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Concise Report mechanistic study, photoredox, spirobi[indene], chain process

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Mechanistic studies on propargyl alcohol-tethered alkylidenecyclopropane with aryldiazonium salt initiated by visible light

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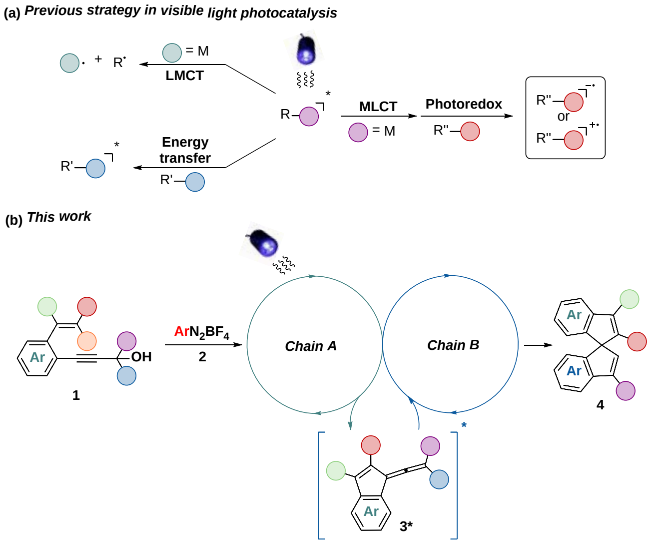
Summary of main observation and conclusion This paper discloses the reaction mechanism of two consecutive but different visible light photo-induced chain processes for the rapid construction of spirobi[indene] skeletons. The first process is triggered by a photo-induced single-electron-transfer (SET) of an electron donor-accepter (EDA) complex. The second process is initiated by a direct SET process between aryldiazonium salt and the excited allenic intermediate. In these two processes, another SET took place respectively on the in situ formed radical intermediate to realize a redox-neutral outcome. The mechanistic studies have been carried out by control experiments, kinetic and spectroscopic analyses, deuterium labeling experiments to support these two chain processes.

Background and Originality Content

In the past decade, photoredox catalysis has played a much crucial role for the efficient construction of molecular complexity in a sustainable manner under mild and environment friendly conditions with a high chemoselectivity.[1] Generally, the most significant feature of this synthetic approach is the use of metal complex/organic dye for the energy transfer or electron energy to a variety of organic substrates via visible-light photoexcitation to generate highly reactive species.[2] Thus far, a series of efficient strategies have been explored in photoredox catalysis such as metal-to-ligand charge transfer (MLCT),[3] ligand-to-metal charge transfer (LMCT),[4] hydrogen atom transfer (HAT),[5] proton-coupled electron transfer (PCET)[6] and so on (Scheme 1a). Moreover, photo-induced intermolecular charge transfer through noncovalent interactions of donor and acceptor molecules is renowned in photochemistry.[7] These exciting findings inspired us to develop a much facilitated photocatalytic protocol in organic synthesis.

Our group has been working on the chemical transformation of strained small rings for the rapid construction of poly- and heterocyclic compounds.[8] On the basis of the aforementioned outstanding photoredox catalytic processes, we attempted to develop new synthetic methods by merging photoredox catalysis strategy with strained small rings to explore new reaction modes with regard to these small carbocyclic compounds. Recently, our group has reported a visible-light photo-induced reaction for rapidly constructing spirobi[indene]s in good yields and with good functional group tolerance (Scheme 1b).[9] However, the related mechanistic studies on this new reaction are insufficient and the real catalytic process has not been clearly unveiled. The preliminary study indicated that this reaction must be initiated by the visible-light irradiation. In addition, the use of a catalytic loading of aryldiazonium salt suggests that an autocatalytic or a chain process might take place during the reaction process. Thus, we envisaged that this reaction may proceed through an unprecedented photochemical pathway. Thus, it is important to further perform the mechanistic investigations on this reaction to well understanding the detailed reaction process, shedding light on the merger of photoredox catalysis with the transformation of strained small rings.

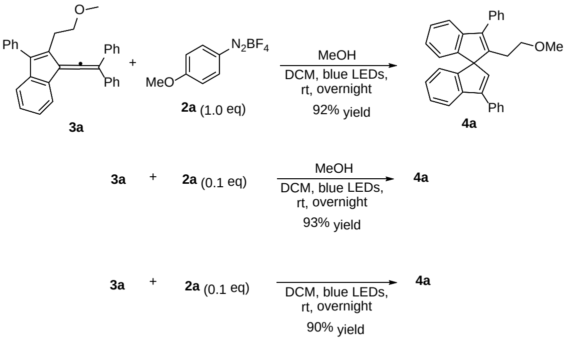
Scheme 1 Previous work and this work.



