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Rapid Construction of Fused Heteropolycyclic Aromatics via Palladium-Catalyzed Domino Arylations of Imidazopyridine Derivatives

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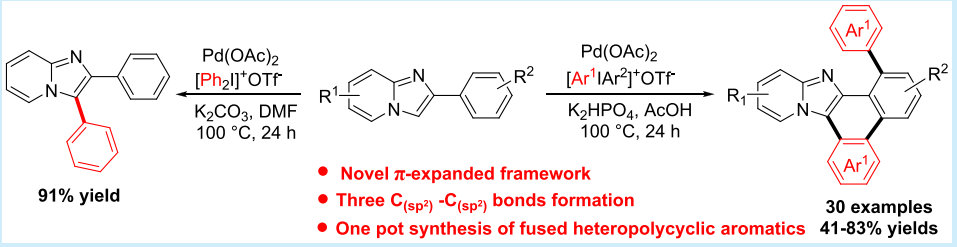
Supporting Information



ABSTRACT: By using diaryliodonium salts, a novel approach of a palladium-catalyzed cascade of diarylation/intramolecular dehydrogenative coupling reaction has been developed in the synthesis of phenanthro-imidazopyridine fused heteropolycycles. The method can tolerate various substrates, and the target products were rapidly constructed in one pot. Furthermore, studies of the detailed reaction mechanism provide an insight into the C−H functionalization of 2-aryl-imidazopyridine derivatives and the C−C bond formations in the presence of palladium catalyst.

Fused heteropolycyclic aromatics continue to stimulate synthetic research in modern chemistry, as both synthetically challenging targets and compounds that possess unique optoelectrochemical properties.[1] Imidazo[1,2-α]pyridine fused π-extended heterocycles represent a prominent framework due to their prevalence in bioactive substances and functional materials.[2] The development of an efficient synthetic method is therefore highly desirable. As a consequence, synthetic efforts were centered around direct functionalization of 2-aryl-imidazo[1,2-α]pyridine derivatives.[3] Among them, extensive research focused on the introduction of functional groups on the C3-position of the imidazo[1,2-α]pyridine motif (Scheme 1Ia),[4] Of particular note, rhodium-catalyzed imidazopyridine-directed *ortho*-amidation and *ortho*-cyanation were recently reported, respectively (Scheme 1Ib).[5] Nevertheless, the catalytic domino/cascade reaction via multiple C−H bonds activation, in which several new bonds were formed sequentially in a single operation for the rapid construction of polyaromatic hydrocarbons, is quite promising. For example, annulations of 2-aryl-imidazo[1,2-α]pyridine with alkynes, *o*-dihaloarenes, or α-diazo esters in the formation of two carbon−carbon bonds were reported in the presence of transition metal catalysts (Scheme 1Ic).[6] On the other hand, diaryliodonium salts were frequently employed in arylations.[7] Seminal contributions from Chen and Mo groups showcased the ability of diaryliodonium salts in cascade annulation for the synthesis of heterocyclic compounds.[8] Recently, hypervalent aryliodine reagents in the presence of palladium catalysts are tremendously attractive to discover novel reaction pathways for multiple C−H functionalization.[9] In this regard, the Jana group reported an elegant work in which the palladium-catalyzed cascade of *C*-arylation/1,2-aryl shift/cross-dehydrogenative coupling of 2-arylindoles with diaryliodonium salts afforded dibenzo-fused carbazoles.[10] The research group of Park and Hong documented diarylation of 2-phenylquinazolin-4(3*H*)-ones through a cascade of *N*-arylation/annulative π-extension in a straightforward manner.[11] In continuation of our interest in exploring the activation of the vicinal C−H bond of diaryliodonium salts for the efficient synthesis of polyaromatic frameworks,[12] in this context, we described herein a feasible procedure of the palladium-catalyzed cascade of the diarylation/intramolecular cross-dehydrogenative coupling reaction of 2-aryl imidazopyridine derivatives using diaryliodonium salts. As a result, a family of phenanthro-imidazopyridine fused heteropolycycles were rapidly constructed in one pot (Scheme 1II).

