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Palladium-Catalyzed Cascade Dearomative Spirocyclization and C−H Annulation of Aromatic Halides with Alkynes

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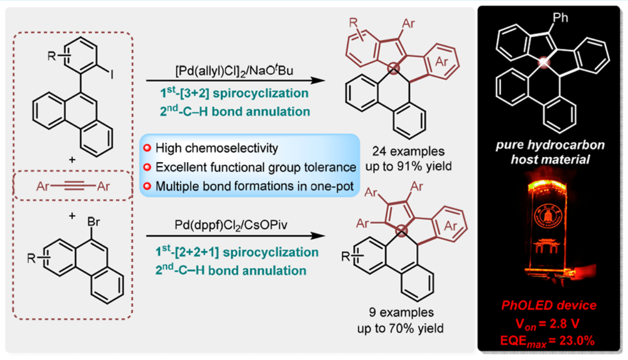
ABSTRACT: Described herein is a palladium-catalyzed intermolecular dearomative annulation of aryl halides with alkynes, which provides a rapid approach to a class of structurally unique spiroembedded polycyclic aromatic compounds. The cascade process is accomplished by a sequential alkyne migratory insertion, Heck-type dearomatization, and C−H bond annulation. Further optoelectronic study indicated this fused spirocyclic scaffold could be a potential host material for OLEDs, as exemplified by a fabricated red PhOLED device with a maximum external quantum efficiency of 23.0%.



Spirocyclic scaffolds have attracted considerable attention in the fields of synthetic chemistry, organic functional materials, and pharmaceuticals.[1] The structures of spirocycles have a crucial influence on their biological activities and photophysical properties such as HOMO−LUMO gaps, redox potentials, carrier mobilities, molecular packing modes, and absorption and emission properties.[2] Considering the wide applications of polycyclic aromatic hydrocarbons (PAHs) as organic semiconductors, the incorporation of the cruciform structural feature into the PAHs could effectively impact the intermolecular $\pi-\pi$ stacking interactions and optoelectronic properties. Upon appropriate π-extension and/or functionalization, these inherently sterically hindered spirocycles could be evolved into advanced materials in organic optoelectronic devices, including the host materials for organic light-emitting diodes (OLEDs) and hole transporting materials for organic solar cells (OSCs).[1a,3] Thus, the development of concise and efficient synthetic methods enabling the rapid assembly of structurally diverse spirofunctionalized polycyclic aromatic hydrocarbons from simple starting materials with excellent functional group tolerance is highly desired, which could boost the innovation of organic functional materials and medicines.

Transition-metal-catalyzed dearomative cyclization of simple planar arenes with alkynes has been regarded as a powerful tool to access three-dimensional spirocyclic architectures.[4] Despite efficiency, the reported methods typically require the employment of electronically activated aromatics as the substrates, such as phenols, naphthols, indoles, and pyrroles, because of the relatively low aromatic stabilization energy and/or beneficial keto−enol tautomerism.[4−7] In 2019, we disclosed a palladium-catalyzed Heck-type dearomative [2 + 2 + 1] spirocyclization of alkyl bromoarenes with internal alkynes.[7] Although this work obviated the using of electronically activated aromatics as starting materials, an alkyl group is necessary to enable a β-hydrogen elimination as the driving force for the expected spirocyclization reaction (Scheme 1a). Recently, the endocyclic C=C bonds of (hetero)arenes have been regarded as nonclassic olefins to enable the dearomative difunctionalization reactions.[8] In this regard, Jia and You reported the catalytic dearomative 1,4-difunctionalization of naphthalenes by capturing the in situ formed π-allyl-palladium species with a second coupling partner (Scheme 1b).[9,10] Inspired by this dearomative difunctionalization strategy, we envisioned that the catalytic Heck-type dearomative spiroannulation of polycyclic aromatic halides with diaryl acetylenes could be achieved without the assistance of an alkyl group, by intercepting the alkyl palladium intermediates with the attached aryl rings on the carbon−carbon triple bonds. The implementation of this rational design relied on the development of a highly efficient and selective catalytic system that enables the thermodynamically unfavored dearomatization process rather than nonspirocyclization and a following C−H annulation process as the termination reaction of the cascade course. Herein, we disclose a palladium-catalyzed cascade dearomative spirocyclization and C−H annulation of aromatic

