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Aerobic Oxidative C−H Olefination of Cyclic *N*-Sulfonyl Ketimines Catalyzed by a Rhodium Catalyst

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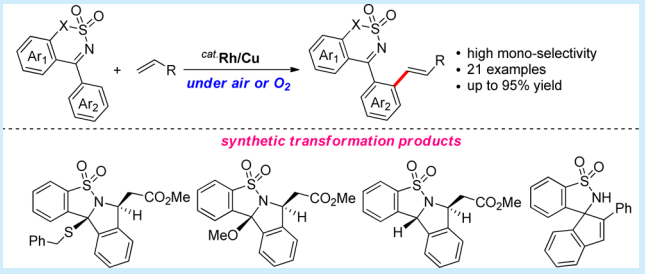
Supporting Information

ABSTRACT: A useful method for the synthesis of *ortho*-olefinated ketimines from readily accessible cyclic *N*-sulfonyl ketimines and various olefins has been achieved. The reactions proceeded by Rh(III)-catalyzed, *N*-sulfonyl ketimine-directed C−H cleavage under aerobic conditions. Further synthetic transformations of the olefinic products led to interesting heterocyclic molecules.



Since the pioneering work by Fujiwara and Moritani on oxidative olefination of the aryl C−H bond,[1] transition-metal-catalyzed oxidative aryl C−H olefination has attracted considerable attention from synthetic chemists.[2] Although such a C−H olefination protocol has been applied to various arenes including simple arenes[3] as well as electron-rich[4] and -deficient arenes,[5] oxidative aryl C−H olefination with the assistance of directing groups is undoubtedly of great importance and usefulness, because the use of directing groups not only facilitate C−H activation but also improve the regioselectivity and reaction efficiency. With such a chelation-directed strategy, a diversity of arenes have successfully been transformed into a plethora of olefinic molecules over the course of the past few years.[6] Despite these achievements, the development of more useful and easily transformable directing groups remains highly desirable.

The *N*-sulfonyl imine motif widely exists in biologically active molecules. For example, compounds containing an *N*-sulfonyl imine moiety are potential inhibitors of HCV (hepatitis C virus) NS5b,[7] kinase,[8] and PFT (protein farnesyltransferase)[9] (Figure 1). On the other hand, the *N*-sulfonyl imines are highly

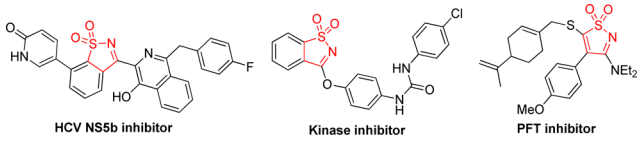


Figure 1. Biologically active molecules containing a *N*-sulfonyl imine moiety.

valuable synthons for the construction of a variety of nitrogen-containing molecules.[10] We can envision that exploring a *N*-sulfonyl imine as a directing group in the C−H functionalization can not only prepare various compounds related to the biologically active molecules but also provide a platform for the synthesis of structurally diverse and complex molecules. However, the *N*-sulfonyl imine rarely acts as an efficient directing group for C−H functionalization because of the low coordination ability of the nitrogen atom which derives from the electron-withdrawing effect of the conjugated sulfonyl group. Recently, Li[11] successfully established a Ru-catalyzed C−H activation/annulation protocol for the synthesis of indenamines from *N*-Ts imines and internal alkynes. Subsequently, Nishimura[12] and Dong[13] developed Ir- and Rh-catalyzed spirocyclic sultam synthesis from cyclic *N*-sulfonyl ketimines and 1,3-dienes or internal alkynes, respectively. In addition, Li[14] reported Rh-catalyzed reactions between *N*-Ts aldimines and olefins leading to *ortho*-olefinated benzaldehydes, in which an excess of copper(II) salt was used as an oxidant and C═NTs was *in situ* hydrolyzed into C═O. Very recently, Dong[15] developed a method for the synthesis of pyridines from *N*-sulfonyl ketimines and alkynes with the N−S bond as an internal oxidant. Despite these advances, the substrate scope in transition-metal-catalyzed, *N*-sulfonyl imine directed C−H functionalization still needs to be expanded further. Herein, we describe a Rh(III)-catalyzed oxidative C−H olefination of cyclic *N*-sulfonyl ketimines with various olefins. This protocol enables the reactions to occur under an air or O_2 atmosphere, furnishing a diversity of *ortho*-olefinated compounds.

