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Efficiency Enhancement of a Photocatalytic Decarbonylation of an Aminocyclopropenone by Benzothiophene Substitution

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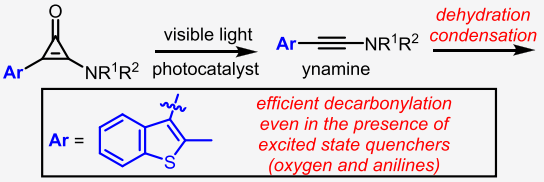
ABSTRACT: To improve the efficiency of the photocatalytic decarbonylation of cyclopropenones, the effects of substituents on cyclopropenone were explored. A benzothiophene-substituted aminocyclopropenone exhibited significantly improved decarbonylation efficiency to produce the corresponding ynamine, which worked as a potent dehydration condensation agent. The benzothiophene derivative was applicable to the photocatalytic reaction in the presence of potential excited-state quenchers such as oxygen and anilines. The high catalyst sensitivity would be attributed to the involvement of triplet energy transfer reaction pathway, which was not observed in the reaction with previously reported aminocyclopropenones.



INTRODUCTION

Photochemical transformations have been used widely for the in situ generation of highly reactive species, such as carbene and radicals, from stable precursors. In addition, photochemical reactions play an important role in the *in vivo* generation of bioactive compounds in a space- and time-controlled manner.[1] Photolabile precursors are generally called "photocaged molecules". In most cases, the photolysis of a photocaged molecule occurs by direct photoexcitation. For the photochemical uncaging reaction, long-wavelength light such as visible light is desirable because it does not decompose ultraviolet (UV)-sensitive molecules within the irradiated area. In contrast, a photocaged molecule sensitive to visible light could undergo undesired decomposition under ambient light conditions.

Photocatalytic reactions can overcome the reactivity−stability dilemma of the photocaged molecules. In some photochemical reactions such as nitrene generation from azide[2] and ring-opening cycloaddition of azirine,[3] direct photoexcitation and photocatalysis conditions yield identical products. In many cases, the photocatalytic reaction can be performed under light irradiation with a longer wavelength than that of direct substrate excitation conditions. Therefore, using a visible-light-responsive photocatalyst, a visible-light stable photocaged molecule could be uncaged under visible-light conditions.

Cyclopropenone is a strained cyclic enone that releases the ring strain on photoexcitation to produce an alkyne and one molecule of carbon monoxide; hence, cyclopropenones are regarded as photocaged alkynes.[4] Owing to the unique chemical reactivity of alkynes, such as ynamine,[5] ynamide,[6] ynol ether,[7] and cyclooctyne,[8] and the numerous reports on bioactive alkynes,[9] photochemical alkyne generation has a versatile potential for chemical and biological applications. To extend the versatility of photolytic alkyne generation, we explored a photocatalytic method to generate alkynes and achieved phototriggered uncaging of visible-light-stable cyclopropenones using a photocatalyst under visible-light conditions.[10] In the reactions, highly reactive ynamine and cyclooctyne were generated from the corresponding cyclopropenones and the resulting active alkynes were used without isolation in subsequent reactions, such as dehydration condensation[11] and alkyne−azide click chemistry.[8] In our previous report, we demonstrated that a UV-sensitive tetrazole[12] can tolerate the photocatalyst/visible-light conditions for the photolysis of cyclopropenones. Compared with the direct excitation method, the photocatalytic approach offers a series of advantages, including the use of cheap and safe visible light and applicability to UV-sensitive substrates (Scheme 1).

When a photocatalytic reaction is performed, undesired quenching of the excited photocatalyst by coexisting redox-sensitive molecules or oxygen could be a major problem.[13] A scheme of the previously developed photocatalytic dehydration condensation is shown in Scheme 2a. First, aminocyclopropenone **1a** is photolyzed under photocatalyst/visible-light conditions to give the corresponding ynamine **2a**. The ynamine reacts with carboxylic acid **3** to produce acyloxyenamine **4**, which is aminolyzed with amine **5** to produce amide **6** and hydrated ynamine **7**.[14] The reaction proceeded efficiently for monoalkyl amines such as 2-phenylethylamine and dialkyl amines such as diethylamine. In contrast, the photolysis of

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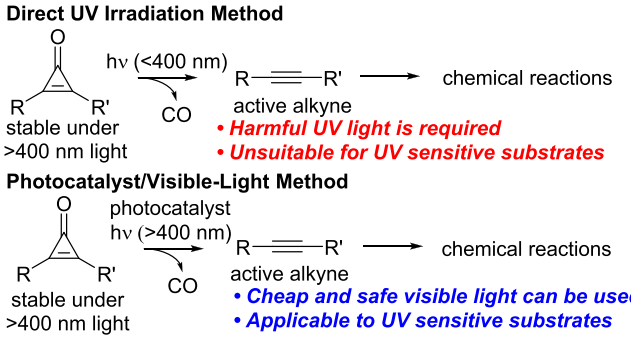
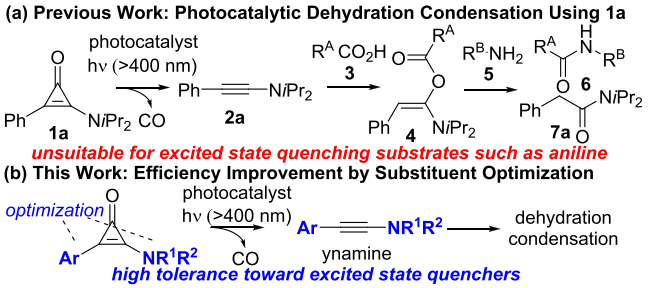
Scheme 1. Phototriggered Active Alkyne Generation Reactions



Scheme 2. Photocatalytic Dehydration Condensation Reaction

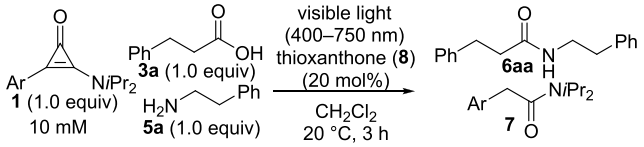


aminocyclopropenone **1a** was disturbed significantly when aromatic amines such as aniline were employed. The condensation reaction with aniline resulted in a low amide yield (12%), and >70% of **1a** remained intact after 24 h of irradiation. According to the correlation of the reaction outcome and the redox potential of the screened catalysts, redox processes are probably involved in the photocatalytic ynamine generation. Therefore, we hypothesized that the efficiency of the photocatalytic reaction could be improved by optimizing the aminocyclopropenone substituents, with an influence on the redox properties of the aminocyclopropenones.[15] In this paper, we examine the effect of aminocyclopropenone substituents on the efficiency of the photocatalytic decarbonylation and demonstrate the photocatalytic uncaging of aminocyclopropenone in the presence of potential excited-state quenchers (Scheme 2b).

RESULTS AND DISCUSSION

We explored the effect of aminocyclopropenone substituents on our previously developed photocatalytic dehydration condensation. A mixture of cyclopropenone **1**, carboxylic acid **3a**, amine **5a**, and thioxanthone (**8**) in CH_2Cl_2 was irradiated with a household fluorescent lamp under a nitrogen atmosphere. After 3 h, the yields of amide **6aa** and recovered **1** were analyzed by ^1H NMR (Table 1). First, the aromatic substituents were investigated. Diisopropylamino group was selected as the amino substituent because it afforded the best results in the phototriggered dehydration condensation in our previous study.[14] The effect of substituents on the phenyl group was studied with 2,4-disubstituted phenyl cyclopropenones **1b–e** because of their synthetic accessibility. Dimethyl-substituted **1c** and difluoro-substituted **1d** exhibited slightly faster photolysis and a higher amide yield, although the effect was not substantial. Overall, the result was not simply

Table 1. Substituent Effect of the Aromatic Group



entry	Ar	**6aa** yield (%)[a]	**1** recovery (%)[a]
1	**1a**	28	66
2	**1b**	32	66
3	**1c**	43	44
4	**1d**	39	60
5	**1e**	34	58
6	**1f**	4	90
7	**1g**	29	70
8	**1h**	39	50
9	**1i**	4	97
10	**1j**	50 (0[b])	40 (>99[b])

[a]NMR yield. [b]Without thioxanthone (**8**).

related to the typical substituent parameters, such as the Hammett constant. Then, other aromatic rings were explored. Naphthyl cyclopropenone **1f** exhibited a significantly lower efficiency. The efficiency of thiophen-2-yl cyclopropenone **1g** was similar to that of **1a**, whereas that of thiophene-3-yl cyclopropenone **1h** was slightly better. A remarkable difference was observed for benzothiophene-substituted cyclopropenones depending on the benzothiophene substitution position. Benzothiophene-2-yl cyclopropenone **1i** exhibited low efficiency, whereas benzothiophene-3-yl cyclopropenone **1j** exhibited high efficiency. Among all of the screened cyclopropenones, **1j** exhibited the fastest cyclopropenone consumption and the highest yield of amide **6aa**. As **1j** was not photolyzed in the absence of photocatalyst **8**, the high reaction efficiency with **1j** is most likely because of its high sensitivity toward the photocatalyst. In the reaction with **1j**, ynamine-derived product **7j** was detected in 36% yield, suggesting the dehydration condensation was caused by an ynamine generated from **1j** in situ.

Next, the substituent effect of the amino group was explored (Table 2). The rate of the aminocyclopropenone decarbonylation was not affected significantly by the substituents on the amino group. In the reaction, the amide yields represent the dehydration condensation reactivity of the ynamines generated from the corresponding aminocyclopropenones.[14] Acetamido-substituted cyclopropenone **1m** gave the corresponding

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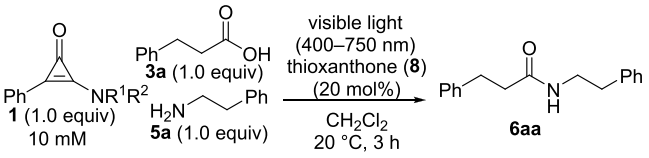
Table 2. Substituent Effect of the Amino Group



entry	NR^1R^2	**6aa** yield (%)[a]	**1** recovery (%)[a]
1	NMePh (**1k**)	13	51
2	NPh_2 (**1l**)	9	65
3	N*i*PrAc (**1m**)	0	71

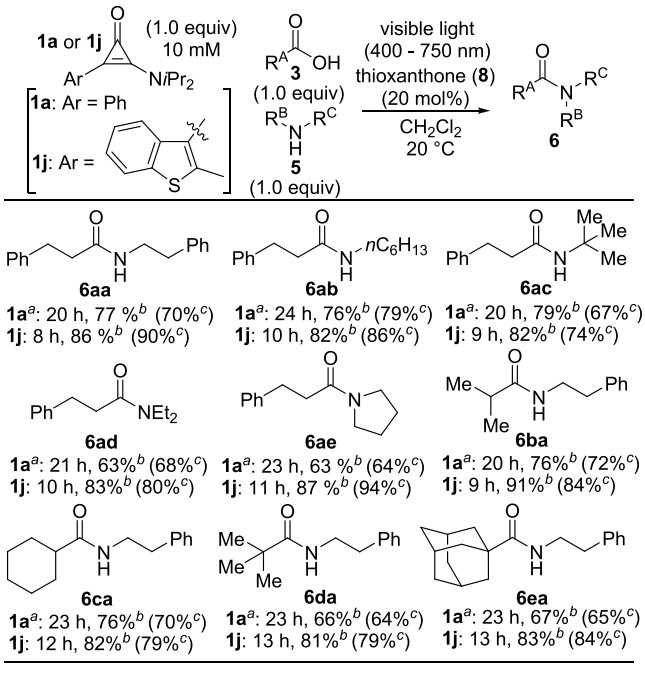
[a]NMR yield.

ynamide at a 17% yield; however, dehydration condensation did not undergo with **1m** because the ynamide was virtually inactive under the reaction conditions. Considering the photolysis efficiency and the reactivity of the produced ynamine, it can be concluded that the dialkylamino group would afford the best results in the photocatalytic dehydration condensation reaction.

