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

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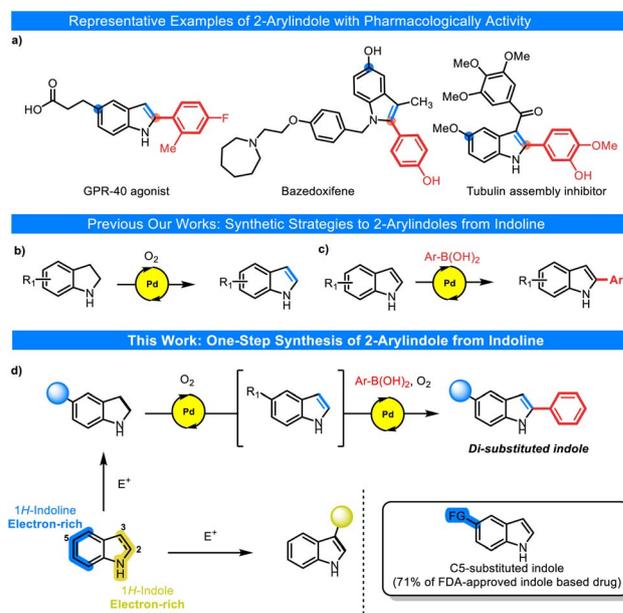
We report an efficient synthetic approach to 2-arylindoles from indolines *via* a one-step process involving Pd-catalyzed oxidative dehydrogenation and a sequential C2-regioselective Heck-type reaction. The mild reaction conditions, which utilize O₂ as the sole oxidant, show a broad substrate scope and 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).¹ 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 regioselective C–H arylation of indole is regarded as one of the most efficient methods for generating a diverse array of 2-arylindole derivatives.³ 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.⁷ 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

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).⁵ 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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Scheme 1 Representative examples of pharmacologically active 2-arylindoles and synthetic strategies to 2-arylindoles



arylindoles directly from indolines (Scheme 1d).^{1b,9} 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,^{5,8} we initially evaluated ligand effects under the standard reaction conditions using phenylboronic acid (**2a**), 10 mol% Pd(OAc)₂, and a ligand in DMF at 80 °C under an O₂ 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.

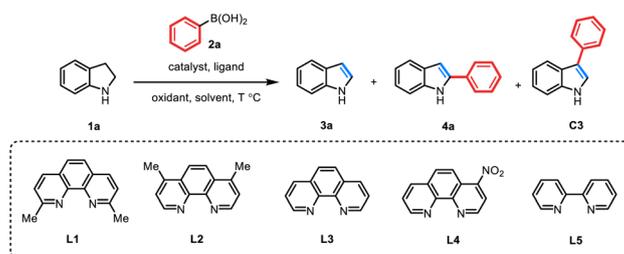
Subsequently, various solvents were screened (entries 6–10). This reaction showed a preference for halogenated benzene solvents over polar solvents, such as DMF, DMSO, H₂O, and DCE. Among these, 1,2-dichlorobenzene (1,2-DCB) was identified as the optimal solvent, affording **4a** in 85% yield. Based 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(II) 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)₂ (10 mol%), neocuproine (20 mol%), and aryl boronic acid (2.5 equiv.) in 1,2-DCB at 40 °C under an O₂ 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

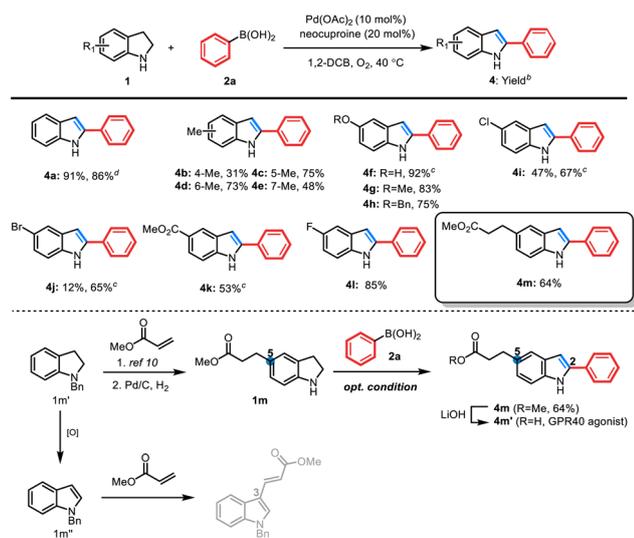
Table 1 Optimization of the reaction conditions



| Entry ^a | Catalyst (10 mol%) | Ligand (20 mol%) | Solvent (0.3 M) | T (°C) | 3a ^b (%) | 4a ^b (%) | C3 ^b (%) |
|--------------------|----------------------------|------------------|------------------|-----------|----------------------------|----------------------------|---------------------|
| 1 | Pd(OAc) ₂ | L1 | DMF | 80 | 71 | 15 | — |
| 2 | Pd(OAc) ₂ | 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 ₂ O | 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 ^c | 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 ^e | Pd(OAc)₂ | L1 | 1,2-DCB | 40 | — | 92(91)^f | — |

