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Visible-light-induced C(sp³)-H activation for a C-C bond forming reaction of 3,4-dihydroquinoxalin-2(1H)-one with nucleophiles using oxygen with a photoredox catalyst or under catalyst-free conditions†

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A convenient photocatalyzed oxidative coupling reaction of 4-alkyl-3,4-dihydroquinoxalin-2(1H)-one and its derivatives with a variety of nucleophiles was developed with a ruthenium photoredox catalyst and oxygen under a household compact fluorescent light. With a slower reaction rate, the cross coupling transformation can be achieved in the absence of an external photocatalyst with a similar isolated yield. An application to the synthesis of natural product cephalandole A was also demonstrated.

Introduction

Carbon-carbon bond-forming reactions constitute one of the foundations in organic synthesis and have attracted extensive exploration since the dawn of organic chemistry.¹ For instance, the direct C-H activation of aryl compounds with transition metals has recently received much attention across the chemistry fields.² Moreover, the emerging strategy for the visible-light photoredox-catalyzed C-C bond forming reactions further enrich the realm of this transformation,³ such as the visible-light photoredox catalyzed indole alkylation⁴ and the oxidative dehydrogenation of N-heterocycles.⁵

On the other hand, quinoxalin-2(1H)-one and benzo[*b*][1,4]oxazin-2-one systems constitute prevailing scaffolds frequently found in many biologically active naturally occurring and unnatural molecules. Consequently, many of them serve as key building blocks in pharmaceutical syntheses, and the derivatives display a wide spectrum of biological activities (Fig. 1).⁶ Owing to these merits, the synthesis of these frameworks has drawn considerable investigations. For example, Huo and his co-workers reported an FeCl₂-catalyzed oxidative C-C bond formation of 3,4-dihydro-1,4-benzoxazin-2-ones with malonic ester, ketone or indoles (Scheme 1).⁷ Xiao and co-workers developed visible light photocatalytic cross-coupling reactions

of amines and carbonyls for the alkylation of 3,4-dihydroquinoxalin-2(1H)-ones.⁸ Zhang *et al.* revealed a direct C-H arylation of quinoxalin-2(1H)-ones with Ph₂IBF₄.⁹ Alternatively, a copper-catalyzed direct coupling of benzoxazin-2-ones with indoles was reported by Lee and coworkers.¹⁰ Nevertheless, despite these advances, an efficient, green, and convenient protocol for the synthesis of these systems remains a topic of high interest in chemical research.¹¹

Informed by this background and as a continuation of our efforts in exploring the visible-light photoredox C-C bond-forming reactions,¹² we envisaged that a direct C(sp³)-C(sp³) oxidative coupling of the quinoxalin-2(1H)-one (or benzo[*b*][1,4]oxazin-2-ones) and alkyl groups could be achieved for the efficient synthesis of these scaffolds. We herein present the outcome of this exploration.

