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Rhodium(III)-Catalyzed Aldehyde C–H Activation and Functionalization with Dioxazolones: An Entry to Imide Synthesis

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Abstract: A rhodium(III)-based catalytic system has been used to develop a C–H bond activation of benzaldehyde derivatives and subsequent functionalization with dioxazolones in order to afford imides. The importance of the nature of the directing group to perform selectively the aldehydic C–H bond activation has been highlighted. The scope investigation showed that this transformation could be applied to various dioxazolones and many benzaldehyde derivatives as well as an acrolein derivative. Derivatization reactions of the imide products demonstrated the synthetic utility of this rhodium-catalyzed aldehydic C–H amidation.

Keywords: C–H activation; Rhodium; Imide; Aldehyde; Dioxazolone

Introduction

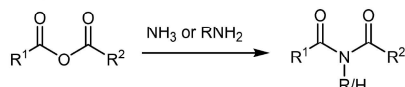
Imides represent an important category of organic products that can be encountered in biologically relevant compounds or used as organic synthons among many other applications.^[1] Various synthetic methodologies have been developed for the preparation of imides, such as the condensation of ammonia or primary amine with acid anhydride, the acylation or the α -oxidation of amides (Scheme 1),^[1] as well as several other strategies.^[2] Of note, only few synthetic routes are based on transition-metal (TM) catalysis, and are mainly limited to the preparation of cyclic imides.^[3]

During the last decade, tremendous advances have been achieved in TM-catalyzed Csp^2 -H bond activation and subsequent functionalization with a wide array of reagents allowing the installation of various functional groups.^[4] Taking advantage of these progresses, we devised a new transformation giving a straightforward access to imides (Scheme 1d). Starting from an aldehyde substrate bearing a directing group (DG) in order to drive the C–H activation, a metallacycle intermediate will be generated before to react with an appropriate functionalization reagent enabling the

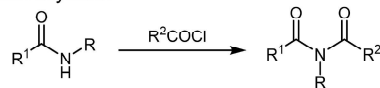
amidation.^[5] In the past two decades, the TM-catalyzed Csp^2 -H activation of arenes and alkenes have received a considerable attention. Despite the cleavage of Csp^2 -H aldehydic bonds is significantly more favorable than the one of Csp^2 -H arene bonds (BDE (benzaldehyde derivatives) = 360–370 kJ.mol⁻¹ vs. BDE (arenes) = 460–470 kJ.mol⁻¹), only few studies focused on the formyl C–H bond activation and most of them used salicylaldehyde as substrate.^[6,7] The main difficulty is that the formyl group can also act as a directing group^[8] and thus might trigger a competitive C–H activation at an unwanted position. Therefore, we anticipated that a strongly coordinating directing group, such as sulfides, could circumvent this issue allowing a chemoselective C–H activation.^[9]

Herein, we disclose the development of a new synthetic procedure giving a straightforward access to imides through a C–H bond activation using a sulfide as suitable directing group and followed by an amidation step with dioxazolones as functionalization reagents.

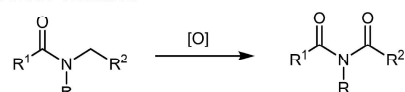
a) Condensation



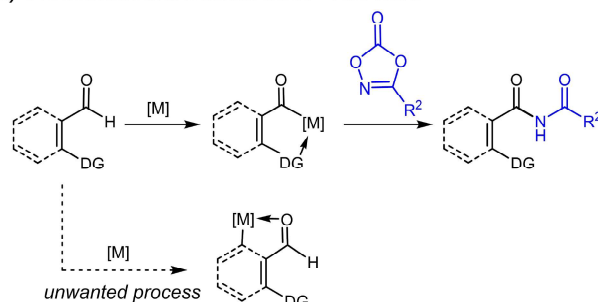
b) Amide acylation



c) Amide oxidation



d) C-H activation/functionalization - This work



Scheme 1. Synthetic routes to imides.

