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Rhodium(III)-Catalyzed Synthesis of Indole Derivatives From Pyrimidyl-Substituted Anilines and Diazo Compounds

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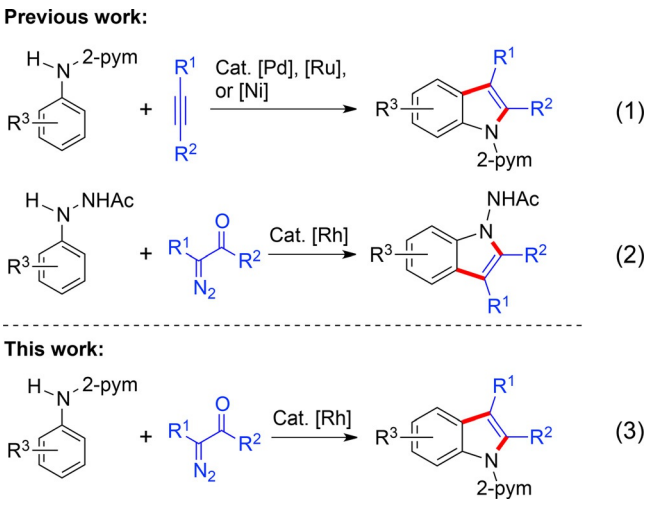
Abstract: An efficient method for the synthesis of indole derivatives from readily available pyrimidyl-substituted anilines and diazo compounds *via* rhodium(III)-catalyzed C–H bond activation has been developed. This cyclization reaction displays excellent functional group compatibility and regioselectivity, which overcomes some drawbacks of the classical indole synthetic methods and provides a facile approach for the construction of multi-substituted indole derivatives. The redox-neutral intermolecular annulation procedure comprises tandem C–H bond activation, cyclization, and condensation steps, releasing water and nitrogen as by-products.

Keywords: C–H activation; diazo compounds; indoles; rhodium

Indoles are among the most important families of nitrogen-containing heterocycles that are present in many natural products, drugs, and other functional molecules.[1] The importance of indole derivatives has driven chemists to continue developing new strategies to access functionalized indole ring systems. Accordingly, various elegant strategies have been reported and used for building the indole skeleton,[2–5] in which the Fischer indole synthesis has remained one of the most widely adopted methods.[6] Generally, the classical indole synthetic methods, starting from arylhydrazines and aldehydes or ketones under acidic conditions, are limited by some drawbacks, such as poor selectivity with unsymmetrical ketones, less functional group tolerance, and the need for strong acids. Therefore, it is highly desirable to develop milder, more efficient, highly regioselective, environmentally benign, and atom-economical methods for the synthesis of indole derivatives.

The pyrimidyl moiety, as an efficient directing group, has been widely employed in C–H bond activation.[4m,5d,g,i,7] The synthesis of indoles from the *N*-2-pyrimidyl-substituted anilines and alkynes catalyzed by palladium, ruthenium, and nickel catalysts was reported by the Li, Ackermann, and Kantam groups [Scheme 1, Eq. (1)].[5d, g,i,7c] Unfortunately, these elegant methods frequently are restricted in the regioselectivity with unsymmetrical alkynes to generate indoles.

Recently, Rh(III)-catalyzed C–H bond functionalization has made great progress in the assembly of various heteroaromatic ring systems,[8] which afford a streamlined and step-economical method for building the desired products without preactivation of the



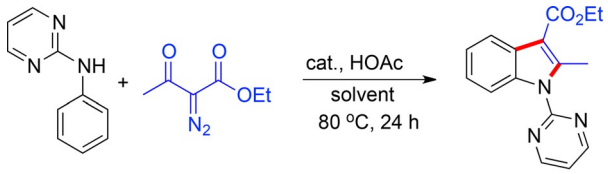
Scheme 1. Transition-metal-catalyzed synthesis of indole derivatives.

coupling partners. Rh(III)-catalyzed intermolecular C–H annulation represents a straightforward and fascinating strategy to access indole derivatives.[4] Very recently, Rh(III)-catalyzed C–H bond activation based on carbene migratory insertion has been developed as a fascinating strategy toward constructing C–C bonds.[9,10] In 2014, we reported the Rh(III)-catalyzed synthesis of 1-aminoindole derivatives from 2-acetyl-1-arylhydrazines and diazo compounds [Scheme 1, Eq. (2)].[10h] As part of our continuing interest in developing Rh(III)-catalyzed new C–H activation reactions,[11] herein, we report an efficient Rh(III) -catalyzed approach to indole derivatives *via* cascade reactions of pyrimidyl-substituted anilines and diazo compounds under mild conditions [Scheme 1, Eq. (3)].

