EurJOC
European Journal of Organic Chemistry

Chemistry Europe
European Chemical Societies Publishing

Accepted Article

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To be cited as: *Eur. J. Org. Chem.* 10.1002/ejoc.202001505

Link to VoR: https://doi.org/10.1002/ejoc.202001505

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Thiocarbamate-directed Cp*Co(III)-Catalyzed Olefinic C-H Amidation: Facile Access to Enamines with High (*Z*)-Selectivity

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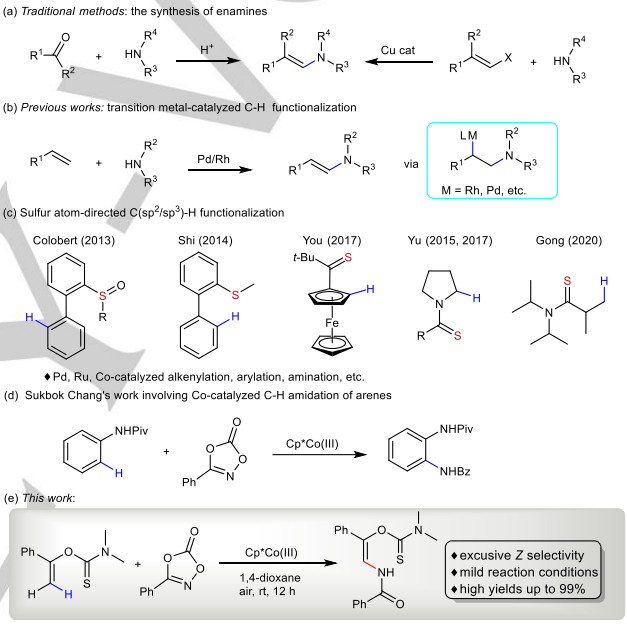
Abstract: A thiocarbamate-directed Cp*Co(III)-catalyzed C-H oxidative amidation of olefins is achieved to synthesize a series of enamines. The key feature of this protocol is the use of earth-abundant cobalt as catalyst and thiocarbamate as directing group, which provides an efficient and simple manner to synthesize enamines in good yields with high (*Z*)-selectivity. This reaction proceeds smoothly under very mild conditions (rt and air), and a wide range of functionalized alkenes as well as dioxazolones were compatible with the standard reaction conditions.

Enamines were usually served as useful precursors to synthesize nitrogen heterocycles, which extensively exist in biologicals, pharmaceuticals, and natural products.[1] Traditional methods for synthesizing enamines were largely depended on the cross-coupling of alkenyl halides with amines and the condensation of aldehydes or ketones with amines (Scheme 1a).[2] However, these methods generally occurred under harsh conditions with a narrow substrate scope. Furthermore, another obstacle is how to effectively control the selectivity of enamines,[3] and this is the main problem and challenge we are facing now.

Different from the traditional methods for synthesizing enamines, transition metal-catalyzed C-H functionalization[4] is highly explored due to the tremendous potential in atom-economy and high efficiency. Remarkable progress has been achieved by employing precious metals such as Pd, Ru, Rh (Scheme 1b).[5] But one significant limitation existing in these systems is that precious metals are few reserve and high cost. Conversely, the earth-abundant 3d transition metal cobalt catalysts have attracted considerable attention due to the low cost and unique activity compared to other counterparts.[6] But there are few examples to realize the Co-catalyzed olefinic selective C-H functionalization.[7] Therefore, it is highly desirable to develop an efficient and convenient strategy to construct C-N bond with high selectivity by using cobalt catalyst in current methodological research.

On the other hand, the directing group strategy that takes advantage of the coordination of chelating atom with transition metal for forging new C–C or C–X bonds seems to be an excellent choice.[8] In previous works, oxygen[9] and nitrogen[10] atoms were commonly used as the electron donors in directing groups, whereas utilizing sulfur atom as directing group in C-H activation was relatively rare for a long time.[11] This may be attributed to its strong-coordinating and potential poison with transition metals.[12] Consequently, employing the sulfur-chelating groups that coordinate with the metal to generate



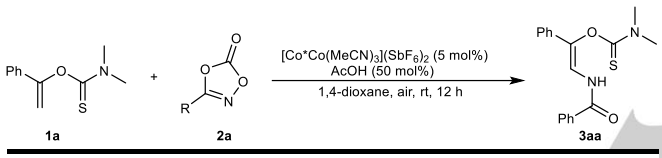
Scheme 1. Background and project synopsis.