Results and Discussion

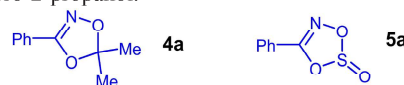
We have optimized the so-called C–H amidation using 2-thiomethylbenzaldehyde **1a** as benchmark substrate, phenyldioxazolone **2a** as functionalization reagent and determined that, through the appropriate choice of conditions, imide **3aa** could be isolated in high yields (Table 1). The catalytic system composed of [Cp*Rh–(III)Cl₂]₂, AgSbF₆ as halide abstractor and NaOAc as additive showed a good efficiency in DCE at 80 °C, since **3aa** was isolated in 83% yield after 20 h (entry 1). Importantly, no C–H activation/functionalization occurring on the aromatic pattern was detected, even when the quantity of **2a** was improved. This highlighted the selectivity of this transformation. Other functionalization reagents suitable for amidation^[5,10] have been tested but no product **3aa** could be detected with dioxazole **4a** and a significantly lower yield was obtained with dioxazol-5-thione **5a** (entries 2 and 3). No reaction occurred with a cobalt-based catalytic system (entry 4). A control experiment showed that the presence of silver salt is mandatory, but it can be replaced by NaBARF, albeit **3aa** was obtained in a lower yield (entries 5 and 6). The removal of sodium acetate or its replacement by potassium or cesium equivalent led to a slight decrease of efficiency (entries 7–9). Carboxylic acids can also be used as additives with comparable results (entries 10–12), but for practical reasons, NaOAc was used in the scope of investigation rather than acetic acid. The C–H amida-

Table 1. Optimization of the reaction conditions with benchmark substrates.^[a]

Entry	Variation from the “standard conditions”	Yield (%)
1	None	83
2	dioxazole 4a instead of 2a	— ^[b]
3	dioxazol-5-thione 5a instead of 2a	52
4	Cp*Co(CO)I ₂ (5 mol%) instead of [Cp*RhCl ₂] ₂	NR
5	no AgSbF ₆	NR
6	NaBARF instead of AgSbF ₆	40
7	No NaOAc	70
8	KOAc instead of NaOAc	55
9	CsOAc instead of NaOAc	60
10	AcOH instead of NaOAc	85
11	BzOH instead of NaOAc	52
12	PivOH instead of NaOAc	61
13	100 °C instead of 80 °C	81
14	60 °C instead of 80 °C	81
15	40 °C instead of 80 °C	42
16	1,4-dioxane instead of DCE	17
17	DME instead of DCE	16
18	Toluene instead of DCE	19
19	TFE instead of DCE	23
20	HFIP instead of DCE	52

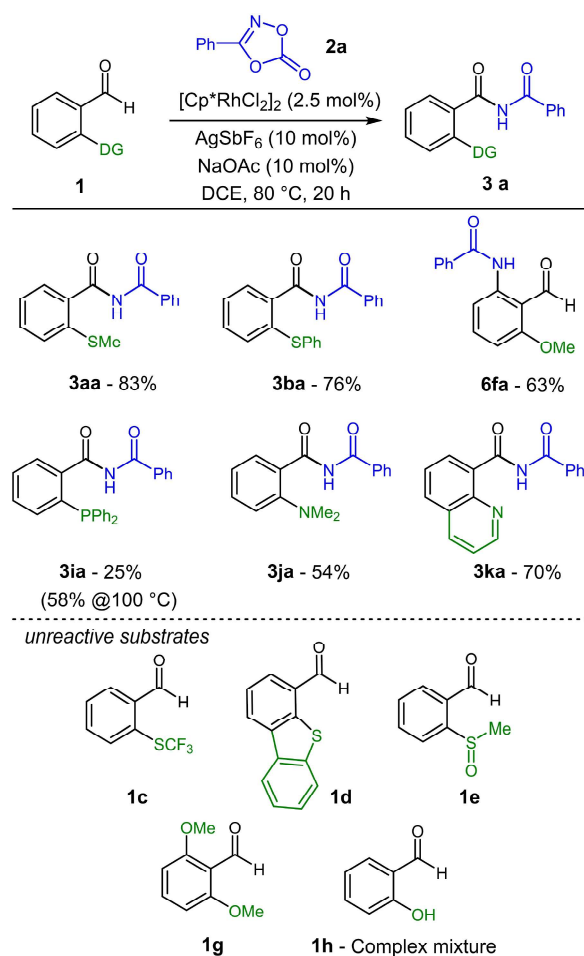
^[a] Reactions conditions: **1a** (76 mg, 0.5 mmol), **2a** (98 mg, 0.6 mmol, 1.2 equiv.), [Cp*RhCl₂]₂ (7.7 mg, 0.0125 mmol, 0.025 equiv.), AgSbF₆ (17 mg, 0.05 mmol, 10 mol%), NaOAc (4.2 mg, 0.05 mmol, 10 mol%), DCE (1 mL).

