JOC The Journal of Organic Chemistry

Article

pubs.acs.org/joc

9,10-Dicyanoanthracene Catalyzed Decarboxylative Alkynylation of Carboxylic Acids under Visible-Light Irradiation

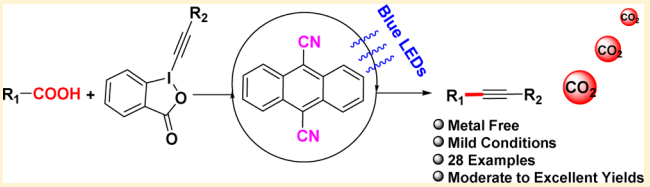
Chen Yang,[†] Jin-Dong Yang,[‡] Yi-He Li,[†] Xin Li,*[,‡] and Jin-Pei Cheng*[,†,‡]

[†]Department of Chemistry and Biology, College of Science, National University of Defense Technology, Changsha 410073, China

[‡]State Key Laboratory of Elemento-organic Chemistry, Collaborative Innovation Center of Chemical Science and Engineering, Nankai University, Tianjin 300071, China

Supporting Information

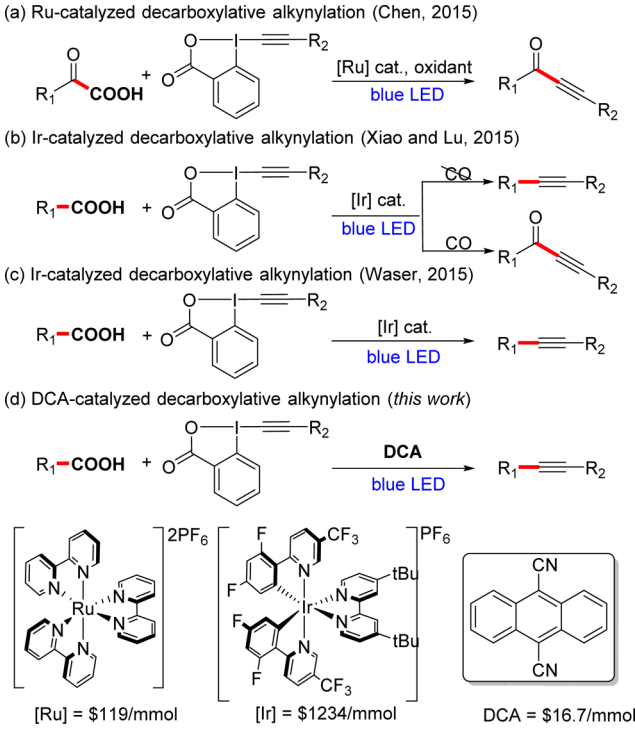
ABSTRACT: A metal-free, visible-light-induced photocatalytic procedure for decarboxylative alkynylation of carboxylic acids was reported. With 9,10-dicyanoanthracene as the photoredox catalyst, the reaction covered a broad scope of α-amino acids, α-oxo acids, and α-keto acids with blue LED irradiation at room temperature under an atmosphere of argon, delivering alkynyl products in moderate to excellent yields. Natural sun light also promoted this alkynylation strategy. This work represents the first example of an organophotocatalytic method for decarboxylative alkynylation of carboxylic acids.



INTRODUCTION

Carboxylic acids, as abundant and inexpensive basic chemicals, have numerous applications in synthetic organic chemistry and industry.[1] One of them is the decarboxylative oxidation of aliphatic carboxylic acids, which has attracted growing attention in the past years.[1a,e] In this regard, the transition-metal-catalyzed decarboxylative procedure is a most conventional method.[2] Since the MacMillan group first introduced photochemistry into the realm of asymmetric catalysis in 2008,[3] visible-light photoredox catalysis has gradually become a competitive tool in many aspects of synthetic chemistry.[4,5] This strategy can be utilized as a versatile tool to trigger many radical reactions under very mild conditions. Recently, visible-light-induced decarboxylative functionalizations of carboxylic acids were developed and have been emerged as a novel, powerful tool to construct C−C and C−X bonds.[5,6] As a result, numerous challengeable transformations on the basis of carboxylic acids, such as alkylation,[6a] amidation,[6b] arylation,[6c] anhydride decarboxylation,[6d] vinylation,[6e] decarboxylative reduction,[6f] halogenation,[6g] trifluoromethylation,[6h] trifluoromethylthiolation,[6i] and hydroxylation[6j] reactions, have been achieved.[5,6] Very recently, visible-light-induced decarboxylative alkynylation reactions have been explored with hypervalent iodine(III) reagents[7] (Scheme 1). The Chen group reported the decarboxylative ynonylation of α-keto acids with ethynylbenziodoxolones and an extra oxidant by employment of a $Ru(bpy)_3(PF_6)_2$ photocatalyst (Scheme 1a).[8] Shortly afterward, the Xiao[9] and Waser[10] group independently developed a direct decarboxylative alkynylation reaction with $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$, avoiding the need for an external oxidant. Xiao, Lu and co-workers found that various carboxylic acids, including aliphatic, α-keto, and α-amino acids, are compatible in the reaction (Scheme 1b). Notably, this methodology can also obtain ynones in the presence of carbon monoxide. Waser and co-workers applied this method to synthesize a series of silyl-, alkyl-, and aryl-substituted alkynes (Scheme 1c). While the above-mentioned strategy of photoinduced decarboxylative

Scheme 1. Photocatalytic Decarboxylative Alkynylation Reactions[11]



Received: September 30, 2016
Published: November 29, 2016

DOI: 10.1021/acs.joc.6b02385
J. Org. Chem. 2016, 81, 12357−12363

alkynylation is quite remarkable, it suffers from the use of either expensive metal photoredox catalysts or an external oxidant and the up-scaling problem related to the cost of noble metal catalysis. Therefore, new approaches to realize the visible-light-induced decarboxylative alkynylation with organic type photoredox catalysts, which can reduce the cost of the reaction, now remain as a formidable challenge and are still highly desirable (Scheme 1d).

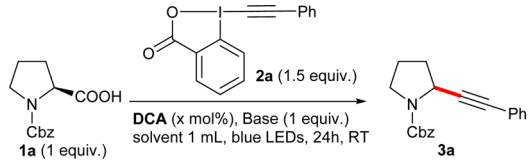
Currently, cheap organic dyes have been proven to be a reliable option to the replacement of those metal photoredox catalysts in many valuable transformations.[4b,f,12,13] Theoretically, if its redox window covered the oxidation potential of carboxylate (E_{ox} = +0.95v (*tert*-butoxycarbonyl)prolinate vs the saturated calomel electroder),[10] an organic dye would be feasible to play the role of a metal photocatalyst. Cyanoarenes, such as 9,10-dicyanoanthracene (**DCA**, E_{red}* = +1.99 V), are classic exemplars with high singlet excited-state oxidation potentials.[4b] Meanwhile, **DCA** possesses a longer singlet lifetime and absorbs visible light (λ_{max} = 422 nm). Additionally, its price is much cheaper than corresponding metal photoredox catalysts (Scheme 1). Although **DCA** has the capability of powerful excited oxidation, to the best of our knowledge, there is no report on the photo-oxidation of carboxylic acids by use of **DCA**.[13] Thus, we saw an opportunity to demonstrate the utility of **DCA** to realize the task of decarboxylative alkynylation (Scheme 1d).[14] Herein, we report the first organophotocatalytic method for decarboxylative alkynylation of carboxylic acids.

