

Rhodium(III)-Catalyzed Cyclative Capture Approach to Diverse 1-Aminoindoline Derivatives at Room Temperature**

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In memory of Ekkehard Winterfeldt

Abstract: A Rh^{III} -catalyzed C–H activation/cyclative capture approach, involving a nucleophilic addition of $C(sp^3)$ –Rh species to polarized double bonds is reported. This constitutes the first intermolecular catalytic method to directly access 1-aminoindolines with a broad substituent scope under mild conditions.

The 1-aminoindoline unit is prevalent in numerous commercial drugs and biologically active compounds (Figure 1),^[1] and has also been widely utilized as a chemical feedstock to access a large number of important skeletal motifs.^[2] 1-Aminoindolines are typically formed by the nitrosylation/reduction of free indolines or by intramolecular amination.^[3] These methods suffer from disadvantages such as multistep synthe-

ses, moderate to poor yields, harsh reaction conditions, and limited substrate scope. Moreover, indoline as the parent heterocycle must be prepared in advance.^[4] To date, no intermolecular catalytic method is available to directly access the 1-aminoindoline core.^[5]

Rh^{III} -catalyzed directed C–H functionalization has emerged as a versatile synthetic approach to access complex molecules.^[6] Recently, several groups have demonstrated that $C(sp^2)$ –Rh intermediates formed by insertion of alkynes into the C–Rh bond could undergo Grignard-type addition to ketone-, imine-, amide-, and ester-based directing groups (Figure 2A).^[7] However, the nucleophilic attack of $C(sp^3)$ –Rh species, generated upon alkene insertion, to polarized double bonds has never been reported, presumably due to problematic preferential β -hydride elimination (Figure 2B).^[8] We wondered whether nucleophilic additions of $C(sp^3)$ –Rh species to polarized unsaturated directing groups might be possible if β -hydride elimination is inhibited. Herein, we introduce diazenecarboxylate as a directing group to trigger a new cyclative capture approach where alkenes undergo insertion followed by intramolecular addition of the $C(sp^3)$ –Rh species to the N=N bond to afford diverse 1-aminoindolines without any external oxidants (Figure 2C). This reaction proceeds at room temperature with a wide range of functionalized substrates, and, moreover, has been extended to the synthesis of pharmaceutically important 1-aminoindoles.

Besides disfavoring β -hydride elimination of the $C(sp^3)$ –Rh species, two other potential difficulties must be overcome: 1) Even though 1,2-diaryl- and 1-alkyl-2-aryl-substituted diazenes have been used as directing groups, diazenecarboxylate has never been used as a directing group;^[9] 2) Although the addition of organometallic reagents to N=N bonds has been reported,^[10] it has not been observed in Rh^{III} -catalyzed C–H activation. Furthermore, the issue of regioselectivity in additions to N=N bonds must also be addressed.

We initially focused on the reaction of *tert*-butyl 2-phenyldiazenecarboxylate **1a** and *n*-butyl acrylate (**2a**) with $[(Cp^*RhCl_2)_2]$ (2.5 mol %) in 1,2-dichloroethane (DCE, 1 mL). After extensive screening, we found that the tandem C–H bond activation/N=N bond addition occurred smoothly in the presence of $[(RhCp^*Cl_2)_2]$ (2.5 mol %; $Cp^* = C_5Me_5$) and AgOAc (10 mol %) in a mixture of HOAc and DCE (1:3) at room temperature for 24 h to afford 1-aminoindoline **3a** in 88 % yield. To confirm the structure, we further converted the oily **3a** to the corresponding 1-aminoindole which formed single crystals suitable for X-ray analysis (see the Supporting

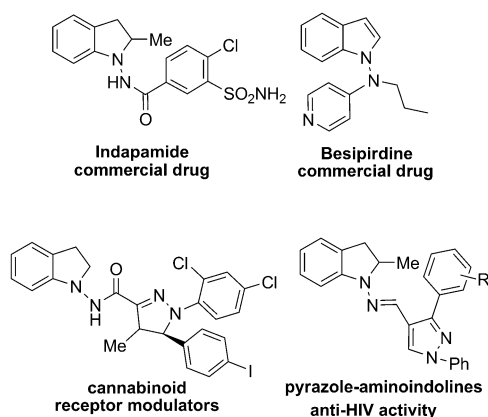


Figure 1. Some biologically active 1-aminoindolines and -indoles.