Our initial investigation focused on the direct synthesis of indole from *N*-2-pyrimidyl-substituted anilines and ethyl diazo acetoacetate (Table 1). By treating **1a** (0.2 mmol) and **2a** (0.24 mmol) in the presence of $[Cp^*Rh(MeCN)_3](SbF_6)_2$ (2.5 mol%) and HOAc (0.2 mmol) at 80 °C under an argon atmosphere in water, the desired product **3aa** was obtained in 40% yield (entry 1). A series of solvents was tested such as DMF, DCE, toluene, MeCN, and MeOH (entries 2–6). To our delight, the isolated yield of **3aa** dramatically increased to 88% when MeOH was used as solvent (entry 6). The yield of **3aa** was slightly decreased to 80% without HOAc (entry 7). Changing HOAc to NaOAc led to a significantly lower coupling efficiency (entry 8), indicating that the reaction works well under acidic conditions. By testing other common catalysts (entries 9–11), $[Cp^*Rh(MeCN)_3](SbF_6)_2$ was demonstrated to be more effective than the others. Finally, we chose the best reaction conditions as **1a** (0.2 mmol) and **2a** (0.24 mmol) in the presence of $[Cp^*Rh(MeCN)_3](SbF_6)_2$ (2.5 mol%) and HOAc (0.2 mmol) at 80 °C.

With the optimized conditions in hand, we investigated the scope of *N*-2-pyrimidyl-substituted anilines (Table 2). *N*-2-Pyrimidyl-substituted anilines with electron-withdrawing and electron-donating groups were all well tolerated. For *para*-position-substituted anilines, high yields (**3ga–la**, 84–99%) of indoles were obtained. *ortho*-Substituted substrates were also suitable for this reaction, affording the desired products in high yields (**3ba–da**, 85–93%). Only one regioisomer was found for *meta*-substituted substrates (**3ea** and **3fa**). Also 2,3- and 2,4-disubstituted anilines can react with **2a** to give the desired products **3ma–pa** in good yields after extension of the reaction time to 48 h.

Table 1. Optimization of reaction conditions[a]

