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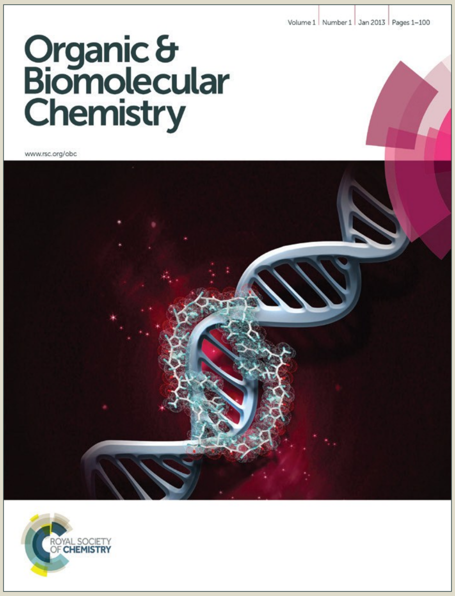

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Reusable Ionic Liquid-Catalyzed Oxidative Coupling of Azoles and Benzylic Compounds *via* sp^3 C–N Bond Formation under Metal-Free Conditions

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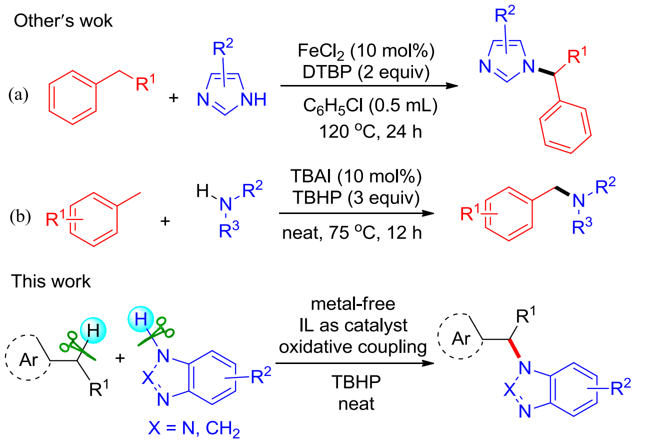
The classical heterocyclic ionic liquid-catalyzed direct oxidative amination of benzylic sp^3 C–H bonds *via* intermolecular sp^3 C–N bond formation for the synthesis of N-alkylated azoles under metal-free conditions has been reported firstly. The catalyst 1-butylpyridinium iodide can be recycled and reused with the similar efficacies for at least eight cycles.

Nitrogen-containing heterocycles and their derivatives are in the focus of the chemical synthesis because they commonly exist in pharmaceuticals, agrochemicals and natural products.[1] As an usual motif in bioactive compounds, developing effective strategies for accessing nitrogen heterocycles remain an important objective.[1d-f, 2] Many azole derivatives, especially the *N*-alkylation and *N*-arylation azoles have also displayed interesting antimycobacterial and antifungal activity.[3] Nucleophilic substitution reaction of azoles with alkyl halides is one of the most classical ways for the synthesis of *N*-alkylation azoles. However, this method suffers from the use of alkyl halides and strong bases which limits its applications. Therefore, the development of more effective routes for constructing the azole derivatives are highly desirable. In recent years, transition-metal-catalyzed C–N bond formations have made great achievements in preparing biologically and medicinally important *N*-aryl/heteroaryl heterocycles.[4] Despite their remarkable potential utility, the toxicity and expense of transition metals limit the practical applications.[5] The discovery of green and efficient C–H bonds transformation under metal-free conditions will be of great value.

