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Sequential Sonogashira/intramolecular aminopalladation/cross-coupling of *ortho*-ethynyl-anilines catalyzed by a single palladium source: rapid access to 2,3-diarylindoles†

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We have developed a practical and efficient one-pot protocol for the synthesis of 2,3-diarylindoles *via* Pd-catalyzed bis-arylative cyclization of various *o*-ethynylanilines with aryl iodides. Mechanism studies showed that a Pd-catalyzed Sonogashira reaction took place firstly, giving an internal alkyne intermediate, which subsequently underwent intramolecular aminopalladation/cross-coupling to give access to 2,3-diarylindoles. The present methodology exhibits a broad substrate scope, producing various 2,3-diaryl indoles bearing two different aryl groups.

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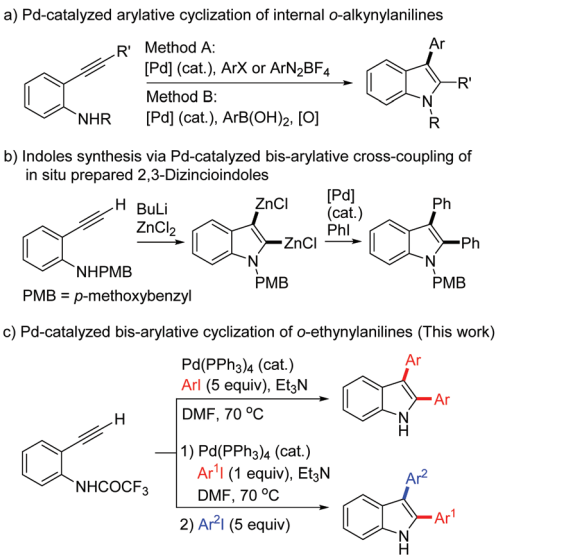
Introduction

Substituted indole nuclei as a classical important N-heterocyclic moiety exist widely in many biologically active natural products and have applications in many drugs showing anticancer, antivirus, antitumor, and inhibition activities.[1] In particular, 2,3-disubstituted indoles have attracted considerable attention owing to their outstanding bio-significant applications. 2,3-Diarylindoles have been found to inhibit tubulin polymerization,[2] and exhibit anti-inflammatory[3] and bioluminescence properties.[4] For example, 2,3-bis(4-methoxyphenyl)indoles (indoxole) have been proven to exhibit a stronger anti-inflammatory activity than common drugs such as aspirin and indomethacin.[5]

Over the past decades, various strategies have been developed for the synthesis of 2,3-disubstituted indole derivatives.[6] *o*-Alkynylanilines are the most commonly used starting materials to prepare substituted indole derivatives. For example, 2,3-disubstituted indole derivatives could be synthesized by Pd-catalyzed cyclization/cross-coupling of *o*-alkynylanilines with either aryl halides[7] or aryldiazonium salts[8] (Scheme 1a, Method A). Alternatively, 2,3-diaryl indoles could also be prepared under Pd catalysis by using arylboronic acids as coupling partners in the presence of an oxidation reagent (Scheme 1a, Method B).[9] Recently, Nakamura and co-workers reported a novel method to synthesize 2,3-disubstituted indoles through Pd-catalyzed cross-coupling of PhI with 2,3-dizincioindole, a vinylene dizinc species, *in situ* prepared *via*



Scheme 1 Synthesis of 2,3-disubstituted indoles *via* the Pd-catalyzed transformation of *o*-ethynylanilines.

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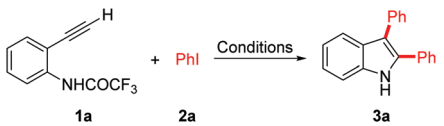
dizincation/cyclization of 2-ethynylanilines with a terminal alkyne.[10] However, this methodology only allows access to the 2,3-diaryl indoles bearing two same aryl groups at 2- and 3-positions. Therefore, we wonder if *o*-alkynylanilines bearing a terminal alkyne, under activation of a Pd catalyst, could undergo bis-arylative cyclization to directly afford 2,3-diaryl indoles through the formation of a vinylene dipalladium intermediate (2,3-dipalladated indole). Herein, we report a Pd-catalyzed bis-arylative cyclization of *o*-ethynyl-anilines to prepare 2,3-diaryl indoles. Several control experiments suggested an internal alkyne intermediate to be the reaction intermediate formed through a Pd-catalyzed Sonogashira reaction, which subsequently underwent intramolecular aminopalladation/cross-coupling to give access to 2,3-diarylindoles. This methodology could also be used to synthesize 2,3-diaryl indoles bearing two different aryl groups at 2- and 3-positions.

