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Rhodium(III)-Catalyzed Oxidative Annulation of 2,2′-Bipyridine N-Oxides with Alkynes via Dual C−H Bond Activation

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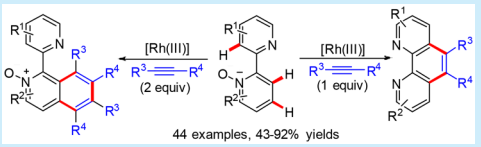
Supporting Information

ABSTRACT: Rh(III)-catalyzed switchable annulation of 2,2′-bipyridine N-oxides with internal alkynes via dual C−H bond activation has been developed. Tuning the reaction conditions enabled the reaction pathway to be switched between rollover and nonrollover annulation, delivering 5,6-disubstituted-1,10-phenanthrolines and 5,6,7,8-tetrasubstituted-1-(pyridin-2-yl)isoquinoline 2-oxides in high yields, respectively. The procedures feature excellent regioselectivity, broad substrate scope, and high tolerance of functional groups. The synthetic utilities of these obtained products were demonstrated in the catalytic reactions.



The past decade has witnessed the tremendous advances of transition-metal-catalyzed direct conversion of inert C−H bonds into C−C and C−X bonds for the synthesis and functionalization of various heterocyclic compounds.[1] It is not surprising that the wide application of 2,2′-bipyridines in coordination chemistry, transition-metal catalysis, supramolecular chemistry, and material science has encouraged the synthetic chemists to explore the feasibility of direct functionalization of these useful compounds under transition-metal catalysis via direct pyridyl C−H bond activation.[2] However, attempts at direct C−H functionalization of 2,2′-bipyridines has been met with limited success, mainly because of their low electrophilicity and the catalyst poisoning by the strong coordination of N atoms.[3] In 2009, Miura and co-workers first reported the regioselective direct alkenylation of 2,2′-bipyridines with terminal silylacetylenes under Rh(I) catalysis.[3a] Later, Chang et al. described the hydroarylation of alkenes and alkynes with 2,2′-bipyridines in the presence of a Rh(NHC) catalytic system.[3b,c] It is believed that the introduction of the NHC ligand allows the facile decomplexation of one of the N atoms from *N*,*N*-chelate complex of 2,2′-bipyridines, thereby facilitating rollover cyclometalation that results in pyridyl C−H activation. Recent studies of the stoichiometric reaction of 2,2′-bipyridine N-oxide with a dimethylplatinum(II) complex by Puddephatt and co-workers revealed a rollover cyclometalation of the N-oxide ring with pyridine as a directing group, and no coordination of the N-oxide oxygen was observed.[4a] Therefore, it is natural to expect that 2,2′-bipyridine N-oxides would be more suitable substrates for direct C−H functionalization under transition-metal catalysis. Unfortunately, the chemistry about the direct functionalization of 2,2′-bipyridine N-oxides has been less investigated, with only one report known in the literature. Tzschucke and co-workers reported the Pd(II)-catalyzed direct halogenation of 2,2′-bipyridine N-oxides via rollover cyclometalation, and the halogenated products could be easily deoxygenated.[4b]

