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 2-pyridylphenols occurred and diverse phenolethers 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 for the formation or modification of phenols or phenolethers has been increasing for the past years. In the area of material science the phenol motif plays a crucial role for the construction of polyphenylethers or their modification, respectively, in order to adjust their macroscopic properties, such as melting or glass temperature for specific applications.[1]

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

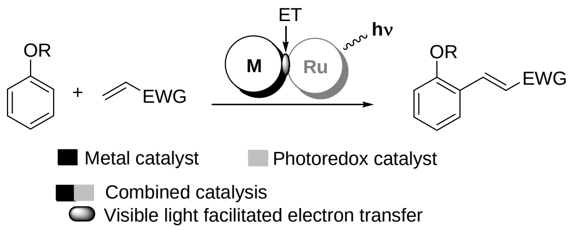
Evidently, the C-H functionalization plays a more and more important role in methodology development since disadvantages, such as prefunctionalization with halogens or reactivity problems with lighter halogens can be overcome. In addition to initial oxidative C-H functionalizations using palladium[3] or rhodium[4] in the Fujiwara-Moritani reaction, first examples of ruthenium were presented. The groups 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 5 mol% [Ru(*p*-

cymene)Cl_2]$_2$ and over-stoichiometric amounts of $Cu(OAc)_2$ (2 equiv.) as cooxidant allowed the efficient coupling of the biaryl moiety with common acrylates. The use of large amounts of copper salts is a general feature in these types of reactions as the *in situ* generated metal complex needs to be reoxidized first before a next catalytic cycle can be started.

In the last years, many different versions have been developed that extended both the olefin component as well as the directing group. Wang und Jeganmohan could not only show that carbamates are well tolerated in a broad variety of aromatic and heteroaromatic compounds, but also that this protocol is applicable to azoxybenzenes[7] and simple aromatic ketones,[8] esters[9] or amides[10] as directing groups, respectively.

Quite recently, the group of Ackermann showed the extension of 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 protocol made use of over-stoichiometric amounts of Cu(II) salts. Eager to make these reactions more environmentally friendly, Wang and coworkers could present a protocol using internal oxidants.[12] *N*-Methoxybenzamides were suitable for the *ortho*-olefination whereas the Ru-complex was subsequently reoxidized by cleavage of the *N*-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.

Since the regeneration of the metal complex represents an electron transfer process, we were wondering if the necessary reoxidation could be facilitated by a photoredox-controlled process using visible light (Scheme 1).



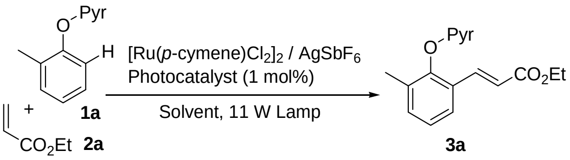
Scheme 1. Combination of photoredox and Ru(II) catalysis in the *ortho*-olefination.

Herein, we report on the first olefination of phenolethers with a combination of metal and photoredox catalysis[13-15] using [Ru(*p*-cymene)Cl_2]$_2$/$AgSbF_6$ und [Ir(ppy)$_2$(bpy)]PF_6.

Based on the excellent work of Ackermann, first experiments replacing the stoichiometric amounts of $Cu(OAc)_2$ with 1 mol% photoredox catalyst were conducted. We were pleased to see that the reaction can in principle lead to conversions of the substrate **1a**. After a broad solvent screening 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 obtained with the Ir-based catalyst in dimethylacetamide. Interestingly, no clear correlation between the solvent properties and yield was observed. Generally, higher yields were obtained for the Ir-based catalyst as compared to [Ru(bpy)$_3$]$(PF_6)_2$, however, this was the case for both polar-aprotic, as well as apolar-aprotic solvents (Table 1).

