Rh-catalyzed Transient Directing Group Promoted C–H Amidation of Benzaldehydes Utilizing Dioxazolones

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Transition-metal catalyzed C–H functionalization of benzaldehydes is of great interest in organic synthesis. Herein, we developed a transient directing group assisted amidation of benzaldehydes catalyzed by rhodium catalyst. With the employment of 10 mol% of 4-trifluoromethyl aniline, the in situ generated imine groups as the directing group efficiently enable this transformation. By using this protocol, a wide range of benzaldehydes were efficiently converted into the corresponding *N*-(2-formylphenyl)benzamides utilizing dioxazolones as the nitrogen source.

Keywords amidation, benzaldehydes, rhodium, C-H functionalization, transient directing group

Introduction

Benzaldehydes are important building blocks in natural products, materials and pharmaceuticals. Recently, transition-metal catalyzed C-H functionalization becomes an intriguing research topic in methodology.[1] The abundance and synthetic versatility of benzaldehydes make aldehyde-directed C−H functionalization an alluring area.[2,3] However, there were only limited reports in this field owning to the weak coordinating ability of an aldehyde group and its instability toward oxidation.[4]

To overcome the above limitations, an optional and promising approach is to introduce transient directing groups which could bind reversibly with substrates. In the traditional directing group assisted C-H bond functionalization, the directing groups could efficiently control the regioselectivity of C–H activation thus enabling regiospecific introduction of other groups. However, the installation of directing groups adds steps and the removal of such auxiliary groups was often challenging, which limit their application in organic synthesis.

Alternatively, a transient directing group strategy might enable the C–H bond functionalization without changing the functional groups of the substrates (Scheme 1, a). Lewis' group represented the pioneering example of selective *ortho* C-H bond alkylation utilizing ortho-metalated ruthenium complexes.[5] Jun and coworkers complete an elegant example by using 2-aminopyridine as external directing group for Rh-catalyzed C–H bond functionalization of aldehydes.[6] In the assistance of catalytic amount of phosphinite liga-

Scheme 1 Transient directing group promoted

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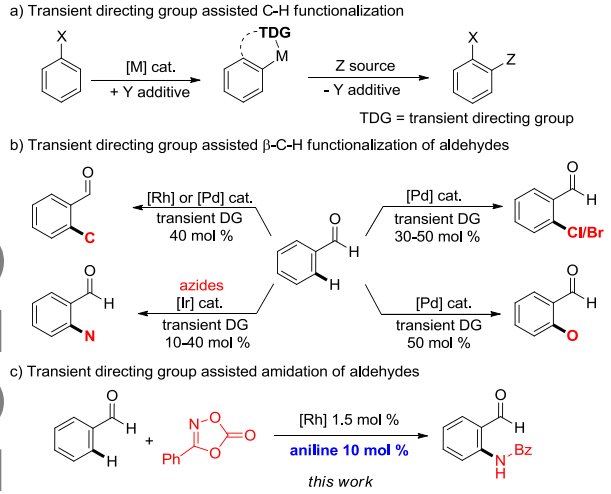
C-H functionalization of benzaldehydes.



ands, Bedford's group reported functionalization of C–H bonds in phenols and alcohols via reversible transesterification.[7] Dong and co-workers developed the C–H functionalization through reversible formation of enamines.[8] Yu and coworkers reported direct C–H arylation with the help of natural amino acid or 2-hydroxynicotinaldehyde as transient directing group.[9] Ge and co-workers reported transient directing group assisted site-selective C–H bond functionalization in the assistance of catalytic amount of glyoxylic acid or 3-aminopropanoic acid.[10] Very recently, the groups of Shi,[11] Murakami,[12] Bull,[13] Xu and Jin,[14] Zhang, Li and Yan,[15] Hu[16] independently developed transient directing group assisted Pd-catalyzed C-H olefination and arylation.

According to this concept, Csp^2–H functionalization of benzaldehydes also attracted considerable attentions using imine as transient directing group. Construction of C-C bond from *ortho* C-H bond of benzaldehydes was revealed by the groups of Seayad,[17] Yu,[18] Sorensen[19] and Wang[20] utilizing transient imine as directing group (Scheme 1, b). The chlorination, and bromination of benzaldehyde substrates was also realized by Yu and coworkers (Scheme 1, b).[18] Recently, Sorensen's group reported Pd(II) catalyzed transient directing groups promoted *ortho* C−H hydroxylation of benzaldehyde substrates.[21] Moreover, by using Ir-catalysis, the groups of Yu,[18] Shi,[22] Chen and He,[23] independently reported transient directing groups promoted C-N bond formation with azide reagents (Scheme 1, b). Very recently, C-H amidation utilizing nitrone as a traceless directing group was realized in constructing functionalized arylaldehydes.[24] According to our continued interest in nitrogenation chemistry for C-N bond formation,[25] we investigated the direct C-H amidation of benzaldehydes. Herein, we report a transient directing group assisted amidation of benzaldehydes catalyzed by rhodium catalyst for the synthesis of *N*-(2-formylphenyl)benzamides (Scheme 1, c). With the employment of 10 mol% of aniline, the in situ generated imine groups as the directing group efficiently enable this transformation.