Recently, Rh(III)-catalyzed C−H bond annulation with alkynes has evolved into a powerful tool for the preparation of highly substituted polycyclic aromatic compounds.[5−7] In particular, several novel fused polycyclic (hetero)arenes could be readily synthesized by annulation reactions of (hetero)-arenes with alkynes under Rh(III) catalysis via double C−H activation involving chelation-assisted *ortho* C−H activation and subsequent rollover or nonrollover C−H activation.[6,7] Notably, the reaction pathway between rollover and nonrollover annulation can be switched by varying the reaction conditions, thereby delivering different types of products from the same substrates. For example, Miura and Satoh et al. found that Rh(III)-catalyzed rollover annulation of 1-phenyl-1*H*-pyrazoles with 1 equiv of alkynes could give 4,5-disubstituted pyrazolo[1,5-*a*]quinolones (Scheme 1a, right), while the nonrollover annulation of 1-phenyl-1*H*-pyrazoles with 2 equiv of alkynes afforded 1-(5,6,7,8-tetrasubstituted naphthalen-1-yl)-1*H*-pyrazoles as the products under slightly modified conditions (Scheme 1a, left).[6a] In a similar way, Dong and co-workers described the selective synthesis of different 7-azaindole derivatives in the annulation of 7-azaindoles with alkynes (Scheme 1b).[6b] More recently, Choudhury et al. demonstrated the rollover and nonrollover annulations of imidazoles with alkynes (Scheme 1c).[6h] Inspired by these elegant studies, we envisioned that tuning the reaction conditions may allow the structurally similar 2,2′-bipyridine N-oxides to undergo chelation-assisted rollover or nonrollover annulation with alkynes to give novel 2,2′-bipyridine derivatives that cannot be readily prepared using known methods. Following our continued interest in catalytic direct C−H functionalization of heteroarenes,[8] herein, we demonstrate that

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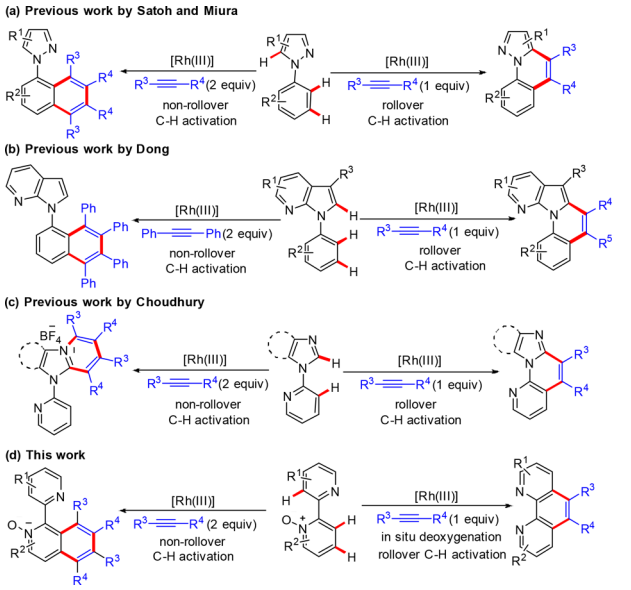
Scheme 1. Rh(III)-Catalyzed Rollover and Nonrollover Annulation of Heteroarenes with Alkynes via Dual C−H Activation

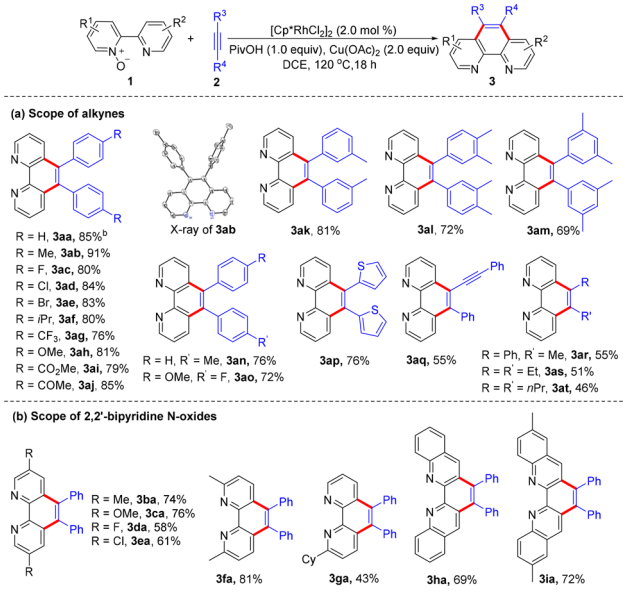


switchable rollover and nonrollover annulation of 2,2′-bipyridine N-oxides with internal alkynes to access 5,6-disubstituted-1,10-phenanthrolines and 5,6,7,8-tetrasubstituted-1-(pyridin-2-yl)isoquinoline 2-oxides, respectively, can be achieved by tuning the reaction conditions in the Rh(III) catalytic systems (Scheme 1d).

