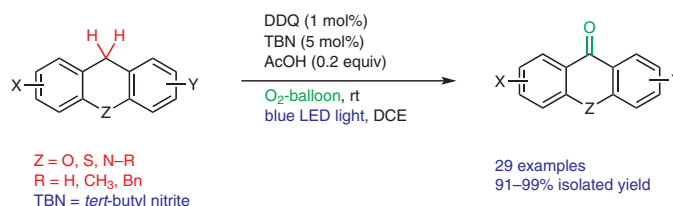


# Visible-Light-Induced Aerobic Oxidation of Benzylic C(sp<sup>3</sup>)-H of Alkylarenes Promoted by DDQ, *tert*-Butyl Nitrite, and Acetic Acid

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**Abstract** A visible-light photocatalytic aerobic oxidation of benzylic C(sp<sup>3</sup>)-H bonds proceeded in the presence of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone, *tert*-butyl nitrite, and acetic acid. Advantages of this aerobic oxidation method include its relatively mild conditions, the use of visible-light irradiation instead of conventional thermal methods, the use of a low catalyst loading, and the ability to oxidize a range of alkylarenes, including xanthenes, thioxanthenes, and 9,10-dihydroacridines, to the corresponding ketones in excellent yields.

**Key words** xanthenones, thioxanthenones, acridinones, oxidation, photocatalysis, benzylic oxidation

It can be said that oxidation is the foundation of many biological and chemical processes.<sup>1</sup> Benzylic C(sp<sup>3</sup>)-H oxidation is an important oxidative transformation that permits the direct conversion of simple raw materials into more-valuable ketones.<sup>2</sup> In the conventional reaction, stoichiometric amounts of hazardous metal oxidants, particularly Cr<sup>3</sup> or Mn<sup>4</sup> compounds, are employed in direct benzylic oxidation reactions. These metal oxidants have gradually been replaced by more-efficient catalytic oxidation systems that largely depend on the use of a transition-metal catalyst and a stoichiometric amount of a terminal oxidant, such as phenyl methyl sulfoxide,<sup>5</sup> polymeric iodosobenzene,<sup>6</sup> *N*-hydroxyphthalimide,<sup>7</sup> *tert*-butyl hydroperoxide,<sup>8</sup> Oxone,<sup>9</sup> etc.<sup>10</sup> However, many of these catalytic oxidation systems do not meet the requirements of green chemistry and sustainable development. In this respect, molecular oxygen (O<sub>2</sub> or air) as the terminal oxidant is considered to be a better option because of its low cost and because water is generated as the sole byproduct from the reaction.<sup>11</sup> However the triplet ground state of molecular oxygen cannot be readily inserted into nonactivated C(sp<sup>3</sup>)-H bonds. Consequently, a transition-metal catalyst, such as Co, Mn, Cu, or Fe, and

harsh reaction conditions are required in benzylic C(sp<sup>3</sup>)-H aerobic oxidations.<sup>12</sup> Unfortunately, these methods often produce problems associated with residues of transition metals, especially in the pharmaceutical industry. Therefore, more and more researchers have become interested in transition-metal-free catalytic oxidations with molecular oxygen as the terminal oxidant.<sup>13</sup> Nontransition-metal-based protocols for benzylic aerobic oxidation have also recently emerged.<sup>14</sup>

Visible-light-induced photocatalysis is a mild and powerful tool for the functionalization of organic molecules.<sup>15</sup> Transition-metal complexes<sup>16</sup> and small organic molecules<sup>17</sup> are often used as the photocatalysts in such photocatalytic reactions. Ruthenium and iridium polypyridyl complexes are representative metal photocatalysts, and their efficient catalytic properties in photocatalytic oxidations have been widely recognized. Moreover, a range of small organic molecules, such as cyanoarenes, benzophenones, pyryliums, acridiniums, and quinones, have been successfully used as catalysts for photocatalytic reactions.