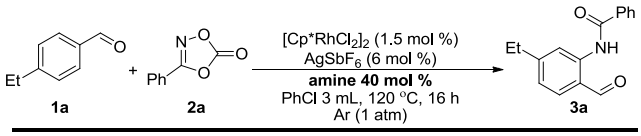
Experimental

$[Cp^*RhCl_2]_2$ (0.0045 mmol, 2.8 mg), $AgSbF_6$ (0.018 mmol, 6.2 mg), benzaldehydes **1** (0.3 mmol), 1,4,2-dioxazol-5-ones **2** (0.45 mmol) and 4-(trifluoromethyl)aniline (0.03 mmol 4.8 mg) were added to a 25 mL Schlenk tube with a magnetic bar under Ar. PhCl (1.5 mL) was added and then the mixture was stirred at 120 ℃ under Ar for 20 h. The solution was then washed with HCl (2 M, 10 mL), extracted with ethyl acetate and evaporated under vacuum. The crude reaction mixture was purified by column chromatography on silica gel to get the desired product.

Results and Discussion

Our initial investigation was carried out using 4-ethylbenzaldehyde (**1a**) and 3-phenyl-1,4,2-dioxazol-5-one (**2a**)[26,27g] in the presence of 1.5 mol % $[Cp^*RhCl_2]_2$ in PhCl for 16 h. Various amines were chosen to test the catalytic activity (Table 1). Interestingly, aniline (**A1**) worked well to produce the desired product **3a** in 62% yield. With 4-methoxyl substituted aniline (**A2**) as the cocatalyst, the yield slightly decreased to 59%. Among those anilines examined, 4-trifluoromethyl aniline (**A3**) was found to be the most effective one to afford the desired product **3a** in 80% yield (Table 2, entry 1). Moreover, alkyl amines such as cyclohexylamine (**A4**) and benzylamine (**A5**) were proved to be less effective. For transient directing groups from amides (**A6, A7**), only trace amount of **3a** was detected. Furthermore, the loading of 4-trifluoromethyl aniline was further screened. Notably, a yield of 74% could also be obtained with only 10 mol % of 4-trifluoromethyl aniline (Table 2, entry 3). Increasing the reaction concentration further improved the efficiency to 81% yield (Table 2, entry 4). Exclusion of either metal catalysts or aniline under standard condition inhibited the reaction (Table 2, entry 5-7). Those results demonstrate that imine might be an transient directing group for Rh-catalyzed C–H bond activation of benzaldehydes.

Table 1 Optimization of transient directing groups. [a]



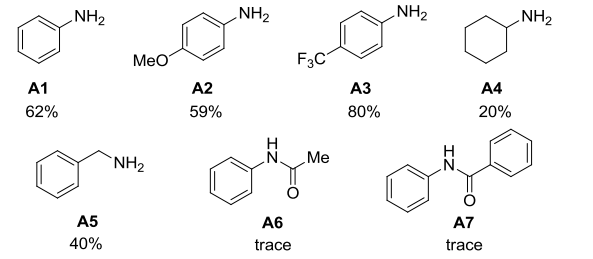
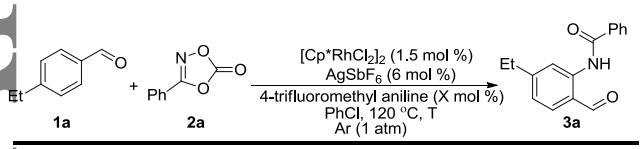


Table 2 Optimization of Reaction Parameters. [a]

