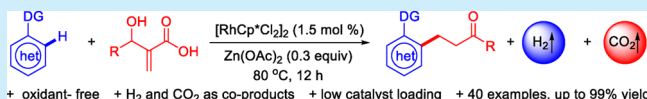


## Rh(III)-Catalyzed Acceptorless Dehydrogenative Coupling of (Hetero)arenes with 2-Carboxyl Allylic Alcohols

Jintao Xia,<sup>†,‡</sup> Zhipeng Huang,<sup>†,‡</sup> Xukai Zhou,<sup>†,‡</sup> Xifa Yang,<sup>†,‡</sup> Feng Wang,<sup>†</sup> and Xingwei Li<sup>\*,†,‡</sup><sup>†</sup>Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China<sup>‡</sup>University of Chinese Academy of Sciences, Beijing 100049, China

## S Supporting Information

**ABSTRACT:** Rhodium(III)-catalyzed C–H activation of (hetero)arenes and redox-neutral coupling with 2-carboxyl allylic alcohols has been realized for the construction of  $\beta$ -aryl ketones. This reaction occurred efficiently at a relatively low catalyst loading via initial dehydrogenative alkylation to give a  $\beta$ -keto carboxylic acid, followed by decarboxylation.



In the past decades, metal-catalyzed C(aryl)–H activation and functionalization<sup>1</sup> has evolved as an attractive alternative to classical organic synthesis which relies heavily on prefunctionalized starting materials for construction of new C–C bonds. By following this strategy, a great number of highly efficient protocols have been developed to deliver various organic functional materials and bioactive molecules.<sup>2</sup> The coupling between an arene and a nucleophilic reagent generally requires a stoichiometric amount of oxidant,<sup>1i,j,3</sup> together with generation of waste, which may limit the atom-economy and pose environmental issues. Ideally, the coupling system includes hydrogen-releasing conditions.

Olefins are commonly used substrates in C–H activation systems.<sup>1e,4</sup> In oxidative olefination of arenes, the employment of either external-oxidation or hydrogen-releasing conditions is dictated by the fate of the metal hydride species M(H)(X) in the catalytic cycle. Elimination of an HX from this metal hydride species leads to a lower valent metal species that is prone to re-oxidation to regenerate the active catalyst. Alternatively, protonolysis of the M–H bond by an acid may give rise to hydrogen evolution. However, this type of dehydrogenative coupling system is rather limited. Despite the challenges, Zhang,<sup>5a</sup> Wang,<sup>5b</sup> Yang,<sup>5c</sup> Jeganmohan,<sup>5d,h</sup> Li,<sup>5e</sup> Dong,<sup>5f</sup> and other groups<sup>6</sup> have independently developed dehydrogenative coupling reactions via C–H activation. On the other hand,  $\beta$ -aryl ketones<sup>7</sup> are versatile synthetic building blocks in organic transformations, and they have been accessed via cross-coupling of aryl (pseudo)halides, arylboronic acids, aryl carboxylic acids, or aryldiazonium salts with allylic alcohols or aldehydes in the presence or absence of external oxidants.<sup>8</sup> Recently, Rh(III)-catalyzed C–H activation has provided new avenues for synthesis of  $\beta$ -aryl ketones. In 2013, the Glorius group and the Jiang group independently reported synthesis of these products via C–H activation of arenes and coupling with allylic alcohols using Cu(OAc)<sub>2</sub> as an oxidant.<sup>9</sup> Our group<sup>10</sup> achieved synthesis of  $\beta$ -aryl ketones by taking advantage of the ring strain in the oxidative coupling of cyclopropanols with arenes. The Lu and Liu groups applied allenol or propargyl alcohols as a coupling reagent for oxidative synthesis of  $\beta$ -aryl

ketones with a quaternary stereogenic center.<sup>11</sup> Although those methods were generally efficient, oxidants were required for the catalyst turnover. Alternatively, hydroarylation of olefins represents a useful method to access  $\beta$ -aryl ketones/aldehydes under redox-neutral conditions.<sup>12</sup> However, the olefins are limited to highly reactive enones/maleimides with stoichiometric amounts of base additives.

