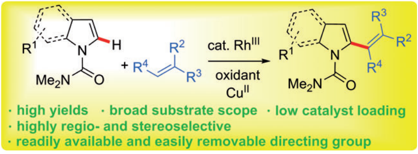
Be economic with your atoms! An efficient Rh-catalyzed oxidative olefination of indoles and pyrroles with broad substrate scope and tolerance is reported (see scheme). The catalytic reaction proceeds with excellent regio- and stereoselectivity. The directing group *N*,*N*-dimethylcarbamoyl was crucial for the reaction and could be removed easily.



· high yields · broad substrate scope · low catalyst loading
· highly regio- and stereoselective
· readily available and easily removable directing group

Homogeneous Catalysis

B. Li, J. Ma, W. Xie, H. Song, S. Xu, B. Wang** .... ▮▮▮▮–▮▮▮▮

Regioselective C2 Oxidative Olefination of Indoles and Pyrroles through Cationic Rhodium(III)-Catalyzed C−H Bond Activation

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Regioselective C2 Oxidative Olefination of Indoles and Pyrroles through Cationic Rhodium(III)-Catalyzed C−H Bond Activation

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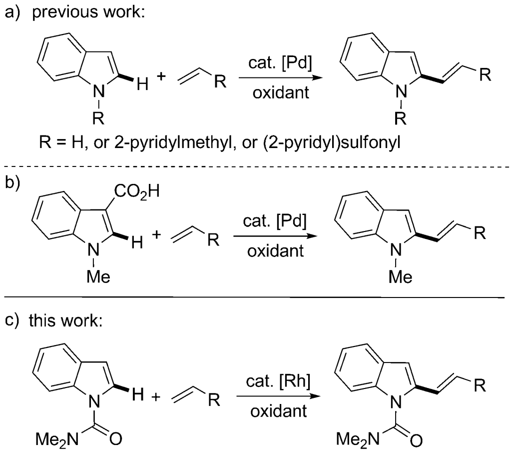
The Mizoroki–Heck reaction is one of the most important metal-catalyzed cross-coupling reactions for the formation of a C−C bond from a C−X bond.[1] However, direct C−H bond transformations allow the use of less expensive and more readily available starting materials without prior functionalization, and thus represent a more atom-economic and step-simplified strategy.[2] As a result, the process of the oxidative olefination of normally unreactive aryl C−H bonds, known as the Fujiwara–Moritani reaction,[3] is an attractive alternative to the traditional Mizoroki–Heck reaction and has made remarkable developments during these years. Among the reports, palladium[4] and rhodium[5] complexes are the most frequently used catalysts for this type of transformation. For these reactions, the use of a directing group especially a readily removable directing group, is the one of the most popular strategies to obtain a selective C−H activation.

The indole skeleton is an important structural unit and is widely found in bioactive natural compounds and pharmaceutical industry products.[6] Therefore, the efficient functionalization of indole derivatives has attracted much attention from both academia and industry, especially with regard to transition-metal-catalyzed C−H bond activation. Over the past decades, many efforts have been focused on regioselective C−H bond arylation at the C2- and C3-positions of indoles.[7] However, the oxidative C−H olefination is much less explored[8] especially for the intermolecular C2 alkenylation of indoles.[8a–c,g,h] A survey of reports on intermolecular C2 oxidative Heck reactions of indoles reveals that only four palladium-catalyzed protocols have been independently developed by the research groups of Ricci,[8g] Gaunt,[8h] Miura and Satoh,[8c] and Carretero and Arrayás.[8a,b] Employing *N*-2-pyridylmethyl as a directing group, Ricci and co-workers reported a Pd^{II}-catalyzed regiocontrolled C2 alkenylation of indole (Scheme 1a). Gaunt et al. demonstrated a selective Pd^{II}-catalyzed C2- or C3- oxidative alkenylation of free (NH) indoles by employing different solvents and additives (Scheme 1a). Later, Miura, Satoh, and co-workers described an exclusive C2 alkenylation method of indoles through Pd^{II}-catalyzed C−H olefination of indole-3-carboxylic acids, in which decarboxylation of the carboxyl group occurred during the reaction process (Scheme 1b). Recently, Carretero and Arrayás et al. developed a *N*-(2-pyridyl)sulfonyl group directed C2 alkenylation of indole with a broad substrate scope of alkenes based on the $[Pd(CH_3CN)_2Cl_2]$ catalyst, in which the directing group could be removed under mild conditions (Scheme 1a). Despite such exciting progress, palladium-catalyzed C2 oxidative alkenylation of indoles suffers from low reaction efficiency, limited substrate scope, and high catalyst loading (often 10 mol %). Moreover, despite the wide application of Rh complexes in the Fujiwara–Moritani reaction, Rh-catalyzed C2 oxidative olefination indoles has rarely been reported.[5l] As a continuation of our interest in metal-catalyzed C−H functionalization,[9] we here disclose our development of cationic Rh^{III}-catalyzed selective oxidative coupling of indoles and pyrroles with alkenes exclusively at the C2-posi-