To begin our studies, we chose 2-phenylimidazo[1,2-α]pyridine (**1a**) and diphenyliodonium triflate (**2a**) as the

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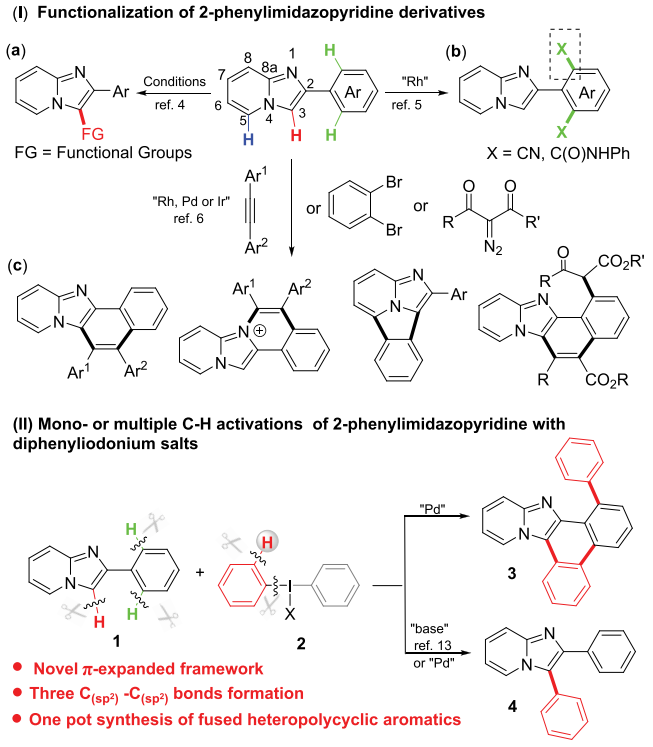
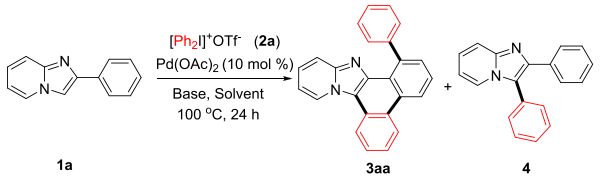
Scheme 1. Background of Functionalization of 2-Phenylimidazopyridine and This Work



model substrates. Inspired by our previous work,[12a] the reaction was performed in the presence of 3.0 equiv of **2a** and 10 mol % $Pd(OAc)_2$ in DMF as the solvent at the temperature of 100 °C (Table 1). However, no desired product was observed with a total recovery of **1a**. Upon the addition of 2.0 equiv of bases of K_2CO_3, a monoarylated product **4** was obtained in an excellent yield of 91% (Table 1, entry 2).[13] Then, we started to change the solvent; neither product **3aa** nor compound **4** was observed in DCE, while product **4** was obtained in 60% yield in EtOH. ^{n}BuOH can afford a trace amount of inseparable compounds which is supposed to be **3aa** later by a thin-layer chromatography experiment (Table 1, entries 3−5). To our delight, a polyarylated product **3aa** was isolated in 65% yield after 24 h when AcOH was employed as the solvent (Table 1, entry 6). While the solvent was changed to trifluoroacetic acid (TFA) with a strong acidity (pK_a of TFA is 0.23, compared to a pK_a of 4.76 for AcOH), the target compound **3aa** was not found (Table 1, entry 7). Subsequently, various bases including KOAc, NaOAc, K_2HPO_4, and K_3PO_4 were screened (Table 1, entries 8, 9, 11, and 12). K_2HPO_4 was proven to be the best choice, affording **3aa** in an excellent yield of 83%. Notably, when the reaction was conducted without base, the yield decreased to 32% in AcOH as the solvent (Table 1, entry 10), which suggested that AcOH played an important role in the reaction (Table 1, entry 1 versus entry 12).[14] We also examined the counteranion effect; the diaryliodonium salt with an anion of OTf gave the best yield of 83% (Table 1, entries 13−15). When we reduced the amounts of diphenyliodonium salt to 2.5 equiv, the isolated yield decreased to 67% (Table 1, entry 16).

With the optimized reaction conditions in hand, we then started to investigate the diaryliodonium salts for this domino arylation process with 2-phenyl-imidazo[1,2-α]pyridine (**1a**).