Results and discussion

Initially, we commenced our study by testing the reaction of *o*-ethynyltrifluoroacetanilides **1a** and iodobenzene **2a** in the presence of several commonly used Pd catalysts and bases (Table 1). By using Et_3N as the base, we examined the reaction in different solvents in the presence of a 10 mol% $Pd(PPh_3)_4$ catalyst at 70 °C for 5 h (Table 1, entries 1–5). To our delight, the desired bis-arylative product **3a** was obtained in a high yield of 82% by using DMF as the solvent (Table 1, entry 5). Extending the reaction time to 8 h, 12 h, 18 h, and 24 h resulted in an increase of the yields up to 86–91%, respectively (Table 1, entries 6–9). At either lower temperature (50 °C) or elevated temperature (100 °C), a lower isolated yield of **3a** was obtained. The reaction conditions were further screened with other palladium catalysts such as $Pd_2(dba)_3$, $Pd(OAc)_2$, $PdCl_2$ and $Pd(PPh_3)_2Cl_2$, but all failed to improve the product yield (Table 1, entries 12–15). When the reaction was carried out by replacing Et_3N with other bases, the desired product **3a** was isolated in lower yields of 10–52% yields (Table 1, entries 16–18). The lower catalyst loading of 5 mol% led to a much lower yield of **3a** (Table 1, entry 19). Reducing the amount of either Et_3N to 3.0 equivalents or PhI to 2.0 and 3.5 equivalents also had no positive effect on the formation of **3a** (Table 1, entries 20–22). Based on these results, the optimal reaction conditions were determined as follows: 10 mol% $Pd(PPh_3)_4$ with 5 equiv. of Et_3N in DMF at 70 °C.

Table 1 Optimization of reaction conditions[a]



1a **2a** **3a**

Entry	Catalyst	Base	Solvent	*T* (°C)	Yield (%)[b]
1	$Pd(PPh_3)_4$	Et_3N	Toluene	70	N.D.
2	$Pd(PPh_3)_4$	Et_3N	CH_3CN	70	<10
3	$Pd(PPh_3)_4$	Et_3N	DCE	70	36
4	$Pd(PPh_3)_4$	Et_3N	DMSO	70	72
5	$Pd(PPh_3)_4$	Et_3N	DMF	70	82
6[c]	$Pd(PPh_3)_4$	Et_3N	DMF	70	86
7[d]	$Pd(PPh_3)_4$	Et_3N	DMF	70	87
8[e]	$Pd(PPh_3)_4$	Et_3N	DMF	70	89
9[f]	**$Pd(PPh_3)_4$**	**Et_3N**	**DMF**	**70**	**91**
10	$Pd(PPh_3)_4$	Et_3N	DMF	50	<10
11	$Pd(PPh_3)_4$	Et_3N	DMF	100	48
12	$Pd_2(dba)_3$	Et_3N	DMF	70	Trace
13	$Pd(OAc)_2$	Et_3N	DMF	70	42
14	$PdCl_2$	Et_3N	DMF	70	53
15	$Pd(PPh_3)_2Cl_2$	Et_3N	DMF	70	74
16	$Pd(PPh_3)_4$	K_2CO_3	DMF	70	<10
17	$Pd(PPh_3)_4$	Cs_2CO_3	DMF	70	<10
18	$Pd(PPh_3)_4$	NaOAc	DMF	70	52
19[f,g]	$Pd(PPh_3)_4$	Et_3N	DMF	70	67
20[f,h]	$Pd(PPh_3)_4$	Et_3N	DMF	70	48
21[f,i]	$Pd(PPh_3)_4$	Et_3N	DMF	70	57
22[f,j]	$Pd(PPh_3)_4$	Et_3N	DMF	70	71

