Rhodium(III)-Catalyzed Direct C-2 Olefination of Unactivated Indoles Utilizing OH/NH₂ as Directing Group

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Abstract: Oxidative C-2 olefination of indoles/pyrrole *via* rhodium(III)-catalyzed direct C–H bond activation is reported. Phenolic OH and aniline NH_2 units were revealed to be effective chelating groups to activate the aryl C–H bond. The reactions proceeded with excellent selectivity and high functional group tolerance, furnishing 2-vinylindoles/2-vinylpyrroles in good yields.

Keywords: directing groups; hydroxy group; indoles; olefination; rhodium

Oxidative olefination reactions, pioneered by Fujiwara and Moritani (Heck-type reactions), have been recognized as atom- and step-economic synthetic tools. Compared with traditional Heck coupling, this strategy possesses significant advantages to achieve complex target skeletons from simple starting materials with no preactivation of arenes.^[1] For the purpose of acquiring high regioselectivity and reactivity, the chelation-assisted strategy has been widely employed in olefination reactions with the aid of directing groups. Examples utilizing directing groups such as carboxyl,^[1e,2] carbonyl,^[3] pyridyl,^[4] amide,^[1f-I,5] imine^[1],6] and ester^[7] have been widely reported by Yu, Miura and Satoh, Glorius, Ackermann, van Leeuwen, and others. Notably, the simple hydroxy or primary amino group appears to be even more desirable due to its easy availability and promising value in the further transformations.^[8] However, since OH and NH₂ groups are highly sensitive and therefore need to have protecting groups appended, reports employing the hydroxy or primary amino group as a directing group in olefination reactions are very rare and the process remains rather challenging [Scheme 1, Eq. $(1)]^{[9]}$



Scheme 1. Hydroxy group- or primary amino group-directed olefination reactions.

On the other hand, 2-vinylindoles are important building blocks for various medical intermediates and functional materials.^[10] As an effective construction method, direct olefination on the indole ring with high selectivities has received considerable attention and related works have been accomplished by Miura and Satoh, Carretero, and others.^[11,12] However, the olefination at the C-2 position of 2,3-unsubstituted indoles is less well addressed since the lower nucleophilicity of C-2 (compared with C-3) makes its olefination a challenging task.^[11,12] Herein, we wish to disclose a Rh(III)-catalyzed C-2 olefination of indoles employing simple OH/NH₂ group as the directing group [Scheme 1, Eq. (2)].

Due to the high selectivity and functional group tolerance provided by only low loadings of Rh complexes,^[4a,5c,13] the initial trial reaction of *N*-(2-hydroxyphenyl)indole (**1a**) with ethyl acrylate (**2a**) was carried out utilizing [RhCp*Cl₂]₂ as the catalyst in the presence of Cu(OAc)₂·H₂O in DMF at 25 °C under a nitrogen atmosphere. Fortunately, the desired 2-olefinated product (*E*)-ethyl 3-[1-(2-hydroxyphenyl)-1*H*-





Entry	[RhCp*Cl ₂] ₂ [mol %]	Solvent ^[d]	Temperature [°C]	Yield [%] ^[e]
1	5	DMF	25	32
2	5	DMF	40	69
3	5	DMF	60	78
4	5	DMF	80	93
5	5	DMF	100	80
6	5	DMSO	80	trace
7	5	toluene	80	74
8	5	dioxane	80	81
9	5	DCE	80	51
10	5	MeCN	80	38
11	5	t-AmOH	80	82
12	5	DMA	80	95
13 ^[b]	5	DMA	80	80
14 ^[c]	5	DMA	80	78
15	2.5	DMA	80	95
16	2	DMA	80	95
17	1.5	DMA	80	90
18	1.25	DMA	80	87

^[a] Unless otherwise specified, the reactions were conducted utilizing 1.0 equiv. of **1a** (0.3 mmol), 1.5 equiv. of **2a**, [RhCp*Cl₂]₂ and 2.1 equiv. of Cu(OAc)₂·H₂O in 2.5 mL of solvent under a nitrogen atmosphere.

- ^[b] The reaction was carried out under an air atmosphere.
- ^[c] The reaction was carried out using 30 mol% of Cu- $(OAc)_2$ ·H₂O under an oxygen atmosphere.
- ^[d] Abbreviations: DMF = N,N-dimethylformamide; DMSO = dimethyl sulfoxide; DCE = 1,2-dichloroethane; DMA = N,N-dimethylacetamide.