2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) is a versatile and powerful oxidant that has been successfully employed in many C-H bond transformations.<sup>18</sup> This is due to its ability to abstract hydrogen and its one-electron reduction potential.<sup>19</sup> We previously developed an efficient versatile DDQ/*tert*-butyl nitrite (TBN)/O<sub>2</sub> catalytic oxidation system, and have successfully applied it to the oxidation of benzylic alcohols, the oxidative deprotection of benzylic-type ethers, and the oxygenation of diarylmethane C(sp<sup>3</sup>)-H moieties.<sup>20</sup> In the DDQ/TBN/O<sub>2</sub> system, DDQ serves as the main catalyst, oxygen is the terminal oxidant, and TBN is a co-catalyst, equivalent to nitric oxide. However, these DDQ/TBN-catalyzed aerobic oxidation reactions are all carried out at elevated temperatures. One of our targets was to perform C(sp<sup>3</sup>)-H oxidations efficiently by photocatalysis to provide a superior outcome to reactions performed un-

der thermal conditions. DDQ can be excited to its triplet excited state by visible light,<sup>21</sup> and the resulting triplet-excited DDQ can even oxidize benzene to phenol.<sup>22</sup> Recently, Brasholz and co-workers successfully applied this photocatalytic system to benzylic oxidation reactions;<sup>23</sup> however, the products selectivities were poor, and the yields of products were low.

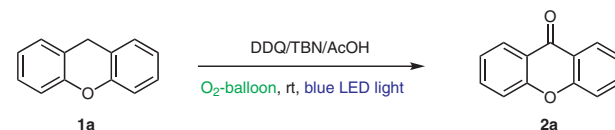
It is well-known that xanthenes, thioxanthenes, and acridones are important organic molecules that can serve as structural motifs in functional molecules, pharmaceutical intermediates, and advanced materials.<sup>24</sup> Inspired by the aforementioned works and by our previous works on DDQ-catalyzed oxidation reactions,<sup>20,25</sup> we attempted to develop a new strategy for visible-light photocatalytic aerobic oxidation of the benzylic C(sp<sup>3</sup>)-H moieties of xanthenes, thioxanthenes, and 9,10-dihydroacridines to give xanthenes, thioxanthenes, and acridones, respectively.

First, we set out to optimize the photooxygenation conditions by using xanthene (**1a**) as a model substrate (Table 1). The photooxygenation reaction was evaluated in the presence of 10 mol% of DDQ, 10 mol% of TBN, and 1 equivalent of acetic acid in 1,2-dichloroethane (DCE) under an oxygen balloon with illumination by an 18 W blue light-emitting diode (LED) at room temperature (Table 1, entry 1). To our delight, xanthen-9-one (**2a**) was obtained in 99% isolated yield after eight hours. We then examined the effects of reducing the loadings of DDQ and TBN. When the loading of DDQ was decreased to 1 mol% and that of TBN was reduced to 5 mol%, **1a** was fully converted into **2a** in ten hours (entry 3). However, reducing the loading of TBN to 2.5 mol% led to a low conversion of **1a**, and the isolated yield of **2a** fell to 55% (entry 4). When TBN was absent, only a trace of **2a** was detected after 12 hours (entry 5), whereas in the absence of DDQ, **2a** was obtained in 12% isolated yield (entry 6). When the photooxygenation reaction was performed in the absence of both DDQ and TBN, as we expected, no reaction took place (entry 7).

TBN can release NO at high temperatures or under acidic conditions.<sup>26</sup> We believe that the acetic acid provides acidic conditions that promote the decomposition of TBN to give NO. We found that 0.2 equivalents of acetic acid were sufficient to permit complete decomposition of TBN (Table 1, entries 8 and 9). TBN also releases NO in light,<sup>23</sup> but this process is less efficient. Thus, the isolated yield of **2a** was only 52% when **1a** was subjected to photooxygenation for 12 hours in the absence of acetic acid (entry 10). As we speculated, only traces of **2a** were formed under a nitrogen atmosphere (entry 11). We also found that the photooxygenation of xanthene proceeded with a much higher yield than the corresponding thermal reaction in darkness (entry 12).