Recently, as an emerging field in C–H activation, the cross-dehydrogenative coupling (CDC) reaction in realizing C–N bonds have become a highly attractive coupling strategy due to its atom-economic manner.[6] One typical example is the oxidative coupling of azoles with benzyl compounds *via* cleavage of nonactivated sp^3 C–H bonds. For instance, in early 2011, Qiu's group established FeCl$_2$-catalyzed amination of benzylic C–H bonds leading to imidazole derivatives in an efficient and straightforward way. But the reaction was conducted at higher reaction temperature in chlorobenzene (Scheme 1a).[7] More recently, Zhu's group reported TBAI-catalyzed highly selective benzylic C–H bond amination protocol using TBHP as an oxidant under metal-free conditions, which had the advantages of milder reaction conditions, shorter reaction times, and higher yields (Scheme 1b).[8]



Scheme 1 Reported and designed routes for the formation of *N*-alkylation azoles *via* oxidative coupling of azoles and benzylic compounds.

Ionic liquids (ILs), also called room-temperature ionic liquids (RTILs), are usually made up of larger organic cations and smaller organic or inorganic anions. Some unique properties such as good thermal stabilities, tunable viscosities, negligible vapor pressures, and generally an anion-dependent miscibility with water and various organic solvents[9] permit ILs to be extensively used in catalysis.[10] In recent years, ILs have also been employed as solvents for transition-metal-catalyzed C–H activation reactions.[11] Recently, we have described an oxidative cross-coupling reaction for C–C bond formation promoted by IL firstly.[12] To the best of our knowledge, up to now, studies of using the classical heterocyclic IL-catalyzed C–H activation reactions for C–N bond formations reactions have not been reported. Herein we present a metal-free, environment-friendly and highly selective benzylic C–H bond amination protocol by using recycled and reused ionic liquid 1-

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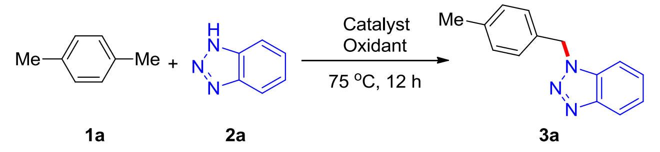
Electronic Supplementary Information (ESI) available: See DOI: 10.1039/ x0xx00000x butylpyridinium iodide ([Bpy]I) as a catalyst and TBHP as an oxidant, which potentially provides a facile entry to substituted and functionalized *N*-alkylation azoles.

The investigation started with the coupling reaction of *p*-xylene (**1a**) and benzotriazole (**2a**) as a mode system (Table 1). In the presence of 10 mol% [Bpy]I, 3.0 equiv of TBHP, the reaction of **1a** and **2a** at 75 °C for 12 h gave 1-(4-methylbenzyl)-1*H*-benzo[*d*][1,2,3]triazole **3a** in 77% yield (Table 1, entry 1). Encouraged by this result, further optimization of the reaction conditions was carried out. When the reaction was catalyzed by other ionic liquids such as [BPy]Br and [BPy]Cl, gave unsatisfactory results (Table 1, entries 2 and 3). The other oxidants instead of TBHP were also screened (Table 1, entries 4−10), the yields decreased dramatically and TBHP was found to be the optimal oxidant. Next, a variety of solvents were tested, including DCE, MeCN, H_2O, PhCl and DMF, and the reactions did not provide higher yields (Table 1, entries 11−15). In addition, lowering the amount of the [Bpy]I resulted in a lower yield of the product (Table 1, entry 16). Increasing the amount of [Bpy]I achieved similar reaction efficiency (Table 1, entry 17). Finally, when the reaction temperature and time were changed, the yields of **3a** were lower than that obtained at 75 °C for 12 h (Table 1, entries 18−21).

