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Visible Light-Induced Pericyclic Cascade Reaction for the Synthesis of Quinolinone Derivatives with an Oxabicyclo[4.2.0]octene Skeleton

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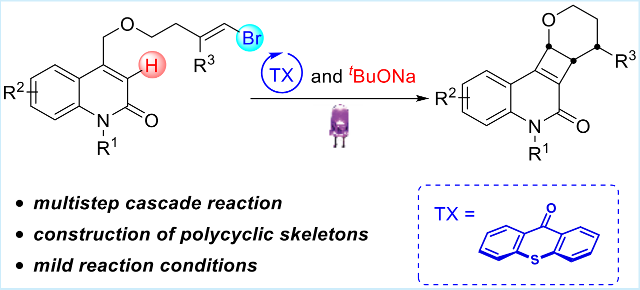
ABSTRACT: A photoinduced pericyclic cascade reaction has been developed to afford oxabicyclo[4.2.0]octenes. Mechanistic studies show that this reaction undergoes [2 + 2]-photocycloaddition, base-promoted elimination, retro-4π-electrocyclization, [1,5]-H shift, and 4π-electrocyclization procedures. This reaction features wide substrate scope, good functional group tolerance, and excellent diastereoselectivity.



Pericyclic cascade reactions have a wide range of applications in the synthesis of natural products and biological molecules.[1] For example, the tandem cyclization strategy comprised of pericyclic reactions was adopted in the syntheses of hirsutellone,[2] artochamins,[3] pleocarpenone,[4] valparicine,[5] parvineostemonine,[6] and daphnilactone[7] (Figure 1), reducing the synthesis steps. Pericyclic reactions mainly include electrocyclic reactions, cycloadditions, and sigmatropic rearrangements. The combination of these protocols will create valuable cascade reactions that allow the formation of complex molecules with simple steps.[8]

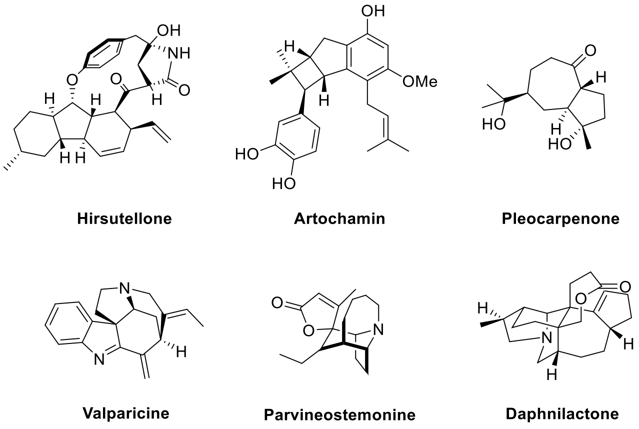


Figure 1. Natural products and biological molecules synthesized by pericyclic cascade reactions.

Over the past decade, a variety of photoreactions have been reported due to the rapid development of visible light photocatalysis.[9] A large number of inorganic and organic catalysts were widely employed in different photocatalytic reactions, featuring either an electron-transfer or an energy-transfer mechanism.[10] [2 + 2]-Photocycloaddition is a powerful tool that engenders the construction of four-membered rings with high atom economy.[11] Owing to the high ring strain, the four-membered rings are prone to undergo ring-opening reactions under proper reaction conditions.[12] The product or intermediate obtained by the ring-opening process can be further employed in subsequent transformations to acquire more complex and valuable structures. Therefore, [2 + 2]-photocycloaddition and its subsequent ring-opening reaction are expected to be important steps in pericyclic cascade reactions.[13] Numerous cascade reactions consisting of [2 + 2]-photocycloaddition and ring-opening have been reported. Bach et al. reported a UV light-induced cascade reaction in the total synthesis of sesquitpenes, wherein the ring-opening of four-membered cyclobutane is the key step (Scheme 1a).[14] Glorius developed a visible light-promoted cascade reaction for the synthesis of benzocyclobutenes. [2 + 2]-Photocycloaddition and vinyl cyclobutane rearrangement were reported to be key steps (Scheme 1b).[15] Clearly, the unique features of [2 + 2]-photocycloadditions and subsequent ring-opening reaction have made them versatile protocols in organic synthesis. Developing tandem reactions on the ground

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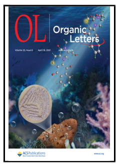

