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Rhodium(III)-Catalyzed Oxidative Allylic C–H Indolylation via Nucleophilic Cyclization

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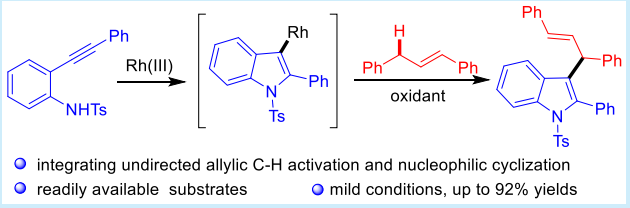
Supporting Information

ABSTRACT: Reported herein is a mild synthesis of 3-allylindoles via Rh(III)-catalyzed allylic C–H activation of olefins and coupling with *o*-alkynylanilines. The reaction proceeded via initial nucleophilic cyclization of *o*-alkynylanilines followed by oxidative coupling with allylic C–H bonds via an η^3-allyl intermediate.



Metal-catalyzed direct C(sp^3)–H bond activation has emerged as a convenient and powerful strategy to deliver numerous important synthetic targets.[1] Although impressive achievements have been made in catalytic C-(sp^3)–H activation (Scheme 1a), a directing group is generally indispensable to ensure reactivity and selectivity of an unactivated C(sp^3)–H bond.[2] Consequently, development of a nondirected strategy to realize activation of a specific C(sp^3)–H bond is of great demand. Among the various classes of C(sp^3)–H bonds, allylic C–H bonds are intrinsically reactive owing to their tendency to form thermodynamically stable η^3-allyl species.[3−6] Thus, following the pioneering work by White, Shi, and others, Pd-catalyzed regioselective allylic functionalization of olefins evolved rapidly.[3] Recently, Blakey[4] and Glorius[5a,b] have successfully developed Cp*Rh(III)-catalyzed allylic C–H amination, etherification, and arylation of terminal and internal alkenes (Scheme 1b). Rovis[6b] and Glorius[5c] also independently realized intermolecular allylic C–H amidation of terminal olefins. Despite these achievements, development of novel allylic C–H functionalization systems is still challenging, especially for C(allylic)–C(aryl) coupling. In reported allylic C–H arylation systems, arenes and aryl boronic acids are common arylating reagents,[5a,b] with the key M–aryl species being generated via C–H activation and transmetalation, respectively. It is well-known that cyclization of alkynes bearing a proximal nucleophilic offers a versatile and atom-economic strategy to access M–C(sp^2) species.[7−11] However, this strategy has not been integrated into activation of C(allylic)–H bonds.

Indoles are prominent heterocyclic structures in numerous natural and synthetic bioactive products. Among the various indole derivatives, 3-allylindoles are useful intermediates in synthetic organic chemistry and promising candidates in drug design.[12] Given the numerous reports of catalytic nucleophilic cyclization of *o*-alkynylanilines for indole synthesis,[8e,f,9c−h,13] it is possible that Cp*Rh(III) complexes may also catalyze the cyclization of *o*-alkynylanilines toward the indolylation of allylic olefins. Thus, our objective was to integrate allylic C–H activation and cyclization of *o*-alkynylanilines via Cp*Rh(III) catalysis under oxidative conditions (Scheme 1c). Despite the design, the following challenges should be addressed: (1) The reaction may stop at the cyclization–protonolysis stage to deliver an unreactive C(3)-unfunctionalized indole. (2) Intermolecular allylic C–H amination may occur to lead to undesired selectivity.[4a] (3) Homocoupling of indoles or olefins may occur to lower the reaction efficiency. We now report a