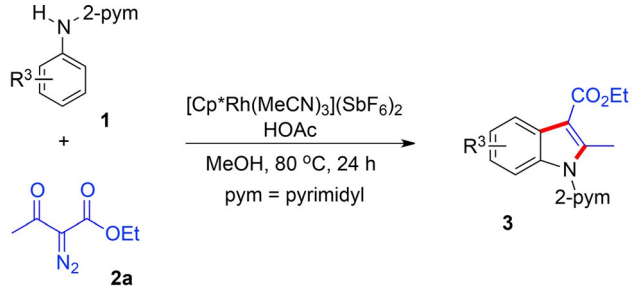


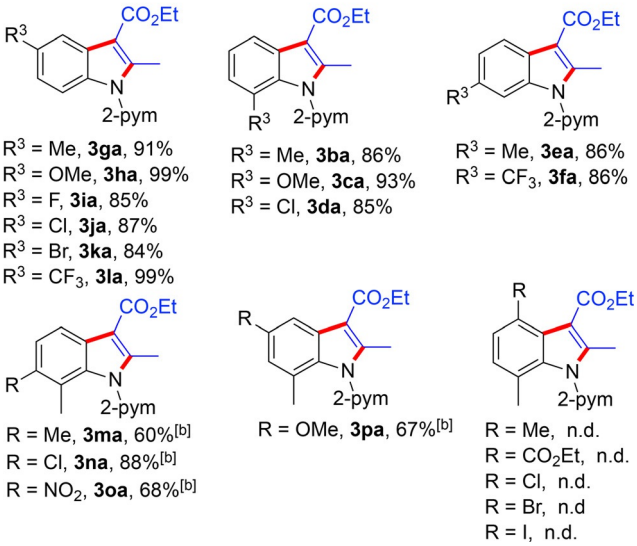
1a **2a** **3aa**

Entry	Catalyst	Solvent	Yield [%][b]
1	$[Cp^*Rh(MeCN)_3](SbF_6)_2$	H_2O	40
2	$[Cp^*Rh(MeCN)_3](SbF_6)_2$	DMF	25
3	$[Cp^*Rh(MeCN)_3](SbF_6)_2$	DCE	42
4	$[Cp^*Rh(MeCN)_3](SbF_6)_2$	toluene	33
5	$[Cp^*Rh(MeCN)_3](SbF_6)_2$	MeCN	15
6	**$[Cp^*Rh(MeCN)_3](SbF_6)_2$**	**MeOH**	**88**
7[c]	$[Cp^*Rh(MeCN)_3](SbF_6)_2$	MeOH	80
8[d]	$[Cp^*Rh(MeCN)_3](SbF_6)_2$	MeOH	27
9	$[Cp^*RhCl_2]_2$	MeOH	57
10	$[Cp^*RhCl_2]_2/AgSbF_6$	MeOH	85
11	$[(p\text{-cymene})RuCl_2]_2/AgSbF_6$	MeOH	55

[a] *Reaction conditions:* **1a** (0.2 mmol), **2a** (1.2 equiv.), catalyst (2.5 mol%), additive (1 equiv.), solvent (2 mL), at the indicated temperature for 24 h, under argon.
[b] Isolated yield.
[c] Without HOAc.
[d] Using NaOAc instead of HOAc.

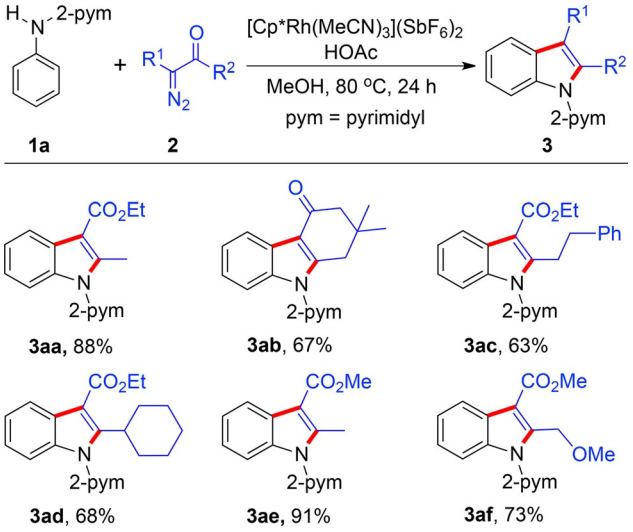
Table 2. Substrate scope of anilines[a]





[a] *Reaction conditions:* **1** (0.2 mmol), **2a** (1.2 equiv.), catalyst (2.5 mol%), HOAc (1 equiv.), MeOH (2 mL), 80 °C, 24 h, under argon; isolated yields are shown.
[b] 48 h.

Table 3. Substrate scope of diazo compounds[a]



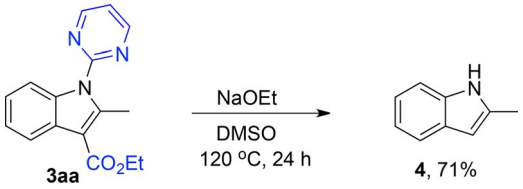
[a] *Reaction conditions:* **1a** (0.2 mmol), **2** (1.2 equiv.), catalyst (2.5 mol%), HOAc (1 equiv.), MeOH (2 mL), 80 °C, 24 h, under argon; isolated yields are shown.

More importantly, tolerance to valuable functional groups such as fluoro (**1i**) and chloro (**1d**, **1j**, and **1n**) offers the opportunity for further transformations. No desired product was formed for the 2,5-substituted substrates, indicating that in highly hindered cases the reaction would shut down.

