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# Visible-light-promoted cyclodesulfurization of phenolic thioureas: an organophotoredox catalytic approach to 2-aminobenzoxazoles

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ABSTRACT

A facile and efficient one-pot operation for the photo-oxidative cyclodesulfurization of *o*-phenolic thioureas to afford 2-aminobenzoxazoles is reported. The protocol could be executed under visible light irradiation employing eosin Y as an organophotoredox catalyst and offers a superior alternative to the existing methods of the cyclodesulfurization of phenolic thioureas. The salient features of the present metal-free approach are the utilization of air and visible light as the greenest and sustainable reagents under mild conditions.



Nature-inspired application of solar energy (visible light) for catalytic activation of organic molecules to achieve synthetically useful transformations has led to a flurry of activity in this area.[1–4] Consequently, visible light photoredox catalysis has recently emerged as a powerful source for the development of novel synthetic methodologies.[5,6] The success of this strategy has been mainly derived from the seminal work of the groups of MacMillan,[1] Yoon,[2] and Stephenson,[3] who employed $Ru(bpy)_3Cl_2$ (bpy = 2,2′-bipyridine) and $Ir(dtbbpy)_3Cl_2$ (dtbbpy = 4,4′-di-*tert*-butyl-2,2′-bipyridine) as efficient photoredox catalysts. Although ruthenium and iridium transition metal complexes have proved to be efficient visible light photoredox catalysts, they suffer from disadvantages such as high cost, potential toxicity, and low sustainability. Thus, as an alternative to the photochemistry of Ru(II) and Ir(II) complexes, a long known dye eosin Y (2′,4′,5′,7′-tetrabromofluorescein) (EY) has been widely used as an organophotoredox catalyst.[7] Advantageously, EY absorbs the green light, which is the most abundant part of the solar light.[7j]

The use of visible light photoredox catalysis has opened up a new route to utilize atmospheric oxygen as an oxidant in organic synthesis. It is mostly employed as an oxidant to regenerate photocatalysts (PC) from their radical anion $PC^{\bullet-}$, which is formed in the catalytic cycle via the excited state (PC*) by single electron transfer (SET) from a donor. The $PC^{\bullet-}$ completes the catalytic cycle by the formation of the superoxide radical ($O_2^{\bullet-}$).[1e,2b,3,6b,e–o,7h] The superoxide radical ($O_2^{\bullet-}$) formed in the photoredox cycle of Ru(II), Ir(II) complexes or eosin Y has also been utilized in situ for oxidative functionalization of organic compounds.[6f]

2-Aminobenzoxazoles are attractive synthetic scaffolds owing to their useful biological properties, and application as important building blocks for pharmaceutical products.[8] They are currently employed in the treatment of a wide variety of disorders, such as HIV, neurodegeneration, and inflammatory diseases.[8] Consequently, 2-aminobenzoxazoles have been described as the target of synthesis in numerous reports involving direct oxidative coupling of benzoxazole with an amine or its surrogates,[8a,9] and nucleophilic displacement of 2-halogenated benzoxazole or its precursor with amine.[10] Also, 2-aminobenzoxazoles can be easily prepared from a facile ring opening of benzoxazoles with secondary amines and oxidative ring closing process has been accomplished with various reagents.[11] The cyclodesulfurization of thioureas has been a popular synthetic strategy for 2-aminobenzoxazoles. Commonly used reagents include DDC,[12a] $AgNO_3$,[12b] $NiO_2$,[12c] HgO,[12d] $LiOH/H_2O_2$[12e] or $KO_2$.[12f] However, all these methods are associated with one or more limitations such as expensive, toxic or metallic catalysts, long reaction times, and lower yields. The latest development of visible-light-triggered oxidative photocatalytic preparation of 2-aminobenzoxazoles involves ring closing reaction of *o*-phenolic amidines, which can be easily prepared from a facile ring opening of benzoxazoles with secondary amines.[13]

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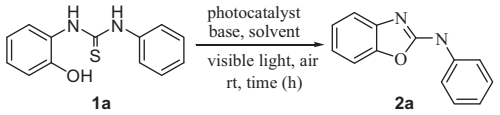
The literature records only a few reports on photocatalytic cyclization reactions involving the sulfur radical (Scheme 1a and b).[14] In view of the above discussion and our continued efforts for developing efficient heterocyclization reactions,[13,15] we envisaged the present eosin Y catalyzed visible-light-mediated aerobic oxidative cyclodesulfurization of *o*-phenolic thioureas to the corresponding 2-aminobenzoxazoles (Scheme 1).

