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Synthesis of Triphenylenes Starting from 2-Iodobiphenyls and Iodobenzenes via Palladium-Catalyzed Dual C–H Activation and Double C–C Bond Formation

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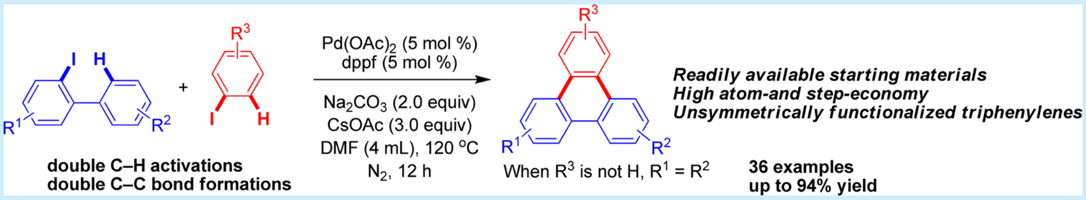
Supporting Information



ABSTRACT: A novel and facile approach for the synthesis of triphenylenes has been developed via palladium-catalyzed coupling of 2-iodobiphenyls and iodobenzenes. The reaction involves dual palladium-catalyzed C–H activations and double palladium-catalyzed C–C bond formations. A range of unsymmetrically functionalized triphenylenes can be synthesized with the reaction. The approach features readily available starting materials, high atom- and step-economy, and access to various unsymmetrically functionalized triphenylenes.

Polycyclic aromatic hydrocarbons (PAHs) are one of the most important classes of organic molecules due to their widespread applications in various fields.[1] Among these, triphenylenes are particularly interesting. As the smallest example of all-benzenoid polycyclic aromatic hydrocarbons, triphenylene has the same fundamental skeleton as many other PAHs and can act as a precursor to synthesize these PAHs.[2] More importantly, triphenylenes have great application potentials in supramolecular and materials chemistry.[3] Triphenylenes have been employed to make functional organic materials such as discotic liquid crystals and organic light-emitting diodes.[4]

Over the past decades, interest in the chemistry of triphenylenes has increased continuously, and the synthesis of triphenylenes has attracted considerable attention.[5] To date, a variety of synthetic strategies for triphenylenes have been developed. One of the common strategies involves the cyclization of *o*-terphenyls.[6] A second popular approach for the synthesis of triphenylenes is the trimerization of arynes.[7] This approach is primarily limited to the synthesis of symmetrical triphenylenes. Furthermore, a variety of other interesting synthetic means are available.[8] More recently, palladium catalysis based methods have gained great attention as they offer facile and efficient strategies for the synthesis of triphenylenes. Miura and co-workers found that *o*-dibromobenzenes could undergo Pd-catalyzed coupling reaction with *o*-phenybenzyl alcohols to form triphenylenes.[9] The Larock group disclosed a novel method for the synthesis of substituted triphenylenes via the palladium-catalyzed annulation of *o*-iodobiphenyls with arynes.[10] The Cheng group developed the carbocyclization of arynes with aryl iodides,[11] and the Zhang group realized the coupling of arynes with 1-(2-bromophenyl)-1*H*-indole.[12] Nishihara and co-workers reported the annulation of *o*-iodobiphenyls with *o*-bromobenzyl alcohols under palladium catalysis, providing an efficient method for the synthesis of highly substituted triphenylenes.[4d,13] Other palladium-catalyzed examples include double cross-coupling of 9-stannafluorenes with 1,2-dibromoarenes,[14] double cross-coupling of 1,2-bis(pinacolatoboryl)arenes with 2,2′-dibromobiaryls,[15] and the intramolecular cyclization of terarylsulfonium salts obtained from dibenzothiophenes.[16] Although these reactions offer versatile methods for the synthesis of triphenylenes, it is still desirable to develop general and facile methods starting from readily available substrates for the synthesis of triphenylenes, particularly substituted ones, which play important roles in materials chemistry.[3a−c]

Recently, our group disclosed that dibenzopalladacyclopentadienes have intriguing reactivities and have been exploited to develop facile and practical synthetic methods.[17] During the research on the synthesis of tetraphenylenes, we isolated a small amount of triphenylene when iodobenzene was added.[17a] Unfortunately, in spite of our great efforts, we failed to improve the yield of triphenylene. Dibenzopalladacyclopentadienes can also be generated from 2-iodobiphenyls under basic conditions,[17b,c] so we envisioned that triphenylenes could be formed by the coupling of 2-iodobiphenyl with iodobenzene under the basic conditions. Herein, we report a new method for the synthesis of triphenylenes starting from readily available

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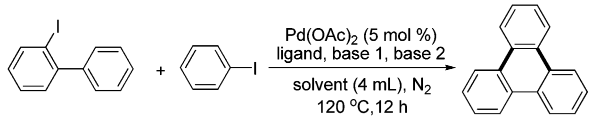
substrates 2-iodobipheyls and iodobenzenes under palladium catalysis.