resembled metal complex species to achieve olefinic amidation will be challenging. In 2013, Colobert,[13] Shi,[14] You[15] and other groups had achieved great progress on the sulfur-atom auxiliary C(sp^2)-H functionalization catalyzed by transition metal (Scheme 1c). In addition, Yu[16] and Gong[17] groups had published the thioamide-directed regioselective C(sp^3)-H activation and realized the enantioselectivity version. In 2015, a cobalt-catalyzed C-H amidation of arenes with doxazolones as new amidating reagents was originally reported by the Chang group (Scheme 1d). However, sulfur atom-directed olefinic C-H oxidative amidation has been rarely exploited. Enlightened by the previous work and our ongoing cobalt catalysis studies,[18] herein we report a thiocarbamate-directed Cp*Co(III) catalyzed olefinic selective C-H amidation. The sulfur atom of thiocarbamate plays a key role in the coordination of the transition metal. And this protocol possesses the advantages of exclusive *(Z)*-selectivity, a wide substrate scope and high isolated yields (Scheme 1e).

We commenced a preliminary investigation by using model substrates thiocarbamate **1a** and dioxazolone **2a** in the

presence of $[Cp^*Co(MeCN)_3](SbF_6)_2$ in DCE under air for 12 h (Table 1). Encouragingly, the reaction proceeded smoothly to afford the C-H amidated product **3aa** in 46% yield (entry 1, Table 1). It was noteworthy that the exclusive *Z*-isomers product **3aa** was observed. Next, subsequent investigation on solvents was conducted (Table S1), and 1,4-dioxane was found to be most effective as compare to other solvents (70% yield, entry 2). The yield decreased obviously (entry 3) when the $[Cp^*Co(MeCN)_3](SbF_6)_2$ was replaced by $Cp^*Co(CO)I_2$. Subsequently, various additives such as K_2CO_3, Na_2CO_3 and acids were evaluated (entries 4-9). It was found that the yield was remarkably improved to 83% with 0.5 equiv of AcOH as the additive (entry 9). Further investigation revealed that the yields decreased while increasing the temperature (Table S5). Surprisingly, when the loading of **2a** was decreased to 1.0 equivalent, an extremely high yield of 94% was observed at room temperature (entry 11). A control experiment confirmed that the reaction didn't occur in the absence of the cobalt catalysts (entry 12). Meanwhile, exchanging the S with O atom in the directing group gave no desired product, demonstrating the necessity of sulfur for this transformation.[19]

Table 1. Optimization of reaction conditions[a]

