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Dual Catalysis

C–H Functionalization of Phenols Using Combined Ruthenium and Photoredox Catalysis: In Situ Generation of the Oxidant**

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Abstract: *A combination of ruthenium and photoredox catalysis allowed the ortho olefination of phenols. Using visible light, the direct C–H functionalization of o-(2-pyridyl)phenols occurred, and diverse phenol ethers were obtained in good yields. The regeneration of the ruthenium catalyst was accomplished by a photoredox-catalyzed oxidative process.*

Phenols represent a common structural motif in natural products and organic materials. Therefore, it is not surprising that the number of publications on the formation or modification of phenols or phenol ethers has been increasing for the past years. In the area of material science, the phenol motif plays a crucial role for the construction of poly(phenol ethers) or their modification to adjust their macroscopic properties, such as their melting or glass-transition temperatures, for specific applications.[1]

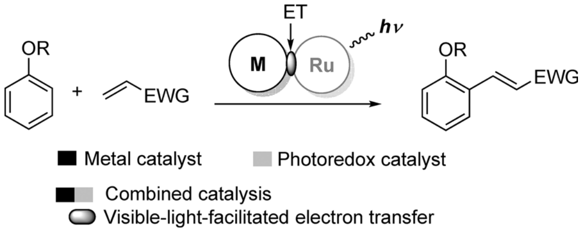
In the field of natural products or bioactive compounds, elegant total syntheses incorporating phenols or phenol ethers as structural motifs have been developed, which were usually centered in the area of C–H activation.[2]

Evidently, C–H functionalization plays a more and more important role in method development as disadvantages, such as prefunctionalization with halogens or reactivity problems with lighter halogens, have been overcome. Aside from initial oxidative C–H functionalizations using palladium[3] or rhodium[4] catalysts in the Fujiwara–Moritani reaction, first examples with ruthenium were presented. The group of Satoh and Miura showed that pyrazole is a suitable directing group (DG) for the *ortho* olefination of 1-phenylpyrazoles.[5] The catalytic system, consisting of [{Ru(*p*-cymene)Cl_2}$_2$] (5 mol%) and $Cu(OAc)_2$ (2 equiv) as the co-oxidant enabled the efficient coupling of the biaryl moiety with common acrylates. The use of large amounts of copper salts is a general feature of these types of reactions as the in situ generated metal complex needs to be reoxidized first before the next catalytic cycle can be started.

Over the last years, the development of many different variants has enabled the use of various olefins and directing groups in such transformations. Wang und Jeganmohan could show that not only carbamates, but also azoxybenzenes[7] and simple aromatic ketones,[8] esters,[9] or amides[10] are suitable directing groups for the olefination of a broad range of aromatic and heteroaromatic compounds.

Quite recently, the group of Ackermann extended the substrate scope to protected phenols.[11] Using a 2-pyridyl protecting group (Pyr), the selective *ortho* olefination of a variety of aromatic and heteroaromatic compounds could be achieved. This procedure made use of over-stoichiometric amounts of Cu^{II} salts. Eager to make these reactions more environmentally friendly, Wang and co-workers developed a procedure that makes use of internal oxidants.[12] *N*-Methoxybenzamides were suitable substrates for the *ortho* olefination as the Ru complex was subsequently reoxidized by cleavage of the methoxy group. Although the use of copper salts could be prevented, this approach possesses a considerable limitation regarding the scope of the reaction as the previously extended scope of directing groups is reduced again.

As the regeneration of the metal complex is an electron-transfer process, we were wondering whether the necessary reoxidation could be facilitated by a photoredox-controlled process using visible light (Scheme 1). Herein, we report the first olefination of phenol ethers by metal and photoredox catalysis using a combination of [{Ru(*p*-cymene)Cl_2}$_2$]/$AgSbF_6$ und [Ir(ppy)$_2$(bpy)]PF_6.[13–15]



Scheme 1. Combination of photoredox and Ru^{II} catalysis for an *ortho* olefination process.

Based on the work of Ackermann, first experiments replacing the stoichiometric amounts of $Cu(OAc)_2$ with 1 mol% of the photoredox catalyst were conducted. We were pleased to see that under these conditions, conversion of substrate **1a** could be observed. During a broad solvent screen with the common photoredox catalysts [Ru(bpy)$_3$](PF_6)$_2$ and [Ir(bpy)(ppy)$_2$]PF_6, the best yield of 60% for product **3a** was achieved with the Ir-based catalyst in dimethylacetamide. Interestingly, no clear correlation between solvent properties and yield was observed. Gener-

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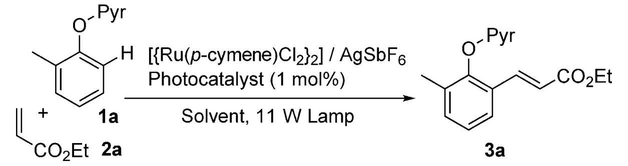
ally, higher yields were obtained for the Ir-based catalyst than with $[Ru(bpy)_3](PF_6)_2$; however, this was the case for both polar aprotic as well as apolar aprotic solvents (Table 1).

