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Access to Aminated Saturated Oxygen Heterocycles via Copper-Catalyzed Aminooxygenation of Alkenes

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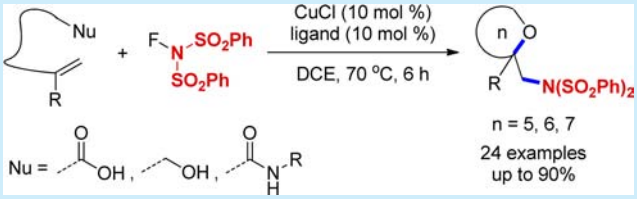
Supporting Information

ABSTRACT: A copper-catalyzed aminooxygenation of unactivated alkenes with various *O*-nucleophiles is described. This novel methodology uses commercially available *N*-fluorobenzenesulfonimide as an amination reagent and provides a simple and efficient approach to a wide range of aminated saturated oxygen heterocycles in moderate to good yields. The reaction features mild reaction conditions, operational simplicity, and a broad substrate scope.



Cyclic structures are ubiquitous in natural products, pharmaceuticals, and bioactive molecules.[1] Among these, saturated oxygen heterocycles, such as lactones and cyclic ethers, are a highly important class of compounds that are frequently found in the structures of many medicinally relevant compounds and biologically active molecules.[1,2] Accordingly, the development of new and efficient synthetic methods for their preparation is an important field of research in organic chemistry.

Over the past decades, considerable efforts have been devoted to the development of simple and efficient methods for constructing saturated oxygen heterocycles.[3] Among these methods, the difunctionalization of alkenes, which allows direct vicinal installation of two functional groups across a C−C double bond, provides a versatile and step-economical route to the synthesis of valuable functionalized saturated heterocycles.[4] Because of the simultaneous incorporation of a second useful functional group during the ring-formation process, the molecular complexity of saturated heterocyclic compounds is enhanced through this strategy. This is beneficial for the discovery of drugs and structural modification of lead compounds. In this context, a variety of studies have been conducted on the difunctionalization of alkenes with the aim of developing simple and novel approaches. For example, in the presence of strongly electrophilic reagents such as halogen and chalcogen reagents, halolactonization[5] and chalcolactonization[6] of unsaturated olefinic carboxylic acids have been established as powerful strategies for synthesizing diversely halogenated and chalcogenated lactones. Moreover, a transition-metal-catalyzed[7] or radical cyclization strategy[8] has been developed to prepare substituted saturated heterocycles. Despite these achievements, continuous efforts are still required, especially for the synthesis of aminated saturated heterocycles due to their importance in organic synthesis and medicine.[9]

The amino group is an important functional group present in many pharmaceuticals, biologically active natural products, and agrochemicals.[10] Chemical and physical properties of heterocycles are altered upon introduction of the amino group, which afford utility in medicinal chemistry and material science.[11] Therefore, it is important to develop synthetic methods for C−N bond formation.[12] *N*-Fluorobenzenesulfonimide (NFSI), which is a commonly used and commercially available amination reagent, has recently attracted much attention. Transition-metal-catalyzed amination of aromatic heterocycles[13] and intermolecular difunctionalization of alkenes[14] using NFSI have been reported.[15] However, examples of the preparation of aminated saturated heterocycles have rare precedents.[16,17] Recently, Michael and co-workers developed an elegant palladium-catalyzed vicinal diamination of alkenes with NFSI to prepare aminated pyrrolidine derivatives.[17] With continuing interest in C−N bond formation reactions,[18] we herein describe a facile copper-catalyzed aminooxygenation of alkenes using NFSI as a source of amine, providing various aminated saturated oxygen heterocycles in moderate to good yields under simple and mild conditions.

