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From Indoles to Carbazoles: Tandem Cp*Rh(III)-Catalyzed C−H Activation/Brønsted Acid-Catalyzed Cyclization Reactions

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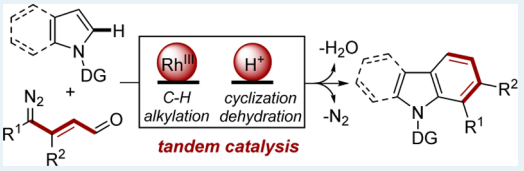
Supporting Information

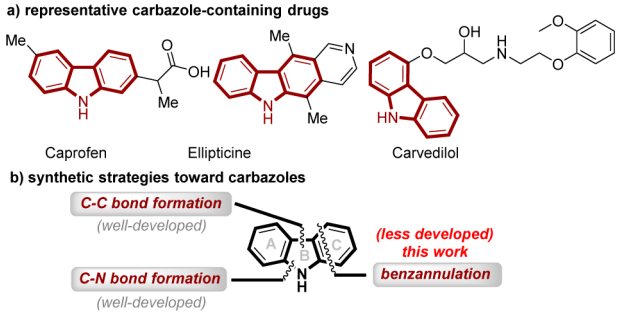
ABSTRACT: A tandem Cp*Rh(III)-catalyzed C−H activation/Brønsted acid-catalyzed intramolecular cyclization allows a facile synthesis of carbazoles from readily available indoles. The reaction proceeds under rather mild reaction conditions with the generation of water and N_2 as the only byproducts. Broad substrate scope, excellent functional group tolerance, and high yields were observed. The benzannulation of pyroles for the synthesis of indoles is also feasible using the same protocol.



KEYWORDS: *Brønsted acid, carbazoles, C−H bond activation, rhodium(III), tandem catalysis*

Carbazoles are important skeletons in functional molecules. For instance, they are widely used in photorefractive materials and organic dyes.[1] In particular, carbazole-containing small molecules are popular in medicinal chemistry as they display various bioactivities (Scheme 1a).[2] As a result, tremendous efforts have been exerted to streamline their synthesis.[3] Traditionally, carbazoles are constructed via the well-known Fischer−Borsche,[4] Bucherer,[5] Cadogan,[6] and Graebe−Ullmann[7] carbazole syntheses. Recently, with the advent and development of organo-transition metal chemistry, methodologies based on transition metal catalysis offer a useful and simple alternative.[8] Not surprisingly, the majority of these methods are targeted on the construction of ring **B**. In contrast, syntheses based on the construction of ring **C** has limited precedent, with a lot of examples necessitating the prefunctionalization of starting material indoles at the α-or/and β-position (Scheme 1b).[9,10] Over the past decade, transition-metal-catalyzed direct C−H functionalization has experienced a fruitful development, allowing for the assembly of diverse C−C and C−heteroatom bonds in an atom- and step-economic manner.[11] In this regard, the carbenoid insertion into C−H bonds, wherein the metal-carbene is proposed to be formed followed by a concerted C−H insertion event, was demonstrated to be powerful and practical in organic synthesis.[12] Recently, an alternative reaction mode involving C−H metalation, metal-carbene formation and migration insertion was found to be operative in Cp*Rh(III),[13] Cp*Ir(III),[14] and Cp*Co(III)[15]-catalyzed C−H coupling reactions with diazo compounds (Scheme 2a).

Scheme 1. (a) Representative Carbazole-Containing Drugs; (b) Synthetic Strategies toward Carbazoles



Very recently, the group of Katukojvala disclosed an efficient synthesis of substituted indoles by using a Rh(II)-catalyzed [4 + 2] benzannulation of pyrroles with enaldiazo ketones or esters as four-carbon synthons (Scheme 2b).[16] The reaction was proposed to occur via a Rh(II)-catalyzed carbonoid C−H insertion/cyclization sequence. Inspired by this elegant work, we devised a tandem catalysis[17,18] strategy for the synthesis of carbazoles from indoles. We envisioned that enaldiazo compounds could serve as intriguing reacting partners in Cp^*Rh^{III}-catalyzed C−H functionalization[19] of indoles to give an enal or aldehyde intermediate (Scheme 2c). Thereafter, in the presence of a Brønsted acid, an intramolecular cyclization/dehydradration reaction could render the synthesis of carbazoles directly from indoles in a one-pot manner. Herein, we report our realization of a tandem Cp*Rh(III) and Brønsted acid catalysis for the benzannulation of indoles, leading to a variety of substituted carbazoles in high efficiency. The reaction occurs under rather mild reaction conditions and generates N_2 and H_2O as the only byproducts. We would like to point out that the application of C−H activation reactions in carbazole syntheses from different starting materials is an active topic in organic synthesis, and a number of elegant examples exist.[20]