Results and Discussion

On the basis of the preliminary study, the acid-catalytic process has been excluded and a simplified reaction pathway has been provided.[9] Meanwhile, the allenic product has been identified under the reaction condition, implying that it was the intermediate to give **4a**. However, the detailed reaction pathway and the evidence to support this mechanism have not been fully clarified. To illustrate the real reaction pathway, we firstly utilized allene intermediate **3a** as substrate to examine its reaction outcome under the standard reaction conditions and identified that the desired product **4a** could be obtained even using 0.1 equiv of **2a** or in the absence of MeOH, suggesting that **3a** was the intermediate for the formation of **4a** (Scheme 2). To simplify the mechanistic investigation, we divided the reaction pathways into two parts: (1) the formation of **3a** from **1a**; (2) the formation of **4a** from **3a**.

Scheme 2 Transformation of **3a** to **4a** under different reaction conditions



Next, we turned our attention to the mechanistic study of the first part starting with evaluation of the role of aryldiazonium salt **2**. It has been well known that aryldiazonium salt **2** can act as an oxidant as it often does in photoredox catalysis. However, the redox potential of **1a** and **2a** did not support its direct oxidation pathway (see cyclic voltammetry at chapter 9 in the Supporting Information). Upon mixing **1a** and **2a**, a significant color change was observed at the beginning of the reaction, implying the formation of an electron donor-accepter (EDA) complex.[7,10] This observation was further supported by appearance of a new absorption peak upon mixing **1a** and **2a** in DCM solution in their electronic spectra (Figure 1). According to their absorption spectra, neither **1a** nor **2a** can be effectively photoexcited by the broad-band blue LED light (380–530 nm). Therefore, it suggested that the radical cation generated upon the visible light photoexcitation of the formed EDA complex followed by a subsequent tandem cyclization, ring opening and nucleophilic attack of MeOH accounted for the formation of **3a**. Moreover, the reaction proceeded smoothly even with a catalytic amount of **2a**, suggesting that **2a** might be an initiator in this reaction. In a catalytic sense, the reaction should therefore be possible to proceed through a chain transfer or an autocatalytic process. The autocatalysis could be easily ruled out since **3a** itself did not catalyze or accelerate the transformation of **1a** to **3a** under the standard conditions (Figures 2a and 2b). Furthermore, a series of control experiments were conducted to investigate the reaction mechanism. The kinetic experiments on reaction rates showed that the concentration of **2a** could affect the reaction rate and the reaction was accelerated if using 0.2 or 0.5 equiv of **2a**. Meanwhile, the shapes of their kinetic curves also implied the existence of an induction period and a chain process (Figure 2c). Next, the light-dark interval experiment confirmed that constant illumination of light is not an essential element for the formation of **3a** after the reaction is initiated (Figure 2d). Moreover, the quantum yield of this reaction was measured to be 5.7, supporting the domination of chain process without light irradiation. These results validated that the second SET did not involve with the excited species and it might take place with a substrate on the ground state to generate a radical cationic species. All these evidences demonstrated the existence of a chain process and the irradiation of visible light is unnecessary while the reaction has been initiated.

Figure 1. (a) UV-vis absorption spectra of **1a**, **2a** and their mixture. (b) The color change after mixing **1a** and **2a**.

