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## Photoredox / rhodium catalysis in C-H activation for the synthesis of nitrogen containing heterocycles

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**The cyclization of acetanilides with alkyne derivatives has been accomplished via a direct C-H functionalization/cyclization pathway in the presence of a photoredox catalyst. The combination of a readily available Rh(III) and photoredox catalyst under irradiation with 11W CFL afforded not only indoles but also pyrrole derivatives in good yields. Mechanistic studies provide evidence for the independent role of each catalyst. In addition, a similar efficiency of the cyclization reaction was achieved with a heterogeneous photoredox catalyst.**

### Introduction

C-H activation methodologies have attracted the attention of many research groups within the chemical community and numerous synthetic procedures for the formation of carbon-carbon and carbon-heteroatom bonds based on C-H bond activation strategies have been developed.<sup>1</sup> Substrates bearing directing groups and pre-activated reaction partners such as diaryl-iodonium salts, organometallic compounds and aryl halides have been employed to obtain cross-coupling products. Oxidative methods with unreactive substrates under the specific combination of metal catalyst and oxidant allowed the enhancement of catalytic efficiency, and the development of synthetic pathways in total synthesis.<sup>2</sup> In addition, this strategy has enabled the late stage functionalization (LSF) of

diverse structures in material and pharmaceutical fields.

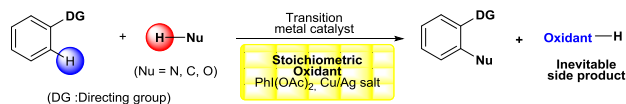
Although remarkable achievements in the area of transition-metal-catalyzed selective C–H bond functionalization have been made, the (over)stoichiometric amounts of oxidants and side products derived from them represent relevant issues which need to be overcome (Scheme 1 i). Hence, many groups focused their research on addressing these issues for further development of organometallic chemistry and tried to find more atom-economic protocols. We became interested in carbon-carbon bond forming transformations under utilization of combined catalytic systems<sup>3,4</sup> which are primarily based on the use of photoredox catalysis<sup>5</sup> to either activate the substrate or to accomplish the regeneration of a catalyst. In this context we have recently developed Heck-type reactions in the presence of photocatalysts as alternative oxidants (Scheme 1 ii).<sup>4</sup> Compared with the previous literature reports, these reactions displayed good reaction productivity and functional group tolerance. Herein, we describe an efficient protocol for the synthesis of *N*-heterocycles such as indoles and pyrroles via metal-catalyzed C-H activation in the presence of a photoredox catalyst and visible light (Scheme 1 iii).

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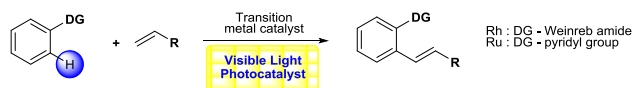
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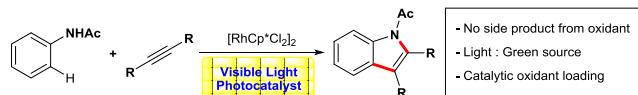
## i) Traditional oxidative cross-coupling reaction



## ii) Previous work : Heck-type reaction with transition metal and photoredox catalyst



## iii) C-C/C-N bond formation with photoredox assistance (This Work)



Scheme 1. Recent developments of combined systems.

