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Combined Catalysis Hot Paper

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Synthesis of Indoles Using Visible Light: Photoredox Catalysis for Palladium-Catalyzed C−H Activation**

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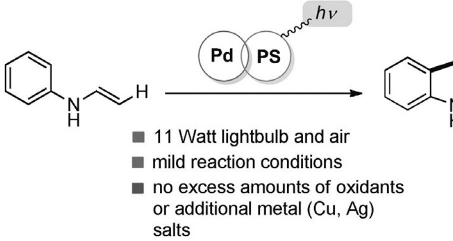
Abstract: *A combined palladium- and photoredox-catalyzed C−H olefination enables the synthesis of indoles. By using visible light, the direct C−H activation of aromatic enamines can be achieved and a variety of indole derivatives can be obtained in good yields under mild reaction conditions.*

The indole motif is one of the most common building blocks among bioactive compounds and natural products and has therefore been a target of numerous methodology developments.[1] In addition to the Fischer indole syntheses,[2] many different synthetic approaches using modern transition-metal catalysis are known. Typically starting from *ortho*-halogenated aniline derivatives, most of the methodologies thus still suffer from the restricted availability or high costs of starting materials.[3] In the field of C−H activation, reactions relying on oxidative palladium(II) chemistry have become a versatile and powerful tool for the synthesis of complex structural motifs. The oxidative Heck reaction, also known as the Fujiwara–Moritani reaction,[4] is a well-understood and broadly applicable transformation in organic synthesis. The use of variable and removable directing groups on the aromatic or heteroaromatic substrate allows *ortho*-olefinations in generally high yields and excellent regioselectivities.[5]

In 2002, van Leeuwen and co-workers reported on the oxidative coupling of anilides with olefins.[6] The use of $Pd(OAc)_2$ in combination with stoichiometric amounts of benzoquinone (BQ) (1 equiv) resulted in successful olefinations. The carbonyl group served as a directing group in these reactions. Furthermore, Lu and co-workers presented an intramolecular Fujiwara–Moritani reaction employing the same Pd/BQ system for the synthesis of carbazoles starting from 3-(3′-alkenyl)indole derivatives.[7] Indoles have also been shown to be suitable substrates for intermolecular olefination reactions. Stoichiometric amounts of $Cu(OAc)_2$ (2 equiv) together with $PdCl_2$ (10 mol%) led to the efficient coupling of N-protected indoles with highly substituted olefins.[8] However, oxidative Heck reactions and related transformations involving different metals, including ruthenium and rhodium, share the same major drawback since the metal–H species that is formed after reductive elimination must be reoxidized by an external oxidant. In recent years many improvements have reduced the amount of stoichiometric metal-based additives, such as copper and silver salts,[9] through use of molecular oxygen.[10] However, still relatively large amounts of oxidants have to be present.

Based on our experience in the field of photoredox catalysis and the recent results of Sanford and co-workers on the coupling of diazonium and iodonium salts with arenes,[11,12] we decided to investigate the palladium-catalyzed C−H olefination of aromatic enamines for the synthesis of indoles. Small amounts of photoredox catalyst[13] in the presence of visible light should facilitate the reoxidation of the Pd catalyst (Scheme 1), thereby obviating the use of an excess of oxidants or metal salts. This method could be considered a highly atom-efficient reaction. Herein, we report on the development of an indole synthesis using a new combination of palladium and photoredox catalysis in the presence of visible light.



Scheme 1. Combination of photoredox and Pd^{II} catalysis for the synthesis of indoles.

We started our investigations with the intramolecular cyclization of aromatic enamines that had previously been described using $Pd(OAc)_2$ and three equivalents of $Cu(OAc)_2$.[14] The replacement of the copper additive with just 1 mol% of the photoredox catalyst led indeed after reaction optimization to the desired product **2a** in 46% yield (Table 1, entry 1). The finding that the photoredox catalyst can be used to regenerate the palladium catalyst encouraged us to test a variety of palladium catalysts in the cyclization reaction, and we found that $Pd(OAc)_2$ led to higher yields than other Pd^{II} precursors. Additional acetonitrile ligands on the palladium with strong or weak coordinating counterions, for example, Cl and BF_4 (Table 1, entries 2 and 3), resulted in only insufficient formation of the desired product.

