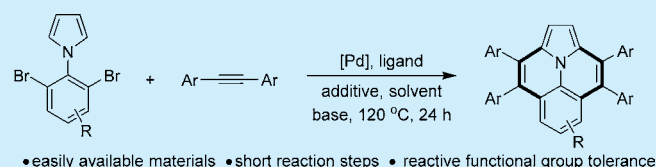


Palladium-Catalyzed Annulation of Internal Alkynes: Direct Access to π -Conjugated UllazinesDanyang Wan,[†] Xiaoyu Li,[†] Ruyong Jiang,[†] Boya Feng,[†] Jingbo Lan,[†] Ruilin Wang,[‡] and Jingsong You^{*,†}[†]Key Laboratory of Green Chemistry and Technology of Ministry of Education, College of Chemistry, and State Key Laboratory of Biotherapy, West China Medical School, Sichuan University, 29 Wangjiang Road, Chengdu 610064, P. R. China[‡]College of Materials Science and Engineering, Sichuan University, 29 Wangjiang Road, Chengdu 610064, P. R. China

S Supporting Information

ABSTRACT: A palladium-catalyzed cyclization reaction of 1-(2,6-dibromophenyl)-1H-pyrroles with alkynes has been developed to construct various π -conjugated indolizino[6,5,4,3-*ija*]quinolones (ullazines) with a reactive functional group tolerance. As illustrative examples, three new ullazine-based sensitizers are synthesized, and the performance of these dyes is examined in DSSC devices, which demonstrates the potential of direct C–H functionalization in the construction of organic optoelectronic materials.



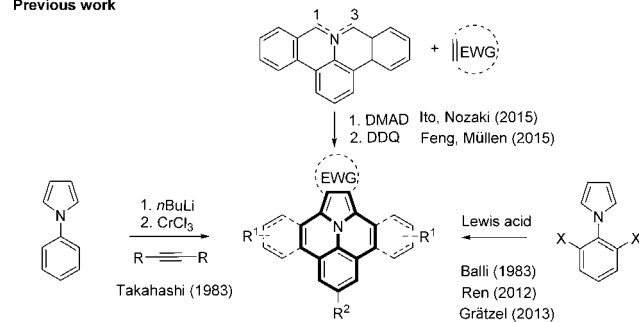
Nitrogen-containing polyaromatic hydrocarbons (PAHs) have been attracting considerable interest owing to their potential applications in high-performance electronic devices such as organic field-effect transistors (OFETs),¹ organic photovoltaics (OPVs),² and organic light-emitting diodes (OLEDs).³ Among these various N-doped π -systems, indolizino[6,5,4,3-*ija*]quinoline (with the trivial name ullazine) (Scheme 1), an isoelectronic compound of pyrene, has received

describing the skeleton synthesis have appeared. The initial route developed by Balli needs a lengthy series of functional group transformations.⁵ Later, Takahashi reported the chromium-mediated annulation reaction to construct this polycyclic system from 1-phenylpyrrole and alkynes to shorten the synthesis steps.⁶ Recently, Grätzel developed an efficient synthesis of ullazine core from easily available starting materials in four steps by utilizing the Fürstner cyclization as the key procedure.^{4a} Almost at the same time, Ren applied the metal-free Friedel–Crafts intramolecular arylation strategy to access the ullazine derivative at room temperature.⁷ Unlike the above-mentioned methods starting from pyrroles, Nozaki⁸ and Müllen⁹ independently employed azomethine ylides and various alkenes or alkynes to synthesize these nitrogen-containing PAHs through 1,3-dipolar cycloaddition reactions. Though these methods are efficient and useful, they might suffer from disadvantages such as tedious synthetic procedures, uneasily available starting materials, and narrow substrate scope, which to a certain extent limit the rapid diversification of ullazines. Thus, the development of more efficient, convenient, and practical methods to construct this skeleton would open a window for screening of ullazine-based electronic materials.

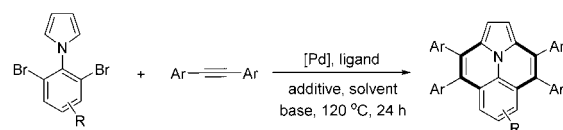
Transition-metal-catalyzed direct C–H functionalization reactions have been significantly developed in recent years, and various types of cyclic compounds have been obtained through catalytic C–H annulations with alkynes.¹⁰ This attractive and powerful strategy has been extensively used in the construction of various PAHs.¹¹ Herein, we describe a novel palladium-catalyzed C–H cyclization of 1-(2,6-dibromophenyl)-1H-pyrroles with alkynes to construct diverse π -conjugated ullazines and elucidate the usefulness of this protocol by applying it in ullazine-based DSSCs.

