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Cascade π-Extended Decarboxylative Annulation Involving Cyclic Diaryliodonium Salts: Site-Selective Synthesis of Phenanthridines and Benzocarbazoles via a Traceless Directing Group Strategy

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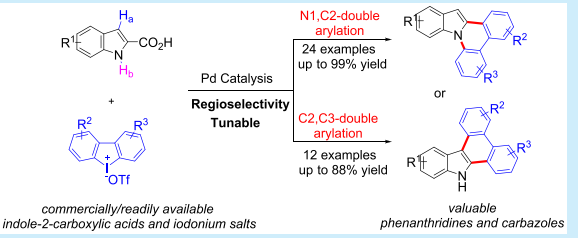
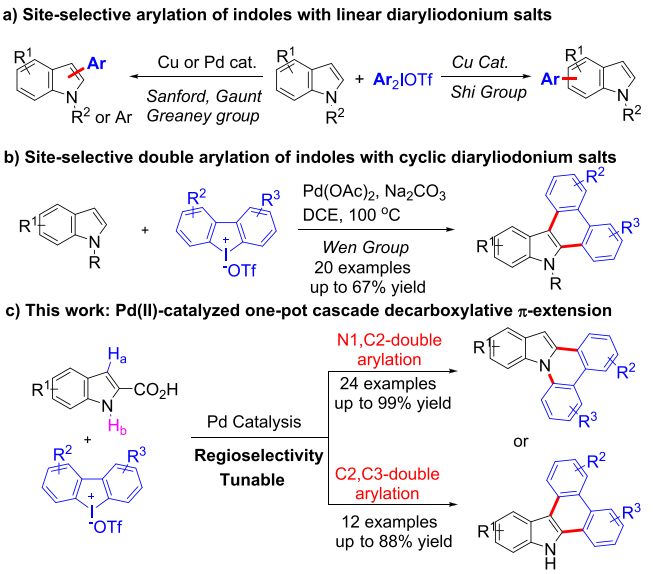
Supporting Information

ABSTRACT: A novel cascade π-extended decarboxylative annulation (PEDA) involved with cyclic diaryliodonium salts is described. Via fine-tuning of the reaction conditions, the Pd(II)-catalyzed site-selective N1/C2 or C2/C3 annulation of commercially available indole-2-carboxylic acids can be achieved, affording valuable phenanthridines or benzocarbazoles, respectively. The key strategy is the carboxylic acid functionality being employed as both a traceless directing group for the *ortho* C−N or C−C coupling and a reactive group for the cascade π-extended decarboxylative annulation in a highly step economical manner.



The indole scaffold is one of the most intensively studied heteroaromatics due to its prevalence in bioactive natural products,[1] drugs,[2] and functional materials.[3] Hence, considerable attention has been focused on the direct and selective functionalization of indole derivatives.[4] However, how to switch and achieve complete regioselectivity is still a challenging task due to the presence of multiple C−H or N−H bonds in the indole structure.[5] Various elegant methods have been developed to enable selective C/N−H functionalization on either the pyrrole-type ring or the benzenoid moiety of indole.[6] Among them, the regioselective construction of aryl−indolyl bonds for the synthesis of arylindoles,[7] the key moieties of a variety of biologically active molecules, is of fundamental importance in organic synthesis.[8] As a readily available electrophilic arylating reagent, the linear diaryliodonium salts[9,10] have been employed for the direct and site-selective arylation of indoles (Scheme 1a). For example, in 2006, the Sanford group reported Pd-catalyzed direct and selective C2−H arylation of indoles under mild conditions.[11] In 2008, by changing the protecting groups on the nitrogen atom, the Gaunt group disclosed a Cu(II)-catalyzed direct and site-selective C2 or C3 arylation of indoles.[12] In 2015, by making use of both aryl groups from the linear diaryliodonium salts, the Greaney group reported a Cu-catalyzed one-pot tandem C3−H/N−H arylation affording various 1,3-diarylindoles.[13] Later, the Shi group achieved the Cu-catalyzed regioselective C−H arylation of indoles at positions C4−C6 (Scheme 1a).[14] Compared to the mono-C−H functionalization of indoles, the one-step double C−H arylative annulation of indoles with cyclic diaryliodomium salts[15,16] had never been reported until the Wen group reported the double C−H functionalization of indoles at positions C2 and C3 affording the benzocarbazoles (Scheme 1b).[17] However, the N1/C2 double annulation cannot be achieved with this protocol.

