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Visible Light Mediated Oxidative C-N Bond Formation/ Aromatization Cascade: A New Photocatalytic Entry to *N*- Arylindoles

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Abstract

Indoles: A joint effort of light and air We have developed a mild aerobic oxidation protocol using visible light photocatalysis to synthesize structurally diverse *N*-arylindoles. The procedure employs 4 mol% [Ru(bpz)₃](PF₆)₂, 18W LED light, and is performed open to the atmosphere. Readily prepared *o*-stryryl anilines are converted to a variety of indoles via a cascade sequence composed of oxidation of anilines, C-N bond formation, and aromatization. A 1,2-carbon shift can be also incorporated into this cascade event to further extend the substrate scope of the method. bpz = 2, 2'-Bipyrazine

Keywords

cascade; indole; photocatalysis; ruthenium; visible light

Indoles are a common heterocyclic motif embedded in a large number of bioactive natural products and pharmaceuticals.^[1] As such, the search for better, sustainable, and more efficient methods of indole synthesis has been a topic of constant interest.^[2,3] Amination of vinyl C-H bonds of styryl anilines provides a direct and potentially more efficient entry to indoles, particularly since styryl anilines are readily prepared by the Buchwald-Hartwig amination^[4] of 2-bromostyrene with an amine. This approach was first established with the assistance of a Pd complex at high temperature by the pioneering work from Hegedus.^[5a,b] However, its use in indole synthesis has been limited. One notable example was a recent work by Buchwald on Pd-catalyzed cyclization of 2-chloro-*N*-(2-vinyl)aniline.^[5c]

Recently, visible light photocatalysis has become a focus of research in organic chemistry and sparked a flurry of activity.^[6] In parallel with other groups' efforts in this field,^[7–11] we^[12] have been engaged in exploring new reactivities of nitrogen radical cations generated via direct oxidation of the corresponding amines by photoexcited ruthenium polypyridyl complexes^[13]. Although this type of oxidation was first discovered in the late 1970s,^[14] its potential in organic synthesis has not been extensively explored until recently. Under visible light photoredox conditions, the fate of nitrogen radical cations has been shown to follow one of three pathways: conversion to an iminium ion with concomitant release of a hydrogen radical,^[15] conversion to an alpha amino radical by deprotonation,^[16] or coupling with an irreversible ring opening process to form a carbon radical distal to the nitrogen atom.^[12b]

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We speculated that other reaction pathways known to nitrogen radical cations, including electrophilic addition to olefins, might be amenable to visible light photocatalysis under similar conditions. Herein we report that nitrogen radical cation **2**, generated from stryryl aniline **1**, can undergo electrophilic addition to the tethered olefin, triggering a cascade event with aromatization (when R²=H in **2**) or C-C bond migration followed by aromatization (when R² ≠ H) to form indoles **3a–b** (Scheme 1). This new photocatalytic entry to indoles is especially attractive, since mild aerobic oxidation conditions (visible light, open to air, and room temperature) are employed.

Stryryl aniline **5a** was chosen as the model substrate for initial investigation (Table 1). Ru(bpz)₃·(PF₆)₂ **4a**^[17] was employed as the photocatalyst and an 18W LED white light was used as the source of visible light. Using 2 mol% of **4a** in CH₃CN and open to air, we were pleased to find that the desired indole product **6a** was formed in 31% yield, although the reaction did not proceed to completion after 24 h (entry 1). Use of O₂ in the place of ambient atmosphere (entry 2) or the use of TFE^[18] as the solvent (entry 3) did not improve the yield. Addition of silica gel^[18] to the reaction mixture significantly accelerated the reaction, which was complete after 12 h and provided indole **6a** in 68% yield (entry 4). Doubling the catalyst loading further shortened the reaction time to 5 h and increased the yield of indole **6a** to 88% (entry 5). Ru(bpy)₃·(PF₆)₂ **4b**^[17b] was found to be inferior to **4a**.^[19] Control studies showed that the catalyst, light, and air were all essential for this transformation (entries 7–9). It is noteworthy that a *p*-alkoxyphenyl group is also critical for the reaction.^[18] When the *p*-methoxyphenyl group of **5b** was replaced by a phenyl group (*N*-phenyl-2-vinylaniline, **5b'**), no reaction was observed under the same conditions. We are currently investigating the role of the *p*-alkoxyphenyl group in the reaction.^[20]

