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Photocatalysis

A Visible-Light-Mediated Oxidative C–N Bond Formation/Aromatization Cascade: Photocatalytic Preparation of *N*-Arylindoles**

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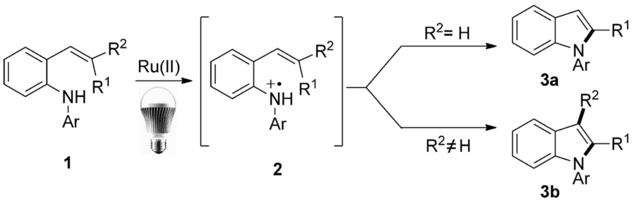
Indoles are heterocyclic motifs that are embedded in a large number of bioactive natural products and pharmaceuticals.[1] As such, the search for sustainable and more efficient methods for the preparation of indoles is of constant interest.[2,3] Amination of vinyl C–H bonds of styryl anilines would provide direct and potentially more efficient access to indoles, particularly because styryl anilines are readily prepared by the Buchwald–Hartwig amination[4] of 2-bromostyrene. When this approach was first reported by the research group of Hegedus, it employed a palladium complex under reaction conditions of high temperature.[5a,b] However, its use in indole synthesis has been limited, although one notable example, in the form of a palladium-catalyzed cyclization of 2-chloro-*N*-(2-vinyl)aniline, was recently reported by Tsvelikhovsky and Buchwald.[5c]

Recently, visible-light photocatalysis has become the subject of a flurry of activity in organic chemistry.[6] In parallel with the efforts of other research groups in this field,[7–11] our research group[12] has been engaged in exploring new types of reactivity of nitrogen-centered radical cations that are generated through direct oxidation of the corresponding amines by using 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 before recent efforts. Under visible-light photoredox conditions, the fate of nitrogen-centered radical cations has been shown to follow one of three reaction pathways: conversion into an iminium ion with concomitant release of a hydrogen radical,[15] conversion into an α-amino radical by deprotonation,[16] or coupling with an irreversible ring-opening process to form a carbon-centered radical that is distal to the nitrogen atom.[12b] We speculated that other reaction pathways that nitrogen-centered radical cations are known to follow, including electrophilic addition to alkenes, might be amenable to visible-light photocatalysis under similar reaction conditions. Herein, we report that nitrogen-centered radical cation **2**, which is generated from styryl aniline **1**, can undergo electrophilic addition to the tethered alkene, thus triggering a cascade reaction involving either aromatization (when $R^2 = H$ in **2**) or C–C bond migration followed by aromatization (when $R^2 \neq H$) to form indoles **3a** and **3b** (Scheme 1). This new photocatalytic approach for preparing indoles is especially attractive because mild aerobic oxidation conditions (visible light, open to air, and room temperature) are employed.



Scheme 1. Visible-light-mediated indole synthesis.

Styryl aniline **5a** was chosen as the model substrate for initial investigation (Table 1). $[Ru(bpz)_3](PF_6)_2$ (**4a**)[17] was employed as the photocatalyst and an 18 W white-light LED was used as the source of visible light. Using 2 mol% of **4a** in CH_3CN and leaving the reaction mixture open to air, we were pleased to find that the desired indole product **6a** was formed in 31% yield, although, even after 24 hours, the reaction had not proceeded to completion (Table 1, entry 1). Either the use of O_2 in the place of ambient atmosphere (Table 1, entry 2) or the use of TFE[18] as the solvent (Table 1, 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 hours, thus providing indole **6a** in 68% yield (Table 1, entry 4). Doubling the catalyst loading further shortened the time necessary for full conversion to 5 hours and led to an increase in the yield of indole **6a** to 88% (Table 1, entry 5). $[Ru(bpy)_3](PF_6)_2$ (**4b**; bpy = 2,2′-bipyridine)[17b] was found to be inferior to **4a**.[19] Control studies showed that the catalyst, light, and air were all essential for this transformation (Table 1, entries 7–9). Notably, a *p*-alkoxyphenyl group on the nitrogen atom 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 reaction conditions. We are currently investigating the role of the *p*-alkoxyphenyl group in the reaction.[20]

