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# Application of Palladium-Catalyzed C(sp<sup>2</sup>)-H Bond Arylation to the Synthesis of Polycyclic (Hetero)Aromatics

Wided Hagui, Henri Doucet and Jean-François Soulé\*

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**Abstract:** Recently, the use of the palladium-catalyzed inter- and/or intra-molecular C–H bond arylations in the building of various  $\pi$ -extended (hetero)aromatic structures has emerged as a suitable alternative to the previous multi-steps synthesis. Such new methodology even allowed to prepare unprecedented  $\pi$ -extended molecules owing a perfect control of the reaction sites. This review gives an overview of various synthesis of Polycyclic Aromatic Hydrocarbons (PAHs) and PolyCyclic Heteroaromatics (PCHs) with planar, bowl-shaped, and helical structures prepared in high efficiency and selectivity *via* Pd-catalyzed C–H bond arylations.

## **Bigger Picture**

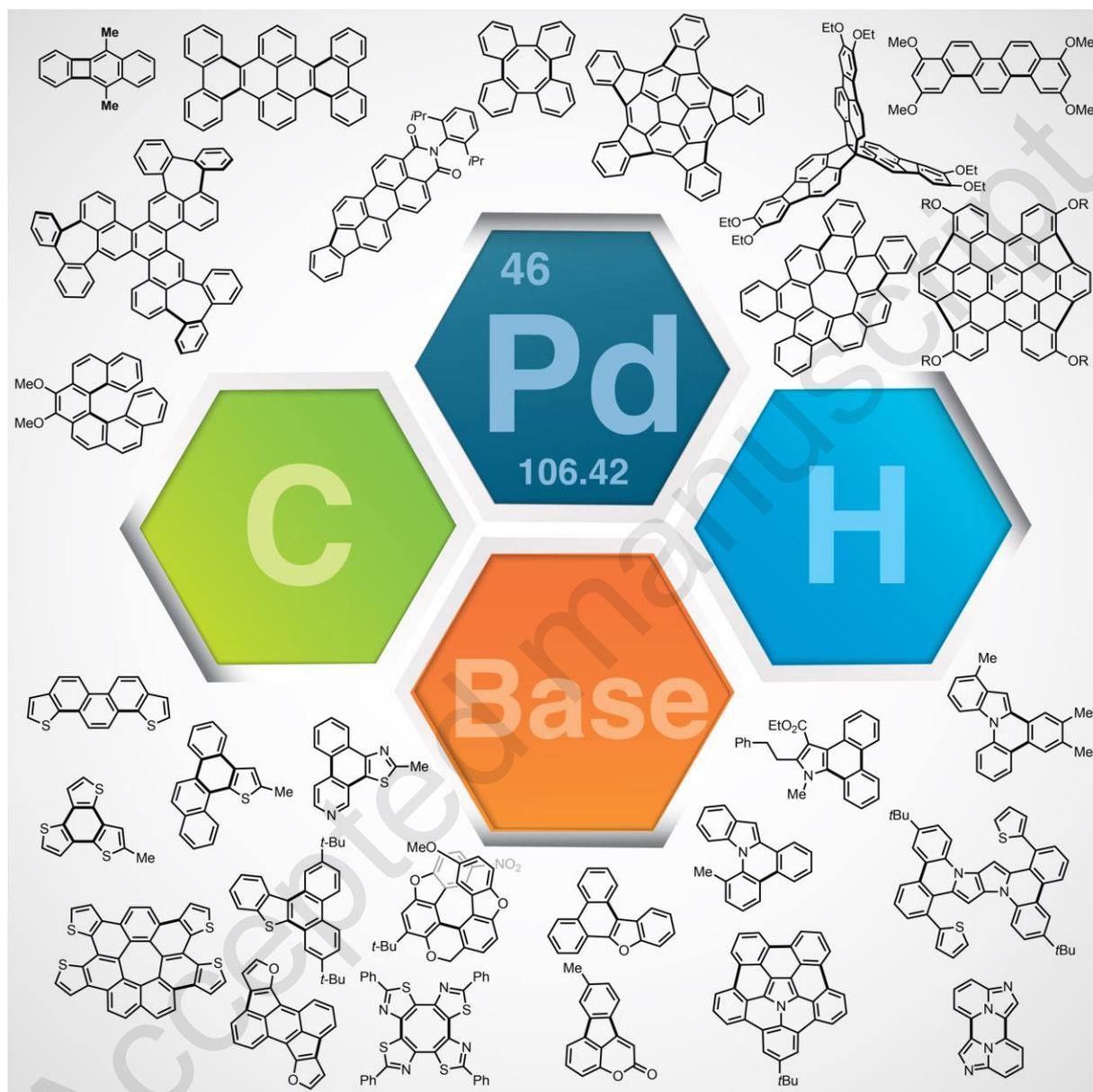
Recently,  $\pi$ -extended compounds such as Polycyclic Aromatic Hydrocarbons (PAHs) and PolyCyclic Heteroaromatics (PCHs) have found important applications in the preparation of optoelectronic devices. The degree of  $\pi$ -extension, the topology of the ring fusion, and the periphery of such molecules are essential factors to control their electronic properties at a molecular level. The traditional approach to prepare nanographenes and heteroatom-doped nanographenes relies on Scholl reaction. However, such methodology suffers from limitations such as functional group compatibility. Catalysis plays a pivotal role in the discovery of new transformations enabling the synthesis of novel molecules, including organic materials. Among various catalytic transformations, Pd-catalyzed C–H bond arylation has emerged as an important tool for the construction of well-decorated polycyclic (hetero)aromatic molecules. Such direct approaches have a considerable impact on the synthesis of PAHs and PCHs by shortening the synthetic scheme and also providing a momentous opportunity to design novel structures.

**eTOC Blurb:** This review highlights the potential of Pd-catalyzed C–H bond arylation for the synthesis of  $\pi$ -extended compounds that include

## **Key World:**

C–H bond arylation - Palladium -  $\pi$ -extended molecules - Planar - Geodesic - Heteroelement

## Graphical Abstract



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## 1. Introduction

Polycyclic Aromatic Hydrocarbons (PAHs) and their analogs containing a heteroatom, PolyCyclic Heteroaromatics (PCHs), are an important class of  $\pi$ -extended compounds, which found multiple applications in material sciences for the preparation of optoelectronic devices, *e.g.*, organic light-emitting diodes (OLEDs), organic photovoltaics (OPVs), or organic field-effect transistors (OFETs).<sup>1-4</sup> These unique properties are directly linked to their chemical structures, which confer a unique arrangement in the space. Indeed, small arenes (benzene, naphthalene, anthracene) have herringbone or “T”-geometry, while larger arenes pack as sandwich herringbone (pyrene, perylene),  $\gamma$ -structure (coronene) and  $\beta$ -structure (tribenzopyrene) (Figure 1 a and c). On the other hand, geodesic PAHs containing both 5- and 6-membered rings such as diindeno[1,2,3-cd]fluoranthene, (benzo)fluoranthene, indacenoprene, or corannulene derivatives exhibit curved structures, similar to fullerenes and their analogs (Figure 1b).<sup>5</sup> The synthesis of such internal strain in  $\pi$ -conjugated frameworks is quite challenging. It should be pointed out that the introduction of heteroelements in these  $\pi$ -extended structures (*e.g.*, benzotrithiophene, benzocoumarin, trioxa[7]helicene or azacorannulene derivatives) often induces a modification of their chemical and/or physical properties (Figure 1c).<sup>6</sup>

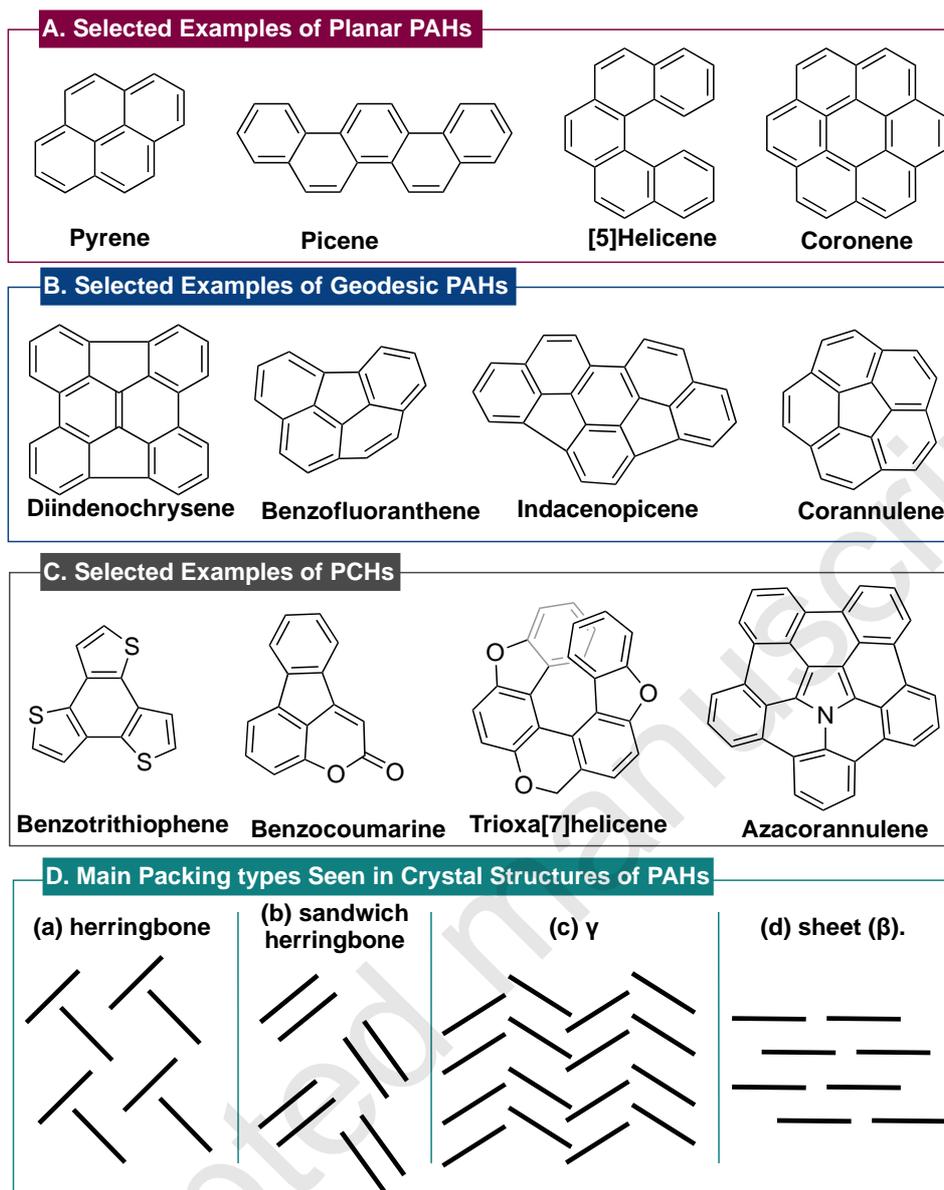


Figure 1. Representative Structures of PAHs and PCHs and Their Packing Modes

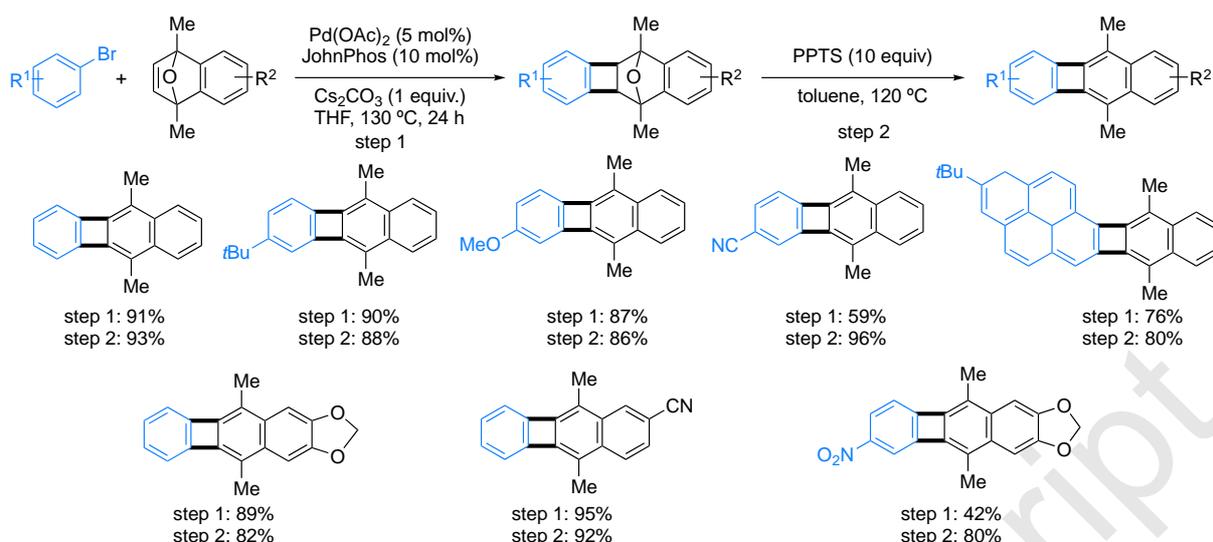
The synthesis of more and more complicated (novel)  $\pi$ -extended molecules with wide structural diversity is a blooming research area. It is also a huge opportunity for chemists to develop new chemical transformations with a high degree of selectivity.<sup>7, 8</sup> Flash-vacuum pyrolysis (FVP) using high temperature, and intramolecular photocyclization reactions were the most traditional approaches for the syntheses of PAHs and PCHs, albeit they suffer from low functional group tolerance and/or tedious access to the key intermediates due to multi-steps synthesis.<sup>9-11</sup> Intramolecular oxidative cyclodehydrogenation reactions, the Scholl reaction, has also been intensively applied in the synthesis of  $\pi$ -extended molecules despite the requirement to use over stoichiometric amounts of oxidant (e.g.,  $\text{FeCl}_3$ ,  $\text{AlCl}_3$ ,  $\text{MoCl}_5$ ,...).<sup>12</sup> With the development of transition-metal catalysis, new protocols for the synthesis of well-decorated  $\pi$ -conjugated

polycycles have been developed such as ring-closing metathesis, alkyne cyclizations, [2+2+2] cycloadditions, C–C bond formations, electrophilic aromatizations.<sup>7, 13, 14</sup> Recently, environmental concerns have significantly affected the way to practice organic synthesis by developing newly sustainable transformations.<sup>15-21</sup> Transition metal-catalyzed direct C–H bond functionalizations adopts this approach owing the use of non prefunctionalized substrates and minimizing the chemical wastes. Among diverse protocols, Pd-catalyzed intra- and/or intermolecular C–H bond arylation has recently attracted a lot of attention for the synthesis of decorated  $\pi$ -conjugated polycycles including some unprecedented structures. In this review, we focus on the application of Pd-catalyzed C–H bond arylation and C–H bond annulation reactions toward the construction of various PAHs and PCHs. This review is organized by the structure type: planar and geodesic PAHs, thio-PCHs, oxo-PCHs and aza-PCHs. Among the designs of  $\pi$ -conjugated polycycles, the reaction conditions, the scope of the reactions and brief mechanistic discussions are also evoked to provide an overview to chemists looking for (i) a useful guide to prepare optoelectronic devices and (ii) to innovate in the design of exotic  $\pi$ -conjugated polycycles.