To test our hypothesis, 1-(pyrimidin-2-yl)-1*H*-indole **1a** was subjected to react with enaldiazo ester **2a** under the catalysis of

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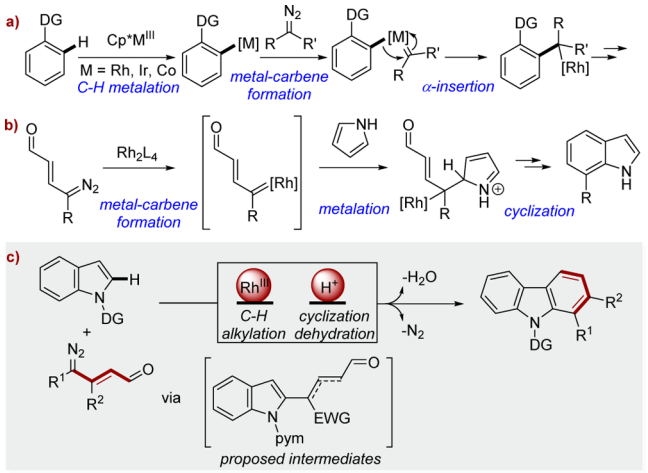
Scheme 2. (a) Cp*Rh(III), Cp*Ir(III), and Co*Co(III)-Catalyzed C−H Coupling with Diazo Compounds; (b) Indole Syntheses via Rh(II)-Catalyzed Carbenoid C−H Insertion/Cyclization Sequence; (c) This Work: Tandem Cp*Rh(III) and Bronsted Acid Catalysis for the Benzannulation of Indoles toward Carbazole Synthesis



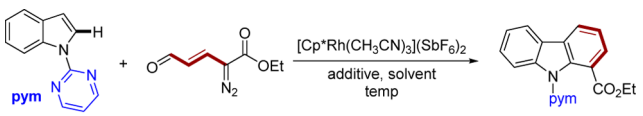
$[Cp^*Rh(CH_3CN)_3](SbF_6)_2$ (5 mol %) in DCE at 35 °C for 20 h (Table 1). Delightedly, the desired benzannulation product **3aa** was obtained, albeit in low yield (10%, entry 1). On the basis of our working hypothesis, we reasoned that the use of acid might facilitate the reaction. Indeed, while the use of CsOAc as additive killed the reactivity (entry 2), the use of PivOH (1.0 equiv) was beneficial for the reaction, giving an improved 33% yield (entry 3). Encouraged by this result, a variety of Brønsted acids were thus screened. Benzoic acid gave a comparable yield (35%, entry 4); however, its stronger acidic analogue, *p*-NO_2PhCOOH, showed superior reactivity (entry 5). Moreover, the use of *p*-TsOH and $(PhO)_2POOH$ further improved the yield to 78% and 91%, respectively (entries 6 and 7). Gratifyingly, the loading of the acid could be decreased to 10 mol %, wherein a similar yield was maintained (entry 8). Control experiments showed that Cp*Rh(III) was essential for this reaction as its omission led to no formation of the desired product (entry 9). A satisfactory yield of 63% was also obtained when 1 mol % of Cp*Rh(III) was employed (entries 10 and 11). Based on a survey of different solvents, $CHCl_3$ gave the best result (entries 12−16). Interestingly, the use of $CHCl_3$/DMF (9:1) as cosolvent delivered **3aa** in an excellent yield of 96%. It is noteworthy that only a slight excess (1.2 equiv) of enaldiazo ester **2a** was used, and no slow addition of **2a** was needed in this reaction (entry 17).