We initiated our research by investigating the coupling reaction of 2-iodobiphenyl and iodobenzene. After extensive screening, we obtained the desired triphenylene in 38% yield when the reaction was carried out in DMF in the presence of $Pd(OAc)_2$, K_2CO_3, and KOAc under N_2 atmosphere (Table 1, entry 1). However, further efforts failed to improve the yield, so we sought the aid of ligands. While PPh_3 gave a similar yield (entry 2), the use of a bidentate phosphine ligand led to a slight increase in yield (entries 3–5). The yield was improved to 60% when dppf was employed (entry 6). Notably, the yield remained almost unchanged when the loadings of $Pd(OAc)_2$ and the ligand were reduced to 5 mol % (entry 7). Next, we examined the impact of bases on the reaction. We found that replacing K_2CO_3 with Na_2CO_3 resulted in an identical yield (entry 8). However, while a combination of Na_2CO_3 and NaOAc gave a lower yield (entry 9), a 71% yield was obtained in the presence of Na_2CO_3 and CsOAc (entry 10). Furthermore, the absence of Na_2CO_3 or CsOAc led to a much lower yield (entries 11 and 12). The reason remains to be investigated. The effect of solvents was also examined. The reactions in NMP or DMSO were lower yielding, and only a small amount of triphenylene was observed for the reactions in *t*-BuOH or THF (entries 13–16). In addition, the reaction in 2 mL of DMF was less effective (entry 17), and the yields decreased when the reaction was carried out at a higher or lower temperature (entries 18 and 19). Finally, the use of 1 or 2 equiv of PhI resulted in lower yields (entries 20 and 21).

Table 1. Optimization of Reaction Conditions for the Pd-Catalyzed Formation of Triphenylene from 2-Iodobiphenyl and Iodobenzene



1a (0.2 mmol) **2a** (1.5 equiv) **3aa**

entry	base 1 (2 equiv)	base 2 (3 equiv)	ligand (mol %)	solvent (4 mL)	yield[a] (%)
1[b]	K_2CO_3	KOAc		DMF	38
2[b]	K_2CO_3	KOAc	PPh_3 (20)	DMF	41
3[b]	K_2CO_3	KOAc	**L1** (10)	DMF	48
4[b]	K_2CO_3	KOAc	**L2** (10)	DMF	46
5[b]	K_2CO_3	KOAc	**L3** (10)	DMF	49
6[b]	K_2CO_3	KOAc	dppf (10)	DMF	60
7	K_2CO_3	KOAc	dppf (5)	DMF	63
8	Na_2CO_3	KOAc	dppf (5)	DMF	63
9	Na_2CO_3	NaOAc	dppf (5)	DMF	45
10	**Na_2CO_3**	**CsOAc**	**dppf (5)**	**DMF**	**71 (70)**[c]
11	Na_2CO_3		dppf (5)	DMF	43
12		CsOAc	dppf (5)	DMF	35
13	Na_2CO_3	CsOAc	dppf (5)	NMP	50
14	Na_2CO_3	CsOAc	dppf (5)	DMSO	41
15	Na_2CO_3	CsOAc	dppf (5)	*t*-BuOH	4
16	Na_2CO_3	CsOAc	dppf (5)	THF	6
17	Na_2CO_3	CsOAc	dppf (5)	DMF[d]	55
18	Na_2CO_3	CsOAc	dppf (5)	DMF	10[e]
19	Na_2CO_3	CsOAc	dppf (5)	DMF	52[f]
20	Na_2CO_3	CsOAc	dppf (5)	DMF	47[g]
21	Na_2CO_3	CsOAc	dppf (5)	DMF	64[h]

[a] The yields were determined by ^1H NMR analysis of the crude reaction mixtures using $CHCl_2CHCl_2$ as the internal standard. [b] $Pd(OAc)_2$ (10 mol %). [c] Isolated yield. [d] 2 mL. [e] 100 °C. [f] 140 °C. [g] 1 equiv of PhI. [h] 2 equiv of PhI. **L1**: $PPh_2CH_2PPh_2$. **L2**: $PPh_2(CH_2)_4PPh_2$. **L3**: bis(dicyclohexylphosphino)ferrocene. dppf: 1, 1′-bis(diphenylphosphino)ferrocene.