[a] Reaction conditions: **1a** (0.47 mmol, 1.0 equiv.), **2a** (5.0 equiv.), base (5.0 equiv.), catalyst (10 mol%) and solvent (3.0 mL), under N_2, 5 h. [b] Isolated yields. N.D. = not detected. [c] Reacted for 8 h. [d] Reacted for 12 h. [e] Reacted for 18 h. [f] Reacted for 24 h. [g] $Pd(PPh_3)_4$ (5 mol%). [h] Et_3N (3.0 equiv.). [i] **2a** (2.0 equiv.). [j] **2a** (3.5 equiv.).

With the optimal reaction conditions in hand, we then investigated the generality and substrate scope of the reaction with a variety of *o*-ethynyltrifluoroacetanilides **1** and aryl iodides (Scheme 2). The reaction was firstly conducted by using different aryl iodides bearing *ortho*-, *meta*- or *para*-substituted electron-donating groups (methyl or methoxyl), and the desired products **3b–3g** were obtained in 35–85% yields. Compared to *meta*- or *para*-substituted aryl iodides, *ortho*-substituted **2b** and **2d** showed lower reactivities, probably due to the steric hindrance of *ortho*-substituents. The reaction also exhibited compatibility with various *para*-substituted aryl iodides, giving the corresponding 2,3-diarylindoles **3f–3l** in moderate to good yields. When using 1-iodonaphthalene, a poor isolated yield of **3m** was obtained. As for the heteroaryl halide applied, 2,3-dithienylindole **3n** was obtained in 65% yield. We further conducted the reaction by using different *o*-ethynyltrifluoroacetanilides under the standard reaction conditions. A variety of *o*-ethynyltrifluoro-acetanilides bearing substituents with different electronic properties proved reactive toward PhI (**3o–3r**). Unfortunately, the transformation failed while using aryl iodides containing a strong electron-withdrawing group (**3s–3u**).

Actually, this transformation involves cross-coupling of ArI twice and intramolecular cyclization once. To gain insight into the reaction mechanism, we carried out several control experiments (Scheme 3). Monitoring the reaction progress, we observed the formation of an internal alkyne **4a** as the major product, along with a small amount of target product **3a** in 30 min (eqn (1), Scheme 3). Extending the reaction time to 2 h afforded **3a** as the major product in 81% yield with a decreased amount of **4a**. In addition, when using one equiv. of Et_3N, internal alkyne **4a**, a Sonogashira reaction product, was obtained in 75% yield, along with trace amounts of the bis-arylative product **3a** (eqn (1), Scheme 3). Increasing the amount of Et_3N to 3 equivalents led to the formation of **3a** as the major product, along with the formation of **4a** (eqn (1),

