, entry 5). Besides, a series of aliphatic thiols afforded the corresponding products in excellent yields within 0.5 h (Table 3, entries 6-11). And the results indicated that there is a peak value when the carbon chain length of the substrate is about six (Table 3, entry 7). Additionally, ethane-1,2-dithiol also provided good yield, up to 93% within 0.5 h (Table 3, entry 11).

Table 3. Thiolation of (4-methoxyphenyl)(phenyl)methanol with a series of thiols catalyzed by [BsCtP][OTf].[a]



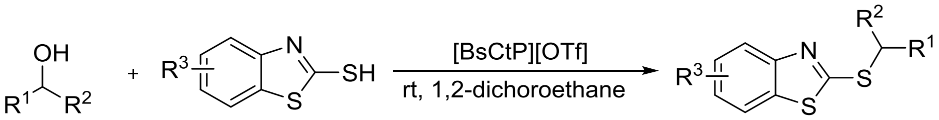
Entry	Thiol	Product	t (h)	Yield (%)[b]
1			0.25	93
2			0.25	99

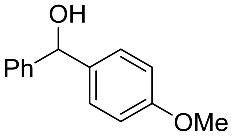
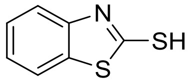
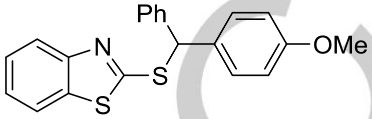
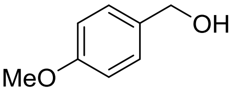
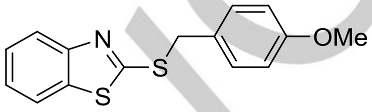
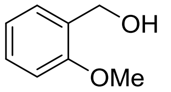
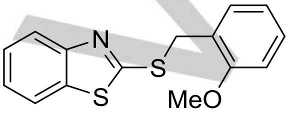
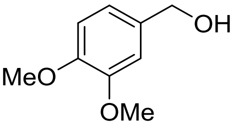
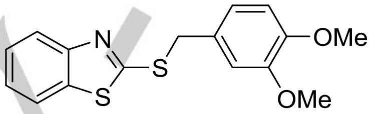
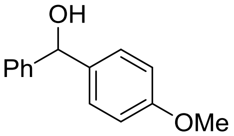
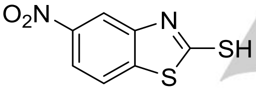
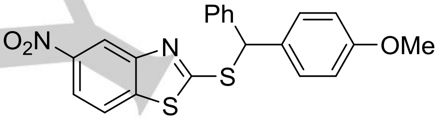
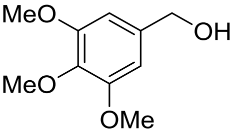
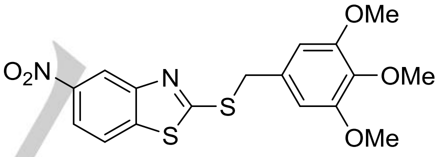
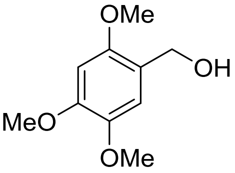
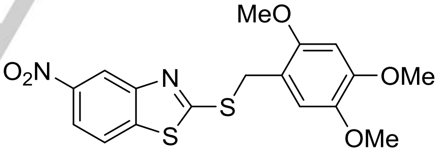
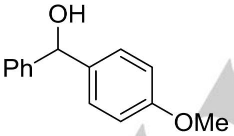
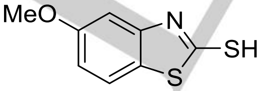
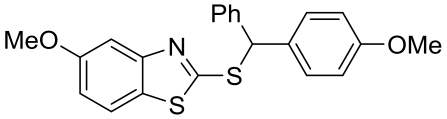
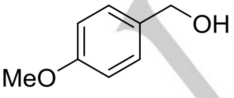
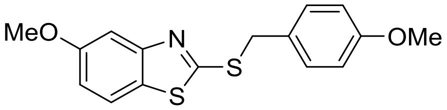
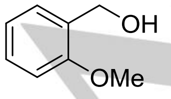
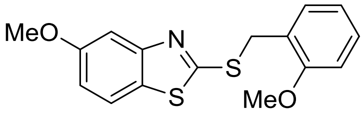
3			0.25	96
4			0.25	90
5			0.25	71
6			0.5	89
7			0.5	96
8			0.5	95
9			0.5	93
10			0.5	85
11			0.5	93

[a] Reaction conditions: (4-methoxyphenyl)(phenyl)methanol (0.5 mmol), thiol (0.6 mmol) and [BsCtP][OTf] (10 mol%, according to alcohol) dissolved in 2 mL of 1,2-dichloroethane were stirred at room temperature for certain time. [b] Isolated yields.

