

Iridium - Catalyzed Aerobic Coupling of Salicylaldehydes with Alkynes: A Remarkable Switch of Oxacyclic Product

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Iridium-Catalyzed Aerobic Coupling of Salicylaldehydes with Alkynes: A Remarkable Switch of Oxacyclic Product

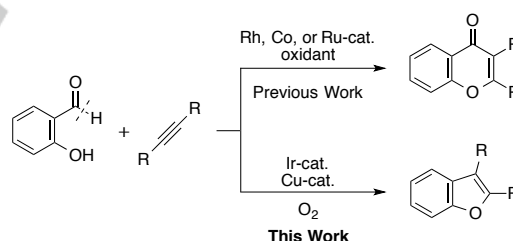
Shintaro Yamane,^[a] Tomoaki Hinoue,^[b] Yoshinosuke Usuki,^[a] Masumi Itazaki,^[a] Hiroshi Nakazawa,^[a] Yoshihiro Hayashi,^[c] Susumu Kawauchi,^[c] Masahiro Miura,^{*[b]} and Tetsuya Satoh^{*[a]}

Dedication ((optional))

Abstract: The iridium(III)/copper(II)-catalyzed dehydrogenative coupling of salicylaldehydes with internal alkynes proceeds efficiently under atmospheric oxygen through aldehyde C–H bond cleavage and decarbonylation. A variety of benzofuran derivatives can be synthesized by the environmentally-benign procedure. DFT calculations suggest that this unique transformation involves the facile deinsertion of CO in the key metallacycle intermediate, which is in marked contrast to the corresponding rhodium(III) catalysis that leads to CO-retentive chromone derivatives.

Aldehydes are definitely highly versatile building blocks in organic synthesis. Among functionalized aromatic aldehydes, salicylaldehyde and its derivatives are readily available and particularly useful for preparing various kinds of valuable fused heterocyclic compounds as well as chelating agents such as salens. Besides conventional condensation reactions involving Claisen and Perkin reactions, latest techniques based on transition-metal-catalysis have attracted attention for their transformation. Thus, we^[1] and other groups^[2] have developed the direct derivatization methods of salicylaldehydes through aldehyde C–H bond arylation and alkenylation.^[3] We also found that salicylaldehydes undergo dehydrogenative annulation with internal alkynes in the presence of a rhodium catalyst and a copper salt oxidant to produce chromone derivatives (Scheme 1, a: previous work).^[4a] Later, similar reactions using cobalt^[4b] and ruthenium^[4c] catalysts were reported for the construction of a variety of flavonoid compounds. During our further studies of transition-metal-catalyzed dehydrogenative coupling reactions,^[5] we succeeded in finding that treatment of the same combination of substrates, salicylaldehydes and alkynes, using an iridium catalyst together with a copper cocatalyst under atmospheric oxygen in place of the rhodium system gives 2,3-disubstituted benzofuran derivatives predominantly, accompanied by dehydrogenation and decarbonylation (Scheme 1, b: this work). Thus, the remarkable switch of product was realized by the simple change of the catalytic system. It should be noted that

this reaction can be carried out using molecular oxygen as a terminal oxidant without waste formation except for water and CO. 2,3-Disubstituted benzofuran structures can be seen in synthetic intermediates in producing various bioactive compounds, natural products, and organic materials.^[6] Therefore, their synthetic methods via transition-metal-catalyzed direct coupling of phenolic substrates with alkynes have been developed.^[7] Although these reactions can be step-economical approaches, the addition of stoichiometric or even excess amounts of metal salts is usually required as oxidants, promoters, or Lewis acids. Liu, Lu, and co-workers reported the rhodium- and ruthenium-catalyzed annulation of *N*-phenoxybenzamides with alkynes utilizing internal oxidants to address the drawback.^[7a] However, an additional step is required to introduce reducible directing groups onto the phenolic substrates. The present reaction provides a straightforward pathway toward useful 2,3-disubstituted benzofuran derivatives from readily available salicylaldehydes through environmentally-benign aerobic dehydrogenative annulation without the addition of a stoichiometric amount of metal salts.



Scheme 1. Dehydrogenative Annulation of Salicylaldehydes with Alkynes.

