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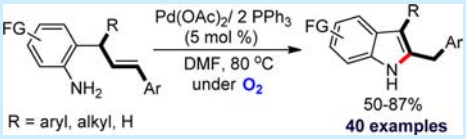
Synthesis of Functionalized Indoles via Palladium-Catalyzed Aerobic Oxidative Cycloisomerization of *o*-Allylanilines

Rajender Nallagonda, Mohammad Rehan, and Prasanta Ghorai*

Department of Chemistry, Indian Institute of Science Education and Research Bhopal, Bhopal 462066, India

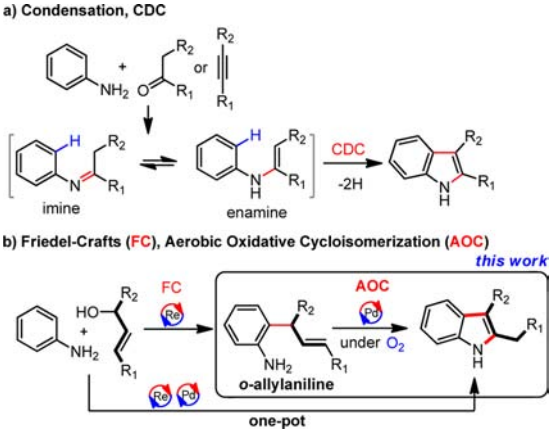
Supporting Information

ABSTRACT: An efficient strategy for the synthesis of 3-substituted 2-benzylindoles from stable and readily available *o*-allylanilines, prepared from anilines and allyl alcohols, has been developed. The reaction occurred via a regioselective *5-exo-trig* intramolecular oxidative cycloisomerization using $Pd(OAc)_2$ as catalyst and molecular oxygen as an oxidant. The reaction showed a broad substrate scope with good to excellent yields.



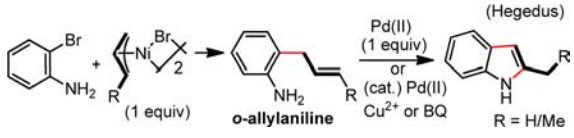
Indoles are probably the most ubiquitous heterocycles in pharmaceuticals and natural products.[1] Therefore, the search for new synthetic strategies for the synthesis of indoles from simple starting materials with a sustainable and atom-economical approach is of continued interest.[2] In recent times, the direct use of anilines instead of modified aniline derivatives such as aryl hydrazines (Fischer indole synthesis)[3] and substituted anilines such as *ortho*-haloanilines (Larock indole synthesis)[4] has emerged as a very powerful strategy. The low cost and wide variety of commercially available anilines make this strategy sustainable and environmentally benign. In this context, a cross-dehydrogenative coupling (CDC) of *N-arylimine* or *enamine*, wherein a coupling of two C−H bonds leads to the formation of C−C bond, opened a new era in indole synthesis (Scheme 1a).[5−7] Such *imine* or *enamine* intermediates are prepared by condensation of anilines with carbonyls. Nevertheless, the requirement of preformed sensitive *imines* or *enamines* is the critical drawback of many such methods.

Scheme 1. Indole Synthesis from Anilines



We became interested in developing a strategy for the synthesis of indoles from *o*-allylanilines driven by the fact that they are stable in nature, and a wide variety of highly substituted analogues are easily accessible from allyl alcohols and commercially available anilines (Scheme 1b).[8] The pioneering work by Hegedus on Pd(II)-mediated intramolecular oxidative cyclization of *o*-allylanilines resulting in the formation of indoles remained the basis of this work (Scheme 2).[9] However, the limitations of their approach were as follows: (i) the synthesis of *o*-allylaniline intermediates was not practical as a stoichiometric allylnickel bromide dimer were used, (ii) the substrate scope was limited (only R = Me), and (iii) the stoichiometric quantities of palladium complex and/or stoichiometric quantities of oxidant such as $Cu(OAc)_2$ or benzoquinone were required. Oxidants such as $Cu(OAc)_2$, AgOAc, $PhI(OAc)_2$, BQ, etc. have been successfully used in many cases.[10] However, the use of dioxygen remains as an "ideal oxidant" and offers an attractive prospect in terms of industrial applications, as well as green and sustainable developments.[11]

Scheme 2. Cross-Coupling, Oxidative Cycloisomerization



3-Substituted 2-benzylindoles are also an important motif in several bioactive molecules (Figure 1).[12] However, there are very limited methods available to synthesize such scaffolds.[13]

Herein, we report an operationally simple and mild method for the synthesis of highly functionalized 3-substituted 2-benzylindoles from *o*-allylanilines catalyzed by $Pd(OAc)_2$ under O_2 as the oxidant with a broad functional group compatibility. Further development of the corresponding one-pot protocol starting from aniline and allylalcohol for the synthesis of indoles