Our studies started with the aminolactonization reaction of unsaturated olefinic carboxylic acid **1a** with NFSI (1.5 equiv) in the presence of CuBr as a catalyst in DCE at 70 °C for 12 h. Unfortunately, no desired aminated lactone **2a** was obtained, and both **1a** and NFSI were recovered (Table 1, entry 1). Investigations were continued by screening different ligands **L1**−**L11** under the same conditions, and we found that neocuproine **L2** is the best ligand for this transformation, which gave **2a** in 73% yield (Table 1, entries 2−12). The structure of **2a** was determined by X-ray analysis (see the Supporting Information).[19] Reactions with various Cu(I) salts including CuCl, CuI, CuOAc, CuTc, CuOTf, and $[(MeCN)_4Cu]BF_4$ were then examined, and CuCl afforded the highest yield (Table 1, entries 13−19). A solvent screening indicated that DCE is the best solvent. Other solvents, such as MeCN, DMF, and 1,4-dioxane, resulted in worse results (Table 1, entries 20−22). The reaction did not proceed at room temperature (Table

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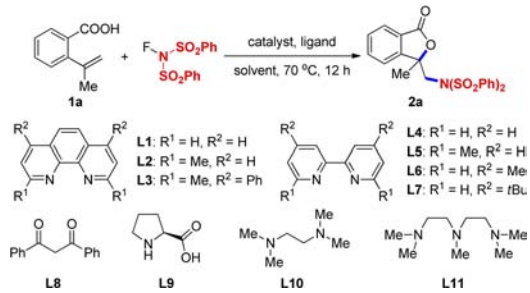
Table 1. Optimization of Reaction Conditions[a]



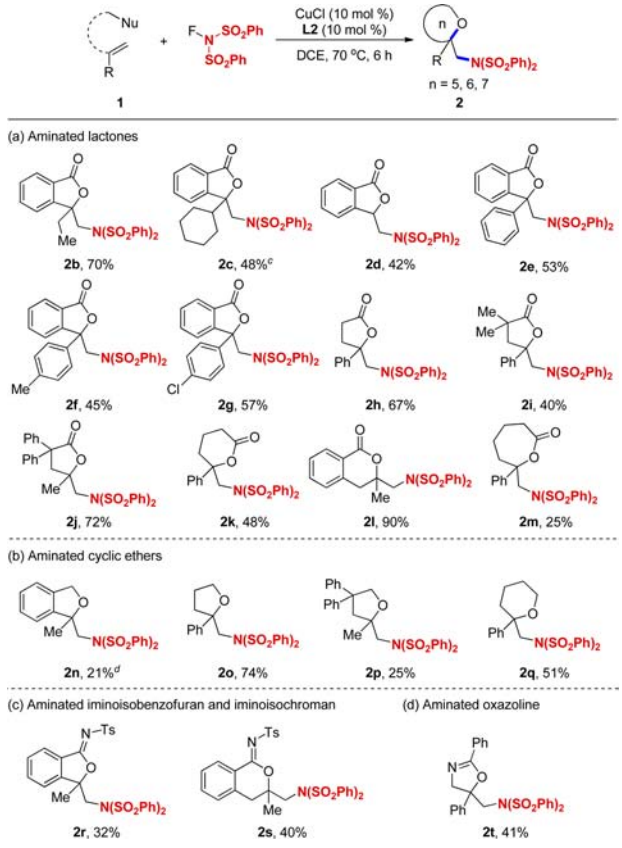
entry	catalyst	ligand	solvent	yield[b] (%)
1	CuBr	none	DCE	0
2	CuBr	**L1**	DCE	66
3	CuBr	**L2**	DCE	73
4	CuBr	**L3**	DCE	72
5	CuBr	**L4**	DCE	58
6	CuBr	**L5**	DCE	72
7	CuBr	**L6**	DCE	49
8	CuBr	**L7**	DCE	59
9	CuBr	**L8**	DCE	42
10	CuBr	**L9**	DCE	53
11	CuBr	**L10**	DCE	49
12	CuBr	**L11**	DCE	58
13	CuCl	**L2**	DCE	80
14	CuI	**L2**	DCE	67
15	Cu_2O	**L2**	DCE	71
16	CuOAc	**L2**	DCE	52
17	CuTc	**L2**	DCE	78
18	CuOTf	**L2**	DCE	55
19	$[(MeCN)_4Cu]BF_4$	**L2**	DCE	63
20	CuCl	**L2**	MeCN	70
21	CuCl	**L2**	DMF	0
22	CuCl	**L2**	1,4-dioxane	0
23[c]	CuCl	**L2**	DCE	0
24[d]	**CuCl**	**L2**	**DCE**	**80**
25	none	**L2**	DCE	0