Table 1. Screening of Reaction Conditions for the Domino Arylation of Imidazopyridine[a]



entry	solvent	base	X	yield of **3aa**[b] (%)	yield of **4** (%)
1	DMF		OTf	0	0
2	DMF	K_2CO_3	OTf	0	91
3	DCE	K_2CO_3	OTf	0	0
4	EtOH	K_2CO_3	OTf	0	60
5	*n*-BuOH	K_2CO_3	OTf	trace	0
6	AcOH	K_2CO_3	OTf	65	0
7	TFA	K_2CO_3	OTf	0	0
8	AcOH	KOAc	OTf	70	0
9	AcOH	NaOAc	OTf	40	0
10	AcOH	K_2HPO_4	OTf	83 (80)[c]	0
11	AcOH	K_3PO_4	OTf	67	0
12	AcOH		OTf	32	0
13	AcOH	K_2HPO_4	BF_4	42	0
14	AcOH	K_2HPO_4	PF_6	58	0
15	AcOH	K_2HPO_4	Br	0	0
16[d]	AcOH	K_2HPO_4	OTf	67	0

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.6 mmol), base (2 equiv), and $Pd(OAc)_2$ as the catalyst (0.02 mmol, 10 mol %) in solvent (4 mL) at 100 °C for 24 h. [b]Isolated yield. [c]A 1 mmol scale reaction was carried out to afford **3aa** in 80% yield. [d]A 2.5 equiv portion of **2a** was used.

As shown in Table 2, we were pleased to find that a range of symmetrical diaryliodonium triflates regardless of the electronic nature of the substituents could be successfully employed in the reaction. The desired products **3ba**−**3ha** were furnished in yields of 57−78% (Table 2, entries 1−7). Moreover, unsymmetrical diaryliodonium triflates bearing a steric mesityl moiety were adopted to this protocol; as expected, the aryl (Ar^1) group with less steric hindrance was selectively transferred to the target products while the formed product containing the mesityl unit was not observed. Of note, when one of the two aryl groups of diaryliodonium triflate is 3,4-dimethylaryl as the Ar^1 unit, two possible products of **3ka** and **3ka′** would be formed as the methyl groups on the different positions of the benzo-fused ring (Table 2, below). However, it was found that only **3ka** was obtained in 43% yield, which indicated that the intramolecular dehydrogenative coupling reaction favored the pathway in a less hindered manner (Table 2, entry 14). Furthermore, 4-methoxyphenyl−phenyliodonium triflate was attempted in the reaction and underwent the exclusive transfer of the phenyl group to the corresponding products in 48% yield (Table 2, entry 15). Moreover, a single crystal of **3ca** was obtained for X-ray crystallographic analysis; the structure of **3ca** was verified unambiguously as presented in Table 2. The structure drawing demonstrated that three carbon (sp^2)−carbon (sp^2) bonds are formed in one pot, which suggested a diarylation with two equivalent diaryliodonium salts and an intramolecular aromatization by the formation of a benzene ring.

We subsequently examined the structural diversity of various 2-arylimidazo[1,2-α]pyridines by assessing the substitution effect on both the heterocyclic framework and the 2-aryl

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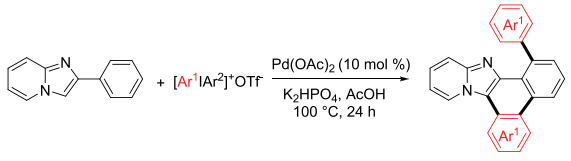
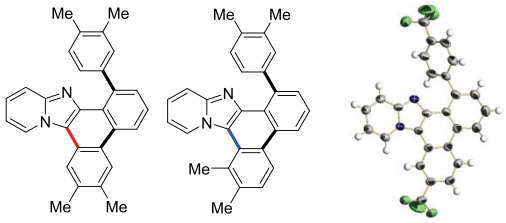
Table 2. Scope of Diverse Iodonium Salts in the Domino Arylation of 2-Phenylimidazopyridine[a]