RESULTS AND DISCUSSION

Using 10 mol % **DCA** as the photocatalyst and a commercially available blue LED strip as the light source, our investigations began with Cbz-protected proline (**1a**) and phenyl ethynylbenziodoxolone (**2a**) (Table 1). The model reaction was initially performed in 1.0 mL of DMF with 1.0 equiv of cesium carbonate, and the desired alkynylated product **3a** was obtained, albeit the yield was only 11% (entry 1). Encouraged by this promising result, we then screened a set of solvents (entries 1−10). Chloroform was designated as optimal due to its delivery of the best result among the examined media (entry 7). The amount and kind of bases were subsequently examined (entries 11−16). Doubling the amount of base further raised the yield of product to 70% (entry 11). With 2 equiv of base, potassium carbonate was found to give the best yield of product **3a** (93%) among the examined bases (entry 16). Lowering the catalyst loading to 5 mol % had little influence on the yield (entry 17). However, the yields decreased sharply with further reduction of the catalyst loading (entries 18−19). Control experiments indicated that a photocatalyst, light source, base and inert atmosphere were necessary for this catalytic system (entries 20−23). Collectively, the optimal conditions were established by performing the reaction with **1a** (0.1 mmol), **2a** (0.15 mmol), K_2CO_3 (0.2 mmol), and **DCA** (5 mol %) in 1.0 mL of chloroform at room temperature under an atmosphere of argon and the irradiation of a blue LED strip (entry 17).

We then evaluated the substrate scope with the optimal reaction conditions (Scheme 2). Cyclic α-amino acids were first examined, and corresponding alkynylated products **3a−3e** were obtained with satisfactory yields (70−92%). Both *N*-Fmoc and *N*-Boc protected amino acids with various aliphatic side chains were compatible, affording decarboxylative products **3f−3p** in moderate to excellent yields (65−96%). Notably, amino acids equipped with functional groups in the side chains, including

Table 1. Optimization of the Reaction Conditions[a]



entry	solvent	base	*x* mol %	% yield[b]
1	DMF	Cs_2CO_3	10	11
2	DMSO	Cs_2CO_3	10	12
3	THF	Cs_2CO_3	10	19
4	EtOAc	Cs_2CO_3	10	37
5	EtOH	Cs_2CO_3	10	52
6	DCM	Cs_2CO_3	10	56
7	$CHCl_3$	Cs_2CO_3	10	62
8	Et_2O	Cs_2CO_3	10	33
9	anisole	Cs_2CO_3	10	52
10	toluene	Cs_2CO_3	10	19
11[c]	$CHCl_3$	Cs_2CO_3	10	70
12[c]	$CHCl_3$	NaOH	10	20
13[c]	$CHCl_3$	TMG	10	6
14[c]	$CHCl_3$	Na_2CO_3	10	47
15[c]	$CHCl_3$	$KHCO_3$	10	43
16[c]	$CHCl_3$	K_2CO_3	10	93
17[c]	**$CHCl_3$**	**K_2CO_3**	**5**	**92**
18[c]	$CHCl_3$	K_2CO_3	3	60
19[c]	$CHCl_3$	K_2CO_3	1	31
20[c]	$CHCl_3$	K_2CO_3	0	no reaction
21[c,d]	$CHCl_3$	K_2CO_3	5	no reaction
22[c,e]	$CHCl_3$	K_2CO_3	5	no reaction
23[c,f]	$CHCl_3$	−	5	<5%

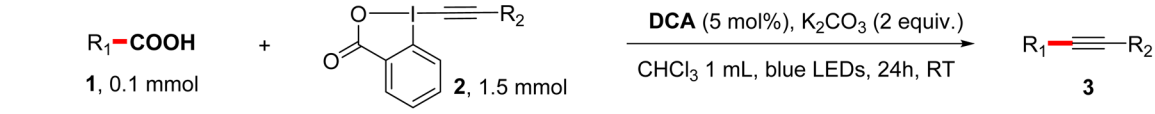
[a]Unless noted, the reaction was carried out with **1a** (0.1 mmol), **2a** (0.15 mmol), base (0.1 mmol), and **DCA** (10 mol %) in 1.0 mL of solvent at room temperature under an atmosphere of argon and the irradiation of a blue LED strip for 24 h. [b]Isolated yield. [c]0.2 mmol base was used. [d]In the absence of a light source. [e]In the presence of air. [f]No base was used.

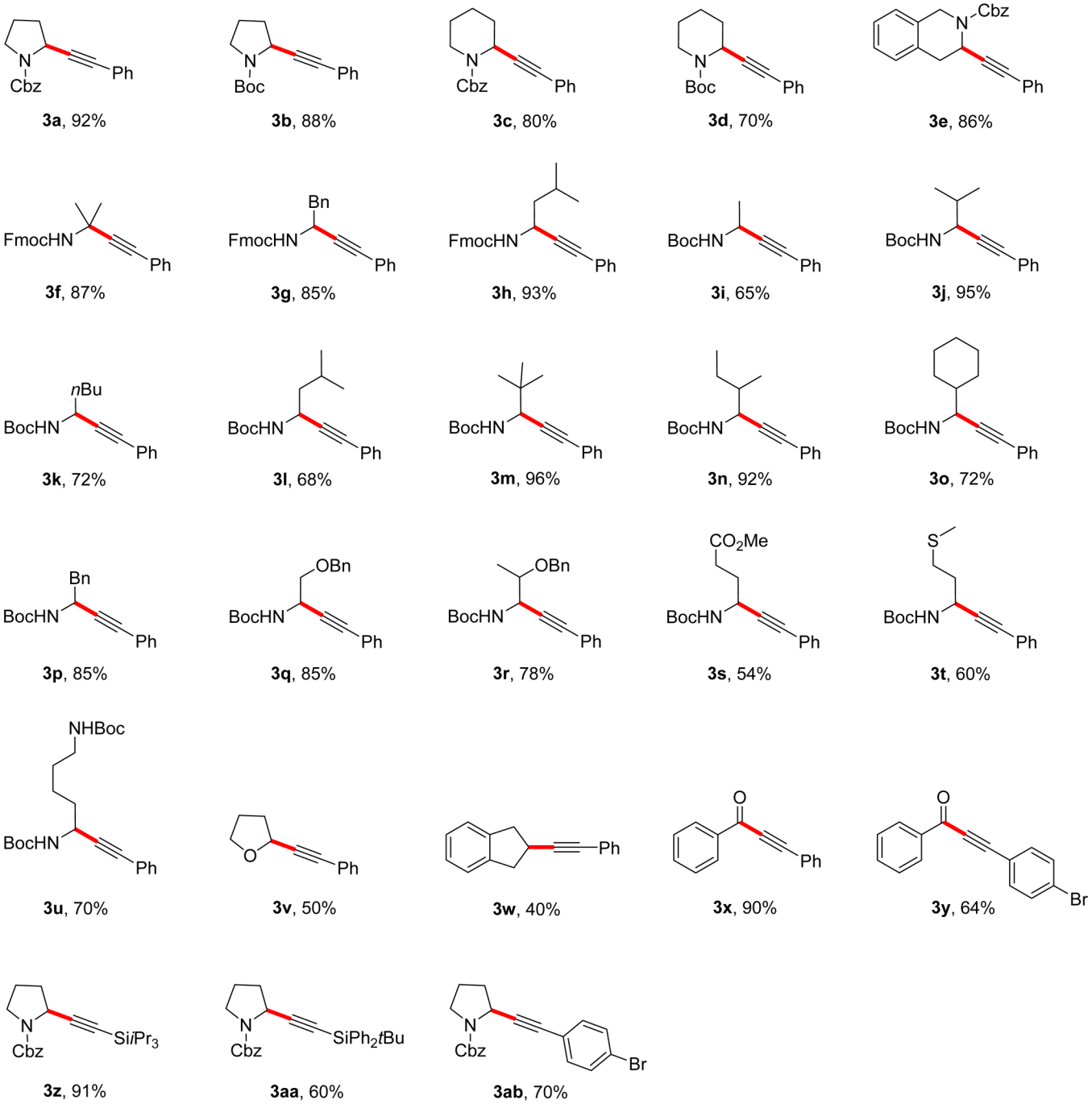
ethers, esters, thioethers, and amines, can also be easily converted to the phenylethynylated products **3q−3u** in 54−85% yields. Moreover, the alkynylation of α-oxo acid can also occur, in which **3v** was isolated in 50% yield. However, the efficiency of this catalytic system for aliphatic carboxylic acid is not as high as that in the case of α-heteroatom acids. Product **3w** was obtained only in 40% yield. To our delight, the reaction also works well in the case of α-keto acids. As a result, the ynonylated products **3x** and **3y** were isolated 90% and 64% yields, respectively. To further explore the substrate scope, the reactivity of three other hypervalent iodine reagents was inspected with **1a**. Silyl as well as electron-poor phenyl substituted ethynylbenziodoxolones underwent the alkynylation smoothly, giving **3z−3ab** in 60−91% yields.