^a 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 O₂, 24 h. ^b Yields were determined by ¹H NMR spectroscopy with 1,3,5-trimethoxybenzene as the internal standard. ^c Additive DMF (1.0 equiv.) in entry 16. ^d Additive DMSO (1.0 equiv.) in entry 16. ^e The reaction was carried out for 48 h. ^f Isolated yield.





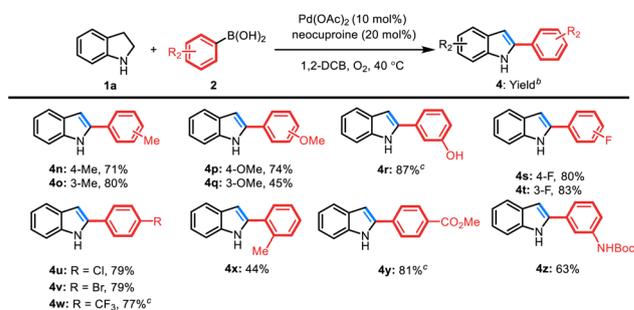
Scheme 2 Substrate scope of indolines. ^aAll reactions were run on a 0.3 mmol scale with indolines **1** (1.0 equiv.), arylboronic acid **2a** (2.5 equiv.), Pd(OAc)₂ (10 mol%), and neocuproine (20 mol%) in 1,2-DCB (1.0 mL) at 40 °C under O₂, 48 h. ^bIsolated yield. ^cThe reaction was carried out at 80 °C for 24 h. ^dYield 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 2,5-disubstituted indoles in moderate yield. In contrast, electron-withdrawing 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 electron-withdrawing groups will decelerate this process, particularly at low temperatures, resulting in relatively poor conversion. Unlike other electron-withdrawing substituents and halogens, fluorine-substituted indoline (**4l**) 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-1*H*-indol-5-yl)propanoic acid (**4m'**).⁹ In general, the synthesis of 2,5-disubstituted 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.¹⁰ 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.

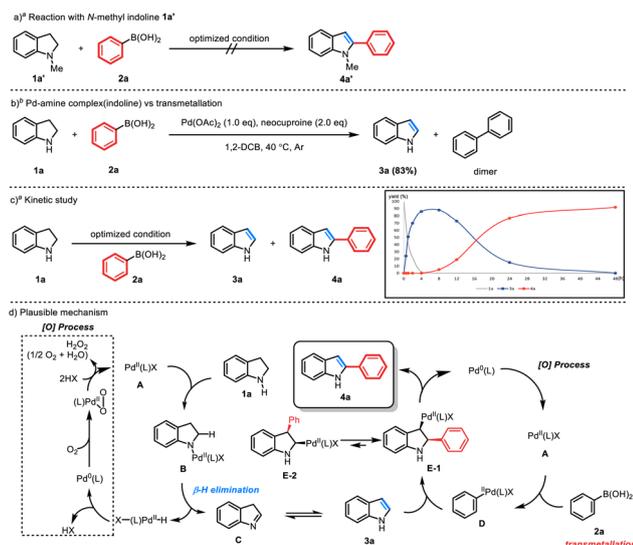
Subsequently, the scope of phenylboronic acids was investigated to evaluate the generality of this protocol (Scheme 3). Electron-donating groups such as Me (**4n** and **4o**), OMe (**4p** and **4q**), and OH (**4r**), as well as electron-withdrawing groups including F (**4s** and **4t**), Cl (**4u**), Br (**4v**), and CF₃ (**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 (**4y**) 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 transmetalation of phenylboronic acid **2a**.¹¹ These results suggest that the coordination of Pd(II) to the N–H of indoline occurs preferentially over transmetalation 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. ^aAll reactions were run on a 0.3 mmol scale with indoline **1a** (1.0 equiv.), arylboronic acids **2** (2.5 equiv.), Pd(OAc)₂ (10 mol%), and neocuproine (20 mol%) in 1,2-DCB (1.0 mL) at 40 °C under O₂, 48 h. ^bIsolated yield. ^cThe reaction was carried out at 80 °C for 24 h.





