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Ruthenium-Catalyzed, Site-Selective C−H Allylation of Indoles with Allyl Alcohols as Coupling Partners

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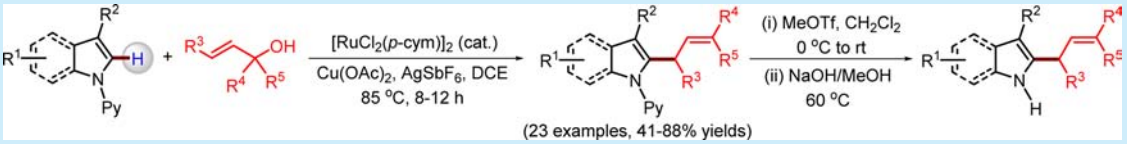
Supporting Information

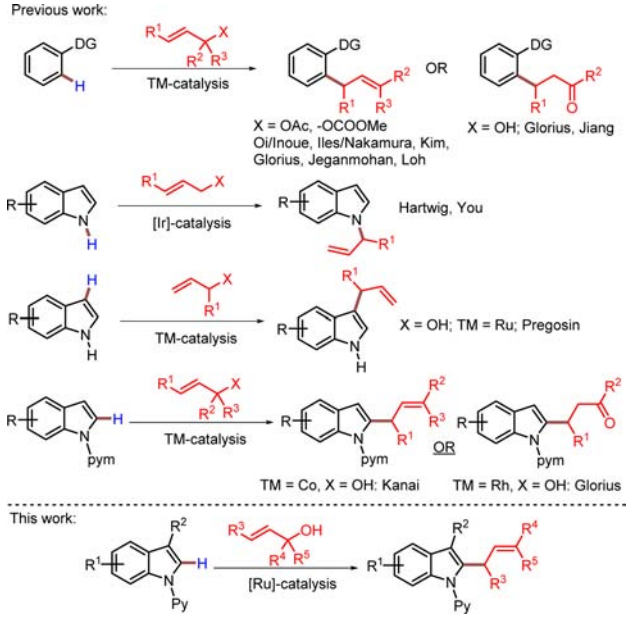


ABSTRACT: A new ruthenium-catalyzed, heteroatom-directed strategy for C−H allylation of indoles is described. The use of allyl alcohols as coupling partners as well as pyridine as the removable directing group is highlighted. This methodology provides access to C2-allylated indoles by utilizing a strategy that does not require prefunctionalization of either of the coupling partners.

The allylation reaction has been a well studied transformation with the palladium-catalyzed Tsuji−Trost allylation bringing about a revolution in this field.[1] Over the years this reaction has undergone a metamorphosis and has been extended to simple arenes as well. Earlier, the reaction was limited to derivatives of allylic alcohols, and in most cases, allyl acetates were used. Now, the reaction has been extended to allylic alcohols as well.[2,3] With the advent of C−H functionalization reactions,[4] the C−H allylation reaction has generated great interest in the scientific community. Selective functionalization of proximal C−H bonds has been made feasible by the use of suitable Lewis basic directing groups.[5] Sometimes, these groups are difficult to remove once the transformation has been carried out. Those directing groups, which can be removed after their utility is over, hold higher synthetic value than those that cannot be done away with.

Nitrogen heterocycles, and in particular indoles, are of great synthetic interest to chemists due to their relevance in biological systems.[6a−d] The functionalization of indoles has therefore merited considerable attention from organic chemists.[6e] In recent years, the C2 C−H functionalization of indoles has proved to be a worthy alternative to traditional functionalization methods that were earlier employed. Considerable work has been done in the area of allylation of arenes via C−H activation.[7−9] The allylation reaction with allyl alcohol derivatives, such as acetates or allyl halides, usually leads to the typical γ-allylated products. The use of allyl alcohols, in turn, can lead to ketones or aldehydes (Scheme 1).[10] The allylation of indoles also has been well studied.[11] Of the four possible scenarios (*N*-allylation,[11a−c] C-2, C-3,[2a,b] or C7[8i] allylation), directed allylation at the C-2 position of indoles has recently gained importance.[11e−h] Here too, the employment of activated allyl alcohols such as allyl acetates or halides results in allylated products, whereas Glorius et al. reported the use of allyl alcohols in the Rh-catalyzed C−H functionalization of indoles, resulting in aldehydes.[10a] Notable is the work of Kanai et al.,[11f] where the same *N*-pyrimidyl substrate was successfully allylated under cobalt catalysis using allyl alcohols.

