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Rhodium(III)-catalyzed coupling of aromatic ketazines or oximes with 2-vinyloxirane via C–H activation

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ABSTRACT

Described herein is a rhodium(III)-catalyzed coupling of aromatic ketazines or oximes with 2-vinyloxirane via directed C–H activation. This reaction proceeds efficiently under mild conditions with a low catalyst loading, especially in conditions with room temperature in the absence of additives for aromatic ketazines. A wide range of substituted substrates is supported and a possible mechanism is proposed according to the experimental results of kinetic isotopic effect, reversibility studies, and catalysis with rhodacycle intermediate **c1**.

Over the past decades, transition-metal-catalyzed directed C–H bond activation, which occurs based on directing groups, has emerged as a powerful tool for the functionalization of various arenes with advantages of step- and atom-economy, high selectivity, and efficiency compared to traditional methods.[1] Among them, Rh-catalyzed directed sp^2 C–H bond activations, based on directing groups such as hydroxyl, carboxyl, amine, and so on, were broadly exploited and used for their excellent catalysis and good tolerance of functional groups.[2] Recently, there are lots of literatures involving the Rh-catalyzed coupling of arenes with diverse coupling partners with products in high yields via C–H activation based on directing groups which contain 'C=N' as substructure.[3] As a kind of important intermediates in organic synthesis, ketazines and oximes, which are used in a wide range of agricultural chemicals, medicines, and materials, have the generic 'C=N' as substructure and it could direct Rh-catalyzed C–H bond activation.[4] Therefore, the method for the functionalization of ketazines and oximes via Rh-catalyzed directed C–H bond activation would have realistic significance compared with traditional methods.[5] In addition, Li et al. showed that 2-vinyloxirane coupled smoothly with various substrates and an allylic alcohol fragment formed could be easily derived.[6] Under this, we carried out further research on the coupling of aromatic ketazines or oximes with 2-vinyloxirane and catalytic mechanism according to a range of mechanism experiments. This study shows broadening of substituted substrates under very mild conditions with $[RhCp^*(MeCN)_3](SbF_6)_2$ or $[RhCp^*Cl_2]_2$ ($Cp^* = C_5Me_5$) as catalysts, a possible mechanism that rhodacycle **c1** is the key intermediate in the catalytic cycle and a kinetic test which identifies the rate-determining step for this transformation.

With acetophenone azine (**1a**) as a model substrate, we initiated our studies by examining the effects of various additives (1.0 equiv) toward the reaction of acetophenone azine (**1a**, 1.0 equiv) and 2-vinyloxirane (**2a**, 1.2 equiv) in THF (2 ml) at 50 °C for 6 h, using $[RhCp^*Cl_2]_2$ (3%)/$AgSbF_6$ (12%) as the catalyst system (Table 1, entries 1–6). It was found that the desired product **3a** was barely observed in entries 1–6 with $[RhCp^*Cl_2]_2$ as catalyst, which revealed ineffectiveness of $[RhCp^*Cl_2]_2$ toward the reaction system. Using $[RhCp^*(MeCN)_3](SbF_6)_2$ as catalyst instead of $[RhCp^*Cl_2]_2$, we subsequently carried out the reaction under various conditions with additives, solvents, temperature, and time (Table 1, entries 7–18). The results suggested that $[RhCp^*(MeCN)_3](SbF_6)_2$ as catalyst worked in the catalytic system with yields of product **3a** more than 38% in all entries. The yields of **3a** both in the presence of NaOAc and absence of additive, which were superior to others, were more than 50% (Table 1, entries 8, 11). Among the set of representative solvents, DCE was found to be optimal (Table 1, entries 13, 16). Although there was no difference on yields between the conditions with NaOAc as additive and no additive

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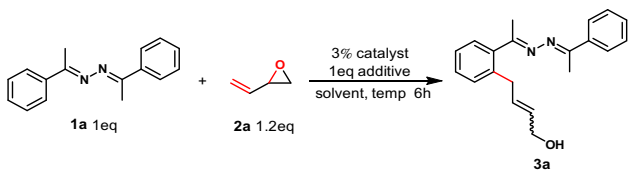
Table 1
Coupling of acetophenone azine (**1a**) with 2-vinyloxirane (**2a**) under various conditions[a,b]