Other results in Table 1 show the effects of various solvents on this reaction. Xanthene (**1a**) was oxidized to **2a** in 14% yield in toluene (Table 1, entry 13), whereas polar solvents inhibited the reaction (entries 14–16). However, in

**Table 1** Optimization of the Reaction Conditions<sup>a</sup>



Entry	Solvent	DDQ (mol%)	TBN (mol%)	AcOH (equiv)	Time (h)	Yield <sup>b</sup> (%)
1	DCE	10	10	1	8	99
2	DCE	5	5	1	8	99
3	DCE	1	5	1	10	99
4	DCE	1	2.5	1	12	55
5	DCE	1	–	1	12	trace
6	DCE	–	5	1	12	12
7	DCE	–	–	1	12	NR <sup>c</sup>
8	DCE	1	5	0.5	12	99
<b>9</b>	<b>DCE</b>	<b>1</b>	<b>5</b>	<b>0.2</b>	<b>12</b>	<b>99</b>
10	DCE	1	5	–	12	52
11 <sup>d</sup>	DCE	1	5	1	12	trace
12 <sup>e</sup>	DCE	1	5	0.2	12	28
13	toluene	1	5	0.2	12	14
14	EtOAc	1	5	0.2	12	trace
15	THF	1	5	0.2	12	trace
16	EtOH	1	5	0.2	12	trace
17	AcOH	1	5	–	12	52

<sup>a</sup> Reaction conditions: **1a** (1 mmol), DCE (5.0 mL), 18 W blue LED, O<sub>2</sub> balloon, rt.

<sup>b</sup> Isolated yield.

<sup>c</sup> NR = no reaction.

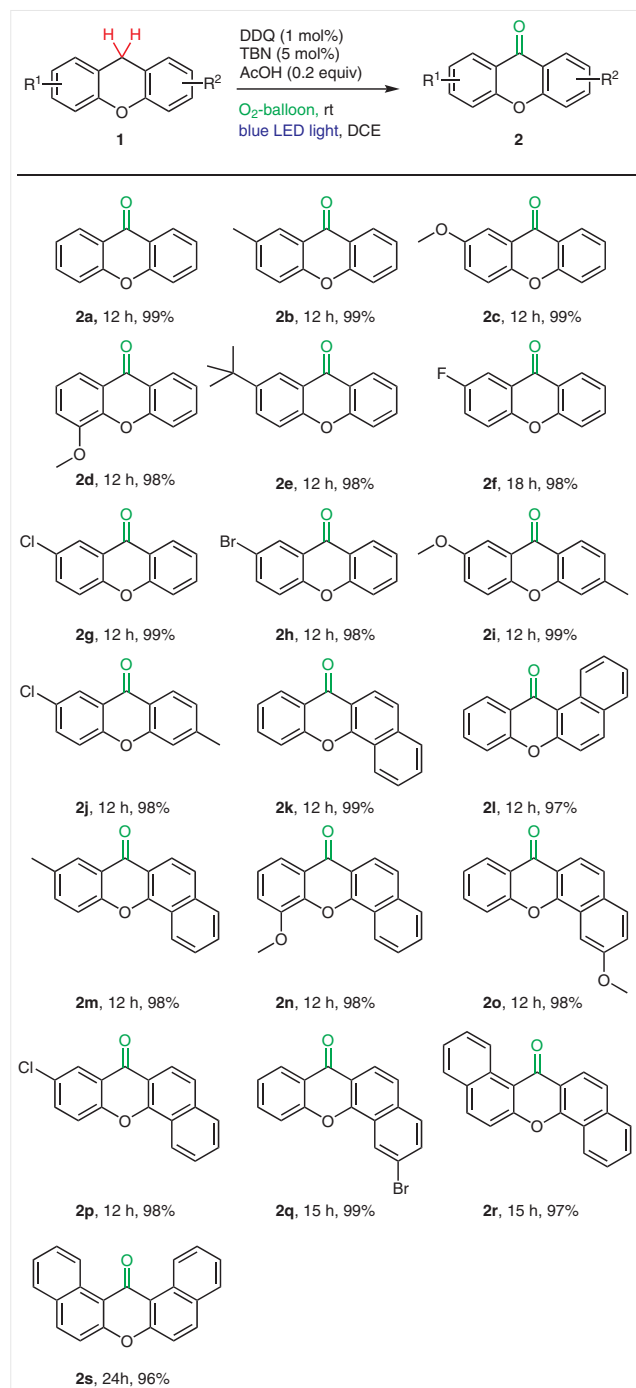
<sup>d</sup> Under N<sub>2</sub>.

