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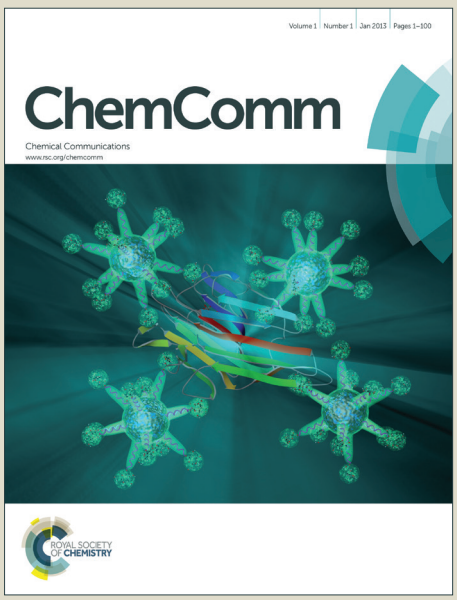

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Rhodium-Catalysed Direct C-H Allylation of *N*-Sulfonyl Ketimines with Allyl Carbonates

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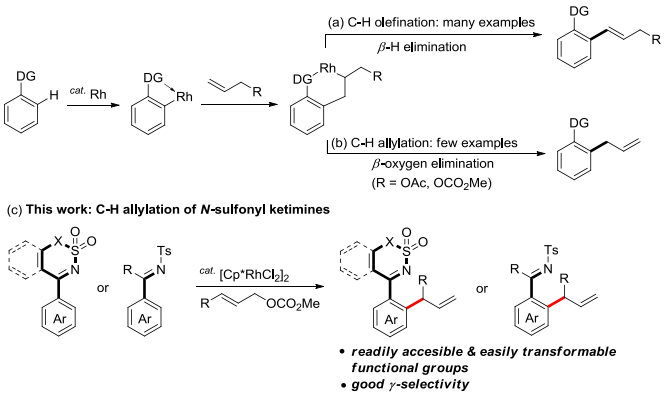
A rhodium-catalysed direct C-H allylation of readily accessible *N*-sulfonyl ketimines with various allyl carbonates has successfully been achieved. The computational studies indicated that olefin insertion and *β*-oxygen elimination steps were involved in the catalytic cycle.

Transition metal-mediated C-H functionalization is a fascinating synthetic strategy for the construction of new chemical bonds from the atom- and step-economic point of view. The past few years have witnessed considerable progress in the conversions of the ubiquitous C-H bonds into synthetically more valuable C-X bonds, such as C-C, C-N, and C-O bonds.[1] Among these transformations, the direct C-H allylation of arenes towards allylarene synthesis is of particular importance because of the prevalence of the allylarene moiety in various natural products and medicinally important molecules[2] as well as the versatile synthetic utilities of the allyl group in organic synthesis.[3] It is known that some electron-rich arenes, such as phenol and mesitylene, could be allylated through Lewis acid promoted-Friedel-Crafts-type reactions.[4] Besides, few activated arenes and directing-group containing arenes could be transformed into the allylarenes based on Pd,[5] Cu,[6] Ru,[7] Re,[8] Ni,[9] Fe[10] and Co[11] catalysts. Despite these achievements, the direct aryl C-H allylation remains largely underdeveloped with regard to substrate scope, selectivity, and reaction efficiency.

Rhodium(III) complexes, $[Cp^*RhCl_2]_2$ in particular, have been widely used in the C-H functionalization due to its good functional group compatibility and high catalytic efficiency, such as C-H olefination (Scheme 1a).[1u,v,y] In the context of aryl C-H allylation, Ma[12] and Cramer[13] independently realized the Rh(III)-catalysed allylation reactions with allenes[14] as the allyl source. Nevertheless, the allenes are generally difficult to prepare and unstable, thus limiting the allene scope. Recently, Bergman and Ellman demonstrated that $[Cp^*RhCl_2]_2$ can catalyse the allylation of *O*-methyl oxime with easily accessible allyl acetate.[15] However, only one example was given in their work. Subsequently, this synthetic strategy was expanded to the amide and pyridine substrates (Scheme 1b).[16,17] Very recently, we developed an efficient method for the synthesis of *ortho*-olefinated cyclic *N*-sulfonyl ketimines through Rh-catalysed C-H activation.[18,19] Inspired by this work and the above-mentioned C-H allylation, we wonder that whether *N*-sulfonyl