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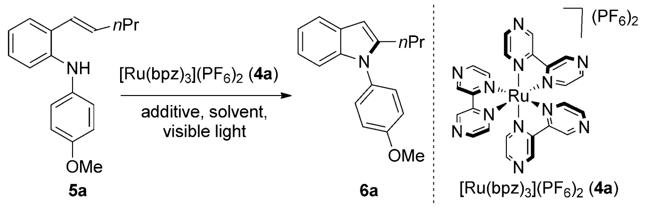
Table 1: Optimization of the catalytic system.

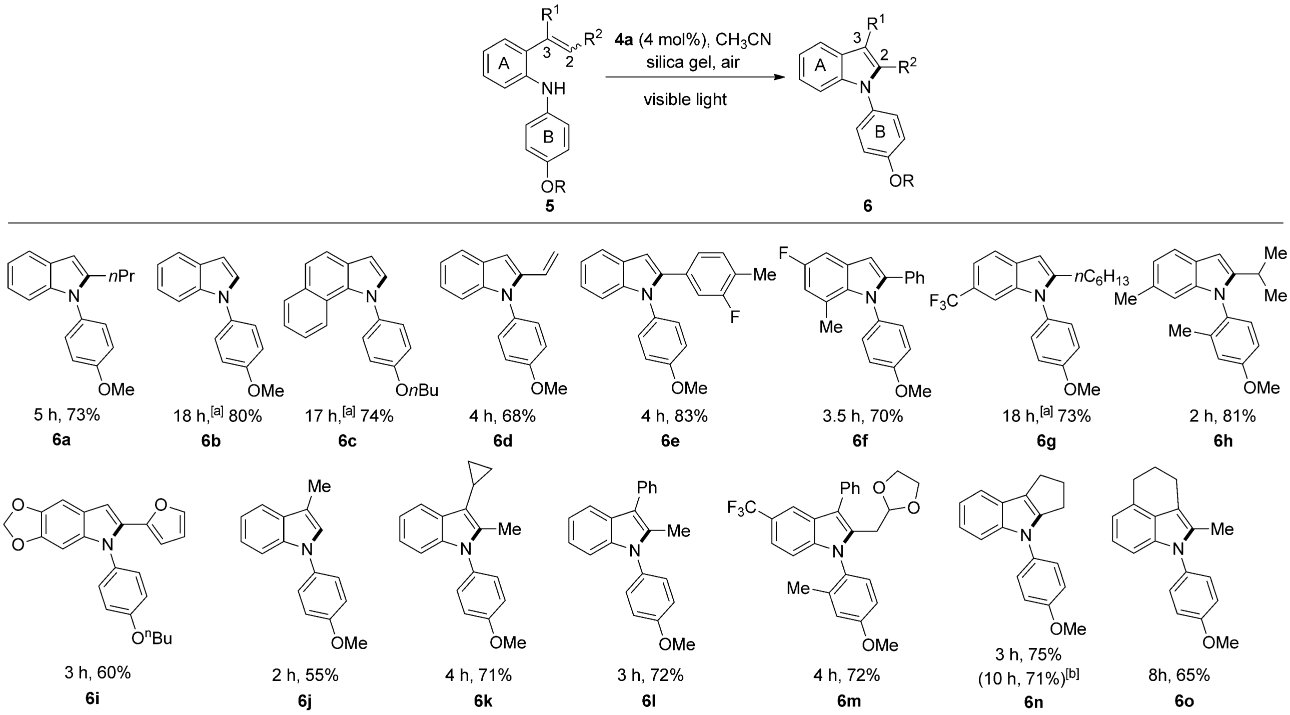


Entry	Reaction conditions[a]	*t* [h]	Conv. of **5a** [%][b]	Yield of **6a** [%][b]
1	**4a** (2 mol %), CH_3CN	24	44	31
2	**4a** (2 mol %), CH_3CN, O_2	24	49	33
3	**4a** (2 mol %), TFE	24	42	21
4	**4a** (2 mol %), silica gel, CH_3CN	12	100	68
5	**4a** (4 mol %), silica gel, CH_3CN	5	100	88
6	**4b** (2 mol %), silica gel, CH_3CN	24	100	19
7	silica gel, CH_3CN, no **4a**, light	24	8	4
8	**4a** (2 mol %), silica gel, CH_3CN, no light	24	4	2
9	**4a** (2 mol %), silica gel, CH_3CN, degassed	24	8	0

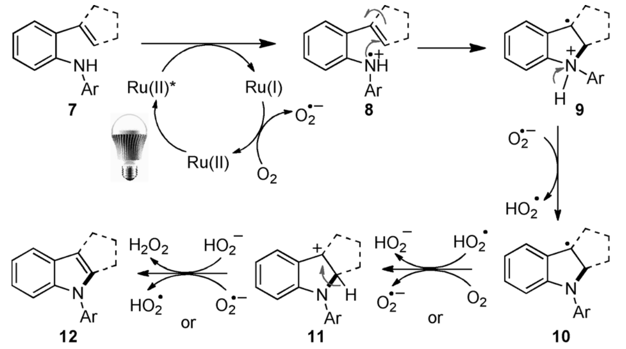
[a] Reaction conditions: **5a** (0.2 mmol), solvent, open to air, irradiation with a white-light LED at RT. [b] Measured by GC using dodecane as an internal standard. bpz = 2,2′-bipyrazine, TFE = trifluoroethanol.

To examine the substrate scope of this method, a series of styryl anilines **5** were prepared using the Buchwald–Hartwig amination of a 2-bromostyrene derivative with anilines. Under the optimized reaction conditions (Table 1, entry 5), styryl anilines **5** were converted into the desired indole products **6** in moderate to good yields (Scheme 2). The presence of electron-donating and electron-withdrawing groups on the aryl ring A were tolerated. A number of alkenes containing various functional groups such as alkanes, alkenes, arenes, and furans were good substrates for this reaction as long as the C2 position was monosubstituted. Disubstituted (2,3- and 3,3-) and trisubstituted (2,3,3-) alkenes were all converted into 2-substituted, 