1a 2 3

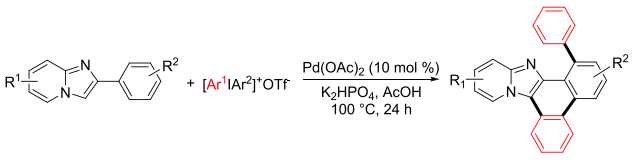
entry	$Ar^1(Ar^2)$	product	yield[b] (%)
1	$(4\text{-}FC_6H_4)_2$	**3ba**	69
2[c]	$(4\text{-}CF_3C_6H_4)_2$	**3ca**	57
3	$(4\text{-}^tBuC_6H_4)_2$	**3da**	73
4	$(4\text{-}MeOC_6H_4)_2$	**3ea**	72
5	$(4\text{-}MeC_6H_4)_2$	**3fa**	74
6	$(4\text{-}PhC_6H_4)_2$	**3ga**	78
7	$(2\text{-}FC_6H_4)_2$	**3ha**	72
8	$4\text{-}FC_6H_4$(Mesityl)	**3ba**	54
9	$4\text{-}MeC_6H_4$(Mesityl)	**3fa**	58
10	$4\text{-}CF_3C_6H_4$(Mesityl)	**3ca**	43
11	$4\text{-}OCF_3C_6H_4$(Mesityl)	**3ia**	63
12	$4\text{-}OPhC_6H_4$(Mesityl)	**3ja**	48
13	$3,5\text{-}F_2C_6H_3(C_6H_4)$	**3aa**	45
14	$3,4\text{-}Me_2C_6H_3$(Mesityl)	**3ka**	43
15	$4\text{-}MeOC_6H_4(C_6H_4)$	**3aa**	48



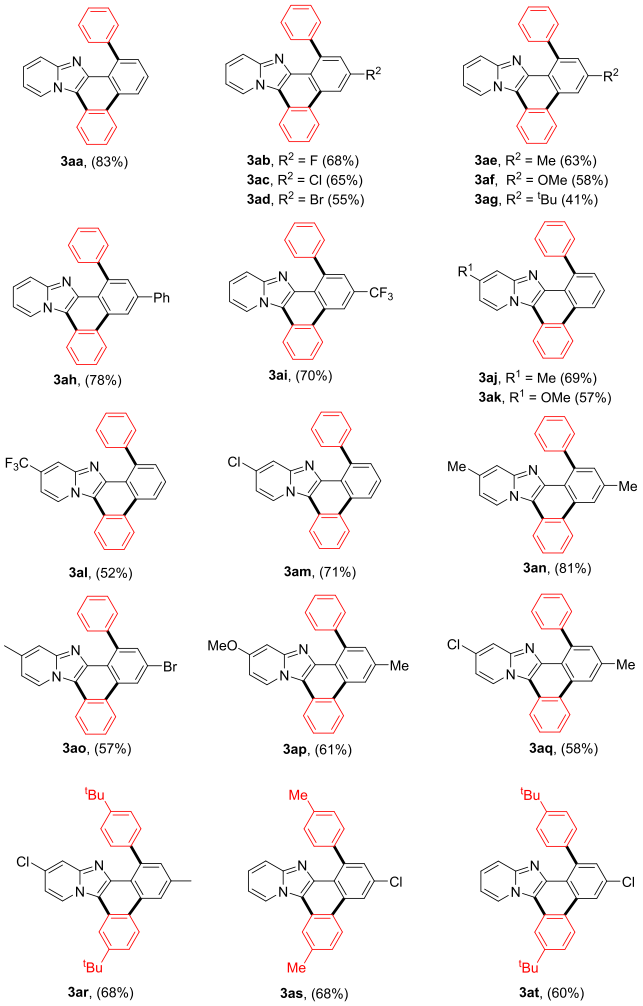
3ka 3ka' 3ca

[a]Reaction conditions: **1** (0.2 mmol), **2** (0.6 mmol), $Pd(OAc)_2$ (10 mol %), and K_2HPO_4 (0.4 mmol) in 4 mL of AcOH at 100 °C for 24 h. [b]Isolated yield after column chromatography. [c]X-ray-derived structural views of **3ca** (carbon atoms in this view are depicted with ellipsoids at the 30% probability level).

Scheme 2. Scope of Imidazopyridine Derivatives for Domino Arylation[a]



1 2 3



[a]Reaction conditions: **1** (0.2 mmol), **2** (0.6 mmol), $Pd(OAc)_2$ (10 mol %), and K_2HPO_4 (0.4 mmol) in 4 mL of AcOH at 100 °C for 24 h; isolated yield after column chromatography.

motifs. First, substrates (R^2) with a broad range of substitution of the 1-aryl group were examined. As shown in Scheme 2, electron-neutral, electron-donating, or electron-withdrawing substituents were generally well-tolerated, affording the desired products **3ab**−**3ai** bearing halogen (**3ab**−**3ad**), methyl (**3ae**), methoxy (**3af**), phenyl (**3ah**), *tert*-butyl (**3ag**), and trifluoromethyl (**3ai**) functionalities in moderate to good yields of 41−78%. We next turned our attention to the substitution on the heterocyclic framework of imidazopyridine (R^1). Fortunately, the reactions all went smoothly to afford the desired products **3aj**−**3aq** in 52−81% yields. Additionally, on the basis of results as shown in Table 2, we attempted the cross-reaction with substituted 2-arylimidazo[1,2-α]pyridine **1** and various diaryliodonium salts **2** bearing a *tert*-butyl or methyl group; the desired products **3ar**−**3at** were afforded in 60−68% yields.