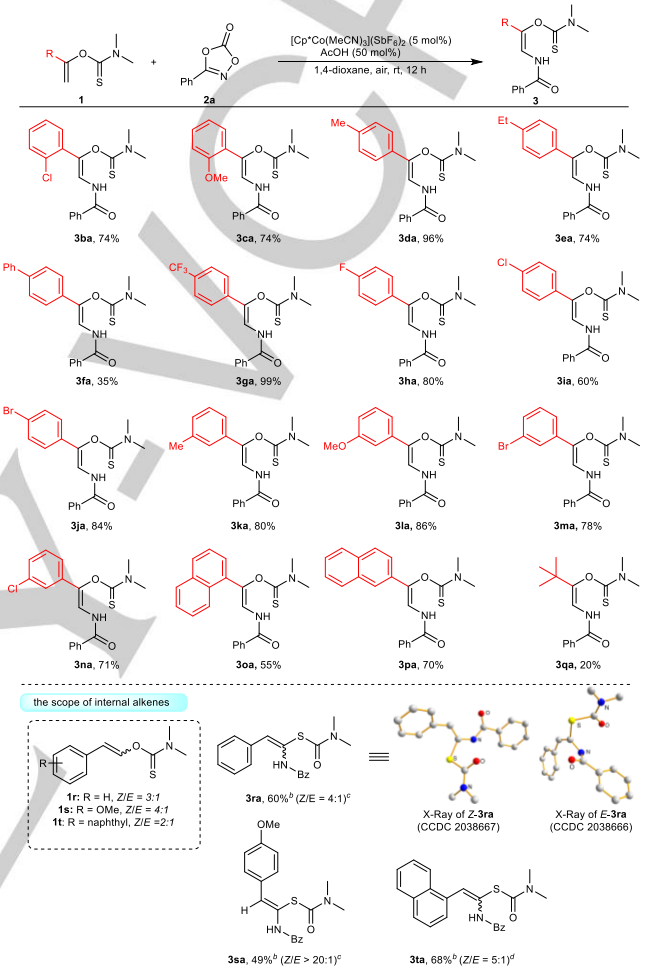


entry	catalyst	T (°C)	additive	yield (%)[a]
1[b]	$[Co^*Co(MeCN)_3](SbF_6)_2$	60	-	46
2	$[Co^*Co(MeCN)_3](SbF_6)_2$	60	-	70
3[c]	$Cp^*Co(CO)I_2$	60	$AgBF_4$	26
4	$[Co^*Co(MeCN)_3](SbF_6)_2$	60	K_2CO_3	72
5	$[Co^*Co(MeCN)_3](SbF_6)_2$	60	$NaHCO_3$	61
6	$[Co^*Co(MeCN)_3](SbF_6)_2$	60	1-AdCOOH	77
7	$[Co^*Co(MeCN)_3](SbF_6)_2$	60	$PhCO_2H$	73
8	$[Co^*Co(MeCN)_3](SbF_6)_2$	60	PivOH	74
9	$[Co^*Co(MeCN)_3](SbF_6)_2$	60	AcOH	83
10	$[Co^*Co(MeCN)_3](SbF_6)_2$	rt	AcOH	87
11[d]	$[Co^*Co(MeCN)_3](SbF_6)_2$	rt	AcOH	94
12	-	rt	AcOH	N.R.
13[e]	$[Co^*Co(MeCN)_3](SbF_6)_2$	rt	AcOH	82%

[a]Reaction conditions: **1a** (0.1 mmol), **2a** (1.5 equiv), $[Co^*Co(MeCN)_3](SbF_6)_2$ (5 mol%), 1,4-dioxane (0.5 mL), air atmosphere, rt, 12 h, isolated yield. [b]DCE as solvent. [c]$Cp^*Co(CO)I_2$ (5 mol%), $AgBF_4$ (10 mol%). [d]**2a** (1.0 equiv). [e]HFIP as solvent.

With the optimal reaction conditions in hand, we firstly examined the scope of **1** (Scheme 2). The substrates bearing EDG or EWG groups (-Cl, -OMe) at the *ortho*-position of the phenyl groups reacted smoothly, affording the corresponding products in good yields (**3ba**, **3ca**). Next, the thiocarbamate substrates with *para*-substituted groups on the aromatic ring were further investigated, both electron-donor (**3da**, **3ea**, **3fa**) and electron-receptor (**3ga**, **3ha**, **3ia**, **3ja**) ones were feasible with good yields (up to 99%). The diverse *meta*-substituted thiocarbamate substrates also participated in the reaction favorably to deliver the desired amidation products in excellent yields (**3ka**, **3la**, **3ma**, **3na**). Besides, when the phenyl was replaced by naphthyl groups, the desired products **3oa** and **3pa** were afforded in good yields (55%-70%). The aliphatic substrate **1q** also reacted well with dioxazolone to afford the desired **3qa** successfully. It should be noted that all the products were exclusive *Z*-isomers in this reaction, which indicated that this protocol possessed a characteristic of high selectivity.

Scheme 2. Cp*Co (III) catalyzed olefinic C-H amidation[a]



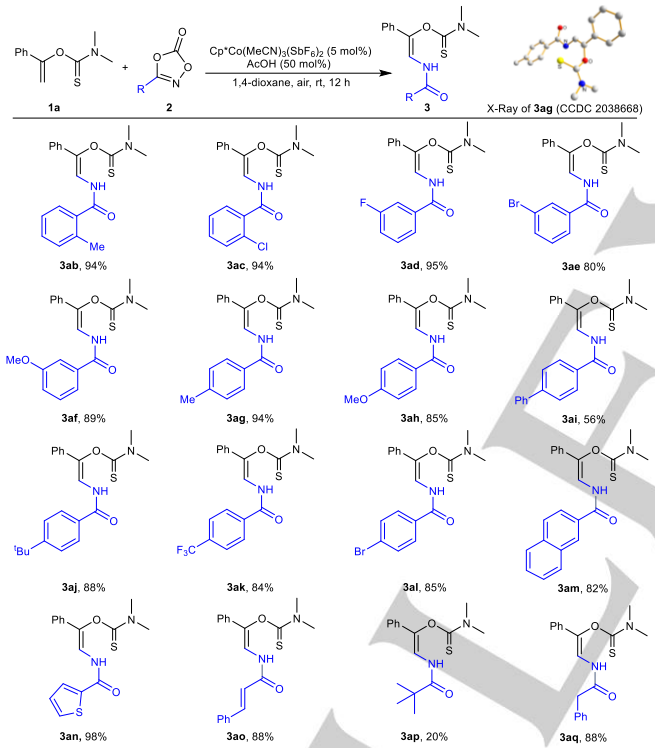
[a]Reaction conditions: **1** (0.2 mmol), **2a** (1.0 equiv), $[Co^*Co(MeCN)_3](SbF_6)_2$ (5 mol%), 1,4-dioxane (1 mL), air atmosphere, rt, 12 h, isolated yield. [b]**2a** (1.5 equiv), $[Cp^*Co(CO)I_2]$ (5 mol%), $AgBF_4$ (10 mol%), AcOH (1.0 eq), HFIP (1 mL), air atmosphere, 12 h, rt. [c]The *Z*/*E* ratio was determined by ^1H NMR of crude product mixture. [d]The *Z*/*E* ratio was determined by isolated yield.

