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Photosensitized, Energy-Transfer-Mediated Cyclization of 2-(1-Arylvinyl)benzaldehydes to Anthracen-9-(10*H*)-ones

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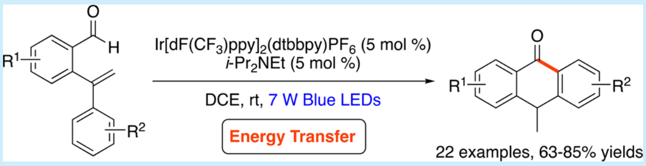
Supporting Information

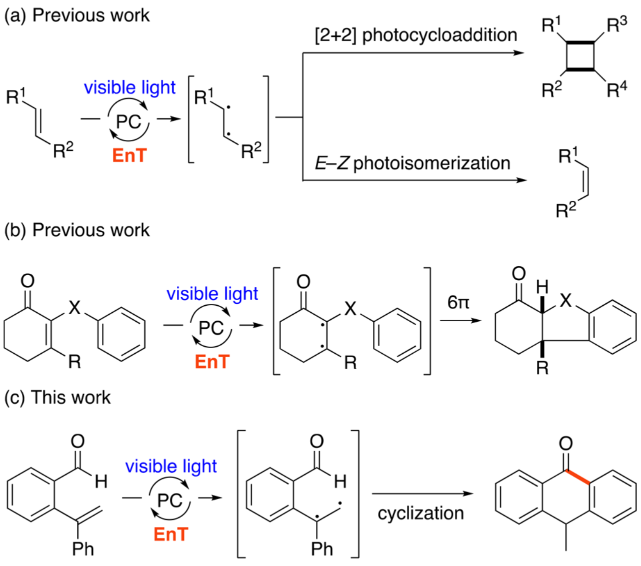
ABSTRACT: A visible-light-induced photocatalytic intramolecular cyclization of 2-(1-arylvinyl)benzaldehydes is reported. The reaction is promoted in the presence of an Ir^{III} photocatalyst and an amine base at room temperature under the irradiation of blue LEDs, affording 10-methylanthracen-9(10*H*)-one derivatives in moderate to good yields with tolerance to various functional groups. A series of mechanistic experiments suggest that the reaction proceeds via energy transfer from the excited Ir^{III} photocatalyst to the substrate to generate a diradical, which then undergoes 1,5-hydrogen shift, 6π electrocyclization, and aromatization leading to the cyclic product.



Over the past decade, photocatalysis using visible light has emerged as a powerful tool for organic synthesis because of its inherent "green chemistry" features.[1] The vast majority of visible-light-induced, photocatalyst-mediated reactions proceed through a single-electron transfer (SET) process between the excited-state photocatalyst and a substrate (photoredox catalysis).[2] Meanwhile, the field of visible-light-mediated energy transfer (EnT) catalysis (photosensitization), in which the excited photocatalyst directly transfers its excited-state energy to a substrate to form a reactive intermediate, has gained increasing attention in recent years.[3,4] In this context, excitation of an alkene to its triplet state (a diradical intermediate) is a representative process enabled by photosensitized energy transfer. However, the majority of known photocatalytic transformations of alkenes enabled by this process are limited to two main reaction types, that is, [2 + 2] photocycloaddition[5] and *E*−*Z* photoisomerization (Scheme 1a).[6] A notable exception is the photocatalytic 6π heterocyclization of cyclic 2-aryloxyketones and related derivatives, which was recently developed by Smith and co-workers (Scheme 1b).[7] Thus, the development of new photosensitized, energy-transfer-mediated transformations of alkenes remains highly desirable.

Herein, we report a visible-light-induced photocatalytic intramolecular cyclization of 2-(1-arylvinyl)benzaldehydes, which is most likely initiated by a photosensitized energy-transfer process (Scheme 1c). The reaction provides a mild, efficient, and atom-economic approach to anthracen-9-(10*H*)-one derivatives, which can be found as structural elements in a variety of natural products and biologically active compounds.[8] The present approach can be compared favorably with conventional approaches to anthracen-9-(10*H*)-ones,[9] such as the intramolecular Friedel−Crafts acylation of 2-benzylbenzoic acid derivatives, which often require excess amounts of strong Brønsted acid or Lewis acid or preactivation of the starting materials into reactive acid halides or anhydrides.[10−12]

Scheme 1. Photocatalytic Transformations of Alkenes via Energy Transfer



We previously reported intramolecular hydroacylation of 2-(1-phenylvinyl)benzaldehyde (**1a**) promoted by a cobalt−diphosphine catalyst activated by a metallic reductant (Zn dust), affording 3-phenyl-1-indanone.[13] The present cyclization reaction was found in our attempt to promote this hydroacylation using a photoredox catalyst and an organic reductant in place of Zn dust.[14] Using the combination of