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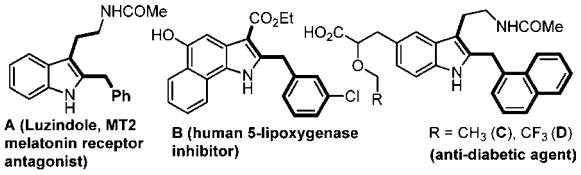
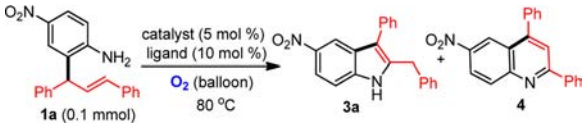


Figure 1. Bioactive 3-substituted 2-benzylindoles.

using oxorhenium/palladium as dual catalytic system has also been developed.

We started our reaction optimization by exploring the oxidative cyclization of *o*-allylaniline (**1a**) under aerobic reaction conditions as summarized in Table 1. Among various

Table 1. Catalyst Optimization



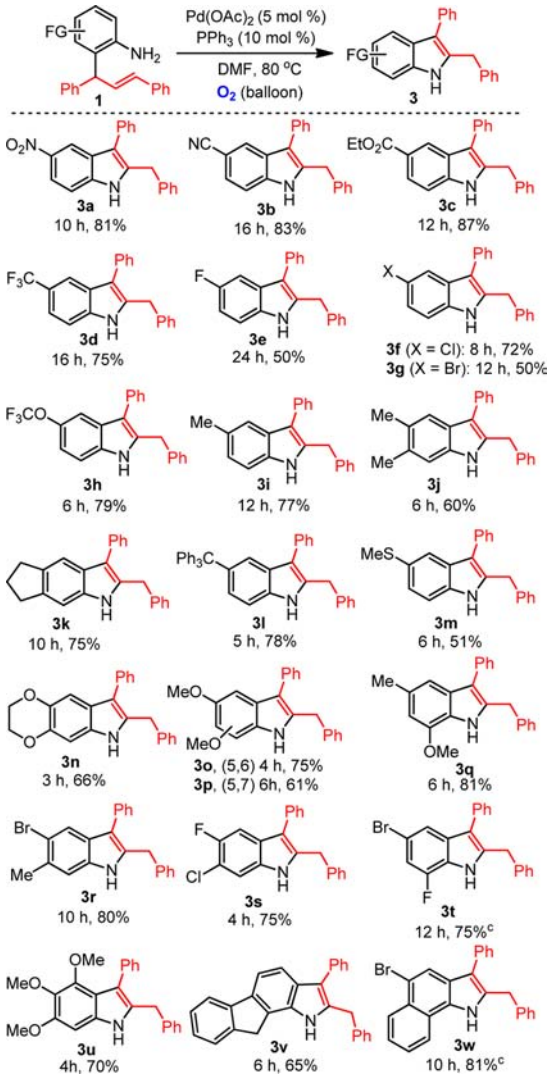
entry	catalyst	ligand	solvent	3a[a] (%)
1	$Pd(PPh_3)_4$		DMF	70
2	$Pd(PPh_3)_2Cl_2$		DMF	9
3	$Pd(OAc)_2$		DMF	83
4	$(ACN)_2Cl_2Pd$[c]		DMF	3
5	$Pd(OAc)_2$	PPh_3	DMF	>95[b]
6	$Pd(OAc)_2$	PPh_3	ACN[c]	40
7	$Pd(OAc)_2$	PPh_3	toluene	80
8	$Pd(OAc)_2$	PPh_3	THF	<10
9	$Pd(OAc)_2$	PPh_3	1,4-dioxane	25
10	$Pd(OAc)_2$	PPh_3	DCE	<10

[a]The conversions were determined based on ^{1}H NMR data of the reaction mixture using acetophenone as internal standard. [b]A trace (<5%) of **4** was observed. [c]ACN = acetonitrile.

palladium catalysts (5 mol %) in DMF at 80 ∘C, $Pd(OAc)_2$ provided relatively the best conversion to the corresponding indole **3a** (entries 1−4). Further, the amount of conversion increased on addition of Ph_3P (10 mol %) as ligand in addition to $Pd(OAc)_2$ catalyst (entry 5). However, the efficiency of the catalyst remained less effective in other solvents such as acetonitrile, toluene, THF, 1,4-dioxane, and 1,2-dichloroethane (DCE) (entries 6−10, respectively). On lowering the reaction temperature as well as catalyst loading, the conversions were diminished (see the Supporting Information).