A screening of substrates for the phototriggered dehydration condensation with **1j** was then performed. A mixture of cyclopropenone **1j**, carboxylic acid **3**, and amine **5** in CH_2Cl_2 was irradiated with visible light under a nitrogen atmosphere until **1j** disappeared, and the yield of amide **6** was analyzed. From the comparison with the result reported previously for **1a** (Scheme 3), we found that **1j** exhibited faster photolysis and gave better yields for all of the substrates.

Cyclopropenone **1j** was especially effective in the reaction with aniline derivatives. The phototriggered dehydration condensation with **1a** was inefficient for the condensation of a carboxylic acid and an aniline, presumably because aniline quenched the excited photocatalyst.[16] Meanwhile, the photocatalytic reactions with **1j** proceeded effectively for anilines

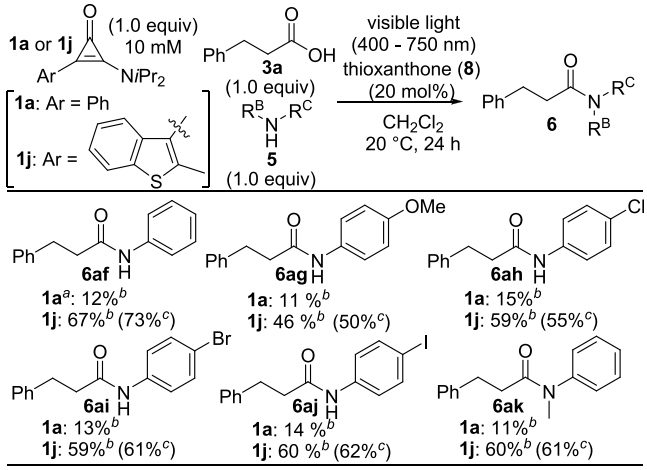
Scheme 3. Substrate Scope of the Photocatalytic Dehydration Condensation



[a]From previous report.[10] [b]NMR yield. [c]Isolated yield.

having various substituents to give the corresponding anilides in yields of 50−73% (Scheme 4). The result can be attributed to the high photocatalyst sensitivity of **1j** compared with that of **1a**.

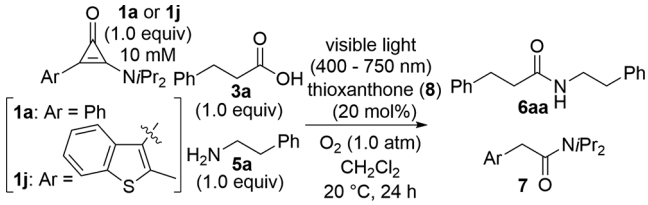
Scheme 4. Photocatalytic Dehydration Condensation of Carboxylic Acids and Aniline Derivatives



[a]From previous report.[10] [b]NMR yield. [c]Isolated yield.

Remarkably, even under an oxygen atmosphere, the photocatalytic dehydration condensation of **3a** and **5a** using **1j** proceeded to give **6aa** in 78% yield, while the reaction using **1a** afforded the product **6aa** only in 54% yield in the same reaction time (Table 3). Although the reaction rate decreased

Table 3. Photocatalytic Dehydration Condensation under Oxygen Atmosphere



entry	**1**	**6aa** yield (%)[a]	**7** yield (%)[a]
1	**1a**	54	37
2	**1j**	78	69

[a]Isolated yield.

compared with the reaction under a nitrogen atmosphere, this result is indicative of the robustness of the reaction with **1j** against excited-state quenchers of the photocatalyst.

To provide a comparison of the reactivity of aminocyclopropenone under photocatalyst and direct excitation conditions, the phototriggered dehydration condensation with **1j** was performed under direct excitation conditions with UV light (280−350 nm) (Table 4). Under direct excitation conditions, phenyl-substituted **1a** was photolyzed in 3 h and the amide yield was 78%. Under the same UV conditions, the reaction with **1j** required 7 h to consume **1j** completely, and **6aa** was obtained in an 84% yield. The different extinction coefficients (ε) of the cyclopropenones hinder precise comparisons of the photosensitivity under direct irradiation conditions. Nevertheless, the results under the UV

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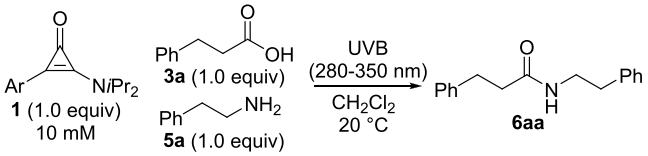
Table 4. Phototriggered Dehydration Condensation with Direct Excitation Conditions



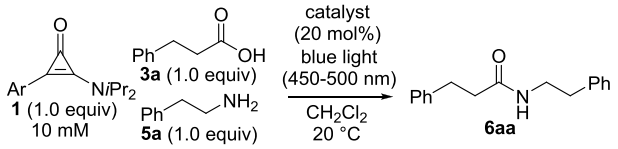
entry	1	reaction time (h)	6aa yield (%)[a]	1 recovery (%)[a]
1	1a	3	78	0
2	1j	7	84	0

[a]NMR Yield.

conditions suggest that the reactivity of cyclopropenones under the photocatalyst conditions is totally different from that under direct excitation conditions.

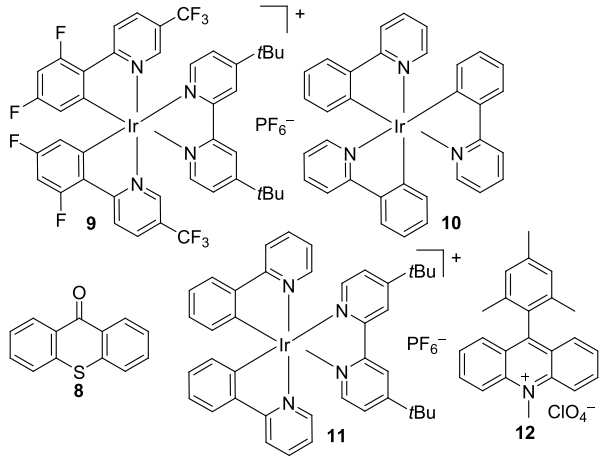
The reactivities of **1a** and **1j** were examined using other photocatalysts (Table 5). $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (**9**)

Table 5. Phototriggered Dehydration Condensation with Various Photocatalysts



entry	1	catalyst	reaction time (h)	6aa yield (%)[a]	1 recovery (%)[a]
1	1a	9	24	69	18
2	1a	10	24	<1	97
3	1a	11	24	<1	>99
4	1a	12	12	32	14
5	1j	9	4	84	<1
6	1j	10	24	47	42
7	1j	11	24	13	80
8	1j	12	24	<1	76

[a]NMR Yield.



catalyzed the reaction with **1j** efficiently, and the efficiency was much higher than that with **1a** (entries 1 and 5). $Ir(ppy)_3$ (**10**) and $Ir(ppy)_2(dtbbpy)PF_6$ (**11**), which were virtually inactive against **1a** catalyzed the reaction of **1j**, and **10** showed a higher efficiency than **11** (entries 2, 3, 6, and 7). In contrast, (Mes-Acr)ClO_4, (**12**) which showed a moderate dehydration condensation activity with **1a** did not catalyze the dehydration condensation with **1j** (entries 4 and 8). Because the recovery of **1j** was not quantitative in the reaction with **12**, **12** might decompose **1j** to a nonynamine product.

The physical properties of the screened photocatalysts are summarized in Table 6. Overall, **1j** exhibited higher reactivity

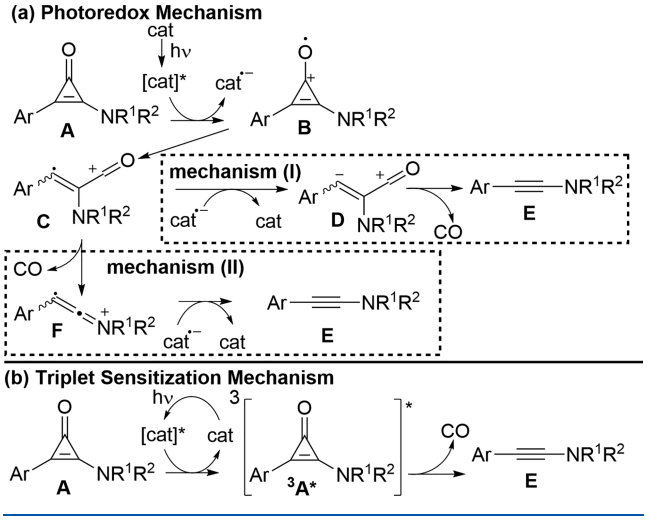
Table 6. Physical Properties of the Photocatalyst 8−12[a]

cat.	E^T (kcal/mol)	E_{red} (C/C$^{\bullet-}$) (V)	E_{red}* (C*/C$^{\bullet-}$) (V)	ref
8	63.4	−1.62	+1.22	17 and 18
9	61.8	−1.37	+1.21	17 and 19
10	58.1	−2.19	+0.31	17 and 19
11	49.2	−1.51	+0.66	17 and 19
12		−0.57	+2.06	20

[a]Previously reported data in the literature. E_{red} and E_{red}* are *versus* saturated calomel electrode (SCE). Measurements were performed in MeCN. C: ground-state catalyst. C*: excited-state catalyst. C$^{\bullet-}$: one-electron reduced catalyst.

against a catalyst with higher triplet energy (E^T), whereas the reactivity of **1a** correlated with reduction potentials (E_{red} (C/C$^{\bullet-}$) and E_{red}* (C*/C$^{\bullet-}$)) of the catalyst. These results suggest triplet sensitization mechanism is dominant for **1j**, whereas the redox mechanism is dominant for **1a** as we reported previously. The plausible mechanisms are shown in Scheme 5. Scheme 5a depicts redox-mediated mechanism.