In order to realize the feasibility of our envisaged preparation of 2-aminobenzoxazoles, a model reaction was carried out by stirring a mixture of *N*-substituted-2-hydroxyphenylthiourea **1a** (1 mmol) with $Cs_2CO_3$ (1.2 mmol) as a base and eosin Y as a photocatalyst in DMF under an air atmosphere (without bubbling air) and irradiation with visible light (green light emitting diodes (LEDs, 4.45 W, $\lambda_{max}$ = 535 nm) at rt. To our delight, the desired product 2-aminobenzoxazole **2a** was obtained in 90% yield after 2 h of irradiation. Then, a series of control experiments were carried out, which indicated that in the absence of any one of the reagents, catalyst/reaction parameters, the present photo-oxidative cyclodesulfurization could not take place (Table 1). Initially, several bases, namely $Na_2CO_3$, $K_2CO_3$, $Cs_2CO_3$, DBU (1,8-diazabicycloundec-7-ene) and DMAP (4-dimethylaminopyridine) were tested and $Cs_2CO_3$ was found to work most efficiently in terms of the yield and reaction time (Table 1, entry 1 vs 3–6). Inorganic bases are more efficient than the amine bases probably because the latter are also involved in the single electron transfer (SET) with the catalyst eosin Y, which reduces the yield considerably. The bases are required to promote the formation of a more electron donor thiolate anion from thioureas. It was noted that the product **2a** was also formed in the absence of a base, but relatively a longer reaction time was required (Table 1, entry 7). A decrease in loading of the catalyst eosin Y from 1 mol % to 0.2 mol % resulted in lower yield of the product (Table 1, entry 1 vs 8), and on increasing the amount of eosin Y from 1 mol % to 2 mol % there was no effect on the yield of the product (Table 1, entry 1 vs 9). It was noted that the product **2a** was not formed in the absence of eosin Y (Table 1, entry 10). Moreover, when the reaction was performed under a nitrogen atmosphere, the desired product **2a** was not formed (Table 1, entry 11). This shows that the presence of $O_2$ is essential for the formation of **2a**. However, the use of an $O_2$ balloon instead of an air atmosphere did not enhance the yield of **2a** (Table 1, entry 1 vs 12). Similarly, when the reaction was conducted in the dark, there was no conversion of **1a** to **2a** (Table 1, entry 13). These results suggest that light, eosin Y, and $O_2$ are essential requirements for the reaction.

With the aforementioned results, we screened several solvents, DMF, DCM, $CH_3OH$, THF, and $CH_3CN$. DMF was found to be the best solvent (Table 1, entry 1 vs 14–17). However, when the reaction was carried out in 18 W CFL (Compact Fluorescent Light) the yield was decreased to 36%. Similarly, the reaction also did not proceed satisfactorily in daylight (Table 1, entry entries 18 and 19), which shows the higher photocatalytic activity of eosin Y in the presence of high intensity green light. In a control study using 2 equiv of TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxyl), a well known radical-trapping reagent, no 2-aminobenzoxazole **2a** was formed, indicating that the reaction presumably involves a radical intermediate (Table 1, entry 20). Moreover, the reaction was also successful on using $Ru(bpy)_3Cl_2$ as a photoredox catalyst under irradiation with blue LEDs (Table 1, entry 21), but we opted to use eosin Y as the organophotoredox catalyst in view of our goal to develop a metal-free protocol.

