OL Organic Letters

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Letter

Rhodium-Catalyzed C(sp^2)−H Alkoxycarbonylation/Acylation of Indolines with Anhydrides as a Carbonyl Source

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Cite This: *Org. Lett.* 2022, 24, 1141−1145

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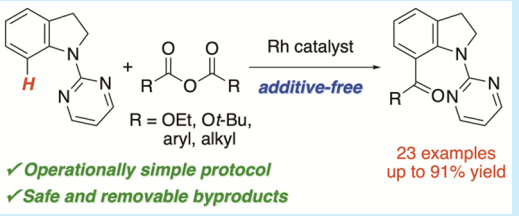
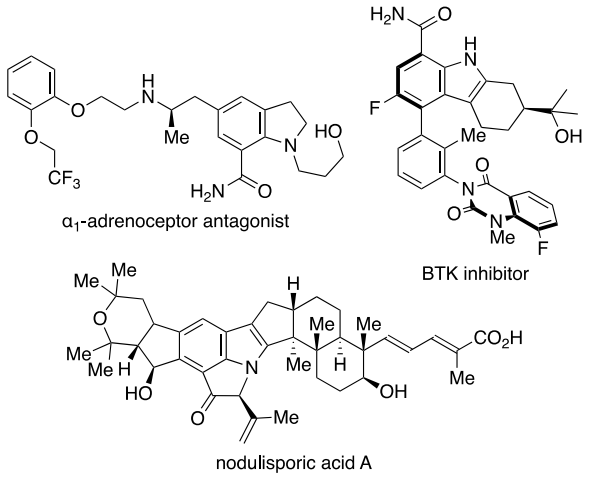
ABSTRACT: We developed rhodium-catalyzed alkoxylcarbonylation/acylation of indolines using anhydrides as a safe and easy-to-handle carbonyl source. This catalytic process represents an additive- and CO-free carbonylation, establishing a simple and straightforward protocol for synthesizing C7-carbonylated indolines. Notably, this reaction provides a successful example of C−H acylation of indolines that results in the formation of α-branched ketones, which were difficult to prepare by previously reported analogous catalytic reactions.



C7-Carbonylated indoles and their derivatives are an important class of biologically active compounds found in many natural products, pharmaceuticals, and agrochemicals (Scheme 1).[1] Common reactions to access C7-carbonylated indoles are palladium-catalyzed carbonylation of 7-haloindoles using carbon monoxide (CO),[2] Stille coupling using (1-ethoxyvinyl)stannane,[3] and nucleophilic addition of C7-metalated indoles to carbonyl donors.[4] Although these well-established protocols provide a reliable route to C7-carbonylated indoles, the prefunctionalization of starting materials makes the reaction less attractive. Moreover, these reactions usually require air- and moisture-sensitive organometallics and harmful reagents. Thus, the development of a simple and efficient procedure to access C7-carbonylated indoles is highly desirable.[5]

Scheme 1. Selected Examples of Biologically Active C7-Carbonylated Indoles and Their Derivatives



C(sp^2)−H functionalization of indolines is one of the most straightforward synthetic pathways for C7-functionalized indoles,[6,7] leading to the investigation of a variety of organic transformations, including carbonylation reactions. In 2002, Chatani et al. reported ruthenium-catalyzed carbonylation of indolines with CO and alkenes.[8] Subsequently, the oxidative amino- and alkoxycarbonylation of indolines under a CO atmosphere has been reported by other groups.[9] In contrast, C(sp^2)−H carbonylation of indolines using various carbonyl sources such as azodicarboxylates,[10] isocyanates,[11] α-keto acids,[12] aldehydes,[13] 1,2-diketones,[14] and glyoxalates[15] has been studied under CO-free conditions (Scheme 2a). Although these carbonyl sources are less toxic and easy to handle, the use of an external additive such as an oxidant and a base limits their application by producing a stoichiometric amount of unwanted byproducts. Consequently, this complicates the experimental procedure and narrows the substrate scope under oxidative or basic reaction conditions. Despite these critical problems, the additive-free C(sp^2)−H carbonylation of indolines is yet to be addressed. We hypothesized that the use of dicarbonates and carboxylic acid anhydrides as a carbonyl source may provide a solution for the additive-free C−H carbonylation of indolines.[16,17] Herein, we describe the additive-free C7-selective carbonylation of indolines using dialkyl dicarbonates and carboxylic acid anhydrides as a safe and easy-to-handle carbonyl source (Scheme 2b).