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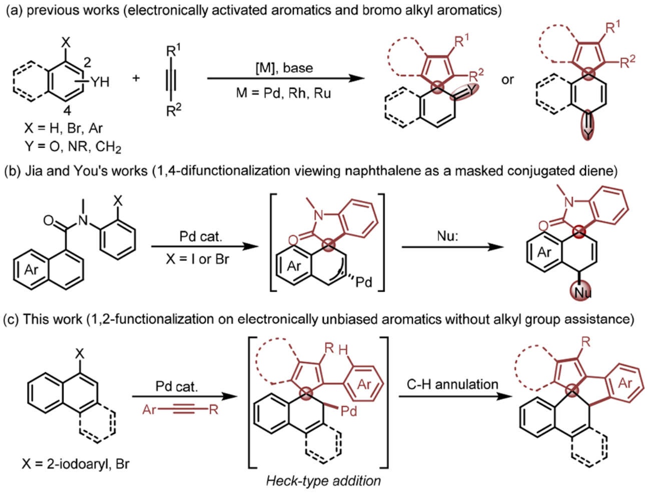
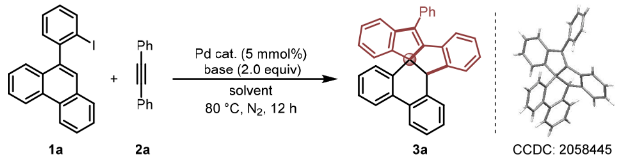
Scheme 1. Transition-Metal-Catalyzed Dearomative Spiroannulation of Aromatics



halides with diaryl acetylenes (Scheme 1c), which enables streamlined synthesis of spiroembedded polycyclic aromatic compounds and rapid assembly of a class of novel pure hydrocarbon host materials for phosphorescent organic light-emitting diodes (PhOLEDs).

At the beginning, the reactions of diphenyl acetylene **2a** with 9-(2-iodophenyl)phenanthrene **1a**, 1-bromonaphthalene, and 9-bromophenanthrene, individually, were conducted under the previously developed catalytic system for spiroannulation of alkyl aryl haloarenes.[7] Not suprisingly, undefined complex mixtures, which were supposed to involve [4 + 2], [3 + 2], and [2 + 2 + 2] cyclized products (based on the GC−MS), were generated in poor yields. Then, **1a** and **2a** were selected as the model substrates for reaction optimization (Table 1). Initial investigation indicated that the palladium source was found to be crucial for the spirocyclization. After extensive screening of the common palladium salts such as $Pd(OAc)_2$, $Pd_2(dba)_3$, $Pd(PPh_3)_4$, $[Pd(allyl)Cl]_2$, and $Pd(acac)_2$ (Table 1, entries 1−5), it was determined that the reaction in the presence of $[Pd(allyl)Cl]_2$, Cs_2CO_3, and toluene could furnish the desired spiroembedded polycyclic product **3a** in 27% yield (Table 1, entry 5). The structure of **3a** was demonstrated by single-crystal X-ray diffraction. Then, the effects of bases were examined (Table 1, entries 6−9). While KO^tBu almost terminated the reaction, NaO^tBu proved to be the most effective base, delivering **3a** in 75% yield (Table 1, entry 9). Benzene solvents such as *o*-xylene, mesitylene, and toluene were the suitable solvents for this reaction (Table 1, entries 10 and 11), whereas other common solvents such as THF, DCE, and DMF were much less effective (Table 1, entries 12−14). Prolonging the reaction time to 18 h could slightly improve the yield to 82% (Table 1, entry 15). Finally, the reaction of **1a** (0.12 mmol), **2a** (0.1 mmol), $[Pd(allyl)Cl]_2$ (5% mmol), NaO^tBu (0.2 mmol), and toluene (1 mL) at 80 °C for 18 h proved to be the optimal conditions, delivering **3a** in 81% isolated yield (Table 1, entry 16) along with the formation of trace amounts of nondearomatized annulation products. The addition of phosphorus ligands such as X-Phos into the catalytic system was detrimental to the reaction efficiency (Table 1, entry 17; see the Supporting Information (SI), Table S1, entries 33−36).