## 2. Preparation of PAHs through Palladium-Catalyzed C–H Bond Arylation

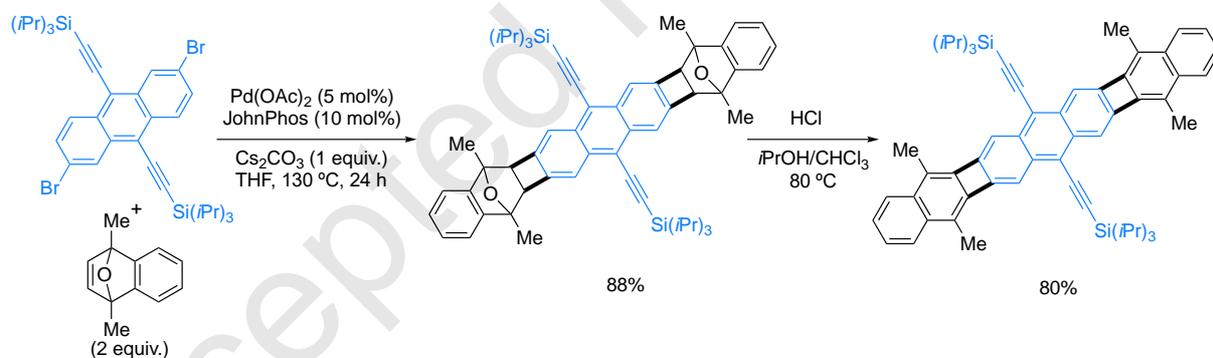
### 2.1. Formation of 4-Membered Rings by Pd-Catalyzed C–H Bond Arylation

[*N*]phenylene is a unique class of PAHs containing fused cyclic hexagonal–square chains (i.e., antiaromatic  $4\pi$ -electron cyclobutadienoid and aromatic  $6\pi$ -electron benzenoid rings). Besides the Vollhardt synthetic approach involving cobalt-catalyzed [2 + 2 + 2] cycloaddition of appropriately designed phenylethynyl substrates under photolysis;<sup>22</sup> in 2017, Xia and co-workers reported a straightforward access to [*N*]phenylene derivatives using Pd-catalyzed C–H bond annulation as the key step for the formation of the 4-membered ring (Scheme 1).<sup>23</sup> Oxanorbornene reacted with aryl bromides to afford the cyclobutadienoid motifs through arene-norbornene annulation reaction (Heck-Catellani reaction type)<sup>24</sup> catalyzed by 5 mol% Pd(OAc)<sub>2</sub> associated with 10 mol% of JohnPhos phosphine ligand and 1 equiv. of Cs<sub>2</sub>CO<sub>3</sub> in THF at 130 °C. Then, aromatization of all the arene-norbornene annulation products was achieved using pyridinium *p*-toluenesulfonate (PPTS) in toluene at 120 °C to afford the corresponding  $4\pi$ -electron cyclobutadienoid-containing PAHs. This synthetic route tolerates a wide range of functional group on both aryl bromide and oxanorbornene partners allowing the synthesis of well-decorated [*N*]phenylene derivatives.



Scheme 1. Synthesis of Polycyclic Conjugated Hydrocarbons Containing Cyclobutadienoids *via* C–H Bond Annulation and Aromatization

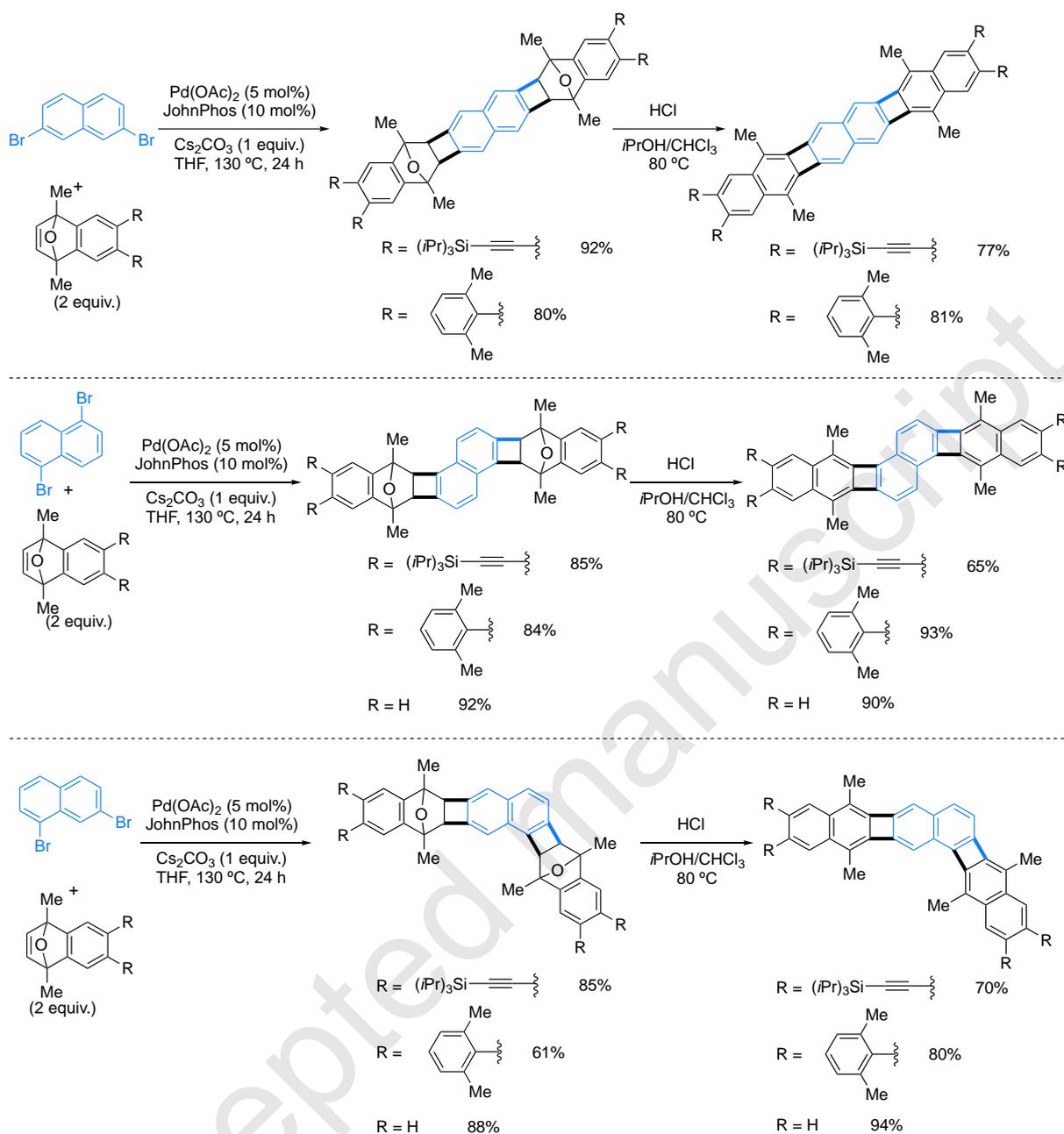
Interestingly, the authors demonstrated the high potential of this methodology by synthesizing an acene-like molecule containing two four-membered rings from dibromo-bis-(triisopropylsilylethynyl)-anthracene and 2 equivalents of oxanorbornene. The arene-norbornene annulation proceeded in 88% yield under standard conditions, while aromatization step required the use of a stronger acid (HCl) (Scheme 2).<sup>23</sup> Notably, exclusive regioselectivity for C–H bond arylation and annulation at 3 and 7 positions of anthracene has been observed.



Scheme 2. Synthesis of Acene-Like Polycyclic Conjugated Hydrocarbons *via* Two-fold C–H Bond Annulation and Aromatization

The authors proposed a catalytic pathway starting with oxidative addition of the aryl bromide to Pd(0) followed by an hydroarylation on the oxanorbornene (Figure 2).<sup>23</sup> The resulting palladium species underwent the cleavage of *ortho* aryl C–H of the aryl bromide to generate a palladacycle. Then, the desired product **A** is generated by reductive elimination. The authors also explained the formation of the by-products **B** and **C**. Besides the C–H cleavage,  $\beta$ -oxygen elimination of the oxanorbornene coupled Pd intermediate may occur to give ring-opened product **B**. The palladacycle intermediate may also undergo *ortho* coupling with another equivalent of aryl bromide before annulation to give product **C**.

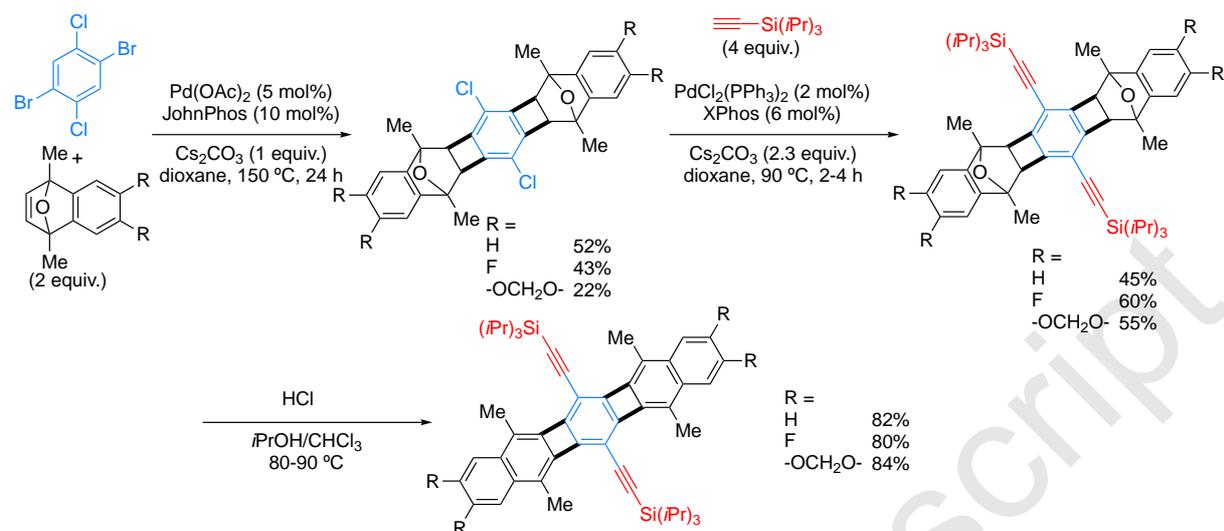




Scheme 3. Synthesis of [3]Naphthylenes *via* Palladium-Catalyzed Arene-Norbornene Annulation of Dibromonaphthalenes with Oxanorbornene

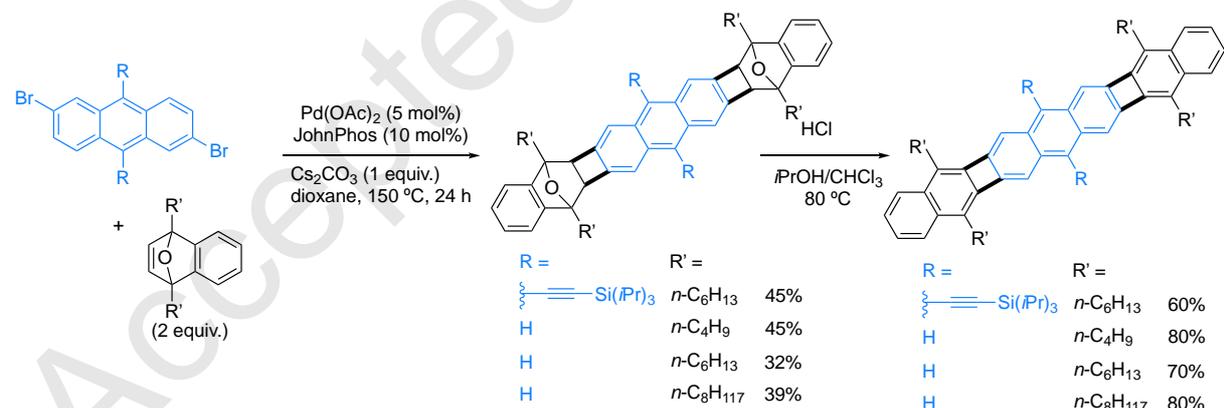
They also succeeded to prepare a compound containing a benzo[1,2:4,5]dicyclobutadiene as central unit through palladium-catalyzed two-fold arene-norbornene annulation of 1,4-dibromo-2,5-dichlorobenzene with oxanorbornene derivatives (Scheme 4).<sup>26</sup> As expected, the reaction has preferentially occurred through the activation of C–Br bonds, while C–Cl bonds could be used in a second step to introduce triisopropylsilyl (TIPS) acetylene motifs *via* two-fold Sonogashira couplings using PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, 2-dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl (Xphos) ligand, and Cs<sub>2</sub>CO<sub>3</sub> in 1,4-dioxane at 90 °C. Finally, an acidic treatment led to the desired PAHs. The introduction of triisopropylsilyl acetylene motifs

allowed to control the molecular packing, which is a critical factor for the performance of organic semiconductors in organic thin film transistors.



