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Controllable Rh(III)-Catalyzed Annulation between Salicylaldehydes and Diazo Compounds: Divergent Synthesis of Chromones and Benzofurans

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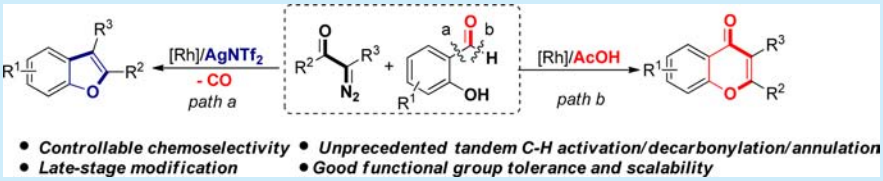
Supporting Information

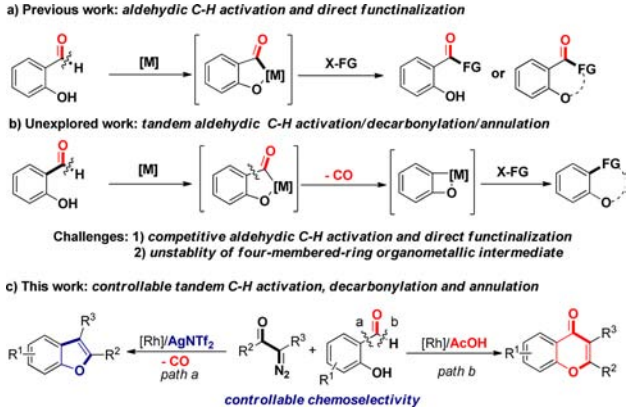


ABSTRACT: A Rh(III)-catalyzed annulation between salicylaldehydes and diazo compounds with controllable chemoselectivity is described. $AgNTf_2$ favored benzofurans via a tandem C−H activation/decarbonylation/annulation process, while AcOH led to chromones through a C−H activation/annulation pathway. The reaction exhibited good functional group tolerance and scalability. Moreover, only a single regioisomer of benzofuran was obtained due to the in situ decarbonylation orientation effect.

In the last two decades, transition-metal-catalyzed C−H activation has been well studied and identified as one of the most powerful tools in organic synthesis.[1] Ideally, the structurally diverse products could be achieved from the same materials via selective C−H functionalization in a controllable manner. Recently, advances have been achieved through the choice of catalysts,[2] ligands,[3] directing groups,[4] and electronic/steric effects.[5] Although the aforementioned methods have been widely investigated, the continuous development of new methods to precisely control the product distribution in C−H activation is still a hot research topic and challenging problem for chemists.

Salicylaldehydes are versatile building blocks in organic synthesis, and numerous endeavors have been devoted to functionalizing salicylaldehydes with alkenes, alkynes, and allenes via a direct aldehydic C−H activation and/or annulation process.[6] The key to the success of these works was the formation of a five-membered-ring organometallic intermediate as shown in Scheme 1a. On the other hand, the synthetic applications of the exotic oxa-metallacycles[7] formed through decarbonylative metalation of salicylaldehydes in annulation have remained unexplored until now[8] (Scheme 1b). To fulfill this objective, predictable challenges might be met: (1) how to regulate the selectivity to realize the facile decarbonylation in the presence of the direct aldehydic C−H functionalization and (2) whether the four-membered oxa-metallacycle generated from decarbonylation exhibits sufficient stability to achieve the subsequent annulation process. On the basis of our continuous interest in transition-metal-catalyzed selective C−H activation and diazo compounds[9] and also to enrich the reaction type of salicylaldehydes, herein we report our results on a Rh(III)-catalyzed tandem C−H activation, decarbonylation, and annulation between salicylaldehydes and diazo compounds[10] toward the construction of benzofurans and chromones in a controllable manner (Scheme 1c). It is necessary to point out that in our reaction the decarbonylation plays an important role in orientation to achieve a single regioisomer of benzofuran, which overcomes the regioselective problems faced by employing phenols as coupling reactants.[11] Moreover, the competitive reaction between the formed metal carbenoid intermediate and the phenolic hydroxyl group of salicylaldehydes has also been well suppressed.[12]