Entry	Catalyst	Additive	Solvent	**3a** Yield (%)
1	$[RhCp^*Cl_2]_2/AgSbF_6$	None	THF	0
2	$[RhCp^*Cl_2]_2$	AgOTf	THF	0
3	$[RhCp^*Cl_2]_2/AgSbF_6$	$Cu(OAc)_2$	THF	Trace
4	$[RhCp^*Cl_2]_2/AgSbF_6$	NaOAc	THF	~5
5	$[RhCp^*Cl_2]_2/AgSbF_6$	HOAc	THF	Trace
6	$[RhCp^*Cl_2]_2/AgSbF_6$	^{t}BuCOOH	THF	0
7	$[RhCp^*(MeCN)_3](SbF_6)_2$	$Cu(OAc)_2$	THF	38
8	$[RhCp^*(MeCN)_3](SbF_6)_2$	NaOAc	THF	55
9	$[RhCp^*(MeCN)_3](SbF_6)_2$	HOAc	THF	21
10	$[RhCp^*(MeCN)_3](SbF_6)_2$	^{t}BuCOOH	THF	47
11	$[RhCp^*(MeCN)_3](SbF_6)_2$	None	THF	52
12	$[RhCp^*(MeCN)_3](SbF_6)_2$	NaOAc	MeOH	35
13	$[RhCp^*(MeCN)_3](SbF_6)_2$	NaOAc	DCE	69
14	$[RhCp^*(MeCN)_3](SbF_6)_2$	NaOAc	MeCN	48
15	$[RhCp^*(MeCN)_3](SbF_6)_2$	NaOAc	Toluene	41
16	$[RhCp^*(MeCN)_3](SbF_6)_2$	None	DCE	68
17[c]	$[RhCp^*(MeCN)_3](SbF_6)_2$	None	DCE	77
18[d]	$[RhCp^*(MeCN)_3](SbF_6)_2$	None	DCE	78

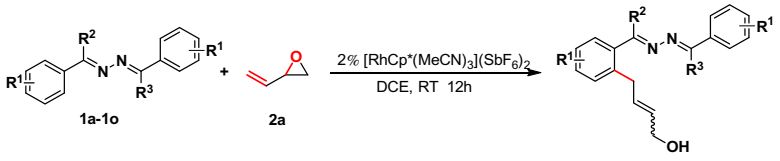
[a] Conditions: **1a** (0.2 mmol, 1.0 equiv), **2a** (1.2 equiv), catalyst (3 mol %), solvent (2 ml), 50 °C, 6 h, all the additives (1.0 equiv) except $AgSbF_6$ (12 mol %).
[b] Yields (<10%) estimated by TLC; Isolated yields estimated by weighing.
[c] Room temperature, 12 h.
[d] Catalyst (2 mol %), room temperature, 12 h.

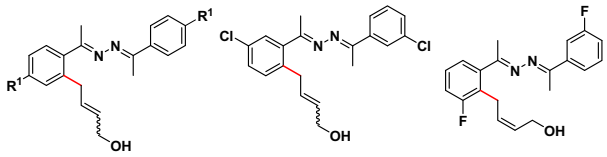
(Table 1, entries 8, 11, 13, 16), the reaction conditions without any additives was still determined to be the first choice for material economy. Further, room temperature and 12 h were determined to be the most appropriate conditions by the results of 77% yield showed in entry 17. By reducing the amount of catalyst to 2 mol % under the conditions in entry 17, the optimal conditions were determined with the isolated 78% yield of product **3a** (Table 1, entry 18).

