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Rhodium-Catalyzed Site-Selective Coupling of Indoles with Diazo Esters: C4-Alkylation versus C2-Annulation

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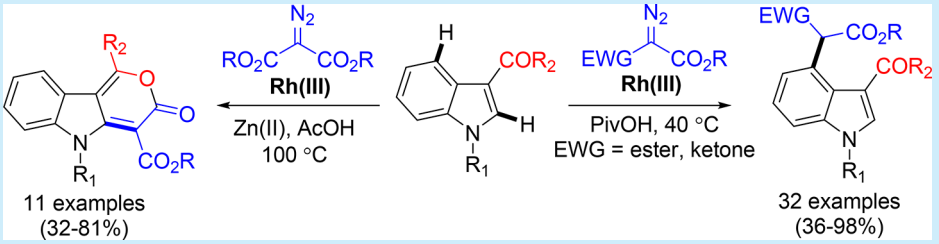
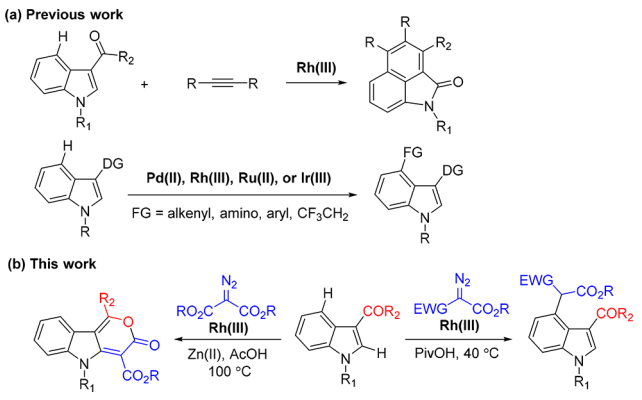
Supporting Information



ABSTRACT: A Rh(III)-catalyzed site-selective C−H activation of C(3)-functionalized indoles in a coupling with diazo esters has been realized with carbonyl as a weakly coordinating group. The coupling selectivity is dictated by the temperature and additives, affording either C4-alkylated indoles or C2-annulated lactones in moderate to excellent efficiency.

Indoles are among the most important heterocyclic structural motifs that have been widely found in a plethora of natural products, functional materials, and pharmaceuticals.[1] Therefore, as a step-economic strategy, metal-catalyzed C−H activation has received increasing attention in indole functionalization.[2] Various C3-selective functionalizations of indoles have been reported via an electrophilic substitution mechanism.[3] Regioselective C2−H functionalization can also be realized using a directing group (DG) or under specific conditions.[4] In contrast, it is a bigger challenge to realize direct functionalization at the C4−C7 positions because of their inherently poor reactivity, which amounts to limited literature reports.[5−7] You and coworkers recently reported the Rh(III)-catalyzed regioselective C4−H activation of indolyl aldehydes or ketones with alkynes as a coupling partner (Scheme 1a).[6c] The Jia, Prabhu, Shi, and You groups also independently reported the functionalization of indoles at the C4 position with a Pd(II), Ru(II), Ir(III), or Rh(III) catalyst, leading to arylation, amination, olefination, and trifluoroethylation (Scheme 1a).[6] Inspired by these outcomes and by Yu's[8] seminal C−H activation using diazo compounds, we reasoned that the unprecedented general C4-alkylation of indole might be realized when a suitable transition-metal catalyst and DG are employed.

Scheme 1. Selective Functionalization of Indoles



Cp*Rh(III) complexes have been recently recognized as competent catalysts for versatile C−H functionalization reactions owing to their high catalytic activity, selectivity, and functional group compatibility.[8−10] Previous reports by Jia, Prabhu, and You revealed that the use of a Rh(III) catalyst could lead to the site-selective functionalization of indoles. Herein, we report Rh(III)-catalyzed C−H activation of indole assisted by a carbonyl DG and divergent couplings with diazo esters at the C2 and C4 positions (Scheme 1b), leading to annulation and alkylation, respectively.

