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Transition-metal-catalyzed C–H functionalization for the direct conversion of C–H bonds to C–C bonds and C–N bonds has evolved into a widespread and effective strategy for fine chemical production.<sup>1</sup> Among these processes, the hydroarylation of C–C double bonds *via* a C–H addition has been well-established and become an effective strategy to access synthetically useful structural motifs.<sup>1</sup> Recently, this alkene hydroarylation reaction has received much attention in an intramolecular fashion<sup>2</sup> (Scheme 1a) because this intramolecular annulation can produce more complex and high value-added structural motifs found in numerous natural products and bioactive molecules (Fig. 1).<sup>3</sup> Despite remarkable progress in this area, most of the annulative protocols developed to date remain limited to one-component intramolecular alkene hydroarylation and functionalization of one side of alkenes. More challenging C–H arylation of intramolecular alkenes followed by a tandem coupling with a different coupling partner have unfortunately proven elusive thus far, thus largely limiting the structural diversity and complexity.

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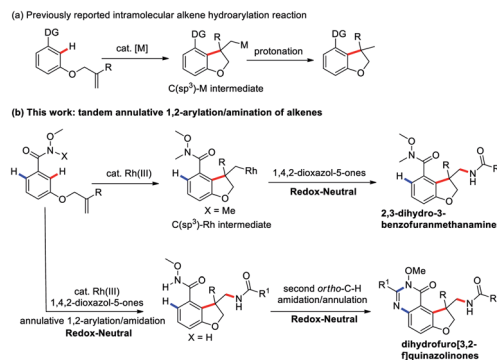
## Rh(III)-catalyzed tandem annulative redox-neutral arylation/amidation of aromatic tethered alkenes†‡

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Transition-metal-catalyzed directed C–H functionalization has emerged as a powerful and straightforward tool to construct C–C bonds and C–N bonds. Among these processes, the intramolecular annulative alkene hydroarylation reaction has received much attention because this intramolecular annulation can produce more complex and high value-added structural motifs found in numerous natural products and bioactive molecules. Despite remarkable progress, these annulative protocols developed to date remain limited to hydroarylation and functionalization of one side of alkenes, thus largely limiting the structural diversity and complexity. Herein, we developed a rhodium(III)-catalyzed tandem annulative arylation/amidation reaction of aromatic tethered alkenes to deliver a variety of 2,3-dihydro-3-benzofuranmethanamine derivatives bearing an all-carbon quaternary stereo center by employing 3-substituted 1,4,2-dioxazol-5-ones as an amidating reagent to capture the transient C(sp<sup>3</sup>)–Rh intermediate. Notably, by simply changing the directing group, a second, unsymmetrical *ortho* C–H amidation/annulation can be achieved to provide tricyclic dihydrofuro[3,2-*f*]quinazolinones in good yields.

On the other hand, nitrogen-containing molecules have gained great attention due to their widespread presence in natural products and widespread use in pharmaceutical science.<sup>4</sup> During the last two decades, transition-metal-catalyzed direct C(sp<sup>2</sup>)–H amination/amidation assisted by chelating directing group is a well-established strategy.<sup>5</sup> Recently, several examples of C(sp<sup>3</sup>)–H amination/amidation have also been reported for the efficient installation of C–N bonds.<sup>6,7</sup> Mechanistically, the reaction is initiated by a chelation-assisted C–H metalation to form a C(sp<sup>3</sup>)–M species, which is then coupled with amination reagents to construct the C–N bonds.

In this context, we wondered if a catalytic annulative C–H arylation of a O-bearing olefin-tethered arenes might be



Scheme 1 Transition-metal-catalyzed C–H functionalization to construct the C–C and C–N bonds.



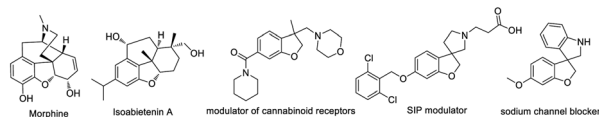


Fig. 1 Representative bioactive 2,3-dihydrobenzofurans.

possible, thus leading to a  $C(sp^3)$ -M intermediate, which upon capture with an amidation reagent to construct a new C-N bond and provide bioactive 2,3-dihydro-3-benzofuranmethanamine derivatives. Inherently, the tandem annulative 1,2-arylation/amidation of alkenes has several challenges. First, the resulting  $C(alkyl)$ -M intermediate is liable to undergo protonation to provide the alkene hydroarylation products.<sup>1,2</sup> Moreover, a potential competing  $\beta$ -H elimination of the resulting  $C(alkyl)$ -M intermediate also required to be suppressed. In addition, compared with the  $C(sp^2)$ -M species, the resulting  $C(alkyl)$ -M species is relatively unstable and also has a low reactivity.