Delightedly, the catalytic system was also suitable for the thiolation of aromatic primary and secondary alcohols with a series of benzothiazole-2-thiol, although the progress needed more time (Table 4). Aromatic secondary alcohols exhibited better activity than that of aromatic primary alcohols (Table 4, entries 1 vs 2-4). Up to 92% yield could be obtained with benzothiazole-2-thiol and (4-methoxyphenyl)(phenyl)methanol as the substrates at room temperature for 2 h (Table 4, entry 1). And the steric hindrance of the substituted groups on the phenyl rings of primary alcohol has certain effect on the activities (Table 4, entries 2-4). *o*-Substituted group led to the decrease of the yield (Table 4, entry 3). The activities of 5-NO_2-benzothiazole-2-thiol also has similar regular. However, electron withdrawing group was not beneficial for the reaction. And about 80% yields could be obtained after prolonging the reaction time to 12 or 24 h (Table 4, entries 5-7). In addition, the activities of the reactions of aromatic primary or secondary alcohols and 5-methoxy benzothiazole-2-thiol were similar (Table 4, entries 8-10).

Table 4. Thiolation of aromatic primary and secondary alcohols with a series of benzothiazole-2-thiol.[a]



Entry	Alcohol	Thiol	Product	t (h)	Yield (%)[b]
1				2	92
2				12	94
3				12	84
4				12	91
5				12	81
6				24	79
7				24	87
8				12	89
9				12	94
10				12	86

[a] Reaction conditions: alcohol (0.5 mmol), benzothiazole-2-thiol derivertive (0.6 mmol) and [BsCtP][OTf] (10 mol%, according to alcohol) dissolved in 2 mL of 1,2-dichloroethane were stirred at room temperature for certain hours. [b] Isolated yields.

Subsequently, a series of catalytic recycle were also tested for the thiolation of (4-methoxyphenyl)(phenyl)methanol with benzo oxazole-2-thiol by employing [BsCtP][OTf] as the catalyst. In each cycle, the solvent was removed firstly by rotary evaporator. Then the separation of the catalyst and the product could be easily achieved via extraction with ethyl acetate and the catalyst was dried in vacuum, and the recovered catalyst could be reused for subsequent reaction directly. Interestingly, the yield was changed from 97% to 92% after six runs (Figure 3). That's to say, the catalyst could be reused for at least six times with slight loss of its catalytic activity. Subsequently, we examined the scalability of our catalytic system by employing (4-methoxyphenyl)(phenyl)methanol and benzooxazole-2-thiol as the substrates under optimized reactions (Scheme 2). Interestingly, 1.64 g of the desired product was obtained with only slightly decrease in yield (94% vs 97%).

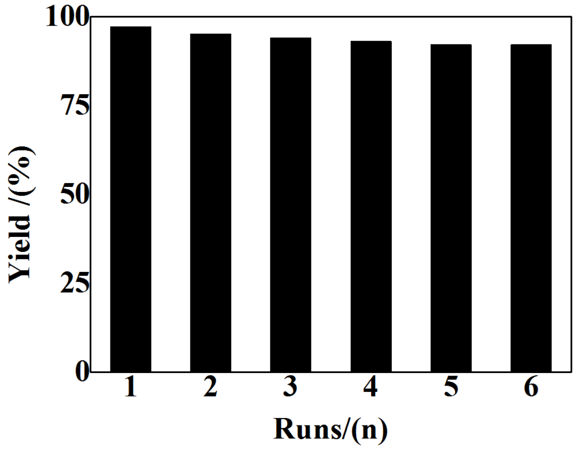
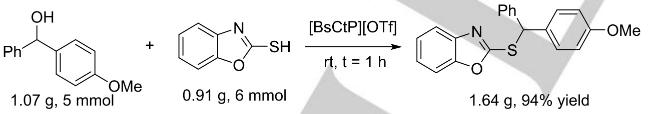
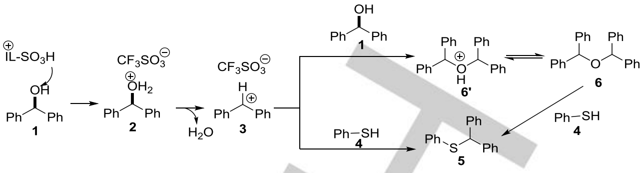


Figure 3. The recyclability of [BsCtP][OTf] in thiolation of (4-methoxyphenyl)(phenyl)methanol with benzooxazole-2-thiol.