Our investigation started with the C−H functionalization of 3-pivaloylindole (**1a**) using diethyl 2-diazomalonate (**2a**) as a coupling reagent (Table 1). In the presence of a $[Cp^*RhCl_2]_2$/$AgSbF_6$ catalyst and PivOH additive, both the 4-alkylated product **3aa** and 2-annulated product **4a** were obtained in low yield and selectivity (entry 1). Both the silver additive and the acid proved necessary (entries 2 and 3). The yield of **4a** was prominently increased by using AcOH and a different silver salt (entry 5). Further introduction of $Zn(OTf)_2$ improved the total yield of **3aa** and **4a**, and the maximum yield of **4a** was reached at 100 °C (entry 6). To our delight, lowering the temperature to 40 °C suppressed the formation of **4a**, and the yield of **3aa** was

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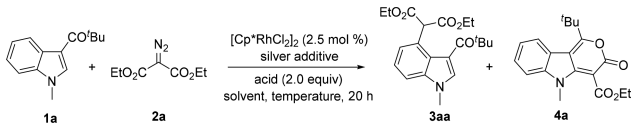
Table 1. Optimization of Reaction Conditions[a]



entry	additive (mol %)	acid	solvent	temp (°C)	yield[b] (%) 3aa	4a
1	$AgSbF_6$ (10)	PivOH	DCE	80	37	31
2		PivOH	DCE	80	0	0
3	$AgSbF_6$ (10)		DCE	80	0	0
4	$AgNTf_2$ (10)	PivOH	DCE	80	29	39
5	$AgNTf_2$ (10)	AcOH	DCE	80	9	48
6[c]	$AgNTf_2$ (10)/ $Zn(OTf)_2$ (50)	AcOH	DCE	100	27	59
7	$AgSbF_6$ (10)	PivOH	DCE	40	96	trace
8	$AgSbF_6$ (10)	PivOH	DCE	25	59	trace
9	$AgBF_4$ (10)	PivOH	DCE	40	93	trace
10	AgOTf (10)	PivOH	DCE	40	51	trace
11	$AgSbF_6$ (10)	PivOH	MeOH	40	88	trace
12	$AgSbF_6$ (10)	PivOH	PhCl	40	87	trace

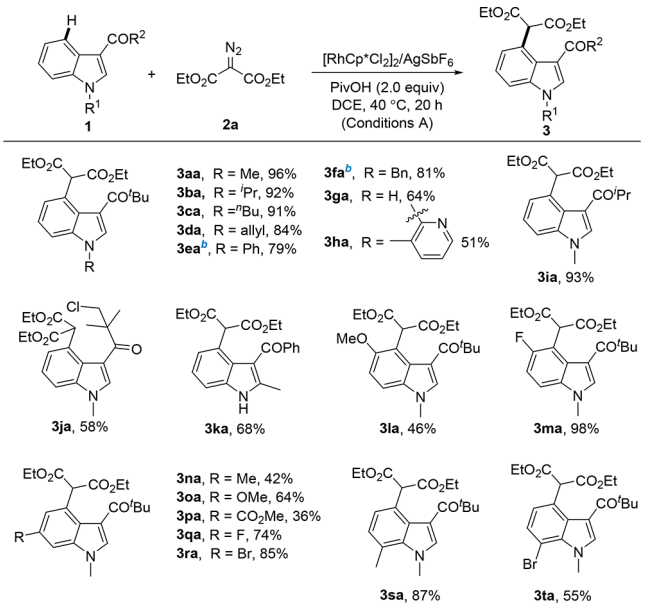
[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.5 mmol), $[Cp^*RhCl_2]_2$ (2.5 mol %), silver salt, acid (2.0 equiv), solvent (2 mL), 40–100 °C, 20 h. [b]Isolated yield. [c]The reaction time was 10 h.

significantly augmented to 96% (entry 7). However, further lowering the temperature resulted in diminished yield (entry 8). The effects of the additive and solvent were further investigated, which revealed that other silver salts or solvents all gave inferior results (entries 8–12). Thus, the conditions in entry7 were adopted for the C4-alkylation (conditions A), while the C2-annulation was performed under conditions B as defined in entry 6.