Scheme 1. C2 oxidative Heck reactions of indoles.

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tion with the use of the easily removed *N*,*N*-dimethylcarbamoyl moiety as the directing group (Scheme 1c).

In the initial study, the coupling reactions of various N-substituted indoles (**1**) with styrene (**2a**) were examined. The choice of the protecting group on indole was found to be crucial, with *N*,*N*-dimethylcarbamoyl being optimal.[10] After many trials, we were pleased to find that treatment of *N*,*N*-dimethyl-1*H*-indole-1-carboxamide (**1a**) (1.0 equiv) and **2a** (3.0 equiv) in the presence of 2.0 mol % of [Rh(CH_3CN)$_3$(Cp*)][SbF_6]$_2$ (Cp* = C_5Me_5) as the catalyst and 2.0 equivalents of $Cu(OAc)_2{\cdot}H_2O$ as the oxidant in THF at 100 °C for 24 h gave the desired Heck-type product **3aa** in near quantitative isolated yield (Table 1, entry 1). The structure of **3aa** was confirmed by ^{1}H and ^{13}C NMR spectroscopy and mass spectrometry. To our delight, the reaction proceeded with excellent regio- and stereoselectivity with the formation of the C2 *E*-alkenylation product exclusively.

With the optimized conditions in hand, we then investigated the reaction of **1a** with various alkenes (**2**; Table 1). The reaction showed broad substrate tolerance with a range of alkenes. Both electron-rich and -poor substituted styrenes efficiently reacted with **1a** to give the desired products **3ab–ai** in good to excellent yields (Table 1, entries 2–9) in a highly regio- and stereoselective manner. The molecular structure of complex **3af** was further confirmed by X-ray diffraction analysis (Figure 1). Under the reaction conditions, the acrylates exhibited much higher reactivity than styrenes: the reactions afforded a mixture of C2-monoalkenylated and C2,C7-dialkenylated products. This was confirmed by the coupling of 2-methyl-substituted indole counterpart **1k** with ethyl acrylate, which proceeded at the C7-position of indole (Scheme 3, vide infra). Upon changing the ratio of the two reactants, C2-monoalkenylated complexes **3aj** and **3ak** were isolated in 77 and 90 % yields as the sole products, respectively (entries 10 and 11). Notably, these two reactions proceeded smoothly even when 1.0 mol % of catalyst was employed. Other alkenes bearing electron-withdrawing groups including (phenylsulfonyl)ethene (entry 12), diethyl vinylphosphonate (entry 13), and acrylonitrile (entry 14) could also be used as the substrates. Unconjugated terminal alkene product **3ao** could be obtained in 49 % yield when allyl acetate acted as the coupling partner (entry 15). Formation of related terminal olefins starting from allyl acetate has been reported.[11]