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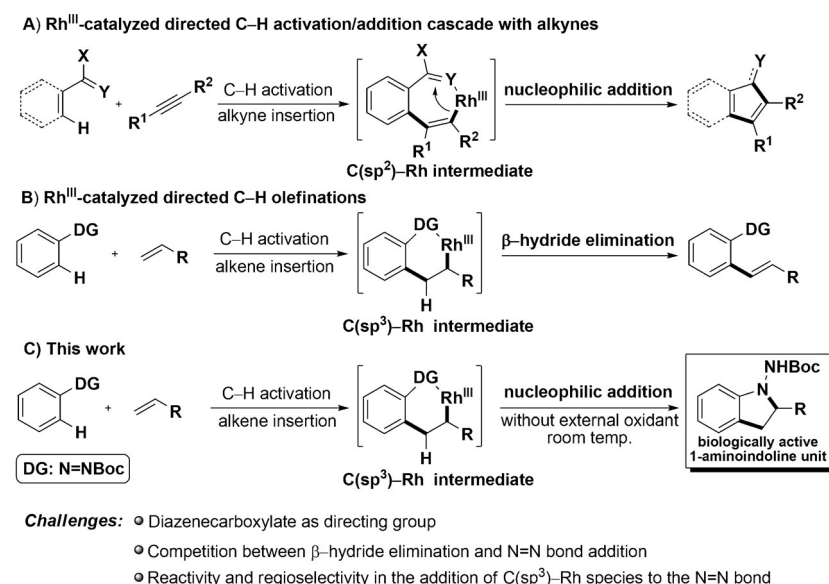
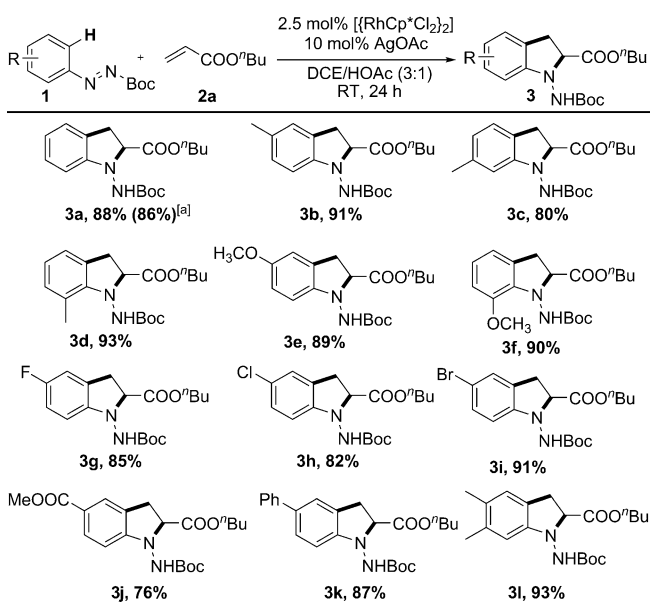


Figure 2. Examples of β -hydride elimination and Grignard-type additions in Rh^{III}-catalyzed C–H functionalization reactions.

Information).^[11] Subsequently, the scope of the aryl-substituted diazenecarboxylate substrates was investigated. A series of 1-aminoindolines bearing substituents at the 5-, 6-, and/or 7-positions were synthesized in good yields (Scheme 1; **3a–l**). A variety of important functional groups such as halogens (F, Cl, and Br), ester, and methoxy groups were well tolerated (Scheme 1; **3e–j**). In addition, we proved that the reaction can be conducted on a gram scale without a significant decrease in yield (ca. 0.9 g of **3a**, 86% yield). It is also worth noting that a remarkable yield was also obtained with a lower catalyst loading (85% yield, 1 mol % $[\text{RhCp}^*\text{Cl}_2]_2$).