With the optimized conditions established, the scope of the substrates with benzylic C−H bonds were investigated (Table 2). It can be seen that various benzyl compounds were found to be compatible under standard reaction conditions (Table 2). Toluenes

Table 1. Reaction optimization[a]

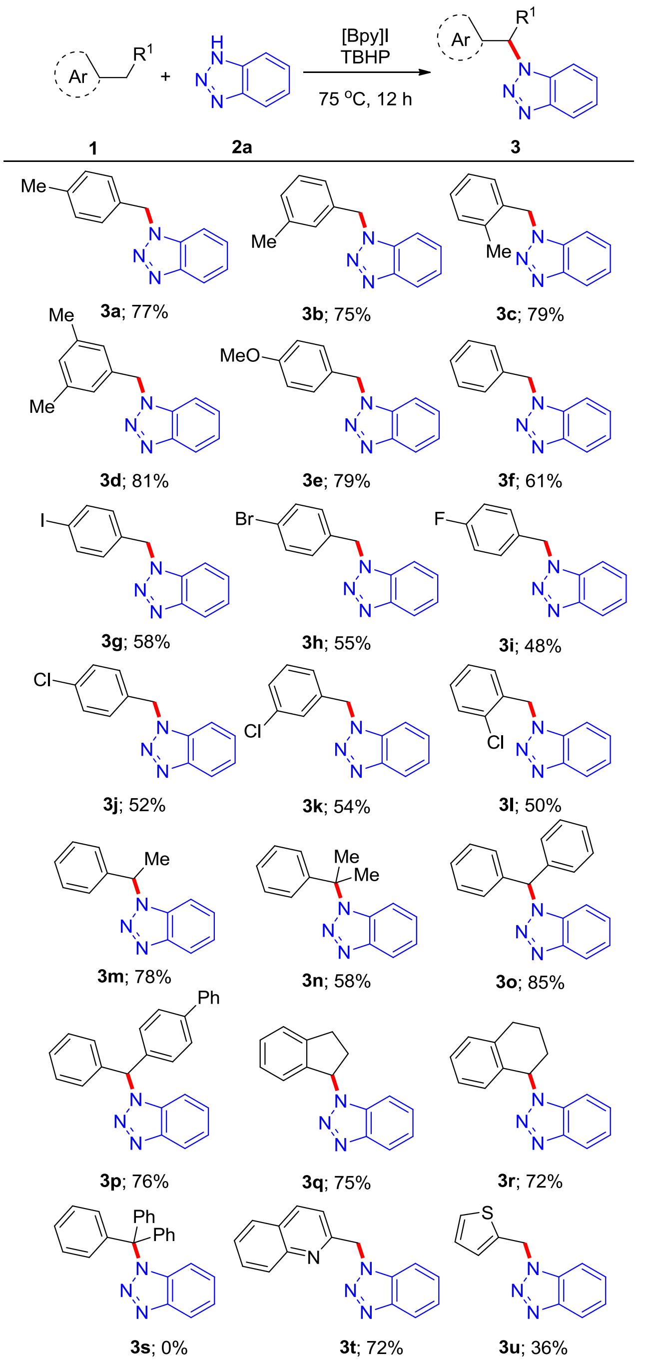


1a **2a** **3a**

Entry	Ionic liquid (mol%)	Oxidant[b]	Solvent	Yield[c] (%)
1	[BPy]I (10)	TBHP	neat	77
2	[BPy]Br (10)	TBHP	neat	trace
3	[BPy]Cl (10)	TBHP	neat	N.R.[d]
4	[BPy]I (10)	DTBP	neat	N.R.
5	[BPy]I (10)	BPO	neat	N.R.
6	[BPy]I (10)	Oxone	neat	N.R.
7	[BPy]I(10)	*m*-CPBA	neat	22
8	[BPy]I (10)	$PhI(OAc)_2$	neat	N.R.
9	[BPy]I (10)	H_2O_2	neat	N.R.
10	[BPy]I (10)	DDQ	neat	N.R.
11	[BPy]I (10)	TBHP	DCE	55
12	[BPy]I (10)	TBHP	MeCN	45
13	[BPy]I (10)	TBHP	H_2O	62
14	[BPy]I (10)	TBHP	PhCl	54
15	[BPy]I (10)	TBHP	DMF	trace
16	[BPy]I (5)	TBHP	neat	58
17	[BPy]I (20)	TBHP	neat	78
18[e]	[BPy]I (10)	TBHP	neat	59
19[f]	[BPy]I (10)	TBHP	neat	69
20[g]	[BPy]I (10)	TBHP	neat	59
21[h]	[BPy]I (10)	TBHP	neat	76