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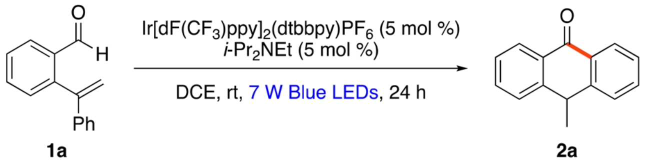
Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$ and *i*-Pr$_2$NEt, the attempted cobalt-catalyzed, visible-light-assisted hydroacylation did not yield the expected indanone product but afforded 10-methylanthracen-9(10*H*)-one (**2a**) as the sole product (see Table S1). We then noted that the cobalt catalyst was not essential and, upon extensive optimization, managed to promote the cyclization using 5 mol % each of the Ir catalyst and the amine in DCE at room temperature under irradiation of blue LEDs, affording **2a** in 83% yield (Table 1, entry 1; see Tables S2−S5 for more details). The reaction was found to be highly sensitive to the photocatalyst. Thus, the use of other common metal and dye photocatalysts, which possess lower triplet energies than that of Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$ (E_T = 60.8 kcal/mol),[3b] led to significantly diminished yields or no desired product (entries 2−5). Organic and inorganic bases other than *i*-Pr$_2$NEt could also be used, albeit with lower reaction efficiency (entries 6−9). DCE emerged as the best solvent among others, including CH$_2$Cl$_2$, MeCN, and DMF (entries 10−12). Control experiments demonstrated that the photocatalyst and visible light are essential (entries 13 and 14). On the other hand, the reaction took place in the absence of the base albeit in a lower yield (entry 15), where the rest of the starting material was not recovered but decomposed into unidentified products.

Table 1. Effect of Reaction Conditions[a]

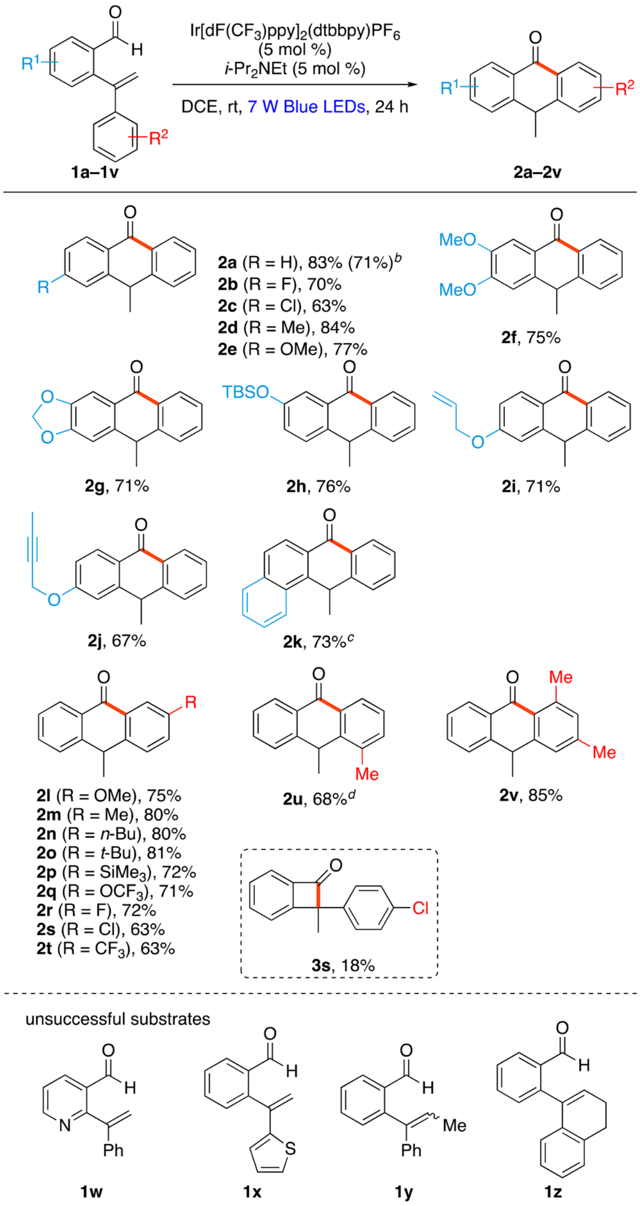


entry	deviation from standard conditions	yield[b] (%)
1	none	81 (83)[c]
2	Ru(bpy)$_3$Cl$_2$•6H$_2$O as the photocatalyst	0
3	Ir(ppy)$_2$(dtbbpy)PF$_6$ as the photocatalyst	4
4	*fac*-Ir(ppy)$_3$ as the photocatalyst	38
5	Eosin Y as the photocatalyst	4
6	Et$_3$N instead of *i*-Pr$_2$NEt	58
7	pyridine instead of *i*-Pr$_2$NEt	45
8	K$_2$CO$_3$ instead of *i*-Pr$_2$NEt	74
9	Cs$_2$CO$_3$ instead of *i*-Pr$_2$NEt	62
10	CH$_2$Cl$_2$ instead of DCE	72
11	MeCN instead of DCE	61
12	DMF instead of DCE	19
13	Ir[dF(CF$_3$)ppy]$_2$(dtb-bpy)PF$_6$ omitted	0
14	in the dark	0
15	*i*-Pr$_2$NEt omitted	31