Scheme 5. Proposed Mechanisms



First, an excited photocatalyst receives one electron from cyclopropenone **A** to give cyclopropenium radical cation **B**. After the oxidation, the three-membered ring of **B** is opened to form intermediate **C**. In mechanism (I), **C** is reduced to obtain **D** by the reduced-state photocatalyst and subsequent decarbonylation gives ynamine **E**. In mechanism (II), the decarbonylation of intermediate **C** gives a ketene iminium radical cation **F**. The one-electron reduction of **F** by the reduced-state photocatalyst gives the ynamine **E**. For efficient photoredox process, the oxidizing activity of excited-state catalyst (C*) and the reducing activity of one electron reduced catalyst (C$^{\bullet-}$) need to be sufficiently high. In contrast, in the triplet sensitization mechanism (Scheme 5b), cyclopropenone is excited to a triplet excited state and subsequent decarbonylation occurs to produce a corresponding ynamine.

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To gain further mechanistic insight into the photocatalytic reaction, a Stern−Volmer fluorescence-quenching experiment and a cyclic voltammetry (CV) experiment were performed for **1a** and **1j** (Figure 1). In the fluorescence-quenching experiment, the quenching rate of catalyst **9** with **1j** (Stern−Volmer constant (K_{SV}) = 0.813 mM^{-1}) was much higher than that with **1a** (K_{SV} = 0.0049 mM^{-1}). The higher K_{SV} value could be attributed to the higher reaction efficiency of **1j** than that of **1a**.

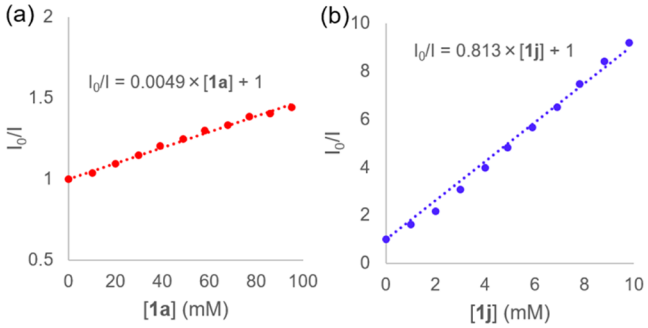

Figure 1. Stern−Volmer plot with $[Ir(dFCF_3ppy)_2dtbbpy]PF_6$ (**9**): (a) **1a** as a quencher and (b) **1j** as a quencher.

In the CV experiment, **1j** showed irreversible oxidation peak at 1.5 V, which is lower than that of **1a** (1.68 V) (Figure 2).

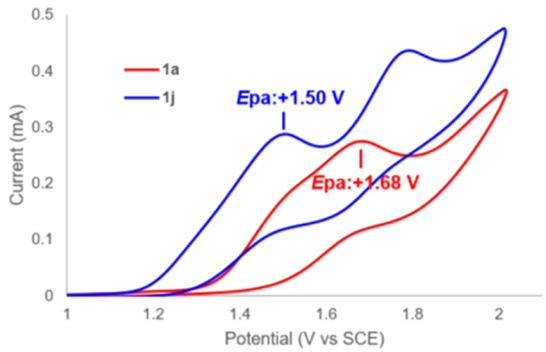

Figure 2. Cyclic voltammogram of **1a** and **1j**. Solvent = MeCN. [analyte] = 10 mM. Supporting electrolyte = 0.1 M $[nBu_4N][PF_6]$. Scan rate = 100 mV/s. The potential was calibrated with ferrocene/ferrocenium couple.

Considering the CV result, contribution of the redox process cannot be completely excluded for the reaction with **1j**, although it would be much less compared to the reaction with **1a**. To rationally explain the effect of the aminocyclopropenone substituents on the efficiency of the redox and the triplet sensitizing mechanism, further investigation such as spectroscopic analysis of reaction intermediates and quantum chemical calculation of possible reaction pathways would be required.

CONCLUSIONS

In summary, the efficiency of the photocatalytic decarbonylation of aminocyclopropenone was improved significantly by optimizing the substituents on the cyclopropenone. According to the catalyst screening, triplet sensitization mechanism, which was not dominant in the reaction with aminocyclopropenone **1a**, would be involved in the reaction with benzothiophene-substituted aminocyclopropenone **1j**. The findings in this research would contribute to broaden substrate scope of the photocatalytic alkyne generation reactions in the presence of potential photocatalyst quenchers. The mechanistic switching phenomenon between triplet energy transfer and electron transfer is reported previously;[21] however, it has not been commonly applied to organic reactions. As seen in our reactions, switching of the mechanism could be an effective strategy for the efficiency improvement of photocatalytic reactions.

EXPERIMENTAL SECTION

General Information. All reactions were performed under air, unless otherwise noted. A 20 W household fluorescent lamp (Panasonic) was used for visible light (400−750 nm) conditions. A 6 W handheld UV lamp (FUNAKOSHI UVM-57) was used for UVB (280−350 nm) conditions. A 1.656 W blue light-emitting diode (LED) lamp (ASONE HL-24) was used for blue light (450−500 nm) conditions. All solvents and commercial reagents were used as provided. Aminocyclopropenones **1a**, **1f**, **1k**, and **1m** were synthesized according to reported procedures.[14,22] For aminocyclopropenone **1l**, previously synthesized material was used. SiO_2 column chromatography was performed employing Kanto Chemical Silica Gel 60 N (spherical, neutral, 40−100 mesh). Thin-layer chromatography (TLC) was performed on silica gel 60 F254 plates. ^1H and ^{13}C NMR were recorded on JEOL JNM-ECS400 (400 MHz) and JNM-ECS600 (600 MHz) spectrometers as noted. Data for ^1H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, br s = broad singlet, d = doublet, t = triplet, q = quartet, qt = quintet, sx = sextet, sep = septet, m = multiplet), coupling constant (Hz), integration, and assignment. Data for ^{13}C NMR are reported in terms of chemical shift. For ^1H NMR, chemical shifts were reported as δ values relative to tetramethylsilane (0 ppm) as an internal standard. For ^{13}C NMR, chemical shifts were calibrated against solvent peaks in $CDCl_3$ (77.00 ppm). UV spectra were recorded on a Shimadzu UV-2400PC spectrophotometer. Fluorescence spectra were recorded on a JASCO FP-6500. Mass spectrometry was performed on a JEOL JMS-T100TD (direct analysis in real time (DART)-time-of-flight (TOF)).

Synthesis of 1a. To a stirred solution of $AlCl_3$ (2.2 g, 16.4 mmol) in $MeNO_2$ (2.5 mL), tetrachlorocyclopropene (0.5 mL, 4.10 mmol) was added at 0 °C under N_2 atmosphere. After 20 min, to the mixture, a solution of benzene (360 μL, 4.02 mmol) in dichloromethane (DCM) (4.0 mL) was added over 10 min. After stirring for 2 h at 0 °C, the mixture was quenched with ice-cooled water (12 mL). The DCM phase was separated, and aqueous phase was extracted with DCM (5 mL × 3). Combined DCM phase was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was dissolved in acetone/water (7.5/2.5 mL) at 0 °C and stirred for 40 min. After reaction completion, the mixture was diluted with DCM (20 mL). The DCM phase was separated and aqueous phase was extracted with DCM (10 mL × 3). Combined DCM phase was dried over Na_2SO_4, filtered, and concentrated *in vacuo* to give 2-chloro-3-phenylcycloprop-2-en-1-one (**14a**) as a yellow oil (652.6 mg). Purity of **14a** was determined to be 68 wt % by quantitative NMR (qNMR) with 1,3,5-trimethoxybenzene as an internal standard (chemical yield of **14a** = 40% over two steps). **14a** was used in the next step without further purification.

To a stirred solution of **14a** (68 wt %, 300.8 mg, 1.24 mmol) in DCM (2.5 mL), a solution of diisopropylamine (420 μL, 2.97 mmol) in DCM (1.0 mL) was added at 0 °C under N_2 atmosphere. After 1.5 h, the mixture was diluted with AcOEt (15 mL); washed with 1 M aqueous HCl (5 mL), water (10 mL × 2), and brine (5 mL); dried over Na_2SO_4; filtered; and concentrated *in vacuo*. The residue was purified by SiO_2 column chromatography (eluent: AcOEt/hexane = 1/4−1/1) to give **1a** as a colorless solid (164.8 mg, 58%). The product **1a** was characterized by ^1H NMR spectrum that was identical to previously reported data.[14]

*2-(Diisopropylamino)-3-phenylcycloprop-2-en-1-one (**1a**).* ^1H NMR (400 MHz, $CDCl_3$) δ 7.60−7.57 (m, 2H), 7.43−7.37 (m, 2H), 7.37−7.33 (m, 1H), 4.19 (sept, J = 6.9 Hz, 1H), 3.62 (sept, J = 6.9 Hz, 1H), 1.386 (d, J = 6.9 Hz, 6H), 1.375 (d, J = 6.9 Hz, 6H).

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Synthesis of 1b. To a stirred solution of $AlCl_3$ (299 mg, 2.24 mmol) in $MeNO_2$ (0.8 mL), tetrachlorocyclopropene (0.2 mL, 1.64 mmol) was added at 0 °C under N_2 atmosphere. After 30 min, to the mixture, DCM (1.6 mL) was added and the mixture was cooled to −78 °C. To the mixture, a solution of 1,3-dimethoxybenzene (206 mg, 1.49 mmol) in DCM (2.4 mL) was added. After stirring for 1 h at −78 °C, the mixture was diluted with DCM (10 mL) and quenched with ice-cooled water (5 mL). The mixture was warmed to 0 °C and stirred for 30 min. Then, the DCM phase was separated and aqueous phase was extracted with DCM (5 mL × 2). Combined DCM phase was dried over Na_2SO_4, filtered, and concentrated *in vacuo*.[a] The residue was purified by SiO_2 column (eluent: AcOEt/hexane = 1:5−1:2) to give a colorless solid. The solid was washed with AcOEt/hexane (1/9) to give 2-chloro-3-(2,4-dimethoxyphenyl)cycloprop-2-en-1-one (**14b**) as a colorless solid (168.6 mg, 50%).

*2-Chloro-3-(2,4-dimethoxyphenyl)cycloprop-2-en-1-one (**14b**).* ^1H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J = 8.7 Hz, 1H), 6.58 (dd, J = 8.7, 2.3 Hz, 1H), 6.49 (d, J = 2.3 Hz, 4.2 Hz, 1H), 3.96 (s, 3H), 3.90 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 166.1, 161.3, 153.1, 149.6, 135.1, 125.8, 105.7, 105.0, 98.2, 55.8, 55.7. High-resolution mass spectrometry (HRMS) (DART) m/z: $[M + H]^+$ calcd for $C_{11}H_{10}ClO_3$ 225.0319; found, 225.0316.

