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Rhodium-Catalyzed Cascade Oxidative Annulation Leading to Substituted Naphtho[1,8-*bc*]pyrans by Sequential Cleavage of C(sp^2)−H/C(sp^3)−H and C(sp^2)−H/O−H Bonds

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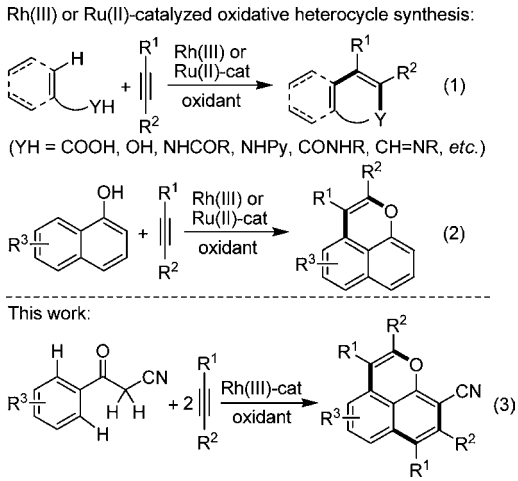
Supporting Information

ABSTRACT: The cascade oxidative annulation reactions of benzoylacetonitrile with internal alkynes proceed efficiently in the presence of a rhodium catalyst and a copper oxidant to give substituted naphtho[1,8-*bc*]pyrans by sequential cleavage of C(sp^2)−H/C(sp^3)−H and C(sp^2)−H/O−H bonds. These cascade reactions are highly regioselective with unsymmetrical alkynes. Experiments reveal that the first-step reaction proceeds by sequential cleavage of C(sp^2)−H/C(sp^3)−H bonds and annulation with alkynes, leading to 1-naphthols as the intermediate products. Subsequently, 1-naphthols react with alkynes by cleavage of C(sp^2)−H/O−H bonds, affording the 1:2 coupling products. Moreover, some of the naphtho[1,8-*bc*]pyran products exhibit intense fluorescence in the solid state.

Transition-metal-catalyzed direct C−H bond transformations have attracted significant interest, because these approaches allow the use of cheaper and more readily available starting materials.[1] In particular, the rhodium-[2] and ruthenium[3]-catalyzed oxidation couplings of various aromatic substrates with alkynes have been extensively investigated, leading to diverse heterocyclic compounds (eqs 1 and 2). Among these examples, most of them proceed by cleavage of C−H/N−H or C−H/O−H bonds, followed by annulation with alkynes. Encouraged by these heterocycle syntheses, we hope to apply this cyclization methodology to construct six-membered carbocyclic skeletons such as naphthalene derivatives. In our initial attempt, we used benzoylacetonitrile as a substrate, expecting to synthesize 1-naphthol product by cleavage of C(sp^2)−H/C(sp^3)−H bonds. To our surprise, not the 1:1 but the unexpected 1:2 coupling product, a naphtho[1,8-*bc*]pyran derivative, was obtained in good yield (eq 3).

Substituted naphtho[1,8-*bc*]pyran moieties are an important structural unit present in various naturally occurring and synthetic compounds that exhibit a broad range of interesting biological[4] and optoelectronic properties.[5] However, only a few synthetic routes are reported in the literature, and most of them require a complicated multistep process or inaccessible starting materials.[4−6] Recently, groups of Satoh and Miura,[2k] and Ackermann[3g] respectively reported rhodium- and ruthenium-catalyzed naphtho[1,8-*bc*]pyran synthesis from a 1-naphthol substrate via hydroxyl-directed C−H bond activation (eq 2). However, very limited substituted 1-naphthol substrates were examined in their work. Therefore, it is of great interest to establish new methods to synthesize substituted naphtho[1,8-*bc*]-pyrans from the accessible starting materials. Herein, we provide a more straightforward approach toward these compounds from readily available substituted benzoylacetonitriles.