<sup>e</sup> 90 °C (oil bath), darkness.

the polar solvent AcOH, a 52% yield of **2a** was obtained (entry 17). On the basis of these experimental results, we chose 1 mol% of DDQ, 5 mol% of TBN and 0.2 equivalents of AcOH in 1,2-dichloroethane with an O<sub>2</sub> balloon as the optimal photooxygenation reaction conditions.

To explore the general applicability of this protocol for the photooxygenation, a number of xanthene derivatives were investigated under the optimal reaction conditions (Scheme 1). All substituted xanthenes showed high reactivities, and the desired substituted xanthenes **2b–s** were obtained in excellent yields.<sup>27</sup> This photooxygenation protocol tolerated various functional groups, including electron-donating groups and electron-withdrawing groups. Xanthenes bearing an electron-donating group (2-methyl, 2-methoxy, 4-methoxy, or 2-*tert*-butyl) underwent smooth transformations to give the corresponding xanthenes **2b–e** in isolated yields of 98–99%. Xanthenes with an electron-withdrawing group (2-F, 2-Cl, or 2-Br) also gave the expected xanthenes **2f–h** in excellent yields. The reaction of **1f**

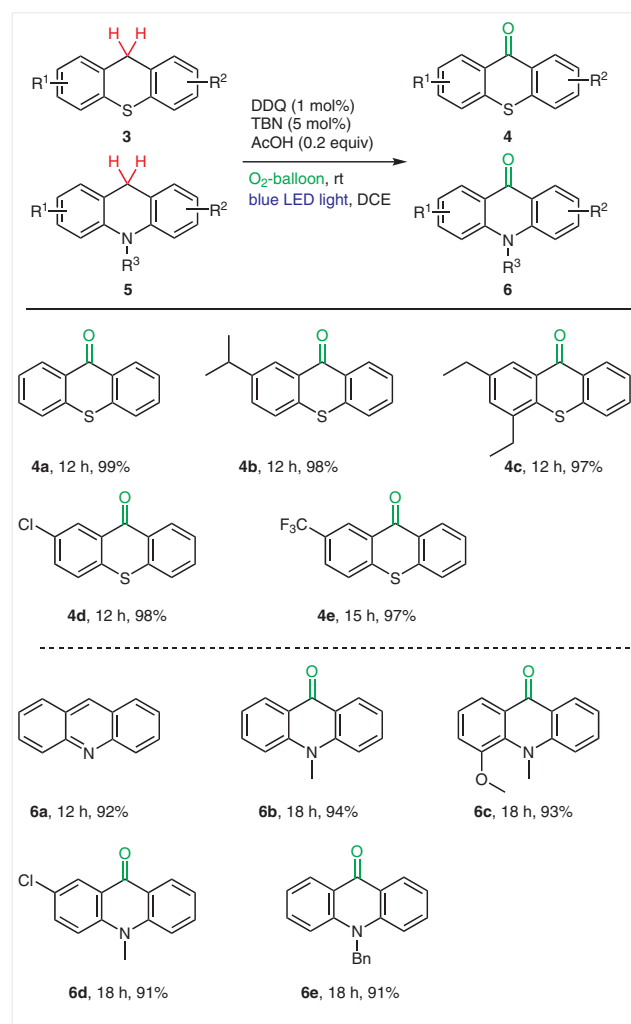
was slightly sluggish, but a satisfactory result could be obtained by prolonging the reaction time to 18 hours. Poly-substituted xanthenes could also be photooxidized smoothly to give the corresponding xanthenes **2i** and **2j**