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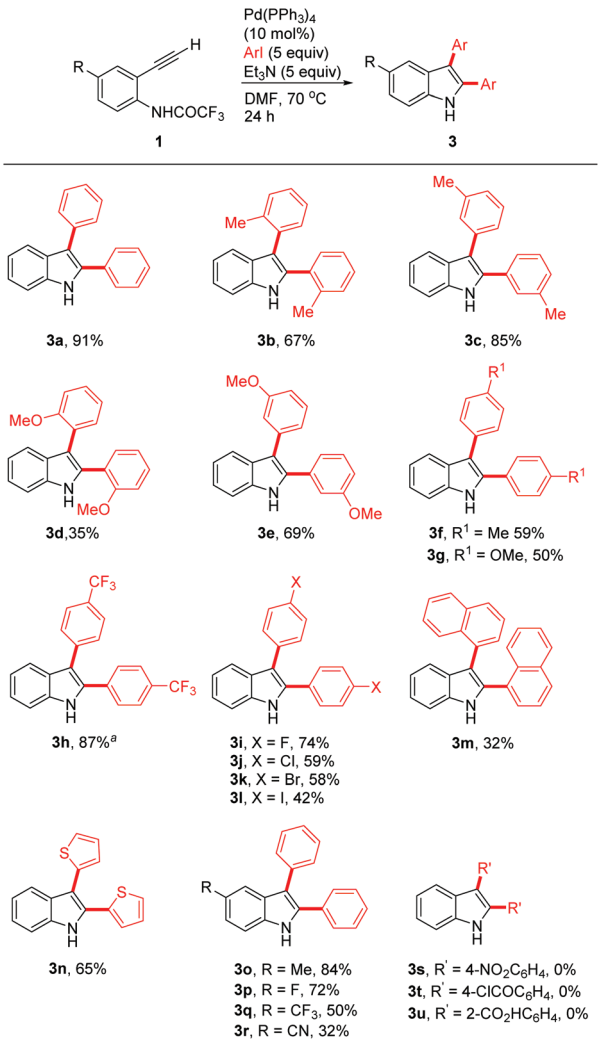
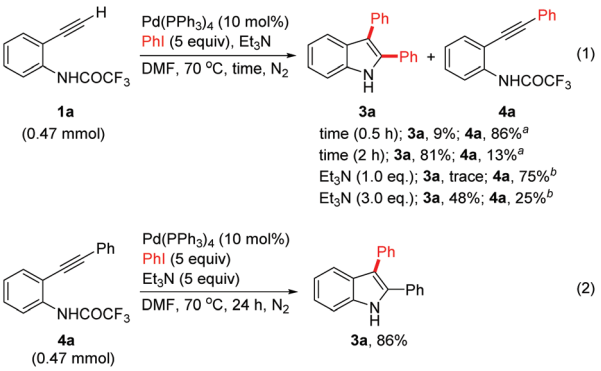


Scheme 2 Substrate scope of *o*-ethynyltrifluoroacetanilides **1** and aryl iodides **2**. **1** (0.47 mmol, 1.0 equiv.), **2** (5.0 equiv.), Et_3N (5.0 equiv.), Pd $(PPh_3)_4$ (10 mol (%) and DMF (3.0 mL), under N_2, 24 h, isolated yields. [a] Reacted for 48 h.



Scheme 3 Mechanism studies. **1a** or **4a** (0.47 mmol, 1.0 equiv.), PhI (5.0 equiv.), Pd$(PPh_3)_4$ (10 mol%) and DMF (3.0 mL), under N_2, isolated yields. [a] Et_3N (5.0 equiv.). [b] Time = 24 h.

Scheme 3). The observations indicate that Sonogashira reaction might be the first step that results in the formation of the intermediate **4a**. The deprotonation takes place firstly at the terminal alkyne, and initiates the Pd-catalyzed Sonogashira process. Cyclization of **4a** followed by the cross-coupling of ArI afforded the bis-arylative product **3a**. Indeed, under the catalysis of palladium, cyclization/cross-coupling of **4a** with PhI gave the desired product **3a** in 86% yield (eqn (2), Scheme 3).

We further wondered if such domino Sonogashira coupling/arylative cyclization was applicable to the synthesis of 2,3-diarylindoles with two different aryl groups at 2- and 3-positions. We firstly optimized the conditions for the Sonogashira reaction of **1a** with 1 equiv. of PhI in DMF under the catalysis of 10 mol% $Pd(PPh_3)_4$ (Table 2). The optimized conditions were as follows: **1a** (1.0 equiv.), PhI (1.0 equiv.), $Pd(PPh_3)_4$ (10 mol%), and Et_3N (2.0 equiv.) were reacted at 50 °C in DMF for 9 h (Table 2, entry 8). After completion of the Sonogashira coupling, monitored by TLC, further arylative cyclization was performed by introducing second ArI (5.0 equiv.) and another portion of Et_3N (3.0 equiv.) (Scheme 4). By the second use of *meta*- or *para*-substituted aryl iodides, the domino Sonogashira coupling/arylative cyclization smoothly afforded the desired products **5a–5c** in 50–86% yields, along with the formation of minor product **3a**. The reaction was also tolerant with 1-iodonaphthalene and heteroaryl halide, giving the corresponding asymmetrical 2,3-diarylindoles **5d** and **5e** in good yields. When using different *para*-halogenated aryl iodides, the mixture products of **5f–5h** and **3a** were obtained in 81–89% yields. Moreover, the Sonogashira-coupling step also worked well with other aryl iodides, and the 2-aryl-3-phenylindoles **5i–5k** could also be obtained in 38–41% yields (Scheme 4).

