



An efficient, eco-friendly and sustainable tandem oxidative amidation of alcohols with amines catalyzed by heteropolyanion-based ionic liquids via a bifunctional catalysis process



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ABSTRACT

An efficient, eco-friendly and sustainable method for the tandem oxidative amidation of alcohols with amines has been reported. Using heteropolyanion-based ionic liquids as the catalyst and *tert*-butyl hydroperoxide as the oxidant, this amidation reaction is operationally straightforward and provides a series of primary, secondary and tertiary amides derivatives in moderate to good yields. Solvent-free media, microwave-promoted conditions and reusability of catalysts are the main highlights. Further, the proposed bifunctional catalysis mechanistic pathway has been briefly investigated in this report.

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1. Introduction

Amide bond formation is one of the key reactions in modern chemistry, material science, pharmaceutical industry and biology.^{1–5} Amides represent a wide range of remarkable pharmacological and agrochemical activities as well as versatile building blocks for the synthesis of various useful molecules, therefore amidation reaction was regard as a high priority research field.^{6–10}

Generally, traditional amide formation involves the reaction of amines with activated carboxylic acid derivatives or coupling with carboxylic acids mediated by a coupling reagent,^{11–13} which are limited in industrial application by poor atom-efficiency, harsh reaction conditions, toxicity issues and excess amount of wastes.^{14,15} Several alternative methods, such as the Beckmann rearrangement,¹⁶ the Staudinger reaction,¹⁷ the Schmidt reaction,¹⁸ hydroamidation of alkynes,¹⁹ iodonium-promoted nitroalkane amine coupling reaction²⁰ and transamidation of primary amides,²¹ have emerged to improve the preparation of amides. Considering

the cheapness, stability and easy availability of alcohols, chemists are now focusing on the direct conversion of alcohols and amines into amides,^{22–47} which is quite attractive in terms of atom economical and environmentally benign considerations. Since 2007, Milstein et al. and other groups have reported the transition metal-catalyzed dehydrogenative amidation of alcohols.^{22–30} Recently, the tandem oxidative amidation of alcohols with amine as another alternative approach has received sustained attention. To date, several metal catalyst systems have been reported, such as Zn,³¹ Fe,^{32–35} Au^{36–38} Cu^{39–40}. However, these methodologies suffer from some common demerits that greatly restricted large scale industrial applications, such as requirement for toxic or expensive metal reagents and oxidants, pre-treatment step to convert amines into their salts, narrow substrate scope and difficulties in separation and recycling of the catalysts. Just recently, several reports afforded attractive approaches for the tandem oxidative amidation chemistry from the view point of green chemistry introducing cascade strategy,⁴¹ metal-free catalysis^{42–46} and catalyst-free reaction,⁴⁷ but with limited substrate scope. Therefore, there is an urgent need to develop more efficient and sustainable catalytic processes for tandem oxidative amidation of alcohols.

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In the last few decades, environmentally benign and sustainable development has been accepted as a common knowledge by chemical industry.⁴⁸ From the view point of organic synthesis, the use of more eco-benign catalysts and their simple recovery are the main targets.^{49,50} So far, ionic liquids (ILs) as efficient and eco-friendly solvents and/or catalysts in organic reactions provide both economical and ecological benefits.^{51,52} Recently, a series of heteropolyanion-based ILs (HPAILs) have emerged as new species of hybrid materials, which were prepared by combining Keggin heteropolyanions with 'task-specific' IL (TSIL) cations containing special functional groups.^{53–55} In addition, protocols containing HPAILs are an attractive alternative for traditional acid-catalyzed^{56–61} or oxidative^{62–68} organic transformations because of their operational simplicity, no toxicity, easy isolation and reusability.

During the last years a large number of publications have shown that microwave (MW)-assisted chemical processing generally leads to the significant rate enhancements, yield and selectivity improvements as well as less environmental pollution matching with the goal of green chemistry.^{69,70} Recently, our group has reported HPAILs as eco-benign and highly efficient catalysts for amidation of carboxylic acid derivatives (Scheme 1(a))^{71–73} and oxidative amidation of aldehydes (Scheme 1(b))⁷⁴ with amines. As a part of our research to pursue novel, efficient and green methods for organic transformations,^{71–78} herein we wish to report the MW-assisted HPAILs catalyzed tandem oxidative amidation of alcohols with amines via a bifunctional catalysis process (Scheme 1(c)).

2. Results and discussions

Based on our previous investigations in HPAILs catalyzed organic reactions,^{71–75} N-substituted imidazole, pyridine and triethylamine based HPAILs were chosen as potential catalysts for this tandem oxidative amidation (Fig. 1).

Our initial studies focused on the reaction of commercially available benzyl alcohol (**1a**) with 2-phenylethylamine (**2a**) as the model substrates to optimize the reaction conditions (Table 1). Firstly, as a control experiment, aqueous *tert*-butyl hydroperoxide (TBHP) was used as the oxidant in the absence of any catalyst and additional solvent under conventional heating at 70 °C. After a prolonged reaction time of 12 h *N*-phenethylbenzamide was achieved in only 26% yield (Table 1, entry 1), whereas addition of 2 mol% amount of [PyPS]₃PW₁₂O₄₀ to the reaction mixture resulted in the desired amide in 61% yield (Table 1, entry 2). The results revealed that this tandem oxidative amidation of alcohol could be promoted by HPAILs. In order to improve the yield, some adjustments to the reaction conditions were made. It was shown that the yield of the reaction apparently increased when the reaction