[a] Reaction conditions: **1a** (1.5 mmol), **2a** (0.3 mmol), oxidant (3.0 equiv), 75 °C, 12 h. [b] TBHP: *tert*-butyl hydroperoxide 70% in water, DTBP: di-*tert*-butyl peroxide, BPO: benzoyl peroxide, Oxone: potassium peroxomonosulfate, *m*-CPBA: *m*-chloroperoxybenzoic acid, H_2O_2 30% in water, DDQ: 2,3-dichloro-5,6-dicyanobenzoquinone. [c] Isolated yield. [d] Not reaction. [e] Reaction temperature: 60 °C. [f] Reaction temperature: 90 °C. [g] Reaction time: 6 h. [g] Reaction time: 18 h.

Table 2. Reactions of benzotriazole with various benzylic compounds[a]

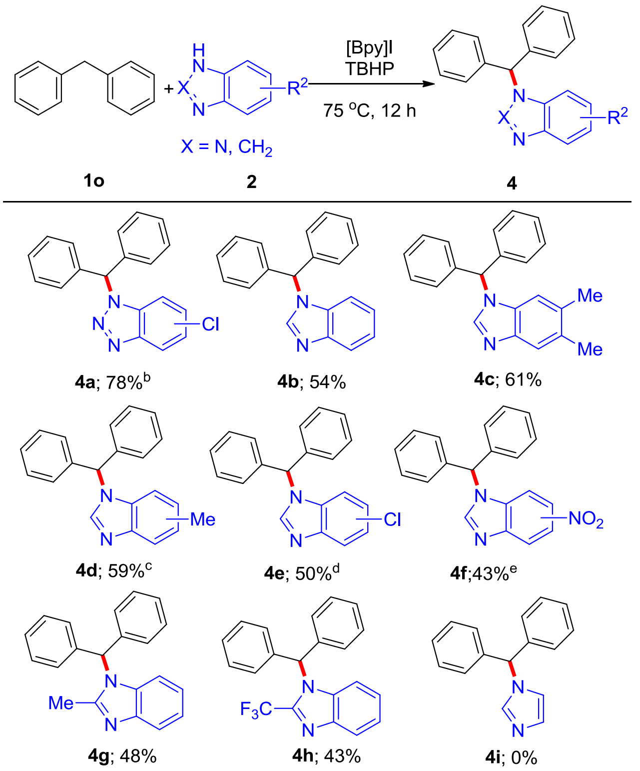


[a] Reaction conditions: **1** (1.5 mmol), **2a** (0.3 mmol), [Bpy]I (10 mol%), TBHP (3.0 equiv), 75 °C, 12 h. Isolated yield.

with electron-donating groups, such as methyl and methoxyl reacted smoothly and obtained the corresponding *N*-alkylated azoles in good yields (Table 2, **3a**–**3e**). Gratifyingly, it was found that toluene reacted well with benzotriazole in 61% yield (Table 2, **3f**). Benzylic compounds beared electron-with-drawing groups, such as fluoro, chloro, bromo and iodo on the benzene ring and moderate yields of the corresponding products were afforded (Table 2, **3g**–**3l**). It should be mentioned that the process also tolerated 2-substituted toluenes (Table 2, **3c**, **3l**). Additionally, 3-substituted toluenes were converted into the desired products in moderate to good yields (Table 2, **3b**, **3d**, **3k**). Direct *N*-alkylation of **2a** with ethylbenzene, cumene and diarylmethanes were successful in this protocol (Table 2, **3m**–**3p**). The triphenylmethane which did not give the expected product was probably caused by steric effect. To our delight, the less activated indane and 1,2,3,4-tetrahydronaphthalene reacted with benzotriazole leading to C–N coupling products in good yields (Table 2, **3q** and **3r**). To further showcase the potential of this methodology, methyl substituted heteroarenes were submitted to the optimized conditions. To our surprise, 2-methylquinoline and 2-methylthiophene were compatible with this transformation, leading to products in 72% and 36% yields, respectively (Table 2, **3t** and **3u**). Notably, *N*-alkylation azoles were also highly selective, affording only mono-amination products.