To address these challenges and with our continuing interest in the  $Rh(III)$ -catalyzed C-H functionalization,<sup>8</sup> we introduced a Weinreb amide as a directing group and 3-substituted 1,4,2-dioxazol-5-ones as the amide sources<sup>9</sup> to trigger a new tandem annulative 1,2-arylation/amidation of alkenes *via* a  $Rh(III)$ -catalyzed C-H activation,<sup>10</sup> providing a variety of synthetically challenging 2,3-dihydro-3-benzofuranmethanamine derivatives bearing an all-carbon quaternary stereo center (Scheme 1b). More importantly, through simply changing the directing group, a second, unsymmetrical *ortho* C-H amidation/annulation could be realized to provide tricyclic dihydrofuro[3,2-*f*]quinazolinone derivatives. This protocol provides a good complement to previously reported carboamination reactions.<sup>11</sup>

To begin our studies, Weinreb amide **1a** was reacted with methyl dioxazolone **3a** in the presence of various catalyst and  $AgSbF_6$  at 70 °C in DCE (Table 1, entries 1–4). The use of  $[Cp^*RhCl_2]_2$  as the catalyst was found to be crucial to give the desired tandem annulative product **4a**, with other catalysts, such as  $[Ru(p\text{-cymene})Cl_2]_2$ ,  $[Cp^*IrCl_2]_2$ , and  $Cp^*Co(CO)I_2$ , resulting in no desired product. Attempt to increase or lower the reaction temperature led to a slightly low yield (entries 5 and 6). Interestingly, when employing a NH-OMe amide **2a** as the substrate and using 3 equivalent of **3a**, a second, unsymmetrical *ortho* C-H amidation/annulation was achieved to provide the tricyclic dihydrofuro[3,2-*f*]quinazolinone **5a** in 50% yield (entry 7). A screen of additives (entries 8–10) identified LiOAc as the optimal additive, affording the desired product **5a** in 93% yield (entry 10). The  $Rh(III)$  catalyst was found to be crucial for this tandem annulative arylation/amidation reaction, with no reactivity in its absence (entries 11 and 12).

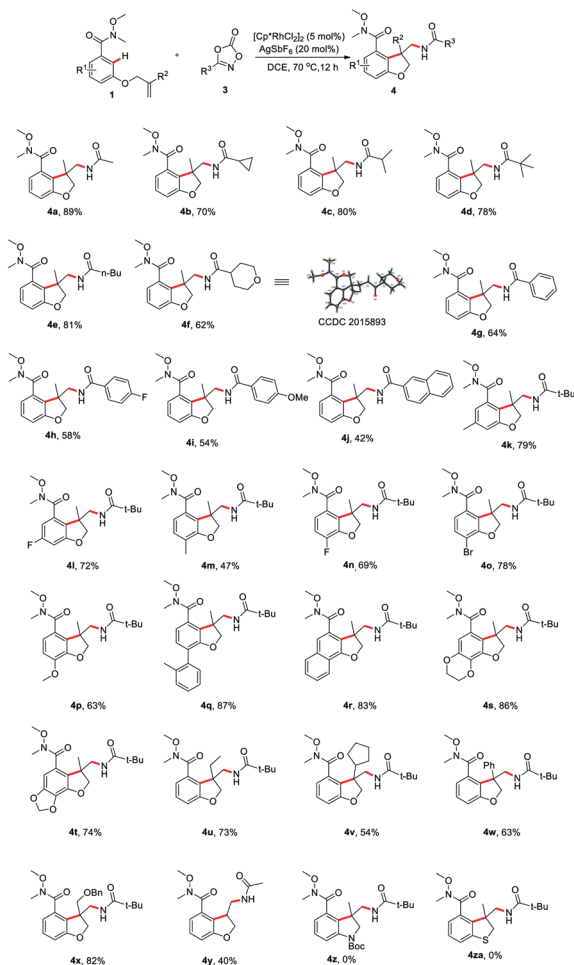
Having determined the optimal reaction conditions, we sought to evaluate the substrate scope (Scheme 2). First, the amidation reagents were explored and 1,4,2-dioxazol-5-ones substituted with primary alkyl (**4a** and **4e**), secondary alkyl (**4b**, **4c** and **4f**), tertiary alkyl (**4d**) and aryl group (**4g–j**) all coupled smoothly with **1a**, providing the 2,3-dihydro-3-benzofuranmethanamines **4a–4j** in good yields. The structure of **4f** was unambiguously confirmed by an X-ray crystallographic analysis (CCDC 2015893). The scope with regards to the arene moiety was then examined. The substrates **1** containing either electron-donating or electron-withdrawing substituents at different positions on the arene ring were well tolerated and provide the desired products **4k–t** in good yields. We were pleased that 2-naphthalenecarboxamide effectively underwent this tandem annulative 1,2-arylation/amidation reaction,

