Letter

# Rhodium(III)-Catalyzed Coupling of Arenes with Cyclopropanols via C-H Activation and Ring Opening

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# Rhodium(III)-Catalyzed Coupling of Arenes with Cyclopropanols via C-H Activation and Ring Opening

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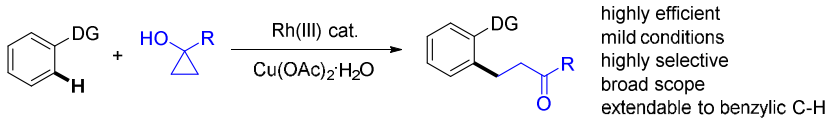
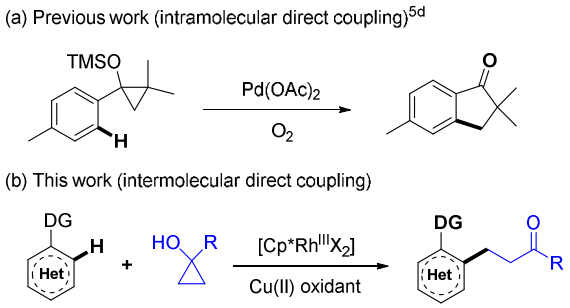



**ABSTRACT:** Rhodium-catalyzed C-H activation of arenes has been established as an important strategy for the rapid construction of new bonds. On the other hand, ring-opening of readily available cyclopropanols has served as a driving force for the coupling with various nucleophiles and electrophiles. Nevertheless, these two important areas evolved separately, and coupling of arenes with cyclopropanols via C-H activation has been rarely explored. In this work, the oxidative coupling between arenes and cyclopropanols has been realized with high efficiency and selectivity under Rh(III)-catalysis, providing an efficient route to access β-aryl ketones. Moreover, the C-H bond has been extended to benzylic C-H bonds.

KEYWORDS : rhodium(III) catalysis, C-H activation, strained ring, ring opening, cyclopropanols

Modern synthetic organic chemistry benefits tremendously from advances in strained ring opening reactions.[1] In recent years the chemistry of strain rings, and particularly three-membered rings, has been extensively investigated.[2] Cyclopropanols are readily available three-membered rings that have been found wide applications in organic synthesis and in many natural products.[3] Driven by the strain, metal-catalyzed and metal-free ring-opening of cyclopropanols has been well-known,[4] especially in metal-catalyzed ring-opening-coupling with both electrophiles and nucleophiles,[5] leading to formation of various types of C-C bonds. Nevertheless, all these synthetic methods required a pre-functionalized coupling partner.

On the other hand, metal-catalyzed C-H activation has emerged as an efficient and step- and atom-economic strategy for C-C bond formation.[6] Among the numerous transition metals, rhodium(III) catalysis have significantly contributed to the arsenal of new bond formation.[7] Despite the significance of both C-H activation and ring opening of cyclopropanols, these two important areas evolved nearly separately. To our knowledge, only one report documented the tandem cyclopropanol rearrangement with intramolecular C-H activation to yield 1-indanones (scheme **1a**).[5d] On the other hand, although several systems of Rh(III)-catalyzed C-H activation of arenes and coupling other three-membered rings have been reported, they all occurred under redox-neutral conditions.[8] We reasoned that Rh(III) catalysts may play a dual role in both C-H activation and in the ring-opening of cyclopropanols. However, given the nucleophilic nature of cyclopropanol, it remains a big challenge whether the mandatory oxidative conditions can be compatible with the C-H activation and the ring-opening processes. Significantly, this coupling process would generate a synthetically important *β*-aryl ketone. We noted that while the *β*-aryl ketone product could be obtained in several cases via Rh(III)-catalyzed hydroarylation of olefins,[9] the reports are very limited because in most systems *β*-H elimination is predominant, leading to oxidative olefination.[10]

