# 1,2-Alkylarylation of Activated Alkenes with Two C–H Bonds by Using Visible-Light Catalysis

Jia-Ling Zhang, Yu Liu, Ren-Jie Song, Guo-Fang Jiang,* Jin-Heng Li*

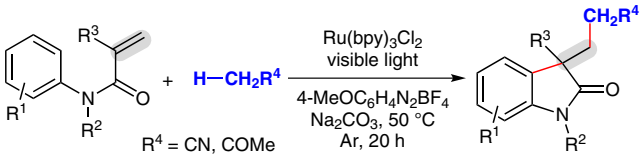
State Key Laboratory of Chemo/Biosensing and Chemometrics, College of Chemistry and Chemical Engineering, Hunan University, Changsha 410082, P. R. of China
Fax +(86)73188713642; E-mail: jhli@hnu.edu.cn; E-mail: gfjiang@hnu.edu.cn

*Received: 15.01.2014; Accepted after revision: 17.02.2014*

**Abstract:** A new visible-light promoted strategy for the difunctionalization of activated alkenes with two C–H bonds has been developed. In the presence of $[Ru(bpy)_3Cl_2]$, 4-$MeOC_6H_4N_2BF_4$, $Na_2CO_3$ and 36 W compact fluorescent light, a variety of *N*-arylacrylamides underwent the 1,2-alkylarylation reaction with acetonitrile or acetone to give the corresponding functionalized oxindoles in moderate to good yields.

**Key words:** alkylarylation, alkenes, acetonitrile, acetone, visible-light catalysis, oxindoles

Difunctionalization of alkenes has proven to be an efficient and versatile synthetic approach to the construction of a range of synthetic intermediates and important bioactive compounds.[1] As a result, the development of new methods for alkene difunctionalization has been an active area of research. Recent alkene difunctionalizations involving C–H functionalization are particularly attractive because of their efficiency and because prefunctionalization processes can be avoided.[2–6] However, available methods for alkene difunctionalizations involving C–H functionalization are still limited. Remarkably, methods for the difunctionalization of alkenes with two C–H bonds are quite rare and most focus on a C–H oxidative functionalization strategy.[2–5] For example, the group of Liu reported the first oxidative arylalkylation of an activated alkene with an aryl C($sp^2$)–H bond and an α-C($sp^3$)–H bond of alkyl nitriles by using the $Pd(OAc)_2$/$PhI(OAc)_2$ catalytic system.[2] Subsequently, the group of Guo and Duan,[3] the group of Liu,[4] and our group[5] independently employed other C($sp^3$)–H bonds of ethers, aryl methanes and cycloalkanes to react with alkenes followed by cyclization with aryl C($sp^2$)–H bonds using peroxides. Nevertheless, it would still be highly desirable to develop new alkene difunctionalization methods by using the double C–H functionalization strategy. Herein, we describe a new visible-light catalysis strategy for the synthesis of functionalized oxindoles through 1,2-alkylarylation of activated alkenes with acetonitrile and aryl C($sp^2$)–H bonds (Scheme 1).[7,8] In addition, this strategy can be expanded to acetone for 1,2-alkylarylation of activated alkenes. Notably, the oxindole unit is a ubiquitous constituent in many natural products and bioactive molecules.[9]