3-substituted, and 2,3-disubstituted indoles, respectively. This method represents a general method for the regioselective introduction of substituents at the C2 and C3 positions of indoles,[2b,e,f] a need that is currently unmet in indole synthesis. Substrates that are sterically hindered in the vicinity of the alkene moiety are well tolerated (**6h**; Scheme 2). When the alkene was part of a carbocycle, fused indoles were obtained as the products (**6n** and **6o**; Scheme 2); the yield of **6n** was high, although the reaction took a longer time to reach completion when it was scaled up to 1 g.

We propose the catalytic cycle that is outlined in Scheme 3. The key steps include: (i) conversion of amine **7** into nitrogen-centered radical cation **8** through oxidation using a photoexcited $[Ru(bpz)_3](PF_6)_2$ (**4a**), (ii) electrophilic addition of nitrogen-centered 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 through deprotonation, thus forming indole **12**. A control study using tetraphenylporphyrin (TPP)[22] in place of **4a** did not lead to the desired indole. This result strongly indicates that the reaction is not mediated by singlet oxygen (see the Supporting Information for details).



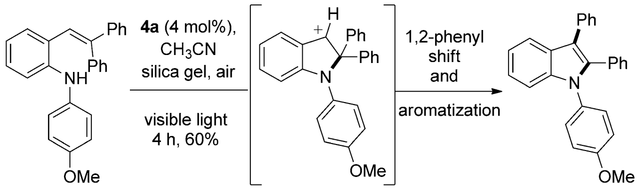
Scheme 2. Substrate scope of the reaction involving C–N bond formation and aromatization. Reaction conditions, unless otherwise noted, 4 mol% $[Ru(bpz)_3](PF_6)_2$, silica gel, air, CH_3CN, irradiation with a 18 W white-light LED. The newly formed C–N bonds are shown in bold. Yields of products isolated using column chromatography are given. [a] Using 6 mol% $[Ru(bpz)_3](PF_6)_2$. [b] Gram-scale reaction.



