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# Palladium-Catalyzed α-Arylation of Enones in the Synthesis of 2-Alkenylindoles and Carbazoles

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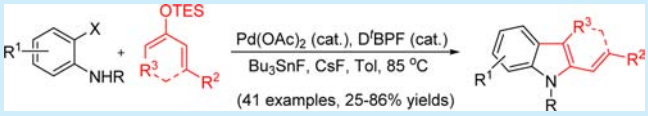
Supporting Information

**ABSTRACT:** A new unified strategy has been developed for the synthesis of substituted 2-alkenylindoles and carbazoles. The strategy uses palladium-catalyzed α-arylation of TES-enol ethers of enones as the key step. The method is highly regioselective, provides good yields, and is expected to have wide application.




Indoles and carbazoles belong to a unique class of nitrogen heterocycles that has gained the attention of synthetic chemists for over a century.[1] It is hardly surprising that tremendous effort has been dedicated to the synthesis of substituted indoles and its derivatives. The 2-alkenylindole core is an important structural constituent of several biologically relevant molecules, which include, among others, asphidophytine,[2] fluvastatin,[3] flinderoles,[4] and chartelline C[5] (Figure 1).

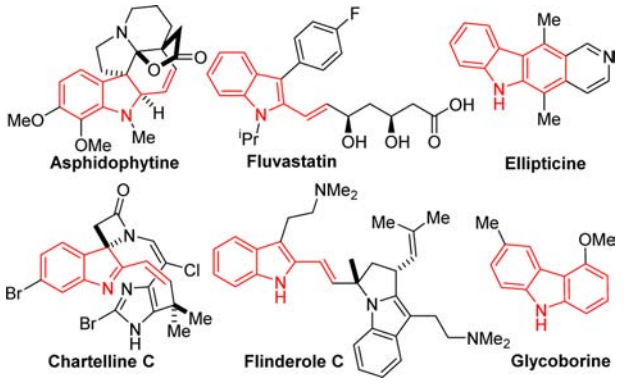
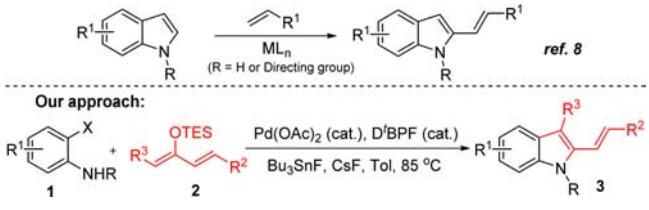



**Figure 1.** 2-Alkenylindole core and carbazoles in biologically relevant molecules.

Apart from being a constituent of such important molecules, 2-alkenylindoles are quite significant starting materials for building architecturally complicated indole-based organic materials.[6]

Not only are these indoles important in cycloaddition reactions while functioning as dienes, they have also been utilized in 6-π electrocyclization reactions of 2,3-dialkenylindoles so as to result in carbazoles.[7] They are also critical starting materials in the synthesis of bioactive 2-alkylindoles.[6d] It is therefore obvious that 2-alkenylindoles have become popular synthetic targets, especially after the advent of the oxidative-Heck reaction and the refinement of the regioselectivity using a variety of C−H functionalization methods.[8] However, in most of these oxidative olefination reactions, activated olefins are employed, which limits the utility of the methods. Other approaches[9] for the synthesis of 2-alkenylindoles include traditional olefination reactions using indoles prefunctionalized at the C-2 position with halides/pseudohalides or often boronates. The main drawback of these methods is the need to synthesize the indole core and then functionalize it. We report herein a new approach for the regioselective assembly of substituted indoles and carbazoles using an α-arylation[10] strategy for TES-enol ethers of enones (Scheme 1). This

**Scheme 1. Previously Reported Approaches and the Present Methodology**




regioselective α-arylation methodology for enones was recently developed in our laboratory[11] in which Hartwig's synergistic catalysis[12] was combined with Kuwajima−Urabe conditions.[13]

Synthetic approaches to indoles using *o*-haloanilines and enolizable ketones or their equivalents by the formation of imines/enamines and subsequent annulation have been well documented in the literature.[14,15] These methods suffer from regioselectivity issues when multiple enolizable positions are available and are therefore limited in substrate scope. In another approach, transition-metal-catalyzed aminations of olefins to form enamines, followed by an intramolecular cyclization reaction, have resulted in the indole framework.[16] However, barring the oxidative-Heck reactions, most of these methods cannot be used for the synthesis of 2-alkenylindoles.

