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# Cp\*Co(III)-Catalyzed *o*-Amidation of Benzaldehydes with Dioxazolones Using Transient Directing Group Strategy

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**Abstract.** Transition metal-catalyzed *ortho*-selective  $C(sp^2)$ -H amidation of weakly coordinating aldehydes remains limited to precious metals such as Ir, Rh, Ru, etc. Herein, we put forward a novel report on *ortho*-amidation of benzaldehydes employing user-friendly dioxazolones under cost-effective and air-stable Cp\*Co(III) catalysis. This catalytic transformation involves transient directing group strategy to enhance the ligating capability of weakly chelating aldehydes.

**Keywords:** Aldehydes; amidation; Co-catalysis; transient directing group, dioxazolones

Directing group (DG) assisted C-H bond activation involves a wide range of coordinating structural elements with strongly or weakly chelating ability depending upon the ligating atoms.<sup>[1]</sup> Functional groups containing oxygen for chelation are considered to be weakly chelating in comparison to that of nitrogen, sulfur and phosphorus.<sup>[2]</sup> Aldehyde, being an easily transformable functional group, shows high potential for medicinally important prototypes as well as synthetic methodologies.<sup>[3]</sup> Despite the fact that formyl group holds a unique reactivity, its exploration in directed C-H bond activations is limited owing to its weak chelation ability and sensitive nature.<sup>[4]</sup> In this context, the transient directing group (TDG) strategy<sup>[1f,5]</sup> has emerged as an excellent alternative for aldehydes since the pioneering work by Jun and co-workers.<sup>[6]</sup>

However, transition metal-catalyzed amidation of benzaldehydes is still limited to precious metals such as Rh,<sup>[7]</sup> Ru,<sup>[8]</sup> and Ir.<sup>[9]</sup> For example, Wang,<sup>[7e]</sup> Kim,<sup>[9a]</sup> and Cui<sup>[9c]</sup> reported Cp\*Rh(III) or Ir(III)-catalyzed *ortho*-amidation of aldehydes using aldimines or nitrones as 'preinstalled directing groups'. In addition to that, Shi,<sup>[5c]</sup> Prabhu,<sup>[7a]</sup> Jiao,<sup>[7b]</sup> Rasheed,<sup>[8]</sup> and He<sup>[9b]</sup> came up with the 'transient directing group strategy (TDG)' employing Rh, Ir and Ru(II) complexes for variety of C-H bond functionalizations. From a cost-effective and sustainable point of view, there is great demand for having an improved procedure under base metal

catalysis, which not only take care of the cost but also amenable to environmentally benign conditions.



**Scheme 1.** Transition metal-catalyzed amidation of benzaldehydes and its surrogates.

In this regard, Cp\*Co(III) catalysts<sup>[10]</sup> have been utilized for C-H bond amidation by Chang<sup>[11]</sup> and later by Jiao,<sup>[12]</sup> Ackermann,<sup>[13]</sup> Li,<sup>[14]</sup> Matsunaga,<sup>[15]</sup> Sundararaju<sup>[16]</sup> and others.<sup>[17]</sup> Interestingly, Dong<sup>[7c]</sup> reported Cp\*Rh(III)-catalyzed and co-workers amidation via in situ generation of a traceless directing group through combination of aldehydes and dioxazolones. Additionally, Zhang<sup>[7d]</sup> reported an elegant H<sub>2</sub>O promoted amidation of benzaldehydes under Cp\*Rh catalysis. To the best of our knowledge, ortho-amidation of aldehydes under first row transition metal catalysis has not been realized yet.[18] Our continuous interest in exploring C-H bond functionalization using weakly chelating directing groups under base metal catalysis<sup>[19]</sup> prompted us to develop an efficient and sustainable procedure for the synthesis of 2-aminobenzaldehydes. Towards this goal, herein, we disclose the cobalt-catalyzed orthoselective  $C(sp^2)$ -H amidation of benzaldehydes with dioxazolones as an easily accessible amidating reagent<sup>[11b,20]</sup> using Cp\*Co(III) as catalyst.