Scheme 3. Proposed mechanistic model.

We suspect that silica gel might play several roles in the reaction, including adsorbing oxygen, being a source of protons, which ensures that the nitrogen-centered radical cation **8** is protonated, and facilitating the oxidation through a proton-coupled electron transfer process.[23] The presence of silica gel alone, that is, in the absence of the ruthenium catalyst, led to no reaction (Table 1, entry 7). Replacing silica gel with either HCl or TsOH led to the decomposition of the starting amine. The use of either AcOH or PPTS in place of silica gel gave the desired indole, although they were not as effective as silica gel (see the Supporting Information for the details). More studies are needed to understand the role(s) of silica gel.

Having proposed that a benzylic carbocation is an intermediate, we suspected that substrates lacking a C2 C–H bond might participate in a 1,2-carbon shift, thus forming a new C–C bond (Scheme 4). The research group of Driver has extensively explored the synthetic utility of this 1,2-carbon shift in their studies of rhodium-catalyzed decomposition of styryl azides, a transformation that presumably involves similar benzylic carbocations.[24] To test this hypothesis, *gem*-diphenyl styryl aniline **13a** was prepared and subjected to the optimized visible-light photocatalytic conditions (Scheme 4). To our delight, the expected 2,3-diphenyl indole **15a** was isolated in 60% yield. This result lent further credence to the possible involvement of benzylic carbocation **14** in the visible-light-mediated reaction.

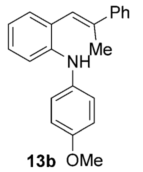
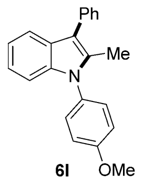
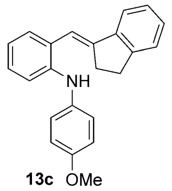
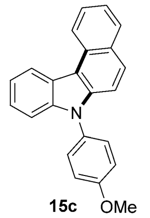
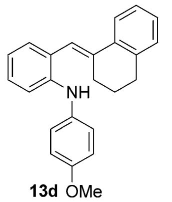
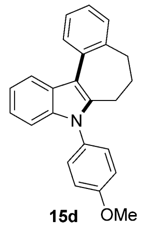
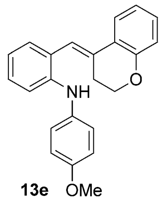
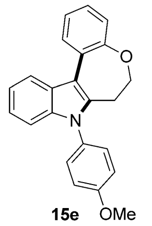
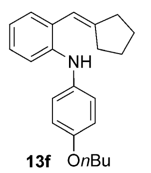
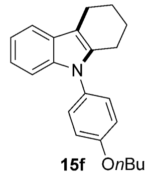


13a **14** **15a**

Scheme 4. Cyclization involving a 1,2-carbon shift.

To further explore the synthetic potential of this 1,2-carbon shift in indole synthesis, a series of gem-disubstituted styryl anilines were synthesized and tested under the optimized reaction conditions (Table 2). Whether the substituents were independent (**13b**), part of a carbocycle (**13c** and **13d**), or part of 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 the C2 position formed part of a cyclopentane ring, the desired ring-expansion product **15 f** was formed, although the efficiency of the transformation was not as high as those involving aryl shifts (Table 2, entry 5). However, when the C2 position bore two methyl groups, the desired methyl-migration product was not formed. Notably, when a tetralene product was formed, further oxidation to a fully aromatized product was observed (Table 2, entry 2).