Scheme 1. C−H Allylation Reactions and Indole Allylations



Our group has also been interested in the C−H functionalization as well as synthesis of indoles via transition metal catalysis.[12] To the best of our knowledge, the ruthenium catalyzed C2 C−H allylation of indoles using allyl alcohols has not been reported. We report herein, the *N*-pyridine directed ruthenium-catalyzed site-selective C−H allylation of indoles and pyrroles, in which unactivated allyl alcohols are employed as coupling partners. The

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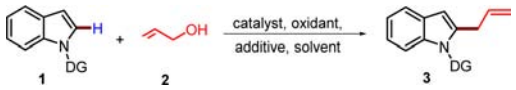
other highlight of this work is the scope of removal of the directing group.

The evolution of the work began with the quest for the best combination of directing groups with the catalyst system. The most important results are summarized in Table 1 (for the

Table 1. Optimization Studies[a]



entry	directing group	catalyst/oxidant/additive/solvent/temp/time	yield (%)
1	2-pyridyl	$Pd(OAc)_2/Cu(OTf)_2/AgSbF_6$/dioxane/ 100 °C/12 h	<5[d]
2	acetyl	$[RuCl_2(p\text{-cym})]_2/Cu(OAc)_2/AgSbF_6$/THF/ 60 °C/12 h	0
3	2-pyrimidyl	$[RuCl_2(p\text{-cym})]_2/Cu(OAc)_2/AgSbF_6$/THF/ 60 °C/12 h	0
4	$-CONMe_2$	$[RuCl_2(p\text{-cym})]_2/Cu(OAc)_2/AgSbF_6$/THF/ 60 °C/12 h	0
5	2-pyridyl	$[RuCl_2(p\text{-cym})]_2/Cu(OAc)_2/AgSbF_6$/ dioxane/100 °C/10 h	70[b]
6	**2-pyridyl**	**$[RuCl_2(p\text{-cym})]_2/Cu(OAc)_2/AgSbF_6$/DCE/ 85 °C/12 h**	**85**[b]
7	2-pyridyl	$[RuCl_2(p\text{-cym})]_2/O_2$ Balloon/$AgSbF_6$/DCE/ 80 °C/10 h	<5[c]
8	2-pyridyl	$[RuCl_2(p\text{-cym})]_2/Cu(OTf)_2/AgSbF_6$/DCE/ 85 °C/10 h	<5[d]
9	2-pyridyl	$[RuCl_2(p\text{-cym})]_2$/NaOAc/$AgSbF_6$/DCE/85 °C/10 h	70[b]
10	2-pyridyl	$[RuCl_2(p\text{-cym})]_2/Cu(OAc)_2/ AgBF_4$ (0.5 equiv)/DCE/85 °C/10 h	67[b]
11	2-pyridyl	$[RuCl_2(p\text{-cym})]_2/Cu(OAc)_2$/DCE/80 °C/ 10 h	0
12	2-pyridyl	$Cu(OAc)_2/AgSbF_6$/DCE/85 °C/12 h	0