Scheme 1. Catalytic C(sp^3)–H Activation

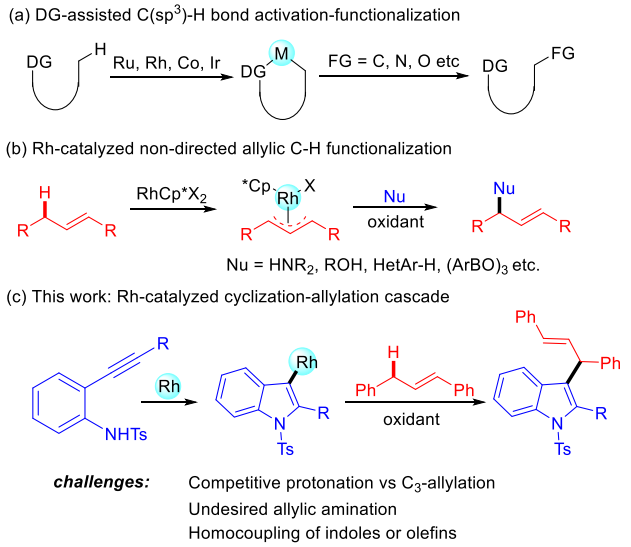


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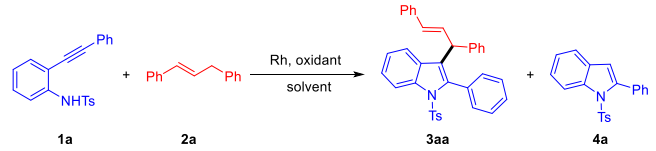
Table 1. Optimization of the Reaction Conditions[a,b]



entry	catalyst (mol %)	oxidant	solvent	T (°C)	yield (%) 3aa	yield (%) 4a
1	$[Cp^*RhCl_2]_2$ (4)/$AgSbF_6$ (16)	$Cu(OAc)_2$	DCM	100	57	41
2	$[Cp^*RhCl_2]_2$ (4)/$AgSbF_6$ (16)	$Cu(OAc)_2$	DCE	100	61	38
3	$[Cp^*RhCl_2]_2$ (4)/$AgSbF_6$ (16)	$Cu(OAc)_2$	$PhCF_3$	100	44	54
4	$[Cp^*RhCl_2]_2$ (4)/$AgSbF_6$ (16)	$Cu(OAc)_2$	TFE	100	55	45
5[c]	$[Cp^*RhCl_2]_2$ (4)/$AgSbF_6$ (16)	$Cu(OAc)_2$	DCE	100	65	35
6[c,d]	$[Cp^*RhCl_2]_2$ (4)/$AgSbF_6$ (16)	$Cu(OAc)_2$	DCE	100	66	34
7[c,d]	$[Cp^*Rh(MeCN)_3](SbF_6)_2$ (5)	$Cu(OAc)_2$	DCE	100	69	31
8[c−e]	$[Cp^*Rh(MeCN)_3](SbF_6)_2$ (5)	$Cu(OAc)_2$	DCE	100	75	22
9[c−e]	$[Cp^*Rh(MeCN)_3](SbF_6)_2$ (5)	AgOAc	DCE	100	82	16
10[c−e]	$[Cp^*Rh(MeCN)_3](SbF_6)_2$ (5)	Ag_2CO_3	DCE	100	25	71
11[c−e]	$[Cp^*Rh(MeCN)_3](SbF_6)_2$ (5)	AgF	DCE	100	60	38
12[c−e]	$[Cp^*Rh(MeCN)_3](SbF_6)_2$ (5)	AgOPiv	DCE	100	53	42
13[c−e]	$[Cp^*Rh(MeCN)_3](SbF_6)_2$ (5)	AgOAc	DCE	120	51	33
14[c−e]	$[Cp^*Rh(MeCN)_3](SbF_6)_2$ (5)	AgOAc	DCE	90	83	16
15[c−e]	$[Cp^*Rh(MeCN)_3](SbF_6)_2$ (5)	AgOAc	DCE	80	85	15
16[c−e]	$[Cp^*Rh(MeCN)_3](SbF_6)_2$ (5)	AgOAc	DCE	70	93 (92)	6
17[c−e]	$[Cp^*RhCl_2]_2$ (4)/$AgSbF_6$ (16)	AgOAc	DCE	70	77	14

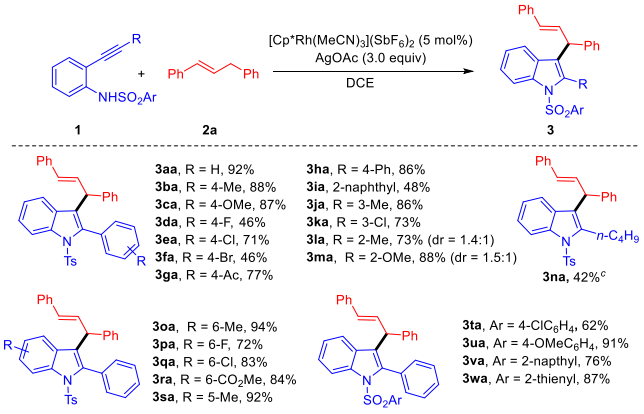
[a]Reaction conditions: **1a** (0.1 mmol), **2a** (1.5 equiv), Rh catalyst, oxidant (2.2 equiv), solvent (2 mL) under N_2 for 12 h. [b]Yields were determined by ^1H NMR spectroscopy using 1,3,5-trimethylbenzene as an internal standard (isolated yield in parentheses). [c]**2a** (2.0 equiv). [d]Under air. [e]Oxidant (3.0 equiv) was used.