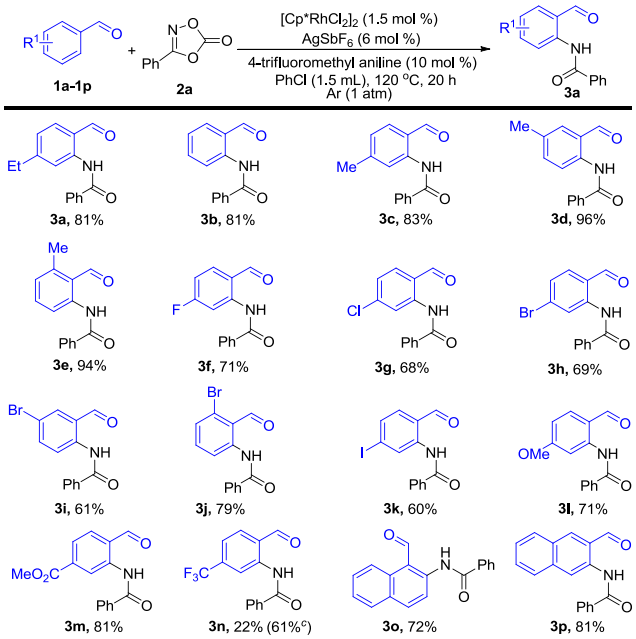


entry	[Rh]	[Ag]	aniline	PhCl	T	yield[b]
1	+	+	40 mol %	3 mL	16 h	80 %
2	+	+	20 mol %	3 mL	16 h	76 %
3	+	+	10 mol %	3 mL	16 h	74 %
4	+	+	10 mol %	1.5 mL	20 h	81 %
5	-	+	10 mol %	1.5 mL	20 h	0
6	+	-	10 mol %	1.5 mL	20 h	0
7	+	+	-	1.5 mL	20 h	0

[a] Reaction conditions: **1a** (0.3 mmol), **2a** (0.45 mmol), $[Cp^*RhCl_2]_2$ (1.5 mol %), $AgSbF_6$ (6 mol %), at 120 ℃ under Ar (1 atm). [b] Isolated yields.

With the optional conditions in hand, we explored the reaction scope by using various substituted benzaldehydes together with 3-phenyl-1,4,2-dioxazol-5-one as the reaction partner (Table 3). All the substrates worked well to produce the desired products in moderate to excellent yields. The *o*-, *m*- and *p*-substituted methyl benzaldehydes were then investigated under these conditions and gave the corresponding products **3c-3e** in 83-96% yields. It was found that the efficiency was not affected by the steric effect. Furthermore, the halogenated benzaldehydes produced the halo-substituted products **3f-3k** in 60-79% yields, which could be used for further coupling transformations as a coupling partner. With electron-donating substituent at the *para*-position, 4-methoxybenzaldehyde gave the desired product **3l** in 71% yields. For substrates with electron-withdrawing group such as CO_2Me, the desired product **3m** was formed in 81% yield. However, the reaction of benzaldehyde with CF_3 group did not work well (**3n**, 22%). With the increasing of 4-trifluoromethyl aniline catalyst to 20 mol %, the yield of **3n** was improved to 61%. Besides, 1-naphthaldehyde and 2-naphthaldehyde showed good reactivity giving the products **3o** and **3p** in good yields with excellent regioselectivity, respectively (72% and 81%).

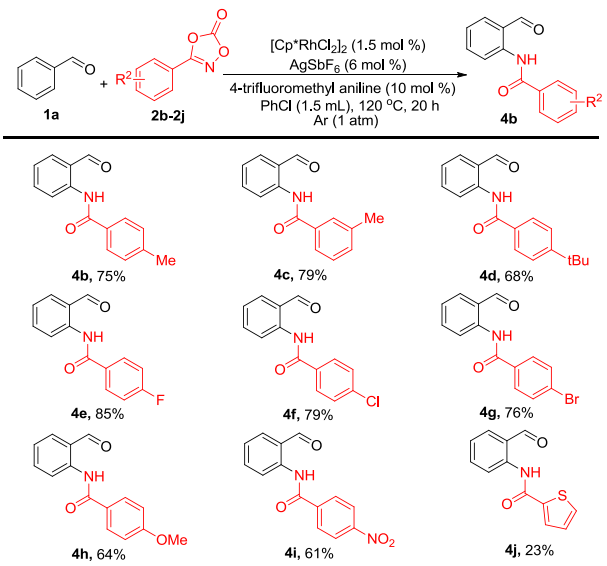
Table 3 The reactions with substituted benzaldehyde [a,b]



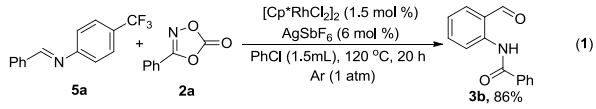
[a] Standard conditions: **1a** (0.3 mmol), **2a** (0.45 mmol), $[Cp^*RhCl_2]_2$ (1.5 mol %), $AgSbF_6$ (6 mol %), 4-trifluoromethyl aniline (10 mol %), PhCl (1.5 mL), stirred at 120 ℃ under Ar (1 atm) for 20 h. [b] Isolated yields. [c] 4-trifluoromethyl aniline (20 mol %) was used.