Table 2: Scope of substrate in the C–N bond formation/1,2-carbon shift/aromatization cascade reaction.[a]

Entry	Styryl 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[c]	 **13f**	 **15f**	16	40

[a] Reaction conditions, unless otherwise noted: 4 mol% $[Ru(bpz)_3](PF_6)_2$, silica gel, air, CH_3CN, irradiation with a 18 W white-light LED. The newly formed C–N and C–C bonds are shown in bold. [b] Yields of product isolated using column chromatography. [c] Using 6 mol% $[Ru(bpz)_3](PF_6)_2$.

In summary, we have developed a visible-light-mediated photocatalytic reaction for the preparation of *N*-arylindoles. These reactions, which were catalyzed by 4 mol% $[\mathrm{Ru(bpz)_3}](\mathrm{PF_6})_2$ (**4a**), were conducted at ambient temperature, and the reaction mixtures were exposed to open air and were illuminated by an 18 W white-light LED. The mild aerobic oxidation conditions were compatible with the presence of 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 toward understanding the roles of the *p*-alkoxyphenyl group and silica gel in these reactions, together with the application of this method to the synthesis of other types of indoles are ongoing in our laboratory.

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[1] For selected recent reviews on biological activities and synthesis of indoles, see: a) S. Cacchi, G. Fabrizi, *Chem. Rev.* **2011**, *111*, PR215; b) A. J. Kochanowska-Karamyan, M. T. Hamann, *Chem. Rev.* **2010**, *110*, 4489; c) M. Bandini, A. Eichholzer, *Angew. Chem.* **2009**, *121*, 9786; *Angew. Chem. Int. Ed.* **2009**, *48*, 9608.

[2] For selected recent examples, see: a) L. Ackermann, A. V. Lygin, *Org. Lett.* **2012**, *14*, 764; b) M. Inman, A. Carbone, C. J. Moody, *J. Org. Chem.* **2012**, *77*, 1217; c) B. Lu, Y. Luo, L. Liu, L. Ye, Y. Wang, L. Zhang, *Angew. Chem.* **2011**, *123*, 8508; *Angew. Chem. Int. Ed.* **2011**, *50*, 8358; d) J. Bonnamour, C. Bolm, *Org. Lett.* **2011**, *13*, 2012; e) Y. Tan, J. F. Hartwig, *J. Am. Chem. Soc.* **2010**, *132*, 3676; f) T. P. Pathak, K. M. Gligorich, B. E. Welm, M. S. Sigman, *J. Am. Chem. Soc.* **2010**, *132*, 7870; g) T.-S. Mei, X. Wang, J.-Y. Yu, *J. Am. Chem. Soc.* **2009**, *131*, 10806; h) Z. Shi, C. Zhang, S. Li, D. Pan, S. Ding, Y. Cui, N. Jiao, *Angew. Chem.* **2009**, *121*, 4642; *Angew. Chem. Int. Ed.* **2009**, *48*, 4572; i) R. Bernini, G. Fabrizi, A. Sferrazza, S. Cacchi, *Angew. Chem.* **2009**, *121*, 8222; *Angew. Chem. Int. Ed.* **2009**, *48*, 8078; j) D. R. Stuart, M. Bertrand-Laperle, K. M. N. Burgess, K. Fagnou, *J. Am. Chem. Soc.* **2008**, *130*, 16474; k) O. Leogane, H. Lebel, *Angew. Chem.* **2008**, *120*, 356; *Angew. Chem. Int. Ed.* **2008**, *47*, 350; l) S. Würtz, S. Rakshit, J. J. Neumann, T. Dröge, F. Glorius, *Angew. Chem.* **2008**, *120*, 7340; *Angew. Chem. Int. Ed.* **2008**, *47*, 7230; m) B. J. Stokes, H. Dong, B. E. Leslie, A. L. Pumphrey, T. G. Driver, *J. Am. Chem. Soc.* **2007**, *129*, 7500; n) T. Tokuyama, T. Yamashita, M. T. Reding, Y. Kaburagi, T. Fukuyama, *J. Am. Chem. Soc.* **1999**, *121*, 3791; o) T. Fukuyama, X. Chen, G. Peng, *J. Am. Chem. Soc.* **1994**, *116*, 3127.