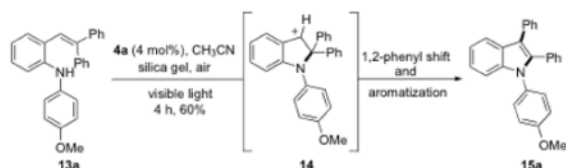
To examine the substrate scope of this method, a series of stryryl anilines **5** were prepared using the Buchwald-Hartwig amination of a 2-bromostyrene derivative with anilines. Under the optimized conditions (entry 7, Table 1), stryryl anilines **5** were converted to the desired indole products **6** in moderate to good yields (Table 2). Electron-donating and electron-withdrawing groups were tolerated on the aryl ring A. A number of alkenes substituted with various functional groups such as alkanes, alkenes, arenes, and furan were effective for this method as long as C2 was monosubstituted. Disubstituted (2,3- and 3,3-) and trisubstituted (2,3,3-) alkenes were all converted uneventfully to 2-substituted, 3-substituted, and 2,3-disubstituted indoles, respectively. Since a general solution to regioselectively introduce substituents at C2 and C3 of indoles is lacking,^[2b,e,f] this method provides an appealing solution to address this unmet need in indole synthesis. Steric hindrance surrounding the alkene is well tolerated as shown by the example of **6h**. When the alkene was part of a carbocycle, fused indoles (**6n**, **6o**) were obtained as the product. The yield of **6n** did not suffer albeit taking a longer time to go to completion when it was scaled up to 1 g.

As a tentative working model, we propose the following catalytic cycle (Scheme 2). The key steps include (i) oxidation of amine **7** by a photoexcited Ru(bpz)₃·(PF₆)₂ **4a** to nitrogen radical cation **8**, (ii) electrophilic addition of nitrogen radical cation **8** to a tethered alkene to generate benzylic radical **9**,^[21] (iii) oxidation of benzylic radical **10** to its corresponding benzylic cation **11**, and finally (iv) aromatization via deprotonation to form indole **12**. A control study using TPP^[22] in place of **4a** did not lead to the desired indole. This result strongly indicated that the reaction was not mediated by singlet oxygen (see the SI for details).

We suspect that silica gel might play several roles in the reaction, including adsorbing oxygen, providing protons to ensure that the nitrogen radical cation **8** is protonated and/or facilitating the oxidation via a proton-coupled electron transfer process.^[23] It alone did not catalyze the reaction (entry 9, Table 1). Replacing silica gel by HCl or TsOH led to the

decomposition of the starting amine. Use of AcOH or PPTS in place of silica gel gave the desired indole, although they were not as effective as silica gel (see SI for the details of these studies). More studies are needed to understand the role(s) of silica gel.

Since a benzylic carbocation was proposed as an intermediate, substrates lacking a C2 C-H bond might participate in a 1,2 carbon shift, where a new C-C bond is formed (eq 1). The Driver group has extensively explored the synthetic utility of this shift in their studies of Rh-catalyzed decomposition of stryryl azides, presumably through similar benzylic carbocations.^[24] To test this hypothesis, gem-diphenyl-substituted stryryl aniline **13a** was prepared and subjected to the optimized visible light photocatalytic conditions (eq 1). To our delight, the expected 2,3-diphenyl indole **15a** was isolated in 60 % yield. This lent further credence to the possible involvement of benzylic carbocation **14** in the visible-light-mediated reaction.



(1)

To further explore the synthetic potential of this 1,2-carbon shift in indole synthesis, a series of gem-disubstituted stryryl anilines were synthesized and tested under the optimized conditions (Table 3). Whether they were independent (**13b**), part of a carbocycle (**13c** and **13d**), or an oxocycle (**13e**), aryl groups preferentially migrated over alkyl groups. However, the 1,2-carbon shift is not limited to the migration of aryl groups only. When C2 was substituted by a cyclopentane ring, the desired ring-expansion product **15f** was formed, although its efficiency was not as high as the aryl shift (entry 5). However, when C2 was substituted by two methyl groups, the desired methyl migration product was not formed. It is noteworthy that, when a tetralene product was formed, further oxidation to a fully aromatized product was observed (entry 2).