We commenced our studies by investigating the reaction of 2,2′-bipyridine N-oxide (**1a**) with 1,2-diphenylethyne (**2a**) (see the Supporting Information (SI)). We first attempted the reaction of **1a** (0.5 mmol) and **2a** (1.0 mmol) with $[Cp^*RhCl_2]_2$ as the catalyst precursor and $Cu(OAc)_2$ as the oxidant in DCE at 120 °C. To our surprise, the reaction only gave a mixture of 5,6-diphenyl-1,10-phenanthroline (**3aa**) and 2,2′-bipyridine in 29% and 20% yields, respectively, and the expected product, 5,6-diphenyl-1,10-phenanthroline 1-oxide (**3aa′**) was not observed (see Table S1, entry 1, in the SI). This result suggests that in situ deoxygenation might occur during the process. The yield of **3aa** could be increased to 45% upon the addition of HOAc as the additive (Table S1, entry 2). Subsequent screening of additives revealed that PivOH turned out to be optimal and provided the product **3aa** in 90% yield (Table S1, entry 5). It appears that deoxygenation of **1a** was suppressed in the presence of acid, as no 2,2′-bipyridine was observed in these reactions (Table S1, entries 2−7). Further optimization showed that the yield of **3aa** dropped significantly when replacing DCE with other solvents (Table S1, entries 8−21), and other oxidants were inferior to $Cu(OAc)_2$ (Table S1, entries 22−30). The reaction did not occur when omitting the oxidant, thereby ruling out the possibility that the N-oxide moiety acts as an internal oxidant in the reaction process (Table S1, entry 43).[9] No reaction proceeded in the absence of $[Cp^*RhCl_2]_2$, suggesting the indispensability of a rhodium catalyst for this reaction (Table S1, entry 44). Notably, neither a dried solvent, nor an inert atmosphere is required in this reaction. Thus, the optimal reaction conditions were set as $[Cp^*RhCl_2]_2$ (2.0 mol %), PivOH (1.0 equiv), and $Cu(OAc)_2$ (2.0 equiv) in DCE at 120 °C for 18 h.

Under the optimized reaction conditions, we then examined the coupling reaction of **1a** with various internal alkynes (see Scheme 2a). Symmetric diarylacetylenes **2b−2j** bearing differ-

Scheme 2. Annulation of 2,2′-Bipyridine N-Oxides with 1 equiv of Internal Alkynes[a]



[a]Reaction conditions: **1** (0.2 mmol), **2** (0.22 mmol), $[Cp^*RhCl_2]_2$ (2.0 mol %), $Cu(OAc)_2$ (2.0 equiv), PivOH (1.0 equiv), DCE (3.0 mL), 120 °C, 18 h. [b]Isolated yield in a gram scale reaction.

ent *para*-substituents on the aryl ring all smoothly underwent a reaction with **1a** to afford the corresponding products (**3ab−3aj**) in 71%−91% yields; the electronic nature of these substituents has little effect on the reaction's efficiency. The structure of **3ab** was confirmed by single-crystal X-ray diffraction (CCDC 1563903). Bis(3-substituted phenyl) acetylenes **2k−2m** also exhibited good reactivity, delivering the target products (**3ak−3am**) in good yields. Similarly, unsymmetrical diarylacetylenes (**2n**,**2o**) proceeded well, allowing for the isolation of **3an** and **3ao** in 76% and 72% yields, respectively. 1,2-Di(thiophen-2-yl)ethyne (**2p**) has been proven to be a viable coupling partner to generate **3ap** in 76% yield. The reaction also tolerated the use of 1,4-diphenylbutadiyne (**2q**), 1-phenyl-1-propyne (**2r**), and dialkylacetylenes (**2s** and **2t**). To showcase the scalability of the current transformation, a gram-scale reaction of **1a** and **2a** was performed to give **3aa** in 85% yield under the standard reaction conditions.

