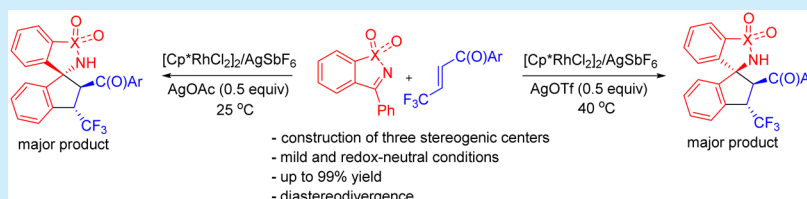


Rh(III)-Catalyzed Diastereodivergent Spiroannulation of Cyclic Imines with Activated Alkenes

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Supporting Information



ABSTRACT: Rh(III)-catalyzed [3 + 2] annulation of cyclic *N*-sulfonyl or *N*-acyl ketimines with activated alkenes has been realized, leading to the synthesis of spirocycles with three continuous stereogenic centers. This atom-economic reaction proceeded efficiently under mild and redox-neutral conditions via a C–H activation pathway, and the coupling is diastereodivergent, with the diastereoselectivity being controlled by silver additives.

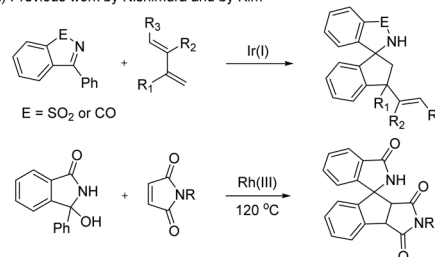
Metal-catalyzed C–H activation and functionalization has provided important approaches for step-economic synthesis of various drug-related chemicals and organics.¹ Among these, tandem [3 + 2] annulation reactions between readily available arenes and unsaturated bonds have been widely investigated.^{2–4} This type of reaction involves a C–H bond activation process followed by in situ transformations of the directing group, which offers a straightforward route to access cyclic compounds⁵ and is especially useful for the construction of spirocycles that are otherwise difficult to synthesize.^{6–13}

Despite this progress, discovery of novel synthetic methods that enable rapid assembly of spirocycles in a highly concise manner remains a formidable challenge.¹⁴ N-containing spirocycles of Type A are important motifs in numerous bioactive products and pesticides (Scheme 1).¹⁵ Previously, a number of metal-catalyzed [3 + 2] spiroannulation reactions for the formation of aminocyclopentene derivatives have been disclosed. For example, the groups of Dong,⁷ Nishimura,^{8d,e} Li,⁹ Wang,¹⁰ and Cramer¹² reported the annulation of aromatics

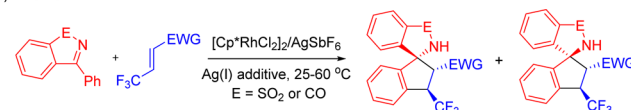
with alkynes. Wei reported the oxidative coupling of benzosultam with heterocycles.¹¹ Nishimura applied Ir(I) catalysis to [3 + 2] annulation of benzosultam and *N*-acyl ketimines with 1,3-dienes via C–H activation (Scheme 2).^{8a–c}

Scheme 2. Construction of Spirocycles by Annulation with Alkenes

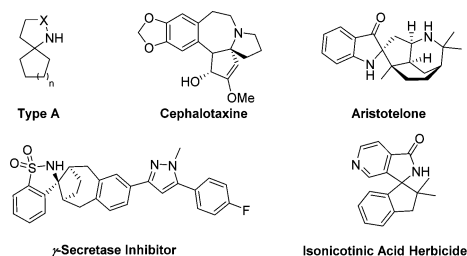
a) Previous work by Nishimura and by Kim



b) This work



Scheme 1. Examples of Important N-Containing Spirocycles



Recently, Kim reported annulative couplings between *N*-acyl ketimines and activated olefins under harsh conditions (Scheme 2),¹³ where the olefins were mostly limited to maleimides, fumarates, and maleates to give a single diastereomer. We now report mild and efficient [3 + 2] spiroannulation between arenes and CF₃-substituted enones with simultaneous con-

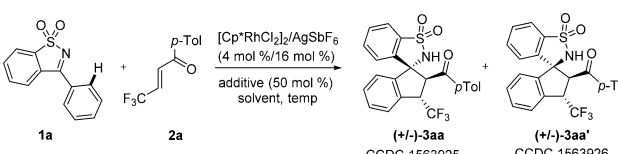
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struction of three continuous stereogenic centers, and the diastereoselectivity could be tuned by the silver additive.