^[b] only degradation was observed. BARF = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate. DCE = dichloroethane. DME = dimethoxyethane. TFE = trifluoroethanol. HFIP = hexafluoro-2-propanol.



tion can be performed at a wide range of temperature (60–100 °C) without either noticeable yield variation or degradation processes (entries 13 and 14). At 40 °C, the reaction occurred but with significantly lower yield (42%, entry 15). Even if various solvents were compatible with the C–H amidation, DCE was, by far, the most effective (entries 16–20). Importantly, substrate **1a** was previously reported in the literature to perform rhodium-catalyzed hydroacylation reactions.^[11] In spite of some similarities, Rh(I)-based catalytic systems developed for hydroacylation were found ineffective for the formation of imides **3**.

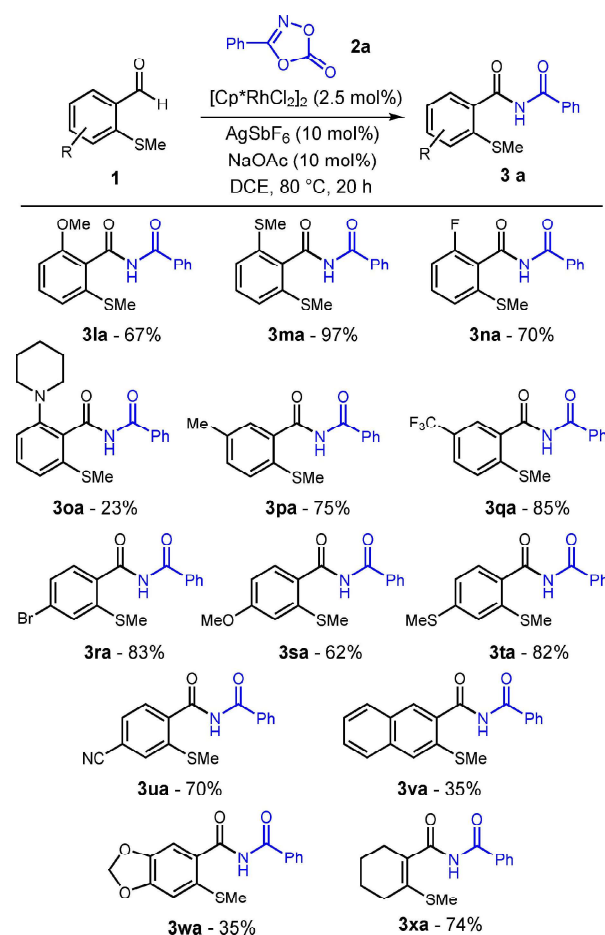
Having established the optimum reaction conditions, we further investigated the scope and the limitations of the aldehydic C–H bond activation/amidation starting with surveying directing groups as they represent a key parameter (Scheme 2). Whereas, thiomethyl and thiophenyl groups were found competent to drive the C–H activation, products **3aa** and **3ba** were isolated in 83% and 76% yield respectively, no reaction occurred with substrates **1c** and **1d**. We believe that the strong electron-withdrawing property of CF₃ decreases the coordinating ability of the sulfide **1c**. The lack of reactivity of **1d** is certainly due to the dibenzothiophene geometry which hampers the 5-membered metallacycle formation. Although sulfoxides are well known to be efficient directing groups in C–H activation processes,^[12] no C–H activation occurred for substrate **1e**. Using a methoxy group instead of methylsulfide, a C–H amidation could be achieved but in *ortho* position to the aldehyde giving rise to compound **6fa** in 63% yield. This result indicates that an aldehyde is a stronger directing group