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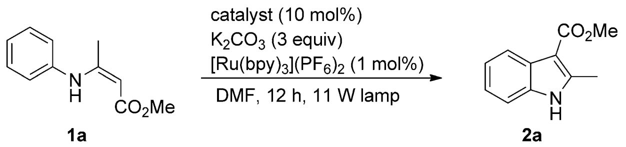
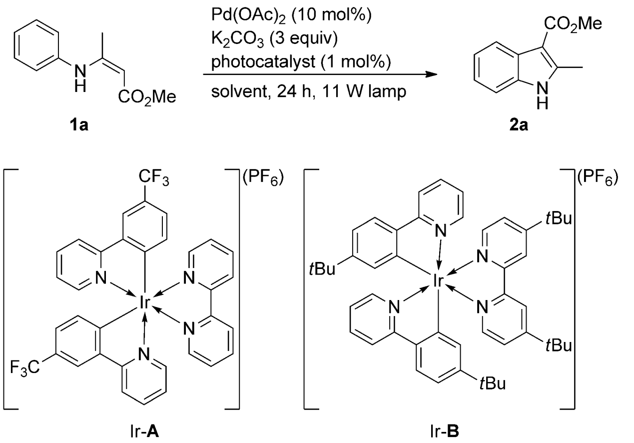
Table 1: Screening of catalyst precursors for the cyclization reaction of arylenamide **1**.



Entry[a]	Catalyst	Yield[b] [%]
1	$Pd(OAc)_2$	46
2	$[Pd(MeCN)_2Cl_2]$	27
3	$[Pd(MeCN)_2(BF_4)_2]$	24
4	$[Pd(PPh_3)_2(OAc)_2]$	–[g]
5	$[\{Cp^*RhCl_2\}_2]/AgSbF_6$	–[c,g]
6	$AgSbF_6$	–[d,g]
7	$[\{Cp^*RhCl_2\}_2]/AgSbF_6$	–[e]
8	$AgSbF_6$	–[f]

[a] Reaction conditions: 0.1 mmol substrate **1**, 3 equiv K_2CO_3, 1 mol% photoredox catalyst, 10 mol% Pd catalyst in DMF at 120 °C with irradiation from an 11 W lightbulb. [b] Yield after column chromatography. [c] 1 mol% Rh catalyst, 4 mol% $AgSbF_6$, 1 equiv K_2CO_3. [d] 5 mol% $AgSbF_6$. [e] 1 mol% Rh catalyst and 4 mol% $AgSbF_6$ in PhCl, 80 °C. [f] 4 mol% $AgSbF_6$ in PhCl, 80 °C. [g] Decomposition of substrate.

Table 2: Screening of reactions conditions for the cyclization reaction.



Entry[a]	Photoredox catalyst	Solvent	Yield[b] [%]
1	$[Ru(bpy)_3](PF_6)_2$	DMF	46
2	$[Ru(bpy)_3](PF_6)_2$	PhCl	–
3	$[Ru(bpy)_3](PF_6)_2$	DCE	–
4	$[Ru(bpy)_3](PF_6)_2$	MeCN	–
5	$[Ru(bpy)_3](PF_6)_2$	EtOH	–
6	$[Ir(bpy)(ppy)_2]PF_6$	DMF	66
7	$[Ir(bpy)(ppy)_2]PF_6$	PhCl	–
8	$[Ir(bpy)(ppy)_2]PF_6$	DCE	–
9	$[Ir(bpy)(ppy)_2]PF_6$	MeCN	–
10	$[Ir(bpy)(ppy)_2]PF_6$	EtOH	–
11	Ir-**A**	DMF	55
12	Ir-**B**	DMF	71
13	$[Ir(bpy)(ppy)_2]PF_6$	DMF	95[c]
14	$[Ir(bpy)(ppy)_2]PF_6$	DMF	42[d]
15	$[Ir(bpy)(ppy)_2]PF_6$	DMF	32[e]
16	–	DMF	–
17	$[Ir(bpy)(ppy)_2]PF_6$	DMF	traces[f]
18	$[Ir(bpy)(ppy)_2]PF_6$	DMF	–[g]
19	$[Ir(bpy)(ppy)_2]PF_6$	DMF	–[h]
20	–	DMF	–[i]
21	–	DMF	–[j,n]
22	$[Ir(bpy)(ppy)_2]PF_6$	DMF	46[k]
23	–	DMF	–[l,n]
24	–	DMF	53[m]

