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Rhodium(III)-Catalyzed *Ortho*-Alkenylation of Anilines Directed by a Removable Boc-Protecting Group

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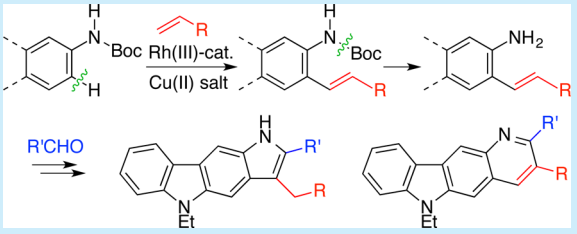
Supporting Information

ABSTRACT: The rhodium(III)-catalyzed *ortho*-alkenylation of *N*-Boc-anilines with alkenes such as acrylate ester and styrene proceeds smoothly through C−H bond cleavage. Obtained *o*-alkenylanilines can be readily transformed to nitrogen-containing fused heteroaromatic compounds including indoles and quinolines.



Transition-metal-catalyzed direct C−H bond functionalization reactions have been significantly developed as powerful synthetic tools in modern organic synthesis. The direct transformations provide straightforward synthetic approaches to complex target molecules from relatively simple starting materials. Among them, the reactions utilizing a directing group are particularly useful because the directing group leads to regioselective functionalization of ubiquitous C−H bonds in organic molecules at the neighboring position.[1,2] For example, *N*-acylanilines undergo *ortho*-selective alkenylation upon treatment with alkenes under palladium,[3] rhodium,[4] or ruthenium[5] catalysis. In contrast to the acylamino directing group,[3−5] the utilization of carbamate moieties including the *tert*-butoxycarbonyl (Boc) function has been less explored.[6] The Boc function is one of the most widely employed protecting groups for amino groups in organic synthesis. Since this can be added and removed on and from amines more readily compared to acyl protecting groups, there is high potential for it to be utilizable as a traceless directing group.[7] During our continuous studies on rhodium-catalyzed *ortho*-selective C−H bond functionalization reactions,[2v,w,8] we have found that *N*-Boc-anilines react with alkenes such as acrylate esters and styrene efficiently in the presence of a rhodium(III) catalyst and a copper salt oxidant through Boc-directed C−H bond cleavage to produce *ortho*-alkenylated aniline derivatives (Scheme 1). Products obtained in this way can be converted to *N*-unprotected 2-alkenylanilines by a conventional deprotection procedure[9] and undergo further functionalization that leads to valuable nitrogen-containing fused heteroaromatic compounds. These new findings are described herein.

In an initial attempt, *N*-Boc-aniline (**1a**) (0.2 mmol) was treated with *n*-butyl acrylate (**2a**) (0.4 mmol) in the presence of $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (0.01 mmol, 5 mol %) and $Cu(OAc)_2·H_2O$ (0.4 mmol) in Am^{t}OH (*tert*-amyl alcohol) under N_2 at 80 °C for 6 h. As a result, an *ortho*-alkenylated product, *n*-butyl (*E*)-3-[2-[(*tert*-butoxycarbonyl)amino]-phenyl]acrylate (**3aa**), was obtained in 68% yield (Table 1, entry 1). Besides *ortho*-alkenylated **3aa**, no *ortho*-alkylated and annulation products were detected. The reaction could be conducted in the presence of a catalytic amount of $Cu(OAc)_2·H_2O$ (0.04 mmol) under air, in spite of its somewhat lower efficiency (entry 2). The use of neutral $[Cp^*RhCl_2]_2$ as a catalyst did not give **3aa** at all (entry 3). While the yield of **3aa** was slightly increased in Bu^{t}OH (entry 4), the reaction was sluggish in other solvents such as EtOH, PhCl, and THF (entries 5−7). Decreasing the reaction temperature to 60 °C enhanced the **3aa** yield up to 82% (entry 8), although a further decrease to 50 °C reduced the yield to 68% (entry 9). The use of anhydrous $Cu(OAc)_2$ in place of $Cu(OAc)_2·H_2O$ gave a somewhat better result (entry 10). The amount of the rhodium catalyst could be cut down to 4 mol % without a significant change of reaction efficiency (entry 11), although a further decrease reduced the product yield (entry 12). The gram-scale synthesis of **3aa** (1.29 g) could be accomplished by a simple scale-up using **1a** (5.2 mmol), **2a** (10.4 mmol), [Cp*Rh-

