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PII: DOI: Reference:	S0040-4039(18)31399-6 https://doi.org/10.1016/j.tetlet.2018.11.052 TETL 50437
To appear in:	Tetrahedron Letters
Received Date:	24 October 2018
Revised Date:	17 November 2018
Accepted Date:	20 November 2018



Please cite this article as: Tu, J., Li, G., Zhao, X., Xu, F., Synthesis of triphenylene derivatives by Pd-catalyzed Suzuki coupling/intramolecular C-H activation between arylboronic acids and dibromobiphenyls, *Tetrahedron Letters* (2018), doi: https://doi.org/10.1016/j.tetlet.2018.11.052

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Tetrahedron Letters journal homepage: www.elsevier.com

Synthesis of triphenylene derivatives by Pd-catalyzed Suzuki coupling/intramolecular C-H activation between arylboronic acids and dibromobiphenyls

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ARTICLE INFO

ABSTRACT

Article history: Received Received in revised form Accepted Available online

Keywords: Annulation Cascade reaction Palladium Boron Polycyclic aromatic hydrocarbons

Introduction

As the result of the advances in organic electronics such as light emitters, semiconductors, liquid crystals, and solar cells, polycyclic aromatic hydrocarbons(PAHs) has been regarded as one of the most important groups of compounds in the field of material science due to their superior optical, electronic and selfassembling properties.1 Hence, efficient synthetic methods for producing functionalized PAHs are undoubtly valuable to accelerate the developments of PAHs-based functional materials. Triphenylenes are the most often synthesized and widely studied due to their unique electronic, biological and liquid crystal properties^{2,3} as well as the applications for organic light-emitting diodes.⁴ However, it is still a great challenge for the construction of triphenylene nucleus because the carbon-carbon bonds used for fusion of the phenyl ring can only be constructed one by one.⁵ In 1998, Guitián and co-workers firstly reported a Pd-catalyzed cyclotrimerization of arynes to produce triphenylenes.⁶ Since then, a variety of triphenylene derivatives were prepared with the similar strategy using o-trimethylsilylaryl triflates as aryne precursors.⁷⁻⁸ The drawbacks such as the high price of otrimethylsilylaryl triflates and the only successful synthesis of symmetrical triphenylenes somehow hinder its more application. In 2006, Larock et al reported a Pd-catalyzed annulation of arynes with 2-halobiaryls, which can be utilized to prepare unsymmetrical triphenylenes.9 Kim et al found a Pd-mediated generation of aryne from methyl 2-bromobenzoates, which underwent a Pd-mediated [2+2+2] cycloaddition to give

An efficient and regioselective synthesis of functionalized triphenylenes via palladium-catalyzed Suzuki-Miyaura coupling and subsequent intramolecular C-H activation between arylboronic acids and dibromobiphenyls was developed. This methodology showed excellent atomic economy and regiospecificity as well as synthetic feasibility of unsymmetrical triphenylenes.

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triphenylenes.¹⁰ Greaney et al developed the synthesis of triphenylenes via Pd-catalyzed [2+2+2] trimerisation of benzyne using cheap benzoic acid¹¹ as well as 2-bromophenylboronic esters¹² as benzyne precursors. Besides these excellent aryne approaches, other important protocols were also developed for triphenylene synthesis in recent years. For example, Miura and co-workers found that o-dibromobenzenes could undergo Pdmediated decarbonylative cross-coupling with o-phenyl benzyl alcohols to prepare triphenylenes.¹³ The Nishihara group disclosed a palladium-catalyzed cascade reaction of oiodobiphenyls with o-bromobenzyl alcohols to form triphenylene.¹⁴ Zhang and co-workers reported the palladiumcatalyzed annulations of 2-iodobiphenyls and iodobenzenes to access functionalized triphenylenes.15 Diaryliodonium salts were also available to react with o-halobenzoic acids or bromoarenes to construct triphenylenes.¹⁶ Moreover, photochemical methods were also developed to generate triphenylene backbones in very high yields.¹⁷ Although these methods significantly expanded the substrate scope for triphenylenes synthesis, to lack regioselectivity and the formation of a mixture of regioisomers were the major problem especially for the generation of highly functionalized triphenylenes including unsymmetrical ones, which generally play especially important roles in material science.

