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An Approach to Tetraphenylenes via Pd-Catalyzed C−H Functionalization

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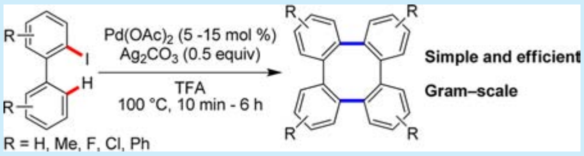
Supporting Information

ABSTRACT: Tetraphenylenes not only are theoretically and experimentally interesting but also have potential applications in a variety of fields such as materials science, supramolecular chemistry, and asymmetric catalysis. A facile and efficient approach is reported for the syntheis of tetraphenylene and its derivatives from 2-iodobiphenyls via Pd-catalyzed C−H activation. A range of substituted tetraphenylenes can be synthesized using this method, and the reaction can be performed on gram scale with relatively high efficiency, demonstrating its practical utility. This novel approach provides easy access to tetraphenylenes and should facilitate research on the application of this type of fascinating molecules.



Tetraphenylene is composed of four benzene rings that are *ortho*-annulated to form an eight-membered ring (Figure 1).[1] It has a nonplanar saddle-shaped structure, with the two opposite pairs of benzene rings oriented above or below the average plane of the molecule.[2] As a molecule with D_{2d} symmetry, tetraphenylene is achiral. However, substituted tetraphenylenes can be chiral due to the high barrier for inversion of the cyclooctatetraene ring.[3,4] Owing to their unique geometry, tetraphenylene and its derivatives are of great theoretical interest. More importantly, there exist numerous potential applications of these compounds in a variety of fields,[2] such as materials science,[5] supramolecular chemistry,[6] and asymmetric catalysis.[7]

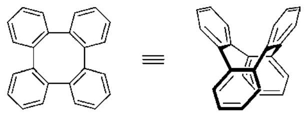

1a

Figure 1. Tetraphenylene and its saddle-shape structure.

Currently, there are three main methods for constructing the skeleton of tetraphenylene (Figure 2).[6b,8] (a) One is homocoupling of 2,2′-dihalobiphenyl via lithiation to provide 2,2′-dimetalbiphenyl and subsequent transition-metal-mediated homocoupling.[9] This method requires harsh conditions. (b) The second is homocoupling of biphenylene by transition-metal-mediated C−C activation[10] or pyrolysis.[11] This approach has very limited substrate scopes, because the synthesis of substituted biphenylenes is often challenging. (c) The third method is Diels−Alder cycloaddition of 1,2,5,6-dibenzocycloocta-3,7-diyne and furan, followed by deoxygenation or hydrogenation/dehydration.[12] Notably, the formation of heterocyclic tetraphenylenes incorporating pyridine via the coupling of 3-bromo-4-phenylpyridines and biphenylene has been reported.[13] The reactions are low-yielding and still require the use of biphenylene, and the synthesis of normal tetrapheneylens via this strategy has not been achieved. Intriguingly, the *de novo* synthesis of chiral tetraphenylenes has been disclosed.[14] Furthermore, tetraphenylenes can be obtained via a double Suzuki reaction or double Ullmann reaction.[15]

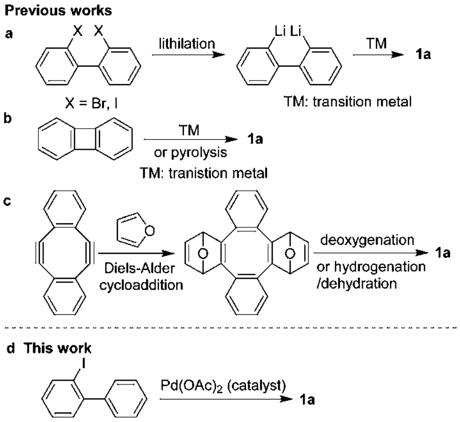


Figure 2. Synthetic methods for tetraphenylene.

In the past decade, the development of novel synthetic methods based on transition-metal-mediated C−H functionalization has attracted considerable interest.[16] Compared to traditional organic reactions that rely on the transformation and interconversion of functional groups, C−H functionalization reactions possess attractive features. The reactions can avoid the use of prefunctionalized starting materials, reduce the formation of unnecessary chemical waste, and provide novel synthetic strategies with higher overall efficiency and fewer reaction steps.

