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# Iridium-Catalyzed [3 + 2] Annulation of Cyclic *N*-Sulfonyl Ketimines with 1,3-Dienes via C−H Activation

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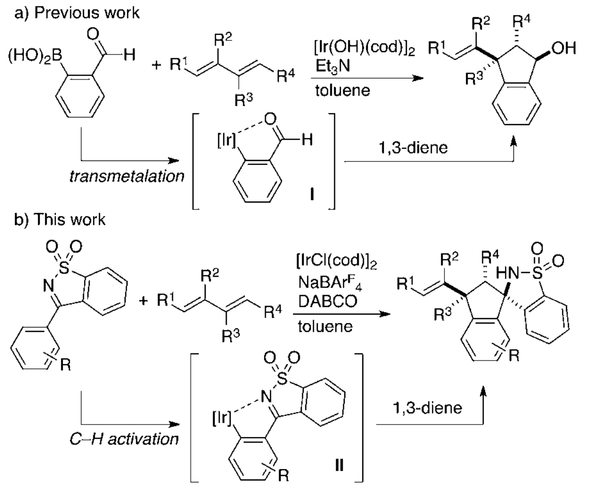
*Supporting Information*

**ABSTRACT:** Ir-catalyzed [3 + 2] annulation of cyclic *N*-sulfonyl ketimines with 1,3-dienes, in which an aryliridium intermediate is formed via C−H activation, gives aminoindane derivatives in high yields with high regio- and diastereoselectivity.

Transition-metal-catalyzed functionalization of aromatic compounds via C−H activation has been recently developed as one of the special topics in organic chemistry.[1] In particular, selective functionalization has been achieved by the use of a directing group appropriately arranged toward the aromatic ring since the first report of successful ruthenium catalysis by Murai and co-workers.[2] In this respect, there have been many reports on the ortho functionalization of aromatic rings bearing carbonyl groups or imines as the directing groups, where arylmetal species are formed via C−H activation.[1,2] The fate of the arylmetal species in the subsequent reaction depends on the reaction partner or the nature of the metal and its ligands. The ortho functionalization of aromatic rings involving a transformation of the directing group is an attractive methodology for achieving the formation of more than two bonds directly, which allows the synthesis of complicated molecules. For example, in 2005, Kuninobu and Takai reported the Re-catalyzed annulation of aromatic aldimines with internal alkynes to give 1-aminoindene derivatives.[3] Rh-catalyzed oxidative coupling of imines with alkynes to give indenone imine and isoquinoline derivatives was reported by Satoh and Miura.[4] Zhao reported Rh-catalyzed [3 + 2] annulation of benzophenone imines with internal alkynes to give 1-aminoindenes,[5] and its asymmetric variant was reported by Cramer.[6] Highly stereoselective annulations of imines with allenes to give 3-alkylidene-1-aminoindanes have also been reported independently by Kuninobu and Takai[3c] and Cramer.[6b] There have been several reports on the catalytic synthesis of 1-indenyl alcohols or their dehydration products by the reactions of aromatic ketones with internal alkynes or allenes in the presence of Ru, Rh, Ir, and Pd catalysts.[7,8]

**Scheme 1. Ir-Catalyzed [3 + 2] Annulation with 1,3-Dienes**



We recently reported the Ir-catalyzed annulation reaction of 2-formylphenylboronic acid with 1,3-dienes to give 1-indanols, where the use of chelating diene ligands is essential (Scheme 1a).[9] The reaction proceeds via 2-formylphenyliridium(I) species **I** as a key intermediate formed by transmetalation, and the following annulation has characteristic features: Of the two double bonds constituting the 1,3-diene substrate, the more electron-rich one participates in the reaction, and of the two carbons of the reacting double bond in the 1,3-diene, the terminal carbon forms a bond with the carbonyl carbon of 2-formylphenylboronic acid. Here we report the new annulation of *N*-sulfonyl ketimines with 1,3-dienes catalyzed by a cationic Ir complex to give aminoindane derivatives (Scheme 1b). Our new approach in this work is focused on the formation of aryliridium(I) intermediate **II** via C−H activation.[10]