By treating benzoylacetonitrile (**1a**) (0.15 mmol) with diphenylacetylene (**2a**) (0.3 mmol) in the presence of catalytic amounts of $[Cp^*RhCl_2]_2$ (0.015 mmol) and $Cu(OAc)_2·H_2O$ (0.6 mmol) in DMF at 100 °C for 10 h, as described above, the 1:2 coupling product, 2,3,7,8-tetraphenylnaphtho[1,8-*bc*]pyran-9-carbonitrile (**3aa**), was obtained in 59% yield (for detailed optimization studies, see Table S1 in the Supporting Information (SI)). The structure of **3aa** was confirmed by its ^1H and ^{13}C NMR spectra, mass spectrometry data, and single-crystal X-ray diffraction analysis. Interestingly, using an equal amount of **1a** and **2a** ([**1a**] = [**2a**] = 0.3 mmol), the 1:1 coupling product was still not observed, while the yield of **3aa** was increased to 81%. When using a lower ratio (0.65: 1) of **1a:2a**, the yield of **3aa** was similar (82%). Under the optimal reactant ratio, MeCN was also an effective solvent and gave **3aa** in 81% yield. In contrast, using other solvents (PhMe, tAmOH, dioxane, PhCl) or other oxidants (Ag_2CO_3, AgOAc), the yield of **3aa** was significantly lower.

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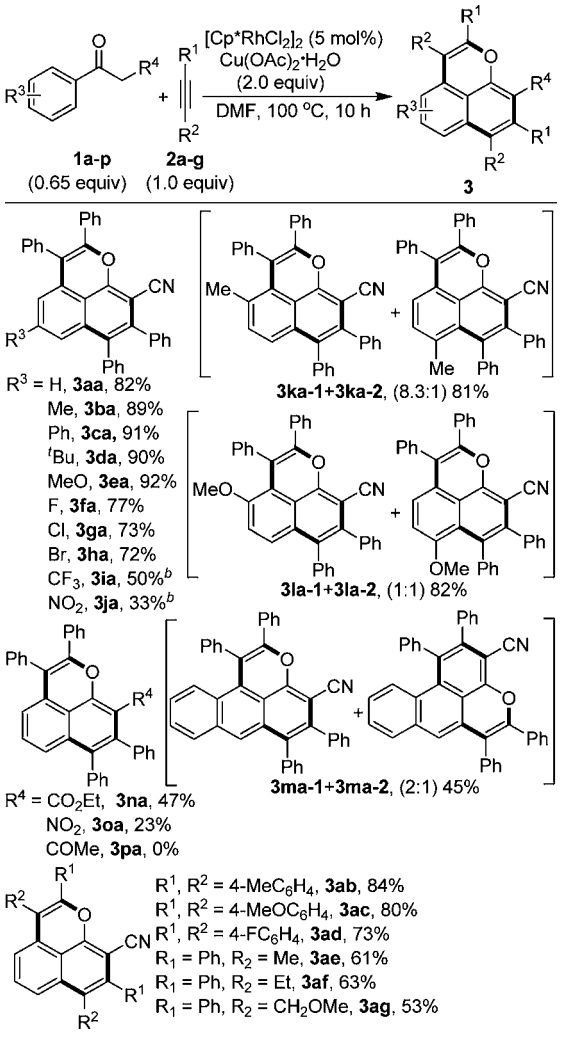
The use of $AgSbF_6$, Et_3N, or NaOAc as an additive was ineffective in increasing the yield of **3aa**. Moreover, decreasing the loading of the $[Cp^*RhCl_2]_2$ resulted in a significantly lower yield.

