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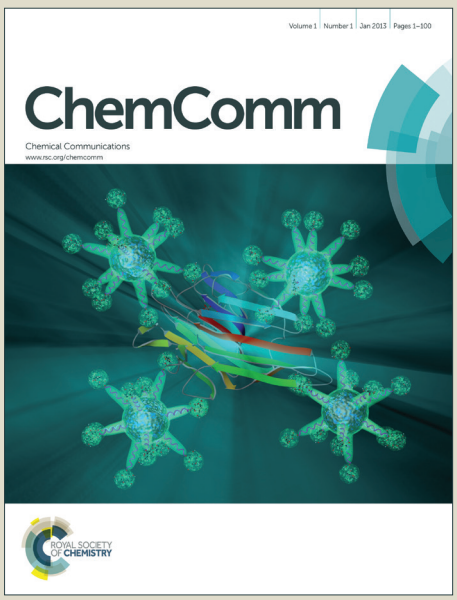

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ARTICLE TYPE

Rhodium(III)-Catalyzed C7-Position C-H Alkenylation and Alkynylation of Indolines†

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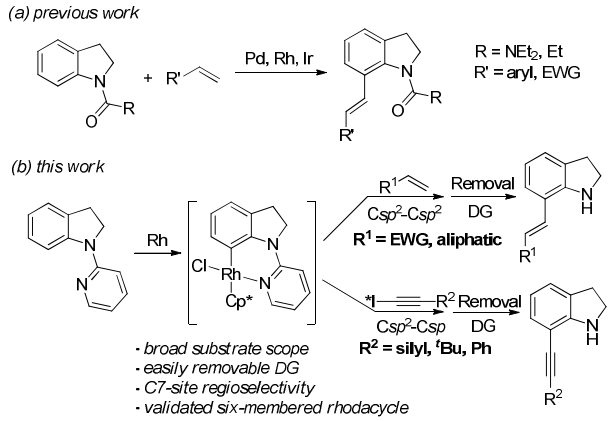
A Rh(III)-catalyzed regioselective C-H alkenylation and alkynylation of indolines is described. This protocol relies on the use of a removable pyridinyl directing group to access valuable C-7 functionalized indoline scaffolds with ample substrate scope and broad functional group tolerance.

The indoline-based alkaloids are ubiquitous structural motifs found in a multitude of biologically active natural products and pharmaceutical compounds as well as organic dyes.[1] Thus, the development of efficient protocols for regioselective synthesis of indoline congeners continues to be of great appeal in the synthetic community.[2] In sharp contrast to the tremendous number of studies made with aromatic systems,[3] regioselective C-H functionalization of indoline by virtue of a directing group attached to the nitrogen atom has been reported sporadically.[4] This strategy offers a direct access to the C-7 functionalization of indolines, in which transition-metal-catalyzed direct alkenylation predominated because of their potential for further manipulations.[4e-i] However, in spite of a plethora of novel synthetic methods have been developed, manifested issues such as removal of undesired external directing group,[5] narrow substrate scope limited to activated or electronically biased alkenes,[6] remained unsolved which drove us to explore a reliable and flexible protocol for the C-7 C-H alkenylation of indolines.

On the other hand, the introduction of an alkynyl group to an aryl C-H bond has drawn considerable interest owing to their diverse reactivity.[7,8] A striking example of the application of this strategy was illustrated in Pd-catalyzed oxidative C-7 alkynlation of indoline with (triisopropylsilyl)acetylene by Chang, albeit with low efficiency.[9] To achieve efficient C-H alkynylation, hypervalent iodine-alkyne reagents[10] featured by ethynylbenziodoxolones (EBXs) came to prominence as a more reactive alknylation source which have been systematically applied to direct alkynylation of electron-rich heterocycles by Waser.[11] Very recently, independent works by us[12], Glorius[13], Li[14] and Chang[15] elegantly broadened the synthetic application of EBXs to the C-H alkynylation of unactivated arenes and olefins by using rhodium or iridium catalysis. In light of these pioneering works and our own interest in the Rh(III)-catalyzed C-H bond functionalization,[16] we report herein Rh(III)-catalyzed C7–alkenylation and alkynylation of indolines by using readily available and easily removable pyridinyl group as a directing group (Scheme 1). This novel protocol exhibits a broad substrate scope, high regioselectivity and the reaction mechanism is investigated in detail.