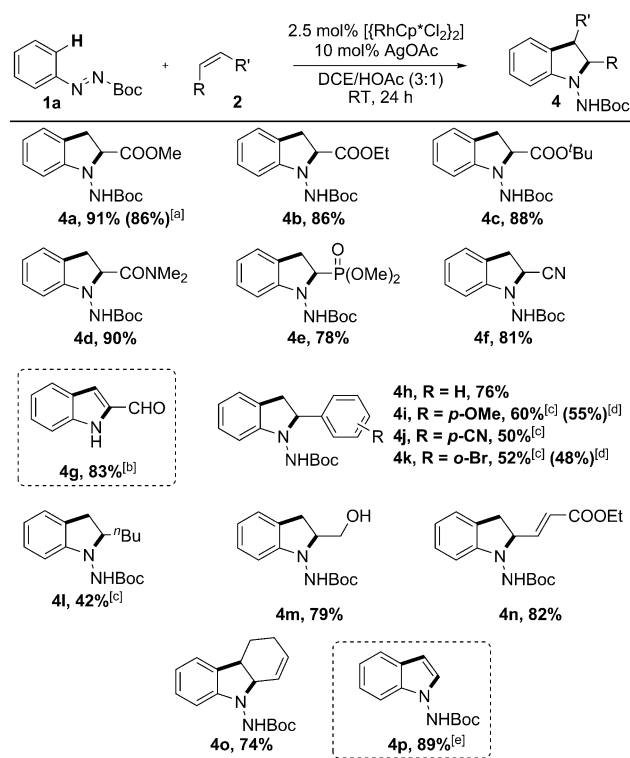


Scheme 1. Scope of aryl-substituted diazenecarboxylates. Reaction conditions: **1** (0.2 mmol), **2a** (1.5 equiv); see SI. [a] 3.0 mmol scale.

We next examined the scope of the alkenes (Scheme 2). A variety of electron-deficient alkenes could be efficiently converted into the corresponding products (Scheme 2; **4a–f**). Unexpectedly, the reaction with acrolein directly afforded the indole-2-carbaldehyde **4g**.^[12] Moreover, various substituted styrenes also reacted with **1a** to furnish the products in moderate yields (Scheme 2; **4h–k**). In addition to styrenes, alkyl alkenes could also give the desired products (Scheme 2; **4l,m**). It is important to note that 1,3-dienes are well-tolerated in this reaction (Scheme 2; **4n,o**). Interestingly, when we switched the substrate to vinyl acetate, we could directly access the aminoindole product **4p** in excellent yield; this reaction might involve an elimination of acetic acid after cyclization.^[13]

To date, synthetic approaches to 1-aminoindoles, which also display very important pharmacological properties,^[14] have been quite limited.^[15] We wondered

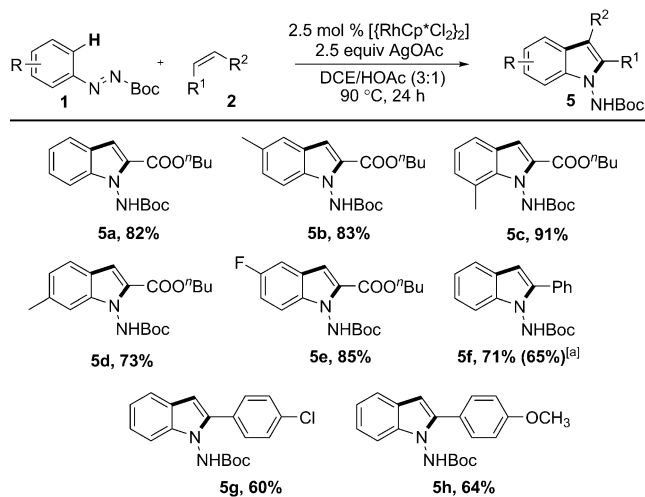
if we could utilize the present transformation for the straightforward synthesis of 1-aminoindoles by introducing an additional oxidant. We found that 1-aminoindole **5a** could be formed when AgOAc was used as the external oxidant under the standard conditions. Further optimization lead to



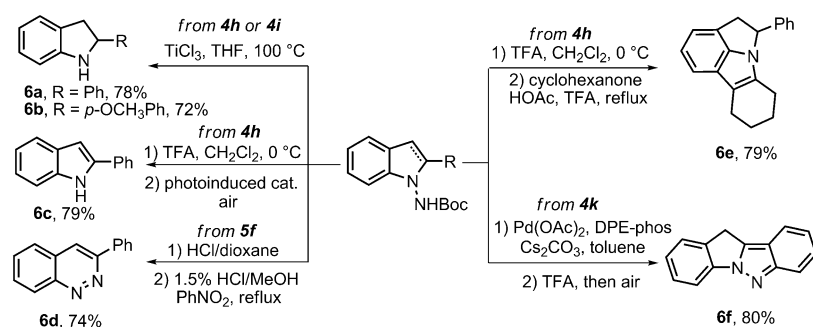
Scheme 2. Scope of alkenes. Reaction conditions: **1** (0.2 mmol), **2** (1.5 equiv); see SI. [a] 3.0 mmol scale. [b] Acrolein was used. [c] 0.4 mmol scale. [d] 2.5 mmol scale. [e] Vinyl acetate was used.

82% yield when the reaction temperature was increased to 90 °C. Using this procedure, a variety of aryl-substituted diazenecarboxylates and alkenes were tested to access various 1-aminoindoles. As shown in Scheme 3, the desired products were generally obtained in good yields.