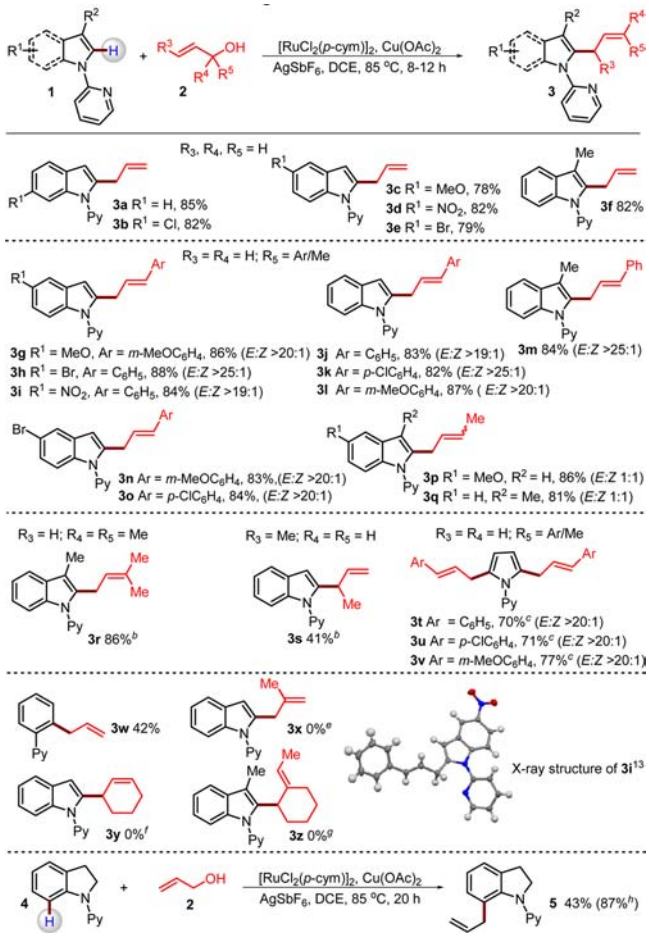
[a]Reaction conditions: unless otherwise mentioned all reactions performed with **1a** (0.3 mmol), **2a** (0.45 mmol), 5 mol % catalyst, 2 equiv of oxidant, and 0.2 equiv of additive in 1.5 mL of solvent. [b]Isolated yield. [c]GC yield. [d]Complex mixture was obtained.

remaining attempts toward optimization, see the Supporting Information (SI)). Initially, simple and readily available palladium catalysts were screened. These efforts, however, did not produce the desired results. The use of other directing groups also did not help (Table 1). The best results were obtained with the *N*-pyridyl directing group, when using ruthenium catalysis, with $AgSbF_6$ as the additive and $Cu(OAc)_2$ as the oxidant. The best solvent for this transformation was dichloroethane. Under some conditions (see the SI), we observed traces of the aldehyde arising from the β-hydride elimination pathway. Under some of the conditions (entry 8, Table 1), the C-3 allylated product was also observed in minor quantities.

This probably arose from the copper salt acting as a Lewis acid to activate the allyl alcohol, thereby resulting in an electrophilic reaction at C-3 of the indole. Under the optimized reaction conditions, the use of a pyrimidine directing group did not result in the desired product; the starting material remained unreacted. The use of both $Cu(OAc)_2$ and $AgSbF_6$ were necessary, which was proved by poor conversions in the absence of any one of these. A control reaction, carried out in the absence of the Ru-catalyst, did not yield the allylated product.

The substrate scope for this transformation is depicted in Scheme 2. The reaction was well-tolerant of all functional groups screened. The reaction worked well for electron-withdrawing and -donating substituents on the indole skeleton. The reaction

Scheme 2. Substrate Scope for the Reaction[a,d]



[a]All reactions were carried out with 0.3 mmol of **1** and 1.5 equiv of **2** unless otherwise noted. All yields are isolated yields. [b]7 mol % catalyst and 0.3 equiv additive were used. [c]2 equiv of allyl alcohol were used. [d]*E:Z* ratio determined by ^1H NMR of reaction mixture. [e]From 2-methylprop-2-en-1-ol. [f]From cyclohex-2-en-1-ol. [g]From 1-(cyclohex-1-en-1-yl)ethan-1-ol. [h]Based on recovered starting material.

worked well with most of allyl alcohols screened for the substrate scope. In almost all cases, the stereochemistry of the resulting olefin was *E*. In some cases isomeric products were observed (entries **3p−q**, Scheme 2). The selectivity was excellent, with the γ-selectivity predominating almost exclusively. With the site selectivity too, only the C-2 C−H functionalization product was observed. There were some notable failures, mainly due to steric reasons (entries **3x−z**, Scheme 2). Another reason could be the lack of feasibility of the β-hydroxide elimination in **3y**. Steric reasons could also be attributed for the low yield in the case of **3s**.