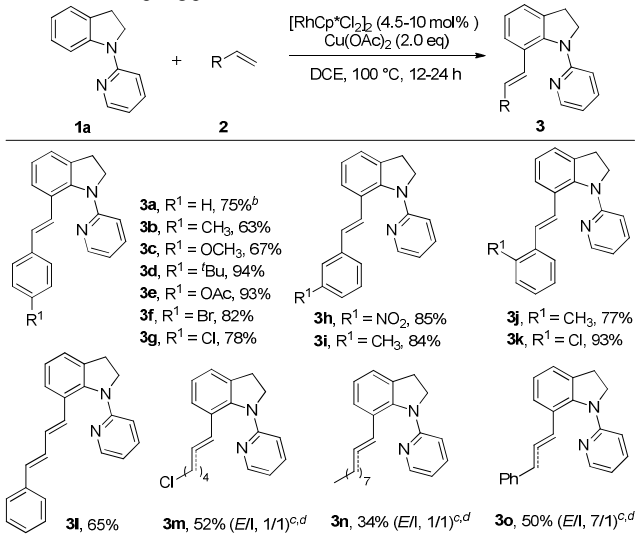


Scheme 1 C-H functionalization of indolines at C-7 position. EWG = electron-withdrawing group, DG = directing group, I^* = benziodoxolones.

We commenced our investigations with the screening of the reaction conditions for the coupling of 1-(pyridin-2-yl)indoline **1a** with styrene in the presence of $[RhCp^*Cl_2]_2$ (4.5 mol%) in 1,2-dichloroethane (DCE) at 100 °C (Table S1 in ESI†). To our delight, the use of AgOAc resulted in C-C bond formation at C-7 position, yielding the desired product **3a** in 48% yield (entry 1), with a high *E* stereoselectivity confirmed by X-ray analysis. Other oxidants such as benzoquinone, Ag_2CO_3 and Ag_2O did not promote the reaction at all (entries 2-4). Surprisingly, $Cu(OAc)_2$ enhanced the product formation, increasing the yield to 83%, with no apparent indoline-to-indole oxidation (entry 5). Other representative solvents such as toluene and tetrahydrofuran resulted in significant decrease of yields (entries 6-7). Control experiment suggested that $[RhCp^*Cl_2]_2$ was indispensable for the catalytic system (entries 8-10).

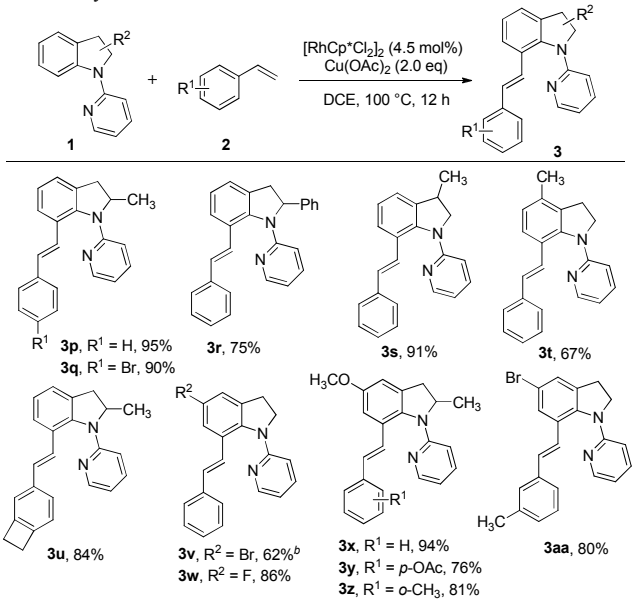
To evaluate the substrate scope of this reaction, the optimized reaction conditions were applied to a wide range of styrenes with different substituents in the phenyl moiety (Table 1). Both electron-donating groups such as methyl (**3b**), methoxy (**3c**), *tert*-butyl (**3d**) or ester (**3e**), and electron-withdrawing groups such as