Scheme 2. Investigation of the directing group influence.

than a methoxy group. This was the only example for which the C–H activation/functionalization process occurred on an aromatic C–H bond. We tried to force the aldehydic C–H bond activation using two methoxy groups, substrate **1g**, but no traces of the expected product could be observed. With salicylaldehyde **1h**, the formation of a complex mixture was obtained. The diphenylphosphino group exhibits suitable coordination properties allowing the formation of imide **3ia**, albeit in low yield but that could be improved to 58% by carrying out the reaction at 100 °C. Nitrogen containing directing groups could also be used to perform C–H amidation, either dimethylamino – **3ja** was isolated in 54% yield – or quinoline – 70% of **3ka** was obtained.

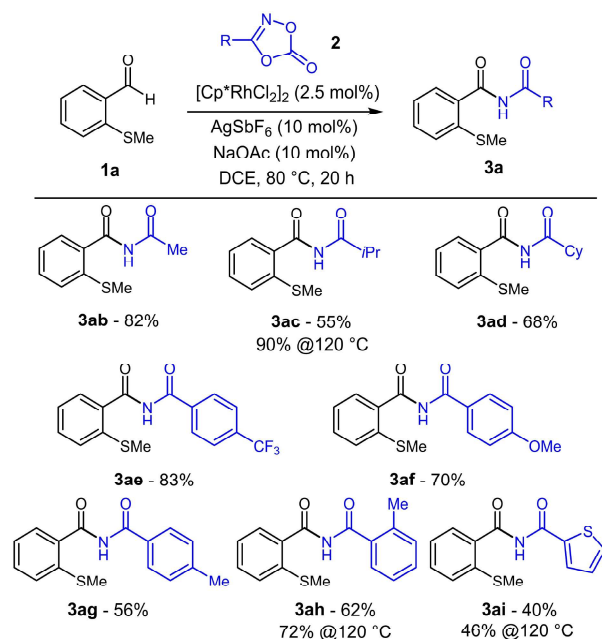
Next, the scope of the imide synthesis was investigated with respect to aldehyde partner (Scheme 3). Whereas the methoxy group was not a suitable directing group for aldehydic C–H bond activation (**1f** and **1g**, Scheme 2), substrate **1i** bearing one methoxy and one methylsulfide groups afforded the expected imide **3ia** with 67% yield. With two MeS



Scheme 3. Scope investigation with respect to aldehyde partner.

substituents in *ortho* positions, the C–H amidation was almost quantitative (**3ma**, 97%). This catalytic system was found tolerant to various substituents such as fluorine or amine in *ortho* position, even if for the latest the yield was low (**3oa**, 23%). In *meta* and *para* positions, electron-withdrawing or -donating groups were compatible and, overall, good yields were isolated (**3pa** to **3ua**). With naphthyl or 1,3-benzodioxole skeletons, lower yields were obtained, 35% for both **3va** and **3wa**. Interestingly, the C–H amidation was not limited to benzaldehyde derivatives, since cyclohexene containing product **3xa** was obtained in 74% yield. We then surveyed various substituted dioxazolones **2** and all of them were found effective as amidation reagent (Scheme 4). Alkyl-substituted dioxazolones **2b–d** gave the expected imides **3** in good yields. For the *isopropyl* substituted imide **3ac** at 80 °C, the yield was moderate but increasing the temperature to 120 °C, up to 90% yield could be reached. Aryl-substituted dioxazolones such as **2e** to **2h**, reacted well to afford the expected imides in good yields for electron-withdrawing and donating groups, and independently of the position of the substituent (*para* or *ortho*, **3ag** vs **3ah**). Heteroaromatic containing dioxazolones were also tolerated and the thiophene substituted imide **3ai** was obtained albeit in moderate 40% that could not be significantly improved by raising the reaction temperature.