**Scheme 1** The 1,2-alkylarylation of alkenes

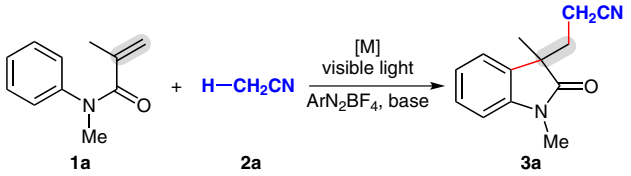
Our investigation commenced with the reaction between *N*-methyl-*N*-phenylmethacrylamide (**1a**) with acetonitrile (**2a**; Table 1).[10] Initially, the reaction of substrate **1a** with **2a**, 4-$MeOC_6H_4N_2BF_4$ (2 equiv.) and $Na_2CO_3$ (2 equiv.) gave the desired product **3a** in 36% yield (entry 1). The yield decreased to 19% with the addition of 4-$MeOC_6H_4N_2BF_4$ (1 equiv.) and no reaction was observed in the absence of 4-$MeOC_6H_4N_2BF_4$ (entries 2 and 3). It has been reported that 4-$MeOC_6H_4N_2BF_4$ could be readily converted into an aryl radical by using visible-light catalysis.[7,8] As expected, the yield of product **3a** dramatically increased to 77% in the presence of $[Ru(bpy)_3Cl_2]$ and visible light (entry 4). Subsequently, two other aryldiazonium salts, 4-$NO_2C_6H_4N_2BF_4$ and 4-$BrC_6H_4N_2BF_4$, were examined, and the results showed that they were less efficient than 4-$MeOC_6H_4N_2BF_4$ (entries 5 and 6). The reaction did not take place without aryldiazonium salts or bases (entries 7 and 8). A series of other bases, including NaOAc, $NaHCO_3$ and $Et_3N$, were tested (entries 9–11) but all were less active than $Na_2CO_3$, and the use of $Et_3N$ resulted in no detectable product **3a**. A study on the effect of reaction temperature revealed that conducting the reaction at 50 °C gave the best results (entries 4, 12 and 13). The use of $[Ir(ppy)_3]$ or Eosin Y instead of $[Ru(bpy)_3Cl_2]$ was also evaluated (entries 14 and 15) and it was found that the reaction was successful with both catalysts, but Eosin Y was less active. It was noted that the reactivity of substrate **1a** decreased in the absence of either visible light or visible-light catalysts (entries 16 and 17). In contrast to the results reported by the group of Fu, Fu and Zhou,[6m] the product from diarylation of acrylamide **1a** with 4-$MeOC_6H_4N_2BF_4$, 3-(4-methoxybenzyl)-1,3-dimethylindolin-2-one, was observed as a side-product (<5% yield) under the present reaction conditions; this is presumably because the present reaction was carried out under basic conditions using highly reactive α-hydrogen-atom-containing solvents.

With the optimal conditions in hand,[10] a variety of *N*-arylacrylamides **1b**–**r** were then investigated to determine the

***SYNLETT*** 2014, 25, 1031–1035
Advanced online publication: 14.03.2014
DOI: 10.1055/s-0033-1340956; Art ID: ST-2014-W0037-L

scope of the 1,2-alkylarylation protocol (Scheme 2). In the presence of $[Ru(bpy)_3Cl_2]$, 4-$MeOC_6H_4N_2BF_4$, $Na_2CO_3$ and 36 W compact fluorescent light, the reaction of N-Bn-substituted substrate **1b** was successful with acetonitrile (**2a**) to give the desired product **3b** in 61% yield. The reactivity of N-Ac-substituted substrate **1c** was less, and only 21% yield of the corresponding product **3c** was isolated. However, *N*-phenylmethacrylamide **1d**, with a free N–H bond, was unreactive and no product **3d** was observed. Gratifyingly, several substituents, including Me, *n*-Bu, MeO, Cl, F, $CF_3$ and SMe, on the aromatic ring of the *N*-aryl moiety were compatible with the optimal conditions, and the reaction gave the expected products **3e**–**n**. For example, substrate **1e**, with a *p*-Me group, underwent the reaction smoothly to afford **3e** in good yield. Notably, substrate **1f**, with a *m*-Me group, gave a mixture of two regioselective isomers **3f** in 70% total yield with 1.5:1 ratio. By using bulky *N*-methyl-*N*-*o*-tolylmethacrylamide, good yield of product **3g** was still achieved. Both Cl or F groups could be tolerated (products **3j**, **3k** and **3n**), thereby facilitating additional modifications at the halogenated position. We found that *N*-(2,3-dihydro-1*H*-inden-5-yl)-*N*-methylmethacrylamide (**1o**) was viable for the reaction, and a mixture of two regioselective isomers **3o** was formed in 64% total yield with 1.6:1 ratio. The optimal conditions could also be applied to substrates with a Ph, $CH_2OH$ or $CH_2OAc$ group at the 2-position of the acrylamide moiety (products **3p**–**r**). However, the use of butyronitrile (**2b**) and 2-phenylacetonitrile (**2c**) instead of acetonitrile (**2a**) was not successful, and substrate **1a** did not react with **2b** under the optimal conditions (products **3s** and **3t**).