Substrates with halosubstituents too worked very well, yielding products which have scope for further functionalization. Interestingly, the pyrroles (**3t−v**, Scheme 2) were also successfully synthesized from the corresponding *N*-pyridyl pyrrole. Since the reaction was not monoselective, we used an excess of the allyl alcohol to obtain the diallylated product directly. Substrate **3w** was also successfully synthesized in moderate yield, proving the efficiency of the pyridyl directing group. The same reaction, when carried out with *N*-pyridyl-2,3-dimethylindole, was extremely sluggish and resulted in a complex mixture, along with the recovered starting material. The *N*-pyridyl indoline **4**, however, reacted well to result in the C-7

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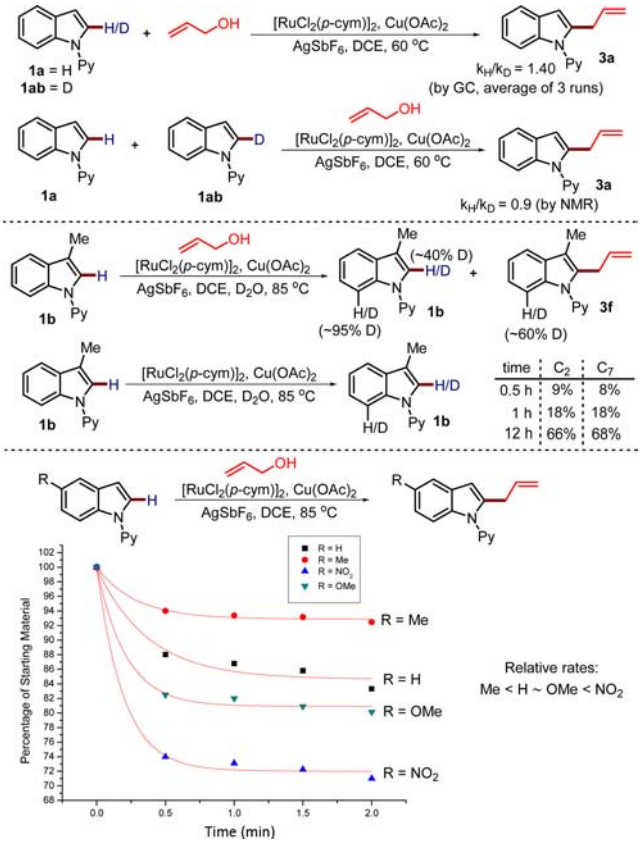
allylated product. Nonetheless, the reaction rate in this case was much lower than that for the corresponding indole.

To shed light on the probable mechanistic pathway involved in the transformation, kinetic isotope effect studies were undertaken (Scheme 3).[14] A moderately low value of 1.40 was obtained