Scheme 1. Site-Selective Arylation of Indoles



Annulative π-extension (APEX) has been frequently employed for the construction of polycyclic arenes that have important applications in material chemistry.[18] Although the number of steps for the synthesis of polycyclic arenes can be reduced by using direct C−H activation in this approach, it is usually very difficult to achieve complete site selectivity due to the presence of multiple C−H bonds in the substrates. Recently, by a π-extended decarboxylative annulation (PEDA) strategy, we reported the synthesis of triphenylenes and

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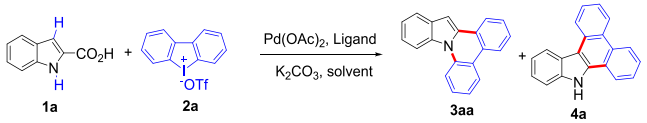
dibenzo[*f*,*h*]quinolines with benzoic acids and cyclic diaryliodonium salts as the starting materials.[19] As a continuation of our research interest in novel arylation chemistry involved with diaryliodonium salts,[20] we envisioned that the carboxylic acid functionality in readily available indole-2-carboxylic acids could be employed as both a directing group for the palladium-catalyzed *ortho* N−H or C−H arylation and a reactive group for the tandem *ipso*-decarboxylative[21] annulation for the synthesis of valuable phenanthridines and benzocarbazoles (Scheme 1c). The challenges for this novel one-pot cascade π-extended decarboxylative annulation (PEDA) are how to avoid side reactions such as protodecarboxylation, etc.,[22] how to achieve the N−H or C−H activation with complete regioselectivity, and how to make the consecutive series of reactions proceed smoothly to achieve the site-selective N1/C2 or C2/C3 annulation.

We initiated the condition optimizations by reacting the commercially available indole-2-carboxylic acids **1a** with cyclic diaryliodonium salt **2a** (Table 1).

Table 1. Optimization of the Reaction Conditions[a]



1a 2a 3aa 4a

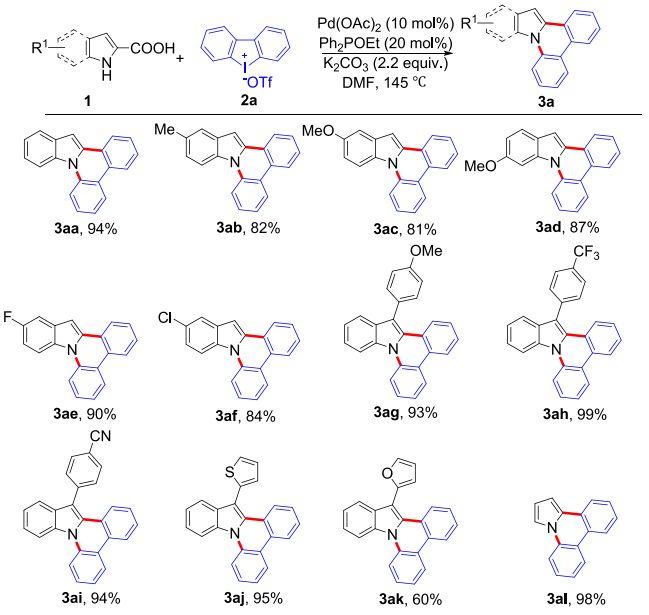
				yield (%)[b]	
entry	**2a** (equiv)	ligand	solvent	**3a**	**4a**
1	1.1	–	DMF	30	–
2[c]	1.1	–	DMF	–	–
3	1.1	–	DMA	10	–
4	1.1	–	DCE	11	–
5	1.1	–	DMSO	30	–
6	1.1	–	HOAc	–	30
7	1.1	PPh_3	DMF	47	–
8	1.1	Ph_2POEt	DMF	58	–
9[d]	1.1	Ph_2POEt	DMF	72	–
10[d]	1.6	Ph_2POEt	DMF	87	–
11[d]	2.0	Ph_2POEt	DMF	94	–
12[d]	2.0	–	DMF	40	10
13[d]	2.0	–	HOAc	–	84

[a]Reaction conditions: **1a** (0.3 mmol), $Pd(OAc)_2$ (10 mol %), ligand (20 mol %), base (2.2 equiv), solvent (1 mL), 12 h, 145 °C, air atmosphere. [b]Isolated yields. [c]Without K_2CO_3 or $Pd(OAc)_2$. [d]With 2 mL of solvent.

