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α-Carbamoylsulfides as *N*-Carbamoylimine Precursors in the Visible Light Photoredox-Catalyzed Synthesis of α,α-Disubstituted Amines

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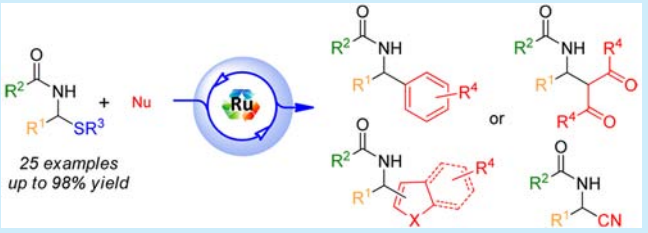
Supporting Information

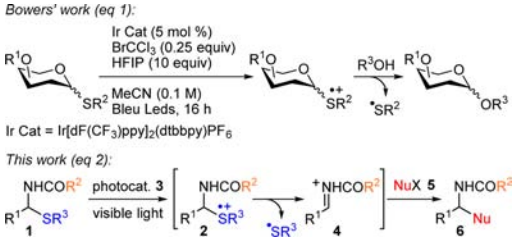
ABSTRACT: A general and practical photoredox-promoted addition of nucleophiles to *N*-acylimines generated *in situ* from α-amidosulfides using $Ru(bpy)_3(PF_6)_2$ as the photocatalyst is reported. The broad scope of the reaction toward various nucleophiles and amidosulfide derivatives was explored. This novel protocol provides a rapid, mild, and efficient access to valuable α,α-disubstituted amines in respectable yields.



The use of masked *N*-acyl and *N*-carbamoylimines has been proven to be a powerful strategy in the preparation of synthetically useful α-substituted amines.[1] Consequently, many precursors containing a good leaving group such as *O*-alkyl, OH, sulfone, halide, benzotriazole, or amide have been investigated for the generation of imines (or iminium ions).[2] However, in some cases, strong acids or bases are required, which precludes the presence of acid- or base-sensitive functional groups. In this regard, we recently reported a NIS (*N*-iodosuccinimide) mediated aza-Friedel−Crafts (aza-FC) reaction using α-carbamoylsulfide as easily available imine precursors.[3] However, while the reaction proceeds under neutral and mild conditions, the formation of molecular iodine during the reaction can limit the substrate scope of the reaction.

As a continuation of this research program, we sought to develop a new method for the preparation of *N*-carbamoylimines from α-carbamoylsulfides that would be mild, practical, and highly functional-group-tolerant. Our approach was inspired by the work of Bowers,[4,5] who showed that photo-oxidation of thioglycosides in the presence of iridium photocatalyst, $BrCCl_3$ and visible light generates oxocarbenium ions, which can be then trapped with alcohols to form *O*-glycosides (Scheme 1, eq 1). We thought that visible light photocatalysis[6,7] could be used to generate *in situ* the *N*-carbamoyliminium **2** from α-aminosulfides **1** under mild conditions (Scheme 1, eq 2). Indeed, the photoinduced single-electron oxidation of the neutral species **1** might produce a sulfur radical cation **2**. The latter could then undergo C−S bond cleavage to give an *N*-acyliminium ion **4**, which can proceed with nucleophiles to provide the addition product **6**.

Scheme 1. Proposed Work Hypothesis



To test this hypothesis, we selected an appropriate reaction for optimization. The initial studies focused on aza-FC reaction of *N*-acylimines generated *in situ* from α-amidosulfides. 1,3,5-Trimethoxybenzene (**5a**) was chosen as the arene nucleophile with *tert*-butyl (1-(ethylthio)-3-phenylpropyl)carbamate (**1a**) as the substrate. To our delight, by using a Ruthenium photoredox catalyst **3a** in CH_3CN, we were able to isolate the desired aza-FC **6a** in 60% yield (Table 1, entry 1). The yield was further improved by adding 10 equiv of hexafluoroisopropyl alcohol (HFIP) or *t*-BuOH as a protic additive (enties 2 and 3). In particular, *t*-BuOH was chosen for the further optimization as it is cheaper. The amount of alcohol was also important, and less or more than 10 equiv *t*-BuOH decreased the yield (entry 3 vs entries 4 and 5). Although the role of alcohol is not fully understood, it may increase the solubility of radical cation **2** as described in previous reports.[4,8] However, in the course of our electrochemical study, we found that the oxidation potential of **1a** was reduced in the presence of *t*-BuOH (see Supporting Information) hence favoring the formation of **4**. In contrast, no beneficial effect was observed when the reaction was performed in the presence of the hazardous $BrCCl_3$ as oxidative quencher (Table 1, entry 6).[4,6] Different photocatalysts **3b−e** (entries 5−7) were also screened. While the organic photocatalyst Eosin Y **3e** (entry 9) was found to be a suitable catalyst for this reaction,[9] a better result was obtained with $[Ru(bpy)_3(PF_6)_2]$ **3a** (entry 3). Next, we studied the reactivity in different solvents, and the yield