With the establishment of the optimal reaction conditions, we next explored the scope of indole substrate for C4 alkylation under the conditions A. As shown in Scheme 2, a range of substituted indoles were examined in the coupling with diethyl 2-diazomalonate (**2a**). The introduction of various *N*-alkyl and -phenyl groups into the indole had marginal influence on the yield of the product (**3aa**–**3fa**, 79–96%). *N*-Pyridylindole and NH indole also reacted with **2a**, giving a relatively lower yield of products (**3ga**, 64% and **3ha**, 51%). In the case of a pyridyl group, the site selectivity remains dominated by the Piv DG (**3ha**). Indoles bearing halogen groups at the C5–C7 positions were fully compatible, affording the desired products in high yields (up to 98%). Furthermore, different ketone directing groups at the C3-position were also tolerated (**3ia**–**ka**). In contrast, poor reactivity and selectivity were observed for a 3-acetyl-substituted indole substrate. In addition, both electron-withdrawing and -donating groups at the C5–C7 positions were consistently tolerated, affording the alkylation products in moderate to excellent yields (**3la**–**ta**).

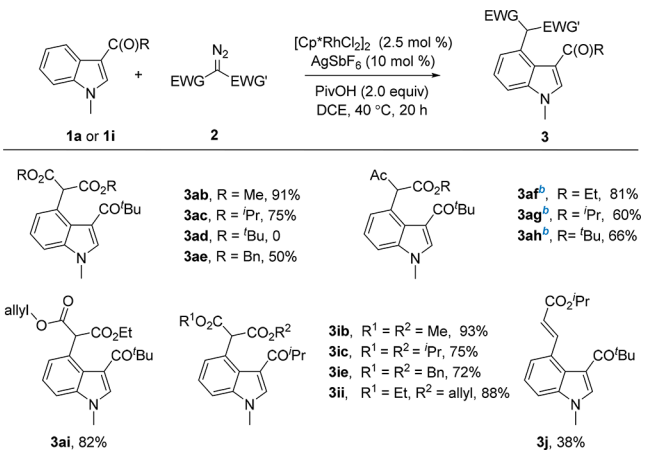
The coupling of indole **1a** or **1h** with various diazo esters was then examined under conditions A (Scheme 3). Various symmetrical or nonsymmetrical diazo malonates all coupled smoothly with such indoles in 50–93% yield. In the case of diazo esters having a larger alkyl group, decreased yields were observed as seen in **3ac**–**ae**. Furthermore, 2-diazo-3-oxobutanoate **2f** and its derivatives (**2g** and **2h**) also reacted successfully with **1a** to afford the desired products (**3af**–**ah**) in 60–81% yields, which were isolated as two tautomers due to keto–enol tautomerization (see the SI). Unfortunately, a donor/acceptor diazo

Scheme 2. Substrate Scope of Indoles for C4-Alkylation[a]



[a]Reaction conditions: indole **1** (0.2 mmol), diazo **2a** (0.5 mmol), $[Cp^*RhCl_2]_2$ (2.5 mol %), $AgSbF_6$ (10 mol %), and PivOH (2.0 equiv) in DCE (2 mL) at 40 °C for 20 h, isolated yield. [b]$[Cp^*RhCl_2]_2$ (5 mol %) and $AgSbF_6$ (20 mol %) were used.

Scheme 3. Substrate Scope of Diazo Compounds for C4-Alkylation[a]



[a]Reaction conditions: indole **1a** or **1i** (0.2 mmol), diazo 2 (0.5 mmol), $[Cp^*RhCl_2]_2$ (2.5 mol %), $AgSbF_6$ (10 mol %), PivOH (2.0 equiv), and DCE (2 mL) at 40 °C for 20 h, isolated yield. [b]The products were isolated as a mixture of two keto–enol tautomers.

compound was not suitable for this alkylation. For example, coupling with isopropyl 2-diazopropanoate (**2j**) produced the C4-alkenylation product **3j** as a result of 1,2-hydrogen shift to the carbene followed by C4-alkenylation.