Table 1 Substrate scope for the alkenylation of **1a** with styrenes and other alkene coupling partners[a]



[a]Unless otherwise noted, the reactions were carried out at 100 °C using **1a** (0.14 mmol), **2** (0.7 mmol), $Cu(OAc)_2$ (0.28 mmol), $[RhCp^*Cl_2]_2$ (0.006 mmol) in DCE (1 mL) for 12 h. Isolated yield. [b]1.0 mmol scale. [c]NaOAc (0.14 mmol) and extra 5 mol% of catalyst added and heated for 24 h. [d]Number in parentheses is the ratio between *E* form and positional isomer.

Table 2 Reaction scope for the alkenylation of indoline derivatives with different styrenes

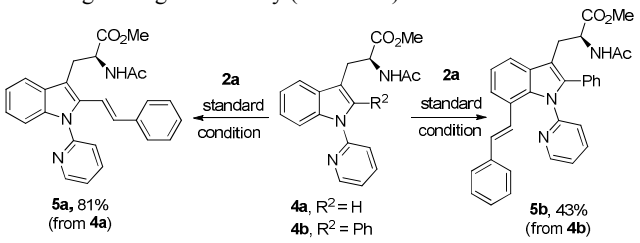


[a]An inseparable diastereomers was obtained in a ratio of 16:1 (*E*/*Z*).

halogens (**3f** and **3g**), could be tolerated at the *para*-position, and the reaction proceeded smoothly providing the corresponding C-7 alkenylindolines in good to excellent yields. Obvious electronic effects on the reactivities were not observed: a nitro group (**3h**) or methyl (**3i**) substituent at the *meta*-position of styrene did not impact the reactivity, thereby delivering the olefinated products in 85 and 84% yield, respectively. To our satisfaction, the challenging *ortho*-substituted styrenes bearing 2-methyl (**3j**) and 2-chloro (**3k**) could also be successfully employed. In addition, the reaction of **1a** with phenyl-1,3-butadiene possessing a conjugated double bond system proceeded smoothly at the terminal alkene position in acceptable yield (**3l**). More importantly, unbiased alkenes, for example, 6-chloro-1-hexene and 1-decene could be introduced under a modified reaction condition, affording a 1:1 mixture of thermodynamically favourable conjugated product together with positional isomers which were probably attributed to the migration of C-C double bond along the aliphatic chain (**3m** and **3n**).[6a] Interestingly, allylbenzene was found to react readily with good stereoselectivity, providing the corresponding product with 7/1 selectivity (**3o**). It is worth mentioning that the problematic issue of branched product was not observed under our protocol.[6e]

Subsequently, a variety of indoline substitution partners were subjected to the C7 alkenylation with styrenes to show the capability of the newly developed transformation (Table 2). The indolines bearing substituents at C2, C3, C4 or C5 position participated well in the coupling, providing the corresponding 7-substituted indolines in 62−95% yield (**3p**−**3aa**). Nevertheless, a chloride at C6 flanking the C7-H bond thwarted the reaction due to the steric congestion neighboured to the reactive site.

Moreover, considering the prevalence of the indole-core existing in complex natural products and drugs, the tryptophan derivative **4a** was subjected to the reaction system to showcase the applicability of this method. As expected, the preferential monoolefination occurred at the C-2 position of compound **4a** in good yield, which is consistent with the previous observations.[17] Hence, we envisioned that preinstalling a substituent at the C-2 position of **4a** would result in exclusive regioselectivity at the C-7 position. To this end, the substrate **4b** was synthesized[18] and then subjected to the standard condition, leading to the desired product **5b** with good regioselectivity (Scheme 2).