In an initial attempt, salicylaldehyde (**1a**) (0.5 mmol) was treated with diphenylacetylene (**2a**) (0.5 mmol) in the presence of catalytic amounts of [Cp*IrCl₂]₂ (0.01 mmol; 2 mol%) and Cu(OAc)₂•H₂O (0.05 mmol; 10 mol%) in xylene (2.5 mL) at 160 °C for 24 h under O₂. As a result, aerobic dehydrogenative coupling proceeded accompanied by decarbonylation to predominantly produce 2,3-diphenylbenzofuran (**3aa**) in 66% yield, along with a minor amount (8%) of 2,3-diphenylchromone (**4aa**)^[4a] (entry 1 in Table 1). Decreasing the amount of Cu(OAc)₂•H₂O to 5 mol% significantly reduced the yield of **3aa** (entry 2). Other copper salts such as Cu(OCOCF₃)₂•H₂O, Cu(OTf)₂•H₂O, and CuO were less effective as co-catalysts than Cu(OAc)₂•H₂O (entries 3-5). The addition of a catalytic amount (10 mol%) of Na₂CO₃ as a base slightly accelerated the reaction and increased the yield of **3aa** (entry 6). NaHCO₃ and KHCO₃ were more effective to increase the yield to 77 and 75%,

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respectively (entries 7 and 8). In addition to these inorganic bases, organic bases were also found to facilitate the reaction. Thus, **3aa** was obtained in 75 and 83% yields by using (*i*-Pr)₂NET and DABCO, respectively (entries 9 and 10). Finally, DBU was found to be the most effective base catalyst to improve the **3aa** yield to 93%, suppressing the formation of **4aa** to 1% (entry 11). Furthermore, **3aa** was produced almost quantitatively under conditions using a slightly excess amount (1.2 equiv.) of **1a** (entry 12). Since stoichiometric amounts of additives are not required, the present reaction can be readily scaled up to a gram scale. Thus, **3aa** was obtained in 78% isolated yield (1.05 g) from **1a** (6 mmol) and **2a** (5 mmol) (entry 13).

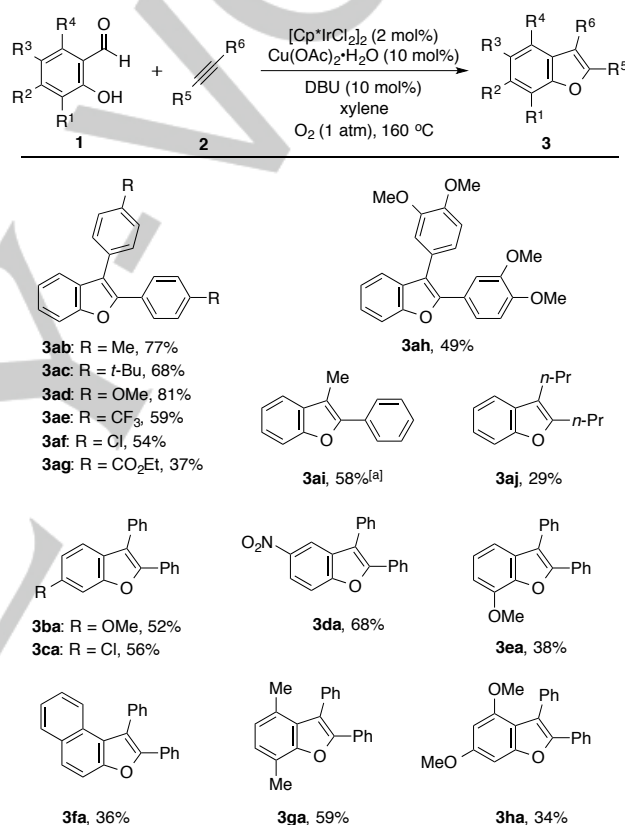
Table 1. Reaction of salicylaldehyde (**1a**) with diphenylacetylene (**2a**)^[a]

entry	Cu-cat.	base	time [h]	Yield [%] ^[b]	
				3aa	4aa
1	Cu(OAc) ₂ ·H ₂ O	–	48	66	8
2 ^[c]	Cu(OAc) ₂ ·H ₂ O	–	24	14	26
3	Cu(OCOCF ₃) ₂ ·H ₂ O	–	48	28	12
4	Cu(OTf) ₂ ·H ₂ O	–	4	0	0
5	CuO	–	4	5	10
6	Cu(OAc) ₂ ·H ₂ O	Na ₂ CO ₃	30	68	11
7	Cu(OAc) ₂ ·H ₂ O	NaHCO ₃	48	77	8
8	Cu(OAc) ₂ ·H ₂ O	KHCO ₃	24	75	10
9	Cu(OAc) ₂ ·H ₂ O	(<i>i</i> -Pr) ₂ NET	24	75	7
10	Cu(OAc) ₂ ·H ₂ O	DABCO	8	83	16
11	Cu(OAc) ₂ ·H ₂ O	DBU	8	93	1
12 ^[d]	Cu(OAc) ₂ ·H ₂ O	DBU	24	99 (84)	1
13 ^[e]	Cu(OAc) ₂ ·H ₂ O	DBU	24	(78)	– ^[f]

