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Rh(III)-catalyzed spiroannulation of 3-arylquinoxalin-2(1*H*)-ones with alkynes: practical access to spiroquinoxalinones†

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The Rh(III)-catalyzed synthesis of spiroquinoxalinone derivatives from 3-arylquinoxalin-2(1*H*)-ones and alkynes *via* a C–H functionalization/[3 + 2] annulation sequence has been developed. This method, featuring low catalyst loading, was amenable to Gram scale synthesis and tolerated a variety of functional groups and substitution patterns on the aryl rings, providing the target products in good to excellent yields.

Introduction

Quinoxalinone derivatives are privileged structural motifs found to have a broad spectrum of biological activities and among them spiro-1,2′-quinoxalin-3′-ones are of particular importance (Fig. 1).[1,2] A handful of first-in-class entities with spiroquinoxalinone scaffolds have been employed as potential antibacterial and antiviral reagents.[2a–c] They are also drug candidates for preventing aging[2d] and inhibiting BET proteins to treat cancers.[2e] Conventionally, two approaches for the synthesis of spiroquinoxalinones are available: one is the nucleophilic aromatic substitution reaction of *ortho*-fluoro substituted nitrobenzenes with cyclic amino acids followed by reductive cyclization amide bond formation;[2] the other is the use of aryl 1,2-diamines as substrates *via* Bargellini reaction.[3] However, these procedures are either of poor atom and step economy or lack of regioselectivity, and therefore the development of methods providing practical access to complex spiroquinoxalinone frameworks that are otherwise difficult to be prepared by the established routes would be highly desirable.

On the other hand, transition metal catalyzed functionalization of C–H bond has been proved to be a practical tool for the construction and modification of valuable molecules with high efficiency and regioselectivity.[4] In this regard, the development of tandem C–H functionalization/[3 + 2] annulation reactions are of intense interest to the synthetic communities especially for the synthesis of N-containing spirocycles, and considerable progresses have been made.[5] Such [3 + 2] annulation processes mainly stem from the pioneer works of Takai, Zhao, Cramer and others who respectively employed Re(I),[6a,b] Ru(II)[6c] and Rh(I)[6d,e] as the catalyst and ketimines as the directing groups to effect the cascade.[6f–i] In 2013, Nishimura and co-workers successfully extended the [3 + 2] annulation prototype to access spirocyclic sultams *via* Ir(I)-catalysis (Scheme 1a).[7a] Since then, a number of transition metal catalyzed C–H metalation followed by nucleophilic insertion cyclization of cyclic *N*-sulfonyl ketimines with alkynes or activated olefins for the construction of spirocyclic sultam cores have been successively reported.[7b–f] In addition, cyclic ketimines activated by electron-withdrawing groups are available to the [3 + 2] spirocyclization reactions as well (Scheme 1b).[8] Duo to the weak nucleophilicity of cyclometalation intermediates generated from C–H activation, activated cyclic ketimines are commonly used to facilitate the intramolecular nucleophilic insertion, and spirocycles bearing cyclic amides on the other rings are generally formed. Taking into account that spirocycles tethered by cyclic amines are also of significant importance,[2] it would be tremendously valuable yet challenging to uncover transition metal catalyzed [3 + 2] spiroannulation reactions in which imines are able to

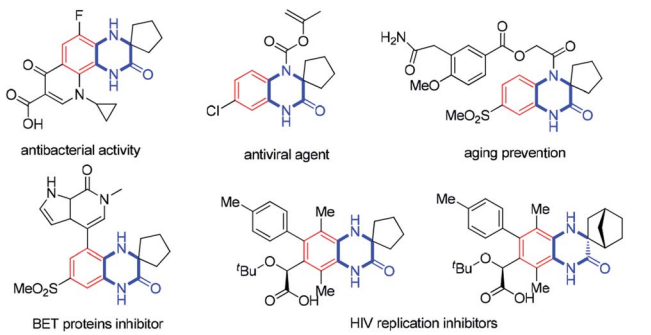

Fig. 1 Selected examples of bioactive spiroquinoxalinones.