Initially, the reaction between cyclic *N*-sulfonyl ketimine **1a**, a readily accessible derivative of saccharin, and methyl acrylate **2a** was chosen as a model reaction to optimize the reaction conditions. After considerable experimentation, we found that the *ortho*-olefinated product **3a** was obtained in 81% yield in the presence of $[Cp^*RhCl_2]_2$ (2.5 mol %), $AgSbF_6$ (10 mol %), and $Cu(OAc)_2$ (50 mol %) at 120 °C in dioxane under air atmosphere within 12 h (entry 1, Table 1).

The key results obtained during the optimization process are summarized in Table 1. Thus, a catalytic amount of $AgSbF_6$ is

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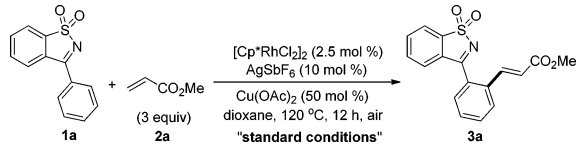
Table 1. Optimization of Reaction Conditions



entry	change from the standard conditions	yield (%)[a]
1	no change	81
2	without $AgSbF_6$	<5
3	$AgBF_4$ instead of $AgSbF_6$	55
4	AgOTf instead of $AgSbF_6$	40
5	20 mol % $Cu(OAc)_2$ instead of 50 mol % $Cu(OAc)_2$	14
6	80 °C instead of 120 °C	42
7	toluene instead of dioxane	0
8	*t*-AmylOH instead of dioxane	51
9	DCE instead of dioxane	<5
10	DMF instead of dioxane	0
11	2 equiv of Ag_2CO_3 instead of $Cu(OAc)_2$/air	54
12	2 equiv of AgOAc instead of $Cu(OAc)_2$/air	29
13	2 equiv of $PhI(OAc)_2$ instead of $Cu(OAc)_2$/air	24

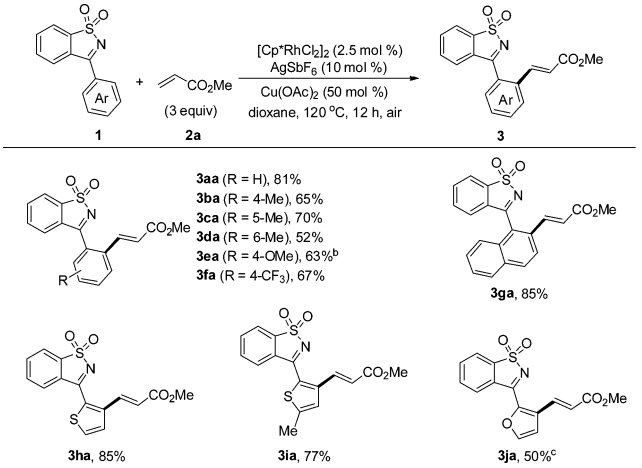
[a]Isolated yields.

crucial to this transformation. The reaction only gave a trace amount of the desired product in the absence of $AgSbF_6$ (entry 2). By replacing $AgSbF_6$ with $AgBF_4$ or AgOTf, the reaction occurred albeit with lower yields of **3a** (entries 3 and 4). Reducing the amount of $Cu(OAc)_2$ from 50 to 20 mol % resulted in a very low yield (entry 5). In addition, the reaction took place at 80 °C affording a 42% yield of **3a** (entry 6). Among the various solvents, only *t*-AmylOH (*tert*-amyl alcohol) showed a moderate yield (entry 8), and other solvents such as toluene, DCE (1,2-dichloroethane), and DMF (*N*,*N*-dimethylformamide) all exhibited negative results (entries 7, 9, and 10). A screening of other oxidants indicated that Ag_2CO_3 provided **3a** in 54% yield (entry 11). However, poor results were obtained when the reaction was carried out with AgOAc or $PhI(OAc)_2$ as the oxidant (entries 12 and 13).