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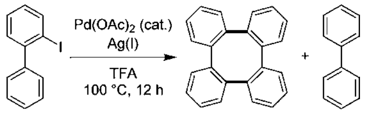
In pursuit of these attractive features, herein, we disclose a novel protocol for the synthesis of tetraphenylenes via Pd-catalyzed C−H activation/coupling of 2-iodobiphenyls (Figure 2d).

As a model system, the Pd-catalyzed homocoupling of 2-iodobiphenyl (**1**) was first examined. Table 1 lists selected examples of conditions that were surveyed during reaction optimization. The investigation commenced by treating **1** with $Pd(OAc)_2$ in trifluoroacetic acid (TFA) at 100 °C (entry 1). However, the reaction failed to form the desired homocoupled product, tetraphenylene (**1a**) (entry 1). Surprisingly, the addition of 1.0 equiv of AgOAc promoted the reaction, providing **1a** in 44% yield, along with a 21% yield of biphenyl (**1b**) as a byproduct (entry 2).[17] Whereas replacing AgOAc with AgOTf or Ag_2O led to a lower or similar yield (entries 3 and 4), the use of 0.5 equiv Ag_2CO_3 improved the yield to 53% (entry 5). Interestingly, when the loading of Ag_2CO_3 or Ag_2O was increased to 1.0 equiv, the desired product **1a** was not observed, and only the byproduct **2a** could be isolated (entries 6 and 7). The reasons remain to be investigated. The yield of **1a** improved to 58% when the reaction was carried out under higher dilution (2.5 mL TFA) (entry 8) and further increased to 70% when the catalyst loading was raised to 15 mol % $Pd(OAc)_2$ (entry 9). In 2.5 mL of TFA solvent, a 50% yield of **1a** could still be obtained when the catalyst loading was reduced to 5 mol % $Pd(OAc)_2$ (entry 10). Conducting the reaction at a lower or higher temperature resulted in lower yields (entries 11 and 12). Notably, the reaction was found to be rapid, reaching completion in only 10 min (entry 13). A control experiment in the absence of $Pd(OAc)_2$ confirmed that it was necessary for formation of **1a** (entry 14). Attempts to perform the reaction in alternative acidic solvents were low-yielding (entries 15 and 16).

Table 1. Optimization of the Reaction Conditions for Pd-Catalyzed Synthesis of Tetraphenylene (1a)



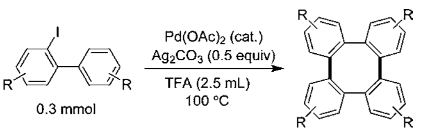
1 0.3 mmol **1a** **1b**

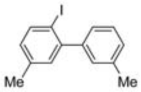
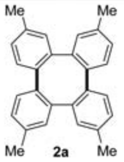
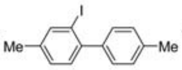
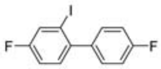
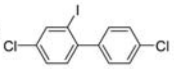
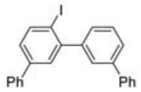
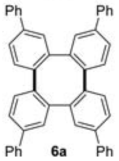
entry	Ag (equiv)	TFA (mL)	$Pd(OAc)_2$ (mol %)	**1a**[a]	**1b**[a]
1	–	1.0	10	0	0
2	AgOAc (1.0)	1.0	10	44	21
3	AgOTf (1.0)	1.0	10	38	9
4	Ag_2O (0.5)	1.0	10	46	15
5	Ag_2CO_3 (0.5)	1.0	10	53	16
6	Ag_2O (1.0)	1.0	10	0	22
7	Ag_2CO_3 (1.0)	1.0	10	0	27
8	Ag_2CO_3 (0.5)	2.5	10	58	12
9	**Ag_2CO_3 (0.5)**	**2.5**	**15**	**70 (68[b])**	**11**
10	Ag_2CO_3 (0.5)	2.5	5	50	14
11[c]	Ag_2CO_3 (0.5)	2.5	15	48	8
12[d]	Ag_2CO_3 (0.5)	2.5	15	40	10
13[e]	**Ag_2CO_3 (0.5)**	**2.5**	**15**	**69**	**8**
14	Ag_2CO_3 (0.5)	2.5	0	0	0
15	Ag_2CO_3 (0.5)	CH_3CO_2H (1.0)	10	trace	9
16	Ag_2CO_3 (0.5)	CF_2HCO_2H (1.0)	10	22	17

[a] The yields were determined by ^1H NMR analysis of crude reaction mixture using $CHCl_2CHCl_2$ as the internal standard. [b] Isolated yield. [c] 120 °C. [d] 80 °C. [e] 10 min.