With the optimized reaction conditions (Table 1, entry 17), the generality of this transformation was then explored (Scheme 3). It was found that **2b** and **2c**, bearing a *tert*-butyl and benzyl ester, respectively, were also suitable coupling partners for this reaction (**3ab** and **3ac**). To our delight, a wide range of substituted indoles were converted smoothly to the corresponding carbazoles in generally good to excellent yields.

Functionalities, regardless of the substitution positions and electronic nature, including ether (**3cb**, **3fb**, **3nb**), cyano (**3ib**), ester (**3db**, **3jb**), nitro (**3kb**, **3ob**), fluoro (**3lb**), chloro (**3gb**, **3mb**, **3qb**), bromo (**3hb**), and even formyl (**3eb**) group, were well tolerated. No corresponding product was obtained when biheterocyclic 1*H*-pyrrolo[2,3-*c*]pyridine **1r** was used, probably arising from the strong coordination ability of the pyridine moiety, which hampers the C−H activation event (**3rb**). It is worth noting that enaldiazo ester **2d**, bearing a methyl substituent, was also tolerated, giving carbazole **3ad** in 55% yield.

It was found that not only enaldiazo esters but also enaldiazo ketones were effective for this benzannulation reaction

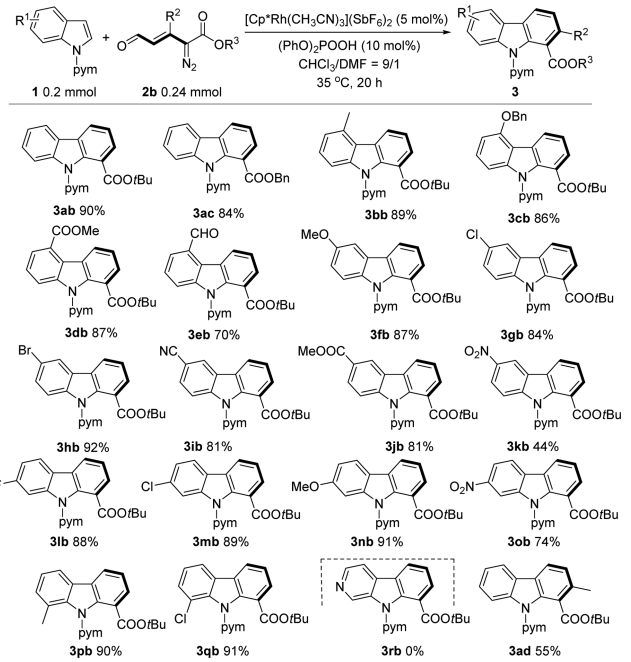
Table 1. Optimization of the Reaction Conditions[a]



entry	Cp*Rh(III) [mol %]	solvent	additive [equiv]	yield [%]
1	5	DCE	-	10
2	5	DCE	CsOAc (1.0)	trace
3	5	DCE	PivOH (1.0)	33
4	5	DCE	PhCOOH (1.0)	35
5	5	DCE	*p*-NO_2PhCOOH (1.0)	65
6	5	DCE	*p*-TsOH (1.0)	78
7	5	DCE	$(PhO)_2POOH$ (1.0)	91
8	5	DCE	$(PhO)_2POOH$ (0.1)	90
9	0	DCE	$(PhO)_2POOH$ (0.1)	0
10	2.5	DCE	$(PhO)_2POOH$ (0.1)	81
11	1	DCE	$(PhO)_2POOH$ (0.1)	63
12	5	MeOH	$(PhO)_2POOH$ (0.1)	trace
13	5	DMF	$(PhO)_2POOH$ (0.1)	trace
14	5	THF	$(PhO)_2POOH$ (0.1)	64
15	5	PhMe	$(PhO)_2POOH$ (0.1)	76
16	5	$CHCl_3$	$(PhO)_2POOH$ (0.1)	92
17	**5**	**$CHCl_3$/DMF (9:1)**	**$(PhO)_2POOH$ (0.1)**	**96**

[a]**1a** (0.1 mmol), **2** (0.12 mmol), $[Cp^*Rh(CH_3CN)_3](SbF_6)_2$ (5 mol %), additive: solvent (1.0 mL), 20 h, 35 °C, isolated yield.