To a stirred solution of **14b** (28 mg, 0.125 mmol) in DCM (0.1 mL), a solution of diisopropylamine (42 μL, 0.299 mmol) in DCM (1.4 mL) was added at 0 °C under N_2 atmosphere. After 1 h, the mixture was diluted with AcOEt; washed with 0.1 M HCl, H_2O, and brine; dried over Na_2SO_4; filtered; and concentrated *in vacuo*. The residue was purified by SiO_2 column (eluent: AcOEt/hexane = 1:2−1:0) to give a colorless solid. The solid was washed with hexane to give **1b** as a colorless solid (20.0 mg, 55%).

*2-(Diisopropylamino)-3-(2,4-dimethoxyphenyl)cycloprop-2-en-1-one (**1b**).* ^1H NMR (600 MHz, $CDCl_3$) δ 7.50 (d, J = 8.6 Hz, 1H), 6.52 (dd, J = 8.6, 2.4 Hz, 1H), 6.47 (d, J = 2.4 Hz, 4.2 Hz, 1H), 4.46 (sept, J = 6.7 Hz, 1H), 3.88 (s, 3H), 3.84 (s, 3H), 3.57 (sept, J = 6.5 Hz, 1H), 1.36 (d, J = 6.9 Hz, 6H), 1.29 (d, J = 6.8 Hz, 6H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 161.7, 158.1, 146.6, 138.9, 132.4, 108.1, 107.2, 104.8, 98.5, 55.5, 52.6, 46.5, 23.6, 21.0. HRMS (DART) m/z: $[M + H]^+$ calcd for $C_{17}H_{24}NO_3$ 290.1756; found, 290.1759.

Synthesis of 1c. To a stirred solution of $AlCl_3$ (858.7 mg, 6.44 mmol) in $MeNO_2$ (1.0 mL), a solution of tetrachlorocyclopropene (0.2 mL, 1.64 mmol) in DCM (0.9 mL) was added at 0 °C under N_2 atmosphere. After 5 min, to the mixture, a solution of *m*-xylene (198 μL, 1.61 mmol) in DCM (0.8 mL) was added over 10 min. After stirring for 2 h at 0 °C, the mixture was quenched with ice-cooled water (5 mL). The DCM phase was separated, and aqueous phase was extracted with DCM (5 mL × 3). Combined DCM phase was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was dissolved in acetone/water (5.6/2.4 mL) at 0 °C and stirred for 1 h. After reaction completion, diisopropylamine (1.13 mL, 8.05 mmol) was added at 0 °C. After 30 min, the mixture was diluted with AcOEt (15 mL); washed with 1 M aqueous HCl (8 mL), water (8 mL), and brine (8 mL); dried over Na_2SO_4; filtered; and concentrated *in vacuo*. The residue was purified by SiO_2 column chromatography (eluent: AcOEt/hexane = 1/4−3/7). The purified material was washed with Et_2O to give **1c** as a colorless solid (217.9 mg, 53% over three steps).

*2-(Diisopropylamino)-3-(2,4-dimethylphenyl)cycloprop-2-en-1-one (**1c**).* ^1H NMR (600 MHz, $CDCl_3$) δ 7.22 (d, J = 7.9 Hz, 1H), 7.06 (s, 1H), 7.00 (d, J = 7.6 Hz, 1H), 4.21 (sept, J = 6.9 Hz, 1H), 3.60 (sept, J = 6.5 Hz, 1H), 1.37 (d, J = 6.5 Hz, 6H), 1.35 (d, J = 6.9 Hz, 6H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 145.9, 140.6, 139.0, 138.8, 131.1, 127.6, 126.2, 122.4, 109.9, 54.6, 47.0, 23.3, 21.0, 20.9, 20.6. HRMS (DART) m/z: $[M + H]^+$ calcd for $C_{17}H_{24}NO$ 258.1858; found, 258.1856.

Synthesis of 1d. To a stirred solution of $AlCl_3$ (858.7 mg, 6.44 mmol) in $MeNO_2$ (1.0 mL), a solution of tetrachlorocyclopropene (0.2 mL, 1.64 mmol) in DCM (0.9 mL) was added at 0 °C under N_2 atmosphere. After 10 min, to the mixture, a solution of difluorobenzene (158 μL, 1.61 mmol) in DCM (0.8 mL) was added over 10 min. After stirring for 3 h at 0 °C, the mixture was warmed to room temperature (rt) and stirred for 5 h. Then, the mixture was quenched with ice-cooled water (5 mL). The DCM phase was separated and aqueous phase was extracted with DCM (5 mL × 5). Combined DCM phase was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was dissolved in acetone/water (3.5/15 mL) at 0 °C and stirred for 20 min. After reaction completion, diisopropylamine (1.13 mL, 8.05 mmol) was added at 0 °C. After 30 min, the mixture was diluted with AcOEt (15 mL); washed with 1 M aqueous HCl (8 mL), water (8 mL), and brine (8 mL); dried over Na_2SO_4; filtered; and concentrated *in vacuo*. The residue was purified by SiO_2 column chromatography (eluent: AcOEt/hexane = 1/4−3/7). The purified material was washed DCM/hexane to give **1d** as a colorless solid (170.8 mg, 40% over three steps).

*2-(2,4-Difluorophenyl)-3-(diisopropylamino)cycloprop-2-en-1-one (**1d**).* ^1H NMR (400 MHz, $CDCl_3$) δ 7.64−7.56 (m, 1H), 6.97−6.87 (m, 2H), 4.26 (sept, J = 6.6 Hz, 1H), 3.64 (sept, J = 6.9 Hz, 1H), 1.38 (d, J = 6.8 Hz, 6H), 1.34 (d, J = 6.9 Hz, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 164.0, 163.9, 161.5, 161.4, 161.0, 160.9, 158.5, 158.4, 146.1, 140.4, 131.94, 131.90, 131.84, 131.80, 111.91, 111.88, 111.70, 111.66, 110.22, 110.18, 110.06, 110.02, 104.5, 104.2, 104.0, 102.4, 53.13, 53.06, 47.0, 23.3, 20.7. HRMS (DART) m/z: $[M + H]^+$ calcd for $C_{15}H_{18}F_2NO$ 266.1357; found, 266.1364.

Synthesis of 1e. To a stirred solution of $AlCl_3$ (858.7 mg, 6.44 mmol) in $MeNO_2$ (1.0 mL), a solution of tetrachlorocyclopropene (0.2 mL, 1.64 mmol) in DCE (0.9 mL) was added at 0 °C under N_2 atmosphere. After 10 min, to the mixture, a solution of dichlorobenzene (184 μL, 1.61 mmol) in 1,2-dichloroethane (DCE) (0.8 mL) was added over 10 min. The solution was warmed to room temperature. After stirring for 2 h at room temperature, the mixture was warmed to 50 °C and stirred for 7 h. Then, the mixture was quenched with ice-cooled water (5 mL). The organic phase was separated and aqueous phase was extracted with DCM (5 mL × 5). Combined organic phase was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. To the residue, acetone/water (2.8/1.2 mL) was added at 0 °C and stirred for 10 min. The mixture in acetone/water was extracted with DCM, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. Then, DCM (5.0 mL) was added to the residue. To the mixture, oxalyl chloride (120 μL, 1.61 mmol) was added at 0 °C. After stirring for 30 min at 0 °C, the mixture was concentrated *in vacuo* to give a crude chlorocyclopropenone. The material was dissolved in DCM (5.0 mL) and stirred at 0 °C. To the solution, diisopropylamine (1.13 mL, 8.05 mmol) was added at 0 °C. After 30 min, the mixture was diluted with AcOEt (20 mL); washed with 1 M aqueous HCl (8 mL), water (8 mL), and brine (8 mL); dried over Na_2SO_4; filtered; and concentrated *in vacuo*. The residue was purified by SiO_2 column chromatography (eluent: AcOEt/hexane = 1/4−2/3) to give **1e** as a colorless solid (123.2 mg, 26% over four steps).

*2-(2,4-Dichlorophenyl)-3-(diisopropylamino)cycloprop-2-en-1-one (**1e**).* ^1H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, J = 1.8 Hz, 1H), 7.34 (d, J = 8.2 Hz, 1H), 7.27 (dd, J = 8.2, 1.8 Hz, 1H), 4.13 (sept, J = 6.8 Hz, 1H), 3.63 (sept, J = 6.7 Hz, 1H), 1.38 (d, J = 6.4 Hz, 6H), 1.34 (d, J = 6.9 Hz, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 145.9, 142.7, 134.9, 134.8, 130.2, 129.8, 127.2, 124.0, 105.8, 54.7, 47.7, 23.5, 21.1. HRMS (DART) m/z: $[M + H]^+$ calcd for $C_{15}H_{18}Cl_2NO$ 298.0765; found, 298.0759.

Synthesis of 1f. To a stirred solution of $AlCl_3$ (596.0 mg, 4.47 mmol) in $MeNO_2$ (0.8 mL), a solution of tetrachlorocyclopropene (0.2 mL, 1.64 mmol) in DCM (2.2 mL) was added at 0 °C under N_2 atmosphere. The solution was cooled to −78 °C. After 10 min, to the mixture, a solution of naphthalene (191.0 mg, 1.49 mmol) in DCM (2.0 mL) was added over 10 min. After stirring for 2 h at −78 °C, the mixture was quenched with ice-cooled water (10 mL). The DCM phase was separated and aqueous phase was extracted with DCM (5 mL × 3). Combined DCM phase was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was dissolved in acetone/water (5.6/2.4 mL) at 0 °C and stirred for 30 min. After reaction completion, the mixture was diluted with DCM (15 mL). The DCM phase was separated and aqueous phase extracted with DCM (5 mL × 3). Combined DCM phase was dried over Na_2SO_4, filtered, and

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concentrated *in vacuo* to give a crude chlorocyclopropenone as a yellow oil. To a stirred solution of the crude chlorocyclopropenone in DCM (8.0 mL), diisopropylamine (1.04 mL, 7.45 mmol) was added at 0 °C. After 40 min, the mixture was diluted with DCM (15 mL); washed with 1 M aqueous HCl (8 mL), water (8 mL), and brine (10 mL); dried over Na_2SO_4; filtered; and concentrated *in vacuo*. The residue was purified by SiO_2 column chromatography (eluent: AcOEt/hexane = 3/2−1/0). The purified material was washed with DCM/hexane to give **1f** as a colorless solid (270.1 mg, 65% over three steps). The product **1f** was characterized by ^{1}H NMR spectrum that was identical to the previously reported data.[14]

*2-(Diisopropylamino)-3-(naphthalene-1-yl)cycloprop-2-en-1-one (**1f**).* ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (d, J = 8.2 Hz, 1H), 7.86 (d, J = 8.2 Hz, 2H), 7.71−7.67 (m, 1H), 7.58−7.54 (m, 2H), 7.50−7.46 (m, 1H), 4.36 (sept, J = 6.8 Hz, 1H), 3.68 (sept, J = 6.8 Hz, 1H), 1.44 (d, J = 6.4 Hz, 6H), 1.42 (d, J = 6.8 Hz, 6H).