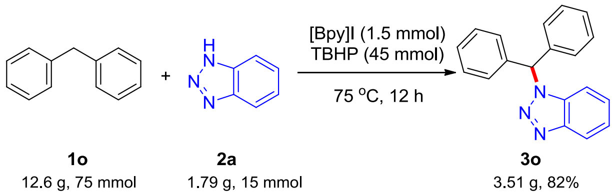
To further define the scope of the synthesis of *N*-alkylated azoles, a series of azoles were applied in this process (Table 3). Benzotriazoles such as 5-chlorobenzotriazole were found to react smoothly to generate the desired coupling product with good yield (Table 3, **4a**). Subsequently, the coupling of a variety of benzimidazoles and diphenylmethane were tested (Table 3, **4b**–**4h**). It should be noted that benzimidazoles with electron-donating groups as well as electron-withdrawing groups ran well in this reaction (Table 3, **4c**–**4h**). 5-Methylbenzimidazole and 5,6-dimethylbenzimidazole generated the corresponding *N*-alkylation azoles **4c** and **4d** with moderate yields. The oxidative coupling of diphenylmethane and benzimidazoles bearing an electron-withdrawing groups at the 5 position also proceeded well (Table 3, **4e**–**4f**). Moreover, 2-substituted benzimidazoles gave the desired products under the optimal conditions in 48% and 43% yields, respectively (Table 3, **4g** and **4h**). Unfortunately, poor regioselectivities were observed in this transformation that 5-substituted benzotriazoles or benzimidazoles gave a mixture of regioisomers (see the Supporting Information). In addition, imidazole did not give the desired product.

Table 3. Reactions of diphenylmethane with various azoles[a]



[a]Reaction conditions: **1o** (1.5 mmol), **2** (0.3 mmol), [Bpy]I (10 mol%), TBHP (3.0 equiv), 75 °C, 12 h. Isolated yield. [b]Separable isomeric products, **4a-1**/**4a-2** = 1 : 1. [c]Inseparable isomeric products. [d]Separable isomeric products, **4e-1**/**4e-2** = 1 : 1. [e]Separable isomeric products, **4f-1**/**4f-2** = 1 : 1.

To demonstrate the synthetic utility of our methodology, an IL-catalyzed scale-up reaction was performed. The oxidative coupling reaction between diphenylmethane and benzotriazole was easily performed under standard reaction conditions to furnish the desired product **3o** in 82% isolated yield (Scheme 2).



Scheme 2 gram-scale oxidative coupling reaction between diphenylmethane and benzotriazole.

An important goal in modern catalyst design is the development of recyclable, inexpensive, environmentally friendly, and efficient catalysts. Thus, the reusability of the IL as catalyst was studied. The recycling reactions were performed with the oxidative coupling between diphenylmethane and benzotriazole. After the reaction was complete, water and ethyl acetate were added, and then the [Bpy]I was separated in the aqueous phase and reused after drying in vacuo. At least eight consecutive runs of reaction were carried out in the same condition and the results showed that ionic liquid catalyst [Bpy]I was recyclable without any significant loss of activity (Figure 1).

