# Journal Pre-proofs

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# Visible-Light-Enabled Regioselective Aerobic Oxidative C(sp<sup>2</sup>)-H Thiocyanation of Aromatic Compounds by Eosin-Y Photocatalyst

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#### ABSTRACT

Herein, visible-light-enabled regioselective aerobic oxidative C(sp<sup>2</sup>)-H thiocyanation of aromatic compounds has been developed by employing eosin-Y as effective photocatalyst and oxygen as the green terminal oxidant. This process featured green, efficient and operationally simple. Furthermore, the practicality and utility of this protocol was demonstrated by the gram scale synthesis. Mechanistic studies suggested that this reaction was realized via a photoredox radical pathway.

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Visible-light photoredox catalysis, featured renewable, environment friendly, readily available and abundant has been experiencing a renaissance in the past decades.<sup>1</sup> Since the pioneering and landmark works by the groups of Bach<sup>2</sup> and MacMillan, <sup>3</sup> the synthetic chemistry field has witnessed the rapid development and breathtaking achievement of organic synthesis photochemical visible-light-promoted through reactions. Consequently, various organic transformations by employing structurally diverse metal-based complexes as photoredox catalysts have been well established.<sup>4</sup> However, in term of more stringent requirements for green chemistry manner and industrial applications, these metal-involved photocatalytic transformations still suffer from expensive and potentially toxic challenges. Accordingly, the metal-free involved organic dyes such as eosin-Y and rose bengal has attracted much attention for their utilization as organic photoredox catalyst via absorbing visible light to generate photoexcited species which usually possess a long life time and prominent redox properties that may engage in a single-electron transfer (SET) process with substrates.<sup>5</sup>

On the other hand, aromatic organosulfur compounds,<sup>6</sup> especially thiocyanate-containing scaffolds are widely existed in many drugs and biological molecules with a plethora of promising biological activities, such as antiviral and antimicrobial activities.<sup>7</sup> The direct C-H thiocyanation reaction is one of the most effective and straightforward synthetic technique to construct C-S bond. Meanwhile, the thiocyanate functional group could be easily converted into various sulfur-containing derivatives, which usually serve as the synthetic precursors of organosulfur molecules.<sup>8</sup> Due to these significant synthetic values and practical applications, Not surprisingly, a large

number of efforts have thus been directed toward the development of new process to access these scaffold.<sup>9</sup> As a consequence, many kinds of methods involved the use of ammonium thiocyanate salts (NH<sub>4</sub>SCN) in the presence of strong oxidants,<sup>10</sup> strong acids,<sup>11</sup> transition metal,<sup>12</sup> corrosive halogen reagents<sup>13</sup> and others<sup>14</sup> have been disclosed. However, despite of their efficiencies, when in term of green chemistry and sustainable development requirement in mind, these mentioned approaches often suffered from many drawbacks obviously. Thus, it is highly desirable to explore alternatively practical, green and environmentally friendly protocol toward aromatic organosulfur



Scheme 1. Thiocyanation strategies for (hetero)aromatic compounds.

skeletons. To the best of our knowledge, only sporadic examples for thiocyanation of indoles,<sup>15</sup> *N*-aryltetrahydroisoquinoline<sup>16</sup> and other heterocycles<sup>17</sup> by using visible-light photocatalytic system ha Journal visible-light-enabled direct thiocyanation of functionalized arenes was virtually very rare. Very recently, the  $Ag/TiO_2$  nanotubes were synthesized painstakingly and utilized as photocatalyst to fulfil the thiocyanation of *N*-bearing (hetero) aromatic compounds was developed by the group of Hosseini-Sarvari.<sup>18</sup> As part of our group research interest in the field of visible-light-mediated photoredox organic chemical transformation.<sup>19</sup> We envisioned that employment of a simple and green organic dye as photocatalyst under the oxygen atmosphere to challenge this thiocyanation reaction. Herein, we describe the regioselective aerobic oxidative C(sp<sup>2</sup>)-H thiocyanation of aromatic compounds by employing commercially available and low-cost eosin-Y as effective photocatalyst and oxygen as the green terminal oxidant.