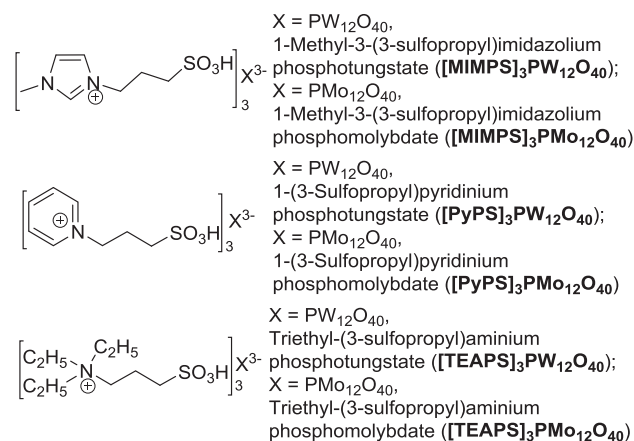
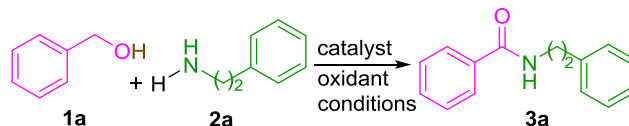


Fig. 1. N-substituted imidazole, pyridine and triethylamine based HPAILs.

Table 1

Optimization of the reaction conditions for oxidative amidation of benzyl alcohol with 2-phenylethylamine.^a



| Entry | Catalyst [mol %] | Oxidant | Time (h) | Yield (%) ^b |
|----------------|--|-------------------------------|----------|------------------------|
| 1 | – | TBHP | 12 | 26 ^c |
| 2 | [PyPS] ₃ PW ₁₂ O ₄₀ [2] | TBHP | 12 | 61 ^c |
| 3 ^d | [PyPS] ₃ PW ₁₂ O ₄₀ [2] | TBHP | 12, 1 | 73 ^d , 86 |
| 4 | [PyPS] ₃ PW ₁₂ O ₄₀ [2] | TBHP | 12, 1 | 70 ^e , 75 |
| 5 | [PyPS] ₃ PW ₁₂ O ₄₀ [2] | H ₂ O ₂ | 1 | <5 |
| 6 | [PyPS] ₃ PW ₁₂ O ₄₀ [2] | Oxone | 1 | <5 |
| 7 | [PyPS] ₃ PW ₁₂ O ₄₀ [2] | <i>m</i> -CPBA | 1 | <5 |
| 8 | [PyPS] ₃ PW ₁₂ O ₄₀ [2] | NaOCl | 1 | <5 |
| 9 | [PyPS] ₃ PW ₁₂ O ₄₀ [2] | TBHP | 1 | 21 ^f |
| 10 | [PyPS] ₃ PW ₁₂ O ₄₀ [2] | TBHP | 1 | 65 ^g |
| 11 | [PyPS] ₃ PW ₁₂ O ₄₀ [2] | TBHP | 1 | 81 ^h |
| 12 | [PyPS] ₃ PW ₁₂ O ₄₀ [1] | TBHP | 1 | 80 |
| 13 | [PyPS] ₃ PW ₁₂ O ₄₀ [3] | TBHP | 1 | 85 |
| 14 | [PyPS] ₃ PMo ₁₂ O ₄₀ [2] | TBHP | 1 | 75 |
| 15 | [MIMPS] ₃ PW ₁₂ O ₄₀ [2] | TBHP | 1 | 79 |
| 16 | [MIMPS] ₃ PMo ₁₂ O ₄₀ [2] | TBHP | 1 | 66 |
| 17 | [TEAPS] ₃ PW ₁₂ O ₄₀ [2] | TBHP | 1 | 65 |
| 18 | [TEAPS] ₃ PMo ₁₂ O ₄₀ [2] | TBHP | 1 | 54 |

^a Reaction conditions: benzyl alcohol **1a** (2 mmol), 2-phenylethylamine **2a** (2.4 mmol), HPAIL catalyst and TBHP (3 equiv., 70% aqueous solution) under MW (700 W) and solvent-free condition at 90 °C in a sealed glass pressure tube.

^b Isolated yields based on benzyl alcohol **1a**.

^c Reaction was conducted under conventional heating at 70 °C.

^d Reaction was conducted under conventional heating at 90 °C.

^e Reaction was conducted under conventional heating at 100 °C.

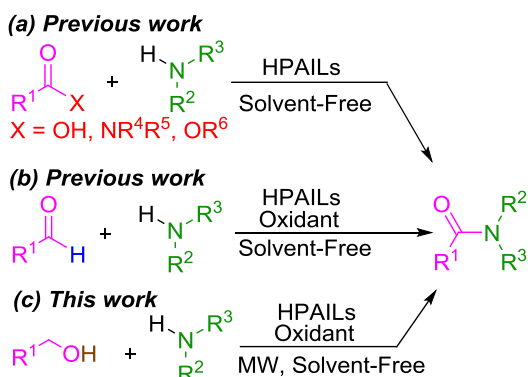
^f TBHP (3 equiv., 5.5 M in decane) was used.

^g TBHP (2.5 equiv., 70% aqueous solution) was used.

^h TBHP (4 equiv., 70% aqueous solution) was used.

ⁱ Optimum reaction condition.

mixture was conventionally heated at 90 °C (Table 1, entry 3, 73% yield), but higher temperature (100 °C) was not beneficial to the product (Table 1, entry 4, 70% yield). We reasoned that the lower yield at higher temperatures could be due to the partial over oxidation of benzyl alcohol to benzoic acid as a side product. To our delight, when MW-assisted heating was introduced, more efficient result was observed (Table 1, entry 3 and 4). Then, other common oxidants including H₂O₂, Oxone, NaOCl, *m*-CPBA were screened, but in all cases only 0–5% amide product formation was



Scheme 1. HPAIL catalyzed amidation reactions developed by our group.

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