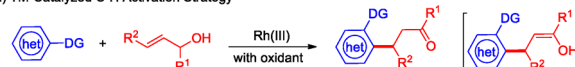
We envisioned that as a special allylic alcohol, 2-carboxyl allylic alcohol may serve as a suitable olefin substrate in C–H activation. Significantly, the migratory insertion of a M–Ar bond into the C = C bond of 2-carboxyl allylic alcohol and subsequent  $\beta$ -H elimination would give a  $\beta$ -keto acid that can readily undergo decarboxylation (Scheme 1c). We speculated

Scheme 1. Catalytic Synthesis of  $\beta$ -Aryl Aldehydes/Ketones

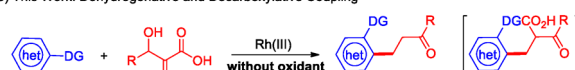
(1) TM-Catalyzed Cross Coupling Strategy



(2) TM-Catalyzed C-H Activation Strategy



(3) This Work: Dehydrogenative and Decarboxylative Coupling



that decarboxylation and dehydrogenation might be integrated into a symbiotic system,<sup>13</sup> especially in the presence of a carboxylic or Lewis acid which may facilitate the protonolysis of the M–H bond for hydrogen evolution. We now report efficient hydrogen-releasing and decarboxylative coupling of arenes and 2-carboxyl allylic alcohols.

We initiated our exploration with the optimization studies of the coupling of *N*-(2-pyrimidinyl)indole (**1a**) and carboxylic

Received: December 13, 2017

acid **2a** (Table 1). Our initial studies revealed ketone **3aa** was isolated in 71% yield using  $[\text{RhCp}^*\text{Cl}_2]_2$  catalyst and

Table 1. Screening of the Reaction Conditions<sup>a</sup>

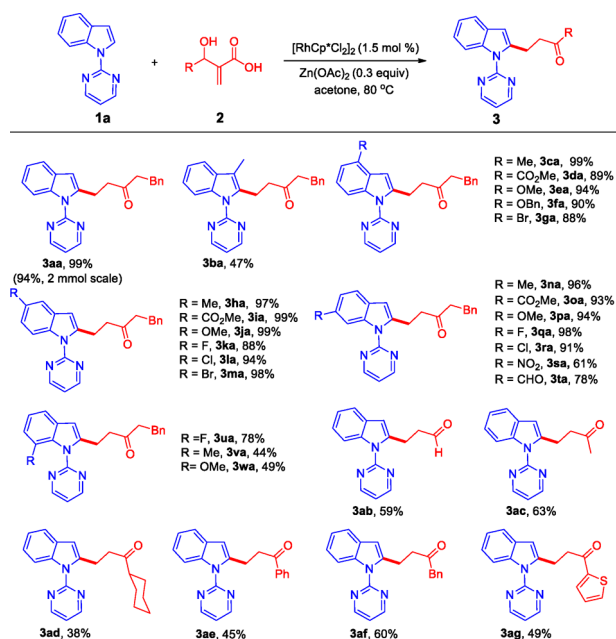
entry	additive (30 mol %)	solvent	yield <sup>b</sup> (%)
1 <sup>c</sup>	Zn(OAc) <sub>2</sub>	DCM	71
2 <sup>c</sup>	Zn(OAc) <sub>2</sub>	DME	70
3 <sup>c</sup>	Zn(OAc) <sub>2</sub>	acetone	74
4	Zn(OAc) <sub>2</sub>	DME	91
5	Zn(OAc) <sub>2</sub>	acetone	99
6	Cu(OAc) <sub>2</sub>	acetone	24
7	AgOAc	acetone	20
8	CsOAc	acetone	trace
9 <sup>d</sup>	Zn(OAc) <sub>2</sub>	acetone	99
10 <sup>e</sup>	Zn(OAc) <sub>2</sub>	acetone	99
11 <sup>e,f</sup>	Zn(OAc) <sub>2</sub>	acetone	99
12		acetone	<5
13 <sup>g</sup>	Zn(OAc) <sub>2</sub>	acetone	

<sup>a</sup>Reaction conditions: **1a** (0.2 mmol), **2a** (0.5 mmol), Rh(III) catalyst, additive in a solvent (3 mL) under nitrogen at 80 °C. <sup>b</sup>Yield of the isolated product. <sup>c</sup>**2a** (0.3 mmol) was used. <sup>d</sup> $[\text{RhCp}^*\text{Cl}_2]_2$  (2.5 mol %). <sup>e</sup> $[\text{RhCp}^*\text{Cl}_2]_2$  (1.5 mol %). <sup>f</sup>Under air. <sup>g</sup>No  $[\text{RhCp}^*\text{Cl}_2]_2$ .

