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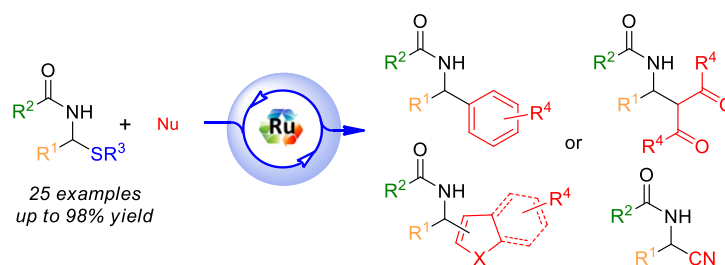
# $\alpha$ -Carbamoylsulfides as *N*-Carbamoylimine Precursors in the Visible Light Photoredox-Catalyzed Synthesis of $\alpha,\alpha$ -Disubstituted Amines

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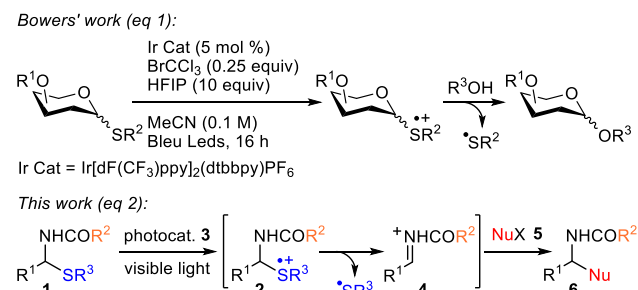
Supporting Information Placeholder



**ABSTRACT:** A general and practical photoredox-promoted addition of nucleophiles to *N*-acylimines generated *in situ* from  $\alpha$ -amidosulfides using  $\text{Ru}(\text{bpy})_3(\text{PF}_6)_2$  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  $\alpha,\alpha$ -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  $\alpha$ -substituted amines.<sup>1</sup> 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).<sup>2</sup> 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  $\alpha$ -carbamoylsulfide as easily available imine precursors.<sup>3</sup> 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.

## Scheme 1. Proposed work hypothesis



As a continuation of this research program, we sought to develop a new method for the preparation of *N*-carbamoylimines from  $\alpha$ -carbamoylsulfides that would be mild, practical, and highly func-

tional-group-tolerant. Our approach was inspired by the work of Bowers,<sup>4,5</sup> who showed that photo-oxidation of thioglycosides in the presence of Iridium photocatalyst,  $\text{BrCCl}_3$  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<sup>6,7</sup> could be used to generate *in situ* the *N*-carbamoyliminium **2** from  $\alpha$ -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**.

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  $\alpha$ -amidosulfides. 1,3,5-Trimethoxybenzene (**5a**) was chosen as 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  $\text{CH}_3\text{CN}$ , 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 equivalents of hexafluoroisopropanol (HFIP) or *t*-BuOH as a protic additive (entries 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 equivalents *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.<sup>4,8</sup> However, in the course of our electrochemical study, we found that the oxidation potential of **1a** was reduced in 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  $\text{BrCCl}_3$  as oxidative quencher (Table 1, entry 6).<sup>4,6</sup> 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,<sup>9</sup> better result was obtained with  $[\text{Ru}(\text{bpy})_3(\text{PF}_6)_2]$  **3a** (entry 3). Next, we studied the reactivity in different solvents, and the yield significantly dropped when MeCN was replaced by tetrahydrofuran (THF),  $\text{CH}_2\text{Cl}_2$  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  $\alpha$ -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.

