

# Merging Photoredox with Copper Catalysis: Decarboxylative Alkynylation of $\alpha$ -Amino Acid Derivatives

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Supporting Information

**ABSTRACT:** A novel and efficient decarboxylative alkynylation of N-(acetoxy)phthalimides of  $\alpha$ -amino acids with terminal alkynes has been developed by merging photoredox with copper catalysis at room temperature, and the reaction provided the valuable propargylamines in

good to excellent yields with assistance of  $[Ru(bpy)_3]Cl_2/CuI$  and visible light. The simple protocol, mild reaction conditions, and high efficiency of this method make it an important strategy for synthesis of diverse molecules containing amino acid fragments.

lkynes are versatile building blocks and intermediates in the Asynthesis of organic materials and biologically active molecules. Sonogashira coupling is a classical and powerful method for the synthesis of alkynes containing aryl  $C(sp^2)$ -C(sp) bonds.<sup>2</sup> However, it still is a challenge to construct alkyl  $C(sp^3)-C(sp)$  bonds. Recently, the alkyl  $C(sp^3)-C(sp)$  bond formation has been addressed by the development of nucleophilic<sup>3</sup> and electrophilic reagents,<sup>4</sup> but the substrate scope is limited thus far. Propargylamines are high value building blocks in organic synthesis, and they are considered as key intermediates for the preparation of many nitrogen-containing, biologically active compounds and important structural elements of natural products and therapeutic drug molecules. The most conventional methods for their synthesis are via transition-metalcatalyzed, especially copper-catalyzed, three-component couplings of aldehydes, amines, and terminal alkynes. Carboxylic acids and their derivatives are ubiquitous in organic molecules, natural products, and biomasses, and some notable decarboxylative examples have recently been developed such as decarboxylative Heck coupling, aldol additions, and asymmetric enolate alkylations. <sup>10</sup> Tunge and co-workers reported an interesting intramolecular decarboxylative C(sp³)-C(sp) coupling from ester derivatives. 11  $\alpha$ -Amino acids widely occur in nature, and their selective functionalization attracts much attention. Liang and Li cooperatively developed a coppercatalyzed decarboxylative coupling of sp<sup>3</sup>-hybridized carbon atoms of  $\alpha$ -amino acids. <sup>12</sup> Recently, visible-light photoredox catalysis has attracted much attention, and it has emerged as a powerful activation protocol in chemical transformations. 13 Sanford and co-workers described the development of a mild method for the cross-coupling of arylboronic acids with CF<sub>3</sub>I via the merger of photoredox and Cu catalysis. 14 Rueping's group developed the alkynylation of tertiary amines with terminal alkynes in the presence of a photoredox catalyst and a metal catalyst. 15 Very recently, Hashmi and co-workers have developed an efficient gold-catalyzed photoredox  $\alpha$ -C(sp<sup>3</sup>)-H alkynylation of tertiary aliphatic amines under irradiation of sunlight. 16 In addition, some progress has been achieved in photoredox

decarboxylative couplings of carboxylic acids and their derivatives as radical precursors. Waser and co-workers have recently developed a decarboxylative alkynylation of carboxylic acids using photoredox catalysis and ethynylbenziodoxolone reagents. We have also developed some interesting visible-light photoredox organic reactions. As part of our continuing study on visible-light photoredox catalysis, we report herein the synthesis of propargylamines from N-(acetoxy)phthalimides of  $\alpha$ -amino acids and terminal alkynes by merging photoredox with copper catalysis at room temperature.

At first, decarboxylative coupling of 1,3-dioxoisoindolin-2-yl 2-(diethylamino)-3-methylbutanoate (1a) with phenylacetylene (2a) by merging photoredox with copper catalysis was chosen as the model to optimize conditions including photocatalysts, copper catalysts, solvents, and time. As shown in Table 1, four copper catalysts were screened using 1.0 mol % of [Ru(bpy)<sub>3</sub>]Cl<sub>2</sub> as the photoredox catalyst and dichloromethane (DCM) as the solvent under argon atmosphere at room temperature for 6 h (entries 1–4), and CuI provided the highest yield (entry 2). No reaction occurred in the absence of copper catalyst (entry 5). Other solvents were investigated (entries 6-9), and the results showed that CH<sub>2</sub>Cl<sub>2</sub> was optimal (compare entry 2 and entries 6–9). The reaction afforded 77% yield when  $[fac-(Ir(ppy)_3)]$  was used as the photocatalyst (entry 10). Only a trace amount of product 3a was observed in the absence of photocatalyst (entry 11). When the time was changed from 6 to 8 h, a similar yield was provided (entry 12). The yield decreased in a short reaction time (entry 13). The reaction did not work without irradiation of visible light (entry 14).