Zn(OAc)<sub>2</sub> additive in DCM under rigorously oxidant-free conditions (entry 1). A similar yield was obtained in DME or acetone solvent (entries 2 and 3). The yield was drastically improved to 91% in DME when the amount of **2a** was increased to 2.5 equiv (entry 4), and a nearly quantitative yield was delivered in acetone (entry 5). These results might indicate hydrogen evolution or hydrogen acceptance by the olefin or acetone. In fact, <sup>1</sup>H NMR analysis of a reaction in acetone-*d*<sub>6</sub> indicated that neither 2-propanol-*d*<sub>6</sub> nor hydrogenation product of the olefin was formed, and absence of the latter was further confirmed by GC–MS and HRMS. The H<sub>2</sub> and CO<sub>2</sub> coproducts were directly observed by online GC–MS analysis. Zn(OAc)<sub>2</sub> play an important role in this system since inferior results were obtained when Cu(OAc)<sub>2</sub>, AgOAc, or CsOAc was used (entries 6–8). Lowering the catalyst loading to 1.5 mol % did not affect the reaction outcome (entries 9 and 10), and the reaction proceeded equally well under air (entry 11). Control experiments confirmed that both  $[\text{RhCp}^*\text{Cl}_2]_2$  and Zn(OAc)<sub>2</sub> were necessary (entries 12 and 13).

With the establishment of the optimal conditions in hand, the scope and limitations of this system (Scheme 2) were next examined. Introduction of electron-donating (OMe, OBn), -withdrawing (CO<sub>2</sub>Me, NO<sub>2</sub>, CHO), and halogen groups (F, Cl, Br) into the C4–C6 positions of the indole were all tolerated, and the products were isolated in 61–99% yields (**3aa**, **3ca**–**ta**). A relatively lower yield was isolated when the C3 (**3ba**) or C7 (**3ua**–**wa**) position was substituted, indicative of steric effects. Of note, useful functional groups such as NO<sub>2</sub> (**3sa**) and CHO (**3ta**) were also compatible. The scope of the 2-carboxyl allylic alcohol was next explored in the coupling with indole **1a**. 2-(Hydroxymethyl)acrylic acid reacted to afford β-aryl aldehyde **3ab** in 59% yield, and moderate yields were delivered when the C3 position of 2-carboxyl allylic alcohol was substituted by a (cyclo)alkyl or a benzyl group (**3ac**–**ag**).

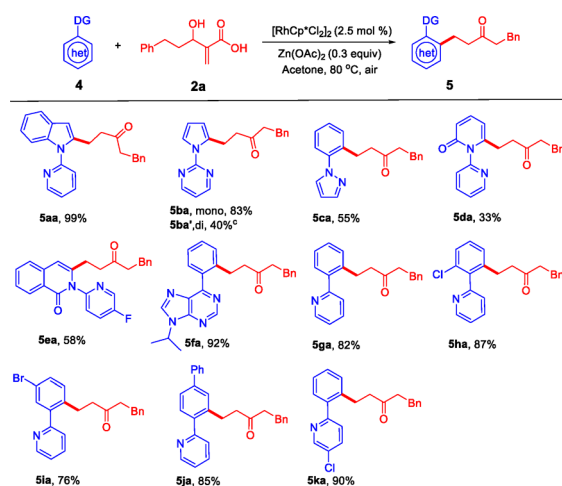
Scheme 2. Scope of Coupling *N*-(2-Pyrimidinyl)indoles and 2-Carboxyl Allylic Alcohols<sup>a,b</sup>



<sup>a</sup>Reaction conditions: **1a** (0.2 mmol), **2** (0.50 mmol),  $[\text{RhCp}^*\text{Cl}_2]_2$  (1.5 mol %), Zn(OAc)<sub>2</sub> (0.3 equiv), acetone (3 mL) at 80 °C under air for 12 h. <sup>b</sup>Isolated yield.