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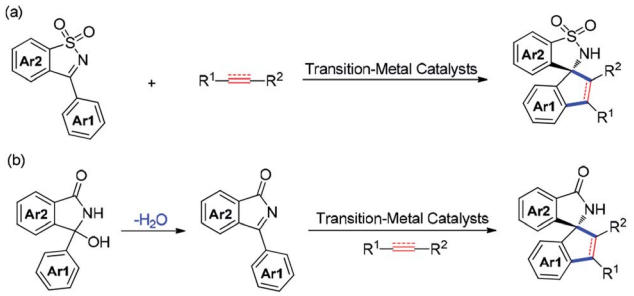


Scheme 1 Synthesis of spirocycles from activated cyclic imines.[7,8] (a) Cyclic *N*-sulfonylketimine. (b) *N*-Acyl ketimines.

participate with concomitant formation of amine rings.[9] Herein, we describe a new approach to the synthesis of spiro-1,2′-quinoxalin-3′-ones *via* the Rh(III) catalyzed C–H activation/[3 + 2] annulation reactions utilizing imine to trap the cyclorhodation species *via* a nucleophilic insertion. With only 1 mol% $[Cp^*RhCl_2]_2$ as the catalyst, we have accomplished the spiroannulation reactions, which was amenable on Gram-scale, of 3-phenylquinoxalinones with alkynes. This protocol is compatible with a broad variety of functional groups and furnishes the desired products in good to excellent yields.

Results and discussion

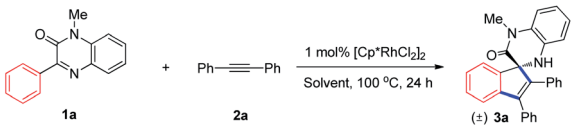
Reaction development

Having the assumption of achieving spiroannulation reactions of cyclic imines in mind, the reaction of 1-methyl-3-phenylquinoxalin-2(1*H*)-one (**1a**)[10] and 1,2-diphenylethyne (**2a**) catalyzed by Rh(III) was selected to verify our hypothesis. Initially, we investigated the effect of solvents on the reaction outcomes using 1 mol% $[Cp^*RhCl_2]_2$ in combination of 4 mol% $AgSbF_6$ as the catalytic system, and gratifyingly obtained the target product with 62% isolated yield when conducted in acetonitrile (Table 1, entry 3). Other solvents, such as DCE, dioxane *etc.*, were inferior (Table 1, entries 1 and 2, see ESI† for more details). Intrigued by those primary results, PivOH was added to the reaction system as additive considering that PivOH might accelerate the C–H activation process and therefore increase the overall yield.[2d,11] As expected, the introduction of one equivalent of PivOH resulted in the improvement of the yield to 86% (Table 1, entry 4). Other proton sources, such as phenol, MsOH and TFA are inferior (see ESI† for more details). The amount of $AgSbF_6$ impacted the transformation dramatically, which did not take place without the addition of $AgSbF_6$ and 6 mol% turned out to be the best furnishing the product in 97% yield (Table 1, entries 5–7). Lowering the catalyst loading to 0.5 mol% and 0.25 mol% decreased the yield even with elevated reaction temperature (Table 1, entries 8–11). Control experiment showed that $[Cp^*RhCl_2]_2$ was indispensable for the reaction (Table 1, entry 12).

Substrate scope

With the optimized reaction conditions established, 3-phenylquinoxalinones with different substituents or substitution patterns on the aryl rings were used to evaluate the substrate