Scheme 4. Synthesis of Dinaphthobenzocyclobutadiene Derivatives via Palladium-Catalyzed Arene-Norbornene Annulation of Dibromonaphthalenes with Oxanorbornene

In 2019, this procedure was employed by Miao and co-workers for the preparation of new semiconductors with bisnaphtho-[2',3':3,4]cyclobut[1,2-b:1',2'-i]anthracene unit bearing alkyl side-chains from 1,4-dialkyl-benzooxanorbornadienes and dibromoanthracenes (Scheme 5).<sup>27</sup> They demonstrated that the molecular packing of these PAHs in the solid state is largely modified by attaching alkyl groups of different lengths to the linear  $\pi$ -backbone and are promising candidates for high-mobility semiconductors.



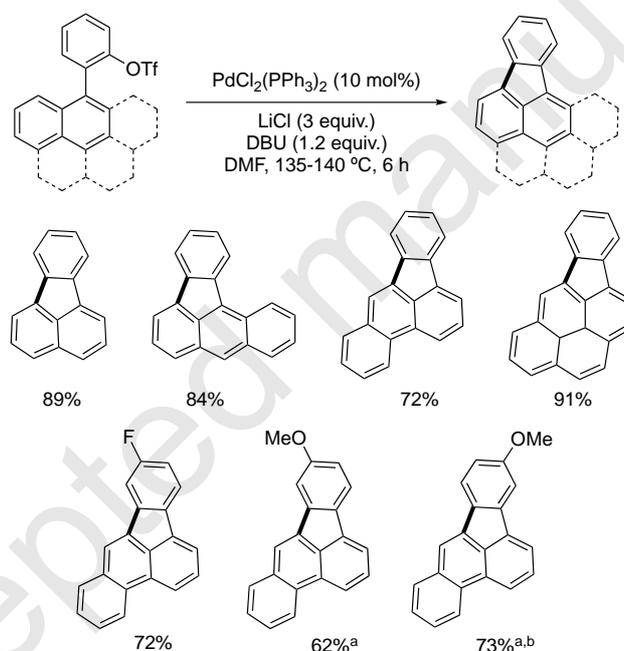
Scheme 5. Synthesis of bisnaphtho-[2',3':3,4]cyclobut[1,2-b:1',2'-i]anthracene Derivatives via Palladium-Catalyzed Arene-Norbornene Annulation of Dibromonaphthalenes with Oxanorbornene

## 2.2. Formation of 5-Membered Rings by Pd-Catalyzed C–H Bond Arylation

### 2.2.1. Synthesis of Fluoranthenes Derivatives

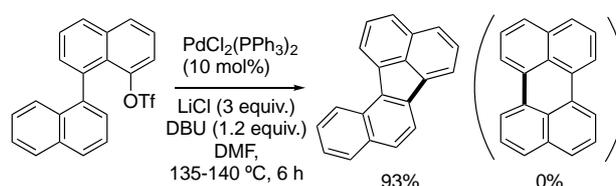
#### a) Pd-Catalyzed 5-Membered Ring C–H Bond Arylation with Aryl Triflates

In 1992, Rice and co-workers were the first to employ palladium-catalyzed intramolecular C–H bond arylation for the preparation of fluoranthenes (Scheme 6).<sup>28</sup> The biaryl precursors were obtained by Corriu-Kumada-Tamao reaction between aryl Grignard reagents bearing a protected *ortho*-phenol and  $\pi$ -extended aryl bromides such as 1-bromonaphthalene, 9-bromoanthracene, 1-bromopyrene, *etc.* Intramolecular C–H bond arylation with arene-triflates were performed using 10 mol% of PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> in the presence of LiCl and DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) as base in DMF at 140 °C allowing the formation of fluoranthene, benzo[*a*]fluoranthene, benzo[*b*]fluoranthene, and indeno[1,2,3-*cd*]pyrene in high yields. In addition, the reaction was also successfully applied to the preparation of compounds bearing substituents on the phenyl-ring such as F or MeO, although electron-rich arenes required an excess amounts of PPh<sub>3</sub> to accelerate the oxidative addition rate of the aryl triflate to Pd(0).



Scheme 6. Synthesis of Fluoranthenes *via* Palladium-Catalyzed Intramolecular Arene-Triflate Coupling. a) Using 4 equiv. of PPh<sub>3</sub>. b) Reaction performed from 3-methoxy-6-(phenanthren-9-yl)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate.

Interestingly, the authors showed that palladium-catalyzed intramolecular arylation of [1,1'-binaphthalen]-8-yl triflate exclusively delivered the 5-membered ring (fluoranthene) without the formation of 6-membered ring product (perylene) (Scheme 7).<sup>29</sup>



Scheme 7. Palladium-Catalyzed 5- vs 6-Membered Ring Formation

The reaction starts by the formation of **B** from aryl triflates with  $\text{PdCl}_2(\text{PPh}_3)_2$  in the presence of  $\text{LiCl}$ . Then, DBU assists the palladation by C–H bond cleavage to give the two isomeric cyclopalladated intermediates **C** and **D**. The regioselectivity of the C–H bond activation is probably due to the formation of 6-membered ring palladacycle **C** rather than 7-membered ring palladacycle **D**, which after reductive elimination gives the corresponding fluoranthene (Figure 3).<sup>29</sup>

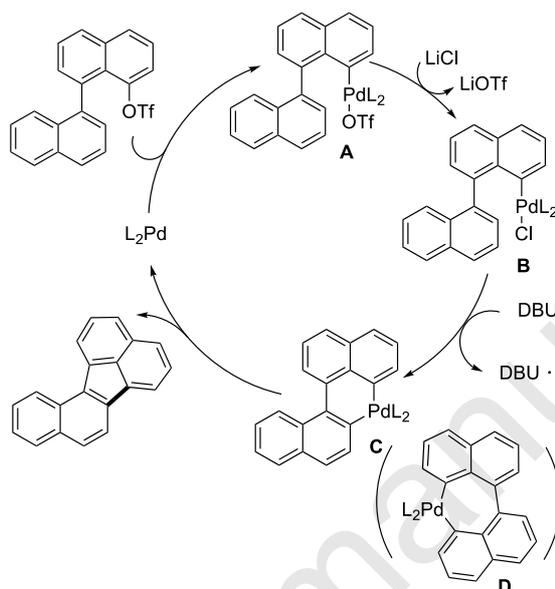
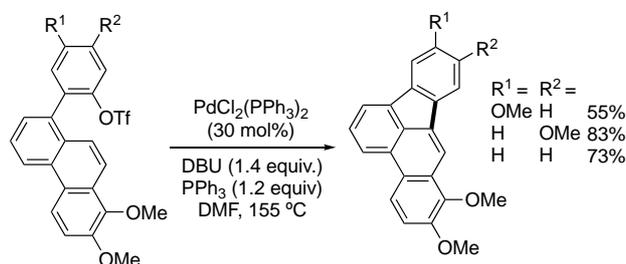


Figure 3. Mechanism for Palladium-Catalyzed Intramolecular Arene-Triflate Coupling

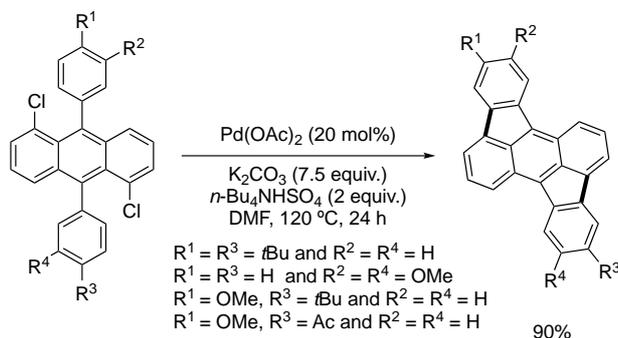
To overcome the previous limitations, i.e., all previously prepared derivatives using this method had a single functional group at positions 4, 5, 6, or 7, they applied the palladium-catalyzed triflate-arene cyclization reaction to the synthesis of polyoxygenated benzo[*b*]fluoranthene derivatives (Scheme 8).<sup>30</sup> It is worth noting that with highly methoxylated substrates, the addition of  $\text{LiCl}$  (thought to be necessary in most cases for palladium-catalyzed reactions involving triflates) had a deleterious effect on the reaction.



Scheme 8. Pd-Catalyzed Triflate-Arene Cyclization of Electron-Rich Biaryl Substrates for the Preparation of Benzo[*b*]fluoranthenes

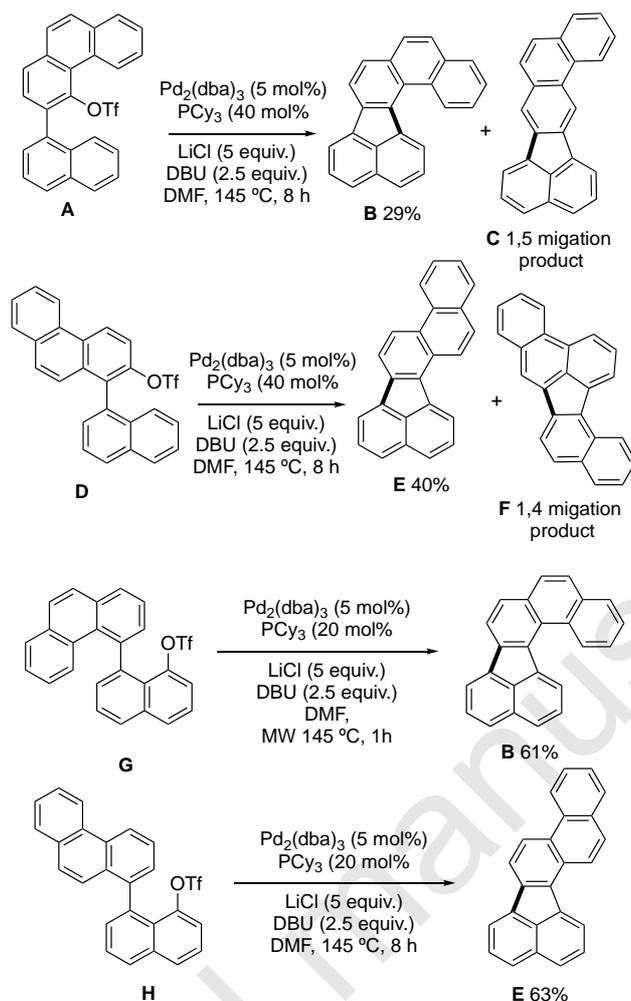
In 1999, Dehaen and co-workers prepared rubicenes in excellent yields *via* a two-fold Pd-catalyzed C–H bond arylation with activation of C–Cl bonds using  $\text{Pd}(\text{OAc})_2$  as catalyst with

$K_2CO_3$  as base and tetrabutylammonium hydrogensulfate as stabilizing agent in DMF at 120 °C (Scheme 9).<sup>31</sup>



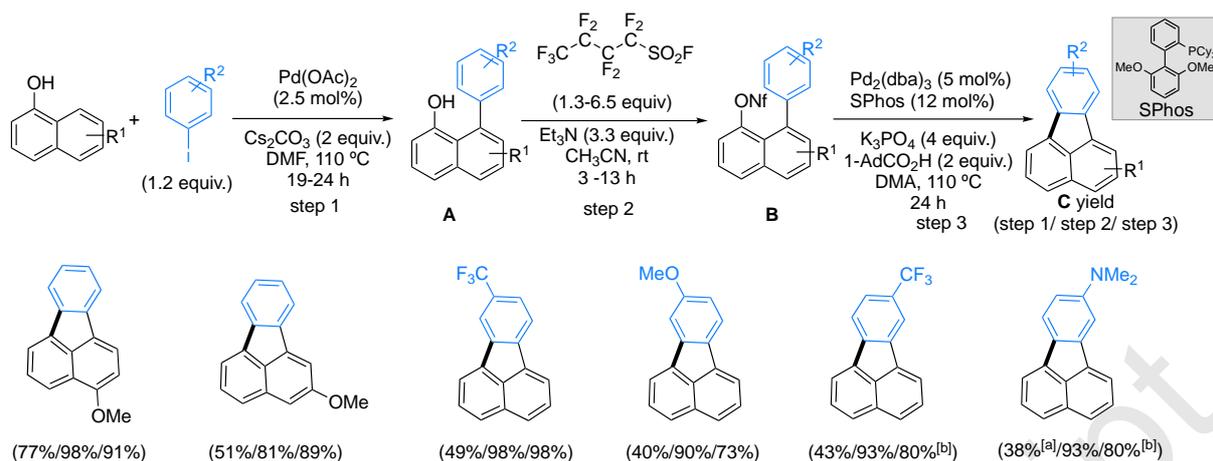
Scheme 9. Synthesis of Rubicenes via Two-Fold Pd-Catalyzed Intramolecular C–H Bond Arylation

In 2018, Harper, Uribe-Romo and co-workers employed this Pd-catalyzed triflate-arene 5-membered ring cyclization for the preparation of a wide range of dibenzo- and naphtho-fluoranthene polycyclic aromatic hydrocarbons (Scheme 10).<sup>32</sup> The triflate intermediates were prepared in three steps *via* a Suzuki coupling with substrates bearing a methoxy group followed by dealkylation using  $BBr_3$ . Then, the phenol intermediates were reacted with triflic anhydride. Most of the substrates afforded the desired PAHs using reaction conditions similar to the previously reported (*c.f.*, Scheme 8),<sup>30</sup> i.e.,  $Pd_2(dba)_3/PCy_3$  associated to DBU as base in DMF. However, with some substrates the ring closing produced significant amount of isomers resulting from 1,5- or 1,4 migrations of palladium. In order to improve the yields into the desired PAHs **B** and **E**, the authors performed the reaction from **G** and **H**, with which the potential rearrangements were avoided.