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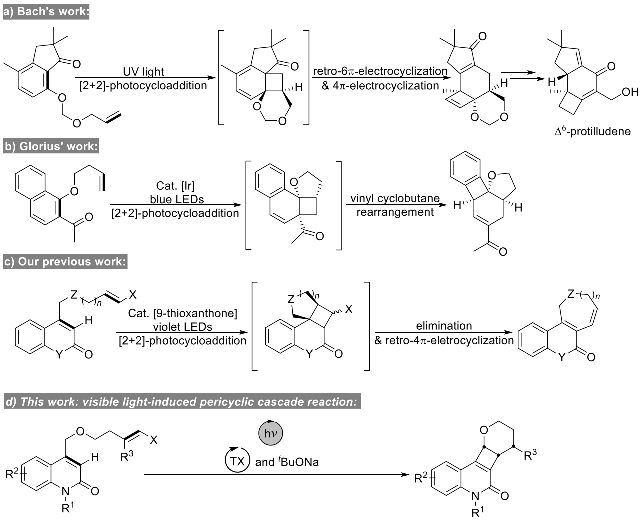
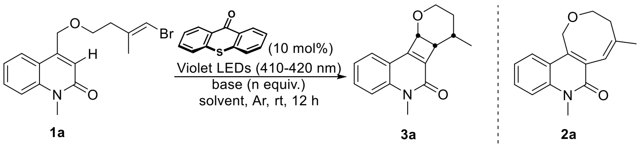
Scheme 1. Pericyclic Cascade Reactions Comprised of [2 + 2]-Photocycloaddition



of these transformations is rewarding. Recently, we reported a cascade reaction that undergoes [2 + 2]-photocycloaddition, hydrogen halide elimination, and retro-4π-electrocyclization to construct seven-or eight-membered rings under visible light catalysis (Scheme 1c).[16] In the investigation of the construction of the eight-membered ring, a rearrangement product with an oxabicyclo[4.2.0]octene skeleton was found after extended reaction time. We deduced that the reaction undergoes a more complicated process, and the eight-membered ring compound is a key intermediate in the further transformation. Herein, a visible light-induced pericyclic cascade reaction is introduced (Scheme 1d), which provides a new way for the construction of polycyclic compounds with oxabicyclo[4.2.0]octene skeletons.

Our previous study showed that irradiation of (*E*)-4-(((4-bromo-3-methylbut-3-en-1-yl)oxy)methyl)-1-methylquinolin-2(1*H*)-one (**1a**) in the present of 5 mol % of thioxanthone and 1.2 equiv of MeONa in acetonitrile within 4 h afforded **2a** in an 89% isolated yield (entry 1, Table 1). Upon further investigation, we discovered that **2a** could be converted into an oxabicyclo[4.2.0]octene **3a** slowly by extending the reaction time (entry 2, Table 1). With this observation, we turned to study the direct transformation from **1a** to **3a**. When the amount of MeONa was increased, the efficiency of the reaction was significantly improved, and **3a** was obtained in a 71% NMR yield (entry 3, Table 1). The reaction in dichloromethane or *n*-hexane gave **3a** in a lower yield (entries 4 and 5, Table 1). To improve the yield of **3a**, the reaction was further conducted using different bases, including KOH, Cs_2CO_3, MeOK, and ^{t}BuONa (entries 6−9, Table 1). The results showed that ^{t}BuONa exhibits the highest efficiency, affording **3a** in an 88% NMR yield (entry 9, Table 1). Further investigation showed that 1 equiv of ^{t}BuONa is sufficient (entries 10 and 11, Table 1). Decreasing the catalyst loading to 5 mol % resulted in a negative impact on the efficiency of this transformation (entry 12, Table 1). Control experiments without light or thioxanthone led to no conversion, and >95% of the starting material was recovered in both cases, indicating that light and thioxanthone were essential (entries 13 and 14, Table 1). Reaction in the absence of base turned out to be complicated, and **3a** could not be detected (entry 15, Table 1).