Table 1: Screening of the reaction conditions for the combined C–H activation.[a]



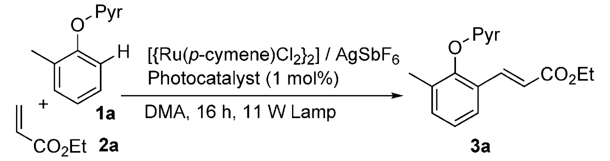
Entry[a]	Photocatalyst	Solvent	Yield [%][b]
1	$[Ru(bpy)_3](PF_6)_2$	DMF	11
2	$[Ru(bpy)_3](PF_6)_2$	PhCl	35
3	$[Ru(bpy)_3](PF_6)_2$	DCE	0
4	$[Ru(bpy)_3](PF_6)_2$	MeCN	0
5	$[Ru(bpy)_3](PF_6)_2$	DMPU	0
6	$[Ru(bpy)_3](PF_6)_2$	DMA	56
7	$[Ru(bpy)_3](PF_6)_2$	TMU	0
8	$[Ir(bpy)(ppy)_2]PF_6$	DMF	49
9	$[Ir(bpy)(ppy)_2]PF_6$	PhCl	42
10	$[Ir(bpy)(ppy)_2]PF_6$	DCE	0
11	$[Ir(bpy)(ppy)_2]PF_6$	MeCN	0
12	$[Ir(bpy)(ppy)_2]PF_6$	DMPU	0
13	$[Ir(bpy)(ppy)_2]PF_6$	DMA	**60**
14	$[Ir(bpy)(ppy)_2]PF_6$	TMU	0

[a] **1a** (0.1 mmol), acrylate (2 equiv), photoredox catalyst (1 mol%), $AgSbF_6$ (0.2 equiv), and Ru catalyst (5 mol%) in the indicated solvent at 120°C under irradiation with a 11 W CFL bulb. [b] Yield of isolated product after column chromatography. DCE = 1,2-dichloroethane, DMA = dimethylacetamide, DMPU = 1,3-dimethyl-3,4,5,6-tetrahydro-2-pyrimidinone, Pyr = pyridyl, TMU = tetramethylurea.

To evaluate the influence of each component on the process, the reaction was performed without the ruthenium dimer (Table 2, entry 2). In this experiment, no conversion was detected, suggesting that the silver salt is not capable of activating the C–H bond of the aryl compound and is therefore responsible for the precipitation of the chloride ligands only. To prove this hypothesis, the Ru dimer was used in the reaction without the silver salt (Table 2, entry 3); as expected, no conversion was observed.

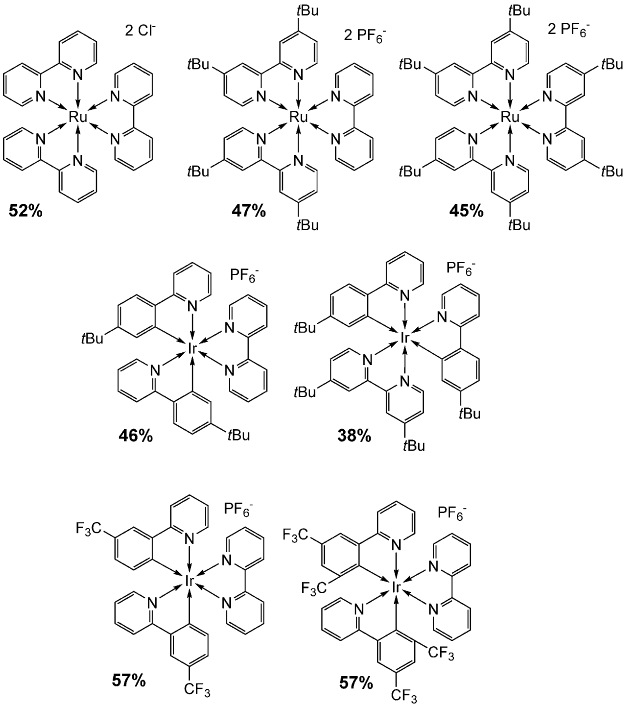
Next, the role of the photoredox catalyst was analyzed. In the absence of the photoredox catalyst, only traces of the desired product **3a** were isolated (Table 2, entry 4). This confirmed that no other oxidant is present in the reaction and that no oxidant is formed during the reaction in the absence of the photoredox catalyst. To exclude a potential C–H activation through the photoredox catalyst, the reaction was performed without the Ru/Ag components, which again gave no conversion (Table 2, entry 5). As it was previously reported that oxo or peroxo species, which can be formed by photoredox processes,[16] can be used for the oxidation of metal complexes, the olefination reaction was conducted under an oxygen atmosphere. No significant improvement of the yield could be observed (Table 2, entry 6). When the photoredox catalyst was omitted, no reoxidation occurred, and therefore, stoichiometric conversion with respect to the Ru/Ag components occurred (Table 2, entry 7). This illustrates that molecular oxygen cannot be used as a reoxidant and cannot be converted into an active species in the absence of the photoredox catalyst. Therefore, peroxo species presumably take part in this reaction.

