## **RSC Advances**



## **PAPER**

View Article Online



Cite this: RSC Adv., 2025, 15, 28131

# One-step synthesis of 2-arylindoles from indolines via Pd-catalyzed oxidative dehydrogenation and C2-selective arylation†

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Received 30th June 2025 Accepted 24th July 2025

DOI: 10.1039/d5ra04628a

rsc.li/rsc-advances

We report an efficient synthetic approach to 2-arylindoles from indolines via a one-step process involving Pd-catalyzed oxidative dehydrogenation and a sequential C2-regioselective Heck-type reaction. The mild reaction conditions, which utilize O<sub>2</sub> as the sole oxidant, show a broad substrate scope and good functional group compatibility.

2-Arylindoles are important structural motifs found in bioactive natural products and synthetic compounds, exhibiting a wide spectrum of pharmacological activities such as anticancer, antimicrobial, and antidiabetic properties (Scheme 1a). Owing to their ubiquitous application in medicinal chemistry, substantial efforts have been made to establish diverse synthetic methodologies for synthesizing 2-arylindoles.2 Among these, the regiospecific C-H arylation of indole is regarded as one of the most efficient methods for generating a diverse array of 2-arylindole derivatives.<sup>3</sup> Recently, the application of innovative synthetic methods, such as direct C-H palladation and Pd-catalyzed Heck-type reactions, has enabled the C2-selective arylation of indoles without a directing group.4,5 To fully exploit the regioselective arylation of indoles for expanding reaction scope, the efficient preparation of multi-substituted indoles is essential, particularly given that most FDA-approved indole-derived drugs are di- or tri-substituted.6 However, the synthesis of such multi-substituted indole derivatives remains challenging, primarily because of the inherent electron-rich nature of the pyrrole ring in indole, especially at the N1 and C3 positions. Electrophilic aromatic substitution reactions, such as acylation, acrylation, halogenation, and nitration, are mainly used for the derivatization of indole, preferentially at the N1 and C3 positions, thereby hindering functionalization at the less reactive C4-C7 positions on the phenyl group.<sup>7</sup> To address this limitation, indoline could be used as a surrogate for indole because its benzene ring possesses a higher electron density than that of indole. This approach successfully enables the

Scheme 1 Representative examples of pharmacologically active 2arylindoles and synthetic strategies to 2-arylindoles

synthesis of multi-substituted indoles but requires a two-step protocol, including an additional oxidation step. Recently, our group reported a breakthrough method for synthesizing indoles from N-free indolines via aerobic oxidation, using a minimal catalytic amount of Pd (Scheme 1b).8 Furthermore, our exploration of the indole scaffold has led to the development of a regioselective Pd(II)-catalyzed aerobic Heck-type reaction for the direct C2-arylation of N-free indoles (Scheme 1c). Inspired by our recent studies on indole chemistry and the challenges associated with accessing multi-substituted indoles, we developed an efficient one-step protocol for synthesizing 2-

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<sup>†</sup> Electronic supplementary information (ESI) DOI: https://doi.org/10.1039/d5ra04628a

arylindoles directly from indolines (Scheme 1d). <sup>16,9</sup> To broaden the structural diversity and enhance functional group compatibility, the reaction was designed to proceed under mild conditions without stoichiometric use of acids, bases, or additives, employing molecular oxygen as the sole oxidant.

To begin this study, 1*H*-indoline (1a) was chosen as the model substrate for reaction optimization (Table 1). Based on our previous reports,<sup>5,8</sup> we initially evaluated ligand effects under the standard reaction conditions using phenylboronic acid (2a), 10 mol% Pd(OAc)<sub>2</sub>, and a ligand in DMF at 80 °C under an O<sub>2</sub> atmosphere (entries 1–5). The use of neocuproine (L1) as the ligand facilitated the oxidative dehydrogenation step, affording indole (3a) in 71% yield and a small amount of the desired C2-aryl indole (4a) in 15% yield. In contrast, common bidentate ligands (L2–L5), although effective in promoting the dehydrogenation of indoline 1a, failed to control the regioselectivity of the subsequent arylation step, predominantly leading to the formation of the undesired C3-arylindole.

Subsequently, various solvents were screened (entries 6–10). This reaction showed a preference for halogenated benzene solvents over polar solvents, such as DMF, DMSO,  $H_2O$ , and DCE. Among these, 1,2-dichlorobenzene (1,2-DCB) was identified as the optimal solvent, affording 4a in 85% yield. Based on previous reports indicating that the use of DMF and DMSO

inhibits the oxidative Heck reaction,  $^{5,8}$  we hypothesized that the coordination of DMF or DMSO to the Pd( $\pi$ ) center may inhibit catalytic turnover. This hypothesis was supported by our observation that the addition of DMF or DMSO under the optimized conditions led to a decreased yield of 4a and incomplete conversion of indole 3a (entries 11 and 12).