## Results and discussion

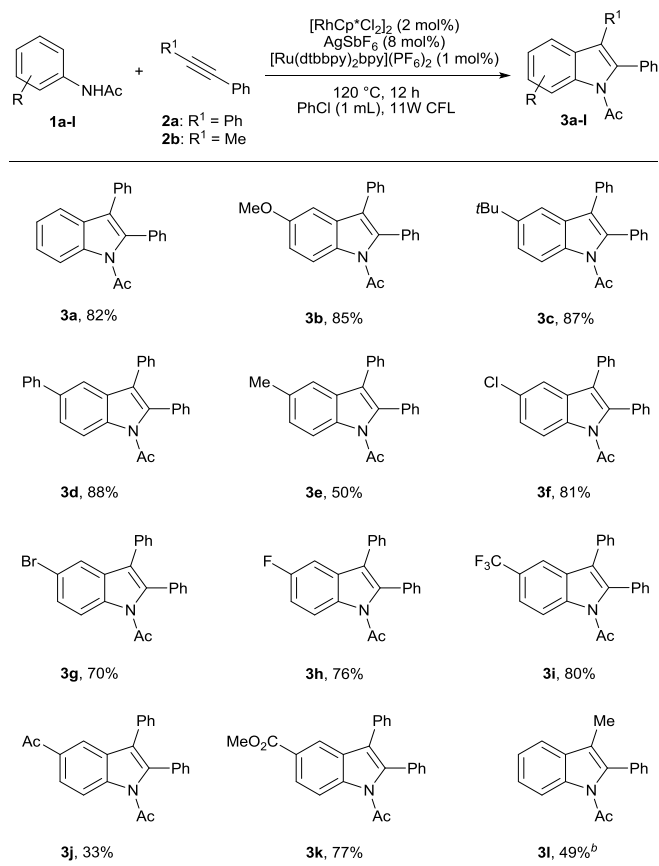
To test our hypothesis regarding a combined catalytic system for the synthesis of indoles,<sup>6,7</sup> acetanilide (**1a**) was reacted with diphenylacetylene (**2a**) in the presence of a Rh(III) catalyst<sup>8</sup> and a Ru photocatalyst under various conditions (Table 1). The desired product **3a** was obtained in 15% yield when  $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$  was applied as oxidant instead of commonly applied  $\text{Cu}(\text{OAc})_2$  (entry 1). Although the yield of the cyclized product was low, this result showed the potential of the photocatalyst to function as oxidant. Different solvents such as  $\text{CH}_3\text{CN}$ , 1,2-DCE, toluene and mesitylene did not provide the desired product and only chlorobenzene<sup>9</sup> exhibited an enhancement of productivity under the same reaction conditions (entries 2–6). Next, the influence of the photocatalyst by varying the ligands and central metal was studied. The electronic variation by changing the external ligands had a significant influence on the reaction outcome. To our delight, in the presence of electron-donating ligands such as dtbbpy, acetanilide efficiently reacted with the alkyne to furnish the desired product **3a** in 40 and 45% yield, respectively (entries 7 and 8). Compared to the ruthenium photocatalysts, the iridium photocatalysts were less effective (entries 9 and 10). Eosin Y, well known as an organic dye for photocatalysis,<sup>10</sup> afforded the desired product with poor efficiency (entry 11). The efficiency of the reaction was totally diminished in the absence of the photocatalyst and this result emphasizes the crucial role of the photocatalyst in the reaction (entry 12). Additionally, the product formation was completely suppressed in the absence of Rh(III) catalyst, implying the involvement of a C-H activation pathway in the reaction mechanism (entry 13). Finally, we have obtained the desired product **3a** in high yield (82%) after prolonged reaction time (entry 14).

Table 1. Optimization of the reaction conditions<sup>a</sup>

Entry	Photocatalyst	Solvent	Yield (%) <sup>b</sup>
1	$[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$	<i>t</i> -AmylOH	15
2	$[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$	$\text{CH}_3\text{CN}$	<1
3	$[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$	1,2-DCE	<5
4	$[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$	Toluene	<1
5	$[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$	Mesitylene	<1
6	$[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$	PhCl	24
7	$[\text{Ru}(\text{dtbbpy})_3](\text{PF}_6)_2$	PhCl	40
8	$[\text{Ru}(\text{dtbbpy})_2(\text{bpy})](\text{PF}_6)_2$	PhCl	45
9	$[\text{Ir}(\text{ppy})_2(\text{bpy})]\text{PF}_6$	PhCl	35
10	$[\text{Ir}(\text{ppy})_2(\text{dtbbpy})]\text{PF}_6$	PhCl	38
11	Eosin Y	PhCl	15
12	-	PhCl	<1
13 <sup>c</sup>	$[\text{Ru}(\text{dtbbpy})_2(\text{bpy})](\text{PF}_6)_2$	PhCl	<1
14 <sup>d</sup>	$[\text{Ru}(\text{dtbbpy})_2(\text{bpy})](\text{PF}_6)_2$	PhCl	82

<sup>a</sup> Reaction conditions: **1a** (0.2 mmol), **2a** (2 equiv),  $[\text{RhCp}^*\text{Cl}_2]_2$  (2 mol %),  $\text{AgSbF}_6$  (8 mol %), photocatalyst (1 mol %) and solvent (1 mL) at 120 °C under irradiation with a 11W CFL bulb. <sup>b</sup> The yield was determined by <sup>1</sup>H NMR spectroscopy. <sup>c</sup> Without Rh catalyst. <sup>d</sup> Reaction conducted for 6 h. 1,2-DCE = 1,2-dichloroethane, bpy = 2,2'-bipyridine, dtbbpy = 4,4'-di-*tert*-butyl-2,2'-bipyridine.

Encouraged by our promising results, we started to investigate the scope and generality of the cyclization by testing various acetanilides and alkynes in the reaction (Table 2). Acetanilides **1b-d** bearing electron-donating substituents in the *para*-position, such as methoxy, *tert*-butyl and phenyl, smoothly participated in the cyclization reaction providing products **3b-d** with excellent efficiencies.