Scheme 1. Synthesis and Further Functionalization of *o*-Alkenylanilines

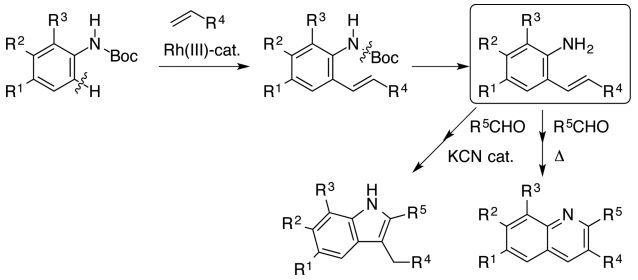


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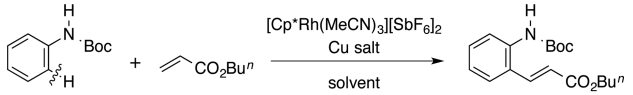
Table 1. Reaction of *N*-Boc-aniline (1a) with *n*-Butyl Acrylate (2a)[a]



1a 2a 3aa

entry	Cu salt	solvent	temp (°C)	yield[b] (%)
1	$Cu(OAc)_2·H_2O$	Am^{t}OH	80	68
2[c]	$Cu(OAc)_2·H_2O$	Am^{t}OH	80	43
3[d]	$Cu(OAc)_2·H_2O$	Am^{t}OH	80	0
4	$Cu(OAc)_2·H_2O$	Bu^{t}OH	80	70
5	$Cu(OAc)_2·H_2O$	EtOH	80	29
6	$Cu(OAc)_2·H_2O$	PhCl	80	36
7	$Cu(OAc)_2·H_2O$	THF	80	53
8	$Cu(OAc)_2·H_2O$	Bu^{t}OH	60	82
9	$Cu(OAc)_2·H_2O$	Bu^{t}OH	50	68
10	$Cu(OAc)_2$	Bu^{t}OH	60	86
11[e]	$Cu(OAc)_2$	Bu^{t}OH	60	87
12[f]	$Cu(OAc)_2$	Bu^{t}OH	60	78
13[g]	$Cu(OAc)_2$	Bu^{t}OH	60	78

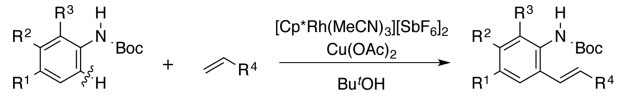
[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (0.01 mmol), and Cu salt (0.4 mmol) in solvent (2 mL) under N_2 for 6 h, unless otherwise noted. [b]Isolated yield based on the amount of **1a** used. [c]$Cu(OAc)_2·H_2O$ (0.04 mmol) was employed under air. [d]$[Cp^*RhCl_2]_2$ (0.005 mmol) was employed in place of $[Cp^*Rh(MeCN)_3][SbF_6]_2$. [e]$[Cp^*Rh(MeCN)_3][SbF_6]_2$ (0.008 mmol) was employed. [f]$[Cp^*Rh(MeCN)_3][SbF_6]_2$ (0.004 mmol) was employed. [g]The reaction was conducted using **1a** (5.2 mmol), **2a** (10.4 mmol), $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (0.16 mmol, 3 mol %), and $Cu(OAc)_2$ (10.4 mmol) in Bu^{t}OH (25 mL) under N_2 at 60 °C for 24 h.

$(MeCN)_3][SbF_6]_2$ (0.16 mmol, 3 mol %), and $Cu(OAc)_2·H_2O$ (10.4 mmol) (entry 13).