With the optimal reaction conditions in hand, various substituted benzoylacetonitriles (**1a−m**) were treated with diphenylacetylene **2a** and gave corresponding naphtho[1,8-*bc*]-pyran derivatives (Table 1). Thus, 4-methyl, 4-phenyl, and 4-*tert*-butyl substituted benzoylacetonitriles **1b−d** afforded naphtho-[1,8-*bc*]pyrans **3ba−3da** in excellent yields (89−91%). Electron-rich substrate **1e** reacted nicely with **2a** and gave **3ea** in 92% yield. In the present catalytic reaction, 4-fluoro-, 4-chloro-, and 4-bromobenzoylacetonitriles **1f−h** could also be tolerated, affording **3fa−3ha** in good yields (72−77%). In contrast, electron-withdrawing 4-trifluoromethyl and 4-nitrobenzoylacetonitriles **1i** and **1j** provided **3ia**, **3ja** in low to moderate yields (50% for **3ia** and 33% for **3ja**). Subsequently, the *meta*-substituted benzoylacetonitrile scope was also explored, generating the expected products in moderate to high yields with modest regioselectivity. Thus, 3-methyl substituted **1k** and *β*-naphthyl derivative **1m** reacted with **2a** to give **3ka-1** and **3ma-1** as the major regioisomers, whereas 3-methoxyl substituted **1l** yielded equal amounts of regioisomers **3la-1** and **3la-2**. Moreover, the effect of changing the nitrile group in **1a** to other substituents was also investigated. Thus, ethyl benzoylacetate (**1n**) and 2-nitro-1-phenylethanone (**1o**) reacted successfully with **2a**, although low to moderate yields were observed (47% for **3na** and 23% for **3oa**). Unfortunately, under the current reaction conditions, 1-phenylbutane-1,3-dione (**1p**) failed to afford the corresponding cycloadduct, possibly because of the formation of a *β*-diketonate−rhodium complex with $[Cp^*RhCl_2]_2$.[7]

Table 1. Scope of Rhodium-Catalyzed Cascade Oxidative Annulation with Alkynes[a]



[a]Isolated yields are given. [b]MeCN was used as solvent.

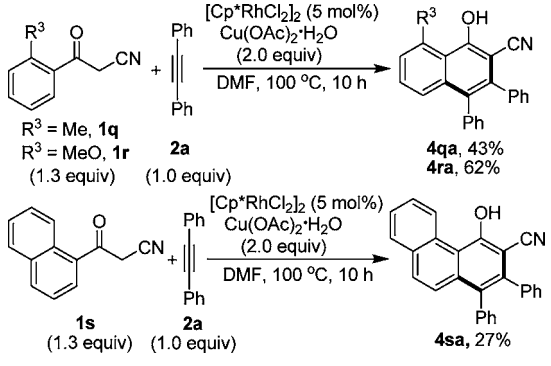
In addition to **2a**, other symmetrical alkynes (**2b−d**) were also tested for the present reaction. Thus, methyl- (**2b**), methoxy- (**2c**), and fluoro- (**2d**) substituted diphenylacetylenes reacted with **1a** and afforded the corresponding naphtho[1,8-*bc*]pyrans **3ab−ad** in high yields (73−84%). To give evidence for the regioselectivity of this reaction, a few unsymmetrical alkynes were employed. In this case, four regioisomeric products could be possible. Surprisingly, 1-phenyl-1-propyne (**2e**), 1-phenyl-1-butyne (**2f**), and propargylic ether (**2g**) gave the single regioisomeric products **3ae−3ag** in moderate to good yields (53−63%). Unfortunately, no selectivity was achieved when 1:1 ratio of different alkynes were used in this cascade reaction (see the SI).

To further demonstrate the efficiency and practicality of this cascade reaction, a scale-up reaction was performed. Thus, gram-scale synthesis of **3aa** was achieved in 79% yield.

Most of the naphtho[1,8-*bc*]pyran derivatives **3** obtained above showed solid-state fluorescence in a range of 490−580 nm (see the SI). Notably, **3aa** was found to exhibit more intense luminescence (λ_{emis} = 535 nm), and the intensity was almost four times stronger than that of tris(8-quinolinolato)aluminum (Alq_3) in the preliminary estimation.

