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Rhodium-catalyzed annulation of hydrazines with vinylene carbonate to synthesize unsubstituted 1-aminoindole derivatives[†]

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Herein, we describe rhodium-catalysed C–H bond activation for [3 + 2] annulation using hydrazide and vinylene carbonate, providing an efficient method for synthesising unsubstituted 1-aminoindole compounds. Characterised by high yields, mild reaction conditions, and no need for external oxidants, this transformation demonstrates excellent regioselectivity and a wide tolerance for various functional groups.

Indole scaffolds,¹ among the most important N-heterocycles, have a wide range of applications, from pharmaceuticals and agrochemicals to renewable energy.² Particularly, 1-aminoindoles³ serve as core components of numerous bioactive molecules, such as commercial drugs like besipirdine^{4b} and indapamide,^{4c} as well as antidepressant and receptor modulators (Fig. 1). Traditional synthetic methods⁵ for these moieties are often complex, involving most synthetic routes requiring multiple steps and electrophilic *N*-aminating reagents, and harsh reaction conditions have limited their synthetic utility and practicality. Consequently, developing more efficient and economically viable synthetic strategies for the 1-aminoindole moiety has attracted significant attention.

Over the past two decades, transition metal-catalysed C–H bond activation⁶ has emerged as a valuable approach for constructing complex molecular scaffolds. Rh(m) complexes,⁷ in particular, have been instrumental in catalysing annulation reactions.⁸ However, only a few studies have been conducted on the synthesis of 1-aminoindole skeletons *via* directed C–H bond activation. Glorius *et al.*^{8a} developed an Rh(m)-catalysed oxidative annulation method using aryl-substituted diazene carboxylates and alkenes, producing C2, C3-disubstituted 1-aminoindoles (Scheme 1a, eqn (1)). Liu *et al.*^{8b} achieved the oxidative annulation of hydrazines with alkynes using 1,3-dinitrobenzene as an oxidant (Scheme 1a, eqn (2)). However, these methods require stoichiometric oxidants.

The coupling of arenes with carbene precursors9 in a redoxneutral manner has introduced important alternatives to oxidative annulation reactions. Wang's group^{10a} realized Rh(III)catalyzed tandem annulation of arylhydrazines with diazo compounds as carbene precursors to yield 1-aminoindole products (Scheme 1b, eqn (3)). Zhu et al.^{10b} successfully used this strategy to synthesise N-aminoindoles via N-Boc cleavage (Scheme 1b, eqn (3)). Cui's group^{10c} he synthesis of 1-aminoindoles through a three-component cyclisation using in situformed hydrazones as guiding groups (Scheme 1b, eqn (3)). Owing to their relatively higher safety and stability, sulfoxonium ylides11 have been demonstrated as carbene surrogates for diazo compounds. Xie12a and Zhang12b independently described a rhodium-catalyzed redox-neutral reaction involving arylhydrazines and sulfoxonium ylides to create C2-substituted 1aminoindole derivatives (Scheme 1b, eqn (4)). Recently, Li and his colleagues13 reported an Rh(III)-catalyzed C-H bond activation reaction of arylhydrazines using iodonium ylides as a carbene precursor (Scheme 1b, eqn (5)). Despite the considerable progress with respect to the synthesis of 1-aminoindole derivatives, the synthesis of C2, C3-unsubstituted 1-aminoindoles through directed C-H bond activation remains underexplored (Scheme 1c, eqn (6)).

Vinylene carbonate¹⁴ is a stable and readily available substance that can be produced on an industrial scale. In 2019,



Fig. 1 Representative bioactive compounds containing 1-aminoindole skeletons.

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Scheme 1 Synthesis of 1-aminoindole compounds by $\mathsf{C-H}$ bond activation.

Miura's group¹⁵ pioneered the use of vinylene carbonate as an acetylene surrogate strategy in C-H functionalization and cascade annulations. Building upon this concept, the facile synthesis of various heterocycles, such as isoquinolines, isocoumarins, quinazolines, quinoline quinolone, pyrazolidinones, cinnolines, and indoles using vinylene carbonate have been realized.¹⁶ In line with our ongoing interest in heterocycle synthesis, we introduce a novel method for synthesising crucial C2, C3-unsubstituted 1-aminoindoles derivatives. This approach involves Rh(III)-catalyzed C-H bond activation and cascade annulation from arylhydrazines and vinylene carbonate (Scheme 1c).