Rh(III)-catalyzed cyclization/oxidative allylation cascade for synthesis of 3-allylindoles.

We commenced our investigation with optimization studies of the coupling of *o*-alkynylaniline (**1a**) and *trans*-1,3-diphenylpropene (**2a**) as model substrates in the presence of a $[Cp^*RhCl_2]_2/AgSbF_6$ catalyst (100 °C). A coupling occurred in the presence of $Cu(OAc)_2$ oxidant to give the desired product **3aa** in 57% yield alongside with indole **4a** as the side product (Table 1, entry 1). Screening of solvents revealed that DCE was the best choice, which afforded the desired product in 61% yield (entries 2−4). The yield of **3aa** was improved to 65% when 2 equiv of **2a** was used (entry 5). The reaction efficiency was essentially unaffected when conducted under air (entry 6). Switching the catalyst to $[Cp^*Rh(MeCN)_3](SbF_6)_2$ (5 mol %) improved the yield to 69% (entry 7). The yield was further improved by increasing the amount of $Cu(OAc)_2$ (entry 8). Although other silver(I) oxidants were less effective (entires 10−12), AgOAc turned out to be ideal for this reaction (82%, entry 9). Gratifyingly, an excellent yield of **3aa** (92%) was isolated when the reaction was performed at 70 °C (entries 13−16). Switching the catalyst to $[Cp^*RhCl_2]_2/AgSbF_6$ gave lower yields due to formation of **4a** (entry 17).

With the optimized conditions in hand, we next explored the scope and limitation of this cyclization/allylation reaction coupling with *trans*-1,3-diphenylpropene **2a** (Scheme 2). The presence of methyl and methoxyl groups at the *para* position of the phenyl ring afford **3ba** and **3ca** in 88% and 87% yield, respectively. Alkynes with halogen and electron-withdrawing groups delivered **3da**−**3ga** in 46−77% yields. Biphenyl and 2-naphthyl groups were also tolerated, affording **3ha** and **3ia** in 86% and 48% yields. For *meta*-substituted substrates **1j** and **1k**, the reaction proceeded efficiently with the corresponding **3ja**

Scheme 2. Scope of Alkynes in Allylation[a,b]



[a]Reaction conditions A: **1** (0.2 mmol), **2a** (2.0 equiv), $[Cp^*Rh(MeCN)_3](SbF_6)_2$ (5 mol %), AgOAc (3.0 equiv), DCE (2 mL), 70 °C for 12 h. [b]Isolated yield after column chromatography. [c]**2a** (3.0 equiv), under 100 °C.

and **3ka** being isolated in 86% and 73% yields. We noted that *o*-Me- and *o*-OMe-substituted substrates **1l** and **1m** led to a formation of a mixture of diastereoisomers caused by hindered rotation of the two aromatic rings. In addition, an alkyl-terminated alkyne was also found to be compatible and afforded product **3na** in 42% yield. Moreover, good coupling efficiency was observed for substrates bearing 5-and 6-alkyl, halogen, or ester groups in the aniline ring, affording coupling products (**3oa**−**3sa**) in 72−94% yields. In addition, product **3qa** has been characterized by X-ray crystallography (CCDC 1890239). Next, we explored the effects of *N*-activating groups of *o*-alkynylaniline. Our results revealed that sulfonamides with

