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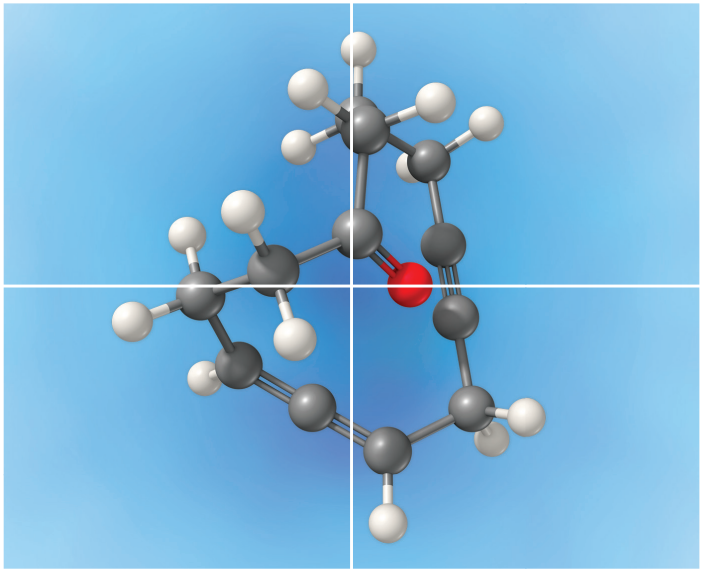

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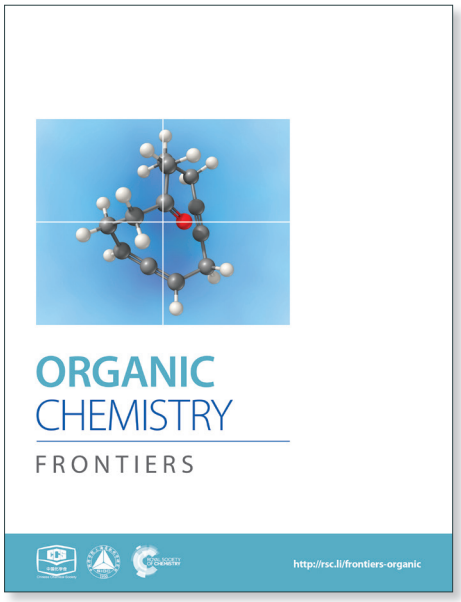

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ARTICLE TYPE

Direct Alkenyl C-H Functionalization of Cyclic Enamines with Carboxylic Acids via Rh Catalysis Assisted by Hydrogen Bonding**

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In Celebration of Max Malacria's 65th Birthday

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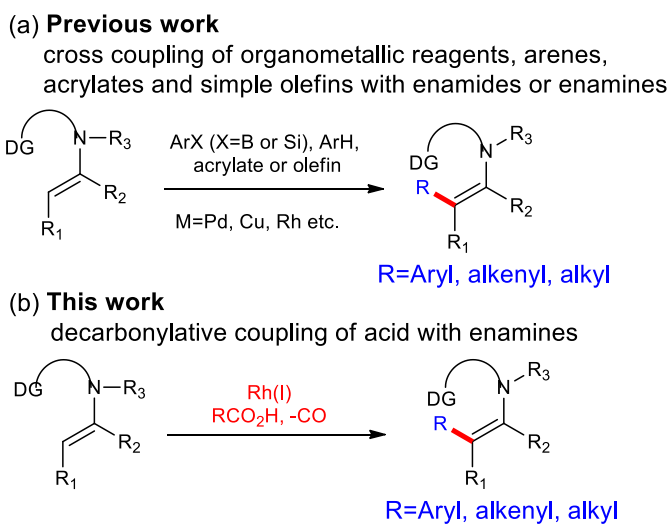
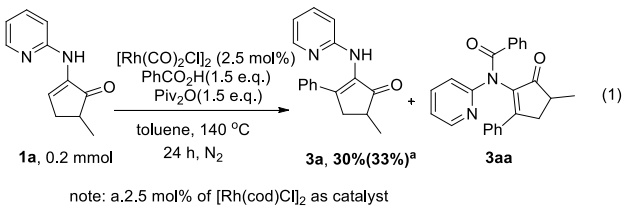
Enamines and enamides are important synthetic intermediates. The transition metal catalyzed C-C coupling through direct β-C-H activation of enamines or enamides is an important method for their functionalizations. But so far the effective coupling partners are limited to organometallic reagents, arenes, olefins, and acrylates. In this study, a highly efficient method was developed to use carboxylic acids, an easily available and cheap carbon source, as coupling partners for the direct β-C-H functionalization of enamines in the presence of Rh(I) catalyst and aminopyridinyl directing group through decarbonylation coupling. The reaction was proved to be assisted by hydrogen bonding. The directing group was easily removed under acid condition. This method provides a useful alternative approach to C-alkylated, and arylated cyclic diketones.