In order to first evaluate the influence of each component on the catalysis, the reaction was performed without ruthenium dimer (Table 2, entry 2). Thereby, no conversion was detected concluding 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 chloride ligands only. To prove this hypothesis, the Ru-dimer without the silver salt was used in the reaction (Table 2, entry 3) that led to no conversion, as expected.

Table 1. Screening of reaction conditions in the combined C-H activation.[a]



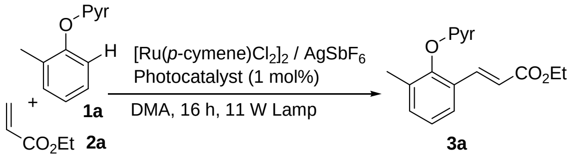
Entry[a]	Photocatalyst	Solvent	Yield[b] (%)
1	$[Ru(bpy)_3](PF_6)_2$	DMF	11
2	$[Ru(bpy)_3](PF_6)_2$	PhCl	35
3	$[Ru(bpy)_3](PF_6)_2$	DCE	0
4	$[Ru(bpy)_3](PF_6)_2$	MeCN	0
5	$[Ru(bpy)_3](PF_6)_2$	DMPU	0
6	$[Ru(bpy)_3](PF_6)_2$	DMA	56
7	$[Ru(bpy)_3](PF_6)_2$	TMU	0
8	$[Ir(bpy)(ppy)_2]PF_6$	DMF	49
9	$[Ir(bpy)(ppy)_2]PF_6$	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] 0.1 mmol **1a**, 2 equiv. acrylate, 1 mol% photoredox catalyst, 5 mol% Ru-catalyst in corresponding solvent at 120 °C using 11 W CFL bulb, Pyr: 2-Pyridyl; [b] yield after column chromatography; DMPU: 1,3-dimethyl-3,4,5,6-tetrahydro-2-pyrimidinone, TMU: Tetramethylurea.

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 shows that no other oxidant is present in the reaction nor is it formed during the reaction independent from the photoredox catalyst. In order to exclude a potential C-H activation through the photoredox catalyst, the reaction was performed without the Ru/Ag components that led to no conversion (Table 2, entry 5). As it was previously reported that oxo- or peroxo species which are typically formed by photoredox processes[16], can be used for the oxidation of metal complexes, the olefination reaction was conducted under an oxygen atmosphere. Thereby, no significant improvement regarding the yield could be observed (Table 2, entry 6). When the oxygen atmosphere was omitted, no reoxidation and therefore stoichiometric conversions concerning the Ru/Ag component occurred. This illustrates that molecular oxygen cannot be used as reoxidant and cannot be converted into an active species in the absence of the photoredox catalyst. Therefore, peroxo species take presumably part in this reaction.

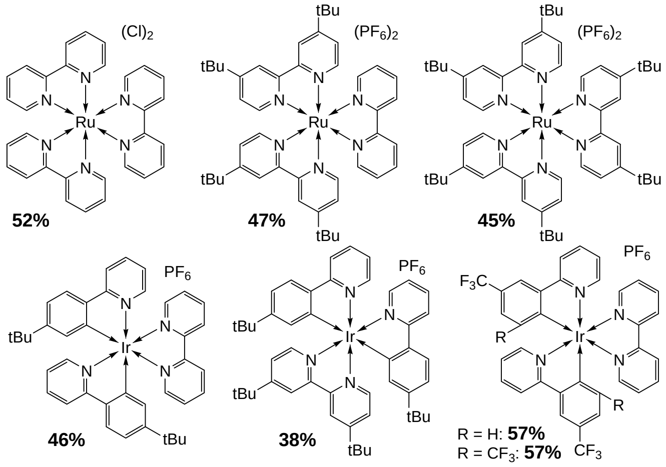
In order to analyze this particular circumstance, the standard reaction was performed in the presence of 1 and 100 mol% photoredox catalyst under an argon atmosphere, respectively (Table 2, entries 8 and 9). The fact that no conversion could be observed using 1 mol% photoredox catalyst proves that the photoredox catalyst itself cannot function as oxidant in the absence of oxygen because no regeneration can take place. In contrast, using 100 mol% of the photoredox catalyst an yield of 38% for the desired product could be obtained (Table 2, entry 9). Since a photoredox cycle can transfer one electron, the conducted reaction shows that the photoredox catalyst itself can also work as oxidant. As final proof of the hypothesis, KO_2 was used as inorganic superoxide anion directly instead of the photoredox catalyst in the reaction under argon atmosphere (Table 2, entry 10). With an isolated yield of 39% the catalysis cycle can be closed again and the peroxo species identified as active oxidant. The reduced yield using KO_2 derive from the instability of the inorganic salt what most probably leads to decomposition at reaction temperatures of 120 °C before full reoxidation of the metal complex could be provided. This moreover illustrates the user-friendly application of the photoredox process that allows users to abandon oxidizing and potentially explosive reagents but also to obtain higher yields by the use of catalytic, photoredox-based generation processes in adequate portions.