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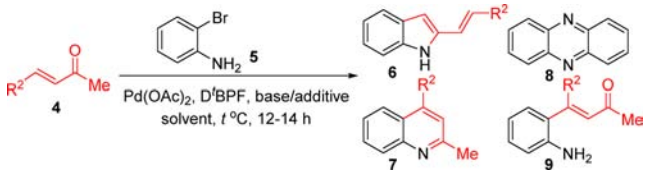
**Table 1. Base-Mediated Arylation Reactions of Enones with *o*-Bromoaniline**

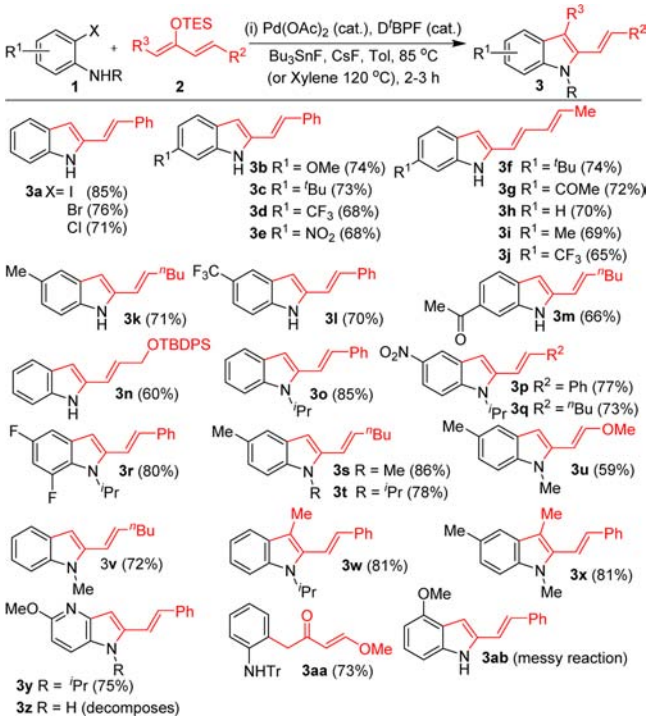



| run | $R^2$ | base/additive | solvent | temp (°C) | yield (%) 6 | 7 | 8 | 9 |
|---|---|---|---|---|---|---|---|---|
| 1 | Ph | TEA | DMF | 120 | <5 | 20 | <5 | 29 |
| 2 | Ph | $K_3PO_4$ | toluene | 85 | 31 | <10 | <5 | <5 |
| 3 | Ph | $K_3PO_4$ | DMF | 120 | 28 | 16 | <10 | <5 |
| 4 | Ph | $Bu_3SnF$,CsF | toluene | 85 | <10 | 15 | <5 | 15 |
| 5 | Ph | NaOAc | toluene | 85 | 34 | <15 | <5 | <5 |
| 6 | $^n$Bu | $K_3PO_4$ | toluene | 85 | messy reaction | | | |
| 7 | $^n$Bu | $K_3PO_4$ | DMF | 120 | messy reaction | | | |
| 8 | Ph | KO$^t$Bu | toluene | 85 | messy reaction | | | |
| 9 | $C_3H_5$ | NaOAc | DMF | 120 | messy reaction | | | |

Initially, in order to develop a new method for the synthesis of substituted 2-alkenylindoles, we attempted to utilize traditional transition-metal-mediated, base-catalyzed $\alpha$-arylation methods. These led mostly to variable mixtures of quinolines,[17] indoles, phenazines, or simple Heck products that were incapable of cyclization owing to the stereochemistry (Table 1). The desired 2-alkenylindoles were usually obtained in minor quantities, and the reaction outcome was mostly substrate dependent.

We then turned to the recently developed methodology in our laboratory for the $\alpha$-arylation of silyl enol ethers of enones[11] and treated them with *o*-haloanilines using palladium catalysis. To our delight, the reaction proceeded very well, and the desired products were obtained in excellent yields (Scheme 2). The reaction with *o*-iodoaniline gave slightly better yields than the bromides or chlorides. However, it is rather difficult to obtain a large library of *o*-iodo- or *o*-chloroanilines; therefore, although the reaction worked very well with iodo- or chloroanilines, we persisted with *o*-bromoanilines as our substrate of choice. The *N*-alkyl-*o*-haloanilines usually gave better results than the simple anilines. The reaction was quite general in terms of substrate scope, and wide variations in anilines and the enones were well tolerated. The current method provides access to 2-alkenylindoles where the C-2 position is functionalized with electron-neutral as well as electron-rich olefins, which is extremely difficult to achieve in oxidative-Heck reactions. It was also very heartening to see that *o*-haloanilines with electron-withdrawing substituents also resulted in a very good transformation (Scheme 2, entries **3l,p−r**). This result is important for the reason that in methods that utilize enamine/imine formations before the annulation, electron-deficient anilines do not perform very well. In our method, a variety of silyl enol ethers could be reacted easily, and the regioselectivity was exclusive to result in 2-alkenylindoles in good to excellent yields. Interestingly, a minor side product was obtained in some of the reactions in the form of the phenazine (of the type **8**, Table 1) arising out of the homodimerization of the aniline (via a dual Buchwald−Hartwig amination).[18] This side reaction was dependent on the reactivity of the silylenol ether and the *o*-haloaniline. When the reactivity of the enol ether was high, the phenazine product was not observed or was obtained in negligible quantities. An

**Scheme 2. Substrate Scope for 2-Alkenylindoles**[a]




[a]Wherever not specified, X = Br; all yields are isolated yields.

important result in the form of azaindoles was also obtained in the form of **3y**. Unfortunately for us, the −*N*H analogue **3z** could not be isolated in pure form. Gratifyingly, the *N*-$^i$Pr azaindole **3y** could be isolated in good yield. Interestingly **3u** was obtained in decent yields from the reaction with Danishefsky diene (TES analogue);[19] whereas **3aa** remained uncyclized due to steric bulk of the trityl group on the nitrogen. Another reason postulated for this was the lower electrophilicity of the carbonyl of the enone. It is important to note that the same *N*-trityl-2-bromoaniline resulted in **3a** when the corresponding silyl enol ether was derived from 4-phenyl-3-buten-2-one. The reaction for **3ab** was not clean, and the compound could not be obtained in pure form.