[a]Reaction conditions: **1a** (0.2 mmol), catalyst (10 mol %), ligand (10 mol %), and NFSI (0.3 mmol) in solvent (1.5 mL) at 70 °C under N_2 for 12 h. [b]Isolated yields. [c]The reaction was conducted at rt. [d]The reaction was conducted for 6 h.

1, entry 23). The yield was not affected when the reaction was conducted for 6 h (Table 1, entry 24). In addition, no **2a** was observed in the absence of copper catalyst (Table 1, entry 25). These results indicate that both the copper salt and ligand are essential for the aminolactonization reaction to take place (Table 1, entries 1 and 25).

With optimized reaction conditions in hand, we next explored the scope of this aminolactonization reaction. Illustrative examples are shown in Scheme 1. 2-Vinylbenzoic acid derivatives **1b–d** underwent the desired cyclization smoothly to deliver the corresponding aminated lactones in moderate to good yields (**2b–d**). Substrates bearing different aryl substituents consistently provided the targeted products in moderate yields regardless of their electronic properties (**2e–g**). Remarkably, the current approach is not restricted to the aminolactonization of aromatic carboxylic acids. Unsaturated aliphatic carboxylic acids could also be successfully converted to the corresponding 5-*exo*-cyclized products under the optimized reaction conditions (**2h–j**). In addition, it was found that six- and even seven-membered ring lactones were accessible using

Scheme 1. Preparation of Various Aminated Saturated Oxygen Heterocycles[a,b]



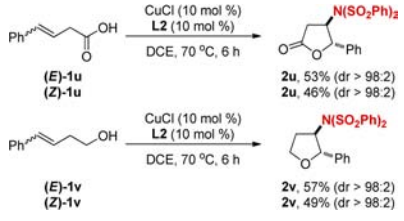
[a]Reaction conditions: see entry 24, Table 1. [b]Isolated yields. [c]Using NFSI (0.34 mmol). [d]Using NFSI (0.4 mmol).

the present protocol (**2k–m**). To show the practicality of this method, we performed a gram-scale reaction of **1a** with NFSI to give **2a** in 68% yield (1.24 g).

Encouraged by the above results, we next turned our attention to the synthesis of aminated cyclic ethers using alcohols as the substrates (Scheme 1). Under the standard reaction conditions, benzylic alcohol **1n** and alkyl alcohol **1p** led to lower yields due to some side reactions. It was found that alcohol substrates carrying no backbone elements favored this cyclization, producing the corresponding products in moderate to good yields (**2o** and **2q**). Moreover, we could show that *N*-substituted amides **1r–t** are also viable substrates for this transformation, which gave the corresponding *O*-cyclized products **2r–t** in moderate yields.

To probe the diastereoselectivity of this reaction, we investigated the aminooxygenation of internal alkenes (Scheme 2). Internal alkene **1u** reacted under the optimized conditions to give the corresponding product **2u** in 53% yield.

