DOI: 10.1002/adsc.201500709

# Iridium- and Rhodium-Catalyzed Carbocyclization between 2-Phenylimidazo[1,2-*a*]pyridine and α-Diazo Esters

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Received: July 26, 2015; Revised: January 4, 2016; Published online: February 17, 2016

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.201500709.

**Abstract:** Iridium(III) and rhodium(III) complexes can catalyze the carbocyclization between 2-phenylimidazo[1,2-*a*]pyridine and α-diazo esters. The reaction occurs *via* C–H activation and dialkylation of the arene followed by intramolecular nucleophilic substitution. Iridium(III) and rhodium(III) catalysis offer complementary scopes with respect to the α-diazo esters.

**Keywords:** carbocyclization; C–H activation; α-diazo esters; iridium(III) and rhodium(III) catalysis; 2-phenylimidazo[1,2-*a*]pyridines

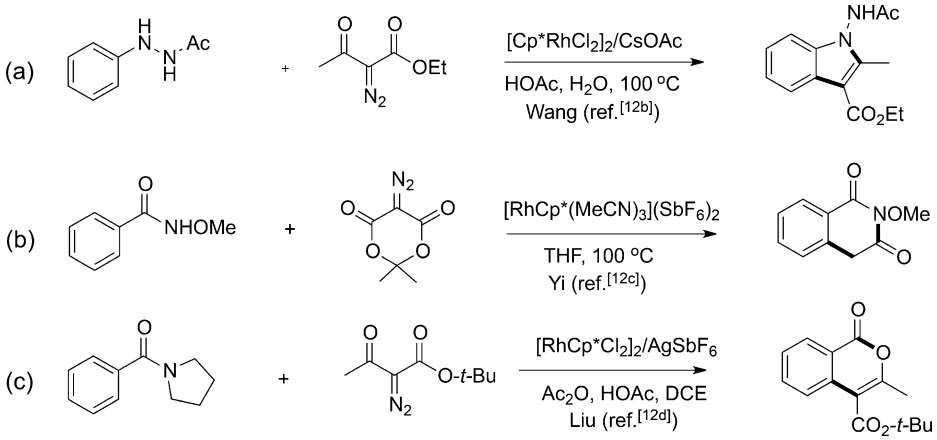
Metal-catalyzed C–H activation and functionalization of arenes have received increasing attention in the past several decades.[1] This strategy effectively and directly utilizes readily available arenes as the substrate, and it has been employed in the construction of various complex structures.[2] In the past several years, Cp*Rh(III)-catalyzed C–H activation of arenes have been increasingly explored. It has been widely accepted that Rh(III)-catalyzed C–H activation and functionalization can proceed with broad substrate scope, functional group tolerance, and high selectivity.[3]

Among these Rh(III)-catalyzed coupling systems, formal insertion of arene C–H bonds into an unsaturated coupling partner is particularly attractive because such reactions are typically redox-neutral. In addition to the redox-economy, the reaction usually proceeds with high atom-economy. The unsaturated coupling partners typically include alkenes/alkynes,[4] organic azides,[5] imines/aldehydes,[6] isocyanates,[7] strained rings,[8] and carbene precursors.[9] This insertion of arenes into carbene precursors (commonly α-diazo carbonyls) is particularly important in that the mechanism differs from the well-explored Rh(II)-catalyzed insertion of $sp^2$ C–H bonds into (activated) carbenes, in which an electrophilic aromatic substitution mechanism is generally followed.[10] Early studies on Rh(III)-catalyzed arene C–H activation–insertion into α-diazo carbonyls only resulted in simple alkylation. In 2015, the Wang group successfully realized an Ir(III)-catalyzed coupling of aromatic C–H bonds with diazomalonates *via* a metal carbene migratory insertion process.[11] Recently, α-diazo carbonyls have been employed as a $C_1$,[12] $C_2$,[13] or $C_3$[14] source in cyclative couplings with bifunctional arenes (Scheme 1). Despite this progress, the synthesis of carbocycles using α-diazo carbonyls as a $C_2$ source has not been reported.