Scheme 4 Mechanistic investigation and supporting experiments.

^aReaction conditions: **1a** or **1a'** (1.0 equiv.), **2a** (2.5 equiv.), Pd(OAc)₂ (10 mol%), neocuproine (20 mol%), and 1,2-DCB (1.0 mL) at 40 °C under O₂, 48 h. ^bReaction conditions: **1a** (1.0 equiv.), **2a** (1.0 equiv.), Pd(OAc)₂ (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-arylidole (**4a**) (Scheme 4c). This confirms that the coordination between **1a** and Pd(II) precedes the transmetalation with arylboronic acid (**2a**). Once **1a** was depleted, the free Pd(II) catalyst underwent transmetalation 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 transmetalation 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.⁵ Finally, anti-β-hydride elimination produces the desired 2-arylidole **4a** in a regioselective manner.

In conclusion, we developed an efficient one-step method to synthesize a variety of 2-arylidole derivatives from their corresponding indolines. The Pd(II)-catalyzed transformation integrates oxidative dehydrogenation and regioselective Heck-type 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-arylidoles 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

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Notes and references

- (a) R. Gastpar, M. Goldbrunner, D. Marko and E. von Angerer, Methoxy-substituted 3-formyl-2-phenylindoles inhibit tubulin polymerization, *J. Med. Chem.*, 1998, **41**, 4965–4972; (b) S. Lal and T. J. Snape, 2-Arylidoles: a privileged molecular scaffold with potent, broad-ranging pharmacological activity, *Curr. Med. Chem.*, 2012, **19**, 4828–4837; (c) R. Plummer, P. Lorigan, N. Steven, L. Scott, M. R. Middleton, R. H. Wilson, E. Mulligan, N. Curtin, D. Wang, R. Dewji, A. Abbattista, J. Gallo and H. Calvert, A phase II study of the potent PARP inhibitor, Rucaparib (PF-01367338, AG014699), with temozolomide in patients with metastatic melanoma demonstrating evidence of chemopotential, *Cancer Chemother. Pharmacol.*, 2013, **71**, 1191–1199.
- (a) H. Song, Z. Y. Yang, C. H. Tung and W. G. Wang, Iron-Catalyzed Reductive Coupling of Nitroarenes with Olefins: Intermediate of Iron-Nitroso Complex, *ACS Catal.*, 2020, **10**, 276–281; (b) C. Xu, V. K. Murugan and S. A. Pullarkat, Domino cyclization-alkylation protocol for the synthesis of 2,3-functionalized indoles from *o*-alkynylanilines and allylic alcohols, *Org. Biomol. Chem.*, 2012, **10**, 3875–3881; (c) H. C. Zhang, H. Ye, A. F. Moretto, K. K. Brumfield and B. E. Maryanoff, Facile solid-phase construction of indole derivatives based on a traceless, activating sulfonyl linker, *Org. Lett.*, 2000, **2**, 89–92.
- (a) C. Sollert, K. Devaraj, A. Orthaber, P. J. Gates and L. T. Pilarski, Ru-Catalysed C-H Arylation of Indoles and Pyrroles with Boronic Acids: Scope and Mechanistic Studies, *Chem.-Eur. J.*, 2015, **21**, 5380–5386; (b)



