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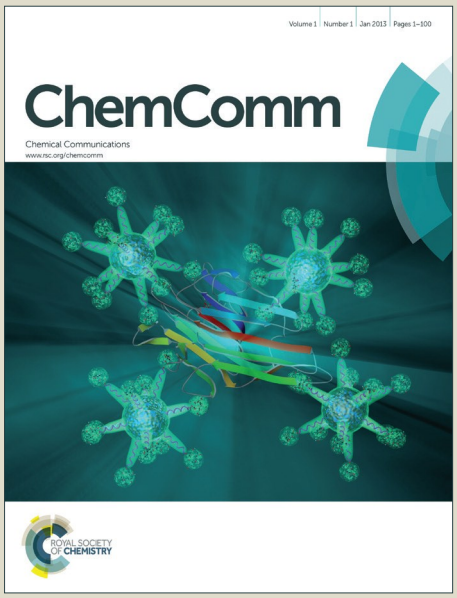




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ARTICLE

# Copper-Catalyzed Oxyamination of Electron-Deficient Alkenes with *N*-Acyloxyamines

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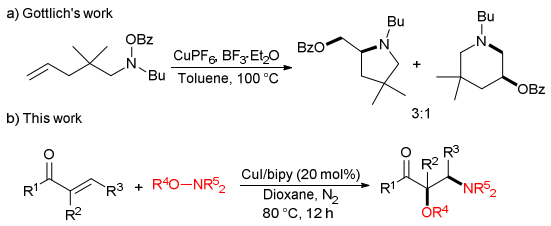
A Cu(I)-catalyzed direct intermolecular oxyamination of electron deficient alkenes is disclosed. This process is characterized by difunctionalization of a variety of *α*,*β*-unsaturated ketones with easily available *N*-acyloxyamine reagents as both amine and oxygen donors, which delivers ester derivatives of *β*-amino alcohols in good yields as well as high regioselectivity. Control studies suggested the involvement of alkyl radical species on the way of product formation.

*β*-Amino alcohol represents as a key structural motif which is frequently found in naturally occurring compounds and bioactive molecules. In addition, optically pure *β*-amino alcohols are extensively used as privileged chiral ligands or auxiliaries in modern organic synthesis.[1] In view of their importance in biological and synthetic chemistry, the pursuit of novel synthetic approaches for the preparation of *β*-amino alcohols have attracted considerable attention from the synthetic organic chemists. In particular, synthetic protocols which afford the amino alcohols in a single step have been of intensive research interest in recent years. In this context, elegant examples for the construction of *β*-amino alcohol derivatives have been developed, for example, the nucleophilic addition to imines/carbonyl compounds,[2] epoxides/aziridines[3] with proper nucleophiles; direct C–H bond functionalization of alcohol derivatives[4] and hydrogenation of amino ketone derivatives.[5] Compared with these strategies, the venerable Sharpless aminohydroxylation, which directly converts simple alkene into amino alcohol is arguably one of the most powerful and convenient ways for the easy access of such skeletons.[6] While expedient, the relative high cost and toxicity of osmium catalyst expose somewhat limits on its practical applications. Therefore, alternative synthetic protocols, which resort to other metallic salts such as Pd,[7] Rh,[8] Cu,[9] Fe[10] as the catalysts have been extensively exploited and proved to be effective complements to the Sharpless aminohydroxylation. Noteworthily, a handful of metal-free and photoredox reactions were also reported most recently.[11] As a cheap and abundant transition metal, Cu has also been employed in catalytic oxyamination of alkenes. For example, In 2002, Gottlich and co-workers reported a Cu-catalyzed intramolecular oxyamination of alkenes (Scheme 1a).[9d] In addition, Yoon and co-workers have developed a Cu(II)-catalyzed addition of *N*-sulfonyl oxaziridine to olefins in 2007.[9j] Although these methods proved to be effective for the introduction of vicinal amino and hydroxyl groups, some drawbacks still remain, such as limited substrate scope and attenuated regioselectivities. Therefore, the development of a novel protocol of intermolecular alkene oxyamination would unarguably be of vital importance from either academic or industrial viewpoints. In recent years, *N*-acyloxyamines were widely studied and used as the amine donors in the transition-metal-catalyzed synthetic elaborations, however, the employment of these reagents as both amine and oxygen donors in a single transformation was far less exploited.[12] Herein, we would like to report a highly regioselective and atom economic protocol of copper(I)-catalyzed intermolecular alkene oxyamination, which, by making use of *N*-acyloxyamine as both the amine and oxygen donors, provides a novel synthetic pathway for the ready access of amino alcohol derivatives (Scheme 1b).[13]