We reasoned that 2-phenylimidazo[1,2-*a*]pyridine[15] is bifunctional in that the nitrogen offers sufficient chelation assistance for C–H activation and the C-3 position offers a reactive nucleophilic site. Thus, its coupling with activated α-diazo esters may lead to an efficient construction of new carbocycles. We now report our studies on Ir(III)- and Rh(III)-catalyzed C–H activation–annulation between 2-phenylimidazo[1,2-*a*]pyridine and α-diazo esters.

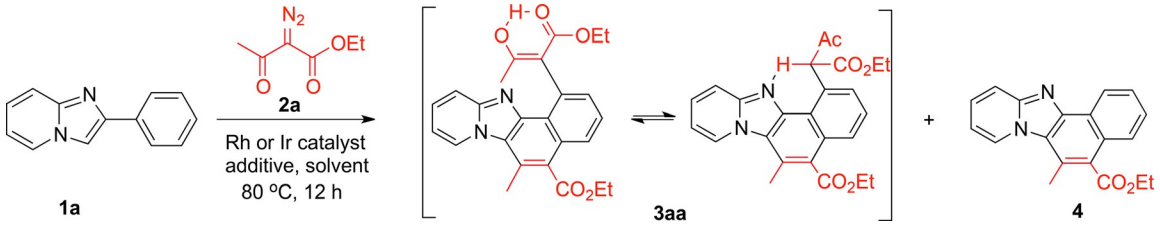
We selected the coupling between 2-phenylimidazo[1,2-*a*]pyridine (**1a**) and ethyl α-diazoacetoacetate (**2a**) as the model reaction for optimization studies (Table 1, see the Supporting Information for details). Our initial screening revealed that when catalyzed by $[RhCp^*(MeCN)_3](SbF_6)_2$ in the presence of PivOH (EtOH, 80 °C), the coupling proceeded in only moderate yield, and the major product (**3aa**) corresponds to dialkylation with subsequent nucleophilic cyclization (entry 1). The yield was only slightly improved when the catalyst was switched to $RhCp^*(OAc)_2$ (entry 2). In contrast, when TFA was employed as an acid additive, the major product was shifted to the monoalkylation–annulation product **4** (entry 3). However, all attempts to further improve the selectivity and efficiency of this coupling met with failure under various rhodium-catalyzed conditions. Thus, we resorted to analogous iridium catalysts because Cp*Ir(III) complexes may also catalyze the coupling of arenes with diazo