Moreover, we tested the reactions of *ortho*-substituted benzoylacetonitriles with **2a**. In this case, there is only one C(sp^2)−H bond activation site, so only one step of the oxidative annulation with alkyne could occur. Under similar reaction conditions, *ortho*-substituted **1q** and **1r** or the *α*-naphthyl derivative **1s** reacted effectively with **2a**, affording substituted 1-naphthols (**4qa** and **4ra**) and 4-phenanthrenol (**4sa**) in low to good yields (27−62%) (Scheme 1). These results indicate that double oxidative insertion of alkynes is a stepwise process, wherein the 1-naphthol acts as an intermediate. Importantly, the reaction offers a convenient way to synthesize some derivatives of 2-naphthonitrile. As described above, the Satoh and Miura group has reported the oxidatve annulation reaction of 1-naphthol with alkyne[2k] affording the corresponding naphtho[1,8-*bc*]pyran product, which supports our hypothesis that 1-naphthol is an intermediate during the

Scheme 1. Rhodium-Catalyzed 1:1 Oxidative Annulation with Alkynes[a]



[a]Isolated yields are given.

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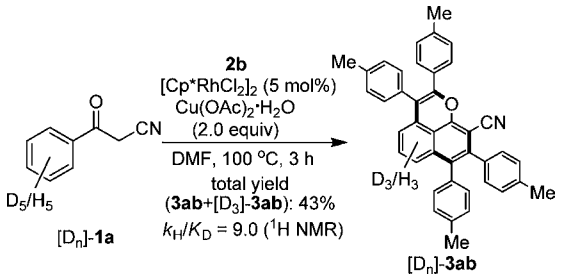
course of these cascade reactions. Therefore, the first-step reaction should be involving the cleavage of C(sp^2)−H/C(sp^3)−H bonds. To the best of our knowledge, no similar transition-metal-catalyzed oxidative annulation reaction with alkyne by cleavage of C(sp^2)−H/C(sp^3)−H bonds has been reported. Very recently, Chen's group reported the intermolecular cylization of *N*-aryl-substituted azole substrates with alkynes via double C(sp^2)−H activation, leading to aza-fused polycyclic quinolines, using a similar strategy.[2b]

To gain more insight to the mechanism of these cascade reactions, we performed a deuterium competition experiment between substrate **1a** and [D_5]-**1a** (Scheme 2 and SI), and a kinetic

Scheme 2. Experiment with Isotopically Labeled Compounds



isotope effect (KIE) of $k_H/k_D \approx 9.0$ was observed. In addition, two parallel independent reactions of **1a** and [D_5]-**1a** illustrated a KIE of $k_H/k_D \approx 2.8$ (see the SI).[8] These results indicated that cleavage of the C−H bond of the phenyl ring was involved in the rate-determining step.

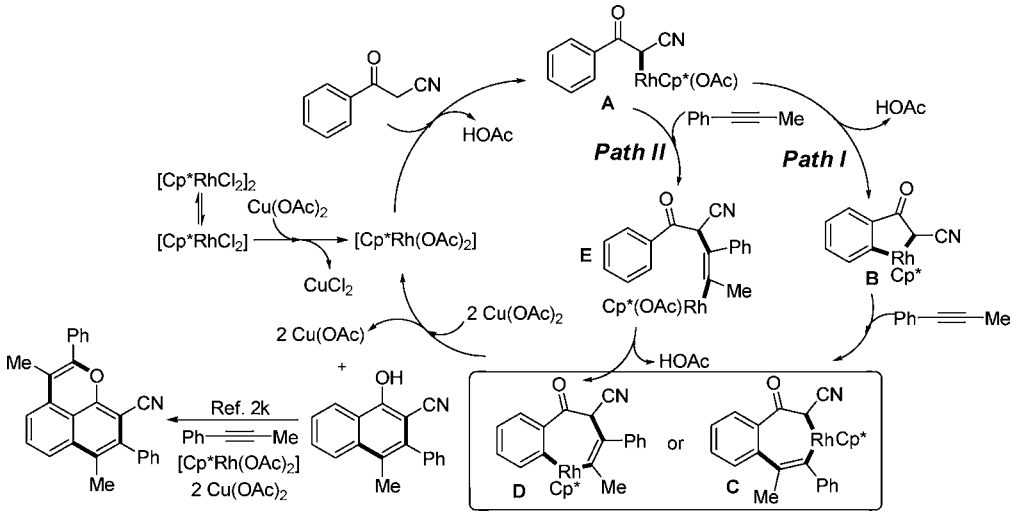
On the basis of known transition-metal-catalyzed C−H bond activation/annulation reactions, a possible mechanism is proposed to the present catalytic reaction (Scheme 3). The first step is likely to be a C(sp^3)−H activation process affording a Rh−C(sp^3) intermediate **A**, owing to the strong acidity of these C(sp^3)−H bonds. Then, a five-membered rhodacycle **B** is formed by a subsequent *ortho* C(sp^2)−H activation process (***Path I***). An intermolecualr deprotonation process for the C−H activation may be involved as proposed by the research group of Dixneuf and Jutand according to the kinetic study.[9] Regioselective insertion of an alkyne into the Rh−C(sp^2) or Rh−C(sp^3) bond of intermediate **B** gives the seven-membered rhodacycle **C** or **D**, respectively. Alternatively, intermediate **A** is proposed to give a vinyl intermediate **E**, which subsequently undergoes an *ortho* C−H bond activation to afford the intermediate **D** (***Path II***). Subsequently, the aromatization-driven reductive elimination of **C** or **D** results in 1-naphthol as the first-step product. The mechanism of the second-step annulation of 1-naphthol with alkyne is consistent with that reported by Satoh and Miura.[2k]