Table 2: Screening of the reaction conditions for the olefination reaction.



Entry[a]	Catalyst	Photocatalyst	Conditions	Yield [%][b]
1	$[Ru]/AgSbF_6$	$[Ir(bpy)(ppy)_2]PF_6$	air	60
2	$AgSbF_6$	$[Ir(bpy)(ppy)_2]PF_6$	air	0
3	[Ru]	$[Ir(bpy)(ppy)_2]PF_6$	air	0
4	$[Ru]/AgSbF_6$	–	air	4
5	–	$[Ir(bpy)(ppy)_2]PF_6$	air	0
6	$[Ru]/AgSbF_6$	$[Ir(bpy)(ppy)_2]PF_6$	O_2	64
7	$[Ru]/AgSbF_6$	–	O_2	6
8	$[Ru]/AgSbF_6$	$[Ir(bpy)(ppy)_2]PF_6$	argon	0
9	$[Ru]/AgSbF_6$	$[Ir(bpy)(ppy)_2]PF_6$	argon	38[c]
10	$[Ru]/AgSbF_6$	–	KO_2 (1 equiv)/ argon	39
11	$[Ru]/AgSbF_6$	$[Ir(bpy)(ppy)_2]PF_6$	air	65[d]
12	$[Ru]/AgSbF_6$	$[Ir(bpy)(ppy)_2]PF_6$	O_2	65[d]

[a] **1a** (0.1 mmol), acrylate (2 equiv), photoredox catalyst (1 mol%), $AgSbF_6$ (0.2 equiv), and the Ru catalyst (5 mol%) in DMA at 120°C using a 11 W CFL bulb. [b] Yield of isolated product after column chromatography. [c] Photoredox catalyst (100 mol%). [d] Photoredox catalyst (3 mol%). [Ru] = [{Ru(p-cymene)Cl_2}$_2$].



To analyze this particular circumstance, the standard reaction was performed in the presence of 1 and 100 mol% of the photoredox catalyst under an argon atmosphere (Table 2, entries 8 and 9, respectively). The fact that no conversion could be observed when 1 mol % of the photoredox catalyst was used confirms that the photoredox catalyst itself cannot function as an oxidant in the absence of oxygen because no regeneration can take place. In contrast, using 100 mol % of the photoredox catalyst, the desired product was obtained in 38 % (Table 2, entry 9). As in one photoredox cycle, only one electron can be transferred, this reaction shows that the photoredox catalyst itself can also function as an oxidant. As a final confirmation of our hypothesis, KO_2 was directly used as an inorganic superoxide anion instead of the photoredox catalyst in the reaction under argon atmosphere (Table 2, entry 10). The desired product was isolated in 39 % yield as the catalytic cycle can be closed, and the peroxo species was identified as a suitable active oxidant. The reduced yields obtained with KO_2 are due to the instability of the inorganic salt, which most probably leads to partial decomposition at the reaction temperature of 120 °C before full reoxidation of the metal complex has been achieved. This finding also illustrates the user friendliness of the photoredox process, as oxidizing and potentially explosive reagents can be avoided while higher yields are obtained.

When the catalyst loading of $[Ir(bpy)(ppy)_2]PF_6$ was increased to 3 mol %, the desired product **3a** could be obtained in 65 % yield (Table 2, entry 11), which lies in the same range as yields obtained with copper-based methods.