Having developed an efficient procedure for the synthesis of triphenylene, we next investigated the substrate scope of this transformation. We first examined the performance of a range of 2-iodobiphenyls under the optimized reaction conditions. Therefore, as shown in Table 2, 2-iodobiphenyls bearing a methoxy group at the 3′ or 4′ position coupled with iodobenzene (entries 1 and 2). It is noted that the reaction selectively occurred at the less hindered position for **1c**, so the reactions of **1b** and **1c** formed the same product **3ba**. The substrate bearing 2′-methoxy group was also suitable, albeit in a lower yield (entry 3). The substrates bearing a methyl or phenyl group were also reactive (entries 4–6). A range of electron-withdrawing substituents were then examined. The trifluoromethyl group was well-tolerated, and triphenylenes were formed in good or excellent yields (entries 7 and 8). However, other electron-withdrawing groups including ester, carbonyl, and nitro gave much lower yields (entries 9–11). In these reactions, a portion of 2-iodobiphenyls was recovered. The reason could be that it is difficult to cleave the C–H bonds of the electron-deficient benzene. Both fluoro and chloro groups, on the iodo-containing benzene ring or the other phenyl group, were well-tolerated under the standard conditions (entries 12–15). 2-Iodobiphenyl bearing two methyl groups was also reactive (entry 16). Furthermore, symmetrically substituted substrates, containing phenyl of trifluoromethyl groups, underwent the double coupling reaction, albeit in lower yields (entries 17 and 18). It is noted that unsymmetrically substituted 2-iodobiphenyls were suitable, affording unsymmetrically functionalized triphenylenes (entries 19 and 20).

Next, the iodobenzene scope was examined. The methoxy groups at the *para* and *meta* positions were compatible, and the reactions afforded methoxylated triphenylene in 91% or 74% yield (entries 21 and 22). It should be mentioned that the reaction for **2c** took place at the less hindered position, forming the same product as that for **2b**. In a similar way, iodobenzenes containing a *m*- or *p*-methyl group formed the same product **3ea** (entries 23 and 24). The chloro and fluoro groups were tolerated in the reaction (entries 25–27), and the reactions of **2g** and **2h** formed the same product **3pa**. 4-Iodobiphenyl and 1-(difluoromethoxy)-4-iodobenzene were also suitable (entries 28 and 29). The reactions of iodobenzenes bearing electron-withdrawing groups such as trifluoromethyl and ester were low yielding (entries 30 and 31). The major reason was that these electron-deficient iodobenzenes tended to undergo homocoupling to form biphenyl byproducts. Bromobenzene was also reactive, albeit in a low yield (entry 32). To obtain multiple substituted triphenylene derivatives, we also examined the reaction of substituted iodobenzenes and 2-iodobiphenyls.

4-Iodoanisole reacted with symmetrically substituted 2-iodobiphenyls to afford multiply substituted triphenylenes in moderate yields (entries 33–35). When unsymmetrically substituted 2-iodobiphenyls were used, two regioisomers were formed (entry 36).

While the detailed mechanism of the reaction remains to be investigated and other reaction pathways cannot be ruled out, based on our previous works, a tentative mechanism can be

