C–H Functionalization

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Rhodium(III)-Catalyzed Dehydrogenative Heck Reaction of Salicylaldehydes**

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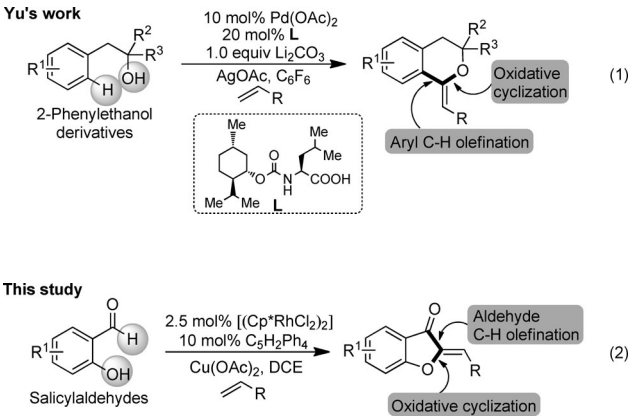
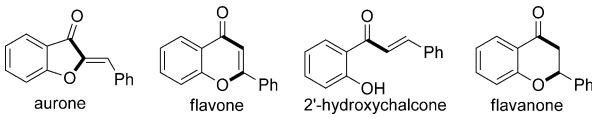
Dedicated to Professor Hans J. Schäfer on the occasion of his 75th birthday

The transition-metal-catalyzed Mizoroki–Heck reaction is one of the most popular and powerful tools for C–C bond formation and offers a straightforward approach for the construction of olefination products.[1] Three kinds of substrates are typically utilized as the coupling partner for the olefin in this reaction: aryl halides or pseudohalides, organometallic reagents, and non-preactivated (hetero)arenes. In terms of atom economy the third type of substrate is the most attractive. Initial studies on the Pd^{II}-catalyzed dehydrogenative Heck reaction[2] (DHR) of benzene with styrene were reported by Fujiwara and Moritani.[3] Compared with the traditional Mizoroki–Heck reaction, this method faces three fundamental challenges: 1) how to expand the scope of substrates; 2) how to control positional selectivity in molecules that contain diverse C–H bonds; and 3) how to make the reaction mild and efficient and, thus, applicable in synthesis.

Much effort has been devoted to solving these problems and significant improvements have been made in recent years.[4] Yu et al. have developed DHR reactions for unactivated $C(sp^3)$–H bonds, electron-deficient aryl C–H bonds, and remote $C(sp^2)$–H bonds.[5] In 2010, the same group developed an unprecedented cascade reaction consisting of a Pd^{II}-catalyzed alcohol-directed aryl C–H olefination and an oxidative intramolecular cyclization which afforded pyran products in the presence of amino acid ligands [Eq. (1)].[5b] Recently, Satoh and Miura et al.,[6] other groups,[7] and we[8] have shown that $\{Rh^{III}Cp^*\}$ complexes[9] catalyzed the DHR of substrates including acetanilides, benzhydroxamic acids, benzoic acids, phenol carbamates, and ketones, and olefins.

We report herein on a Rh^{III}-catalyzed regioselective DHR of aldehyde C–H bonds with different classes of olefins [Eq. (2)]. In combination with a recent report on the Pd^{II}-catalyzed carbonylative Heck reaction of halides,[10] this methodology affords another way to complete the Heck reaction on carbonyl groups.[11] Most importantly, it provides access to the structural motifs of valuable natural products and bioactive molecules such as aurone,[12] flavone,[13] 2′-hydroxychalcone,[14] and flavanone[15] (Scheme 1).





Scheme 1. Structures of biologically active natural products.

The selective functionalization of aldehyde C–H bonds has been quite an active research area.[16] To date, there have been two main strategies for the direct functionalization of aldehyde C–H bonds with olefins: 1) oxidative addition of low-valent transition-metal complexes (especially Rh^I catalysts) to aldehyde C–H bonds[17] and 2) umpolung of aldehydes with N-heterocyclic carbenes (NHCs).[18] In the context of either of these methods, aldehyde C–H bonds can add to C=C bonds yielding ketone derivatives by hydroacylation. However, extending the DHR to aldehyde C–H bonds remains undeveloped, with no examples reported to date. Satoh and Miura demonstrated the Rh-catalyzed oxidative coupling between salicylaldehydes and internal alkynes, involving the cleavage of the aldehyde C–H bond and producing chromone derivatives.[6f] Inspired by this work, we envisioned that salicylaldehydes should be a suitable class of substrates to achieve DHR with aldehyde C–H bonds.