Synthesis of 1g. To a stirred solution of $AlCl_3$ (875 mg, 6.56 mmol) in $MeNO_2$ (0.8 mL), a solution of tetrachlorocyclopropene (0.2 mL, 1.64 mmol) in DCM (1.6 mL) was added at 0 °C under N_2 atmosphere. After stirring for 10 min, the mixture was cooled to −78 °C. To the mixture, a solution of thiophene (119 μL, 1.49 mmol) in DCM (1.6 mL) was added over 10 min. After stirring for 25 min at −78°C, the mixture was diluted with DCM (10 mL) and quenched with ice-cold water (5 mL). The DCM phase was separated, and the aqueous phase was extracted with DCM (5 mL × 2). Combined DCM phase was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was dissolved in acetone/water (4.0/1.0 mL) at 0 °C and stirred for 30 min. After completion of the hydrolysis, a solution of diisopropylamine (1.26 mL, 8.96 mmol) in DCM (10 mL) was added at 0 °C. After 20 min, the DCM phase was separated, and the aqueous phase was extracted with DCM (5.0 mL × 2). The DCM phases were combined, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by SiO_2 column chromatography (eluent: AcOEt/hexane = 1/3−2/1). The purified material was washed with hexane to give **1g** as a brown solid (240.8 mg, 69% over three steps).

*2-(Diisopropylamino)-3-(thiophen-2-yl)cycloprop-2-en-1-one (**1g**).* ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (dd, J = 3.7, 0.9 Hz, 1H), 7.37 (dd, J = 5.0, 0.9 Hz, 1H), 7.09 (dd J = 5.0, 3.7 Hz, 1H), 4.17 (sept, J = 6.9 Hz, 1H), 3.62 (sept, J = 6.9 Hz, 1H), 1.39 (d, J = 6.9 Hz, 6H), 1.36 (d, J = 6.9 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 143.4, 136.8, 130.1, 128.0, 127.2, 126.1, 104.1, 54.0, 48.5, 23.4, 21.6. HRMS (DART) m/z: $[M + H]^+$ calcd for $C_{13}H_{18}NOS$ 236.1109; found, 236.1102.

Synthesis of 1h. To a stirred solution of $AlCl_3$ (596.0 mg, 4.47 mmol) in $MeNO_2$ (0.8 mL), a solution of tetrachlorocyclopropene (0.2 mL, 1.64 mmol) in DCM (2.2 mL) was added at 0 °C under N_2 atmosphere. The solution was cooled to −78 °C. After 10 min, to the mixture, a solution of 2,5-dimethylthiophene (169 μL, 1.49 mmol) in DCM (2.0 mL) was added over 10 min. After stirring for 1.5 h at −78 °C, the mixture was quenched with ice-cooled water (5 mL). The DCM phase was separated and aqueous phase was extracted with DCM (5 mL × 3). Combined DCM phase was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was dissolved in acetone/water (7.2/1.8 mL) at 0 °C and stirred for 40 min. After reaction completion, diisopropylamine (1.04 mL, 7.45 mmol) was added at 0 °C. After 1 h, the mixture was diluted with AcOEt (15 mL); washed with 1 M aqueous HCl (8 mL), water (8 mL), and brine (8 mL); dried over Na_2SO_4; filtered; and concentrated *in vacuo*. The residue was purified by SiO_2 column chromatography (eluent: AcOEt/hexane = 1/4−3/7). The purified material was washed with DCM/hexane to give **1h** as a pale yellow solid (216.3 mg, 55% over three steps).

*2-(Diisopropylamino)-3-(2,5-dimethylthiophen-3-yl)cycloprop-2-en-1-one (**1h**).* ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.59−6.58 (m, 1H), 4.08 (sept, J = 6.8 Hz, 1H), 3.58 (sept, J = 6.8 Hz, 1H), 2.72 (s, 3H), 2.42 (s, 3H), 1.35 (s, 6H), 1.34 (s, 6H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 144.1, 141.3, 136.9, 136.8, 123.3, 122.4, 105.7, 53.4, 47.2, 23.0, 20.7, 14.7, 14.1. HRMS (DART) m/z: $[M + H]^+$ calcd for $C_{15}H_{22}NOS$ 264.1422; found, 264.1420.

Synthesis of 1i. To a stirred solution of $AlCl_3$ (747.4 g, 5.96 mmol) in $MeNO_2$ (0.8 mL), a solution of tetrachlorocyclopropene (0.2 mL, 1.64 mmol) in DCM (2.2 mL) was added at 0 °C under N_2 atmosphere. The solution was cooled to −78 °C. After 15 min, to the mixture, a solution of 3-methylbenzo[b]thiophene (195.4 μL, 1.49 mmol) in DCM (2.0 mL) was added over 10 min. After stirring for 40 min at −78 °C, the mixture was quenched with ice-cooled water (5 mL). The DCM phase was separated and aqueous phase was extracted with DCM (10 mL × 3). Combined DCM phase was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was dissolved in acetone/water (4.2/1.8 mL) at 0 °C and stirred for 30 min. After reaction completion, diisopropylamine (1.13 mL, 8.05 mmol) was added at 0 °C. After 30 min, the mixture was diluted with AcOEt (15 mL); washed with 1 M aqueous HCl (8 mL), water (8 mL), and brine (8 mL); dried over Na_2SO_4; filtered; and concentrated *in vacuo*. The residue was purified by SiO_2 column chromatography (eluent: AcOEt/hexane = 1/4−3/7). The purified material was washed with Et_2O and DCM/hexane to give **1i** as a colorless solid (166.7 mg, 37% over three steps).

*2-(Diisopropylamino)-3-(3-methylbenzo[b]thiophen-2-yl)-cycloprop-2-en-1-one (**1i**).* ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 (d, J = 7.9 Hz, 1H), 7.73 (d, J = 7.9 Hz, 1H), 7.41−7.35 (m, 2H), 4.29 (sept, J = 6.9 Hz, 1H), 3.62 (sept, J = 6.5 Hz, 1H), 2.75 (s, 3H), 1.40 (d, J = 6.8 Hz, 6H), 1.37 (d, J = 6.5 Hz, 6H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 144.0, 139.7, 139.4, 137.6, 136.4, 125.6, 124.6, 122.7, 122.3, 120.7, 104.3, 54.4, 47.7, 23.5, 21.3, 13.2. HRMS (DART) m/z: $[M + H]^+$ calcd for $C_{18}H_{22}NOS$ 300.1422; found, 300.1429.

Synthesis of 1j. To a stirred solution of $AlCl_3$ (2.0 g, 14.9 mmol) in $MeNO_2$ (2.0 mL), a solution of tetrachlorocyclopropene (0.5 mL, 4.10 mmol) in DCM (5.0 mL) was added at 0 °C under N_2 atmosphere. The solution was cooled to −78 °C. After 10 min, to the mixture, a solution of 2-methylbenzo[b]thiophene (552.9 mg, 3.73 mmol) in DCM (6.5 mL) was added over 10 min. After stirring for 1 h at −78 °C, the mixture was quenched with ice-cooled water (5 mL). The DCM phase was separated and aqueous phase was extracted with DCM (5 mL × 3). Combined DCM phase was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was dissolved in acetone/water (13.5/15 mL) at 0 °C and stirred for 30 min. After reaction completion, diisopropylamine (2.6 mL, 18.7 mmol) was added at 0 °C. After 1 h, the mixture was diluted with AcOEt (15 mL); washed with 1 M aqueous HCl (16 mL), water (16 mL), and brine (16 mL); dried over Na_2SO_4; filtered; and concentrated *in vacuo*. The residue was purified by SiO_2 column chromatography (eluent: AcOEt/hexane = 1/4−2/3). The purified material was washed with DCM/hexane to give **1j** as a colorless solid (513.6 mg, 46% over three steps).

*2-(Diisopropylamino)-3-(2-methylbenzo[b]thiophen-3-yl)-cycloprop-2-en-1-one (**1j**).* ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.75 (d, J = 8.2 Hz, 1H), 7.73 (d, J = 8.3 Hz, 1H), 7.37 (t, J = 7.9 Hz, 1H), 7.30 (t, J = 7.6 Hz, 1H), 4.09 (br s, 1H), 3.60 (br s, 1H), 2.69 (s, 3H), 1.39 (br s, 6H), 1.29 (br s, 6H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 146.6, 142.1, 141.7, 138.5, 138.0, 124.4, 124.1, 122.0, 121.8, 119.1, 104.5, 53.3, 46.8, 23.4, 21.0, 15.4. HRMS (DART) m/z: $[M + H]^+$ calcd for $C_{18}H_{22}NOS$ 300.1422; found, 300.1435.

Synthesis of 1k. To a stirred solution of **14a** (68 wt %, 147.7 mg, 0.61 mmol) in DCM (1.4 mL), *N*-methylaniline (163 μL, 1.50 mmol) was added at 0 °C under N_2 atmosphere. After 1 h, the mixture was diluted with DCM (15 mL); washed with 1 M aqueous HCl (5 mL), water (10 mL), and brine (5 mL); dried over Na_2SO_4; filtered; and concentrated *in vacuo*. The residue was purified by SiO_2 column chromatography (eluent: AcOEt/hexane = 1/4−0/1) to give **1k** as a colorless solid (139.2 mg, 97%). The product **1k** was characterized by ^{1}H NMR spectrum that was identical to previously reported data.[14]

*2-(Methyl(phenyl)amino)3-phenylcycloprop-2-en-1-one (**1k**).* ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (br s, 2H), 7.45−7.16 (m, 8H), 3.75 (s, 3H).

Synthesis of 1m. To a stirred solution of isopropylacetamide (227 mg, 2.24 mmol) in tetrahydrofuran (THF) (4.0 mL), *n*BuLi (1.6 M in hexane, 1.3 mL, 2.10 mmol) was added at −78 °C under N_2 atmosphere. After stirring for 15 min, the mixture was transferred to a

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solution of **14a** (73 wt %, 314 mg, 1.40 mmol) in THF (6.0 mL) under N_2 atmosphere. After 1 h, 1 M aqueous HCl (5.0 mL) was added to the solution and the mixture was warmed to rt. The mixture was extracted with DCM (10 mL × 3), dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by SiO_2 column chromatography (eluent: AcOEt/hexane = 1/3−1/1) to give **1m** as a pale yellow solid (210 mg, 65%). The product **1m** was characterized by ^{1}H NMR spectrum that was identical to previously reported data.[14]

*N-Isopropyl-N-(3-oxo-2-phenylcycloprop-1-en-1-yl)acetamide (**1m**).* ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81 (d, J = 3.8 Hz, 2H), 7.53−7.49 (m, 3H), 4.68 (br s, 1H), 2.54 (s, 3H), 1.51 (d, J = 7.2 Hz, 6H).