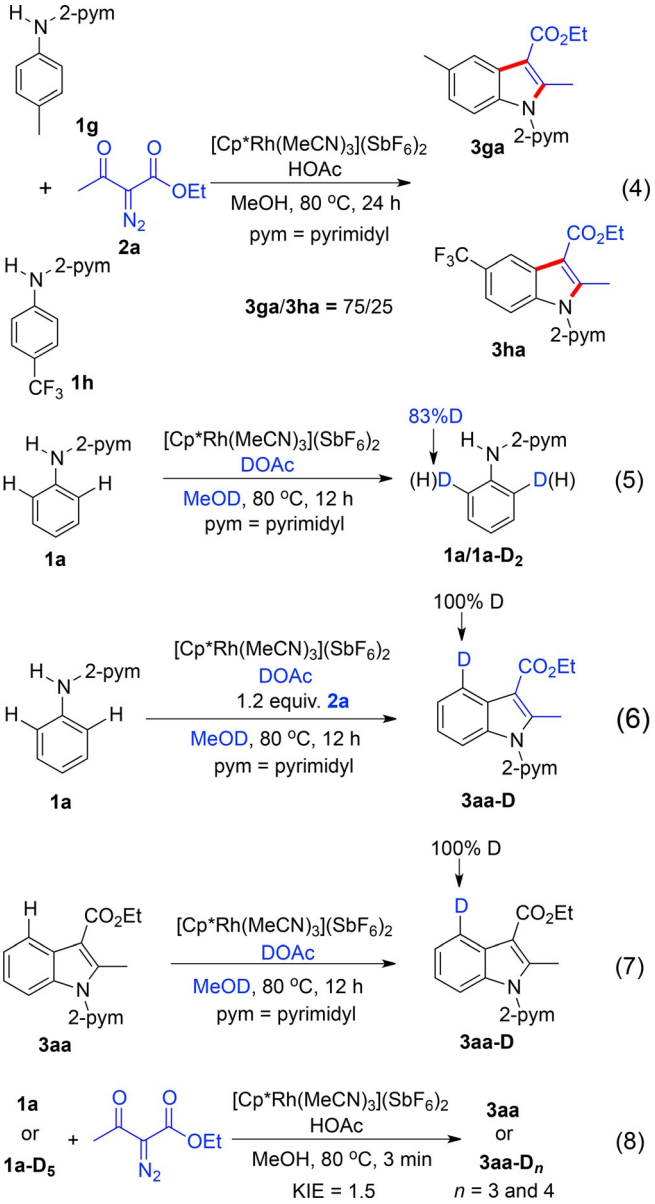
Next, we investigated the reactions of various diazo compounds with **1a**. As shown in Table 3, diazo substrates bearing substituents such as ketone, ester, alkyl, and cycloalkyl afforded the corresponding 2,3-disubstituted indoles in 63–91% yield. Interestingly, reaction of 2-diazo-5,5′-dimethylcyclohexane-1,3-dione (**2b**) with **1a** also proceeded smoothly to give **3ab** in 67% yield.

For future practical applications, removal of the directing group *N*-2-pyrimidyl was done with sodium ethoxide in DMSO. Unexpectedly, both *N*-2-pyrimidyl and ester groups were removed in a one-pot reaction to deliver the corresponding NH-free indole **4** in 71% yield (Scheme 2).

