Heteroarenes

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Indole Synthesis by Rhodium(III)-Catalyzed Hydrazine-Directed C–H Activation: Redox-Neutral and Traceless by N–N Bond Cleavage**

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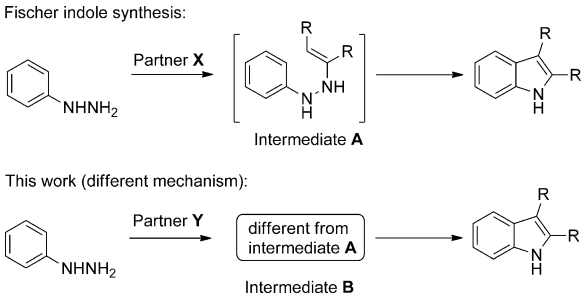
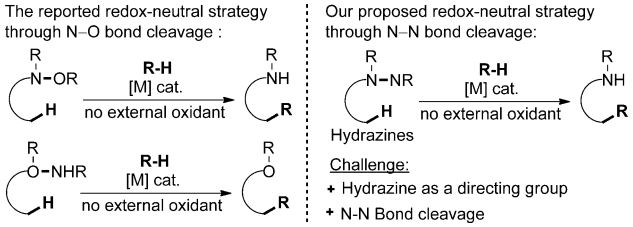
Indole is one of the most common motifs in natural bioactive products, marketed drugs, and other functional molecules.[1] There is continued interest in the development of simple and general synthetic methods to access this structural moiety.[2] Of the many methods developed, the Fischer indole synthesis has remained one of the most widely adopted approaches.[3] In the classical Fischer indole synthesis an aromatic hydrazine reacts with an aldehyde or ketone via the ene–hydrazine intermediate **A** (Scheme 1). In the past, research has focused



Scheme 1. Fischer indole synthesis and a new method inspired by it.

on the discovery of new methods to prepare the *N*-aryl hydrazones or ene–hydrazines to improve the scope of Fischer indole synthesis, for example by hydrohydrazination.[4] The investigation of synthetic alternatives to the Fischer indole synthesis that also start from hydrazines seems to be largely unexplored (Scheme 1).

In recent years, transition-metal-catalyzed directed C–H activation has been developed as a powerful and straightforward synthetic approach to complex molecules from less-functionalized substrates.[5] As a consequence of the oxidative character of these reactions, the use of an external oxidant is generally required. The use of a directing and oxidizing group (DG^{ox}) as an internal oxidant has emerged as an attractive alternative in C–H activation chemistry.[6–9] Oxidizing directing groups in the transition-metal-catalyzed C–H functionalization typically contain an N–O bond (Scheme 2, left).



Scheme 2. Strategies for redox-neutral C–H activation.

Normally, the oxidation of a low-valent metal by these internal oxidants will result in the cleavage of the N–O bond. Generally, the use of an internal oxidant can lead to improved levels of reactivity and selectivity and also to a broader scope than when external oxidants are used. The development of innovative oxidizing directing groups, which enable novel transformations to deliver valuable structures under mild and simple reaction conditions, is highly desirable. Although some examples in organic synthesis clearly show that N–N bond cleavage can occur,[10] there seems to be no report of an oxidizing directing group that utilizes an N–N bond-cleavage step (Scheme 2, right).

Rh^{III}-catalyzed C–H bond activation of arenes involving oxidizing directing groups and coupling with alkynes has been widely explored for heteroarene formation.[8,11] However, Rh^{III}-catalyzed C–H annulation directed by oxidizing directing groups have not been used to access the indole scaffold.[12] We envisioned that the Rh^{III}-catalyzed reaction of easily available arylhydrazines and various alkynes would constitute a new route for the regioselective synthesis of diverse N–H indoles without any external oxidant, if arylhydrazine could be used as an oxidizing directing group. Arguably, this pathway must follow a mechanism different from that of the Fischer indole synthesis. In this, we may face some formidable challenges: 1) Arylhydrazines appear not to have been used as directing groups in the transition-metal-catalyzed directed C–H activation; 2) N–N bond cleavage typically requires harsh reaction conditions, and it has never been used in redox-neutral reactions. Herein, we meet these challenges and successfully apply 2-acetyl-1-arylhydrazines as oxidizing