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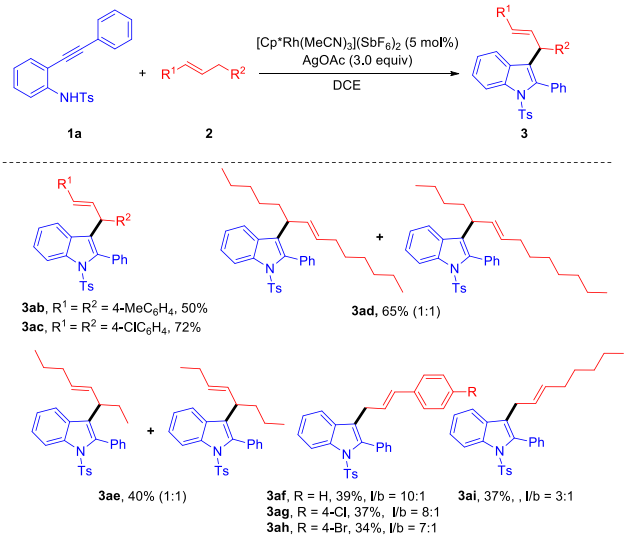
different functional groups furnished the corresponding products **3ta**–**3wa** in good to excellent yields (62–91%). Unfortunately, TMS-substituted o-alkynylaniline, unprotected *o*-alkynylaniline, and *o*-alkynylphenol failed to deliver any of the desired coupling products (see the SI).

The scope of the internal and terminal olefins was next explored under slightly modified reaction conditions (Scheme 3). Tolyl- and chlorophenyl-substituted diarylpropene **2b** and **2c** coupled smoothly with *o*-alkynylaniline **1a**, affording the 3-allylation indoles in good yields (**3ab**, **3ac**). Then the internal olefins 7-tetradecene and 4-octene were examined, which both delivered the corresponding 3-allylindoles as 1:1 regioisomers (**3ad**, **3ae**). Terminal olefins were also tolerated and give a 10:1 and 3:1 regioisomeric ratio favoring the linear product (**3af**, **3ai**). Substituted allylbenzenes were also tolerated and gave the desired products **3ag** and **3ah** in 37% and 34% yields with 8:1 and 7:1 l/b ratios, respectively. However, no product was obtained when ester-, aldehyde- and acid-functionalized olefins were used, and cyclic olefins were also found to be incompatible (see the SI).

Scheme 3. Substrate Scope of Olefins[a,b]

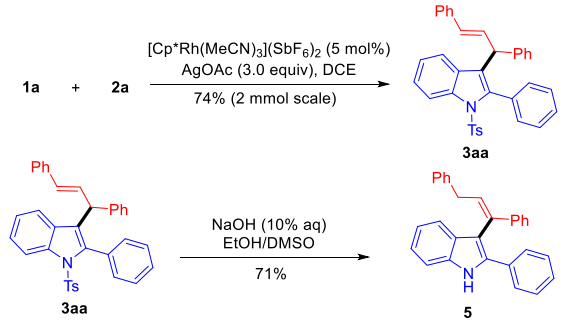


[a]Reaction conditions B: **1a** (0.2 mmol), **2** (3.0 equiv), [Cp*Rh(MeCN)$_3$](SbF$_6$)$_2$ (5 mol %), AgOAc (3.0 equiv), DCE (2 mL), 100 °C for 12 h. [b]Isolated yield after column chromatography.

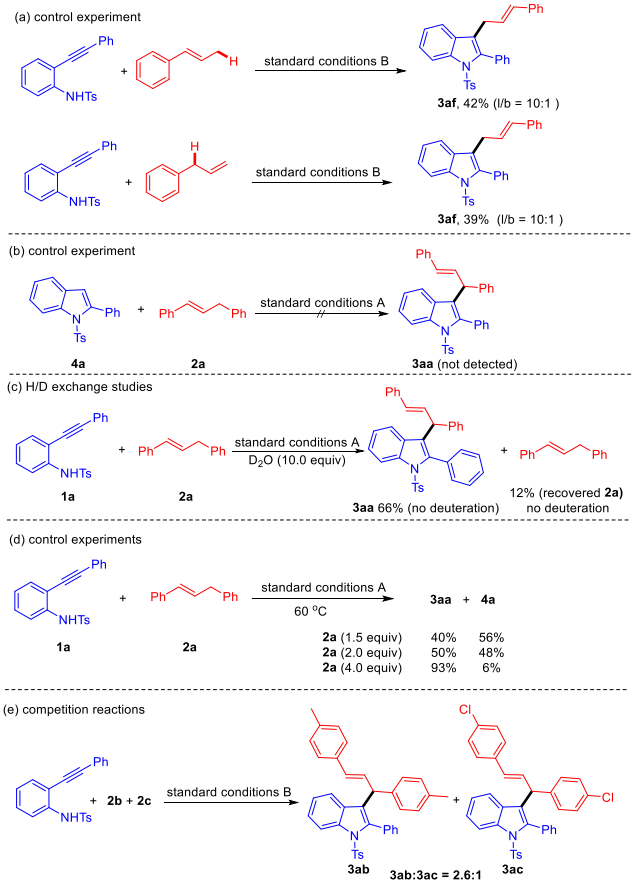
To demonstrate the practicability of this reaction, a 2 mmol scale reaction was conducted and **3aa** was isolated in 74% yield (0.8 g). To further investigate the synthetic application of this product, we next investigated deprotection of the sulfonyl group (Scheme 4). Thus, treatment of **3aa** with NaOH afforded NH indole **5** in 72% yield.[14]