Enamines and enamides are important synthetic intermediates.[1] They have broad utility in catalytic asymmetric C-C bond forming processes such as aza–ene,[2] Michael,[3] Friedel–Crafts,[4] cycloaddition,[5] and arylation.[6] The transition metal catalyzed C-C coupling through direct β-C-H activation of enamines or enamides is an important method for their functionalizations.[7] The effective coupling partners include organometallic reagents,[6c, 6d, 6g] arenes,[6f] olefins[7k] and acrylates[7i, 7j, 8] (scheme 1a).

Recent years, the development of decarboxylative coupling reactions of carboxylic acids has made significant progresses. [9] Its applications have extended to arylation,[10] alkenylation,[11]acylation,[7h, 12] and etherification.[13] However, the decarbonylative coupling reactions of carboxylic acids were less developed.[14] Recently, Yu,[15] and our group[16] have independently developed a method for rhodium-catalyzed decarbonylative cross-coupling of acid derivatives with arenes. This method features a stable five-membered rhodium species as intermediate. It, however, can only activate aromatic C-H bond, and the pyridine as directing group is hardly removable. In our continuing efforts to extend the application scope of the decarbonylative system,[16-17] we became interested to implement decarbonylative coupling of acids with enamines installed with removable directing groups (DGs)[18] through non-aromatic sp^2 C-H activation (Scheme 1b),[19] aiming at developing this transformation into a more general and economical method for the β functionalization of enamines. The challenges facing this endeavour include: 1) the enamine may not be stable under acid conditions at high temperature; 2) the non-aromatic sp2 C-H bond may not be significantly active towards the previous catalyst system; 3) the six-membered rhodium species may not be as active as the previous five-membered one.

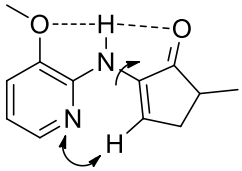


Scheme 1. Transition metal catalyzed cross coulplings through direct β-H activation of enamides or enamines



Scheme 2. The initial results obtained with the previous catalytic system

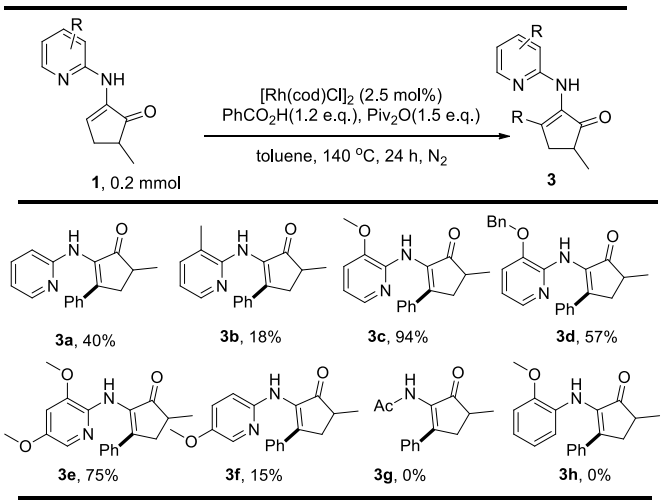
We firstly tested the reaction of enamine **1a**, which has been used by Dong group,[7k] with benzoic acid under the standard



