

3-Acylindoles Synthesis: Ruthenium-Catalyzed Carbonylative Coupling of Indoles and Aryl Iodides

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(5) Supporting Information

ABSTRACT: A novel and convenient procedure for the synthesis of 3-acylindoles from simple indoles and aryl iodides has been established. Through ruthenium-catalyzed carbon-ylative C-H functionalization of indoles, with $Mo(CO)_6$ as the solid CO source, the desired indol-3-yl aryl ketones were isolated in moderate to good yields. Not apply Mellylindoles



isolated in moderate to good yields. Not only N-alkylindoles but also N-H indoles can be applied here.

uring the past years, transition-metal catalysts have been extensively explored as a topic of new C-C bond formation through direct C-H activation.¹ Among the various noble metal catalysts, ruthenium catalysts are attractive due to their relative low cost and high reaction selectivity.^{2,3} Several challenging transformations have been realized with ruthenium complex as the catalyst, such as C-H alkenylation,⁴ arylation,⁵ and alkyne annulations.⁶ However, the reports on rutheniumcatalyzed carbonylation reactions are still very limited. In 1992, Moore's group reported a Ru₃(CO)₁₂-catalyzed sp² C-H carbonylation of aromatic heterocycles with olefins.⁷ This reaction exhibited high regioselectivity and high catalyst turnover frequencies. Subsequently, Murai's group studied the $Ru_3(CO)_{12}$ -catalyzed carbonylative coupling reaction of imidazoles with olefins, which has good yields, impressive catalytic efficiency, and wide functional group compatibility.⁸ Then Chatani and co-workers demonstrated Ru₃(CO)₁₂catalyzed carbonylative transformation of sp² C-H and sp C-H with pyridine as the directing group.9 The desired carbonylation products were formed in moderate to good yields. More recently, Beller's group reported a $[Ru(cod)Cl_2]_{n-1}$ catalyzed directing group assisted carbonylative C-H activation of arenes.¹⁰ The reactions were carried out in water and arvl iodides and styrenes were used as the coupling partners. Indoles have been studied as well, but the presence of the directing group was essential.

On the other hand, 3-acylindoles are common structural motifs in many biologically active compounds, natural products,¹¹ and pharmaceutical compounds,¹² such as indiacen A, indiacen B, and MK-0533. Additionally, 3-acylindoles have been applied as key intermediates for synthesis of some other value-added compounds as well.^{13g} Because of the versatile values and applications, their preparation attracts much interest. Traditional procedures include Friedel–Crafts acylations,¹³ Vilsmeier–Haack-type reactions,¹⁴ and indole Grignard reactions.¹⁵ The most frequently used Friedel–Crafts reaction requires troublesome *N*-protection, especially for indoles bearing an electron-donating group with a stoichiometric Lewis acid promoter and strict exclusion of moisture. Hence, alternative methods for 3-acylindole preparation are highly

desired. Carbonylative 3-acylation of indoles is one of the most straightforward procedures. In 2015, Arndtsen's group demonstrated a palladium-catalyzed carbonylative coupling of heterocycles with aryl iodides via C-H functionalization.¹⁶ 3-Acylindoles can be effectively produced under CO pressure. Meanwhile, Guan and co-workers described a novel palladiumcatalyzed carbonylative coupling of indoles with aromatic boronic acids.¹⁷ With the addition of I₂ and KOH, via in situ generation of 3-iodoindole intermediates,¹⁸ good yields of 3acylindoles can be prepared with a wide range of functional groups tolerance. More recently, the application of visible light in carbonylative synthesis of 3-acylindoles has been realized by the groups of Gu^{19} and Li and Liang^{20} as well. With the assistance of photoredox catalysts under high CO pressure (70-80 bar), 3-acylindoles were formed at room temperature. In this paper, we report here a new procedure for the synthesis of 3-acylindoles. With ruthenium as the catalyst using simple indoles and readily available aryl iodides as the substrates, the desired 3-acylindoles can be produced even from N-H indoles. Notably, $Mo(CO)_6$ has been applied as the solid and safe CO source here.²

Our initial investigation began with 1,2-dimethyl-1*H*-indole (1a, 1 equiv) and iodobenzene (2a, 2 equiv), $[RuCl_2(p-cymene)]_2$ (5 mol %), and $[Mo(CO)_6]$ (1 equiv) in HFIP (hexafluoroisopropanol). To our delight, 20% yield of the desired carbonylation product 3a was formed after 30 h at 100 °C (Table 1, entry 1). Subsequently, various ruthenium catalysts such as CpRuCl(PPh₃)₂, $[RuCl_2(cod)]_n$, and $RuCl_2(PPh_3)_3$ were tested (Table 1, entries 2–4). Unfortunately, none of them could give improved results. Then the effects of bases and acids were investigated (Table 1, entries 5–14). TFA was found to be the best in this reaction, whereas K_2HPO_4 , Li₂CO₃, LiBr, LiCl, KH₂PO₄, and MesCO₂H (2, 4, 6-trimethylbenzoic acid) were all found to be inferior. Et₃N and DBU inhibited the reaction completely, and no conversion of 1a was observed (Table 1, entries 5 and 6). Only a trace of