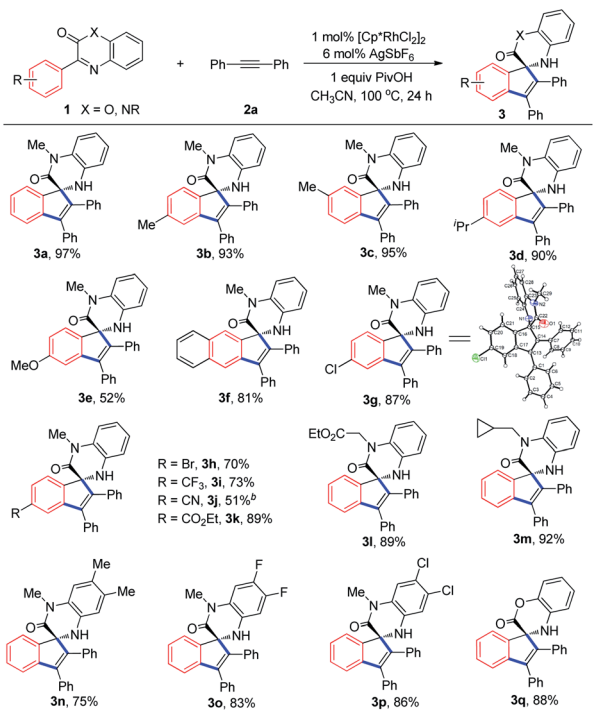
Table 1 Optimization of the reaction conditions[a]



Entry	$AgSbF_6$ (mol%)	Solvent	Additive	Yield[b] (%)
1	4	DCE	—	<10
2	4	Dioxane	—	<10
3	4	CH_3CN	—	62
4[c]	4	CH_3CN	PivOH	86
5	5	CH_3CN	PivOH	91
6	6	CH_3CN	PivOH	97
7	0	CH_3CN	PivOH	0
8[c]	3	CH_3CN	PivOH	76
9[d]	1.5	CH_3CN	PivOH	60
10[c,e]	3	CH_3CN	PivOH	78
11[d,e]	1.5	CH_3CN	PivOH	65
12[f]	6	CH_3CN	PivOH	0

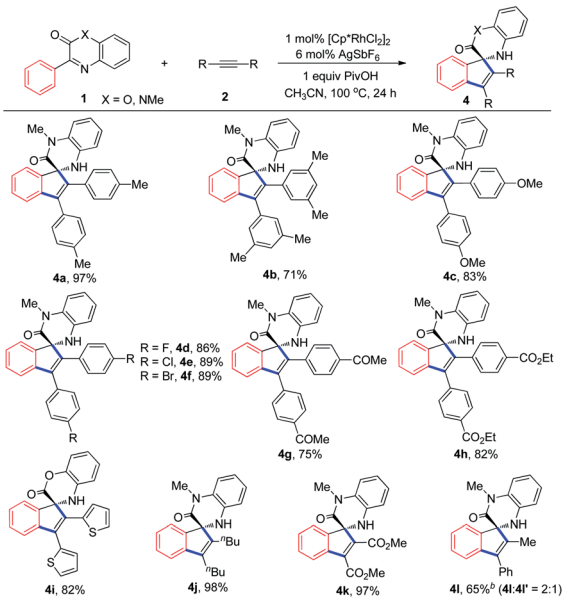
[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.22 mmol), $[Cp^*RhCl_2]_2$ (1 mol%), $AgSbF_6$ (4 mol%), additive (1 equiv.), 2 mL of solvent, 100 °C, 24 h. [b] Isolated yields. [c] 0.5 mmol scale, 0.5 mol% of $[Cp^*RhCl_2]_2$ was used. [d] 0.5 mmol scale, 0.25 mol% of $[Cp^*RhCl_2]_2$ was used. [e] The reaction ran at 120 °C for 24 h. [f] In the absence of $[Cp^*RhCl_2]_2$.

Table 2 Substrate scope of quinoxalinones[a]