[a] Reaction conditions: 0.1 mmol substrate **1**, 3 equiv K_2CO_3, 1 mol% photoredox catalyst, 10 mol% Pd catalyst in DMF at 120 °C with irradiation from an 11 W lightbulb. [b] Yield after column chromatography [c] 3 mol% photoredox catalyst, O_2^{2-} was detected during the reaction. [d] 1 equiv K_2CO_3. [e] No base. [f] Ar atmosphere. [g] No Pd catalyst. [h] No Pd, no base. [i] No Pd. [j] O_2 atmosphere. [k] Ar atmosphere, photoredox catalyst. [l] 1.5 equiv KO_2, Ar atmosphere. [m] 0.5 equiv KO_2, Ar atmosphere. [n] Decomposition of substrate.

When $[Pd(PPh_3)_2(OAc)_2]$ was applied in the reaction, only decomposition of the starting material could be observed (Table 1, entry 4), showing that the reaction is highly dependent on the electronic and steric character of the palladium(II) catalyst. Since rhodium was also reported as a catalyst to activate aryl C–H bonds, the commonly used $[\{Cp^*RhCl_2\}_2]/AgSbF_6$ catalyst system was also tested in the cyclization reaction. However, only decomposition of the starting material was observed in DMF or chlorobenzene when either $[\{Cp^*RhCl_2\}_2]/AgSbF_6$ or only $AgSbF_6$ was present in the reaction (Table 1, entries 5–8).

Our previous research on Ru and Ir complexes in photoredox catalysis showed a dramatic dependence on the solvent system.[15] Thus we not only screened different photoredox catalysts but also examined their behavior in a variety of solvents. Again, the performance of the catalyst system was solvent dependent. Conversions were only observed in DMF, and using the iridium-based photoredox catalyst $[Ir(bpy)(ppy)_2]PF_6$ an yield of 66% for the expected indole was achieved (Table 2, entry 6). Chlorinated solvents, such as DCE and chlorobenzene, as well as polar-aprotic and -protic solvents, such as acetonitrile and ethanol (Table 2, entries 4, 5, 9, and 10) did not lead to any conversion.[16]

Next, the electronic and steric properties of $[Ir(bpy)(ppy)_2]PF_6$ were analyzed. A change to electron-deficient ligands (Ir-**A**, Table 2, entry 11) led to decreased yields of 55%, whereas with electron-rich ligands (Ir-**B**, Table 2, entry 12) indole **2a** was obtained in slightly higher yields of 71%. Finally, with the standard photoredox catalyst, 3 mol% of $[Ir(bpy)(ppy)_2]PF_6$ resulted in 95% yield (Table 2, entry 13).

In order to investigate the role of the inorganic base, reactions with lower amounts of K_2CO_3 (Table 2, entries 14 and 15) were conducted. The use of less base led to lower yields and showed that 3 equivalents are crucial for an efficient reaction. Afterwards, control experiments, which might also provide information regarding the mechanism of the reaction, were undertaken.