We began our optimization studies by treating benzaldehyde **1a** with dioxazolones **2a** (1.2 equiv.) in the presence of Cp\*Co(CO)I<sub>2</sub> (10 mol%) along with AgSbF<sub>6</sub> (30 mol%) and aniline (20 mol%) under argon in 2,2,2-trifluoroethanol (TFE) (0.2 M) at 80 °C for 24 h. The expected ortho-amidated product **3aa** was isolated in 45% isolated yield (entry 1, Table 1). Next, we screened various amines as the transient directing group; among them aniline was found to be more suitable for the high-product formation (see ESI, Table-S2). Changing the solvent to 1,2-dichloroethane (DCE) and elevating the temperature to 100 °C led to the formation of **3aa** in 56% yield (entries 2-3). Solvents such as acetonitrile, *t*-AmOH were also examined but none of them worked better than DCE (entries 4-5).

#### Table 1. Reaction optimization and control experiments<sup>a</sup>

			i) [Co] - 10 mol % AgSbF <sub>6</sub> - 30 mol % PhNH <sub>2</sub> - 20 mol % additive - 20 mol %		NH NH	
	N	S ii) H	olvent (1 mL <sup>+</sup> work up	.), T °C, Time	0	$\bigcirc$
1a	2a				3aa	
Entry	Catalyst	Solvent	Temp. (°C)	Additive	Time (h)	Yield (%) <sup>b</sup>
1	Cp*Co(CO)I2	TFE	80	-	24	45
2	Cp*Co(CO)I2	DCE	80	-	24	48
3	Cp*Co(CO)I <sub>2</sub>	DCE	100	-	24	56
4	Cp*Co(CO)I2	CH <sub>3</sub> CN	100	-	24	NR
5	Cp*Co(CO)I <sub>2</sub>	t- AmOH	100	-	24	26
6	$[Cp*CoI_2]_2$	DCE	100	-	24	NR
7	CoCl <sub>2</sub> .6H <sub>2</sub> O	TFE	80	-	24	NR
8	Co(acac) <sub>2</sub>	TFE	80	-	24	NR
9	Cp*Co(CO)I2	DCE	100	NaOPiv	24	59
10	Cp*Co(CO)I2	DCE	100	PhCOONa	24	20
11	Cp*Co(CO)I <sub>2</sub>	DCE	100	NaOAc	24	10
12	Cp*Co(CO)I <sub>2</sub>	DCE	100	TFA	24	25
13	Cp*Co(CO)I <sub>2</sub>	DCE	100	CH <sub>3</sub> COOH	24	35
14	Cp*Co(CO)I2	DCE	120	NaOPiv	24	61
15 <sup>c</sup>	Cp*Co(CO)I2	DCE	120	NaOPiv	24	69
16 <sup>d</sup>	Cp*Co(CO)I2	DCE	120	NaOPiv	24	74
$17^d$	Cp*Co(CO)I <sub>2</sub>	DCE	120	NaOPiv	12	91
$18^{d,e}$	Cp*Co(CO)I <sub>2</sub>	DCE	120	NaOPiv	12	38
$19^{d,e}$	Cp*Co(CO)I <sub>2</sub>	DCE	120	NaOPiv	24	38
20 <sup>f</sup>	Cp*Co(CO)I <sub>2</sub>	DCE	120	NaOPiv	12	51
21 <sup>g</sup>	Cp*Co(CO)I2	DCE	100	-	24	NR

<sup>*a*</sup> Reaction conditions: benzaldehyde (**1a**, 0.20 mmol), aniline (20 mol%), catalyst (10 mol%), AgSbF<sub>6</sub> (30 mol%), 3-phenyl-1,4,2-dioxazol-5-one (**2a**, 1.2 equiv.), additive (20 mol%), solvent (1.0 mL), heated at given temperature under Argon atmosphere, hydrolyzed the reaction mixture with 3 N HCl. <sup>*b*</sup>Isolated yield. <sup>*c*</sup>Aniline (40 mol%). <sup>*d*</sup>Aniline (60 mol%). <sup>*e*</sup>Catalyst (5 mol%). <sup>*f*</sup>AgSbF<sub>6</sub> (20 mol%). <sup>*g*</sup>Without aniline.