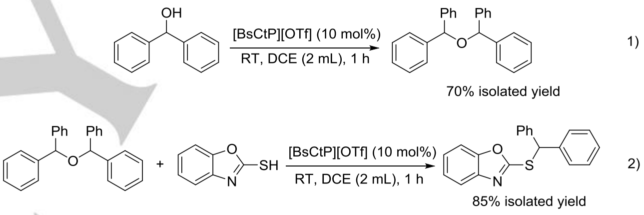


Scheme 2. Scale-up experiment.

According to previous research and the above results,[22,23] we proposed a possible mechanism for the thiolation of alcohols (Scheme 3). Carbocations may be the key intermediate. Initially, the acidic condition was very important for the reaction (Table 1, entry1-3 vs 4-12) and there is certain interaction between the proton of the ionic liquids and hydroxyl of the alcohols, which is beneficial for the formation of intermediate **2**. Meanwhile, $CF_3SO_3^-$ would stabilize the cations **2** and **3**. During the formation of carbocations, anion and cation of the ionic liquids may have synergistic effect. Moreover, the results indicated that the activities of secondary alcohols were usually better than that of primary alcohols (Table 4). The phenomena also demonstrated that stabilized carbocations would be benefit for the reaction. Then substrate **4** would react with **3** by the nucleophilic attack, generating the desired product. On the other hand, **3** also could react with **1** to produce intermediate **6** and **6'**, which further react with material **4** to provide **5**. And some control experiments were carried out to prove our speculation (Scheme 4). Intermediate **6** could be detected under our optimized reaction conditions with lower reaction rate. And the desired product was obtained from intermediate **6** and thiol under some reaction conditions.



Scheme 3. Proposed mechanism for the thiolation of alcohols.



Scheme 4. Control experiments for the thiolation of alcohols.

Conclusions

We have developed a metal-free and efficient protocol by employing muti-functionalized ionic liquids (long chain and acid) derived from pyrrolidine as the catalyst for the thiolation of alcohols. The system was suitable for the reaction of aromatic primary and secondary alcohols with benzooxazole-2-thiol, benzothiazole-2-thiol, aromatic and aliphatic thiols, providing the corresponding products with up to 99% yield within 0.25 h at room temperature. Cations, anions and the chain length of ionic liquids based on pyrrolidine have certain relationship with their corresponding activities. Moreover, [BsCtP][OTf] exhibited good recyclability and there was just small decrease in yield after six runs. And the gram-scale reaction was also successfully demonstrated. Besides, a mechanism involving carbocation was proposed. Developing new reactions catalyzed by muti-functionalized ionic liquids is in progress in our laboratory.

Experimental Section

General

NMR spectra were recorded on BRUKER AVANCETM III spectrometers. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were obtained as solutions in CDCl$_3$ or D$_2$O. Chemical shifts were reported in parts per million (ppm, δ) and referenced to CHCl$_3$ (δ 7.26) or D$_2$O (δ 4.88). GC-MS analyses were performed using an Agilent 6850 system (FID) and ion source of mass spectrometer is EI. Mass spectra (MS) were recorded on Waters ZQ4000 mass instrument (ESI). IR spectra were recorded by FT-IR spectroscopy Nexus 870.

Most chemicals used for synthetic procedures were reagent grade and the residue were purified using a silica gel column unless specified otherwise. All reactions were monitored by TLC with silica gel coated plates and detected by UV absorption (254 nm). And silica gel (200-300 microns) was used for all chromatography.

Preparation procedure for ionic liquids of *N*-cetyl-[*N*-(4-sulfonbutyl) pyrrolidine] trifluoromethanesulfonate ([BsCtdP][OTf])