To expand the synthetic applicability of the products, three experiments were performed. The model reaction was first carried out under natural sun light (Scheme 3a). After 10 h, the desired product **3a** was obtained in 83% yield. The satisfactory yield of a gram-scale reaction exhibited the convenient scaled-up ability of this catalytic system (Scheme 3b). We subsequently converted product **3m** to a *N*-allylated product **4**, which is the precursor in the preparation of cyclic product **5** (Scheme 3c).[15]

DOI: 10.1021/acs.joc.6b02385
J. Org. Chem. 2016, 81, 12357−12363

Scheme 2. Reaction Scope of Photocatalytic Decarboxylative Alkynylation[a,b]



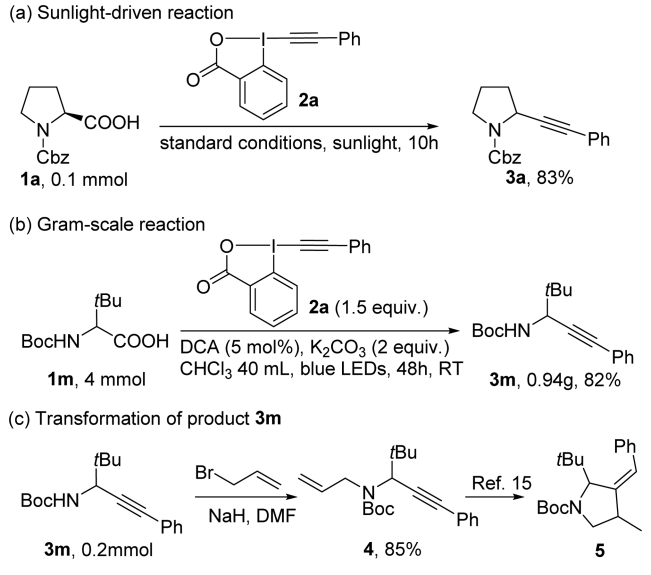


[a]The reaction was carried out with **1** (0.1 mmol), **2** (0.15 mmol), K_2CO_3 (0.2 mmol), and **DCA** (5 mol %) in chloroform (1.0 mL) at room temperature under an atmosphere of argon and the irradiation of a blue LED strip for 24 h. [b]Isolated yield.

To probe the mechanism, a standard Stern−Volmer analysis was conducted (Figure 1).[16] Under basic conditions, it was found that the excited state of *DCA can be quenched by substrate **1a**. However, no obvious change of *DCA luminescence in the presence of variable concentrations of **2a** was observed. Although comprehensive studies will be needed to gain a good understanding of the current strategy, a putative mechanism was proposed to describe the decarboxylative alkynylation reactions based on the quenching experiments and previously studied photoredox catalysis (Scheme 4).[9,10] Under the irradiation of a light source, excited **DCA** would oxidize the deprotonated acid **1**. This progress would lead to the formation

DOI: 10.1021/acs.joc.6b02385
J. Org. Chem. 2016, 81, 12357−12363

Scheme 3. Synthetic Utility of the Methodology



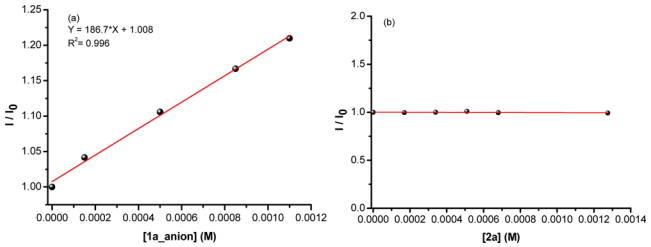
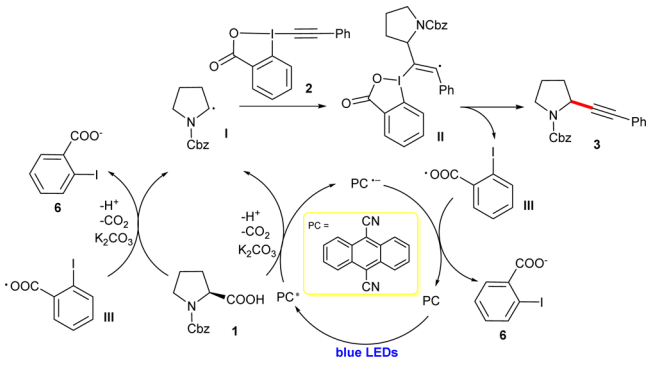


Figure 1. Stern–Volmer quenching studies for (a) **1a**_anion, (b) **2a**.

Scheme 4. Proposed Reaction Mechanism



of a reduced species and carboxyl radical. Because of a negative bond dissociation enthalpy of the carboxyl radical,[17] a carbon radical intermediate **I** would be quickly generated through the release of CO_2. Addition of **I** to substrate **2** would deliver an unstable radical adduct **II**, which would undergo a β-elimination to yield the desired product **3** and benziodoxolonyl radical **III**. The redox potential of the reduced photocatalyst is −0.91 V,[4b] which is comparable with the well-known iridium catalyst ($E^{red}[Ir^{III}/Ir^{II}]$ = −1.37 V)[9,10] used in decarboxylative transformations. Thus, radical **III** can be reduced to 2-iodobenzoate **6** by this species, finishing the catalytic cycle and regenerating the catalyst. Besides, a chain propagation pathway cannot be excluded at present.[18] The intermediate **III** could work as a direct oxidant for the deprotonated acid **1** to yield another radical intermediate **I**, which would react with substrate **2** to give the product **3**.