**Scheme 1.** Rh-catalyzed cyclative coupling with diazo esters serving a $C_2$ source.

**Table 1.** Optimization studies.[a]



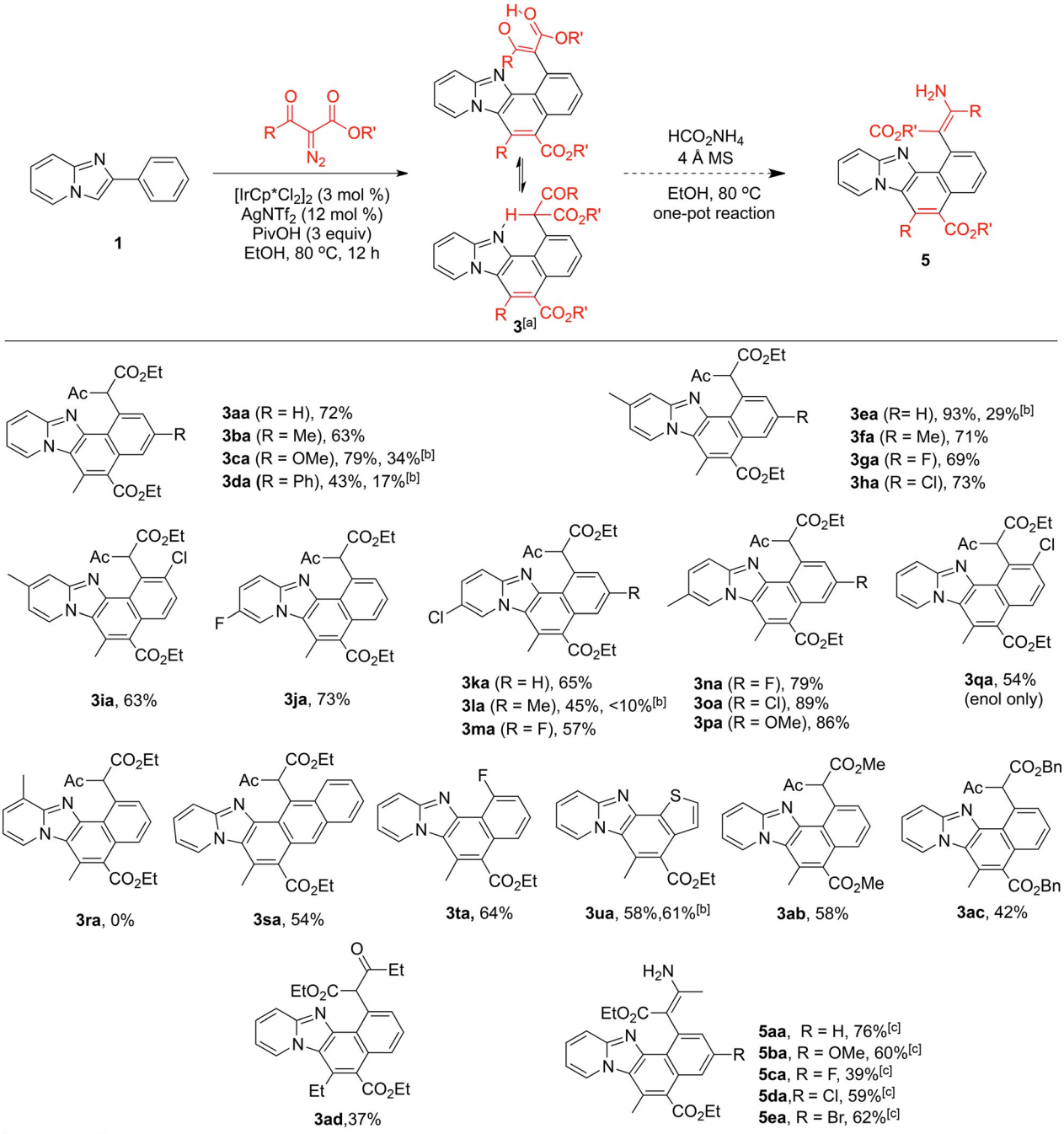

| Entry | Catalyst | Additive | Solvent | Yield [%][b] | |
|---|---|---|---|---|---|
| | | | | **3aa** | **4** |
| 1 | $[RhCp^*(MeCN)_3](SbF_6)_2$ | PivOH | EtOH | 47 | <5 |
| 2 | $RhCp^*(OAc)_2$ | PivOH | EtOH | 53 | 17 |
| 3 | $RhCp^*(OAc)_2$ | TFA | EtOH | <5 | 55 |
| 4 | $[IrCp^*Cl_2]_2/AgNTf_2$ | – | EtOH | 17 | <5 |
| 5 | $[IrCp^*Cl_2]_2/AgNTf_2$ | TFA | EtOH | 25 | 27 |
| 6 | $[IrCp^*Cl_2]_2/AgNTf_2$ | HOAc | EtOH | 36 | 23 |
| 7 | $[IrCp^*Cl_2]_2/AgNTf_2$ | PivOH | EtOH | 72 | <5 |
| 8 | $[IrCp^*Cl_2]_2/AgSbF_6$ | PivOH | EtOH | 63 | 21 |
| 9 | $[IrCp^*Cl_2]_2/AgOTf$ | PivOH | EtOH | 65 | 18 |
| 10 | $[IrCp^*Cl_2]_2/AgNTf_2$ | PivOH | DCE | <5 | <5 |
| 11 | $[IrCp^*Cl_2]_2/AgNTf_2$ | PivOH | MeCN | ND | ND |
| 12 | $AgNTf_2$ | PivOH | EtOH | ND | ND |