[a] Reaction conditions: **1a** (0.5 mmol), **2a** (0.5 mmol), [Cp*IrCl₂]₂ (0.01 mmol), Cu-cat. (0.05 mmol), and base (0.05 mmol) in xylene (2.5 mL) under O₂ (1 atm) at 160 °C, unless otherwise noted. [b] GC yield based on the amount of **2a** used. Value in parentheses indicates yield after purification. [c] With Cu(OAc)₂·H₂O (0.025 mmol). [d] With **1a** (0.6 mmol). [e] With **1a** (6 mmol), **2a** (5 mmol), [Cp*IrCl₂]₂ (0.1 mmol), Cu(OAc)₂·H₂O (0.5 mmol), and DBU (0.5 mmol) in xylene (10 mL). [f] Not determined.

Under the optimized conditions (entry 12 in Table 1), **1a** coupled with 4,4'-substituted diphenylacetylenes **2b-g** to give the corresponding 2,3-diarylbenzofurans **3ab-3ag** (Scheme 2). Similarly, 3,3',4,4'-tetramethoxydiphenylacetylene (**2h**)

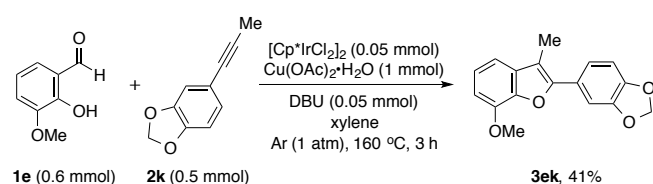
underwent the annulation with **1a** to produce **3ah**. The reaction of an unsymmetrical alkyne, 1-phenyl-1-propyne (**2i**), with **1a** afforded 2-phenyl-3-methylbenzofuran (**3ai**) predominantly. Only a trace amount (ca. 1%) of a regioisomer was detected by GC-MS and ¹H NMR. Compared to aromatic alkynes, an aliphatic one, 4-octyne (**2j**), was less reactive under the standard conditions to give **3aj** in a lower yield. Commercially available, variously substituted salicylaldehydes **1b-h** also underwent the annulative coupling with **2a** to produce **3ba-3ha**. It should be noted that sterically hindered 4- and/or 7-substituted benzofuran frameworks are readily constructed by the present procedure. These frameworks seem to be difficult to prepare by the previous coupling of phenolic substrates with alkynes.^[7]



Scheme 2. Reaction scope of salicylaldehydes and alkynes. Reaction conditions: **1** (0.5–0.6 mmol), **2** (0.5 mmol), [Cp*IrCl₂]₂ (0.01 mmol), Cu(OAc)₂·H₂O (0.05 mmol), and DBU (0.05 mmol) in xylene (2.5 mL) under O₂ (1 atm) at 160 °C for 4–48 h, unless otherwise noted. Yields after purification were listed. [a] A trace amount (ca. 1%) of regioisomer was also detected by GC-MS and ¹H NMR.

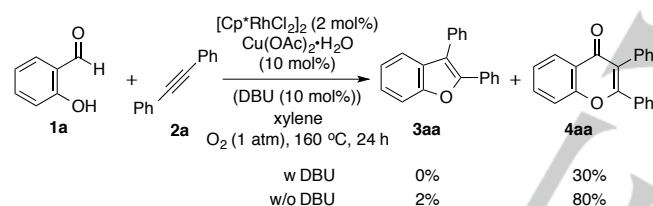
The present annulation method was found to be applicable to the synthesis of an analogue of naturally occurring, bioactive eupomatoid-1.^[8] Thus, treatment of **1e** (0.6 mmol) with alkyne **2k** (0.5 mmol) using [Cp*IrCl₂]₂ (0.05 mmol) and Cu(OAc)₂·H₂O (1 mmol) in the presence of DBU (0.05 mmol) in xylene (2.5 mL) at 160 °C for 3 h under Ar gave **3ek** in 41% yield (Scheme 3).^[9] As in the case using **2i** (Scheme 2), only a trace amount (less than 1%) of regioisomer was detected by GC-MS and ¹H NMR,

indicating high regioselective nature of the present annulation reaction.