In addition, transition metal especially palladium-catalyzed cyclization/C3-allylation of *N*-allyl *o*-ethynylaniline is an efficient method to synthesize 2,3-disubstituted indole deriva-

Table 2 Optimization of Sonogashira reaction conditions[a]

Entry	Et_3N (equiv.)	T (°C)	Time (h)	Yield[b] (%)
1	1.0	70	2	60
2	2.0	70	2	78
3	3.0	70	2	70
4	2.0	25	4	48
5	2.0	50	4	73
6	2.0	70	4	70
7	2.0	50	7	71
8	**2.0**	**50**	**9**	**82**
9	2.0	50	11	51

[a] Reaction conditions: **1a** (0.47 mmol, 1.0 equiv.), **2a** (1.0 equiv.), Et_3N, $Pd(PPh_3)_4$ (10 mol%) and DMF (3.0 mL), under N_2. [b] The yields were determined by ^1H NMR using 1,3,5-trimethoxybenzene (1.0 equiv.) as the internal standard.

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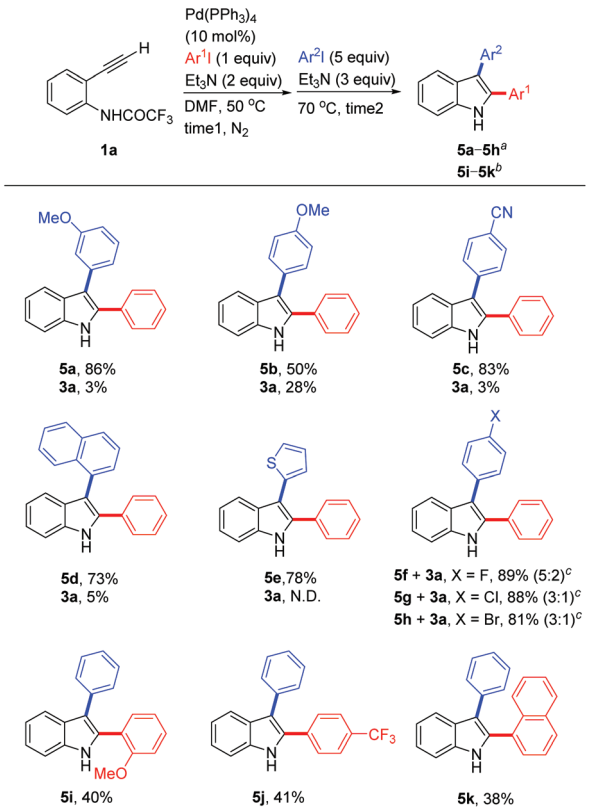
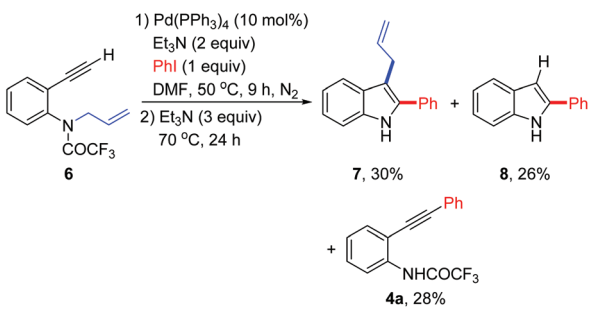


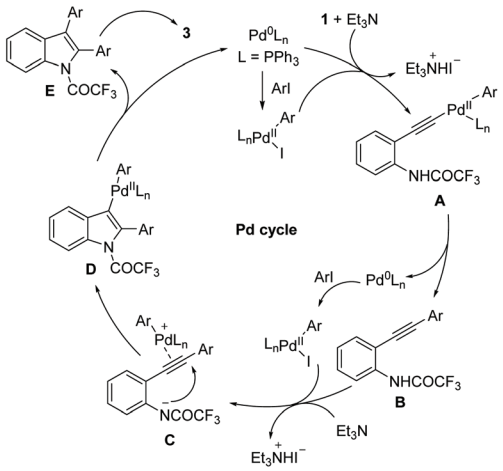
Scheme 4 The synthesis of 2,3-diarylindoles **5a–5k**. **1a** (0.47 mmol, 1.0 equiv.) and DMF (3.0 mL), under N_2, isolated yields. [a] Time1 = 9 h, time2 = 24 h. [b] Time1 = 24 h, time2 = 10 h. [c] Mixed yields, the ratio of **5** to **3a**. N.D. = not detected.