[a] *Reaction conditions:* arene (0.2 mmol), diazo ester **2a** (0.5 mmol), Rh or Ir catalyst (3 mol% for dimer), $AgNTf_2$ (12 mol%), acid additive (0.6 mmol) in a solvent (2 mL) at 80 °C for 12 h.
[b] Isolated yields.

esters.[11,16] Our screening indicated that $[IrCp^*Cl_2]_2$ (3 mol%)/$AgNTf_2$ (12 mol%) in the presence of PivOH additive constitutes an optimal catalyst system, and the product **3aa** was isolated in 72% yield (entry 7). Using other acids (entries 4–6), silver salts (entries 8 and 9), or solvents (entries 10 and 11) all resulted in lower efficiency and selectivity. The PivOH additive likely facilitates C–H activation and enhances the electrophilicity of the ketone functionality toward subsequent cyclization.[17] Control experiments confirmed that a rhodium or iridium catalyst is necessary. Product **3aa** has been fully characterized as a ketone-enol mixture in the solution. Of note, intramolecular hydrogen bonding has been elucidated by $^1H$ NMR spectroscopy in each component [$\delta = 13.2$ for O···H and 7.80 for N···H (br, s) in $CDCl_3$], and these O···H and N···H species existed in equilibrium in a 1:3.8 ratio ($CDCl_3$).

Having identified the optimal conditions, we next examined the scope and limitations of this coupling system (Scheme 2). Introduction of electron-donating, electron-withdrawing, and halogen groups into the *para* position of the benzene ring of the arene substrate is well tolerated (**3aa–4da** and also **3aa–5fa**).




[a] Ratio of ketone:enol is typically 3.8:1.
[b] Using $RhCp^*(OAc)_2$ (6 mol%), PivOH (0.6 mmol) instead of the current catalyst system, isolated yields after chromatography.
[c] Yields of enamines after one-pot reaction.

**Scheme 2.** Iridium-catalyzed C–H activation–annulation. *Reaction conditions:* 2-phenylimidazo[1,2-*a*]pyridine (0.2 mmol), diazo ester (0.5 mmol), $[IrCp^*Cl_2]_2$ (3 mol%), $AgNTf_2$ (12 mol%), PivOH (0.6 mmol), EtOH (2 mL), 80 °C, 12 h, isolated yields after chromatography.