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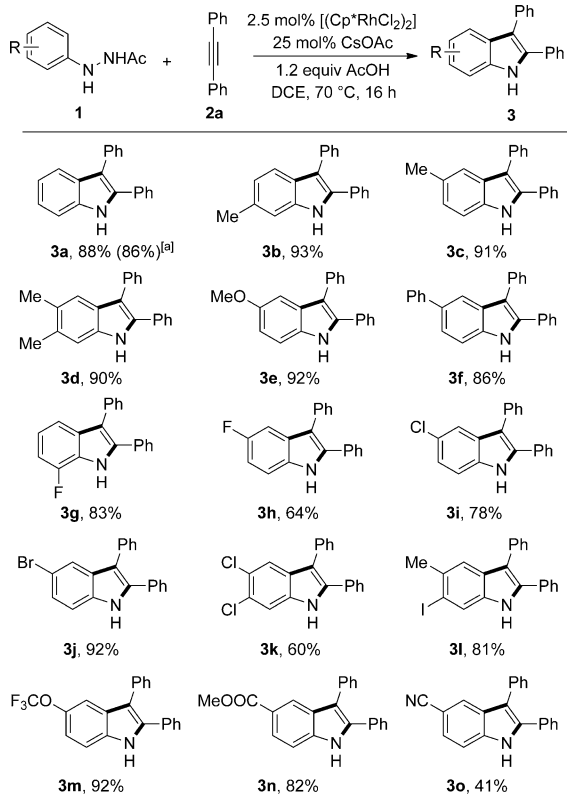
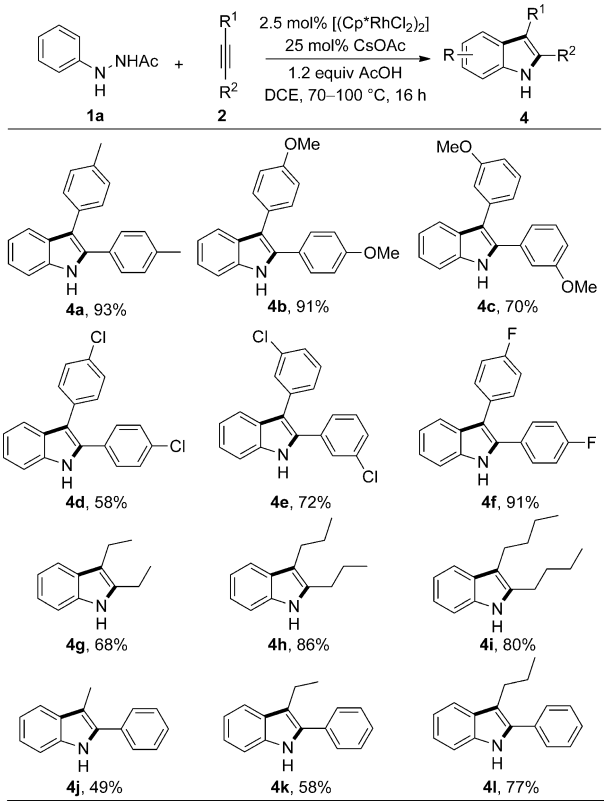
directing groups to access diverse N–H indoles without any external oxidant.