In summary, we have developed a visible light mediated photocatalytic method for the synthesis of *N*-arylindoles. These reactions were conducted at ambient temperature with the aid of 4 mol% [Ru(bpz)₃](PF₆)₂ **4a**, 18W LED white light, and open to air. The mild aerobic oxidation conditions were shown to be compatible with a variety of functional groups. More importantly, these studies revealed for the first time that arylamines could participate in C-N bond formation directly under visible light photoredox conditions. Studies leading to understand the roles of the *p*-alkoxyphenyl group and silica gel in these reactions, and application of this method to the synthesis of other types of indoles are ongoing in our laboratory.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

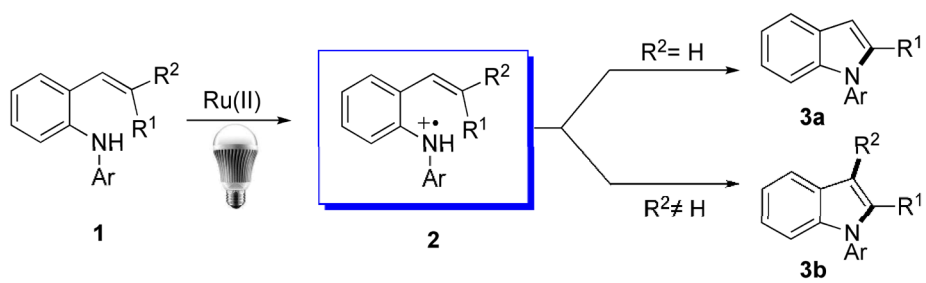
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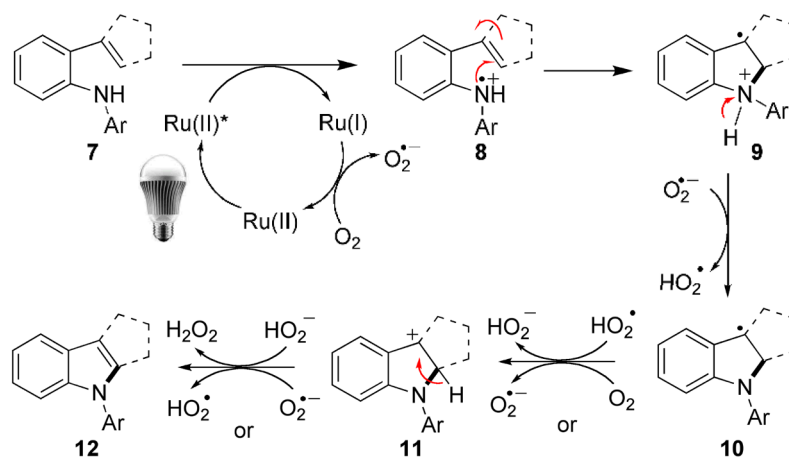
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18. Fluorocarbon solvents and silica gel enhance the solubility of molecular oxygen (see: Lee HB, Sung MJ, Blackstock SC, Cha JK. *J Am Chem Soc.* 2001; 123:11322. [PubMed: 11697988])
19. The effectiveness of the catalysts correlates with the redox potentials of Ru^{2+*/Ru¹⁺} (vs. SCE): Ru(bpz)₃, 1.3 V; Ru(bpy)₃, 0.78 V. The values are taken from reference 17a.
20. Electron rich *p*-alkoxyphenyl groups lower the oxidation potential of anilines: see cyclic voltammogram of **5b** and **5b'** in SI.
21. Formation of 3-cyclopropyl-substituted indole **6k** in high yield does not rule out our proposed mechanism. Bullock reported that, because of the stabilization provided by the benzyl group, ring opening of the cyclopropylbenzyl radical is much slower (2.7×10^5) than that of the cyclopropylmethyl radical (2.1×10^8), which would allow for competitive oxidation of benzylic radical **10** to benzylic cation **11** (see: Masnovi J, Samsel EG, Bullock RM. *J Chem Soc, Chem Commun.* 1989:1044.
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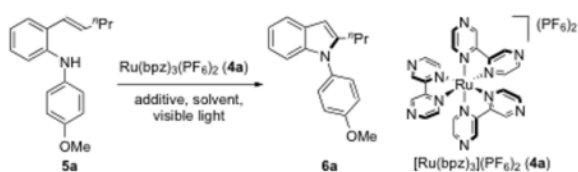
Scheme 1.
Visible light mediated indole synthesis.



Scheme 2.
Proposed Mechanistic Model.

Table 1

Optimization of the catalytic system.