**Table 1**
Optimization of reaction conditions[a]



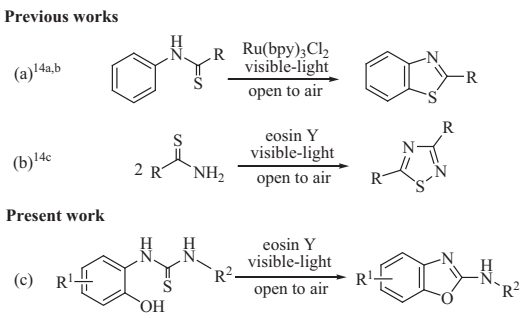

**1a** **2a**

| Entry | Solvent | Air | Photocatalyst | Base (1.2 mmol) | Time (h) | Yield[b] (%) |
|---|---|---|---|---|---|---|
| 1 | DMF | + | EosinY (1 mol %) | $Cs_2CO_3$ | 2 | 90 |
| 2 | DMF | + | EosinY (1 mol %) | $Cs_2CO_3$ | 4 | 90 |
| 3 | DMF | + | EosinY (1 mol %) | $K_2CO_3$ | 4 | 78 |
| 4 | DMF | + | EosinY (1 mol %) | $Na_2CO_3$ | 4 | 63 |
| 5 | DMF | + | EosinY (1 mol %) | DBU | 4 | 58 |
| 6 | DMF | + | EosinY (1 mol %) | DMAP | 4 | n.d. |
| 7 | DMF | + | EosinY (1 mol %) | — | 30 | 76 |
| 8 | DMF | + | EosinY (0.2 mol %) | $Cs_2CO_3$ | 2 | 40 |
| 9 | DMF | + | EosinY (2 mol %) | $Cs_2CO_3$ | 2 | 90 |
| 10 | DMF | + | — | $Cs_2CO_3$ | 12 | n.d. |
| 11 | DMF | $N_2$ | EosinY (1 mol %) | $Cs_2CO_3$ | 12 | n.d. |
| 12[c] | DMF | + | EosinY (1 mol %) | $Cs_2CO_3$ | 2 | 90 |
| 13[d] | DMF | + | EosinY (1 mol %) | $Cs_2CO_3$ | 12 | n.d. |
| 14 | DCM | + | EosinY (1 mol %) | $Cs_2CO_3$ | 2 | 69 |
| 15 | $CH_3OH$ | + | EosinY (1 mol %) | $Cs_2CO_3$ | 2 | 75 |
| 16 | THF | + | EosinY (1 mol %) | $Cs_2CO_3$ | 2 | 67 |
| 17 | $CH_3CN$ | + | EosinY (1 mol %) | $Cs_2CO_3$ | 2 | 72 |
| 18[e] | DMF | + | EosinY (1 mol %) | $Cs_2CO_3$ | 2 | 36 |
| 19[f] | DMF | + | EosinY (1 mol %) | $Cs_2CO_3$ | 2 | 13 |
| 20[g] | DMF | + | EosinY (1 mol %) | $Cs_2CO_3$ | 2 | n.d. |
| 21[h] | DMF | + | $Ru(bpy)_3Cl_2$ (1 mol %) | $Cs_2CO_3$ | 2 | 88 |

[a] All reactions were run with **1a** (1 mmol), base (1.2 mmol), and solvent (3 mL), open to air (without bubbling air), irradiation through the flask's bottom side using Luxeon Rebel power green LEDs [2.50 W, $\lambda_{max}$ = 535 nm] at rt.
[b] Isolated yield of **2a**; n.d. = not detected.
[c] $O_2$ balloon was used.
[d] Reaction was carried out in the dark.
[e] 18 W CFL.
[f] Daylight.
[g] The reaction was quenched with TEMPO (2 equiv).
[h] Luxeon Rebel power blue LEDs [4.45 W, $\lambda_{max}$ = 447.5 nm] used for irradiation.

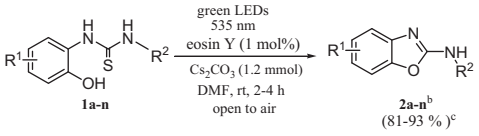
Encouraged by the above studies, we investigated the substrate scope under the optimized reaction conditions and results are summarized in Table 2. *o*-Phenolic thioureas bearing electron-donating or electron-withdrawing substituents generally afforded 2-aminobenzoxazoles in good to excellent yields (81–93%). However, phenolic thioureas with an electron-withdrawing group afforded slightly higher yields (Table 2, entries **2d**–**2h**, **2m,** and **2n**) as compared to those bearing an electron-donating group (Table 2, entries **2b**, **2c,** and **2j**). Interestingly, thioureas with various functionalities such as $CH_3$, $C_2H_5$, $OCH_3$, Br, Cl, F, $CF_3$, and $NO_2$ were well tolerated to give aminobenzoxazoles **2** in excellent yields and high purity.