Scheme 1. Synthesis of Ullazines

Previous work



This work



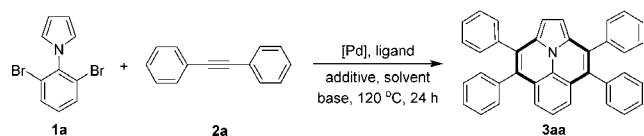
extensive interest in the photovoltaic field for its excellent performance as a strong donating group.⁴ The ullazine core has a planar 16 π -system that can facilitate a strong intramolecular charge transfer (ICT) and modification of multiple substitution sites, which indicate a good potential for more optoelectronic applications. However, facile and versatile methods to ullazines are extremely rare in the literature, and only a few reports

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We initiated our investigation by utilizing 1-(2,6-dibromophenyl)-1*H*-pyrrole (**1a**) and 1,2-diphenylacetylene (**2a**) as model substrates to produce 3,4,8,9-tetraphenylindolizino[6,5,4,3-*ija*]quinoline **3aa** (Table 1). Pleasingly, the expected

Table 1. Optimization of Reaction Conditions^a



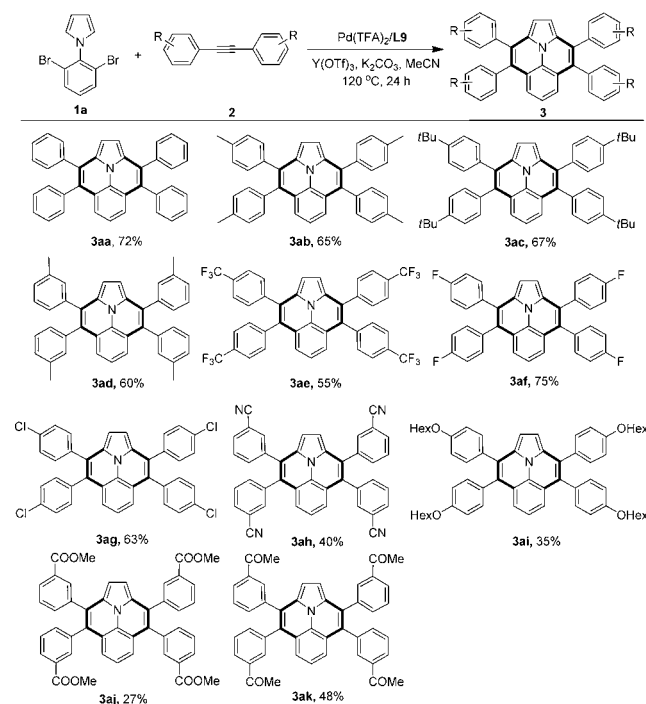
entry	catalyst ^b	additive	base	yield (%)
1 ^{c,d}	PdCl ₂ (PPh ₃) ₂	LiCl	NaOAc	7
2 ^{c,e}	PdCl ₂ (PPh ₃) ₂	LiCl	NaOAc	trace
3 ^{c,d}	PdCl ₂ (PPh ₃) ₂	LiCl	Et ₃ N	trace
4 ^c	PdCl ₂ (PPh ₃) ₂	LiCl	NaOAc	10
5 ^c	PdCl ₂ (PPh ₃) ₂	LiCl	K ₂ CO ₃	10
6 ^c	PdCl ₂ (PPh ₃) ₂	Y(OTf) ₃	K ₂ CO ₃	15
7	PdCl ₂ (PPh ₃) ₂	Y(OTf) ₃	K ₂ CO ₃	27
8	Pd(OAc) ₂ , L1	Y(OTf) ₃	K ₂ CO ₃	trace
9	Pd(OAc) ₂ , L2	Y(OTf) ₃	K ₂ CO ₃	33
10	Pd(OAc) ₂ , L3	Y(OTf) ₃	K ₂ CO ₃	trace
11	Pd(OAc) ₂ , L4	Y(OTf) ₃	K ₂ CO ₃	24
12	Pd(OAc) ₂ , L5	Y(OTf) ₃	K ₂ CO ₃	55
13	Pd(OAc) ₂ , L6	Y(OTf) ₃	K ₂ CO ₃	29
14	Pd(OAc) ₂ , L7	Y(OTf) ₃	K ₂ CO ₃	13
15	Pd(OAc) ₂ , L8	Y(OTf) ₃	K ₂ CO ₃	trace
16	Pd(TFA) ₂ , L5	Y(OTf) ₃	K ₂ CO ₃	70
17	Pd(TFA) ₂ , L9	Y(OTf) ₃	K ₂ CO ₃	72
18	Pd(TFA) ₂ , L9	LiCl	K ₂ CO ₃	20
19 ^f	Pd(TFA) ₂ , L9	Y(OTf) ₃	K ₂ CO ₃	51