tives.[11] Therefore, we also tested the domino Sonogashira coupling/cyclization of *N*-allyl *o*-ethynylaniline **6**. Under the catalysis of $Pd(PPh_3)_4$, the C2-arylation and C3-allylation product **7** was obtained in 30% yield, and the 2-phenyl indole **8** and **4a** were also observed (Scheme 5).

Based on the above results, we proposed a plausible mechanism for the Pd-catalyzed bis-arylative cyclization of *o*-ethynyltrifluoroacetanilides (Scheme 6). Initially, the oxidative addition of aryl iodide to Pd(0) results in an aryl palladium species, which reacts with the terminal alkyne to form the pal-



Scheme 5 Domino Sonogashira coupling/cyclization of *N*-allyl *o*-ethynylaniline **6**.



Scheme 6 Proposed reaction mechanism.

ladium acetylide **A** in the presence of Et_3N. The subsequent reductive elimination of **A** gives the internal alkyne **B**. Deprotonation of the Pd-activated alkyne species **C** results in the formation of the key vinyl palladium intermediate **D** through intramolecular aminopalladation. Continuously, **D** further undergoes reductive elimination to afford the *N*-protected indole intermediate **E**. Finally, deacylation of **E** gives the target product **3** and simultaneously regenerates the Pd(0) species to the next catalytic cycle.

Conclusions

In conclusion, we have developed a practical and efficient one-pot process for the synthesis of highly functionalized 2,3-diarylindoles *via* Pd-catalyzed bis-arylative cyclization by coupling *o*-ethynylanilines with aryl iodides. In addition, 2,3-diarylindoles with two different aryl groups at 2- and 3-positions could also be obtained by the bis-arylative cyclization process. The mechanism studies showed that an internal alkyne **4a** might be the reaction intermediate formed by copper-free Sonogashira coupling, which underwent intramolecular aminopalladation/cross-coupling to afford the final bis-arylative cyclization product.

Experimental

General procedure for the synthesis of 2,3-diaryl indoles 3a–3u

A nitrogen-filled round-bottom flask was charged with **1** (0.47 mmol), $Pd(PPh_3)_4$ (54 mg, 0.047 mmol) and anhydrous DMF (3 mL), and then Et_3N (238 mg, 0.33 mL, 2.35 mmol) and aryl iodides **2** (2.35 mmol) were added in order. After the solution was stirred at 70 °C for 24 h, the reaction was quenched with water (3 mL) and the aqueous layer was extracted with DCM (10 mL × 3). The combined organic layer was dried over MgSO, the volatile component was removed under vacuum, and then the resulting residue was purified by silica gel

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column chromatography (PE/EtOAc) to afford pure products **3a–3u**.

General procedure for the synthesis of 2,3-diaryl indoles 5a–5h

A nitrogen-filled round-bottom flask was charged with **1a** (100 mg, 0.47 mmol), $Pd(PPh_3)_4$ (54 mg, 0.047 mmol) and anhydrous DMF (3 mL), and then Et_3N (0.13 mL, 0.94 mmol) and PhI (96 mg, 52 μL, 0.47 mmol) were added in order. After the solution was stirred at 50 °C for 9 h, another portion of Et_3N (0.2 mL, 1.41 mmol) and second aryl iodide (2.35 mmol) were added to the reaction mixture. After the solution was stirred at 70 °C for another 24 h, the reaction was quenched with water, and the aqueous layer was extracted with DCM. The combined organic layer was dried over MgSO, the volatile component was removed under vacuum, and then the crude product was purified by column chromatography (PE/EtOAc) using silica gel to afford pure products **5a–5h**.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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