**Table 1** Screening Optimal Conditions[a]




| Entry | [M] (mol%) | $ArN_2BF_4$ | Base | *T* (°C) | Yield (%)[b,c] |
|---|---|---|---|---|---|
| 1[d] | – | 4-$MeOC_6H_4N_2BF_4$ | $Na_2CO_3$ | 50 | 36 |
| 2[d,e] | – | 4-$MeOC_6H_4N_2BF_4$ | $Na_2CO_3$ | 50 | 19 |
| 3[d] | – | – | $Na_2CO_3$ | 50 | 0 |
| 4 | $Ru(bpy)_3Cl_2$ (5) | 4-$MeOC_6H_4N_2BF_4$ | $Na_2CO_3$ | 50 | 77 |
| 5 | $Ru(bpy)_3Cl_2$ (5) | 4-$NO_2C_6H_4N_2BF_4$ | $Na_2CO_3$ | 50 | 15 |
| 6 | $Ru(bpy)_3Cl_2$ (5) | 4-$BrC_6H_4N_2BF_4$ | $Na_2CO_3$ | 50 | 38 |
| 7 | $Ru(bpy)_3Cl_2$ (5) | – | $Na_2CO_3$ | 50 | trace |
| 8 | $Ru(bpy)_3Cl_2$ (5) | 4-$MeOC_6H_4N_2BF_4$ | – | 50 | 0 |
| 9 | $Ru(bpy)_3Cl_2$ (5) | 4-$MeOC_6H_4N_2BF_4$ | NaOAc | 50 | 70 |
| 10 | $Ru(bpy)_3Cl_2$ (5) | 4-$MeOC_6H_4N_2BF_4$ | $NaHCO_3$ | 50 | 50 |
| 11 | $Ru(bpy)_3Cl_2$ (5) | 4-$MeOC_6H_4N_2BF_4$ | $Et_3N$ | 50 | 0 |
| 12 | $Ru(bpy)_3Cl_2$ (5) | 4-$MeOC_6H_4N_2BF_4$ | $Na_2CO_3$ | 25 | trace |
| 13 | $Ru(bpy)_3Cl_2$ (2) | 4-$MeOC_6H_4N_2BF_4$ | $Na_2CO_3$ | 80 | 23 |
| 14 | $Ir(ppy)_3$ (5) | 4-$MeOC_6H_4N_2BF_4$ | $Na_2CO_3$ | 50 | 75 |
| 15 | Eosin Y (5) | 4-$MeOC_6H_4N_2BF_4$ | $Na_2CO_3$ | 50 | 49 |
| 16[d] | $Ru(bpy)_3Cl_2$ (5) | 4-$MeOC_6H_4N_2BF_4$ | $Na_2CO_3$ | 50 | 34 |
| 17 | – | 4-$MeOC_6H_4N_2BF_4$ | $Na_2CO_3$ | 50 | 38 |