Table 1.	Optimization	of reaction	conditions <sup>[a]</sup>
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I				H
	<sup>N</sup> ` <sup>Bn</sup> + NH₄SCN	Catalyst (5	5 mol%)	Bn N`Bn
		Solvent, Light	source, O <sub>2</sub> NCS	~~
	2 Catalvet	Solvent	Light source	Ja Vield [b]
	Catalyst	Solvent	Light source	I leiu 🤖
1	Eosin Y	DMF	Green LEDs	68
2	$Ru(bpy)_3(PF_6)_2$	DMF	Green LEDs	65
3	Fe(bpy) <sub>3</sub> (PF <sub>6</sub> ) <sub>2</sub>	DMF	Green LEDs	trace
4	Co(bpy) <sub>3</sub> (PF <sub>6</sub> ) <sub>2</sub>	DMF	Green LEDs	trace
5	TiO <sub>2</sub>	DMF	Green LEDs	6
6	Rose Bengal	DMF	Green LEDs	49
8	Eosin Y	DMF	CFL	54
9	Eosin Y	DMF	Blue LEDs	58
10	Eosin Y	DMF	Red LEDs	20
11	Eosin Y	CH <sub>3</sub> OH	Green LEDs	58
12	Eosin Y	THF	Green LEDs	71
13	Eosin Y	CH <sub>3</sub> CN	Green LEDs	85
14	Eosin Y	DMSO	Green LEDs	37
15	Eosin Y	CH <sub>2</sub> Cl <sub>2</sub>	Green LEDs	35
16 <sup>[c]</sup>	Eosin Y	CH <sub>3</sub> CN	Green LEDs	63
17 <sup>[d]</sup>	Eosin Y	CH <sub>3</sub> CN	Green LEDs	78
18 <sup>[e]</sup>	Eosin Y	CH <sub>3</sub> CN	Green LEDs	82
19 <sup>[f]</sup>	Eosin Y	CH <sub>3</sub> CN	Green LEDs	81
20 <sup>[g]</sup>	Eosin Y	CH <sub>3</sub> CN	-	0
21 <sup>[h]</sup>	-	CH <sub>3</sub> CN	Green LEDs	0

<sup>[</sup>a] Reaction conditions: **1a** (0.2 mmol), **2** (0.6 mmol) and catalyst (5 mol%) in Solvent (2 mL) and  $O_2$  atmosphere under 30 W green LEDs irradiation at room temperature for 24 h. [b] Isolated yield. [c] 1.0 equiv. NH<sub>4</sub>SCN was used. [d] 2.0 equiv. NH<sub>4</sub>SCN was used. [e] 4.0 equiv. NH<sub>4</sub>SCN was used. [f] Air instead of  $O_2$ , [g] In the dark. [h] Without photocatalyst.

We began our studies by using eosin-Y as photocatalyst to investigate this  $C(sp^2)$ -H thiocyanation reaction of *N*benzylaniline **1a** with NH<sub>4</sub>SCN under the 30 W green LEDs and O<sub>2</sub> atmosphere in DMF at room temperature for 24 h (Table 1). To our delight, the regiospecificity thiocyanation product **3a** at the *para*-position of *N*-benzylaniline was obtained in 68% isolated yield (entry 1). Encouraged by this initial result, we next



[a] Reaction conditions: **1a** (0.2 mmol), **2** (0.6 mmol) and Eosin Y (5 mol%) in CH<sub>3</sub>CN (2 mL) and O<sub>2</sub> atmosphere under 30 W green LEDs irradiation at room temperature for 24 h. [b] Isolated yield. [c] 36 h.