Following solvent optimization, the effect of the reaction temperature was investigated. As the temperature increased, the reaction efficiency significantly decreased, accompanied by the formation of inactive Pd black. Notably, conducting the reaction at 40 °C with a prolonged reaction time provided the highest yield of 92% (entries 13-16). This relatively low reaction temperature was consistent with the mild conditions required for a broad substrate scope. Minor optimization of boronic acid loading and Pd(II) catalyst was also conducted to confirm the optimal conditions for Pd(OAc)<sub>2</sub> (10 mol%), neocuproine (20 mol%), and aryl boronic acid (2.5 equiv.) in 1,2-DCB at 40 °C under an O<sub>2</sub> atmosphere, as listed in entry 16 (ESI Table S1†). A series of control experiments confirmed that all reaction components, including the Pd catalyst, ligand, oxygen, and reaction temperature, were essential for this reaction (ESI Table S2†).

With the optimized conditions in hand, we examined the substrate scope of the indolines (Scheme 2). Indolines bearing

Table 1 Optimization of the reaction conditions

Entrya	Catalyst (10 mol%)	Ligand (20 mol%)	Solvent (0.3 M)	T (°C)	3a <sup>b</sup> (%)	<b>4a</b> <sup>b</sup> (%)	C3 <sup>b</sup> (%)
1	Pd(OAc) <sub>2</sub>	L1	DMF	80	71	15	_
2	Pd(OAc) <sub>2</sub>	L2	DMF	80	61	_	7
3	$Pd(OAc)_2$	L3	DMF	80	41	_	34
4	$Pd(OAc)_2$	L4	DMF	80	30	_	31
5	$Pd(OAc)_2$	L5	DMF	80	35	_	33
6	$Pd(OAc)_2$	L1	DMSO	80	51	7	
7	$Pd(OAc)_2$	L1	$H_2O$	80	12	41	_
8	$Pd(OAc)_2$	L1	DCE	80	28	53	
9	$Pd(OAc)_2$	L1	PhCl	80	14	73	_
10	$Pd(OAc)_2$	L1	1,2-DCB	80	3	85	_
11 <sup>c</sup>	$Pd(OAc)_2$	L1	1,2-DCB	40	14	60	_
$12^d$	$Pd(OAc)_2$	L1	1,2-DCB	40	24	60	_
13	$Pd(OAc)_2$	L1	1,2-DCB	100	_	24	_
14	$Pd(OAc)_2$	L1	1,2-DCB	120	_	5	_
15	$Pd(OAc)_2$	L1	1,2-DCB	60	_	87	_
16 <sup>e</sup>	Pd(OAc) <sub>2</sub>	L1	1,2-DCB	40	_	92(91) <sup>f</sup>	_

<sup>&</sup>lt;sup>a</sup> All reactions were run on a 0.3 mmol scale with indoline **1a** (1.0 equiv.), phenylboronic acid **2a** (2.5 equiv.), Pd(II) catalyst (10 mol%), and neocuproine (20 mol%) in solvent (1.0 mL) at *T* °C under O<sub>2</sub>, 24 h. <sup>b</sup> Yields were determined by <sup>1</sup>H NMR spectroscopy with 1,3,5-trimethoxybenzene as the internal standard. <sup>c</sup> Additive DMF (1.0 equiv.) in entry 16. <sup>d</sup> Additive DMSO (1.0 equiv.) in entry 16. <sup>e</sup> The reaction was carried out for 48 h. <sup>f</sup> Isolated yield.

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Pd(OAc)<sub>2</sub> (10 md)% neocuproine (20 md)% 1,2-DCB, O<sub>2</sub>, 40 °C 4: Yield<sup>b</sup>

Me 4 4a: 91%, 86%<sup>d</sup> 4b: 4-Me, 31% 4c: 5-Me, 75% 4f: R-H, 92%<sup>c</sup> 4i: 47%, 67%<sup>c</sup> 4d: 6-Me, 73% 4e: 7-Me, 48% 4h: R=Bn, 75%

Br 4 12%, 65%<sup>c</sup> 4k: 53%<sup>c</sup> 4l: 85% 4m: 64%

Display="Bloth" Am: 64%

LICH 4 m (R=Me, 64%)

LICH 4 m' (R=H, GPR40 agonist)