Table 1 Optimization of reaction conditions<sup>a</sup>

Entry	X	Catalyst (5 mol%)	Additive (20 mol%)	Solvent	T (°C)	Yield of <b>4a</b> (%)	Yield of <b>5a</b> (%)
1	Me	$[Cp^*RhCl_2]_2$	—	DCE	70	89	0
2	Me	$[Ru(p\text{-cymene})Cl_2]_2$	—	DCE	70	0	0
3	Me	$[Cp^*IrCl_2]_2$	—	DCE	70	0	0
4	Me	$Cp^*Co(CO)I_2$	—	DCE	70	0	0
5	Me	$[Cp^*RhCl_2]_2$	—	DCE	90	69	0
6	Me	$[Cp^*RhCl_2]_2$	—	DCE	50	70	0
7 <sup>b</sup>	H	$[Cp^*RhCl_2]_2$	—	DCE	70	0	50
8 <sup>b</sup>	H	$[Cp^*RhCl_2]_2$	$Cu(OAc)_2$	DCE	70	0	87
9 <sup>b</sup>	H	$[Cp^*RhCl_2]_2$	KOAc	DCE	70	0	86
10 <sup>b</sup>	H	$[Cp^*RhCl_2]_2$	LiOAc	DCE	70	0	93
11 <sup>b</sup>	H	—	LiOAc	DCE	70	0	0
12	Me	—	—	DCE	70	0	0

<sup>a</sup> Conditions: **1a** (0.1 mmol), **3a** (0.12 mmol), catalyst (5 mol%),  $AgSbF_6$  (20 mol%) and additive (20 mol%) in DCE (1 mL) for 12 h. Yield isolated by column chromatography. <sup>b</sup> Conditions: **2a** (0.1 mmol), **3a** (0.3 mmol), catalyst (5 mol%),  $AgSbF_6$  (20 mol%), additive (20 mol%) in DCE (1 mL) for 12 h. Yield isolated by column chromatography.

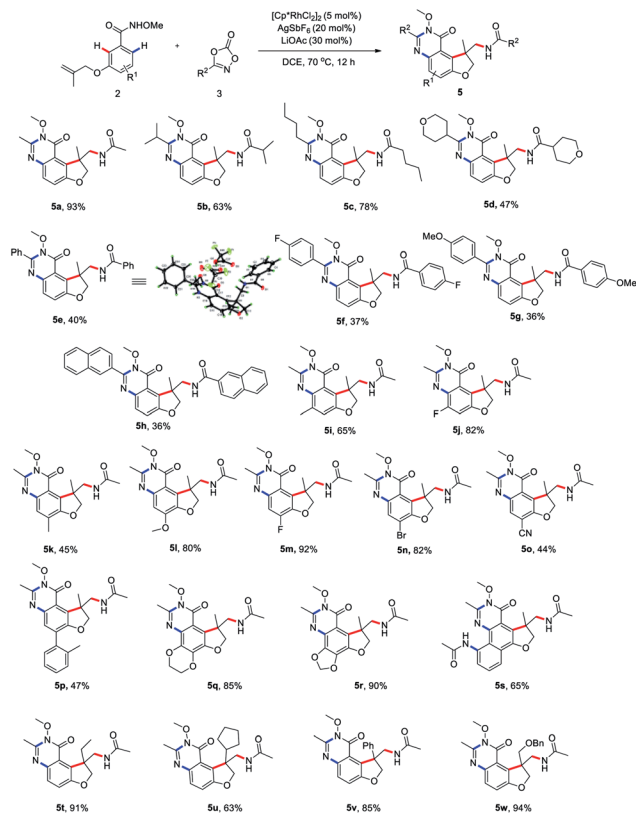




**Scheme 2** Substrate scope of tandem annulative arylation/amidation reaction of aromatic tethered alkenes. Conditions: **1** (0.1 mmol), **3** (0.12 mmol),  $[Cp^*RhCl_2]_2$  (5 mol%),  $AgSbF_6$  (20 mol%) in DCE (1 mL) at 70 °C for 12 h. Yield isolated by column chromatography.