We next investigated the scope of 2,2′-bipyridine N-oxides (Scheme 2b). We found that 5,5′- and 6,6′-disubstituted 2,2′-bipyridine N-oxides (**1b−1f**) reacted smoothly with **2a** to provide the corresponding products (**3ba−3fa**) in 58%−81% yields. In the case of 6-cyclohexyl-[2,2′-bipyridine] 1-oxide (**1g**), the product **3ga** was isolated only in 43% yield, probably because of the steric effect. Delightfully, 2,2′-biquinoline 1-oxides (**1h**,**1i**) could also engage in the reaction to deliver the expected products (**3ha**, **3ia**) in good yields.

During the course of optimization of the reaction conditions for the production of **3aa**, we serendipitously found that the reaction of **1a** and **2a** in DCE at 100 °C with $[Cp^*RhCl_2]_2$ as the catalyst precursor and $Cu(OAc)_2$ as the oxidant gave 5,6,7,8-tetraphenyl-1-(pyridin-2-yl)isoquinoline 2-oxide (**4aa**) (23% yield, 18 h) as the solo product, in the absence of any

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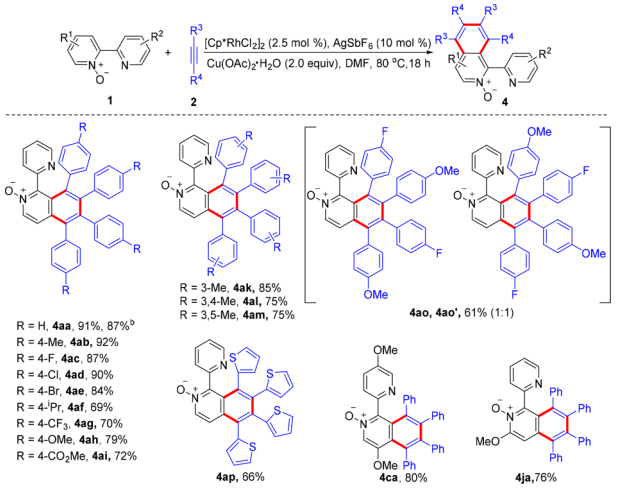
additive. This observation prompted us to further explore this transformation. After extensive optimization, we found that the combination of $[Cp^*RhCl_2]_2$, $AgSbF_6$ and $Cu(OAc)_2{\cdot}H_2O$ could work effectively to catalyze the reaction of 2,2′-bipyridine N-oxide with 2 equiv of internal alkynes in DMF at 80 °C to give the corresponding 5,6,7,8-tetrasubstituted-1-(pyridin-2-yl)isoquinoline 2-oxides (**4aa**−**4ai**, **4al**, and **4am**) in good to excellent yields with good tolerance of functional groups in both coupling partners (see Scheme 3). We noted that

Scheme 3. Annulation of 2,2′-Bipyridine N-Oxides with 2 equiv of Internal Alkynes[a]

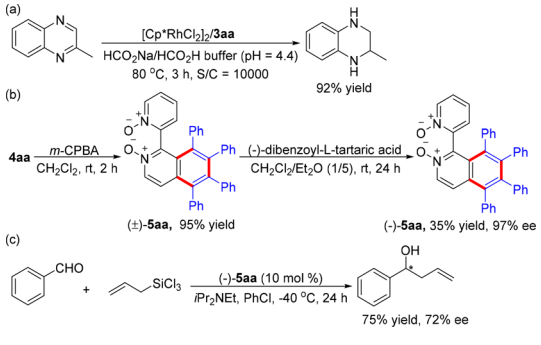


[a]Reaction conditions: $[Cp^*RhCl_2]_2$ (2.5 mol %), $AgSbF_6$ (10 mol %), **1** (0.2 mmol), **2** (0.5 mmol), $Cu(OAc)_2{\cdot}H_2O$ (2.0 equiv), DMF (3.0 mL), 80 °C, 18 h. [b]Isolated yield in a gram-scale reaction.

unsymmetrical alkyne **2o** was also applicable, but a mixture of two inseparable regioisomers was isolated in an ∼1:1 ratio (**4ao** and **4ao′**). When 1,2-di(thiophen-2-yl)ethyne (**2p**) was used, **4ap** was obtained in 66% yield. Reactions of **1c** and **1j** with **2a** proceeded smoothly to produce **4ca** and **4ja** in 80% and 76% yields, respectively. Further study indicated that **1a** could be transformed to **4aa** in a gram-scale with 87% yield, demonstrating the scalability of this transformation.