First, the ethoxycarbonylation of 1-(pyrimidin-2-yl)indoline (**1a**) as a model substrate was investigated (Table 1). An initial

Received: December 11, 2021
Published: January 31, 2022

https://doi.org/10.1021/acs.orglett.1c04195
Org. Lett. 2022, 24, 1141−1145

Scheme 2. C7-Carbonylation of Indolines under CO-Free Conditions

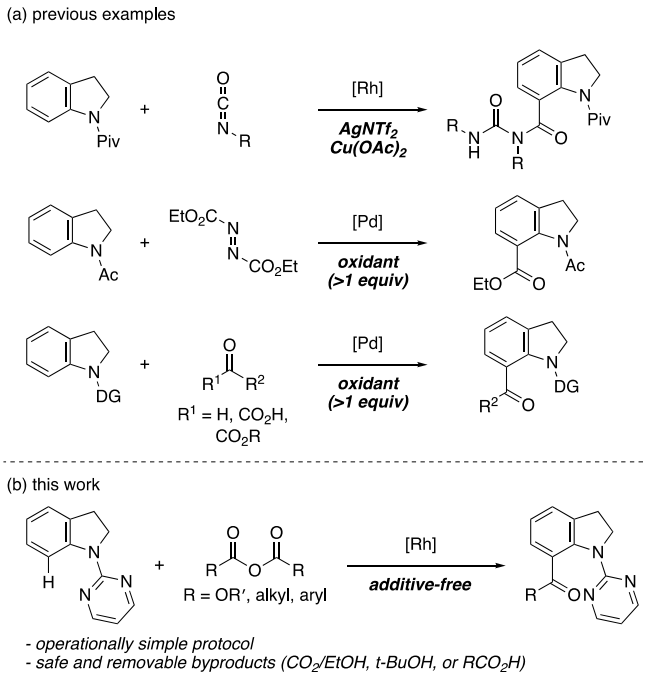
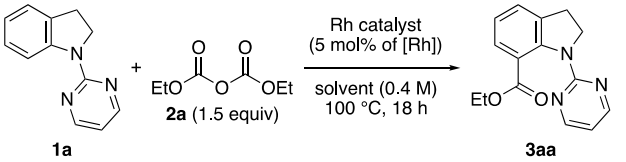


Table 1. Optimization of Reaction Conditions[a]



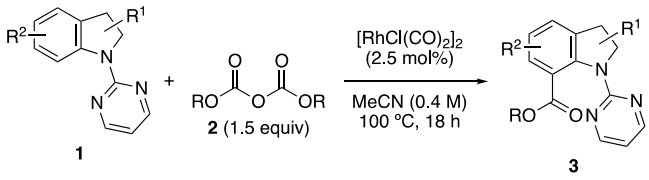
entry	Rh catalyst	solvent	yield[b] (%)
1	$[Rh(cod)_2]OTf$	1,4-dioxane	25
2	$[RhCl(cod)]_2$	1,4-dioxane	0
3	$RhCl(PPh_3)_3$	1,4-dioxane	0
4	$[RhCl(CO)_2]_2$	1,4-dioxane	86
5	$Rh(acac)(CO)_2$	1,4-dioxane	8
6	$[Cp^*RhCl_2]_2$	1,4-dioxane	0
7	$[Cp^*Rh(MeCN)_3](SbF_6)_2$	1,4-dioxane	0
8	$[RhCl(CO)_2]_2$	THF	83
9	$[RhCl(CO)_2]_2$	toluene	79
10	$[RhCl(CO)_2]_2$	DCE	91
11	$[RhCl(CO)_2]_2$	DMF	11
12	$[RhCl(CO)_2]_2$	MeCN	99 (88)
13	–	MeCN	0