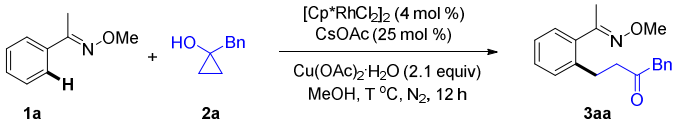



Scheme 1. Combination of C-H activation with ring-opening of cyclopronanols

We initiated our studies with the coupling between oxime ether **1a** and 1-benzylcyclopropanol (**2a**, Table 1). When **1a** and **2a** were treated with $[Cp^*RhCl_2]_2$ (4 mol %), CsOAc (25 mol %), and $Cu(OAc)_2{\cdot}H_2O$ oxidant in methanol (100 °C), the desired product **3aa** was isolated in only 27% yield (entry **1**). The replacement of CsOAc with $AgSbF_6$ as an additive only resulted in lower yield (entry **2**). Using $[Cp^*Rh(OAc)_2]$ as a catalyst also led to lower yield (entry **3**). Effects of the reaction temperature were then examined, and coupling at 40 °C or a higher temperature all gave inferior results (entry **4-5, 7-8**). Thus,

the optimal efficiency was reached when the reaction was performed at rt. Screening also revealed that other common solvents such as DCE, MeCN, and toluene are not viable.

Table 1. Optimization Studies[a]

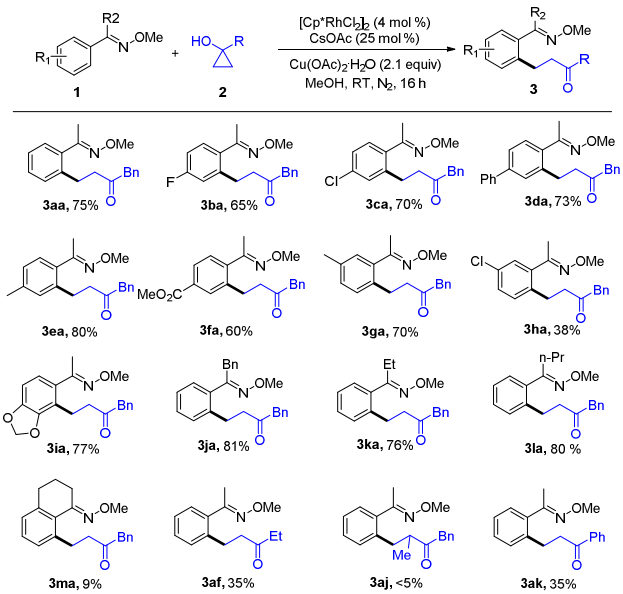



1a 2a 3aa

| entry | catalyst | temp (°C) | yield (%)[b] |
|---|---|---|---|
| 1 | $[Cp^*RhCl_2]_2$ | 100 | 27 |
| 2[c] | $[Cp^*RhCl_2]_2$ | 100 | 9 |
| 3[d] | $[Cp^*Rh(OAc)_2]$ | 100 | 20 |
| 4 | $[Cp^*RhCl_2]_2$ | 80 | 33 |
| 5 | $[Cp^*RhCl_2]_2$ | 60 | 42 |
| 6[e] | $[Cp^*RhCl_2]_2$ | 60 | 42 |
| 7 | $[Cp^*RhCl_2]_2$ | 40 | 64 |
| 8 | $[Cp^*RhCl_2]_2$ | RT | 70 |
| 9[f] | $[Cp^*RhCl_2]_2$ | RT | 75 |
| 10[g] | $[Cp^*RhCl_2]_2$ | RT | 75 |

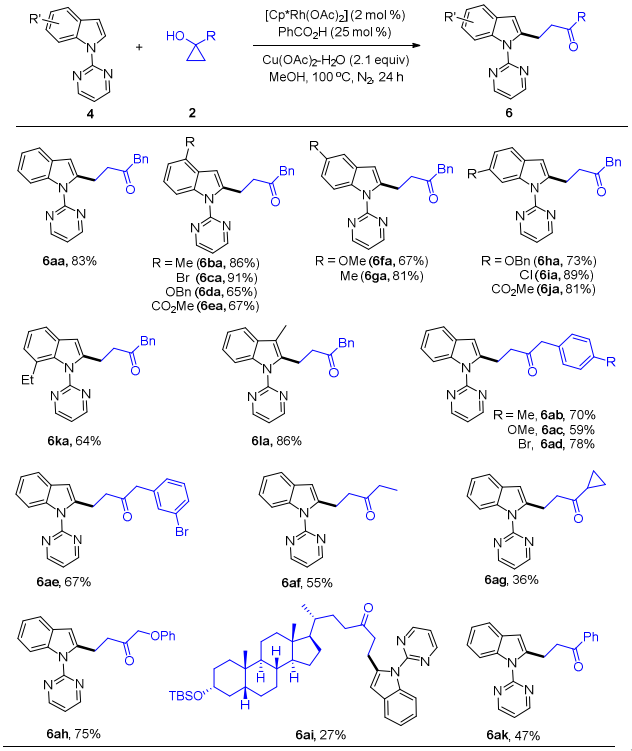
[a] Reactions were carried out using $[Cp^*Rh(Cl)_2]_2$ (4 mol %), CsOAc (25 mol %), $Cu(OAc)_2{\cdot}H_2O$ (2.1 equiv), **4a** (0.2 mmol), and 2a (0.25 mmol) in a solvent (2 mL) for 12 h. [b] Isolated yield after column chromatography. [c] $AgSbF_6$ (16 mol %) instead of CsOAc (25 mol %). [d] $[Cp^*Rh(OAc)_2]$ (8 mol %) was used with no additive. [e] CsOPiv instead of CsOAc. [f] The reaction was performed for 16 h. [g] The reaction was performed for 20 h.