Table 1. Optimization of Reaction Conditions[a,b]

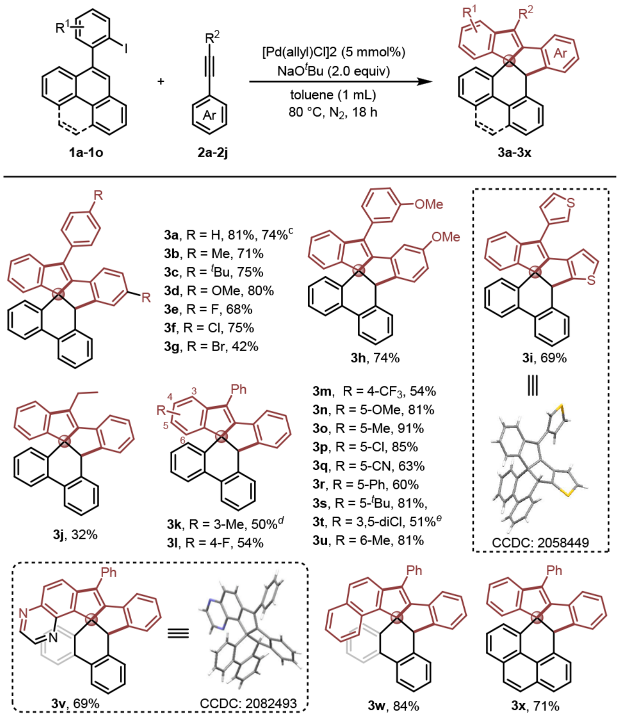


entry	base	Pd. cat	solvent	yield (%)
1	Cs_2CO_3	$Pd(OAc)_2$	toluene	n.d.
2	Cs_2CO_3	$Pd_2(dba)_3$	toluene	trace
3	Cs_2CO_3	$Pd(PPh_3)_4$	toluene	n.d.
4	Cs_2CO_3	$Pd(acac)_2$	toluene	n.d.
5	Cs_2CO_3	$[Pd(allyl)Cl]_2$	toluene	27
6	K_2CO_3	$[Pd(allyl)Cl]_2$	toluene	19
7	K_3PO_4	$[Pd(allyl)Cl]_2$	toluene	48
8	KO^tBu	$[Pd(allyl)Cl]_2$	toluene	trace
9	NaO^tBu	$[Pd(allyl)Cl]_2$	toluene	75
10	NaO^tBu	$[Pd(allyl)Cl]_2$	*o*-xylene	71
11	NaO^tBu	$[Pd(allyl)Cl]_2$	mesitylene	65
12	NaO^tBu	$[Pd(allyl)Cl]_2$	THF	25
13	NaO^tBu	$[Pd(allyl)Cl]_2$	DCE	n.d.
14	NaO^tBu	$[Pd(allyl)Cl]_2$	DMF	42
15[c]	NaO^tBu	$[Pd(allyl)Cl]_2$	toluene	82
16[c,d]	**NaO^tBu**	**$[Pd(allyl)Cl]_2$**	**toluene**	**89(81[f])**
17[c,d,e]	NaO^tBu	$[Pd(allyl)Cl]_2$	toluene	38

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.15 mmol), Pd cat. (5 mol %), base (0.2 mmol), and solvent (1 mL) at 80 °C for 12 h under N_2. [b] NMR yield using dibromomethane as an internal standard. [c] Run for 18 h. [d] **1a** (0.12 mmol) and **2a** (0.1 mmol) were used. [e] X-Phos (20 mol %) was added. [f] Yields of isolated products. DCE = 1,2-dichloroethane; THF = tetrahydrofuran; DMF = *N*,*N*-dimethylformamide; n.d. = not detected.