**Table 1. Survey of reaction conditions for the photocatalyzed alkylation of 1.**

1a R = Et  
1b R = Ph  
1c R = Bn  
1d R = *t*-Bu

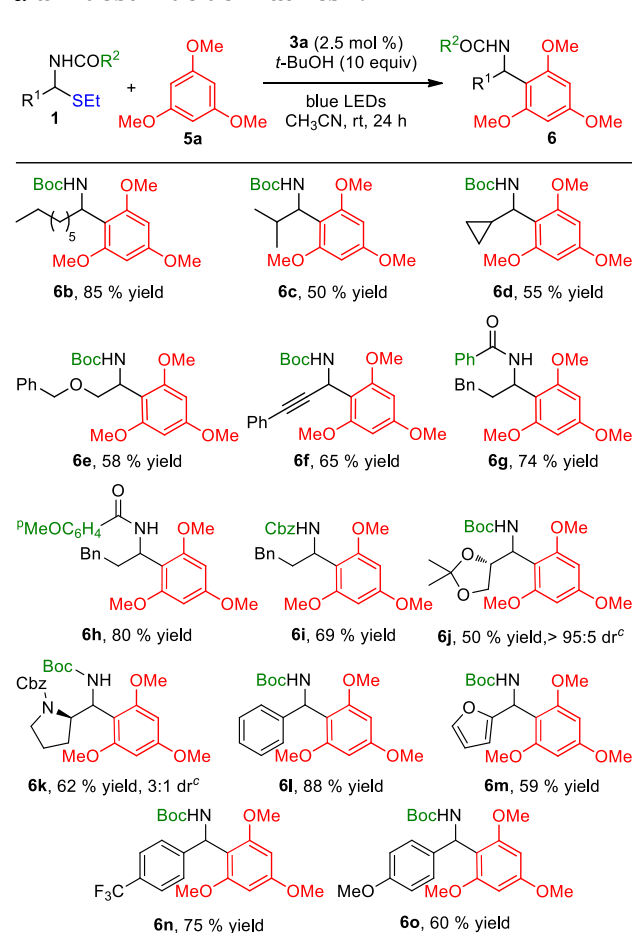
entry	1	photocat. 3	additive (x equiv)	6a yield (%) <sup>a,b</sup>
1	1a	$\text{Ru}(\text{bpy})_3(\text{PF}_6)_2$ ( <b>3a</b> )	-	60
2	1a	<b>3a</b>	HFIP (10)	77
3	1a	<b>3a</b>	<i>t</i> -BuOH (10)	85
4	1a	<b>3a</b>	<i>t</i> -BuOH (5)	77
5	1a	<b>3a</b>	<i>t</i> -BuOH (20)	63
6	1a	<b>3a</b>	<i>t</i> -BuOH (10)	67 <sup>c</sup>
7	1a	$\text{Ru}(\text{bpy})_3\text{Cl}_2$ ( <b>3b</b> )	<i>t</i> -BuOH (10)	65
8	1a	$\text{Ir}(\text{ppy})_2(\text{dtbbpy})(\text{PF}_6)$	<i>t</i> -BuOH (10)	70
9	1a	Eosin Y ( <b>3e</b> )	<i>t</i> -BuOH (10)	63 <sup>d</sup>
10	1a	<b>3a</b>	<i>t</i> -BuOH (10)	60 <sup>e</sup>
11	1a	<b>3a</b>	<i>t</i> -BuOH (10)	90 <sup>f</sup>
12	1b	<b>3a</b>	<i>t</i> -BuOH (10)	57
13	1c	<b>3a</b>	<i>t</i> -BuOH (10)	63
14	1d	<b>3a</b>	<i>t</i> -BuOH (10)	91
15	1a	<b>3a</b>	<i>t</i> -BuOH (10)	- <sup>h, i</sup>
16	1a	<b>3a</b>	<i>t</i> -BuOH (10)	- <sup>h</sup>

<sup>a</sup>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. <sup>b</sup>Yields referred to chromatographically pure product. <sup>c</sup> $\text{BrCCl}_3$  (0.025 mmol) was used as oxidative quencher. <sup>d</sup>Irradiated with green LEDs. <sup>e</sup>MeCN (2 mL) was used. <sup>f</sup>MeCN (0.5 mL) was used. <sup>h</sup>Starting material was recovered. <sup>i</sup>Without any irradiation.

We next examined the scope of  $\alpha$ -amido or  $\alpha$ -carbamoylsulfides **1** that participate in this photocatalyzed aza-FC reaction. As summarized in Scheme 2, the reaction of aliphatic  $\alpha$ -carbamoylsulfides whether linear or  $\alpha$ -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.<sup>3a</sup> This was demonstrated as the  $\alpha$ -carbamoylsulfides

**1f** being converted into the *N*-Boc propargylic amine **6f** which is an important building blocks for the synthesis of nitrogen-containing compounds.<sup>2m,10</sup> 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,<sup>3</sup> enantioenriched  $\alpha$ -carbamoylsulfides **1j** and **1k** whose corresponding  $\alpha$ -substituted imines are known to be sensitive towards racemization, were successfully engaged in this reaction.<sup>11</sup> For instance, the imine precursors derived from *D*-glyceraldehyde acetonide **1j** led to aza-FC adduct **6j** as a single diastereomer 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  $\alpha$ -amidosulfides effectively participated in this reaction, leading to the aza-FC adducts **6l-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**).