[a] Standard conditions: **1a** (0.1 mmol), Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$ (0.005 mmol, 5 mol %), and *i*-Pr$_2$NEt (0.005 mmol, 5 mol %) in DCE (0.8 mL) at room temperature under irradiation of 7 W blue LEDs and a nitrogen atmosphere. [b] Determined by GC using *n*-tridecane as an internal standard. [c] Isolated yield in parentheses.

With the optimized catalytic system in hand, we explored the scope of the intramolecular cyclization using various 2-(1-arylvinyl)benzaldehyde derivatives (Scheme 2). A variety of electron-withdrawing or -donating groups could be introduced to the benzaldehyde moiety, affording the corresponding products **2b**−**j** in moderate to good (63−84%) yields. Thus, substituents such as halogen (F, Cl), alkoxy, siloxy, alkenyl, and alkynyl groups could be well tolerated without very obvious electronic impact, while somewhat lower yield was obtained with the chlorinated substrate (see **2c**). The reaction of **1a** could be performed on 5 mmol scale albeit in a somewhat lower yield of 71%. 1-(1-Phenylvinyl)-2-naphthaldehyde **1k** also underwent the photocatalytic cyclization to give the desired product **2k** in 73% yield. Likewise, a variety of substituents could be introduced to the *para* position of the other aryl group of the substrate, affording the desired products **2l**−**t** in 63−85% yields. Note that somewhat lower yields were observed for the substrate-bearing electron-withdrawing CF$_3$ group (see **2v**) compared with those bearing electron-donating groups such as methoxy and alkyl groups (see **2l**−**o**). Interestingly, the reaction of the *p*-chloro-substituted substrate **1s** was accompanied by a benzocyclobutanone derivative **3s** as a byproduct (18% yield). While other substrates did not give isolable and characterizable amount of

Scheme 2. Substrate Scope[a]

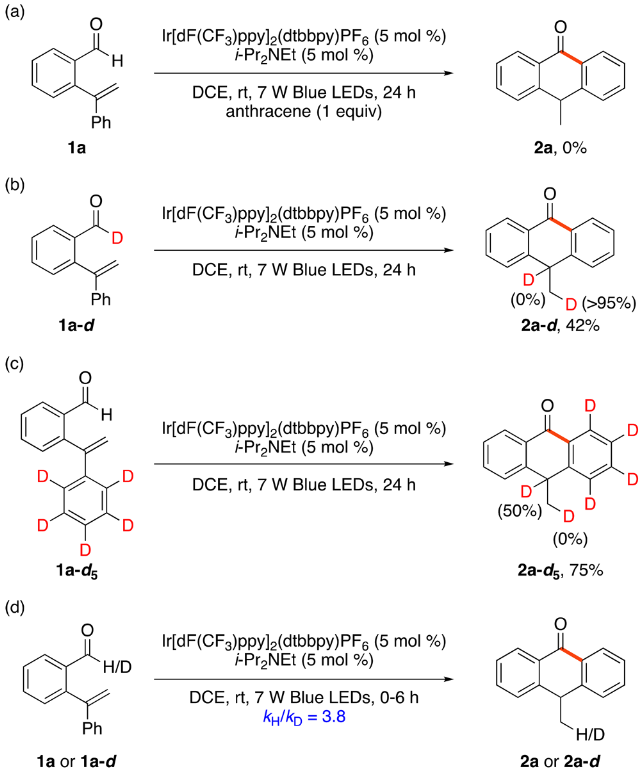


[a] Standard conditions: **1** (0.3 mmol), Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$ (0.015 mmol, 5 mol %), and *i*-Pr$_2$NEt (0.015 mmol, 5 mol %) in DCE (2.4 mL) at room temperature under irradiation of 7 W blue LEDs and a nitrogen atmosphere. [b] 5 mmol scale, 48 h. [c] 48 h. [d] 72 h.

benzocyclobutanone byproducts, the formation of **3s** would be relevant to the mechanism of the present cyclization (vide infra). The reaction also tolerated substrates bearing 2-tolyl and 3,5-dimethylphenyl groups, affording the corresponding products **2u** and **2v** in good yields. Unfortunately, substrates bearing a heteroaryl group such as pyridine and thiophene or a β-substituent on the alkene moiety (**1w**−**z**) failed to produce the desired products.