Scheme 10. Synthesis of Fluorescent Dibenzo- and Naphtho-Fluoranthenes via Pd-Catalyzed Fluoranthene Ring-Closing Reactions

In 2016, Manabe and co-workers described a three-steps synthetic method for the preparation of fluoranthenes, involving Miura's intermolecular C–H bond arylation, nonaflation, and 5-membered ring intramolecular C–H bond cyclization (Scheme 11).<sup>33</sup> In order to introduce an aryl group at the C8 position of 1-naphthols, they employed the conditions described by Miura for the C–H bond arylation of with halobenzenes,<sup>34</sup> i.e., 2.5 mol% of Pd(OAc)<sub>2</sub> as catalyst and Cs<sub>2</sub>CO<sub>3</sub> as base in DMF at 110 °C. For less reactive aryl bromides, they employed PdCl<sub>2</sub>(PCy<sub>3</sub>)<sub>2</sub> as catalyst. Then, the 8-aryl-1-naphthols **A** were transformed into nonaflates **B** to perform subsequent intramolecular C–H bond arylation using a combination of Pd<sub>2</sub>(dba)<sub>3</sub>, SPhos ligand, K<sub>3</sub>PO<sub>4</sub> as the base, in DMA to afford the fluoranthenes **C** in good yields. Interestingly, excellent site selectivities (>99:1) were observed in the synthesis of fluoranthene bearing *meta* substituents and the C–H bond arylation occurred at the less sterically hindered position.

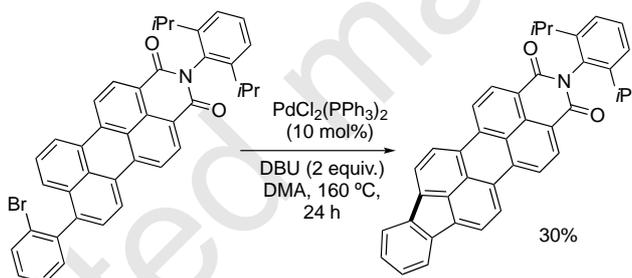


[a] From 3-bromo-*N,N*-dimethylaniline using  $\text{PdCl}_2(\text{PCy}_3)_2$  (10 mol %),  $\text{Cs}_2\text{CO}_3$  (3.6 equiv), DMF, 110 °C, 18–24h. [b] >99:1

Scheme 11. Three-Steps Synthesis of Fluoranthenes through Pd-Catalyzed Inter- and Intramolecular C–H Arylations

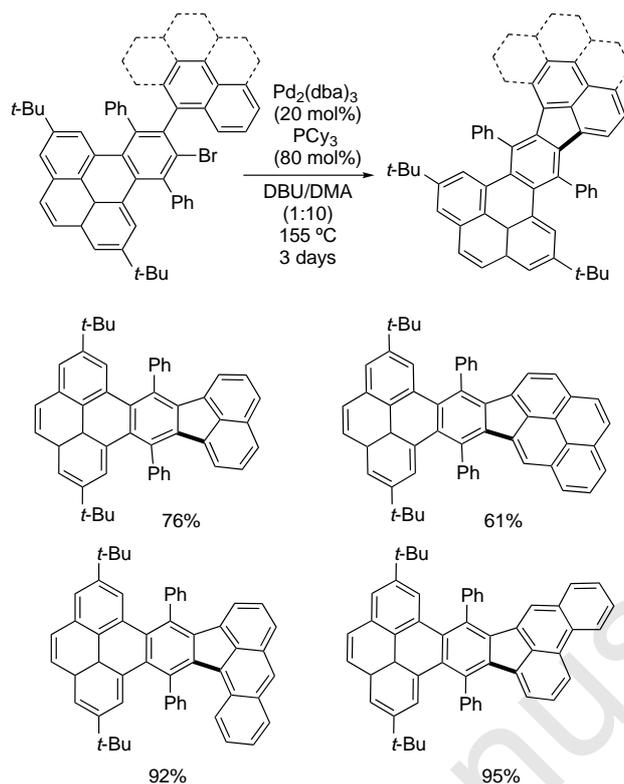
### b) Pd-Catalyzed 5-Membered Ring C–H Bond Arylations with Aryl Halides

In 2005, Müllen *et al* reported a variant of the Pd-catalyzed triflate-arene 5-membered ring cyclization using an aryl bromide instead of an aryl triflate (Scheme 12).<sup>35</sup> They were able to synthesize an indenoperylene dicarboximide in moderate 30% yield using  $\text{PdCl}_2(\text{PPh}_3)_2$  as catalyst in the presence of DBU as base in DMA.



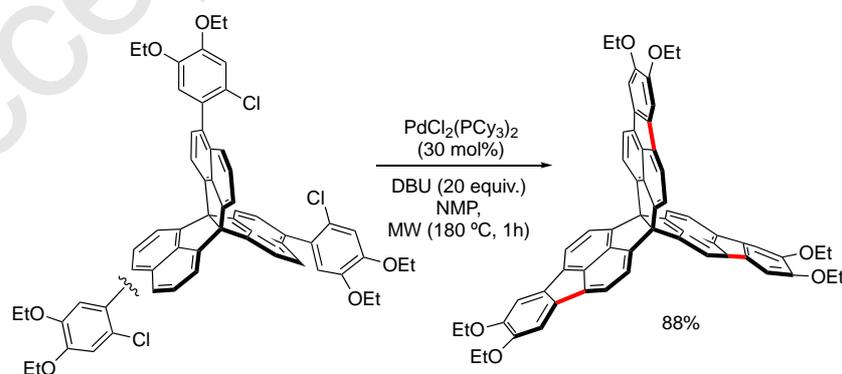
Scheme 12. Synthesis of Core-Extended Perylene Carboximide Dye Containing an Indenoperylene Unit

In 2016, a similar Pd-catalyzed 5-membered ring intramolecular C–H bond arylation was employed by Xiao, Song and co-workers for the preparation of a novel family of unsymmetrical twistacene analogs (Scheme 13).<sup>36</sup> The annulation reactions occurred in good yields with 1-naphthyl, 1-pyrenyl, 1-anthracenyl and 9-phenanthrenyl substituted twistacenes using 20 mol% of  $\text{Pd}_2(\text{dba})_3$  as catalyst associated with 80 mol% of  $\text{PCy}_3$  in the presence of DBU as base in DMA. These twistacene analogs emitted strong solution fluorescence covering a wide range from cyan to yellow.



Scheme 13. Synthesis of Twistacene Analogs *via* Pd-Catalyzed Intramolecular C–H Bond Arylations

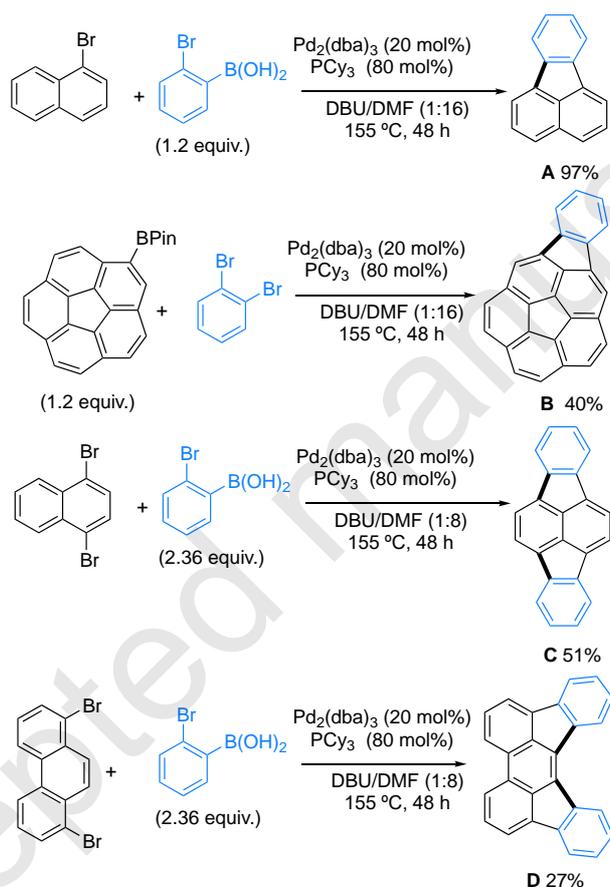
In 2016, the Pd-catalyzed intramolecular reaction for access to 5-membered rings has been employed by Hirao, Kubo and co-workers for the preparation of a novel  $\pi$ -extended trinaphtho[3.3.3]propellane derivative (Scheme 14).<sup>37</sup> The three fold cyclization of a mixture of isomers of 3,10,15-/3,10,16-tris(2-chloro-4,5-diethoxyphenyl)trinaphtho[3.3.3]propellane intermediate was carried out using 30 mol%  $\text{PdCl}_2(\text{PCy}_3)_2$  catalyst in the presence of distilled DBU in NMP at  $180\text{ }^\circ\text{C}$  under microwave irradiation to give the PAH in 88% yield. Interestingly, the authors showed that this propellershaped molecule exhibited intra- and inter-molecular electronic communications among the fluoranthene moieties.



Scheme 14. Synthesis of a Trinaphtho[3.3.3]propellane *via* Pd-Catalyzed Intramolecular C–H Bond Arylation

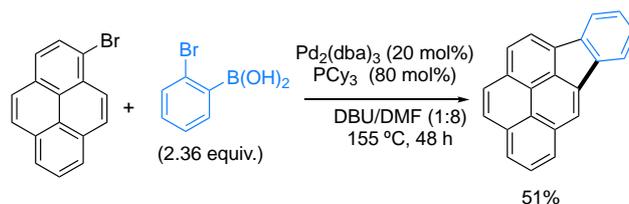
### c) Pd-Catalyzed Cross-Coupling Reaction – C–H Bond Annulation

In 2003, de Meijere and co-workers optimized the conditions for the Suzuki-type coupling cascade reaction for the synthesis of indeno[1,2,3]-annulation of polycyclic aromatic hydrocarbons (Scheme 15).<sup>38</sup> They found that in the presence of a huge amount of  $\text{Pd}_2(\text{dba})_3/\text{PCy}_3$  as catalyst in DMF with DBU as base, 1-bromonaphthalene reacted with 2-bromobenzeneboronic acid as the annelation partner to afford fluoranthene in high yield. Then, they applied this cross-coupling-cyclization cascade to other substrates such as pinacol corannuleneboronate with 1,2-dibromobenzene, or 1,4-dibromonaphthalene with 2-bromobenzeneboronic acid.



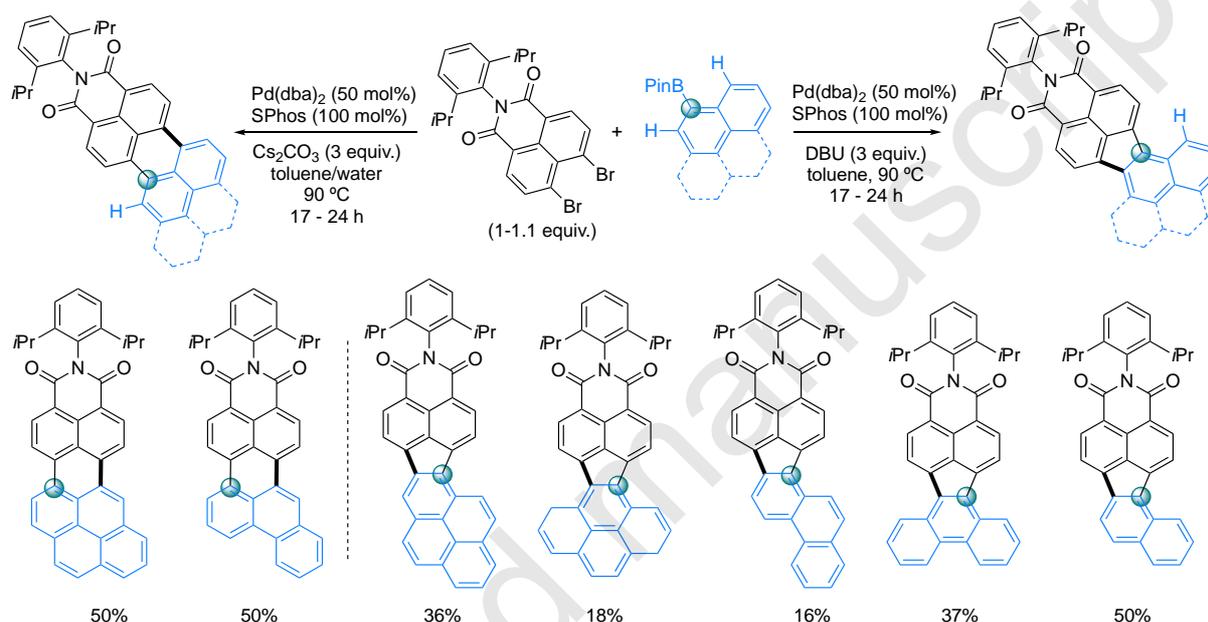
Scheme 15. Pd-Catalyzed Suzuki-Type Coupling Cascade for the Preparation of Indeno[1,2,3]-Annelation of Polycyclic Aromatic Hydrocarbons

Later, Scott and co-workers applied this Suzuki-annulation cascade reaction for the preparation of a monoindenopyrene from 1-bromopyrene (Scheme 16).<sup>39</sup>



Scheme 16. Pd-Catalyzed Suzuki-Type Coupling Cascade for the Synthesis of a Monoindenopyrene

In 2017, Würthner and co-workers employed a similar annulation protocol for the synthesis of polycyclic aromatic dicarboximides (Scheme 17).<sup>40</sup> They investigated the Pd-catalyzed cross-coupling annulation reaction of a dibrominated naphthalimide with arylboronic acid pinacol esters using Pd(dba)<sub>2</sub> as catalyst and Cs<sub>2</sub>CO<sub>3</sub> or DBU as base, in toluene. Interestingly, they discovered that the use of an inorganic base (Cs<sub>2</sub>CO<sub>3</sub>) in these cascade reactions led exclusively to 6-membered ring annulation, while the use of organic base (DBU) afforded the corresponding 5-membered ring annulated products. Notably, a very high loading in palladium (50 mol%) was required for both reaction conditions.