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Table 1. Optimization of Reaction Conditions^a



	Ia	24		Ja	
entry		catalyst	base/acid	additive	yield ^b (%)
1	[RuC	$l_2(p$ -cymene)] ₂			22 (20)
2	CpRu	$Cl(PPh_3)_2$			0
3	[RuC	$l_2(cod)]_n$			<5
4	RuCl	$(PPh_3)_3$			0
5	[RuC	$l_2(p$ -cymene)] ₂	Et ₃ N		0
6	[RuC	$l_2(p$ -cymene)] ₂	DBU		0
7	[RuC	$l_2(p$ -cymene)] ₂	K ₂ HPO ₄		15
8	[RuC	$l_2(p$ -cymene)] ₂	Li ₂ CO ₃		32
9	[RuC	$l_2(p-cymene)]_2$	LiBr		40
10	[RuC	$l_2(p$ -cymene)] ₂	LiCl		35
11	[RuC	$l_2(p$ -cymene)] ₂	KH ₂ PO ₄		42 (40)
12	[RuC	$l_2(p$ -cymene)] ₂	CH ₃ SO ₃ H		<5
13	[RuC	$l_2(p$ -cymene)] ₂	MesCO ₂ H		28
14	[RuC	$l_2(p$ -cymene)] ₂	TFA		45
15 [°]	[RuC	$l_2(p$ -cymene)] ₂	TFA		48
16 ^c	[RuC	$l_2(p$ -cymene)] ₂	TFA	FeCl ₃	44
17 ^c	[RuC	$l_2(p$ -cymene)] ₂	TFA	$MgCl_2$	46
18 ^c	[RuC	$l_2(p$ -cymene)] ₂	TFA	$ZnCl_2$	50
19 ^c	[RuC	$l_2(p$ -cymene)] ₂	TFA	$ZnBr_2$	55
20 ^{c,d}	[RuC	$l_2(p$ -cymene)] ₂	TFA	$ZnBr_2$	35
21 ^{<i>c,e</i>}	[RuC	$l_2(p$ -cymene)] ₂	TFA	\mathbf{ZnBr}_2	62 (61)
22 ^{c,f}	RuC	$l_2(p$ -cymene)] ₂	TFA	$ZnBr_2$	57

^{*a*}Conditions: **1a** (0.2 mmol, 1 equiv), **2a** (0.4 mmol, 2 equiv), catalyst (0.01 mmol, 5 mol %), $Mo(CO)_6$ (0.2 mmol, 1 equiv), base/acid (0.2 mmol, 1 equiv), additive (0.08 mmol, 40 mol %), HFIP (1 mL), stirring at 100 °C for 30 h under air. ^{*b*}Yields were determined by GC using *n*-hexadecane as the internal standard. Isolated yield is in parentheses. ^{*c*}TFA (0.06 mmol, 30 mol %). ^{*d*}Mo(CO)₆ (0.1 mmol, 0.5 equiv). ^{*c*}Mo(CO)₆ (0.3 mmol, 1.5 equiv). ^{*f*}Mo(CO)₆ (0.4 mmol, 2 equiv).

carbonylation product 3a could be detected when CH₂SO₂H was added (Table 1, entry 12). Further study showed that a lower amount of TFA led to higher yield (48%; Table 1, entry 15). To further improve the outcome, different additives were used in this reaction (Table 1, entries 16–19). Surprisingly, we found that ZnBr₂ can give the carbonylation product in 55% yield (Table 1, entry 19). Replacement of ZnBr₂ with FeCl₃, MgCl₂, or ZnCl₂ proved detrimental to the efficiency of the process, with product 3a being formed in diminished 44%, 46%, and 50% yield, respectively (Table 1, entries 16-18). Notably, the amount of $Mo(CO)_6$ played a crucial role for the outcome of this reaction (Table 1, entries 20 and 21). The yield could be improved by increasing the amount of $Mo(CO)_6$ to 1.5 equiv, and we could obtain the carbonylation product 3a in 61% yield (Table 1, entry 21). In addition, the model reaction was also performed with other CO sources such as formic acid, CO, $Cr(CO)_{6}$, $Co_2(CO)_{8}$, and $Fe_2(CO)_{9}$. However, none of them gave better results (see the Supporting Information). These results imply that $Mo(CO)_6$ might play several roles in this transformation. In the case of temperature testing, we found that less than 5% of the desired product was formed at 80 °C and the yield decreased as well at higher temperature (120 °C; 28% yield). Importantly, no product could be detected in the absence of ruthenium catalyst. Additionally, less than 10% of the desired product could be detected when the reaction was performed under pure O_2 (1 bar) pressure or argon atmosphere. These results suggest that the oxygen in air joined in the reaction, but pure oxygen destroyed the catalyst activity.