Subsequently, the substrate scope of the C2-annulation reaction was investigated under conditions B (Scheme 4). Introduction of substituents such as methyl and methoxyl at the C6-position of the *N*-protected indole was tolerated, affording the corresponding annulated products **4b** and **4c** in moderate yields (51–63%). Furthermore, unprotected NH indoles were also amenable to the reaction conditions, giving the desired products **4d**–**g** in moderate to good yields (32–81%). Besides, different ketone directing groups at the C3 position of indoles

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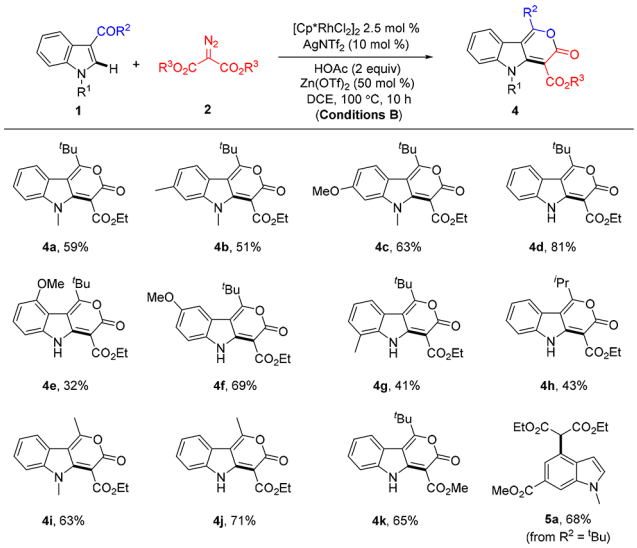
Scheme 4. Scope of C2-Annulation of Indoles[a]

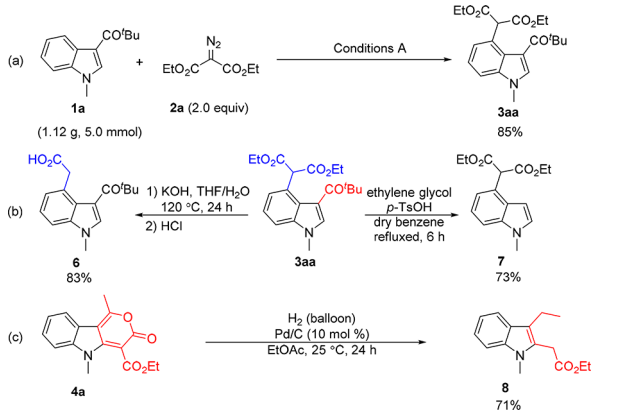


[a]Reaction conditions: indole **1** (0.2 mmol), diazo ester **2** (0.5 mmol), $[Cp^*RhCl_2]_2$ (2.5 mol %), $AgSbF_6$ (10 mol %), $Zn(OTf)_2$ (0.5 equiv), AcOH (2.0 equiv), and DCE (2 mL) at 100 °C for 10 h, isolated yield.

were also investigated, giving the target products (**4h**–**j**) in moderate yields (43–71%). In all cases, a small amount of the corresponding 4-alkylation product was also generated. In contrast, the electron-withdrawing group was not suitable for this transformation. For example, an ester-substituted indole at the C6 position produced the DG-removed C4-alkylated product **5a** under the standard conditions as a result of C(4)-alkylation followed by in situ removal of the DG.

The synthetic utility of the alkylation system was next demonstrated in a scale-up reaction. Thus, a 5 mmol reaction of **1a** and **2a** afforded the alkylation product **3aa** in 85% yield (Scheme 5a). Treatment of **3aa** with KOH led to hydrolysis–