Scheme 2. Aminooxygenation of Internal Alkene 1u and 1v



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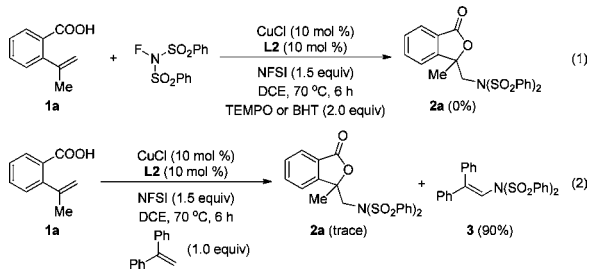
Interestingly, **2u** was formed with excellent *trans*-selectivity (>98:2). The relative configuration of **2u** was determined by ROESY analysis. The bis-sulfonylamidyl group and phenyl group are arranged in an *anti*-fashion presumably because of steric repulsion between the bis-sulfonylamidyl and phenyl groups. Internal alkene **1v** also proved to be a suitable substrate for this transformation, which reacted with excellent *trans*-selectivity (>98:2) to give the product **2v** in 57% yield. Finally, we prepared *Z*-isomers of **1u** and **1v** and subjected them to identical conditions. These reactions gave **2u** and **2v** in moderate yields with excellent *trans*-selectivity (>98:2).

To gain mechanistic insights into the reaction pathway, some control experiments were performed (Scheme 3). First, the

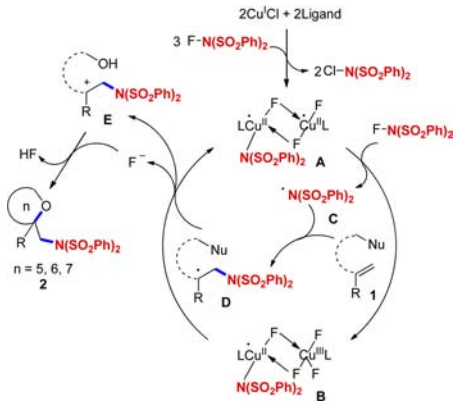
Scheme 3. Mechanistic Experiments



aminooxygenation reaction was completely suppressed in the presence of 2,6-di-*tert*-butyl-4-methylphenol (BHT) or 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) as a radical scavenger, and **1a** was recovered in almost 100% yield. Moreover, when the radical trapper 1,1-diphenylethylene was subjected to the standard reaction conditions, only traces of the targeted product **2a** were identified, and a 90% of **3** was obtained.[14f] These results suggest that a bis-sulfonylamidyl radical addition pathway is likely involved in these reactions.

On the basis of the above experimental observations, a possible reaction mechanism is illustrated in Scheme 4. As

Scheme 4. Proposed Reaction Mechanism



previously suggested,[20] the CuCl precatalyst is first transformed into the active dinuclear Cu^{II}–Cu^{II} catalyst **A** through Cl/F exchange reactions with NFSI. Subsequently, **A** gets oxidized by NFSI via one-electron F atom transfer pathway to generate a reactive bis-sulfonylamidyl radical **C** along with the dinuclear Cu^{II}–Cu^{III} intermediate **B**.[21,22] Radical addition to alkene **1** produces the carbon-centered radical **D**. **D** is further oxidized by **B** to generate the cationic intermediate **E** and fluoride anion. This process allows the regeneration of the dinuclear Cu^{II}–Cu^{II} catalyst **A**. Finally, deprotonation by the fluoride anion and cyclization of **E** provides the product **2**.

In summary, we have presented a simple and efficient method for the preparation of aminated saturated oxygen heterocycles including lactones, cyclic ethers, iminoisobenzofurans, iminoisochromans, and oxazolines via copper-catalyzed aminooxygenation of unactivated alkenes. The novel transformation uses the commercially available NFSI as the amination reagent. Reactions are operationally simple and display a broad substrate scope. Furthermore, aminooxygenation of internal alkenes occurs with excellent diastereoselectivity. Further studies on the mechanism, the scope, and the synthetic applications are ongoing in our laboratory.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.7b00182.

Experimental details and characterization data for the products (PDF)

X-ray crystallographic data for **2a** (CIF)

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Notes

The authors declare no competing financial interest.

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