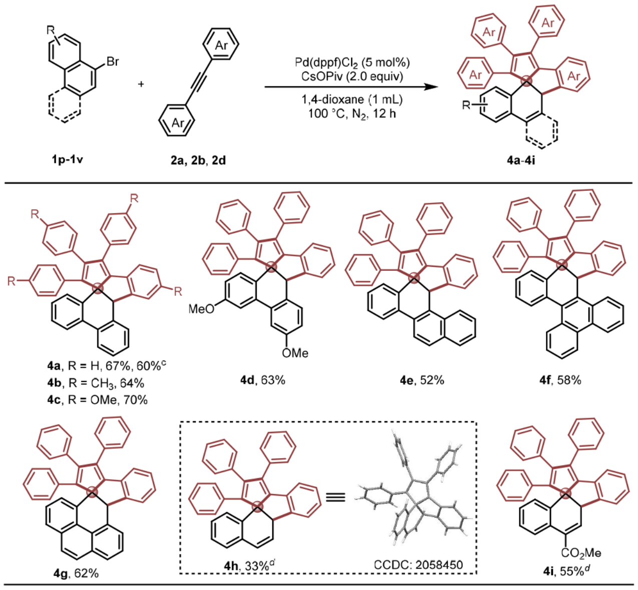
With the optimized reaction conditions in hand, we first evaluated the substrate scope using different alkynes (Table 2). Diaryl acetylenes with either electron-donating groups (methyl, *t*-butyl, methoxy) and electron-withdrawing groups (fluoro, chloro, bromo) at the *para* or *meta* position of phenyl rings worked well under the standard conditions, giving the spirocyclic products in 42−81% yields (**3a**−**h**). The good functional tolerance with halo groups could provide a valuable opportunity for further derivation (see the SI, part VII). Generally, the electron-rich alkynes appeared to be beneficial for the reaction (**3b**−**d** vs **3e**−**g**). Additionally, di(thiophen-3-yl)ethyne (**2i**) could undergo a tandem annulation with a 69% product yield (**3i**), and the terminal C−H annulation regioselectively occurred at C2 position of thienyl, which was identified by X-ray crystallographic analysis. To our delight, phenyl alkyl alkynes, such as but-1-yn-1-ylbenzene (**2j**), could also be suitable substrates albeit in lower yield (**3j**). However, terminal alkynes such as phenylacetylene failed to undergo this spiroannulation. Next, the substrate scope of biaryl halides was studied. Biaryl iodides with diverse functional groups, including trifluoromethyl, methoxy, methyl, chloro, cyano, phenyl, and *t*-butyl, at different positions on the iodinated aryl rings were investigated, leading to the spirocyclic analogues in 50−91% yields (**3k**−**u**). Furthermore, biaryl halides involving quinoxalinyl, naphthyl, and pyrenyl moieties were also suitable substrates, giving a sterically congested spirocyclic compound in moderate to high yields (**3v**−**x**). Unfortunately, the reaction of 1-(2-iodophenyl)naphthalene with **2a** did not provide the desired product.

Table 2. Scope of Biaryl Iodides and Internal Alkynes[a,b]