Having developed an efficient protocol for Pd-catalyzed homocoupling of 2-iodobiphenyl (**1**), we next investigated the substrate scope of this reaction. A range of symmetrically substituted 2-iodobiphenyls were examined. As shown in Table 2, substrates bearing two *meta*- or *para*-methyl groups (**2** and **3**) were competent in the coupling reaction (entries 1 and 2). Notably, the homocoupling of **2** took place selectively at the less hindered *ortho*-C−H bond; as a consequence, **2** and **3** both formed the same tetramethylated tetraphenylene product (**2a**). Both fluoro and chloro groups were well-tolerated in the reaction, giving desired homocoupled products in 62% and 41% yields, respectively (entries 3 and 4). 3′,5-Diphenyl-2-iodobiphenyl (**5**) was also reactive (entry 5), affording a new method for the synthesis of **6a**, a tetraphenylene derivative bearing multiple phenyl substituents. Substrates bearing ester, carbonyl, nitro, or methoxy groups were examined. No desired products were formed, or the yields were very low. The bromo group was not tolerated in the reaction.

Table 2. Substrate Scope for Pd-Catalyzed Synthesis of Substituted Tetraphenylenes



entry	substrate	$Pd(OAc)_2$ (mol %)	time (h)	product	yield (%)[a]
1	 **2**	10	1.0	 **2a**	60
2	 **3**	15	1.0	 **2a**	68
3	 **4**	10	3.0	 **4a**	60
4[b]	 **5**	10	3.0	 **5a**	39
5[b]	 **6**	15	1.0	 **6a**	52

[a] Isolated yields. [b] 0.1 mmol scale in 1.0 mL of TFA.

Next, we examined the cross-coupling of two different 2-iodobiphenyls. Equimolar quantities of 2-iodophenyl and a 2-iodobiphenyl derivative containing chloride or methoxy

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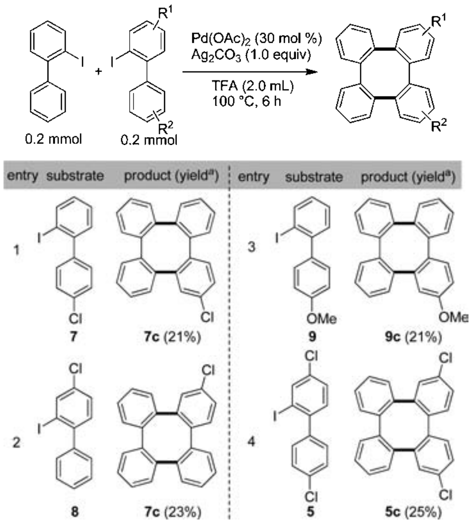
substituents were subject to the standard conditions (Table 3). We targeted these two functional groups due to the possibility of performing further downstream diversification. These reactions proceeded to form the corresponding cross-coupled products in yields ranging from 21% to 25%. The low yields in these cases are primarily due to competitive formation of homocoupled products (see Table S1 in the Supporting Information).

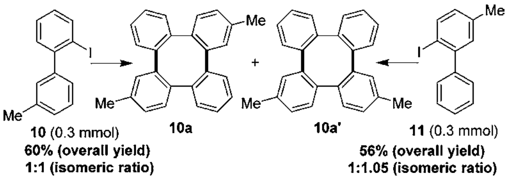
Table 3. Pd-Catalyzed Cross-Coupling of 2-Iodobiphenyls



[a] Isolated yields.

To gain insight into the reaction mechanism, additional experiments were designed and carried out. Thus, 3′- and 5-methyl-2-iodobiphenyl substrates were subjected to the standard conditions (Scheme 1). Intriguingly, both reactions afforded an inseparable mixture of two isomeric products, **10a** and **10a′**. Fortunately, the isomers could be separated following oxidation to the corresponding tetraphenylene dicarboxylic acids with $KMnO_4$.[9d] Notably, the reactions with **10** and **11** not only formed the same two products but also resulted in nearly identical yields and isomeric ratios. In addition, in the cross-coupling reaction of **1** with **7** or **8** (Table 3, entries 1 and 2), the homocoupled product of 7 or **8** was observed. More importantly, the homocoupling reactions of **7** and **8** also yielded the same products based on ^{1}H NMR analysis. These results are consistent with the two reactions proceeding via a common intermediate, which should be Pd(2,2′-biphenyl) (Scheme 3, **B**).