With an optimized catalytic system in hand, we proceeded to evaluate the generality of the optimal reaction conditions with a variety of aromatic ketazines as shown in Table 2. The reactions with aromatic ketazines substituted on aryl assessed initially showed that *para*-substituted substrates with higher efficiency afforded products **3a**–**3e** in yields of 67–83%, compared with others affording products in yields of 53–67%. Electron-donating substrates showed better activity than electron-withdrawing substrates in the catalytic system. Notably, *meta*-substituted substrates exhibited good regioselectivity that the coupling occurred at a defined position on aryl. Subsequently, the scope of aromatic ketazines with diverse substituents on ketazine was studied in optimal conditions. The results showed that these substrates also had high efficiency with affording products **3i**–**3m** in yields of 59–85% and substituents on ketazine exhibited steric hindrance. In these cases, *cis*–*trans* isomerism of all products was observed except product **3g** with only *cis* isomer. Moreover, products **3f** and **3g** exhibited disparate regioselectivity in the catalytic system. Benzylidene azine as substrate delivered no product, which probably revealed that the long distance between the directing N-atom and C-atom on activation site, resulted from bond angles, blocked metalation–cyclization of substrate with Rh-catalyst.[7]

Then, we preliminarily examined the coupling of acetophenone azine (**1a**) with other alkenes (Scheme 1). The results suggested

Table 2
Substrate scope of aromatic ketazines[a,b]

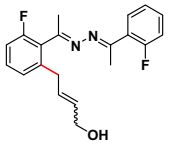




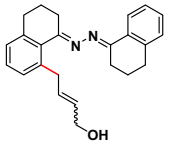
3a: R^1=H, 78.2% (***E***/***Z*** = 1.21:1)
3b: R^1=Me, 80.4% (***E***/***Z*** = 1.18:1)
3c: R^1=OMe, 82.7% (***E***/***Z*** = 1.09:1)
3d: R^1=Cl, 74.5% (***E***/***Z*** = 1.22:1)
3e: R^1=F, 67.2% (***E***/***Z*** = 1.16:1)

3f: 66.8% (***E***/***Z*** = 0.95:1)

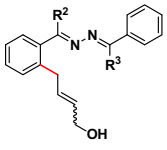
3g: 53.1% (***E***)



3h: 59.4% (***E***/***Z*** = 0.86:1)

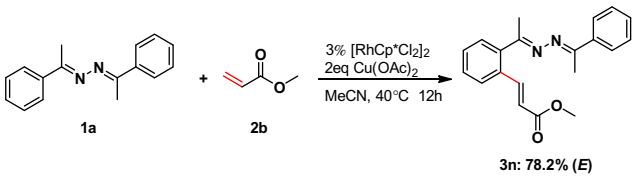


3l: 63.8% (***E***/***Z*** = 0.58:1)



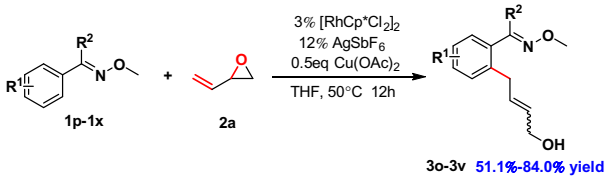
3i: R^2=Et, R^3=Et, 74.0% (***E***/***Z*** = 1.24:1)
3j: R^2=^{n}Pr, R^3=^{n}Pr, 73.5% (***E***/***Z*** = 1.26:1)
3k: R^2=Ph, R^3=Ph, 58.9% (***E***/***Z*** = 2.74:1)
3m: R^2=Me, R^3=H, 84.5% (***E***/***Z*** = 1.29:1)
R^2=H, R^3=H, **no product**

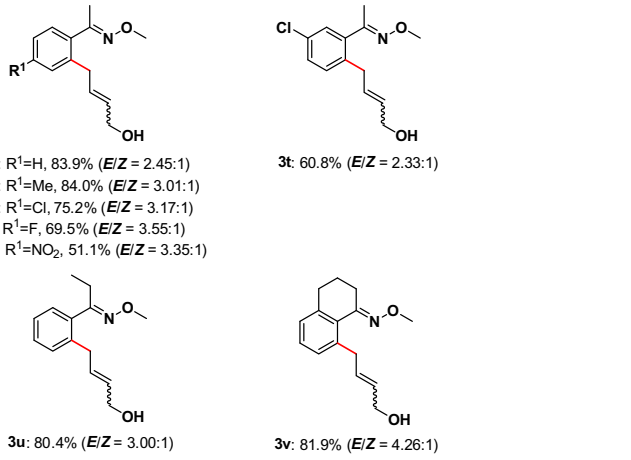
[a] Reaction conditions presented in entry 18, Table 1.
[b] Isolated yields given unless otherwise noted.