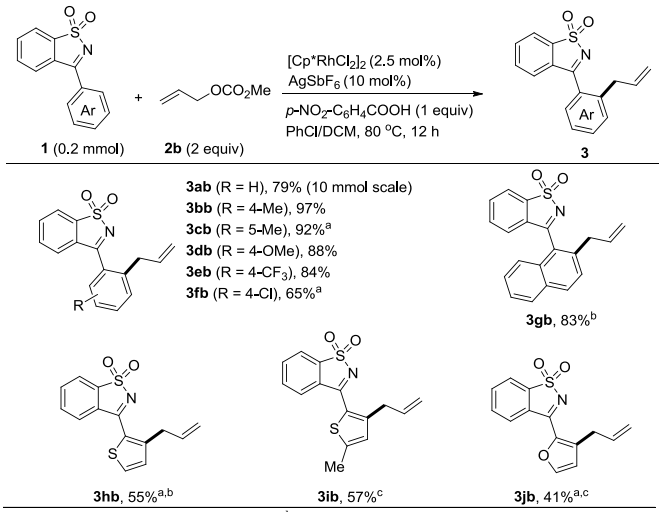
Scheme 1. Rh(III)-catalysed C-H olefination and allylation reactions. DG = Directing Group

ketimines, useful synthons in organic synthesis[20] and widely existing units in biologically active molecules,[21] could be easily allylated with suitable allyl electrophiles. We can envision that the introduction of an allyl group into the *ortho* position of the ketimines would provide a platform to prepare structurally complex and diverse molecules through manipulation of the imine and allyl groups. Herein, we disclose a straightforward approach for the C-H allylation of *N*-sulfonyl ketimines with readily accessible allyl carbonates in the presence of a rhodium catalyst (Scheme 1c). This protocol allows the allylation reactions to proceed efficiently with broad substrate scope and good *γ*-selectivity. The obtaining allylarenes were easily converted into several interesting compounds. The computational studies indicated that olefin insertion and *β*-oxygen elimination steps were involved in the catalytic cycle.

We commenced our study by choosing *N*-sulfonyl ketimine **1a**, a readily accessible derivative of saccharin, and allyl acetate **2a** as model substrates to optimize the reaction conditions (see Table S1 in the Supplementary Information for detailed results). Although the reaction took place in the presence of $[Cp^*RhCl_2]_2$ (2.5 mol%) and $AgSbF_6$ (10 mol%) at 120 ^oC in dioxane, only 41% yield was obtained (entry 1, Table S1). The investigation of various additives showed that the addition of 1 equiv of 4-nitrobenzoic acid improved the yield to 62% (entry 8, Table S1).[22] After a further screening of the solvents and the allyl electrophiles with different leaving groups,

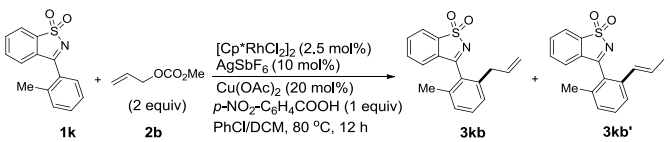
we found that the C-H allylation reaction occurred smoothly using allyl carbonate **2b** as the allyl source in the presence of $[Cp^*RhCl_2]_2$ (2.5 mol%), $AgSbF_6$ (10 mol%) and 4-nitrobenzoic acid (1 equiv) at 80 °C in PhCl/DCM within 12 h (entry 17, Table S1).

Table 1. Substrate scope of cyclic *N*-sulfonyl ketimines.



[a]The reaction was run at 120 °C. [b]$Cu(OAc)_2$ (20 mol%) was used. [c]$Cu(OAc)_2$ (50 mol%) and $AgSbF_6$ (40 mol%) were used.