Scheme 17. Synthesis of Polycyclic Aromatic Dicarboximides *via* Pd-Catalyzed Base-Selective Annulation of Dibromonaphthalimide with Aryl Boronate Esters

They proposed that the switch of selectivity is due to a different mechanism during the C–H bond activation/functionalization. In the presence of Cs<sub>2</sub>CO<sub>3</sub>, the reaction occurred *via* a Heck-type reaction, while the use of DBU favors CMD or SEAr type pathways (Figure 4).<sup>40</sup>

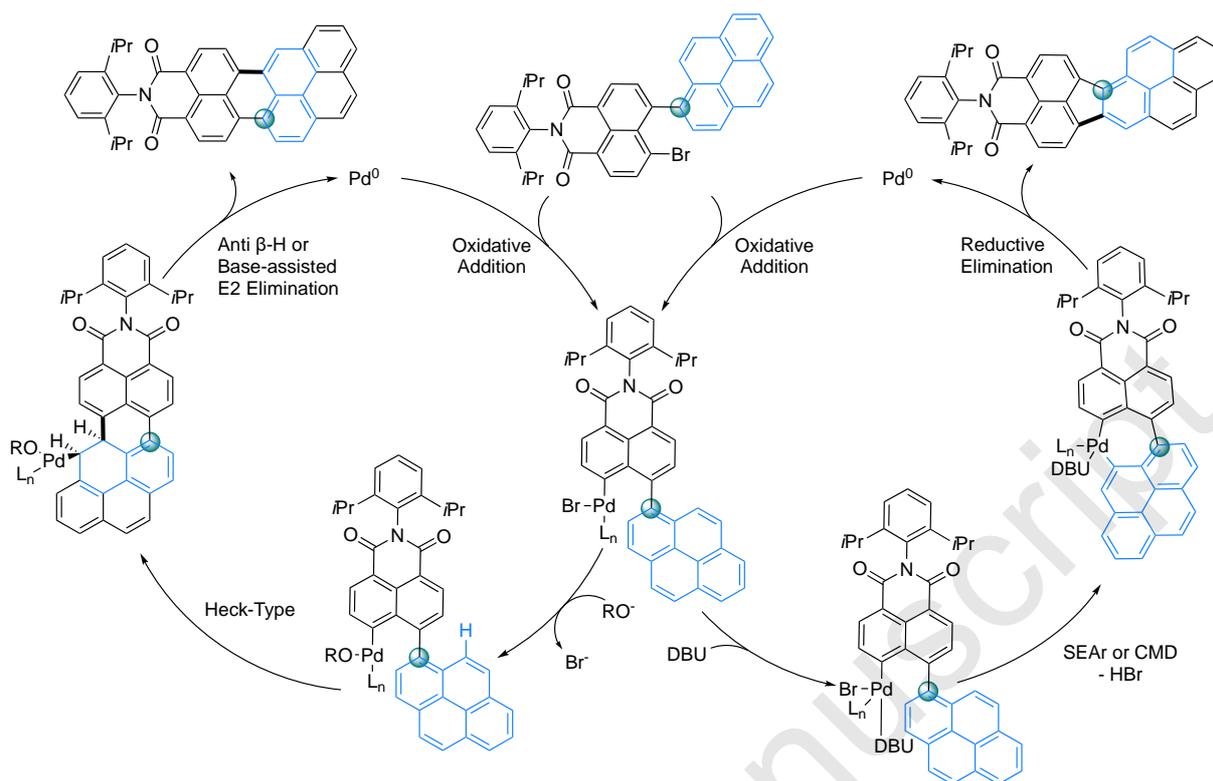
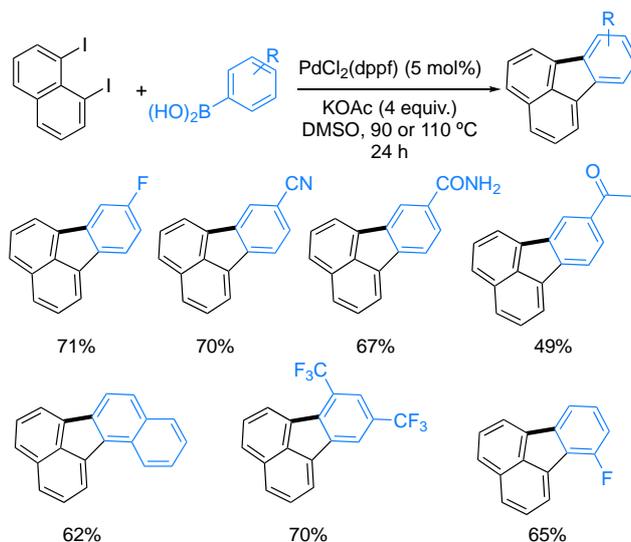


Figure 4. Proposed Mechanisms for Pd-Catalyzed Base-Selective 6- Versus 5-Membered Ring Annulations

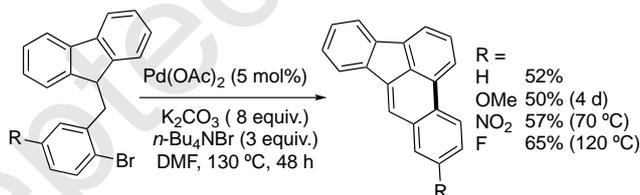
In 2017, Metin, Türkmen and co-workers reported the synthesis of fluoranthene derivatives *via* one-pot tandem Suzuki–Miyaura couplings followed by C–H bond annulation (Scheme 18).<sup>41</sup> Coupling reactions between 1,8-diiodonaphthalene and substituted arylboronic acids in the presence of 5 mol% PdCl<sub>2</sub>(dppf) associated to KOAc as base in DMSO afforded the fluoranthene derivatives. A wide variety of *para*-, *meta*- and *ortho*-substituted aryl boronic acids has been successfully employed. However, this reaction was limited to the use of 1,8-diiodonaphthalene. Moreover, the authors demonstrated that this annulation reaction also proceeded using heterogeneous catalysis such as reduced graphene oxide (rGO)-CuPd nanocatalyst, which can be easily recycled.



Scheme 18. Synthesis of Fluoranthenes through One-Pot Pd-Catalyzed Suzuki–Miyaura Couplings – Intramolecular C–H Bond Arylations

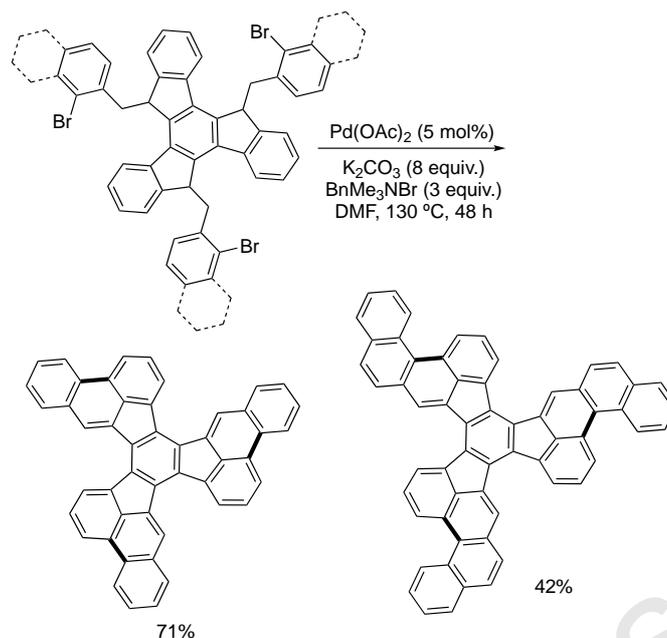
### 2.2.2. Synthesis of Bowl-Shaped PAHs

Echavarren and co-workers reported the synthesis of benz[*e*]acephenanthrylenes *via* the intramolecular C–H bond arylation of fluorenes substituted by a 2-bromobenzyl at C9 position using 5 mol% Pd(OAc)<sub>2</sub> in the presence of K<sub>2</sub>CO<sub>3</sub> as base and *n*-Bu<sub>4</sub>NBr in DMF at 130 °C (Scheme 19).<sup>42</sup> Depending on the substituents on the aryl bromide, the reaction proceeded more or less efficiently due to the oxidative addition rate of the C–Br bond to Pd(0). The reaction involved a C–H bond arylation step followed by a rearomatization.



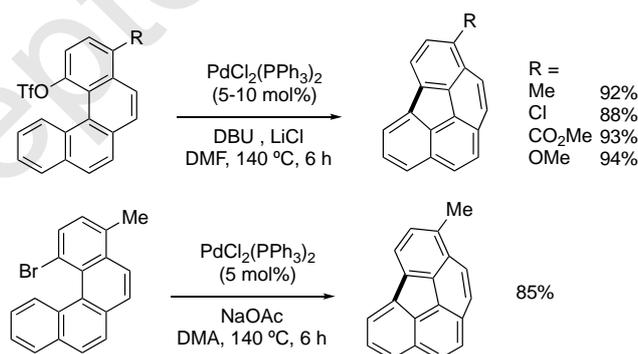
Scheme 19. Synthesis of Benz[*e*]acephenanthrylene Derivatives *via* Palladium-Catalyzed Intramolecular C–H Bond Arylation

Echavarren and co-workers extended this reaction to truxene unit for the synthesis of crushed fullerene derivatives by palladium-catalyzed three-fold C–H bond arylation–rearomatization (Scheme 20).<sup>43-45</sup>



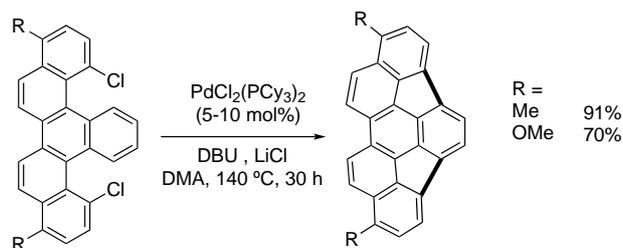
Scheme 20. Synthesis of “Crushed Fullerenes” through Palladium-Catalyzed Intramolecular C–H Bond Arylations

In 2000, Shelvin and co-workers reported the synthesis of benzo[*ghi*]fluoranthenes by palladium-catalyzed intramolecular arylation of benzo[*c*]phenanthren-1-yl triflates, which were synthesized in 3-4 steps *via* photolysis of stilbene derivatives (Scheme 21, top).<sup>46</sup> These coupling reactions proceeded smoothly in the presence of various substituents including strong electron donors using  $\text{PdCl}_2(\text{PPh}_3)_2$  as catalyst in the presence of DBU as base in DMF at 140 °C. The authors demonstrated that a 1-bromobenzo[*c*]phenanthrene also undergoes palladium-catalyzed intramolecular C–H bond arylation for the formation of a 5-membered ring using more classical NaOAc/DMA system (Scheme 21, bottom).



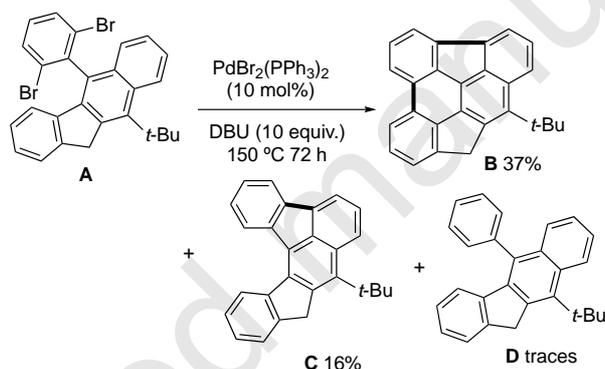
Scheme 21. Synthesis of Benzo[*g,h,i*]fluoranthenes by Palladium-Catalyzed Intramolecular C–H Bond Arylations

The same group also reported the synthesis of bowl-shaped fullerene fragments, as indaceno[3,2,1,8,7,6-*p,q,r,s,t,u,v*]picenes, by a double palladium-catalyzed intramolecular C–H bond arylation using similar reaction conditions (Scheme 22).<sup>47</sup> Based on X-ray analysis, the authors demonstrated that such strained molecules display a local maximum curvature slightly larger than that in corannulene (8.4°), and about 3° smaller than that in C<sub>60</sub>.



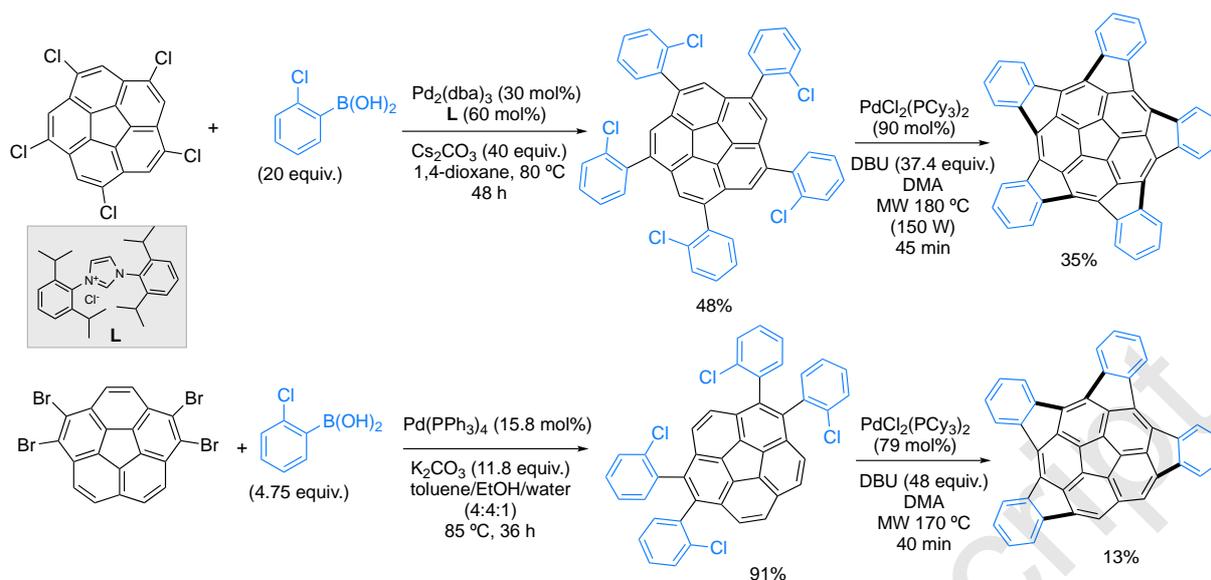
Scheme 22. Synthesis of Bowl-Shaped Fullerene Fragments by Palladium-Catalyzed Intramolecular C–H Bond Arylations

In 2006, Wang *et al.* succeeded to prepare bowl-shaped polycyclic aromatic hydrocarbons *via* Pd-catalyzed intramolecular arylation reactions with the simultaneous formation of 5- and 6-membered rings (Scheme 23).<sup>48</sup> 5 steps were required to prepare the key intermediate 5,6-dibromophenyl)-10-(1,1-dimethylethyl)-11H-benzo[*b*]fluorene (**A**), which was treated with 10 mol % of PdBr<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> in the presence of DBU to produce the buckybowl **B**. Notably, reductive debromination either on one side or on both sides also occurred, giving rise to the monocyclized hydrocarbon **C** as a minor product and a small amount of **D**.