**Scheme 2. Substrate scope of the aza-FC reaction of  $\alpha$ -amidosulfide derivatives 1.<sup>a,b</sup>**

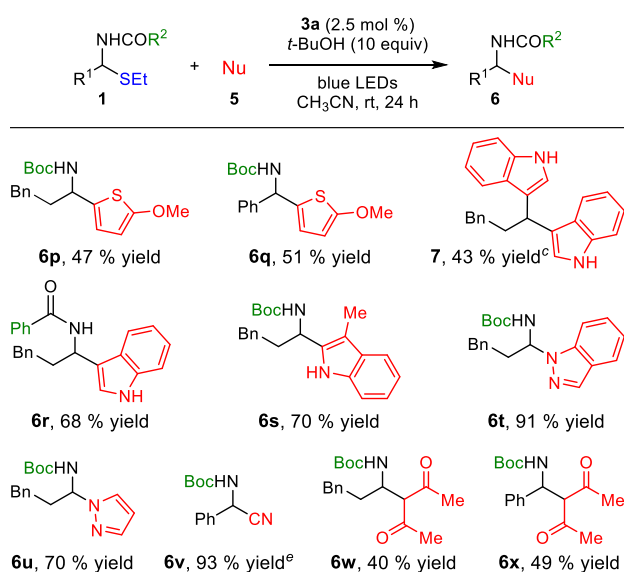


<sup>a</sup>Reaction conditions: **1** (0.10 mmol), 1,3,5-trimethoxybenzene **5a** (0.15 mmol), **3a** (0.025 equiv), *t*-BuOH (10.0 equiv) in MeCN (0.5 mL) irradiated at rt for 24 h. <sup>b</sup>Yields referred to chromatographically pure product. <sup>c</sup>dr determined by <sup>1</sup>H-NMR analysis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

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-5d** afforded the C-alkylated aza-FC products **6p**, **6q**, **6r** and **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.<sup>3</sup> In the case of indole **5c**, bis(indolyl) product derived **7**, which display important biological activities,<sup>12</sup> 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**.<sup>2d-f,13</sup> 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 % 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**.

### Scheme 3. Substrate scope with respect to the nucleophile.<sup>a,b</sup>

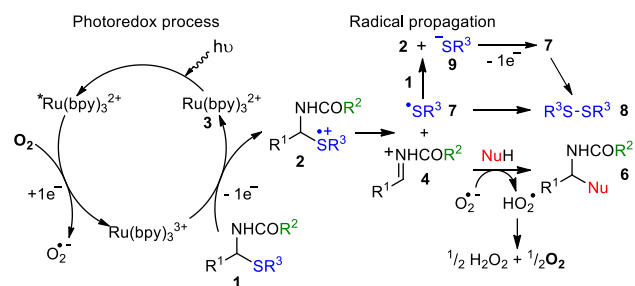


<sup>a</sup>General conditions: **1** (0.10 mmol), nucleophile **5** (0.15 mmol), **3a** (0.025 equiv), *t*-BuOH (10.0 equiv) in MeCN (0.5 mL) irradiated at rt for 24 h. <sup>b</sup>Yields referred to chromatographically pure product. <sup>c</sup>From **1a**. <sup>d</sup>With KCN (0.3 mmol) and a mixture MeCN:H<sub>2</sub>O (0.5 mL:0.5 mL).

To gain more insight into the pathway of this photocatalytic reaction, several control experiments were conducted. We have first measured the oxidation potential of the  $\alpha$ -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<sub>3</sub>CN. This indicates that the electron-transfer pathway after its excitation of Ru<sup>2+</sup> is not possible, as the oxidation potential of \*Ru<sup>2+</sup> (0.77 V vs. SCE in CH<sub>3</sub>CN) is too low.<sup>6,14</sup> To proceed, the reaction requires the formation of stronger oxidizing Ru<sup>3+</sup> (1.33 V vs. SCE in CH<sub>3</sub>CN) via oxidative quenching of \*Ru<sup>2+</sup>. Since BrCCl<sub>3</sub> was an inefficient quencher (Table 1, entry 6), we hypothesized that molecular oxygen might act as an oxidative quencher of \*Ru<sup>2+</sup>. 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 slight decrease of reaction time (see Supporting Information). On the basis of the above results as well as other reports,<sup>6,15</sup> a plausible mechanism for this process is outlined in Scheme 4. The oxidative quenching of \*Ru<sup>2+</sup> by the O<sub>2</sub> generates

the Ru<sup>3+</sup> and superoxide radical anion (O<sub>2</sub><sup>•-</sup>). Sulfur radical cation **2**, formed by the Ru<sup>3+</sup>-promoted oxidation of **1**, undergoes a fragmentation to generate the iminium **4**, S-centered radical (sulfanyl radical) **7** and Ru<sup>2+</sup>. Subsequent addition of nucleophiles to **4**, followed by hydrogen atom abstraction mediated by superoxide radical ion, provides the desired products **6** and hydroperoxyl radical (HO<sub>2</sub><sup>•</sup>). It is also possible that O<sub>2</sub> could be regenerated in course of disproportionation reactions of hydroperoxyl radical (HO<sub>2</sub><sup>•</sup>). This might explain why that addition of O<sub>2</sub> 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.,<sup>16</sup> 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 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<sup>3+</sup> photocatalyst.

### Scheme 4. Plausible reaction mechanism.



In summary, we have developed a practical photoredox-catalyzed synthesis of *N*-carbamoyl  $\alpha,\alpha$ -disubstituted amines from readily available  $\alpha$ -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 diastereoselectivity was also achieved by using a chiral  $\alpha$ -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

Detailed experimental procedures and spectral data for all new compounds are provided. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Author Contributions

\*These authors contributed equally. All authors have given approval to the final version of the manuscript.

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