Recently, the transition-metal catalyzed cross-coupling reactions of organometals with organic halides provided an efficient access to regio- and stereospecific C-C bonds

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formation.¹⁸ And thus, the step-wise double cross-coupling reactions of organodimetallic reagents and dihalides afforded a straightforward and efficient method for highly functionalized triphenylenes synthesis. King et al reported the uncatalyzed reaction of [Zr(2,2'-biphenyldiyl)₃][Li·(THF)₄]₂, as an equivalent of 1,4-dimetal reagent with o-dihalobenzenes to form triphenylenes in 2006.19d Shimizu et al developed the double cross-coupling of 9-stannafluorenes, a 1,4-dimetal equivalent, with o-dibromoarene for triphenylene synthesis.^{20c} In 2011, Shimizu reported a palladium-catalyzed double cross-coupling reaction of 1,2-dimetal reagent, o-diborylbenzene with 2,2'dibromobiphenyl to synthesize triphenylene.^{21d} Nevertheless, either 1,4-dimetal reagents or 1,2-dimetal reagents were generally prepared from the corresponding dihalogenated compounds and up to date only limited these reagents and their equivalents such as diboryl reagent,²¹ distannyl reagent,20 reagent,22 platinacycles,23 zirconacycles,19 dilithium nickelacycles²⁴ were developed and successfully applied in transition-metal catalyzed annulation reactions. Considering the wider availability and cheaper price of mono-metallic reagents, to develop an efficient annulation process to prepare PAHs such as triphenylene derivatives using mono-metal reagents instead of dimetal reagents will undoubtly be more atom-economic and appealing.

For this consideration, we designed the annulations between



Scheme1. Design of synthesis of triphenylene via Suzuki-Heck type cascade.

arylboronic acids and 2,2'-dibromobiphenyls to construct the triphenylene backbone (Scheme 1). In the reaction, the arylboronic acid 1 firstly underwent Suzuki-Miyaura cross-coupling reaction with dibromobiphenyl 2a and gave an intermediate I with a remaining C_{Ar} -Br bond. The intermediate I subsequently formed an intermediate II via oxidative addition with Pd⁰ catalyst. Consequently, an intramolecular C-H activation and reductive elimination process finally generated the triphenylene 3.

Result and discussion

An initial attempt to construct triphenylene backbone was performed from 4-nitrophenylboronic acid and 2,2'-dibromobiphenyl **2a** using Pd(OAc)₂, PPh₃, and Cs₂CO₃ in toluene at reflux. Gratifyingly, 2-nitrotriphenylene was successfully isolated in 18% yield (Table 1, entry 1). For PAHs synthesis, high reaction temperature was generally favorable to the cyclization. Nevertheless, only trace product was monitored in this cascade process when DMF was utilized as solvent at reflux (Table 1, entry 2).

The effects of THF and 1,4-dioxane as solvents were also investigated and the yield was improved to 33% in 1,4-dioxane at reflux (Table 1, entry 4). The screening of bases (Table 1, entries 5-

8) revealed that strong inorganic base (KOH, entry 5) and organic base

(DABCO, 1,4-Diazabicyclo[2.2.2]octane, entry 6) were ineffective in this transformation.

 Table 1. Optimization of the reaction conditions^a

	B(OH) ₂ Br				
	- +	[Pd], [L] 	▸└╱		
	O ₂ N	Br Base,Reflux			
	1a 2a		N 3a	0 ₂	
Entry	[Pd]	[L]	Base	$\text{Yield}(\%)^b$	
1^c	Pd(OAc) ₂	PPh ₃	Cs_2CO_3	18	
2^d	Pd(OAc) ₂	PPh ₃	Cs_2CO_3	Trace	
3 ^e	Pd(OAc) ₂	PPh ₃	Cs_2CO_3	16	
4	Pd(OAc) ₂	PPh ₃	Cs_2CO_3	33	
5	Pd(OAc) ₂	PPh ₃	KOH	Trace	
6	Pd(OAc) ₂	PPh ₃	DABCO	n.r.	
7	Pd(OAc) ₂	PPh ₃	K_2CO_3	22	
8	Pd(OAc) ₂	PPh ₃	K_3PO_4	17	
9	Pd(PPh ₃) ₄	PPh ₃	Cs_2CO_3	17	
10	Pd ₂ (dba) ₃	PPh ₃	Cs_2CO_3	14	
11	PdCl ₂	PPh ₃	Cs_2CO_3	Trace	
12	$Pd(PPh_3)_2Cl_2$	PPh ₃	Cs_2CO_3	30	
13	$Pd(PhCN)_2Cl_2$	PPh ₃	Cs_2CO_3	18	
14	$Pd(PCy_3)_2Cl_2$	PPh ₃	Cs_2CO_3	40	
15	$Pd(PCy_3)_2Cl_2$	PCy ₃	Cs_2CO_3	32	
16	$Pd(PCy_3)_2Cl_2$	X-phos ^f	Cs_2CO_3	21	
17	$Pd(PCy_3)_2Cl_2$	Xantphos ^g	Cs_2CO_3	Trace	
18	$Pd(PCy_3)_2Cl_2$	S-phos ^h	Cs_2CO_3	58	
19	$Pd(PCy_3)_2Cl_2$	P(4-MeOPh) ₃	Cs_2CO_3	75	
20	$Pd[P(4\text{-}MeOPh)_3]_2Cl_2$	P(4-MeOPh) ₃	Cs_2CO_3	35	
21 ⁱ	$Pd(PCy_3)_2Cl_2$	P(4-MeOPh) ₃	Cs_2CO_3	84	