With the optimized reaction conditions in hand, we examined the scope of the present oxidative cyclization reaction of *o*-allylanilines, as summarized in Scheme 3. *o*-Allylanilines with substitution on aniline moiety with electron-withdrawing substituents such as nitro, cyano, ethylester, trifluoromethyl, halogens (F-, Cl-, and Br-) and trifluoromethoxy groups proceeded smoothly to afford the desired indoles (**3a−h**) in good to excellent yield. Similarly, with electron-donating groups, including methyl, dimethyl, trityl, methylthio, and dialkoxy on the aryl moiety, were effectively converted to the corresponding 2-benzyl-3-phenylindoles **3i−n**, respectively. Various di- (**3j−k,n−t**) and tri- (**3u**) substitutions on the aryl ring were nicely tolerated to provide the highly functionalized indoles. Other types of aryl groups, such as 9*H*-fluorene-2-allyl-1-amine and 4-bromo-2-allylnaphthylamine, were equally applicable to provide fused tetracyclic **3v** and tricyclic **3w** indoles, respectively, in good yields. Notably, halogen

Scheme 3. Variation of Arylamine[a,b]



[a]Reaction conditions: *o*-allylaniline **1** (0.20 mmol), $Pd(OAc)_2$ (5 mol %), Ph_3P (10 mol %), DMF (0.5 mL). [b]Isolated yields after column chromatography. [c]10 mol % of $Pd(OAc)_2$ and 20 mol % of PPh_3 was used at 100 °C.

substitutions, such as bromo- and chloro-, which are sensitive to palladium-catalyzed reaction conditions, are also compatible with the present reaction conditions to provide the corresponding indoles (**3f−g,r−t,w**).

Next, we examined the oxidative cyclization of *o*-allylanilines containing substitutions on allyl counterparts, which are summarized in Scheme 4. Various symmetrically substituted 1′,3′-diarylallyls such as *p*-methyl, *p*-chloro-, and *p*-bromo-phenyls attached to anilines at the *ortho*-position reacted smoothly to provide the desired indoles (**5a−c**, respectively) in moderate yields. Similar reactivity was found with *o*-allylaniline having *α*-naphthyl as the aryl counterpart on allyl moiety (**5d**). Starting with an inseparable mixture of unsymmetrically substituted 1′,3′-diaryl *o*-allylanilines, a equimolar mixture of corresponding substituted indoles (**5e,f**) was obtained. The synthesis of 2-benzyl-3-methylindoles (**5g,h**) was achieved from the corresponding unsymmetrical substituted 1′-methyl-3′-aryl allyls. Moreover, 2-benzylindoles containing long alkyl chain (**5i**), o-acetyl ethyl (**5j**), and *γ*-successfully synthesized using

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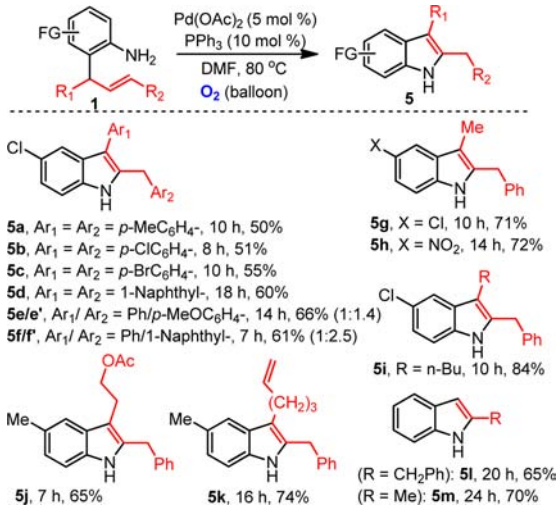
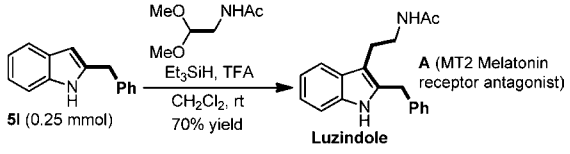
Scheme 4. Variation of Allyl Counterpart[a,b]



[a]Reaction conditions: *o*-allylaniline **1** (0.20 mmol), $Pd(OAc)_2$ (5 mol %), Ph_3P (10 mol %), DMF (0.5 mL). [b]Isolated yields.

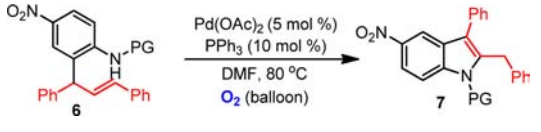
this method from the ethylenepropyl (**5k**) on 3-position have also been corresponding *o*-allylanilines. Notably, these 2-benzylindoles containing *o*-acetyl ethyl (**5j**) or *γ*-ethylenepropyl (**5k**) on the 3-position could potentially be converted to many biologically active substituted indoles such as indole **A**−**C** (shown in Figure 1). For example, the synthesis of MT2 melatonin receptor antagonist, luzindole (**A**), has been synthesized from **5l** in a single straightforward step as shown in Scheme 5.[12c] In addition to 2-benzylindoles, 2-alkylindoles could easily be synthesized using this strategy; for example, 2-methylindole (**5m**) was prepared from 2-allylaniline.

