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Rh(III)-Catalyzed [4 + 2] Self-Annulation of *N*-Vinylarylamides

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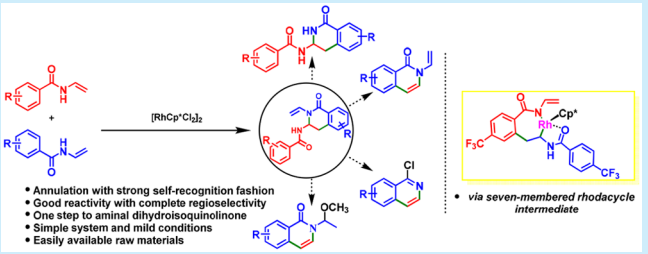
Supporting Information

ABSTRACT: An efficient rhodium(III)-catalyzed self-annulation of *N*-vinylarylamide has been developed. This reaction features a simple system and good reactivity with complete regioselectivity. The protocol provides easy access to an aminal incorporated dihydroisoquinolinone, which proved to be a versatile synthetic synthon. The kinetic isotope effect experiments showed that C−H activation is the rate-limiting step, and competition studies revealed the annulation exhibits a strong self-recognition mode. In addition, a seven-membered rhodacycle species was isolated and established as the key reaction intermediate.



Aminal incorporated dihydroisoquinolinones are important structural motifs in bioactive molecules and drug candidates.[1] For example, the polycyclic compounds containing a substructure core as shown in Figure 1 are agents for the treatment of respiratory syncytical virus infections.[2] In addition, due to the presence of a synthetically important aminal functionality,[3] the aminal dihydroisoquinolinone would be easily transformed into structurally diverse isoquinolinones. As a result, numerous strategies for preparation of such a compound have appeared in the literature (Scheme 1).[4] So far, the most common approaches rely on the reaction of delicately designed substrates with amine, diamine, or vinylamine, etc. For example, the condensation of keto/aldehyde−acid/acyl chloride compound with diamine,[5] the reaction of isocoumarin with amine,[6] or palladium-catalyzed cyclization−amination of *N*-allene benzamides[7] could all construct such a skeleton. However, these established methods are limited to specific and not easily available substrates.

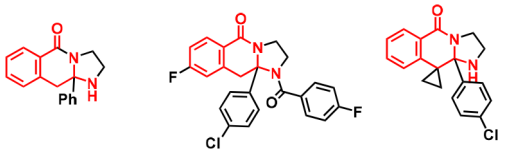
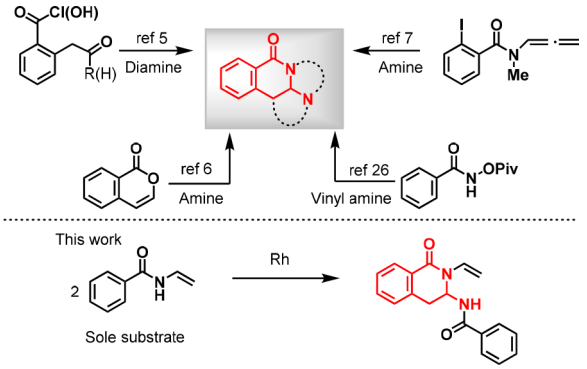


Figure 1. Representive agents for the treatment of respiratory syncytical virus infections.

In 2010, Fagnou and co-workers first reported the Cp*Rh-catalyzed 4 + 2 annulation of benzamides with internal alkynes for construction of the isoquinolinone derivatives by using CONHOMe as the directing group.[8] Since this seminal work, various amide directing groups modified by pivaloyloxy,[9] alkyl,[10] aryl,[11] or 8-AQ (aminoquinoline)[12] have been investigated to effect this type of reaction. These protocols either require an external oxidant or redox-neutral conditions, depending on whether an NH−O bond exists in the directing groups. The coupling partners have been extended from internal alkyne[12a,13] to terminal alkynes,[14] alkenes,[12b,15] arenes,[16] benzyne,[17] allenes,[18] ketenimines,[19] and α-halo- or pseudohaloketones.[20] Several examples of intramolecular reactions have also been reported by Rovis,[21] Glorius,[22] Van der Eyken,[23] and others.[24] These intramolecular reactions allowed for simultaneously building of multiple rings and provided an efficient method to synthesize more complex scaffolds.[25] While the utility of this process for synthesis of various isoquinolinone cores has been well documented, it has