N-cetyl pyrrolidine (5.90 g, 0.020 mol) and 1,4-butane sultone (2.25 mL, 0.022 mol) were charged into a 100 mL round bottom flask and stirred at 40 °C for 10 h. The formed white solid zwitterion was washed repeatedly with ether and ethyl acetate to remove any unreacted starting materials and dried in vacuum. Then, a stoichiometric amount of trifluoromethanesulfonic acid (1.80 mL, 0.020 mol) was added dropwisely to the above intermediate dissolved in toluene and the mixture was stirred for 12 h at 80 ^{o}C, resulting in the formation of *N*-cetyl-[*N*-(4-sulfonbutyl)pyrrolidine] trifluoromethanesulfonate ([BsCtP][OTf]). The ionic liquid phase was washed repeatedly with ethyl acetate to remove non-ionic residues, and dried in vacuum. The ionic liquid (11.2 g, 96% yield) was formed quantitatively with high purity as assessed by NMR, IR and MS spectroscopy. ^{1}H NMR (400 MHz, D$_2$O) δ 0.76 (t, *J* = 5.6 Hz, 2H), 1.18-1.23 (m, 27H), 1.59-1.77 (m, 5H), 2.05-2.10 (m, 4H), 2.79 (t, *J* = 7.2 Hz, 3H), 3.12-3.23 (m, 4H), 3.42-3.50 (m, 4H); ^{13}C NMR (100 MHz, D$_2$O) δ 13.8, 21.5, 21.7, 22.7, 23.1, 24.2, 26.3, 29.2, 29.6, 29.8, 29.9, 30.0, 30.1, 30.2, 32.1, 50.1, 59.2, 59.6, 62.8, 72.0, 89.6, 118.3, 121.4, 202.8; IR: 3321, 2952, 1628, 1589, 1459, 1407, 1291, 1228, 1165, 1059, 1028, 897, 761, 719, 638, 573, 574, 478; MS (ESI): [m/z]+ = 399.1, [m/z]- = 148.9.

Representative procedure for the thiolation of alcohols

Alcohol (0.5 mmol), thiol (0.6 mmol) and catalyst (10 mol%, according to alcohol) were added into a Schlenk tube in 1,2-dichloroethane (2 mL) and stirred at room temperature for certain time. Then the reaction solution was subjected to GC analysis or silicon column to determine the product yield.

The NMR data of the products

2-(benzhydrylthio)benzo[d]oxazole[38]

White solid, ^{1}H NMR (400 MHz, CDCl$_3$) δ 6.35 (s, 1H), 7.17-7.26 (m, 4H), 7.30-7.39 (m, 5H), 7.49 (d, *J* = 8.0 Hz, 4H), 7.55 (d, *J* = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 55.2, 109.9, 118.7, 124.0, 124.2, 127.7, 128.3, 128.7, 140.0, 141.9, 157, 163.4.

2-(phenyl(4-tolyl)methylthio)benzo[d]oxazole[38]

White solid, ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.36 (s, 3H), 6.51 (d, *J* = 8.0 Hz, 1H), 6.98-7.02 (m, 1H), 7.15-7.19 (m, 5H), 7.25-7.28 (m, 2H), 7.34-7.36 (m, 4H), 7.55 (s, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 21.2, 64.8, 123.9, 124.5, 128.4, 128.5, 128.6, 128.8, 129.5, 131.1, 133.1, 136.3, 138.4, 147.1.

2-((4-methoxyphenyl)(phenyl)methylthio)benzo[d]oxazole[38]

White solid, ^{1}H NMR (400 MHz, CDCl$_3$) δ 3.81 (s, 1H), 6.50 (d, *J* = 7.6 Hz, 1H), 6.86-6.90 (m, 2H), 6.98-7.02 (m, 1H), 7.14-7.27 (m, 6H), 7.34-7.37 (m, 3H), 7.53(s, 1H).^{13}C NMR (100 MHz, CDCl$_3$) δ 55.3, 64.6, 110.4, 112.2, 114.2, 123.9, 124.5, 128.2, 128.4, 128.8, 130.0, 131.1, 136.4, 147.1, 159.6, 181.0.

2-((4-chlorophenyl)(phenyl)methylthio)benzo[d]oxazole[38]

Colorless liquid, ^{1}H NMR (400 MHz, CDCl$_3$) δ 6.32 (s, 1H), 7.17-7.28 (m, 5H), 7.30-7.38 (m, 3H), 7.43-7.45 (m, 4H), 7.45-7.56 (m, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 54.5, 109.9, 118.7, 124.1, 124.3, 128.0, 128.2, 128.7, 128.8, 129.7, 133.5, 138.6, 139.3, 141.7, 151.7, 163.0.

2-((3-chlorophenyl)(phenyl)methylthio)benzo[d]oxazole[38]

Colorless liquid, ^{1}H NMR (400 MHz, CDCl$_3$) δ 6.32 (s, 1H), 7.15-7.26 (m, 5H), 7.29-7.41 (m, 4H), 7.43-7.45 (m, 2H), 7.50 (s, 1H), 7.54-7.56 (m, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 54.7, 110.0, 118.8, 124.2, 124.4, 126.6, 128.0, 128.1, 128.3, 128.5, 128.9, 130.0, 134.6, 139.2, 141.8, 142.2, 151.8, 163.0.