Table 1. Optimization of Reaction Conditions for the Pericyclic Cascade Reaction[a]



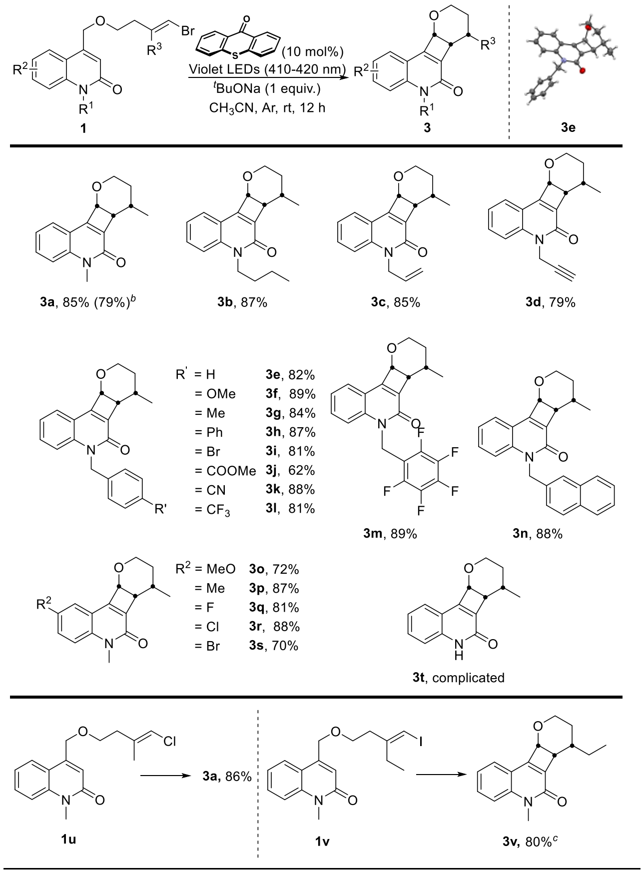
entry	base (equiv)	solvent	yield of **3a**[b] (%)
1[c]	MeONa (1.2)	CH_3CN	0 (89)[d]
2	MeONa (1.2)	CH_3CN	10[e]
3	MeONa (4)	CH_3CN	71[e]
4	MeONa (4)	CH_2Cl_2	13[e]
5	MeONa (4)	hexane	18[e]
6	KOH (4)	CH_3CN	5[e]
7	Cs_2CO_3(4)	CH_3CN	15[e]
8	MeOK (4)	CH_3CN	25[e]
9	^{t}BuONa (4)	CH_3CN	88
10	^{t}BuONa (2)	CH_3CN	87
11	^{t}BuONa (1)	CH_3CN	87 (85)[f]
12[g]	^{t}BuONa (1)	CH_3CN	17[e]
13[h]	^{t}BuONa (1)	CH_3CN	NR
14[i]	^{t}BuONa (1)	CH_3CN	NR
15	–	CH_3CN	0

[a] A solution of **1a** (0.1 mmol), thioxanthone (10 mol %), and base in anhydrous solvent (10 mL) was irradiated by 30 W violet LEDs (410−420 nm) at rt under argon atmosphere for 12 h. [b] Yields were determined by ^{1}H NMR analysis of the crude reaction mixture using CH_2Br_2 (0.1 mmol) as internal standard. [c] A solution of **1a** (0.1 mmol), thioxanthone (5 mol %), and NaOMe (0.12 mmol) in anhydrous MeCN (10 mL) was irradiated by 5 W violet LEDs (390−410 nm) at rt under argon atmosphere for 4 h. [d] Yield of **2a**, ref 16. [e] Some unidentified byproducts were formed. [f] Isolated yield of **3a**. [g] 5 mol % of thioxanthone was applied. [h] The reaction was carried out under exclusion of light. [i] No thioxanthone was applied.

Therefore, violet LEDs, 10 mol % of thioxanthone, 1 equiv of ^{t}BuONa, acetonitrile, and room temperature were chosen as the standard conditions for this pericyclic cascade reaction.