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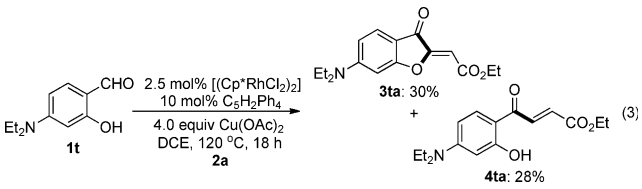
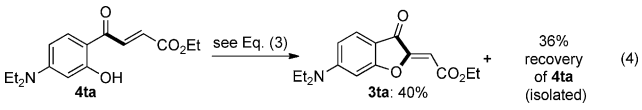
With this hypothesis in mind, we selected salicylaldehyde (**1a**) and ethyl acrylate (**2a**) as substrates and $Cu(OAc)_2$ as the oxidant in *tert*-amyl alcohol as the solvent at a reaction temperature of 120 °C. In our initial studies, the efficiency of several catalysts like $[\{RuCl_2(p\text{-cymene})\}_2]$, $[Cp^*Rh(CH_3CN)_3](SbF_6)_2$, and $[(Cp^*RhCl_2)_2]$ was tested (see the Supporting Information). Interestingly, the cyclization product **3aa** was produced in 23% yield in the presence of the latter catalyst; this product may result from DHR of the aldehyde C–H bond and subsequent intramolecular oxidative cyclization. Gratifyingly, **3aa** was obtained in 48% yield when we increased the amount of oxidant. The product yield was increased to 63% when the solvent was changed to DCE. 1,2,3,4-Tetraphenyl-1,3-cyclopentadiene was found to be an effective ligand,[6f,19] affording **3aa** in 76% yield. Under these conditions, decreasing either the catalyst loading or the reaction temperature led to lower yields of **3aa**.

With a set of optimized conditions in hand, we examined the scope of the DHR of aldehyde C–H bonds and the subsequent oxidative cyclization of C–O bonds (Scheme 2). We were pleased to find that electron-deficient olefins such as butyl acrylate (**2b**) and methyl vinyl ketone (**2c**) were also suitable substrates for this transformation. Furthermore, a variety of salicylaldehydes could be converted to the desired products using these olefins. Electron-donating groups such as methoxy (**1c**), ethoxy (**1d**), and methylthio (**1e**) as well as electron-withdrawing groups such as carboxylate (**1n**) and nitro (**1o**) were tolerated on the salicylaldehyde. In particular, the halogen-containing substrates (**1f–k**) reacted efficiently. Substrates **1l** and **1m** derived from **1h** by Suzuki and Heck reactions, respectively, are also compatible with the process. As expected, the naphthaldehyde substrates **1q** and **1r** and the benzopyran substrate **1s** can also be converted into interesting products (**3qa–sa**). Interestingly, when we selected **1t** as the substrate, the desired product **3ta** was obtained only in 30% yield. The uncyclized product **4ta**, which was isolated in 28% yield, may act as an intermediate in this reaction [Eq. (3)]. To prove this hypothesis, we employed **4ta** as the starting material under our standard reaction conditions and, indeed, observed the formation of **3ta** in 40% yield [Eq. (4)].