With the optimal conditions in hand, we next examined the scope and generality of this coupling system (Scheme 2). Various *para* substituted *O*-methyl oximes readily coupled with **2a** under the standard conditions to afford the products in 60%-80% yield (**3ba-3fa**). Meanwhile, electron-donating groups tends to enhance the efficiency (**3ea, 3ia**), and electron-withdrawings or halogen groups at the *para* and *meta* positions of the benzene ring led to lower yields (**3ba, 3fa, and 3ha**). Moreover, the imine substrate is not limited to acetophenone imines, and the reaction yield was comparably high when the carbon chain in the imine moiety was elongated or when a benzyl substituent was introduced to the α-position (**3ja, 3ka, and 3la**). However, the reaction yield was poor when the substrate is conformationally rigid or sterically bulky (**3ma** and **3aj**). Furthermore, 1-ethyl- and 1-phenyl-substituted cyclopropanol coupled with *O*-methyl oximes afford **3af** and **3ak** in 35% yield. In all cases, the reaction proceeded with high regio-selectivity and high mono-/di- selectivity. Furthermore, essentially no enone byproduct via overoxidation of the saturated ketone was observed.




Scheme 2. Substrate Scope of Oximes.[a,b] [a]Reactions were carried out using $[Cp^*RhCl_2]_2$ (4 mol %), CsOAc (25 mol %), $Cu(OAc)_2{\cdot}H_2O$ (2.1 equiv), 1 (0.2 mmol), and 2a (0.25 mmol) in a MeOH (2 mL) at room temperature for 16 h. [b]Isolated yield after column chromatography.

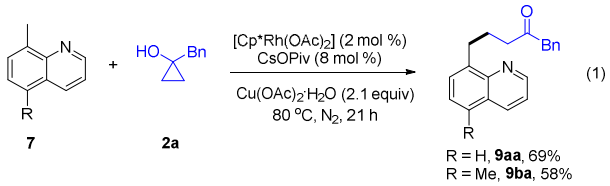
Encouraged by these initial findings, we sought to further define the scope of this coupling reaction using other arenes. It was found that *N*-pyrimidinylindoles could serve as a viable substrate.[11] Through extensive optimization of the reaction conditions in the coupling of indole **4a** and **2a** (See Table S1 in the SI), the product **6aa** was obtained in 83% yield under the following reaction conditions: $[Cp^*Rh(OAc)_2]$ (2 mol %), $PhCO_2H$ (25 mol %), and $Cu(OAc)_2{\cdot}H_2O$ in MeOH (100 °C, 24 h). The benzoic acid additive likely facilitated C-H activation of the arene as in a CMD mechanism.[12] While *N*-pyrimidinylindoles can be highly efficient in many Rh(III)-catalyzed C-H activation systems, the reaction needed to be performed at 100 °C, but only a low loading of the catalyst was necessary. With the establishment of these optimum conditions, the scope of *N*-pyrimidinylindole was first evaluated (Scheme 3). Generally, introduction of both electron-donating (**6da, 6fa, 6ha**) and –withdrawing (**6ea, 6ia, 6ja**) substituents into different positions of the benzene ring was well tolerated, and the reaction efficiency was marginally affected by such electronic perturbation. Furthermore, the reaction efficiency was essentially not affected when a 7-ethyl or a 3-methyl group was introduced, indicating that the reaction tolerated steric effects at these two positions.