**Scheme 1.** Cu(I)-catalyzed oxyamination of alkenes.

At the very beginning, 1-phenylprop-2-en-1-one **1a** and 4-benzoyloxymorpholine **2a** were chosen as the model reaction partners for the optimization of reaction conditions (see ESI for details). When **1a** (1.0 equiv) and **2a** (1.1 equiv) were

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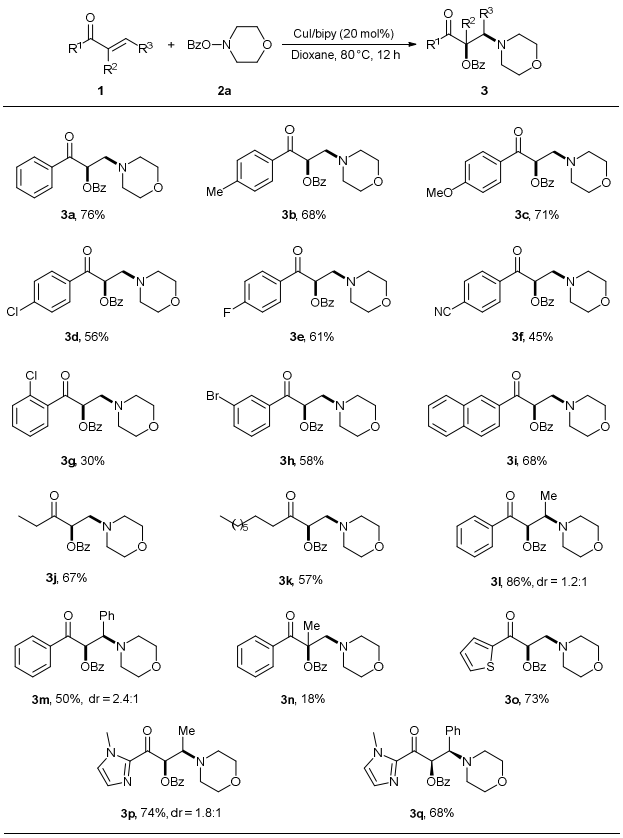
subjected to a catalytic amounts of CuI (20 mol%) with *o*-phenanthroline (20 mol%) as the ligand in dioxane under nitrogen atmosphere at 80 °C for 12 h, to our delight, 50% yield of desired product **3a** was obtained. The following ligand screening revealed 2,2'-dipyridine to be the ligand of choice, which delivered **3a** in 76% yield. Further examination of copper catalysts revealed that only copper halide such as CuCl, CuBr and CuI exhibited catalytic reactivity for this reaction and the yield increased in the order Cl<Br<I, thus indicating a significant effect of halide counter ion for this process.[14] The role of halide in this particular transformation was further confirmed in another control reaction wherein the addition of a substoichiometric amount of $Bu_4NI$ (0.5 equiv) enabled the aminoacyloxylation with $Cu(MeCN)_4PF_6$ (20 mol%) as the reaction catalyst which failed to give any product in its own right. Moreover, control experiments clearly demonstrated the indispensability of copper catalysts in this transformation.