When benzoylacetonitrile **1a** reacts with unsymmetrical alkynes (**1e−g**), single regioisomeric products **3ae−3ag** were obtained. These results reveal that, in the seven-membered rhodacycle **C** or **D**, the phenyl group of the unsymmetrical alkyne is far away from the phenyl ring of benzoylacetonitrile substrate. According to the known literatures[2] related to regioselective insertion of an unsymmetrical alkyne to a Rh−C bond (involving a Rh−C(sp^3) bond[2m]), in the seven-membered rhodacycle the phenyl group of the alkyne gets close to the Rh-atom and is far away from the C-atom. So intermediate **C** is more reasonble than intermediates **D** and **E**, and ***Path I*** might be a plausible mechanism.

Recently, the Glorius[10] and Cheng[11] groups have respectively developed a rhodium-catalyzed method to synthesize indenols from aryl ketones (including substituted acetophenones) and alkynes, via ketone-assisted C−H activation. They proposed a five-membered rhodacycle intermediate with the O-atom coordinated to the Rh-atom. In contrast to their five-membered carbocyclic product synthesis, our results reveal another reaction path of acetophenones with alkynes via C−H activation and subsequent annulation, affording six-membered carbocyclic products. We envision that the different acidity of the C(sp^3)−H bond at the α-position of acetophenone may be responsible for the distinct results. The pK_a value of **1a** in DMSO is 10.2,[12] while that of acetophenone is 24.7.[13]

In summary, we have developed rhodium-catalyzed cascade oxidative annulation reactions of benzoylacetonitriles with alkynes, affording substituted naphtho[1,8-*bc*]pyrans in good yields. Moreover, these cascade reactions are highly regioselective with unsymmetrical alkynes. Further experiments revealed that the first-step reaction proceeds by sequential cleavage of C(sp^2)−H/C(sp^3)−H bonds and annulation with an alkyne, leading to 1-naphthols as the intermediate products. Subsequently, 1-naphthols react with alkyne by cleavage of C(sp^2)−H/O−H bonds, affording the 1:2 coupling products. Some of the naphtho[1,8-*bc*]pyran products exhibit intense fluorescence in the solid state, and this cascade

Scheme 3. Proposed Mechanistic Pathway for the Formation of 1-Naphthol Derivatives



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method may contribute to the design of new molecular materials. Further applications of this method in the synthesis of other six-membered carbocyclic ring-containing targets and a detailed mechanistic investigation are in progress.

■ ASSOCIATED CONTENT

Supporting Information

Detailed experimental procedures, characterization of all new compounds, and X-ray structures of **3aa**, **3ka-1**, **3la-2**, **3ma-1**, **3ae**, and **3af**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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