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Cascade cyclization reactions of alkylidenecyclopropanes for the construction of polycyclic lactams and lactones by visible light photoredox catalysis†

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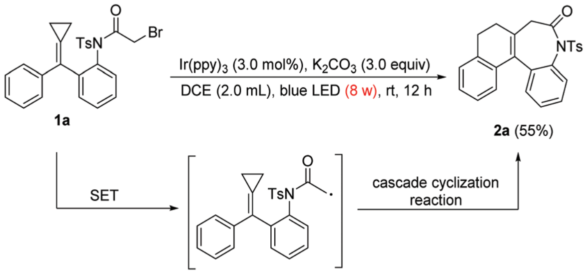
A visible light photocatalytic cascade cyclization reaction of alkylidenecyclopropanes for the rapid construction of seven- and eight-membered ring-containing polycyclic lactams and lactones has been developed. The process is proposed to proceed through a radical pathway, and the suggested radical intermediate was captured by TEMPO successfully. An intermolecular version of the reaction was also achieved, affording a variety of methyl dialinoacetate products.

The past ten years have witnessed a flourish in visible light photocatalysis,[1] and the photocatalytic variants of many important reactions have been achieved, such as cross-coupling reactions, cycloadditions, fluorinations, *etc*.[2] Using light as the driving force in the reaction, the photocatalytic reaction can often proceed under mild reaction conditions. Meanwhile, photocatalysts can serve as both electron donors and acceptors in catalytic reaction cycles[1b,3] and many stoichiometrically used oxidants and reductants in traditional reactions can be replaced by air, oxygen and amines, leading to a more economical and sustainable chemical synthesis.[1a,4]

Alkylidenecyclopropanes are important building blocks due to their high activities and diverse reactivities, and they have been widely used in organic synthesis.[5] To further explore their potential usefulness in organic chemistry, persistent efforts have been made by our group and many other groups, and significant progress and interesting results have been achieved, including some light driven reactions about a decade ago.[6] Considering the immense potential of visible light photocatalysis in organic synthesis, we attempt to combine it with alkylidenecyclopropane chemistry, in order to achieve new and efficient transformations of alkylidenecyclopropanes into useful structural motifs.

Inspired by the previous work,[7] we hypothesized that substrate **1a** having the alkylidenecyclopropane moiety under visible light photocatalysis could produce a radical intermediate by the cleavage of the C–Br bond at the α-position of the carbonyl group, and a cascade cyclization reaction would probably take place to afford polycyclic compounds. Thus, **1a** was prepared, and we subsequently examined its reactivity under visible light photocatalysis (Scheme 1). To our delight, when **1a** (0.2 mmol) together with Ir(ppy)$_3$ (3 mol%) and K$_2$CO$_3$ (3.0 equiv.) was exposed to blue LED light for 12 h, polycyclic product **2a** was obtained successfully in a yield of 55% (Scheme 1 and Table 1, entry 6). The structure of **2a** was confirmed by X-ray crystal diffraction. Its ORTEP drawing is shown in Fig. 1 and the CIF data are presented in the ESI.†

Encouraged by the success of the first attempt of this reaction, we tried to optimize the reaction conditions (Table 1). Firstly, we screened several commonly used photocatalysts. Photocatalysts such as eosin Y, fluorescein and Ru(bpy)$_3$Cl$_2$·6H$_2$O could not catalyze this reaction, and the reaction still did not work when we employed white and green



Scheme 1 Our design and first attempt of the photo-catalyzed reaction.