The annulation reaction of cyclic *N*-sulfonyl ketimines with 1,3-dienes was found to take place in the presence of a cationic Ir complex generated from [IrCl(cod)]$_2$ (cod = 1,5-cyclooctadiene). Thus, ketimine **1a** was allowed to react with 2.0 equiv of isoprene (**2m**) in the presence of [IrCl(cod)]$_2$ (5 mol % Ir), triethylamine (5 mol %), and NaBAr$^F_4$ [Ar$^F$ = 3,5-(CF$_3$)$_2$C$_6$H$_3$] in toluene at 80 °C for 20 h, giving an 81% yield of aminoindane **3am** together with a 5% yield of its regioisomer **4am**; the formation of other diastereomers of each product was not detected (Table 1, entry 1). The structure of **3am**[11] as shown in Table 1 indicates that the more substituted carbon−carbon double bond of isoprene (**2m**) preferentially reacted to form two carbon−carbon bonds, one at the ortho position of the phenyl group and the other at the imine carbon, and its 1,3-*cis* relative stereochemistry is similar to that observed in our previous studies on the annulation of 2-formylphenylboronic acid with 1,3-

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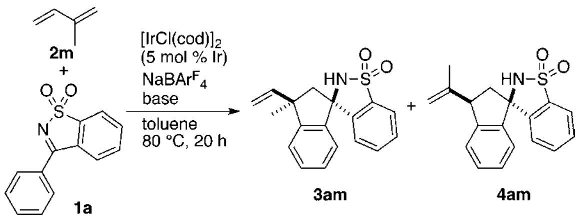
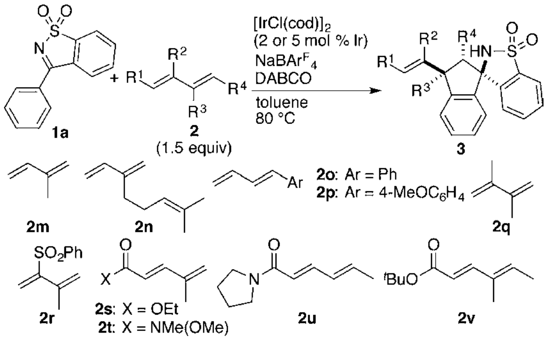
### Table 1. Ir-Catalyzed [3 + 2] Annulation of 1a with 2m[a]

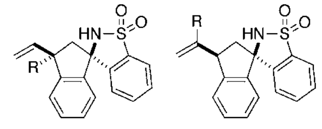
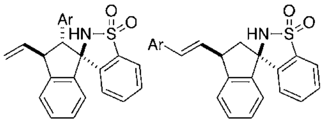
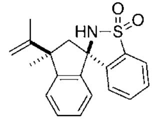
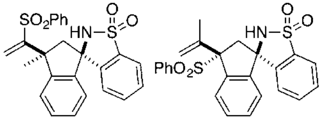
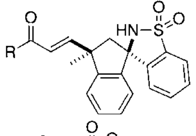
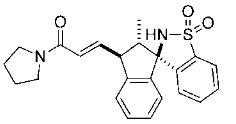
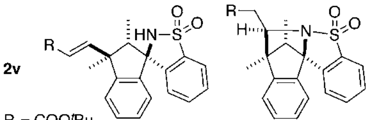


| entry | base | yield (%)[b] 3am | 4am |
|---|---|---|---|
| 1 | Et$_3$N | 81 | 5 |
| 2 | EtN$^i$Pr$_2$ | 54 | 3 |
| 3 | DABCO | 94 | 5 |
| 4 | pyridine | 61 | 4 |
| 5 | 2,6-lutidine | 70 | 5 |
| 6 | – | 0 | 0 |
| 7[c] | DABCO | 48 | 2 |
| 8[d] | DABCO | 92 | 5 |

[a]Reaction conditions: ketimine **1a** (0.10 mmol), **2m** (0.20 mmol), [IrCl(cod)]$_2$ (5 mol % Ir), NaBAr$^{\mathrm{F}}_4$ (10 mol %), and base (5 mol %) in toluene (0.4 mL) at 80 °C for 20 h. [b]Determined by $^1$H NMR analysis. [c]Performed without NaBAr$^{\mathrm{F}}_4$. [d]Performed with 1.5 equiv of **2m** (0.15 mmol) in the presence of [IrCl(cod)]$_2$ (2 mol % Ir), NaBAr$^{\mathrm{F}}_4$ (4 mol %), and DABCO (2 mol %).