Our initial studies revealed that, in the presence of $[\text{Cp}^*\text{RhCl}_2]_2/\text{AgSbF}_6$ (4 mol %/16 mol %) and $\text{Cu}(\text{OAc})_2$ (50 mol %), the coupling of *N*-sulfonyl ketimine **1a** with CF_3 -substituted enone **2a** in DCE afforded two spirocycles (**3aa** and **3aa'**) in overall quantitative yield with a dr of 1.3:1 (Table 1, entry 1). Both products have been characterized by X-ray

Table 1. Optimization Studies^{a,b}



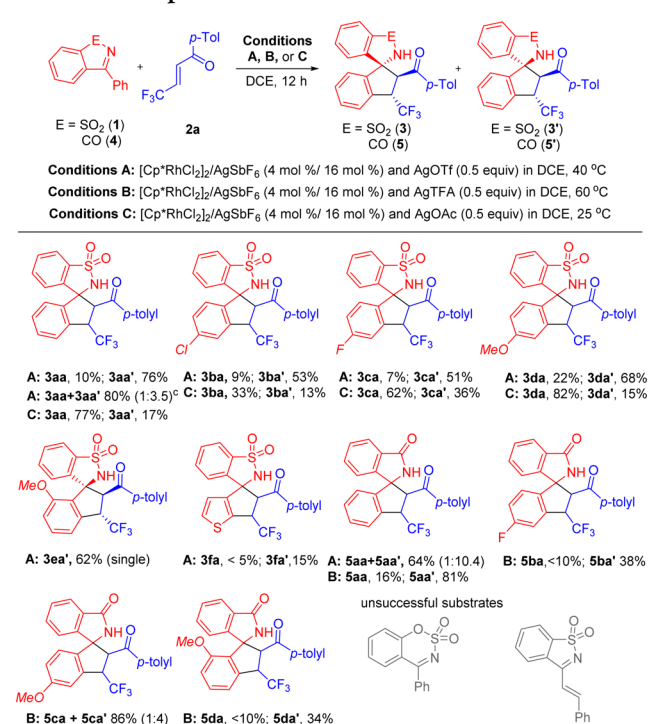
entry	solvent	additive	yield (%)	dr	temp (°C)
1	DCE	$\text{Cu}(\text{OAc})_2$	>99	1.3:1	60
2	TFE	$\text{Cu}(\text{OAc})_2$	>99	1:1	60
3	MeOH	$\text{Cu}(\text{OAc})_2$	trace	—	60
4	DCE	$\text{Cu}(\text{OAc})_2$	>99	1.6:1	40
5 ^c	DCE	$\text{Cu}(\text{OAc})_2$	nr	—	40
6	DCE	—	75	1:4	40
7	DCE	AgOAc	95	3.4:1	40
8	DCE	AgOAc	94	4.4:1	25
9	DCE	AgTFA	84	1:4.6	40
10	DCE	AgSbF_6	72	1:5	40
11	DCE	AgOTf	86	1:7.8	40
12 ^d	DCE	AgOTf	83	1:4.7	40

^aReaction conditions: **1a** (0.2 mmol), **2a** (0.24 mmol), $[\text{Cp}^*\text{RhCl}_2]_2/\text{AgSbF}_6$ (4 mol %/16 mol %), and an additive (50 mol %) in a solvent (2.0 mL) for 12 h under Ar. ^bIsolated yield. The dr of **3aa**:**3aa'** was determined by ^1H NMR spectroscopy. ^cNo AgSbF_6 was used. ^d AgNTf_2 was used instead of AgSbF_6 (16 mol %).

crystallography. Changing the solvents turned out to be futile (entries 2,3), and decreasing the reaction temperature only slightly increased the diastereoselectivity (entry 4). Screening of additives revealed that AgOAc was effective to increase the diastereoselectivity up to 4.4:1 (entry 8), but using AgTFA or AgOTf gave the inverse diastereoselectivity (entries 9 and 11). Control experiments were also carried out. In the absence of AgSbF_6 , no product was detected. However, the products could be generated without any additive (entry 6). When AgSbF_6 was used as a halide scavenger as well as a silver additive (entry 10) or when AgNTf_2 was used as a halide scavenger (entry 12), the reaction proceeded with a lower yield and diastereoselectivity. Finally, we chose the conditions in entries 8 (Conditions C) and 11 (Conditions A) as the diastereodivergent standard conditions.