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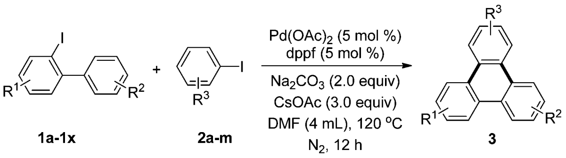
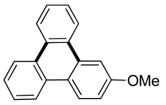
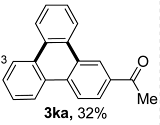
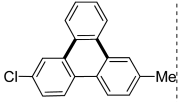
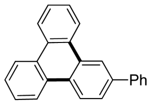
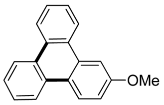
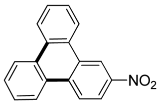
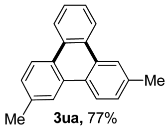
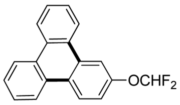
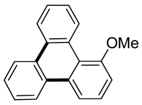
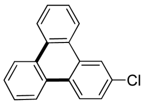
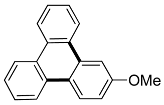
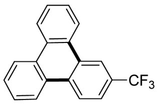
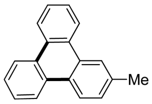
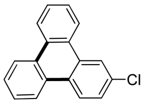
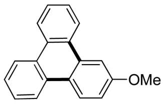
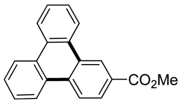
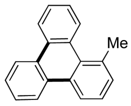
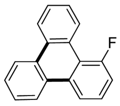
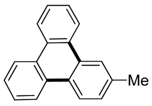
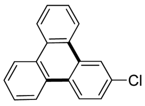
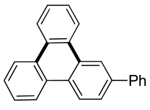
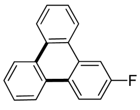
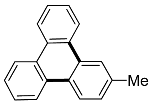
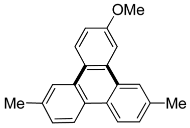
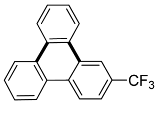
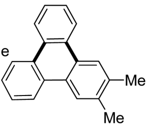
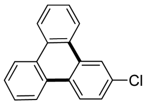
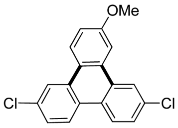
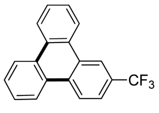
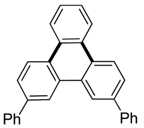
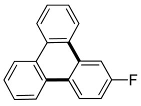
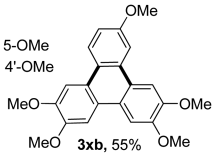
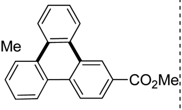
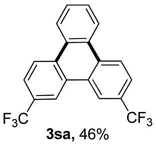
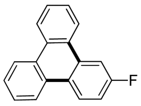
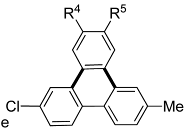
Table 2. Substrate Scope with Respect to 2-Iodobiphenyls



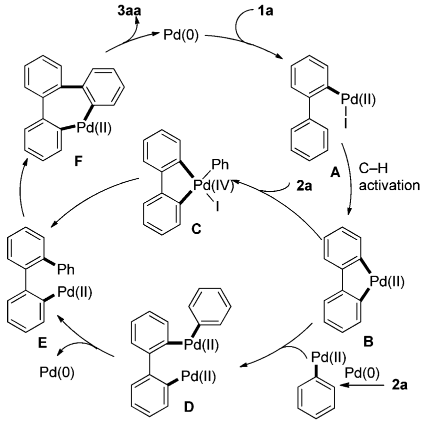
entry	substrate	product^a	entry	substrate	product^a	entry	substrate	product^a	entry	substrate	product^a
1	**1b**: R^1 = H R^2 = 4'-OMe **2a**: R^3 = H	 **3ba**, 76%	10	**1k**: R^1 = H R^2 = 4'-COCH$_3$ **2a**: R^3 = H	 **3ka**, 32%	19	**1t**: R^1 = 4-Cl R^2 = 4'-Me **2a**: R^3 = H	 **3ta**, 73%	28	**1a**: R^1 = H R^2 = H **2i**: R^3 = 4-Ph	 **3ga**, 60%
2	**1c**: R^1 = H R^2 = 3'-OMe **2a**: R^3 = H	 **3ba**, 81%	11	**1l**: R^1 = H R^2 = 3'-NO$_2$ **2a**: R^3 = H	 **3la**, 32%	20	**1u**: R^1 = 5-Me R^2 = 4'-Me **2a**: R^3 = H	 **3ua**, 77%	29	**1a**: R^1 = H R^2 = H **2j**: R^3 = 4-OCHF$_2$	 **3aj**, 50%
3	**1d**: R^1 = H R^2 = 2'-OMe **2a**: R^3 = H	 **3da**, 60%	12	**1m**: R^1 = H R^2 = 3'-Cl **2a**: R^3 = H	 **3ma**, 71%	21	**1a**: R^1 = H R^2 = H **2b**: R^3 = 4-OMe	 **3ba**, 91%	30	**1a**: R^1 = H R^2 = H **2k**: R^3 = 4-CF$_3$	 **3ha**, 44%
4	**1e**: R^1 = H R^2 = 3'-Me **2a**: R^3 = H	 **3ea**, 76%	13	**1n**: R^1 = 5-Cl R^2 = H **2a**: R^3 = H	 **3ma**, 55%	22	**1a**: R^1 = H R^2 = H **2c**: R^3 = 3-OMe	 **3ba**, 74%	31	**1a**: R^1 = H R^2 = H **2l**: R^3 = 4-CO$_2$Me	 **3ja**, 32%
5	**1f**: R^1 = H R^2 = 2'-Me **2a**: R^3 = H	 **3fa**, 66%	14	**1o**: R^1 = H R^2 = 2'-F **2a**: R^3 = H	 **3oa**, 72%	23	**1a**: R^1 = H R^2 = H **2d**: R^3 = 4-Me	 **3ea**, 72%	32	**1a**: R^1 = H R^2 = H **2m** = 1-Bromo-4-chlorobenzene	 **3ma**, 19%
6	**1g**: R^1 = H R^2 = 4'-Ph **2a**: R^3 = H	 **3ga**, 62%	15	**1p**: R^1 = 5-F R^2 = H **2a**: R^3 = H	 **3pa**, 65%	24	**1a**: R^1 = H R^2 = H **2e**: R^3 = 3-Me	 **3ea**, 67%	33	**1v**: R^1 = 4-Me R^2 = 4'-Me **2b**: R^3 = 4-OMe	 **3vb**, 56%
7	**1h**: R^1 = H R^2 = 4'-CF$_3$ **2a**: R^3 = H	 **3ha**, 94%	16	**1q**: R^1 = H R^2 = 3'-Me,4'-Me **2a**: R^3 = H	 **3qa**, 79%	25	**1a**: R^1 = H R^2 = H **2f**: R^3 = 4-Cl	 **3ma**, 44%	34	**1w**: R^1 = 4-Cl R^2 = 4'-Cl **2b**: R^3 = 4-OMe	 **3wb**, 66%
8	**1i**: R^1 = H R^2 = 3'-CF$_3$ **2a**: R^3 = H	 **3ha**, 81%	17	**1r**: R^1 = 5-Ph R^2 = 3'-Ph **2a**: R^3 = H	 **3ra**, 57%	26	**1a**: R^1 = H R^2 = H **2g**: R^3 = 4-F	 **3pa**, 55%	35	**1x**: R^1 = 4-OMe, 5-OMe R^2 = 3'-OMe, 4'-OMe **2b**: R^3 = 4-OMe	 **3xb**, 55%
9	**1j**: R^1 = H R^2 = 4'-CO$_2$Me **2a**: R^3 = H	 **3ja**, 56%	18	**1s**: R^1 = 5-CF$_3$ R^2 = 3'-CF$_3$ **2a**: R^3 = H	 **3sa**, 46%	27	**1a**: R^1 = H R^2 = H **2h**: R^3 = 3-F	 **3pa**, 50%	36	**1t**: R^1 = 4-Cl R^2 = 4'-Me **2b**: R^3 = 4-OMe **3tb-A** R^4 = H, R^5 = OMe **3tb-B** R^4 = OMe, R^5 = H	 **3tb**, 62%^{b}

