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PII: DOI: Reference:	S0040-4039(19)30145-5 https://doi.org/10.1016/j.tetlet.2019.02.024 TETL 50618
To appear in:	Tetrahedron Letters
Received Date: Revised Date: Accepted Date:	<ul><li>21 December 2018</li><li>9 February 2019</li><li>12 February 2019</li></ul>



Please cite this article as: Balaboina, R., Swamy Thirukovela, N., Vadde, R., Sekhar Vasam, C., Amide bond synthesis *via* silver(I) *N*-heterocyclic carbene-catalyzed and *tert*-butyl hydroperoxide-mediated oxidative coupling of alcohols with amines under base free conditions, *Tetrahedron Letters* (2019), doi: https://doi.org/10.1016/j.tetlet. 2019.02.024

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### **Graphical Abstract**





Tetrahedron Letters

journal homepage: www.elsevier.com

### Amide bond synthesis *via* silver(I) *N*-heterocyclic carbene-catalyzed and *tert*butyl hydroperoxide-mediated oxidative coupling of alcohols with amines under base free conditions

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#### ARTICLE INFO

Article history: Received Received in revised form Accepted Available online

*Keywords:* oxidative amidation silver(I) *N*-heterocyclic carbenes hemiaminal TBHP ABSTRACT

We present a base free method for amide bond construction *via* oxidative coupling of alcohols with amines catalyzed by Silver(I) *N*-heterocyclic carbenes (Ag(I)-NHCs) and mediated by *tert*-butyl hydroperoxide(TBHP) in ethanol. The results of controlled experiments suggest that the oxidative coupling proceeds through the formation of aldehyde, then subsequent attack by amine to give hemiaminal, which can then be oxidized to amide.

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Amide bonds are essential disconnections in organic retrosynthesis.<sup>1</sup> Early methods to form the amide bond using carboxylic acids or it's derivatives are super-stoichiometric and create considerable amount of waste.<sup>2</sup> Thus, a variety of catalytic amide bond formations have been investigated using a range of organic functionalities as starting materials including alcohols,<sup>3</sup> carbonyls,<sup>4</sup> oximes,<sup>5</sup> primary amides,<sup>6</sup> terminal alkynes,<sup>7</sup> alkyl arenes,<sup>8</sup> esters,<sup>9</sup> aryl boronic acids,<sup>10</sup> and aryl halides.<sup>11</sup>(Figure 1)



Figure 1. Catalytic amide bond syntheses.

Since alcohols are relatively abundant and stable starting materials, catalytic coupling of alcohols with amines *via* either dehydrogenative<sup>3g-j,12</sup> or oxidative path<sup>3k-1,13</sup> has been recognized as environmentally benign and atom-economic process.

Because the catalytic dehydrogenative amidation of alcohol occurs in the absence of oxidant, it is critical to direct the transformation of hemiaminal intermediate that formed from alcohol-amine coupling to the amide or imine.<sup>3d,12a</sup> Conversely, catalytic oxidative amidation is generally a tandem process, in which an oxidant converts selectively the alcohol to aldehyde and then hemiaminal intermediate selectively to the amide.3k,3m,13 Although the platinum group metal catalyzed amide bond processes have been established deeper insights of mechanistic path,<sup>3a-d,12a-d</sup> however their high cost and toxicity provides opportunity to explore relatively cheaper and non-toxic transition metal catalysts. In this context, there are few reports disclosed the utilization of homogeneous/heterogeneous iron,<sup>14</sup> copper,<sup>15</sup> silver,<sup>16</sup> and zinc<sup>17</sup> catalysts in oxidative amidation of alcohol, which however requires a base or an additive in stoichiometric amounts or relatively higher catalyst loadings. The report by Beller<sup>17</sup> is the exception to disclose a base free oxidative amidation via alcohol-amine coupling catalyzed by Zinc/TBHP system. However, there was no information about the possible reaction mechanism for the optimized catalytic conditions and the reported amide yields obtained from aryl and aralkyl amines are not appreciable.

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Silver (I) *N*-heterocyclic carbenes (Ag(I)-NHCs) are one of the highly resourceful organometallics since they are (i) carbene transfer agents to synthesize many other powerful metal-NHC catalysts, (ii) good antibacterial agents, (iii) precursors for nanoparticles and liquid crystals and (iv) able to catalyze a variety of C-C and C-heteroatom bond forming reactions as emphasized by us<sup>18</sup> and others.<sup>19</sup> A report by Jiang and colleagues described the use of Ag(I)-NHCs (NHC = *N*,*N'*-Disubstituted imidazol-2-ylidene based carbenes) in a one-pot aerobic oxidative coupling of alcohols with amines in toluene to produce imines in the presence of a base.<sup>19a</sup> Imines are also an important class of nitrogen compounds in chemistry.