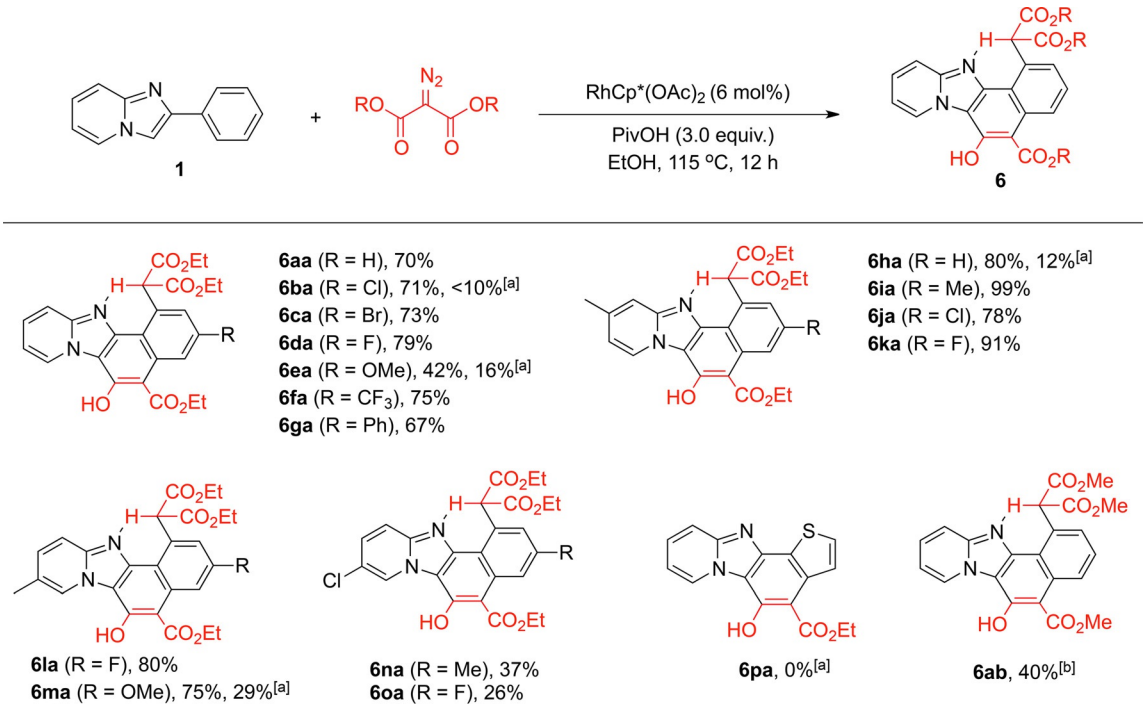
The reaction was equally efficient when 2-(*meta*-chloro)phenylimidazo[1,2-*a*]pyridine was used (**3ia** and **3qa**), and the cyclization process proved to be site-selective as indicated by NOESY analyses (distal to the Cl). This observed site-selectivity may be ascribable to steric effects. The *ortho* disposition of the chloro group with respect to the alkyl in the product caused the enol form to be the major component for **3ia**, and the extreme goes to **3qa** where only the enol form was observed. In addition, 2-phenylimidazo[1,2-*a*]pyridines bearing alkyl and halogen substituents at the 6- or 7-position all coupled smoothly under the

standard conditions. The presence of halogen groups should offer a handle for further chemical manipulation. Furthermore, disubstituted arenes with substituents at both the pyridine backbone and the benzene ring proved viable. However, the reaction is sensitive to steric perturbation at the 8-position; essentially no reaction occurred when 8-methyl-2-phenylimidazo[1,2-*a*]pyridine was employed (**3ra**). When 2-(thiophen-2-yl)imidazo[1,2-*a*]pyridine was subjected to the standard conditions, the desired product was isolated in 58% yield (**3ua**). The ester moiety can be extended to several other diazo esters (**3ab–3ad**), albeit with slightly lower yields. In nearly all cases, the annulated β-keto ester product existed as a mixture of isomers as a result of keto-enol tautomerization, with a typical ratio of enol:ketone = 1:4 ($CDCl_3$). Notably, enamination of the annulated β-keto ester product can be achieved in a one-pot reaction (Scheme 2), from which products **5aa–5ea** were isolated as a single isomer in moderate to good yield. Comparisons of Ir(III) and Rh(III) catalysis were conducted for several substrates, which indicate that Ir(III) catalysts exhibit higher reactivity.

Extension of the diazo substrate to diethyl diazomalonates, unfortunately, met with poor efficiency under Ir(III) catalysis. To our delight, switching the catalyst to $RhCp^*(OAc)_2$ (6 mol%) in the presence of PivOH (EtOH, 115 °C) significantly improved the efficiency (Scheme 3), and the same type of dialkylation–annulation product (phenol) was isolated. Thus, Rh(III) and Ir(III) catalysts offered a complementary substrate scope.[18] As given in Scheme 3, the scope of the 2-phenylimidazo[1,2-*a*]pyridine is in line with that in the Ir-catalyzed system, where electron-donating, electron-withdrawing, and halogen groups at both rings are tolerated. In contrast to the smooth synthesis of **3ua** under Ir(III) and Rh(III) catalysis, coupling between 2-(thiophen-2-yl)imidazo[1,2-*a*]pyridine and diethyl 2-diazomalonate failed in both cases (**6pa**). Comparisons of Ir(III) and Rh(III) catalysis were conducted using diethyl 2-diazomalonate, which indicates that Rh(III) is more efficient (**6ba**, **6ea**, **6ha**, **6ma**). Overall, the phenol products were isolated in moderate to high yields (up to 99%). The structures of the products have been fully characterized and in all cases, the methine hydrogen is hydrogen-bonded to the nitrogen, with no enol form being detected. In particular, addition of $D_2O$ to a $CDCl_3$ solution of **6ga** caused the disappearance of the phenolic proton, while the N···H was essentially not affected.

