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Ru^{II}-Catalyzed Vinylative Dearomatization of Naphthols via a $C(sp^2)$–H Bond Activation Approach

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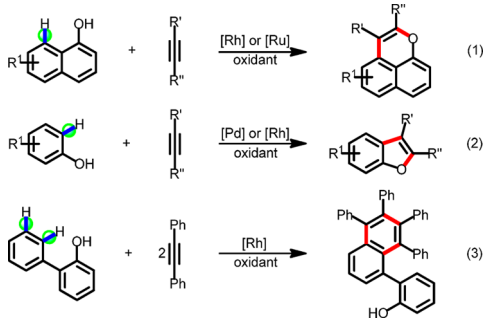
Supporting Information

ABSTRACT: Intermolecular annulation reactions of 1-aryl-2-naphthols with internal alkynes proceed efficiently in the presence of a Ru catalyst and a Cu oxidant to generate spirocyclic compounds by sequential cleavage of the $C(sp^2)$-H bond, migratory insertion of the alkyne, and dearomatization of the naphthyl ring. Various spirocyclic molecules bearing an all-carbon quaternary stereocenter could be obtained by this novel method with good yields and excellent regioselectivity, and the current process tolerates a variety of synthetically important functional groups.

The ubiquitous phenols are a class of privileged chemical feedstock being widely utilized in organic synthesis, and a plethora of natural products and valuable materials have been prepared from these readily available starting materials.[1] To streamline substantial advances in this arena, more efficient and economical methods for phenol functionalization are highly desirable.

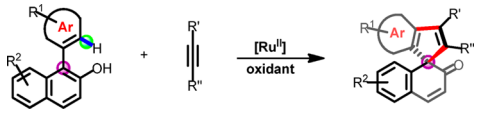
Transition-metal-catalyzed C-H functionalization has unimpeachably emerged as a powerful tool to render shorter synthetic routes for complex molecules by eliminating the need for prior preparation of activated substrates.[2] Notably, Rh-,[3] Pd-,[4] and Ru-catalyzed[5] C-H activation followed by an annulation reaction with alkynes has been frequently used as a rapid approach to construct various heterocycles and carbocycles. In particular, incorporating phenol derivatives in these reactions has been of very recent interest, and several elegant transformations involving 1-naphthols,[6] simple phenols,[7] and 2-arylphenols[6a] have been successfully implemented to give rise to planar annulation products (eqs 1–3). Meanwhile, some other facile



metal-catalyzed phenol-related reactions to generate diverse benzofurans,[8] dibenzofurans,[9] and dibenzopyranones[10] were also realized by using the C-H activation tactics. Notwithstanding these pioneering examples, further development of versatile phenol functionalization processes is needed to enrich the scope and utility of this category of synthetically valuable transformations.

In this context we will focus on a Ru-catalyzed oxidative annulation reaction by coupling of phenol derivatives with internal alkynes (Scheme 1). This catalytic method provides a straightforward avenue to access 3D spirocyclic compounds bearing the spiro[indene-1,1′-naphthalene] skeleton, which is an important but synthetically challenging structural motif in various biologically active natural products[11] and optoelectronic materials.[12] The significance of this transformation is further highlighted by the evolution of dearomatization of naphthyl rings in the substrates compelled by a C-H activation strategy. Dearomatization of phenols often serves as a key step in the rapid construction of highly functionalized alicyclic molecules.[1c,d] However, progress of metal-catalyzed direct dearomatization of phenol derivatives to form C-C bonds has been relatively slow, and the majority of the few protocols established in this area were mainly limited by employing preactivated agents such as aryl halides as coupling partners.[13] Thereby, metal-catalyzed C-H activation would be a complementary approach for phenol dearomatization. Until now, a handful of phenol-involved, metal-catalyzed C-H activation reactions have been described,[6−10] but the envisioned dearomatization of phenol rings has not yet been disclosed. Herein we report the first successful example of transition-metal-catalyzed vinylative dearomatization of naphthols through an unprecedented C-H activation/dearomatization tandem process.