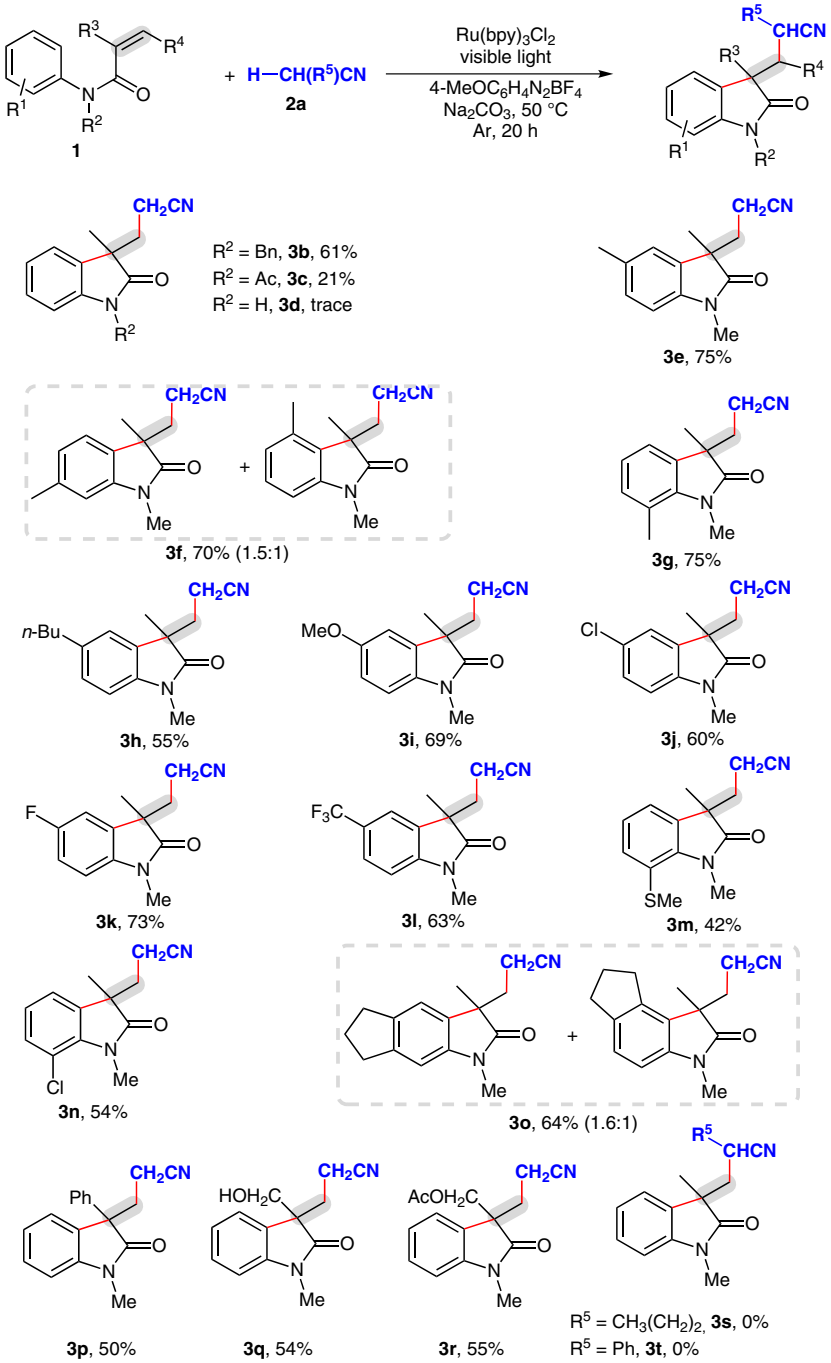
[a] Reaction conditions: **1a** (0.3 mmol), **2a** (1 mL), [M], 4-$MeOC_6H_4N_2BF_4$ (2 equiv), base (2 equiv), 36 W compact fluorescent light, argon atmosphere, 20 h.
[b] Some side products, including 3-(4-methoxybenzyl)-1,3-dimethylindolin-2-one (diarylation of acrylamide **1a** with aryl diazonium salt) and 4,4′-dimethoxybiphenyl, were observed by GC-MS analysis.
[c] Isolated yield.
[d] Without additional light.
[e] 4-$MeOC_6H_4N_2BF_4$ (1 equiv) was used.

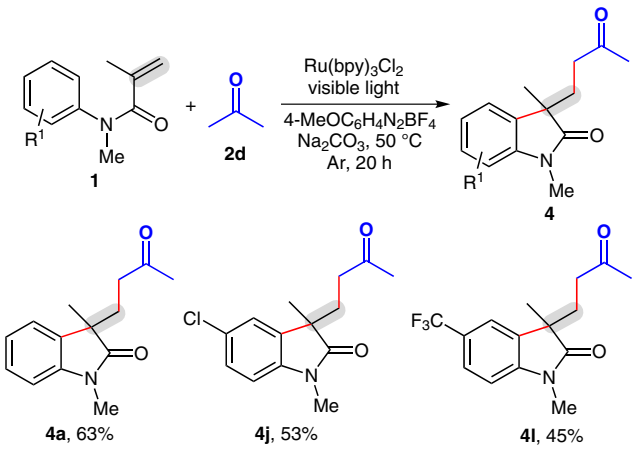
Interestingly, this 1,2-alkylarylation protocol could be applied to acetone (**2d**; Scheme 3). Thus, treatment of *N*-methyl-*N*-phenylmethacrylamide (**1a**) with **2d**, $[Ru(bpy)_3Cl_2]$, 4-$MeOC_6H_4N_2BF_4$, $Na_2CO_3$ and 36 W compact fluorescent light afforded the desired product **4a** in 63% yield. The reactions with **2d** were also successful with substrates **1j** and **1l**, giving the corresponding products **4j** and **4l** in moderate yields. Unfortunately, attempts at the 1,2-alkylarylation of **1a** with other ketones, such as acetylbenzene or cyclohexanone, failed.