^aThe reaction was performed with **1a** (0.25 mmol), **2a** (0.75 mmol, 3.0 equiv), catalyst (0.05 mmol), ligand (0.10 mmol), additive (0.50 mmol), and base (0.75 mmol) in 2.0 mL of MeCN under a N₂ atmosphere. Isolated yield. ^bL1 = 2-(di-*tert*-butylphosphino)biphenyl, L2 = tris(2-methoxyphenyl)phosphine, L3 = butyldi-1-adamantylphosphine, L4 = X-phos, L5 = tricyclohexylphosphine, L6 = 2-(dicyclohexylphosphino)biphenyl, L7 = 1,3-bis(diphenylphosphino)propane, L8 = 1,10-phenanthroline, L9 = tri-*tert*-butylphosphine tetrafluoroborate. ^cPdCl₂(PPh₃)₂ (10 mol %) was used. ^d*N,N*-Dimethylacetamide was used instead of MeCN. ^eToluene was used instead of MeCN. ^fThe reaction temperature was 100 °C.

annulation reaction occurred when 10 mol % of PdCl₂(PPh₃)₂ was used as a catalyst and 3.0 equiv of NaOAc as a base (Table 1, entry 1). The solvent and base parameters were next explored, and the use of MeCN and K₂CO₃ slightly improved the yield (Table 1, entries 2–5). Taking consideration of the vital function of Lewis acid additives in some alkyne-involved annulations,¹² Y(OTf)₃ was added to improve the yield of **3aa** to 15% (Table 1, entry 6). It is well-known that catalyst precursor plays the decisive role in transition-metal-catalyzed coupling reactions of sp²/sp³ C–H bonds with aryl halides.¹³ Thus, a variety of catalysts and ligands were screened, and the best results were obtained when Pd(TFA)₂/L9 was used (Table 1, entries 8–17). In addition, several Lewis acid additives were screened under the optimized conditions, and the results were not superior to Y(OTf)₃ (Table S1).

With the optimized conditions now in hand, we next investigated the substrate scope of this method. As summarized in Scheme 2, various alkynes with both electron-donating and electron-withdrawing groups smoothly underwent the cyclization reaction with **1a**, delivering a series of ullazines in

Scheme 2. Scope of Alkynes^a

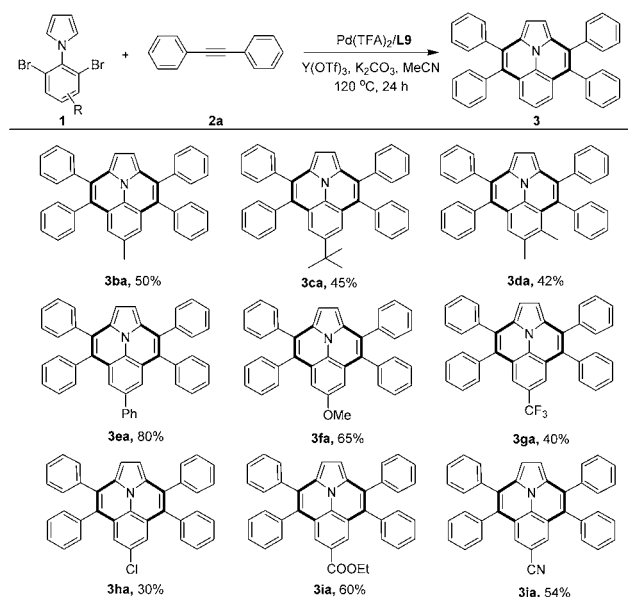


^aReaction conditions: **1a** (0.25 mmol), **2** (0.75 mmol, 3.0 equiv), Pd(TFA)₂ (0.05 mmol), *t*Bu₃P·HBF₄ (0.10 mmol), Y(OTf)₃ (0.50 mmol), and K₂CO₃ (0.75 mmol) were stirred in MeCN (2.0 mL) at 120 °C for 24 h under a N₂ atmosphere.