We then surveyed various substituted dioxazolones **2** and all of them were found effective as amidation reagent (Scheme 4). Alkyl-substituted dioxazolones

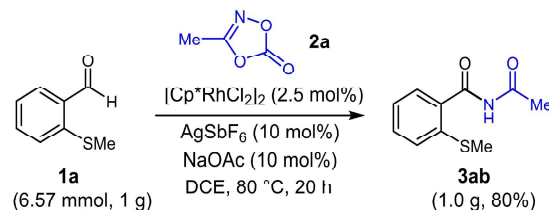


Scheme 4. Scope investigation with respect to dioxazolones.

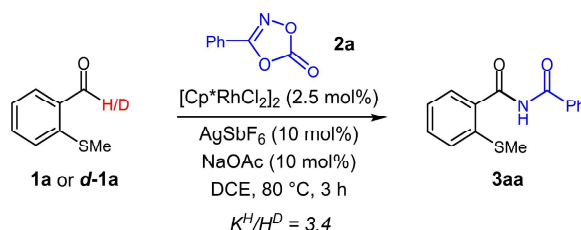
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In order to prove the synthetic robustness of the C–H amidation on gram-scale, a reaction was performed on 6.57 mmol. As depicted in Scheme 5, using the standard conditions with 2.5 mol% of [Cp*Rh-(III)Cl₂]₂ as catalyst loading, imide **3ab** was isolated in 80% yield.

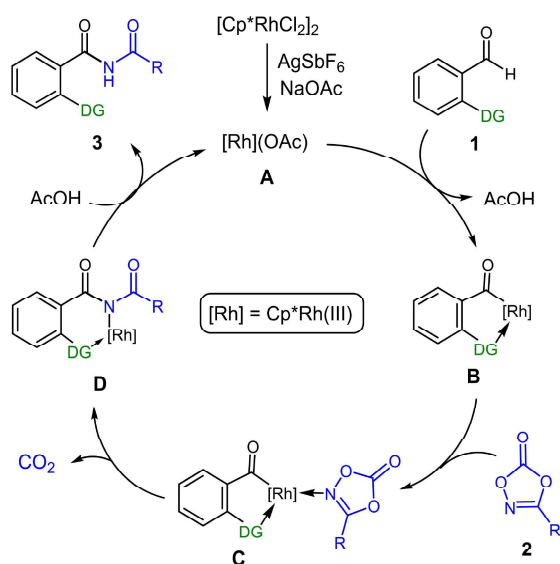
To gain insight into the mechanism, a kinetic isotope effect (KIE) study was conducted with parallel experiments using **1a** and its deuterium-labeled analogue **d-1a**. (Scheme 6).^[13] The kinetic isotopic value of (*k_H*/*k_D*) 3.4 indicated that the C–H bond cleavage would be involved in the rate-limiting step of the reaction. On the basis of this experiment and results from the literature,^[10d,e,14] a plausible mechanism is depicted in Scheme 7. The treatment of the dimer [RhCp*Cl₂]₂ with AgSbF₆ and NaOAc would generate the rhodium(III) intermediate **A** as catalytic active species. The C–H bond activation, the rate determining step, would occur through an acetate assisted concerted metalation/deprotonation (CMD) pathway to give rise to the rhodacycle **B** with acetic acid release. Then, the coordination of the nitrogen of dioxazolone **2** to the Rh



Scheme 5. Large scale experiment.



Scheme 6. Kinetic isotopic effect.



Scheme 7. Plausible mechanism.

center (intermediate **C**) is followed by a migratory insertion and the extrusion of CO_2 (intermediate **D**). Finally, the protodemetalation of intermediate **D** with acetic acid releases imide **3** and regenerates the catalytic active species **A**.