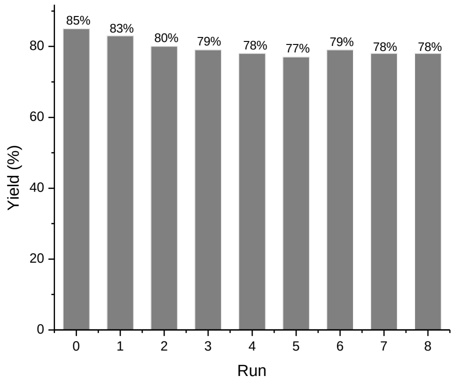
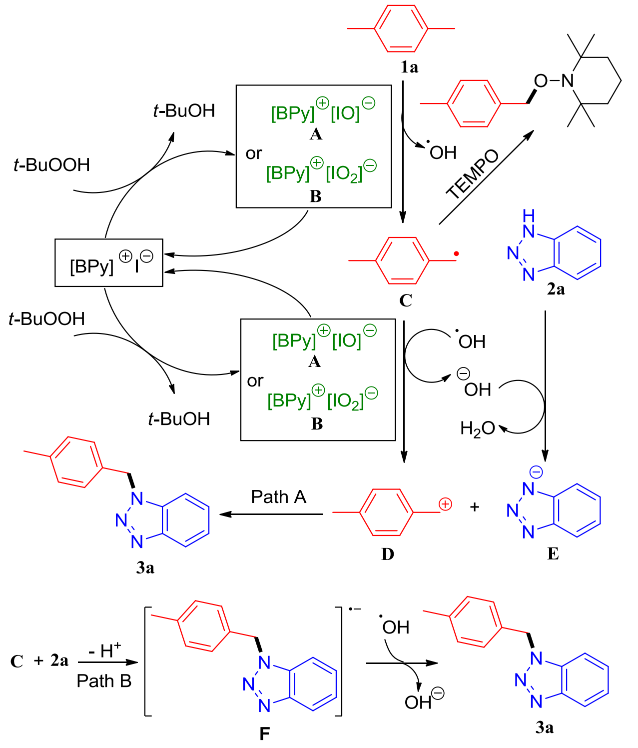


Figure 1 Recycling reactions.

In order to elucidate the reaction mechanism, control experiments were carried out. When 1 equiv. TEMPO (2,2,6,6-tetramethylpiperidine-*N*-oxyl) as a radical scavenger was added to the reaction mixture under the optimal conditions, the yield of **3a** was decreased to trace. When the amount of TEMPO was increased to 5 equiv., the desired product **3a** was not afforded. The benzyl radical intermediate was trapped and the oxyamination product was isolated in 55% yield. The results indicated the reaction involves a radical process.

According to the above results as well as the known literatures[7-8,13], a plausible mechanism is proposed (Scheme 3). Initially, [BPy]I is oxidized by TBHP to form the {[Bpy]$^+$[IO]$^-$} **A** or {[Bpy]$^+$[IO$_2$]$^-$} **B** species. Subsequently, homolysis of a benzyl C–H bond is induced by **A** or **B** and give a benzyl radical **C**. The benzyl radical is liable to be oxidized by active iodine species **A** or **B** to form the benzyl cation **D**, with a hydroxide ion being released. After that, the benzotriazole is deprotonated by the hydroxide ion to generate the anionic specie **E**. Finally, the nucleophilic reaction of specie **E** with the benzyl cation **D** forms the desired product **3a** (Scheme 3, path A). In addition, benzyl radical **C** react with azole to give the *N*-benzyl azole radical anion **F**, followed by a SET process by losing an electron with the assistance of hydroxyl radicals to provide the desired product **3a** (Scheme 3, path B).



Scheme 3 The proposed mechanism.

Conclusions

In conclusion, we have described an IL-catalyzed the direct amination of benzyl sp^3 C–H bond in mild and green condition. This metal-free catalytic system is suitable for the oxidative coupling reactions between a wide range of azoles and benzyl substrates. Moreover, the inexpensive ionic liquid [Bpy]I is recyclable and reused for eight cycles without showing any significant loss of catalytic activity. This facile and environmentally friendly protocol has opened up the application field of ionic liquids catalyzed C-H bond activation.

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