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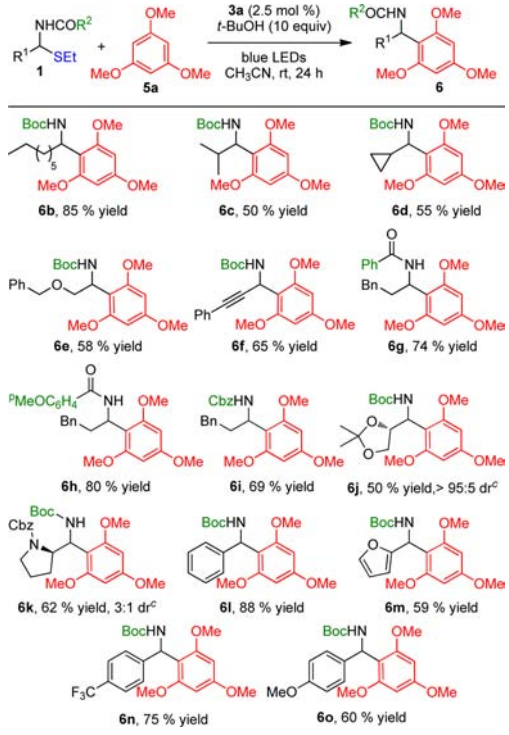
Table 1. Survey of Reaction Conditions for the Photocatalyzed Alkylation of 1

entry	1	photocat. 3	additive (*x* equiv)	6a yield (%)[a,b]
1	1a	$Ru(bpy)_3(PF_6)_2$ (3a)		60
2	1a	3a	HFIP (10)	77
3	1a	3a	*t*-BuOH (10)	85
4	1a	3a	*t*-BuOH (5)	77
5	1a	3a	*t*-BuOH (20)	63
6	1a	3a	*t*-BuOH (10)	67[c]
7	1a	$Ru(bpy)_3Cl_2$ (3b)	*t*-BuOH (10)	65
8	1a	$Ir(ppy)_2(dtbbpy)(PF_6)$ (3c)	*t*-BuOH (10)	70
9	1a	Eosin Y (3e)	*t*-BuOH (10)	63[d]
10	1a	3a	*t*-BuOH (10)	60[e]
11	1a	3a	*t*-BuOH (10)	90[f]
12	1b	3a	*t*-BuOH (10)	57
13	1c	3a	*t*-BuOH (10)	63
14	1d	3a	*t*-BuOH (10)	91
15	1a	3a	*t*-BuOH (10)	*g*,*h*
16	1a		*t*-BuOH (10)	*g*

[a]General conditions: 1 (0.10 mmol), 1,3,5-trimethoxybenzene **2a** (0.15 mmol), **3** (0.025 equiv), additive in MeCN (1.0 mL) irradiated at rt for 24 h. [b]Yields referred to chromatographically pure product. [c]$BrCCl_3$ (0.025 mmol) was used as oxidative quencher. [d]Irradiated with green LEDs. [e]MeCN (2 mL) was used. [f]MeCN (0.5 mL) was used. [g]Starting material was recovered. [h]Without any irradiation.

Scheme 2. Substrate Scope of the aza-FC Reaction of α-Amidosulfide Derivatives 1[a,b]



[a]Reaction conditions: **1** (0.10 mmol), 1,3,5-trimethoxybenzene **5a** (0.15 mmol), **3a** (0.025 equiv), *t*-BuOH (10.0 equiv) in MeCN (0.5 mL) irradiated at rt for 24 h. [b]Yields referred to chromatographically pure product. [c]The dr was determined by ^1H NMR analysis of crude mixtures

significantly dropped when MeCN was replaced by tetrahydrofuran (THF), CH_2Cl_2, or *t*-BuOH (see Supporting Information). The reaction was improved further by increasing the substrate concentration (Table 1, entry 11). Further studies revealed that the nature of the substituent on the S atom of the α-amidosulfides influenced the efficiency of the reaction (entries 12−14). The use of S-aryl (**1b**, entry 12) and S-benzyl (**1c**, entry 13) derivatives resulted in lower yields than with the S-*t*-butyl (**1d**, entry 14) and S-Et (**1d**, entry 11) derivatives. It is noteworthy that no reaction occurred in the absence of a photocatalyst or light (Table 1, entries 15 and 16). These experiments indicate that the photoredox catalysis is essential for this process.