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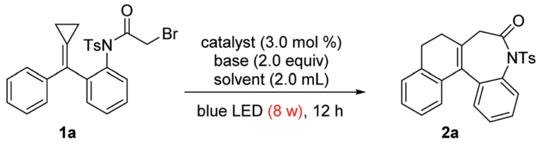
Table 1 Optimization of reaction conditions



Entry[a]	Catalyst	Base	Solvent	Yield[b]/%
1[c]	Eosin Y	K_2CO_3	DCE	NR
2[c]	Fluorescein	K_2CO_3	DCE	NR
3[c]	$Ru(bpy)_3{\cdot}Cl_{26}H_2O$	K_2CO_3	DCE	NR
4	$Ir(ppy)_2(dtbpy)PF_6$	K_2CO_3	DCE	10
5	$Ir[dF(CF_3)ppy]_2(dtbpy)PF_6$	K_2CO_3	DCE	5
6	***$Ir(ppy)_3$***	***K_2CO_3***	***DCE***	***55***
7	$Ir(ppy)_3$	Cs_2CO_3	DCE	52
8	$Ir(ppy)_3$	Pyridine	DCE	10
9	$Ir(ppy)_3$	Et_3N	DCE	15
10	$Ir(ppy)_3$	K_2CO_3	Toluene	47
11	$Ir(ppy)_3$	K_2CO_3	CH_3CN	33
12	$Ir(ppy)_3$	K_2CO_3	DCM	50
13[d]	$Ir(ppy)_3$	K_2CO_3	DCE	54
14[e]	$Ir(ppy)_3$	K_2CO_3	DCE	53

[a] Reaction conditions: **1a** (0.2 mmol), photocatalyst (3.0 mol%) and base (3.0 equiv.) were placed in a reaction tube and Ar was charged. Then 2.0 mL solvent was added and the mixture was stirred exposing to blue LED light (8 W) at room temperature for 12 h. NR = no reaction. [b] Isolated yield. All the starting materials had been consumed and instead of forming **2a**, the rest of them might have decomposed into unknown complexes. [c] White light (40 W) and green LED light (8 W) were also employed and no desired product **2a** was obtained. [d] 1.5 mL DCE. [e] 2.5 mL DCE.

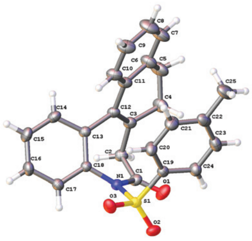
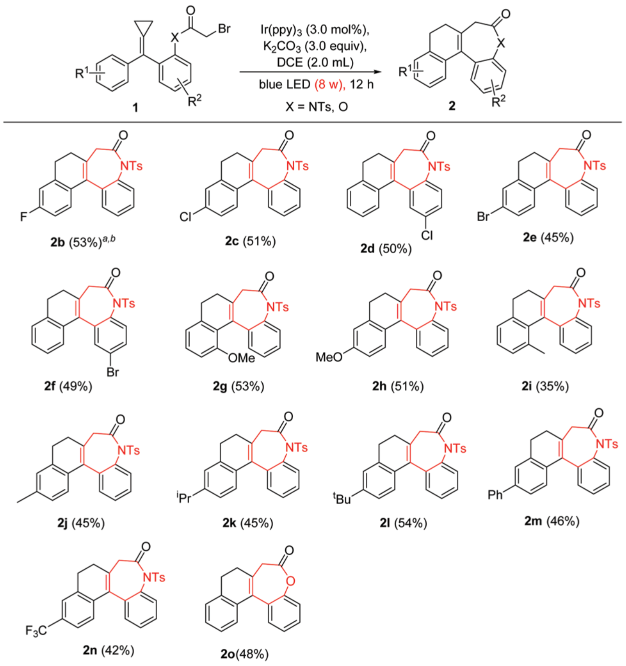


Fig. 1 The X-ray crystal structure of **2a**.

light sources instead of blue LED light (Table 1, entries 1–3). However, Ir-relevant photocatalysts smoothly catalyzed this reaction to afford the desired product **2a** (Table 1, entries 4 and 5) and $Ir(ppy)_3$ used in our first attempt was still the best (Table 1, entry 6). This maybe implied that the redox potentials of Ir-relevant photocatalysts were the most suitable for this reaction. Then, different bases were screened. The use of the inorganic base Cs_2CO_3 afforded **2a** in a yield of 52% (Table 1, entry 7), which is similar to that obtained using K_2CO_3. However, employing organic bases including pyridine and NEt_3 decreased the yield of **2a** to 10% and 15%, respectively (Table 1, entries 8 and 9), which implied that organic bases might hamper the redox cycle of the photocatalyst in the reaction. Different solvents were also screened, and the use of toluene, CH_3CN and DCM as solvents afforded product **2a** in yields ranging from 30% to 50% (Table 1, entries 10–12). In comparison, DCE was the most appropriate choice. The adjustment of the volume of solvent did not improve the yield of **2a** (Table 1, entries 13 and 14). The reaction conditions used in the first attempt were still the best reaction conditions.