We applied the optimized conditions to the reactions of methyl acrylate **2a** with an array of different *N*-sulfonyl ketimines (Scheme 1). The coupled products bearing *o*- and *p*-methyl, *p*-trifluoromethyl as well as naphthyl groups were obtained in 52−85% yields (**3ba**−**3da**, **3fa**, and **3ga**). In the case of a *m*-methyl ketimine substrate, the C−C bond formation took place exclusively at the less-hindered site (**3ca**). Although the ketimine substrate with a *p*-methoxy group only gave **3ea** in 14% yield under the standard reaction conditions, the addition of 3 equiv of acetic acid strongly promoted the reaction, providing a 63% yield of the desired product. Strangely, for substituted furan, the olefination reaction proceeded sluggishly under the reaction conditions for **3ea**. However, **3ja** was obtained in a synthetically useful yield when switching acetic acid to pivalic acid. Although the exact role of the acetic acid and pivalic acid in the reactions remains unclear, it has been known that acidic conditions are beneficial to the C−H cleavage.[16−18] More importantly, thiophenes also smoothly underwent the oxidative olefination, affording the products in good yields (**3ha**−**3ia**). Notably, under Li's conditions, the *N*-Ts aldimines of heterocycles such as furan coupled with olefins sluggishly, with <10% of the desired product formation.[14]

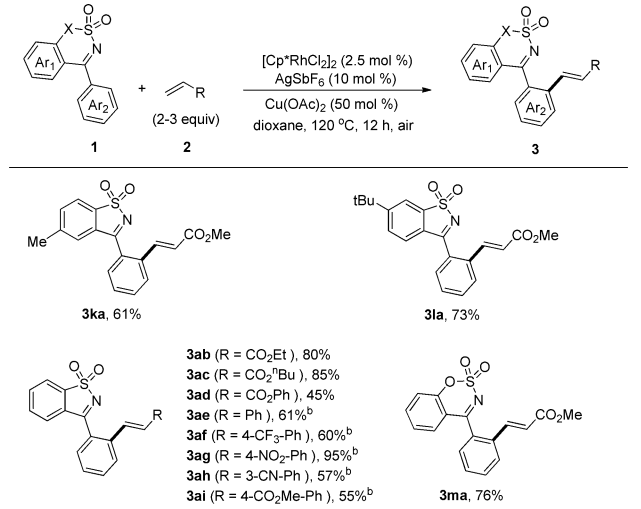
We next performed the coupling reactions of *N*-sulfonyl ketimines **1** with a variety of olefins (Scheme 2). Ketimines

Scheme 1. Rh-Catalyzed Oxidative Olefination of *N*-Sulfonyl Ketimines with Methyl Acrylate[a]



[a]See Supporting Information for reaction details. [b] 3 equiv of HOAc were used. [c] 3 equiv of PivOH were used.

Scheme 2. Rh-Catalyzed Oxidative Olefination of Cyclic *N*-Sulfonyl Ketimines with Various Olefins[a]



[a]See Supporting Information for reaction details. [b] Reactions were carried out under 1 atm of O_2.

with methyl or *tert*-butyl substituents underwent olefination smoothly to give the desired products in synthetically useful yields (**3ka** and **3la**). Among different acrylates, ethyl acrylate and *n*-butyl acrylate reacted with **1a** excellently, giving rise to the corresponding products in 80% and 85% yields, respectively (**3ab** and **3ac**). However, phenyl acrylate reacted with **1a** sluggishly and only gave **3ad** in 45% yield. In contrast to the acrylates, other electron-poor olefins such as cinnamaldehyde, acrylonitrile, and methyl methacrylate did not give the corresponding olefinated products at all, which indicated that the coupling reactions largely depended on the electronic or steric effect of the olefins. Besides the activated olefins, nonactivated olefins such as styrene were also applicable in the Rh(III)-catalyzed oxidative olefination reactions when the oxidant was switched from $Cu(OAc)_2$/air to $Cu(OAc)_2/O_2$. The oxidative conditions were compatible with a variety of functional groups including trifluoromethyl, nitro, cyano, and ester, delivering the olefinic compounds in moderate to

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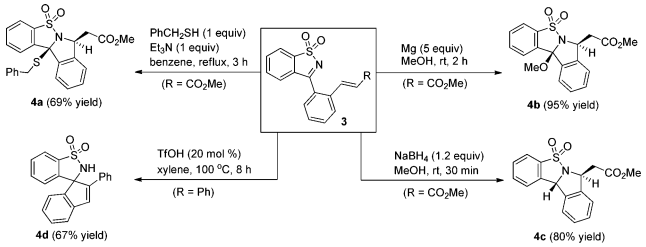
excellent yields (**3ae**−**3ai**). In addition, the reaction of cyclic ketimine **3m** with methyl acrylate under the standard conditions also proceeded to give the desired product **3ma** in 76% yield.