### Table 2. Ir-Catalyzed [3 + 2] Annulation of Ketimine 1a with 1,3-Dienes 2[a]



| entry | diene 2 | product | yield (%)[b] |
|---|---|---|---|
| 1 | 2m | <br>3am: R = Me 4am<br>3an: R = CH$_2$CH$_2$CH=CMe$_2$ 4an | 96 (3am/4am = 94:6) |
| 2[c,d] | 2n | | 90 (3an/4an = 92:8) |
| 3[c,e] | 2o | <br>3ao: Ar = Ph 4ao<br>3ap: Ar = 4-MeOC$_6$H$_4$ 4ap | 92 (3ao/4ao = 95:5) |
| 4[c,e] | 2p | | 99 (3ap/4ap = 98:2) |
| 5 | 2q | 3aq  | 96 |
| 6[c,f] | 2r | <br>3ar 4ar | 3ar: 82<br>4ar: 5 |
| 7 | 2s | 3as: R = EtO  | 99 |
| 8[c] | 2t | 3at: R = NMe(OMe) | 95 |
| 9 | 2u | 3au  | 95 |
| 10 | 2v | <br>R = COO$^t$Bu 3av 5av | 98 (3av/5av = 98:2) |

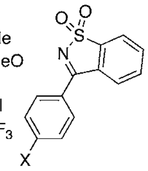
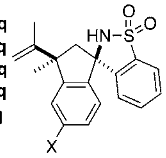
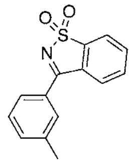
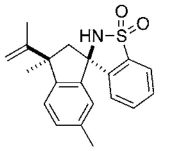
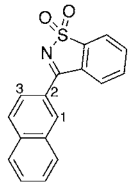
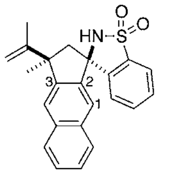
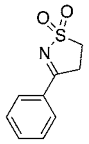
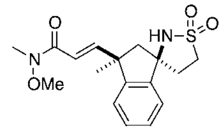
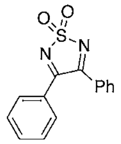
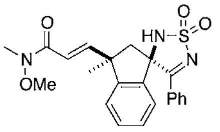
[a]Reaction conditions: ketimine **1a** (0.20 mmol), **2m** (0.30 mmol), [IrCl(cod)]$_2$ (2 mol % Ir), NaBAr$^{\mathrm{F}}_4$ (4 mol %), and DABCO (2 mol %) in toluene (0.8 mL) at 80 °C for 20 h. [b]Isolated yields. The isolated yields of the mixtures of isomers are shown in entries 1–4 and 10. [c]Performed with [IrCl(cod)]$_2$ (5 mol % Ir), NaBAr$^{\mathrm{F}}_4$ (10 mol %), and DABCO (5 mol %). [d]Performed with 2.0 equiv of **2n** for 48 h. [e]For 12 h. [f]For 48 h.

dienes.[9] The nature of the base significantly affects the yields of the annulation products. Thus, the reaction in the presence of EtN$^i$Pr$_2$, a bulkier base than triethylamine, gave **3am** and **4am** in yields of 54 and 3%, respectively (entry 2), while the use of the less bulky and less basic 1,4-diazabicyclo[2.2.2]octane (DABCO) gave higher yields of the annulation products (**3am**, 94%; **4am**, 5%; entry 3). Pyridine and 2,6-lutidine were less effective than DABCO (entries 4 and 5), and the reaction without a base gave no annulation products (entry 6).[12] Modest conversion of **1a** was observed in the reaction without NaBAr$^{\mathrm{F}}_4$ (entry 7), indicating that the cationic Ir complex efficiently catalyzes the present reaction. The reaction with reduced amounts of the diene (1.5 equiv) and the Ir catalyst (2 mol % Ir) also proceeded well, giving high yields of the annulation products (**3am**, 92%; **4am**, 5%; entry 8).