In order to demonstrate the synthetic usefulness of the rhodium-catalyzed C–H amidation of benzaldehyde derivatives, some transformations of imide **3ab** have been performed (Scheme 8). As sulfones and sulfoxides were not suitable directing groups to promote the aldehyde C–H activation, we converted the thiomethyl

into these functions. The treatment of **3ab** with 3 equivalents of *meta*-chloroperoxybenzoic acid (*m*-CPBA) gave the expected sulfone **7ab** in moderate yield (52%, Scheme 8a). Following the procedure described by Uemura,^[15] the enantioselective oxidation of **3ab** has been tested. Sulfoxide **8ab** was isolated in moderate yield (44%) and with a low enantiomeric excess (34% ee, Scheme 8b). Finally, the treatment of **3ab** with one equivalent of SelectfluorTM in acetonitrile at 80 °C for 16 h gave benzoisothiazol-3-one **9ab** with a good yield (Scheme 8a).^[16] Of note, benzoisothiazolinone skeletons are widely used in drug design due to their biological activities spanning from antimicrobial to antipsychotic.

Conclusion

In summary, we have developed a synthetic route to imides using a rhodium-catalyzed aldehydic C–H activation and functionalization with dioxazolones. This C–H amidation was found robust, scalable (up to gram scale) and tolerant toward various functional groups. Even if most of this study focused on methylsulfide as directing group, we demonstrated the importance of the directing group nature and proved that other functions can be successfully used such as phenylsulfide, phosphino and amino groups or quinoline. Interestingly, this transformation was not limited to benzaldehyde derivatives, since cyclohexene containing product **3xa** was obtained in 74% yield. Further applications related to this rhodium-catalyzed intermolecular transformation are currently under investigation in our laboratory.

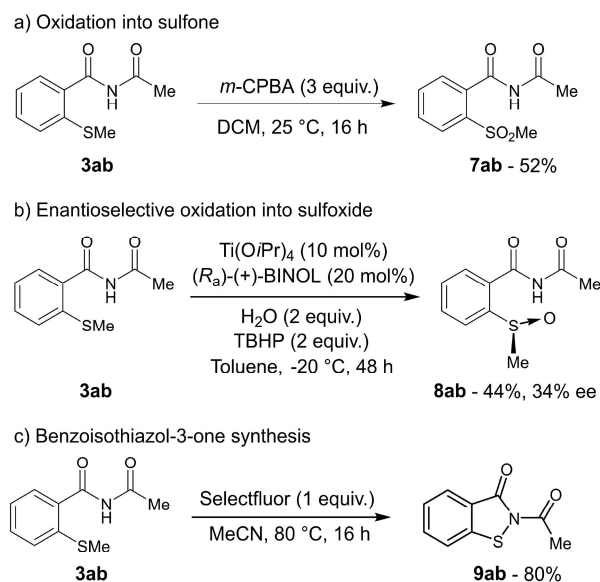
Experimental Section

General Procedure for the C–H Activation and Functionalization with Dioxazolone

In the glovebox, a 10 mL Schlenk tube was charged with $[\text{Cp}^*\text{RhCl}_2]_2$ (7.7 mg, 0.0125 mmol, 2.5 mol%) and AgSbF_6 (17 mg, 0.05 mmol, 10 mol%). Outside the glovebox, NaOAc (4.2 mg, 0.05 mmol, 10 mol%) and DCE (0.5 mL) were added and the resulting solution was stirred for 20 min. at 25 °C. Aldehyde **1** (0.05 mmol, 1 equiv.), dioxazolone **2** (0.6 mmol, 1.2 equiv.) and DCE (0.5 mL) were added in turn and the reaction mixture was stirred for another 10 minutes at 25 °C, before to heat it at 80 °C for 20 h. The reaction mixture was then cooled to room temperature, filtered through a Celite[®] bed, and the solvent was evaporated under reduced pressure. The crude product was purified by silica gel column chromatography to obtain the pure product.

Acknowledgements

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Scheme 8. Synthetic applications of compound **3ab**.

etry analyses (Spectropole, Fédération des Sciences Chimiques de Marseille), Arnaud Treuvey (Ecole Centrale Marseille) for IR spectroscopy and Dr. Muriel Albalat (iSm2, Aix Marseille Université) for chiral HPLC analysis.

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