To initiate our investigation of this reaction, we selected 1N'phenylacetohydrazide (1a) and vinylene carbonate (2a) as the model substrates for the coupling reaction (Table 1). We were pleased to discover that the desired 1-aminoindole product 3aa was obtained in 66% yield in the presence of a catalytic combination of $[Cp*RhCl_2]_2$ and $Zn(OAc)_2$ in DMF (Table 1, entry 1). NMR spectroscopy and high-resolution mass spectrometry confirmed the structure of 3aa, which was further validated *via* X-ray crystallographic analysis¹⁷ (Fig. 2). A control experiment demonstrated the necessity of the Rh(m) catalyst; alternative catalysts such as Cp*Co(CO)I₂, $[Cp*IrCl_2]_2$ and [p $cymeneRuCl_2]_2$ did not facilitate the reaction (Table 1, entries 3– 5). The use of the cationic catalyst $[Cp*Rh(MeCN)_3](SbF_6)_2$

Table 1 Optimization of the reaction conditions^a

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	$[Cp*IrCl_2]_2$	$Zn(OAc)_2$	DMF	nd	
	$[p-CymeneRuCl_2]_2$	$Zn(OAc)_2$	DMF	nd	
	None	$Zn(OAc)_2$	DMF	nd	
	$[Cp*RhCl_2]_2$	NaOAc	DMF	nd	
	[Cp*RhCl ₂] ₂	KOAc	DMF	nd	
	$[Cp*RhCl_2]_2$	$Zn(OAc)_2$	t-BuOH	94	
0	$[Cp*RhCl_2]_2$	$Zn(OAc)_2$	MeCN	91	
1	[Cp*RhCl ₂] ₂	$Zn(OAc)_2$	DME	86	
2	$[Cp*RhCl_2]_2$	$Zn(OAc)_2$	DCE	85	
3	[Cp*RhCl ₂] ₂	$Zn(OAc)_2$	Dioxane	80	
4^c	$[Cp*RhCl_2]_2$	$Zn(OAc)_2$	TAA	76	
5	[Cp*RhCl ₂] ₂	$Zn(OAc)_2$	Toluene	70	
6	$[Cp*RhCl_2]_2$	$Zn(OAc)_2$	CH_3OH	nd	
7 ^c	[Cp*RhCl ₂] ₂	$Zn(OAc)_2$	t-BuOH	66	
8^d	$[Cp*RhCl_2]_2$	$Zn(OAc)_2$	t-BuOH	80	
9^e	$[Cp*RhCl_2]_2$	$Zn(OAc)_2$	t-BuOH	90	
0^{f}	[Cp*RhCl ₂] ₂	$Zn(OAc)_2$	t-BuOH	90	

^{*a*} **1a** (0.20 mmol), **2a** (0.40 mmol), catalyst (5 mol%), additive (20 mol%), solvent (2.0 mL), N₂, 80 °C, 16 h. ^{*b*} Isolated yield. ^{*c*} 60 °C. ^{*d*} 100 °C. ^{*e*} For 12 h. ^{*f*} For 20 h.

resulted in a decreased yield (Table 1, entry 2). Various additives were screened, but it was disappointing that no reaction occurred when NaOAc or KOAc was used (Table 1, entries 7 and 8). A range of solvents was tested, including *t*-BuOH, MeCN, DME, DCE, dioxane, TAA, toluene and CH₃OH, with *t*-BuOH proving to be the optimal solvent, achieving a 94% yield of the target product **3aa** (Table 1; entry 9). When CH₃OH was used as the solvent, the reaction did not proceed (Table 1, entry 16). The reaction efficiency was negatively affected by both increments and decrements in reaction temperature (Table 1, entries 17 and 18). Altering the reaction duration to 12 or 20 h resulted in a reduced yield (Table 1, entries 19 and 20).