Procedure for Tables 1 and 2. Aminocyclopropenone **1** (50 μmol), 3-phenylpropionic acid **3a** (7.5 mg, 50 μmol), 2-phenylethylamine **5a** (6.4 μL, 50 μmol), thioxanthone (2.1 mg, 10 μmol), and DCM (5.0 mL) were added into a screw-capped test tube filled with N_2 gas equipped with a magnetic stir bar. The mixture was irradiated with a household fluorescent lamp (400−750 nm) that was placed 4.0 cm from the reaction vessel. The temperature was kept at 20 °C using a temperature-controlled water bath. After 3 h irradiation, the mixture was diluted in DCM; washed with aqueous 1 M $KHSO_4$, aqueous $NaHCO_3$, and brine; dried over Na_2SO_4; filtered; and concentrated *in vacuo*. The product yield was determined by qNMR using 1,3,5-trimethoxybenzene as an internal standard.

Procedure for Scheme 3. Aminocyclopropenone **1** (50 μmol), carboxylic acid **3** (50 μmol), amine **5** (50 μmol), thioxanthone (2.1 mg, 10 μmol), and DCM (5.0 mL) were added into a screw-capped test tube filled with N_2 gas equipped with a magnetic stir bar. The mixture was irradiated with a household fluorescent lamp (400−750 nm) that was placed 4.0 cm from the reaction vessel. The temperature was kept at 20 °C using a temperature-controlled water bath. The reaction progress was monitored by preparative TLC (PTLC). After **1** disappeared, the mixture was diluted in DCM; washed with aqueous 1 M $KHSO_4$, aqueous $NaHCO_3$, and brine; dried over Na_2SO_4; filtered; and concentrated *in vacuo*. The NMR yield of the dehydration condensation product was determined by qNMR using 1,3,5-trimethoxybenzene as an internal standard. The isolated yield was determined after purification by PTLC.

*Condensation of **3a** and **5a**.* **1j** (15.0 mg, 50 μmol), 3-phenylpropionic acid (**3a**) (7.5 mg, 50 μmol), 2-phenylethylamine (**5a**) (6.3 μL, 50 μmol), thioxanthone (2.12 mg, 10 μmol), and DCM (5.0 mL) were added into a screw-capped test tube filled with N_2 gas equipped with a magnetic stir bar. The mixture was stirred and irradiated with a household fluorescent lamp that was placed 4.0 cm from the reaction vessel. Temperature was kept at 20 °C using a temperature-controlled water bath. After 10 h, the mixture was diluted with DCM; washed with 1 M aqueous $KHSO_4$, saturated aqueous $NaHCO_3$, and brine successively; dried over Na_2SO_4; filtered; and concentrated *in vacuo*. NMR yield was determined to be 86% by qNMR using 1,3,5-trimethoxybenzene as an internal standard. Isolation yield was determined after purification with PTLC (AcOEt/hexane = 2/3) to give **6aa** as a colorless solid (11.4 mg, 90%). The product **6aa** was characterized by ^{1}H NMR spectrum that was identical to previously reported data.[23]

*N-Phenethyl-3-phenylpropanamide (**6aa**).* ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30−7.18 (m, 8H), 7.10−7.08 (m, 2H), 5.31 (br s, 1H), 3.48 (td, J = 6.9, 6.5 Hz, 2H), 2.94 (t, J = 7.9 Hz, 2H), 2.74 (t, J = 6.9 Hz, 2H), 2.42 (t, J = 7.9 Hz, 2H).

*Condensation of **3a** and **5b**.* **1j** (15.0 mg, 50 μmol), 3-phenylpropionic acid (**3a**) (7.5 mg, 50 μmol), *n*-hexylamine (**5b**) (6.6 μL, 50 μmol), thioxanthone (2.12 mg, 10 μmol), and DCM (5.0 mL) were added into a screw-capped test tube filled with N_2 gas equipped with a magnetic stir bar. The mixture was stirred and irradiated with a household fluorescent lamp that was placed 4.0 cm from the reaction vessel. Temperature was kept at 20 °C using a temperature-controlled water bath. After 10 h, the mixture was diluted with DCM; washed with 1 M aqueous $KHSO_4$, saturated aqueous $NaHCO_3$, and brine successively; dried over Na_2SO_4; filtered; and concentrated *in vacuo*. NMR yield was determined to be 82% by qNMR using 1,3,5-trimethoxybenzene as an internal standard. Isolation yield was determined after purification with PTLC (AcOEt/hexane = 3/7) to give **6ab** as a colorless solid (10.1 mg, 86%). The product **6ab** was characterized by ^{1}H NMR spectrum that was identical to previously reported data.[24]

*N-Hexyl-3-phenylpropanamide (**6ab**).* ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, J = 7.8 Hz, 2H), 7.21−7.19 (m, 3H), 5.26 (br s, 1H), 3.20 (dt, J = 6.9, 6.4 Hz, 2H), 2.97 (t, J = 7.3 Hz, 2H), 2.46 (t, J = 7.4 Hz, 2H), 1.44−1.37 (m, 2H), 1.29−1.23 (m, 6H), 0.88 (t, J = 6.9 Hz, 3H).

*Condensation of **3a** and **5c**.* **1j** (15.0 mg, 50 μmol), 3-phenylpropionic acid (**3a**) (7.5 mg, 50 μmol), *tert*-butylamine (**5c**) (5.3 μL, 50 μmol), thioxanthone (2.12 mg, 10 μmol), and DCM (5.0 mL) were added into a screw-capped test tube filled with N_2 gas equipped with a magnetic stir bar. The mixture was stirred and irradiated with a household fluorescent lamp that was placed 4.0 cm from the reaction vessel. Temperature was kept at 20 °C using a temperature-controlled water bath. After 9 h, the mixture was diluted with DCM; washed with 1 M aqueous $KHSO_4$, saturated aqueous $NaHCO_3$, and brine successively; dried over Na_2SO_4; filtered; and concentrated *in vacuo*. NMR yield was determined to be 82% by qNMR using 1,3,5-trimethoxybenzene as an internal standard. Isolation yield was determined after purification with PTLC (AcOEt/hexane = 2/3) to give **6ac** as a colorless solid (7.6 mg, 74%). The product **6ac** was characterized by ^{1}H NMR spectrum that was identical to previously reported data.[25]

*N-(tert-Butyl)-3-phenylpropanamide (**6ac**).* ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30−7.26 (m, 2H), 7.21−7.19 (m, 3H) 5.09 (br s, 1H), 2.94 (t, J = 7.8 Hz, 2H), 2.38 (t, J = 7.8 Hz, 2H), 1.28 (s, 9H).

*Condensation of **3a** and **5d**.* **1j** (15.0 mg, 50 μmol), 3-phenylpropionic acid (**3a**) (7.5 mg, 50 μmol), diethylamine (**5d**) (5.2 μL, 50 μmol), thioxanthone (2.12 mg, 10 μmol), and DCM (5.0 mL) were added into a screw-capped test tube filled with N_2 gas equipped with a magnetic stir bar. The mixture was stirred and irradiated with a household fluorescent lamp that was placed 4.0 cm from the reaction vessel. Temperature was kept at 20 °C using a temperature-controlled water bath. After 10 h, the mixture was diluted with DCM; washed with 1 M aqueous $KHSO_4$, saturated aqueous $NaHCO_3$, and brine successively; dried over Na_2SO_4; filtered; and concentrated *in vacuo*. NMR yield was determined to be 83% by qNMR using 1,3,5-trimethoxybenzene as an internal standard. Isolation yield was determined after purification with PTLC (AcOEt/hexane = 1/1) to give **6ad** as a colorless solid (8.2 mg, 80%). The product **6ad** was characterized by ^{1}H NMR spectrum that was identical to previously reported data.[26]

*N,N-Diethyl-3-phenylpropanamide (**6ad**).* ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31−7.18 (m, 5H), 3.38 (q, J = 7.2 Hz, 2H), 3.22 (q, J = 7.2 Hz, 2H), 2.98 (t, J = 8.2 Hz, 2H), 2.61−2.57 (m, 2H), 1.13−1.08 (m, 6H).

*Condensation of **3a** and **5e**.* **1j** (15.0 mg, 50 μmol), 3-phenylpropionic acid (**3a**) (7.5 mg, 50 μmol), pyrrolidine (**5e**) (4.1 μL, 50 μmol), thioxanthone (2.12 mg, 10 μmol), and DCM (5.0 mL) were added into a screw-capped test tube filled with N_2 gas equipped with a magnetic stir bar. The mixture was stirred and irradiated with a household fluorescent lamp that was placed 4.0 cm from the reaction vessel. Temperature was kept at 20 °C using a temperature-controlled water bath. After 11 h, the mixture was diluted with DCM; washed with 1 M aqueous $KHSO_4$, saturated aqueous $NaHCO_3$, and brine successively; dried over Na_2SO_4; filtered; and concentrated *in vacuo*. NMR yield was determined to be 87% by qNMR using 1,3,5-trimethoxybenzene as an internal standard. Isolation yield was determined after purification with PTLC (AcOEt/hexane = 7/3) to give **6ae** as a colorless solid (9.6 mg, 94%). The product **6ae** was characterized by ^{1}H NMR spectrum that was identical to previously reported data.[27]

*3-Phenyl-1-(pyrrolidin-1-yl)propan-1-one (**6ae**).* ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30−7.18 (m, 5H), 3.46 (t, J = 6.8 Hz, 2H), 3.29 (t, J = 6.9 Hz, 2H), 2.99 (t, J = 7.8 Hz, 2H), 2.56 (t, J = 8.2 Hz, 2H), 1.92−1.78 (m, 4H).

*Condensation of **3b** and **5a**.* **1j** (15.0 mg, 50 μmol), isobutyric acid (**3b**) (4.6 μL, 50 μmol), 2-phenylethylamine (**5a**) (6.3 μL, 50 μmol), thioxanthone (2.12 mg, 10 μmol), and DCM (5.0 mL) were

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added into a screw-capped test tube filled with N_2 gas equipped with a magnetic stir bar. The mixture was stirred and irradiated with a household fluorescent lamp that was placed 4.0 cm from the reaction vessel. Temperature was kept at 20 °C using a temperature-controlled water bath. After 9 h, the mixture was diluted with DCM; washed with 1 M aqueous $KHSO_4$, saturated aqueous $NaHCO_3$, and brine successively; dried over Na_2SO_4; filtered; and concentrated *in vacuo*. NMR yield was determined to be 91% by qNMR using 1,3,5-trimethoxybenzene as an internal standard. Isolation yield was determined after purification with PTLC (AcOEt/hexane = 1/1) to give **6ba** as a colorless solid (8.0 mg, 84%). The product **6ba** was characterized by ^{1}H NMR spectrum that was identical to previously reported data.[14]

*N-Phenethylisobutyramide (**6ba**).* ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33−7.29 (m, 2H), 7.23−7.18 (m, 3H), 5.38 (br s, 1H), 3.52 (dt, J = 6.9, 6.1 Hz, 2H), 2.82 (t, J = 6.9 Hz, 2H), 2.27 (sept, J = 6.9 Hz, 1H), 1.11 (d, J = 6.9 Hz, 6H).