With the optimized conditions in hand (Table 1, entry 21), we began to investigate the scope of iodoarenes subsequently. As shown in Scheme 1, carbonylation of 1,2-dimethyl-1*H*-

Scheme 1. 3-Acylindole Synthesis: Variation of Aryl Iodides^a



"Reaction conditions: 1,2-dimethyl-1*H*-indole 1a (0.2 mmol, 1 equiv), iodoarenes 2 (0.4 mmol, 2 equiv), $[RuCl_2(p-cymene)]_2$ (0.01 mmol, 5 mol %), Mo(CO)₆ (0.2 mmol, 1 equiv), TFA (0.06 mmol, 30 mol %), ZnBr₂ (0.08 mmol, 40 mol %), HFIP (1 mL), 100 °C, 30 h, air, isolated yield.

indole with iodoarenes proceeded smoothly under our standard reaction conditions. Using iodoarenes with either electrondonating or electron-withdrawing groups led to the formation of the corresponding carbonylation products in moderate to good yields. Substrates can tolerate various functional groups such as Bn, OCH₃, CF₃, Cl, F, and COOMe. However, iodoarenes substituted with OH or NO₂ could not give the desired carbonylation product. No carbonylation products could be obtained with 3-iodopyridine as the substrate. Importantly, the position of substituent R¹ had a critical effect on this carbonylation reaction. Iodoarenes substituted with functional groups in the *meta* position could give higher yields than that in the *para* position (3e vs 3f, 3i vs 3j).

Next, various indoles were investigated for further extending the substrates scope (Scheme 2). *N*-Substituted indoles can be readily carbonylated with iodoarenes to provide moderate to good yields of the corresponding carbonylation products (4a– d). A yield of 70% can be achieved with –COOMe-decorated aryl iodide. Remarkably, free *NH*-indoles can be successfully applied as well (4e–i) and gave good yields of the desired products with total chemoselectivity. Here, the obtained N-H free 3-acylindole products (4e–i) are ready for further C–N coupling reactions. However, we could not detect the products 4j or 4k when indole or 3-methyl-1*H*-indole was used as the substrate. These results revealed that the methyl group on the





^aReaction conditions: indoles **1a** (0.2 mmol, 1 equiv), iodoarenes **2** (0.4 mmol, 2 equiv), $[RuCl_2(p-cymene)]_2$ (0.01 mmol, 5 mol %), Mo(CO)₆ (0.2 mmol, 1 equiv), TFA (0.06 mmol, 30 mol %), ZnBr₂ (0.08 mmol, 40 mol %), HFIP (1 mL), 100 °C, 30 h, air, isolated yield.

2-position of indoles played a crucial role in the carbonylative C-H activation reaction. Additionally, heterocycles such as benzothiazole, benzothiophene, and pyrrole were also tested in the reaction conditions, but none of them could give the desired carbonylation products.

On the basis of the above results and literature, we postulated a possible reaction mechanism for the ruthenium-catalyzed carbonylation of indoles (Scheme 3). First, indoles were activated and transformed into the corresponding organometallic reagents in the presence of $ZnBr_2$, TFA, and

Scheme 3. Proposed Reaction Mechanism



molybdenum slat. The in situ generated zinc reagent then moved to transmetalation with ruthenium catalyst to produce the ruthenium intermediate **A**. Following this, the ruthenium species **A** underwent oxidative addition upon formation of intermediate **B**. Subsequently, intermediate **C** was generated through the coordination and insertion of CO into the Ru–C bond. Finally, the terminal product could be eliminated through reductive elimination, and the active ruthenium catalyst for the next catalytic cycle was regenerated under the presence of air.

In summary, we have developed an interesting procedure for the synthesis of 3-acylindoles. Through ruthenium-catalyzed carbonylative C–H functionalization with $Mo(CO)_6$ as the solid CO source, moderate to good yields of the desired products can be prepared with good functional group tolerance.

ASSOCIATED CONTENT

Supporting Information

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Experimental procedures and NMR spectra for obtained compounds (PDF)

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Notes

The authors declare no competing financial interest.

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