Substituted *N*-sulfonyl ketimines (**1a–f**) were allowed to undergo annulation with **2a** under Conditions A to explore the scope of the arene substrate (Scheme 3). It was observed that an electron-donating group such as methoxyl (**1d**) benefited the reaction while electron-withdrawing groups such as *para*-F (**1c**) decreased the reaction efficiency. The position of the substituent also affected the reaction. In contrast to ketimine **1d**, ketimine **1e** with an *ortho*-OMe group coupled with **2a** to give a single product in good yield (**3ea'**, 62%). This is likely due to the steric effect that leads to a more crowded transition state during insertion of the imine group. The ketimine **1f** with a thienyl group only reacted with a low yield. When the reactions were carried out under Conditions C with the AgOAc

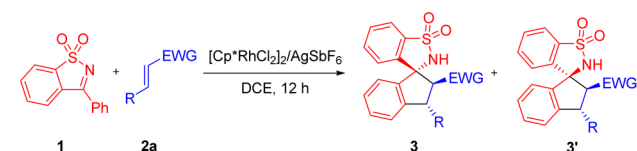
Scheme 3. Scope of Ketimine Substrates^{a,b}



^aThe reaction was performed under Conditions A, B, or C in DCE (2.0 mL) under Ar for 12 h. ^bIsolated yield. The dr was determined by ^1H NMR spectroscopy. ^cThe reaction was performed at a scale of 2.5 mmol of **1a** under Conditions A.

additive, the products were all obtained in good to excellent yields and moderate dr's (46–98% total yield, 1.7–5.5:1 dr). It has been reported that *N*-acyl ketimine generated *in situ* from 3-hydroxy-3-aryllisoindolin-1-ones by dehydration can undergo [3 + 2] annulation with alkynes.^{8c,e} Thus, **4a** was chosen to react with **2a** under the standard conditions A, furnishing the desired products **5aa** and **5aa'** in totally 64% yield and 1:10.4 dr. By simple optimization using the AgTFA additive (Conditions B; see Supporting Information (SI)), the products were obtained in excellent yield (97%) and moderate dr (1:5.2). Several substituted *N*-acyl ketimines (**4b–4d**) were then examined, and they all gave moderate to high yield (42%–86%, 1:4–8 dr). To demonstrate the synthetic utility of the catalytic reaction, a 2.5-mmol-scale synthesis of **3aa** and **3aa'** was performed and a high yield was realized (Conditions A, 80%, 1:3.5 dr).

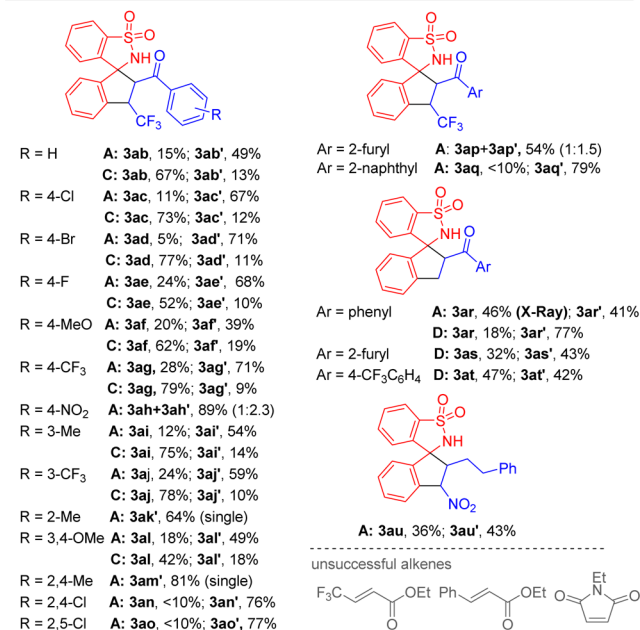
The scope of alkenes was also established (Scheme 4), and the reaction system allowed the annulations of various CF_3 -substituted enones and aryl vinyl ketones. CF_3 -substituted enones bearing halogen groups (**2c–e**), methoxyl (**2f**), CF_3 (**2g**), and NO_2 (**2h**) at the *para*-position of the phenyl group all reacted smoothly with **1a** under Conditions A to give the corresponding products in moderate to excellent yield and dr (59–99% yield, 1:2.3–14 dr). The reactions were efficient with introduction of EWGs such as CF_3 (**2g**) and NO_2 (**2h**). Substrates bearing an *ortho*- or *meta*-substituent (**2i–2k**) were also examined, and they exhibited good reactivity. Notably, only product **3ak'** was detected when 2-methyl-substituted alkene (**2k**) was used as a coupling partner (64%). Coupling of alkenes with disubstituted aryl (**2l–2o**), furyl (**2p**), and naphthyl (**2q**) all afforded the desired products with good efficiency and selectivity. Switching to the AgOAc additive consistently