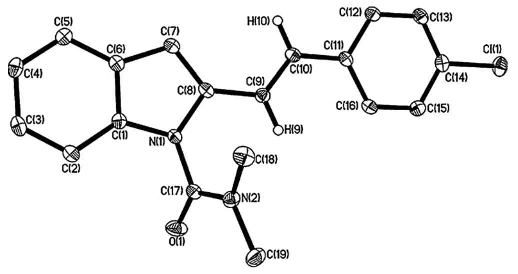
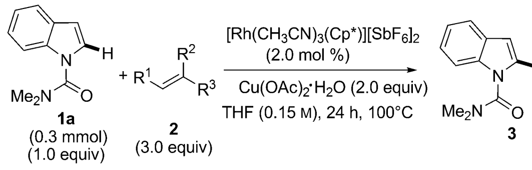
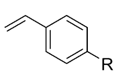
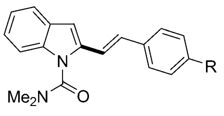
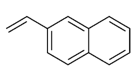
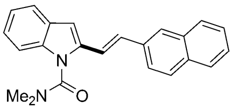
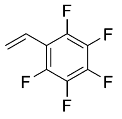
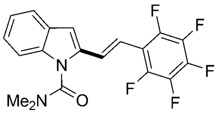
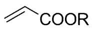
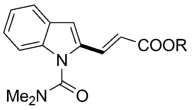
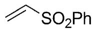
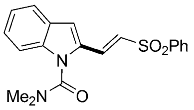
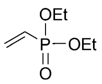
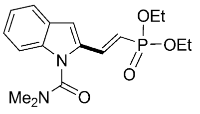
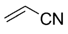
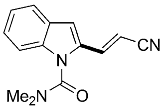
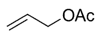
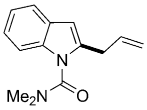
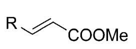
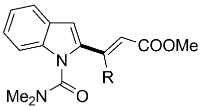
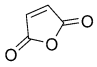
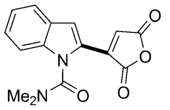
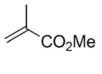
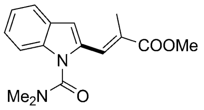
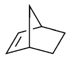
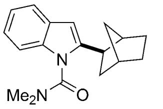


Figure 1. ORTEP of compound **3af**; thermal ellipsoids are set at 30 % probability. Hydrogen atoms except H(9) and H(10) have been omitted for clarity.

Table 1. Olefin scope of the rhodium-catalyzed oxidative C2 olefination of **1a**.



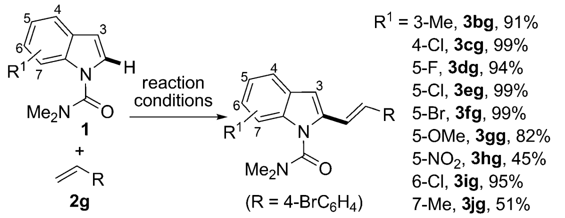
Entry	Alkene	Product	Yield [%][a]
1			R = H, **3aa**, 99 %
2			Me, **3ab**, 96 %
3			*t*Bu, **3ac**, 99 % (**3ac**, 98 %)[b]
4			OMe, **3ad**, 94 %
5			F, **3ae**, 83 %
6			Cl, **3af**, 99 %
7			Br, **3ag**, 99 %
8			**3ah**, 80 %
9			**3ai**, 86 %
10			R = Et, **3aj**, 77 %[c] (**3aj**, 78 %)[b]
11			*n*Bu, **3ak**, 90 %[c]
12			**3al**, 75 %
13			**3am**, 90 %
14			**3an**, 53 %[d,e]
15			**3ao**, 49 %[f]
16			R = Me, **3ap**, 98 %
17			Ph, **3aq**, 47 %
18			**3ar**, 32 %[d,e]
19			**3as**, 50 %[d,e]
20			**3at**, 92 %[f,g]

[a] Isolated yield. [b] The data in parentheses refers to the yield performed on a 3.0 mmol scale. [c] **1a** (1.5 equiv), alkene (1.0 equiv), and Rh cat. (1 mol %). [d] Rh catalysts (5.0 mol %). [e] 36 h. [f] Rh catalyst (4.0 mol %). [g] 48 h.