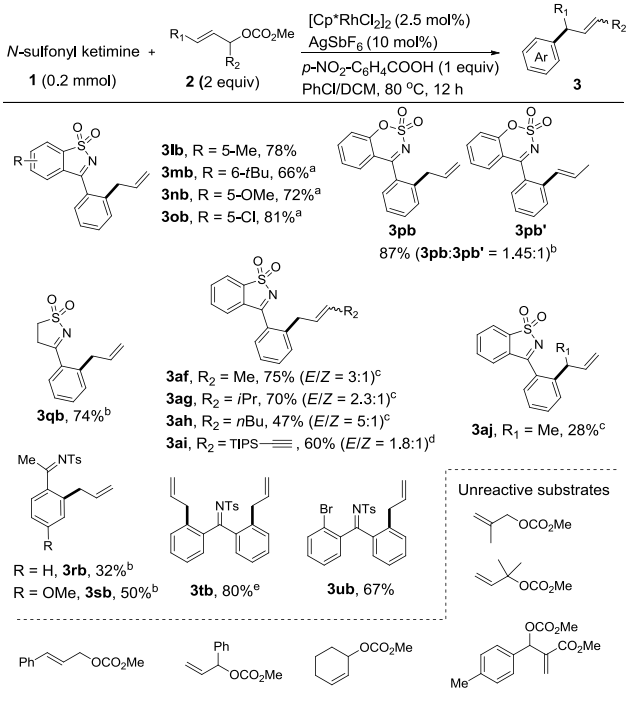
With the optimal reaction conditions in hand, we next explored the substrate scope with respect to cyclic *N*-sulfonyl ketimines (Table 1). The substrates bearing *p*-methyl, *p*-methoxy, *p*-trifluoromethyl, and *p*-chloro groups afforded the corresponding products in moderate to excellent yields (**3bb**, **3db**-**3fb**). For the substrate bearing a methyl substituent at the *meta*-position of the ketimine aryl ring, the C-C bond formation took place exclusively at the less-hindered site (**3cb**). In the case of a naphthyl-substituted ketimine, only 16% yield was obtained under the standard reaction conditions. In order to improve the yield of **3gb**, we invesigated the effect of additive under the standard conditions. Fortunately, we found that the introduction of 20 mol% of $Cu(OAc)_2$ significantly promoted the reaction, delivering **3gb** in 83% yield.[15] Moreover, heterocyclic compounds, thiophenes and furan, also underwent the direct allylation to give synthetically useful yields with the $Cu(OAc)_2$ as a promoter (**3hb**-**3jb**). It is noteworthy that a reaction between a *ortho*-methyl substituted ketimine **1k** and **2b** gave a 2:1 ratio of two isomers derived from a migration of C=C double bond (Scheme 2).



Scheme 2. Reaction between *N*-sulfonyl ketimine **1k** and **2b**.

In order to demonstrate the broad substrate scope of this method, more *N*-sulfonyl ketimines and allyl carbonates were investigated (Table 2). Ketimines bearing methyl, *tert*-butyl, methoxy, and chloro substituents underwent allylation smoothly to give the desired products in good yields (**3lb**-**3ob**). Besides ketimines derived from saccharins, cyclic ketimines **1p** and **1q** were also suitable substrates in the C-H allylation reactions, yet requiring 50 mol% of $Cu(OAc)_2$ as an additive (**3pb** and **3qb**). Ketimine **1p** coupled with **2b** to

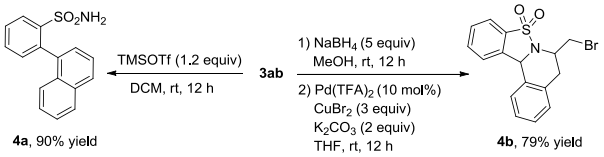
Table 2. Substrate scope of *N*-sulfonyl ketimines and allyl carbonates.