Scheme 1. Coupling of acetophenone azine (**1a**) with methyl acrylate (**2b**). (a) Reagents and conditions: **1a** (0.2 mmol, 1.0 equiv), **2b** (1.2 equiv), $[RhCp^*Cl_2]_2$ (3 mol %), MeCN (2 ml), 40 °C, 12 h, $Cu(OAc)_2$ (2.0 equiv) as oxidant. (b) Only (*E*)-configuration afforded, isolated yields given.

Table 3
Substrate scope of *O*-methyl oximes[a,b]



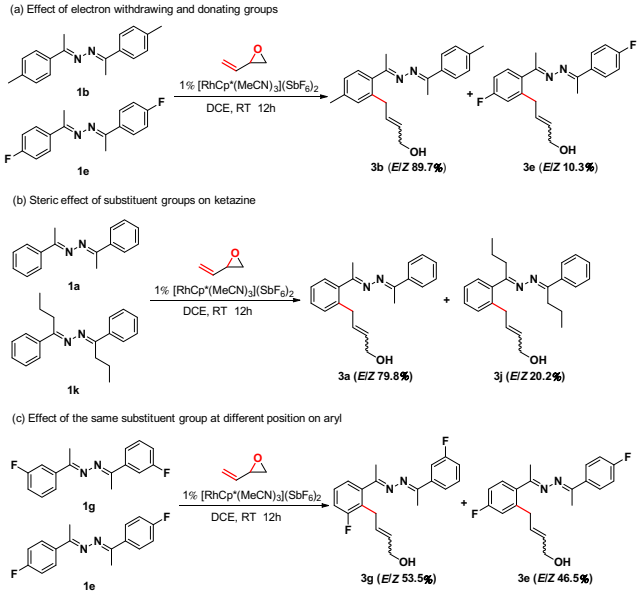


[a] Conditions: **1p** (0.2 mmol, 1.0 equiv), **2a** (1.2 equiv), $[RhCp^*Cl_2]_2$ (3 mol %), $AgSbF_6$ (12 mol %), THF (2 ml), 50 °C, 12 h, $Cu(OAc)_2$ (0.5 equiv).
[b] (*E*,*Z*)-Configuration afforded, isolated yields given.

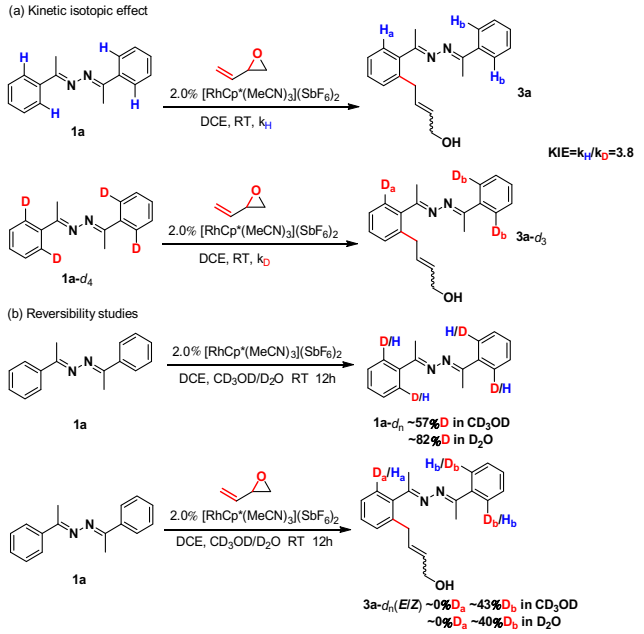
that product **3n** was afforded in a yield of 78% under the conditions with $[RhCp^*Cl_2]_2$ as catalyst. Compared to the coupling of 2-vinyloxirane via internal oxidative C–H activation with oxirane-substructure as oxidant, the coupling of methyl acrylate occurred by external oxidative C–H activation with $Cu(OAc)_2$ as oxidant.