Herein for the first-time we describe the results of a basefree and additive free, Ag(I)-NHC catalyzed alcohol-amine oxidative coupling using *tert*-butyl hydroperoxide (TBHP) as an oxidant to produce selectively the amide-bond in high yields in a green solvent ethanol. We also made efforts to derive appropriate mechanism with the support of controlled experiments.

Our investigation began with the oxidative amidation of benzyl alcohol **1a** with aniline **2a** in ethanol as a model reaction to optimize the catalytic condition for the selective synthesis of amide **3a**. The results are present in Table 1. Firstly, a control experiment was conducted using TBHP as the oxidant in the absence of any catalyst and base at 60 °C i.e. below the b.p. value of ethanol. The reaction was almost none even after prolonged reaction periods as observed initially by TLC. Next, the addition of 5 mol% of Ag-salts (AgOAc, AgOTf, AgSbF<sub>6</sub> and AgBF<sub>4</sub>)as catalysts to the reaction mixture in the presence of TBHP has resulted in the formation of desired amide **3a**, but the yield was observed in the range of 18-29% yield after 24 hrs (Table 1, entries 2-5). Nevertheless, the results indicate Ag(I) metal centre is capable of promoting base free oxidative amidation of alcohol with amine selectively to amide using TBHP.

In order to improve the catalytic conditions (yield and reaction times), we next investigated the efficacy of pre-synthesized Ag(I)-NHCs (Figure 2, a-f) as catalysts in the above oxidative coupling. At first, the catalytic ability of 5 mol% Ag(I)-NHC (R = (a) mesityl, Figure 2) was tested in the coupling of 1a with 2aand obtained corresponding amide **3a** in 81% yield after 16 hours (Table 1, entry 6). Since Ag(I)-NHCs are organometallic catalysts, we have also carried out additional experiments using 4, 3 and 2 mol% concentration of Ag(I)-NHCs in the oxidative coupling 1a with 2a. To our surprise, there was no change in the vield of **3a** (Table 1, entries 6-9). However, there was a sudden decrease in the yield of amide 3a when 1 mol% of Ag(I)-NHC (a) was utilized. (Table 1, entry 10). The other 2 mol% Ag(I)-NHCs depicted in Figure 2 have also performed well as catalysts in the oxidative coupling of 1a with 2a in providing high yields of amide 3a (Table 1, entries 11-15) and indicates that the Ag(I)-NHCs used in our work are more efficient than normal Ag(I)-salt catalysts in ethanol. On the other hand, oxidative coupling between 1a and 2a at room temperature was unsuccessful. Only the TBHP-promoted benzyl alcohol oxidation to benzaldehyde was noticed (Table 1, entry 18).

The catalytic efficiency of Ag(I)-NHC (a) was also studied in the presence of  $H_2O_2$  and  $O_2$  promoted coupling between **1a** and **2a** 

in ethanol at 60 °C. It was noticed that the oxidative coupling reaction mediated by  $O_2$  gave trace amounts of aldehyde and imine (Table 1, entry 17), whereas the  $H_2O_2$  mediated oxidative coupling gave exclusively amide **3a** (Table 1, entry 16).



Solvent effect studies were conducted by replacing ethanol with various non-polar, polar aprotic and polar protic and found that ethanol solvent is a good choice for the establishment of present oxidative amidation protocol (see, ESI).

Table 1. Optimization of catalytic conditions.



Entry	Catalyst(mol%)	Oxidant	Time	Temn	Vield
Liftiy	Catalyst(mor/o)	Oxidant	(hrs)	(°C)	$(\%)^{b}$
1		TBHP	24	60	
2	AgOAc (5)	TBHP	24	60	18
3	AgOTf (5)	TBHP	24	60	24
4	$AgSbF_6(5)$	TBHP	24	60	29
5	AgBF <sub>4</sub> (5)	TBHP	24	60	27
6	Ag(I)-NHC (a) (5)	TBHP	16	60	<mark>81</mark>
7	Ag(I)-NHC (a) (4)	TBHP	16	60	<mark>81</mark>
8	Ag(I)-NHC (a) (3)	TBHP	16	60	<mark>81</mark>
9	Ag(I)-NHC (a) (2)	TBHP	16	60	<mark>81</mark>
10	Ag(I)-NHC (a) (1)	TBHP	18	60	65
11	Ag(I)-NHC (b) (2)	TBHP	16	60	83
12	Ag(I)-NHC (c) (2)	TBHP	16	60	78
13	Ag(I)-NHC (d) (2)	TBHP	16	60	82
14	Ag(I)-NHC (e) (2)	TBHP	16	60	81
15	Ag(I)-NHC (f) (2)	TBHP	16	60	84
16	Ag(I)-NHC (a) (2)	H <sub>2</sub> O <sub>2</sub>	16	60	64
17	Ag(I)-NHC (a) (2)	air	16	60	
18	Ag(I)-NHC (a) (2)	TBHP	24	RT	

<sup>a</sup> Reaction conditions: Reaction was carried out using **1a** (1 mmol), **2a** (1.2 mmol) and TBHP (3 mmol) in ethanol (3 mL). <sup>b</sup> Isolated yields after column chromatography.