Fig. 2 Molecular structure of 3aa

With the optimized conditions established, we explored the substrate scope of 1-acetyl-2-phenylhydrazine (Scheme 2). The transformation exhibited a broad substrate scope, accommodating 2-acetyl-1-arylhydrazines with various substituents. 2-Acetyl-1-arylhydrazines, whether bearing electron-donating group (e.g., Me, OMe, and OCF_3) or electron-withdrawing groups (e.g., CF₃, CN, NO₂) at the para position, all reacted effectively with vinylene carbonate, yielding the corresponding products (3ba-3ka) in moderate to good yields. This functional group compatibility proves highly beneficial for synthesizing complex molecules. Furthermore, substrates with halogen substituents (e.g. F, Cl and Br) at different positions were welltolerated, enabling further derivatisation through coupling reactions. This transformation demonstrated excellent regioselectivity, with coupling occurring at the less hindered position for meta-substituted substrates (3la-3na). The reaction seems to be sensitive to steric hindrance, as ortho-substituted phenylacetohydrazines (1m-1o) exhibited limited reactivity (3oa-3ra). When disubstituted derivatives were used in the reaction with vinylene carbonate, the product yield was reduced (3ga, 3ra).



BuOH (2 mL), 80 °C, under N₂ for 16 h. Isolated yields after column

Moreover, when N'-(naphthalen-2-yl)acetohydrazide (1s) was used, the C-H bond at the 3-position, with less steric hindrance was preferred to be functionalized (3sa : 3sa' = 5 : 1, 88%).

Our investigation also included hydrazines with different substitutions at the R^2 position. A pivaloyl (Piv) group led to the formation of 1-aminoindole derivatives (**3ta**) in 58% yield, while an *N*-Boc substituent failed to produce the desired product (**3ua**). Additionally, disubstituted hydrazine **1v** was also explored and the corresponding product (**3va**) could be isolated in 42% yield.

To demonstrate the synthesis utility of our catalytic system, we performed a scaled-up reaction with 6 mmol of hydrazine (1a), obtaining product 3aa in 86% yield (Scheme 3).

A series of experiments was conducted to investigate the reaction mechanism (Scheme 4). Initially, an H/D exchange study was carried out under standard conditions in the presence of D₂O. Only 10% deuterium was incorporated at the C3 position of 3aa but not at other positions (Scheme 4a). The results indicate a protonation process was possibly involved in the transformation. Furthermore, a kinetic isotope effect (KIE) experiment was investigated. An intermolecular competitive KIE experiment using equivalent substrates 1a and 1a-d5 was implemented, revealing a KIE value of 1.4 (Scheme 4b). Moreover, a KIE value of 1.1 was detected based on parallel experiments (Scheme 4b). These results suggested that the C-H bond cleavage might not be involved in the rate-determining step of the overall reaction. Additionally, an intermolecular competition reaction between 1g and 1i was carried out in a one-pot fashion under the optimized reaction conditions, and the products were isolated in a 9:1 ratio (3ga/3ia), demonstrating higher reactivity for the electron-rich substrate (Scheme 4c).

Based on the aforementioned experiments and previous reports,¹⁸ we propose two possible catalytic cycle pathways (Scheme 5, path a and path b). The cycle begins with the activation of a C-H bond, catalysed by rhodium(III), leading to the formation of a five-membered rhodacycle intermediate A. Subsequently, intermediate A coordinates with vinylene carbonate and undergoes migratory insertion of vinylene carbonate into the Rh-C bond, resulting in the formation of a seven-membered metallacycle complex B. Rhodacycle B may further undergo intramolecular amide attack towards Rh, yielding the six-membered E (path a). This is followed by C-N reductive elimination, which is succeeded by the formation of a bond into the adjacent C-O bond, giving rise to intermediate F. Formal β -oxygen elimination is affected to liberate the desired product (3aa) along with the regenerated catalyst, and the extrusion of CO_2 (path a).



Scheme 3 Gram-scale synthesis.

chromatography.



Scheme 4 Mechanistic studies.



Scheme 5 Proposed mechanism.

An alternative possibility is that 1,2-Rh–C bond migration and decarboxylation may occur from intermediate **B**, resulting in the formation of intermediate **C** (path b). Subsequently, a protonolysis process generates the corresponding aldehyde intermediate **D**, along with the regeneration of the Cp*Rh(m). After eliminating water through intramolecular condensation, the final product **3aa** is formed.

Conclusions

In summary, we developed a new method for the stepeconomical synthesis of C2, C3-unsubstituted 1-aminoindole derivatives. This method involves rhodium-catalysed annulation of hydrazines with vinylene carbonate and is scalable to a gram-scale level without substantial yield loss. This protocol showcases a broad substrate scope and exceptional tolerance for various functional groups.

Conflicts of interest

There are no conflicts to declare.

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