Scheme 3. Hydrogen bonding

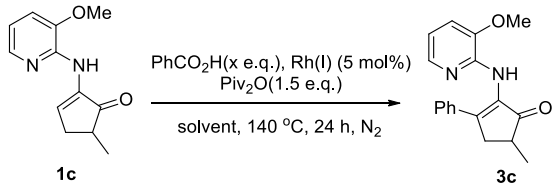
conditions we previously used. Delightfully, the desired product **3a** was obtained, albeit with only 30% isolated yield (80% conversion) (Scheme 2). The costly more effecitive catalyst $[Rh(cod)Cl]_2$ afforded comparable yield. **3aa** was observed as a main byproduct due to the amidation of the product. In order to supress the side reaction, we installed a methyl group in the 3-position of the directing pyridinyl group (**1b**) [20] in hope that the amidation could become less easy to occur due to steric hindrance (Table 1). But **1b** turned out to be unstable and got decomposed fairly fast under the reaction condition. We then turned to the use of a methoxyl group (**1c**) at the same position considering that the methoxyl group is not only a steric hindrance provider, but also a hydrogen bond donor. If strong hydrogen bondings could be formed as depicted in Scheme 3[20-21], the substrate should not only have better stability under the reaction condtion, but also be able to facilitate the activation of the vinyl C-H bond since the directing group is fixed in a most favorable orientation towards the vinyl C-H bond. As expected, the reaction of **1c** gave a dramatically increased yield. Notably, when the 3-methoxy group was replaced with a benzoxy group (**3d**), the yield was lowered to some degree. Moving the methoxy group to the 5-position of the pyridine ring (**3f**) or adding one more methoxy group to the 5-position (**3e**) also decreased the yield. On the other hand, if the aminopyridine DG is replaced by either acetamido group (**3g**) or 2-methoxyphenylamino group (**3h**), the reaction completely lost the reactivity, clearly indicating that the pyridinyl DG is crucial for the reactivity.

Table 1. Directing group controlled decarbonylative coupling [a].



[a] Isolated yield.

Table 2. Exploration of reaction conditions [a]



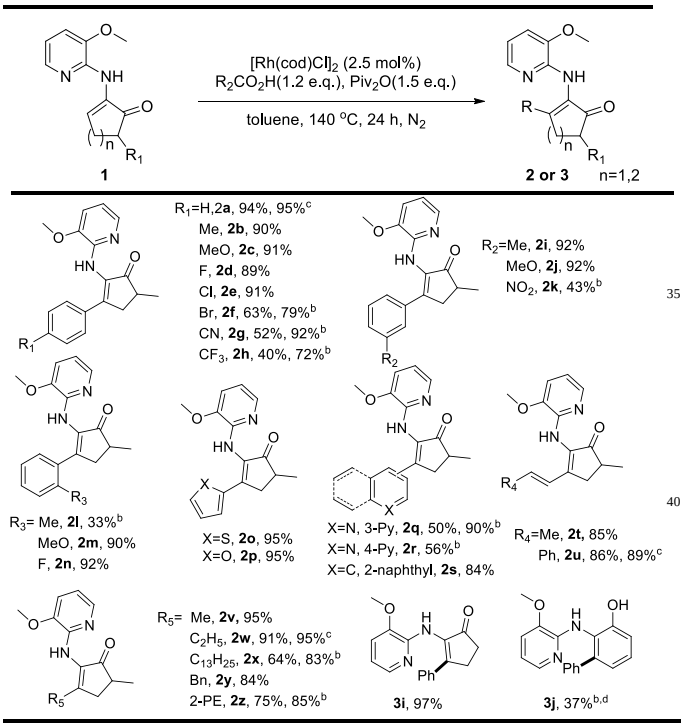
Entry	Catalyst	Solvent	Acid (e.q.)	Yield(%)[b]
1	$[Rh(cod)Cl]_2$	Toluene	1.5	93(85)
2	$[Rh(CO)_2Cl]_2$	Toluene	1.5	91(81)
3	$Rh(CO)_2(acac)$	Toluene	1.5	77
4	$[Rh(cod)(OH)]_2$	Toluene	1.5	<5
5	$[Rh(cod)Cl]_2$	Toluene	1.2	99(94)
6	$[Rh(CO)_2Cl]_2$	Toluene	1.2	98(92)
7[c]	$[Rh(cod)Cl]_2$	Toluene	1.2	73
8[d]	$[Rh(CO)_2Cl]_2$	Toluene	1.2	68
9	$[Rh(cod)Cl]_2$	o-xylene	1.2	93
10	$[Rh(cod)Cl]_2$	PhCl	1.2	95
11	$[Rh(cod)Cl]_2$	CH_3CN	1.2	0
12	$[Rh(cod)Cl]_2$	DCE	1.2	0
13	$[Rh(cod)Cl]_2$	Toluene	1.2	73
14	$[Rh(cod)Cl]_2$	Toluene	1.2	70