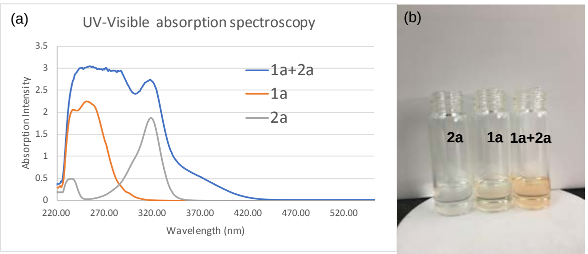
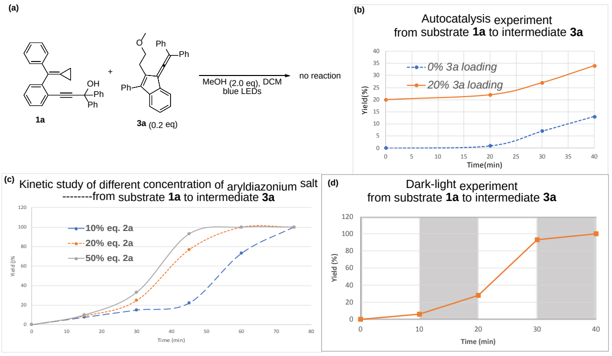
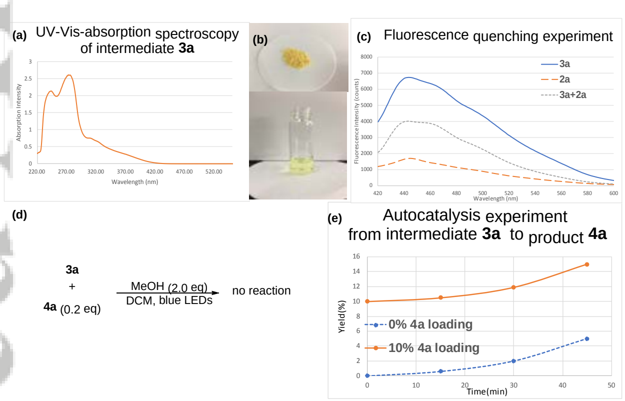


Figure 2. (a) A direct autocatalytic examination experiment of **1a** to **3a**. (b) Autocatalytic examination experiment of **1a** to **3a** under the reaction conditions. (c) The kinetic experiments from **1a** to **3a**. (d) Light/dark cycle experiments for the templet reaction from **1a** to **3a**.

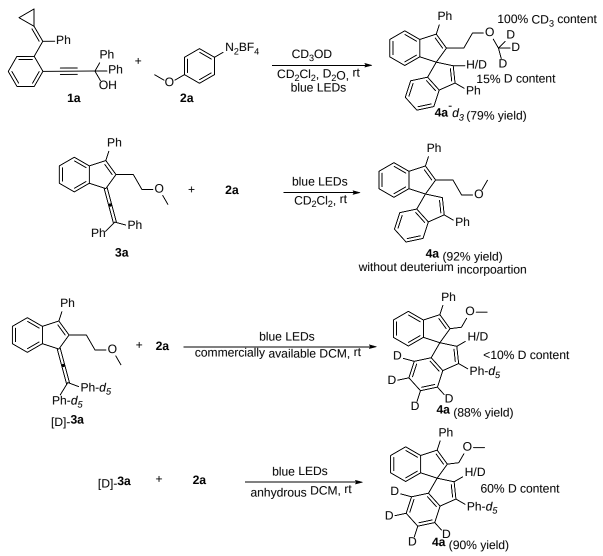


Notably, the allenic product **3a** is a bright yellow solid, indicating the possibility on the absorption of visible light irradiation. As expected, the UV-vis absorption spectrum of **3a** showed a broad absorption band over 400 nm (Figures 3a and 3b). On the basis of its absorption spectrum, fluorescence quenching experiment of **3a** demonstrated that its excited state could be quenched by aryldiazonium salt **2a**, indicating that a SET process or an energy transfer could take place between **3a** and **2a** (Figure 3c). Thus, we assumed that the second reaction pathway might proceed via a SET process to generate the radical cation of **3a** under the reaction condition. In a seminal work by Wu and his coworkers, it has been shown that the allenic moiety of **3a** could be oxidized to radical cation followed by a nucleophilic attack.[11] Indeed, while using catalytic amount of **2a**, the reaction could proceed smoothly from **3a** to **4a**, suggesting a similar chain process or autocatalytic pathway. The measurement on the fluorescence decay of compound **3a** indicated that its fluorescence lifetime is 0.80 ns (see page S26 in the Supporting Information). The control experiments showed that **4a** itself could not catalyze the transformation of **3a** to **4a**, and upon treating **3a** with **4a** (10 mol%) under the reaction conditions, no accelerated transformation could be realized from **3a** to **4a**, thereby excluding the autocatalytic pathway (Figures 3d and 3e). Therefore, the second reaction pathway might have a similar chain process as that of the first pathway. To explain the formation of product **4a**, we hypothesized that the radical cation of **3a** was quenched by an intramolecular Friedel-Crafts-type cyclization to generate a spirobi[indene] skeleton fused alkenyl radical, which underwent a hydrogen transfer to afford the final product.