The results obtained for the Ir-catalyzed annulation of ketimine **1a** with various types of 1,3-dienes are summarized in Table 2. In the same fashion as isoprene (**2m**, entry 1), myrcene (**2n**) underwent the reaction at the more substituted double bond of the 1,3-diene moiety with high regioselectivity to give a 90% yield of the annulation products (entry 2). The same regioselectivity was also observed for 1-phenyl-1,3-butadiene (**2o**) and 1-(4-methoxyphenyl)-1,3-butadiene (**2p**), where the more substituted double bond preferentially participated in the reaction (entries 3 and 4).[13] The reaction of 2,3-dimethyl-1,3-butadiene (**2q**) gave **3aq** exclusively in 96% yield (entry 5). Entries 6–9 demonstrate that electron-deficient dienes substituted with sulfonyl and carbonyl groups (sulfonylbutadiene **2r**, dienoate **2s**, and dienamides **2t** and **2u**) are also reactive toward the present annulation, with the reaction taking place at the more electron-rich double bond with very high regioselectivity, except for **2r**, which gave **3ar** and **4ar** in yields of 82 and 5%, respectively. The reaction of dienoate **2v** having a trisubstituted double bond gave the annulation product **3av** as well as a small amount of transannular product **5av** (98% yield, **3av**/**5av** = 98:2; entry 9). It was confirmed that **5av**[11] was formed from **3av** by intramolecular addition of the sulfonamide group. Thus, **5av** was isolated in 91% yield by treatment of a 98:2 mixture of **3av** and **5av** with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) at room temperature for 15 h.

Table 3 summarizes the results obtained for the reaction of several ketimines **1** with 1,3-diene **2q** or **2t**. The reactions of ketimines **1b**–**f** having para-substituted phenyl groups gave high

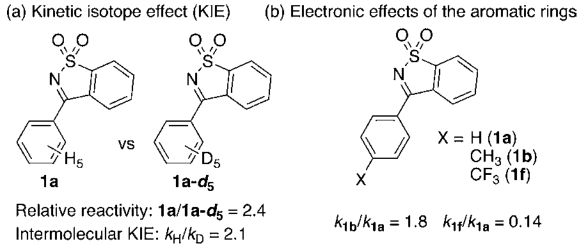
**Table 3. Ir-Catalyzed [3 + 2] Annulation of Ketimines 1 with 1,3-Dienes 2**[a]

| entry | 1 | | product | | isolated yield (%) |
|---|---|---|---|---|---|
| 1 | **1b**: X = Me |  | **3bq** |  | 98 |
| 2 | **1c**: X = MeO | | **3cq** | | 96 |
| 3 | **1d**: X = F | | **3dq** | | 94 |
| 4 | **1e**: X = Cl | | **3eq** | | 96 |
| 5[b,c] | **1f**: X = CF$_3$ | | **3fq** | | 89 |
| 6[b] | **1g** |  | **3gq** |  | 97 |
| 7 | **1h** |  | **3hq** |  | 98[d] (91/9) |
| 8[b,e] | **1i** |  | **3it** |  | 79 |
| 9[b,e] | **1j** |  | **3jt** |  | 82 (5)[f] |

[a] Reaction conditions: ketimine **1** (0.20 mmol), **2** (0.30 mmol), $[IrCl(cod)]_2$ (2 mol % Ir), $NaBAr^F_4$ (4 mol %), and DABCO (2 mol %) in toluene (0.8 mL) at 80 °C for 20 h. [b] Performed with 5 mol % Ir. [c] For 48 h. [d] Isolated yield of **3hq** and its regioisomer. [e] Performed with 3 equiv of **2t** at 100 °C for 48 h. [f] Isolated yield of a double annulation product.

