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Letter

Two-in-One Strategy for the Pd(II)-Catalyzed Tandem C–H Arylation/Decarboxylative Annulation Involved with Cyclic Diaryliodonium Salts

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Supporting Information

ABSTRACT: We report here a two-in-one strategy for the Pd(II)-catalyzed tandem C-H arylation/decarboxylative annulation between readily available cyclic diaryliodonium salts and benzoic acids. The carboxylic acid functionality can be used as both a directing group for the *ortho*-C-H arylation and the reactive group for the tandem decarboxylative annulation. By a step-economical double cross-coupling



annulation procedure, the privileged triphenylene frameworks were efficiently constructed, which have potential applications in material chemistry.

The regioselective functionalization of aromatic C–H bonds using directing groups (DGs) has become a prevalent strategy for the construction of new bonds in arenes.¹ Nitrogen-containing heterocycles, amines, alcohols, carbonyl-related groups, and so on have been employed as DGs for the transition-metal (TM)-catalyzed direct C–H functionalization. These DGs could be divided into the following four categories (Scheme 1): (a) The DGs are usually hard to remove and thus





remain in product 2 after the arene C–H bond functionalization of substrate 1.² (b) The DG could be easily removed or further modified to give 3 via intermediate 2.³ (c) The traceless DGs were removed in one pot to give product 4 via the functionalized product 5.⁴ (d) The new transient DGs in 6 were formed by adding a catalytic amount of external reagents and reacting with functional groups (FGs) in substrate 1 (here FG = DG), which can be reversibly removed in situ after the C–H bond functionalization to give 2.⁵ Although the above strategies have been successfully employed for the arene C–H bond functionalization at a specific site within a molecule, a more atom- and step-economical "two-in-one" strategy is of high demand, in which the DG can be employed as both a directing and a reactive group to give 3 in a one-pot cascade reaction. 6

The aromatic carboxylic acids have been frequently employed for TM-catalyzed reactions because of their ready availability and chemical structure diversity. Previous research has well demonstrated that the acid functionality can be employed as a reactive group for ipso-decarboxylative crosscoupling reactions;⁸ also, it can be used as a removable or traceless DG for *ortho*-arene C-H functionalization.⁹ Although a few classes of transformations by employing the carboxylic acids as traceless DGs have been explored to date,¹⁰ only a small range of substrates such as benzoic acid 7a are effective, plus the carboxylic acid DGs were simply removed in situ or by additional steps via protodecarboxylation from 8 to give 9^{11} and had not been used as reactive groups for further decaboxylative cross-coupling reactions (Scheme 2a). Recently, by a decarboxylative annulation strategy, we reported the synthesis of triphenylenes¹² and dibnzo[f_ih]quinolines 12_1^{13} which are known as privileged structures for organic light-emitting diode (OLED) materials.¹⁴ However, the prefunctionalized ortho-halogenated (hetero)aromatic carboxylic acid 10 is required (Scheme 2b).

In continuation of our research interest¹⁵ in novel arylation chemistry involved with diaryliodonium salts,^{16–19} we envisioned that the valuable triphenylene skeleton 13 might be constructed in an atom- and step-economical one-pot reaction via a "two-in-one" strategy with simple substrates 7 and 11 as the starting materials (Scheme 2c), in which the acids can be employed as both DGs for the palladiumcatalyzed *ortho*-arene C–H arylation and reactive groups for

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Scheme 2. Acid-Directed Arene ortho-Arylation Chemistry



the tandem *ipso*-decarboxylative cyclization. The challenges for this highly efficient cascade protocol are how to avoid the side reactions, such as the protodecarboxylation,¹¹ and how to make the consecutive series of reactions proceed smoothly.