With the optimal conditions in hand, we then examined the substrate scope (Scheme 2). Generally speaking, the products were obtained in moderate yields; although all the starting materials were consumed, some of them were decomposed to unknown complexes. Substrates **1b–1d** bearing the F/Cl substituent afforded the desired products **2b–2d** in a similar yield of about 50%; substrates **1e** and **1f** bearing the –Br substituent afforded the corresponding products **2e** and **2f** in relatively lower yields of 45% and 49%, respectively. Substrates **1g** and **1h** bearing a methoxyl group also afforded the corresponding products **2g** and **2h** in yields of 53% and 51%, respectively. It seemed that the electronic effect of the substituents on the substrates did not have remarkable influence on the yields of the products. Alkyl group substituted substrates **1i–1l** underwent the reaction smoothly, affording products **2i–2l** in yields ranging from 35% to 54%. The phenyl substituted substrate **1m** afforded product **2m** in a yield of 46%. Substrate **1n** having the CF_3 substituent underwent the reaction smoothly, affording product **2n** in a yield of 42%. A polycyclic lactone product **2o** was also obtained in a yield of 48%.

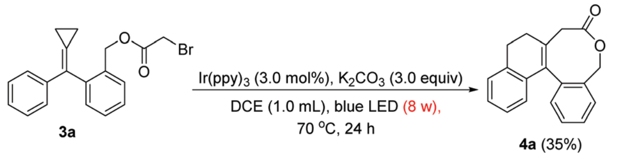


Scheme 2 Substrate scope of **1**. [a] Reaction conditions: **1** (0.2 mmol), $Ir(ppy)_3$ (3.0 mol%) and K_2CO_3 (3.0 equiv.) were placed in a reaction tube and Ar was charged. Then 2.0 mL solvent was added and the mixture was stirred upon exposure to blue LED light (8 W) at room temperature for 12 h. [b] Isolated yield.

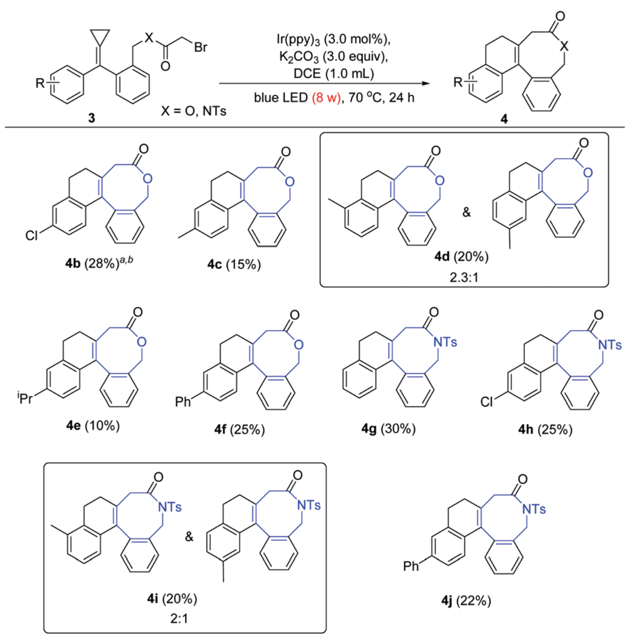
After successfully obtaining a series of polycyclic lactams and lactones containing seven-membered rings, we further proceeded to synthesize polycyclic compounds containing eight-membered rings. With a slight adjustment of the conditions, we found that when DCE was reduced to 1.0 mL, the temperature was increased to 70 °C and reaction time was prolonged to 24 h (see the ESI†), and product **4a** was also obtained smoothly, though in a relatively lower yield (Scheme 3).