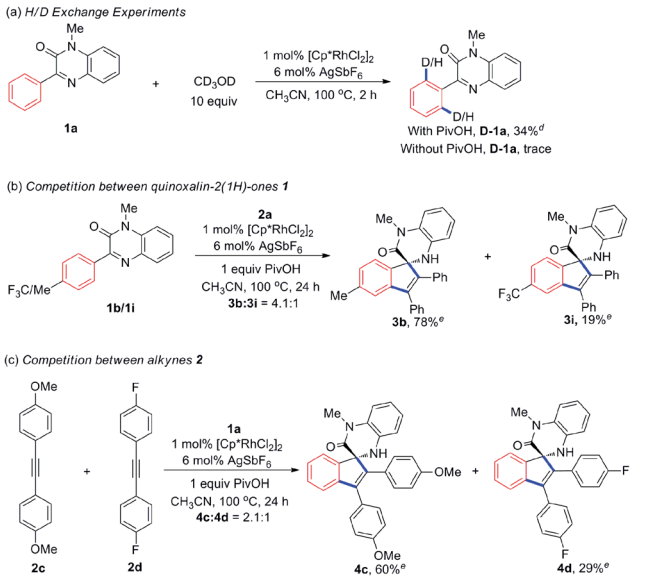


[a] Reaction conditions: **1** (0.2 mmol), **2a** (0.22 mmol), $[Cp^*RhCl_2]_2$ (1 mol%), $AgSbF_6$ (6 mol%), PivOH (1 equiv.), CH_3CN (2 mL), 100 °C, 24 h. Isolated yields. [b] $[Cp^*RhCl_2]_2$ (2 mol%) and $AgSbF_6$ (12 mol%) were used.

Table 3 Substrate scope of alkynes[a]

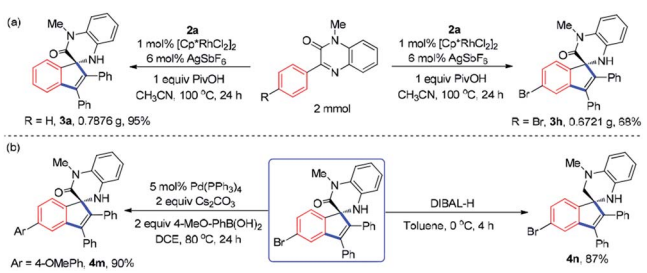


[a] Reaction conditions: **1** (0.2 mmol), **2** (0.22 mmol), $[Cp^*RhCl_2]_2$ (1 mol%), $AgSbF_6$ (6 mol%), PivOH (1 equiv.), CH_3CN (2 mL), 100 °C, 24 h. Isolated yields. [b] Major isomer.



Scheme 3 Primary mechanistic observations. [a]H/D exchange experiments. [b]Competition between quinoxalin-2(1*H*)-ones **1**. [c]Competition between alkynes **2**. [d]Determined by NMR. [e]NMR yield using 1,3,5-trimethoxybenzene as the internal standard.

scope of the reaction. As depicted in Table 2, methyl, isopropyl and methoxyl-substituted quinoxalinones as well as 3-(naphthalen-2-yl)quinoxalinone were all suitable substrates for the transformation and the desired products were generally obtained with satisfying yields (**3b–3f**). The reaction preferred to occur at the less hindered site since **3c** and **3f** were exclusively formed. The reaction was also compatible with chloro, bromo and electron-withdrawing substituents, such as trifluoromethyl, nitrile and ester groups, and delivered the corresponding products in good yields (**3g–3k**). The structure of **3g** was unambiguously determined by X-ray diffraction analysis.[12] 3-Phenylquinoxalinones bearing ester and cyclopropyl groups on the amide moiety could be easily transformed into the target products with yields of 89% and 92% respectively (**3l** and **3m**). Methyl, fluoro and chloro substituents on the quinoxalinone rings did not affect the reaction much (**3n–3p**). Conversion of 3-phenyl-2*H*-benzo[*b*][1,4]oxazin-2-one to the spirocyclization product was achieved as well (**3q**). The reaction conditions are generally compatible with electron-donating and electron-withdrawing substituents on both aryl rings, and electron-donating groups tend to lower the reaction yields. Furthermore, because of the coordination of nitrile group to the active Rh centre impeded the catalytic cycle, only 30% yield of **3j** was obtained when 1 mol% of $[Cp^*RhCl_2]_2$ was used.

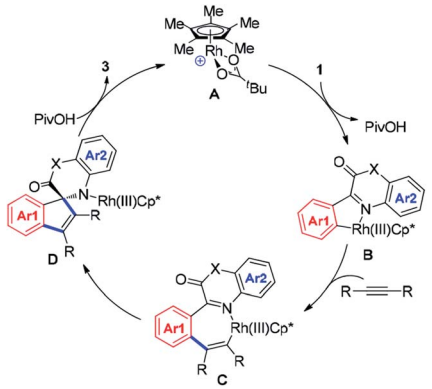


Scheme 2 Gram scale synthesis and product derivations. (a) Gram scale synthesis of **3a** and **3h**. (b) Derivations of **3h**.