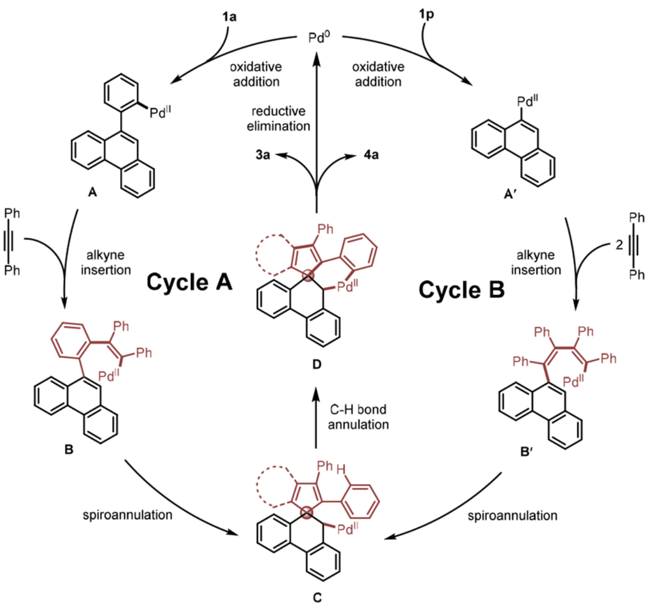
[a]Reaction conditions: **1** (0.12 mmol), **2** (0.1 mmol), $[Pd(allyl)Cl]_2$ (5.0 mol %), and NaO^{t}Bu (0.2 mmol) in toluene (1 mL) at 80 °C for 18 h under N_2. [b]Yields of isolated products. [c]Scale of 3 mmol. [d]At 100 °C. [e]At 110 °C.

Table 3. Scope of Bromoarenes and Internal Alkynes[a,b]



[a]Reaction conditions: **1** (0.1 mmol), **2** (0.15 mmol), $Pd(dppf)Cl_2$ (5.0 mol %), and CsOPiv (0.2 mmol) in 1,4-dioxane (1 mL) at 100 °C for 12 h under N_2. [b]Yields of isolated products. [c]Scale of 3 mmol. [d]At 110 °C.

Scheme 2. Plausible Mechanistic Pathway



Besides the cascade [3 + 2] spirocyclization/C−H annulation of biaryl halides with internal alkynes, condensed aromatic bromides could also work with alkynes to undergo a cascade [2 + 2 + 1] spirocyclization/C−H annulation to furnish the spirocyclic scaffolds. After reoptimization of the reaction conditions (see SI, Table S2), spirofeatured polycyclic aromatic compound **4a** was obtained in 67% yield accompanied by approximately 10% yield of the [2 + 2 + 2] annulated byproduct (1,2,3,4-tetraphenyltriphenylene). As exemplified in Table 3, symmetrical diaryl alkynes and bromoarenes with functional groups such as methyl, methoxy, and carboxylic ester could be converted to the desired spirocycles in 55−70% yields (**4a**−**d** and **4i**). Of particular note, bromo substrates with larger π-conjugated arenes such as chrysene, benzo[*g*]chrysene, and pyrene could also participate in this reaction, providing the congested spirocyclic products in 52−62% yields (**4e**−**g**).

To preliminarily investigate the reaction mechanism, an intermolecular competitive experiment between **2a** and **2a**-d_{10} with **1a** was conducted (see the SI, part VIII). The kinetic isotope effect ($k_H/k_D \approx 1.63$) suggested that terminal C−H cleavage of the aryl ring of alkynes might not be involved in the rate-determining step.

Based on the above results and previous reports,[7,9,10] a proposed mechanism is shown in Scheme 2. Initially, oxidative addition of Pd(0) to the C−X bond affords aryl Pd(II) species **A** (cycle A) or **A′** (cycle B), which then undergoes migratory insertion with diaryl acetylenes to deliver the alkenyl palladium species **B** (cycle A) or 1,3-dienyl palladium speices **B′** (two migratory insertions, cycle B). Following Heck-type dearomative spiroannulation produces benzylic Pd(II) species **C**, which subsequently participates in the C−H annulation to deliver the palladacycle intermediate **D**. Finally, reductive elimination provides the targeting spirocyclic product **3a** or **4a** and releases the Pd(0) species to complete the catalytic cycle.