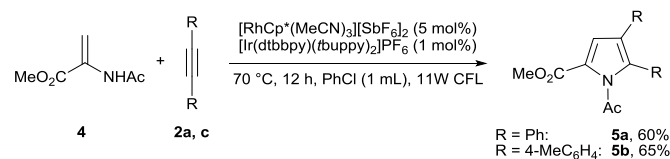
**Table 2.** Substrate scope of acetanilide derivatives<sup>a</sup>

<sup>a</sup> Reaction conditions: acetanilide (0.2 mmol), alkyne (2 equiv),  $[\text{RhCp}^*\text{Cl}_2]_2$  (2 mol %),  $\text{AgSbF}_6$  (8 mol %),  $[\text{Ru}(\text{dtbbpy})_2(\text{bpy})](\text{PF}_6)_2$  (1 mol %) and chlorobenzene (1 mL) at 120 °C under irradiation with a 11 W CFL bulb. Yield of the isolated product is given. <sup>b</sup>  $[\text{Ir}(\text{dtbbpy})_2(\text{bpy})]\text{PF}_6$  was employed instead of the Ru photocatalyst.

Methyl-substituted acetanilide **1e** provided the desired product in moderate yield. In addition, chloro-, bromo- and fluoroacetanilides **1f-h** were compatible with the reaction conditions. Notably, dehalogenated indole was not detected after reaction with 4-chloroacetanilide. Substrates **1i-l** possessing various sensitive functional groups such as trifluoromethyl, ketone or ester all smoothly underwent cyclization reaction to provide the desired products **3i-l** in moderate to good yields. Promisingly, not only symmetric internal alkyne **2a** but also unsymmetric alkyne **2b** afforded the desired product **3l** with moderate yield.<sup>11</sup>

Next we focused our attention on broadening the applicability of our developed protocol and attempted the synthesis of pyrroles. A catalytic system consisting of an iridium based photocatalyst and a Rh acetonitrile complex, known to be more reactive than  $[\text{RhCp}^*\text{Cl}_2]_2$ , were employed in this case (Scheme 2). Pleasingly, acetamidoacrylate (**4**) reacted at 70 °C with diphenylacetylene and 4-methyl substituted diphenylalkyne, to give the corresponding products **5a** and **5b** in good yields. We were delighted to observe that Rh(III) / photoredox combined catalytic system offers a direct access to

pyrrole skeleton presumably guided by the chelation-assisted olefinic C–H metalation (Scheme 2).

**Scheme 2.** Pyrrole synthesis via photocatalytic cyclization procedure.

Over the last years, photoactive inorganic semiconductor reagents have been employed in organic synthesis and exhibited excellent efficiency.<sup>12</sup> In order to further improve the practicability of our protocol, we tested heterogeneous photocatalysts under the optimized conditions (Table 3). Notably, we found that the use of  $\text{WO}_3$  affords almost comparable results when compared to the reaction performed in the presence of the Ru photocatalyst (Table 3, entry 2). Further reagents such as  $\text{BiVO}_3$ ,  $\text{ZnO}$  and  $\text{TiO}_2$  also provided the desired product, however, their efficiency was lower compared to  $\text{WO}_3$ .

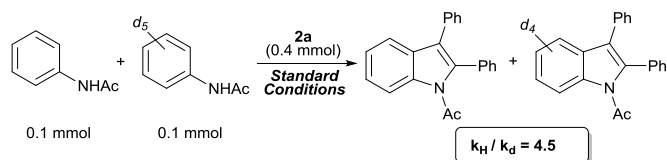
**Table 3.** Indole synthesis with heterogeneous photocatalyst

Reaction scheme showing the synthesis of indole **3a** from acetanilide **1a** and alkyne **2a**. The reaction conditions are:  $[\text{RhCp}^*\text{Cl}_2]_2$  (2 mol%),  $\text{AgSbF}_6$  (8 mol%), Heterogeneous Photocatalyst (1 equiv),  $\text{PhCl}$  (1 mL), 11 W CFL, 120 °C, 12 h.