Subsequently, we investigated the substrate scope with respect to the internal alkynes (Table 3). Symmetrical alkynes having both electron-donating and electron-withdrawing groups on the aryl rings reacted smoothly with **1a**, giving yields ranging from 71% to 97% (**4a–4h**). The chloro and bromo substitutes within **4e** and **4f** provide the possibility for further derivations. 1,2-Di(thiophen-2-yl)ethyne was found to be able to participate in the reaction even if Rh(III) catalyst has been reported by several research groups to activate the α-position of thiophenes (**4i**).[13] Similarly, other kind of symmetrical alkynes were appropriate reaction partners too (**4j–4k**). Under the optimized conditions, prop-1-yn-1-ylbenzene, an unsymmetrical alkyne, afforded two separable isomers in excellent yield with moderate selectivity (**4l**). Although both symmetrical and unsymmetrical internal alkynes are suitable substrates, terminal alkynes, such as phenylacetylene and ethyl propiolate, failed to deliver the desired products.

Synthetic utilities

To demonstrate the synthetic utility of the transformation, the reactions of **1a** and **1h** with **2a** were then conducted on Gram scale using the standard reaction conditions and satisfying yields, namely 95% and 68%, were acquired (Scheme 2a). Moreover, subsequent conversions of the spirocyclic products were viable. For example, **3h** could undergo Suzuki-coupling



Scheme 4 Plausible mechanism for the Rh(III)-catalyzed spiroquinoxalinone synthesis.

with phenylboronic acid yielding the biaryl product (**4m**) with high efficiency (Scheme 2b). The reduction of amide group in **3h** with DIBAL-H at 0 °C was realized bringing about spirotetrahydroquinoxaline derivative **4n** in 87% yield.

Mechanistic studies

To gain insights into the reaction mechanism, an H/D exchange experiment was firstly carried out. Interestingly, we observed 34% of H/D exchange upon the addition of PivOH, which is in sharp contrast to the result when PivOH was absent (Scheme 3a). This phenomenon indicates that PivOH might help to accelerate the chelation-directed C–H activation process.[2d,11] Intermolecular competition experiment between **1b** and **1i** disclosed that the electron-rich quinoxalinones were more reactive, suggesting a PivOH-assisted electrophilic substitution mechanism for C–H cyclorhodation (Scheme 3b).[14] Additional competition experiment with regard to alkynes revealed that the reaction favored to convert electron-rich alkynes to spirocyclic product (Scheme 3c), which can be explained by a kinetic coordination of alkyne to metal center and is consistent with the previous reports on Rh(III)-catalyzed annulation reactions.[7e,14a,15]

Proposed reaction mechanism

Based on the observations and considerations above, a plausible mechanism was proposed and depicted in Scheme 4. Cationic rhodium **A** coordinated with quinoxalinone **1** followed by the electrophilic substitution of rhodium to the aryl ring to generate rhodacycle **B** with the assistance of $PivO^-$. Subsequently, a seven-membered metallacycle complex **C** came into being *via* the insertion of alkyne, and intramolecular addition of nucleophilic Rh–C bond to imine within **C** simultaneously occurred affording intermediate **D**. On protonation by PivOH, the spirocyclic products **3** were formed with the concomitant releasing of the Rh(III) catalyst. PivOH acted as proton shuttle in the catalytic cycle thus benefited the overall yield.[11b]

Conclusions

In conclusion, we have devised a practical access to spiroquinoxalinone derivatives from cyclic imines and alkynes *via* a tandem Rh(III)-catalyzed C–H functionalization/[3 + 2] annulation sequence. By employing only 1 mol% of Rh(III) catalyst, spiroquinoxalinones bearing a broad range of functional groups and substitution types could be efficiently synthesized on Gram scale with good to excellent yields. Key mechanistic findings illustrated the reason why PivOH was of beneficial effect on the reaction yield. Further studies on the annulation reaction of unactivated cyclic imines affording complex molecules of important biological applications are in progress.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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