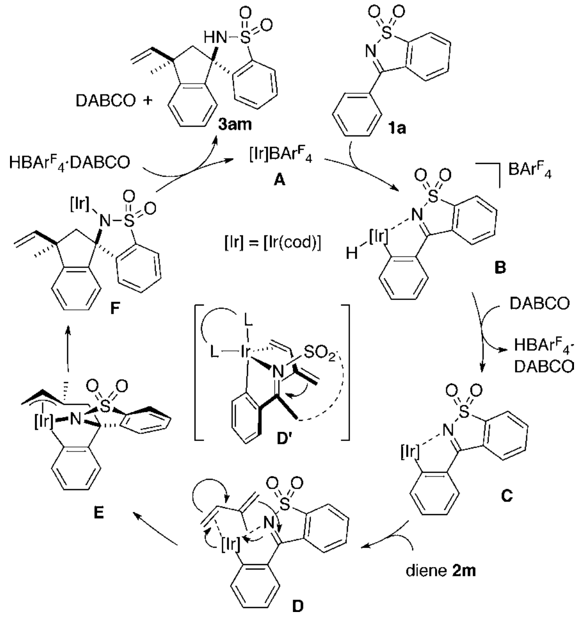
yields of the annulation products **3bq**–**3fq** (entries 1–5), although the strongly electron-withdrawing CF$_3$ group of **1f** retarded the reaction, requiring a longer reaction time (48 h) in the presence of an increased amount of the catalyst (5 mol % Ir) (entry 5). In the reaction of meta-substituted ketimine **1g**, a less sterically hindered C–H bond was selectively activated to give **3gq** in 97% yield (entry 6). The selectivity of the C–H activation in the reaction of ketimine **1h** substituted with 2-naphthyl was similar to that observed for meta-substituted ketimine **1g**, and **3hq** was obtained as a major product, although the regioselectivity was not very high because of the formation of the annulation product resulting from C–H activation at C1 (entry 7). Ketimines **1i** and **1j**, which are not fused with a benzene ring, reacted slowly and required a higher catalyst loading and a prolonged reaction time (entries 8 and 9). The annulation of **1i** with dienamide **2t** under harsh conditions (100 °C for 48 h) gave **3it** in 79% yield (entry 8). In the reaction of diimine **1j**, one phenyl group preferentially participated in the reaction to give **3jt** in 82% yield with the formation of a small amount (5% yield) of a double annulation product (entry 9).[14]

**Scheme 2. Relative Reactivity of Imines 1 with 2q**



The preliminary results of competition experiments to gain some mechanistic insight are shown in Scheme 2. In separate reactions with diene **2q**, a significant difference in the reactivities of **1a** and **1a**-$d_5$ was observed: **1a** reacted 2.4 times faster than **1a**-$d_5$ (Scheme 2a).[15] In addition, $k_H/k_D = 2.1$ was observed for the intermolecular competition reaction of **1a** and **1a**-$d_5$ with **2q**, indicating that the C–H bond cleavage occurs during the turnover-limiting step or reversibly before the other turnover-limiting step.[16] On the other hand, the electronic nature of the substituents on the benzene ring of imine **1** influenced the reactivity. Thus, relatively electron-rich **1b** having a methyl group at the 4-position reacted 1.8 times faster than nonsubstituted **1a**, and electron-deficient **1f** reacted slower than **1a** (Scheme 2b).

**Scheme 3. Proposed Catalytic Cycle**



On the basis of the regiochemistry observed in the present annulation reaction, which is similar to that in the reaction of 2-formylphenylboronic acid with 1,3-dienes,[9] we postulate the catalytic cycle shown in Scheme 3. Ortho C–H activation of ketimine **1a** assisted by coordination of the imine nitrogen to Ir forms arylhydridoiridium(III) species **B**.[10g,17] Deprotonation of **B** promoted by DABCO forms aryliridium(I) species **C**.[17] Nucleophilic attack of the electron-rich terminal carbon of diene **2m** at the imine carbon in intermediate **D**, where the other double bond of the diene coordinates to Ir, forms π-allyliridium(III) intermediate **E** via oxidative cyclization.[9a] **E** undergoes reductive elimination to form a carbon–carbon bond, giving imidoiridium(I) species **F**, and subsequent protonolysis gives aminoindane **3am** and regenerates the cationic Ir complex **A**. Alternatively, protonation of **E** to form a cationic π-allyliridium(III) species and subsequent reductive elimination would give the annulation product. The stereoselectivity of the product **3am** is tentatively explained by the model of the fivecoordinate intermediate **D**′[9a] leading to the π-allyliridium complex **E**.

In summary, we have developed a new type of annulation reaction of cyclic *N*-sulfonyl ketimines with 1,3-dienes using an Ir catalyst that gives aminoindane derivatives with high regio- and stereoselectivity.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

Experimental procedures, compound characterization data, and crystallographic data (CIF). 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.

## ■ ACKNOWLEDGMENTS

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(12) Appropriate basicity and size of the base are necessary for the catalytic activity. The p$K_a$ values of the conjugate acids of the bases are as follows: $Et_3N$, 10.8; DABCO, 8.8; pyridine, 5.2.

(13) The regioselectivity leading to **3ao** is different from that observed in our previous reaction of **2o** with 2-formylphenylboronic acid (ref 9a), where the terminal alkene of **2o** participated in the reaction.

(14) The reaction of **2q** with *N*-tosylbenzophenone imine or the *N*-tosylimine derived from *p*-methoxybenzaldehyde gave no annulation products under the standard reaction conditions.

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