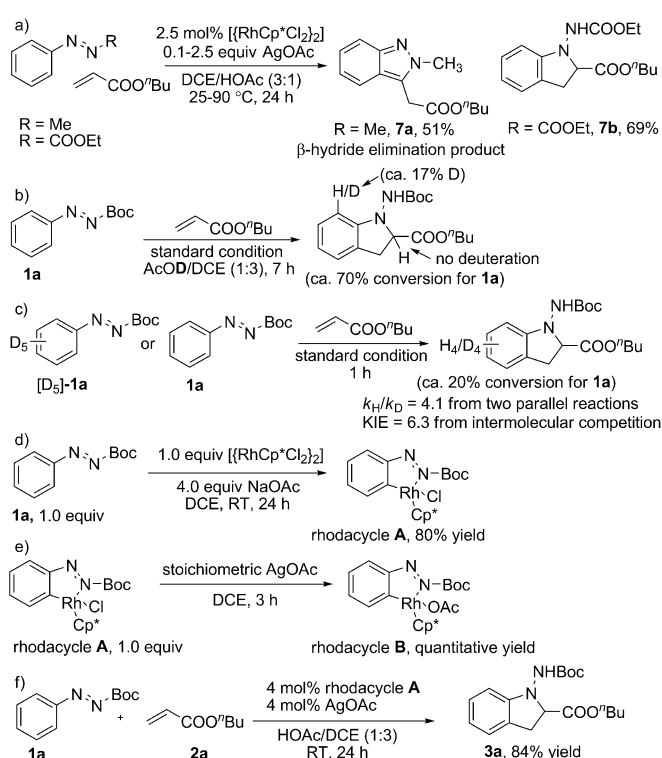
Furthermore, we demonstrated the synthetic usefulness of the 1-aminoindolines by conducting five additional transformations with our products (Scheme 4). First, the N–N bond of the 1-aminoindoline was easily cleaved to yield the free indolines **6a,b** using TiCl_3 .^[16] We could also submit compound **4h** to an initial deprotection, followed by a photocatalytic oxidation with $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(\text{dtbbpy})]\text{PF}_6$ ($\text{dF}(\text{CF}_3)\text{ppy}$ = 2-(2,4-difluorophenyl)-5-trifluoromethylpyridine, dtbbpy = 4,4'-di-*tert*-butyl-2,2'-bipyridine), visible light, and air to afford the free indole **6c**.^[17] Cinnoline **6d** could also be prepared from 2-phenyl-1-aminoindoline in good yield.^[18] The tetracyclic fused indole skeleton **6e**, which exists in numerous privileged pharmaceuticals and natural alkaloids,^[2g–i] could also be constructed from 1-aminoindoline by a Fischer indole synthesis (Scheme 4; **6e**). In addition, we also made the backbone of indolo[1,2-*b*]indazoles, which have been shown to be potent inhibitors to DNA topoisomerases I and II (Scheme 4; **6f**).^[19]



Scheme 3. Synthesis of 1-aminoindoles. Reaction conditions: **1** (0.2 mmol), **2** (1.5 equiv); see SI. [a] 3.0 mmol scale.



Scheme 4. Applications of 1-aminoindolines/1-aminoindoles. DPE-phos = Bis[(2-diphenylphosphino)phenyl] ether, TFA = trifluoroacetic acid.



Scheme 5. Mechanistic experiments.

A series of mechanistically insightful experiments were carried out. First, we submitted 1-methyl-2-phenyldiazene as the substrate to the standard conditions with *n*-butyl acrylate (Scheme 5a). The β -hydride elimination takes place preferentially to afford the product **7a** in moderate yield.^[20] However, if we change the Boc group to $-\text{COOEt}$, the cyclative capture step occurs smoothly to afford 1-aminoindoline **7b** in 69% yield (Scheme 5a). These observations imply that the carboxyl substituent in our directing group might be crucial in precluding β -hydride elimination. When the reaction was performed with AcOD to roughly 70% conversion, deuterium incorporation was observed at the C7-position of **3a** (Scheme 5b). This deuteration might be induced by reversible C–H activation or acid-catalyzed tautomerism. Also, deuterium incorporation was not observed at the C2-position of the product (Scheme 5b), which indicates that migratory insertion of alkene might be irreversible. Furthermore, deuterium incorporation was also observed using substrate **1a** in AcOD/DCE in the absence of Rh catalyst implying that the acid-catalyzed tautomerism might occur during the reaction (see SI). The kinetic isotope effect (KIE) experiment was also carried out to independently assess the rate of reaction for *ortho*-C–H versus *ortho*-C–D activation. The value of $k_{\text{H}}/k_{\text{D}}$ = 4.1 from two parallel reactions as well as the value of KIE = 6.3 from intermolecular competition indicated that the C–H bond-cleavage process is likely involved in the rate-determining step (Scheme 5c).