**Scheme 1** Photooxygenation of xanthenes. *Reaction conditions:* substrate **1a–s** (1 mmol), DDQ (1 mol%), TBN (5 mol%), AcOH (0.2 equiv), DCE (5 mL), 18 W blue LED, O<sub>2</sub> balloon, rt. Reaction times and isolated yields are reported for each product.

quantitatively. Much to our delight, when benzo-fused xanthenes were used as substrates, they were fully converted into xanthenes **2k–q** in isolated yields of 97–99%. Because of the low solubility of 14*H*-dibenzo[*a,h*]xanthene (**1r**), its reaction had to be prolonged to 15 hours to improve the isolated yield of **2r**. Notably, for the sterically hindered substrate 14*H*-dibenzo[*a,j*]xanthene (**2s**), the reaction time had to be extended to 24 hours.

Having showed that our photocatalytic system is capable of highly efficient benzylic C(sp<sup>3</sup>)-H oxidation of xanthenes, we turned our attention to the photooxygenation of thioxanthenes to form thioxanthenes (Scheme 2). Thioxanthenes are a class of compounds that have great potential in biological applications and in the development of photosensitive materials.<sup>24d,e,f</sup> As shown in Scheme 2, the experimental results for the oxidization of thioxanthenes were

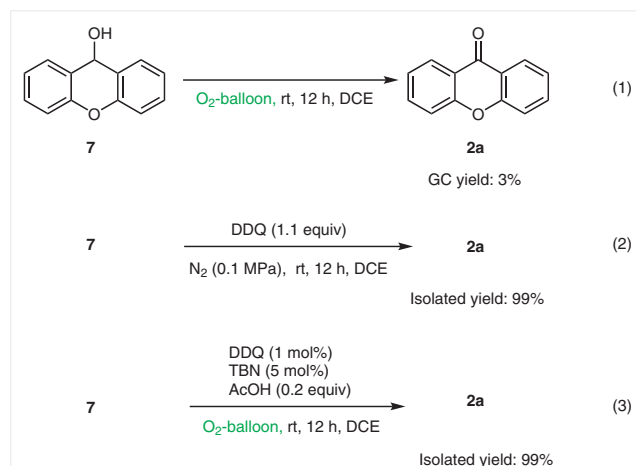


**Scheme 2** Photooxygenation of thioxanthenes and 9,10-dihydroacridines. *Reaction conditions:* substrate **3** or **5** (1 mmol), DDQ (1 mol%), TBN (5 mol%), AcOH (0.2 equiv), DCE (5 mL), 18 W blue LED, O<sub>2</sub> balloon, rt. Reaction times and isolated yields are reported for each product.

similar to those of xanthenes, and the corresponding thioxanthenes **4a–d** were obtained in isolated yields of 97–99%. Substrates bearing a strongly electron-withdrawing group, such as trifluoromethyl, required longer reaction times (**4e**). In addition to xanthenes and thioxanthenes, 9,10-dihydroacridines were also submitted to this photooxygenation protocol to obtain acridones. Acridones have a wide range of biological properties, the most striking of which is the selective inhibition of various human pathogenic viruses.<sup>24g,h</sup> However, we found that 9,10-dihydroacridine underwent aromatization, instead of oxygenation, to give acridine (**6a**), whereas *N*-methyl- and *N*-benzyl-9,10-dihydroacridines were photooxygenated smoothly to give the desired acridones in 91–94% isolated yields (**6b–e**).