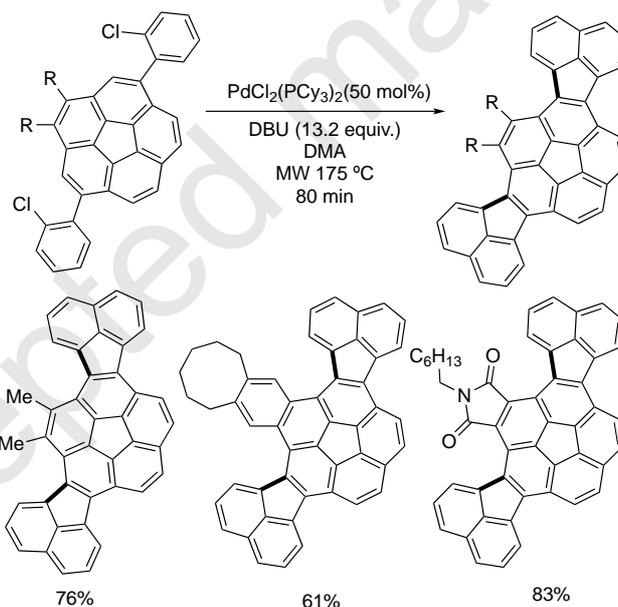
Scheme 23. Synthesis of Bowl-Shaped Polycyclic Aromatic Hydrocarbons by Palladium-Catalyzed 5- and 6-Membered Ring Intramolecular C–H Bond Arylations

In 2007, Scott's group achieved the synthesis of pentaindenocorannulene and tetraindenocorannulene from 1,3,5,7,9-pentachlorocorannulene or 1,2,5,6-tetrabromocorannulene with 2-chlorophenylboronic acid using their previously reported conditions,<sup>38</sup> i.e., Suzuki coupling followed by a C–H bond annulation in a two steps procedure (Scheme 24).<sup>49, 50</sup> Interestingly, these two bowl-shaped PAHs have curvatures surpassing that of C<sub>60</sub>. A large amount of 2-chlorophenylboronic acid was required to prepare the intermediates *via* one-pot five or four Suzuki couplings. The five or four annulation reactions were performed in one-pot using nearly a stoichiometric amount of palladium catalyst to afford the  $\pi$ -extended aromatics in low yields. Later, they employed this strategy for the preparation of a wide family of modified indenocorannulenes.<sup>51</sup>



Scheme 24. Application of Pd-Catalyzed Suzuki Coupling Followed by C–H Bond Annulation for the Synthesis of Pentaindenocorannulene and Tetraindenocorannulene

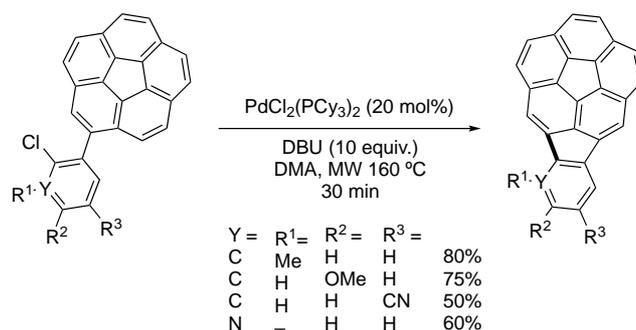
This synthetic scheme was later employed by Baldrige, Siegel and co-workers for the preparation of dimethyldiindenocorannulene, cyclooctendiindenocorannulene and heptyldiindenocorannulene maleimide (Scheme 25).<sup>52</sup>



Scheme 25. Application to the Preparation of Diindenocorannulenes

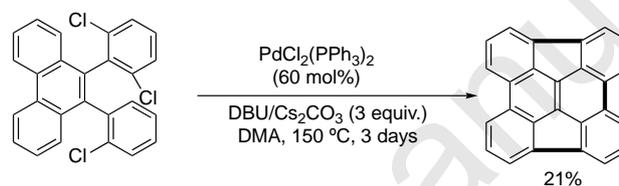
Remarkably, the same group demonstrated that in contrast to the chiral corannulenes, periannulated corannulenes, such as indenocorannulenes, shown increased barriers for bowl-to-bowl inversion that open new strategies for the design of stable chiral atropisomeric bowls.<sup>53</sup> Using the previous synthetic scheme, they were able to prepare an array of such chiral atropisomeric indenocorannulenes (Scheme 26). However, resolution of the enantiomers by

high-performance liquid chromatography over chiral support phases should be conducted in order to obtain optically active bowls.



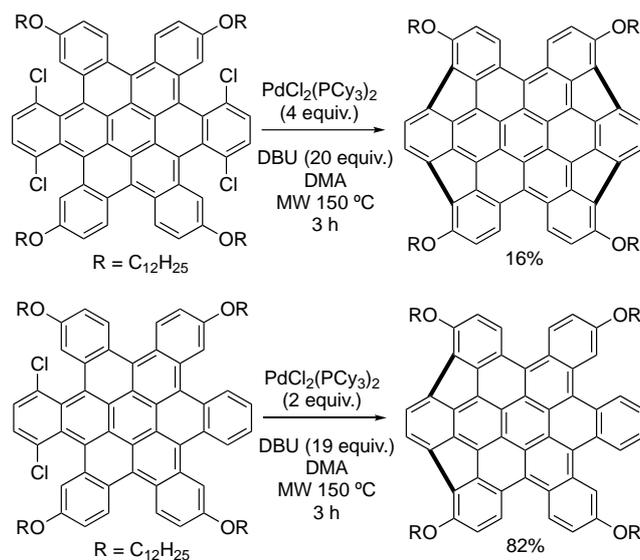
Scheme 26. Synthesis of Chiral Atropisomeric Indenocorannulene Bowls

Diindeno[1,2,3,4-*defg*;10,20,30,40-*mno*p]chrysene can also be prepared in around 20% yield from 9-(2-chlorophenyl)-10-(2,6-dichlorophenyl)phenanthrene by palladium-catalyzed three fold intramolecular arylations, as demonstrated by Wu and co-workers (Scheme 27).<sup>54</sup>



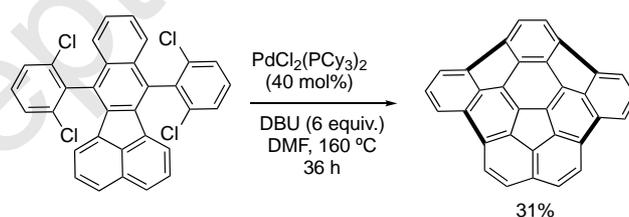
Scheme 27. Synthesis of Diindeno[1,2,3,4-*defg*;10,20,30,40-*mno*p]chrysene

In 2010, Steigerwald, Nuckolls and co-workers achieved the synthesis of a highly non-planar hexabenzocoronene derivative in very low yield (16%) *via* the *in-situ* formation of four 5-membered rings through Pd-catalyzed four intramolecular C–H bond arylations using 4 equivalents of PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> as catalyst associated to DBU as base in DMA (Scheme 28, top).<sup>55</sup> The incorporation of *n*-dodecyloxy hydrocarbon side-chains increased the solubility. In contrast, when only a double ring-closure was engaged, the reaction proceeded in a higher yield of 82% (Scheme 28, bottom).



Scheme 28. Synthesis of Bowl-Shaped Hexabenzocoronenes *via* Pd-Catalyzed Multiple C–H Bond Intramolecular Arylations

In 2011, Wu and co-workers introduced 5-membered rings into  $sp^2$  hexagonal networks for the formation of aromatic bowls, which are subunits of buckminsterfullerene (Scheme 29).<sup>56</sup> Such corannulene fragments, so-called mixed buckybowl are obtained from benzo[*k*]fluoranthene, which is prepared *via* Pd-catalyzed [(2 + 2) + 2] cycloaddition reaction of 1,8-bis((2,6-dichlorophenyl)ethynyl)naphthalene with iodobenzene. In the presence of 40 mol%  $PdCl_2(PCy_3)_2$  as catalyst and DBU as base, four cyclizations occurred to generate the desired buckybowl in 31% yield. The authors also quantified the curvature of this buckybowl with the determination of pyramidalization angle (POAV) from the crystallographic structure. This corannulene fragments exhibited an POAV angle of 12.75°. As a comparison, the values of planar benzene and  $C_{60}$  are observed to be 0° and 11.6°



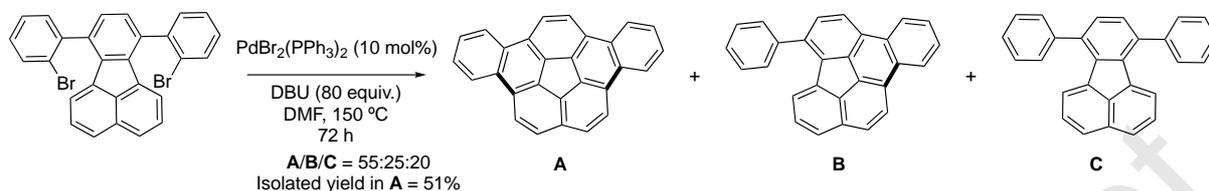
Scheme 29. Pd-Catalyzed Four Intramolecular C–H Bond Arylations for the Preparation of a Highly Curved Buckybowl Containing Corannulene

## 2.3. Formation of 6-Membered Rings by Pd-Catalyzed C-H Bond Arylation

### 2.3.1. Synthesis of Fluoranthene Derivatives and Bowl-Shaped PAHs

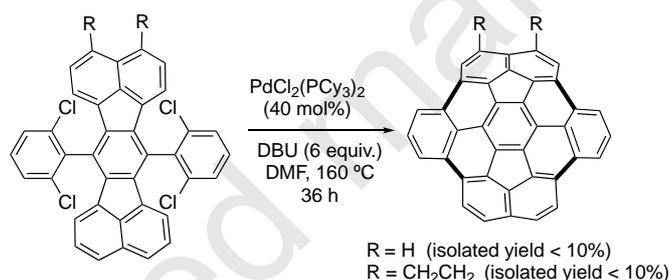
In 2000, Scott and co-workers demonstrated that the synthesis of dibenzo[*a,g*]corannulenes can be performed from 7,10-di(2-bromophenyl)-fluoranthene in 51% yield *via* Pd-catalyzed two-fold intramolecular 6-membered ring C–H bond arylation using 10 mol% of  $PdBr_2(PPh_3)_2$  in

the presence of a large excess amount of DBU as base in DMF (Scheme 30).<sup>57</sup> Notably, previous protocols to prepare dibenzo[*a,g*]corannulene involved flash vacuum pyrolysis, which suffer from several drawbacks: i) low to modest yields, ii) very poor functional group tolerance, iii) side-reactions due to the high temperatures employed (1000-1100 °C).



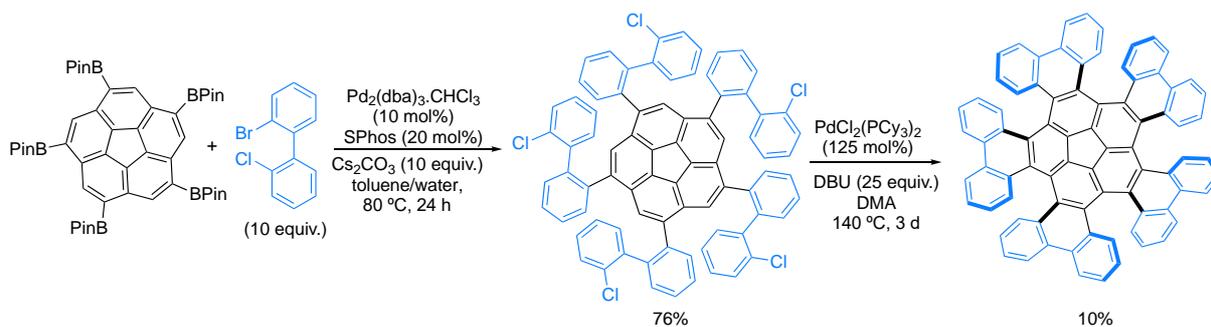
Scheme 30. Synthesis of Dibenzo[*a,g*]corannulene via Palladium-Catalyzed Two-Fold Intramolecular C–H Bond Arylations

Wu and co-workers reported in 2013 the synthesis of highly curved bowl-shaped fragments of fullerenes via the incorporation of two 5-membered rings into  $\text{sp}^2$  hexagonal networks (Scheme 31).<sup>58, 59</sup> The key step is the one-pot formation of four C–C bonds via intramolecular 6-membered ring C–H bond arylations using 20 mol% of  $\text{PdCl}_2(\text{PCy}_3)_2$  in the presence of 6 equivalents of DBU. However, the bowl-shaped PAHs were isolated in very poor yields (around 10%).