Scheme 1. Ru^{II}-Catalyzed Dearomatization of Naphthols



In an initial attempt, we investigated the envisioned oxidative coupling of 2-phenylphenol with 1-phenyl-1-propyne (**2a**) under various reaction conditions. Unfortunately, the desired dear-

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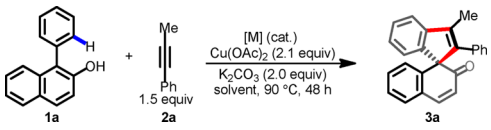
omatization product could only be obtained at extremely low yield (<5%), although the most frequently used $[(Cp^*RhCl_2)_2]$, $Pd(OAc)_2$, and $[RuCl_2(p\text{-cymene})_2]$ catalysts combined with different weak oxidants $[Cu(OAc)_2$, Ag_2CO_3, Ag_2O, AgOAc] have been tested. To this end, we turned our attention to other substrates with substituted phenol rings. Gratifyingly, 1-phenyl-2-naphthol (**1a**) was found to be very effective for this unprecedented transformation (Table 1). At the outset,

Table 1. Optimization of the Reaction Conditions



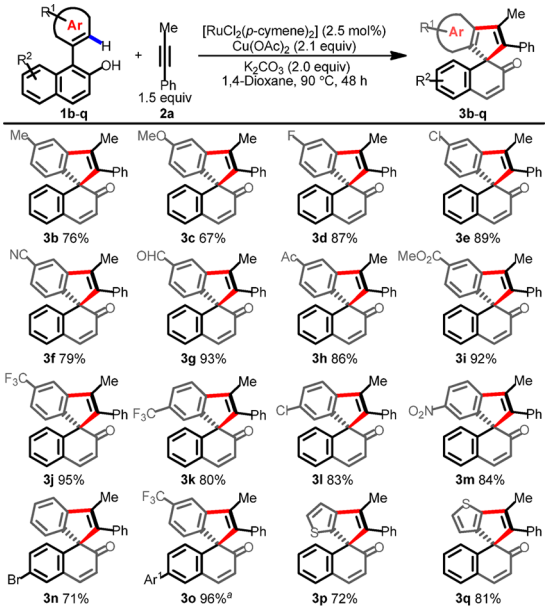
entry	[M], amount (mol%)	solvent	yield (%)[a]
1	$[RuCl_2(p\text{-cymene})_2]$, 2.5	^{t}AmOH	48
2	$[RuCl_2(p\text{-cymene})_2]$, 2.5	toluene	36
3	$[RuCl_2(p\text{-cymene})_2]$, 2.5	DME	62
4	$[RuCl_2(p\text{-cymene})_2]$, 2.5	DCE	18
5	$[RuCl_2(p\text{-cymene})_2]$, 2.5	DMF	19
6	$[RuCl_2(p\text{-cymene})_2]$, 2.5	1,4-dioxane	85
7[b]	$[RuCl_2(p\text{-cymene})_2]$, 2.5	1,4-dioxane	38
8[c]	$[RuCl_2(p\text{-cymene})_2]$, 2.5	1,4-dioxane	42
9	$Pd(OAc)_2$, 5.0	1,4-dioxane	<5
10	$[(Cp^*RhCl_2)_2]$, 2.5	1,4-dioxane	26

[a]Isolated yield. [b]K_2CO_3 was not added. [c]10 mol% K_2CO_3 was used.

$[RuCl_2(p\text{-cymene})_2]$ was chosen as the catalyst for the reactions being carried out at 90 °C with stoichiometric $Cu(OAc)_2$ as the oxidant. After surveying a variety of solvents in the presence of K_2CO_3, the best result was obtained by using 1,4-dioxane (entry 6). Further control experiment proved that 2.0 equiv of K_2CO_3 was necessary for promoting higher product yield (entries 7 and 8). $Pd(OAc)_2$ showed inferior result (entry 9), although it has been extensively employed in a great number of oxidative annulation reactions with alkynes. Next, complex $[(Cp^*RhCl_2)_2]$ was evaluated, and it resulted in 26% yield of **3a** entry 10). Overall, the best result was achieved using 2.5 mol% of $[RuCl_2(p\text{-cymene})_2]$, 2.1 equiv of $Cu(OAc)_2$, and 2.0 equiv of K_2CO_3 in 1,4-dioxane at 90 °C for 48 h, providing **3a** in 85% yield with excellent regioselectivity (only one regioisomer was observed). The structure of **3a** was unambiguously assigned by NMR spectroscopy and X-ray studies (SI).[14] With respect to the regioselectivity, the methyl-phenyl alkyne **2a** was installed in a manner that phenyl group is adjacent to the spirocyclic carbon center, which is consistent with literature precedent.[5] Compared to previous reports,[13e−g] which have been limited to the dearomatization of 1-alkyl-2-naphthols by using metal catalysis, this new catalytic approach allows the dearomatization of larger aromatic frameworks (1-aryl-2-naphthols).