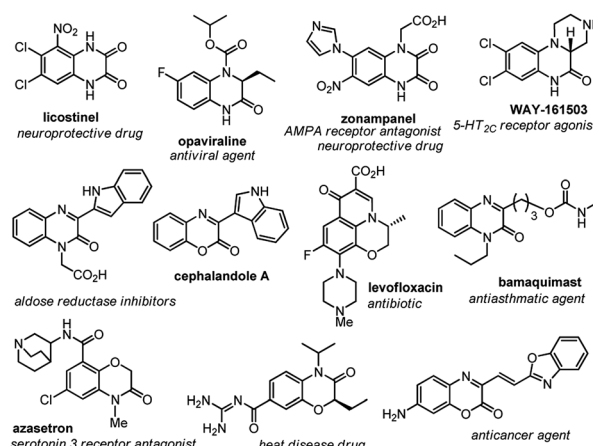


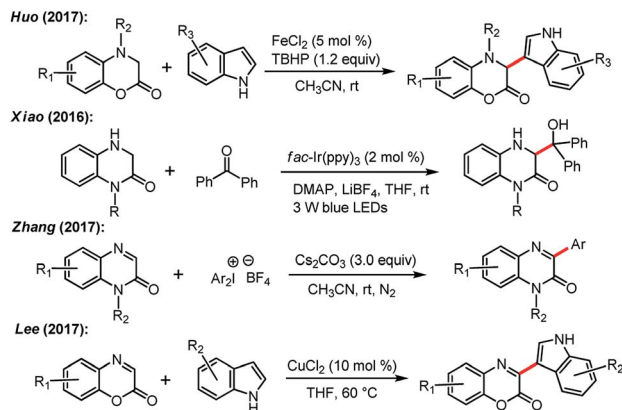
Fig. 1 Selected examples of naturally occurring and pharmaceutically active quinoxalin-2(1H)-one or benzo[*b*][1,4]oxazin-2-ones.

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Scheme 1 Direct synthesis of quinoxalin-2(1*H*)-one or benzo[*b*][1,4]oxazin-2-one derivatives via oxidative coupling.

Results and discussion

Initially, a solution of **1c**, indole (**2a**, 2 equiv.), and Ru(bpy)₃·Cl₂·6H₂O (2 mol%) in CH₃CN (0.05 M) under a balloon of oxygen was irradiated with a household 24 W compact fluorescent plug-in light (CFL) bulb with a distance of around 10 cm at room temperature for 4 h and gave 54% yield of the expected adduct **3ca** after chromatographic purification (Table 1, entry 1).

Table 1 Screening of conditions for the cross-coupling reaction^a

Entry	Cat. (mol%)	Condition ^b	Solvent	Time (h)	Yield ^c (%)
1	2	O ₂ , light	CH ₃ CN	4	54
2 ^d	2	O ₂ , light	CH ₃ CN	4	40
3 ^e	2	O ₂ , light	CH ₃ CN	4	15
4	2	O ₂ , light	MeOH	4	76
5	2	O ₂ , light	CH ₂ Cl ₂	4	63
6	2	O ₂ , light	CHCl ₃	4	51
7	2	O ₂ , light	Acetone	4	43
8	2	O ₂ , light	DMF	4	~0 ^f
9 ^g	2	Air, light	MeOH	7	71
10	2	O ₂ , dark	MeOH	72	Trace
11	—	O ₂ , dark	MeOH	72	~0
12	—	O ₂ , light	MeOH	14	69
13	—	Air, light	MeOH	20	63
14 ^h	2	O ₂ , light	MeOH	4	74
15 ⁱ	2	O ₂ , light	MeOH	4	75

^a Unless otherwise noted, the reactions were performed on a 0.05 M concentration of **1c** (1.0 equiv.), **2a** (2.0 equiv.) with 2 mol% of catalyst in solvent under O₂ atmosphere at ambient temperature (~25–30 °C).

^b Light source: a 24 W household CFL light bulb (cool daylight).

^c Isolated yields of **3ca**. ^d **1c** (1.0 equiv.), **2a** (2.0 equiv.), and the reaction was performed on a 0.1 M concentration. ^e **1c** (1.0 equiv.), **2a** (1.0 equiv.), and the reaction was performed on a 0.1 M concentration. ^f Trace amount of **3ca** with complicated mixtures.