2-((2-chlorophenyl)(phenyl)methylthio)benzo[d]oxazole[38]

Colorless liquid, ^{1}H NMR (400 MHz, CDCl$_3$) δ 6.79 (s, 1H), 7.17-7.27 (m, 5H), 7.30-7.34 (m, 2H), 7.37-7.39 (m, 2H), 7.47-7.49 (m, 2H), 7.51-7.56 (m, 1H), 7.67 (dd, *J* = 2.0, 7.6 Hz, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 51.8, 109.9, 118.9, 124.0, 124.3, 127.2, 127.9, 128.5, 128.7, 129.0, 129.8, 130.0, 133.9, 137.5, 138.4, 141.8, 151.8, 162.9.

2-(bis(4-chlorophenyl)methylthio)benzo[d]oxazole[38]

Colorless liquid, ^{1}H NMR (400 MHz, CDCl$_3$) δ 6.29 (s, 1H), 7.21-7.27 (m, 1H), 7.28-7.32 (m, 4H), 7.39-7.46 (m, 6H), 7.55-7.57 (m, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 53.8, 110.0, 118.8, 124.3, 124.4, 129.0, 129.7, 133.9, 138.0, 141.6, 151.7, 162.6.

2-(bis(4-methoxyphenyl)methylthio)benzo[d]oxazole[38]

White solid, ^{1}H NMR (400 MHz, CDCl$_3$) δ 3.80 (s, 6H), 6.52 (d, *J* = 7.6 Hz, 1H), 6.86-6.89 (m, 4H), 6.99-7.03 (m, 1H), 7.14-7.20 (m, 5H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.46 (s, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 55.3, 64.1, 110.4, 112.2, 114.1, 123.9, 124.5, 128.4, 129.7, 131.1, 147.1, 159.5, 180.9.

2-(4-methoxybenzylthio)benzo[d]oxazole[39]

White solid, ^{1}H NMR (400 MHz, CDCl$_3$) δ 3.80 (s, 3H), 4.54 (s, 2H), 6.85-6.88 (m, 2H), 7.23-7.32 (m, 2H), 7.37-7.45 (m, 3H), 7.62-7.64 (m, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 36.2, 55.3, 109.9, 14.2, 118.4, 124.0, 124.3, 127.7, 130.3, 141.8, 151.8, 159.3, 1647.

2-(3,4-dimethoxybenzylthio)benzo[d]oxazole[39]

White solid, ^{1}H NMR (400 MHz, CDCl$_3$) δ 3.86 (s, 3H), 3.87 (s, 3H), 4.53 (s, 2H), 6.81 (d, *J* = 8.8 Hz, 1H), 6.99-7.01 (m, 2H), 7.22-7.31 (m, 2H), 7.44 (d, *J* = 7.6 Hz, 1H), 7.62 (d, *J* = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 36.7, 55.8, 55.9, 109.9, 111.2, 112.2, 118.4, 121.5, 124.0, 124.3, 128.1, 141.9,148.8, 149.0, 151.8, 164.6.

2-(4-(phenoxymethyl)benzylthio)benzo[d]oxazole[39]

White solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.54 (s, 2H), 5.05 (s, 2H), 6.92-6.95 (m, 2H), 7.23-7.45 (m, 10H), 7.62-7.64 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 36.2, 70.1, 109.9, 115.1, 118.4, 124.0, 124.4, 127.5, 127.9, 128.0, 128.6, 130.4, 136.8, 141.7, 151.8, 158.6, 164.8.

benzhydryl(phenyl)sulfane[40]

White solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.54 (s, 1H), 7.10-7.24 (m, 7H), 7.29 (t, *J* = 7.6 Hz, 4H), 7.41 (d, *J* = 7.6 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 57.4, 126.6, 127.2, 128.4, 128.5, 128.7, 130.5, 136.1, 141.0.

phenyl(phenyl(*p*-tolyl)methyl)sulfane[40]

Colorless liquid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.30 (s, 3H), 5.52 (s, 1H), 7.08-7.24 (m, 9H), 7.28-7.31 (m, 3H), 7.40 (d, *J* = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.1, 57.1, 126.4, 127.1, 128.2, 128.4, 128.5, 128.7, 129.2, 130.3, 136.4, 136.9 138.0 141.2.

((4-chlorophenyl)(phenyl)methyl)(phenyl)sulfane[40]

Colorless liquid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.49 (s, 1H), 7.13-7.38 (m, 14H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 56.9, 126.9, 127.5, 128.4, 128.7, 128.9, 129.8, 130.8, 133.1, 135.7, 139.7, 140.6.

(4-methoxybenzyl)(phenyl)sulfane[41]

White solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.78 (s, 3H), 4.07 (s, 2H), 6.80-6.83 (m, 2H), 7.15-7.31 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 38.5, 55.3, 113.9, 126.3, 128.8, 129.4, 129.8, 129.9, 136.6, 158.8.