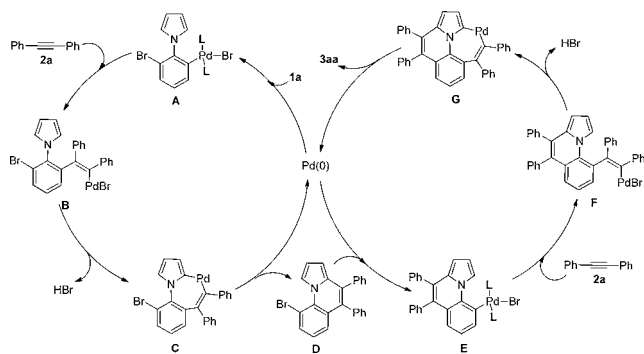
moderate to good yields. *tert*-Butyl, one of the most commonly used groups to improve the solubility of PAHs,¹⁴ could be tolerated in this reaction to afford **3ac** in a 67% yield. In particular, the tolerance of the hexyloxy group will be of great importance to reduce the π – π interaction of ullazines and facilitate the applications in organic semiconductors (Scheme 2, **3ai**).¹⁵ Moreover, some reactive functional groups such as nitrile, ester, and ketone were tolerated in our catalytic system (Scheme 2, **3ah**, **3aj**, and **3ak**). Unfortunately, heteroaryl-containing alkynes such as pyridine and thiophene compounds are not tolerated, and this method is not suitable for synthesizing asymmetrical compounds.

Subsequently, the scope of this annulation reaction was extended to various substituted dibromophenylpyrroles (Scheme 3). It was observed that a variety of functional groups such as alkyl, alkyloxy, trifluoromethyl, chloro, ester, and nitrile were tolerated under the optimized conditions (Scheme 3, **3ca**, **fa**–**ja**). However, the substituent that was installed in the *meta*-position on the arene had a negative effect on this cyclization reaction and slightly reduced the yield (Scheme 3, **3da**). An extended π -conjugated ullazine **3ea** was obtained in a good yield when 1-(3,5-dibromo[1,1'-biphenyl]-4-yl)-1*H*-pyrrole **1e** was utilized as a substrate.

Based on the palladium-catalyzed annulation reaction reported by Larock,¹⁶ a plausible mechanism for this transformation is described in Scheme 4. The reaction starts with an oxidative addition of **1a** with Pd(0) to give the intermediate **A**, which subsequently reacts with alkyne to afford the palladium(II) complex **B**. This vinylic palladium intermediate then undergoes a ring-closing reaction via an electrophilic attack on the C–2 position of pyrrole, forming the monoannulated product **D** after reductive elimination. The further annulation

Scheme 3. Scope of 2,6-Dibromophenylpyrroles^a

Scheme 4. Proposed Catalytic Pathway



of **D** with alkyne through a similar catalytic cycle gives the desired product **3aa**.

Finally, we elucidated the usefulness of the current method by using it for the synthesis of new ullazine-based sensitizers. The concise synthesis of **5a**, **5b**, and **5c** could be performed by the sequential palladium-catalyzed cyclization of dibromophenylpyrrole with alkyne, Vilsmeier–Haak reaction, and Knoevenagel condensation with cyanoacetic acid or rhodanine-3-acetic acid (Scheme 5).

The absorption spectra of ullazine-based dyes **5a–c** in CH₂Cl₂ solution and on TiO₂ film are displayed in Figure 1. Both **5a** and **5b** have a strong absorbance in the range of 400–550 nm, while the absorption band of **5c** is distinctly red-shifted by >50 nm, indicating an enhanced capacity of light-harvesting. Subsequently, the ground-state oxidation potential ($E_{1/2}^{\text{ox}}$) and HOMO–LUMO transition energy value (E_{0-0}) of each dye were estimated from cyclic voltammetry (CV) and absorption/emission spectra (Table S2 and Figure S1). The $E_{1/2}^{\text{ox}}$ values range from 0.86–0.96 V vs NHE, which are more positive than that of the iodide/triiodide redox shuttle, and the $E_{1/2}^{\text{ox}}$ values were calculated to be –1.17 to –1.48 V vs NHE, ensuring the

