Synthesis of 2-Substituted Indoles through Visible Light-Induced Photocatalytic Cyclizations of Styryl Azides

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Abstract: A visible light-induced photocatalytic intramolecular cyclization of styryl azides has been developed in the presence of the ruthenium complex Ru(bpy)₃Cl₂ (0.5 mol%) as photocatalyst at room temperature. The present photocatalytic strategy features operational simplicity as well as high functional group tolerance, and provides a facile access to various 2-substituted *N*-free indoles in good to excellent yields. Importantly, the present process can employ sunlight as the light source to afford the corresponding products without loss of reaction efficiency.

Keywords: azides; heterocyclic compounds; indoles; photoredox catalysis; visible light

Indoles and their derivatives are a family of privileged heterocyclic structures commonly found in a number of natural products and many biologically active molecules.^[1] Among them, 2-substituted indoles represent a subclass of biologically and synthetically useful scaffolds.^[2] Thus, the development of efficient methods to construct these molecules has evoked considerable attention from both academic and industrial communities.^[3] Traditional methods for the preparation of 2substituted indoles are mainly based on the Fischer indole synthesis,^[4] which always requires the heating of phenylhydrazines with aldehydes or ketones under acid catalysis. However, harsh reaction conditions sometimes limit the functional group tolerance. Over the past 10 years, transition metal-catalyzed C-H functionalization processes have been established as alternative protocols for the synthesis of 2-substituted indoles. In this context, the Driver group has reported a rhodium-catalyzed intramolecular C–H amination of aryl azides and azidoacrylates, which represents one of the most significant and efficient methods for the assembly of various indoles and polycyclic indole derivatives.^[5] Other practical methods include transition metal-catalyzed arylation reactions at the C-2 position of indoles with arylboronic acids,^[6] aryltrifluoroborate salts,^[7] and hypoiodide reagents,^[8] as well as direct dual C–H functionalization.^[9] Despite these impressive advances, the development of new and efficient methodologies for the synthesis of 2-substituted indoles under mild and environmentally friendly conditions remains highly desirable.

Recently, visible light-induced photocatalysis has been nicely applied to the construction of useful and important carbocycles and heterocycles due to its sustainable character.^[10,11] For example, the group of Zheng in 2012 developed an elegant example of indole synthesis through a visible light photocatalytic oxidative C-N bond formation/aromatization sequence of styrylanilines.^[12] They found that only the para-alkoxyphenyl-protected styrylanilines proved to be suitable for this transformation (Scheme 1, a). Quite recently, Rueping and co-workers disclosed a visible light photocatalytic protocol to construct Nalkylindoles via an intramolecular cyclization of the α -amino radical to tethered alkenes (Scheme 1, b).^[13] In addition, azides have been used as versatile reagents to participate in a variety of transformations for the construction of diversely functionalized nitrogen-containing molecules due to their sensitivity to thermolysis, photolysis or transition metals.^[14] For example, Liu and co-workers recently described a visible



Ar Ar = *p*-alkoxyphenyl

Rueping's work - synthesis of N-alkylindoles



This work - synthesis of N-free indoles



Scheme 1. Visible light photocatalysis in indole synthesis.

light-induced reduction of azides to the corresponding amines with high efficiency.^[15] As part of our ongoing research program on the visible light photoredox catalysis^[16] and indole synthesis,^[17] we report herein a highly efficient route to construct *N*-free 2-substituted indoles from the readily available styryl azides *via* a visible light-induced photocatalysis (Scheme 1, c).

Initially, the styryl azide 1a was selected as the model substrate to optimize the reaction conditions. As summarized in Table 1, indole 2a was isolated in 88% yield when the reaction was performed in CH_3CN with 2 mol% $Ru(bpy)_3Cl_2 \cdot 6H_2O$ as the photocatalyst (Table 1, entry 1). Encouraged by this preliminary result, the effects of other reaction media were then investigated. Notably, the reaction in DMF or EtOH occurred smoothly to give the desired indole product in 96% and 93% yields, respectively (Table 1, entries 2 and 3). Other reaction media such as acetone and THF resulted in inferior results (Table 1, entries 4 and 5). It is worth noting that changing the concentration of **1a** leads to no increase in the yield of 2a (Table 1, entry 6). Further investigation revealed that the catalyst loading could be reduced to 0.5 mol% without apparent erosion of the reaction efficiency (Table 1, entries 7 and 8). Importantly, when the reaction was carried out in the absence of the photocatalyst or visible light irradiation, only 12% or a trace amount of 2a was obtained after 24 h (Table 1, entries 9 and 10). The reaction without the degas process only provided the corresponding product in moderate yield (Table 1, entry 11).