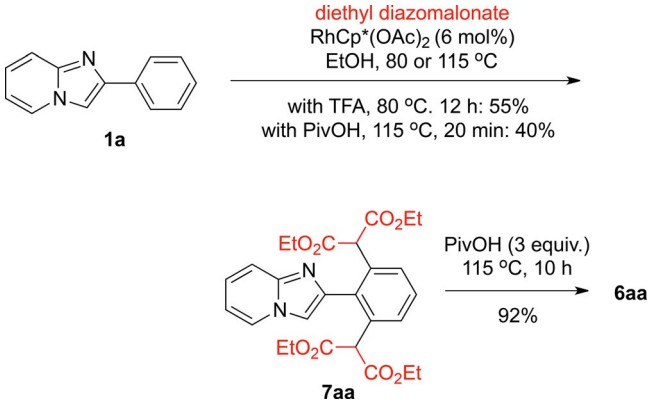
Interestingly, when this reaction was conducted at a low temperature or conducted for a shortened reaction time, only the dialkylation product (**7aa**) was isolated (Scheme 4). Treatment of **7aa** with PivOH in




[a] $[IrCp^*Cl_2]_2$ (3 mol%), $AgNTf_2$ (12 mol%), PivOH (0.6 mmol) EtOH, 80 °C, isolated yields after chromatography.
[b] MeOH was used as a solvent.

**Scheme 3.** Scope of rhodium-catalyzed C–H activation–annulation. *Reaction conditions:* 2-phenylimidazo[1,2-*a*]pyridine (0.2 mmol), diazo ester (0.5 mmol), $RhCp^*(OAc)_2$ (6 mol%), PivOH (0.6 mmol), EtOH (2 mL), 115 °C, 12 h, isolated yield after column chromatography.




**Scheme 4.** Establishment of a dialkylation intermediate.

EtOH (115 °C) led to high conversion to the annulated product even in the absence of any rhodium catalyst. This indicated that the final annulation process is not metal-catalyzed, and furthermore it is turnover-limiting in the overall catalytic cycle.

Several experiments have been performed to probe the reaction mechanism. Treatment of 2-phenylimidazo[1,2-*a*]pyridine with $[Cp^*IrCl_2]_2$ and NaOAc in $CH_2Cl_2$ led to an iridacycle **8** in 84% yield [Eq. (1)]. Complex **8**[19] was fully characterized, including by X-ray crystallography (see Figure 1). When **8** was applied as a catalyst together with $AgNTf_2$ for the coupling of **1a** and **2a**, the product **3aa** was isolated in a yield (74%) closely comparable to that obtained under the standard conditions [Eq. (2)]. To further explore the C–H activation process, a KIE experiment has been performed by two parallel competitions [Eq. (3)], which gave a $k_H/k_D = 1.1$. This suggested that the C–H activation process is not involved in the turnover-limiting step.