affording the desired product **4r** in good yield. Notably, the various substituted allyl groups such as ethyl, cyclopentyl, phenyl, and phenoxyethyl groups were found to be compatible with the reaction conditions (**4u-x**). In addition, 3-N-tethered and 3-S-tethered substrates failed to give the desired tandem annulative products **4z** and **4za**.

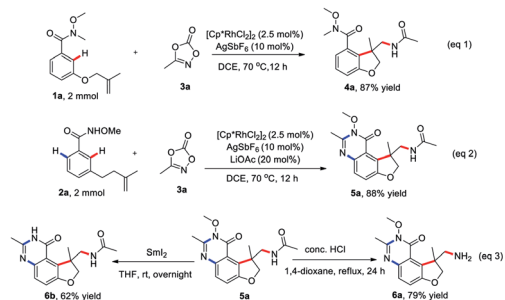
Next, we proceeded to explore the scope of this unsymmetrical twofold C–H functionalization reaction (Scheme 3). Under the optimal reaction conditions, amidating reagents bearing alkyl or aryl groups are fully tolerated, affording the tricyclic dihydrofuro[3,2-*f*]quinazolinones **5a–5h** in good yields. The structure of **5e** was unambiguously confirmed by an X-ray crystallographic analysis (CCDC 2014245). Electronic and steric modification of the aryl group was also tolerated. Both electron-deficient (**5j**, **5m–o**) and electron-rich (**5i**, **5k**, **5l**, **5q** and **5r**) substrates gave the corresponding tricyclic systems in good yields. *Meta* and *para* substitutions of a methyl group were also tolerated and delivered the products **5i** and **5k**, indicating a high tolerance for steric hindrance. Interestingly, when 2-naphthalenecarboxamide was used, a third C–H amidation of



**Scheme 3** Substrate scope of unsymmetrical twofold C–H functionalization reaction. Conditions: **2** (0.1 mmol), **3** (0.30 mmol),  $[Cp^*RhCl_2]_2$  (5 mol%),  $AgSbF_6$  (20 mol%),  $LiOAc$  (20 mol%) and DCE (1 mL) at 70 °C for 12 h. Yield isolated by column chromatography.

naphthalene ring took place, affording the product **5s** in 65% yield. Notably, the current method effectively resulted in the ethyl-, cyclopentyl, phenyl, and phenoxyethyl-substituted products **5t–w** bearing an all-carbon quaternary stereo center in good yield, respectively.

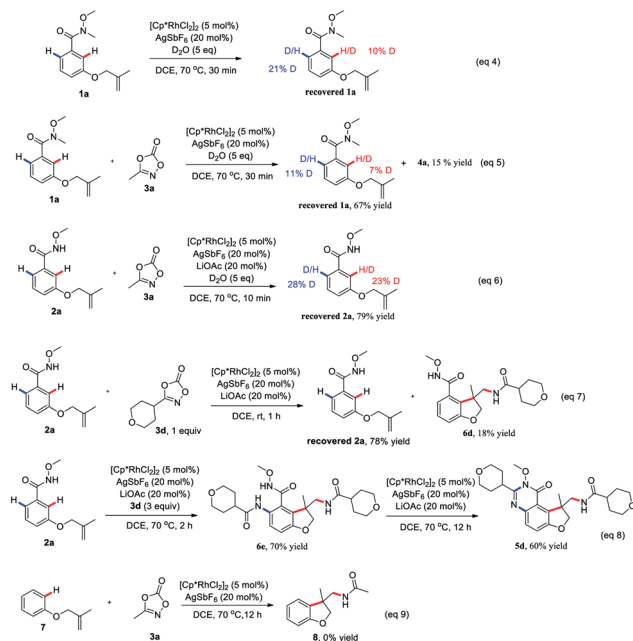
To check the practicability of this protocol, this two procedures could be readily scaled up with comparable efficiency in the presence of 2.5 mol% of Rh(III) catalyst on a 2.0 mmol scale (eqn (1) and (2)). The product **5a** could be readily converted into potential useful intermediates, such as amines **6a** and free amino quinazolinone analog **6b**, respectively (eqn (3)).