This protocol was also successfully applied for highly substituted alkenes, including 1,2- and 1,1-disubstituted alkenes. An excellent yield was obtained with (*E*)-methyl crotonate, affording the desired product **3ap** (Table 1, entry 16).[12] (*E*)-Methyl cinnamate, maleic anhydride, and methyl methacrylate were also suitable coupling partners to provide the corresponding trisubstituted alkene products **3aq**, **3ar**, and **3as**, respectively (entries 17–19).

Interestingly, the coupling of norbornene with indole **1a** yielded the alkylated product **3at** instead of the expected alkenylated one (Table 1, entry 20). The molecular structure was confirmed by X-ray diffraction analysis and a pair of enantiomers was observed (Figure 2).

The scope of the reaction with respect to the indole reactant was also explored for this alkenylation process (Scheme 2). Both electron-rich and -poor indole substrates bearing various groups at different positions (C3 to C7) of the indole ring participated well in the reaction, providing the corresponding products **3bg–jg**. The indole counterpart with 7-methyl group gave the desired product in a moderate yield, this might be due to the steric hindrance between the C7 methyl and *N*,*N*-dimethylcarbamoyl directing group. Moreover, many functional groups, such as fluoro (**3dg**), chloro (**3cg**, **3eg**, and **3ig**), bromo (**3fg**), methoxy (**3gg**), and nitro (**3hg**) substituents, were compatible in the present catalytic reaction.



Scheme 2. Scope of the rhodium-catalyzed oxidative C2 olefination of indoles. Isolated yields are given. Reaction conditions: **1** (1.0 equiv), **2g** (3.0 equiv), $[Rh(CH_3CN)_3(Cp^*)][SbF_6]_2$ (2.0 mol %), and $Cu(OAc)_2{\cdot}H_2O$ (2.0 equiv) in THF (0.15 M) at 100 °C for 24 h. For products **3hg** and **3jg**, 4.0 mol % of the Rh catalyst was used and the reaction was conducted for 36 h.

It should be noted that when indole **1k**, in which the reactive C2-position was blocked, reacted with ethyl acrylate the C7 alkenylation complex resulted in 27 % yield as the only product instead of the C3-position alkenylation product (Scheme 3). This result is in contrast to the previous report catalyzed by Pd complex. It could be rationalized by the formation of the six-membered rhodacycle (**A**) from the C–H activation of the C7-position with the assistance of the *N*,*N*-dimethylcarbamoyl directing group.

Moreover, the reactions were conducted on a large scale (3.0 mmol) with good performance: 98 and 78 % isolated yields for **3ac** and **3ai**, respectively (Table 1). The dimethylcarbamoyl group can be easily removed by using KO*t*Bu in THF at room temperature or NaOH in EtOH at 90 °C (Scheme 4).[13] Both of these results highlight the potential synthetic utility of this method.

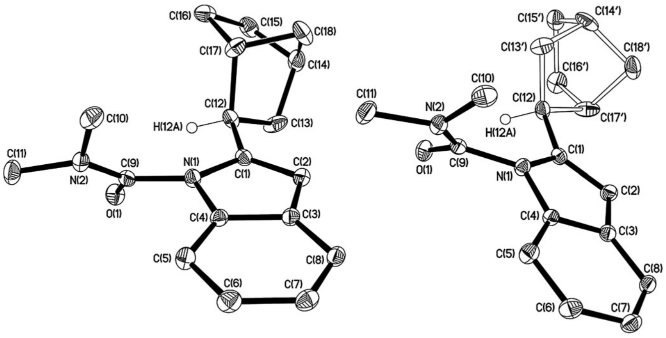
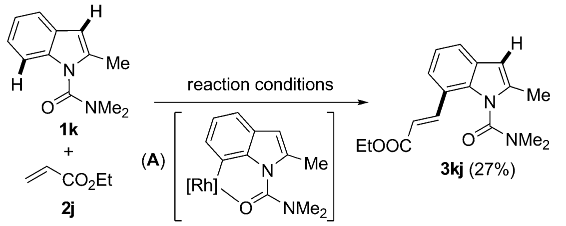
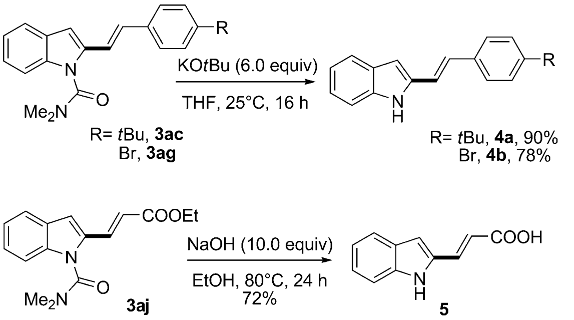