[a]The reaction was run at 120 °C. [b]$Cu(OAc)_2$ (50 mol%) was used. [c]$[Cp^*RhCl_2]_2$ (5 mol%), $Cu(OAc)_2$ (20 mol%), and $AgSbF_6$ (20 mol%) were used. [d]$Cu(OAc)_2$ (20 mol%) was used. [e]$Cu(OAc)_2$ (20 mol%) and **2** (6 equiv) were used. TIPS = triisopropylsilyl

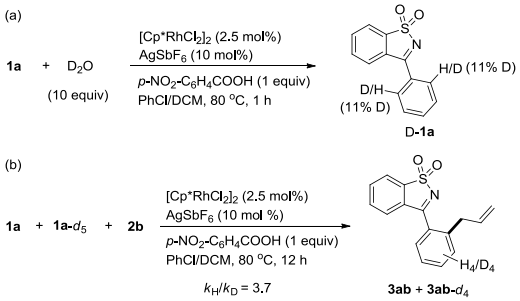
produce a mixture containing the allylation and olefination products with a ratio of 1.45:1. Among the allyl electrophilic partners, the branched allyl carbonates with substituents at the 2-position, such as Me, *i*Pr, *n*Bu, and alkynyl, showed moderate to good reactivities with up to 5:1 ratio of *E*/*Z* diasteroisomer (**3af**-**3ai**). These allylation reactions all required the use of $Cu(OAc)_2$ with enhanced amounts of $[Cp^*RhCl_2]_2$ and $AgSbF_6$. More importantly, allyl carbonate with γ-methyl substituent also reacted with **2b** albeit with only 29% yield (**3aj**), indicative of the sensitivity of this transformation to steric hindrance. Unfortunately, methyl (2-methylallyl) carbonate, methyl (2-methylbut-3-en-2-yl) carbonate, cinnamyl methyl carbonate, methyl (1-phenylallyl)carbonate, cyclohex-2-en-1-yl methyl carbonate and allyl carbonate derived from Morita–Baylis–Hillman adduct were unreactive. This direct allylation method is also applicable to acyclic *N*-sulfonyl ketimines. Imines derived from acetophenone and *p*-methoxyacetophenone underwent allylation reactions to give the desired products in synthetically useful yields (**3rb** and **3sb**). In the case of an imine derived from benzophenone, the reaction exclusively gave a di-allylation product even though using an equimolar amount of allyl carbonate (**3tb**). The introduction of a bromo as a blocking group into the *ortho* position afforded a 65% yield of **3ub**. The tolerance of the bromo substituent provides an opportunity for further functional group manipulations *via* classic metal-catalysed cross-coupling reactions.

The usefulness of the allyl functional groups was demonstrated by access to interesting molecules (Scheme 3). **3ab** was efficiently transformed into sulfonamide **4a** with TMSOTf as a Lewis acid at room temperature, which would have proceeded through an intramolecular Alder-ene reaction[23] followed by an elimination reaction. In addition, sultam **4b** was prepared through C=N bond reduction and Pd-catalysed intramolecular aminobromination reaction.[24]



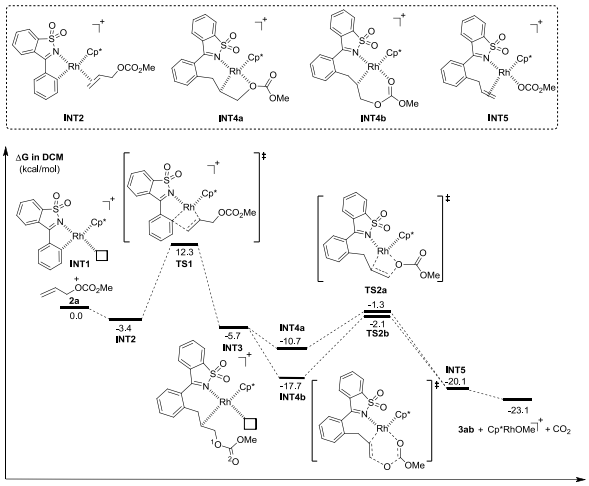
Scheme 3. Synthetic utilities of the allylated *N*-sulfonyl ketimines.

To provide insight into the possible mechanism, we conducted H/D exchange experiment and competition reactions (Scheme 4). The result of H/D exchange experiment between **1a** and 10 equiv of deuterium oxide showed that 11% D was introduced into the two *ortho* positions of the ketimine aryl ring (Scheme 4a). An intermolecular competition reaction between **1a** and **1a**-d_5 was performed, giving a primary kinetic isotope effect of 3.7 (Scheme 4b). These results suggested that the reaction involved a Rh-mediated reversible C-H activation process, which was consistent with our previous observation in the Rh-catalysed aryl C-H olefination.[18] Furthermore, an intermolecular competition reaction of **1d** and **1e** with **2b** was also carried out. GC analysis of the resulting mixture revealed that **3db** was the major product, indicating that the more electron-rich ketimine is significantly kinetically favored.