To gain deeper insight into the individual regeneration processes mediated by the superoxide anion and the photoredox catalyst, the dependence of the yield on the reaction time was determined for both oxidants (Figure 1). The individual regeneration processes for hydride oxidation were analyzed individually, either with KO_2 (2 equiv) or with the photoredox catalyst (2 equiv) under an argon atmosphere; both processes proceeded much slower than under the standard reaction conditions (3 mol % photoredox catalyst, air) and therefore led to lower yields after 24 hours. However, when both processes were combined under the standard reaction conditions, where both the photoredox processes as well as the steps involving the superoxide anion generated in situ can be executed simultaneously, an increase in the reactivity was observed, and higher yields were obtained. This can be explained by the fact that only small amounts of the highly reactive superoxide anions are formed by the photoredox process, which are then rapidly consumed and therefore not present in excess amounts. In contrast, when larger amounts are present, side and consecutive reactions will cause lower yields of the desired product.

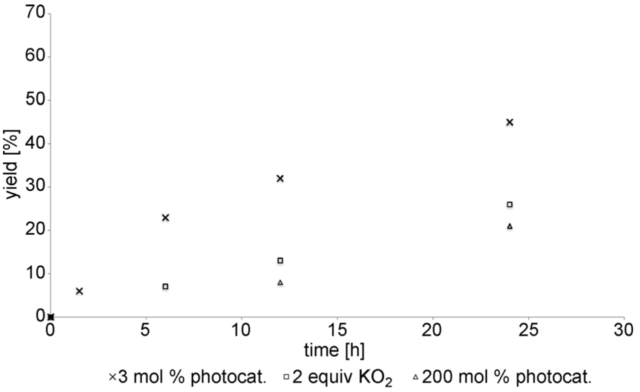
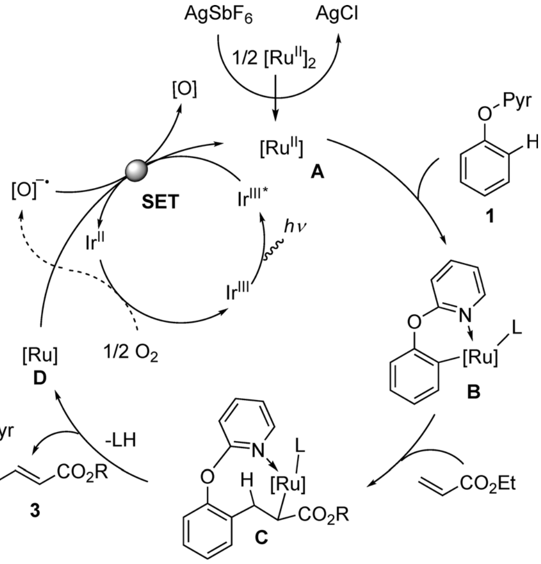


Figure 1. Yield–time correlation of the olefination reaction.

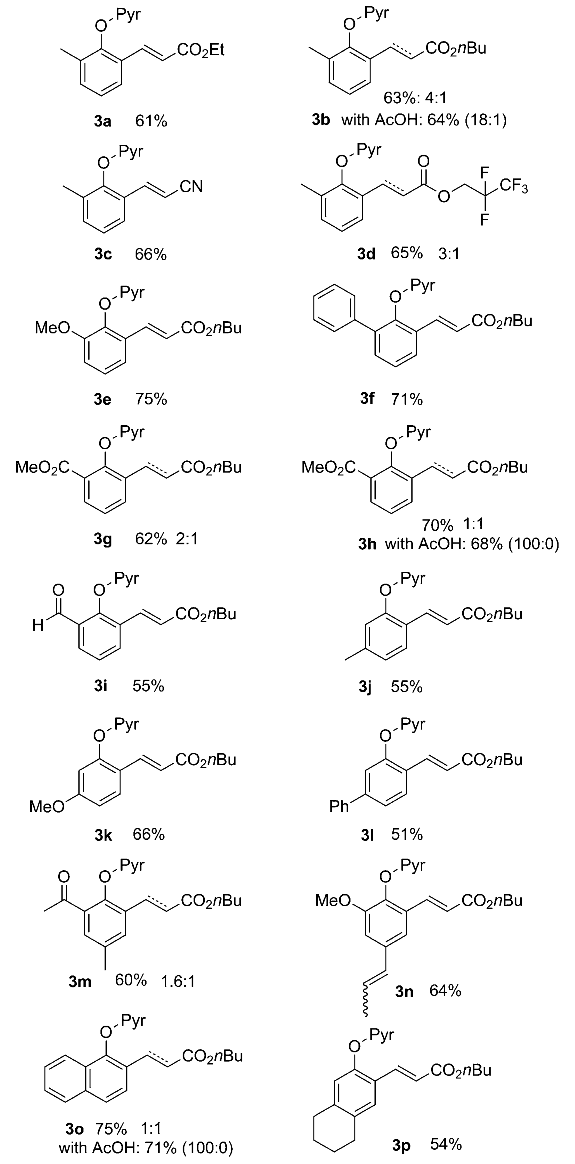
Using the obtained data, the following reaction mechanism can be postulated (Scheme 2): After the active Ru^{II} catalyst **A** has been formed by precipitation of the chloride ligands attached to the Ru dimer, *ortho* C–H activation of substrate **1** to intermediate **B** occurs with the help of the directing pyridine moiety. After insertion of the olefinic compound, which yields intermediate **C**, and reductive elimination of product **3**, ruthenium complex **D** is obtained. Photoredox catalyst Ir^{III*}, which has been excited with visible light, is now capable of oxidation by electron transfer, thus regenerating the catalytically active Ru species **A**. The resulting Ir^{II} complex is now reoxidized to Ir^{III} by molecular oxygen, and a superoxide anion is generated. The superoxide anion itself may then oxidize Ru complex **D** by accepting an electron.



