



# Visible light photoredox catalysis: aerobic oxidation of perimidines to perimidinones



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## ABSTRACT

Aerobic oxidation of a series of 2,3-dihydro-1*H*-perimidines to the corresponding 4- and 6-perimidinones via visible light photoredox catalysis using Ru(bpy)<sub>3</sub><sup>2+</sup> as a catalyst was reported. The scope and limitation of this oxidation were investigated and a possible photochemical mechanism was proposed.

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## 1. Introduction

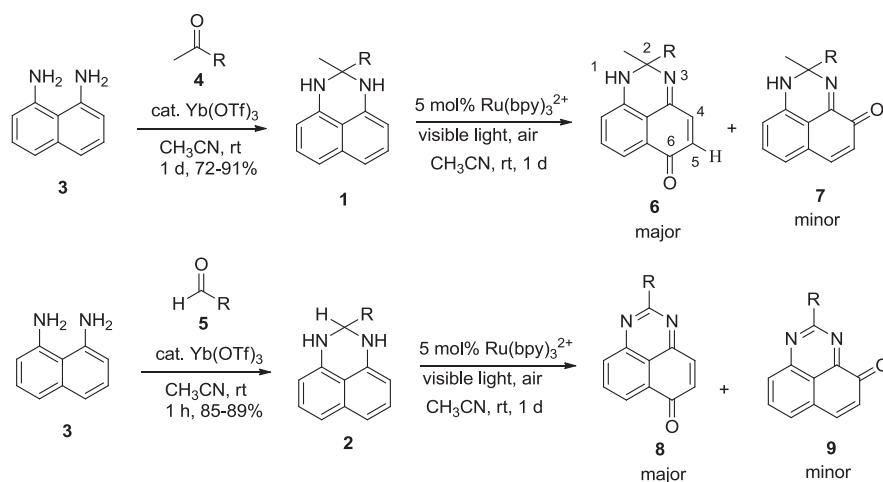
Chemical transformation via photocatalysis with visible light is one of the emerging strategies to meet the increasing demand for more sustainable chemical processes.<sup>1</sup> Up to date, visible light photoredox catalysis (VLPC) has been successfully applied to various organic transformations, including aza-Henry reaction,<sup>2</sup> asymmetric alkylation,<sup>3</sup> [2+2] cycloaddition,<sup>4</sup> Diels–Alder reaction,<sup>5</sup> reductive dehalogenation,<sup>6</sup> oxidations,<sup>7</sup> etc. Among the VLPC-based oxidations, previous reactions involved the use of the less environmentally benign organic compounds such as aryldiazonium ion<sup>8</sup> tetrachloromethane<sup>9</sup> or bromotrichloromethane<sup>10</sup> as the external oxidants. Recent catalytic oxidation processes, however, focus primarily on utilizing molecular oxygen as the terminal oxidant, since the latter is more atom-economical and generates no waste after reduced. For instance, Zen<sup>11</sup> and co-workers have reported the selective and efficient photocatalytic oxidation of sulfides to sulfoxides with O<sub>2</sub> using tris(bipyridine) ruthenium complexes (Ru(bpy)<sub>3</sub><sup>2+</sup>) as a photoredox catalyst. Itoh and co-workers have reported the aerobic oxidation of alcohols to carboxylic acids under visible light irradiation of fluorescent lamp with a catalytic amount of magnesium bromide diethyl etherate<sup>12</sup> or 2-chloroanthraquinone.<sup>13</sup> These successful examples prompted us to explore other oxygen-mediated oxidation transformations via

VLPC to replace the use of conventional oxidants such as Fremy's salt, which generally suffers from low yields or requires excess stoichiometric amounts of reagents.<sup>14</sup> Here, we describe the oxidation of a series of 2,3-dihydro-1*H*-perimidines to the corresponding 4- and 6-perimidinones via visible light photocatalysis under aerobic conditions. The 4- and 6-perimidinones can potentially serve as precursors for further preparation of 1,8-diaminonaphthalene-based spiroheterocyclic photochromic colorants.<sup>15</sup> The scope and limitation of this oxidation were investigated and the photochemical mechanism was proposed on the basis of the experimental results.

## 2. Results and discussion

Scheme 1 depicts the preparation of 2,3-dihydro-1*H*-perimidines **1** and **2**. It involved the Yb(OTf)<sub>3</sub>-catalyzed condensation cyclization<sup>16</sup> of naphthalene-1,8-diamine (**3**) with acetophenones or benzaldehydes to give 2,3-dihydro-1*H*-perimidines **1** and **2**, respectively. The aerobic oxidation of **1** and **2** via visible light photoredox catalysis using Ru(bpy)<sub>3</sub><sup>2+</sup> as a catalyst in acetonitrile generated the perimidinones **6**, **7** and **8**, **9** in moderate to good yields. The photooxidation was performed in various solvents and acetonitrile was found to be the optimal one. Tables 1 and 2 summarize the results of the studies. The molecular structures of the major products **6** and **8** were all elucidated by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy. The perimidinones **6** and **8** could be spectroscopically identified by the observation of the characteristic downfield doublet absorption of the 5-H hydrogen at 6.69–6.73 and

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**Scheme 1.** Preparation of perimidines **1–2** and their photooxidation products **6–9**.