After obtaining the optimized, dual catalytic conditions, we investigated substrate scope on the decarboxylative alkynylation of *N*-(acetoxy)phthalimides (1) with terminal alkynes (2). As shown in Table 2, various terminal alkynes were tested using 1a as the partner, and the results showed that both aliphatic and

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Table 1. Optimization of Conditions for Decarboxylative Coupling of 1,3-Dioxoisoindolin-2-yl 2-(Diethylamino)-3methylbutanoate (1a) with Phenylacetylene (2a) by Merging Photoredox with Copper Catalysis<sup>a</sup>

entry	photo- catalyst	Cu catalyst	solvent	time (h)	yield (%) <sup>b</sup>
1	A	Cu(CH <sub>3</sub> CN) <sub>4</sub> PF <sub>6</sub>	$CH_2Cl_2$	6	70
2	A	CuI	$CH_2Cl_2$	6	89
3	A	CuBr	$CH_2Cl_2$	6	72
4	A	CuSCN	$CH_2Cl_2$	6	NR
5	A		$CH_2Cl_2$	6	$NR^c$
6	A	CuI	ClCH <sub>2</sub> CH <sub>2</sub> Cl	6	75
7	A	CuI	CH <sub>3</sub> CN	6	62
8	A	CuI	CHCl <sub>3</sub>	6	17
9	A	CuI	DMF	6	55
10	В	CuI	$CH_2Cl_2$	6	77
11		CuI	$CH_2Cl_2$	6	trace <sup>d</sup>
12	A	CuI	$CH_2Cl_2$	8	89
13	A	CuI	$CH_2Cl_2$	4	80
14	A	CuI	$CH_2Cl_2$	6	$NR^e$

<sup>a</sup>Reaction conditions: irradiation of visible light with 40 W CFL and argon atmosphere, 1,3-dioxoisoindolin-2-yl 2-(diethylamino)-3-methylbutanoate (1a) (0.6 mmol), phenylacetylene (2a) (0.3 mmol), photocatalyst (3  $\mu$ mol), Cu catalyst (0.03 mmol), solvent (2.0 mL), rt (~25 °C), 4–8 h in a sealed Schlenk tube. <sup>b</sup>Isolated yield. <sup>c</sup>No addition of copper catalyst. <sup>d</sup>No addition of photocatalyst. <sup>e</sup>No light. NR = No reaction. CFL = compact fluorescent light.

aromatic alkynes were effective substrates (see 3a-1). Subsequently, N-(acetoxy)phthalimides containing different amino acid units were investigated, and the substrates with aliphatic amino acid side chains (see 3m-s) provided yields higher than those with a phenyl side chain (see 3t-v). We investigated diverse substrates with different N-substituents on the amino acids, and they all gave the corresponding propargylamines in good to excellent yields (see 3w-ad). The decarboxylative alkynylation by merging photoredox with copper catalysis exhibited some functional group tolerance, including ethers (see 3d, 3i, 3p, 3v, 3z, 3aa, and 3ac), C-F bond (see 3e), C-Cl bonds (see 3f, 3g, 3o, 3s, and 3ad), ester (see 3j), and amides (see 3k and 3l).

As shown in Scheme 1, we attempted a gram-scale synthesis of compound 3d under the standard conditions. Reaction of 1a with 4-ethynylanisole 2d provided the target product 3d in a high yield (86%). Therefore, the present method is very effective for decarboxylative alkynylation of  $\alpha$ -amino acid derivatives with terminal alkynes.

To explore the mechanism for the visible-light photoredox decarboxylative alkynylation, the reaction of 1,3-dioxoisoindolin-2-yl 2-(diethylamino)-3-methylbutanoate (1a) with phenylacetylene (2a) was performed in the presence of 2 equiv of 2,2,6,6-tetramethyl-1-piperidinyloxy as the radical-trapping

Table 2. Decarboxylative Alkynylation of  $\alpha$ -Amino Acid Derivatives (1) with Terminal Alkynes (2) by Merging Photoredox with Copper Catalysis

<sup>a</sup>Reaction conditions: irradiation of visible light with 40 W CFL and argon atmosphere, N-(acetoxy)phthalimide of  $\alpha$ -amino acid (1) (0.6 mmol), alkyne (2) (0.3 mmol),  $[Ru(bpy)_3Cl_2]$  (3  $\mu$ mol), CuI (0.03 mmol), CH<sub>2</sub>Cl<sub>2</sub> (2.0 mL), rt (~25 °C), 6-24 h in a sealed Schlenk tube. <sup>b</sup>Isolated yield.