*Condensation of **3c** and **5a**.* **1j** (15.0 mg, 50 μmol), cyclohexanecarboxylic acid (**3c**) (6.4 mg, 50 μmol), 2-phenylethylamine (**5a**) (6.3 μL, 50 μmol), thioxanthone (2.12 mg, 10 μmol), and DCM (5.0 mL) were added into a screw-capped test tube filled with N_2 gas equipped with a magnetic stir bar. The mixture was stirred and irradiated with a household fluorescent lamp that was placed 4.0 cm from the reaction vessel. Temperature was kept at 20 °C using a temperature-controlled water bath. After 12 h, the mixture was diluted with DCM; washed with 1 M aqueous $KHSO_4$, saturated aqueous $NaHCO_3$, and brine successively; dried over Na_2SO_4; filtered; and concentrated *in vacuo*. NMR yield was determined to be 82% by qNMR using 1,3,5-trimethoxybenzene as an internal standard. Isolation yield was determined after purification with PTLC (AcOEt/hexane = 2/3) to give **6ca** as a colorless solid (9.2 mg, 79%). The product **6ca** was characterized by ^{1}H NMR spectrum that was identical to previously reported data.[23]

*N-Phenethylcyclohexanecarboxamide (**6ca**).* ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33−7.18 (m, 5H), 5.44 (br s, 1H), 3.51 (dt, J = 6.9, 6.4 Hz, 2H), 2.81 (t, J = 6.4 Hz, 2H), 2.00 (tt, J = 11.9, 3.2 Hz, 1H), 1.82−1.64 (m, 5H), 1.48−1.11 (m, 5H).

*Condensation of **3d** and **5a**.* **1j** (15.0 mg, 50 μmol), pivalic acid (**3d**) (5.1 mg, 50 μmol), 2-phenylethylamine (**5a**) (6.3 μL, 50 μmol), thioxanthone (2.12 mg, 10 μmol), and DCM (5.0 mL) were added into a screw-capped test tube filled with N_2 gas equipped with a magnetic stir bar. The mixture was stirred and irradiated with a household fluorescent lamp that was placed 4.0 cm from the reaction vessel. Temperature was kept at 20 °C using a temperature-controlled water bath. After 13 h, the mixture was diluted with DCM; washed with 1 M aqueous $KHSO_4$, saturated aqueous $NaHCO_3$, and brine successively; dried over Na_2SO_4; filtered; and concentrated *in vacuo*. NMR yield was determined to be 81% by qNMR using 1,3,5-trimethoxybenzene as an internal standard. Isolation yield was determined after purification with PTLC (AcOEt/hexane = 3/7) to give **6da** as a colorless solid (8.1 mg, 79%). The product **6da** was characterized by ^{1}H NMR spectrum that was identical to previously reported data.[26]

*N-Phenethylpivalamide (**6da**).* ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33−7.30 (m, 2H), 7.25−7.18 (m, 3H), 5.60 (br s, 1H), 3.50 (dt, J = 6.9, 6.4 Hz, 2H), 2.82 (t, J = 6.9 Hz, 2H), 1.14 (s, 9H).

*Condensation of **3e** and **5a**.* **1j** (15.0 mg, 50 μmol), 1-adamanthancarboxylic acid (**3e**) (5.1 mg, 50 μmol), 2-phenylethylamine (**5a**) (6.3 μL, 50 μmol), thioxanthone (2.12 mg, 10 μmol), and DCM (5.0 mL) were added into a screw-capped test tube filled with N_2 gas equipped with a magnetic stir bar. The mixture was stirred and irradiated with a household fluorescent lamp that was placed 4.0 cm from the reaction vessel. Temperature was kept at 20 °C using a temperature-controlled water bath. After 13 h, the mixture was diluted with DCM; washed with 1 M aqueous $KHSO_4$, saturated aqueous $NaHCO_3$, and brine successively; dried over Na_2SO_4; filtered; and concentrated *in vacuo*. NMR yield was determined to be 83% by qNMR using 1,3,5-trimethoxybenzene as an internal standard. Isolation yield was determined after purification with PTLC (AcOEt/hexane = 1/4) to give **6ea** as a colorless solid (11.9 mg, 84%). The product **6ea** was characterized by ^{1}H NMR spectrum that was identical to previously reported data.[23]

*(3r,5r,7r)-N-Phenethyladamantane-1-carboxamide (**6ea**).* ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32 (t, J = 7.6 Hz, 2H), 7.25−7.22 (m, 1H), 7.19 (d, J = 6.8 Hz, 2H), 5.57 (br s, 1H), 3.50 (dt, J = 6.8, 6.4 Hz, 2H), 2.80 (t, J = 6.9 Hz, 2H), 2.01 (s, 3H), 1.78 (d, J = 2.8 Hz, 6H), 1.70 (dd, J = 17.1, 12.4 Hz, 6H).

1.0 mmol Scale Reaction of the Photocatalyst Promoted Dehydration Condensation of 3a and 5a Using 1j. **1j** (299.4 mg, 1.0 mmol), **3a** (150.2 mg, 1.0 mmol), **5a** (126 μL, 1.0 mmol), thioxanthone (42.5 mg, 0.20 mmol), and DCM (100 mL) were added into a Pyrex flask equipped with a magnetic stir bar and N_2 balloon. The mixture was stirred and irradiated with a household fluorescent lamp that was placed 5.0 cm from the reaction vessel. Temperature was kept at 20 °C using a temperature-controlled water bath. After 33 h, the mixture was washed with 1 M aqueous $KHSO_4$, saturated aqueous $NaHCO_3$, and brine successively; dried over Na_2SO_4; filtered; and concentrated *in vacuo*. The residue was purified by SiO_2 column chromatography (eluent: AcOEt/hexane = 1/9−3/7) to give **6aa** as a colorless solid (207.7 mg, 82%) and **7j** as a colorless solid (214.6 mg, 74%). The 1.0 mmol scale reaction in flask was much less efficient than the 0.05 mmol scale reaction in test tube due to the lower irradiation efficiency.

*N,N-Diisopropyl-2-(2-methylbenzo[b]thiophen-3-yl)acetamide (**7j**).* ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 7.4 Hz, 1H), 7.71 (d, J = 7.8 Hz, 1H), 7.31 (td, J = 7.6, 0.9 Hz, 1H), 7.25 (td, J = 7.6, 0.9 Hz, 1H), 3.96 (sept, J = 6.9 Hz, 1H), 3.79 (s, 2H), 3.34 (sept, J = 6.4 Hz, 1H), 2.51 (s, 3H), 2.77 (d, J = 6.9 Hz, 6H), 0.99 (d, J = 6.4 Hz). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 168.9, 140.1, 138.0, 135.9, 125.3, 124.0, 123.5, 121.9, 121.4, 49.1, 46.1, 35.2, 20.55, 20.48, 14.1. HRMS (DART+) calcd for $C_{17}H_{24}NOS$ ([M + H$^+$]$^+$): 290.1579, found: 290.1565.

Phototriggered Dehydration Condensation under Oxygen Atmosphere (Table 3). Aminocyclopropenone **1** (50 μmol), carboxylic acid **3a** (7.5 mg, 50 μmol), amine **5a** (6.3 μL, 50 μmol), thioxanthone (2.1 mg, 10 μmol), and DCM (5.0 mL) were added into a test tube equipped with a magnetic stir bar and an oxygen-filled balloon. The mixture was irradiated with a household fluorescent lamp (400−750 nm) that was placed 4.0 cm from the reaction vessel. The temperature was kept at 20 °C using a temperature-controlled water bath. The reaction progress was monitored by TLC. After 24 h irradiation, the mixture was diluted in DCM; washed with aqueous 1 M $KHSO_4$, aqueous $NaHCO_3$, and brine; dried over Na_2SO_4; filtered; and concentrated *in vacuo*. The isolated yields of condensation product **6aa**, hydrated ynamine **7**, and recovery of **1** were determined after purification by PTLC.

With aminocyclopropenone **1a**, amide **6aa** and ynamine-derived product **7a** were obtained in 54 and 37% yields, respectively. With aminocyclopropenone **1j**, amide **6aa** and ynamine-derived product **7j** were obtained in 78 and 69% yields, respectively.

Procedure for Scheme 4. Aminocyclopropenone **1** (50 μmol), 3-phenylpropionic acid **3a** (7.5 mg, 50 μmol), aniline **5** (50 μmol), thioxanthone (2.1 mg, 10 μmol), and DCM (5.0 mL) were added into a screw-capped test tube filled with N_2 gas equipped with a magnetic stir bar. The mixture was irradiated with a household fluorescent lamp (400−750 nm) that was placed 4.0 cm from the reaction vessel. The temperature was kept at 20 °C using a temperature-controlled water bath. After 24 h irradiation, the mixture was diluted in DCM; washed with aqueous 1 M $KHSO_4$, aqueous $NaHCO_3$, and brine; dried over Na_2SO_4; filtered; and concentrated *in vacuo*. The NMR yield of the dehydration condensation product was determined by qNMR using 1,3,5-trimethoxybenzene as an internal standard. The isolated yield was determined after purification by PTLC.

*Condensation of **3a** and **5f**.* **1j** (15.0 mg, 50 μmol), 3-phenylpropionic acid (**3a**) (7.5 mg, 50 μmol), aniline (**5f**) (4.6 μL, 50 μmol), thioxanthone (2.12 mg, 10 μmol), and DCM (5.0 mL) were added into a screw-capped test tube filled with N_2 gas equipped with a magnetic stir bar. The mixture was stirred and irradiated with a household fluorescent lamp that was placed 4.0 cm from the reaction vessel. Temperature was kept at 20 °C using a temperature-controlled

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water bath. After 24 h, the mixture was diluted with DCM; washed with 1 M aqueous $KHSO_4$, saturated aqueous $NaHCO_3$, and brine successively; dried over Na_2SO_4; filtered; and concentrated *in vacuo*. NMR yield was determined to be 67% by qNMR using 1,3,5-trimethoxybenzene as an internal standard. Isolation yield was determined after purification with PTLC (AcOEt/hexane = 1/4) to give **6af** as a colorless solid (8.2 mg, 73%). The product **6af** was characterized by ^{1}H NMR spectrum that was identical to previously reported data.[23]

*N,3-Diphenylpropnamide (**6af**).* ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42 (d, J = 7.9 Hz, 2H), 7.31−7.28 (m, 4H), 7.26−7.21 (m, 3H), 7.09 (t, J = 7.2 Hz, 1H), 7.05 (br s, 1H), 3.05 (t, J = 7.6 Hz, 2H), 2.66 (t, J = 7.6 Hz, 2H).