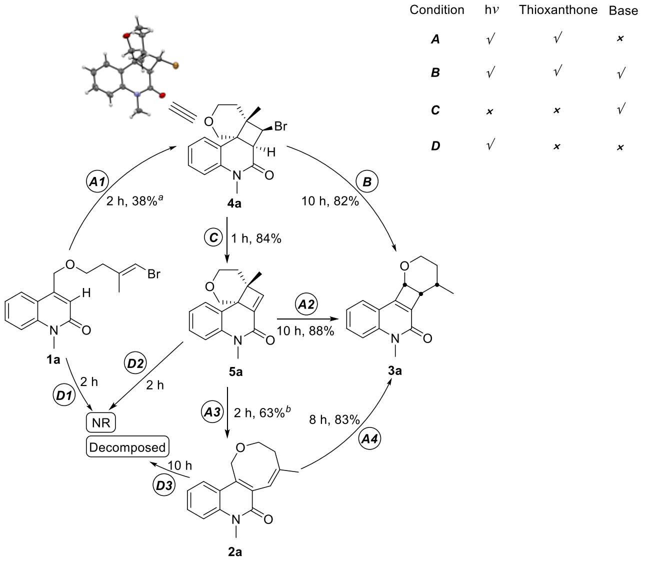
With the standard reaction conditions in hand, we explored the substrate scope of this pericyclic cascade reaction (Table 2). The reactivity of various *N*-substituted reactants was tested at first. Methyl and *n*-butyl *N*-substituents were found to be highly efficient, affording **3a** and **3b** in good yields. Allyl and propargyl moieties that were potentially reactive in [2 + 2]-photocycloaddition were also tolerated, yielding the corresponding products **3c** and **3d** in 85 and 79% yield, respectively. The *N*-benzyl group did not retard the reaction efficiency, delivering **3e** in an 82% yield. Then, the tolerance of the functional groups was examined. Substrate with 4-methoxybenzyl showed good reactivity and gave **3f** in an 89% yield. 4-Methylbenzyl or 4-phenylbenzyl decorated reactants efficiently participated in the cascade reaction, leading to **3g** and **3h** in 84 and 87% yield, respectively. 4-Bromobenzyl was also tolerated, giving **3i** in an 81% yield. Notably, 4-methoxycarbonylbenzyl, 4-cyanobenzyl, and 4-trifluoromethylbenzyl were also compatible under the reaction conditions and formed the corresponding products **3j**−**3l** in moderate to good yields. To further expand the scope at R^1, a substrate with perfluorobenzyl was applied, and **3m** was obtained in 89% yield. Reactants containing other R^1 substitution, like 2-naphthylmethyl, also worked well, affording the corresponding product **3n** in a good yield. Then, the scope of R^2 was studied. Substrates with strong

Table 2. Substrate Scope Investigations[a]



[a] A solution of **1** (0.2 mmol), thioxanthone (10 mol %), and ^{t}BuONa (1 equiv) in anhydrous MeCN (20 mL) was irradiated by violet LED (410−420 nm) at rt under argon atmosphere for 12 h. [b] 1.108 g of **1a** was applied. [c] An extended reaction time of 24 h was applied.

Scheme 2. Detailed Mechanism Studies



Condition	hν	Thioxanthone	Base
A	√	√	×
B	√	√	√
C	×	×	√
D	√	×	×

[a] The reaction generated **2a** in a 16% yield. Some unidentified byproducts were formed. [b] The reaction generated **3a** in a 21% yield as well.

electron-donating groups (EDG), such as methoxy, were tried and gave **3o** in a 72% yield. Weak EDG, such as methyl, installed on R^2 was also tolerated, and **3p** was obtained in good yield. Halogenated compounds were acquired in moderate to good yields. The substrate with hydrogen on the nitrogen (**1t**) was also tested but turned out to be complicated. Notably, the leaving group (*vide infra*) was not limited to bromo, as chlorine and iodine proved also to be feasible, affording the desired products in 86 and 80% yield, respectively. The practical utility of the method was illustrated by conducting a gram-scale experiment of **1a**, affording **3a** in a 79% isolated yield. The structure of **3** was confirmed by X-ray crystal structure analysis of **3e**, providing solid evidence for the diastereoselectivity of the three stereocenters.