Scheme 1. Transition-Metal-Catalyzed C−H Activation of Salicylaldehydes



We set out our investigation with salicylaldehyde **1a** and ethyl 2-diazo-3-oxobutanoate **2a** as model substrates. A preliminary

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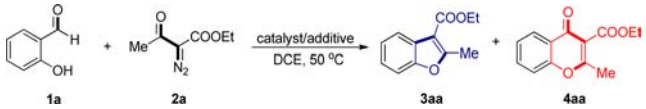
attempt with 2.5 mol % of $[RhCp^*Cl_2]_2$ and 20 mol % AgOAc in 2 mL of DCE at 50 °C offered the decarbonylation/annulation product **3aa** in 21% yield with the direct aldehydic C−H activation/annulation product **4aa** in 55% yield (Table 1, entry 1). When $AgSbF_6$ was tested, **3aa** could be produced in 52% yield (Table 1, entry 2). The yield of **3aa** was further increased to 90% when $AgNTf_2$ was used (Table 1, entry 4). Decreasing the amount of $AgNTf_2$ or reducing the reaction temperature led to lower yields (Table 1, entries 5 and 6). To improve the yield of **4aa**, some additives were then examined. When AcOH was used, **4aa** could be furnished in 44% yield with a certain amount of **1a** and **2a** unconverted (Table 1, entry 7). By further increasing the temperature to 80 °C, the yield of **4aa** was promoted to 82% (Table 1, entry 10). Neither **3aa** nor **4aa** could be obtained without the loading of $[RhCp^*Cl_2]_2$ (Table 1, entries 11 and 12).

Table 1. Optimization of Reaction Conditions[a]