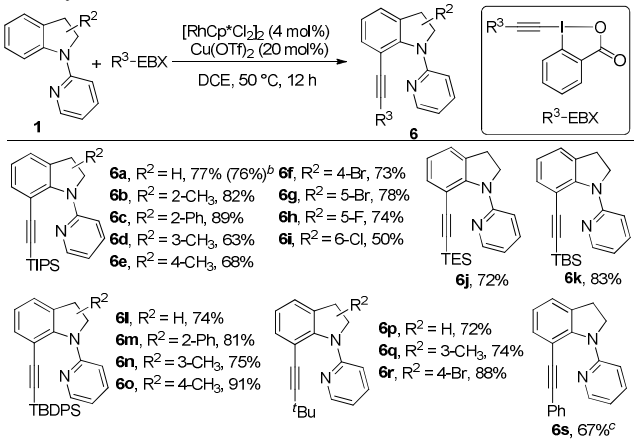
Scheme 2 Alkenylation of tryptophan derivatives

Encouraged by the results for the formation of Csp^2-Csp^2 bond, we became interested in the reactivity of indoline for constructing Csp^2-Csp bond at the C-7 position. Initial examination was focused on the reaction of the model substrate **1a** with commonly used hypervalent iodine reagent TIPS-EBX. The alkynylation reaction occurred smoothly in the presence of $[RhCp^*Cl_2]_2$ (4 mol%), $Cu(OTf)_2$ (11 mol%) in DCE at 50 °C, delivering 77% of **6a** as the best yield. Catalyst, additive and temperature were all shown to be crucial to this transformation (see Table S2 in ESI† for details).

Consequently, we explored the generality and limitation of this alkynylation protocol under the optimized condition (Table 3). In general, a wide range of indoline derivatives are compatible with this protocol, furnishing the desired products in moderate to good yields under relatively mild conditions. Regardless of the

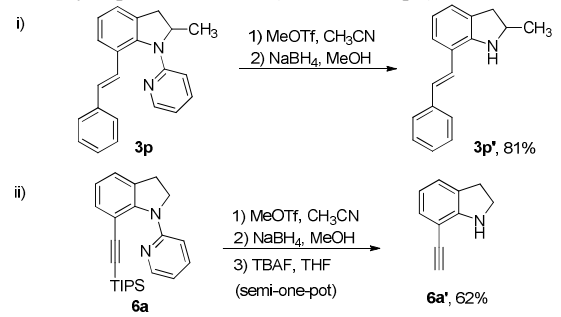
electronic nature and steric effect of the substituents on the indolines, the alkynylation reaction with TIPS-EBX proceeds well (**6b**−**6i**). Remarkably, the relative hindered indoline bearing a chloride group at the C-6 position, which had served as a limited substrate in the alkenylation reaction, could afford the product **6i** in 50% isolated yield. Furthermore, other hypervalent alkynyl iodine reagents was also examined with readily accessible indolines. The reaction exhibited high efficiency with different alkynes such as TES-EBX, TBS-EBX, TBDPS-EBX, and ^{t}Bu-EBX to furnish the corresponding products in good yields (**6j**−**6s**). Impressively, phenyl-based hypervalent alkynyl iodine, which usually failed to facilitate high level of conversion as an alkynylation reagent,[12,14] was also successfully engaged in such transformation (**6s**), with the reaction being complete within a shorter time even at room temperature.

Table 3 Substrate scope for the alkynylation of indoline derivatives with a variety of R^3-EBX [a]



[a]Unless otherwise noted, the reactions were carried out at 50 °C using **1** (0.14 mmol), TIPS-EBX (0.18 mmol), $Cu(OTf)_2$ (0.016 mmol), $[RhCp^*Cl_2]_2$ (0.0056 mmol) in DCE (1 mL) for 12 h. Isolated yield. [b]1.0 mmol scale. [c]R^3-EBX (0.36 mmol), $Zn(OTf)_2$ (0.028 mmol) at rt for 3 h.