Acyclic diphenylmethane was also subjected to this protocol; however, the conversion of diphenylmethane was only 15% after 24 hours.

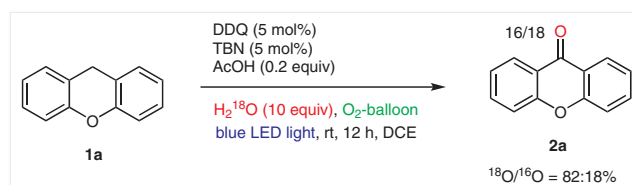
To understand the reaction mechanism, we attempted to identify the reaction intermediate in the photooxygenation of xanthene. HPLC was used to monitor the progress of the reaction. We found that an intermediate was gradually generated during the reaction and that its content remained at about 12–18% for two to ten hours. This intermediate was unstable but could be isolated by column chromatography on alkaline aluminum oxide. The pure intermediate needed to be cryopreserved. On the basis of NMR and MS analyses, the intermediate was identified as xanthydro (**7**; 9*H*-xanthen-9-ol). To gain insight into the oxidation of xanthydro, several control experiments were performed. We found that **7** could be transformed into **2a** in 3% GC yield under a dioxygen atmosphere in 12 hours (Scheme 3, equation 1). When **7** was treated with 1.1 equivalents of DDQ, a 99% yield of **2a** was obtained (Scheme 3, equation 2). The DDQ/TBN/O<sub>2</sub> catalytic oxidation system



**Scheme 3** Control experiments for the oxidation of xanthydro **7**

can replace stoichiometric DDQ.<sup>20</sup> Thus, when **7** was treated with 1 mol% of DDQ and 5 mol% of TBN in the presence of 0.2 equivalents of acetic acid under 0.1 MPa of O<sub>2</sub>, **2a** was obtained in 99% yield (Scheme 3, equation 3).

To confirm that the oxygen in the product is derived from water, an isotopic trace experiment was conducted with stoichiometric water labelled with <sup>18</sup>O. This resulted in 82% <sup>18</sup>O labelling of **2a**, as observed by MS analysis (Scheme 4); however, the molecular-ion peak of intermediate **7** could not be detected, due to its instability in MS.



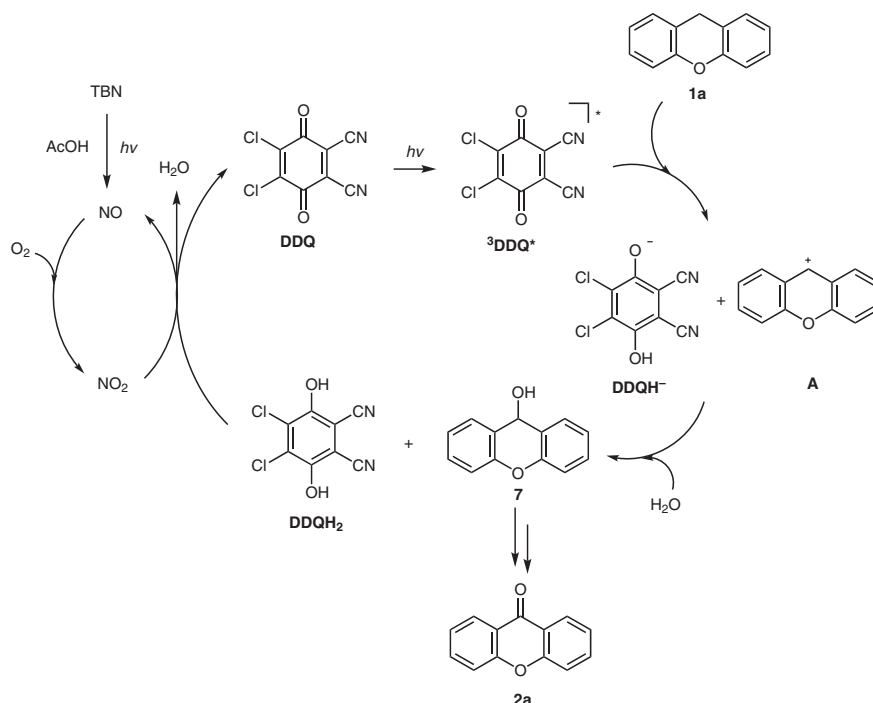
**Scheme 4** The isotopic tracer experiment