After intensive screening of the catalytic systems (see the Supporting Information), it was found that the N1/C2 cyclized product indolo[1,2-*f*]phenanthridine **3aa** was obtained in 30% yield without the detection of C2/C3 cyclized carbazole **4a** with $Pd(OAc)_2$ (10 mol %) as the catalyst and K_2CO_3 (2.2 equiv) as the base in DMF at 145 °C for 12 h (Table 1, entry 1). There is no reaction in the absence of either base or Pd catalyst (Table 1, entry 2). A base screening (see the Supporting Information) and a solvent screening (Table 1, entries 3−5) were then carried out; unfortunately, there was no improvement in the yield of **3aa**. Surprisingly, when HOAc was used as the solvent, the site selectivity was switched completely with C2/C3 cyclized carbazole **4a** isolated as the only product (Table 1, entry 6). A ligand screening was then conducted. It was found the yields were improved to 47% and 58% when triphenylphosphine (PPh_3) and ethyl diphenylphosphinite (Ph_2POEt), respectively, were used as the ligands (Table 1, entries 7 and 8, respectively). The yield was further increased to 72% when the reaction was conducted in a more diluted solution (Table 1, entry 9). To our delight, it was found the yield can be improved significantly by increasing the amount of iodonium salt **2a** (Table 1, entries 10 and 11), and finally, the reaction gave phenanthridine **3aa** in 94% yield when 2.0 equiv of **2a** was used (Table 1, entry 11). In the absence of Ph_2POEt, a mixture of **3a** and **4a** was obtained in 40% and 10% yields, respectively, with DMF as the solvent (Table 1, entry 12), and the yield of carbazole **4a** was improved to 84% with HOAc as the solvent (Table 1, entry 13).

With optimum conditions in hand, we first examined the substrate scope of this novel acid-directed double N1/C2 arylative annulation protocol with various commercially available indole-2-carboxylic acid derivatives (Scheme 2).

Scheme 2. Carboxylic Acids for N1/C2 Annulation



First, the substrates without substitutents at position C3 were tested. Substrates with methyl or methoxyl substituents gave the corresponding products in good to excellent yields (**3aa**−**3ad**). Substrates displaying extra halogenated functionalities such as F or Cl were tolerated under the reaction conditions (**3ae** and **3af**). Second, 3-aryl-indole-2-carboxylic acid substrates were examined. All of the substrates with strong electron-donating or -withdrawing substituents in the phenyl ring afforded the corresponding cyclized products **3ag**−**3ai** in excellent yields. Both 3-thiophenyl and 3-furanyl indole-2-carboxylic acids are effective, as well (**3aj** and **3ak**). It was found that the reaction with simple pyrrole-2-carboxylic acid as the substrate also gave the pyrrolo[1,2-*f*]phenanthridine **3al** in 98% yield.

To fully establish the scope of this one-pot N1/C2 annulation process, a range of substituted cyclic diaryliodonium salts were prepared and subjected to the optimized reaction protocol with indole-2-carboxylic acids and pyrrole-2-carboxylic acids (Scheme 3).[23] The symmetrical cyclic diaryliodonium salts were examined first (**3ba**−**3bh**). Both the indole-2-carboxylic acid and the pyrrole-2-carboxylic acid reacted with the cyclic diaryliodonium salts bearing simple

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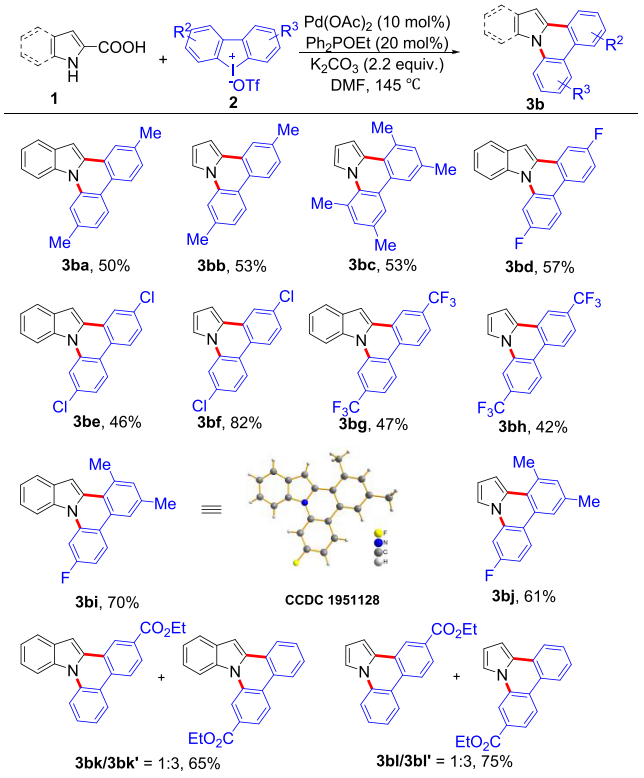
Scheme 3. Cyclic Diaryliodonium Salts for N1/C2 Annulation