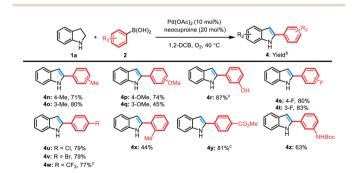
Scheme 2 Substrate scope of indolines. <sup>a</sup>All reactions were run on a 0.3 mmol scale with indolines 1 (1.0 equiv.), arylboronic acid **2a** (2.5 equiv.), Pd(OAc)<sub>2</sub> (10 mol%), and neocuproine (20 mol%) in 1,2-DCB (1.0 mL) at 40 °C under O<sub>2</sub>, 48 h. <sup>b</sup>Isolated yield. <sup>c</sup>The reaction was carried out at 80 °C for 24 h. <sup>d</sup>Yield for the scaled-up experiment (3.0 mmol of **1a** used).

methyl substituents at benzene core positions (4b-e) were smoothly converted into disubstituted indoles in moderate yields. Notably, the C4-methyl substituted indoline afforded the desired C2-arylindole 4b in relatively low yield, accompanied by the formation of a C3-arylated regioisomer. This result may be attributed to steric interactions among the C4-methyl group, neocuproine and the arylboronic acid, which likely hinder the Heck-type arylation step.5 Electron-rich alkoxy indolines (4f-h) readily underwent this transformation to afford the desired 2,5disubstituted indoles in moderate yield. In contrast, electronwithdrawing indolines bearing halogen and ester substituents (4i-k) exhibited relatively lower reactivity. The dehydrogenation step might be initiated by substituting the indoline N-H with an electrophilic Pd(II) species. It is likely that the electronwithdrawing groups will decelerate this process, particularly at low temperatures, resulting in relatively poor conversion. Unlike other electron-withdrawing substituents and halogens, fluorine-substituted indoline (41) exhibited relatively better reactivity, presumably due to the mesomeric effect of fluorine, which enhanced the nucleophilicity of the indoline nitrogen. Nevertheless, increasing the reaction temperature enabled moderate conversion of these substrates (4i-k). A gram-scale reaction performed under the optimized conditions afforded 4a in 86% yield, highlighting the feasibility of the protocol. To demonstrate the utility of our method in rapidly assembling biologically relevant multi-substituted indoles, we applied it to the synthesis of a known GPR40 agonist, 3-(2-phenyl-1H-indol-5-yl)propanoic acid (4m').9 In general, the synthesis of 2,5disubstituted indoles requires multistep procedures involving prefunctionalized intermediates prepared from aniline derivatives. The reported synthesis of the GPR40 agonist proceeds in seven steps. In contrast, the GPR40 agonist was efficiently

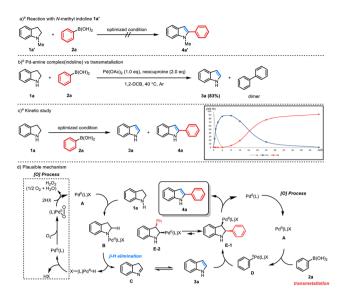
synthesized in a four-step sequence using this strategy. The key intermediate (**1m**) was prepared by exploiting the inherent nucleophilic character of the C5 position in indoline. Our protocol successfully transformed **1m** into the desired 2,5-disubstituted indole (**4m**) *via* sequential dehydrogenation and oxidative arylation. Final hydrolysis afforded the GPR40 agonist (**4m**') in four steps.

Subsequently, the scope of phenylboronic acids was investigated to evaluate the generality of this protocol (Scheme 3). Electron-donating groups such as Me (4n and 4o), OMe (4p and 4q), and OH (4r), as well as electron-withdrawing groups including F (4s and 4t), Cl (4u), Br (4v), and CF<sub>3</sub> (4w), were well tolerated, regardless of the substituent position (para or meta). Furthermore, ortho-methyl-containing 2-arylindole (4x) was obtained in a moderate yield. Notably, the base-labile ester (4v) and acid-labile Boc protecting group (4z) were compatible with this transformation, affording the corresponding products in moderate to good yields. This broad functional group tolerance is likely attributable to mild acid- and base-free conditions. We further evaluated the compatibility of aliphatic boronic acids, including methylboronic acid and cyclohexylboronic acid, under the optimized reaction conditions. However, the corresponding 2-alkylindole products were not detected. Only the simple indole was formed in moderate yield (ESI Table S3†).