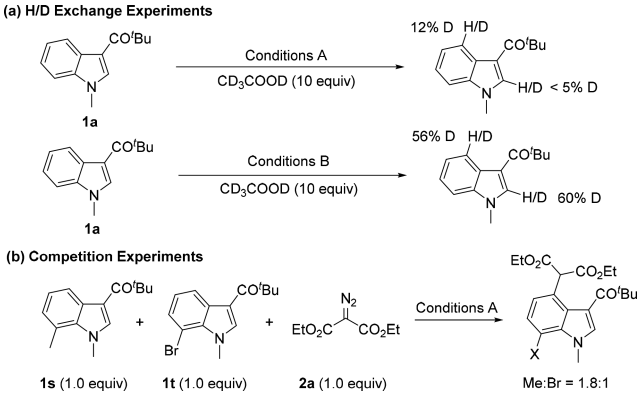
Scheme 5. Gram-Scale Synthesis and Synthetic Applications



decarboxylation to give product **6** in 83% yield (Scheme 5b,). The carboxyl group in **6** should provide handles for further functionalization. The DG in **3aa** was readily removed using a general method (Scheme 5b). Furthermore, when catalyzed by Pd/C, the annulated product **4a** can be selectively hydrogenated together with decarboxylation to give a 2,3-dialkylated indole **8** in good yield, with aromatization being a driving force (Scheme 5c).

Several experiments have been conducted to briefly probe the mechanism of the alkylation system (Scheme 6). Two H/D-

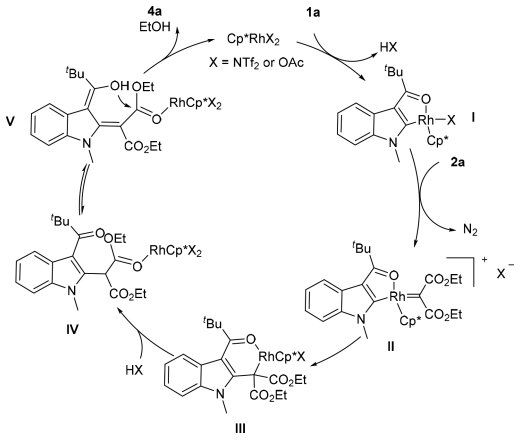
Scheme 6. Mechanistic Investigations



exchange experiments have been conducted between indoles **1a** and CD_3COOD (Scheme 6a). Under conditions A, only the C4-H was partially deuterated. In contrast, both the C2-H and C4-H underwent deuteration under conditions B. Besides the reversibility of the C–H activation (if any), these outcomes on H/D exchange are inconsistent with the site-selectivity of our C–H functionalization systems, and the C2-H activation should carry a higher barrier likely due to steric effects. Thus, the C4-alkylation is the kinetic product, while the C2-annulation product is likely the thermodynamic product. Furthermore, a competitive coupling between **1s** and **1t** with diazo ester **2a** yielded a mixture of **3sa** (Me) and **3ta** (Br) in a ratio of 1.8:1 under conditions A, suggesting that the C–H alkylation reaction is kinetically favored for a more electron-rich indole (Scheme 6b).

On the basis of the literature reports,[8,11] a plausible mechanism of the annulation reaction is proposed in Scheme 7. Starting from a Cp^*RhX_2 catalyst, a five-membered

Scheme 7. Proposed Mechanism of the Annulative Coupling



rhodacyclic intermediate **I** is generated via C2-H activation of indole **1a**. Coordination of an incoming diazo ester (**2a**) is followed by denitrogenation to afford a metal–carbene species **II**. Subsequent migratory insertion of the Rh-aryl bond into the carbene moiety gives alkyl species **III**. Protonolysis of the intermediate **III** then generates a 2-alkylated intermediate **IV**, which could tautomerize to **V**.[11c] Finally, under assistance of the Rh or the zinc catalyst, the ester carbonyl group is activated toward nucleophilic attack to furnish the annulated product **4a**, together with regeneration of the active Rh(III) catalyst.

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In summary, we have developed the Rh(III)-catalyzed efficient and site-selective C−H activation systems of indoles with diazo esters as a coupling partner. A variety of indoles and diazo compounds are amenable to the coupling systems, affording the C4-alkylation or C2-annulation products in good selectivity. The selectivity is collectively controlled by reaction temperature and additives. This protocol features a relatively low catalyst loading and compatibility with diverse functional groups, thus providing a straightforward strategy to access functionalized indoles.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.7b03099.

Detailed experimental procedures, characterization of new compounds, and copies of NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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