**Table 1**  
Photooxidation of **1a–e** under VLPC

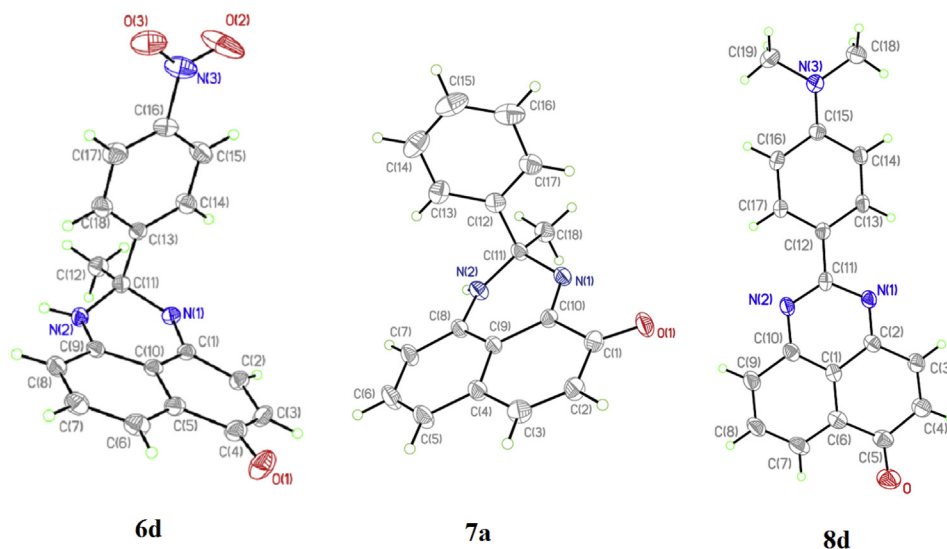
Entry <sup>a</sup>	Substrate	R	Major product	Yield <sup>b</sup> (%)	Minor product	Yield <sup>b</sup> (%)
1	<b>1a</b>	Phenyl	<b>6a</b>	77	<b>7a</b>	12
2	<b>1b</b>	<i>p</i> -Methoxyphenyl	<b>6b</b>	82	<b>7b</b>	9
3	<b>1c</b>	<i>o</i> -Methoxyphenyl	<b>6c</b>	83	<b>7c</b>	10
4	<b>1d</b>	<i>p</i> -Nitrophenyl	<b>6d</b>	80	<b>7d</b>	7
5	<b>1e</b>	Methyl	<b>6e</b>	82	<b>7e</b>	12

<sup>a</sup> Subjected to irradiation with a 23 W household fluorescence lamp ( $\lambda_{\max} \approx 465$  nm).

<sup>b</sup> Isolated yield after purification by chromatography on SiO<sub>2</sub>.

7.00–7.05 ppm, respectively (see [Scheme 1](#) for atom numbering). Selective compounds such as **6d** (R=*p*-nitrophenyl), **7a** (R=phenyl), and **8d** (R=*p*-dimethylaminophenyl) were further characterized by the X-ray crystallography as shown in [Fig. 1](#).<sup>17</sup> Since no reaction was observed when **1** was irradiated with visible light in the absence of Ru(bpy)<sub>3</sub><sup>2+</sup> in acetonitrile for 24 h, this result suggests the photooxidation is indeed catalyzed by the ruthenium complex.

In an effort to investigate the scope and limitation of this photoredox catalysis, several aminonaphthalene derivatives (**10–13**) were synthesized to explore their structure–reactivity relationship toward VLPC, as shown in [Schemes 2 and 3](#). Compounds **10** and **11** were accessed by sequential methylations of **1a** using methyl iodide in the presence of potassium carbonate as a base at room temperature. The perimidinone **12** was prepared by treating naphthalene-1,8-diamine (**3**) with sodium cyanate under acidic conditions via the literature procedure.<sup>18</sup> The amide **13** was readily available by base-promoted acetylation of naphthalen-1-amine (**15**) with acetyl chloride. With these four compounds in hand, their photochemical reactivity toward VLPC was then evaluated. While aerobic oxidation of *N*-monomethylated **10** generated the expected perimidinone product **14**, no product was obtained for photooxidation of *N,N*-dimethylated **11** under the same reaction conditions ([Scheme 2](#)).



**Fig. 1.** ORTEP crystal structures of **6d**, **7a**, and **8d**.

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