CONCLUSIONS

In conclusion, we have developed an efficient, organo-photocatalytic method for decarboxylative alkynylation of carboxylic acids for the first time. The reaction can be carried out at room temperature by using visible light with only 5 mol % of cheaply organic type photocatalyst **DCA**. A set of amino acids, as well as α-oxo acids and α-keto acids, can be smoothly converted to the corresponding products in moderate to excellent yields through the current strategy. The feature of this methodology, that is the metal-free, optional-solar-light-driven, feasibly scaled-up, and synthetic-utility product, may make itself useful in organic synthesis and industry.

EXPERIMENTAL SECTION

General Information. Commercial reagents were used as received, unless otherwise stated. The purchased solvents were dried over molecular sieves and degassed by three cycles of freeze–pump–thaw before use in the reaction. ^1H and ^{13}C NMR were recorded on a spectrometer. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard. The following abbreviations were used to designate chemical shift mutiplicities: s = singlet, d = doublet, t = triplet, q = quartet, h = heptet, m = multiplet, br = broad. All first-order splitting patterns were assigned on the basis of the appearance of the multiplet. Splitting patterns that could not be easily interpreted are designated as multiplet (m) or broad (br). Mass spectra were obtained using the ESI mode with a double focusing mass analyzer. The hypervalent iodine(III) reagents were prepared according to known methods reported by the Waser group.[10]

General Procedure for the Decarboxylative Alkynylation Reaction. Carboxylic acids **1** (0.1 mmol), ethynylbenziodoxolones **2** (0.15 mmol), K_2CO_3 (0.2 mmol), **DCA** (1.1 mg), and a magnetic stir bar were added to an oven-dried 10 mL Schlenk tube. The reaction mixture was degassed three times. 1 mL of degassed chloroform was then added to the mixture in the presence of a flow of argon. The solution was placed at a distance of about 5 cm from a 5 W blue LED strip and irradiated for 24 h. Afterward, the crude mixture was purified by column chromatography (eluent: petroleum ether/ethyl acetate 40:1 to 5:1) to give the product **3**.

Procedure for the Sunlight-Driven Decarboxylative Alkynylation Reaction. **1a** (0.1 mmol), **2a** (0.15 mmol), K_2CO_3 (0.2 mmol), **DCA** (1.1 mg), and a magnetic stir bar were added to an oven-dried 10 mL Schlenk tube. The reaction mixture was degassed three times. 1 mL of degassed chloroform was then added to the mixture in the presence of a flow of argon. The solution was stirred under solar light for 10 h (Location: 39°6′2″ *N*, 117°9′51″ *E*). Afterward, the crude mixture was purified by column chromatography (eluent: petroleum ether/ethyl acetate 10:1) to give the product **3a** in 83% yield as a colorless oil.

Procedure for the Gram-Scale Reaction. **1m** 0.92g (4 mmol), **2a** 2.08g (6 mmol), K_2CO_3 1.12g (0.2 mmol), **DCA** (40 mg), 40 mL of chloroform, and a magnetic stir bar were added to an oven-dried 100 mL two-neck flask. The reaction mixture was degassed by using a freeze–pump–thaw procedure three times. The solution was placed at a distance of about 5 cm from a 5 W blue LED strip and irradiated for 48 h. Afterward, the crude mixture was purified by column chromatography (eluent: petroleum ether/ethyl acetate 30:1) to give the product **3m** (0.94 g) in 82% yield as a yellow oil.

Procedure for the Transformation of Product 3m. The transformation was performed according to a known method reported by the Shin group.[19] Under an atmosphere of argon, 0.2 mmol of **3m** and 0.6 mL of anhydrous DMF were added to an oven-dried 10 mL Schlenk tube. The solution was cooled to 0 °C, and 10 mg of NaH (60% dispersion in mineral oil) were then added. When gas evolution ceased, 36.4 mg of allyl bromide were added. The reaction mixture was

DOI: 10.1021/acs.joc.6b02385
J. Org. Chem. 2016, 81, 12357–12363

warmed to room temperature and stirred for 4 h. When the reaction was completed, 2.8 mL of water were added. The resulting aqueous layer was extracted with Et_2O (4 mL × 3). The combined organic layer was dried with Na_2SO_4 for 4 h. Na_2SO_4 was removed by filtration, and the solvent was evaporated. The residue was purified by chromatography (petroleum ether/ethyl acetate, 15:1) to give **4** (55.4 mg, 85%) as a light yellow oil.

Procedure for the Luminescence Quenching Experiments. The experiments were carried out on a fluorescence spectrophotometer. All samples were prepared in MeOH solution. To a glass cuvette, solutions of photocatalyst, quencher, and MeOH were added to obtain a total volume of 5.0 mL. Before determination, the solution was degassed by three freeze−pump−thaw cycles and backfilled with argon. When **1a** was used as the quencher, 1.5 equiv of NaOH were added. The concentration of DCA was 1.4×10^{-6} M. All samples were irradiated at 401 nm, and emission was determined at 432 nm.

*Benzyl 2-(Phenylethynyl)pyrrolidine-1-carboxylate (**3a**).* Colorless oil; 28.1 mg, 92% yield. Analytical data matched previously reported values.[10] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41−7.14 (m, 10H), 5.30−5.02 (m, 2H), 4.82−4.64 (m, 1H), 3.56−3.49 (m, 1H), 3.41−3.33 (m, 1H), 2.20−2.02 (m, 3H), 1.96−1.86 (m, 1H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.7, 137.1, 132.0, 131.8, 128.5, 128.3, 128.2, 128.1, 127.8, 127.7, 123.0, 89.6, 82.4, 66.9, 49.3, 48.8, 46.3, 45.9, 34.1, 33.4, 24.6, 23.9 ppm.

*tert-Butyl 2-(Phenylethynyl)pyrrolidine-1-carboxylate (**3b**).* Colorless oil; 23.9 mg, 88% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45−7.36 (m, 2H), 7.35−7.24 (m, 3H), 4.96−4.60 (m, 1H), 3.62−3.27 (m, 2H), 2.24−1.87 (m, 4H), 1.52 (s, 9H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.3, 131.7, 128.6, 128.1, 123.3, 82.9, 81.6, 79.8, 48.9, 45.7, 28.6, 23.9, 17.5 ppm. HRMS (ESI): calcd for $[C_{17}H_{21}NO_2 + H]^+$ 272.1651, found 272.1644.

*Benzyl 2-(Phenylethynyl)piperidine-1-carboxylate (**3c**).* Light yellow oil; 25.5 mg, 80% yield. Analytical data matched previously reported values.[20] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50−7.28 (m, 10H), 5.46 (br. s, 1H), 5.30−5.20 (m, 2H), 4.14 (d, J = 13.1 Hz, 1H), 3.27 (t, J = 13.0 Hz, 1H), 2.05−1.90 (m, 2H), 1.85−1.70 (m, 3H), 1.60−1.45 (m, 1H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.2, 136.9, 131.9, 128.6, 128.4, 128.3, 128.1, 127.9, 123.0, 87.3, 84.6, 67.4, 45.1, 40.9, 30.9, 25.5, 20.2 ppm.

*tert-Butyl 2-(Phenylethynyl)piperidine-1-carboxylate (**3d**).* Colorless oil; 20.0 mg, 70% yield. Analytical data matched previously reported values.[21] ^{1}H NMR (400 MHz, $CDCl_3$) δ7.45−7.38 (m, 2H), 7.33−7.26 (m, 3H), 5.28 (s, 1H), 3.96 (d, J = 13.5 Hz, 1H), 3.11 (t, J = 12.8 Hz, 1H), 1.93−1.78 (m, 2H), 1.77−1.61 (m, 3H), 1.49 (s, 9H), 1.49−1.40 (m, 1H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.8, 131.9, 128.4, 128.2, 123.3, 87.8, 84.3, 80.1, 44.9, 40.7, 30.9, 25.5, 20.3 ppm.