To showcase the utility of these annulation products, we first attempted the application of **3aa** as the ligand in an Rh(III)-catalyzed transfer hydrogenation of quinoxaline in water, and the desired 1,2,3,4-tetraquinoxaline was obtained in 92% yield (Scheme 4a).[10] Considering the potential of 2,2′-bipyridine *N*,*N*′-dioxides as promising chiral organocatalysts,[3b] (−)-**5aa**

Scheme 4. Synthetic Application of 2,2′-Bipyridine N-Oxide Derivatives

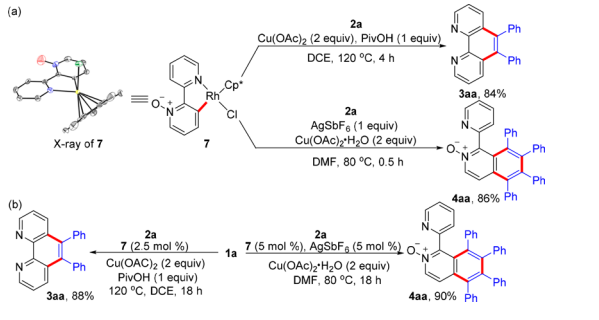


was then synthesized via N-oxidation of **4aa** with *m*-CPBA to give racemic **5aa** and subsequent optical resolution of racemic **5aa** with (−)-dibenzoyl-L-tartaric acid (Scheme 4b). With (−)-**5aa** (10 mol %) as the catalyst, the allylation of benzaldehyde with trichloroallylsilane delivered the target product 1-phenylbut-3-en-1-ol in 75% yield and 72% ee (Scheme 4c).[3b,7c] In addition, products **4** could be readily deoxygenated by PCl_3, and the measurement of absorption and emission spectra of these obtained 2,2′-bipyridines were performed (see the SI). Notably, 5,6,7,8-tetrakis(4-chlorophenyl)-1-(pyridin-2-yl)isoquinoline (**6ad**) exhibited strong fluorescence emission at a broad range of 360−475 nm.

To address the question of in situ deoxygenation in the formation of products **3**, several control experiments were conducted (see the SI). No reaction was observed when treating 2,2′-bipyridine with **2a** under the standard reaction conditions. The HRMS analysis of the reaction system of **1a** and **2a** under the standard conditions confirmed the generation of 5,6-diphenyl-1,10-phenanthroline 1-oxide (**3aa′**) during the reaction process. Furthermore, when **3aa′** was subjected to the standard reaction conditions, **3aa** was obtained in 95% yield. Further study indicated that this catalytic deoxygenation of **3aa′** proceeded equally well in the absence of $Cu(OAc)_2$ and PivOH, but the reaction did not occur without using $[Cp^*RhCl_2]_2$. These results show that DCE could act both as a solvent and a reductant in this Rh(III)-catalyzed deoxygenation reaction.

In order to gain more insight into the reaction mechanisms, additional experiments were performed. The reversibility of C−H activation was first examined (see the SI). The observed H/D scrambling in the deuterium labeling experiments between **1a** and CD_3CO_2D under the standard conditions in the absence of alkyne suggested that a reversible C−H activation step may be involved in the two transformations. However, no deuteration of **1a**, **3aa**, and **4aa** was observed when performing the same reactions in the presence of **2a**, revealing the possible involvement of an irreversible alkyne insertion.[11] The reaction of **1a** with $[Cp^*RhCl_2]_2$ led to the formation of a five-membered cyclometalated rhodium(III) intermediate **7**, the structure of which was confirmed by single-crystal X-ray diffraction (XRD) studies (CCDC 1563904). The coordination of pyridine N-oxide oxygen atom to Rh(III) center was not observed.[12] The stoichiometric reactions of **2a** with **7** afforded the products **3aa** and **4aa** in high yields in shorter reaction times (Scheme 5a). Further studies showed that **7** could catalyze the annulation reactions of **1a** with **2a** to give the expected products **3aa** and **4aa** in essentially the same yields to those obtained under the standard reaction conditions (Scheme 5b). These results clearly indicate the potential intermediacy of