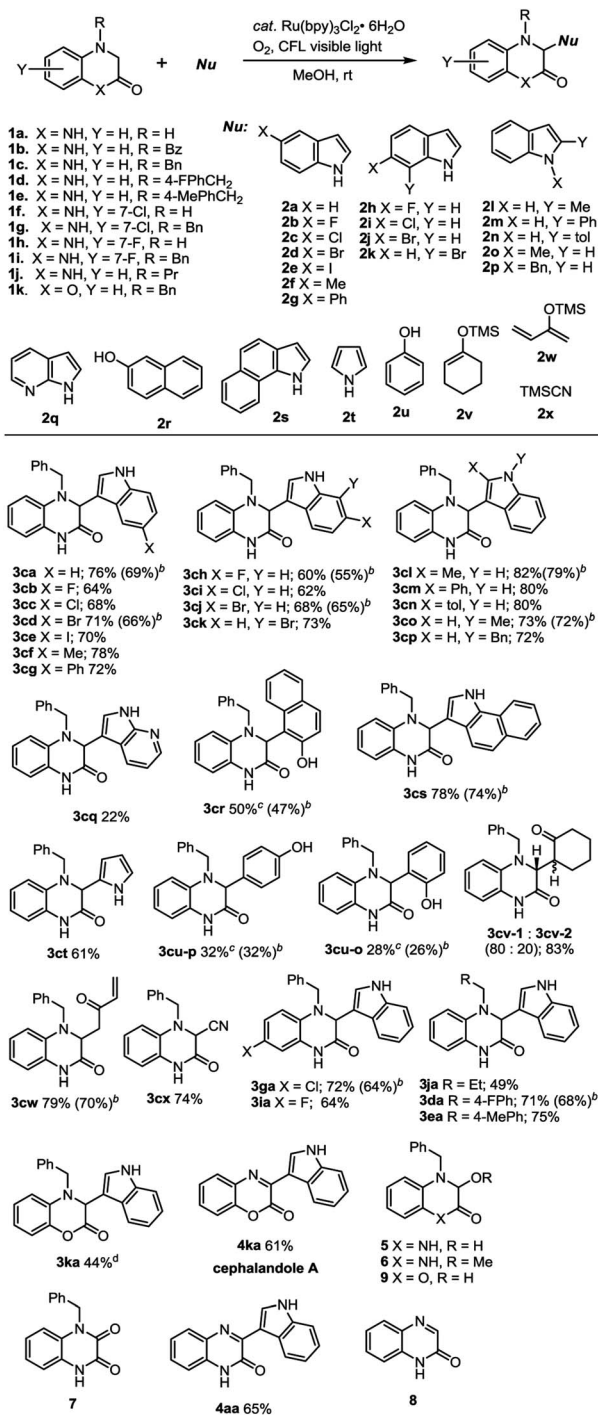
^g Under a balloon of air. ^h In the presence of 24 blue LEDs. ⁱ Using Ir(ppy)₃ as photocatalyst.

Increasing the reaction concentration to 0.1 M, or reducing the indole **2a** to 1 equivalent under the same reaction conditions gave lower yields (40% and 15% yields, respectively, Table 1, entries 2–3).

A series of solvents were evaluated, and methanol was found to be the best choice of the solvent in the reaction to give 76% yield of **3ca**, while CH₂Cl₂, CHCl₃, acetone, and DMF afforded lesser or poor yields (entries 4–8). The reaction under air afforded similar yields, but proceeded slightly slower as the oxygen concentration decreased (Table 1, entry 9). Importantly, the reaction in the dark under oxygen atmosphere in the presence of a ruthenium catalyst or in the absence of the catalyst gave only trace amounts or no observation of the product **3ca**, respectively, after 72 h (Table 1, entries 10–11). Apparently, visible light plays an essential role in the reaction. Notably, the reaction with the CFL irradiation in the absence of catalyst under the oxygen or air atmosphere still provided the adduct **3ca** in yields of 69% and 63%, respectively, albeit these conditions required significantly longer reaction time, compared to the catalyst conditions (Table 1, entries 12 and 13 vs. entries 4 and 9). Briefly, entry 4 in Table 1 was identified as the best condition with respect to both the yields and the reaction time.