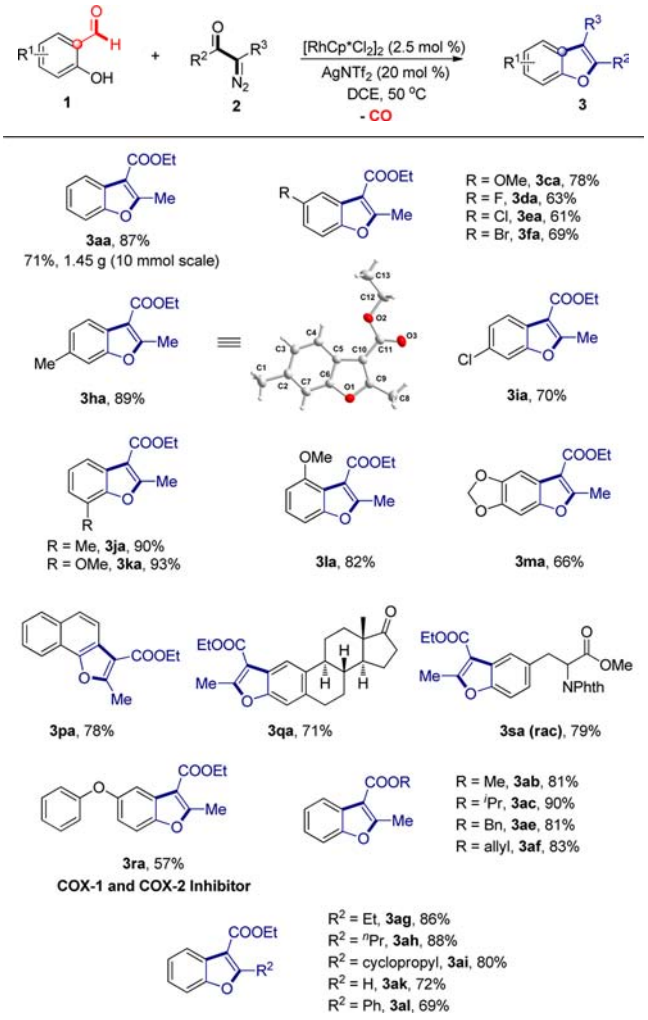


entry	catalyst	additive	yield (3aa/4aa)[b]
1	$[RhCp^*Cl_2]_2$	AgOAc	21/55
2	$[RhCp^*Cl_2]_2$	$AgSbF_6$	52/31
3	$[RhCp^*Cl_2]_2$	$AgBF_4$	43/0
4	$[RhCp^*Cl_2]_2$	$AgNTf_2$	90 (87)[c]/0
5[d]	$[RhCp^*Cl_2]_2$	$AgNTf_2$	69/0
6[e]	$[RhCp^*Cl_2]_2$	$AgNTf_2$	56/0
7	$[RhCp^*Cl_2]_2$	AcOH[f]	0/44
8	$[RhCp^*Cl_2]_2$	PivOH[f]	0/32
9	$[RhCp^*Cl_2]_2$	MSA[f]	0/0
10[g]	$[RhCp^*Cl_2]_2$	AcOH[f]	0/82[c]
11		$AgNTf_2$	0/0
12		AcOH[f]	0/0

[a]Reaction conditions: **1a** (0.5 mmol, 1.0 equiv), **2a** (1.0 mmol, 2.0 equiv), catalyst (0.0125 mmol, 2.5 mol %), additive (20 mol %), DCE (2 mL), 50 °C, 12 h under air atmosphere. [b]Yields were determined by ^1H NMR using dibromomethane (δ = 4.80) as an internal standard. [c]Isolated yields. [d]10 mol % of $AgNTf_2$ was used. [e]Room temperature. [f]2.0 equiv of additives. [g]80 °C.

With the optimized conditions in hand, the substrate scope for the synthesis of benzofurans was examined as shown in Table 2. When 5-methoxysalicylaldehyde was investigated, **3ca** was obtained in 78% yield. 5-Halogen-substituted products **3da**−**fa** were prepared in 61−69% yields. In previous works,[12] when 3-substituted phenols were used as coupling reactants, it was difficult to obtain a single regioisomer of 4-substituted or 6-substituted benzofuran. Here, our methods provided a practical way to settle this problem with the in situ decarbonylation orientation effect. When 4-methylsalicylaldehyde was tested, only 6-methylbenzofuran **3ha** was obtained, and the structure was identified by single-crystal X-ray analysis.[13] Salicylaldehydes with substituents at the C3 or C6 positions performed smoothly to offer **3ja**−**la** in 82−93% yields. 1-Hydroxy-2-naphthaldehyde **1p** delivered **3pa** in 78% yield. Considering that the benzofuran skeleton is widespread in drugs and natural products, late-stage modification of estrone and tyrosine were tested, and the desired products **3qa** and **3sa** were prepared in 71% and 79% yields. Compound **3ra**,[14] identified as a COX-1 and COX-2 inhibitor, was also synthesized conveniently in 57% yield. When the ester group of **2a** was altered from an ethyl group to methyl, isopropyl, benzyl, and allyl groups, **3ab**−**af** were obtained in 81−90% yields. When the R^2 group was replaced with ethyl, *n*-propyl, and cyclopropyl groups, **3ag**−**ai** were prepared in 80−88% yields. 2-Unsubstituted and 2-phenyl-substituted **3ak** and **3al** were obtained in 72% and 69% yields. When the reaction was scaled up to 10 mmol, **3aa** could be prepared in 71% yield (1.45 g).

Table 2. Substrate Scope for the Synthesis of Benzofurans[a,b]



[a]Reaction conditions: **1** (0.5 mmol, 1.0 equiv), **2** (1.0 mmol, 2.0 equiv), $[RhCp^*Cl_2]_2$ (0.0125 mmol, 2.5 mol %), $AgNTf_2$ (20 mol %), DCE (2 mL), 50 °C for 12 h under air atmosphere. [b]Isolated yields.