Scheme 5. Mechanistic Studies



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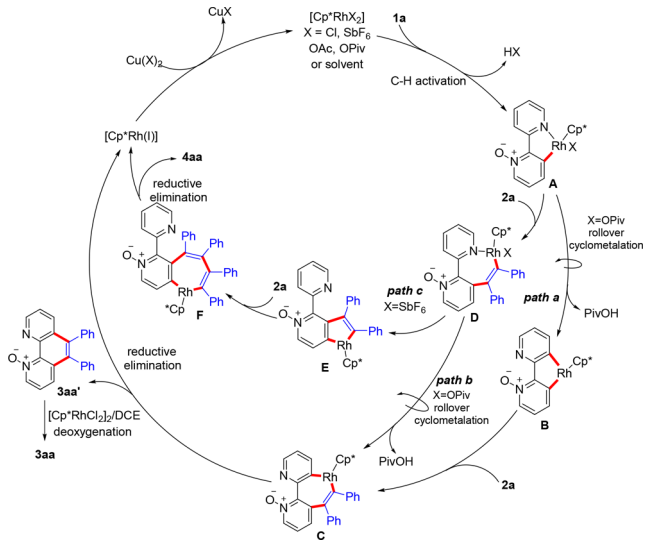
the five-membered rhodacycle species in the two catalytic processes.

Based on these observations and the literature precedents,[5−7] possible catalytic cycles for both transformations are given in Scheme 6. First, cyclometalation of **1a** generates a five-membered rhodacyclic intermediate **A**. In the presence of PivOH (X = OPiv), path a is favored to deliver a rhodacyclic intermediate **B** via a rollover cyclometalation, because of the strongly basic and coordinating nature of OPiv anion. Insertion of alkyne **2a** gives a seven-membered rhodacycle **C** (path a), which undergoes reductive elimination to deliver product **3aa′** and a Rh(I) species. The Rh(I) is reoxidized by $Cu(OAc)_2$ to regenerate the active Rh(III) catalyst for the next catalytic cycle, and Rh(III)-catalyzed deoxygenation of **3aa′** affords the product **3aa**. Alternatively, intermediate **A** possibly first reacts with **2a** to afford a seven-membered rhodacycle **D**, and the presence of strongly basic and coordinating OPiv anion facilitates the following rollover cyclorhodation to produce **C** (path b). With weakly basic and less coordinating SbF_6 anion, the second intramolecular C−H activation of **D** occurs preferably to furnish a five-membered rhodacycle **E** (path c). After insertion of **2a** once again and subsequent reductive elimination, product **4aa** is obtained with the regeneration of the active Rh(III) catalyst.

Scheme 6. Plausible Mechanism



In summary, we have achieved Rh(III)-catalyzed chelation-assisted switchable annulation of 2,2′-bipyridine N-oxides with internal alkynes via double C−H activation. The neutral Rh(III) catalytic system favored rollover annulation to give 5,6-disubstituted-1,10-phenanthrolines, whereas the cationic Rh(III) catalytic system worked well for nonrollover annulation to deliver 5,6,7,8-tetrasubstituted-1-(pyridin-2-yl)isoquinoline 2-oxides. The protocols have the advantages of high efficiency and functional group tolerance, excellent regioselectivity and broad substrate scope, enabling them to become attractive complements to the existing methods for the synthesis of useful 2,2′-bipyridine derivatives.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.8b01434.

Detailed experimental procedures, characterization data, and copies of ^1H and ^{13}C NMR spectra of products (PDF)

Accession Codes

CCDC 1563903 and 1563904 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, U.K.; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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