[a] The reactions were carried out with 0.2 mmol of **1c** in the presence of 5.0 mol % Rh(I) catalysts and benzoic acid in 2.0 mL solvent, N_2, 140 °C for 24 h; [b] Isolated yields in parenthesis. [c] 1.25 mol% of $[Rh(cod)Cl]_2$ was added. [d] 1.25 mol% of $[Rh(CO)_2Cl]_2$ was added. [e] The reaction was carried out at 110 °C. [f] The reaction was carried out without degassing.

Thus, we chose **1c** as substrate for further studies. A brief survey on the catalyst showed that $[Rh(CO)_2Cl]_2$ has similar catalytic activity as $[Rh(cod)Cl]_2$ (entry 2 vs 1), whereas $Rh(CO)_2(acac)$ is substantially less active (entry 3). In contrast, $[Rh(cod)OH]_2$ exhibited almost no activity (entry 4). When the amount of acid was reduced from 1.5 to1.2 eqiv, and the yield was further increased to 94% and 92% (entries 5 and 6). Lowering the catalyst amount from 2.5% to 1.25% caused some decrease in yield (entries 7 and 8). O-xylene and chlorobenzene as solvents also gave excellent yields (entries 9 and 10). In contrast, the reaction completely lost the reactivity when other nonaromatic solvents such as acetonitrile and dichloroethane were used (entries 11 and 12). When the reaction temperature was lowered from 140 to 110 ℃, the reaction was significantly slowed down and only afforded a moderate yield (entry 13). If the reaction was initiated without degassing, again moderate yield was obtained (entry 14).

With the optimized reaction conditions in hands, various acids were subjected to reactions with **1c** to explore the substrate scope (Table 3). In general, good to high yields were obtained for relatively electron-rich aromatic acids under condition A, including benzoic acids bearing various substituents (**2a-f**, **2i**, **2j**, **2m**, **2n** and **3i**), naphthyl caboxylic acid (**2s**), and heteroaromatic thiophenyl and furanyl carboxylic acids (**2o** and **2p**). Although steric hindered and electron-deficient aromatic acids (**2l**, **2g**, **2h**, **2k**, **2q** and **2r**) only afforded moderate yields under condition A, much better results could be attained with these substrates under condition B. Importantly, cinnamic acid (**2u**), crotonic acid (**2t**)

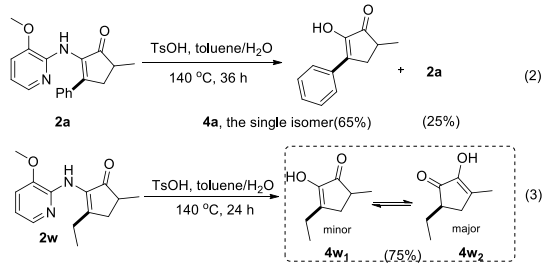
Table 3. Exploration of the substrate scopes of acid and diketone [a]



[a] The reactions were carried out in the scale of 0.2 mmol **1**, 1.2 eqiv acid, 140 °C, N_2. Condition A: in the presence of 2.5 mmol % $[Rh(cod)Cl]_2$ as catalyst, reacted for 24 h.; Condition B: in the presence of 2.5 mo% $[Rh(CO)_2Cl]_2$ as catalyst, reacted for 36 h; isolated yield. [b] The isolated yield given under condition B. [c] The reaction was scaled up to 1.0 mmol under condition A. [d] Aromatic oligomer was exclusively formed under condition B.