We next examined the scope of α-amido or α-carbamoylsulfides **1** that participate in this photocatalyzed aza-FC reaction. As summarized in Scheme 2, the reaction of aliphatic α-carbamoylsulfides whether linear or α-branched, afforded the corresponding aza-FC adducts **6b**−**6e** in moderate to excellent yields. The photocatalytic system also proved to be efficient for various imines bearing functional groups such as benzyl ether (**1e**), acetal (**1j**), and amine (**1k**). Most remarkably, these imine precursors bearing an alkyne functional group such as (**1i**), which were totally unstable in our previous NIS-assisted protocol, worked well.[3a] This was demonstrated as the α-carbamoylsulfides **1f** being converted into the *N*-Boc propargylic amine **6f** which is an important building block for the synthesis of nitrogen-containing compounds.[2m,10] Several protecting groups bonded to the nitrogen of **1**, including carbamates (**6a** and **6i**) and amides (**6g** and **6h**), were tolerated. We also found that, contrary to our previous studies,[3] enantioenriched α-carbamoylsulfides **1j** and **1k** whose corresponding α-substituted imines are known to be sensitive toward racemization, were successfully engaged in this reaction.[11] For instance, the imine precursors derived from *D*-glyceraldehyde acetonide **1j** led to aza-FC adduct **6j** as a single disastereomer with no racemization. Similarly, *L*-proline derivative **1k** yielded to an enantiomerically pure mixture (3:1) of two inseparable diastereomers in 62% yield. On the other hand, various aromatic and heteroaromatic α-amidosulfides effectively participated in this reaction, leading to the aza-FC adducts **6l** and **6m** in good yields. No noticeable difference in reactivity was observed when electron-rich and electron-poor functional groups were present in the aromatic ring (**6n** and **6o**).

Extension of this novel photoredox protocol to other nucleophiles than **5a** was delightfully successful (Scheme 3). Under the same conditions, various heterocycles such as 2-methoxythiophene **5b** and indoles **5c** and **5d** afforded the C-alkylated aza-FC products **6p**−**6s** in moderate to good yields. It is worth noting that this is complementary to our early developed NIS-catalyzed approach in which the 3-alkylindoles furnished only *N*-alkylated products.[3] In the case of indole **5c**, bis(indolyl) product derived **7**, which displays important biological activities,[12] was isolated as a single product. Interestingly, no acid was required to promote the double addition of **5c** to the *in situ*-generated *N*-Boc imine **1a**.[2c−e,13] On the other hand, reaction of amide-protected **1g** with indole **5c** under similar reaction conditions only delivered the desired aza-FC product **6r**, indicating the influence of protecting groups on the reactivity of **4**. The process also worked with nitrogen nucleophiles such as indazole **5e** and pyrazole **5f** yielding to **6t** and **6u** in 91% and 70%

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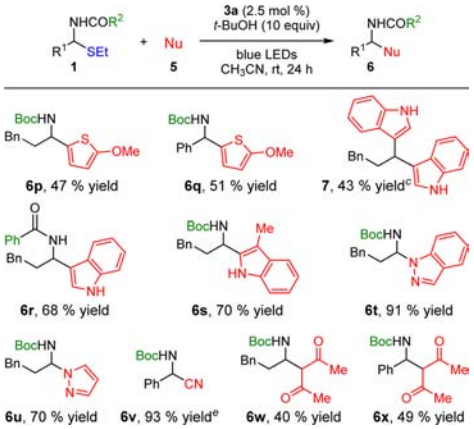
Scheme 3. Substrate Scope with Respect to the Nucleophile[a,b]

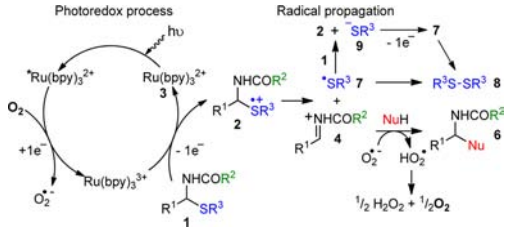


[a]General conditions: **1** (0.10 mmol), nucleophile **5** (0.15 mmol), **3a** (0.025 equiv), *t*-BuOH (10.0 equiv) in MeCN (0.5 mL) irradiated at rt for 24 h. [b]Yields referred to chromatographically pure product. [c]From **1a**. [d]With KCN (0.3 mmol) and a mixture MeCN/H_2O (0.5 mL:0.5 mL).

yield, respectively. We further explored the potential for a Strecker-type reaction. Surprisingly, when attempting to trap the *N*-carbamoyl iminium **1a** with TMSCN, we did not isolate any desired product. Fortunately, the use of KCN **5g** was successful leading to **6v** in excellent yield. Next, we found that 1,3-dicarbonyls such as acetylacetone **5h** underwent addition to **1a** and **1l** yielding to Mannich product **6w** and **6x**. Although the yields were moderate, no acid or base was added to trigger the nucleophilic addition of **5h**.