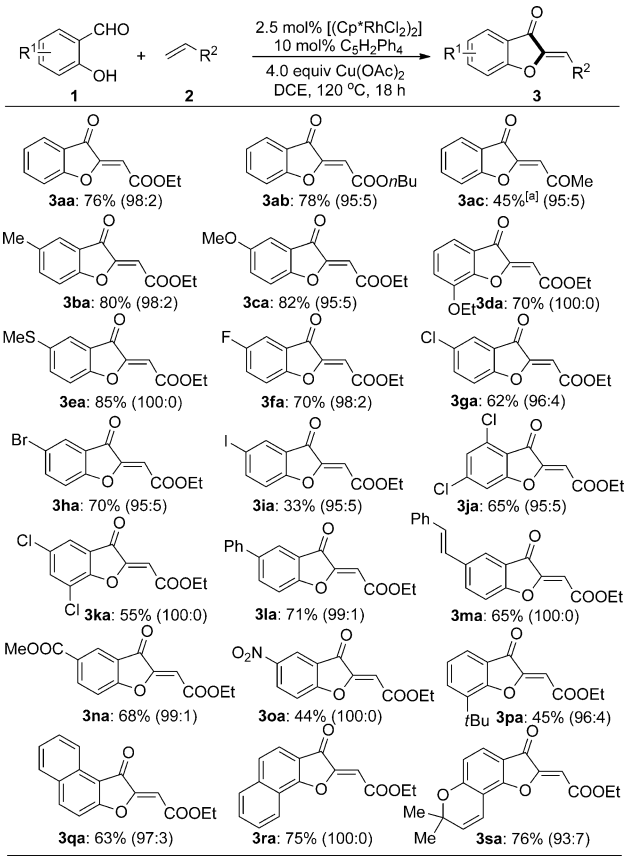




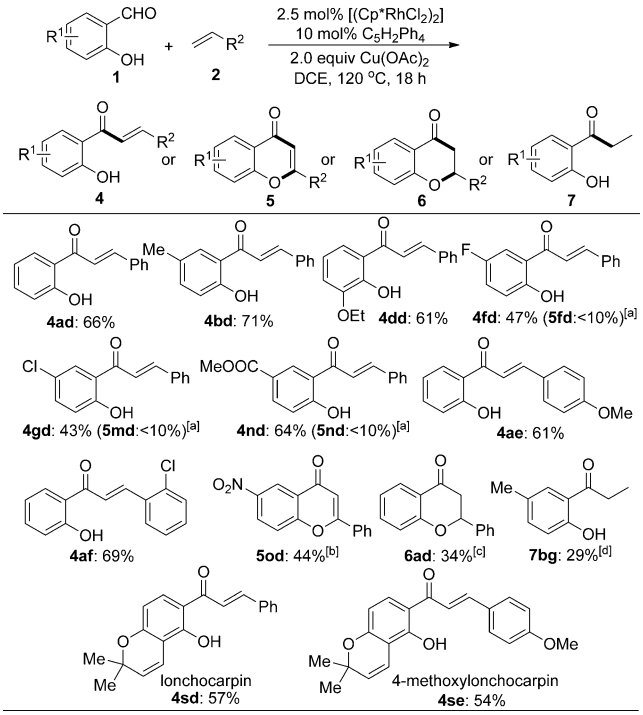
Other olefin substrates such as styrene and ethylene were also investigated with salicylaldehydes as reaction partners (Scheme 3). We found that electron-neutral and electron-rich salicylaldehydes (**1a**, **1b**, and **1d**) afforded only olefinated products without further cyclization even when the amount of oxidant was increased. The successive oxidative cyclization was inhibited presumably because styrene is less electrophilic than ethyl acrylate. The reaction with moderately electron-poor salicylaldehydes (like **1n**) can also produce chalcone derivatives (**4nd**) with some flavone-type by-products. Halide functional groups on either the salicylaldehydes or styrene were tolerated (**4fd**, **4gd**, and **4af**). The most electron-poor substrate, 5-nitrosalicylaldehyde, selectively afforded **5od** in 44% yield. When Ag_2CO_3 was used as the oxidant, only flavanone **6ad** resulting from DHR of the aldehyde C–H bond and subsequent Michael addition. In addition, when ethylene gas (5 bar) was used as a substrate only the hydroacylation product **7bg** was obtained in 29% yield.

Lonchocarpin (**4sd**) and 4-methoxylonchocarpin (**4se**) are isolated from *Lonchocarpus utilus* and *L. subglaucescens*, plants found in tropical America, Africa, and the Caribbean islands. They exhibit a range of biological and pharmacological properties including antimutagenic, antimicrobial, antiulcer, and antitumor activities.[20] Compounds **4sd** and **4se** could be synthesized using this methodology in just two steps from commercially available reagents.