The arene substrates are not limited to *N*-pyrimidinylindoles (Scheme 3). *N*-Pyridylindole also coupled smoothly with **2a** in

Scheme 3. Scope of Other Arene Substrates<sup>a,b</sup>



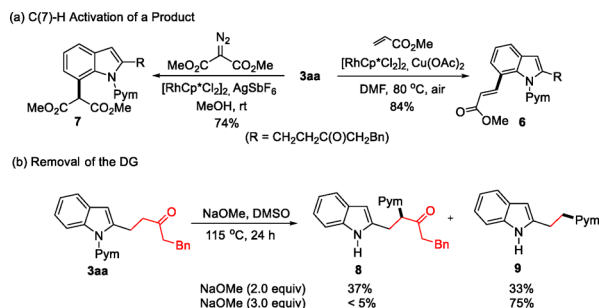
<sup>a</sup>Reaction conditions: **4** (0.2 mmol), **2a** (0.5 mmol),  $[\text{RhCp}^*\text{Cl}_2]_2$  (2.5 mol %), Zn(OAc)<sub>2</sub> (0.3 equiv), acetone (3 mL), 80 °C under air for 12 h. <sup>b</sup>Isolated yields. <sup>c</sup>**2a** (1.0 mmol) was used.

high efficiency (**5aa**). Pyrrole **4b** coupled with **2a** only to give the monoalkylated product (**5ba**) in 83% yield, while both mono- (**5ba**) and dialkylated (**5ba'**) products were obtained when the amount of **2a** was increased to 5 equiv. In addition, *N*-phenylpyrrole was amenable to the reaction conditions (**5ca**, 55%). Coupling of pyridone derivatives with **2a** provided products **5da** and **5ea** in moderate yields. Purine and pyridine were also applicable directing groups for C–H activation of

benzene rings, as in formation of **5fa–ka** in good to excellent yields.

Several derivatization reactions were carried out to demonstrate the synthetic applications. Scaling up the reaction to 2 mmol gave **3aa** in 94% yield (Scheme 2). Further C(7)–H functionalization of **3aa** with methyl acrylate and dimethyl 2-diazomalonate afforded the olefination product **6** and alkylation product **7**, respectively (Scheme 4a). Attempted removal of the

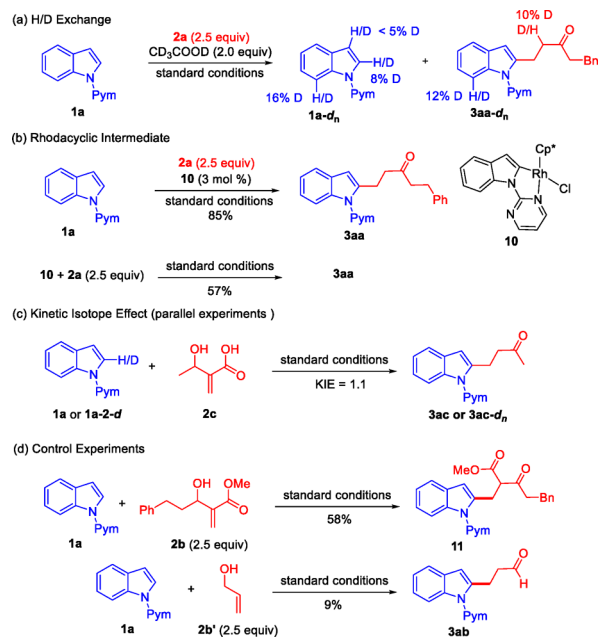
#### Scheme 4. Diversification of the Products



pyrimidyl group in **3aa** afforded an NH indole **8** together with 2-(2-(pyrimidin-2-yl)ethyl)-1H-indole (**9**), where **8** was generated via Smiles rearrangement (Scheme 4b).<sup>10a,14</sup> Furthermore, only **9** was isolated when NaOMe was used in 3 equiv amounts.