Other cobalt precursors did not afford the amidated product, however no product formation observed with Cp\*CoI<sub>2</sub> dimer; this is unexpected and unexplainable at this stage (entries 6-8). In order to improve the efficiency of the product formation, a series of carboxylate additives such as NaOPiv, PhCO<sub>2</sub>Na, NaOAc were tested and among them NaOPiv offered satisfactory yield (entries 9-11). Acid additives such as trifluoroacetic acid (TFA) and CH<sub>3</sub>COOH were proved to be inefficient (entries 12-13). Increasing the temperature up to 120 °C could offer the amidated product in 61% yield (entry 14). Excellent yield of **3aa** was obtained when the loading of aniline increased to 60 mol% and the reaction time was reduced to 12 h (entries 15-17, for more details see ESI). Further decreasing of the loading of the catalyst as well as silver salt led to reduction in the isolated yield (entry 18-20, Table 1). No product formation occurred when aniline was not employed as transient directing group (entry 21). Further, control experiments showed that catalyst, AgSbF<sub>6</sub> and additive are important to obtain the expected *ortho*amidated product in high yield (see ESI, Table-S1).



Scheme 2. Reaction Scope.<sup>*a*</sup>

<sup>*a*</sup> Reaction conditions: benzaldehyde (**1a-1s**, 0.20 mmol), dioxazolone (**2**, 1.2 equiv), aniline (60 mol%), Cp\*Co(CO)I<sub>2</sub> (10 mol%), AgSbF<sub>6</sub> (30 mol%) and NaOPiv (20 mol%) in DCE at 120 °C for 12 h under argon atmosphere. <sup>*b*</sup>Isolated yield. <sup>*c*</sup>3-(trifluoromethyl)aniline (60 mol%).

With the optimized reaction conditions in hand, *ortho*-amidation was applied to various aldehydes (Scheme 2). In general, a wide range of benzaldehydes was employed under optimized reaction conditions. Delightedly, various electronwithdrawing groups and electron-donating groups on

benzaldehydes afforded desired amidated products in good to excellent yields. To begin with, halogens at ortho- and para-positions worked well and expected products were isolated in excellent yields (Scheme 2a, **3ba-3fa**). Next, with trifluoromethyl group at meta position, C-H activation occurred selectively at less hindered side but a very low yield of 23% was observed, possibly due to the electron deficient orthoposition, but when 3-(trifluoromethyl)aniline was used as TDG in the place of aniline then improved yield of 42% (3ga) was obtained. It is noteworthy that nitro group at ortho-position, which appears to be problematic in C-H activations offered excellent yield (Scheme 1, 3ha). Under the standard conditions, alkyl groups at ortho-, meta- and para-positions afforded good yields (Scheme 1, 3ia-3la). Methoxy group at ortho- and para-positions gave lower yields but improved yields were obtained when 3-(trifluoromethyl)aniline was replaced by aniline (3ma-3na). Delightedly, sensitive yet useful group such as allylphenyl ethers afforded **30a** in 66% yield. Similarly, 2-phenyl, 1-naphthyl and 2-naphthyl benzaldehydes worked well under the optimized conditions (3pa-3ra). Finally, we also tested 3,4dichlorobenzaldehyde **1s**, which afforded the amidated product in satisfactory yield of 68% (3sa). We next investigated the generality of the dioxazolones using benzaldehyde **1a** as coupling partner (Scheme 2b). Aryl dioxazolones with alkyl and methoxy substitution (2b-2d) worked well to afford the amidated products in good yields (3ab-**3ad**). Furthermore, 3-(naphthalen-1-yl)-1,4,2dioxazol-5-one afforded lower yield, but with 3-(trifluoromethyl)aniline on the place of aniline gave good yield of 74% (3ae). It is noteworthy that the benzyl, pentyl and cyclohexyl dioxazolones performed well to afford desired products in excellent yields (3af-3ah). Finally, we also tested the heteroaromatic thiophene derived dioxazolone 3-(thiophen-2-yl)-1,4,2-dioxazol-5-one, which also worked well and afforded 3ai in 61% yield.