With the optimal reaction conditions established, different aryl-substituted styryl azides **1** were then employed to examine the generality of the methodology. As shown in Table 2, structural variations of the aryl ring at the C-2 position of indole were possible. Table 1. Optimization of the reaction conditions.^[a]

$$\begin{tabular}{|c|c|c|c|c|} \hline Ph & \frac{2 \mbox{ mol}\% \mbox{ Ru}(\mbox{ bpy})_3 \mbox{ Cl}_2 \cdot 6 \mbox{ H}_2 \mbox{ O} \\ \hline \mbox{ solvent, r.t.} & & \end{tabular} \\ \hline \mbox{ N}_3 & \end{tabular} & \end{tabular} \\ \hline \mbox{ 1a} & -\end{tabular} & \end{tabular} \\ \hline \mbox{ N}_2 & \end{tabular} \\ \hline \mbox{ Ph} \\ \hline \mbox{ H} \\ \hline \mbox{ H} \\ \hline \mbox{ H} \\ \hline \mbox{ Ru}(\mbox{ bpy})_3 \mbox{ Cl}_2 \cdot 6 \mbox{ H}_2 \mbox{ O} \\ \hline \mbox{ N} \\ \hline \mbox{ H} \\ \hline \mbox{ H} \\ \hline \mbox{ H} \\ \hline \mbox{ Ru}(\mbox{ bpy})_3 \mbox{ Cl}_2 \cdot 6 \mbox{ H}_2 \mbox{ O} \\ \hline \mbox{ N} \\ \hline \mbox{ H} \\ \hline \$$

Entry	Solvent	Conc. [M]	Time [h]	Yield [%] ^[b]
1	CH ₃ CN	0.05	24	88
2	DMF	0.05	24	96
3	EtOH	0.05	24	93
4	acetone	0.05	24	74
5	THF	0.05	24	7
6	DMF	0.1	24	93
7 ^[c]	DMF	0.05	24	96
8 ^[d]	DMF	0.05	24	96
9 ^[e]	DMF	0.05	24	12
$10^{[f]}$	DMF	0.05	24	trace
11 ^[g]	DMF	0.05	24	63

[a] Unless otherwise noted, the reaction conditions are as follows: **1a** (0.3 mmol), Ru(bpy)₃Cl₂·6H₂O (2 mol%), solvent (6 or 3 mL), 3 W white LEDs, at room temperature.

^[b] Yield of the isolated product.

^[c] 1 mol% Ru(bpy)₃Cl₂· $^{\circ}$ 6H₂O was used.

^[d] 0.5 mol% Ru(bpy)₃Cl₂·6H₂O was used.

^[e] Without the use of photoredox catalyst.

^[f] In the absence of light source.

^[g] Without degas.

Incorporation of an electron-donating group (e.g., methyl, *tert*-butyl, phenoxy) or an electron-withdrawing group at the *para* position of the benzene ring (such as the fluoro, chloro, trifluoromethyl, cyano) was well tolerated, affording the corresponding indoles in 69–99% yields (**2b–g**, **2i**). Moreover, the disubstituted and trisubstituted arenes also proved to be suitable (**2h**, **2j**). Notably, it seems that the steric and electronic effects have some impact on the reaction efficiency. For instance, the substrate containing a nitro group at the *ortho*-position of the benzene ring gave indole **2k** in only 46% yield after 60 h. To our delight, styryl azide **1l** bearing a naphthalene ring was also tolerated and provided 2-(naphthalen-1-yl)-1*H*-indole **2l** in 81% yield.

In addition, a variety of substituents on the indole ring was also investigated to further extend the generality of this transformation (Table 3). Variation of the electronic properties of the R¹ group at the C-5 position of the indole ring could be achieved without loss of reaction efficiency. Thus, a range of 5-substituted indoles (e.g., fluoro, chloro, bromo, ester, and methyl) was synthesized in good to excellent yields (**2m–o**, **2q**, **2s**). A difluoro-substituted substrate also appeared to be suitable to give the corresponding product **2p** in 91% yield. Surprisingly, it was found that 4-methylsubstituted indole (**2r**) was obtained in only moderate yield (68%), which was probably due to the unexpected light-induced E to Z isomerazition of the starting





^[a] Unless otherwise noted, the reaction conditions are as follows: 1 (0.3 mmol), Ru(bpy)₃Cl₂·6H₂O (0.5 mol%), DMF (6 mL), 3 W white LEDs, at room temperature. Yield of the isolated product is given.

material. Also, the Z isomer is reluctant to undergo the desired cyclization (see the mechanistic studies in Scheme 3). More importantly, the photocatalytic protocol was successfully extended to the synthesis of 5methoxy-2-vinyl-1H-indole (2v) and 2-benzoyl-substi-



tuted indole (2w), which could be useful for further transformations.^[18]