Scheme 5. Synthesis of Ullazine-Based Sensitizers

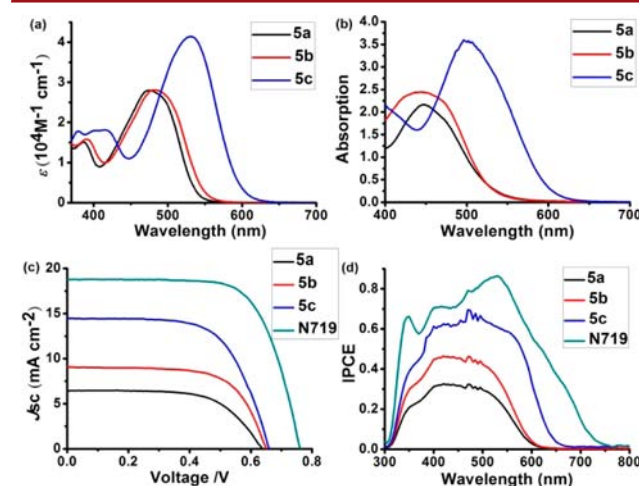
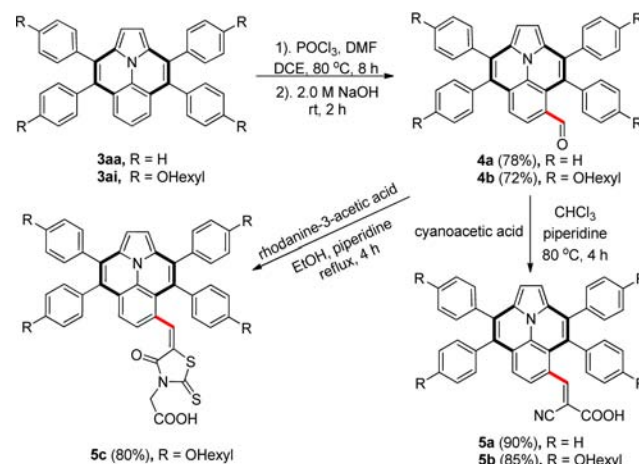


Figure 1. Absorption spectra of **5a–c** (a) in CH₂Cl₂ solution (1.0×10^{-5} M) and (b) on TiO₂ film; (c) photocurrent–voltage (*J*–*V*) plots obtained with **5a–c** and N719 under simulated AM 1.5G irradiation (100 mW/cm²); (d) incident photon-to-current efficiency (IPCE) curves of the DSSCs based on **5a–c** and N719.

transmission of an electron from the excited dye to the TiO₂ conduction band.¹⁷

The performance of these ullazine-based dyes was then examined in DSSC devices under simulated AM 1.5G irradiation (Figure 1). As shown in Table S3, the cell based on **5a** exhibits the lowest conversion efficiency (η) of 2.6% ($J_{\text{sc}} = 6.45 \text{ mA cm}^{-2}$, $V_{\text{oc}} = 0.635 \text{ V}$, and FF = 0.633), perhaps due to a low solubility. Thus, we added four alkoxy chains to **5a**, and the η value of **5b**-based DSSC was increased to 3.9% ($J_{\text{sc}} = 9.06 \text{ mA cm}^{-2}$, $V_{\text{oc}} = 0.649 \text{ V}$, and FF = 0.663). When the anchoring group was changed to give **5c** as a sensitizer, the highest power conversion efficiency ($\eta = 6.1\%$, $J_{\text{sc}} = 9.06 \text{ mA cm}^{-2}$, $V_{\text{oc}} = 0.649 \text{ V}$, and FF = 0.663) was obtained, and the incident photon-to-electron conversion efficiency (IPCE) of **5c**-based DSSC device shows a broad band in the region of 300–600 nm with a maximum of 70% at 471 nm (Figure 1).

In conclusion, we have developed a facile and efficient method to construct various π -conjugated ullazines via the palladium-catalyzed direct C–H cyclization of dibromophenylpyrroles with alkynes. This method is compatible with various electron-donating groups and electron-withdrawing groups such as alkyloxy, chloro, ester and nitrile, which could be

used in further synthetic transformations. The usefulness of this protocol is elucidated by the concise synthesis of three new ullazine-based sensitizers. A power conversion efficiency (PCE) of 6.1% is obtained under simulated AM 1.5G irradiation, which demonstrates that the protocol developed herein would provide an opportunity to assemble various ullazines rapidly that could be used in organic optoelectronic materials. Other applications of this method are currently underway in our laboratory.

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acs-orglett.6b01182](https://doi.org/10.1021/acs.orglett.6b01182).

Detailed experimental procedures, characterization data, and copies of ^1H and ^{13}C NMR spectra of key intermediates and final products (PDF)

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Notes

The authors declare no competing financial interest.

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