A series of experiments have been performed to elucidate the reaction mechanism (Scheme 5). H/D exchange between **1a**

#### Scheme 5. Preliminary Mechanistic Studies

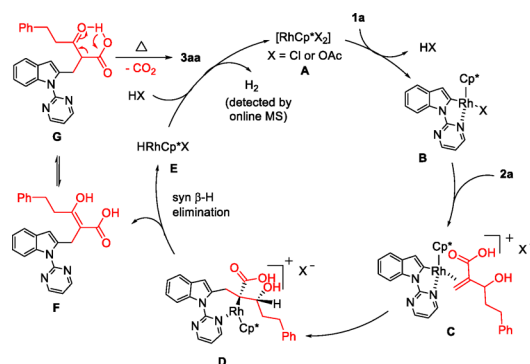


and  $\text{CD}_3\text{CO}_2\text{D}$  has been carried out in the presence of **2a** (Scheme 5a). Deuterium incorporation at the C2 and C7 positions was observed for the recovered indole substrate, suggestive of reversible C–H activation. In addition, H/D exchange at the  $\alpha$ -position of the carbonyl group of the product was also detected. Rhodacyclic complex **10** was then synthesized, and it showed good activity in both stoichiometric and catalytic reactions (Scheme 5b), indicating relevancy of a C–H activation pathway. To further probe the C–H activation

process, insignificant kinetic isotope effect ( $k_{\text{H}}/k_{\text{D}} = 1.1$ ) of the reaction of indole **1a** was then obtained on the basis of two rate constants, suggesting that the C–H cleavage was not involved in the turnover-limiting step (Scheme 5c). A control experiment using the analogous ester suggested the reaction likely involve  $\beta$ -hydride elimination (Scheme 5d). In another control experiment, coupling of simple allyl alcohol under the standard conditions only afforded product **3ab** in 9% yield, indicating olefination activation by the carboxylic group (Scheme 5d).

On the basis of mechanistic studies and literature reports,<sup>15</sup> a plausible mechanism is proposed in Scheme 6. Starting from

#### Scheme 6. Proposed Mechanism



$[\text{RhCp}^*(\text{OAc})\text{X}]$  ( $\text{X} = \text{OAc}$  or  $\text{Cl}$ ), cyclometalation of indole produces a rhodacycle **B**. Subsequent coordination of **2a** gives a cationic olefin intermediate **C**, which undergoes selective migratory insertion to generate a tertiary alkyl species **D**, and this process is likely promoted by the  $\text{Zn}(\text{OAc})_2$  additive which activates the carbonyl.<sup>15a,16</sup> Subsequent  $\beta$ -hydride elimination provides a rhodium hydride species **E** together with the enol form of a  $\beta$ -keto acid. The  $\beta$ -keto acid **G** undergoes facile decarboxylation to furnish the final product. The rhodium hydride **E** is then protonolyzed by  $\text{HX}$  to regenerate the active rhodium species with hydrogen liberation. It is possible that the protonolysis is also facilitated by  $\text{Zn}(\text{OAc})_2$ .

In conclusion, we have developed an efficient process to access  $\beta$ -aryl ketones via  $\text{Rh}(\text{III})$ -catalyzed C–H activation of arenes and coupling with 2-carboxyl allylic alcohols, and the reactions tolerated a wide range of substrates with good functional group compatibility with  $\text{H}_2$  and  $\text{CO}_2$  as the coproducts. Efforts to explore other dehydrogenative coupling systems are underway in our laboratories.

#### ■ ASSOCIATED CONTENT

##### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.7b03881.

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

#### ■ AUTHOR INFORMATION

##### Corresponding Author

\*E-mail: xwli@dicp.ac.cn.

##### ORCID

Feng Wang: 0000-0002-9167-8743

Xingwei Li: 0000-0002-1153-1558



## Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

Financial support from the NSFC (Nos. 21525208 and 21472186) and the new technology of methanol conversion of Dalian Institute of Chemical Physics (Chinese Academy of Sciences) are gratefully acknowledged.

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