(4-chlorophenyl)((4-methoxyphenyl)(phenyl)methyl)sulfane[41]

White solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.77 (s, 1H), 5.47 (s, 1H), 6.80-6.84 (m, 2H), 7.13 (s, 4H), 7.20-7.32 (m, 5H), 7.38-7.40 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.3, 57.0, 114.0, 127.3, 128.3, 128.6, 128.9, 129.5, 132.0, 132.6, 134.7, 140.9, 158.8.

(4-methoxyphenyl)((4-methoxyphenyl)(phenyl)methyl)sulfane[41]

White solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.74 (s, 3H), 3.76 (s, 3H), 5.32 (s, 1H), 6.69-6.73 (m, 2H), 6.79-6.83 (s, 2H), 7.18-7.22 (m, 3H), 7.25-7.30 (m, 4H), 7.37 (d, *J* = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.3, 58.6, 113.8, 114.3, 126.1, 127.0, 128.3, 128.4, 129.5, 133.4, 134.6, 141.6, 158.6, 159.3.

((4-methoxyphenyl)(phenyl)methyl)(p-tolyl)sulfane[41]

White solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.33 (s, 3H), 3.68 (s, 3H), 5.48 (s, 1H), 6.77-6.80 (m, 2H), 6.92-7.01 (m, 2H), 7.07-7.11 (m, 2H), 7.15-77.18 (m, 1H), 7.22-7.31 (m, 4H), 7.37-7.40 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.6, 55.3, 55.9,114.0, 126.2, 126.4, 127.3, 128.5, 128.7, 129.7, 129.8, 130.1, 133.2, 135.8, 137.9, 141.4, 158.9.

((4-methoxyphenyl)(phenyl)methyl)(naphthalen-2-yl)sulfane[42]

White solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.75 (s, 3H), 5.64 (s, 1H), 6.82 (d, *J* = 8.8 Hz, 2H), 7.19-7.45 (m, 10H), 7.60-7.65 (m, 3H), 7.71-7.73 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.2, 56.7, 113.9, 125.8, 126.3, 127.2, 127.3, 127.6, 128.0, 128.1, 128.4, 128.6, 128.7, 129.5, 131.9, 133.0, 133.6, 133.8, 141.2, 158.7.

benzyl((4-methoxyphenyl)(phenyl)methyl)sulfane[43]

White solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.34 (s, 3H), 3.77 (s, 3H), 5.49 (s, 1H), 6.81-6.83 (m, 2H), 6.96-6.99 (m, 4H), 7.01-7.12 (m, 5H), 7.29-7.41 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.4, 55.3, 113.9, 55.68, 126.1, 126.3, 127.2, 128.3, 128.5, 129.5, 129.6, 130.0, 133.1, 135.7, 137.8, 141.2, 158.7.

ethyl((4-methoxyphenyl)(phenyl)methyl)sulfane[44]

Colorless liquid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.11 (t, *J* = 7.6 Hz, 3H), 2.29 (q, *J* = 7.2 Hz, 2H), 3.65 (s, 3H), 5.06 (s, 1H), 6.72-6.76 (m, 2H), 7.09-7.12 (m, 1H), 7.18-7.26 (m, 4H), 7.32 (d, *J* = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.2, 25.2, 52.0, 54.2, 112.8, 125.9, 127.2, 127.4, 128.3, 132.5, 140.8, 157.5.

hexyl((4-methoxyphenyl)(phenyl)methyl)sulfane[41]

Colorless liquid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.57 (t, *J* = 6.8 Hz, 3H), 1.18-1.35 (m, 6H), 1.49-1.57 (m, 2H), 2.35 (t, *J* = 7.2 Hz, 2H), 3.71 (s, 3H), 5.10 (s, 1H), 6.79-6.83 (m, 2H), 7.15-7.19 (m, 1H), 7.25-7.33 (m, 4H), 7.40 (d, *J* = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 22.6, 28.7, 29.1, 31.5, 32.4, 53.6, 55.3, 113.9, 127.1, 128.3, 128.6, 129.4, 133.8, 142.0, 158.7.