With the best condition in hand (Table 1, entry 4), a series of **1** and nucleophile **2** were reacted, and the most promising outcomes are summarized in Scheme 2. The reactions of **1c** and indole (**2a–2p**) with Ru(bpy)₃Cl₂·6H₂O (2 mol%) in MeOH under a balloon of oxygen were irradiated with a household 24 W compact fluorescent (CFL) plug-in light bulb at room temperature and provided the corresponding adduct **3ca–3cp** in good yields, ranging from 60% to 82%. The reactions with the indoles (**2b**, **2c**, **2h**, and **2i**), which bore electron-withdrawing substituents (*e.g.*, F and Cl), gave lesser yields of the corresponding **3cb**, **3cc**, **3ch**, and **3ci**, probably due to the lesser nucleophilicity of these indoles. The photoredox reactions with 2-alkyl indoles (**2l**, **2m**, and **2n**) provided high yields of adducts (**3cl**, **3cm**, and **3cn**). Reactions with the protected indoles (**2o** and **2p**) did not increase the yields (**3co** and **3cp**). The reaction with other aromatic compounds, such as 7-azaindole (**2q**), naphthalen-2-ol (**2r**), 1*H*-benzo[*g*]indole (**2s**), pyrrole (**2t**) and phenol (**2u**) were feasible, although a low yield was obtained in the case of 7-azaindole (**2q**), and two regioisomeric products **3cu-p** and **3cu-o** were observed in the reaction with phenol (**2u**). The reactions of silyl enol ethers (**2v** and **2w**) and **1c** smoothly provided the corresponding adducts in good yields (83% and 79% yield, respectively), albeit with a 4 : 1 stereoisomeric ratio of **3cv-1** and **3cv-2**. Exposure of TMSCN **2x** to **1c** under the reaction conditions provided 74% yield of **3cx**. On the other hand, the reactions of chloro- and fluoro-dihydroquinoxalin-2(1*H*)-one (**1g** and **1i**) with indole **2a** afforded the corresponding products (**3ga** and **3ia**) in 72% and 64% yields, respectively. It is noteworthy that the reaction with propyl-substituted dihydroquinoxalinone (**1j**) with indole **2a** gave a lesser yield of adduct **3ja** (49% yield), as compared to the reactions with benzyl-substituted dihydroquinoxalinones (**1c**, **1d** and **1e**), where **3ca**, **3da** and **3ea** were obtained in 76%, 71%, and 75% yields, respectively. Notably, the same reaction condition with benzoyl substituted dihydroquinoxalinones (**1b**) gave no observable product, with





^a Unless otherwise noted, the reactions were performed with **1** (1 equiv) and **2** (2 equiv) with 2 mol % of Ru(bpy)₃Cl₂·6H₂O in MeOH at ambient temperature. Percentage (%) for isolated yields after chromatography purification. ^b Yields in parenthesis for the reaction in the absence of Ru(bpy)₃Cl₂·6H₂O (catalyst free condition). ^c Reaction conducted with **2** (10 equiv) in CH₂Cl₂. ^d Reaction conducted in CH₃CN.

Scheme 2 Examples of the photoredox cross-coupling reaction.^a

recovery of most of the starting compounds. Alternatively, the reaction of 3,4-dihydroquinoxalin-2(1*H*)-one (**1a**) and indole (**2a**) with Ru(bpy)₃Cl₂·6H₂O (2 mol%) in MeOH was slow, **1a** was consumed in 2 days, and converted to quinoxalin-2(1*H*)-one (**8**), monitored by crude ¹H NMR, followed by the transformation to

afford the product **4aa** in 65% yield, after 5 days irradiation.¹³ In another batch of the reaction, where the irradiation was continued for only 2 days, and **8** was isolated in 71% yield. Apparently, the initial SET photo-oxidation and the subsequent oxidation afforded **8**. The nucleophilic addition of indole towards **8**, activated by acid (generated in the photo reaction condition), followed by oxidation gave the adduct **4aa**.¹⁴ Later, the protocol was applied in the concise synthesis of cephalindole A (**4ka**).¹⁵ Irradiation of **1k** and indole (**2a**) in the presence of Ru(bpy)₃Cl₂·6H₂O (2 mol%) in CH₃CN for 48 h provided adduct **3ka** in 44% yield, along with 21% yield of the product **9**.¹⁶ Subsequently, debenzoylation of **3ka** (H₂, 10% Pd/C, THF, 16 h, rt), followed by the dilution with THF and the addition of DDQ with stirring under nitrogen atmosphere for 1 h gave 61% overall yield of cephalindole A (**4ka**) in a one-pot, two-step operation.