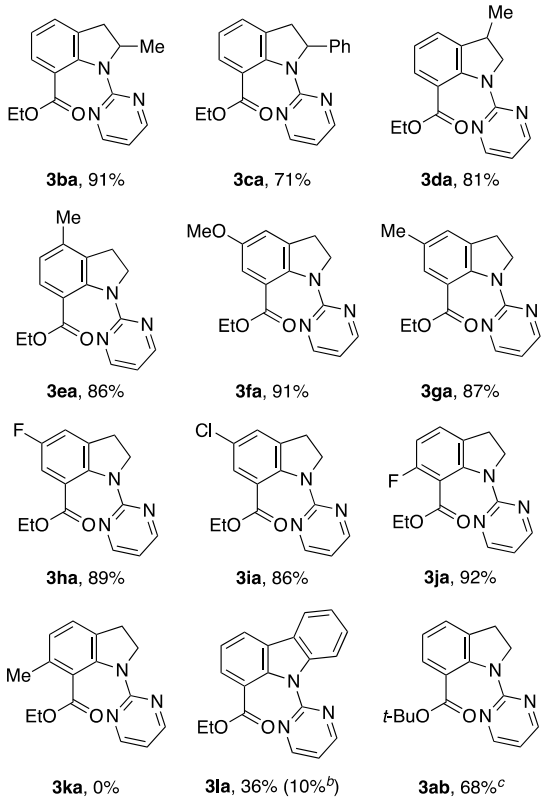
[a]Standard conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), and Rh catalyst (5 mol % of [Rh]) in the solvent (0.5 mL) at 100 °C for 18 h. [b]Yields were determined by ^1H NMR analysis using 1,2,4,5-tetramethylbenzene as an internal standard. Value in parentheses indicates isolated yield, which represents the average of two runs.

reaction was performed using diethyl dicarbonate (**2a**) as an ethoxycarbonyl source in the presence of $[Rh(cod)_2]OTf$. The reaction was conducted at 100 °C for 18 h and yielded the desired indoline-7-carboxylic acid ester **3aa** (entry 1). Based on these results, other rhodium catalysts such as $[RhCl(cod)]_2$, $RhCl(PPh_3)_3$, $[RhCl(CO)_2]_2$, $Rh(acac)(CO)_2$, $[Cp^*RhCl_2]_2$, and $[Cp^*Rh(MeCN)_3](SbF_6)_2$ were tested; $[RhCl(CO)_2]_2$ proved to be the optimal catalyst for this process (entries 2–7). Acetonitrile gave the best results among the solvents examined (entries 8–12). A control experiment revealed that the rhodium catalyst was essential for this reaction (entry 13).

With the optimized reaction conditions in hand, the additive-free alkoxycarbonylation using various indoline derivatives was investigated (Table 2). Indolines bearing a

Table 2. Substrate Scope of Indolines[a]





[a]Reaction conditions: **1** (0.2 mmol), **2** (0.3 mmol), and $[RhCl(CO)_2]_2$ (2.5 mol %) in MeCN (0.5 mL) at 100 °C for 18 h. Isolated yields represent the average of two runs. [b]Yield of the double alkoxycarbonylation product. [c]2.0 equiv of Boc_2O was used.

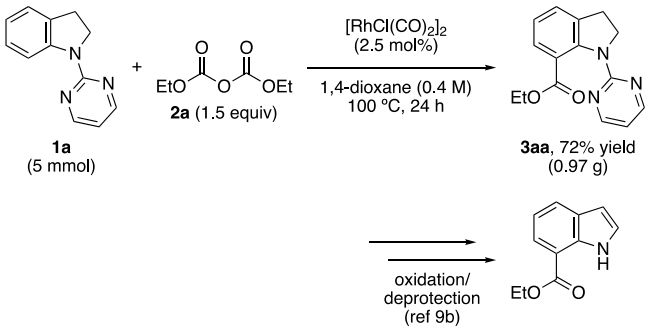
methyl and a phenyl group at the 2- or 3-position resulted in the formation of the desired indoline-7-carboxylic acid esters in good to high yields (**3ba–da**). Introducing a methyl group at the 4-position did not influence the reactivity (**3ea**). Indolines bearing electron-donating and electron-withdrawing substituents at the C5 position delivered the desired products in 86–91% yields (**3fa–ia**). Although a 6-fluoro indoline produced the desired product in high yield (**3ja**), the reaction of a 6-methyl indoline was sluggish presumably due to steric hindrance (**3ka**). A carbazole transformed into monoester **3la** in moderate yield (36%) along with a small amount (10%) of the double alkoxycarbonylation product. Gratifyingly, **1a** was coupled with di-*tert*-butyl dicarbonate to provide a good yield of **3ab**.