With the optimal reaction conditions in hand, the substrate scope with respect to alkene partner was subsequently studied and the results were summarized in Table 2. Generally, aryl ($R^1$)-substituted vinyl ketones proved to be well suited for this transformation. Vinyl ketones with aryl fragments containing either electron-rich or electron-deficient substituents all worked smoothly and produced vicinal acyloxyl amine derivatives in moderate to good yields. For example, when substrates bearing electron-donating groups such as methyl and methoxyl (**1b** and **1c**) were employed, products **3b** and **3c** were obtained in 68% and 71% yields, respectively. Slightly lower yields were observed in the case of using substrates with electron-withdrawing groups, such as chloride, fluoride and cyanide. It is noteworthy that while *o*-chlorophenyl vinyl ketone **1g** led to the product **3g** in only 30% yield, 56% of desired product **3d** was obtained when *p*-chlorophenyl vinyl ketone **1d** was subjected to the standard reaction conditions. The discrepancy between **1g** and **1d** was tentatively attributed to the bidentate chelation of chlorine and ketone moieties in the case of **1g**, which rendered the copper catalyst residing away from the alkene moiety thus impeding the ensuing migratory insertion step. The oxyamination process was also evaluated with sterically more encumbered substrates. It was found that *β*-substituted enone substrates were nicely accommodated and tended to afford the difunctionalization products in good yields, albeit with low diastereoselectivities observed in the cases of **3l** and **3m**. In contrast, α-substituted congener **1n** led to a much lower yield, which is likely due to the steric congestion, thus disfavouring the migratory insertion of the copper intermediate to the alkene moiety. Upon extending the scope to alkyl and heteroaryl vinyl ketones, high yields were also obtained. Much to our surprise, while **1p** afforded the product **3p** as a mixture of diastereoisomers in the ratio of 1.8:1, the related substrate **1q**, however, provided product **3q** as a single isomer and the exact reason for this discrepancy is presently uncertain (the structure of **3q** was confirmed by single-crystal X-ray diffraction analysis).[15] It is worth mentioning that while acrylates, at the present stage, were proved to be not viable substrates in this oxyamination reaction, the feasibility of *N*-methylimidazoyl vinyl ketone enables a facile access of these targets by post-elaborations.

**Table 2:** Substrate scope of activated alkenes.[a]




[a] Unless otherwise noted, the reactions were carried out at 80 °C using **1** (0.1 mmol), **2a** (0.11 mmol), CuI (0.02 mmol) and 2,2'-dipyridine (0.02 mmol) in solvent (1.0 mL) for 12 h. [b] Yield of isolated products are given.

In order to further evaluate the reaction generality and limitation with respect to the *N*-acyloxyamine reagents, a series of *N*-acyloxyamines were synthesized and examined and the results were summarized in Table 3. It was found that moderate to good yields of desired products could be obtained by modifying either the amino or ester fragments. For example, when pyrrolidine based *N*-benzoxyamine was subjected to the optimized reaction condition with **1a**, the desired product **3r** was obtained in 72% yield. Pleasingly, this transformation was not limited to cyclic hydroxylamine derivatives and when dibenzylamine or diethylamine based *N*-benzoxyamine substrates were employed, the reaction worked smoothly to deliver the corresponding difunctionalized products in synthetically useful yields (**3s**, **3t**). Furthermore, the ester group in the hydroxylamine derivatives could also be decorated and when **2e** was employed the reaction readily occurred to provide the desired product **3u** in 55% yield. It needs to be pointed out that the products obtained from acyclic *N*-acyloxyamine derivatives were not very stable, which underwent degradation either under the standard reaction conditions or decomposed on silica gel chromatograph. For

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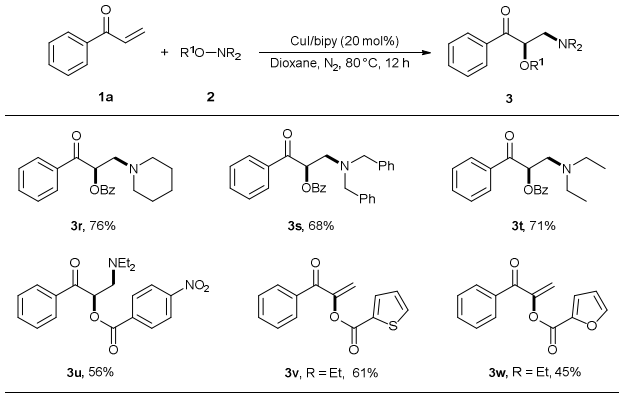
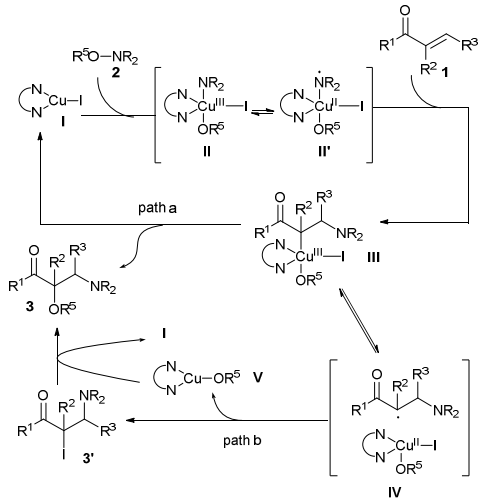
example, when *N,N*-diethyl acyloxyamine derivatives **2f** and **2g** were examined, *α*-acyloxylated enones **3v** and **3w** were obtained instead of the *α*-acyloxyl-*β*-amino ketones in the yields of 53% and 37%, respectively. Although the yields were only moderate, it constituted to be a shortcut for the easy access of *α*-acyloxylated enone derivatives, which, however, were previously obtained through multistep-reactions with 1,2-diketones or prefunctionalized substrates as starting materials.[16]