((4-methoxyphenyl) (phenyl) methyl)(octyl)sulfane[41]

Colorless liquid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87 (t, *J* = 6.8 Hz, 3H), 1.21-1.35 (m, 10H), 1.50-1.57 (m, 2H), 2.36 (t, *J* = 7.2 Hz, 2H), 3.76 (s, 3H), 5.11 (s, 1H), 6.81-6.85 (m, 2H), 7.18-7.23 (m, 1H), 7.27-7.35 (m, 4H), 7.41 (d, *J* = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 22.7, 28.9, 29.1, 29.2, 31.8, 32.3, 53.5, 55.3, 113.9, 127.0, 128.3, 128.5, 129.4, 133.8, 142.0, 158.6.

dodecyl ((4-methoxyphenyl)(phenyl)methyl)sulfane[41]

Colorless liquid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, *J* = 6.4 Hz, 3H), 1.23-1.30 (m, 18H), 1.50-1.57 (m, 2H), 2.36 (t, *J* = 7.2 Hz, 2H), 3.75 (s, 3H), 5.10 (s, 1H), 6.81-6.85 (m, 2H), 7.17-7.22 (m, 1H), 7.27-7.34 (m, 4H), 7.40 (d, *J* = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 32.7, 28.9, 29.1, 29.2, 29.4, 29.5, 29.6, 29.7, 29.7, 32.0, 32.4, 53.5, 55.3, 113.9, 127.0, 128.3, 128.5, 129.4, 133.8, 142.0, 158.6.

((4-methoxyphenyl)(phenyl)methyl)(octadecyl)sulfane[41]

White solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.89(t, *J* = 6.8 Hz, 3H), 1.24-1.26 (m, 30H), 1.51-1.58 (m, 2H), 2.37 (t, *J* = 7.2 Hz, 2H), 3.78 (s, 3H), 5.11 (s, 1H), 6.84 (d, *J* = 8.4 Hz, 2H), 7.21-7.43 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.7, 28.9, 29.1, 29.2, 29.4, 29.5, 29.6, 29.7, 29.7, 29.7, 31.9, 32.3, 53.5, 55.2, 113.9, 127.0, 128.2, 128.5, 129.3 133.7, 141.9, 158.6.

1,2-bis((4-methoxyphenyl)(phenyl)methylthio)ethane[44]

Colorless liquid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.53 (s, 4H), 3.74 (s, 6H), 5.05 (s, 2H), 6.79-6.83 (m, 4H), 6.18-6.22 (m, 2H), 7.12-7.29 (m, 8H), 7.33-7.35 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 32.0, 53.5, 55.3, 114.0, 127.2, 128.3, 128.6, 129.4, 133.3, 141.5, 158.8.

2-((4-methoxyphenyl)(phenyl)methylthio)benzo[d]thiazole[41]

White solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.79 (s, 3H), 6.85-6.89 (m, 2H), 6.92 (d, *J* = 8.4 Hz, 1H), 7.03-7.07 (m, 1H), 7.16-7.20 (m, 1H), 7.23-7.28 (m, 4H), 7.31-7.35 (m, 3H), 7.45 (dd, *J* = 0.8, 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.3, 63.5, 114.1, 115.7, 121.1, 124.3, 126.0, 127.0, 127.9, 128.2, 128.3, 128.7, 129.9, 136.4, 140.9, 159.3, 190.7.

2-(4-methoxybenzylthio)benzo[d]thiazole[27]

White solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.79 (s, 3H), 4.58 (s, 2H), 6.84-6.88 (m, 2H), 7.29-7.33 (m, 1H), 7.36-7.45 (m, 3H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.92 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 37.5, 55.3, 114.1, 121.0, 121.4, 124.4, 126.2, 127.9, 130.4, 135.1, 152.8, 159.2, 166.9.

2-(2-methoxybenzylthio)benzo[d]thiazole[45]

White solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.86 (s, 3H), 4.63 (s, 2H), 6.89 (t, *J* = 7.2 Hz, 2H), 7.24-7.30 (m, 2H), 7.39-7.47 (m, 2H), 7.73 (d, *J* = 7.6 Hz, 1H), 7.91 (d, *J* = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 32.7, 55.5, 110.6, 120.6, 130.0, 121.5, 124.2, 124.6, 126.0, 129.3, 130.8, 135.3, 153.2, 157.6, 167.5

2-(3,4-dimethoxybenzylthio)benzo[d]thiazole[27]

Colorless liquid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.84 (s, 3H), 3.85 (s, 3H), 4.55 (s, 2H), 6.79 (d, *J* = 8.0 Hz, 1H), 6.97-7.01 (m, 2H), 7.26-7.30 (m, 1H), 7.39-7.43 (m, 1H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.89 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 37.8, 55.8, 55.9, 111.1, 112.2, 121.0, 121.4, 121.5, 124.3, 126.1, 128.4, 135.3, 148.6, 148.9, 153.1, 166.5 .