Scheme 5. Synthesis of Bioactive 3-Substituted 2-Benzylindole



The feasibility of cyclization of *N*-protected *o*-allylanilines under the current reaction conditions were also tested (see Table 2). In the case of *N*-Boc-protected *o*-allylaniline **6a**, oxidative cyclization occurred to provide the corresponding indole without having Boc-group (**3a**, entry 1). Using Bn and Me as protecting group, the cyclization did not occur at all (entries 2 and 3). Further, in case of *N*-allyl (**6d**), the allylic group is deprotected without proceeding for cyclization (entry 4).

Table 2. Reaction with N-Protected *o*-Allylanilines[a]

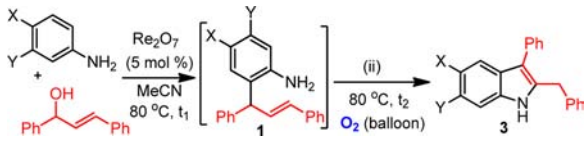


entry	PG- (**6**)	time (h)	**7**[b] (%)	recovered[b] (%)	other product[b] (%)
1	Boc- (**6a**)	24	–	**6a**, 16	**3a**, 80
2	Bn- (**6b**)	24	–	**6b**, 78	–
3	Me- (**6c**)	24	–	**6c**, 90	–
4	Allyl- (**6d**)	24	–	**6d**, –	**1a**, 90

[a]Reaction conditions: same as Scheme 3. [b]Isolated yields.

Finally, a one-pot, sequential FC-allylation of anilines with allyl alcohol using Re_2O_7 as catalyst followed by palladium-catalyzed oxidative cyclization to provide 3-substituted 2-benzylindoles has been demonstrated (see Table 3). Although moderate yields are obtained, nevertheless, the one-pot method is expected to be of high synthetic utility.

Table 3. One-Pot Protocol: Co-operative Catalysis[a]

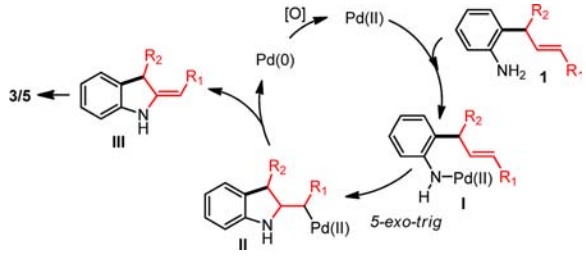


entry	X	Y	t_1 (h)	t_2 (h)	**3**[b] (%)
1	O_2N	H	14	10	**3a**, 51
2	NC	H	20	20	**3b**, 52
3	EtO_2C	H	20	24	**3c**, 48
4	Me	Me	10	3	**3j**, 52

[a]Reaction conditions: (i) alcohol (0.20 mmol), aniline (0.24 mmol), Re_2O_7 (5 mol %) in CH_3CN; (ii) $Pd(OAc)_2$ (10 mol %), Ph_3P (20 mol %), DMF (0.5 mL). [b]Isolated yields after column chromatography.

On the basis of this work and previous reports,[9,14] a tentative mechanism for the current cyclization reaction is proposed in Scheme 6. The initial step involves palladium-catalyzed

Scheme 6. Proposed Mechanism for Current Oxidative Cyclization



aminopalladation of 2-allylaniline **I** via an intramolecular 5-*exo-trig* cyclization to generate intermediate **II**.[14] Subsequent *β*-hydride elimination affords intermediate **III**, which undergoes isomerization to form product **3** or **5**. In this catalytic cycle, the Pd(0) was assumed to be oxidized by molecular oxygen to regenerate the active Pd(II) catalyst.

In summary, a versatile catalytic method for the synthesis of 3-substituted 2-benzylindoles through palladium-catalyzed intramolecular oxidative annulation of *o*-allylanilines has been disclosed. Molecular oxygen is used as an oxidant. A sequential synthesis of *o*-allylaniline, starting from corresponding aniline and substituted allyl alcohols, followed by oxidative cycloannulation has also been demonstrated. In view of the high pharmaceutical importance of the functionalized indoles, this simple and practical synthetic strategy may become another route to indoles. Extension of the present reaction demonstrated toward the synthesis of related heterocyclic moieties and detailed mechanistic investigations are currently in progress in our laboratory.

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■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures, characterization data, and copies of NMR spectra for all products. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: pghorai@iiserb.ac.in.

Notes

The authors declare no competing financial interest.

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■ DEDICATION

Dedicated to Professor James Takacs on the occasion of his 60th Birthday.

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