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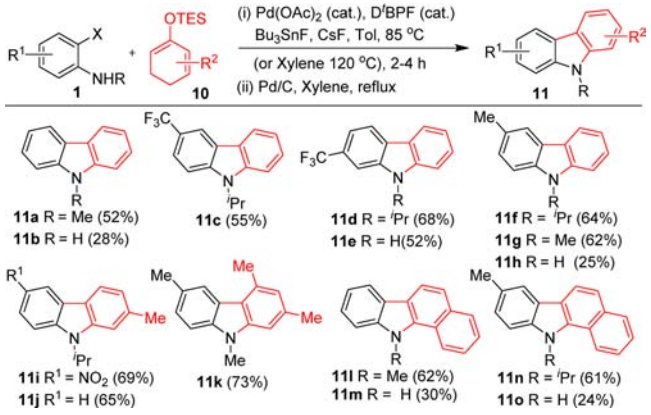
Just as indoles, carbazoles are important structural motifs of several bioactive molecules and have been the subject of interest of synthetic chemists.[20] We successfully extended this methodology to the synthesis of carbazoles. Reactions with the silyl enol ethers of cyclohexenones resulted in very clean conversions to the tricyclic core structures which could be easily aromatized to the parent carbazole (Scheme 3). In this

**Scheme 3. Substrate Scope for Substituted Carbazoles**[a]

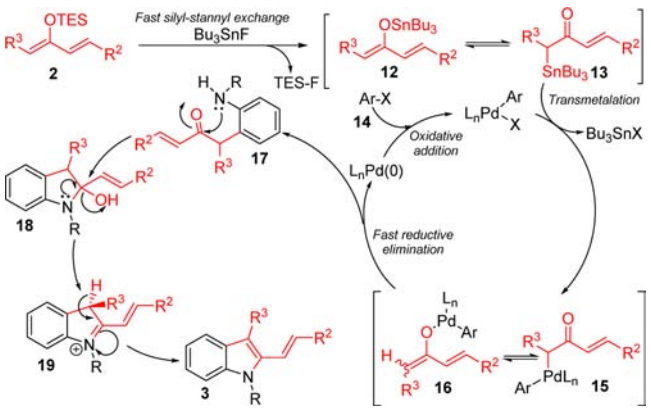



[a]All yields are isolated yields.

case, too, the yields with *N*-alkyl-*o*-haloanilines were found to be much better than the corresponding anilines where the amine functionality was unsubstituted. The reactivity of the cyclohexenone silylenol ether was found to be slightly lower than silylenol ethers of other acyclic enones. Therefore, in these cases, the phenazine byproduct was obtained in 10−30% yields. The highlight of this work is the fact that **11i** and **11j** were obtained as exclusive regioisomers. It is important to note that the regioselective synthesis of these, via base-mediated $\alpha$-arylation of corresponding cyclohexanones, is not possible. Of the compounds depicted in Scheme 3, **11l−o** were obtained from silylenol ethers of 2-tetralone and are not from enone systems. Our method therefore constitutes a quick intermolecular assembly of carbazoles in which a wide variation in form of the *o*-haloaniline and the cyclohexenone could be effected.

A plausible mechanism for the transformation is depicted in Scheme 4.[11] Upon formation of **17** via a palladium-catalyzed $\alpha$-arylation reaction of the TES-enol ether of the enone with the *o*-haloaniline, the condensation reaction of the aniline with the

**Scheme 4. Plausible Mechanism**




enone results in the annulation to indole **3**. The simple fact that the $\alpha$-arylation occurs before the condensation drives the regioselectivity in this reaction.

In summary, we have developed a new strategy, via palladium-catalyzed $\alpha$-arylation, for the synthesis of 2-alkenylindoles and carbazoles. In this approach, we utilized silylenol ethers of enones to direct the regioselectivity and offer a better alternative approach to the oxidative-Heck reaction of indoles. This methodology stands out because simple metal-catalyzed base-mediated $\alpha$-arylation reactions with enones do not result exclusively in 2-alkenylindoles. This is also true for regioselective synthesis of substituted carbazoles which cannot be achieved by the base-mediated reaction. Further application of this strategy in a synthesis of other heterocycles and mechanistic studies is currently underway.

## ■ ASSOCIATED CONTENT

### Supporting Information

Experimental procedures and full spectroscopic data for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest.

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