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



Entry[a]	Catalyst	Photocatalyst	Cond.	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] / $AgSbF_6$	--	1 eq. KO_2/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] 0.1 mmol **1a**, 2 equiv. acrylate, 1 mol% photoredox catalyst, 5 mol% [Ru]-catalyst in corresponding solvent at 120 °C using 11 W CFL bulb. [b] yield after column chromatography. [c] 100 mol% photoredox catalyst, O_2^{2-} was detected during the reaction. [d] 3 mol% photoredox catalyst. [Ru]: [Ru(*p*-cymene)Cl$_2$]$_2$

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

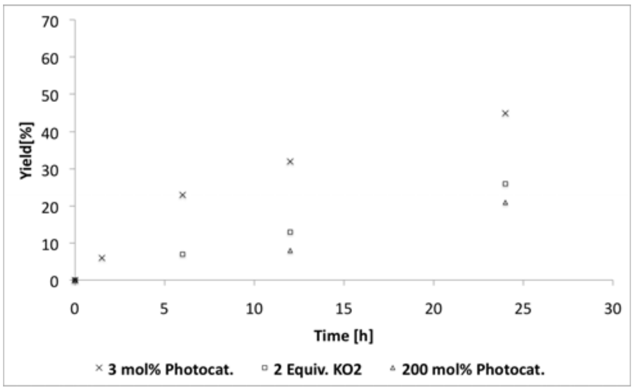
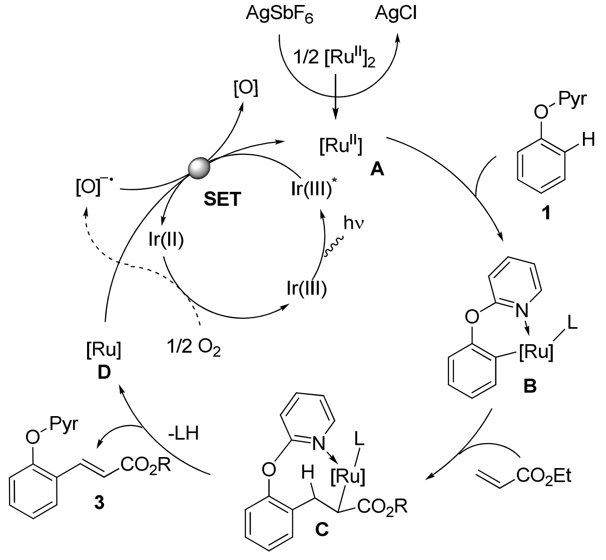


Figure 1. Yield-time correlation of the olefination reaction.