Figure 2. ORTEP of compound **3at**; thermal ellipsoids are set at 30 % probability. Hydrogen atoms except H(12A) have been omitted for clarity.

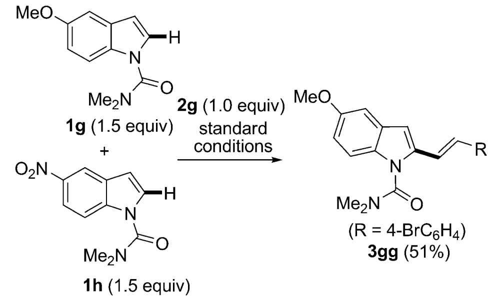


Scheme 3. Rhodium-catalyzed oxidative C7 olefination of indole **1k**. Reaction conditions: **1k** (1.0 equiv), **2j** (3.0 equiv), $[Rh(CH_3CN)_3(Cp^*)][SbF_6]_2$ (1.0 mol %), and $Cu(OAc)_2{\cdot}H_2O$ (2.0 equiv) in THF (0.15 M) at 100 °C for 48 h.

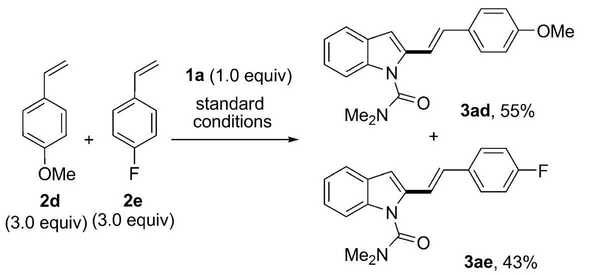


Scheme 4. Removal of the carbamate group.

Given the high efficiency of the rhodium(III) catalyst, we conducted mechanistic studies to probe the working mode of the reaction. First, intermolecular competition experiments between indoles **1g** and **1h** with a single equivalent of alkene **2g** under the standard conditions revealed that electron-rich indole **1g** is transformed preferentially (Scheme 5). Then, intermolecular competition experiments between substituted styrenes **2d** and **2e** with a single equivalent of indole **1a** indicated that the electron-rich styrene is more reactive under this catalytic system (Scheme 6). Finally, we conducted experiments with isotopically labeled sub-

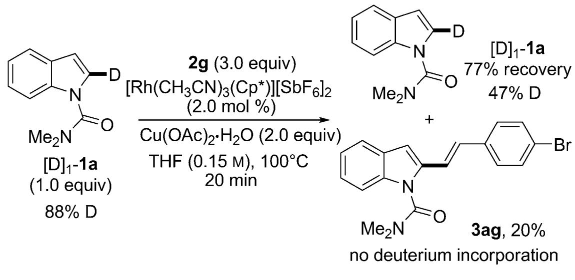


Scheme 5. Intermolecular competition experiments with indoles **1g** and **1h**.



Scheme 6. Intermolecular competition experiments with alkenes **2d** and **2e**.