The substrate scope for the synthesis of chromones was then examined, and the results are shown in Table 3. 5-Methyl- and 5-methoxysalicylaldehydes gave **4ba** and **4ca** in 85% and 90% yields. Salicylaldehydes with halogen groups at the C5 position offered **4da** and **4fa** in 83% and 79% yields. Compound **4ga** with a strong electronic-withdrawing group (NO_2) was obtained in 50% yield. The C3- or C4-substituted salicylaldehydes offered the corresponding products in 80−87% yields. 6-Hydroxybenzo-[*d*][1,3]dioxole-5-carbaldehyde delivered **4ma** in 70% yield. Substrates with phenyl and 2-thienyl groups at the C5 position yielded **4na** and **4oa** in 68% and 60% yields. When 1-hydroxy-2-naphthaldehyde **1p** was examined, **4pa** was obtained in 58% yield. Estrone and tyrosine derivatives **4qa** and **4sa** with a chromone skeleton were prepared in 80% and 91% yields. Methyl, *tert*-butyl, and benzyl 2-diazo-3-oxobutanoates yielded **4ab**, **4ad**, and **4ae** in 81%, 77%, and 82% yields. Alkyl- and aryl-substituted diazo compounds in the R^2 position offered **4ag**, **4ah**,

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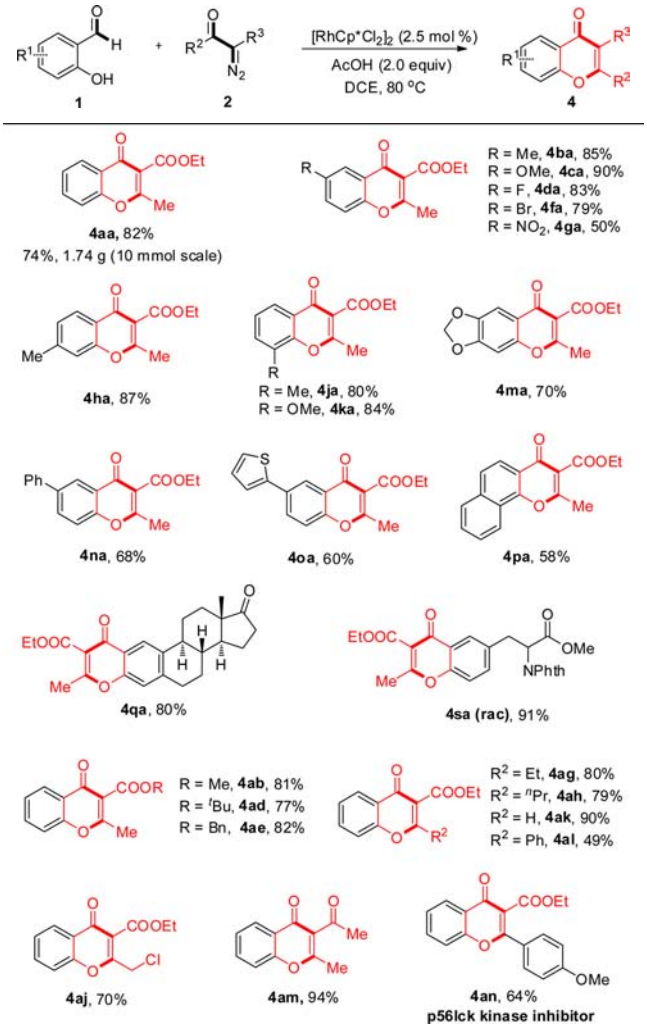
Table 3. Substrate Scope for the Synthesis of Chromones[a,b]