Scheme 3. Mechanistic Studies

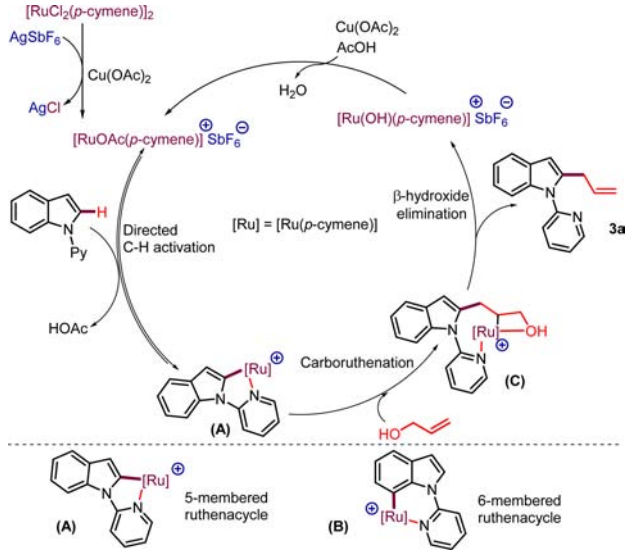


for individual experiments, whereas a value of 0.9 was obtained via competitive studies, thereby indicating absence of a primary kinetic isotope effect. To check for reversibility of the formation of the ruthenacycle, quenching studies were undertaken, in both the presence and absence of the coupling partner. In the presence of the coupling partner, the recovered starting material (after 5 min) had a deuterium content of about 40% at C2. Surprisingly, in the presence of D_2O, the reaction seemed to accelerate considerably. In the absence of the coupling partner, the reaction resulted in about 66% deuterium incorporation into the starting material at C2 (after 12 h, Scheme 3), thereby proving the reversibility of the formation of the ruthenacycle. In both experiments, the C7 position was also deuterated (Scheme 3).

We also attempted to explore the electronic effect of the C5 substituent on the rate of the reaction. The 5-nitro substrate seemed to react faster whereas the 5-methyl substrate was comparatively the slowest. The unsubstituted and the 5-methoxy substrates had quite similar rates.

A plausible reaction pathway is proposed in Scheme 4, based on our observations as well as literature reports. The first step is the generation of the cationic Ru(II) catalyst, followed by coordination of the metal to the pyridine nitrogen. This is then followed by the proximal C−H activation at C-2, to result in the ruthenacycle **A**. Insertion of the allyl alcohol via carboruthenation results in **C**. The intermediate **C** now has the option of β-hydride elimination or β-hydroxide elimination. It could be

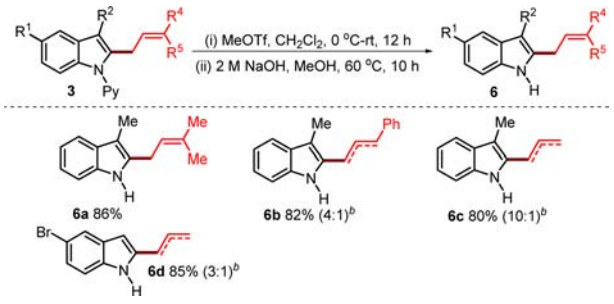
Scheme 4. Plausible Mechanism



postulated that the oxophilicity of the metal may drive the reaction to choose the latter pathway. The regeneration of the active catalyst by $Cu(OAc)_2$ and AcOH completes the catalytic cycle. Observation of the γ-selectivity and previous reports[7g,11f] seem to rule out the S_N2' pathway as well as the formation of the π-allyl intermediate. The fact that considerable deuterium incorporation was observed at the C7 position in our quenching studies with D_2O indicated a reversible C−H activation and ruthenacycle formation at C7. However, this six-membered ruthenacycle (**B**) is expected to have a relatively lower stability than the five-membered ruthenacycle (**A**) formed from the C2 C−H activation (Scheme 4). This would probably explain the preferential formation of the C2 allylated product over the C7 allylated one.

We were also successful in the removal of the pyridyl directing group.[15] The reaction with MeOTf followed by alkali treatment resulted in a clean conversion to the NH-indole (Scheme 5). In some cases, isomerization of the olefin was also observed in the deprotection reaction.

Scheme 5. Removal of the Pyridine Directing Group[a]



[a]All yields are isolated yields. [b]Ratio of terminal alkene/internal alkene.

In summary, we have developed a new Ru(II) catalyzed C−H allylation method for indoles using unactivated allyl alcohols. A removable *N*-pyridyl directing group was employed in the reaction, thereby increasing the utility of the reaction. The site selectivity for C−H functionalization was exclusive, and the allylation reaction was highly γ-selective. The transformation was

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a clean reaction with very good yields for most substrates. This is one of the few allylation methods in which unactivated allyl alcohols are employed as coupling partners and the catalyst system is simple and rather inexpensive.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b00217.

Experimental procedures and full spectroscopic data for all new compounds (PDF)

Crystal structure data (X-ray) for compound **3i** (CIF)

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Notes

The authors declare no competing financial interest.

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