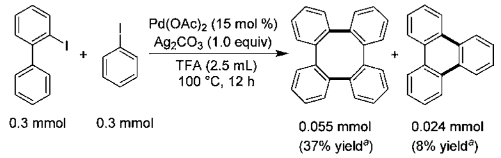
Scheme 1. Pd-Catalyzed Coupling of Unsymmetrically Substituted 2-Iodobiphenyls



[a] Conditions: 15 mol % $Pd(OAc)_2$, 0.5 equiv of Ag_2CO_3, 2.5 mL of TFA, 100 °C, 1 h.

When equimolar amounts of 2-iodophenyl and iodobenzene were stirred under the standard conditions, tetraphenylene was isolated in 37% yield, along with 8% of triphenylene (Scheme 2). Therefore, the homocoupling of Pd(2,2′-biphenyl) should be ruled out as the pathway of formation of tetraphenylene, unless the reaction of 2-iodobiphenyl with iodobenzene proceeds via a different mechanism from the coupling of 2-iodobiphenyl.

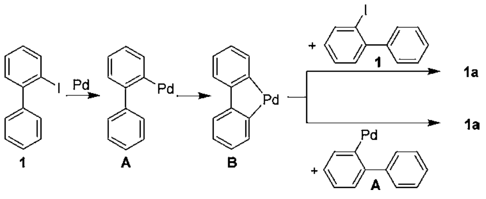
Scheme 2. Pd-Catalyzed Coupling of 2-Iodobiphenyl and Iodobenzene



[a] The yields were determined by ^{1}H NMR analysis of a mixture of tetraphenylene and triphenylene.

While the detailed mechanism of this reaction remains the topic of ongoing investigation in our laboratory, the above-mentioned experimental results are consistent with the mechanism shown in Scheme 3 involving the formation of Pd(2,2′-biphenyl) **B**. Therefore, 2-iodobiphenyl is transformed into **B**, likely via the oxidative addition of the iodide to Pd followed by subsequent C−H activation. The resulting complex **B** reacts with a second molecule of 2-iodobiphenyl to generate tetraphenylene. Alternatively, Pd(2,2′-biphenyl) **B** may react with complex **A** to form **1a**. At this stage, the oxidation states of palladium during the catalytic cycle have not been determined. Furthermore, byproduct biphenyls should result from the protonation of complex **A** or **B**. When the reaction of **3** was carried out in TFA-*d*, 2-deutero-4,4′-dimethylbiphenyl and 2,2′-dideutero-4,4′-dimethylbiphenyl were formed, which indicated that both complex **A** and **B** are responsible for the formation of biphenyl.

Scheme 3. Tentative Mechanism for the Formation of Tetraphenylene via Pd-Catalyzed Coupling of 2-Iodobiphenyl

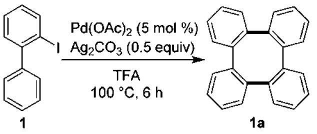


[a] Ligands are omitted for clarity.

To test whether the reaction was amenable to scale-up for generating preparatively useful quantities of material (Scheme 4), we attempted a reaction using 1.0 or 3.0 g of 2-iodobiphenyl (**1**). Gratifyingly, **1** was thus converted into tetraphenylene (**1a**) in 50% or 48% yield with only 5 mol % $Pd(OAc)_2$.

In summary, a simple and efficient protocol for the synthesis of tetraphenylenes from 2-iodobiphenyls has been developed via Pd-catalyzed C−H functionalization. Compared to alternatives, this approach is advantageous in terms of simplicity, operational

Scheme 4. Gram-Scale Synthesis of Tetraphenylene via Pd-Catalyzed Coupling of 2-Iodobiphenyl



(**1** = 1.0 g, 3.57 mmol, TFA 10 mL, 50% yield)
(**1** = 3.0 g,10.71 mmol, TFA 30 mL, 48% yield)

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convenience, and atom economy. A range of substituted tetraphenylenes could be synthesized using this protocol. The preparative utility of this transformation was demonstrated in an example that was carried out on gram scale with 5 mol % $Pd(OAc)_2$. This transformation represents a novel C−H coupling reaction of 2-iodobiphenyls. Further studies aimed at elucidating the detailed mechanism and expanding the scope 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.6b00641.

> 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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