*Condensation of **3a** and **5g**.* **1j** (15.0 mg, 50 μmol), 3-phenylpropionic acid (**3a**) (7.5 mg, 50 μmol), 4-methoxyaniline (**5g**) (6.2 mg, 50 μmol), thioxanthone (2.12 mg, 10 μmol), and DCM (5.0 mL) were added into a screw-capped test tube filled with N_2 gas equipped with a magnetic stir bar. The mixture was stirred and irradiated with a household fluorescent lamp that was placed 4.0 cm from the reaction vessel. Temperature was kept at 20 °C using a temperature-controlled water bath. After 24 h, the mixture was diluted with DCM; washed with 1 M aqueous $KHSO_4$, saturated aqueous $NaHCO_3$, and brine successively; dried over Na_2SO_4; filtered; and concentrated *in vacuo*. NMR yield was determined to be 46% by qNMR using 1,3,5-trimethoxybenzene as an internal standard. Isolation yield was determined after purification with PTLC (AcOEt/DCM = 1/19) to give **6ag** as a colorless solid (6.4 mg, 50%).

*N-(4-Methoxyphenyl)-3-phenylpropanamide (**6ag**).* ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32−7.29 (m, 4H), 7.26−7.21 (m, 3H), 6.96 (br s, 1H), 6.84−6.82 (m, 2H), 3.78 (s, 3H), 3.05 (t, J = 7.6 Hz, 2H), 2.63 (t, J = 7.6 Hz, 2H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 170.2, 156.4, 140.7, 130.8, 128.6, 128.4, 126.4, 121.9, 114.1, 55.5, 55.4, 39.3, 31.7. HRMS (DART) m/z: $[M + H]^+$ calcd for $C_{16}H_{18}NO_2$ 256.1338; found, 256.1350.

*Condensation of **3a** and **5h**.* **1j** (15.0 mg, 50 μmol), 3-phenylpropionic acid (**3a**) (7.5 mg, 50 μmol), 4-chloroaniline (**5h**) (6.4 mg, 50 μmol), thioxanthone (2.12 mg, 10 μmol), and DCM (5.0 mL) were added into a screw-capped test tube filled with N_2 gas equipped with a magnetic stir bar. The mixture was stirred and irradiated with a household fluorescent lamp that was placed 4.0 cm from the reaction vessel. Temperature was kept at 20 °C using a temperature-controlled water bath. After 24 h, the mixture was diluted with DCM; washed with 1 M aqueous $KHSO_4$, saturated aqueous $NaHCO_3$, and brine successively; dried over Na_2SO_4; filtered; and concentrated *in vacuo*. NMR yield was determined to be 59% by qNMR using 1,3,5-trimethoxybenzene as an internal standard. Isolation yield was determined after purification with PTLC (DCM 100%) to give **6ah** as a colorless solid (7.1 mg, 55%).

*N-(4-Chlorophenyl)-3-phenylpropanamide (**6ah**).* ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 (d, J = 8.6 Hz, 2H), 7.30 (t, J = 7.4 Hz, 2H), 7.26−7.23 (m, 5H), 7.03 (br s, 1H), 3.05 (t, J = 7.6 Hz, 2H), 2.65 (t, J = 7.6 Hz, 2H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 170.3, 140.4, 136.2, 129.3, 129.0, 128.7, 128.4, 126.5, 121.1, 39.4, 31.5. HRMS (DART) m/z: $[M + H]^+$ calcd for $C_{15}H_{15}ClNO$ 260.0842; found, 260.0852.

*Condensation of **3a** and **5i**.* **1j** (15.0 mg, 50 μmol), 3-phenylpropionic acid (**3a**) (7.5 mg, 50 μmol), 4-bromoaniline (**5i**) (8.6 mg, 50 μmol), thioxanthone (2.12 mg, 10 μmol), and DCM (5.0 mL) were added into a screw-capped test tube filled with N_2 gas equipped with a magnetic stir bar. The mixture was stirred and irradiated with a household fluorescent lamp that was placed 4.0 cm from the reaction vessel. Temperature was kept at 20 °C using a temperature-controlled water bath. After 24 h, the mixture was diluted with DCM; washed with 1 M aqueous $KHSO_4$, saturated aqueous $NaHCO_3$, and brine successively; dried over Na_2SO_4; filtered; and concentrated *in vacuo*. NMR yield was determined to be 59% by qNMR using 1,3,5-trimethoxybenzene as an internal standard. Isolation yield was determined after purification with PTLC (DCM/hexane = 19/1) to give **6ai** as a colorless solid (9.3 mg, 61%).

*N-(4-Bromophenyl)-3-phenylpropanamide (**6ai**).* ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, J = 9.2 Hz, 2H), 7.32−7.28 (m, 4H), 7.24−7.21 (m, 3H), 7.04 (br s, 1H), 3.04 (t, J = 7.8 Hz, 2H), 2.65 (t, J = 7.8 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.3, 140.4, 136.7, 131.9, 128.7, 128.4, 126.5, 121.4, 116.8, 39.5, 31.5. HRMS (DART) m/z: $[M + H]^+$ calcd for $C_{15}H_{15}BrNO$ 304.0337; found, 304.0337.

*Condensation of **3a** and **5j**.* **1j** (15.0 mg, 50 μmol), 3-phenylpropionic acid (**3a**) (7.5 mg, 50 μmol), 4-iodoaniline (**5j**) (11.0 mg, 50 μmol), thioxanthone (2.12 mg, 10 μmol), and DCM (5.0 mL) were added into a screw-capped test tube filled with N_2 gas equipped with a magnetic stir bar. The mixture was stirred and irradiated with a household fluorescent lamp that was placed 4.0 cm from the reaction vessel. Temperature was kept at 20 °C using a temperature-controlled water bath. After 24 h, the mixture was diluted with DCM; washed with 1 M aqueous $KHSO_4$, saturated aqueous $NaHCO_3$, and brine successively; dried over Na_2SO_4; filtered; and concentrated *in vacuo*. NMR yield was determined to be 60% by qNMR using 1,3,5-trimethoxybenzene as an internal standard. Isolation yield was determined after purification with PTLC (DCM 100%) to give **6aj** as a colorless solid (10.9 mg, 62%).

*N-(4-Iodophenyl)-3-phenylpropanamide (**6aj**).* ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.58 (d, J = 8.6 Hz, 2H), 7.30 (t, J = 7.6 Hz, 2H), 7.23−7.19 (m, 5H), 7.06 (br s, 1H), 3.03 (t, J = 7.6 Hz, 2H), 2.64 (t, J = 7.6 Hz). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 170.3, 140.4, 137.9, 137.4, 128.7, 128.4, 126.5, 121.6, 87.4, 39.5, 31.4. HRMS (DART) m/z: $[M + H]^+$ calcd for $C_{15}H_{15}BrNO$ 352.0198; found, 352.0193.

*Condensation of **3a** and **5k**.* **1j** (15.0 mg, 50 μmol), 3-phenylpropionic acid (**3a**) (7.5 mg, 50 μmol), *N*-methylaniline (**5k**) (5.5 μL, 50 μmol), thioxanthone (2.12 mg, 10 μmol), and DCM (5.0 mL) were added into a screw-capped test tube filled with N_2 gas equipped with a magnetic stir bar. The mixture was stirred and irradiated with a household fluorescent lamp that was placed 4.0 cm from the reaction vessel. Temperature was kept at 20 °C using a temperature-controlled water bath. After 24 h, the mixture was diluted with DCM; washed with 1 M aqueous $KHSO_4$, saturated aqueous $NaHCO_3$, and brine successively; dried over Na_2SO_4; filtered; and concentrated *in vacuo*. NMR yield was determined to be 60% by qNMR using 1,3,5-trimethoxybenzene as an internal standard. Isolation yield was determined after purification with PTLC (AcOEt/DCM = 1/99) to give **6ak** as a colorless solid (7.3 mg, 61%).

*N-Methyl-N,3-phenylpropanamide (**6ak**).* ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37−7.35 (m, 2H), 7.32−7.29 (m, 1H), 7.23−7.21 (m, 2H), 7.16 (t, J = 7.2 Hz, 1H), 7.05 (d, J = 7.2 Hz, 2H), 7.02 (d, J = 7.2 Hz, 2H), 3.25 (s, 3H), 2.91 (t, J = 7.9 Hz, 2H), 2.37 (t, J = 7.9 Hz, 2H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 172.2, 144.0, 141.3, 129.7, 128.4, 128.3, 127.7, 127.3, 126.0, 37.3, 36.0, 31.8. HRMS (DART) m/z: $[M + H]^+$ calcd for $C_{16}H_{18}NO$ 240.1388; found, 240.1380.

Procedure for Table 4. Aminocyclopropenone **1** (50 μmol), 3-phenylpropionic acid **3a** (7.5 mg, 50 μmol), 2-phenylethylamine **5a** (6.4 μL, 50 μmol), and DCM (5.0 mL) were added into a screw-capped test tube filled with N_2 gas equipped with a magnetic stir bar. The mixture was irradiated with a UVB lamp (280−350 nm) that was placed 8.0 cm from the reaction vessel. The temperature was kept at 20 °C using a temperature-controlled water bath. The reaction progress was monitored by TLC. After **1** disappeared, the mixture was diluted in DCM; washed with aqueous 1 M $KHSO_4$, aqueous $NaHCO_3$, and brine; dried over Na_2SO_4; filtered; and concentrated *in vacuo*. The product yield was determined by qNMR using 1,3,5-trimethoxybenzene as an internal standard.

Procedure for Table 5. Aminocyclopropenone **1** (50 μmol), 3-phenylpropionic acid **3a** (7.5 mg, 50 μmol), 2-phenylethylamine **5a** (6.4 μL, 50 μmol), photocatalyst (10 μmol), and DCM (5.0 mL) were added into a screw-capped test tube filled with N_2 gas equipped with a magnetic stir bar. The mixture was irradiated with a blue LED (450−500 nm) that was placed 4.0 cm from the reaction vessel. The temperature was kept at 20 °C using a temperature-controlled water bath. The reaction progress was monitored by TLC. After 24 h,[b] the mixture was diluted in DCM; washed with aqueous 1 M $KHSO_4$, aqueous $NaHCO_3$, and brine; dried over Na_2SO_4; filtered; and concentrated *in vacuo*. The yields of the condensation product and

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recovered aminocyclopropenone were determined by qNMR using 1,3,5-trimethoxybenzene as an internal standard.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.0c02997.

Detailed experimental procedure for the synthesis of aminocyclopropenones (**1a**−**m**), UV−vis spectra of aminocyclopropenones (**1a**−**m**) and photocatalysts (**8**−**12**), cyclic voltammogram of **1a** and **1j**, and fluorescence spectra for the Stern−Volmer fluorescence-quenching experiment (PDF)

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Notes

The authors declare no competing financial interest.

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■ ADDITIONAL NOTES

[a]^{1}H NMR was recorded at 45 °C (above the coalescence temperature of the rotamers).

[b]For entry 4, the reaction was stopped after 12 h because multiple byproduct started to appear and the reaction rate significantly decreased. For entry 5, aminocyclopropenone **1j** disappeared after 4 h; therefore, the reaction was stopped after 4 h irradiation.

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