In order to gain deeper insights into the individual regeneration processes mediated by the superoxide anion and the photoredox catalyst, yield-time plots with the corresponding oxidants were conducted (Figure 1). The individual regeneration processes for the hydride oxidation, analyzed individually, - either with KO_2 (2 equiv.) or photoredox catalyst (200 mol%) under an argon atmosphere – proceeded much slower compared to standard reaction conditions (3 mol% photoredox catalyst under air) and therefore led to lower yields after 24 h. However, when both processes are combined in the standard reaction conditions, in which both the photoredox as well as the *in situ* generated superoxide anion processes can be executed simultaneously, an increase in the reactivity takes place and higher yields are obtained.

This can be explained by the fact that only small amounts of the highly reactive superoxide anions are formed by the photoredox process that consecutively are being rapidly consumed and therefore are notpresent in excess amounts. If in contrast larger amounts are present, side and consecutive reactions will be the reason for lower yields of the desired product.

Using the obtained data, the following reaction mechanism can be formulated: After obtaining the active Ru(II) catalyst **A** via 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 yielding intermediate **C** and reductive elimination of product **3**, ruthenium complex **D** is obtained. The, with visible light irradiated photoredox catalyst Ir(III)* is now capable of oxidation via electron transfer regenerating the catalytically active Ru-species **A**. The resulting Ir(II)-complex is now oxidized back to Ir(III) by molecular oxygen and a superoxide anion is generated. The superoxide anion itself is then able again, by electron acceptance, to oxidize the Ru complex **D**.

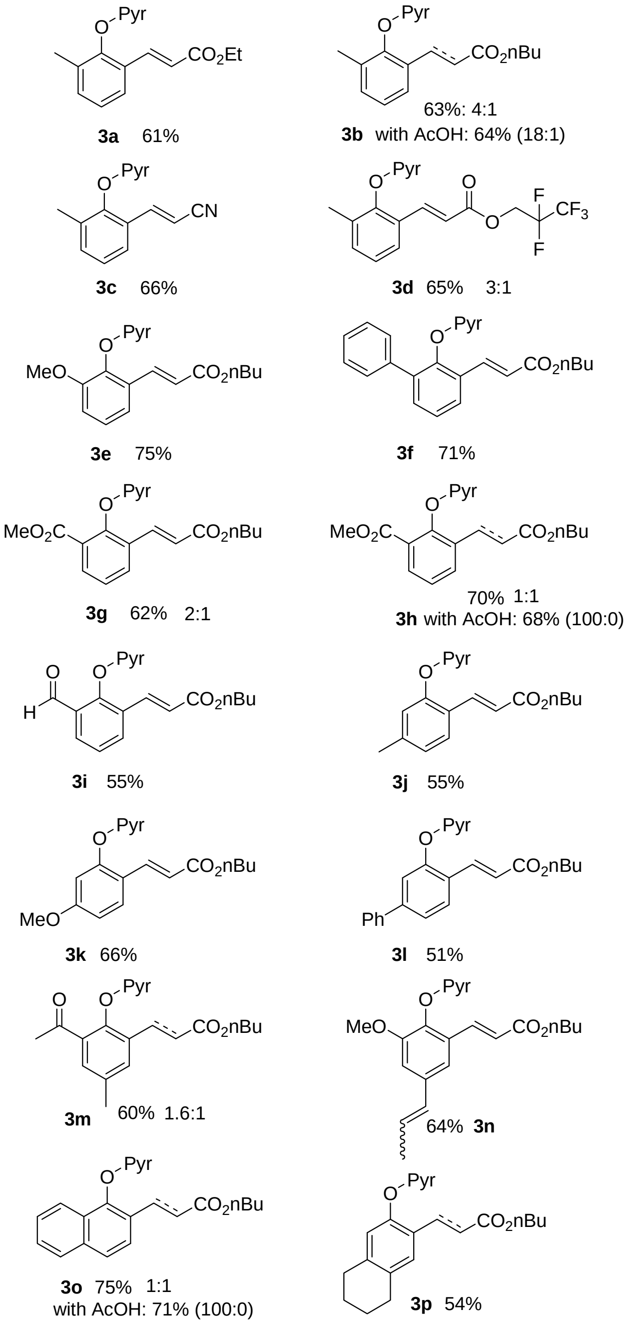


Scheme 2. Proposed mechanism for the combined olefination reaction.