To help understand the mechanism of this 1,2-alkylarylation protocol, the quantum yield was determined (Figure S1 in the Supporting Information). The quantum yield (Φx) was found to be approximately 0.099, suggesting that the 1,2-alkylarylation protocol proceeded through a photoinduced mechanism.[11]

Consequently, the mechanism outlined in Scheme 4 is proposed.[2–4] The 4-methoxyphenyl radical is readily formed from 4-$MeOC_6H_4N_2BF_4$ under the action of the base/$[Ru(bpy)_3Cl_2]$/visible-light system under heating.[4,5] Subsequent selective hydrogen atom abstraction by the 4-




**Scheme 2** Scope of the reaction with *N*-arylacrylamides **1**. *Reagents and conditions*: **1** (0.3 mmol), **2a** (1 mL), $[Ru(bpy)_3Cl_2]$ (5 mol%), 4-$MeOC_6H_4N_2BF_4$ (2 equiv), $Na_2CO_3$ (2 equiv), 36 W compact fluorescent light, argon atmosphere, 50 °C, 20 h.




**Scheme 3** 1,2-Alkylarylation of alkenes (**1**) with acetone (**2d**)

methoxyphenyl radical from either $CH_3CN$ or cation radical **A**, which is generated in situ from $CH_3CN$ (**2a**) through visible-light catalysis, yields the $\cdot CH_2CN$ radical. Addition of the $\cdot CH_2CN$ radical to the activated alkene gives radical intermediate **B**, intramolecular cyclization of which then produces radical intermediate **C**. Finally, hydrogen atom abstraction from the $CH_3CN$ cation radical **A** by radical intermediate **C** takes place to generate the $^{\cdot}CH_2CN$ radical and product **3a**. The $^{\cdot}CH_2CN$ radical can be formed directly from the reaction between $CH_3CN$ (**2a**) and 4-methoxyphenyl radical in the presence of a base under heating conditions, albeit with lower efficiency.

In summary, we have disclosed a new visible-light catalysis strategy for the difunctionalization of activated alkenes with alkyl C($sp^3$)–H bonds (acetonitrile or acetone) and aryl C($sp^2$)–H bonds. This strategy provides a new route to functionalized oxindoles from N-arylacrylamides and either acetonitrile or acetone. The measured quantum yield for the process (Φx = 0.099) indicates that the 1,2-alkylarylation protocol proceeds through a photoinduced mechanism.

## Acknowledgment

We thank the Hunan Provincial Natural Science Foundation of China (No. 13JJ2018), the Specialized Research Fund for the Doctoral Program of Higher Education (No. 20120161110041), and the Natural Science Foundation of China (No. 21172060) for financial support.