[3] S. Jana, M. D. Clements, B. K. Sharp, N. Zheng, *Org. Lett.* **2010**, *12*, 3736.

[4] a) D. S. Surry, S. L. Buchwald, *Chem. Sci.* **2011**, *2*, 27; b) J. F. Hartwig, *Acc. Chem. Res.* **2008**, *41*, 1534.

[5] a) P. J. Harrington, L. S. Hegedus, *J. Org. Chem.* **1984**, *49*, 2657; b) P. J. Harrington, L. S. Hegedus, K. F. McDaniel, *J. Am. Chem. Soc.* **1987**, *109*, 4335; c) D. Tsvelikhovsky, S. L. Buchwald, *J. Am. Chem. Soc.* **2010**, *132*, 14048.

[6] For recent reviews on photoredox catalysis, see: a) J. Xuan, W.-J. Xiao, *Angew. Chem.* **2012**, *124*, 6934; *Angew. Chem. Int. Ed.* **2012**, *51*, 6828; b) J. W. Tucker, C. R. J. Stephenson, *J. Org. Chem.* **2012**, *77*, 1617; c) J. M. R. Narayanam, C. R. J. Stephenson, *Chem. Soc. Rev.* **2011**, *40*, 102; d) F. Teplý, *Collect. Czech. Chem. Commun.* **2011**, *76*, 859; e) T. P. Yoon, M. A. Ischay, J. Du, *Nat. Chem.* **2010**, *2*, 527; f) K. Zeitler, *Angew. Chem.* **2009**, *121*, 9969; *Angew. Chem. Int. Ed.* **2009**, *48*, 9785.

[7] a) D. A. Nagib, D. W. C. MacMillan, *Nature* **2011**, *480*, 224; b) P. V. Pham, D. A. Nagib, D. W. C. MacMillan, *Angew. Chem.* **2011**, *123*, 6243; *Angew. Chem. Int. Ed.* **2011**, *50*, 6119; c) H.-W. Shih, M. N. V. Wal, R. L. Grange, D. W. C. MacMillan, *J. Am. Chem. Soc.* **2010**, *132*, 13600; d) D. A. Nagib, M. E. Scott, D. W. C. MacMillan, *J. Am. Chem. Soc.* **2009**, *131*, 10875; e) D. A. Nicewicz, D. W. C. MacMillan, *Science* **2008**, *322*, 77.

[8] a) J. D. Parrish, M. A. Ischay, Z. Lu, S. Guo, N. R. Peters, T. P. Yoon, *Org. Lett.* **2012**, *14*, 1640; b) S. Lin, M. A. Ischay, C. G. Fry, T. P. Yoon, *J. Am. Chem. Soc.* **2011**, *133*, 19350; c) J. Du, L. R. Espelt, I. A. Guzei, T. P. Yoon, *Chem. Sci.* **2011**, *2*, 2115; d) Z. Lu, M. Shen, T. P. Yoon, *J. Am. Chem. Soc.* **2011**, *133*, 1162; e) M. A. Ischay, Z. Lu, T. P. Yoon, *J. Am. Chem. Soc.* **2010**, *132*, 8572.

[9] a) J. W. Tucker, C. R. J. Stephenson, *Org. Lett.* **2011**, *13*, 5468; b) L. Furst, J. M. R. Narayanam, C. R. J. Stephenson, *Angew. Chem.* **2011**, *123*, 9829; *Angew. Chem. Int. Ed.* **2011**, *50*, 9655; c) J. D. Nguyen, J. W. Tucker, M. D. Konieczynska, C. R. J. Stephenson, *J. Am. Chem. Soc.* **2011**, *133*, 4160; d) C. Dai, J. M. R. Narayanam, C. R. J. Stephenson, *Nat. Chem.* **2011**, *3*, 140; e) L. Furst, B. S. Matsuura, J. M. R. Narayanam, J. W. Tucker, C. R. J. Stephenson, *Org. Lett.* **2010**, *12*, 3104; f) J. M. R. Narayanam, J. W. Tucker, C. R. J. Stephenson, *J. Am. Chem. Soc.* **2009**, *131*, 8756.