For the scope of dioxazolones, the applicability was further investigated using benzaldehyde **1a** as the partner reagent (Scheme 3). For alkyl substituted 3-Phenyl-1,4,2-dioxazol-5-one reagents, these reactions worked well to afford the amide products (**4b-4d**) in good yields. It is noteworthy that halogenated dioxazolones performed well to afford the corresponding amide products (**4e-4g**) in 76% - 85% yield. Furthermore, electron-donating and electron-withdrawing substituents worked well to afford **4h** and **4i** in 64% and 61% yields, respectively. Meanwhile, except for phenyl substituted 1,4,2-dioxazol-5-one reagent, the reaction with 3-(thiophen-2-yl)- 1,4,2-dioxazol-5-one as nitrogen source could also afford the corresponding thiophene ring product **4j** in 23% yield.

Table 4 Scope with respect to dioxazolones [a,b]

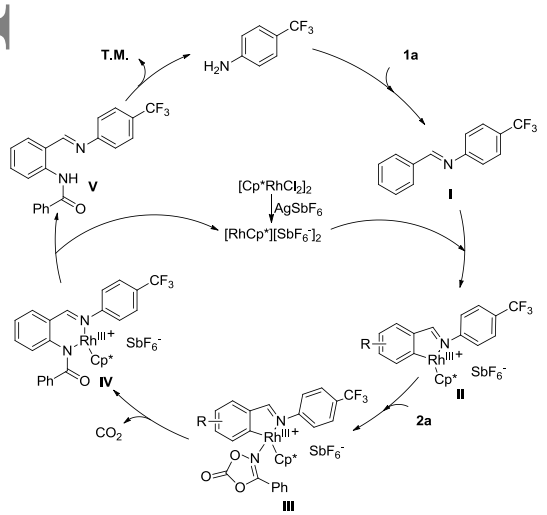


[a] Standard conditions: **1a** (0.3 mmol), **2a** (0.45 mmol), $[Cp^*RhCl_2]_2$ (1.5 mol %), $AgSbF_6$ (6 mol %), 4-trifluoromethyl aniline (10 mol %), PhCl (1.5 mL), stirred at 120 ℃ under Ar (1 atm) for 20 h. [b] Isolated yields.



(1)

To probe the reaction mechanism, imine substrate 5a was synthesized in advance and was employed under the standard reaction conditions without addition of 4-trifluoromethyl aniline (Eq. 1). The amide product 3b was obtained in 86% yield in this case, which indicates that imines could serve as the key intermediates in this transformation.



Scheme 2 Proposed Mechanism

Based on the results and previously reported studies,[27] a plausible mechanism was proposed (Scheme 4). Initially, condensation between 4-trifluoromethyl aniline and **1a** generates the intermediate **I**. Meanwhile, active catalyst cationic [Cp*RhIII] is generated with the assistance of $AgSbF_6$. The cationic catalyst would coordinate with the imine intermediate **I** and undergoes C−H bond activation to generate the rhodacyclic intermediate **II**. Coordination of 3-phenyl-1,4,2-dioxazol-5-one **2a** to rhodium(III) affords intermediate **III**. With the release of CO_2 and migratory insertion, Rh(III) amido species (**IV**) is then formed. Subsequently, the protonation of intermediate **IV** occurs to regenerate cationic Cp*Rh(III) catalyst and furnish the amidation process with **V** as product. Finally the hydrolysis of amide intermediate **V** occurs to form target molecule and release the aniline catalyst for a new catalytic cycle.

Conclusions

In conclusion, we have achieved an efficient Rh-catalyzed approach diverse *N*-(2-formylphenyl)- benzamides through the transient directing group assisted C-H activation. 4-Trifluoromethyl aniline was approved as a good co-catalyst in this case. This reaction complements β-C–H functionalization of benzaldehydes with a broad substrate scope and moderate to excellent yields. Further mechanistic studies and other applications are now under investigation.

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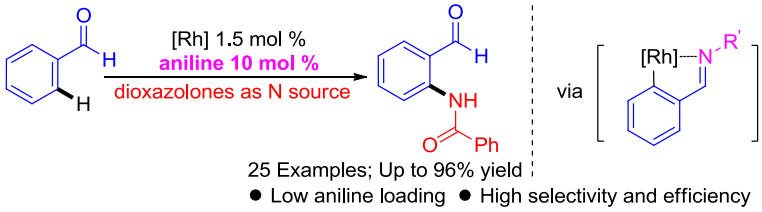
Rh-catalyzed Transient Directing Group Promoted C–H Amidation of Benzaldehydes Utilizing Dioxazolones



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Transition-metal catalyzed C–H functionalization of benzaldehydes is of great interest in organic synthesis. Herein, we developed a transient directing group assisted amidation of benzaldehydes catalyzed by rhodium catalyst. With the employment of 10 mol% of 4-trifluoromethyl aniline, the in situ generated imine groups as the directing group efficiently enable this transformation. By using this protocol, a wide range of benzaldehydes were efficiently converted into the corresponding *N*-(2-formylphenyl)benzamides utilizing dioxazolones as the nitrogen source.