## Supporting Information for this article is available online at http://www.thieme-connect.com/ejournals/toc/synlett.

## References and Notes

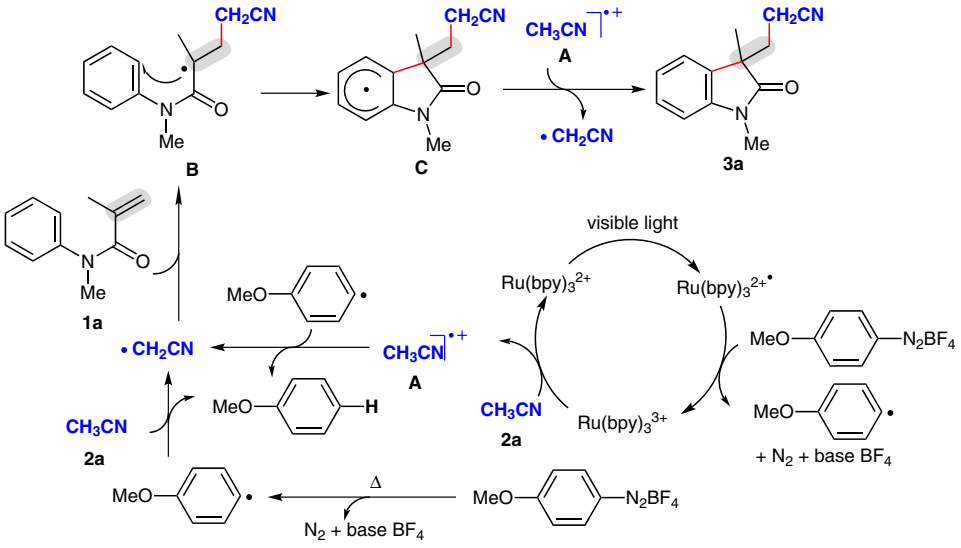
(1) For recent reviews, see: (a) Sibbald, P. A. *PhD Dissertation*; University of Washington: USA, **2009**. (b) Jacques, B.; Muñiz, K. In *Catalyzed Carbon-Heteroatom Bond Formation*; Yudin, A. K., Ed.; Wiley-VCH: Weinheim, **2011**, 119–135. (c) Bergmeier, S. C. *Tetrahedron* **2000**, *56*, 2561. (d) Beccalli, E. M.; Broggini, G.; Martinelli, M.; Sottocornola, S. *Chem. Rev.* **2007**, *107*, 5318. (e) Kotov, V.; Scarborough, C. C.; Stahl, S. S. *Inorg. Chem.* **2007**, *46*, 1910. (f) Li, G.; Kotti, S. R. S. S.; Timmons, C. *Eur. J. Org. Chem.* **2007**, 2745. (g) Muñiz, K. *Angew. Chem. Int. Ed.* **2009**, *48*, 9412. (h) McDonald, R. I.; Liu, G.; Stahl, S. S. *Chem. Rev.* **2011**, *111*, 2981. (i) Xie, Y.-X.; Song, R.-J.; Xiang, J.-N.; Li, J.-H. *Chin. J. Org. Chem.* **2012**, *32*, 1555. (j) Zhang, C.; Tang, C.; Jiao, N. *Chem. Soc. Rev.* **2012**, *41*, 3464.

(2) (a) Wu, T.; Mu, X.; Liu, G.-S. *Angew. Chem. Int. Ed.* **2011**, *50*, 12578. (b) Zhang, H.; Chen, P.; Liu, G.-S. *Synlett* **2012**, *23*, 2749.

(3) (a) Meng, Y.; Guo, L.-N.; Wang, H.; Duan, X.-H. *Chem. Commun.* **2013**, *49*, 7540. (b) Zhou, Z.-Z.; Hua, H.-L.; Luo, J.-Y.; Chen, Z.-S.; Zhou, P.-X.; Liu, X.-Y.; Liang, Y.-M. *Tetrahedron* **2013**, *69*, 10030. (c) Zhou, S.-L.; Guo, L.-N.; Wang, H.; Duan, X.-H. *Chem. Eur. J.* **2013**, *19*, 12970. (d) Wang, H.; Guo, L.-N.; Duan, X.-H. *Org. Lett.* **2013**, *15*, 5254. (e) Wang, H.; Guo, L.-N.; Duan, X.-H. *Chem. Commun.* **2013**, *49*, 10370.

(4) Li, Z.; Zhang, Y.; Zhang, L.; Liu, Z.-Q. *Org. Lett.* **2014**, *16*, 382.

(5) (a) Wei, W.-T.; Zhou, M.-B.; Fan, J.-H.; Liu, W.; Song, R.-J.; Liu, Y.; Hu, M.; Xie, P.; Li, J.-H. *Angew. Chem. Int. Ed.*




**Scheme 4** Possible mechanism

**2013**, *52*, 3638. (b) Zhou, M.-B.; Wang, C.-Y.; Song, R.-J.; Liu, Y.; Wei, W.-Y.; Li, J.-H. *Chem. Commun.* **2013**, *49*, 10817. (c) Zhou, M.-B.; Song, R.-J.; Ouyang, X.-H.; Liu, Y.; Wei, W.-T.; Deng, G.-B.; Li, J.-H. *Chem. Sci.* **2013**, *4*, 2690.