We started the condition optimizations by reacting acid 7a with hypervalent iodine reagent 11a (Table 1). With the

Table 1. Optimization of the Reaction Conditions^a

CO ₂ H • 7a	OTf 11a (2 eq.)	cat.(10 mmol base (2.0 eq. solvent (2 mL),	%)) 145°C, 16 h	13aa
entry	cat.	base	solvent	yield (%) ^b
1	CuI	K ₂ CO ₃	DMF	0
2	RuCl ₃	K_2CO_3	DMF	trace
3	PdCl ₂	K_2CO_3	DMF	15
4	$Pd(OAc)_2$	K ₂ CO ₃	DMF	30
5	$Pd(OAc)_2$	Na_2CO_3	DMF	46
6	$Pd(OAc)_2$	Cs ₂ CO ₃	DMF	13
7	$Pd(OAc)_2$	KO ^t Bu	DMF	43
8	$Pd(OAc)_2$	K ₃ PO ₄	DMF	55
9	$Pd(OAc)_2$	K ₃ PO ₄	DMSO	36
10	$Pd(OAc)_2$	K ₃ PO ₄	DMAc	44
11	$Pd(OAc)_2$	K ₃ PO ₄	NMP	23
12 ^c	$Pd(OAc)_2$	K ₃ PO ₄	DMF	67
13 ^c	$Pd(OAc)_2$	K ₃ PO ₄	DMF ^d	81

^{*a*}Optimized reaction conditions: 7a (0.4 mmol), 11a (0.2 mmol), Pd(OAc)₂ (10 mol %), K_3PO_4 (0.4 mmol), DMF (4 mL), 145 °C, 16 h. ^{*b*}Isolated yields. ^{*c*}7a (2 equiv). ^{*d*}DMF (4 mL).

benzoic acid as the limiting reagent, the TM catalysts were initially screened (see the SI), and it was found that the Pd(OAc)₂ was the optimum catalyst with potassium carbonate in dimethylformamide (DMF) (2 mL) at 145 °C (Table 1, entries 1–4). The bases were then screened, and the reaction with K₃PO₄ as the base gave the highest 55% yield (Table 1, entries 5–8). There was no improvement in yield when other solvents were screened (Table 1, entries 9–11) or the additional ligand was added (see the SI). The yields were dropped by decreasing the reaction temperature or the amount of catalyst (see the SI). To our delight, the yield was increased to 67% when an excess of benzoic acid 7a (2 equiv) was used (Table 1, entry 12), and the yield was further improved to 81% when the reaction was conducted in a more diluted solution (Table 1, entry 13). The reactions were negative in the absence of either base or catalyst (see the SI). Finally, a 10 mmol scale reaction was carried out, and triphenylene **13aa** was obtained in 72% yield (1.64 g; see the SI).

With the optimal conditions in hand, various commercially available carboxylic acids were first examined (Scheme 3). In

Scheme 3. Substrate Scope of Carboxylic Acids



general, the carboxylic acids with alkyl (13ab and 13ak), strong electron-donating (13ac, 13ad, 13ao, and 13ap) or -withdrawing (13ag-aj) substituents, or halogen (13ae and 13af) all gave moderate to good yields. It is worth mentioning that various FGs such as phenolic hydroxyl (13ac), halogen (13ae and 13af), formyl (13ah), cyano (13ai), nitro (13aj), and so on were untouched under the optimized reaction conditions. The reaction went smoothly when there was an electronic-donating substituent on the ortho position of the acid functionality (13ak and 13am). However, with 2nitrobenzoic acid as the substrate, the yield was poor, probably because the side reaction of protodecarboxylation happened. A mixture of products (13an and 13an') was obtained in 79% yield with 2-naphthoic acid as the substrate. Pleasingly, the heteroaromatic carboxylic acids were also effective and gave the corresponding products in good yield (13aq-at).

To further test the substrate scopes of this cascade one-pot annulation process, various cyclic diaryliodoniums with different substituents were prepared and treated under the optimized conditions (Scheme 4).²⁰ The symmetric hypervalent reagents (13ba-be) were examined first, and all gave the desired products in moderate yield, respectively. Next, various unsymmetric diaryliodoniums were tested, and the reactions gave the corresponding products in moderate to good yield (13ak-bj). Halogen-containing groups such as F, Cl, and CF₃ (13ba-be, 13bf, and 13bg), nitro (13al), and ester (13bj) on cyclic diaryliodonium salts were untouched under the optimized conditions.