^a Reaction conditions: **1a** (0.6 mmol), **2a** (0.5 mmol), [Pd] (5 mol%), Ligand (5.5 mol%), Base (3.0 equiv.), Solvent (5.0 mL), 24h. ^b Isolated yield. ^c Using toluene as solvent. ^d Using DMF as solvent. ^e Using THF as solvent. ^f X-phos: 2-(dicyclohexyl-phosphino)-2',4',6'-triisopropyl-1,1'biphenyl. ^g Xantphos: 9,9-dimethyl-4,5-bis(diphenylphosphi-no)xanthene. ^h S-phos: 2-dicyclohexylphos-phino-2',6'-dimethoxy-1,1'biphenyl. ⁱ [Pd] (10 mol%), Ligand (11 mol%).

Further examination of various palladium species and phosphine ligands was then carried out. Pd⁰ catalysts such as Pd(PPh₃)₄ and Pd₂(dba)₃ showed lower catalytic ability than Pd(OAc)₂ in this cascade process (entries 9 and 10). The performance of other Pd^{II} catalysts such as $PdCl_2$, $Pd(PPh_3)_2Cl_2$, $Pd(PhCN)_2Cl_2$, and Pd(PCy₃)₂Cl₂ were next evaluated (entries 11-14). Pd(PCy₃)₂Cl₂ showed the best catalytic ability and the yield of 2-nitrotriphenylene was increased to 40% (entry 14). Further screening of the phosphine ligands revealed that PCy₃ and X-Phos exhibited lower efficiency and Xantphos was completely ineffective. S-phos showed positive activity and the yield was increased to 58% (entry 18). The P(4-MeOPh)3 was the best ligand in this transformation, finally improving the yield to 75%. And thus, Pd[P(4-MeOPh)₃]₂Cl₂ was next selected to perform the transformation. A sharply decreased yield of 3a was observed (entry 20), which indicated the role of each phosphine in the catalytic cycle was completely different and the details were unclear. By further increasing the amounts of

 $Pd(PCy_3)_2Cl_2$ and $P(4-MeOPh)_3$ into 10 mol% and 11 mol% respectively, the isolated yield of desired 2-nitrotriphenylene was finally enhanced to 84% (entry 21).

With the optimal reaction conditions in hand, we next investigated the substrate scope of the cascade annulation process (Table 2).

Table 2. Synthesis of triphenylenes^{*a*,*b*}



^a Reaction conditions: **1** (0.6mmol), **2** (0.5mmol), $Pd(PCy_3)_2Cl_2$ (10 mol%), P(4-MeOPh)₃ (11 mol%), Cs₂CO₃ (3.0 equiv.), 1,4-dioxane (5 mL). ^b Isolated yield. ^c 2.0 equiv. aryboronic acids were used.

Phenylboronic acids with a para-substitutent such as methyl(1b), fluoro(1f), chloro(1g), cyano(1h), CF₃(1i) and ester(1l and 1m) all smoothly performed the cascade cyclization with 2.2'dibromobiphenyl 2a to produce the functionalized unsymmetric triphenylenes in moderate to high yields. Phenylboronic acids with electron-withdrawing groups were more reactive and gave higher yields. Meaningfully, the halo substituents such as fluoro (3f and 3j) and chloro (3g and 3k) on the benzene ring were well tolerated. The triphenylenes containing halo atoms are very useful for they can be easily further derivatized by means of simple coupling strategies and the likes. The 1-naphthylboronic acid (1d) and 2-biphenylboronic acid (1e) also effectively underwent the cascade coupling reactions with 2,2'-dibromobiphenyl 2a to afford sterically hindered triphenylenes. Moreover, no isomers of 1,8-cyclized product of 1napthylboronic acid and 2,2'-cyclized product of 2-biphenylboronic acid were observed, which indicated that these two transformations showed excellent regioselectivity. Sterically demanding orthosubstituted phenylboronic acids (1b' and 1e) were also well tolerated in this procedure. Although sterically hindered 2-methylboronic acid performed the annualtion with 2,2'-dibromobiphenyl **2a** affording the desired product **3b'** in 31% yield, the yield was successfully improved to 52% when 2 equivaluents of 2-methylphenylboronic acid were used. The substituted dibromobiphenyl, 4,4,5,5-tetramethyl-2,2'-dibromobiphenyl **2b** also exhibited good reactivity and smoothly conducted the annulations with arylboronic acids to generate the corresponding triphenylenes (**3n-3s**).