In preliminary experiments, primary phenylhydrazine was treated with $[(Cp^*RhCl_2)_2]$ (2.5 mol%), CsOAc (25 mol%), and diphenylacetylene (**2a**, 1.1 equiv) in 1,2-dichloroethane (DCE, 1 mL) at 70°C for 16 h, and was completely unreactive (Table S1 in the Supporting Information, entry 1). Further, we evaluated the influence of different substituents on the phenylhydrazine nitrogen atom (Table S1). When we used 2-acetyl-1-phenylhydrazine as the directing group, we could obtain product **3a** in 12% yield without adding any external oxidant. After screening several parameters, we found that the C–H annulation between 2-acetyl-1-phenylhydrazine and diphenylacetylene (**2a**) could occur smoothly with 88% yield in the presence of $[(Cp^*RhCl_2)_2]$ (2.5 mol%), CsOAc (25 mol%), and HOAc (1.2 equiv) in DCE at 70°C for 16 h (Table S1, entry 5). Subsequently, the scope of 2-acetyl-1-arylhydrazine compounds was investigated by using diphenylacetylene as the internal alkyne. As shown in Scheme 3, a series of indoles bearing substituents at the 5-, 6-, and/or 7-positions were synthesized in good to excellent yields regardless of whether the 2-acetyl-1-arylhydrazines were electron-rich, electron-poor, or sterically demanding (Scheme 3, **3a–o**). It is important to stress that the reactions occurred preferably at the sterically more accessible position when a *meta* substituent was attached to the phenyl ring of the hydrazine compounds (Scheme 3, **3b**). This method was remarkably compatible with a variety of important functional groups on the phenyl ring of the hydrazines such as halogens (F, Cl, Br, and I) and ester, cyano, and methoxy groups, which could be subjected to further synthetic transformations (Scheme 3, **3e**, and **3g–o**). It is also worth noting that our method is not only suitable for diverse monosubstituted 2-acetyl-1-arylhydrazines but also disubstituted 2-acetyl-1-arylhydrazines as well (Scheme 3, **3d**, **3k**, and **3l**). In addition, we proved that the reaction can be conducted on a gram scale without a significant decrease in yield (2.3 g of **3a**, 86% yield).

We next examined the scope of internal alkynes in the redox-neutral C–H bond annulation (Scheme 4). Overall, we were pleased with the generality of this method. Various internal alkynes reacted smoothly to afford the desired 2,3-disubstituted indoles in satisfactory yields. A variety of symmetric diaryl-substituted alkynes could be efficiently converted into the corresponding products and the substituents had a nearly neglible electronic effect (Scheme 4, **4a–f**). Symmetrical aliphatic alkynes such as 3-hexyne, 4-octyne, and 5-decyne also reacted with 2-acetyl-1-phenylhydrazine to



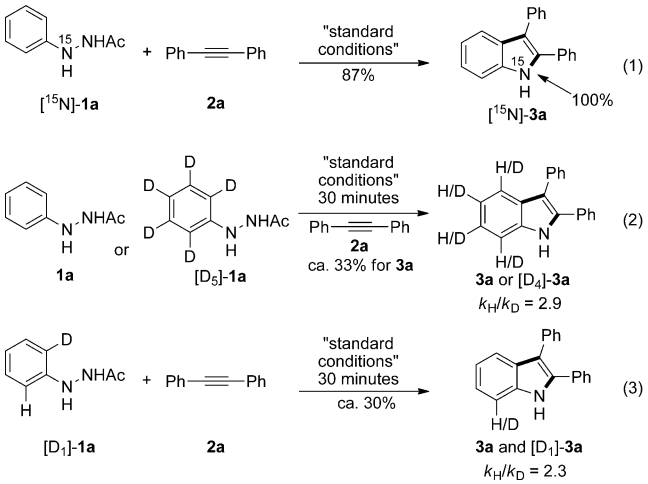
Scheme 3. The reactions of diverse 2-acetyl-1-arylhydrazines with diphenylacetylene. Reactions were carried out using $[(Cp^*RhCl_2)_2]$ (2.5 mol%), CsOAc (25 mol%), AcOH (1.2 equiv), 2-acetyl-1-arylhydrazine (0.2 mmol), and diphenylacetylene (0.22 mmol) in DCE (1 mL) for 16 h at 70°C under an argon atmosphere. Yield of isolated product is given. [a] 10 mmol scale reaction.



Scheme 4. The reactions of 2-acetyl-1-phenylhydrazine with diverse internal alkynes. Reactions were carried out using $[(Cp^*RhCl_2)_2]$ (2.5 mol%), CsOAc (25 mol%), AcOH (1.2 equiv), 2-acetyl-1-phenylhydrazine (0.2 mmol), and internal alkyne (0.22 mmol) in DCE (1 mL) at 70°C under an argon atmosphere for 16 h. Yield of isolated product is given. For **4d** and **4g–l**, the reaction temperature was increased to 100°C. The low yields of **4j–l** can be attributed to the incomplete consumption of 2-acetyl-1-phenylhydrazine; the formation of only one regioisomer was observed.

furnish the desired products in moderate to good yields when the reaction temperature was increased to 100 °C (Scheme 4, **4g–l**). In addition to symmetric alkynes, some unsymmetrical alkynes could also give the desired products, impressively with complete regioselectivity. For various alkyl phenyl acetylenes, only one regioisomer was obtained (Scheme 4, **4j–l**).