To gain insight into the reaction mechanism, we performed a series of experiments. First, a light on/off experiment showed that the cyclization product **2a** formed only under irradiation of blue LEDs (Figure S2), demonstrating that the transformation needed continuous irradiation of visible light. Second, Stern−Volmer quenching experiments demonstrated that the olefinic substrate **1a** efficiently quenches the excited state of the Ir photocatalyst (Figure S3). The S_0−T_1 gap for **1a** was calculated to be 53.8 kcal/mol (B3LYP/6-311+G,[2d]p)), suggesting that the energy of the triplet state of $^*Ir^{III}$ (E_T = 60.8 kcal/mol) is sufficient for sensitizing **1a** to its triplet state. In accordance with this observation, the addition of 1 equiv of anthracene, a common triplet state quencher (E_T = 42.6 kcal/mol),[3a,15] completely shut down the cyclization of **1a** (Scheme 3a). These facts are consistent with the hypothesis that the present reaction proceeds through a photocatalytic energy transfer pathway.

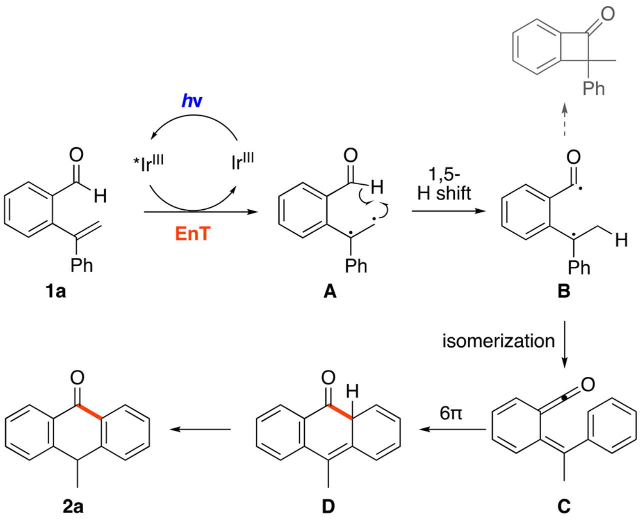
Scheme 3. Mechanistic Experiments



In order to trace the fate of the hydrogen atoms on the formyl and the *ortho* positions as well as to probe the rate-determining step, we next performed experiments using deuterium-labeled substrates. The substrate bearing a deuterated formyl group, **1a**-***d***, underwent cyclization with a clean transfer of the deuterium atom to the methyl position of the product **2a**-***d*** (Scheme 3b). On the other hand, the reaction of the pentadeuterated substrate **1a**-d_5 resulted in incomplete (50%) transfer of the *ortho*-deuterium atom into the 10-position of the product (Scheme 3c). Furthermore, comparison of initial rates of parallel individual reactions of **1a** and **1a**-***d*** gave a kinetic isotope effect (KIE) of 3.8, suggesting that the formyl C−H bond cleavage is the rate-determining step.

On the basis of the above experimental results and related literature precedents,[3−6] we propose a reaction mechanism of the present cyclization as shown in Scheme 4. Initially, irradiation of the Ir photocatalyst with visible light generates excited state $^*Ir^{III}$, which can sensitize the substrate **1a** via an energy-transfer process to form a triplet diradical intermediate **A**. Subsequently, 1,5-hydrogen shift of **A** gives a 1,4-diradical intermediate **B**, which would then undergo intersystem crossing and isomerization to an *o*-quinodimethane-type intermediate **C**. The formation of the benzocyclobutane byproduct **3s** may be rationalized by intramolecular radical−radical coupling of 1,4-diradical intermediate analogous to **B**. Finally, 6π electrocyclization of **C** and subsequent aromatization would furnish the product **2a**. The failure of the reaction of the internal alkene substrates **1y** and **1z** might be attributed to the difficulty of 1,5-hydrogen shift of the corresponding diradical intermediates. Note that the role of the base remains unclear at this moment.

Scheme 4. Proposed Reaction Pathway



In summary, we have developed an intramolecular cyclization reaction of 2-(1-arylvinyl)benzaldehydes under visible-light photocatalysis, affording anthracen-9(10*H*)-one derivatives in moderate to good yields. The reaction features high atom economy, mild conditions, simple operation, and good functional group compatibility. The reaction likely involves photosensitized energy transfer as the key step, and the proposed mechanism would inspire further exploration of photocatalytic transformations of alkene-containing molecules.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.9b00182.

Detailed experimental procedures and characterization data for new compounds (PDF)

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Notes

The authors declare no competing financial interest.

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