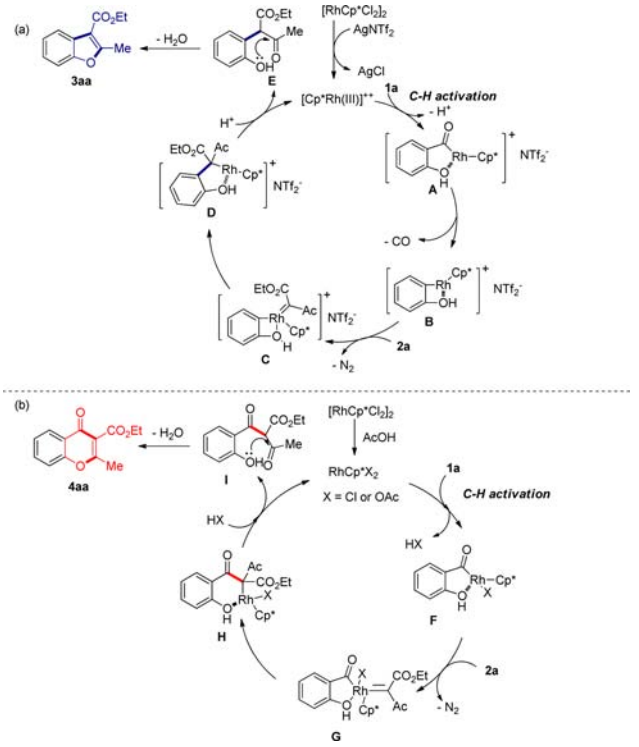


[a]Reaction conditions: **1** (0.5 mmol, 1.0 equiv), **2** (1.0 mmol, 2.0 equiv), $[RhCp^*Cl_2]_2$ (0.0125 mmol, 2.5 mol %), AcOH (2.0 equiv), DCE (2 mL), 80 °C for 12 h under air atmosphere. [b]Isolated yields.

and **4al** in 80%, 79%, and 49% yields. Ethyl 2-diazo-3-oxopropanoate **1k** gave **4ak** in 90% yield. Compound **4aj** with a chloro group in the R^2 position was obtained in 70% yield. When 3-diazopentane-2,4-dione **2m** was tested, **4am** was obtained in 94% yield. Flavone derivative **4an**[15] with antityrosine-kinase activity could be prepared in 64% yield. When the model reaction was conducted on a 10 mmol scale, **4aa** was obtained in 1.74 g (74% yield).

On the basis of our control experiments (see the Supporting Information for details) and previous reports,[16] the plausible reaction pathway for the Rh(III)-catalyzed annulation between salicylaldehydes and diazo compounds with controllable chemoselectivity is proposed as shown in Scheme 2. When $AgNTf_2$ is used as an additive (Scheme 2a), the cationic complex Cp*Rh(III) is generated, participating in the directed C−H activation of salicylaldehyde to offer intermediate **A**. Catalyst with a weaker coordinating counterion (such as Tf_2N^-) prefers the decarbonylation, while the stronger counterions (Cl^-, AcO^-) are unlikely to fulfill this role.[17] We speculated that the Ag^+ may also play an important role in promoting the decarbonylation process, while the specific role is unclear at the present stage. A sequential decarbonylation process occurs to generate the four-

Scheme 2. Plausible Reaction Pathway



membered oxa-metallacycle **B**, which reacts with **2a** to offer the Rh−carbene complex **C** with the release of N_2. Then the intermediate **D** is generated after the migratory insertion process, which is protonated to form **E** with the regeneration of the active rhodium catalyst. Later, the intramolecular dehydration condensation of **E** yields the product **3aa**. When AcOH was used as the additive (Scheme 2b), the hydroxyl-directed C−H activation of **1a** affords the intermediate **F**, which reacts with **2a** directly to produce a five-membered-ring Rh−carbene complex **G**. Next, the migratory insertion yields intermediate **H**, which is then protonated to form **I** with the regeneration of the active catalyst. Chromone **4aa** is achieved through the intramolecular dehydration condensation of intermediate **I**.

In conclusion, we have developed a rhodium-catalyzed annulation between salicylaldehydes and diazo compounds with controllable chemoselectivity. $AgNTf_2$ favored benzofurans via a tandem C−H activation/decarbonylation/annulation process, while AcOH led to chromones through a C−H activation/annulation pathway. The reaction exhibited good functional group tolerance and scalability, and only a single regioisomer of benzofuran was obtained due to the in situ decarbonylation orientation effect. To expand the application of our method, late-stage modification was conducted to provide estrone and tyrosine derivatives with chromone and benzofuran skeletons in high efficiency, and two reported bioactive molecules were also conveniently synthesized. The preliminary mechanism study illustrated that a four-membered oxa-metallacycle might be generated during the C−H activation/decarbonylation step.

■ ASSOCIATED CONTENT

Supporting Information

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^{1}H and ^{13}C NMR spectra for all new compounds (PDF)
X-ray crystallographic data for **3ha** (CIF)

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Notes

The authors declare no competing financial interest.

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(13) Crystallographic data for **3ha** have been deposited with the Cambridge Crystallographic Data Centre as deposition no. CCDC 1450291. Detailed information can be found in the Supporting Information.

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