To demonstrate the efficacy of this transformation, the reaction of **1a** with **2a** in 1,4-dioxane[18] was performed on a 5

https://doi.org/10.1021/acs.orglett.1c04195
Org. Lett. 2022, 24, 1141–1145

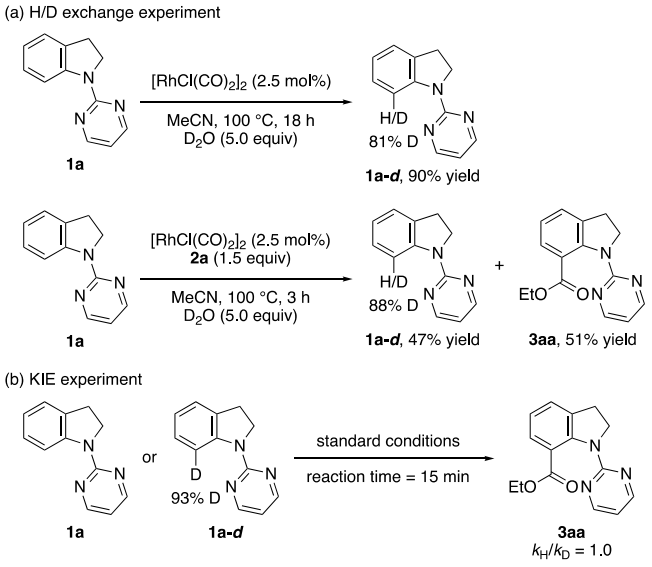
mmol scale (Scheme 3). The reaction proceeded smoothly to furnish the product **3aa** in good yield. The pyrimidyl directing group in the product could be removed in two steps.[9b]

Scheme 3. Large-Scale Reaction



A series of control experiments were performed to elucidate the reaction mechanism (Scheme 4). First, H/D exchange

Scheme 4. Control Experiments



experiments were conducted by subjecting **1a** with D_2O (5.0 equiv) to the standard reaction conditions in the presence or absence of diethyl dicarbonate (**2a**). A significant H/D scrambling was observed at the C7 position in both cases, which supports the reversibility of the C−H activation step. Furthermore, the kinetic isotope effect experiment (k_H/k_D = 1.0) revealed that the C−H bond cleavage might not be involved in the rate-determining step.

Based on the experimental results and previous reports in the literature,[16,19] the reaction mechanism for the additive-free alkoxycarbonylation is proposed (Figure 1). The C−O bond of dicarbonate **2** undergoes oxidative addition to rhodium(I) **A** to form a rhodium(III) intermediate **B** along with the extrusion of CO_2. The C7-selective C−H activation of indoline **1** by intermediate **B** provides six-membered rhodacycle **C**, which subsequently transforms into the desired product **3** via reductive elimination, and the active catalyst **A** is regenerated. However, another reaction mechanism involving initial oxidative addition of **1a** to **A** to form a rhodium(III) intermediate cannot be ruled out at this stage.[5,19b]

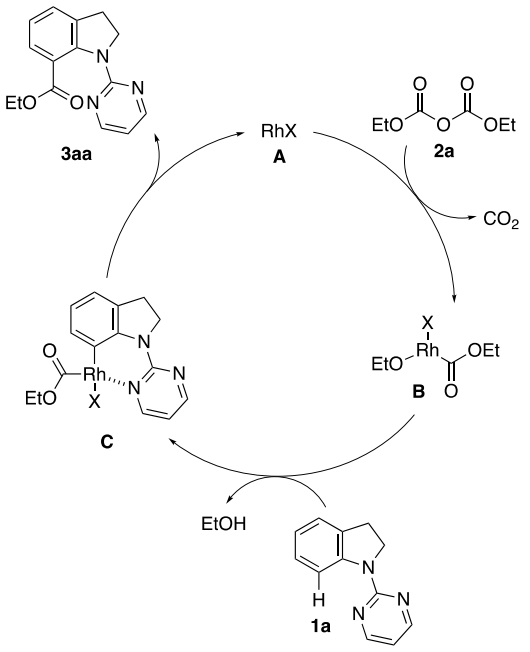


Figure 1. Proposed reaction mechanism for the rhodium-catalyzed additive-free alkoxycarbonylation of **1a** with **2a**.

Next, the C7-selective acylation of indolines using symmetrical carboxylic acid anhydrides was investigated. Although carboxylic acid anhydrides are known to be good acyl sources in the C3-selective Friedel−Crafts acylation of indoles,[20] the corresponding C7-acylation has scarcely been reported.[5] This is due to the decarbonylation process that occurs at high temperatures (>130 °C).[19] It was assumed that the C7-acylation of indolines using a carboxylic acid anhydride might proceed without decarbonylation if the optimized reaction conditions were applied. The reaction of indoline **1a** with acetic anhydride was initially examined under the optimal conditions for the alkoxycarbonylation. Unfortunately, the desired acylated indoline **5aa** was obtained in moderate yield along with a small amount of the methylation product, 7-methyl-1-(pyrimidin-2-yl)indoline, which formed via decarbonylation. Thus, the reaction conditions were slightly modified, and the optimal conditions for the acylation were identified as follows: 5 mol % of $[Rh(CO)_2Cl]_2$ in DMF at 80 °C for 24 h.[21]