Under the different conditions with the coupling of aromatic ketazines, oximes proved to have a broad substrate scope in $[RhCp^*Cl_2]_2/AgSbF_6$ catalytic system with $Cu(OAc)_2$ as additive and afforded products **3o**–**3v** in considerable yield (Table 3). As well as aromatic ketazines, electron-donating oximes gave a higher yield than electron-withdrawing ones. There was almost no difference in reaction efficiency between substituents on aryl and oxime. The results also showed that the coupling reaction was not sensitive to the steric effect of substituents on oxime. Clearly, all of the coupling reactions via C–H activation occurred at the *ortho*-position on aryl, which demonstrated the key role of directing groups.

Subsequently, mechanism experiments were carried out with aromatic ketazines as a template. On the basis of competition experiment, the chemoselectivity of the rhodium-catalysis was further understood that it revealed the difference of yields on the scope of substrates which resulted from the effects of electronic property, steric property, and substituted position (Scheme 2).



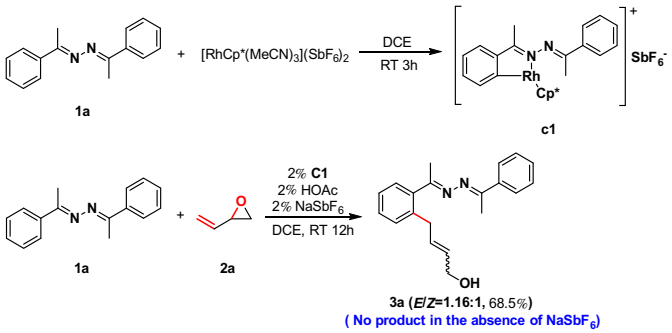
Scheme 2. Competition experiment. (a) The substrate ratio determined to be 1:1. (b) Percentage in bracket estimated by ^1H NMR meaning proportion of each product in total not yield.



Scheme 3. Deuterium experiments. (a) Deuteration rate estimated by ^1H NMR.

Additionally, the significant difference on effect of electronic property probably suggested that C–H activation followed the electrophilic aromatic substitution (EAS) mechanism rather than concerted metalation–deprotonation (Scheme 2a).[8] The steric effect of substituents on ketazine was probably reflected in that substrates with large substituents on ketazine tended to form (*Z*)-configuration which was unable to direct C–H activation (Scheme 2b).

The kinetic isotope effect (KIE) was measured to be 3.8 by using two parallel reactions, which indicated the reaction involving the rate-limiting C–H bond activation (Scheme 3a).[9] Additionally, an H/D exchange was remarkably observed by employing CD_3OD/D_2O as the proton donor under conditions without 2-vinyloxirane



Scheme 4. Catalysis of rhodacycle intermediate **c1**. (a) HOAc as proton donor for that the process of separating rhodacycle **c1** resulted in proton lack.

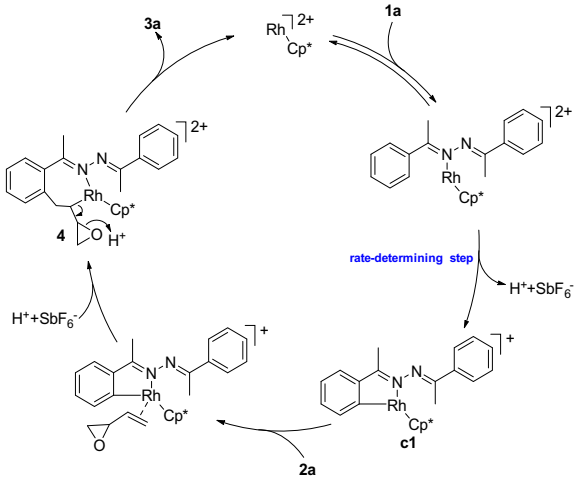
and it revealed the reversibility of C–H activation. With CD_3OD/D_2O added to the standard reaction system, irreversibility of migratory insertion of double bond was observed (Scheme 3b) (note that some deuterium protons (D_b) of **3a**-d_n resulted from Rh-catalyzed C–H activation rather than migratory insertion).