*Benzyl 3-(Phenylethynyl)-3,4-dihydroisoquinoline-2(1H)-carboxylate (**3e**).* Colorless oil; 31.6 mg, 86% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39−6.99 (m, 14H), 5.72−5.42 (m, 1H), 5.14 (s, 2H), 4.87 (d, J = 16.6 Hz, 1H), 4.52 (d, J = 16.5 Hz, 1H), 3.20 (dd, J = 15.6, 5.2 Hz, 1H), 2.92 (d, J = 15.9 Hz, 1H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.2, 141.6, 136.6, 134.1, 133.2, 131.9, 129.1, 128.7, 128.4, 128.2, 128.1, 126.7, 126.6, 126.2, 122.7, 87.0, 83.5, 67.7, 66.8, 43.3, 34.9, 29.8 ppm. HRMS (ESI): calcd for $[C_{25}H_{21}NO_2 + H]^+$ 368.1651, found 368.1645.

*(9H-Fluoren-9-yl)methyl 2-Methyl-4-phenylbut-3-yn-2-ylcarbamate (**3f**).* White solid; mp:144−149 °C; 33.2 mg, 87% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 7.5 Hz, 2H), 7.62 (d, J = 7.5 Hz, 2H), 7.49−7.20 (m, 9H), 5.08 (s, 1H), 4.42 (d, J = 6.7 Hz, 2H), 4.23 (t, J = 7.0 Hz, 1H), 1.69 (s, 6H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.5, 144.1, 141.4, 131.9, 128.3, 127.8, 127.2, 125.2, 122.9, 120.1, 92.7, 81.3, 66.4, 48.3, 47.4, 29.5 ppm. HRMS (ESI): calcd for $[C_{26}H_{23}NO_2 + H]^+$ 382.1807, found 382.1808.

*(9H-Fluoren-9-yl)methyl 1,4-Diphenylbut-3-yn-2-ylcarbamate (**3g**).* White solid; mp: 100−104 °C; 37.7 mg, 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, J = 7.6 Hz, 2H), 7.62 (d, J = 7.6 Hz, 2H), 7.48−7.29 (m, 14H), 5.08−4.72 (m, 2H), 4.54 (dd, J = 10.6, 7.0 Hz, 1H), 4.42 (t, J = 8.7 Hz, 1H), 4.26 (t, J = 6.9 Hz, 1H), 3.22−2.85 (m, 2H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.3, 143.9, 141.5, 131.8, 130.2, 128.6, 128.5, 128.4, 127.9, 127.2, 127.1, 125.3, 125.2, 122.5, 120.1, 87.7, 84.8, 67.0, 47.4, 45.1, 42.0 ppm. HRMS (ESI): calcd for $[C_{31}H_{25}NO_2 + H]^+$ 444.1964, found 444.1957.

*(9H-Fluoren-9-yl)methyl 5-Methyl-1-phenylhex-1-yn-3-ylcarbamate (**3h**).* White solid; mp: 93−98 °C; 38.1 mg, 93% yield. Analytical data matched previously reported values.[9] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, J = 7.5 Hz, 2H), 7.62 (d, J = 6.9 Hz, 2H), 7.46−7.27 (m, 9H), 5.01 (d, J = 9.0 Hz, 1H), 4.76 (q, J = 8.0 Hz, 1H), 4.51−4.40 (m, 2H), 4.25 (t, J = 7.0 Hz, 1H), 1.91−1.82 (m, 1H), 1.66 (t, J = 7.4 Hz, 2H), 1.00 (d, J = 6.6 Hz, 6H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.6, 144.0, 141.4, 131.8, 129.1, 128.4, 128.4, 127.9, 127.8, 127.2, 125.2, 122.8, 120.1, 88.8, 83.3, 66.9, 47.4, 45.6, 42.7, 25.2, 22.8, 22.2 ppm.

*tert-Butyl 4-Phenylbut-3-yn-2-ylcarbamate (**3i**).* White solid; mp: 76−80 °C; 15.9 mg, 65% yield. Analytical data matched previously reported values.[22,23] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44−7.36 (m, 2H), 7.35−7.28 (m, 3H), 4.95−4.55 (m, 2H), 1.50−1.42 (m, 12H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.9, 131.8, 128.4, 122.9, 90.0, 82.2, 80.0, 39.2, 28.5, 23.1 ppm.

*tert-Butyl 4-Methyl-1-phenylpent-1-yn-3-ylcarbamate (**3j**).* Light yellow oil; 26.0 mg, 95% yield. Analytical data matched previously reported values.[23] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45−7.37 (m, 2H), 7.33−7.27 (m, 3H), 4.82 (brs, 1H), 4.54 (brs, 1H), 2.03−1.93 (m, 1H), 1.47 (s, 9H), 1.04 (d, J = 5.1 Hz, 6H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.2, 131.8, 128.4, 128.3, 123.1, 87.6, 83.9, 79.9, 49.4, 33.6, 28.5, 19.0 ppm.

*tert-Butyl 1-Phenylhept-1-yn-3-ylcarbamate (**3k**).* Light yellow oil; 20.7 mg, 72% yield. Analytical data matched previously reported values.[23] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44−7.38 (m, 2H), 7.32−7.27 (m, 3H), 4.78 (s, 1H), 4.62 (d, J = 9.5 Hz, 1H), 1.78−1.66 (m, 2H), 1.51−1.32 (m, 13H), 0.92 (t, J = 7.2 Hz, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.9, 131.7, 128.3, 128.2, 122.9, 89.1, 82.8, 80.0, 43.6, 36.4, 28.5, 27.9, 22.3, 14.2 ppm.

*tert-Butyl 5-Methyl-1-phenylhex-1-yn-3-ylcarbamate (**3l**).* Light yellow oil; 19.5 mg, 68% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45−7.35 (m, 2H), 7.33−7.28 (m, 3H), 4.82−4.60 (m, 2H), 1.81−1.94 (m, 1H), 1.67−1.54 (m, 2H), 1.47 (s, 9H), 0.97 (d, J = 5.4 Hz, 6H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.0, 131.8, 128.4, 128.3, 123.1, 89.3, 82.9, 79.9, 45.8, 42.2, 28.5, 25.3, 23.0, 22.1 ppm. HRMS (ESI): calcd for $[C_{18}H_{25}NO_2 + H]^+$ 288.1964, found 288.1958.

*tert-Butyl 4,4-Dimethyl-1-phenylpent-1-yn-3-ylcarbamate (**3m**).* Yellow oil; 27.6 mg, 96% yield. Analytical data matched previously reported values.[23] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45−7.38 (m, 2H), 7.31−7.27 (m, 3H), 4.78 (d, J = 9.9 Hz, 1H), 4.46 (d, J = 9.9 Hz, 1H), 1.47 (s, 9H), 1.04 (s, 9H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.5, 131.8, 128.4, 128.3, 123.2, 88.2, 83.8, 79.8, 52.9, 36.2, 28.5, 26.1 ppm.