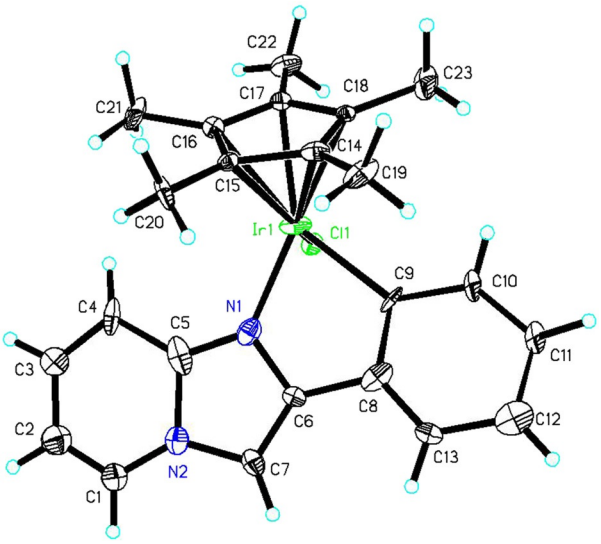
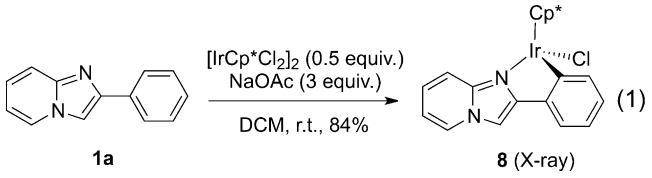
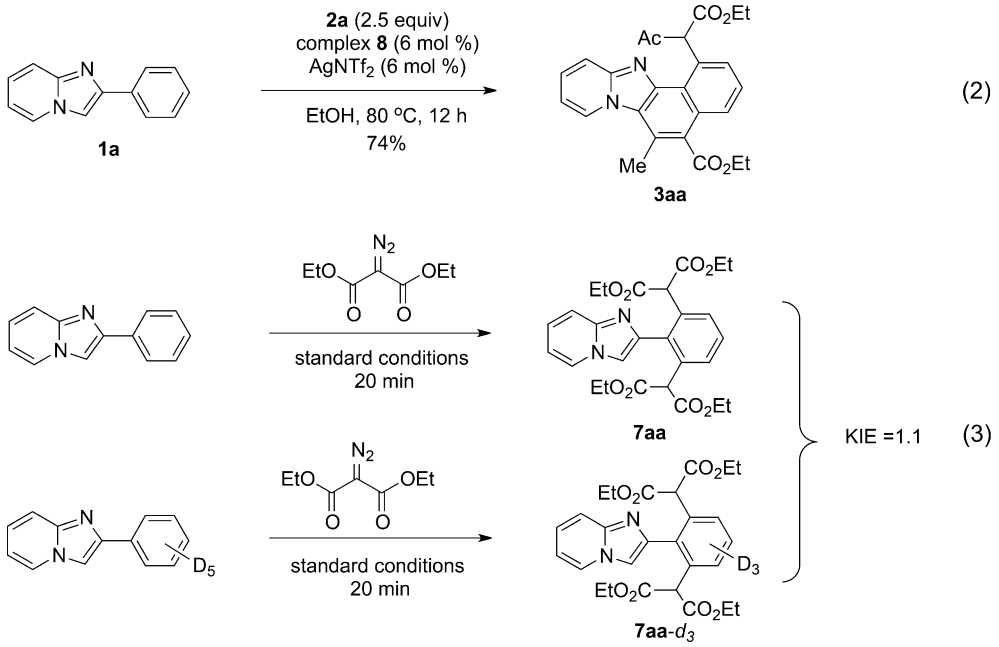
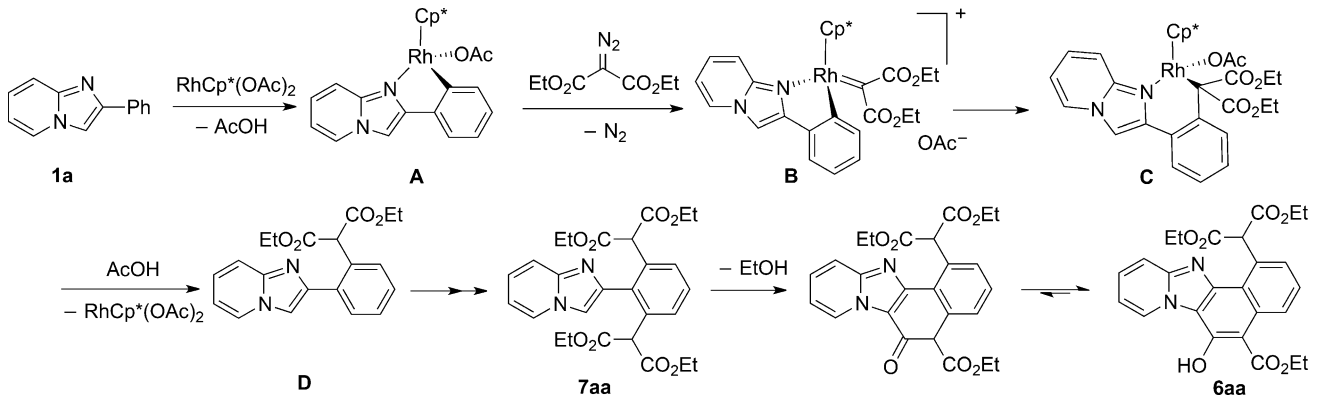