2-(((4-Methoxyphenyl)(phenyl)methyl)thio)-5-nitrobenzo[d]thiazole[41]

White solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.81 (s, 3H), 6.86-6.91 (m, 2H), 6.98 (d, *J* = 9.2 Hz, 1H), 7.19-7.24 (m, 4H), 7.35-7.40 (m, 3H), 7.95 (dd, *J* = 2.4, 9.2 Hz, 1H), 8.29 (s, 1H), 8.34 (d, *J* = 2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.3, 63.9, 114.4, 114.8, 116.8, 122.0, 127.4, 127.8, 128.1, 128.4, 129.1, 129.8, 135.7, 144.2, 145.2, 159.6, 192.3.

5-nitro-2-((3,4,5-trimethoxybenzyl)thio)benzo[d]thiazole[41]

Yellow solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.84 (s, 3H), 3.86 (s, 6H), 4.61 (s, 2H), 6.70 (s, 2H), 7.94 (d, *J* = 8.8 Hz, 1H), 8.33 (dd, *J* = 2.4, 9.2 Hz, 1H), 8.69 (d, *J* = 2.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 38.3, 56.2, 60.9, 106.3, 117.5, 121.2, 122.0, 130.8, 135.7, 137.9, 144.2, 153.4, 156.8, 173.5.

5-nitro-2-((2,4,5-trimethoxybenzyl)thio)benzo[d]thiazole[41]

Yellow solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.72 (s, 3H), 3.88 (s, 3H), 3.97 (s, 3H), 5.09 (s, 2H), 7.01 (s, 1H), 7.49 (d, *J* = 9.2 Hz, 1H), 8.22 (dd, *J* = 2.4, 9.2 Hz, 1H), 8.35 (d, *J* = 2.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 43.5, 56.1, 56.5, 56.6, 97.1, 112.9, 113.0, 113.2, 116.8, 123.0, 128.0, 143.6, 144.7, 145.7, 150.0, 151.1, 192.0.

5-methoxy-2-((4-methoxyphenyl)(phenyl)methylthio)benzo[d]thiazole[46]

White solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.46 (s, 3H), 3.80 (s, 3H), 6.46 (d, *J* = 2.4 Hz, 1H), 6.78 (dd, *J* = 6.4, 8.8 Hz, 1H), 6.86-6.90 (m, 2H), 7.23-7.35 (m, 8H), 8.33 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.3, 55.5, 63.6, 101.1, 112.3, 114.2, 118.2, 121.3, 128.0, 128.3, 128.8, 129.9, 136.6, 142.1, 158.4, 159.3, 191.6.

5-methoxy-2-(4-methoxybenzylthio)benzo[d]thiazole[27]

White solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.79 (s, 3H), 3.88 (s, 3H), 4.55 (s, 2H), 6.84-6.88 (m, 2H), 6.95 (dd, *J* = 2.4, 8.8 Hz, 1H), 7.36-7.43 (m, 3H), 7.59 (d, *J* = 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 37.5, 55.3, 55.7, 104.5, 114.0, 114.1, 121.2, 126.9, 127.9, 130.3, 154.2, 159.0, 159.2, 167.9.

5-methoxy-2-(2-methoxybenzylthio)benzo[d]thiazole[27]

White solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.86 (s, 3H), 3.88 (s, 3H), 4.62 (s, 2H), 6.88-6.94 (m, 3H), 7.24-7.29 (m, 1H), 7.43-7.46 (m, 2H), 7.57 (d, *J* = 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 38.3, 55.5, 55.6, 104.5, 110.6, 113.9, 120.5, 121.1, 124.5, 126.9, 129.3, 130.7, 154.3, 157.6, 158.9, 168.7.

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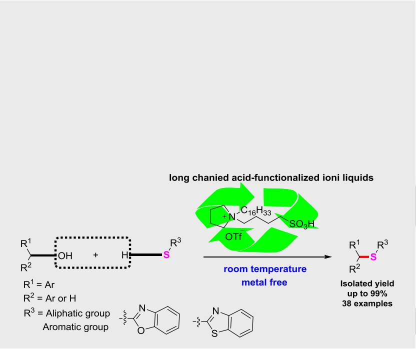
FULL PAPER

Long chained and SO_3H-functionalized ionic liquids derived from pyrrolidine were employed as metal-free, efficient and recyclable catalyst for thiolation of alcohols with several kinds of thiols, providing up to 99% yield within 0.25 h at room temperature.



Thiolation *

Chengxia Miao, Hongfeng Zhuang, Yating Wen, Feng Han, Qing-Feng Yang, Lei Yang, Zhen Li, and Chungu Xia**

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Efficient Thiolation of Alcohols Catalyzed by Long Chained Acid-functionalized Ionic Liquids under Mild Conditions