^[e] Isolated yield of **3a** based on **1a**.

indol-2-yl]acrylate (**3a**) was obtained in 32% yield (Table 1, entry 1). On raising the temperature, the reaction gave better yields of product **3a** (69–93%, entries 2–5); up to 93% yield of **3a** could be obtained at under 80°C (entry 4). Subsequent solvent examination demonstrated that DMA was a better choice, giving **3a** in a higher yield of 95% (entries 6–12). The further results demonstrated that the reaction could also be conducted under an air atmosphere with **3a** furnished in 80% yield (entry 13). Upon decreasing the amount of $Cu(OAc)_2 \cdot H_2O$ to 30 mol% under an oxygen atmosphere, the reaction furnished **3a** in a relative lower yield (78%, entry 14). Gratifyingly, a 95% yield of **3a** could be obtained with an only 2 mol%

loading of $[RhCp*Cl_2]_2$ (entry 16). However, employment of an even lower amount of catalyst reduced the yield of **3a** (entries 17 and 18).

With the optimized conditions in hand, we next explored the substrate scope of this reaction with a series of substituted N-(2-hydroxyphenyl)indoles 1 and alkenes 2. As shown in Table 2, various indoles 1 bearing substituents on C-3 to C-7 positions were successfully allowed to react with ethyl acrylate (2a) to give the corresponding coupling products 3a-i in good to excellent yields (70-97%). Substituents on the indole moiety of substrates 1 such as F, Br, NO₂, alkyl and alkoxy were smoothly introduced, which are attractive due to their potential value to be further transformed to other useful functional groups.^[8] It seems that the weak electron-withdrawing and electron-donating groups in the indoles had negligible effects on the olefination reaction. However, the presence of a strong electron-withdrawing substituent such as the nitro group (6-nitro-substituted indole 1f) decreased the reactivity of product 3f to some extent (71%, Table 2). Bromo and fluoro substituents were well tolerated under the optimal conditions, demonstrating the high functional group tolerance of this Rh catalysis. Interestingly, the presence of a methyl group on the C-3 position of indole **1i** (R^1 =3-Me) did not reduce the yield, giving product **3i** in 84% yield. This experimental fact strongly indicated that the C-H rhodation occurred on the C-2 position of substrate 1 and demonstrated that the 3-methyl substituent did not show much of an ortho-steric effect (Figure 1, B-1). In contrast, the starting material **1h** equipped with a methyl group on the C-7 position of indole ring led to 3h in a lower yield (70%, Table 2). The reduced yield of **3h** might be attributed to the steric hindrance between the H atom and the 7-methyl group (Figure 1, B-2) which disturbed the planarity of the intermediate rhodacycle B and then deteriorated the reaction yield (Figure 1, compare B-2 with B-3).^[1h]

Indole derivatives 1j ($R^2 = F$) and 1k ($R^2 = Me$) bearing fluoro and methyl substituents on the phenolic moiety could also react with 2a successfully, providing C-2 olefinated products 3j and 3k in 87% and 84% yields, respectively (Table 2). Further studies revealed that acrylates 2 from alcohols other than ethanol could also give coupling products 3l-o in 83–96% yields. Moreover, vinyl ketones 1-phenylprop-2-en-1one (2f) and but-3-en-2-one (2g) could be smoothly employed and afforded the corresponding products 3p and 3q in good yields.

Having the successful experience in realizing the 2olefination of indoles, we further intended to explore the C-2 olefination of pyrroles bearing two H atoms which may undergo hydrorhodation on both positions *ortho* to the N atom. Notably, both mono- and bisolefinated pyrroles are important skeletons widely found in natural products and material chemistry,^[11] Table 2. Hydroxy group-directed C-2 olefination of indoles.^[a,b]



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UPDATES

Table 2. (Continued)



^[a] Unless otherwise specified, the reactions were conducted utilizing 1.0 equiv. of 1 (0.3 mmol), 1.5 equiv. of 2, 2 mol% of [RhCp*Cl₂]₂ and 2.1 equiv. of Cu(OAc)₂·H₂O in 2.5 mL of DMA at 80 °C for 10 h under a nitrogen atmosphere.

^[b] Isolated yield of **3** based on **1**.