Recently, the development of pure hydrocarbon (PHC) host materials has attracted much attention in the field of OLEDs.[11] To evaluate the potential of the spirocyclic scaffolds as PHC host materials, compound **3a** was selected as the prototype molecule for investigation. A preliminary investigation on the photophysical properties of **3a** indicated that the maximum absorption and emission were at 331 and 438 nm in toluene (1.0×10^{-5} M), respectively. The singlet energy (E_{S1}) and triplet energy (E_{T1}) of **3a** were calculated to be 3.31 and 3.08

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eV based on the fluorescence emission and phosphorescence emission spectra, respectively (see the SI, Figure S5a,b and Table S7). The electrochemical property of **3a** was studied by cyclic voltammetry (CV) in CH_2Cl_2 (see the SI, Figure S5c). The HOMO energy was measured to be −5.71 eV, and the LUMO was evaluated to be −2.36 eV based on the values of E_{HOMO} and E_g (see the SI, Table S7 and Figure S6). Thermogravimetric analysis (TGA) showed a high decomposition temperature at 328 °C (5% weight loss, see the SI, Figure S5d). Based on these results, a red phosphorescent organic light-emitting diode (PhOLED) device was fabricated using **3a** as a host material with a device configuration of ITO/HAT-CN (5 nm)/NPB (30 nm)/TCTA (10 nm)/Ir-$(mphmq)_2$(tmd):**3a** (5%, 25 nm)/TmPyPb (50 nm)/LiF (0.8 nm)/Al (100 nm) (Figure 1a,b). As shown in Figure 1c, the emission spectra demonstrated sufficient energy transfer from **3a** to the red emitter. The PhOLED device exhibited a low turn-on voltage (V_{on}) of 2.8 V, and the maximum external quantum efficiency (EQE_{max}) was up to 23.0%, indicating the spiroembedded polycyclic aromatic scaffolds could be potential host materials in the OLED field (Figure 1d,e).

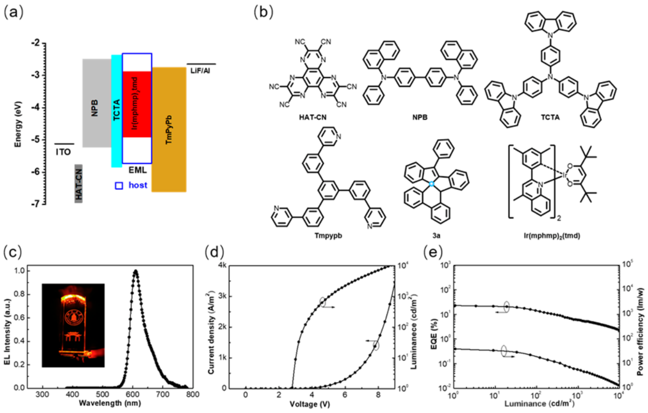

Figure 1. (a) Device structure and energy-level diagram of PhOLED device. (b) Molecular structures used in the device. (c) Electroluminescence spectra at the luminance of 1000 cd/m^2. (d) Luminance and current density versus voltage curves. (e) External quantum efficiency and power efficiency versus luminance curves of the device.

In summary, we have developed a novel palladium-catalyzed cascade dearomative spirocyclization and C−H annulation of aromatic halides with diaryl acetylenes, providing straightforward and efficient access to diverse functionalized spiroembedded polycyclic aromatic compounds. This reaction features a broad substrate scope, excellent functional group tolerance, good chemoselectivities, and scale-up synthesis. Furthermore, as an illustrated example, spirocycle **3a** was successfully used as the pure hydrocarbon host material to fabricate a red phosphorescent light-emitting device with an EQE_{max} of 23.0%, suggesting the potential application of this scaffold in the OLEDs.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.1c01736.

> Detailed experimental procedures, characterization data, copies of ^1H and ^{13}C NMR spectra of final products, and crystallographic data and X-ray crystal structures of **3a** (CCDC-2058445), **3i** (CCDC-2058449), **3v** (CCDC-2082493), and **4h** (CCDC-2058450) (PDF)

Accession Codes

CCDC 2058445, 2058449−2058450, and 2082493 contain 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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