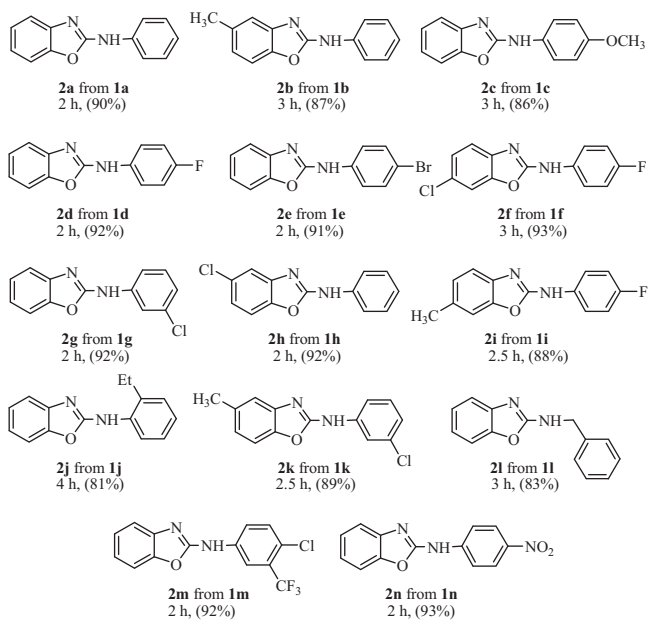
In view of an easy and high yielding conversion of *o*-aminophenols into the corresponding phenolic thioureas with aryl isothiocyanates,[12e] we proceeded for one-pot synthesis of 2-aminobenzoxazole **2a** starting directly from commercially available phenyl isothiocynate and 2-aminophenol (Scheme 2). Thus, we stirred phenyl isothiocynate (1 mmol) and



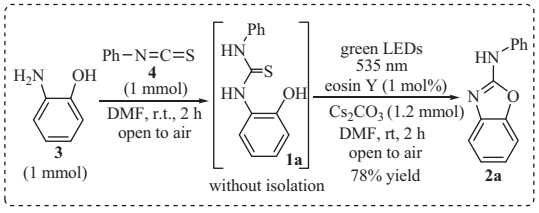

**Scheme 1.** Aerobic oxidative cyclization via sulfur radicals.

**Table 2**
Substrate scope for the conversion of *N*-substituted-2-hydroxyphenylthioureas into 2-aminobenzoxazoles[a]



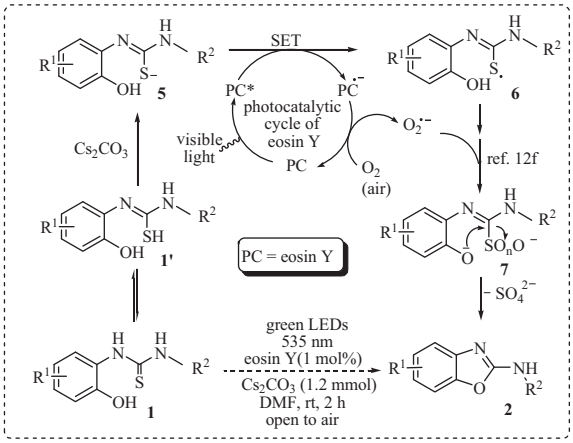

[a] For experimental procedure, see Ref. 17.
[b] All compounds are known and were characterized by comparison of their spectral data with those reported in the literature.[16]
[c] Yields of isolated pure compounds **2**.




**Scheme 2.** One-pot sequential reactions for the synthesis of 2-aminobenzoxazole.

2-aminophenol **3** (1 mmol) in DMF (3 mL) at room temperature for 2 h. After confirming the complete conversion of phenyl isothiocynate to corresponding *o*-phenolic thioureas by TLC, $Cs_2CO_3$ (1.2 mmol), and eosin Y (1 mol %) were added and the reaction mixture was irradiated with visible light (green light emitting diodes (LEDs), $\lambda_{max}$ = 535 nm) at room temperature for 2 h. The reaction resulted in the clean formation of **2a** in a very good yield (78%).

On the basis of the above observations and the literature precedents,[6f,12f,14] a plausible mechanism for the present visible-light-initiated photo-oxidative cyclodesulfurization of *N*-substituted-2-hydroxylphenylthioureas **1** to afford 2-aminobenzoxazole derivatives **2** is depicted in Scheme 3. The base $Cs_2CO_3$ abstracts thiolic H from phenolic thioureas **1′** to form more oxidizable sulfur anion **5**. Eosin Y (PC) upon absorption of light goes to its excited state (PC*). Single electron transfer (SET) between sulfur anion **5** and PC* affords sulfur radical **6** and $PC^{\cdot-}$. The photoredox cycle of PC (eosin Y) is completed by the aerobic oxidation of




**Scheme 3.** Plausible pathway for the photo-oxidative cyclodesulfurization of *o*-phenolic thioureas.

$PC^{\cdot-}$ to its ground state (PC). The in situ generated $O_2^{\cdot-}$ radical combines with sulfur radical **6** to form intermediate **7**. Finally, the cyclization of **7** affords the desired products **2**.