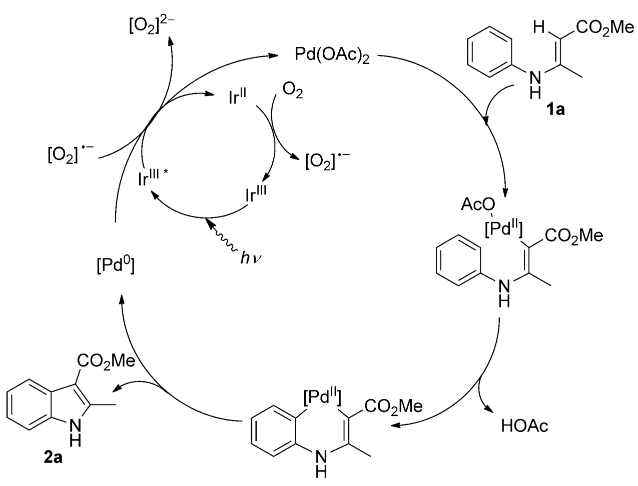
First, leaving out the photoredox catalyst (Table 2, entry 16) led to no formation of product, showing that no other oxidant is present or formed during the reaction. When no oxygen was present, only minimal conversion could be observed (Table 2, entry 17), leading to the conclusion that the photoredox catalyst can function as an external oxidant. This is further verified when 100 mol% of the photoredox catalyst was used under an argon atmosphere. In this case the corresponding product could be isolated in 46% yield (Table 2, entry 22).[17] This means that the palladium catalyst can be reoxidized by the photoredox catalyst in the absence of oxygen.

However, it cannot be excluded that peroxy species, which are formed by photoredox processes and could be detected as O_2^{2-} anions during the reaction,[18] simultaneously serve as an external oxidant and have therefore beneficial effects on the reaction. In order to prove this hypothesis, potassium superoxide was used as an oxidant source under an argon atmosphere in the absence of a photoredox catalyst. A yield of 53% for the reaction conducted with 0.5 equivalents of KO_2 confirmed that the in situ formed superoxide anion serves as an external oxidant. When more than stoichiometric amounts of KO_2 were used, decomposition of both starting material and product was observed.

To exclude the possibility that oxygen acts as an external oxidant, the reaction was performed under oxygen atmosphere in the absence of the photoredox catalyst (Table 2, entry 21). Here, only decomposition of the starting material was observed. In order to analyze any background reaction, the ring-closing reaction was performed once without palladium catalyst, without palladium and base, and without any additive (Table 2, entries 18–20). In all cases, no conversion of starting material **1** could be observed, allowing the conclusion that only the complete catalyst system—palladium, photoredox catalyst, and base—is active in the reaction.

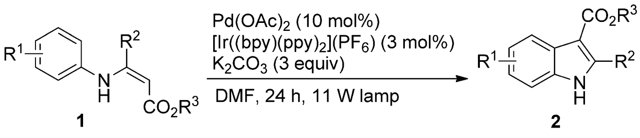
Based on this information, we propose the following mechanism: in the first step, C–H activation of the olefin of **1a** takes place, followed by the activation of the arene (Scheme 2). After reductive elimination, indole **2a** is produced and the resulting Pd^0 can now be reoxidized by either the photoredox catalyst or the in situ formed superoxide anion yielding the catalytically active Pd^{II} species.

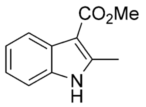
With the optimal reaction conditions and a general understanding of the mechanism in hand, we evaluated the substrate scope of the ring-closing olefination reaction (Table 3). Different electron-donating groups in *para* position led to slightly lower yields of 80%, 73%, and 79% for the *p*-OMe, *p*-OPh, and *p*-Me derivatives **2b–d**, respectively. The substrate with an electron-deficient *p*-Cl substituent (**1e**) gave the corresponding product in very good 83% yield. Opposite results were obtained when variations in the *ortho* position

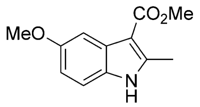


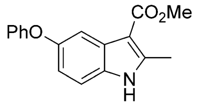
Scheme 2. Proposed mechanism for the Pd-catalyzed intramolecular olefination reaction.