On the other hand, as previously observed in Table 1, some reactions were studied in the absence of photocatalyst (catalyst-free condition) with CFL light and successfully provided the corresponding adducts, albeit in slightly lower yields (as shown in the parenthesis in Scheme 2 and ESI, Scheme S1[†]), but required longer reaction time for the completion. The feasibility of this catalyst-free and visible-light photo reaction is of particular interest due to its green and cost-effective strategy.¹⁷ The UV-vis absorption spectrum of **1c** in MeOH showed no obvious absorption at low concentrations in the visible region. However, upon increasing the concentration (to 0.05 M, the concentration used in the experiments), a small absorption band appeared in the visible region (380–480 nm), which implied that, due to aggregation, **1c** could absorb visible light and undergo photo-activation.^{18,19} Consequently, the UV-vis absorption spectrum of the 1 : 2 mixture of **1c** and indole (**2a**) in methanol, after 30 min, showed a significant broad absorption in the UV-vis around 380–520 nm. Indeed, the mixture was colorless in the dark for hours, but turned to pale yellow after 30 min CFL irradiation.¹⁹ The structure of adducts **3ca**, **3cd**, **3ga**, **5**, and **7** was unequivocally confirmed by their single-crystal X-ray crystallographic diffraction analyses (Fig. 2).¹⁹

To shed some light on the reaction mechanism, the light/dark experiment was conducted by on-off switching of the

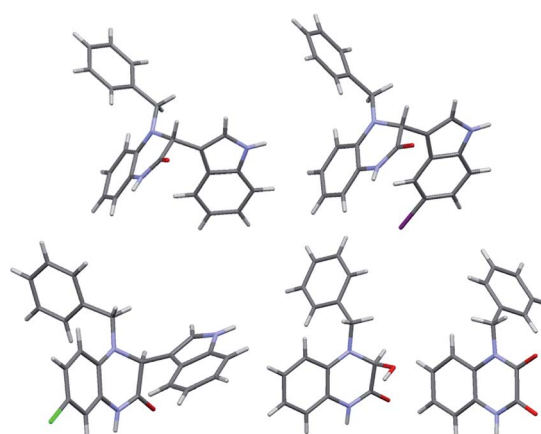


Fig. 2 Stereo plots of the X-ray crystal structures of **3ca**, **3cd**, **3ga**, **5** and **7**: C, gray; O, red; N, blue; Br, purple; Cl, green.



light at different intervals for the reactions of **1c** to **3ca** under standard conditions (Fig. S2†).¹⁹ The reaction ceased during the periods in the dark and restarted when the light source was switched on once again. The observations excluded a light-initiated chain process and clearly revealed the essential role of visible-light photocatalysis through the reaction process.²⁰ In addition, a radical trapping experiment was carried out to probe the radical nature of this reaction. A methanolic solution of **1c** and indole with 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO), an efficient radical scavenger and a radical mechanism indicator, was irradiated with 24 W CFL light under oxygen atmosphere. The reaction was inhibited, and even after 48 h irradiation less than 8% of the product **3ca** was observed (estimated by crude ¹H NMR), and most of **1c** was recovered after chromatographic purification. In addition, MS analysis of the reaction mixture showed the presence of the 394.2 molecular ion which reflected the presence of $[\mathbf{1c}\text{-TEMPO} + \text{H}]^+$. This observation further reveals the involvement of a radical process in the reaction mechanism.²¹