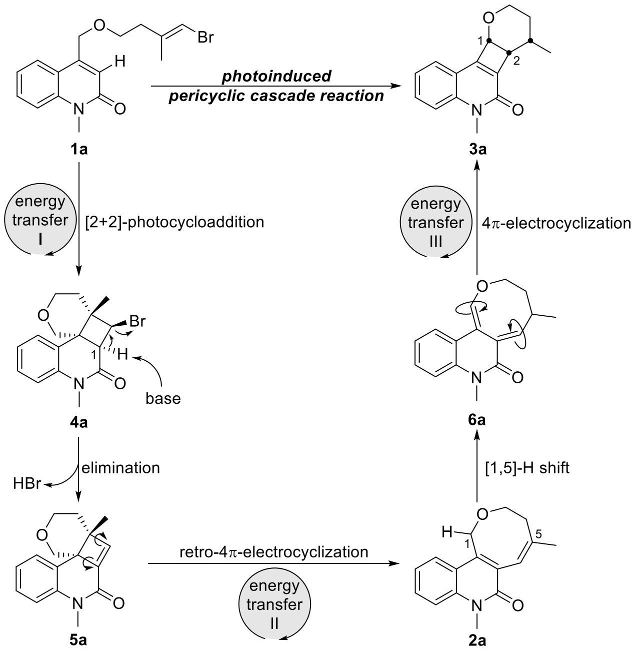
Control experiments were performed to explore the reaction mechanism (Scheme 2). Subjecting **1a** to condition A for 2 h yielded 38% of the [2 + 2]-photocycloaddition product **4a** (A1, Scheme 2), whose structure was determined by X-ray single-crystal diffraction analysis. Further application of **4a** to condition B for 10 h gave 82% of **3a** (B, Scheme 2). These two steps demonstrated that the [2 + 2]-photocycloaddition product **4a** was the key intermediate of the cascade reaction. Next, application of **4a** to condition C resulted in cyclobutene product **5a** (C, Scheme 2). It has been found that irradiating **5a** under condition A for 10 h gave 88% of **3a** (A2, Scheme 2). These evidence showed that the cyclobutene compound **5a** was another important intermediate from **4a**, formed by a base-promoted elimination process. When reducing the irradiation time of **5a** to 2 h under condition A, the eight-membered ring product **2a** was formed and obtained in 63% isolated yield, along with 21% of **3a** (A3, Scheme 2). Subjecting **2a** to condition A for 8 h gave 83% of **3a** (A4, Scheme 2). These results demonstrated that the eight-membered ring compound **2a** was an important intermediate and can be transformed from the cyclobutene **5a** via a retro-4π-electrocyclization process. Direct irradiation of **1a** or **5a** without thioxanthone gave no reaction at all (D1 and D2, Scheme 2). **2a** was totally decomposed under condition D (D3, Scheme 2). These experiments indicated that the transformations of **1a**, **2a**, and **5a** in the cascade reaction proceed through a thioxanthone catalyzed photochemical pathway.

It was worthy to note that the triplet energy of thioxanthone (265 kJ/mol)[17] is higher than that of **1a** (237 kJ/mol),[18] which indicated that the energy-transfer process occurring between thioxanthone (T_1) and substrate **1a** (S_0) might be possible.

Based on the above-described observations and previous investigations, a plausible mechanism for this pericyclic cascade reaction can be proposed (Scheme 3). Under visible light irradiation, brominated cyclobutane **4a** is formed via the first energy transfer-based [2 + 2]-photocycloaddition. Subsequently base-promoted elimination of hydrogen bromide afforded the cyclobutene intermediate **5a**. A second energy transfer leads to retro-4π-electrocyclization of **5a**, forming eight-membered ring product **2a**. Then, **2a** undergoes [1,5]-H shift to form intermediate **6a**.[19] Considering that the hydrogen atoms attached to C1 and C2 of **3a** adopt a *cis*-conformation, a photoinduced disrotatory 4π-electrocyclization is likely to occur in the transformation of **6a** to **3a**, which is consistent with the Woodward−Hoffmann rules.[20]

In summary, a visible light-induced pericyclic cascade reaction has been developed. This reaction proceeds through [2 + 2]-photocycloaddition, base-promoted elimination, retro-4π-electrocyclization, [1,5]-H shift, and 4π-electrocyclization, affording quinolinone derivatives with an oxabicyclo[4.2.0]-

Scheme 3. Possible Reaction Mechanism for This Pericyclic Cascade Reaction



octene skeleton. This cascade reaction shows excellent diastereoselectivity, which has potential applications in the synthesis of complex nature products containing polycyclic skeletons.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.1c00642.

> Figure S1, Figure S2, experimental procedures and characterization of compounds, and crystal information for compound **3e** and **4a** (PDF)

Accession Codes

CCDC 2045528 and 2061362 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: + 44 1223 336033.

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Notes

The authors declare no competing financial interest.

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(18) For detailed information about the phosphorescence emission spectrum of **1a**, please see Figure S3 in the Supporting Information.

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