To elucidate the reaction mechanism, we performed a series of control experiments (See ESI for more details). The kinetic isotope effect (KIE) value was found to be 1.7, which indicates the possible involvement of C-H activation in rate-limiting step of the catalytic cycle (ESI, Va). Additionally, a competitive reaction of electron-releasing 4methylbenzaldehyde (1k) and electron-withdrawing phenyl-1,4,2-4-chlorobenzaldehyde (1e) with dioxazol-5-one (2a) furnished the amidated products in a ratio of 2:1, suggesting that reaction might proceed through electrophilic C-H bond activation. (ESI, Vb). We further synthesized the aldimine (4) of benzaldehyde and aniline, which worked well under standard conditions confirming that the aniline acts as transient directing group (ESI, Vc).

To demonstrate the synthetic utility of *ortho*amidated benzaldehydes, **3aa** was transformed to valuable products (**5-8**) as described in Scheme 3.



Scheme 3. Synthetic applications and transformations.

Keeping in mind the importance of olefins in organia synthesis, aldehydic group was transformed to the alkene with methyltriphenylphosphonium iodide, affording **5** in 91% yield.<sup>[7e]</sup> An efficient intermolecular cyclization of 3aa with aq. NH<sub>3</sub> in isopropanol solvent at 90 °C afforded 2phenylquinazoline **6** in 79% yield.<sup>[21]</sup> Next, Co<sup>II</sup>/TBHP system converted 3aa to benzoxazin-4one derivative 7 in 80% yield via intermolecular cyclization.<sup>[22]</sup> Finally, quinolone derivative 8 was synthesized using dimethyl acetylenedicarboxylate as a coupling partner.<sup>[23]</sup>



Scheme 4. Plausible mechanism.

Based on literature reports<sup>[7a,c-d,10-11,13,15-16]</sup> and our preliminary control experiments, we proposed a plausible reaction mechanism (Scheme 4). Initially, the cationic Co<sup>III</sup> complex **A** can undergo initial ligand exchange with in situ generated aldimines from benzaldehyde **1a** and aniline to give complex **B**. Next, carboxylate-assisted concerted metalation– deprotonation afforded cobaltacycle **C**. Then, the coordination of dioxazolones to the cobalt center of the intermediate **C**, followed by CO<sub>2</sub> extrusion would lead to the Co-nitrenoid species **E**. The formation of a new C-N bond by migratory insertion of nitrenoid species between Co-C bond would lead to six membered cobaltacycle **F**. Finally, protodemetalation will regenerate the active catalyst and acidic hydrolysis of intermediate **G** will deliver the desired product **3aa**.

In conclusion, Cp\*Co(III)-catalyzed *ortho*-C(sp<sup>2</sup>)-H amidation of benzaldehydes has been achieved using dioxazolones as user friendly amidating reagent under transient directing group strategy. A key feature of this protocol involves readily available cobalt catalyst, ambient conditions, broad substrate scope as well as useful synthetic transformations of amidated benzaldehydes. Further applications and other mechanistic studies are currently under investigation in our laboratory.

### **Experimental Section**

General Procedure for the *o*-Amidation of Aryl Aldehyde: An oven-dried Schlenk tube was charged with a Teflon coated magnetic stir bar; under argon atmosphere was added aryl aldehyde (0.20 mmol, 1.0 equiv.), Aniline (0.12 mmol, 60 mol%), Cp\*Co(CO)I<sub>2</sub> (9.5 mg, 0.02 mmol, 10 mol%), silver hexafluoroantimonate (AgSbF<sub>6</sub>) (20 mg, 0.06 mmol, 30 mol%), dioxazolone derivative (0.24 mmol, 1.2 equiv.) and sodium pivalate (5 mg, 0.04 mmol, 20 mol%) followed by 1,2-dichloroethane (DCE) (1 mL).The closed Schlenk tube was placed in preheated oil bath at 120 °C for 12 hours. After 12 h the reaction mixture was allowed to cool to room temperature. The reaction mixture was filtered through a small silica pad, worked up with 3 N HCl, and extracted with ethyl acetate (2 x 10 mL). The organic layer was washed with brine solution and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. Removal of organic solvent followed by column chromatography (EtOAc/Hexane) on silica gel afforded the amidated product.

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## UPDATE

Cp\*Co(III)-Catalyzed *o*-Amidation of Benzaldehydes with Dioxazolones Using Transient Directing Group Strategy

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