Subsequently, we began to investigate the substrate scope of this newly developed methodology. The acrylate component was thereby first varied. It was apparent that this only had a small influence on the reaction and the products were isolated with comparable good yields (Table 3, row 1 and 2). Electron-donating substituents in *ortho*-position even increased the yield up to 75% for a OMe-group. The electron-poor compounds **3g-i** could also be successfully applied in the olefination reaction that moreover underlines the applicability of the reaction due to its tolerance against aldehydes, ketones, and esters. Subsequently also *meta*-substituted substrates, as well as substrates with more complex substitution patters were applied and successfully olefinated (Table 3, rows 5-8). Independent from the electronic or steric character of the substrates, partial hydrogenation of the double bond was observed. This consecutive hydrogenation based on the ruthenium-hydride complex led then to a mixture of the olefinic and hydrogenated product. This reactivity of homogeneous ruthenium complexes has been previously reported by other groups in different contexts.[17]

In order to determine whether the obtained ratio of the olefin-alkane-components can be controlled, naphthyl derivative **1o** was chosen as model substrate and different additives were tested under the standard reaction conditions. Since the consecutive reaction involves participation of a hydride, we decided to test a variety of acids with different acidities as additives. We were pleased to see that the middle-strong acetic acid (Table 1, SI) not only gave comparable yields for product **3o** but also that addition of the acid suppressed any consecutive hydrogenation. When the strong acid TsOH was used, the obtained ratio of olefin to alkane was only 6:1 with a yield of 46%. Different weak acids such as a benzoic acid derivative or diphenyl phosphate indeed led to a 100% selectivity in favor of the olefin but to lower yields compared to acetic acid. Addition of water as co-solvent led to lower yields of 23% with an olefin to alkane ratio of 2:1. Acetic acid proved to be an efficient additive also for other representative substrates like **3b** and **3h** for the suppression of consecutive hydrogenations in similar yields.

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



3a 61%

3b 63%: 4:1
with AcOH: 64% (18:1)

3c 66%

3d 65% 3:1

3e 75%

3f 71%

3g 62% 2:1

3h 70% 1:1
with AcOH: 68% (100:0)

3i 55%

3j 55%

3k 66%

3l 51%

3m 60% 1.6:1

3n 64%

3o 75% 1:1
with AcOH: 71% (100:0)

3p 54%

[a] 0.2 mmol substrate **1**, 1 equiv. AcOH, 2 equiv. Olefin, 3 mol% $[Ir(bpy)(ppy)_2]PF_6$, 5 mol% Ru-catalyst / 20 mol% $AgSbF_6$ in DMA at 120 °C using a CFL bulb, yields after column chromatography, ratios given for olefin:alkane.

In summary, we report a new combination of photoredox and metal catalysis for the olefination reaction of phenols via C-H activation. The unique interplay of metal and photoredox catalysis allowed the directed reoxidation of the metal-hydride intermediate which allowed a catalytically performed regeneration of the catalyst.

Mechanistic studies revealed that a maximization of the regeneration reaction could be obtained when small amounts of superoxide anions, formed by photoredox-generated processes, were generated which could also work as oxidant. Since only small amount of oxidants are generated, side reactions of substrate and product could not be observed that allows the use of oxidant-sensible molecules. Based on mechanistic studies we could show that using acid additives or adjusting the catalyst ratios, respectively, allow the selective synthesis of olefinated phenol derivatives in good yields. As the yields are comparable with stoichiometric, copper-based reactions, an extension to other C-H functionalizations could be possible and feasible. Besides, the combination of metal and photoredox catalysis should be transferable to other C-H functionalizations.

Keywords: CH Functionalizations • Photoredoxcatalysis • Superoxide Anion • visible light • alkenylation

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