Scheme 2. Proposed mechanism for the combined olefination reaction.

Subsequently, we began to investigate the substrate scope of this newly developed method. The acrylate component was varied first. It was apparent that substituents on this substrate only had a small influence on the reaction, and the products were isolated with comparable, good yields (Table 3, rows 1 and 2). Electron-donating substituents in the *ortho* position even increased the yield up to 75 % for a methoxy group (**3e**). The electron-poor substrates **3g–i** could also be successfully used in the olefination reaction. Furthermore, the applicability of the reaction was underlined by its tolerance towards aldehydes, ketones, and esters. Subsequently, also *meta*-substituted substrates as well as substrates with more complex substitution patterns were successfully olefinated (Table 3, rows 5–8). Independent from the electronic or steric character of the substrates, partial hydrogenation of the double bond

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



[a] **1** (0.2 mmol), AcOH (1 equiv), olefin (2 equiv), [Ir(bpy)(ppy)$_2$]PF$_6$ (3 mol%), and the Ru catalyst (5 mol%)/AgSbF$_6$ (20 mol%) in DMA at 120°C using a CFL bulb. Yields of isolated products after column chromatography; the olefin/alkane ratios are also given.

was observed. This consecutive hydrogenation catalyzed by the ruthenium hydride complex then led to a mixture of the olefinic and hydrogenated products. This reactivity of ruthenium complexes has previously been described by other groups in different contexts.[17]

To determine whether the obtained ratio of the olefin and alkane components can be controlled, naphthyl derivative **1o** was chosen as a model substrate, and different additives were tested under the standard reaction conditions. As the consecutive reaction involves the participation of a hydride, we decided to test a variety of acids with different acidities as additives. We were pleased to see that with medium-strong acetic acid (Table S1), we not only observed comparable yields for product **3o**, but also that the addition of the acid suppressed any consecutive hydrogenation. When the strong acid *para*-toluenesulfonic acid (TsOH) was used, the olefin/alkane ratio was only 6:1 with an overall yield of 46%. Different weak acids, such as a benzoic acid derivatives or diphenyl phosphate, indeed led to a 100% selectivity in favor of the olefin, but to lower yields than acetic acid. The addition of water as a co-solvent led to lower yields (23%) with an olefin/alkane ratio of 2:1. Acetic acid also proved to be an effective additive for other representative substrates, including **3b** and **3h**, for the suppression of consecutive hydrogenation processes while giving the desired products in similar yields.

In summary, we have reported a new combination of photoredox and metal catalysis for the olefination reaction of phenols by C–H activation. The unique interplay of metal and photoredox catalysis allowed the direct reoxidation of the metal hydride intermediate for the catalytic regeneration of the catalyst. Mechanistic studies revealed that the regeneration reaction can be maximized with small amounts of superoxide anions, which are formed by photoredox processes and could also function as the oxidant. As only small amounts of oxidant are generated, side reactions of substrate and product could not be observed, and oxidant-sensitive molecules can be employed. Based on mechanistic studies, we could show that with acid additives, olefinated phenol derivatives may be synthesized in good yields. As the yields are comparable with those of similar transformations that employ stoichiometric amounts of copper, an extension to other C–H functionalizations should be possible and feasible. Furthermore, the combined use of metal and photoredox catalysts should be transferable to other C–H functionalizations.

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