Under the standard conditions in the absence of 2-vinyloxirane, the rhodacycle **c1** was obtained. Afterward, we examined catalysis of rhodacycle **c1** in the reaction. With only HOAc added to supply protons for the catalytic system and using rhodacycle **c1** instead of $[RhCp^*(MeCN)_3](SbF_6)_2$, the reaction afforded no product, which was caused by that weak acidity of HOAc hindered proton from migrating to 2-vinyloxirane. When adding HOAc and $NaSbF_6$ to supply H^+ and SbF_6^-, the product **3a** was obtained in yield of 68.5% (Scheme 4). We concluded that it is difficult to form $HSbF_6$ from weakly acidic HOAc, however, owing to slight solubility of NaOAc formed by HOAc and $NaSbF_6$, a certain amount of $HSbF_6$ could exist in the reaction to deliver completely free protons.

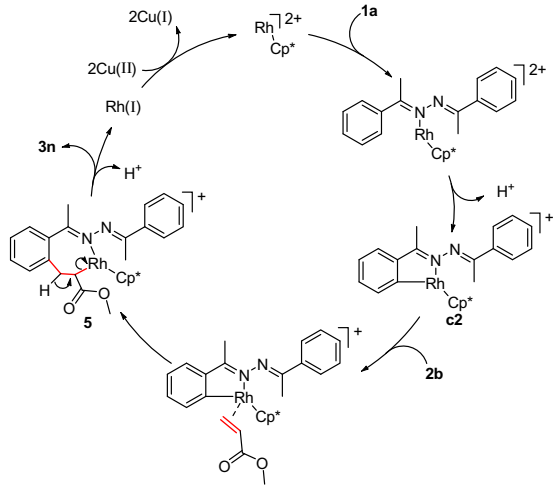
Based on these studies, a reasonable catalytic cycle for aromatic ketazine is proposed (Scheme 5). We hypothesize that the proposed catalytic cycle initiates with the formation of the previously proposed rhodacycle intermediate **c1** via [$RhCp^*$]-catalyzed C–H activation. Immediately, a seven-membered rhodacycle (**4**) is formed by migratory insertion of double bond of 2-vinyloxirane (**2a**) into the C-Rh bond.[10] Finally, rhodacycle (**4**) delivers the product **3a** with substructure of allyl alcohol and Rh(III) simultaneously by β-elimination and proton capture. The entire procedure of the catalytic cycle for oxime should be consistent with that for aromatic ketazine due to their structural similarity and relevance of catalytic system. As for $Cu(OAc)_2$ added as additive, it could be used as weak base rather than oxidant to provide a suitable pH-atmosphere, which is concluded on the basis that the coupling reaction of oxime occurs under conditions with other additives such as $Zn(OAc)_2$.

Subsequently, we synthesized rhodacycle **c2** and examined catalysis of rhodacycle **c2** that it worked in the catalytic system (S12–S14, Supporting Information). Finally, we proposed a possible catalytic cycle for methyl acrylate sketched in Scheme 6. Differently from the catalytic cycle of the coupling with 2-vinyloxirane, the catalytic cycle for methyl acrylate occurred by external oxidative C–H activation with $Cu(OAc)_2$ as oxidant. After migratory insertion of double bond into the Rh-C bond, intermediate **5** simultaneously delivers product **3n** by β-H elimination and Rh(I) that is oxidized to Rh(III) by external oxidant $Cu(OAc)_2$.[11]

In summary, we have developed an effective methodology to achieve the direct *ortho*-coupling of aromatic ketazines or oximes with 2-vinyloxirane, and proposed a possible catalytic cycle for aromatic ketazine by mechanism experiments including KIE, H/D exchange, substrates competition, and catalysis of Rh(III) complex intermediate **c1**. This methodology, which especially for functionalization of aromatic ketazines is attractive with the low loading of Rh-catalyst, mild reaction temperature, and no additives added, supports a wide range of differently substituted substrates. Moreover, there were no by-products formed in the coupling reaction of aromatic ketazines and it could belong to green chemistry. Also, the product with an allylic alcohol fragment can be easily derived. The above features and chemo-selectivity should lead to some applications, especially derivation and modification of aromatic organics with the generic 'C=N' as substructure.



Scheme 5. Mechanism proposal of coupling with 2-vinyloxirane. (a) (SbF_6^-) as ligand of rhodium complex omitted.



Scheme 6. Mechanism proposal of coupling with methyl acrylate. (a) (Cl^-) as ligand of rhodium complex omitted.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2015.08.025.

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