(6) For papers on the other oxidative difunctionalizations of alkenes involving C–H fuctionalization, see: (a) Jaegli, S.; Dufour, J.; Wei, H.-L.; Piou, T.; Duan, X.-H.; Vors, J.-P.; Neuville, L.; Zhu, J. *Org. Lett.* **2010**, *12*, 4498. (b) Piou, T.; Neuville, L.; Zhu, J. *Angew. Chem. Int. Ed.* **2012**, *51*, 11561. (c) Mu, X.; Wu, T.; Wang, H.-Y.; Guo, Y.-L.; Liu, G.-S. *J. Am. Chem. Soc.* **2012**, *134*, 878. (d) Wu, T.; Zhang, H.; Liu, G.-S. *Tetrahedron* **2012**, *68*, 5229. (e) Li, Y.-M.; Sun, M.; Wang, H.-L.; Tian, Q.-P.; Yang, S.-D. *Angew. Chem. Int. Ed.* **2013**, *52*, 3972. (f) Wang, H.; Guo, L.-N.; Duan, X.-H. *Adv. Synth. Catal.* **2013**, *355*, 2222. (g) Wei, X.-H.; Li, Y.-M.; Zhou, A.-X.; Yang, T.-T.; Yang, S.-D. *Org. Lett.* **2013**, *15*, 4158. (h) Li, X.; Xu, X.; Hu, P.; Xiao, X.; Zhou, C. *J. Org. Chem.* **2013**, *78*, 7343. (i) Matcha, K.; Narayan, R.; Antonchick, A. P. *Angew. Chem. Int. Ed.* **2013**, *52*, 7985. (j) Xie, J.; Xu, P.; Li, H.-M.; Xue, Q.-C.; Jin, H.-M.; Cheng, Y.-X.; Zhu, C.-J. *Chem. Commun.* **2013**, *49*, 5672. (k) Li, Y.-M.; Wei, X.-H.; Li, X.-A.; Yang, S.-D. *Chem. Commun.* **2013**, *49*, 11701. (l) Fan, J.-H.; Zhou, M.-B.; Liu, Y.; Wei, W.-T.; Ouyang, X.-H.; Song, R.-J.; Li, J.-H. *Synlett* **2014**, *25*, 657. (m) Fu, W.; Xu, F.; Fu, Y.; Zhu, M.; Yu, J.; Xu, C.; Zou, D. *J. Org. Chem.* **2013**, *78*, 12202. (n) Xu, P.; Xie, J.; Xue, Q.; Pan, C.; Cheng, Y.; Zhu, C. *Chem. Eur. J.* **2013**, *19*, 14039. (o) Shen, T.; Yuan, Y.; Jiao, N. *Chem. Commun.* **2014**, *50*, 554. (p) Xu, X.; Tang, Y.; Li, X.; Hong, G.; Fang, M.; Du, X. *J. Org. Chem.* **2014**, *79*, 446.

(7) For special reviews on visible-light photoredox catalysis, see: (a) Melchiorre, P. *Angew. Chem. Int. Ed.* **2009**, *48*, 1360. (b) Zeitler, K. *Angew. Chem. Int. Ed.* **2009**, *48*, 9785. (c) Yoon, T. P.; Ischay, M. A.; Du, J. *Nat. Chem.* **2010**, *2*, 527. (d) Narayanam, J. M. R.; Stephenson, C. R. J. *Chem. Soc. Rev.* **2011**, *40*, 102. (e) Teplý, F. *Collect. Czech. Chem. Commun.* **2011**, *76*, 859. (f) Ravelli, D.; Fagnoni, M. *ChemCatChem* **2012**, *4*, 169. (g) Xuan, J.; Xiao, W.-J. *Angew. Chem. Int. Ed.* **2012**, *51*, 6828. (h) Hari, D. P.; König, B. *Angew. Chem. Int. Ed.* **2013**, *52*, 4734.