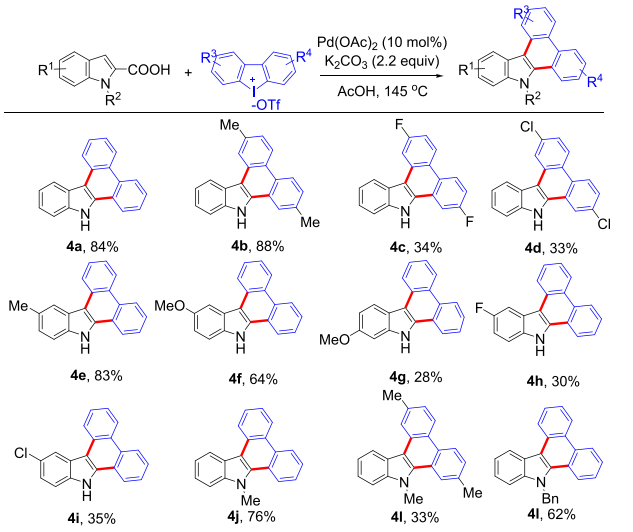


methyl substituents and gave the corresponding products in moderate yields. The halogen (F and Cl) and strong electron-withdrawing groups such as CF_3 were tolerated under the optimum conditions, affording the corresponding products in moderate to good yields (**3bd**–**3bh**). The unsymmetrical cyclic diaryliodonium salts were then tested (**3bi**–**3bl**). Cyclized products **3bi** and **3bj** were isolated as single products, and the structure of **3bi** was further confirmed by single-crystal X-ray diffraction analysis, which demonstrated that N-arylation took place from the less hindered side of the salt and formed the C–N bond first. For the unsymmetrical cyclic diaryliodonium salt with an ester substituent on one of the phenyl rings, the reactions afforded a mixture of products in moderate yields, and the main product was formed from the nitrogen attacking from the electron deficient ring of the salt.

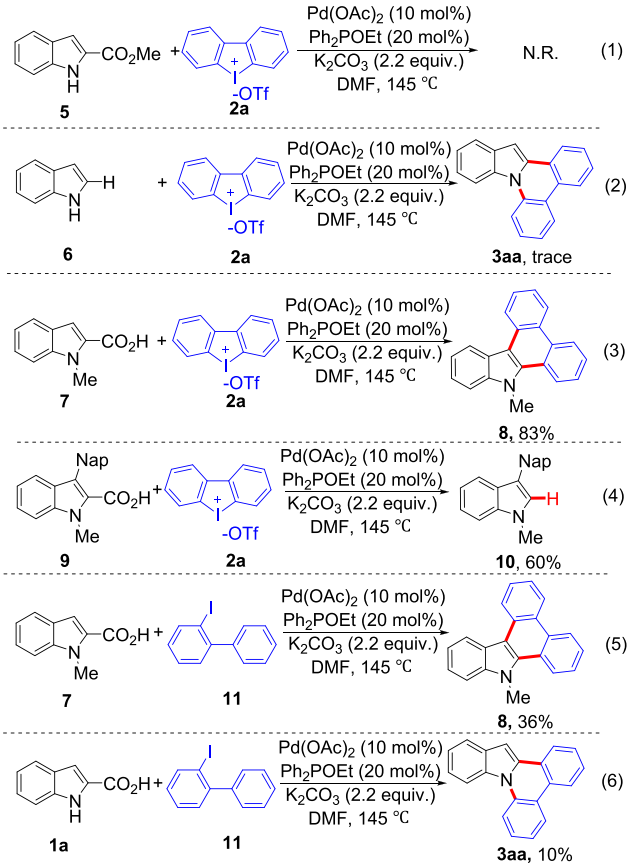
The substrate scope for the cascade one-pot C2/C3 annulation was then examined (Scheme 4). The indole-2-carboxylic acids without substituents on position N1 were tested first (**4a**–**4i**). All gave the corresponding C2/C3 annulated products with complete site selectivity. However, the substrates with halogen substituents gave the products in poor yields (**4c**, **4d**, **4h**, and **4i**). The indole-2-carboxylic acids with a methyl or benzyl substituent at position N1 were effective and gave the desired products **4j**–**4l** successfully.