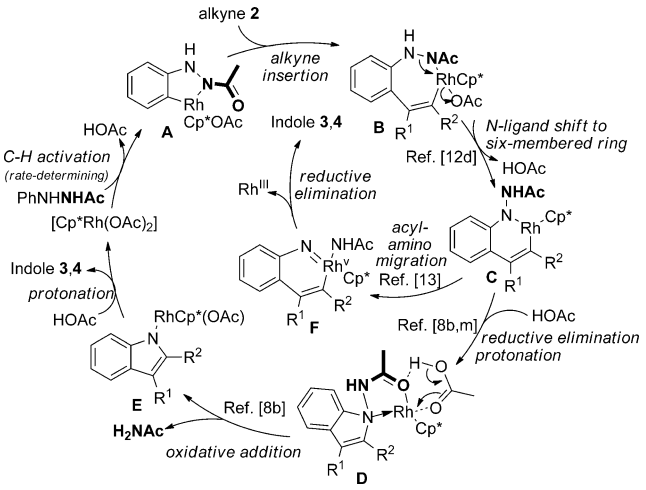
To probe the reaction mechanism, a series of isotope and deuteration experiments were carried out (Scheme 5). First we conducted the reaction with ^{15}N-labeled substrate [^{15}N]-**1a**



Scheme 5. Isotope-labeling experiments and deuteration experiments for the study of the kinetic isotope effects.

and diphenylacetylene (**2a**) under the standard conditions and the product [^{15}N]-**3a** was obtained smoothly in 87 % yield. ^{15}N NMR and ESI-MS analyses confirmed that the indole nitrogen originates from the hydrazine nitrogen directly attached to the aromatic ring [Scheme 5, Eq. (1)]. A separate experiment using the pentadeuterated substrate [D_5]-**1a** was carried out to independently assess the rate of reaction for *ortho*-C–H versus C–D bond cleavage. A measurement of $k_H/k_D = 2.9$ indicated that the C–H bond cleavage should be the rate-determining step [Scheme 5, Eq. (2)]. The intramolecular kinetic isotope effect (KIE) was also determined to be $k_H/k_D = 2.3$ by treatment of [D_1]-**1a** with **2a** [Scheme 5, Eq. (3)], providing additional evidence regarding the reactions.

The yields obtained with [Cp*Rh(OAc)$_2$] as the catalyst were similar to those obtained with the [(Cp*RhCl$_2$)$_2$]/CsOAc system, thus indicating that [Cp*Rh(OAc)$_2$] might be the active catalyst. On the basis of deuteration experiments and literature precedence,[8] we propose a directed C–H bond cleavage to form intermediate **A** as the first step, which is followed by alkyne insertion, thus affording the seven-membered rhodacycle **B** (Scheme 6). This metallacycle presumably rearranges to a more stable six-membered Rh complex **C** (Scheme 6).[12d] Complex **C** might undergo a reductive elimination, protonation, and oxidative addition to break the N–N bond with the aid of acetic acid to form intermediate **E**, which is finally protonated by acetic acid to yield the desired indole and regenerate the catalyst.[8b,m] Alternatively, complex **C** could lead to a cyclic Rh^V nitrene intermediate **F**



Scheme 6. Proposed mechanism of the hydrazine-directed redox-neutral C–H annulation giving indoles.

by acylamino migration,[13] and **F** could easily undergo reductive elimination to form the desired heterocycle and to regenerate the Rh^{III} catalyst (Scheme 6).

In summary, we have developed a mild and efficient rhodium(III)-catalyzed redox-neutral C–H activation/cyclization of 2-acetyl-1-arylhydrazines with alkynes to prepare unprotected indoles. The reaction did not require any external oxidant and because of the cleavage of the N–N bond the directing group was traceless in the product (loss of NHAc). In addition, the catalytic protocol was highly regioselective when some unsymmetrical internal alkynes were employed. Starting from similar hydrazine substrates, this method now provides an alternative to the Fischer indole synthesis. Considering the valuable structure of the products and good functionality tolerance, this reaction should be of synthetic utility.

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