We next sought to investigate the mechanism of this reaction. By the formation of three carbon (sp^2)−carbon (sp^2) bonds (a, b, and c in Scheme 3), all of the five possible reaction intermediates were assumed: the formation of single (1) a-bond (**4**) or (2) b-bond (**5**) first; the simultaneous formation of two bonds first such as (3) a-bond and c-bond (**6**), (4) a-bond and b-bond (**7**), or (5) b-bond and c-bond (**8**). The intermediates **4**−**7** were therefore prepared and attempted in the reaction under the standard conditions, respectively. The results are shown in Scheme 3; compounds **4** and **7** did not transform into **3aa** while **4** could form compound **7** in a good yield of 89%. The reaction of **6** with **2a** gave a low yield of **3aa** as well (Scheme 3, 1). It suggested that the reaction initiated with the formation of b- and c-bonds but not the a-bond.

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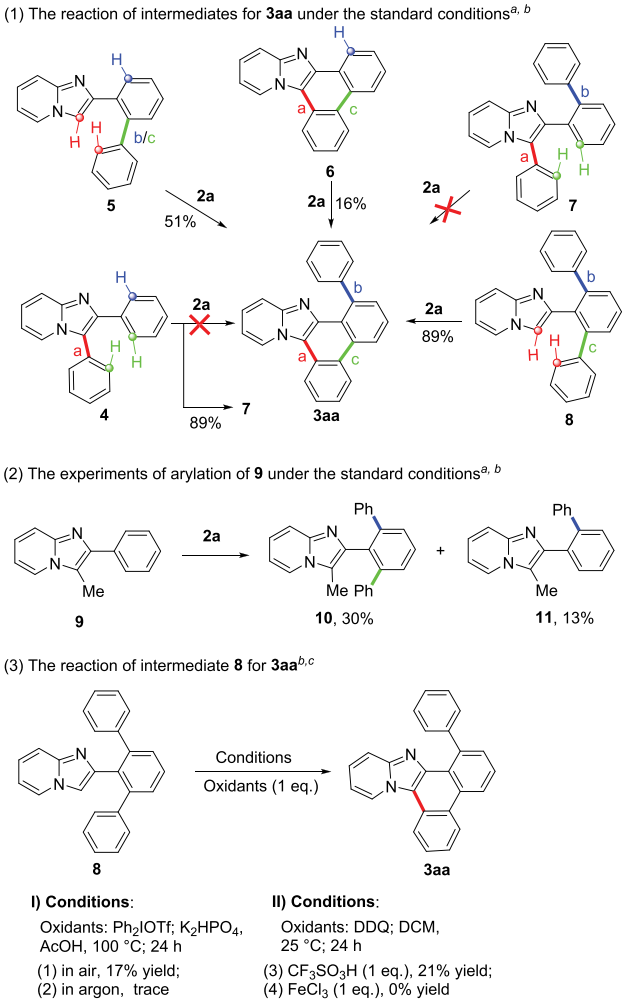
Scheme 3. Controlled Reactions



[a]Standard conditions: **4**, **5**, **6**, or **7** (0.2 mmol), **2** (0.6 mmol), $Pd(OAc)_2$ (10 mol %), and K_2HPO_4 (0.4 mmol) in 4 mL of AcOH, 100 °C, 24 h. [b]Isolated yield after column chromatography. [c]DDQ = 2,3-dichloro-5,6-dicyano-1,4-benzoquinone.

Moreover, compounds **5** and **8** afforded **3aa** in good yields. Hence, it is reasonable to conclude that the a-bond was formed lastly. Further experiments of the arylation of **9** bearing a methyl group at the 3-position furnished diphenylated **10** as well as monophenylated product **11** (Scheme 3, 2). More importantly, a scale-up reaction (10 g) of the model reaction of **1a** with **2a** was carried out; a separable amount of **8** was isolated and characterized by NMR and MS spectra.