[10] T. Koike, M. Akita, *Chem. Lett.* **2009**, *38*, 166.

[11] a) D. P. Hari, P. Schroll, B. König, *J. Am. Chem. Soc.* **2012**, *134*, 2958; b) Y.-Q. Zou, J.-R. Chen, X.-P. Liu, L.-Q. Lu, R. L. Davis, K. A. Jørgensen, W.-J. Xiao, *Angew. Chem.* **2012**, *124*, 808; *Angew. Chem. Int. Ed.* **2012**, *51*, 784; c) D. Kalyani, K. B. McMurtrey, S. R. Neufeldt, M. S. Sanford, *J. Am. Chem. Soc.* **2011**, *133*, 18566; d) M.-H. Larraufie, R. Pellet, L. Fensterbank, J.-P. Goddard, E. Lacôte, M. Malacria, C. Ollivier, *Angew. Chem.* **2011**, *123*, 4555; *Angew. Chem. Int. Ed.* **2011**, *50*, 4463; e) M. Neumann, S. Fuldner, B. König, K. Zeitler, *Angew. Chem.* **2011**, *123*, 981; *Angew. Chem. Int. Ed.* **2011**, *50*, 951; f) R. S. Andrews, J. J. Becker, M. R. Gagné, *Org. Lett.* **2011**, *13*, 2406; g) Y. Su, L. Zhang, N. Jiao, *Org. Lett.* **2011**, *13*, 2168; h) M. Zlotorzynska, G. M. Sammis, *Org. Lett.* **2011**, *13*, 6264; i) T. Maji, A. Karmakar, O. Reiser, *J. Org. Chem.* **2011**, *76*, 736; j) Y. Chen, A. S. Kamlet, J. B. Steinman, D. R. Liu, *Nat. Chem.* **2011**, *3*, 146; k) Q. Liu, Y.-N. Li, H.-H. Zhang, B. Chen, C.-H. Tung, L.-Z. Wu, *J. Org. Chem.* **2011**, *76*, 1444; l) L. Zhou, H. Yang, P. J. Wang, *Org. Chem.* **2011**, 76, 5873; m) R. S. Andrews, J. J. Becker, M. R. Gagné, *Angew. Chem.* **2010**, *122*, 7432; *Angew. Chem. Int. Ed.* **2010**, *49*, 7274; n) J. B. Borak, D. E. Falvey, *J. Org. Chem.* **2009**, *74*, 3894.

[12] a) M. Zhu, N. Zheng, *Synthesis* **2011**, 2223; b) S. Maity, M. Zhu, R. S. Shinabery, N. Zheng, *Angew. Chem.* **2012**, *124*, 226; *Angew. Chem. Int. Ed.* **2012**, *51*, 222.

[13] For photophysical and redox properties of $\mathrm{Ru^{II}}$, see: a) A. Inagaki, M. Akita, *Coord. Chem. Rev.* **2010**, *254*, 1220; b) A. Juris, V. Balzani, F. Barigelletti, S. Campagna, P. Belser, A. V. Zelewsky, *Coord. Chem. Rev.* **1988**, *84*, 85; c) K. Kalyanasundaram, M. Grätzel, *Coord. Chem. Rev.* **1998**, *177*, 347; d) K. Kalyanasundaram, *Coord. Chem. Rev.* **1982**, *46*, 159.

[14] For selected early studies on photoreduction of $\mathrm{Ru^{II}}$–polypyridyl complexes by amines, see: a) P. J. DeLaive, J. T. Lee, H. W. Sprintschnik, H. Abruña, T. J. Meyer, D. G. Whitten, *J. Am. Chem. Soc.* **1977**, *99*, 7094; b) P. J. DeLaive, T. K. Foreman, C. Giannotti, D. G. Whitten, *J. Am. Chem. Soc.* **1980**, *102*, 5627.