With the optimized conditions in hand (Table 1, entry 10), the *ortho*-alkenylation of **1a** with various alkenes **2b−f** was examined (Table 2). A series of acrylates **2b−e** reacted with **1a** smoothly to produce the corresponding *o*-alkenylaniline derivatives **3ab−ae** in 83−87% yields (entries 1−4). Besides acrylates, acrylamides such as *N*,*N*-dimethylacrylamide and *N*-(*tert*-butyl)acrylamide and acrylonitrile did not react with **1a** at all under standard conditions. In the case using styrene (**2f**), *o*-styrylaniline derivative **3af** could be obtained in 60% yield by increasing the catalyst loading and reaction temperature (entry 6). Next, the reactions of variously substituted *N*-Boc-anilines **1b−g** with **2a** were examined. A series of 4-substituted *N*-Boc-anilines possessing methyl, methoxy, bromo, and butoxycarbonyl groups underwent *ortho*-alkenylation to afford **3ba−ea** (entries 7−10). In the case with *N*-Boc-3-methylaniline (**1f**), the alkenylation took place exclusively at the less hindered position (entry 11). The reaction of *N*-Boc-2-methylaniline (**1g**) was found to be sluggish, probably due to steric reasons (entry 12). Interestingly, the reaction of *tert*-butyl (9-ethyl-9*H*-carbazol-3-yl)carbamate (**1h**) with **2a** proceeded efficiently and regioselectively to give C2-alkenylated carbazole derivative **3ha** as a sole product in an excellent yield (entry 13).

On the basis of the literature information,[4,6] a plausible mechanism for the *ortho*-alkenylation of **1** with **2** is illustrated in Scheme 2. Coordination of the Boc group of **1** to the rhodium center triggers C−H bond cleavage at the *ortho*-position to form a rhodacycle intermediate **A**. Then, alkene insertion to form **B** and subsequent *β*-hydrogen elimination

Table 2. Reaction of *N*-Boc-anilines 1 with Alkenes 2[a]

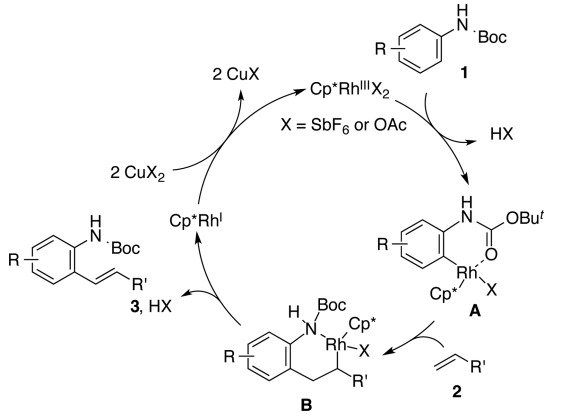


1 2 3

entry	1	2	product	yield (%)[b]
1	**1a**	**2b**: R = Bu^i	**3ab**: R = Bu^i	87
2		**2c**: R = Bu^t	**3ac**: R = Bu^t	86
3		**2d**: R = Cy	**3ad**: R = Cy	83
4		**2e**: R = Me	**3ae**: R = Me	83
5[c]	**1a**	**2f**	**3af**	35
6[c,d]				60
7	**1b**: R^1 = Me, R^2 = R^3 = H	**2a**	**3ba**: R^1 = Me, R^2 = R^3 = H	82
8	**1c**: R^1 = OMe, R^2 = R^3 = H		**3ca**: R^1 = OMe, R^2 = R^3 = H	83
9	**1d**: R^1 = Br, R^2 = R^3 = H		**3da**: R^1 = Br, R^2 = R^3 = H	69
10	**1e**: R^1 = CO_2Bu^n, R^2 = R^3 = H		**3ea**: R^1 = CO_2Bu^n, R^2 = R^3 = H	55
11	**1f**: R^2 = Me, R^1 = R^3 = H		**3fa**: R^2 = Me, R^1 = R^3 = H	78
12	**1g**: R^3 = Me, R^1 = R^2 = H		**3ga**: R^3 = Me, R^1 = R^2 = H	43
13	**1h**	**2a**	**3ha**	96

[a]Reaction conditions: **1** (0.2 mmol), **2** (0.4 mmol), $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (0.008 mmol), $Cu(OAc)_2$ (0.4 mmol) in Bu^{t}OH (2 mL) under N_2 at 60 °C for 6 h, unless otherwise noted. [b]Isolated yield based on the amount of **1** used. [c]$[Cp^*Rh(MeCN)_3][SbF_6]_2$ (0.01 mmol) was employed. [d]At 80 °C.

Scheme 2. Plausible Mechanism for the Reaction of 1 with 2



may take place to give **3**. The rhodium(I) species generated by releasing HX at the last step can be reoxidized by a copper salt to regenerate a rhodium(III) active species.