Scheme 3. Benzannulation Reaction of Indoles with Enaldiazo Esters



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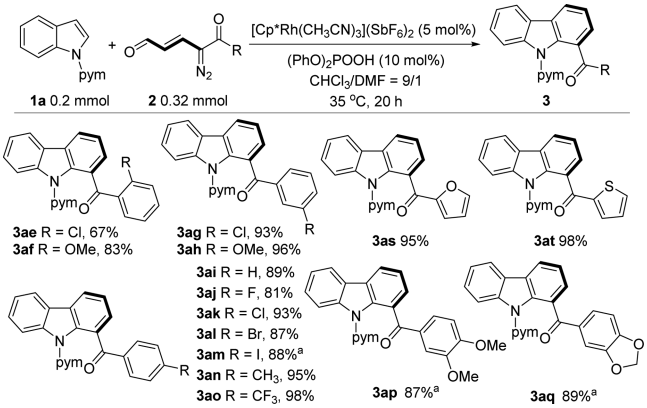
(Scheme 4). In these cases, 1.6 equiv of enaldiazo ketones were subjected to maintain a higher yield. Again, the reaction was

Scheme 4. Benzannulation Reaction of Indoles with Enaldiazo Ketones

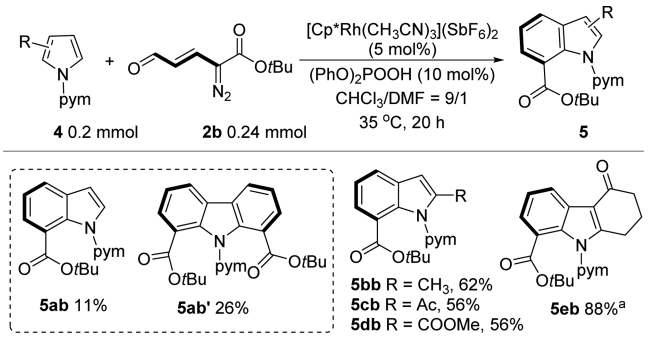


[a]50 °C was used. An additional 3 mol % of $[Cp^*Rh(CH_3CN)_3](SbF_6)_2$ was added after 24 h, and the reaction was stirred for another 8 h.

exceptionally general while reacting with diversely substituted enaldiazo ketones. Numerous commonly encountered functionalities as well as heteroaryl groups including furan and thiophene were well tolerated.

Having established the benzannulation of indoles for carbazoles synthesis, we set to investigate the feasibility of benzannulation of pyrroles using the same protocol (Scheme 5). The reaction of 2-(1*H*-pyrrol-1-yl)pyrimidine **4a** with **2b**

Scheme 5. Benzannulation Reaction of Pyrroles with Enaldiazo Esters

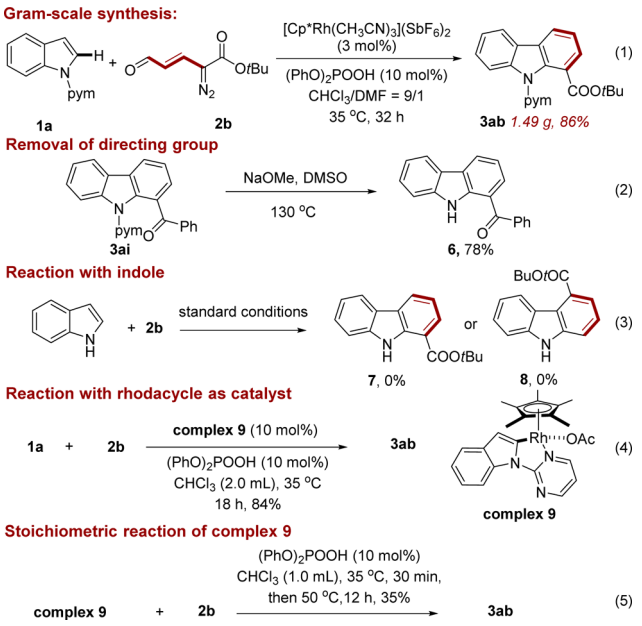


[a]**2b** (0.32 mmol, 1.6 equiv) was used.

delivered bis-benzannulation product carbazole **5ab′** in 26% yield, along with indole **5ab** in 11% yield. With substituted pyrroles, the corresponding indole products were successfully constructed in satisfactory to good yields (**5bb**-**5eb**). Notably, the electron-withdrawing acetyl and ester groups at the α-position were tolerated, which is complementary to Katukojvala's work wherein only electron-withdrawing groups located at the β-position of pyrroles were presented.