Finally, removal of the pyridinyl directing group is crucial for realizing the generality of this method. On the basis of quaternization-hydride reduction strategy, the pyridine moiety of alkenyl indoline **3p** can be cleaved efficiently under mild condition by treatment of methyl trifluoromethanesulfonate (MeOTf) followed by $NaBH_4$ reduction (Scheme 3, eq i).[19] In the case of **6a**, a one-pot removal/desilylation procedure provided the terminal alkynyl indoline **6a'** in 62% overall yield in a more synthetically expedient manner (Scheme 3, eq ii).



Scheme 3 Removal of pyridinyl group and desilylation

To gain insight into the C-H activation mechanism, H/D exchange experiment was carried out in the presence of CD_3OD without addition of styrene. It was discovered that the starting material was completely recovered with a significant incorporation of deuterium at the C-7 position of indoline **1a**, supporting that the reversible C7-H insertion occurred under the Rh catalysis (see ESI† for details).

More mechanistic experiments were conducted to probe the fundamental catalytic process. The thermodynamically stable six-membered rhodacycle **c1** derived from **1a** was prepared independantly at this stage,[20] which was unequivocally determined by single-crystal analysis (Fig. 1). A stoichiometric amount of **c1** reacted with styrene or TIPS-EBX in shorter time (Scheme 4, eq i), indicating that C-H functionalization is likely to be the rate-determining step. Whilst rhodacyclic complex was applied as a catalyst to the reaction of substrate **1a** with styrene or TIPS-EBX under the standard conditions, corresponding product **3a** or **6a** was isolated in essentially the same yields, with respect to those obtained with $[RhCp^*Cl_2]_2$ (Scheme 4, eq ii). This suggests that **c1** is probably involved as an active intermediate or a direct precursor in the catalytic cycle.

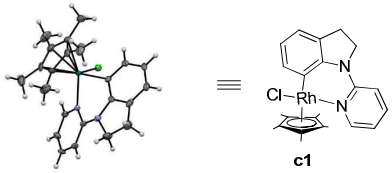
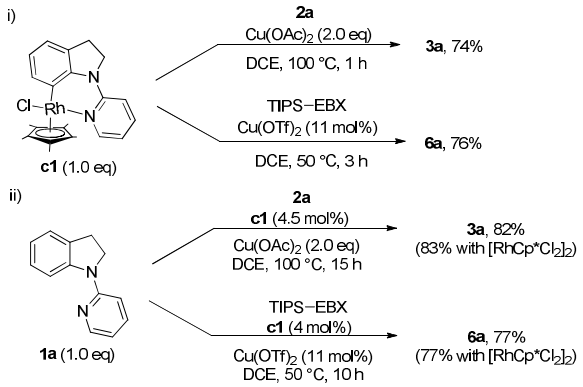


Fig. 1 ORTEP of rhodacyclic compound **c1** derived from **1a**



Scheme 4 i) Stoichiometric reactions of complex **c1** with styrene or TIPS-EBX; ii) Alkenylation and alkynylation catalyzed by complex **c1**.

In summary, we have developed a mild, efficient, and versatile Rh(III)-catalyzed direct C7 alkenylation and alkynylation of indolines using pyridinyl as a removable directing group. Based on the strong coordination of pyridinyl group with rhodium in the C-H insertion step, the regioselective C7-functionalized indolines were obtained with broad substrate scope and functionality tolerance. A catalytically competent six-membered rhodacycle has been synthesized, revealing a key intermediate species in the catalytic cycle. Supporting data includes the isolation of the rhodacycle and the demonstration of its catalytic activity. This protocol provides a convenient route for the construction of Csp^2-C$sp^2$and Csp^2-Csp bond of indoline scaffolds with synthetic ease.

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Notes and references

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