On the basis of reports in the literature and our experimental results, we propose a plausible reaction mechanism for the visible-light-induced aerobic oxidation of **1a** to **2a** promoted by the DDQ/TBN catalytic system in the presence of AcOH, as shown in Scheme 5. Initial photolysis and acylolysis of TBN liberates NO, which is readily oxidized to NO<sub>2</sub> by O<sub>2</sub>. DDQ is excited to its triplet excited state (<sup>3</sup>DDQ\*) by visible light.<sup>22</sup> The reaction of <sup>3</sup>DDQ\* with **1a** generates DDQH<sup>•</sup> and 9*H*-xanthen-9-yl cation (**A**) by a single-electron transfer/hydrogen-atom transfer (SET/HAT) pathway or by a HAT/SET pathway.<sup>22,23,28</sup> Nucleophilic trapping of the cation **A** by H<sub>2</sub>O (from the undried solvent and AcOH) gives xanthydro (**7**), which can be further oxidized to the product **2a** by DDQ/TBN/O<sub>2</sub>. Meanwhile DDQH<sup>•</sup> is protonated to 4,5-dichloro-3,6-dihydroxyphthalonitrile (DDQH<sub>2</sub>). This is oxidized to DDQ by NO<sub>2</sub>, which is immediately reduced to NO, with release of H<sub>2</sub>O as a byproduct.

In conclusion, we have successfully applied the DDQ/TBN/AcOH catalytic system to benzylic aerobic oxidation under visible light. Triplet-excited DDQ (<sup>3</sup>DDQ\*) exhibits an ultra-high oxidation activity. A range of alkylarenes, including xanthenes, thioxanthenes, and 9,10-dihydroacridines, were oxidized to the corresponding ketones in excellent yields. On the basis of the identification of the intermediate, we propose a plausible reaction mechanism. This photocatalytic protocol is more efficient than the conventional thermal protocol.

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Scheme 5 Plausible reaction mechanism

## Supporting Information

Supporting information for this article is available online at <https://doi.org/10.1055/s-0037-1610678>.

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- (27) **Xanthone (2a; 9H-Xanthen-9-one); Typical Procedure**  
A15-mL Schlenk tube equipped with a magnetic stirrer bar was charged with xanthone (**1a**; 182 mg, 1.0 mmol) and DDQ (2.3 mg, 1 mol%). The air in the tube was replaced with O<sub>2</sub> and the tube was sealed with a rubber plug. TBN (5.9 μL, 5 mol%), AcOH (12.0 mg, 20 mol%), and DCE (5.0 mL) were added. The Schlenk tube was placed in a dark box and illuminated with a 18 W blue LED. The mixture was stirred vigorously under an O<sub>2</sub> balloon

until the reaction was complete (GC). The mixture was then concentrated on a rotary evaporator, and the residue was purified by column chromatography (silica gel, PE-EtOAc) to give a white solid; yield: 194 mg (99%); mp 174–175 °C.

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.35–8.33 (m, 2 H), 7.73–7.70

(m, 2 H), 7.48 (d,  $J$  = 8.5 Hz, 2 H), 7.39–7.36 (m, 2 H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 177.2, 156.2, 134.8, 126.7, 123.9, 121.9, 118.0. MS (EI):  $m/z$  (%): 196.11 (93)  $[\text{M}]^+$ , 139.10 (100).  
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