In order to gain insight into the mechanism of the reaction, we performed parallel experiments with deuterium-labeled substrates (see the Supporting Information). The kinetic isotope effect (KIE) value for the C–H olefina-

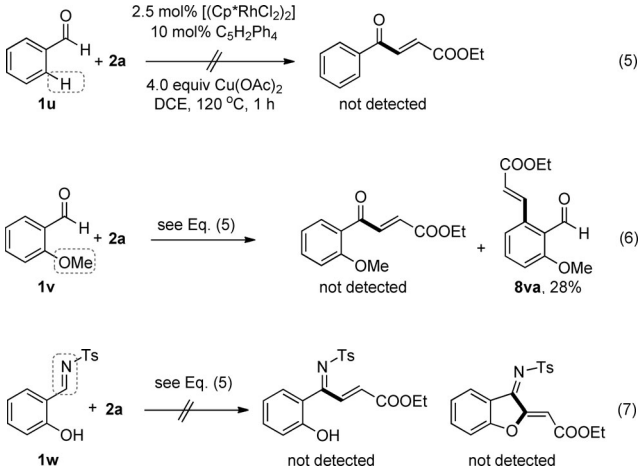


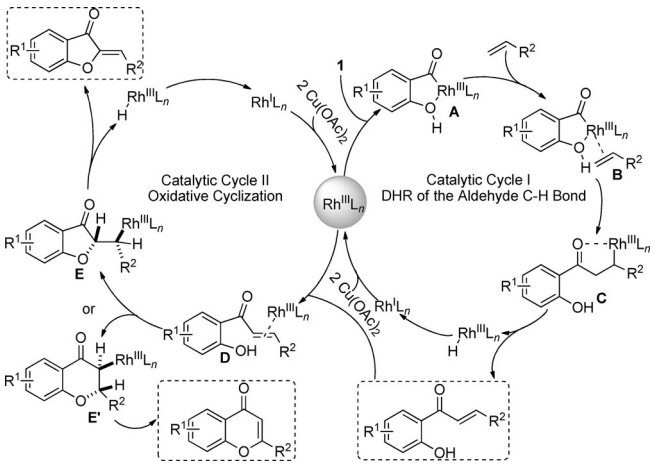
Scheme 2. Rh^{III}-catalyzed cyclization of salicylaldehydes and electron-deficient olefins. General reaction conditions: **1** (0.2 mmol), **2** (0.4 mmol), $[(Cp^*RhCl_2)_2]$ (2.5 mol%), $C_5H_2Ph_4$ (10 mol%), $Cu(OAc)_2$ (0.8 mmol), DCE (1.0 mL), 120 °C, 18 h, under Ar; values in parentheses indicate the *Z*/*E* ratios, which were determined by ^1H NMR analysis of the crude products. [a] Reaction temperature 90 °C.



Scheme 3. C–H olefination of salicylaldehydes with other olefins. General reaction conditions: **1** (0.2 mmol), **2** (0.4 mmol), $[(Cp^*RhCl_2)_2]$ (2.5 mol%), $C_5H_2Ph_4$ (10 mol%), $Cu(OAc)_2$ (0.4 mmol), DCE (1.0 mL), 120 °C, 18 h, under Ar. [a] Determined by ^1H NMR analysis of crude products. [b] 4.0 equiv $Cu(OAc)_2$ was used. [c] 2.0 equiv Ag_2CO_3 was used as oxidant instead of $Cu(OAc)_2$. [d] Ethylene atmosphere (5 bar).

tion of **1a** with ethyl acrylate **2a** and styrene **2d** were 1.3 and 1.2, respectively, suggesting that the C–H cleavage is fast and not involved in the rate-determining step.[21] When the simpler benzaldehyde (**1u**) was utilized as the substrate, the corresponding chalcone was not formed [Eq. (5)]. 2-Methoxybenzaldehyde (**1v**) underwent DHR only at the CHO-directed *ortho* aromatic C–H bond [Eq. (6)]. Therefore, the presence of a hydroxy group in the substrate was critical in triggering the initial C–H bond-functionalization event. Meanwhile, when imine **1w** was subjected to the standard reaction conditions, no desired products were observed, thus indicating the important role of the carbonyl group for this transformation [Eq. (7)].





Scheme 4. Plausible reaction mechanism.