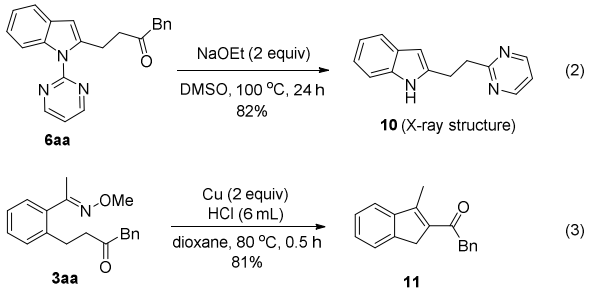

Scheme 3. Substrate Scope of *N*-Pyrimidinylindoles.[a,b]
[a]Reactions were carried out using $[Cp^*Rh(OAc)_2]$(2 mol %), $PhCO_2H$ (25 mol %), $Cu(OAc)_2{\cdot}H_2O$ (2.1 equiv), **4** (0.2 mmol), and **2a** (0.4 mmol) in MeOH (2 mL) at 100 °C for 24 h. [b]Isolated yield after column chromatography.

The scope of the cyclopropanol substrate was then examined. In general, various *para*-substituted 1-benzylcyclopropanols all underwent smooth coupling with *N*-pyrimidinylindole (**4a**) under the standard conditions to afford the ketone products in 59%-78% yields (**6ab, 6ac, 6ad**). Furthermore, *meta*-bromo-substituted 1-benzylcyclopronanol coupled with comparably high efficiency (**6ae**). The substituent in the cyclopronanol ring is not limited to a benzyl group, and alkyl, cyclopropyl, and phenyl-substituted cyclopropanols are also viable albeit with slightly lower yield (**6af, 6ag,** and **6ak**), where the reduced yield seems to result from the formation of a detectable amount of corresponding $\alpha,\beta$-unsaturated ketone. To our delight, a high isolated yield was secured for the product **6ah** which originated from the coupling using a 1-phenoxmethylcyclopronal. Interestingly, a natural product-derived cyclopropanol also exhibited activity, albeit with 27 % yield.

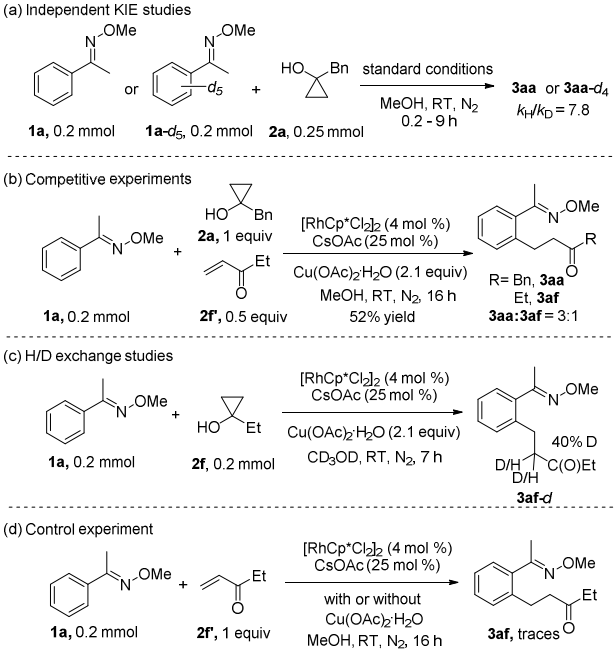
Additional experiments have been carried out to move beyond the activation of arene C-H bonds. 8-Methylquinolines coupled smoothly with 1-benzylcyclopropanol to deliver the $\gamma$-aryl ketone products in good yields (**eq 1**).[13] This reaction represents the first example of coupling of benzylic C-H bond with a strained ring, leading to $C(sp^3)$-$C(sp^3)$ formation.




Derivatization reactions have been carried out to demonstrate the synthetic utility. In an attempt to remove the pyrimidyl DG (eq 2), the expected NH indole was not observed. Surprisingly, while the product (**10**) is an NH indole as established unambiguously by X-ray crystallography, the pyrimidyl group was retained with a formal 1,4-shift (see SI for proposed mechanism). In another experiment, treatment of **3aa** with copper powder in HCl/dioxane led to an indene product **11** in high yield (eq 3).