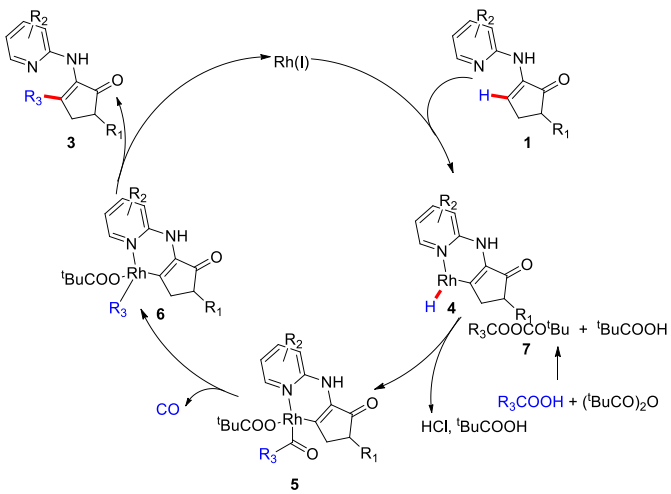
and various aliphatic acids (**2v-z**) also proved to be good substrates for the reaction, furnishing the corresponding alkenyl and alkyl enamine products in good-to-excellent yields. It should be noted that no branched product due to isomerization was observed for long chain aliphatic acids, which partially ruled out the formation of cationic and radical intermediates during the course of reaction. It should be noted that enamine **1i** devoid of the methyl group on the five- membered ring also proved to be excellent substrate, affording product **3i** in 97% yield. In addition, the six-membered cyclic enamine **1j** was found to be much less active. It reacted with benzoic acid to furnish the desired product **3j** only with 37% yield.

To demonstrate the practicability of the present reaction system, the reaction was conducted in a 1.0 mmol scale. Expectedly, the desired products (**2a**, **2u**, **2w**) were achieved with excellent yields. On the other hand, the 3-methoxypyridinyl amino DG of product **2a** and **2w** proved to be easily removable under modified condition of Dong and co-workers previously used, affording the desired diketone products **4a** and **4w** in good yield (Eqs 2 and 3). Thus, this present method provides an convient method for the preparation of *C*-alkylated[7k] and *C*-arylated[22] products of 1,2-diketones.



Scheme 4. Remove of the directing group

Finally, a mechanism model[16] was proposed for the present reaction system as follows (scheme 5). The vinyl C-H bond was inserted by rhodium(I) with the assistance of the DG. The carboxylic acid should react with $(^tBuCO)_2O$ to form anhydride **7**, which then interacts with **4** to generate complex **5**. The decarbonylation of **5** gives rise to intermediate **6**, which undergoes reductive elimination to produce the desired product **3** with the regeneration of the rhodium(I) catalyst .



Scheme 5. Proposed mechanism for decarbonylative coupling of enamine

In summary, we have successfully developed the first Rh-catalyzed decarbonylative coupling of cyclic enamine with simple carboxylic acids. 3-Methoxy-2-pyridinyl amino group proved to be a highly effective directing group for this transformation. A broad range of acids were subjected to the coupling to afford β-aryl, alkenyl and alkylation enamine products with high yields. The directing group proved to be easily removalbe, thus rendering the present reaction system a convient and efficient approach to *C*-alkylated and *C*-arylated1,2-diketone compounds. This work should have broad implications and serve as a seminal study toward catalytic ketone functionalization.

Experimental section

General procedure for the decarbonylative coupling of carboxylic acids with cyclic enamines

$[Rh(cod)Cl]_2$ (0.005 mmol, 2.4 mg) or $[Rh(CO)_2Cl]_2$ (0.005 mmol, 1.9 mg), enamine **1** (0.2 mmol), and carboxylic acid (0.24 mmol) were added to a Schlenk flask, which was then degassed with N_2 for three times. $(^tBuCO)_2O$ (0.3 mmol) and 2 mL of

anhydrous toluene were added, and the reaction mixture was subsequently heated and kept at 140°C in oil bath for the indicated time with stirring. After cooling to room temperature, 1 mL of a concentrated ammonia solution was added. The mixture was directly subjected to column chromatograph on silica gel with petroleum ether/EtOAc (12:1-5:1) as eluent to afford the desired product **2** or **3**.

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Notes and references

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† Electronic supplementary information (ESI) available: ^{1}H NMR, ^{13}C NMR, and HRMS data and copies of NMR spectra for all starting materials and products. See DOI: 10.1039/b000000x/

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