**Table 3:** Substrate scope of *N*-acyloxyamine.




[a] Yield of isolated products are given. [b] Purified with alkaline aluminium oxide column chromatography.

To probe the reaction mechanism, 2 equivalent TEMPO was charged into the model reaction and the yield of desired product decreased significantly from 76% to 29% (see ESI for details of control experiments). It seems a radical intermediate was involved in this process although the TEMPO trapped intermediate was not detected. In addition, a small amount of *α*-iodo-*β*-amino side product **3a'** was observed in the reaction mixture determined by $^1$H NMR, reminiscent of halogen transfer from Cu(II)-X to alkyl radical intermediate.[17] Furthermore, when **3a'** was subjected into the standard reaction conditions the desired product **3a** could be obtained in 30% yield. Taken together, these results indicated that compound **3a'** probably stems from a radical intermediate derived from **1a** and a Cu(II) complex and might be an intermediate on the way to product **3a** formation. Furthermore, it was found that either *cis*- or *trans*-chalcone gave a mixture of diastereomers with essentially the same ratio, which further lent support the involvement of a radical intermediate, thus resulting in the loss of stereo information of starting materials. Therefore, a provisionally proposed reaction mechanism for this Cu(I)-catalyzed oxyamination of *α,β*-unsaturated ketones was depicted in Scheme 2. Initially, the oxidative addition of CuI complex **I** with *N*-benzyloxyamine forms an aminocopper intermediate **II**, which is in equilibrium with aminyl radical species **II'**. Then intermediate **II** undergoes a sequence of alkene complexation and migratory insertion to form alkyl-Cu(III) species **III**. At this stage, two possible reaction pathways could be envisioned for the access of oxyamination product **3**: the first (path a) comprises a selective reductive elimination to produce the desired product **3a** while the other pathway (path b) lies on the involvement of *α*-iodo-*β*-amino ketone **3'** as the key reaction intermediate, which evolves into the product **3** with simultaneous regeneration of the active copper catalyst **I** upon further interaction with acyloxycopper complex **V**.[9d,13] It needs to be further pointed out that 2-iodo-3-morpholino-1-phenylpropan-1-one **3a'** was always observed at a very low level along with product **3a** accumulating by a real-time monitoring of the reaction between **1a** and **2a** and the characteristic $^1$H-NMR signal of **3a'** disappeared when the reaction completed. This observation indicates the radical pathway b is viable for the reaction however it may be less favoured than the ionic pathway a. The existence of equilibrium between the radical intermediate **IV** and the alkyl-Cu(III) complex **III** is consistent with the similar diastereoselectivities obtained from both *E* and *Z* enones.




**Scheme 2.** Proposed reaction mechanism.

In conclusion, we have reported a copper(I)-catalyzed regioselective aminoacyloxylation of electron deficient alkenes. This reaction works efficiently and delivers the ester derivatives of *β*-amino alcohol. Compared with previous reports, this reaction features a 100% atom economy fashion with both amino and oxygen functionalities originating from the sole *N*-acyloxyamine reagents without any added acid or amine derivatives for promotion. By tuning the amino or ester fragments, a diversity of functionalized *β*-amino alcohol derivatives could be easily accessed in a straightforward manner and a variety of synthetically useful functional groups were well tolerated under reaction conditions.

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