Scheme 4. Scope of Alkenes^{a,b}

Conditions A: [Cp*RhCl₂]₂/AgSbF₆ (4 mol %/16 mol %) and AgOTf (0.5 equiv) in DCE, 40 °C

Conditions C: [Cp*RhCl₂]₂/AgSbF₆ (4 mol %/16 mol %) and AgOAc (0.5 equiv) in DCE, 25 °C

Conditions D: [Cp*RhCl₂]₂/AgSbF₆ (4 mol %/16 mol %) and AgOMs (0.5 equiv) in DCE, 25 °C

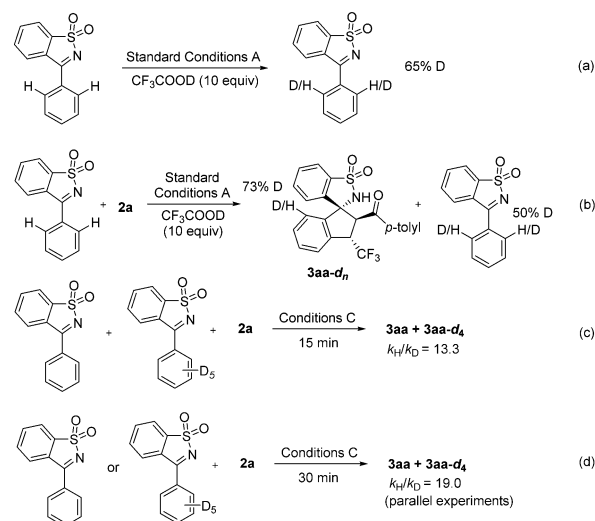


^aThe reaction was performed under Conditions A, C, or D in DCE (2.0 mL) under Ar for 12 h. ^bIsolated yield. The dr was determined by ¹H NMR spectroscopy.

changed the diastereoselectivity with a good yield and moderate selectivity. In most cases, the two diastereomers are isolable. Aryl vinyl ketones (**2r–2t**) and nitroalkene (**2u**) were also compatible. With a simple change of the silver additive to AgOMs (see SI), the coupling afforded the annulated products in excellent yield with moderate dr (Conditions D). In contrast, some common alkenes failed to show any reactivity.

To gain some insight into the mechanism of this reaction, H/D exchange experiments were carried out. H/D exchange with AcOH-*d*₄ was detected at the *ortho*-positions of the phenyl group of **1a** in the presence or absence of olefin **2a** under Conditions A (Scheme 5a). H/D exchange was also observed at the *ortho'* position of product **3aa** (**3aa'** was not analyzed, Scheme 5b). These results indicated reversibility of the C–H cleavage. KIE experiments were then conducted by both intermolecular competition and independent reactions using **1a** and **1a-d**₅. Consistently large KIEs were obtained, indicating that cleavage of the C–H bond is probably involved in the turnover-limiting step (Scheme 5c and 5d). The large magnitude might also suggest a tunneling effect in C–H activation.¹⁶ A possible mechanism is given in the SI on the basis of our experimental results and literature precedents. Cyclometalation of **1a** affords a five-membered rhodacyclic intermediate. Subsequent key processes include the regio- and diastereoselective insertion of the alkene to give a Rh(III)-enolate, in which the stereochemistry of the olefin is retained (trans orientation). The Rh–C(enolate) then undergoes silver

Scheme 5. H/D Exchange and KIE Experiments



additive-dependent migratory insertion into the imine moiety. In the presence of a more cationic AgOTf salt, the silver cation likely facilitates the migratory insertion by activation of the carbonyl to place the carbonyl and the nitrogen in a cis orientation through a N,O-chelation to the Rh or Ag for stabilization.

In summary, we have realized Rh(III)-catalyzed efficient [3 + 2] annulation for the synthesis of diverse spirocycles with three stereogenic centers under mild conditions. The reactions are highly efficient and atom-economical. The diastereoselectivity can be tuned by the silver additive. Two types of cyclic ketimine directing groups proved to be viable, and the scope of alkenes was investigated and found to be quite satisfactory. Given the rapid assembly of spirocycles, mild and oxidant-free conditions, broad substrate scope, and diastereodivergence, this method may find applications in the synthesis of related complex structures.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.7b02678.

Crystallographic data (CIF, CIF, CIF)

Detailed experimental procedures, characterization of new compounds, and copies of NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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