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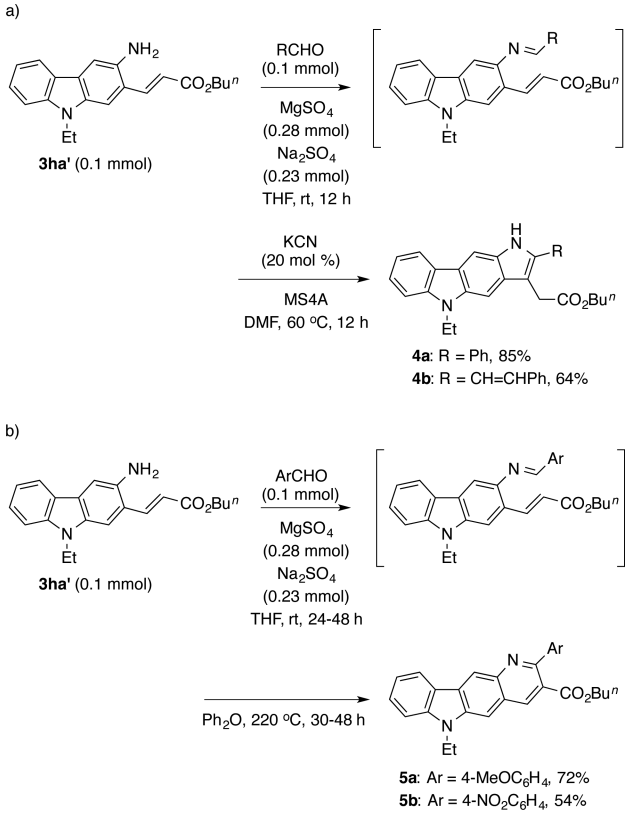
It was confirmed that the Boc moiety of *ortho*-alkenylated products **3** can be readily removed by a conventional method under acidic conditions.[8] For example, treatment of **3aa** with CF_3CO_2H at rt for 12 h gave deprotected *n*-butyl (*E*)-2-aminocinnamate (**3aa′**) quantitatively (Scheme S1).[10] Next, we examined further derivatization of thus-obtained *N*-unprotected 2-alkenylanilines **3′**. First, **3ha′** was treated with benzaldehyde using $MgSO_4/Na_2SO_4$ as dehydrative condensation reagents in THF at room temperature for 12 h. Without isolation, the crude aldimine intermediate was subjected to a Stetter-type reaction.[11] Thus, the imine was successively treated with a catalytic amount of KCN and molecular sieves 4 Å (MS4A) in DMF at 60 °C for 12 h to produce a pyrrolo[3,2-*b*]carbazole derivative **4a** in 85% yield (Scheme 3a). In a similar manner, 2-styrylated pyrrolo[3,2-*b*]carbazole **4b** could be prepared through the reaction of **3ha′** with cinnamaldehyde. On the other hand, the aldimine intermediates could also be transformed into pyrido[3,2-*b*]carbazole derivatives through thermal electrocyclic reaction (Scheme 3b).[12] Thus, the aldimine formed in situ by dehydrative condensation of **3ha′** with 4-methoxybenzaldehyde was heated at 220 °C in diphenyl ether for 30 h. As a result, pyrido[3,2-*b*]carbazole **5a** was obtained in 72% yield. 4-Nitrobenzaldehyde also reacted with **3ha′** to give **5b** in 54% yield. It should be noted that pyrrolo- and pyridocarbazole skeletons can be seen in a variety of natural products and biologically active compounds.[13] The present *ortho*-alkenylation/annulation sequences provide straightforward synthetic routes toward such classes of compounds. It is also noted that *o*-aminocinnamates like compounds **3′** have also been transformed to not only indoles and quinolines[11,12,14] but also other nitrogen-containing fused heterocyclic compounds including indoloquinoline, isoquinolonoquinazoline, chromenoquinoline, and benzoimidazothiazine derivatives.[15]

Scheme 3. Transformation of Compound 3ha′ to Indole and Quinoline Derivatives



In summary, we have demonstrated that *N*-Boc-anilines readily undergo *ortho*-alkenylation upon treatment with alkenes in the presence of a rhodium(III) catalyst and a copper salt oxidant. In this reaction, the Boc function acts as a removable directing group. Further derivatization of the produced *o*-alkenylanilines to nitrogen-containing multicyclic aromatic compounds has also been achieved.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.7b00569.

Experimental procedures, results for additional experiments, and characterization data of products (PDF)

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Notes

The authors declare no competing financial interest.

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