Meanwhile, the substrate **1r** as internal alkene was performed to discuss the applicability of this method. Surprisingly, the amidation product **3ra** with oxygen and sulfur exchanged was observed under standard conditions, [20] albeit with a low yield (Table S9). When 1,4-dioxane was replaced by HFIP in the system (Table S9), there was an obvious yield enhancement of **3ra** (33%).[21] Further optimization on cobalt catalysts and additives was conducted (Tables S9-S16), and the yield of **3ra** was improved to 60% in the presence of $Cp^*Co(CO)I_2$ and $AgBF_4$ in HFIP. Next, several internal olefinic substrates were investigated. The *para*-methoxyl substituted substrate was well-tolerated and gave the O/S exchanged product **3sa** in 49% yield with high (*Z*)-selectivity. The naphthalene-substituted internal olefinic substrate **1t** was suitable for this transformation as well, giving the amidated product **3ta** in 68% yield with *Z*/*E* ratio of 5:1. And the *Z*/*E*-

isomers structures of **3ra** (*Z* isomer: CCDC 2038667; *E* isomer: CCDC 2038666) were further confirmed by X-ray crystallography analysis (Tables S18-S19).

Subsequently, the scope of dioxazolones **2** was evaluated and the results were listed in Scheme 3. Dioxazolones with electron-donating and -withdrawing groups at the *ortho*, *meta* positions of the phenyl groups were well tolerated. And the desired products **3ab**-**3af** were obtained in extremely high yields with excellent (*Z*)-selectivity. Additionally, *para*-phenyl-substituted dioxazolones also worked well, leading to **3ag**-**3al** in good yields (56%-94%). And the structure of **3ag** (CCDC 2038668) was further confirmed by X-ray crystallography analysis. Moreover, when the phenyl was replaced with a naphthalene or thiophene moiety (**3am**, **3an**), the reaction also proceeds smoothly (82% and 98%). Notably, the olefinic and aliphatic dioxazolones were compatible with good functional tolerance, affording the corresponding enamine products **3ao**-**3aq** in moderate to high yields.

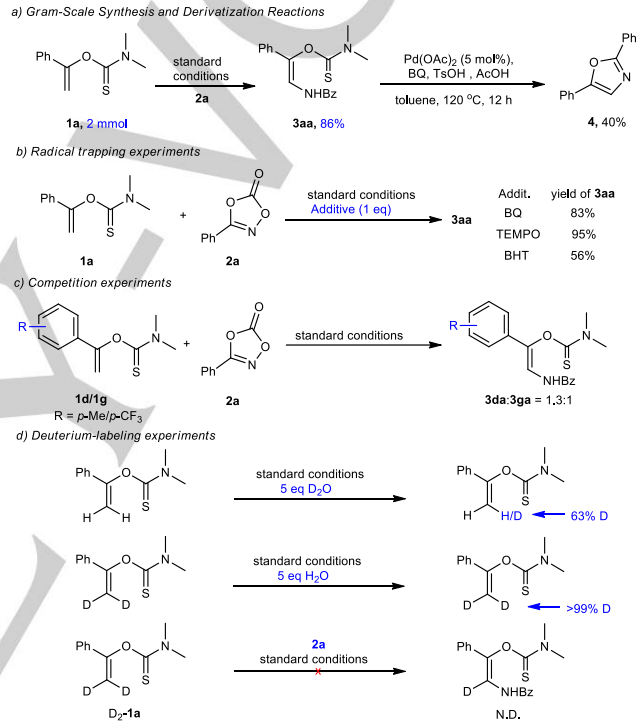
Scheme 3. Substrate scope of dioxazolones[a]



[a]Reaction conditions: **1a** (0.2 mmol), **2** (1.0 equiv), $[Co^*Co(MeCN)_3](SbF_6)_2$ (5 mol%), 1,4-dioxane (1 mL), air atmosphere, rt, 12 h, isolated yield.