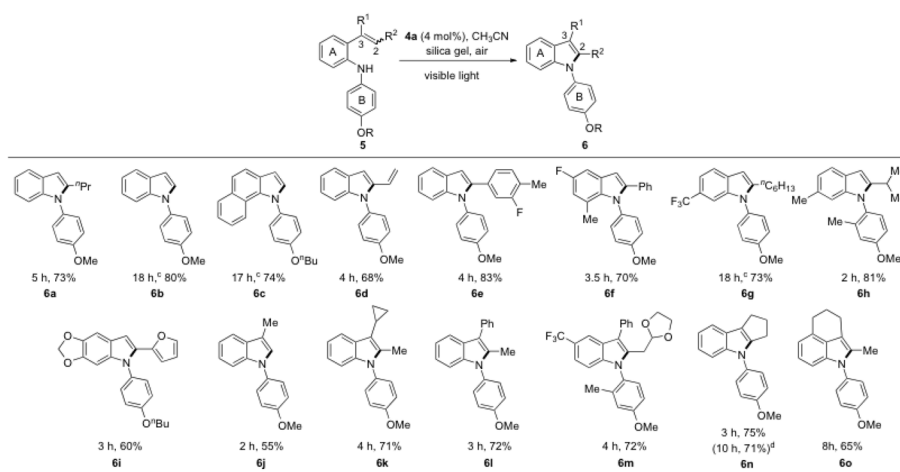


Entry	Conditions ^[a]	t [h]	Conv. of 5a [%] ^[b]	Yield of 6a [%] ^[b]
1	4a (2 mol%), CH ₃ CN	24	44	31
2	4a (2 mol%), CH ₃ CN, O ₂	24	49	33
3	4a (2 mol%), TFE	24	42	21
4	4a (2 mol%), silica gel, CH ₃ CN	12	100	68
5	4a (4 mol%), silica gel, CH ₃ CN	5	100	88
6	4b (2 mol%), silica gel, CH ₃ CN	24	100	19
7	Silica gel, CH ₃ CN, no 4a , light	24	8	4
8	4a (2 mol%), silica gel, CH ₃ CN, no light	24	4	2
9	4a (2 mol%), silica gel, CH ₃ CN, degassed	24	8	0

^[a] Conditions: **5a** (0.2 mmol), solvent, open air, irradiation with a white LED light at rt.

^[b] Measured by GC using dodecane as an internal standard.

Table 2

Scope of Indoles via C-N Bond Formation/Aromatization.^[a, b]

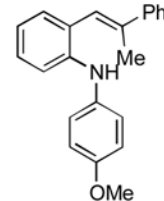
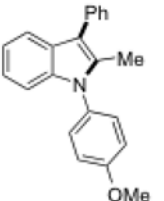
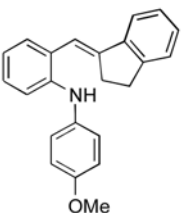
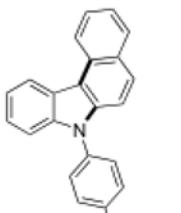
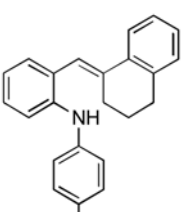
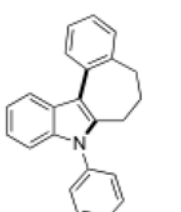
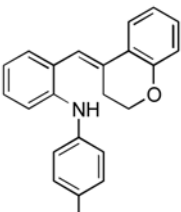
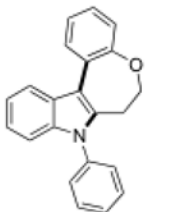
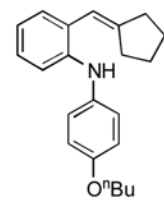
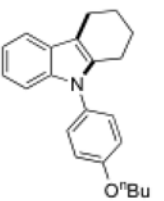
^a Conditions, unless otherwise noted: 4 mol% Ru(bpz)₃(PF₆)₂, silica gel, air, CH₃CN, irradiation with a 18 W LED white light. The newly formed C-N bonds are shown in bold.

^b Isolated yields after column chromatography.

^c Using 6 mol% Ru(bpz)₃(PF₆)₂.

^d Gram scale reaction.

Table 3Scope of Indoles via C-N Bond Formation/1,2-Carbon Shift/Aromatization.^[a]

Entry	Stryryl Anilines	Indole Product	t [h]	Yield [%] ^[b]
1	 13b	 6l	4.5	62
2	 13c	 15c	6	52
3	 13d	 15d	6	60
4	 13e	 15e	6	58
5	 13f	 15f	16	40

^a Conditions, unless otherwise noted: 4 mol% Ru(bpz)₃(PF₆)₂, silica gel, air, CH₃CN, irradiation with a 18 W LED white light. The newly formed C-N and C-C bonds are shown in bold.

^b Isolated yields after column chromatography.

^c Using 6 mol% Ru(bpz)₃(PF₆)₂. Newly formed C-N and C-C bonds are shown in bolds.