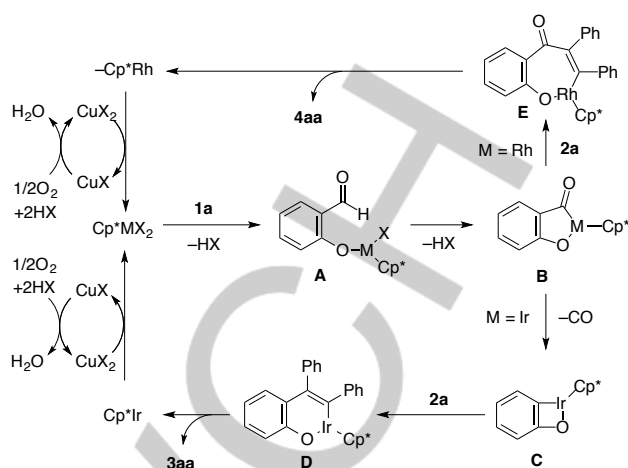
Scheme 3. Synthesis of **3ek**.

We previously performed the rhodium-catalyzed reaction of **1** with **2** in the presence of $[\text{RhCl}(\text{cod})]_2/\text{C}_5\text{H}_2\text{Ph}_4$ and $\text{Cu}(\text{OAc})_2\cdot\text{H}_2\text{O}$.^[4a] To confirm the origin of the product switch, we reinvestigated the reaction of **1a** and **2a** using $[\text{Cp}^*\text{RhCl}_2]_2$ under otherwise identical conditions to the present transformation (Scheme 4). As a result, chromone **4aa** was produced exclusively, albeit with 30% yield, no benzofuran **3aa** being detected. It was of interest that a significantly enhanced yield of **4aa** (80%) was obtained by eliminating DBU, along with a small amount (2%) of **3aa**. Thus, the product switch is definitively attributable to the nature of the metals employed.



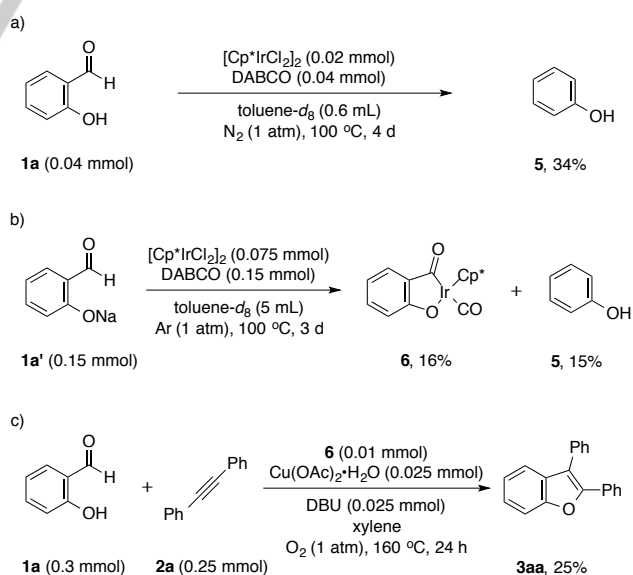
Scheme 4. Cp^*Rh -catalyzed reaction of **1a** with **2a**. GC yields are shown.

A plausible mechanism for the reaction of **1a** with **2a** is illustrated in Scheme 5. In the case using an iridium catalyst, coordination of the hydroxy function of **1a** to Cp^*IrX_2 and subsequent aldehyde C–H bond cleavage in a resulting intermediate **A** take place to form a five-membered iridacycle intermediate **B**.^[10] Then, **B** undergoes decarbonylation, alkyne insertion into the aryl–Ir bond of **C**, and reductive elimination from the resulting six-membered iridacycle intermediate **D** to produce **3aa**. The $\text{Cp}^*\text{Ir}(\text{I})$ species generated at the last step may be reoxidized by a $\text{Cu}(\text{II})$ cocatalyst to regenerate the $\text{Ir}(\text{III})$ active species along with $\text{Cu}(\text{I})$. The latter may be reoxidized under O_2 in the present reaction system. Meanwhile, under rhodium catalysis, the intermediate **B** ($\text{M} = \text{Rh}$) may undergo alkyne insertion retaining the carbonyl forming a seven-membered rhodacycle **E** and final reductive elimination to give **4aa**.