Scheme 1. Strategies for Synthesis of Aminal Isoquinolinone



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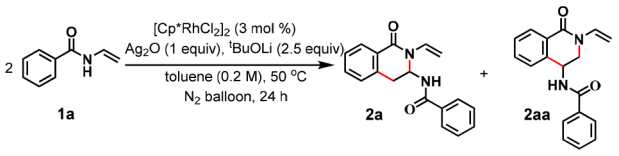
rarely been used to prepare the aminal incorporated isoquinolinone.[26] In considering the development of a more direct and practical route for the synthesis of such a compound, we recognized that a Rh(III)-catalyzed 4 + 2 reaction using *N*-vinylbenzamide as substrate could provide a solution. In this strategy, a rhodacycle is initially formed via a sequential N−H/C−H activation, followed by a regioselective C═C insertion to the Rh−C bond, giving the intermediate with the nitrogen atom closely oriented to the rhodium center, wherein a reductive elimination could afford the dihydroisoquinolinone with an aminal group.[27] Guided by this rationale, we anticipate that the *N*-vinylarylamide would be a promising candidate for the synthesis of such a compound. However, it is surprising to note that no *N*-vinylarylamides have thus far been explored in this kind of 4 + 2 reaction, possibly in large part due to its ease of polymerization.[28] In this report, we disclose an unprecedented Rh (III)-catalyzed 4 + 2 annulation reaction between two molecules of *N*-vinylarylamides, the annulation products of which prove to be versatile synthetic intermediates.

We began our investigation with *N*-vinylbenzamide **1a** as the substrate. As shown in Table 1, under the optimal conditions,

Table 1. Optimization of the Reaction Conditions[a,b]



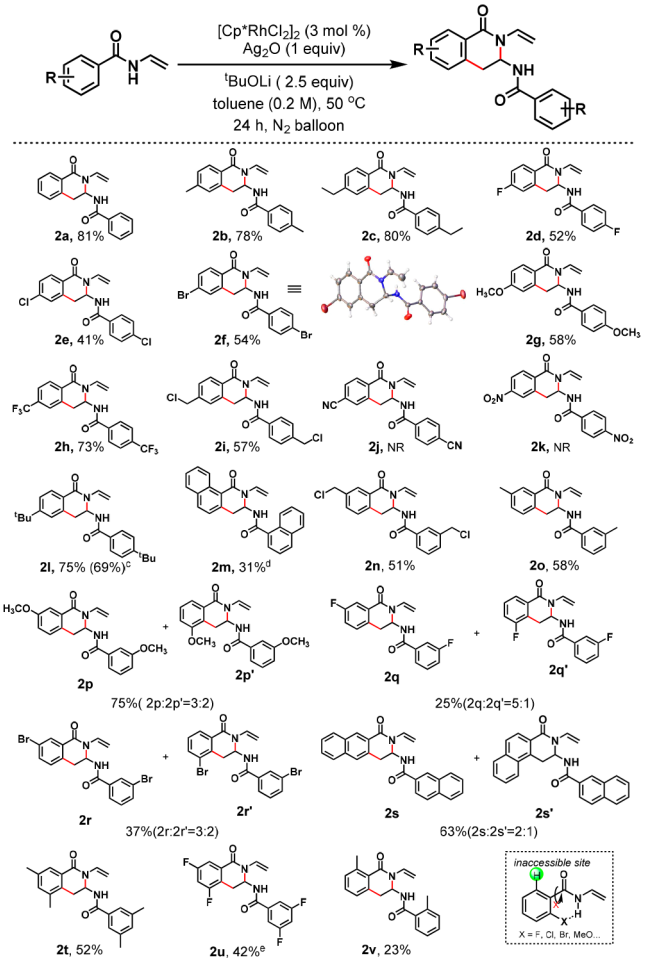
entry	deviation from standard conditions	yield of **2a** (%)
1	no change	81
2	$RhCl_3$, $[Cp^*IrCl_2]_2$, $PdCl_2$ or $Co(OAc)_2$ instead of $[Cp^*RhCl_2]_2$	0
3	at 70 °C[d]	55
4	in absence of oxidant[e]	trace
5	Ag_2CO_3 instead of Ag_2O[c,d]	36
6	KOAc instead of ^{t}BuOLi[c,d]	38
7	in absence of base[c,d]	9
8	in absence of both the oxidant and the base	0[f]
9	DCE instead of toluene[c,d]	40
10	no N_2 balloon protection	72