A series of experiments have been conducted to gain mechanistic insight into this coupling system (Scheme 5). First, we performed two independent couplings of allylbenzene and (*E*)-prop-1-en-1-ylbenzene and *o*-alkynylaniline **1a**, and the product was obtained in nearly the same yield and regioselectivity (Scheme 5a). This result indicates the common intermediacy of a π-allyl species in these reactions. Furthermore, indole **4a** proved to be inactive for this transformation (Scheme 5b). Therefore a Rh(III)-indolyl, instead of a protonolyzed indole, is the active species. The C–H activation step in the coupling of **1a** and **2a** was found to be irreversible under the reaction conditions, as evidenced by

Scheme 4. Scale-up Reaction and Derivatization of 3aa



Scheme 5. Mechanistic Studies



absence of deuterium incorporation in both 3-allylindoles (**3aa**) and the recovered olefin (Scheme 5c). We also evaluated the sequence of cyclization versus allylic C–H activation. By increasing the amount of olefin **2a** with a fixed amount of **1a** substrate, the ratio of **3aa**/**4a** also increased (Scheme 5d). This observation indicated that cyclization occurred prior to C–H activation (vide infra). Our competition experiment also showed that the C–H functionalization is kinetically favored for a more electron-rich allylic C–H bond (Scheme 5e).

On the basis of the preliminary mechanistic studies and previous reports,[4,5] a plausible catalytic cycle for the reaction of **1a** and **2a** is proposed (Scheme 6). An active catalyst Cp*RhX$_2$ was generated via ligand exchange. Coordination of the *o*-alkynylaniline **2a** then gives a metal-bound alkyne intermediate **A**. Subsequent nucleophilic cyclization gives a Rh(III) indolyl species **B**. Off-cycle competitive protonolysis of the Rh-indolyl bond accounts for the cyclization byproduct.

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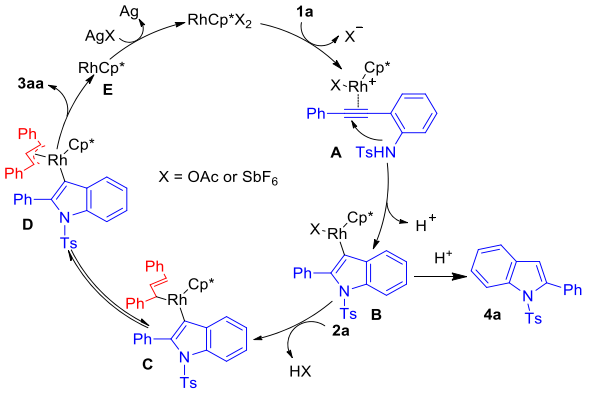
Scheme 6. Plausible Mechanism



C−H activation of **1a** promoted by **B** produces a rhodium intermediate **C**, which rapidly isomerizes to a Rh(III)-(η^3)-allyl intermediate **D**.[5a,15] Reductive elimination then affords the 3-allylindole product, and the resultant Rh(I) intermediate is reoxidized by AgOAc to regenerate the Rh(III) for the next catalytic cycle. We reasoned that the competition between protonolysis and allylic C−H activation is leveraged to the latter with an increasing amount of the olefin, which is consistent with our observation (Scheme 5d). If the irreversible allylic C−H activation would take place prior to the cyclization, the ratio of the indole byproduct should be independent of the amount of olefin.

In conclusion, we have realized mild synthesis of 3-allylindoles by a Rh(III)-catalyzed nucleophilic cyclization/allylation cascade. This coupling strategy employs the abundant chemical feedstocks of olefins and *o*-alkynylanilines without prefunctionalization of the substrate. Further studies on Rh(III)-catalyzed cyclization and couplings with other unsaturated substrates are underway in our laboratories.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.9b01553.

Experimental procedures, spectral data of new compounds, and crystallographic data of **3qa** (PDF)

Accession Codes

CCDC 1890239 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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