- V. K. Tiwari, N. Kamal and M. Kapur, Ruthenium-Catalyzed Heteroatom-Directed Regioselective C–H Arylation of Indoles Using a Removable Tether, *Org. Lett.*, 2015, **17**, 1766–1769; (c) X. J. Zhu, J. H. Su, C. Du, Z. L. Wang, C. J. Ren, J. L. Niu and M. P. Song, Cobalt(II)-Catalyzed Oxidative C–H Arylation of Indoles and Boronic Acids, *Org. Lett.*, 2017, **19**, 596–599.
- 4 (a) N. R. Deprez, D. Kalyani, A. Krause and M. S. Sanford, Room temperature palladium-catalyzed 2-arylation of indoles, *J. Am. Chem. Soc.*, 2006, **128**, 4972–4973; (b) B. S. Lane and D. Sames, Direct C–H bond arylation: selective palladium-catalyzed C2-arylation of *N*-substituted indoles, *Org. Lett.*, 2004, **6**, 2897–2900; (c) N. Lebrasseur and I. Larrosa, Room temperature and phosphine free palladium catalyzed direct C-2 arylation of indoles, *J. Am. Chem. Soc.*, 2008, **130**, 2926–2927; (d) S. D. Yang, C. L. Sun, Z. Fang, B. H. Li, Y. Z. Li and Z. J. Shi, Palladium-catalyzed direct arylation of (hetero)arenes with aryl boronic acids, *Angew. Chem., Int. Ed.*, 2008, **47**, 1473–1476; (e) J. L. Zhao, Y. H. Zhang and K. Cheng, Palladium-catalyzed direct C-2 arylation of indoles with potassium aryltrifluoroborate salts, *J. Org. Chem.*, 2008, **73**, 7428–7431.
- 5 Y.-S. Yang, S. Lee, S. H. Son, H.-S. Yoo, Y. H. Jang, J.-W. Shin, H.-J. Won, J. Sim and N.-J. Kim, Ligand-controlled regiodivergent direct arylation of indoles oxidative boron Heck reaction, *Org. Chem. Front.*, 2022, **9**, 5906–5911.
- 6 E. Vitaku, D. T. Smith and J. T. Njardarson, Analysis of the Structural Diversity, Substitution Patterns, and Frequency of Nitrogen Heterocycles among U.S. FDA Approved Pharmaceuticals, *J. Med. Chem.*, 2014, **57**, 10257–10274.
- 7 (a) H. S. Ma, T. Y. Yu, L. X. Chi, C. Huang, X. W. Li, R. Zhang and C. Deng, Recent advances in theoretical studies on transition-metal-catalyzed regioselective C–H functionalization of indoles, *J. Mol. Model.*, 2022, **28**, 287; (b) T. A. Shah, D. Bhusan, S. Pradhan and T. Punniyamurthy, Transition-metal-catalyzed site-selective C7-functionalization of indoles: advancement and future prospects, *Chem. Commun.*, 2019, **55**, 572–587; (c) K. Urbina, D. Tresp, K. Sipps and M. Szostak, Recent Advances in Metal-Catalyzed Functionalization of Indoles, *Adv. Synth. Catal.*, 2021, **363**, 2723–2739.
- 8 H.-S. Yoo, Y.-S. Yang, S. L. Kim, S. H. Son, Y. H. Jang, J.-W. Shin and N.-J. Kim, Syntheses of 1*H*-Indoles, Quinolines, and 6-Membered Aromatic *N*-Heterocycle-Fused Scaffolds via Palladium(II)-Catalyzed Aerobic Dehydrogenation under Alkoxide-Free Conditions, *Chem.–Asian J.*, 2021, **16**, 3469–3475.
- 9 (a) D. O. Yoon, X. Zhao, D. Son, J. T. Han, J. Yun, D. Shin and H. J. Park, SAR Studies of Indole-5-propanoic Acid Derivatives To Develop Novel GPR40 Agonists, *ACS Med. Chem. Lett.*, 2017, **8**, 1336–1340; (b) X. D. Zhao, D. O. Yoon, J. Yoo and H. J. Park, Structure-Activity Relationship Study and Biological Evaluation of 2-(Disubstituted phenyl)-indole-5-propanoic Acid Derivatives as GPR40 Full Agonists, *J. Med. Chem.*, 2021, **64**, 4130–4149.
- 10 (a) W. L. Jia, N. Westerveld, K. M. Wong, T. Morsch, M. Hakkennes, K. Naksomboon and M. A. Fernández-Ibáñez, Selective C–H Olefination of Indolines (C5) and Tetrahydroquinolines (C6) by Pd/S,O-Ligand Catalysis, *Org. Lett.*, 2019, **21**, 9339–9342; (b) K. Naksomboon, J. Poater, F. M. Bickelhaupt and M. A. Fernández-Ibáñez, Selective C–H Olefination of Aniline Derivatives via Pd/S,O-Ligand Catalysis, *J. Am. Chem. Soc.*, 2019, **141**, 6719–6725.
- 11 A. J. J. Lennox and G. C. Lloyd-Jones, Selection of boron reagents for Suzuki–Miyaura coupling, *Chem. Soc. Rev.*, 2014, **43**, 412–443.
- 12 D. L. Bruns, D. G. Musaev and S. S. Stahl, Can Donor Ligands Make Pd(OAc)₂ a Stronger Oxidant? Access to Elusive Palladium(II) Reduction Potentials and Effects of Ancillary Ligands via Palladium(II)/Hydroquinone Redox Equilibria, *J. Am. Chem. Soc.*, 2020, **142**, 19678–19688.
- 13 T. Diao, P. White, I. Guzei and S. S. Stahl, Characterization of DMSO Coordination to Palladium(II) in Solution and Insights into the Aerobic Oxidation Catalyst, Pd(DMSO)₂(TFA)₂, *Inorg. Chem.*, 2012, **51**, 11898–11909.