To demonstrate the utility of the *ortho*-olefinated products, further synthetic transformations were conducted (Scheme 3).

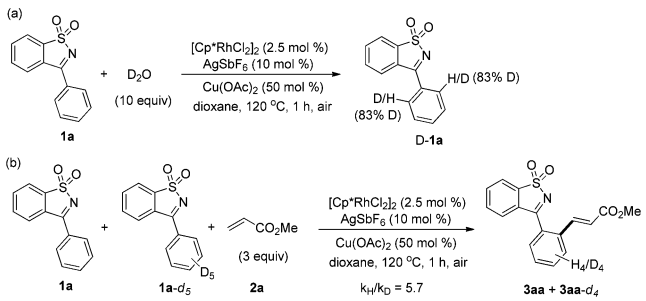
Scheme 3. Synthetic Transformations of 3



In the presence of nucleophiles such as benzyl mercaptan and MeOH, polycyclic products **4a** and **4b** were easily prepared in 69% and 95% yields, respectively. Such reactions would have proceeded through intermolecular nucleophilic attack of the C═N bond and subsequent intramolecular Michael addition of the resulting sulfonamide to the C═C bond. In addition, the reaction of **3aa** with $NaBH_4$ delivered polycyclic product **4c** in good yield under mild reaction conditions. Interestingly, spirocyclic sultam **4d** was obtained in a synthetically useful yield with TfOH as a catalyst, which might be formed through a Prins-type reaction.[19]

To probe the possible mechanism, we performed some isotope labeling experiments (Scheme 4). First, an H/D

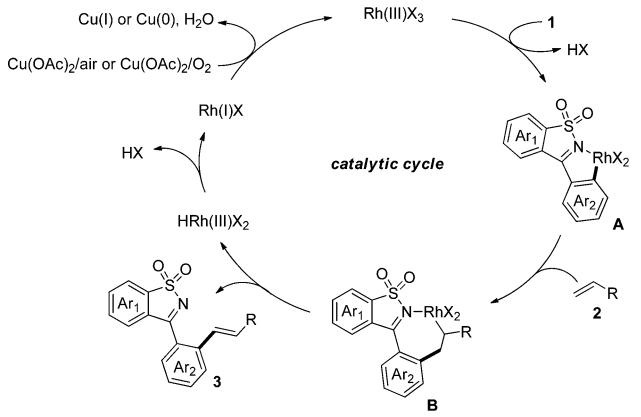
Scheme 4. Deuteration Experiments



exchange experiment was conducted between **1a** and deuterium oxide (Scheme 4a). In the presence of 10 equiv of D_2O, it was found that 83% D was incorporated into the two *ortho* positions of the ketimine aryl ring. Next, an intermolecular competition reaction between **1a** and **1a**-d_5 was performed, showing a significantly primary kinetic isotope effect of 5.7 (Scheme 4b).[20] The above-mentioned data suggested that a reversible C−H activation process is involved in the Rh(III)-catalyzed olefination.[21,22]

On the basis of the above results and recent achievements in Rh(III)-catalyzed oxidative C−H olefination,[6i,n−p,s,u,14] we suggested a possible catalytic cycle shown in Scheme 5. First, cyclic *N*-sulfonyl ketimine **1** reacted with a rhodium catalyst to form a five-membered rhodacycle species **A**[13,23] with elimination of HX through chelation-directed C−H activation. Subsequently, olefin **2** inserted into the C−Rh bond to give an intermediate **B** that is prone to *β*-H elimination, delivering the desired product **3** and $HRh(III)X_2$ species. The latter then

Scheme 5. Possible Catalytic Cycle



decomposed into Rh(I)X by loss of HX. Finally, the Rh(III) is regenerated by oxidation of the Rh(I)X with the aid of Cu(OAc)/air or $Cu(OAc)/O_2$ to fulfill the catalytic cycle.

In summary, we have developed a useful method for the synthesis of a wide range of *ortho*-olefinated cyclic *N*-sulfonyl ketimines that served as useful starting materials for the rapid construction of interesting heterocyclic molecules. Further studies focusing on the transition-metal-mediated C−H bond functionalization of *N*-sulfonyl ketimines and their applications for the construction of heterocyclic skeletons are currently underway.

■ ASSOCIATED CONTENT

Supporting Information

Detailed experimental procedures, characterization of products, and copies of NMR spectra. 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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