Having the optimized conditions in hand (alcohol/amine = 1/1.2 ratio, 3 equivalents of TBHP, 2 mol% Ag(I)-NHC, 60 °C, ethanol) we have further extended this protocol to synthesize different primary and secondary amides and the results were

shown in **table 2**. The substituted benzyl alcohols containing electron-withdrawing groups transformed easily to corresponding primary amides (Table 2, entries 3e and 3i-3l) than those containing electron-donating groups (Table 2, entries 3f-3h). With respect to the reactivity of amines, it found that all the linear aryl primary amines have coupled efficiently with the alcohol partners in providing respective primary amides (Table 2, 3i-3q). In the case of anilines, those anilines bearing electron-releasing groups have given slightly higher yields of primary amides (Table 2, entries 3c-3d) than the other anilines (Table 2, entries 3g-3h).

Besides, we have also utilized secondary amines as partners to alcohols in oxidative coupling. It was noticed that the oxidative coupling reactions using both the acyclic and aryl alkyl secondary amines (Table 2, entries 3r-3v) are less efficient than cyclic secondary amines (Table 2, entries 3w-3y). All the synthesized products were characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR and mass spectrometry.

#### Table 2. Substrate scope.



<sup>a</sup> Reaction conditions: **1(a-j)** (1 mmol), **2(a-m)** (1.2mmol), Ag(I)-NHC (a) (2 mol%) and TBHP (3 mmol) in ethanol (3 mL) at 60 °C temperature for 12-18 hours. <sup>b</sup> Isolated yields after column chromatography.

In order to understand the reaction mechanism, we have done few supporting studies (Scheme 1).

(i) When the benzyl alcohol **1a** was treated only with TBHP in the presence of Ag(I)-NHC, exclusively benzaldehyde **1aa** was formed in 91 % yield (CC) in ethanol at 60 °C.

(ii) When benzaldehyde **1aa** was coupled with aniline **2a** in the absence of TBHP, formation of schiff base **1ab** was noticed.

(iii) When benzaldehyde **1aa** was coupled with aniline **2a** in the presence of TBHP, formation amide **3a** was noticed.

From the equation **i**, **ii**, and **iii** it is confirmed that our approach proceeds through the *in situ* formation of aldehydes rather than ester and TBHP oxidant is responsible for the formation of desired amides through the oxidation of *in situ* generated hemiaminal that obtained by the coupling benzaldehyde with aniline in ethanol.



Scheme 1. Controlled experiments.

Based on the above supporting studies and from the literature support<sup>14b,14c,19a,20</sup> we proposed the plausible mechanism as shown in scheme 2. Initially Alkoxide-silver NHC-complex intermediate A was formed by the coordination of NHC-Ag-Cl to the alcohol. This intermediate A is activated by TBHP to afford the intermediate **B** in which Ag-metal centre having (+2)oxidation state. Later, intermolecular β-hydrogen abstraction of intermediate **B** takes place to provide the aldehyde and tertbutanol. Finally, the catalytic cycle is completed by the attack of labile Cl ion on free radical NHC-Ag-O to regenerate NHC-Ag-Cl along with the release of molecular oxygen. The regenerated NHC-Ag-Cl will start the next phase of catalytic cycle by coordinating to *in situ* formed aldehyde which subsequently reacts with amine to form hemiaminal intermediate C. The hemiaminal **C** reacts with TBHP to give the intermediate **D**. Then the same process was observed as that of intermediate B to give desired amides and tBuOH (intermediate D to amide). Finally, the NHC-Ag-Cl is renewed by the reaction of labile Cl ion on NHC-Ag-O<sup>'</sup> radical by releasing molecular oxygen.



Scheme 2. Proposed mechanism.

In conclusion, we have developed a base free direct amidation from alcohols and primary/secondary amines through a tandem oxidation process that catalyzed by Ag(I)-NHC

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organometallics and mediated by TBHP in ethanol. The catalytic conditions developed in the present work for the amide bond construction are comparable or relatively better than the previous works in terms of yield and selectivity.

#### Acknowledgements

The authors are thankful to the DST-SERB, New Delhi, India File No. SR/S1/IC-31/2011, DST-India (DST/INT/SA/P-15/2011 Indo-South Africa project) for financial support.

#### Supplementary data

Experimental details, characterization data of 3(a-y) products can be found, in the online version, at http://dx.doi.org/

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**Tetrahedron Letters** 

Highlights of this manuscript are;

- ➤ Ag(I)-NHC catalysed base-free synthesis of amide-bond from alcohol-amine coupling.
- Acceleration > TBHP is an effective oxidant than  $H_2O_2$  & O<sub>2</sub> to produce selectively amide than

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