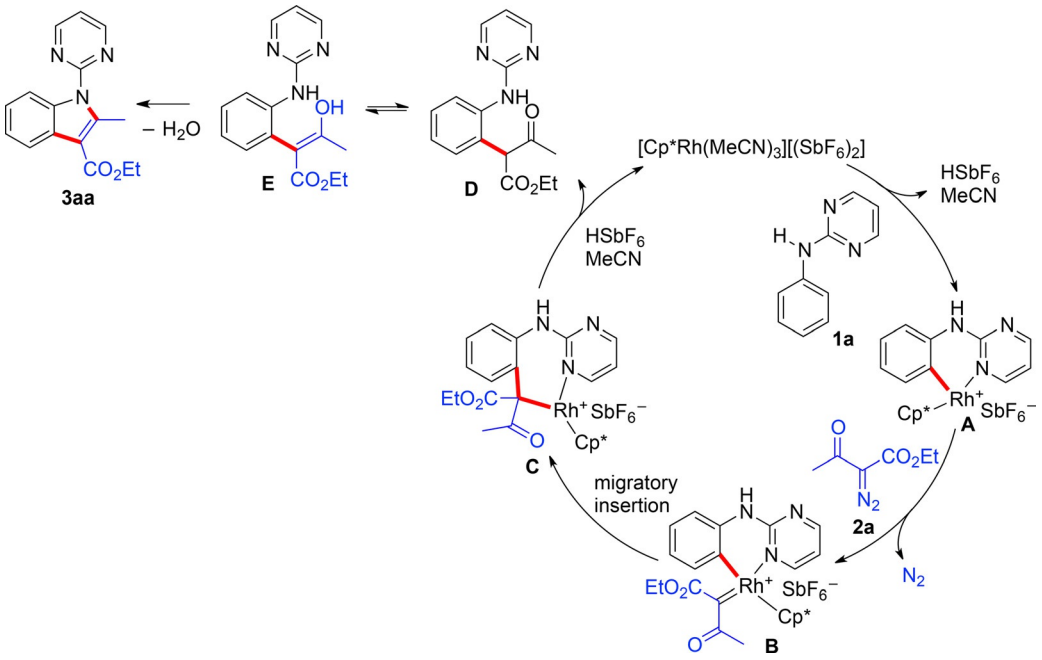
To further understand the reaction, a set of competition experiments was undertaken to probe the relative activity of different substrates. *para*-Substituted substrates **1g** and **1h** were chosen in the intermolecular competition experiment [Scheme 3, Eq. (4)]. This result revealed that the electron-rich substrates are more active for the reaction to generate the corresponding indole product. H/D exchange of **1a** without and with **2a** in the presence of $[Cp^*Rh(MeCN)_3](SbF_6)_2$ was observed when MeOD was used as solvent [Scheme 3, Eq. (5) and Eq. (6)]. However, it cannot be concluded if the H/D exchange is reversible, because the product **3aa** can also occur the H/D exchange in the presence of $[Cp^*Rh(MeCN)_3](SbF_6)_2$ [Scheme 3, Eq. (7)]. The kinetic isotope effect experiment was carried out, which gave a k_H/k_D ratio of 1.5 [Scheme 3, Eq. (8)], suggesting that the C–H bond cleavage may be involved in the rate-determining step.



Scheme 2. Removal of the directing group.



Scheme 3. Mechanistic studies.



Scheme 4. Proposed reaction pathway.

Based on the experimental results and previous work,[10d,i,u] we propose a possible mechanism for the present catalytic reaction (Scheme 4). $[Cp^*Rh(MeCN)_3](SbF_6)_2$ is firstly coordinated with **1a** and subsequent cyclometallation occurs to give six-membered rhodacycle intermediate **A** by releasing $HSbF_6$. The coordination of the carbene derived from the diazo compound **2a** to rhodium affords the rhodium-carbene intermediate **B**. Subsequently, the migratory insertion of the carbene into the Rh–C bond leads to intermediate **C**, which is protonated to form intermediate **D** and release the catalytic species for the next catalytic cycle. At last, tautomerization of intermediate **D** delivers enol intermediate **E** and further elimination of water by intramolecular condensation affords the final product **3aa**. In the presence of HOAc, a ligand exchange can occur to give the catalytic species $[Cp^*Rh(OAc)(MeCN)]^+$, which reacts with **2a** to form the intermediate **A** by releasing the weak acid HOAc to promote the reaction. The catalytic species $[Cp^*Rh(OAc)(MeCN)]^+$ can be regenerated by reaction of intermediate **C** with HOAc.

In conclusion, we have developed an efficient route for the synthesis of indole derivatives from readily available pyrimidyl-substituted anilines and diazo compounds *via* rhodium(III)-catalyzed C–H bond activation. This cyclization reaction displays excellent functional group compatibility and regioselectivity; it overcomes some drawbacks of the classical indole synthetic methods and provides a facile approach for the building of multi-substituted indole derivatives. The redox-neutral intermolecular annulation procedure comprises tandem C–H bond activation, cyclization, and condensation steps, releasing H_2O and N_2 as by-products.

Experimental Section

General Procedure

A mixture of a pyrimidyl-substituted aniline (**1**) (0.2 mmol, 1.0 equiv.), diazo compound (**2**) (0.24 mmol, 1.2 equiv.), $[Cp^*Rh(MeCN)_3](SbF_6)_2$ (4.2 mg, 0.005 mmol, 2.5 mol%), and dry MeOH (2.0 mL) in a Schleck tube equipped with a stir bar was stirred at 80 °C for 24 h under an argon atmosphere. Afterwards, it was transferred to a round-bottom flask. Silica was added to the flask, and volatiles were evaporated under reduced pressure. The purification was performed by flash column chromatography on silica gel (EtOAc/petroleum ether = 1:10).

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