**Figure 1.** X-ray crystallographic structure of **8**.[19]




A proposed catalytic cycle is given in Scheme 5 on the basis of our mechanistic studies and previous reports of related systems.[13b,c] Taking the rhodium-catalyzed annulative coupling between **1a** and diethyl diazomalonate as an example, nitrogen coordination






**Scheme 5.** Proposed catalytic cycle.

and cyclometalation affords a rhodacycle **A**. Coordination of diethyl diazomalonate is followed by dediazoniation to afford a rhodium carbene species **B**. Migratory insertion of the Rh–C bond into the activated carbene generates a rhodium(III) alkyl **C**, which undergoes protonolysis to lead to the monoalkylation product **D**. This process is reiterated to give the dialkylated product **7aa**. Subsequent intramolecular nucleophilic attack of the imidazo[1,2-*a*]pyridine ring at the ester group under assistance of PivOH furnished the annulated phenol product after keto-enol tautomerization.

In summary, we have realized iridium- and rhodium-catalyzed C–H activations of 2-phenylimidazo[1,2-*a*]pyridine in the 1:2 coupling with activated α-diazo esters. The reaction proceeded *via* a dialkylated arene, followed by intramolecular nucleophilic attack of the C-3 position of the imidazole ring at the proximal carbonyl group. Rhodium and iridium catalysts exhibited complementary scope of the diazo substrate. Mechanistic studies indicated that the final nucleophilic cyclization process is turnover-limiting. These coupling systems utilized readily available arenes and unsaturated coupling partners for the construction of carbocycles. This method may find applications in the synthesis of complex structures.

## Experimental Section

### Procedure A

2-Phenylimidazo[1,2-*a*]pyridine (0.2 mmol),[20] ethyl α-diazoacetoacetate[21] (0.5 mmol), $[IrCp^*Cl_2]_2$ (3 mol%)/$AgNTf_2$ (12 mol%), and PivOH (0.6 mmol) were charged into a pressure tube, to which was added EtOH (2 mL) under $N_2$ atmosphere. The reaction mixture was stirred at 80 °C for 12 h. After that, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using PE/EA to afford compound **3aa** as a white solid; yield: 72%.

### Procedure B

2-Phenylimidazo[1,2-*a*]pyridine (0.2 mmol), ethyl α-diazoacetoacetate (0.3 mmol), $RhCp^*(OAc)_2$ (6 mol%), TFA (0.6 mmol) were charged into a pressure tube, to which was added EtOH (2 mL) under $N_2$ atmosphere. The reaction mixture was stirred at 80 °C for 12 h. After that, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using PE/EA to afford compound **4** as a white solid; yield: 55%.

## Acknowledgements

*We thank the Dalian Institute of Chemical Physics, Chinese Academy of Sciences, and the NSFC (Nos. 21472186 and 21272231) for financial support.*

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