*tert-Butyl 4-Methyl-1-phenylhex-1-yn-3-ylcarbamate (**3n**).* Colorless oil; 26.4 mg, 92% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (dd, J = 6.7, 3.0 Hz, 2H), 7.33−7.27 (m, 3H), 4.90−4.74 (m, 1H), 4.71−4.56 (m, 1H), 1.73 (d, J = 9.6 Hz, 1H), 1.65−1.53 (m, 2H), 1.47 (s, 9H), 1.02 (dd, J = 6.7, 3.2 Hz, 3H), 0.99−0.93 (m, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.2, 131.9, 131.8, 128.4, 128.3, 128.3, 123.1, 88.3, 83.6, 79.9, 48.2, 40.4, 29.8, 28.5, 26.4, 25.2, 15.5, 11.8 ppm. HRMS (ESI): calcd for $[C_{18}H_{25}NO_2 + H]^+$ 288.1964, found 288.1958.

*tert-Butyl 1-Cyclohexyl-3-phenylprop-2-ynylcarbamate (**3o**).* White solid; mp: 92−96 °C; 22.6 mg, 72% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45−7.37 (m, 2H), 7.32−7.27 (m, 3H), 4.83 (d, J = 9.2 Hz, 1H), 4.52 (dd, J = 9.3, 5.9 Hz, 1H), 1.91−1.74 (m, 4H), 1.71−1.63 (m, 2H), 1.46 (s, 9H), 1.33−1.08 (m, 5H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.2, 131.8, 128.4, 128.3, 123.1, 88.1, 83.8, 79.9, 48.7, 43.2, 29.4, 28.5, 26.4, 26.1, 26.0 ppm. HRMS (ESI): calcd for $[C_{20}H_{27}NO_2 + H]^+$ 314.2120, found 314.2121.

*tert-Butyl 1,4-Diphenylbut-3-yn-2-ylcarbamate (**3p**).* Light yellow solid; mp: 85−90 °C; 27.3 mg, 85% yield. Analytical data matched previously reported values.[9] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41−7.28 (m, 10H), 4.93 (m, 1H), 4.83 (m, 1H), 3.14−3.02 (m, 2H), 1.48 (d, J = 1.9 Hz, 9H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.8, 136.8, 131.7, 130.1, 128.5, 128.4, 127.0, 122.8, 88.3, 84.4, 80.1, 44.7, 42.2, 28.5 ppm.

DOI: 10.1021/acs.joc.6b02385
J. Org. Chem. 2016, 81, 12357−12363

*tert-Butyl 1-(Benzyloxy)-4-phenylbut-3-yn-2-ylcarbamate (**3q**).* Colorless oil; 29.9 mg, 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46−7.26 (m, 10H), 5.06 (s, 1H), 4.86 (s, 1H), 4.71−4.58 (m, 2H), 3.68 (d, J = 4.8 Hz, 2H), 1.47 (s, 9H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.1, 138.0, 131.9, 128.6, 128.5, 128.4, 127.9, 127.8, 122.8, 87.1, 83.3, 80.2, 73.4, 72.3, 43.6, 28.5 ppm. HRMS (ESI): calcd for $[C_{22}H_{25}NO_3 + Na]^+$ 374.1732, found 374.1730.

*tert-Butyl 4-(Benzyloxy)-1-phenylpent-1-yn-3-ylcarbamate (**3r**).* Colorless oil; 28.5 mg, 78% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55−7.22 (m, 10H), 5.18−4.98 (m, 1H), 4.82−4.53 (m, 3H), 3.84−3.72 (m, 1H), 1.46 (m, 9H), 1.36−1.25 (m, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.3, 155.0, 138.4, 131.8, 131.7, 128.4, 128.4, 128.3, 128.3, 128.2, 127.8, 127.7, 122.9, 87.6, 86.1, 84.1, 83.3, 79.9, 79.9, 76.6, 75.9, 71.8, 71.0, 47.6, 28.4, 16.6, 16.3 ppm. HRMS (ESI): calcd for $[C_{23}H_{27}NO_3 + H]^+$ 366.2069, found 366.2061.

*Methyl 4-(tert-Butoxycarbonylamino)-6-phenylhex-5-ynoate (**3s**).* Colorless oil; 17.1 mg, 54% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49−7.35 (m, 2H), 7.34−7.27 (m, 3H), 4.86 (s, 1H), 4.69 (s, 1H), 3.68 (s, 3H), 2.60−2.43 (m, 2H), 2.15−2.01 (m, 2H), 1.46 (s, 9H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.6, 154.9, 131.9, 128.6, 128.4, 122.6, 87.8, 83.9, 80.3, 51.9, 43.1, 31.6, 30.6, 28.5 ppm. HRMS (ESI): calcd for $[C_{18}H_{23}NO_4 + H]^+$ 318.1705, found 318.1700.

*tert-Butyl 5-(Methylthio)-1-phenylpent-1-yn-3-ylcarbamate (**3t**).* Light yellow oil; 18.3 mg, 60% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46−7.36 (m, 2H), 7.33−7.27 (m, 3H), 4.89 (brs, 1H), 4.78 (brs, 1H), 2.73−2.63 (m, 2H), 2.14 (s, 3H), 2.11−1.94 (m, 2H), 1.46 (s, 9H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.9, 131.9, 128.6, 128.4, 122.7, 88.0, 83.8, 80.2, 43.0, 36.0, 30.4, 28.5, 15.7 ppm. HRMS (ESI): calcd for $[C_{17}H_{23}NO_2S + H]^+$ 306.1528, found 306.1525.

*tert-Butyl 7-Phenylhept-6-yne-1,5-diyldicarbamate (**3u**).* Colorless oil; 28.2 mg, 70% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43−7.36 (m, 2H), 7.32−7.27 (m, 3H), 4.81 (s, 1H), 4.70−4.50 (m, 2H), 3.20−3.02 (m, 2H), 1.82−1.68 (m, 2H), 1.60−1.46 (m, 4H), 1.46 (s, 9H), 1.43 (s, 9H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.2, 155.0, 131.8, 128.4, 122.9, 88.8, 83.2, 80.0, 79.2, 43.5, 40.5, 36.3, 29.7, 28.6, 23.0 ppm. HRMS (ESI): calcd for $[C_{23}H_{34}N_2O_4 + H]^+$ 403.2597, found 403.2594.

*2-(Phenylethynyl)tetrahydrofuran (**3v**).* Light yellow oil; 8.6 mg, 50% yield. Analytical data matched previously reported values.[9] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45−7.41 (m, 2H), 7.32−7.27 (m, 3H), 4.85−4.79 (m, 1H), 4.08−3.96 (m, 1H), 3.90−3.82 (m, 1H), 2.32−1.78 (m, 4H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 131.9, 128.4, 128.4, 123.0, 89.2, 84.6, 68.8, 68.1, 33.6, 25.6 ppm.

*2-(Phenylethynyl)-2,3-dihydro-1H-indene (**3w**).* White solid; mp: 48−51 °C; 8.7 mg, 40% yield. Analytical data matched previously reported values.[9] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43−7.36 (m, 2H), 7.31−7.26 (m, 3H), 7.25−7.20 (m, 2H), 7.19−7.14 (m, 2H), 3.49−3.39 (m, 1H), 3.35−3.24 (m, 2H), 3.16−3.08 (m, 2H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.1, 131.7, 128.3, 127.8, 126.7, 124.5, 123.9, 93.1, 80.7, 40.5, 30.9 ppm.