Scheme 31. Preparation of buckybowls via Pd-Catalyzed Four Intermolecular C–H Bond Arylations

In 2018, Itami, Segawa et al. succeed in the preparation of an original structure of quintuple [6]helicene with a corannulene core from corannulene in three steps including a Pd-catalyzed five-fold intramolecular direct arylation (Scheme 32).<sup>60</sup> Firstly, they performed a five-fold Suzuki–Miyaura coupling of pentaborylcorannulene (with 2-bromo-2'-chlorobiphenyl to afford the key intermediate. Then, this intermediate was heated in DMA at 140 °C over 3 days in the presence of 1.25 equivalent of  $\text{PdCl}_2(\text{PCy}_3)_2$  and 10 equivalents of DBU to generate the quintuple [6]helicene with a corannulene in 10% yield. Notably, previous strategy involving oxidative cyclization (Scholl reaction) of pentakis(biphen-2-yl)corannulene failed to deliver the quintuple [6]helicene, but gave warped nanographenes containing 6- and 7-membered rings.<sup>61</sup>



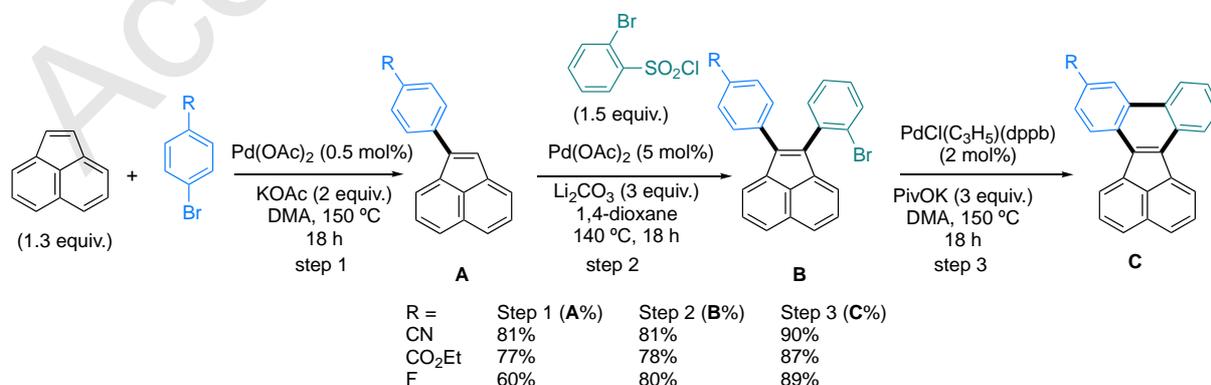
Scheme 32. Pd-Catalyzed Five-Fold Intramolecular Direct Arylation for the Synthesis of a [6]Helicene

In 2016, Segawa, Itami *et al.* employed their Pd-catalyzed annulative  $\pi$ -extension reaction technology to corannulene using silicon-bridged aromatics as  $\pi$ -extending agents to produce phenanthro[9,10-*a*]corannulene in one-step (Scheme 33).<sup>62</sup>



Scheme 33. Preparation of Phenanthro[9,10-*a*]corannulene using Pd-Catalyzed Annulative  $\pi$ -Extension of Corannulene

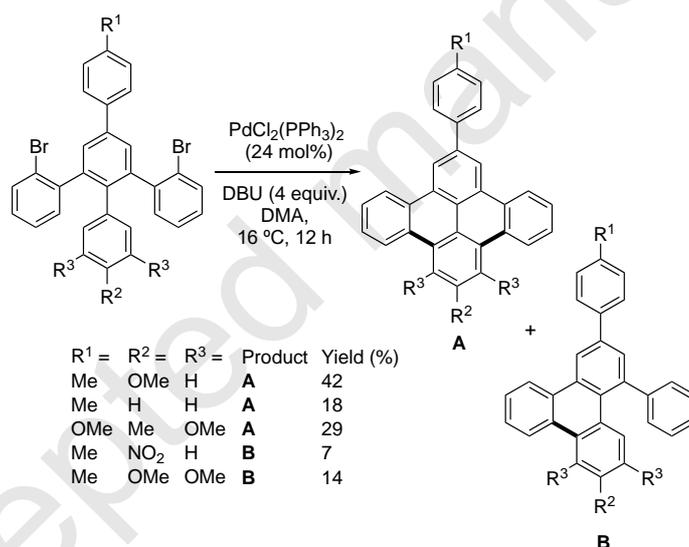
In 2018, our group reported the synthesis of dibenzo[*j,l*]fluoranthenes from acenaphthylene *via* three successive C–H bond arylations (Scheme 34).<sup>63</sup> Acenaphthylene was mono-arylated at C1-position using aryl bromides as aryl sources using phosphine-free Pd(OAc)<sub>2</sub>/KOAc catalytic system in DMA. The C2-arylations of 1-arylacenaphthylenes were more challenging and should be performed with more reactive benzenesulfonyl chlorides in the presence of 5 mol% Pd(OAc)<sub>2</sub> associated with Li<sub>2</sub>CO<sub>3</sub> as base in 1,4-dioxane. One major advantage of Pd-catalyzed desulfitative couplings is that they are tolerant toward C–halo bonds.<sup>64</sup> We took this advantage to introduce a 2-bromophenyl motif at C2-position of 1-arylacenaphthylene. Then, dibenzo[*j,l*]fluoranthenes were obtained in good yields through an intramolecular C–H bond arylation using 2 mol% of a diphosphine palladium catalyst and PivOK as base.



Scheme 34. Synthesis of Dibenzo[*j,l*]fluoranthenes *via* Pd-Catalyzed Successive C–H Bond Arylations

### 2.3.2. Synthesis of Triphenylenes and Related Derivatives

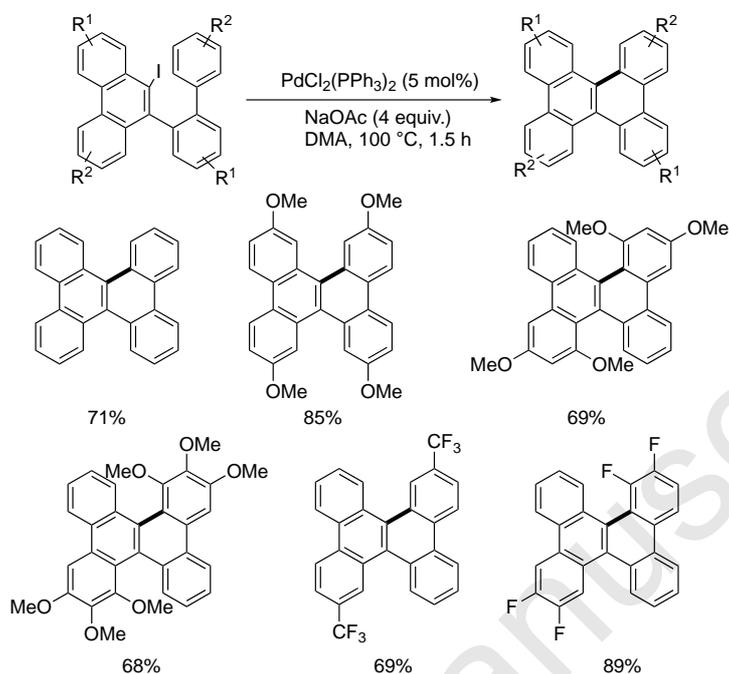
In 2003, Höger and co-workers were one of the first groups to employ palladium-catalyzed intramolecular C–H bond arylation to synthesize functionalized PAHs, such as dibenzo[*fg,op*]naphthalenes (Scheme 35).<sup>65</sup> The functionalized 1,2,3,5-tetraarylbenzenes containing properly located bromo groups were prepared from the condensation of pyrylium salts containing bromo substituents at the 2 and 2' positions with sodium 2-phenyl acetates.<sup>66</sup> Then, intramolecular C–H bond arylation was performed in the presence of PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub> associated with DBU (1,8-diazabicyclo(5.4.0)undec-7-ene) as base in DMA at 160 °C. Dibenzo[*fg,op*]naphthalenes were obtained in variable yields depending on the substitution pattern. In some case, the formation of minor amounts of the corresponding triphenylenes was observed. The authors also applied this methodology to the synthesis of monofunctionalized dibenzonaphthalenes *via* late stage transition-metal catalyzed C–C coupling reactions of dibenzo[*fg,op*]naphthalene triflate.<sup>67</sup>



Scheme 35. Synthesis of Alkoxy-Functionalized Dibenzo[*fg,op*]naphthalenes

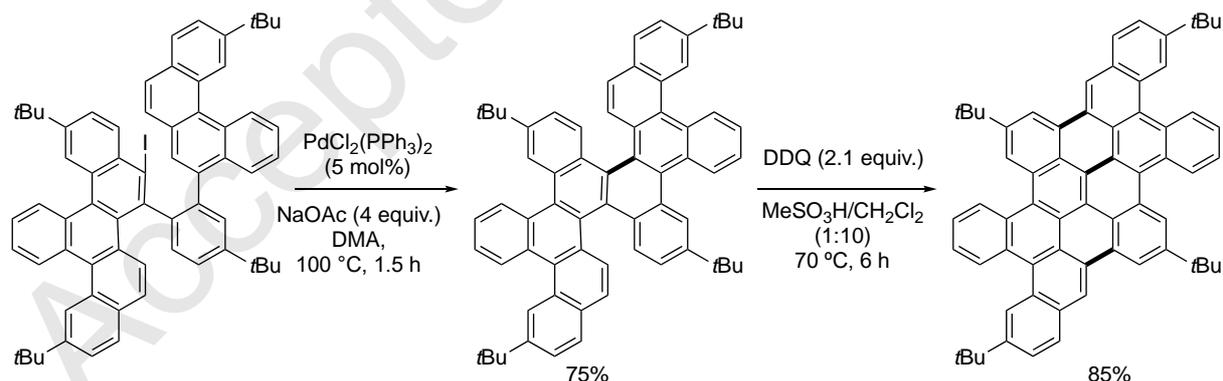
Liu and co-workers designed a new synthetic scheme for the preparation of dibenzo[*g,p*]chrysenes through palladium-catalyzed intramolecular C–H bond arylation using 5 mol% PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> in the presence of NaOAc as base in DMA at 100 °C (Scheme 36).<sup>68, 69</sup> When the aromatic ring which undergoes C–H bond activations bears electron-donating substituents, higher yields in dibenzo[*g,p*]chrysenes were obtained. However, the reaction seemed to be sensitive to steric factors. Interestingly, from difluorinated substrates a strong fluorine effect<sup>70-73</sup> was observed resulting in a high regioselectivity control at the *ortho* position

of the fluorine atom with an increase of the reactivity, as the desired dibenzo[*g,p*]chrysene was obtained in 89% yields.



Scheme 36. Synthesis of Functionalized Dibenzo[*g,p*]chrysenes by Palladium-Catalyzed Intramolecular C–H Bond Arylation

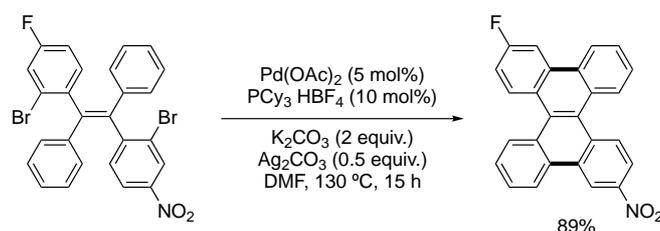
In continuous research efforts on the synthesis of large PAHs, Lui and co-workers reported the use for their previous methodology, namely palladium-catalyzed intramolecular C–H bond arylation, to access to dibenzo[*g,p*]chrysenes, which were again cyclized into large planar PAHs using DDQ-oxidation (Scheme 37).<sup>74</sup>



Scheme 37. Synthesis of Large Planar PAHs with Low  $\pi$ -Sextets by Palladium-Catalyzed Intramolecular C–H Bond Arylation Followed by DDQ-oxidation

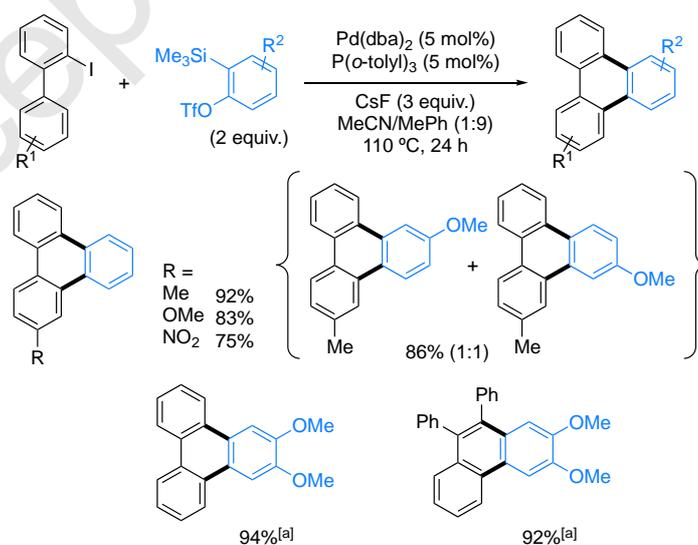
During their investigations on the addition of trimethylstanyllithium to diarylacetylenes, Tsuji, Nakamura and co-workers synthesized 2-bromo-4-fluoro-1-iodobenzene and 2-bromo-1-iodo-4-nitrobenzene, which undergo palladium catalyzed two-fold intramolecular C–H bond

arylation allowing the formation of a dibenzochrysene derivative in 89% yield as single isomer (Scheme 38).<sup>75</sup>



Scheme 38. Stereoselective Synthesis of a Dibenzochrysene Derivative by Palladium-Catalyzed Two-Fold Intramolecular C–H Bond Arylation

Based on their previous study on the synthesis of fluoren-9-ones through palladium-catalyzed annulation of arynes with 2-halobenzaldehydes,<sup>76</sup> in 2005, Larock and co-workers reported an elegant method for the preparation of fused polycyclic aromatics involving palladium-catalyzed annulation of arynes using 2-halobiaryls, in which an intramolecular C–H bond arylation occurred (Scheme 39).<sup>77</sup> Pd(dba)<sub>2</sub> associated with P(*o*-tolyl)<sub>3</sub> in the presence of CsF as base was found to promote the carboannulation of arynes (generated from *ortho*-(trimethylsilyl)phenyl triflate by the action of F<sup>−</sup> anion) by 2-iodobiphenyls. Triphenylene derivatives were obtained in high yields from 2-iodobiphenyl substituted at 4' position by Me, MeO and NO<sub>2</sub> groups. When the 4-methoxy-substituted aryne precursor (i.e., 4-methoxy-2-(trimethylsilyl)phenyl triflate) was employed, a mixture of two isomers was obtained in a 1:1 ratio. The authors mentioned this experiment as an evidence for the formation of an aryne intermediate. The reaction was also operative from 2-bromobiphenyl in comparable yield. Notably, carboannulation of arynes was also operative with vinylic halides, such as (2-bromoethene-1,1,2-triyl)tribenzene.



Scheme 39. Synthesis of Fused Polycyclic Aromatics by Palladium-Catalyzed Annulation of Arynes Using 2-Halobiaryls. [a] MeCN/MePh = 1:3.