[a]Standard conditions: *N*-vinylbenzamide (0.2 mmol), $[Cp^*RhCl_2]_2$ (3 mol %), oxidant (0.2 mmol), base (0.5 mmol), solvent (0.2 M), 50 °C, 24 h. [b]Isolated yield. [c]Reaction run at 70 °C. [d]Without N_2 balloon protection. [e]Reaction run at 130 °C. [f]*(Z)-N,N′*-(But-1-ene-1,3-diyl)dibenzamide was obtained.

$[Cp^*RhCl_2]_2$ (3 mol %), Ag_2O (1 equiv), and ^{t}BuOLi (2.5 equiv) in toluene (0.2 M) at 50 °C for 24 h, the desired aminal incorporated isoquinolinone **2a** was obtained in 81% isolated yield without the isomer **2aa** being detected (Table 1, entry 1). Other commonly used catalyst precursors in this kind of reaction, such as $[Cp^*IrCl_2]_2$, $PdCl_2$, $RhCl_3{\cdot}3H_2O$, $Co(OAc)_2$, were all ineffective (Table 1, entry 2). Although the substrate was completely converted by elevating the temperature to 70 °C, the yield of product decreased rapidly accompanied by a large amount of unidentified byproducts (Table 1, entry 3). The oxidant proved to be the prerequisite for this reaction, and in comparison with Ag_2O, other oxidants such as Ag_2CO_3, $AgNO_3$, and CF_3COOAg led to a decreased yield, while $AgSbF_6$ completely inhibited the reaction (Table 1, entries 4 and 5 and Table S3). Moreover, the effects of the other bases and solvents are inferior to the effects of ^{t}BuOLi and toluene (Table 1, entries 6, 7, and 9). Interestingly, at a higher temperature of 130 °C, the absence of oxidant and base led to an unexpected hydro-olefinated product *(Z)-N,N′*-(but-1-ene-1,3-diyl)dibenzamide in 35% yield without any **2a** being detected (Table 1, entry 8). Finally, the reaction yield is slightly reduced without the protection of N_2 balloons (Table 1, entry 10).

With the optimal conditions in hand, we next examined the scope of the substrate. As can be seen in Scheme 2, the

Scheme 2. Scope of the *N*-Vinylarylamides[a,b]



[a]Reaction conditions: *N*-vinylarylamides (0.2 mmol), $[Cp^*RhCl_2]_2$ (3 mol %), Ag_2O (0.2 mmol), and ^{t}BuOLi (0.5 mmol), toluene (0.2 M), 50 °C, 24 h, N_2 balloon atmosphere. [b]Isolated yield. [c]1.2 mmol of **1l** was used. [d]Reaction run at 60 °C. [e]KOAc instead of ^{t}BuOLi.

annulation reaction generally occurs smoothly with a variety of substituents in 23−80% yields with complete regioselectivity. The introduction of alkyl and CF_3 groups to the *para* position has a marginal effect on the reaction, delivering the desired products in 73−80% yields (**2b**, **2c**, **2h**, and **2l**). In contrast, the *para*-halogen, chloromethyl, and OMe substitution only led to moderate yields, ranging from 41 to 58% (**2e−g**, **2i**), allowing for further transformation if needed. Unfortunately, the strong electron-withdrawing substituents, such as CN and NO_2 groups, led to no reactivity (**2j**, **2k**), with the majority of the starting materials recovered. In the case of the *meta*-substituted substrates (**2p−r**), low site-selectivity was observed