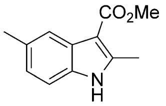
Table 3: Substrate scope of the cyclization reaction.[a]

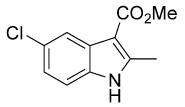


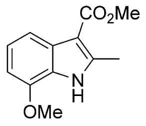

2a: 95%

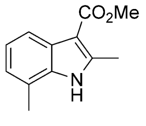

2b: 80%

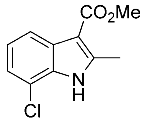

2c: 73%

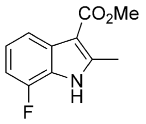

2d: 79%

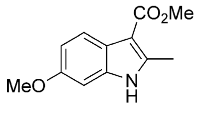

2e: 83%


2f: 78%

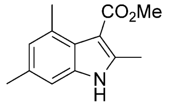

2g: 78%

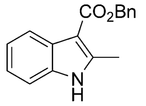

2h: 65%

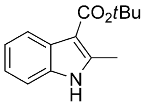

2i: 60%

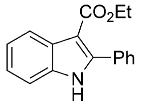

2j: 57%


2k: 71%(1:1.3)


2l: 71%


2m: 74%


2n: 80%


2o: 91%

[a] Reaction conditions: 0.2 mmol substrate **1**, 3 equiv K_2CO_3, 3 mol% $[Ir(bpy)(ppy)_2]PF_6$, 10 mol% Pd catalyst in DMF at 120 °C with irradiation from an 11 W lightbulb; yield after column chromatography.

were investigated. The substrate with an electron-rich donating OMe group provided indole **2f** in 78 % yield, whereas a chloro-substituted indole **2h** could only be isolated in moderate yield of 65 %. The lowest yields were obtained when *o*-F- (**1i**) and *m*-OMe-based (**1j**) anilines were applied in the olefination reaction. Also, multisubstituted anilines **1k** and **1l** were tested in this reaction. The tricylic compound **2k** was isolated as a mixture of regioisomers in 71 % yield. Furthermore, different enamine esters were successfully applied in the reaction and the corresponding products were isolated in moderate yield (74 %) for the benzyl ester (**2m**) to good yield (80 %) for the *tert*-butyl ester (**2n**). A very good yield of 91 % could be obtained for compound **2o** which shows that the electronic or steric character in the C2 or C3 position does not have any significant influence on the reaction.

In conclusion, we have reported on a new combined photoredox- and palladium-catalyzed system for the synthesis of highly functionalized indoles. Using catalytic amounts of a photoredox catalyst in the presence of visible light, the typical high loadings of external oxidants could be avoided. Mechanistic studies revealed for the first time that either a) the photoredox catalyst in the absence of oxygen or b) the in situ formed superoxide anions in the presence of oxygen and photoredox catalyst function as the external oxidant. Notably, the safe and practical method described herein represents an alternative[19] to common procedures involving peroxo species. Since only small amounts of the oxidant are generated that are furthermore immediately consumed, side reactions of substrate or product can be avoided. Thus, oxidant-sensitive substrates can be used and this makes this method highly suitable for syntheses.

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[16] This implies that the redox potentials of the photoredox catalysts differ from known potentials recorded in water or acetonitrile. Experiments in order to record their potentials are currently in progress. First results already showed that this will not be an easy task because of their low solubility in chlorobenzene and DCE.

[17] This is in accordance to the theory as only one electron per photoredox catalyst molecule can be transferred.

[18] Hydrogen peroxide was detected with the aid of colorimetric assay reagents both in undiluted reaction media as well as after dilution with water.

[19] For another elegant method, see: D. P. Kranz, A. G. Griesbeck, R. Alle, R. Perez-Ruiz, J. M. Neudörfl, K. Meerholz, H.-G. Schmalz, *Angew. Chem. Int. Ed.* **2012**, *51*, 6000–6004; *Angew. Chem.* **2012**, *124*, 6102–6106.