To gain more insight into the pathway of this photocatalytic reaction, several control experiments were conducted. We first measured the oxidation potential of the α-carbamoylsulfides **1** used in our studies. The oxidation potential of the sulfur atom of **1a** was found to be 1.17 V vs SCE in CH_3CN. This indicates that the electron-transfer pathway after its excitation of Ru^{2+} is not possible, as the oxidation potential of $*Ru^{2+}$ (0.77 V vs SCE in CH_3CN) is too low.[6,14] To proceed, the reaction requires the formation of stronger oxidizing Ru^{3+} (1.33 V vs SCE in CH_3CN) via oxidative quenching of $*Ru^{2+}$. Since $BrCCl_3$ was an inefficient quencher (Table 1, entry 6), we hypothesized that molecular oxygen might act as an oxidative quencher of $*Ru^{2+}$. Indeed, when the reaction was carried under anaerobic condition, only starting material **1a** was recovered (see Supporting Information), thus confirming the oxidative quenching role of molecular oxygen. A parallel experiment showed that the addition of oxygen results in a slight decrease of reaction time (see Supporting Information). On the basis of the above results as well as other reports,[6,15] a plausible mechanism for this process is outlined in Scheme 4. The oxidative quenching of $*Ru^{2+}$ by the O_2 generates

Scheme 4. Plausible Reaction Mechanism



the Ru^{3+} and superoxide radical anion ($O_2^{\bullet-}$). Sulfur radical cation **2**, formed by the Ru^{3+}-promoted oxidation of **1**, undergoes a fragmentation to generate the iminium **4**, S-centered radical (sulfanyl radical) **7**, and Ru^{2+}. Subsequent addition of nucleophiles to **4**, followed by the hydrogen atom abstraction mediated by the superoxide radical ion, provides the desired products **6** and hydroperoxyl radical ($HO_2^{\bullet}$). It is also possible that O_2 could be regenerated in course of disproportionation reactions of hydroperoxyl radical ($HO_2^{\bullet}$). This might explain why that addition of O_2 into the reaction medium was not necessary (see Supporting Information). Meanwhile the sulfanyl radical **7**, formed upon cleavage of the C−S bond, may evolve according to two different routes: (a) either **7** dimerizes to form disulfide **8** or (b) **7** propagates the radical chain reaction by oxidation of **1** leading to **2** and thiolate anion **9**. The latter, based on the work Matsuda et al.,[16] can be photooxidized to produce the disulfide **8** via **7**. To distinguish between these two plausible reaction pathways, we performed additional experiments. We irradiated **1a** in the presence of 1,3,5-trimethoxybenzene (**5a**) and **3a** with blue LEDs for 1 h (see Supporting Information). In this condition, **6a** was isolated in 8% yield (instead of 90% after 24 h of irradiation, Table 1, entry 11). However, an increase in yield (30%) was obtained when **1a** was stirred under dark conditions for 24 h after 1 h irradiation. These latter experiments indicate that although chain-propagating one-electron oxidation by **7** seems effective, it is not the dominant pathway. Consequently, it is reasonable to assume that **2** was mainly generated by electron transfer from the oxidized Ru^{3+} photocatalyst.

In summary, we have developed a practical photoredox-catalyzed synthesis of *N*-carbamoyl α,α-disubstituted amines from readily available α-amidosulfides under mild conditions. This methodology has wide scope, including several examples of nucleophiles, and moderate to excellent yields. A promising asymmetric amine synthesis with excellent diasteroselectivity was also achieved by using chiral α-amidosulfides. Moreover, the photoredox protocol relies on the use of nonhazardous chemicals, features a simple experimental procedure, and is performed under mild conditions. We believe that such a protocol could find useful applications in view of the synthesis of functionalized building blocks, potentially biologically active substances, and natural products.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b00442.

Detailed experimental procedures and spectral data for all new compounds (PDF)

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Notes

The authors declare no competing financial interest.

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