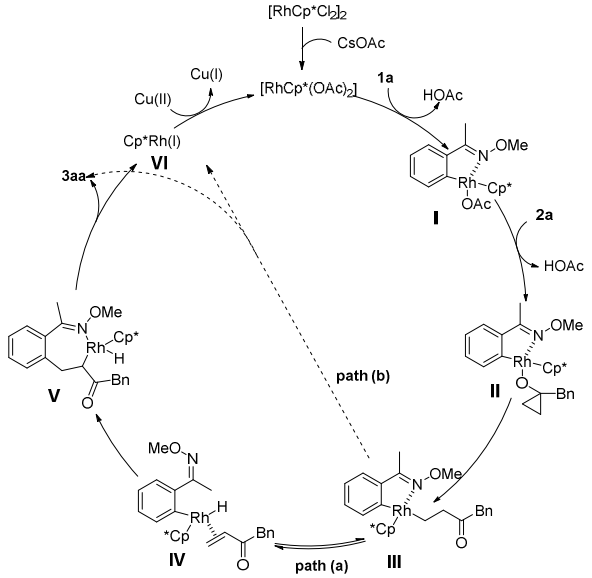



The mechanism of C-H activation/coupling of oxime ether **1a** has been explored (Scheme 4). To gain insights into the C-H activation process, kinetic isotope effect has been measured from parallel experiments under identical conditions using **1a** and **1a**-$d_5$ with **2a** being a coupling partner (Scheme 4a). A value of $k_H/k_D = 7.8$ was obtained on the basis of two rate constants. This large value indicated that C-H bond cleavage is likely involved in the turnover-limiting step.




Scheme 4. Mechanistic Studies

The detection of a small amount of enone byproducts in some cases suggests the involvement of $\beta$-H elimination and olefin species. Thus, several experiments have been performed to probe this process. When the coupling of **1a** and **2a** was performed in the presence of ethyl vinyl ketone (EVK, 0.5 equiv), GC analysis revealed the incorporation of EVK (Scheme 4b), indicating that olefin species and accordingly a $\beta$-H elimination process should be pertinent. This conclusion is also consistent with the fact that H/D exchange was achieved at the one of the alpha positions in product **3af**,[14] where $CD_3OD$ may provide D to lead to a Rh-D species that undergoes reversible $\beta$-D elimination (Scheme 4c). To probe the stage or sequence of olefin formation, **1a** was allowed to couple directly with EVK (Scheme 4d). However, only traces of the hydroarylation product was detected with or without $Cu(OAc)_2$ (Scheme 4d). This suggests that participation of cyclopropanol in the form of an enone via initial oxidative opening prior to cyclometalation is unlikely.




Scheme 5. Proposed catalytic cycle.

On the basis of our results and previous reports,[5g,15] a plausible mechanism is given in Scheme 5. Starting from $[Cp^*Rh(OAc)_2]$, cyclorhodation of substrate **1a** forms a rhodacycle **I**, and ligand exchange with a cyclopropanol affords alkoxide **II** which subsequently undergoes $\beta$-carbon elimination to produce a Rh(III) alky species **III**.[8a,8e-g] $\beta$-hydride elimination of **III** should reversibly occur to provide Rh(III) hydride **IV** with dissociation of the imine chelator (pathway (a)). This proposal is in good agreement with the inactivity of oxime ether **1m** (product **3ma**) because the rigidity enforced by the extra fused cyclohexanone ring should disfavor imine dechelation. Migratory insertion of the aryl into the olefin of **IV** followed by C-H reductive elimination (or protonolysis) of **V** furnished product **3aa** together with a Rh(I), which is oxidized by Cu(II) to regenerate the active Rh(III) catalyst. Although an alternative direct C-C reductive elimination of **III** may also lead to **3aa** (pathway (b)), we reason that this is less likely because both oxime **1m** (in the coupling with **2a**) and cyclopropanol **2j** (in the coupling with **1a**) should be expected to react with comparable reactivity in this pathway, while poor reactivity for **2j** would be expected in pathway (a) because access to a Rh(III) tertiary alkyl via migratory insertion is unlikely.

In summary, we have achieved the first combination of C-H bond activation with ring opening of cyclopropanols under Rh(III)-catalysis, furnishing an efficient route to access $\beta$-aryl ketones. The reaction may proceed under mild conditions with broad scope, high regioselectivity, and good functional group tolerance. Both oxime ethers and *N*-pyrimidylindoles proved to be viable arene substrates. Furthermore, this coupling system has been extended to the activation of benzylic C-H bonds. This work broadened the scope of strained rings in C-H activation chemistry, and future studies are directed to the C-H activation and ring opening-coupling with other less reactive rings.

## ASSOCIATED CONTENT

**Supporting Information**.
General experimental procedures, characterization data, $^1H$ and $^{13}C$ NMR spectra of some starting materials and new products (PDF), and X-ray crystallographic data of compound **10** (CIF). This information 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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