The dibenzochrysene (DBC) is a twisted polycyclic aromatic



Scheme2. Preparation of dibenzochrysene.

hydrocarbon. Its derivatives can be applied to the preparation of sensors, nonlinear optical and liquid-crystalline materials, etc. The preparation of parent dibenzochrysene and its derivatives generally requires multistep syntheses.²⁵ In our previous work, we reported a highly efficient approach to 9,10-diaryl substituted phenanthrenes, which could be converted to dibenzochrysenes via the Scholl reaction using CuCl₂ and AlCl₃ as an oxidant.²⁶ With present developed methodology, when 9-phenanthrylboronic acid was directly utilized to react with 2,2'-dibromobiphenyls, one-step synthesis of dibenzochrysenes was realized (Scheme 2). Furthermore, this transformation showed high regioselectivity, only 9,10-cylized product was found and no 1,9-cyclized product was observed.

To further investigate the regioselectivity of this cyclization

Table 3. Synthesis of triphenylenes with meta-substitutedarylboronic $acid^a$

R R	B(OH) ₂ + Br	Pd(PCy ₃) ₂ Cl ₂ , P(4-OMePh) ₃ Cs ₂ CO ₃ , 1,4-dioxane,100°C	
	Za		3 3'
Entry	1 (R)	Time(h)	Yield ^b
1	1u (NO ₂)	24	57%(3a')
2	1v (CH ₃)	36	37%(3b+3b' ;1:1.4)
3	1w (F)	24	38%(3f')
4	1x (Cl)	24	41%(3g')
5	1y (CF ₃)	24	32%(3i+3i' ;1:1.1)

^a Reaction conditions: **1** (0.6mmol), **2** (0.5mmol), Pd(PCy₃)₂Cl₂ (10 mol%), P(4-MeOPh)₃ (11 mol%), Cs₂CO₃ (3.0 equiv.), 1,4-dioxane (5 mL). ^b Isolated yield. ^c 2.0 equiv. aryboronic acids were used.

strategy, arylboronic acids with a *meta*-substituent were then tested to perform the cascade cyclization with 2,2'-dibromobiphenyl **2a** (Table 3). For *meta*-substituted arylboronic acids, there generally might produce two regioisomeric mixtures, triphenylene **3** and triphenylene **3'**. To our surprise, arylboronic acids with *meta*substitutents such as nitro(**1u**), fluoro(**1w**) and chloro(**1x**) showed excellent regiospecificity. Only sterically more hindered triphenylenes **3'** cyclized between C1 and C2 of arylboronic acids were produced and no cyclized triphenylenes **3** between C1 and C6 of arylboronic acids were found, which indicated that the steric effect was not the major factor to determine the regioselectivity. When 3methylphenylboronic acid **1v** and 3-trifluoromethylphenylboronic 4

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acid **1y** were used to react with 2,2'-dibromobiphenyl **2a** respectively, a regioisomeric mixture was generated. 1,6-Cyclized triphenylene and 1,2-cyclized triphenylene were produced and could not be isolated by silica chromatography since they own completely same retention factor value. The ¹HNMR analysis showed the ratio of **3b** to **3b'** was 1:1.4 and the ratio of **3i** to **3i'** was 1:1.1. The reason for such regioselectivity was unknown.

Conlusions

In conclusion, we have developed a highly efficient palladiumcatalyzed cascade annulations from 2,2'-dibromobiphenyls and arylboronic acids for the synthesis of various functionalized triphenylenes. This is the first case that mono-metallic reagents were used to prepare triphenylenes. Compared with the previous double couplings of dimetallic reagents with dihaloarenes, this methodology showed very excellent atomic economy and reduction of synthesis cost. Compared with the conventional cyclotrimerization of arynes, the present strategy showed high regioselectivity and the synthetic feasibility of unsymmetrical triphenylenes. For some metasubstituted arylboronic acids, this cyclization process showed excellent regiospecificity. This methodology also provides a highly efficient and low-cost approach to dibenzochrysene derivatives starting from simple, commercially available reactants in one step. Further studies on the application of the present annualtion strategy for the preparation of other functional material are in progress.

Acknowledgments

We are grateful for the financial support from the National Natural Science Foundation of China (21302117 and 21572123), the Natural Science Foundation of Shaanxi Province (2018JM2049) and Fundamental Research Funds for the Central Universities (GK201603047 and GK201601003).

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Highlights

- mono-metallic reagents were firstly used to prepare triphenylenes
- excellent atomic economy and regioselectivity
- the synthetic feasibility of unsymmetrical triphenylenes.
- an efficient and low-cost approach to dibenzochrysene derivatives

Graphical Abstract

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