With the optimized reaction conditions in hand, the reaction scope was first examined by varying the substitution patterns on the naphthol coupling partner (Table 2). Overall, an important number of desired spirocyclic products were successfully prepared, affording good yields (up to 96%) with excellent regioselectivity for unsymmetrical alkyne **2a** (>19:1). Various substituents on the phenyl ring were found to be tolerable in this process, including electron-neutral or electron-donating groups (EDGs) such as methyl (**3b**) and methoxy (**3c**) groups, and electron-withdrawing groups (EWGs) such as fluoro (**3d**), chloro (**3e**,**l**), cyano (**3f**), formyl (**3g**), acetyl (**3h**), ester (**3i**),

Table 2. Survey the Scope of Naphthol Coupling Partner

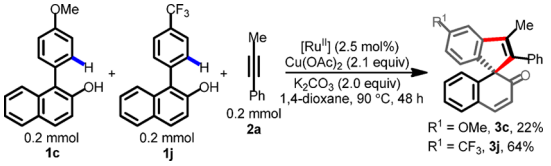


[a]Ar^1 = p-CF_3-C_6H_4.

trifluoromethyl (**3j**,**k**), and nitro (**3m**) groups. Satisfactorily, the reactions of substrates which possess a *m*-substituted phenyl group (**3k**−**m**) occurred regioselectively at the less sterically hindered 6-postion, whereas the other regioisomer was not observed. However, the existence of a substituent on the *ortho* position dramatically hampered the cyclization (<5% yield), presumably because of steric hindrance. As expected, substitutions at the naphthyl ring were tolerated as well (**3n**,**o**). It is noteworthy that potentially labile halogen functionalities remained intact in the reactions (**3e**,**l**,**n**), thus offering excellent handles for further synthetic manipulations. More importantly, the value of this method was further amplified by the successful replacement of upper phenyl group with heterocycles such as thiophene system (**3p**,**q**). Most strikingly, **1q** underwent highly regioselective C-H functionalization at the α-position of thienyl ring to generate **3q** as the major product (>19:1:1:1).[15]

As shown in Table 2, the steric factor of aryl ring in **1b**−**m** has been thoroughly studied. To reveal a more instructive principle of the electronic effect of substrate **1** on this transformation, illustrative competition experiments between **1c** and **1j** were conducted (Scheme 2). The results highlighted EWGs on the aryl moiety to be beneficial.

Scheme 2. Intermolecular Competition between Naphthols 1



Next, we sought to investigate the scope of alkynes. The results demonstrated that the oxidative annulation process occurred smoothly with various symmetrical and unsymmetrical alkynes (Table 3). Regarding the alkynes containing aromatic substituents, both EDGs (methoxy) and EWGs (fluoride, trifluoromethyl) were tolerated (**3b′**−**d′**). Moreover, the reactions of alkynes with heterocyclic substitutent proceeded

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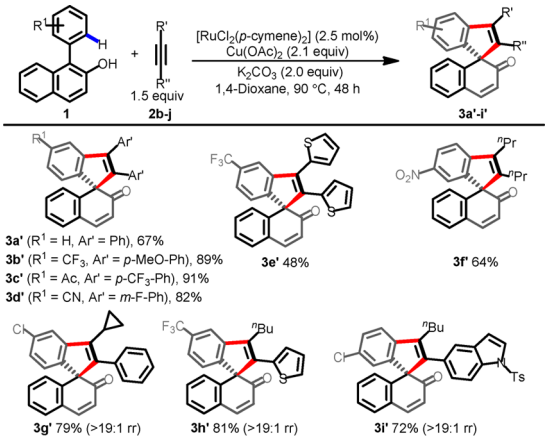
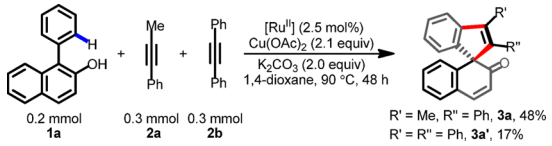
Table 3. Survey the Scope of Alkyne Coupling Partner 2



properly to give corresponding product in moderate yield (**3e′**). Notably, a dialkylacetylene could undergo the envisioned cyclization with a naphthol derivative as well (**3f′**). However, terminal alkynes are not applicable under the current reaction conditions. To further study the regioselectivity of this transformation, several representative unsymmetrical alkynes including aryl, heteroaryl and alkyl substituents were subjected to the reaction conditions (**3g′**−**i′**). The results indicated that the initial C-C bond formation in the alkyne insertion step favorably occurred at the alkyne carbon bearing the alkyl substituent, and the desired products were obtained with excellent regioselectivity (>19:1). Remarkably, the regioselectivity of the formation of **3g′** is superior to the recently reported Ru-catalyzed oxidative annulations with cyclopropyl-substituted alkynes.[5q]

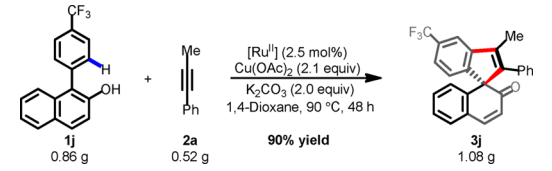
To compare the activity difference of alkynes, we carried out a set of competition experiments (Scheme 3), which indicated the favored product **3a** being derived from electron-rich alkyne **2a**.