Figure 3. (a) UV-vis absorption spectrum of **3a**. (b) The physical property of **3a**. (c) The fluorescence quenching experiment. (d) A direct autocatalytic examination experiment of **3a** to **4a**. (e) Autocatalytic examination experiment of **3a** to **4a** under the reaction conditions.

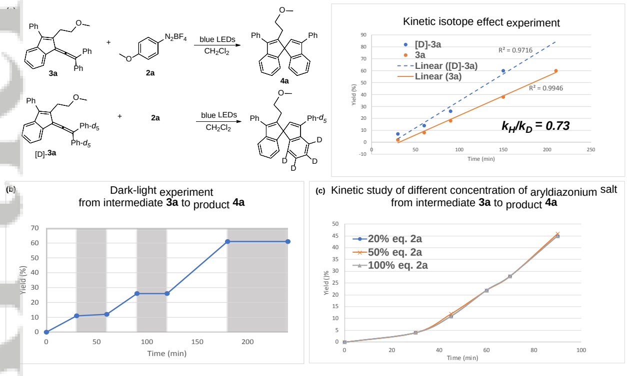


Scheme 3 The deuterium labeling experiments.



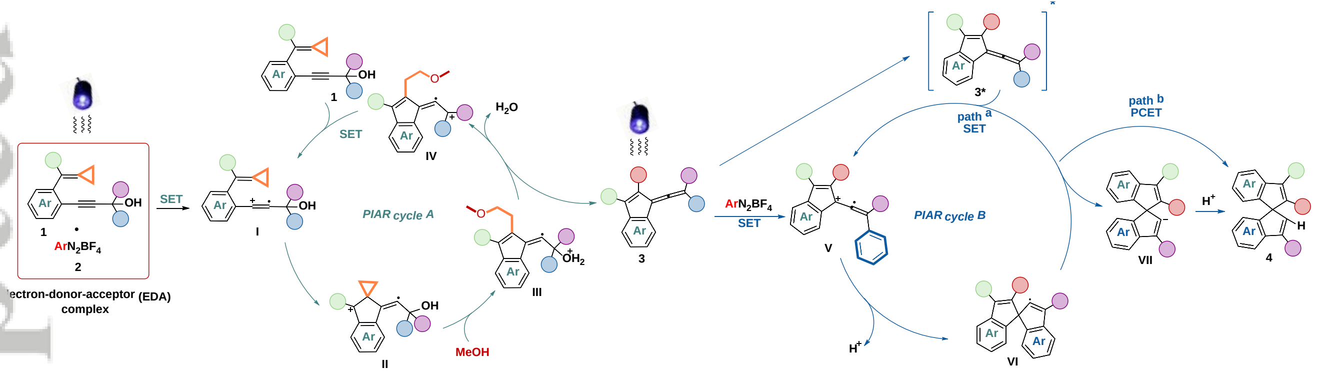
Another key issue is to illustrate the way of alkenyl radical to capture a H atom to produce **4a**, whether it comes from a HAT process or a SET process. To clarify this point, a series of deuterium labeling experiments were carried out. As shown in Scheme 3, when the reaction was performed by using **1a** as the starting material in CD_2Cl_2 in the presence of deuterium oxide (5.0 equiv) and CD_3OD (2.0 equiv), only 15% of the alkenyl hydrogen in product **4a** was deuterated. In the meantime, no deuterium incorporation was observed when the reaction was carried out in CD_2Cl_2 using intermediate **3a** as the starting material. Next, we prepared the deuterated **3a** to further investigate the hydrogen source and found that when the reaction was carried out in anhydrous DCM, **4a** was obtained in 90% yield along with 60% deuterium incorporation; however, when the reaction was directly performed in commercially available DCM, **4a** was formed in 88% yield without significant deuterium incorporation (< 10% D content), due to the higher water content (0.035%) of commercially available DCM (see Karl Fischer analytic result in the Supporting Information). These results suggested that the H atom is derived from an electrophilic addition pathway rather than a HAT process. Meanwhile, a kinetic isotope experiment gave a k_H:k_D = 0.73, also indicating an electrophilic pathway in the hydrogen transfer process (Figure 4a). In addition, the intermolecular HAT between alkenyl radical and the phenyl group in **3a** could be also ruled out, suggesting a complete proton transfer process. More importantly, the light-dark interval experiment confirmed that constant illumination of light is an indispensable element for formation of **4a** from allenic intermediate **3a** (Figure 4b). This experimental result may validate that the photoexcitation of **3a** to **3a*** is an essential element for the chain transfer process. Furthermore, the kinetic experiments illustrated that the reaction rate was not related to the concentration of **2a** from reaction pathway of **3a** to **4a**, demonstrating that the rate of SET between **3a*** and **2a** is much slower than that of **3a*** and alkenyl radical species (Figure 4c). The quantum yield of this process was measured to be 0.5, which implied the chain process without light irradiation is not a dominant process, partially supporting the chain process with the continuous light irradiation (see page S16 in the Supporting Information). The similar shape of the kinetic curves suggested the existence of a similar induction period and chain process as that of the first reaction pathway.