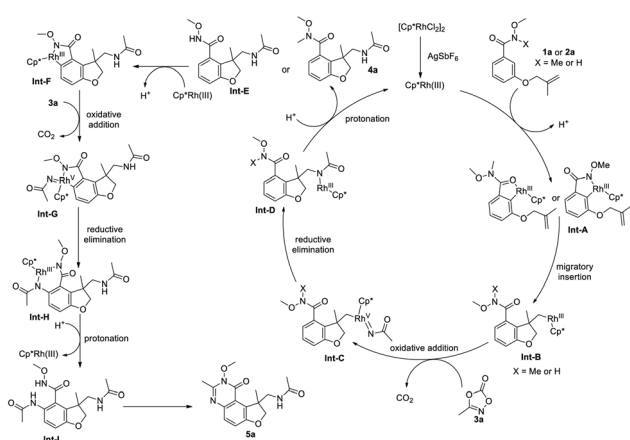
To gain insight into the reaction mechanism, hydrogen/deuterium (H/D) exchange were carried out. A H/D exchange at the *ortho*-position of the amide group in the re-isolated **1a**



and **2a** was observed in the absence or presence of **3a**, indicative of the reversibility of the *ortho* C–H activation (eqn (4)–(6)). Treatment of **2a** with 1 equivalent of **3d** at room temperature for 1 h delivered the **6d** as the sole product, indicating that the intramolecular tandem annulative 1,2-arylation/amidation of alkenes is faster than *ortho* C–H amidation/annulation (eqn (7)). In addition, the use of 3 equivalent of **3d** at 70 °C for 2 h provided **6e** as the main product and subsequent treatment of **6e** under the standard conditions gave **5d** in 60% yield (eqn (8)), indicating that the second *ortho* C–H amidation occurs first, followed by an intramolecular dehydration to give the desired quinazolinone product. Finally, treatment of substrate **7** with **3a** under the standard reaction conditions did not give any product **8**, ruling out the possibility of the insertion of a nitrene to double bond (eqn (9)).



Based on above-mentioned experimental results, a plausible reaction pathway is proposed in Scheme 4.  $[\text{Cp}^*\text{RhCl}_2]_2$  precursor reacts with  $\text{AgSbF}_6$  to form an active cationic  $\text{Rh}(\text{III})$



Scheme 4 Proposed reaction mechanism.

species, which undergoes a C–H bond activation to form cyclometalated complex **Int-A**. Coordination of the tethered olefin and a subsequent migratory insertion affords the intermediate **Int-B**, which undergoes an oxidative addition into the N–O bond of **3a**, followed by a  $\text{CO}_2$  extrusion, to provide the  $\text{Rh}(\text{v})$  nitrenoid species **Int-C**. Reductive elimination occurs to deliver the intermediate **Int-D** which then is protonated to release product **4a** or **Int-E** and regenerate the catalyst. **Int-E** can undergo a second *ortho* C–H activation to give **Int-F**, which can be oxidized by **3a** again to afford the  $\text{Rh}(\text{v})$  nitrenoid species **Int-G**, with a  $\text{CO}_2$  extrusion. Subsequent reductive elimination and protonation give the **Int-I** which undergoes an intramolecular dehydration to deliver the product **5a**.

## Conclusions

In summary, we have developed an unprecedented rhodium-catalyzed tandem annulative arylation/amidation reaction of aromatic tethered alkenes by using 3-substituted 1,4,2-dioxazol-5-ones as an amidating reagent. This robust transformation proceeds with a broad functional group tolerance under relatively mild and redox-neutral reaction conditions, releasing  $\text{CO}_2$  as the single byproduct. A wide variety of 2,3-dihydro-3-benzofuranmethanamine derivatives bearing an all-carbon quaternary stereo center can be accessed with high yields. Notably, by simply changing the directing group, a second, unsymmetrical *ortho* C–H amidation/annulation can be achieved to provide tricyclic dihydrofuro[3,2-f]quinazolinone derivatives in good yields.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

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