(8) For pioneering papers on the use of aryldiazonium salts in organic synthesis, see: (a) Sandmeyer, T. *Ber. Dtsch. Chem. Ges.* **1884**, *17*, 1633. (b) Sandmeyer, T. *Ber. Dtsch. Chem. Ges.* **1884**, *17*, 2650. (c) Hodgson, H. H. *Chem. Rev.* **1947**, *40*, 251. The Pschorr reaction: (d) Pschorr, R. *Ber.* **1896**, *29*, 496. (e) Leake, P. H. *Chem. Rev.* **1956**, *56*, 27. (f) Cano-Yelo, H.; Deronzier, A. *J. Chem. Soc., Perkin Trans. 2* **1984**, 1093. (g) Cano-Yelo, H.; Deronzier, A. *J. Chem. Soc., Faraday Trans. 1* **1984**, 3011. (h) Cano-Yelo, H.; Deronzier, A. *Tetrahedron Lett.* **1984**, *25*, 5517.

(9) For selected reviews and papers, see: (a) Jensen, B. S. *CNS Drug Rev.* **2002**, *8*, 353. (b) Millemaggi, A.; Taylor, R. J. K. *Eur. J. Org. Chem.* **2010**, 4527. (c) Zhou, F.; Liu, Y.-L.; Zhou, J. *Adv. Synth. Catal.* **2010**, *352*, 1381. (d) Deak, G.; Doda, M.; Gyorgy, L.; Hazai, L.; Sterk, L. *J. Med. Chem.* **1977**, *20*, 1384. (e) Numata, A.; Yang, P.; Takahashi, C.; Fujiki, R.; Nabae, M.; Fujita, E. *Chem. Pharm. Bull.* **1989**, *37*, 648. (f) Hibino, S.; Choshi, T. *Nat. Prod. Rep.* **2001**, *18*, 66.

(10) **1,2-Alkylarylation of Activated Alkenes with Acetonitrile; Typical Procedure:** To a Schlenk tube were added *N*-methyl-*N*-phenylmethacrylamide (**1a**; 0.3 mmol), 4-$MeOC_6H_4N_2BF_4$ (2 equiv), $[Ru(bpy)_3Cl_2]$ (5 mol%), $Na_2CO_3$ (2 equiv), and acetonitrile (**2a**; 1 mL). The tube was charged with argon and the mixture was stirred at 50 °C (oil bath temperature) under irradiation with a 36 W compact fluorescent light for the indicated time until complete consumption of starting material was observed (reaction monitored by TLC and/or GC-MS analysis).Upon completion, the reaction mixture was cooled to room temperature, diluted in $Et_2O$ (3 mL), and washed with brine (3 mL). The aqueous phase was re-extracted with $Et_2O$ (3 mL) and the combined organic extracts were dried over $Na_2SO_4$, concentrated in vacuum, and the resulting residue was purified by silica gel column chromatography (hexane–EtOAc, 5:1) to afford the desired product **3a**.
**3-(1,3-Dimethyl-2-oxoindolin-3-yl)propanenitrile (3a):**[2] Brown oil. $^1$H NMR (400 MHz, $CDCl_3$): δ = 7.34–7.30 (m, 1 H), 7.18 (d, *J* = 7.2 Hz 1 H), 7.11 (t, *J* = 7.6 Hz, 1 H), 6.88 (d, *J* = 7.6 Hz, 1 H), 3.22 (s, 3 H), 2.34–2.29 (m, 1 H), 2.11–1.98 (m, 3 H), 1.39 (s, 3 H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 178.8, 143.1, 131.6, 128.6, 123.0, 122.6, 118.8, 108.5, 47.3, 33.4, 26.3, 23.4, 12.8. MS (EI, 70 eV): *m*/*z* (%) = 214 (37) $[M]^+$, 161 (35), 160 (100).

(11) (a) Gorner, H.; Khun, H. J. *J. Chem. Soc., Perkin Trans. 2* **1999**, 2671. (b) Pelliccioli, A. P.; Wirz, J. *Photochem. Photobiol. Sci.* **2002**, *1*, 441.