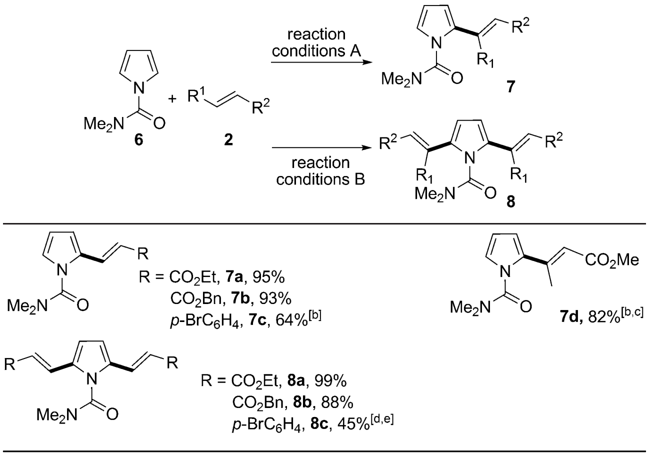
strate. When the C2-position deuterated starting material [D]$_1$-**1a** was subjected to the reaction conditions (Scheme 7), a significant D/H exchange was observed in the recovered starting material, which suggested that the C–H bond metalation step is probably reversible.



Scheme 7. Experiment with isotopically labeled substrate.

After achieving the oxidative olefination reactions with indoles, we next tried to expand our methodology to another widely used substrate, pyrroles, which are useful building blocks and the core motif of many natural products.[14] Up to now, only two protocols of direct C–H alkenylation catalyzed by Pd complex were reported.[8a,b,15] Table 2 outlines the results of our reactions. Gratifyingly, under our Rh-catalyzed reaction conditions, ethyl acrylate and benzyl acrylate reacted with pyrrole **6** smoothly to afford C2-monoalkenylated (**7a** and **7b**) or C2,C5-dialkenylated (**8a** and **8b**) products in high yields, by changing the ratio of the two reactants. A similar method was successfully applied for *p*-bromostyrene but a lower efficiency was observed (**7c** and **8c**). It should be pointed out that the internal alkene (*E*)-methyl crotonate was also a suitable candidate for this reaction, which reacted with **6** to give **7d** in 82 % yield.

Table 2. Scope of the rhodium-catalyzed oxidative C2 olefination of indole.[a]



R = CO_2Et, **7a**, 95%
CO_2Bn, **7b**, 93%
p-BrC_6H_4, **7c**, 64%[b]

7d, 82%[b,c]

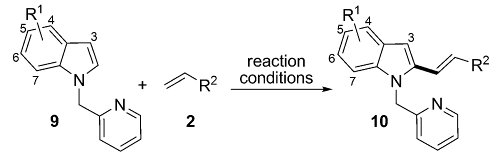
R = CO_2Et, **8a**, 99%
CO_2Bn, **8b**, 88%
p-BrC_6H_4, **8c**, 45%[d,e]

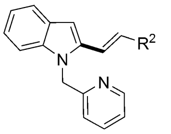
[a] Isolated yields are given. Reaction conditions A: **6** (1.5 equiv), **2** (1.0 equiv), $[Rh(CH_3CN)_3(Cp^*)][SbF_6]_2$ (1.0 mol %), and $Cu(OAc)_2{\cdot}H_2O$ (2.0 equiv) in THF (0.15 M) at 100 °C for 24 h. Reaction conditions B: **6** (1.0 equiv), **2** (5.0 equiv), $[Rh(CH_3CN)_3(Cp^*)][SbF_6]_2$ (2.0 mol %) and $Cu(OAc)_2{\cdot}H_2O$ (4.0 equiv) in THF (0.15 M) at 100 °C for 24 h. [b] 2.0 mol % of the Rh catalyst was used. [c] **6** (1.0 equiv) and **2** (2.0 equiv) were used. [d] 4.0 mol % of the Rh catalyst was used. [e] 30% of monoalkenylation product **7c** was also obtained.

To further highlight the high efficiency of our rhodium catalytic system, the *N*-2-pyridylmethyl, which was introduced by Ricci and co-workers was also tested. It was found not to be suitable for the oxidative coupling with styrene under our Rh-catalyzed system. However, it proved to be a good directing group in the reaction with more active acrylates (Table 3). In the presence of 1.0 mol % of catalyst, a series of acrylates reacted smoothly with **9a** to produce the corresponding Heck-type products **10a–e** in high yields. Furthermore, the substituents at the indole ring did not have a significant impact in the reactivity, the corresponding alkene derivatives **10g–o** were formed in high yields. The molecular structure of complex **10b** was confirmed by X-ray diffraction analysis (Figure 3).