[15] a) D. B. Freeman, L. Furst, A. G. Condie, C. R. J. Stephenson, *Org. Lett.* **2012**, *14*, 94; b) Y.-Q. Zou, L.-Q. Lu, L. Fu, N.-J. Chang, J. Rong, J.-R. Chen, W.-J. Xiao, *Angew. Chem.* **2011**, *123*, 7309; *Angew. Chem. Int. Ed.* **2011**, *50*, 7171; c) C. Wang, Z. Xie, K. E. deKrafft, W. Lin, *J. Am. Chem. Soc.* **2011**, *133*, 13445;

d) D. P. Hari, B. König, *Org. Lett.* **2011**, *13*, 3852; e) M. Rueping, S. Zhu, R. M. Koenigs, *Chem. Commun.* **2011**, *47*, 12709; f) M. Rueping, D. Leonori, T. Poisson, *Chem. Commun.* **2011**, *47*, 9615; g) J. Xuan, Y. Cheng, J. An, L.-Q. Lu, X.-X. Zhang, W.-J. Xiao, *Chem. Commun.* **2011**, *47*, 8337; h) A. G. Condie, J. C. González-Gómez, C. R. J. Stephenson, *J. Am. Chem. Soc.* **2010**, *132*, 1464.

[16] a) Y. Miyake, K. Nakajima, Y. Nishibayashi, *J. Am. Chem. Soc.* **2012**, *134*, 3338; b) P. Kohls, D. Jadhav, G. Pandey, O. Reiser, *Org. Lett.* **2012**, *14*, 672; c) A. McNally, C. K. Prier, D. W. C. MacMillan, *Science* **2011**, *334*, 1114.

[17] a) R. J. Crutchley, A. B. P. Lever, *J. Am. Chem. Soc.* **1980**, *102*, 7128; b) D. P. Rillema, G. Allen, T. J. Meyer, D. Conrad, *Inorg. Chem.* **1983**, *22*, 1617.

[18] Fluorocarbon solvents and silica gel enhance the solubility of molecular oxygen, see: H. B. Lee, M. J. Sung, S. C. Blackstock, J. K. Cha, *J. Am. Chem. Soc.* **2001**, *123*, 11322.

[19] The effectiveness of the catalysts correlates with the redox potentials of Ru^{2+*}/Ru^{1+} (versus SCE): $[Ru(bpz)_3]$, 1.3 V; $[Ru(bpy)_3]$, 0.78 V. The values are taken from Ref. [17a].

[20] Electron-rich *p*-alkoxyphenyl groups lower the oxidation potential of anilines: see cyclic voltammogram of **5b** and **5b′** in the Supporting Information.

[21] The formation of 3-cyclopropyl 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: J. Masnovi, E. G. Samsel, R. M. Bullock, *J. Chem. Soc. Chem. Commun.* **1989**, 1044.

[22] For the use of TPP as a photosensitizer to generate singlet oxygen, see: G. Jiang, J. Chen, J.-S. Huang, C.-M. Che, *Org. Lett.* **2009**, *11*, 4568.

[23] For a review on proton-coupled electron transfer, see: M. H. V. Huynh, T. J. Meyer, *Chem. Rev.* **2007**, *107*, 5004.

[24] a) B. J. Stokes, S. Liu, T. G. Driver, *J. Am. Chem. Soc.* **2011**, *133*, 4702; b) K. Sun, S. Liu, P. M. Bec, T. G. Driver, *Angew. Chem.* **2011**, *123*, 1740; *Angew. Chem. Int. Ed.* **2011**, *50*, 1702; c) M. Shen, B. E. Leslie, T. G. Driver, *Angew. Chem.* **2008**, *120*, 5134; *Angew. Chem. Int. Ed.* **2008**, *47*, 5056.