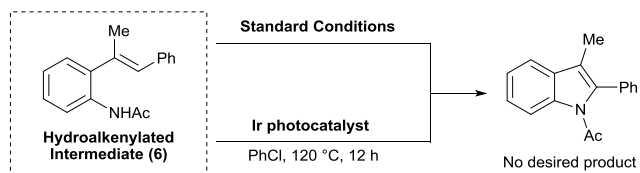
Entry	Heterogeneous Photocatalyst	Yield (%)
1	$\text{BiVO}_3$	64
2	$\text{WO}_3$	78
3	$\text{ZnO}$	58
4	$\text{ZnS}$	<1
5	$\text{TiO}_2$	55

In order to get more information on the reaction mechanism and the role of the photocatalyst, several experiments were carried out (Scheme 3). Firstly, a competition experiment between acetanilide and its deuterated analogue revealed a significant kinetic isotope effect (KIE),  $k_{\text{H}}/k_{\text{D}} = 4.5$ ,<sup>13</sup> which lies in the same range as values obtained through copper oxidant methods.<sup>7</sup> Thus, this result indicated that the photocatalyst does not inhibit the rhodium catalysis cycle. Secondly, the cyclized product was not detected when hydroalkenylated substrate **6** was subjected to the optimal reaction conditions and photocatalytic conditions in the absence of Rh(III) catalyst. Hence the existence of **6** as a reaction intermediate could be ruled out based on this observation.

## i) KIE experiment

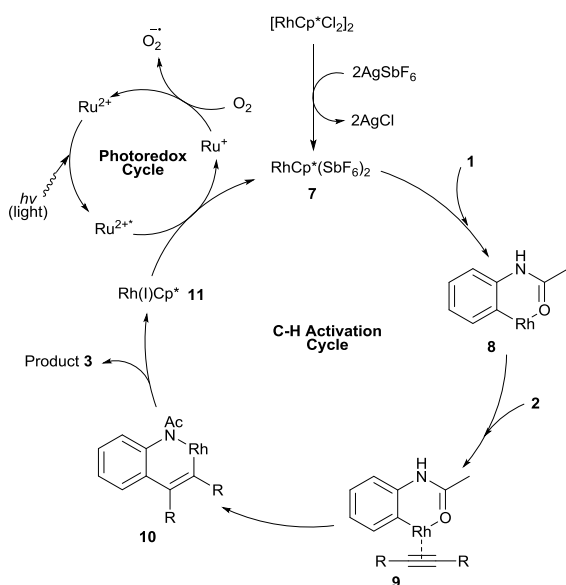


## ii) Hydroalkenylated intermediate test



Scheme 3. KIE experiment and intermediate test.

Based on the above mechanistic studies and relevant literature reports, we propose a plausible catalytic cycle in Scheme 4. Upon treatment with the silver salt, the neutral dimeric rhodium precursor is converted into its cationic monomeric species that promotes the C-H bond cleavage of the substrates. The active species **7** provides the five-membered metallacycle **8** via coordination with the Lewis-basic oxygen of the acetyl directing group. Coordination of alkyne to Rh will initiate a subsequent carbo-rhodation to afford Rh(III) alkenylated species **10**. The desired product is released from **10** by C-N reductive elimination along with Rh(I) species **11**. Simultaneously, the  $Ru^{2+}$  complex is excited by visible light providing a  $Ru^{2+*}$  species, which is then reductively quenched by Rh(I) to regenerate Rh(III) catalyst for further reaction and  $Ru^+$ . The resulting  $Ru^+$  complex is now reoxidized to  $Ru^{2+}$  by molecular oxygen from air, and a superoxide anion is generated.



Scheme 4. Plausible reaction mechanism.

## Conclusion

In conclusion, we have developed an efficient method for the sequential construction of carbon-carbon and carbon-nitrogen bonds by functionalization of  $sp^2$  C-H bonds in acetanilide derivatives via C-H activation and photoredox pathway. The protocol exhibits good functional group tolerance and offers an efficient and environmental friendly alternative to reactions involving traditional (over)stoichiometric amounts of oxidants. In addition, the transformation can be efficiently performed with heterogeneous inorganic photocatalysts. Mechanistic studies demonstrated that Rh(III) and the photocatalyst provide the desired product via photoredox regeneration cycle of the Rh-catalyst. Based on the mechanistic insights obtained in this study, an additional advance is anticipated in C-H activation assisted by photoredox catalysis, enabling the development of more efficient and selective catalytic systems with broader applicability.

## Experimental

General procedure for the synthesis of compound **3**

To an oven-dried screw-capped tube were added acetanilide (0.2 mmol), alkyne (0.4 mmol),  $[RhCp^*Cl_2]_2$  (2 mol%),  $AgSbF_6$  (8 mol%), photocatalyst (1 mol%) and PhCl (1.0 mL). The mixture was irradiated by an 11W lamp (distance ca. 3 cm) after placing it on an aluminum block heated at 120 °C for 12 h. The reaction was cooled to room temperature, filtered through a plug of celite, and the celite was washed with  $CH_2Cl_2$  (15 mL). The filtrate was concentrated and then evaporated to dryness under high vacuum. The desired product was isolated by column chromatography.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

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