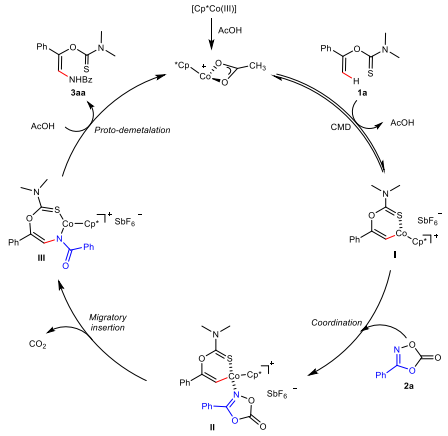
To demonstrate the synthetic utility of the Co-catalyzed amidation reaction, a large-scale reaction was performed with a high yield (86%). Notably, further derivatization of enamines products could be carried out smoothly. The biologically important 2,5-disubstituted oxazole could be synthesized by using $Pd(OAc)_2$ with BQ, TsOH, and AcOH in one-pot, which thus promoted the potential application value in synthesis. (Scheme 4a). In order to gain further insight into the mechanism, following experiments were performed. Upon addition of stoichiometric amounts of radical scavengers, the formation of **3aa** was not suppressed except for the BHT, which suggested that this process might not involve a free radical (Scheme 4b). Then, competitive experimental results demonstrate that the electron-rich substrates have better reactivity. (Scheme 4c). Furthermore, H/D exchange could be detected when **1a** was stirred under standard conditions with 5 eq D_2O, indicating that the C-H cleavage was reversible (Scheme 4d). However, when the deuterated D_2-**1a** was added to the model condition with 5 eq H_2O, the D/H exchange product was not observed according to the ^1H NMR analysis. Then we put the deuterated substrate D_2-**1a** and dioxazolone into the standard conditions, but it was found that the reaction could not react at all (Scheme 4d). This result indicates that the C−H bond cleavage may be involved in the rate-limiting step.

Scheme 4. Large scale and mechanistic experiments



Based on the above mechanistic experimental results, a plausible mechanism is proposed. First, the Cp*Co(III) undergoes ligand exchange with AcOH, followed by a thiocarbamate-assisted concerted-metalation-deprotonation (CMD)[22] to generate intermediate **I**. Then the nitrogen of dioxazolone coordinates with intermediate **I** to afford the Co(III) intermediate **II**. Subsequently, intermediate **II** undergoes migratory insertion and releases CO_2 to deliver intermediate **III**. Finally, demetalation of intermediate **III** affords the **3aa** and regenerates Co(III) catalyst for a new catalytic cycle.

In conclusion, an efficient Cp*Co(III)-catalyzed olefinic C-H oxidative amidation strategy using thiocarbamate as directing group to synthesize (*Z*)-selective enamines has been developed. The exclusive (*Z*)-selectivity, earth-abundant cobalt catalyst, excellent functional group tolerance and mild conditions make this reaction to be an attractive protocol for the construction of $C(sp^2)$−N bonds of olefins. This strategy also provides a simple and practical method to access structurally diverse enamine derivatives. Further applications in other related types of olefinic C−H functionalization are actively ongoing in our laboratory.



Scheme 5. Proposed mechanism

Acknowledgements

Here we would like to express our sincere thanks to the National Natural Science Foundation of China (21772179), the Program for Science & Technology Innovation Talents in Universities of Henan Province (19HASTIT038).

Keywords: C-H activation • cobalt catalysis • enamines • thiocarbamate • (Z)-selectivity

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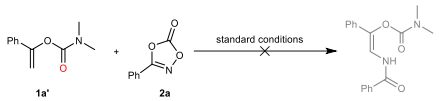

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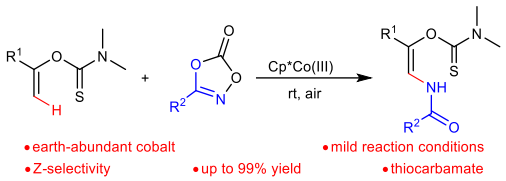

A Thiocarbamate-directed earth-abundant Cp*Co(III)-catalyzed C-H amidation of olefins to synthesize (*Z*)-selective enamines was explored. And the mild reaction conditions and a yield of up to 99% make the strategy more practical and attractive for constructing a new C-N bond.