me 5c).^[21] Additionally, it was observed that the reactivities of aryl-substituted diazenecarboxylates with an electron-donating substituent (e.g., OCH₃) are obviously higher than those with an electron-withdrawing substituent (e.g., *p*-COOMe), which is consistent with an electrophilic C–H activation mechanism.^[22]

Furthermore, we prepared the rhodacycle **A** (Scheme 5d),^[23] which can be easily transformed to rhodacycle **B** in the presence of stoichiometric silver acetate (Scheme 5e). Importantly, when 4 mol% rhodacycle **A** served as the catalyst in the presence of 4 mol% AgOAc in HOAc/DCE (1:3) at RT, the reaction of **1a** and **2a** works efficiently (Scheme 5f), suggesting the plausible intermediacy of a cyclometalated complex **B** in the catalytic cycle. Furthermore, we monitored the reaction of rhodacycle **B** with methyl acrylate in CD₂Cl₂ by ¹H NMR spectroscopy (see SI). No reaction was observed in the absence of HOAc. When HOAc was added to the reaction system, the signal of product **4a** was detected immediately. Presumably HOAc promotes the dissociation of the coordinated acetate of rhodacycle **B** to form the key intermediate cation **C** to initiate this reaction.^[22]

On the basis of our preliminarily mechanistic experiments and literature precedence,^[6,7] we propose that a directed C–H bond cleavage forms intermediate **B** as the first step after generation of [RhCp*(OAc)₂]. An acetate ligand of rhodacycle **B** dissociates to give the cationic complex **C** with assistance from HOAc;^[22] this is followed by alkene coordination and insertion, thus affording the rhodacycle **E** (Scheme 6). The resulting seven-membered metallacycle presumably rearranges to the more stable six-membered coordinately saturated Rh species **F** by chelation with the Boc substituent,^[24] which efficiently prevents competitive β-hydride elimination.^[25] Complex **F** might undergo a nucleophilic addition to the N=N bond to form intermediate **G**, which is finally protonated by HOAc to yield the desired 1-aminoindoline.

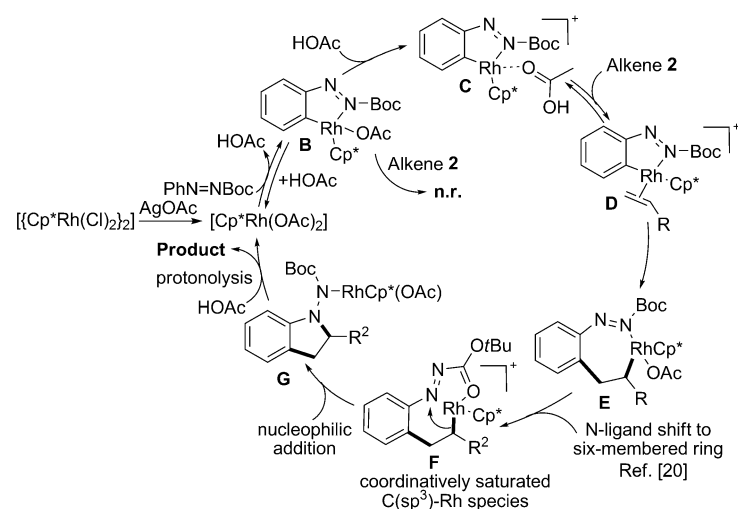
In summary, we have developed the first Rh^{III}-catalyzed synthesis of 1-aminoindolines and 1-aminoindoles from aryl-substituted diazenecarboxylates and alkenes. Mechanistic

studies support a pathway that proceeds via reversible C–H activation, alkene insertion, and Grignard-type addition. This intermolecular annulation proceeds under mild conditions, does not require external oxidants, and displays a broad scope with respect to the substituents.

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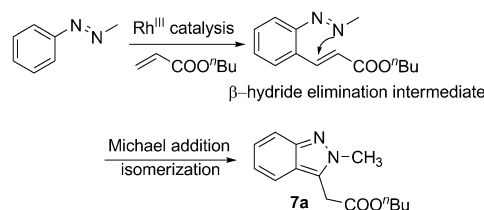
Keywords: C–H functionalization · directing groups · heterocycles · indolines · rhodium



Scheme 6. Proposed reaction mechanism.

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