To further understand the formation of the a-bond, intramolecular aryl−aryl dehydrogenative coupling reactions of **8** were conducted in the presence of a variety of oxidants (Scheme 3, 3). When diphenyliodonium triflate was used as the oxidant,[15] the desired product of **3aa** could be formed in air. Moreover, we performed the oxidative aromatic couplings (Scholl reaction) of **8** mediated by the strong Brønsted acid of TfOH or Lewis acid of $FeCl_3$ with additional oxidants of DDQ; **3aa** was isolated in 21% yield with TfOH. However, no reaction occurred in the case of $FeCl_3$. These results implied that the formation of the a-bond of **3aa** could proceed in acidic conditions in the presence of oxidants. In comparison with the palladium-catalyzed phenylation of **1a** with **2a** in DMF as the solvent as described in Table 1, protic acetic acid as the solvent might shield the highly reactive C−H bond at the 3-position of 2-arylimidazopyridine derivatives. We therefore proposed a catalytic mechanism as shown in Figure 1. The reaction of **1a**

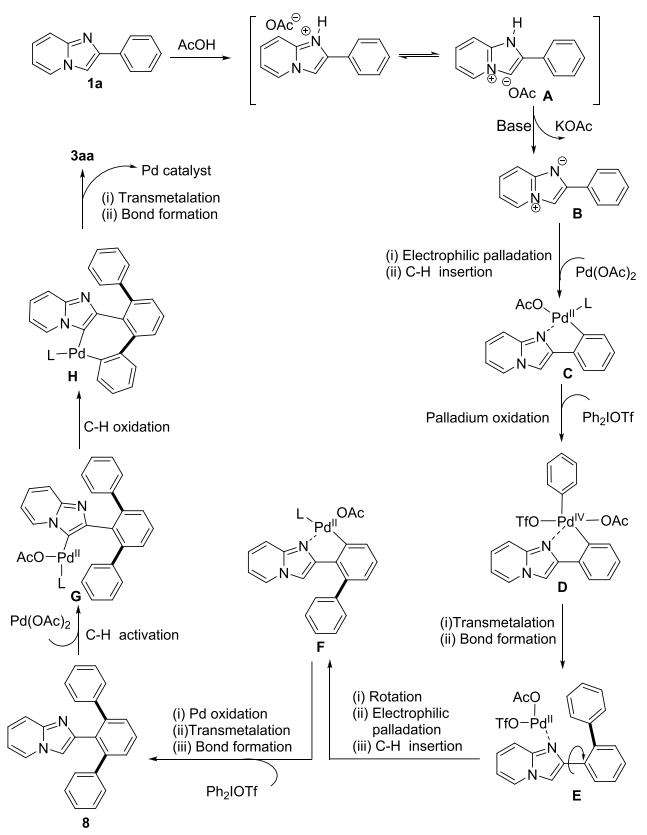


Figure 1. Proposed mechanism for domino arylation.

with AcOH formed a salt (**A**), as shown in Figure 1, whose positive cation diminished the reactivity of the C−H group at the 3-position of **A** by electron-withdrawing inductive effects. Furthermore, the associated anion of OAc might shield the reactivity of the C−H group at the 3-position of **A** by steric hindrance. **A** gave **B** bearing nucleophilic nitrogen with base. Then, the reaction was initiated by electrophilic palladation and C−H insertion to generate palladacycle **C**. Oxidation of **C** afforded the Pd(IV) complex of **D** with Ph_2IOTf as oxidants. C−C bond formation of **E** by a reductive elimination from the high-valent palladium center.[16] The second C−C bond formation proceeded via **F** by bond rotation of **E** in a similar manner. Finally, an intramolecular dehydrogenative coupling reaction by palladium-catalyzed C−H activations releases **3aa** from **8** which was an isolated intermediate, and the Pd species is regenerated from the catalytic cycle.

In summary, we have developed a palladium-catalyzed cascade of the diarylation/intramolecular dehydrogenative coupling reaction of imidazopyridine derivatives using diaryliodonium salts, which provides an access to a variety of *ortho*-phenanthro-imidazopyridine fused heteropolycycles. The advantage of the current protocol is that it can tolerate various substrates, and the target polyaromatic compounds were rapidly constructed in one pot. Further investigation of the detailed reaction mechanism and optimization of reaction conditions to achieve a broader scope is ongoing in our laboratory.

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■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.9b00761.

Experimental procedures, and characterization data and spectra of new compounds (PDF)

Accession Codes

CCDC 1900251 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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