Scheme 5. Possible mechanism

In a control experiment, **1a** (0.04 mmol) was treated with stoichiometric amounts of $[\text{Cp}^*\text{IrCl}_2]_2$ (0.02 mmol) and DABCO (0.04 mmol) in the absence of **2a** in $\text{toluene-}d_8$ at 100°C for 4 d, resulting in the formation of a decarbonylation product, phenol (**5**), in 34% yield (Scheme 6a). In this reaction, an iridacycle similar to **C** appears to be formed and then be protonated to release **5**. When sodium 2-formylphenolate (**1a'**) was used in place of **1a** to suppress the protonation, a five-membered iridacycle **6** that corresponds to CO-coordinated **B** (16%) could be isolated (Scheme 6b). The structure was verified by X-ray crystallography.^[9] It was confirmed that **6** shows a catalytic activity in the reaction of **1a** with **2a** (Scheme 6c). The slower reaction rate could be attributed to the coordinated CO which should be eliminated for the complex to enter the catalytic cycle.



Scheme 6. Control experiments.

DFT calculations were also performed to clarify the reaction paths for the coupling reaction of **1a** with **2a** catalyzed under iridium and rhodium catalyses (Figures S2 and S3), which gave different products. As a result, it shows that the product difference between the iridium- and rhodium-catalyzed reactions is dominated by the equilibrium in the decarbonylation of the five-membered metallacycle intermediate. The Gibbs free energy diagram of the decarbonylations in the iridium- and rhodium-catalyzed reactions is shown in Figure 1. Gibbs free energy change of the iridium-catalyzed reaction was a negative value (-3.7 kcal mol $^{-1}$), while that of the rhodium-catalyzed reaction was a positive value (3.5 kcal mol $^{-1}$). This indicates that the equilibrium of the iridium-catalyzed reaction is toward the four-membered metallacycle intermediate, while that of the rhodium-catalyzed reaction is toward the five-membered metallacycle intermediate. Therefore, the alkyne insertion to the four- and five-membered metallacycle intermediates leads to distinct products in the iridium- and rhodium-catalyzed reactions, respectively.

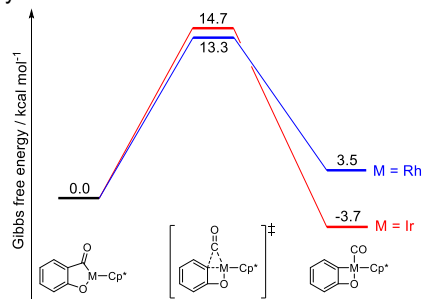


Figure 1. Gibbs free energy diagram (in kcal mol $^{-1}$) of the decarbonylation of the five-membered metallacycle intermediates (M = Ir, Rh). The red and blue lines indicate the diagram of the iridium- and rhodium-catalyzed reactions, respectively.

In summary, we have demonstrated that various benzofuran derivatives can be effectively prepared from readily available salicylaldehydes and alkynes via iridium/copper catalyzed aerobic dehydrogenative coupling. The procedure can be applied to the synthesis of an analogue of naturally occurring, bioactive eupomatenoid-1. We also succeeded in interpreting the difference of products between the reactions under iridium and rhodium catalyses by DFT calculations.

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Keywords: C–H activation • iridium • annulation • dehydrogenation • oxygen heterocycles

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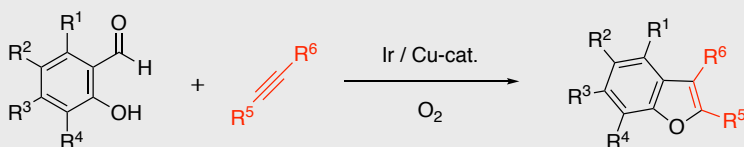
COMMUNICATION

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Layout 2:

COMMUNICATION



Construction of Benzofurans was achieved through a novel iridium(III)/copper(II)-catalyzed dehydrogenative coupling of salicylaldehydes with internal alkynes involving aldehyde C–H bond cleavage and decarbonylation. This reaction proceeds efficiently under atmospheric oxygen. To clarify the mechanism of this unique annulation, DFT calculations have been performed.

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