^[c] Np-2=2-naphthalenyl.



Figure 1. The effects of methyl group in the formation of rhodacycle intermediate **B**.

indicating that the preparation of mono- or bis-olefinated pyrroles with selectivity is of great importance. Thus, control experiments under different conditions were conducted. Under the standard conditions, the reaction of N-(2-hydroxyphenyl)pyrrole (4a) with acrylate 2a gave bis-olefinated product 5a as the major product in 56% yield, together with 29% of monoolefinated product 5b [Eq. (3)].



As predicted, enhancement of the amount of acrylate **2a** to 3.0 equiv. afforded bis-olefinated pyrrole **5a** as the sole product in 91% isolated yield [Scheme 2, Eq. (4)]. Interestingly, it was found possible to control the selectivity to achieve the mono-olefination prod-



Scheme 2. Rh-catalyzed direct C-2 olefination of *N*-(2-hydroxyphenyl)pyrrole. Conditions I: **4a** (1.0 equiv.), **2a** (3.0 equiv.), [RhCp*Cl₂]₂ (2 mol%) and Cu(OAc)₂·H₂O (4.2 equiv.) in DMA at 80 °C for 24 h. Conditions II: **4a** (1.0 equiv.), **2a** (1.0 equiv.), [RhCp*Cl₂]₂ (2 mol%) and Cu(OAc)₂·H₂O (2.1 equiv.) in DMA at 50 °C for 5 h.

uct **5b** in 84% isolated yield by decreasing the amount of **2a** to 1.0 equiv. and lowering the temperature to 50°C [Scheme 2, Eq. (5)].

Moreover, applications of the cross-coupling products were explored. As shown in Eq. (6), the intramolecular oxa-Michael reation of 2-vinylindole **3q** was conducted in the presence of Et₃N (20 mol%) in CH₂Cl₂ at room temperature. The reaction proceeded smoothly and afforded the annulation product 1-(6*H*benzo[5,6][1,4]oxazino[4,3-*a*]indol-6-yl)propan-2-one (**6a**) in excellent yield (94%). It should be noted that the l,4-benzoxazine heterocyclic system has served as a rich source for a variety of pharmaceutical agents.^[14]



2a R ¹ 7a	R^2 R^2 $+$ R^2 $+$ $R^$	hCp*Cl ₂] ₂ (5 mol%) <u>Cu(OAc)₂·H₂O</u> R ¹ DMA, 80 °C I ₂	NH ₂ 8a-g
Entry	$R^{1}(7)$	R ² (2)	Yield [%] ^[b]
1	H (7a)	CO ₂ Et (2a)	76 (8a)
2	4-ÒBn ('	7b) 2a	78 (8b)
3	4-Me (7	c) 2a	75 (8c)
4	5-OMe (7d) 2a	80 (8d)
5	5-F (7e)	2 a	82 (8e)
6	7a ` ´	CO ₂ - <i>t</i> -Bu (2	63 (8f)
7	7a	$\overline{\text{CO}_2\text{Bn}}$ (2d)	79 (8g)

Table 3. Amino group-directed C-2 olefination of indoles.^[a]

[a] The reactions were conducted utilizing 1.0 equiv. of 7 (0.3 mmol), 1.5 equiv. of 2, 5 mol% of [RhCp*Cl₂]₂ and 2.1 equiv. of Cu(OAc)₂·H₂O in 2.5 mL of DMA at 80 °C for 12 h under a nitrogen atmosphere.

^[b] Isolated yield of **8** based on **7**.

Having successfully applied the OH group as the dierecting group of the olefination, we envisioned that the NH₂ group may also be applied for the construction of 2-olefinated indole products of great potential value. With this notion in mind, we then examined the reaction of N-(2-aminophenyl)indoles 7 with alkenes 2. To our delight, the coupling products 8 could also be obtained in good yields (63–82%, Table 3). Unexpectedly, substrates 7 equipped with electron-donating methoxy or electron-withdrawing fluoro substituents on the C-5 could furnish both corresponding products 8d and 8e in higher yields (80% and 82%, entries 4 and 5). In addition, in the case of

the utilization of *tert*-butyl acrylate (2c), the olefinated product was isolated in a slightly lower yield (63%, entry 6).