To gain insight into the mechanism of this oxidative transformation, a series of mechanistic experiments were conducted. First, N-methyl indoline (1a') failed to undergo the transformation under the optimized conditions, indicating that the oxidative dehydrogenation requires a free N-H moiety (Scheme 4a). To determine the initial step of the transformation, the reaction was performed under Ar using stoichiometric amounts of Pd(OAc)2 in the presence of indoline (1a) and phenylboronic acid (2a) (Scheme 4b). In this case, the dehydrogenated indole (3a) was obtained without the formation of a phenyl-phenyl dimer, which is typically generated via the transmetallation of phenylboronic acid 2a.11 These results suggest that the coordination of Pd(II) to the N-H of indoline occurs preferentially over transmetallation with boronic acid, indicating that the oxidative dehydrogenation of indoline precedes aryl transfer. Further kinetic analysis of the reaction



Scheme 3 Substrate scope of arylboronic acids. <sup>a</sup>All reactions were run on a 0.3 mmol scale with indoline 1a (1.0 equiv.), arylboronic acids 2 (2.5 equiv.), Pd(OAc)<sub>2</sub> (10 mol%), and neocuproine (20 mol%) in 1,2-DCB (1.0 mL) at 40 °C under O<sub>2</sub>, 48 h. <sup>b</sup>Isolated yield. <sup>c</sup>The reaction was carried out at 80 °C for 24 h.



Scheme 4 Mechanistic investigation and supporting experiments. <sup>a</sup>Reaction conditions: **1a** or **1a**′ (1.0 equiv.), **2a** (2.5 equiv.), Pd(OAc)<sub>2</sub> (10 mol%), neocuproine (20 mol%), and 1,2-DCB (1.0 mL) at 40 °C under O<sub>2</sub>, 48 h. <sup>b</sup>Reaction conditions: **1a** (1.0 equiv.), **2a** (1.0 equiv.), Pd(OAc)<sub>2</sub> (1.0 equiv.), neocuproine (2.0 equiv.), and 1,2-DCB (1.0 mL) at 40 °C under Ar, 48 h.

revealed that 1*H*-indoline **1a** was rapidly converted into indole **3a**. After complete consumption of **1a**, **3a** was transformed into 2-arylindole (**4a**) (Scheme 4c). This confirms that the coordination between **1a** and Pd(II) precedes the transmetallation with arylboronic acid (**2a**). Once **1a** was depleted, the free Pd(II) catalyst underwent transmetallation to form a Pd-aryl species, enabling the desired C2-arylation of **3a**.

Based on the above mechanistic investigations and previous literature, 5,8 we propose a plausible reaction mechanism, as depicted in Scheme 4d. The reaction is initiated by coordination of the free N-H of indoline (1a) to the Pd(II) catalyst (A), forming the complex B.8 Subsequent β-hydride elimination from B generates the imine intermediate C, which readily tautomerizes to the more stable indole 3a. The resulting Pd-H complex sequentially regenerates its initial state A via aerobic oxidation. Once indoline 1a is completely consumed, the neocuproine ligand facilitates transmetallation between phenylboronic acid and Pd(II) over electrophilic substitution with indole, leading to the formation of the Pd-aryl complex **D** in a nonpolar solvent.12,13 Subsequent Heck-type addition of the prepared indole 3a favors the formation of intermediate E-1 over E-2 influenced by the steric and electronic effects of the Pd-aryl complex D, as previously investigated.<sup>5</sup> Finally, anti-β-hydride elimination produces the desired 2-arylindole 4a in a regioselective manner.

In conclusion, we developed an efficient one-step method to synthesize a variety of 2-arylindole derivatives from their corresponding indolines. The  $Pd(\pi)$ -catalyzed transformation integrates oxidative dehydrogenation and regionselective Hecktype arylation under mild acid- and base-free conditions. This protocol tolerates a broad range of functional groups and does not require high temperature or additives. Notably, our

approach offers a straightforward synthetic strategy for accessing diverse multi-substituted 2-arylindoles *via* direct functionalization of the indoline scaffold. This method addresses a significant challenge in the fields of heterocyclic and medicinal chemistry and has the potential to broaden the chemical space of indole-based scaffolds.

## Data availability

The data supporting this article have been included as part of the ESI† and the additional data used and/or analysed during the current study are available from the corresponding author on reasonable request.

#### Conflicts of interest

There are no conflicts to declare.

#### **Acknowledgements**

This work was supported by National Research Foundation (NRF) grants funded by the Korean government (NRF-2022R1A2C1009252, NRF-2021R1C1C1010044, and NRF-RS-2024-00399805), and by the BK21 FOUR Program of the Graduate School, Kyung Hee University (GS-1-JO-NON-20240398).

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