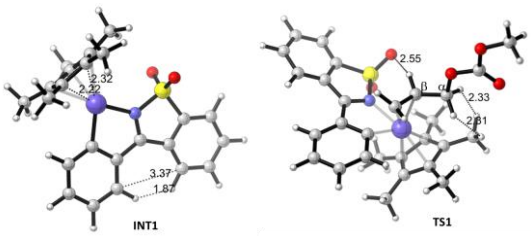


Scheme 4. Deuteration experiments.

Subsequently, we sought to use density functional theory (DFT) calculations to gain more understanding of the reaction mechanism (Scheme 5). A coordinatively unsaturated cationic species (**INT1**) was postulated to be formed by the reaction of **1a** and $[Cp^*RhCl_2]_2$ through C-H cleavage.[25] In the optimized structure of **INT1** (Scheme 6), the isothiazole ring and the phenyl ring are in the same plane with the Rh atom. It indicates that the introduction of a methyl group into the *ortho* position of the phenyl ring should disturb this plane structure. The formation of two isomers in the reaction of **1k** and **2b** may result from the steric effect, and possibly involve a different mechanism.[26] A similar result of the reaction between **1p** and **2b** producing two isomers (**3pb** and **3pb'**) was also due to the same reason that the steric hindrance disturbed the plane structure as shown in Scheme S6 (see the Supplementary Information for detailed results). With the allyl carbonate **2b** as a substrate, **INT1** formed a four-coordinate Rh(III) complex (**INT2**) which should undergo olefin insertion through **TS1** to furnish a coordinatively unsaturated Rh(III) intermediate (**INT3**). The energy barrier for the olefin insertion was 15.7 kcal/mol. In the **TS1** as shown in Scheme 6, the space around β-C of **2b** is limited by the isothiazole ring and Cp^*, showing short distance between β-H and SO_2, and between α-H and Cp*. This may explain why the methyl (2-methylallyl) carbonate was unreactive under the same reaction conditions. Two different coordinative models from **INT3** were proposed, coordination of the oxygen atoms (^{1}O and ^{2}O) of methyl carbonate with Rh to form **INT4a** and **INT4b**, respectively. The transition states (**TS2a** and **TS2b**) of β-oxygen elimination from **INT4a** and **INT4b** were identified with four and six membered ring, respectively. Although the energy of transition state **TS2a** (-1.3 kcal/mol) was similar with **TS2b** (-2.1 kcal/mol), the **INT4b** showed much lower energy (-17.7 kcal/mol) than **INT4a** (-10.7 kcal/mol), which indicated that the pathway involving the coordination of C=O with Rh was favored. The forming four-coordinate Rh(III) complex (**INT5**) *via* the β-oxygen elimination[27] readily underwent decarboxylation[28] to produce the allylarene **3ab** and $[Cp^*Rh(III)OMe]^+$. The latter may react with **1a** to generate **INT1** to fulfill the catalytic cycle. It is note that we have tried to understand the possible role of the 4-nitrobenzoic acid and $Cu(OAc)_2$ using DFT, unfortunately, we failed to identify any reasonable TS in this mechanism. Hence, the exact role of these two additives remains unclear at this moment.



Scheme 5. Energy profile of olefin insertion and allylarene formation with relative Gibbs free energies [kcal/mol].



Scheme 6. Optimized structure of intermediates **INT1** and **TS1**. The bond distances of the optimized structures are in angstroms.

In conclusion, we have developed a straightforward route to the synthesis of allylated *N*-sulfonyl ketimines *via* Rh-catalysed C-H functionalization. This reaction utilized the *N*-sulfonyl ketimine as a directing group and showed good γ-selectivity. The realization of such approach enriches the methods for the preparation of the allylarenes.[29] The computation studies indicated that the allylarene formation involved the olefin insertion and the β-oxygen elimination. These results could direct us to explore more synthetic methods regarding the synthesis of useful compounds. Our ongoing work is devoted to expanding the direct C-H allylation to a broad spectrum of substrates.

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