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Surprisingly, the reaction of 2-naphthalenyl acrylate (2e) with N-(2-aminophenyl)indole (7a) did not terminate at the olefination stage to give the expected olefinated product. Instead, the C-2 olefination product/intermediate might subsequently undergo an intramolecular aza-Michael addition to furnish the annulated compound 9a directly as the single product [68%, Scheme 3, Eq. (7)]. Similarly, phenyl acrylate was examined and furnished 5,6-2h also dihydroindolo[1,2-a]quinoxaline **9b** in 51% yield [Scheme 3, Eq. (8)]. The differences observed for these aryl acrylates and alkyl acrylates (Table 3) with respect to aza-Michael reactions are likely caused by the differences of the stereoelectronic effects of the acrylate intermediate/product. Notably, no direct annulation product was observed when N-(2-hydroxyphenyl)indole 1a was reacted with 2e (Table 2), which may lie in the difference in nucleophilicity between the aniline NH₂ group and the phenolic OH group.

On the basis of the experimental results and known Rh-catalyzed C–H bond activation reactions, a plausible catalytic cycle for the reaction was proposed (Scheme 4).^[1a,d,13] Coordination of the oxygen atom of the phenolic moiety (from **1a**) to the RhX₃ species gave Rh(III) species **A**. Similar with the previous works on C-2 olefination^[12] and alkylation^[15] of indoles, subsequent direct C–H bond activation at the C-2 position generated the six-membered rhodacycle intermediate **B**. Subsequent alkene insertion led to the seven-membered rhodacycle **C**.^[5c,16] Finally, β -H elimination of intermediate **C** offered product **3a** and the resulting RhX species was oxidized by the CuX₂ salt to regenerate RhX₃ species.

In summary, we have developed an Rh(III)-catalyzed direct C-2 olefination of unactivated indoles/ pyrrole *via* the C–H activation strategy. Notably,



Scheme 3. Reactions of 7a with 2-naphthalenyl acrylate (2e) and phenyl acrylate (2h).

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Scheme 4. Plausible mechanism.

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simple phenolic OH and aniline NH_2 groups were successfully introduced as efficient directing groups, which are ubiquitous structural units in natural products and provide for the ready transformation of the 2-olefinated products to other interesting skeletons. The Michael reaction of the so obtained 2-vinylindoles was also revealed to furnish fused heterocyclic compounds in a one-pot or a stepwise manner. Due to the high selectivity of the reaction, the wide scope of the substrates, the good-to-excellent yields and the promising utilization of the products, this methodology may be of great potential value.

Experimental Section

Typical Procedure

Under a nitrogen atmosphere, 2-(1H-indol-1-yl)phenol (1a) (62.8 mg, 0.3 mmol), [Cp*RhCl₂]₂ (3.7 mg, 0.006 mmol) and $Cu(OAc)_2$ ·H₂O (125.7 mg, 0.63 mmol) were added to a 25mL Schlenk tube equipped with a magnetic stirrer. Then 2.5 mL of DMA and ethyl acrylate (2a) (45.0 mg, 0.45 mmol) were added. The reaction mixture was stirred at 80°C. When the reaction was complete as monitored by TLC, the reaction mixture was filtered through a short column of silica gel and eluted with CH₂Cl₂. The filtrate was concentrated under reduced pressure. The residue was purified by silica gel chromatography (petroleum ether/ethyl acetate = 10/1) to afford **3a** as a yellow solid; yield: 87.6 mg (95%); mp 122.7–122.8°C. ¹H NMR (400 MHz, CDCl₃): $\delta =$ 7.65 (d, J = 7.2 Hz, 1 H), 7.41–7.35 (m, 2 H), 7.22–7.02 (m, 6H), 6.99 (d, J=8.0 Hz, 1H), 6.16 (d, J=16.0 Hz, 1H), 5.80 (s, 1H), 4.06-4.01 (m, 2H), 1.22 (t, J=7.6 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): $\delta = 167.1$, 152.7, 139.7, 135.4, 133.0, 130.7, 129.7, 127.9, 124.5, 123.1, 121.5, 121.4, 121.2, 118.0, 117.2, 110.8, 106.4, 60.6, 14.1; IR (neat): $\nu = 3353$, 3054, 2979, 1684, 1627, 1277, 1180 cm⁻¹; HR-MS (EI): m/z = 307.1212, calcd. for C₁₉H₁₇NO₃ (M⁺): 307.1208.

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