evaluated the catalytic reactivities of different photocatalysts. Fisrtly, metal-based complexes such as  $Ru(bpy)_3(PF_6)_2$ , Fe(bpy)<sub>3</sub>(PF<sub>6</sub>)<sub>2</sub> and Co(bpy)<sub>3</sub>(PF<sub>6</sub>)<sub>2</sub> were used as photocatalyst in the reaction (entries 2-4), Unexpectedly, only Ru(bpy)<sub>3</sub>(PF<sub>6</sub>)<sub>2</sub> as catalyst was effective to the thiocyanation process, affording the desired product with moderate yield (entry 2). Titanium dioxide (TiO<sub>2</sub>) usually serve as a practical and impactful heterogeneous photocatalyst was also tested in this reaction but giving the target product with only 6% yield (entry 5). Actually, the organic dye rose bengal was also found to be effective to promote this thiocyanation reaction for affording the desired product with 49% yield (entry 6). Next, we investigated the effects of different light sources on the reaction, including 30 W compact fluorescent lamps (CFL), 30 W blue LEDs and 30 W red LEDs, and the results demonstrated that green LEDs was the most favorable light source for this thiocyanation process (entries 8-10). Solvent usually have a large effect in the visible-light-photoredox promoted reactions. Thus, several common solvents such as CH<sub>3</sub>OH, THF, CH<sub>3</sub>CN, DMSO, and CH<sub>2</sub>Cl<sub>2</sub> were examined, and CH<sub>3</sub>CN was turned out to be the best, which can provide the desired product with 85% isolated yield (entry 13). Furthermore, the amount of NH<sub>4</sub>SCN was also screened, and 3.0 equiv. NH<sub>4</sub>SCN was proved to appropriate choice, while reducing or improving the equivalent of NH<sub>4</sub>SCN did not bring better results (entries 16-18). Therefore, the optimized reaction conditions were obtained using 5 mol % of eosin Y as photocatalyst and 3.0 equiv. NH<sub>4</sub>SCN in CH<sub>3</sub>CN under 30 W green LEDs irradiation in ambient O<sub>2</sub> at room temperature for 24 h. Of note, the reaction could not occur without photocatalyst or light irradiation (entries 20-21), which clearly revealed that they were indispensable conditions for this photocatalytic transfromation.

With the optimized reaction conditions in hand, the substrate scopes for the thiocyanation reaction of aromatic amines with  $NH_4SCN$  was explored. As shown in the Table 2, various

tertiary amine regardless of the positions and electronic properties of the substituents on the phenyl ring and nitrogen atom moiety could be well employed, the regiospecificity thiocyanation product at the para-position of aromatic amines were obtained with moderate to good yields. Specifically, different substituents including Bn, Me, Et, Pr and Ph groups on the nitrogen atom moiety could were well tolerated the reaction conditions, and the corresponding products were obtained in 80-90% yields (3a-e). When the substituent group Cl at the orthoposition of *N*-methylaniline could give the product (**3f**) with 84% yield, which is better than that at meta-position of Nmethylaniline (3g). Substrates bearing both electron-donating and electron-withdrawing group at either ortho- or meta-position of the N-benzylaniline were also tolerated and afforded the corresponding products with moderate to good yields (3h-I). Moreover, kinds of primary aromatic amines bearing various substituent groups at diffierent position on the phenyl ring moiety were also compatible with template reaction conditions, producing the expected products in 73-93% yields. (3m-p). Notably, when the aniline bearing two isopropyl groups at the ortho position was also well tolerated to afford the product (3g) in 95% yield. It is worth mentioning that the tertiary amine was still proved as a good substrate in our catalytic system and the target product was obtained in 89% yield, which is far superior to the result of Ag/TiO<sub>2</sub> nanotubes photocatalyst in previous report<sup>[18]</sup>. In addition, When phenol was used as the substrate, this C(sp<sup>2</sup>)-H regiospecificity thiocyanation reaction also occured and afforded the expected product (3s) with 53% yield in 36 h. However, when 1-naphthol was used as the substrate, Surprisingly, the target thiocyanation product was not obtained.

To demonstrate the utility and practicality of this visiblelight-enabled regioselective oxidative  $C(sp^2)$ -H thiocyanation reaction, the large-scale reaction between *N*-benzylaniline **1a** (6.0 mmol, 1.098 g) and NH<sub>4</sub>SCN was performed under the optimal reaction conditions with prolonging the reaction time to 48 h, and the corresponding product **3a** was obtained in 81% yield (1.45 g). Analogously, when the primary amine **1m** (8.0 mmol, 0.744 g) was used as substrate, the corresponding product **3m** was obtained in 80% yield (0.96 g).