Subsequently, the scope of acylation with various symmetrical carboxylic acid anhydrides was investigated (Table 3). Indoline **1a** was coupled with acetic anhydride and propionic anhydride to form the corresponding 7-acylated indolines **5aa** and **5ab**, respectively, in good yields. Notably, acylation of **1a** with cyclohexanecarboxylic anhydride provides the α-branched ketone **5ac** in 79% yield. This is a successful example of the direct catalytic alkacylation of indolines that yields α-branched ketones, for which efficient coupling reactions have not been reported to date.[12−15] Benzoic anhydrides and their derivatives also served as good coupling partners for this acylation. Benzoic anhydride reacted smoothly with **1a** to afford the desired product **5ad** in 78% yield. Methyl-substituted benzoic anhydrides rendered the desired products **5ae−ag** with good efficiency. Varying the electronic properties of benzoic anhydrides did not significantly affect the reactivity (**5ah−aj**). A heteroaroyl group was also introduced into **1a** to form

https://doi.org/10.1021/acs.orglett.1c04195
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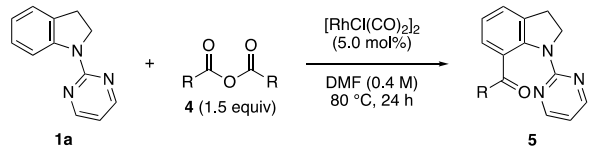
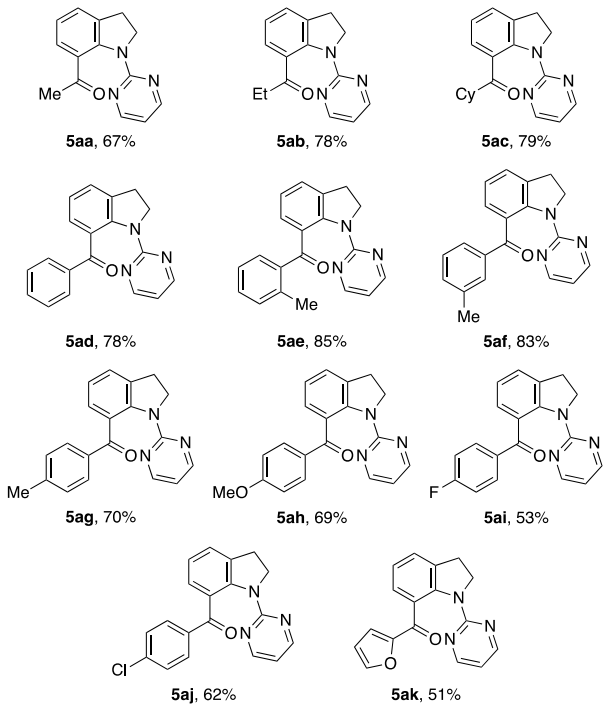
Table 3. Substrate Scope of Carboxylic Acid Anhydrides[a]





[a]Reaction conditions: **1a** (0.2 mmol), **4** (0.3 mmol), and $[RhCl(CO)_2]_2$ (5.0 mol %) in DMF (0.5 mL) at 80 °C for 24 h. Isolated yields represent the average of two runs.

5ak in good yield. Thus, our additive-free protocol was applied to a variety of anhydrides without any undesired side reactions.

In summary, we performed additive-free alkoxycarbonylation of indolines using dialkyl dicarbonates as the alkoxycarbonyl source. Furthermore, this additive-free protocol was applied to the acylation of indolines with a variety of aliphatic and aromatic carboxylic acid anhydrides. Unlike previously reported catalytic reactions, our reaction system achieved the formation of α-branched ketones via the acylation of indolines. We believe that these findings will advance the catalytic alkoxycarbonylation/acylation of $C(sp^2)$−H bonds under additive- and CO-free conditions.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.1c04195.

Experimental procedures, characterization data, and copies of NMR spectra for new compounds (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by JSPS KAKENHI Grant Numbers JP21K14633 and JP21K05061.

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(21) See the Supporting Information for the details of the optimization.

https://doi.org/10.1021/acs.orglett.1c04195
Org. Lett. 2022, 24, 1141−1145