To further understand this cascade decarboxylative annulative π-extension protocol, we carried out the following control experiments (Scheme 5). First, the effect of the carboxylic functional group was evaluated. It was found the reaction did not take place if the carboxylic functional group was masked as ester **5**, which demonstrates the essential directing effect of carboxylic acid (Scheme 5, eq 1). Only a trace amount of **3aa** was obtained if the carboxylic acid group was removed from the substrate (Scheme 5, eq 2). The impact

Scheme 4. Substrates for C2/C3 Annulation



Scheme 5. Control Experiments



of the substitutents on the pyrrole-type ring was then tested. With N-blocked indole-2-carboxylic acids **7** with a substrate, carbazole product **8** was obtained in 83% yield (Scheme 5, eq 3). If substrate **9** was used as the substrate with both N1 and C3 positions blocked, proto-decarboxylated product **10** was obtained in 60% yield (Scheme 5, eq 4). Finally, if cyclic diaryliodonium salt **2a** was replaced with 2-iodo-1,1′-biphenyl **11** and reacted with **7** and **1a** separately, carbazole product **4j** and phenanthridine product **3aa** were obtained in only 36% and 10% yields, respectively (Scheme 5, eqs 5 and 6).

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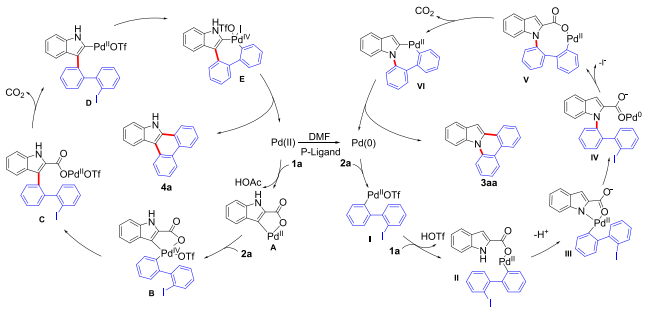
On the basis of the experiments described above, the proposed reaction mechanisms are shown in Scheme 6. With

Scheme 6. Proposed Mechanism



HOAc as the solvent, the catalytic cycle would start with a C−H activation by Pd(II) species to give a five-membered cyclopalladate(II) intermediate **A**. Because the N atom is more electronegative than the C atom, a ring opening of cyclic diaryliodonium salt **2a** then occurs at the C position, which has a lower barrier, and a Pd(IV) complex **B** would be generated, which is the key step that determines the regioselectivity of this reaction. A reductive elimination would give the C−C coupled intermediate **C**. After sequential decarboxylation (**D**), oxidative addition (**E**), and reductive elimination, carbazole product **4a** would form. When DMF is used as the solvent with Ph_2POEt as an additive, a Pd(0)/Pd(II) catalytic cycle instead of the aforementioned Pd(II)/Pd(IV) pathway is proposed. The catalytic cycle would start with the ring opening of cyclic diaryliodonium salt **2a** by in situ-generated Pd(0) to give Pd(II) species **I**, which would be attacked by indole-2-carboxylic acids **1a** to give intermediate **II**. The following key step, N−H activation, might generate a five-membered cyclopalladate(II) species **III** that would undergo sequential reductive elimination, oxidative addition, decarboxylation, and reductive elimination to give phenanthridine product **3aa**.

In summary, we have successfully developed a cascade π-extended decarboxylative annulation (PEDA) strategy for the construction of privileged phenanthridine and benzocarbazole scaffolds from commercially available indole-2-carboxylic acids and readily available cyclic diaryliodonium salts. This highly step economical process involves the Pd(II)-catalyzed site-selective *ortho* N1 or C2 arylation followed by tandem intramolecular decarboxylative annulation. The key is the successful development of a two-in-one traceless directing group strategy by which the carboxylic acid functionality was employed as both a directing group for the Pd-catalyzed N−H/C−H arylation and a reactive group for the cascade intramolecular decarboxylative annulation.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.9b03775.

Experimental procedures and spectroscopic characterization data (PDF)

Accession Codes

CCDC 1951128 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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