A conceivable mechanism is proposed in Scheme 3. Initially, irradiation of $\text{Ru}(\text{bpy})_3^{2+}$ by CFL visible light provides the active $\text{Ru}(\text{bpy})_3^{2+*}$, which oxidizes amine **1c** via a single electron transfer (SET) process to give the radical cation **A** and $\text{Ru}(\text{bpy})_3^+$. The species $\text{Ru}(\text{bpy})_3^+$ can be oxidized by O_2 and regenerated to start the new catalytic cycle.²² Deprotonation of the intermediate **A** affords the radical **B**, and the subsequent conversion provides the imine intermediate **C**. Subsequently, reaction of indole with imine **C** provide the adduct **3ca**. Side reaction of the intermediate **B** could occur by reaction with oxygen or H_2O_2 to give **5** and **7**. The side reaction becomes dominant when the aforementioned nucleophilic substitution of imine **C** occurs with weak nucleophiles (e.g., **2u**, **2q**, **2r**). For the reaction with such a weak nucleophile, a competition of the MeOH and weak nucleophile with iminium **C** can occur and leads to the formation of side product **6** as well.²³ Alternatively, in the absence of external ruthenium photocatalyst, substrate **1c**, which acts as a photosensitizer, was slowly excited by CFL light irradiation.^{18a} The activated **1c*** underwent an energy transfer

process with the ground state $^3\text{O}_2$ to render the singlet $^1\text{O}_2$, and regenerate the ground state **1c**. The produced singlet $^1\text{O}_2$ can undergo single-electron-transfer oxidation of **1c** to give a radical cation **A** and $\text{O}_2^{\cdot-}$, which could further react with **1c** to yield O_2^{2-} and additional radical cation **A** followed by the subsequent reaction process.²⁴ Alternatively, the photoreaction with the catalyst-free condition might be allowed due to the electron donor-acceptor complex.²⁵ The results in the presence of ruthenium photocatalyst (e.g., Table 1, entry 4) indicate that the addition of an external photosensitizer significantly increases the reactivity, in consonance with the occurrence of an additional photoinduced electron transfer pathway.

Conclusions

In summary, we have established a visible-light induced C–C bond formation reaction of 4-alkyl-3,4-dihydroquinoxalin-2(1H)-one and indoles as well as a variety of other nucleophiles. This reaction protocol not only contributed a convenient process with a household compact fluorescence lamp for the synthesis of related heterocycles, but also manifested an illustration of a catalyst-free photoreaction. The structures of several products were established by X-ray crystallographic analyses.²⁶ Given the extensive interest of heterocycles in synthetic and medicinal chemistry and the growing interest in photocatalysis as well as the imperative need of acquiring green chemistry processes, this study could provide a valuable contribution to chemical synthesis. Further expansions of these reactions and demonstration of the process in elaborated systems are now in progress.

Conflicts of interest

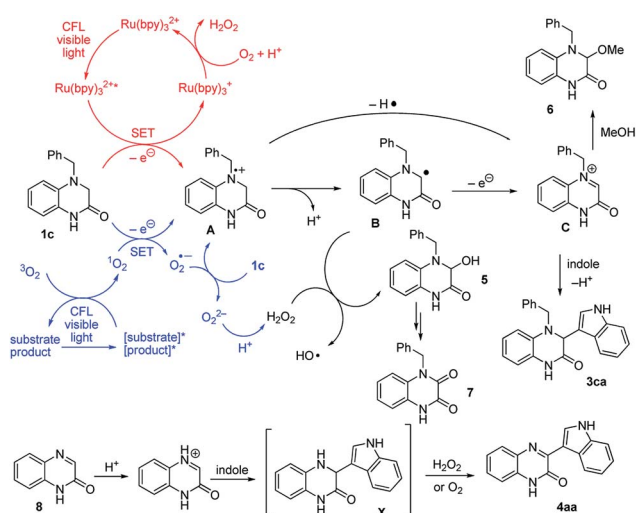
The authors declare no competing financial interest.

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Scheme 3 Plausible reaction mechanism.



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- 26 During the preparation of this manuscript, a related photocatalysis of 3,4-dihydro-2H-benzo[b][1,4]oxazin-2-one was published, G.-Y. Zhang, K.-K. Yu, C. Zhang, Z. Guan and Y.-H. He, *Eur. J. Org. Chem.*, 2018, 525. Nevertheless, the current studies provide more examples, including the 3,4-dihydroquinoxalin-2(1H)-one, extensive study and the catalyst free condition, as well as the X-ray analysis of adducts.