On the basis of these investigations, a mechanism is proposed in Scheme 4. Coordination of the 2-hydroxy group of salicylaldehydes to a $Rh^{III}L_n$ species appears to be the key for the selective cleavage of the aldehyde C–H bond to afford **A**.[6f,22] This rhodacycle can coordinate one equivalent of alkene to form **B**, which undergoes alkene insertion giving intermediate **C**. Subsequently, β-hydride elimination of **C** generates the uncyclized product and a $Rh^{III}H$ species. This species can undergo reductive elimination to yield a Rh^I complex, which is then reoxidized by Cu^{II} to $Rh^{III}L_n$ (catalytic cycle I). If this resulting olefination product contains an electron-withdrawing group on the alkene (i.e., $R^2 = COOR$, COR) or the salicylaldehyde (i.e., $R^1 = NO_2$), a subsequent alkoxyrhodation cyclization will take place by a 5-*exo* or 6-*endo*-trig pathway generating **E** or **E′**. Similar to Yu's work,[5b] we observed the *Z*-type product,[23] which means this cyclization process proceeds by *anti* addition and then *syn*-β-hydride elimination to afford the oxidized cyclization product and the $Rh^{III}H$ species. In the presence of another two equivalents of $Cu(OAc)_2$, the resulting Rh^I species can transfer to the catalytically active $Rh^{III}L_n$ (catalytic cycle II).

In summary, we have developed a catalytic DHR with aldehyde C–H bonds, complementing the Heck reaction on carbonyl substrates. This methodology is attractive because the starting materials are readily available and the products are valuable. Moreover, we have applied this methodology to the synthesis of lonchocarpin and 4-methoxylonchocarpin, showing the practicality and value of this method.

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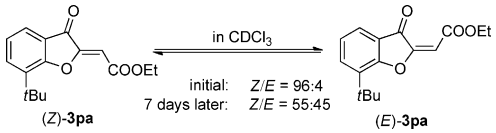
[21] a) W. Jones, *Acc. Chem. Res.* **2003**, *36*, 140; b) E. Simmons, J. Hartwig, *Angew. Chem.* **2012**, *124*, 3120; *Angew. Chem. Int. Ed.* **2012**, *51*, 3066.

[22] The coordination mode of the hydroxy group to an $Rh^{III}L_n$ species is still unclear. Miura et al. proposed that the phenolic oxygen atom in salicylaldehyde coordinates with the Rh^{III} species as an anionic ligand: a) K. Kokubo, K. Matsumasa, M. Miura, M. Nomura, *J. Org. Chem.* **1997**, *62*, 4564; b) K. Kokubo, K. Matsumasa, Y. Nishinaka, M. Miura, M. Nomura, *Bull. Chem.*

Soc. Jpn. **1999**, *72*, 303; Liu et al. obtained clear evidence by X-ray structure analysis of an intermedate in a Pd^{II}-catalyzed reaction that the phenol group coordinated as a neutral ligand: c) B. Xiao, T.-J. Gong, Z.-J. Liu, J.-H. Liu, D.-F. Luo, J. Xu, L. Liu, *J. Am. Chem. Soc.* **2011**, *133*, 9250. In Scheme 4 we depict the phenol group coordinated with Rh^{III} as a neutral σ donor; however, anionic coordination cannot be ruled out at present stage.

[23] We found that *Z*-type products can isomerize to *E*-type ones at room temperature. For example (*Z*)-**3pa**:



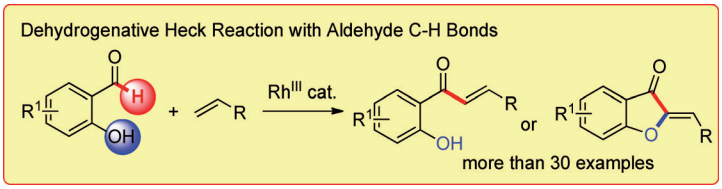
Thus, the small amounts of the *E* isomer might arise from this equilibrium rather than from β-hydride elimination.

Communications

C–H Functionalization

Z. Shi, N. Schröder,
F. Glorius* _____ ■■■■–■■■■

Rhodium(III)-Catalyzed Dehydrogenative Heck Reaction of Salicylaldehydes



Your CHOice! An efficient Rh^{III}-catalyzed dehydrogenative Heck reaction (DHR) of salicylaldehydes with different classes of olefins extends the oxidative Heck reaction to aldehyde C–H bonds. Several structural motifs similar to natural products and bioactive molecules such as aurones, flavones, 2′-hydroxychalcones, and flavanones could be efficiently produced. Initial mechanistic studies give insight into the reaction mechanism.