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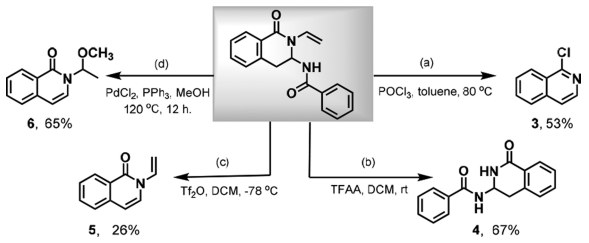
because two *ortho*-C−H bonds are available. An inseparable mixture of two annulation isomers was formed in 3:2−5:1 ratios, with the less crowded one as the major product. Similar phenomena were also observed for *N*-vinyl-2-naphthamide (**2s**). Interestingly, the reaction displayed excellent selectivity for the substrates bearing methyl or chloromethyl groups at the *meta* position, with the annulation occurring exclusively at the sterically less hindered position in moderate yields (**2n**, **2o**). Moreover, 3,5-dimethyl- and -difluorine-substituted substrates which can avoid the site-selectivity problem also gave synthetically useful yields (**2t**, **2u**). Finally, the *ortho*-substituted *N*-vinylbenzamides could also undergo this type of reaction, albeit in a low yield (**2v**). However, no product was obtained with the *ortho*-halogenated *N*-vinylbenzamides. This could be attributed to a conformational restriction exerted by hydrogen-bonding between the halogen atom and the amide NH hydrogen, which makes the *ortho* C−H bond an inaccessible site for Rh(III) to form the important rhodacycle intermediate.

Product **2a** is a synthetically useful intermediate and can be transformed into various useful molecules (Scheme 3). By

Scheme 3. Useful Transformation

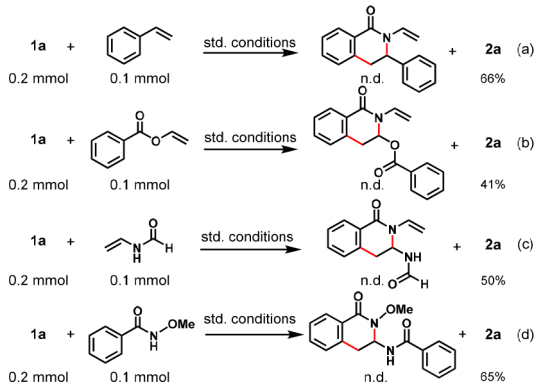


employing different conditions, the benzamido and vinyl groups can be removed simultaneously (**3**) or individually (**4**, **5**). They can also be further functionalized to install another functionality (**6**). Importantly, during the formation of compounds **3**, **5**, and **6**, an equal amount of benzamide was isolated as a byproduct, which can be reused by conversion into the *N*-vinylbenzamide.[29]

A series of intermolecular competition experiments were conducted to gain insight into the mechanism. The 2:1 molar ratio of **1a** and a commonly used annulation partner, such as styrene, vinyl benzoate, *N*-vinylformamide, or *N*-methoxybenzamide, were subjected to the standard conditions. The 4 + 2 annulation only occurs between two molecules of **1a** without a cross-annulation product being detected (Scheme 4). These data reveal a strong self-recognition mode in the formal 4 + 2 reaction of *N*-vinylbenzamide.

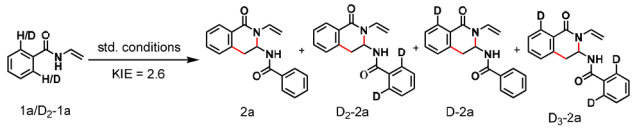
To determine the turnover-limited step of the catalytic cycle, the kinetic isotope effect (KIE) experiment was carried out by treating a 1:1 molar ratio of **1a** and D_2-**1a** with $[Cp^*RhCl_2]_2$, Ag_2O, and ^{t}BuOLi under the standard conditions for 5 h. Then the separated targeted products were subjected to ^{1}H NMR measurement, which gave a KIE value of 2.6, indicating that the C−H bond cleavage was the rate-determining step (Scheme 5a). Subsequently, we reacted **1h** with 25 mol % of $[Cp^*RhCl_2]_2$ in the presence of ^{t}BuOLi without Ag_2O and successfully obtained the important intermediate **D** in 32% isolated yield, accompanied by a trace amount of dirhodium complex **B′**; their structures were confirmed by NMR spectroscopy, HRMS, and X-ray structural analysis, respectively. The catalytic amount of **D** could successfully convert **1h**