Scheme 3. Intermolecular Competition between Alkynes 2



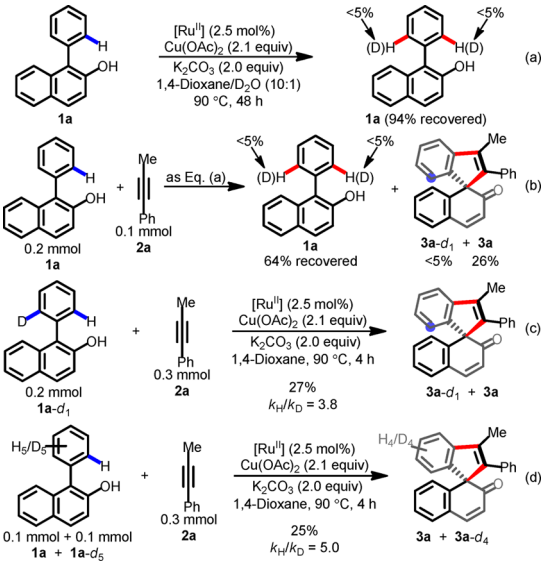
With the aim of evaluating the efficiency and practicality of this catalytic process, a scale-up experiment (3 mmol of **1j**) was carried out (Scheme 4). As a result, gram-scale preparation of **3j** (1.08 g) was achieved in 90% yield with >19:1 regioselectivity.

Scheme 4. Gram-Scale Preparation of 3j



To shed more light on the reaction mechanism, a series of deuterium-labeling experiments were performed (Scheme 5). With D_2O as solvent, no deuterium was detected in the recovered **1a**. Repeating this experiment in the presence of 0.5 equiv of **2a**, no deuterium was found in either product **3a** or recovered **1a**. These results indicates that cycloruthenation is irreversible under

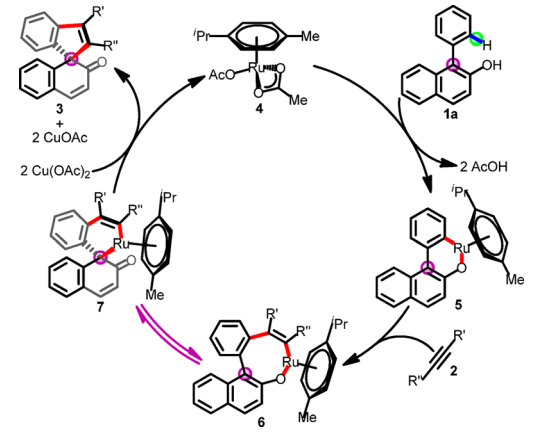
Scheme 5. Deuteration Experiments



the reaction conditions. Moreover, the kinetic isotope effects were observed in both intramolecular (k_H/k_D = 3.8) and intermolecular (k_H/k_D = 5.0) competition experiments, which suggests that the C-H bond cleavage is most likely involved in the rate-limiting step and might follow the concerted metalation/deprotonation mechanism.[16]

Based on the above results and previous reports,[3−5] a possible mechanism is proposed (Scheme 6). First, deprotonation and an

Scheme 6. Proposed Mechanism



irreversible C-H bond cleavage occurs to give a six-membered ruthenacycle **5**. This would be then followed by coordination with alkyne **2** and subsequent regioselective migratory insertion to form a rather strained eight-membered intermediate **6**. The most important step of this reaction should be the unique enol-keto tautomerization of the phenol ring to deliver the key intermediate **7**, which is a C-bound Ru enolate. To our knowledge, there is one similar intermediate to ruthenacycle **7** being proposed in a Ru-catalyzed reaction.[4c,5n] Finally, reductive elimination takes place to release product **3** and concomitantly regenerates Ru^{II} catalyst **4** to furnish the catalytic cycle.

In summary, we have developed the first Ru-catalyzed vinylative dearomatization reaction of 1-aryl-2-naphthols relying on a C-H activation strategy. This transformation provides a facile route to access a class of highly functionalized spirocyclic

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compounds with good yields and excellent regioselectivity. Further investigations into the scope and mechanism of this reaction, as well as extensive explorations of related enantioselective transformations, are in progress.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures, spectral data for all new compounds, and crystallographic data in cif format. 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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