In conclusion, we have developed a new, efficient, and mild strategy for the synthesis of 2-aminobenzoxazoles by cyclodesulfurization of *o*-phenolic thioureas. The protocol utilizes visible light and atmospheric oxygen as inexpensive and sustainable reagents and eosin Y as an organophotoredox catalyst. The reaction could also be rendered as one pot and afforded 2-aminobenzoxazole in 78% yield starting directly from 2-aminophenol and phenyl isothiocyanate.

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17. *General procedure for the synthesis of 2-aminobenzoxazoles* ***2****:* A mixture of *N*-substituted-2-hydroxyphenylthiourea[12e] **1** (1 mmol), eosin Y (1 mol %), $Cs_2CO_3$ (1.2 mmol), and DMF (3 mL) was taken in a flask open to air and stirred at rt under irradiation with visible light (green light emitting diodes (LEDs, 4.45 W, $\lambda_{max}$ = 535 nm) for 2–3 h (Table 2). After completion of the reaction (monitored by TLC), water (5 mL) was added and the mixture was extracted with ethyl acetate (3 × 5 mL). The combined organic phase was dried over anhydrous $Na_2SO_4$, filtered, and evaporated under reduced pressure. The resulting crude product was purified by silica gel chromatography using a mixture of hexane/ethyl acetate (4:1) as eluent to afford an analytically pure sample of product **2**. All the compounds **2** are known and were characterized by comparison of their spectral data with those reported in the literature.[16] Characterization data of representative compounds **2** are given below:
Compound **2a**:[16] $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$: 10.54 (br s, 1H, NH), 7.76 (d, 2H, *J* = 8.0 Hz, ArH), 7.47 (t, 2H, *J* = 8.4 Hz, ArH), 7.36 (t, 2H, *J* = 8.0 Hz, ArH), 7.19 (t, 1H, *J* = 7.2 Hz, ArH), 7.09 (t, 1H, *J* = 7.2 Hz, ArH), 7.03 (t, 1H, *J* = 7.2 Hz, ArH); $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta$: 158.40, 147.45, 142.89, 139.19, 129.40, 124.41, 122.53, 122.05, 118.00, 117.04, 109.34. MS: *m*/*z* 211 $[M+H]^+$. HRMS (FAB) calcd for $C_{13}H_{11}N_2O$: 211.0871 $[M+H]^+$, found: 211.0868.
Compound **2g**:[16] $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$: 10.87 (br s, 1H, NH), 7.95 (s, 1H, ArH), 7.59 (d, 1H, *J* = 7.6 Hz, ArH), 7.51 (d, 2H, *J* = 7.6 Hz, ArH), 7.40 (t, 1H, *J* = 8.0 Hz, ArH), 7.21 (t, 1H, *J* = 7.6 Hz, ArH), 7.15 (t, 1H, *J* = 7.6 Hz, ArH), 7.09 (d, 1H, *J* = 7.2 Hz, ArH); $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta$: 157.89, 147.39, 142.49, 140.65, 133.90, 131.07, 124.58, 122.49, 122.16, 117.35, 117.28, 116.55, 109.54, MS: *m*/*z* 245 $[M+H]^+$. HRMS (FAB) calcd for $C_{13}H_{10}ClN_2O$: 245.0482 $[M+H]^+$, found: 245.0484.
Compound **2l**:[16] $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 7.19-7.43 (m, 8H, ArH), 7.14 (t, 1H, *J* = 7.6 Hz, ArH), 7.00 (t, 1H, *J* = 7.6 Hz, ArH), 6.81 (br s, 1H, NH), 4.70 (s, 2H, CH2); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 162.31, 148.45, 142.75, 137.86, 128.80, 127.74, 127.59, 123.95, 120.80, 116.18, 108.82, 46.91. MS: *m*/*z* 225 $[M+H]^+$. HRMS (FAB) calcd for $C_{14}H_{13}N_2O$: 225.1028 $[M+H]^+$, found: 225.1025.