*1,3-Diphenylprop-2-yn-1-one (**3x**).* Yellow solid; mp: 44−48 °C; 18.6 mg, 90% yield. Analytical data matched previously reported values.[9] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, J = 7.0 Hz, 2H), 7.73−7.66 (m, 2H), 7.69−7.59 (m, 1H), 7.57−7.45 (m, 3H), 7.48−7.38 (m, 2H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.2, 137.0, 134.3, 133.2, 131.0, 129.7, 128.8, 128.8, 120.3, 93.3, 87.0 ppm.

*3-(4-Bromophenyl)-1-phenylprop-2-yn-1-one (**3y**).* Yellow solid; mp: 98−103 °C; 18.2 mg, 64% yield. Analytical data matched previously reported values.[24] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, J = 7.7 Hz, 2H), 7.64 (t, J = 7.4 Hz, 1H), 7.60−7.48 (m, 6H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.0, 136.9, 134.5, 134.4, 132.3, 129.7, 128.8, 125.8, 119.2, 91.8, 87.8 ppm.

*Benzyl 2-((Triisopropylsilyl)ethynyl)pyrrolidine-1-carboxylate (**3z**).* Colorless oil; 35.1 mg, 91% yield. Analytical data matched previously reported values.[10] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44−7.27 (m, 5H), 5.16 (d, J = 2.9 Hz, 2H), 4.68−4.34 (m, 1H), 3.66−3.47 (m, 1H), 3.44−3.30 (m, 1H), 2.27−1.85 (m, 4H), 1.15−0.90 (m, 21H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.7, 136.0, 127.5, 126.9, 126.8, 107.0, 81.8, 66.1, 48.0, 45.1, 33.4, 22.8, 17.7, 10.3 ppm.

*Benzyl 2-((tert-Butyldiphenylsilyl)ethynyl)pyrrolidine-1-carboxylate (**3aa**).* Colorless oil; 28.1 mg, 60% yield. Analytical data matched previously reported values.[10] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84−7.66 (m, 4H), 7.46−7.12 (m, 11H), 5.32−5.02 (m, 2H), 4.82−4.64 (m, 1H), 3.72−3.36 (m, 2H), 2.34−1.87 (m, 4H), 1.04 (s, 9H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.7, 136.8, 135.7, 133.4, 129.6, 128.6, 127.8, 110.3, 82.1, 67.2, 49.1, 46.3, 34.3, 27.1, 24.0, 18.7 ppm.

*Benzyl 2-((4-Bromophenyl)ethynyl)pyrrolidine-1-carboxylate (**3ab**).* Colorless oil; 26.9 mg, 70% yield. Analytical data matched previously reported values.[10] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45−7.27 (m, 8H), 7.16 (d, J = 8.1 Hz, 1H), 5.43−4.95 (m, 2H), 4.85−4.69 (m, 1H), 3.66−3.34 (m, 2H), 2.22−1.82 (m, 4H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.6, 133.4, 133.3, 131.6, 128.6, 128.1, 127.9, 127.8, 122.5, 90.8, 81.4, 67.0, 49.3, 48.8, 46.4, 46.0, 34.0, 33.3, 29.9, 23.9 ppm.

*tert-Butyl allyl(4,4-dimethyl-1-phenylpent-1-yn-3-yl)carbamate (**4**).* Light yellow oil; 27.8 mg, 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47−7.33 (m, 2H), 7.36−7.28 (m, 3H), 6.06−5.82 (m, 1H), 5.29−4.86 (m, 3H), 4.18−3.79 (m, 2H), 1.46 (s, 9H), 1.06 (s, 9H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.1, 135.4, 130.7, 127.4, 127.2, 122.3, 114.5, 85.7, 85.1, 79.0, 56.5, 47.7, 36.9, 27.5, 26.0 ppm. HRMS (ESI): calcd for $[C_{21}H_{29}NO_2 + Na]^+$ 350.2096, found 350.2095.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b02385.

^{1}H and ^{13}C NMR spectral data for compounds **3a**−**3ab** and **4** (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: xin_li@nankai.edu.cn (X.L.).
*E-mail: chengjp@most.cn (J.-P.C.).

ORCID

Xin Li: 0000-0001-6020-9170

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We are grateful to the Foundation for Specially-Appointed Professors at National University of Defense Technology and the National Natural Science Foundation (Grant Nos. 21390400 and 21421062) at Nankai University for financial support. C.Y. also thanks Dr. He-Lue Sun at Nankai University for help in conducting luminescence quenching experiments.

■ REFERENCES

(1) (a) Li, H.; Miao, T.; Wang, M.; Li, P.; Wang, L. *Synlett* **2016**, *27*, 1635. (b) Straathof, A. J. J. *Chem. Rev.* **2014**, *114*, 1871. (c) Goossen, L. J.; Goossen, K. *Top. Organomet. Chem.* **2012**, *44*, 121. (d) Gallezot, P. *Chem. Soc. Rev.* **2012**, *41*, 1538. (e) Rodríguez, N.; Goossen, L. J. *Chem. Soc. Rev.* **2011**, *40*, 5030.

(2) For selected examples, see: (a) Zhang, L.; Hang, Z.; Liu, Z.-Q. *Angew. Chem., Int. Ed.* **2016**, *55*, 236. (b) Liu, C.; Wang, X.; Li, Z.; Cui, L.; Li, C. *J. Am. Chem. Soc.* **2015**, *137*, 9820. (c) Neely, J. M.; Rovis, T. *J. Am. Chem. Soc.* **2014**, *136*, 2735. (d) Liu, X.; Wang, Z.; Cheng, X.; Li, C. *J. Am. Chem. Soc.* **2012**, *134*, 14330. (e) Bi, H.-P.; Zhao, L.; Liang, Y.-M.; Li, C.-J. *Angew. Chem., Int. Ed.* **2009**, *48*, 792.

(3) Nicewicz, D. A.; MacMillan, D. W. C. *Science* **2008**, *322*, 77.

(4) For selected reviews on visible light photochemistry, see: (a) Skubi, K. L.; Blum, T. R.; Yoon, T. P. *Chem. Rev.* **2016**, *116*, 10035. (b) Romero, N. A.; Nicewicz, D. A. *Chem. Rev.* **2016**, *116*, 10075. (c) Ravelli, D.; Protti, S.; Fagnoni, M. *Chem. Rev.* **2016**, *116*, 9850.

DOI: 10.1021/acs.joc.6b02385
J. Org. Chem. 2016, 81, 12357−12363

(d) Lang, X.; Zhao, J.; Chen, X. *Chem. Soc. Rev.* **2016**, *45*, 3026. (e) Kärkäs, M. D.; Porco, J. A.; Stephenson, C. R. J. *Chem. Rev.* **2016**, *116*, 9683. (f) Corrigan, N.; Shanmugam, S.; Xu, J.; Boyer, C. *Chem. Soc. Rev.* **2016**, *45*, 6165. (g) Chen, J.-R.; Hu, X.-Q.; Lu, L.-Q.; Xiao, W.-J. *Chem. Soc. Rev.* **2016**, *45*, 2044. (h) Prier, C. K.; Rankic, D. A.; MacMillan, D. W. C. *Chem. Rev.* **2013**, *113*, 5322. (i) Xuan, J.; Xiao, W.-J. *Angew. Chem., Int. Ed.* **2012**, *51*, 6828. (j) Narayanam, J. M. R.; Stephenson, C. R. J. *Chem. Soc. Rev.* **2011**, *40*, 102. (k) Yoon, T. P.; Ischay, M. A.; Du, J. *Nat. Chem.* **2010**, *2*, 527.