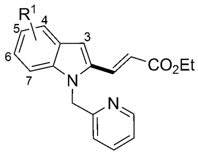
In summary, we have developed an efficient Rh-catalyzed oxidative olefination of indoles and pyrroles assisted by the *N*,*N*-dimethylcarbamoyl protecting group with broad substrate scope tolerance. The catalytic reaction proceeds in an excellent regio- and stereoselective manner. In this reaction, low catalyst loadings are required. The use of a readily available and easily removable *N*,*N*-dimethylcarbamoyl as a directing group also highlights the potential synthetic utility of this protocol. Further studies to explore this new method and metal-catalyzed oxidative C–H bond transformations are under investigation.

Table 3. Scope of the rhodium-catalyzed oxidative C2 olefination of indole **9**.[a]





R^2 = CO$_2$Me, **10a**, 88%
CO$_2$Et, **10b**, 88%
CO$_2$*n*Bu, **10c**, 87%[b]
CO$_2$*t*Bu, **10d**, 79%[b]
CO$_2$Bn, **10e**, 93%
SO$_2$Ph, **10f**, 47%[b]



R^1 = 3-Me, **10g**, 75%
4-Cl, **10h**, 90%
5-F, **10i**, 90%
5-Cl, **10j**, 88%
5-Br, **10k**, 95%

R^1 = 5-OMe, **10l**, 81%
5-NO$_2$, **10m**, 81%
6-Cl, **10n**, 90%
7-Me, **10o**, 78%

[a] Isolated yields are given. Reaction conditions: **9** (1.0 equiv), **2** (2.0 equiv), [Rh(CH$_3$CN)$_3$(Cp*)][SbF$_6$]$_2$ (1.0 mol %), and Cu(OAc)$_2$·H$_2$O (2.0 equiv) in THF (0.15 M) at 100 °C for 24 h. [b] 2.0 mol % of the Rh catalyst was used.

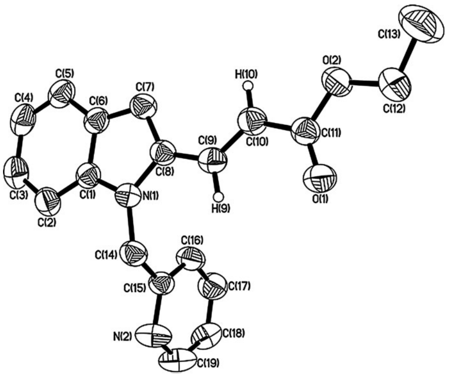


Figure 3. ORTEP of compound **10b**; thermal ellipsoids are set at 30% probability. Hydrogen atoms except H(9) and H(10) have been omitted for clarity.

Experimental Section

General procedure for the rhodium-catalyzed oxidative coupling of 1 with alkenes: A mixture of indole substrate **1** (0.30 mmol, 1.0 equiv), [Rh(CH$_3$CN)$_3$(Cp*)][SbF$_6$]$_2$ (5.00 mg, 0.006 mmol, 2.0 mol%), Cu(OAc)$_2$·H$_2$O (120.0 mg, 0.60 mmol, 2.0 equiv), and alkene (**2**) (0.9 mmol, 3.0 equiv) was combined in a Schlenk tube followed by addition of THF (2.0 mL) under an Ar atmosphere. The reaction mixture was then heated to 100 °C with stirring for 24 h. Afterwards, the vial was cooled to room temperature. Silica was added to the flask and the volatiles were evaporated under reduced pressure. Purification was performed by flash column chromatography on silica gel to give the corresponding pure product **3**.

CCDC-941050 (**3af**), 941051 (**3at**), and 941052 (**10b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Keywords: C–H activation · homogeneous catalysis · indoles · oxidative olefination · rhodium

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