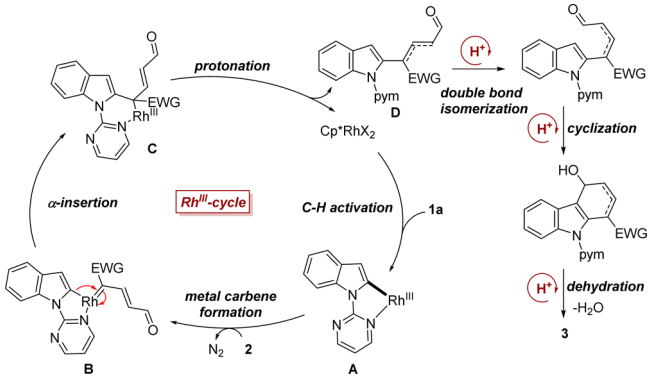
A gram-scale reaction was conducted to evaluate the reaction efficacy on preparative scale. In total, 1.49 g of carbazole **3ab** was obtained in 86% yield with 3 mol % of Cp*Rh(III) catalyst when the reaction was run for 32 h, demonstrating that the reaction is practical (eq 1, Scheme 6). The removal of the directing group went smoothly upon the treatment of NaOMe in DMSO, giving the free carbazole **6** in 78% yield (eq 2).

Scheme 6. Gram-Scale Synthesis, Removal of Directing Group, and Mechanistic Studies



To probe the reaction mechanism, indole was subjected to the reaction instead of **1a**, and no formation of carbazole **7** or **8** was detected (eq 3), suggesting the importance of pyrimidyl group for this transformation. This result might also indicate a reaction mechanism distinct from Katukojvala's work.[16] In addition, when rhodacycle A, prepared according to a literature procedure,[21] was used as a the catalyst, a high yield of 84% was obtained (eq 4). Furthermore, the stoichiometric reaction of complex **9** with **2b** without **1a** gave a yield of 35% (eq 5). These results support a C−H activation/carbene formation sequence is operative in this reaction. On the basis of the above-mentioned experimental results, a plausible mechanism was outlined in Scheme 7. Initially, Cp*Rh(III)-catalyzed C−H activation takes place to give a rhodacycle **A**, which is followed by the metal-carbene formation with enaldiazo compounds to give intermediate **B**. A subsequent α-insertion gives alkyl-Rh(III) species **C**, which upon protonation delivers the regioisomeric alkenes **D**. Several intermediates, which were converted slowly to the final product, were found by TLC

Scheme 7. Mechanistic Rationale



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analysis but were unstable upon isolation. We suspect these intermediates might be a mixture of **D**. Thereafter, the double bond could be isomerized in the presence of Brønsted acid, thereby setting the stage for the intramolecular cyclization. A Friedel−Crafts cyclization and a subsequent dehydration reaction provides the final product **3**. These two steps might also be promoted by the Brønsted acid.

We have identified a Cp*Rh(III)/H^+ tandem catalytic system, which allows the facile construction of carbazoles from indoles. The reaction proceeds under mild reaction conditions with the generation of H_2O and N_2 as the only byproducts. Broad substrate scope, excellent functional group tolerance, and high yields were observed. Besides, the reaction is practical and operationally simple to handle. The benzannulation of pyrroles to indoles is also feasible using the same protocol. Giving the importance of carbazoles and indoles in biologically active compound, we expect this protocol to find many applications.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.5b01801.

Experimental details of the synthesis and characterization of starting materials and final compounds; copies of ^{1}H NMR and ^{13}NMR spectra of all new compounds (PDF)

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Notes

The authors declare no competing financial interest.

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