(5) For reviews on photoinduced decarboxylative functionalizations, see: (a) Huang, H.; Jia, K.; Chen, Y. *ACS Catal.* **2016**, *6*, 4983. (b) Xuan, J.; Zhang, Z.-G.; Xiao, W.-J. *Angew. Chem., Int. Ed.* **2015**, *54*, 15632.

(6) Selected photoinduced decarboxylative examples, see: (a) Chu, L.; Ohta, C.; Zuo, Z.; MacMillan, D. W. C. *J. Am. Chem. Soc.* **2014**, *136*, 10886. (b) Liu, J.; Liu, Q.; Yi, H.; Qin, C.; Bai, R.; Qi, X.; Lan, Y.; Lei, A. *Angew. Chem., Int. Ed.* **2014**, *53*, 502. (c) Zuo, Z.; Ahneman, D. T.; Chu, L.; Terrett, J. A.; Doyle, A. G.; MacMillan, D. W. C. *Science* **2014**, *345*, 437. (d) Le, C. C.; MacMillan, D. W. C. *J. Am. Chem. Soc.* **2015**, *137*, 11938. (e) Noble, A.; MacMillan, D. W. C. *J. Am. Chem. Soc.* **2014**, *136*, 11602. (f) Cassani, C.; Bergonzini, G.; Wallentin, C.-J. *Org. Lett.* **2014**, *16*, 4228. (g) Rueda-Becerril, M.; Mahé, O.; Drouin, M.; Majewski, M. B.; West, J. G.; Wolf, M. O.; Sammis, G. M.; Paquin, J.-F. *J. Am. Chem. Soc.* **2014**, *136*, 2637. (h) Beatty, J. W.; Douglas, J. J.; Cole, K. P.; Stephenson, C. R. J. *Nat. Commun.* **2015**, *6*, 7919. (i) Candish, L.; Pitzer, L.; Gómez-Suárez, A.; Glorius, F. *Chem. - Eur. J.* **2016**, *22*, 4753. (j) Song, H.-T.; Ding, W.; Zhou, Q.-Q.; Liu, J.; Lu, L.-Q.; Xiao, W.-J. *J. Org. Chem.* **2016**, *81*, 7250.

(7) (a) Wang, L. J.; Liu, J. *Eur. J. Org. Chem.* **2016**, *2016*, 1813. (b) Yoshimura, A.; Zhdankin, V. V. *Chem. Rev.* **2016**, *116*, 3328.

(8) Huang, H.; Zhang, G.; Chen, Y. *Angew. Chem., Int. Ed.* **2015**, *54*, 7872.

(9) Zhou, Q.-Q.; Guo, W.; Ding, W.; Wu, X.; Chen, X.; Lu, L.-Q.; Xiao, W.-J. *Angew. Chem., Int. Ed.* **2015**, *54*, 11196.

(10) Le Vaillant, F.; Courant, T.; Waser, J. *Angew. Chem., Int. Ed.* **2015**, *54*, 11200.

(11) Prices for $Ru(bpy)_3(PF_6)_2$, $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$, and 9,10-dicyanoanthracene are available at http://www.sigmaaldrich.com.

(12) Selected organic photocatalysis: (a) Theriot, J. C.; Lim, C. H.; Yang, H.; Ryan, M. D.; Musgrave, C. B.; Miyake, G. M. *Science* **2016**, *352*, 1082. (b) Romero, N. A.; Margrey, K. A.; Tay, N. E.; Nicewicz, D. A. *Science* **2015**, *349*, 1326. (c) Ghosh, I.; Ghosh, T.; Bardagi, J. I.; König, B. *Science* **2014**, *346*, 725. (d) Ohkubo, K.; Fujimoto, A.; Fukuzumi, S. *J. Am. Chem. Soc.* **2013**, *135*, 5368. (e) Hamilton, D. S.; Nicewicz, D. A. *J. Am. Chem. Soc.* **2012**, *134*, 18577. (f) Hari, D. P.; Schroll, P.; König, B. *J. Am. Chem. Soc.* **2012**, *134*, 2958. (g) Neumann, M.; Füldner, S.; König, B.; Zeitler, K. *Angew. Chem., Int. Ed.* **2011**, *50*, 951.

(13) Recent applications of DCA on visible-light photochemistry: (a) Pandey, G.; Laha, R. *Angew. Chem., Int. Ed.* **2015**, *54*, 14875. (b) Hofstra, J. L.; Grassbaugh, B. R.; Tran, Q. M.; Armada, N. R.; de Lijser, H. J. P. *J. Org. Chem.* **2015**, *80*, 256. (c) Ikeda, H.; Nomura, T.; Akiyama, K.; Oshima, M.; Roth, H. D.; Tero-Kubota, S.; Miyashi, T. *J. Am. Chem. Soc.* **2005**, *127*, 14497.

(14) Phenanthrene and 1, 4-dicyanobenzene were reported as a redox-photosensitized reagent to pomote decarboxylative alkylation under UV-light irradiation: (a) Yoshimi, Y.; Masuda, M.; Mizunashi, T.; Nishikawa, K.; Maeda, K.; Koshida, N.; Itou, T.; Morita, T.; Hatanaka, M. *Org. Lett.* **2009**, *11*, 4652. (b) Yoshimi, Y.; Itou, T.; Hatanaka, M. *Chem. Commun.* **2007**, 5244. (c) Itou, T.; Yoshimi, Y.; Morita, T.; Tokunaga, Y.; Hatanaka, M. *Tetrahedron* **2009**, *65*, 263.

(15) Chen, M.; Weng, Y.; Guo, M.; Zhang, H.; Lei, A. *Angew. Chem., Int. Ed.* **2008**, *47*, 2279.

(16) Turro, N. J. *Modern Molecular Photochemistry*; Benjamin/Cummings: Menlo Park, CA, 1978.

(17) (a) Internet Bond-energy Databank (*i*BonD) Home Page. http://ibond.nankai.edu.cn. (b) Luo, Y.-R. *Comprehensive Handbook of Chemical Bond Energies*; CRC Press: Boca Raton, FL, 2007.

(18) Cismesia, M. A.; Yoon, T. P. *Chem. Sci.* **2015**, *6*, 5426.

(19) Lee, E.-S.; Yeom, H.-S.; Hwang, J.-H.; Shin, S. *Eur. J. Org. Chem.* **2007**, *2007*, 3503.

(20) Scarpi, D.; Begliomini, S.; Prandi, C.; Oppedisano, A.; Deagostino, A.; Gómez-Bengoa, E.; Fiser, B.; Occhiato, E. G. *Eur. J. Org. Chem.* **2015**, *2015*, 3251.

(21) Cheng, G.; Wang, X.; Su, D.; Liu, H.; Liu, F.; Hu, Y. *J. Org. Chem.* **2010**, *75*, 1911.

(22) Schmidt, N. G.; Simon, R. C.; Kroutil, W. *Adv. Synth. Catal.* **2015**, *357*, 1815.

(23) Kano, T.; Kobayashi, R.; Maruoka, K. *Org. Lett.* **2016**, *18*, 276.

(24) Tang, S.; Zeng, L.; Liu, Y.; Lei, A. *Angew. Chem., Int. Ed.* **2015**, *54*, 15850.

DOI: 10.1021/acs.joc.6b02385
J. Org. Chem. 2016, 81, 12357−12363