Scheme 4. Competition Experiments

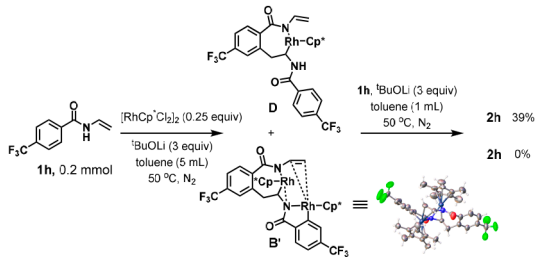


Scheme 5. Mechanism Study

(a) KIE experiment



(b) Seeking the active intermediate



into the expected product **2h** under the otherwise identical standard conditions, whereas **B′** was fully recovered and could not catalyze the reaction. It is clearly shown that the intermediate **D** is most likely the reaction catalytic species, while **B′** is catalytically inactive (Scheme 5b). More importantly, these results provide direct evidence for the five- and seven-membered rhodacycle species[30] involved in the reaction process. The failure in isolation of the mononuclear five-membered rhodacyle species is most likely due to the rapid double bond insertion to the Rh−C bond, which might be the reason why the annulation exhibited a strong self-recognition mode in competition studies.

On the basis of the above results and the related literature,[31] a plausible reaction mechanism is proposed in Scheme 6. First, in the presence of ^{t}BuOLi, catalyst precursor $[Cp^*RhCl_2]_2$ is activated to species **A**, which subsequently cleaves the N−H and *ortho* C−H bonds of **1h** to give the key five-membered rhodacycle complex **B**. Thereafter, rapid coordination of another molecule **1h** via the double bond gives rise to intermediate **C**, which undergoes double bond insertion into the Rh−C bond in two ways to furnish the seven-membered rhodacycle **D** or **D′**. The amide carbonyl group coordinates to rhodium(III) in intermediate **D**, forming a five-membered ring, which provides an extra stabilization of about 21.1 kcalmol^{-1} in comparison with **D′** (see the Supporting Information). A possible benefit from this extra stabilization is that the completely regioselective insertion of the double bond occurs to afford intermediate **D**. Then reductive elimination from **D**

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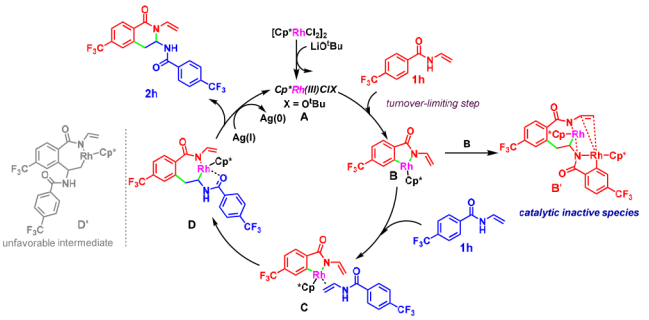
Scheme 6. Proposed Mechanism



gives the desired product **2h** and releases the Rh(I) species. Finally, Rh(I) is oxidized by Ag(I) to regenerate the Rh(III) catalyst. Alternatively, rhodium complex **B** coordinates with another molecule **B** followed by double-bond insertion to afford dirhodium complex **B′**, which has proven to be very stable and fails to deliver any of the desired product. This is probably the catalyst deactivation pathway.

In conclusion, we have developed the first example of a Rh(III)-catalyzed intermolecular *N*-vinylbenzamide annulation reaction featuring a simple and mild reaction system. This unique formal 4 + 2 annulation reaction provides a useful method for the synthesis of the aminal-incorporated dihydroisoquinolinone from the sole easily available *N*-vinylbenzamides. The products proved to be easily transformed into various types of important compounds.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.8b02872.

Experimental details and full spectroscopic data for all new compounds (PDF)

Accession Codes

CCDC 1857356 and 1863830 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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