The substrate scope was also examined by employing a variety of alkylidenecyclopropanes **3** bearing $-$Cl/Me/^{i}Pr/Ph groups. The desired polycyclic lactams and lactones **4b–4j** containing eight-membered rings were obtained in yields ranging from 10% to 30% (Scheme 4). In comparison, the yield of **4** was much lower than that of **2** presumably due to the large size of the eight-membered ring. The reactions of substrates **3d** and **3i** took place, affording products **4d** and **4i** as mixtures of regioisomers in 2.3 : 1 and 2 : 1 ratios, respectively.

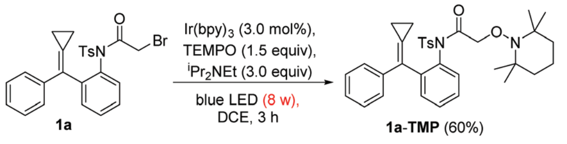
To gain some insights into the mechanism, TEMPO was used to capture radical intermediates involved in the reaction. Fortunately, compound **1a-TMP** was successfully obtained in a yield of 60% (Scheme 5). This provided evidence for the proposed radical pathway.



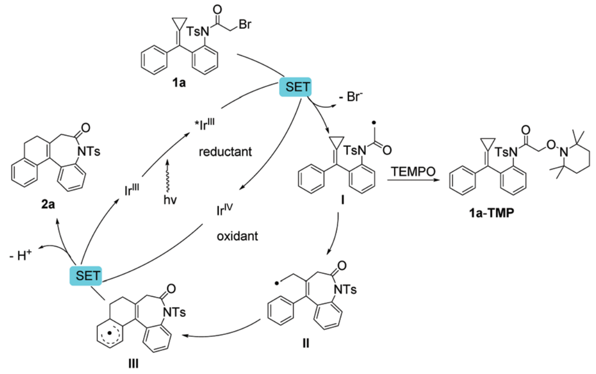
Scheme 3 Attempt to construct polycyclic compound **4a** using substrate **3a**.



Scheme 4 Substrate scope of **3**. [a] Reaction conditions: **3** (0.2 mmol), Ir(ppy)$_3$ (3.0 mol%) and K_2CO_3 (3.0 equiv.) were placed in a reaction tube and Ar was charged. Then 2.0 mL solvent was added and the mixture was stirred upon exposure to blue LED light (8 W) at 70 °C for 12 h. [b] Isolated yield.



Scheme 5 Capture of the radical intermediate with TEMPO.

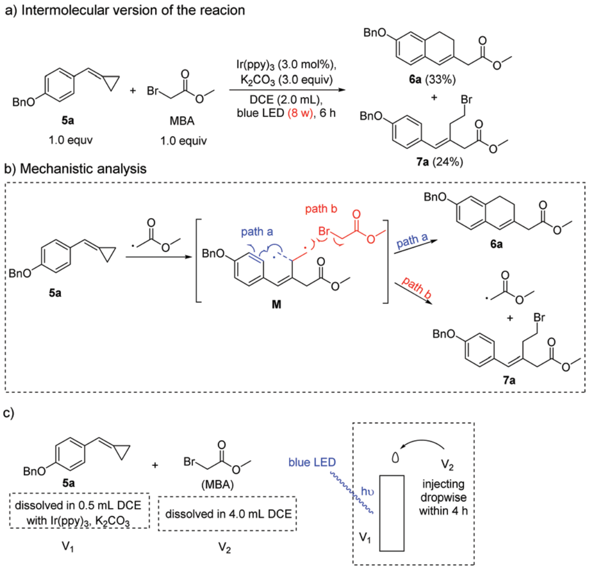


Scheme 6 A plausible pathway for the reaction.