To further demonstrate the synthetic utility, a gram scale reaction with substrate **1a** was also conducted [Eq. (1)]. The designed reaction proceeded smoothly to afford the desired product in comparable yield after 30 h. More importantly, the sunlight-driven process also proved feasible to afford the indole product with the same reaction efficiency, which further highlighted the synthetic advantages of this methodology.^[19]

To probe the possible reaction route towards indole formation, cyclic voltammetry (CV) data of substrate **1a** $(-1.8 \text{ V vs. SCE})^{[20]}$ was firstly measured, which indicated that $[\text{Ru}(\text{bpy})_3]^{2+*}$ (-0.8 V) was unable to give an electron to reduce the corresponding substrate **1a**. Therefore, a plausible reaction mechanism for this photocatalytic transformation *via* an energy trans-



Scheme 2. Proposed mechanism.

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Table 3. Visible light-induced indole synthesis: variation of

- [a] Unless otherwise noted, the reaction conditions are as follows: 1 (0.3 mmol), $Ru(bpy)_3Cl_2 \cdot 6H_2O$ (0.5 mol%), DMF (6 mL), 3 W white LEDs, at room temperature.
- Yield of the isolated product is given. ^[b] The E/Z ratio of the starting material was 12.5:1.
- [c]
- The Z and E isomers existed in the starting material, the ratio was 2.4:1.

fer^[16d,21,24] was favored and is depicted in Scheme 2. Initially, visible light excitation of $[Ru(bpy)_3]^{2+}$ might generate the excited state $[Ru(bpy)_3]^{2+*}$. An energy transfer process occurred between 1a and the excited state $[Ru(bpy)_3]^{2+*}$ to give the nitrene intermediate A with release of N_2 . Note that it has been previously documented that the nitrenes could easily be generated by photolysis or thermolysis of the azides.^[22] Finally, a concerted nitrene insertion reaction through transition state **B** delivers the desired product. In order to detect the possible nitrene insertion process, a D-labeling experiment was also performed to gain some insights [Scheme 3, Eq. (3)]. The kinetic isotope effect (KIE) of the reaction was $K_H/K_D = 1.2$ upon 51% conversion of the starting material, which suggested that the concerted nitrene insertion process was likely to be involved.^[23] Moreover, the fact that the reaction with substrate 1x led to no formation of methyl migration product 2x further confirmed such a possible mechanism [Eq. (4)], which also excluded the nitrene addition pathway through transient intermediate C. Additionally, it was found that the exposure of a Z/E mixture of styryl azide substrates to the standard conditions resulted in Z/E isomerization based on the results highlighted in Eq. (5) and the case of 1r in Table 3. Thus, it can be concluded that the cis-configurated substrates could not directly generate the corresponding products due to the blockage of the nitrene-insertion process.

In conclusion, a mild and efficient method for the facile construction of various N-free 2-substituted indoles has been developed by a visible light-induced intramolecular cyclization of styryl azides.^[24] Importantly, the reaction occurs smoothly at room temperature in the presence of low catalyst loading [0.5 mol%



Scheme 3. Control experiments.

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Ru(bpy)₃Cl₂·6H₂O] and provides the corresponding products in good to excellent yields.^[24] Further extensive mechanistic studies and synthetic applications of this transformation are currently underway in our laboratory.

Experimental Section

General Procedure

To a 25-mL Schlenk flask equipped with a magnetic stirrer bar were added **1a** (0.3 mmol), Ru(bpy)₃Cl₂·6H₂O (0.0015 mmol) and 6 mL DMF. The resulting mixture was vigorously degassed through a 'freeze-pump-thaw' procedure three times. Then the solution was stirred at room temperature under irradiation of 3 W white LEDs at a distance of approximately 5 cm. Upon completion of the reaction, as monitored by TLC, the crude mixture was poured into 20 mL H₂O and extracted with Et₂O (30 mL × 3).The combined organic layer was dried over Na₂SO₄ and the solvent was removed under reduced pressure. The crude product was subjected to flash chromatography on silica gel (silica: 200–300; eluent: petroleum ether/ethyl acetate =10:1) to provide pure indole **2a** as a light yellow solid; yield: 96%.

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- [24] During the preparation of this manuscript, we became aware that Yoon and co-workers had published a work about visible light-induced cyclization of vinyl azides by transition metal photocatalysis, giving a variety of pyrroles with good yields: E. P. Farney, T. P. Yoon, *Angew. Chem.* 2014, 126, 812–816; *Angew. Chem. Int. Ed.* 2014, 53, 793–797. In the course of our optimization study, we also found that Ir(ppy)₂(dtbbpy)PF₆ proved to be suitable for the reaction and resulted in a 98% yield of 2a.

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