Scheme 2. Gram-scale synthesis

Subsequently, In order to further understand the reaction mechanism, a series of control experiments were performed.<sup>20</sup> As shown in Scheme 3, Firstly, the radical traping experiments were carried out. When the common radical quenchers 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) and 2,6-di-tertbutyl-4-methylphenol (BHT) was added to the reaction under the standard conditions, the target product **3a** was only obtained with 10% and 13% GC yield, respectively (Scheme 3, a, b). These results revealed that the reaction may underwent free radical pathway. Besides, When nitrogen instead of oxygen was used in

proceed and the similar result was obtained when the reaction was carried out in the dark (Scheme 3, c, d). According to the aforementioned results, it can be strongly deduced that the reactions proceed through visible-light-induced aerobic radical mechanism. Moreover, when the para-position of N-arylamine was occupied by methoxy group, no ortho-thiocyanated product was formed, and the starting material was recovered completely, demonstrating high para-selectivity in this C-H thiocyanation reaction (Scheme 3, e). Of note, Similar phenomenon of regioselectivity at the para-position has been also appeared in earlier reports <sup>10b,18</sup>. In addition, luminescence quenching experiments (Scheme 4) and cyclic voltammetry test to investigate the reaction mechanism were also conducted (see SI for more details). Based on the results of fluorescence quenching experiments, the more notable decrease of fluorescence intensity of Eosin Y was recorded with increasing the concentration of NH<sub>4</sub>SCN, which might suggest that NH<sub>4</sub>SCN is more easily to undergo single-electron transfer process with the excited state photocatalyst (EY\*) under the standard reaction conditions. On the other hand, the obvious oxidation peaks of N-benzylaniline and NH<sub>4</sub>SCN were observed +0.95 V, +0.75V (vs Ag/AgCl) respectively, which might suggest that NH<sub>4</sub>SCN would be more easily than N-benzylaniline to be oxidated under the standard reaction conditions in our catalytic system. (Figure S4).



Scheme 3. Control experiments

On the basis of our observations of the control experiments and previous literatures,<sup>17a</sup> a plausible mechanism has been proposed in Scheme 4. Initially, Eosin-Y (EY) is being photoexcited in the presence of green LEDs light irradiation to converted into an excited state EY\*, and then SCN- anion is being oxidized to SCN• radical through single-electron transfer. Subsequently, the SCN• radical attacked the substrate 1 to generate another radical intermediate **A**, which was oxidized quickly to form the cationic intermediate **B**. Then the cationic intermediate **B** via deprotonation process to turn into the target product **3**. In addition, oxygen may plays a crucial role to complete the photoredox cycle through oxidation of the EY•radical anion back to the ground state EY, Which enter into the next catalytic cycle (Scheme 5).

## Tetrahedron





Scheme 5. Proposed reaction mechanism

In summary, we have developed regiospecificity oxidative  $C(sp^2)$ -H thiocyanation of aromatic compounds by employing eosin-Y as photocatalyst and oxygen as the green oxidant. A variety of aromatic amines including primary amine, secondary amine and tertiary amine could proceed well to afford the corresponding products with moderate to good yields. This method featured green, efficient and environmentally friendly Moreover, the practicality and utility of this protocol was also demonstrated by the gram-scale synthesis and Mechanistic studies suggested that this reaction was realized via a photoredox radical pathway.

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#### Notes

The authors declare no competing financial interest.

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- 20. See SI for more details.

#### **Supplementary Material**

Supplementary data associated with this article can be found in the online version, at xxx.



## **Highlights**

- 1.Visible-light-enabled regioselective
- C(sp<sup>2</sup>)-H thiocyanation

2. Eosin-Y as photocatalyst and oxygen as the green oxidant.

3. Green, efficient and operationally simple

4. Broad substrate scopes and gram scale synthesis