Figure 4. (a) Experiment of kinetic isotope effect; (b) Light/dark cycle experiments for the templet reaction of **3a** to **4a**; (c) The kinetic experiment from **3a** to **4a**.



On the basis of above mechanistic investigations and the pervious results, a plausible reaction mechanism for this novel process is outlined in Scheme 4. The visible light irradiation of an *in situ* generated electron donor-accepter (EDA) complex between propargyl alcohol-tethered alkylidenecyclopropane **1** and aryldiazonium salt **2** would generate a radical cation **I** via a SET event, which underwent a cyclization to give intermediate **II**. The cyclopropane in intermediate **II** underwent a ring-opening process upon nucleophilic attack of methanol to deliver the corresponding radical intermediate **III**, and the release of water leads to a radical cation **IV**. It can accept an electron from another molecule of propargyl alcohol-tethered alkylidenecyclopropane **1** to give the indene fused allenic product **3**. The two SET processes constituted the first chain process. Visible light direct irradiation of **3** could produce a excited **3*** species, which underwent another SET event with aryldiazonium salt **2** to afford a radical cationic species **V**. Once **V** was formed, it would rapidly undergo an intramolecular Friedel-Crafts reaction to give a cyclized radical intermediate **VI** along with the release of a proton. At this stage, another SET process could take place between **VI** and the excited **3*** to afford **V** and the alkenyl anion **VII**, which captured a proton to afford the desired spirobi[indene] derivative **4** (path a). However, we could not exclude the possiblity of a direct PCET from **VI** to **4** without the formation of intermeidate **VII** at the present stage (path b).[6] The two SET processes constituted the second chain process.

Scheme 4. Proposed reaction mechanism



Conclusions

In summary, we have disclosed the reaction pathway to rapidly construct spirobi[indene] skeletons, and a two consequent chain processes has been suggested. This process has been established through the detailed mechanistic investigations. This unusual process occurs, through utilizing photoactive substrate in chain process with visible light irradiation. Upon photo-irradiation, the redox-active intermediate can be generated as radical ion or the substrate can be excited to the singlet or triplet state to take part in the following chain transfer process. To the best of our knowledge, this is the unique example of a photo-induced chain process with a photoactive substrate in organic synthesis. The utilization of this novel synthetic method for the synthesis of natural products or pharmaceutical molecules is currently under investigation.

Supporting Information

The supporting information for this article is available on the WWW under https://doi.org/10.1002/cjoc.2020xxxxx.

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Entry for the Table of Contents

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Title: Mechanistic studies on propargyl alcohol-tethered alkylidenecyclopropane with aryldiazonium salt initiated by visible light

Jiaxin Liu,[a] Yin Wei*,[a] and Min Shi[a,b]

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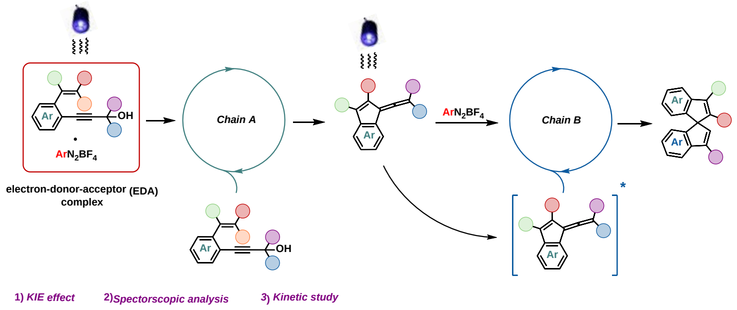

The plausible reaction mechanism of a visible-light photo-induced reaction for rapidly constructing spirobi[indene]s has been established through systematically mechanistic studies.