[a] Yields are those of purified and isolated products. [b] The ratio of the two isomers is 1:2.44.

proposed as shown in Scheme 1. Therefore, the catalytic cycle should begin with the oxidative addition of 2-iodobiphenyl to Pd(0) to form complex **A**. Intramolecular C−H activation yields palladacycle **B**. Next, **B** undergo oxidative addition with iodobenzene to give Pd(IV) complex **C**. The subsequent reductive elimination generates Pd(II) complex **E**. At this stage, an alternative pathway for the formation of **E** from **B** cannot be ruled out. Complex **B** could undergo transmetalation-type exchange of aryl ligands with the phenylpalladium(II) species, which is formed by the oxidative addition of iodobenzene to Pd(0) to afford dinuclear arylpalladium complex **D**.[18] The reductive elimination of complex **D** leads to complex **E**.

In conclusion, a novel and facile approach for the synthesis of triphenylenes has been developed. The starting materials 2-iodobiphenyls and iodobenzenes are readily available. The reaction involves two palladium-catalyzed C−H activations and two palladium-catalyzed C−C bond formation steps, which makes the reaction atom- and step-economic. A range of unsymmetrically functionalized triphenylenes can be synthesized with this method. Therefore, the approach features readily

Scheme 1. Proposed Mechanism for the Pd-Catalyzed Formation of Triphenylene from 2-Iodobiphenyl and Iodobenzene[a]



[a]Complex **E** undergo a second intramolecular C−H activation to give complex **F**.[19] The final reductive elimination generates triphenylene and releases a Pd(0) species to initiate a second catalytic cycle.

available starting materials, atom- and step-economy, and comparatively broad substrate scope. A tentative mechanism involved in the reaction has been proposed. Further studies aimed at elucidating the detailed mechanism and improving the reaction 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.6b02071.

Detailed experimental procedures, spectroscopic data, and characterization of products (PDF)

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Notes

The authors declare no competing financial interest.

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