3ac (6 h. 84%)

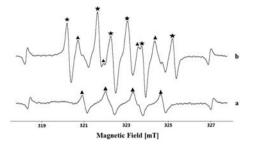
Scheme 1. Synthesis of Compound 3d on Gram Scale by Merging Photoredox with Copper Catalysis under Standard Conditions

agent under the standard conditions, and no reaction occurred, which demonstrated that the reaction could undergo a free-

3ad (6 h, 81%)

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radical intermediate process. We investigated the types of the radicals produced during the reaction by electron spin resonance (ESR). As shown in Figure 1a, a solution of active ester 1a (100



**Figure 1.** Investigations of mechanism for the decarboxylative alkynylation by ESR. ESR spectra of the mixtures under different conditions: (a) Capillary with solution of active ester **1a** (100 mM), Ru(bpy) $_3$ Cl $_2$  (1 mM), CuI (10 mM), DMPO (100 mM), and CH $_2$ Cl $_2$  (200  $\mu$ L) was irradiated under Ar for 1 min and then detected by ESR. (b) Capillary with solution of active ester **1a** (50 mM), Ru(bpy) $_3$ Cl $_2$  (1 mM), and CuI (10 mM) in CH $_2$ Cl $_2$  (100  $\mu$ L) was irradiated under Ar for 5 min, and then DMPO (100 mM) in DCM (100  $\mu$ L) was injected with a syringe, and the resulting solution was detected by ESR.

mM), Ru(bpy) $_3$ Cl $_2$  (1 mM), CuI (10 mM), 5,5-dimethyl-1-pyrroline N-oxide (DMPO) (100 mM), and CH $_2$ Cl $_2$  (200  $\mu$ L) was bubbled with Ar for 5 min, and a small amount of solution was transferred into a capillary. The capillary was irradiated with a 40 W CFL bulb for 1 min and analyzed by ESR. A quartet peak signal (marked with triangles) was observed with a g value of 2.003,  $A_N$  = 1.33 mT,  $A_H$  = 1.21 mT, and it was presumed to be from an adduct of a nitrogen radical (corresponding to the nitrogen radical of I in Scheme 2) with DMPO. As shown in Figure 1b, a capillary with a solution of active ester a (50 mM), Ru(bpy) $_3$ Cl $_2$  (1 mM), and CuI (10 mM) in CH $_2$ Cl $_2$  (100  $\mu$ L) was irradiated with a 40 W CFL bulb for 5 min under Ar atmosphere, and then DMPO (100 mM) in CH $_2$ Cl $_2$  (100  $\mu$ L) was injected into the solution with a syringe. The resulting mixture was transferred into a capillary and analyzed by ESR, and

Scheme 2. Plausible Mechanism for the Decarboxylative Alkynylation by Merging Photoredox with Copper Catalysis

two groups of radical signals were observed; they were from adducts of a carbon or nitrogen radical with DMPO (corresponding to I and IV, respectively, in Scheme 2). A sextet peak signal (marked with the stars) with a g value of 2.003,  $A_{\rm N}$  = 1.44 mT,  $A_{\rm H}$  = 2.11 mT was assigned to be from an adduct of a carbon radical with DMPO. <sup>21</sup>

A plausible mechanism for the decarboxylative alkynylation is proposed in Scheme 2 according to the results above and the previous research.  $^{7,13-19}$  Irradiation of  $Ru(bpy)_3^{2+}$  with visible light gives the excited-state  $[Ru(bpy)_3^{2+}]^*$ , and the photoexcited catalyst was reduced by the tertiary amine in 1 to provide  $Ru(bpy)_3^+$  and radical cation  $L^{22}$  A single electron transfer from  $Ru(bpy)_3^+$  to phthalimide in another 1 leads to radical anion II, regenerating catalyst  $Ru(bpy)_3^{2+}$ , with subsequent cleavage of phthalimide anion III and carbon dioxide from II to provide carbon radical IV. IV is then oxidized by an excited catalyst  $[Ru(bpy)_3^{2+}]^*$  to regenerate the  $Ru(bpy)_3^+$  state and deliver an iminium ion  $V^{23}$  Meanwhile, treatment of terminal alkyne with CuI in the presence of III yields VII, freeing phthalimide VI and I $^-$ , and nucleophilic attack of VII to V affords the desired target product  $3,^{7,23}$  liberating the copper catalyst.

In summary, we have developed a novel and efficient decarboxylative alkynylation of  $\alpha$ -amino acid derivatives with terminal alkynes by merging photoredox with copper catalysis at room temperature. Valuable propargylamines were prepared in good to excellent yields with tolerance of various functional groups. The method exhibited some advantages, including readily available  $\alpha$ -amino acid derivatives and terminal alkynes as the staring materials, a simple protocol, mild reaction conditions, high efficiency, and no addition of extra base and additive. The present method provides a convenient and practical strategy for dual catalysis by merging photoredox with transition-metal catalysis, and we believe that it will find wide applications in organic synthesis.

#### ASSOCIATED CONTENT

## S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b03888.

Experimental details, NMR data (PDF)

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### **Notes**

The authors declare no competing financial interest.

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