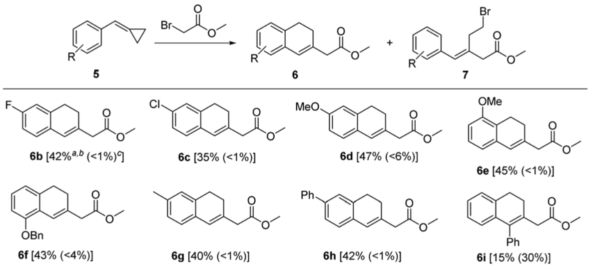
Based on the previous reports[7b,c,8] and the above experimental results, we proposed a radical reaction mechanism for this photo-catalyzed reaction (Scheme 6). Firstly, substrate **1a** produces an active radical intermediate **I** through a SET process, and then intermediate **I** undergoes cascade cyclization to afford intermediates **II** and **III**. Afterwards, through another SET process and deprotonation, the desired polycyclic product **2a** can be generated. It should be noted here that K_2CO_3 as the auxiliary base is also critical for this reaction; without the base, the substrate will be quickly decomposed in the presence of HBr generated during the reaction process and the yield will be dramatically decreased.

Furthermore, we developed an intermolecular version of the visible light photocatalyzed reaction on the basis of the above results. The reaction of **5a** and methyl bromoacetate (MBA) occurred under the same conditions, and the desired product **6a** was obtained in a yield of 33%, together with a radical chain product **7a** in a yield of 24% (Scheme 7a). Based on the proposed mechanism (Scheme 6), we proposed that the key radical intermediate **M** probably underwent either cyclization (*via* path a) to give product **6** or a chain reaction with MBA (*via* path b) to generate product **7**. We hypothesized that if the concentration of MBA was kept low enough, intermediate **M** would be favorably transformed into **6a** through path a while path b would be greatly suppressed (Scheme 7b). Thus, MBA was injected dropwise into the reaction system through a syringe pump within 4 h and the yield of **6a** successfully increased to 54% while the yield of **7a** decreased to 10% (Scheme 7c; for details, see the ESI†).

We also investigated the substrate scope of **5** for this reaction (Scheme 8). Substrates **5b–5h** bearing –F/Cl/Me/MeO/Ph/OBn groups underwent this reaction to afford products **6b–6h** in yields ranging from 35% to 47% while the radical chain products **7b–7h** were obtained in dramatically suppressed yields.



Scheme 7 Intermolecular reaction of **5a** with MBA.

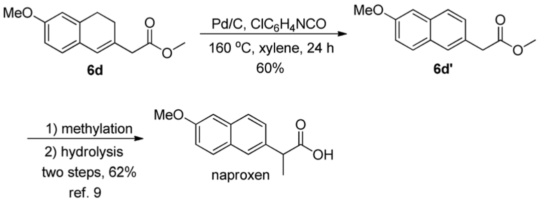


Scheme 8 Substrate scope for the intermolecular reaction. ^{a} Reaction conditions: **5** (0.2 mmol), Ir(ppy)$_3$ (3.0 mol%) and K$_2$CO$_3$ (3.0 equiv.) were placed in a reaction tube. Ar was charged and 0.5 mL DCE was added. Then upon exposure to blue LED light (8 W), MBA (0.2 mmol) dissolved in 4.0 mL DCE was injected dropwise through a syringe pump within 4 h. ^{b} Isolated yields of product **6**. ^{c} Yields of **7** determined by ^{1}H NMR spectroscopy with 1,3,5-trimethoxybenzene as an internal standard.

As for substrate **5e**, it transformed regiospecifically into product **6e**. For substrate **5i**, the corresponding product **6i** was only obtained in a yield of 15% while the yield of **7i** increased to 30%, presumably due to the electronic effect (see the ESI†).

Products **6** can be used as precursors of many valuable compounds. For example, **6d** can be dehydrogenated to form **6′d** (available at a high price on the market) and then naproxen (non-steroidal anti-inflammatory drug) after further methylation and hydrolysis (Scheme 9).[9]

In summary, a facile method for the synthesis of polycyclic lactams and lactones containing seven-membered or eight-membered rings by visible light photocatalysis has been developed and a plausible radical pathway is proposed. An intermolecular version of the reaction was also achieved which could afford various substituted methyl dialinoacetate products used as valuable precursors for further transformations.



Scheme 9 Synthetic transformation of **6d**.

Conflicts of interest

There are no conflicts of interest to declare.

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