To demonstrate the utility of these triphenylene products, a triphenylene-based electron-transport material (ETM) **16**, with high electron affinity and a coplanar structure, was

Scheme 4. Substrate Scope of Cyclic Diaryliodoniums



prepared efficiently from 13bc by Suzuki–Miyaura coupling reactions (Scheme 5). Previously, it took five steps to prepare compound 16, and it has been used in OLEDs and showed better performance than conventional ETMs.²¹

Scheme 5. Synthesis of Triphenylene-Based Electron-Transport Material



To further understand this novel method, the following experiments were conducted (Scheme 6). First, under the optimized conditions, there is no reaction with methyl benzoate 17 as the substrate, which demonstrates the vital importance of carboxylic acid functionality (Scheme 6, eq 1). The electronic effect of the substituents on the acids was then examined (Scheme 6, eq 2). The product 13ad was obtained as the major product when a mixture of 7d, 7j, and 11a was treated under the optimized reaction conditions, which indicated that the electron-rich acid reacted much faster. With *ortho*-chloro benzoic acid 7u as the substrate, a mixture of triphenylene products 13au with chlorine and 13aa without chlorine was obtained in 54% yield, which formed from ortho C-H arylation/decarboxylative annulation and dechlorinative arylation/decarboxylative annulation respectively (Scheme 6, eq 3).

We further carried out the following experiments to better understand the reaction mechanism. First, we prepared the *ortho*-phenyl benzoic acid 18 and treated it with cyclic diaryliodonium salt 11a under the optimized conditions. The

Scheme 6. Mechanistic Experiments



triphenylene products 19a and 19b were obtained in moderate yield which were formed via ortho-C-H_a activation. The other product 20 formed via bay-C-H_b activation was not detected (Scheme 6, eq 4). There was no triphenylene product 13aa formed when 7a was treated under the optimized reaction conditions alone in the absence of cyclic diaryliodonium salt 11a. Furthermore, by reacting 7a with 2-methylfuran, no cyclized product 21 was obtained (Scheme 6, eq 5), which showed that a benzyne intermediate did not form in this cyclization reaction.²² The reaction still went smoothly with the addition of TEMPO, which indicated that a radical mechanism might not involve (Scheme 6, eq 6). An intermolecular competition experiment with equimolar amounts of 7a and $[D_5]$ -7a was then conducted (Scheme 6, eq 7), and the reaction gave a crude mixture of $13bh/[D_4]$ -13bh with a ratio of 2:1 by ¹H NMR analysis. Meanwhile, two parallel reactions of 7a and $[D_5]$ -7a under the optimum

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conditions were conducted (Scheme 6, eq 8). The reaction rates of 7a and $[D_5]$ -7a provided a kinetic isotope effect (KIE) of only $k_H/k_D \approx 1.3$. These results indicated that the cleavage of the C–H bond was not involved in the rate-determining step. The difference between these two KIE values suggests that the rate-determining step might happen before the cleavage of the C–H bond, and the electrophilic metalation is probably involved in the rate-determining step.

On the basis of the above experiments, this cascade one-pot protocol might involve an acid-directed *ortho*-C-H arylation/ intramolecular decarboxylative annulation sequence (Scheme 7). First, a five-membered Pd(II) complex I may be generated

Scheme 7. Possible Reaction Pathways



from the benzoic acid 7a, which then attacks 11a to afford the Pd(IV) intermediate II. Reductive elimination and then decarboxylation would afford the iodide IV, which could give the seven-membered Pd(IV) complex V by oxidative addition to the C–I bond. Finally, a reductive elimination would release the desired product 13aa to complete the catalytic cycle. Alternatively, a Pd(II)–(III) catalytic cycle might be involved with the bimetallic Pd(III) species VI.²³

In summary, a one-pot protocol for the construction of privileged triphenylene core was developed with commercially available (hetero)aromatic carboxylic acids and readily available cyclic diaryliodonium salts as the starting materials. Various functionalized triphenylenes were efficiently prepared which could be further transformed into an ETM, and different FGs were tolerated under the Pd-catalyzed ligand-free conditions. The key is the development of a two-in-one strategy by which the acid functionalities were employed as both the DGs for the Pd-catalyzed ortho-C-H arylation and the reactive groups for the cascade intramolecular decarboxylative annulation, which was supported by the mechanistic studies. This simple and novel method would allow easy access to fused polyaromatics of interest in optoelectronics research,²⁴ and the further applications of this method for the preparation of small graphene nanoribbons are ongoing in our lab.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.or-glett.9b02429.

Experimental procedures and spectroscopic characterization data (PDF)

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Notes

The authors declare no competing financial interest.

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