The authors proposed two possible pathways differentiated by the first palladium oxidative addition step, which are depicted in Figure 5.<sup>77</sup> In left cycle, the Pd(0) undergoes oxidative cyclization with the aryne **A**, resulting from the desilylation of *ortho*-(trimethylsilyl)phenyl triflate promoted by CsF, to generate palladacycle **B**. Then, the reaction with 2-iodobiphenyl allows the formation of organopalladium intermediate **D**, which undergoes intramolecular C–H activation to generate the palladacycle **E**. Subsequent reductive elimination yields the annulation product and regenerates the Pd(0) catalyst. In the cycle on the right, oxidative addition of 2-iodo-biphenyl to Pd(0) firstly occurs to generate arylpalladium intermediate **C**, followed by reaction with the aryne derivative to afford intermediate **D**, then a similar pathway led to the desired triphenylene derivative.

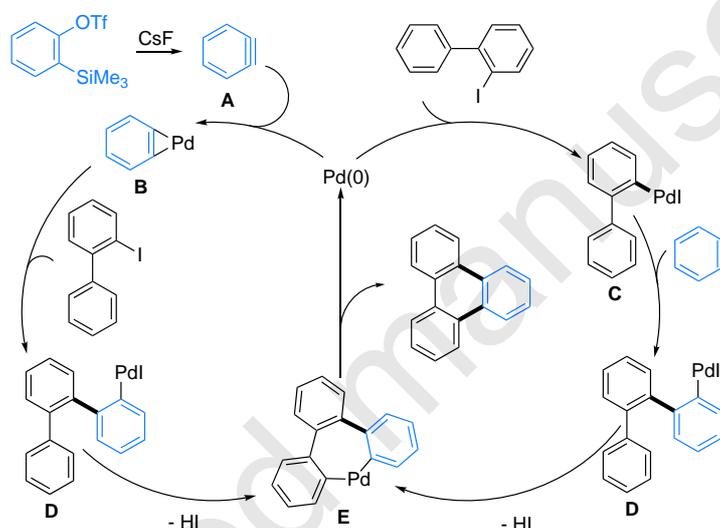
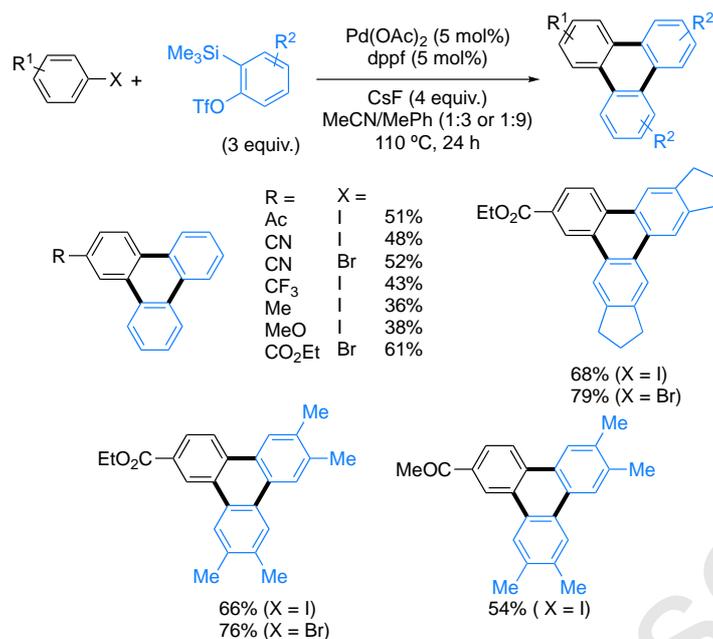


Figure 5. Proposed Mechanism for Palladium-Catalyzed Annulation of Arynes Using 2-Halobiaryls

Two years later, the same group extended the scope of this annulation reaction to the synthesis of biphenyl motif through palladium-catalyzed double annulation of aryne in “one-pot” (Scheme 40).<sup>78</sup> This strategy to generate polycyclic aromatics by the reaction of an aryl iodide and two aryne was inspired by a previous report by Miura on the synthesis of tetrasubstituted naphthalenes involving Pd-catalyzed double annulation of an internal alkyne.<sup>79</sup> Slightly modified reaction conditions resulting of the use of Pd(OAc)<sub>2</sub>/dppf instead of Pd(dba)<sub>2</sub>/P(*o*-tolyl)<sub>3</sub> as catalyst were employed to promote the double annulation process. Aryl halides bearing electron-withdrawing groups at the *para* position efficiently undergo this aryne double annulation process to generate moderate to good yields of the corresponding multisubstituted polycyclic aromatics; whereas electron-rich aryl halides were less reactive. However, only *para*-substituted aryl halides were employed, probably due to regioselectivity issues of the annulation. In most of the cases, aryl bromides gave better yields than the corresponding aryl iodides.



Scheme 40. Synthesis of Fused Polycyclic Aromatics *via* Palladium-Catalyzed Aryne Annulation by Aryl Halides

The proposed mechanism for this palladium-catalyzed double annulation process is shown in the Figure 6. Firstly, arylpalladium(II) **A** is formed through the oxidative addition of the aryl halide to the Pd(0) catalyst. Then, arylpalladium **A** coordinated to the aryne followed by the insertion of the aryne allows the formation of the biaryl palladium intermediate **B**. This process is reproduced once to form the triaryl palladium intermediate **C**. Intramolecular C–H bond activation affords the 7-membered ring palladacyclic intermediate **D**, which undergoes reductive elimination to generate the double annulation product in concert with the regeneration of the Pd(0) catalyst.

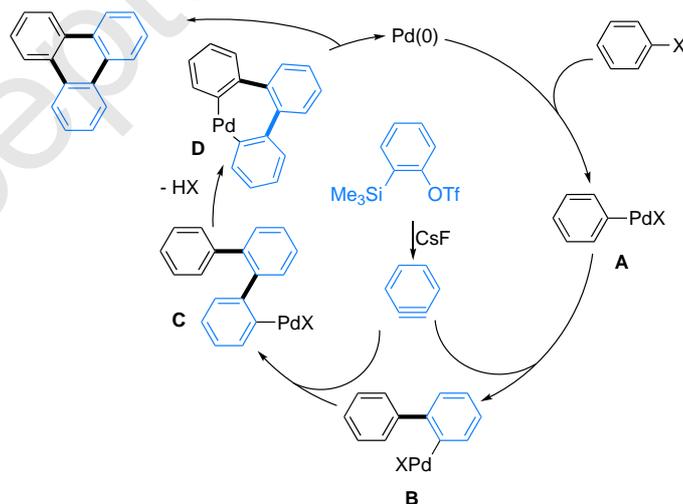
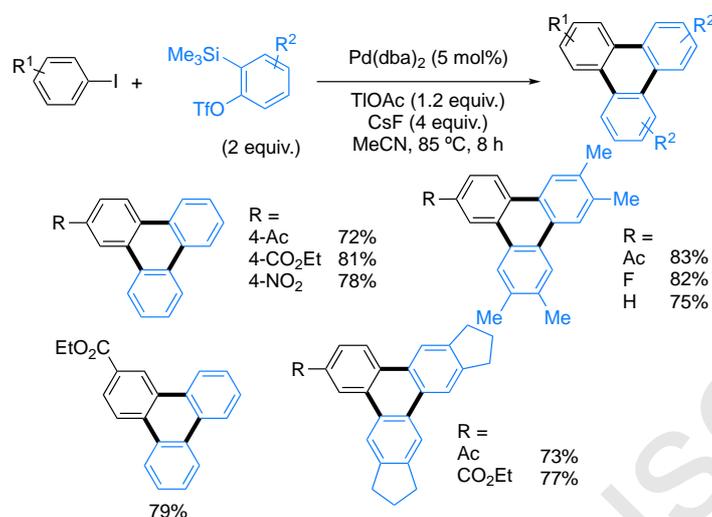


Figure 6. Proposed Mechanism for the Palladium-Catalyzed Double Annulation of Arynes by Aryl Halides

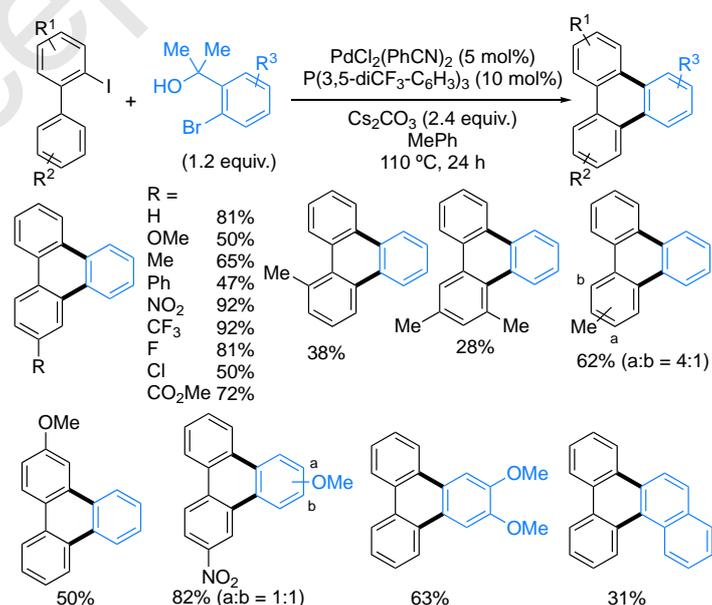
One year before, Cheng *et al.* had reported exactly the same reaction (Scheme 41).<sup>80</sup> Pd(dba)<sub>3</sub> under phosphine free conditions was employed as catalyst in the presence of CsF. The authors

found that the use of 1.2 equiv. of TIOAc remarkably improved the yield of the annulation reaction. Only electron-deficient aryl iodides were employed, and the same products were obtained whatever *para* or *meta* the substituent positions.



Scheme 41. Palladium-Catalyzed Carbopalladation and Carbocyclization of Arynes with Aryl Halides

In 2013, Nishihara and co-workers reported an alternative route for the preparation of triphenylene derivatives involving palladium-catalyzed annulation of *ortho*-iodobiphenyls with *ortho*-bromobenzyl alcohols (Scheme 42).<sup>81, 82</sup> In the presence of  $\text{PdCl}_2(\text{PhCN})_2$ , an electron deficient triaryl phosphine and  $\text{Cs}_2\text{CO}_3$  as base, the annulation of *ortho*-iodobiphenyls with *ortho*-bromobenzyl alcohols took place, through sequential decarbonylative coupling/intramolecular C–H arylation, allowing the formation of multisubstituted triphenylenes in moderate to high yields. Various substituents at all positions were tolerated, and when the substrate had two reaction sites, the less hindered C–H bond predominantly underwent the reaction.



Based on the detection of 2-bromo-*ortho*-terphenyl intermediate **D**, the authors proposed a mechanism involving two catalytic cycles (Figure 7). One of the cycles starts with the oxidative addition of *ortho*-iodobiphenyl to give arylpalladium iodide **A** followed by an exchange of ligand (iodide vs alkoxide) assisted by the base affording the aryl(alkoxy)-palladium **B**. The sequential  $\beta$ -carbon elimination delivers the diarylpalladium complex **C** with a release of acetone. Reductive elimination produces the 2-bromo-*ortho*-terphenyl intermediate **D** and then regenerates the Pd(0) catalyst. **D** is again engaged in oxidative addition to Pd(0) to generate **E**, which undergoes concerted metalation/deprotonation (CMD) process. The resulting 7-membered ring pallacycle **F** affords the desired triphenylene after reductive elimination.

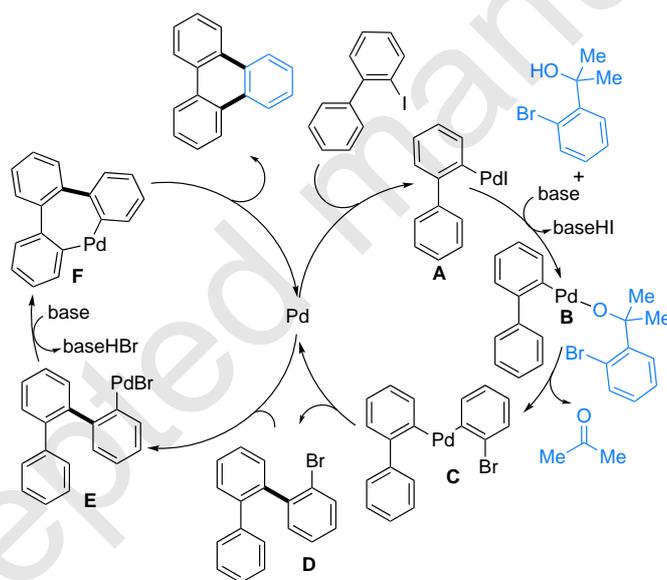
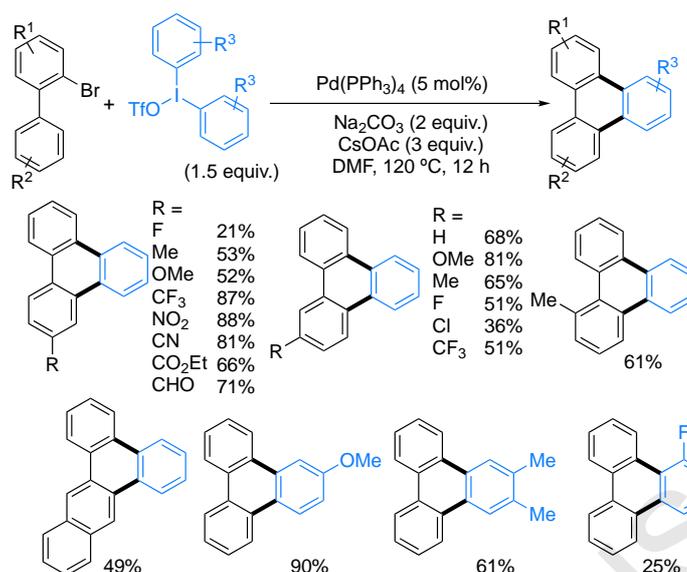


Figure 7. Proposed mechanism for Palladium-Catalyzed Annulation of *ortho*-Iodobiphenyls with *ortho*-Bromobenzyl Alcohols

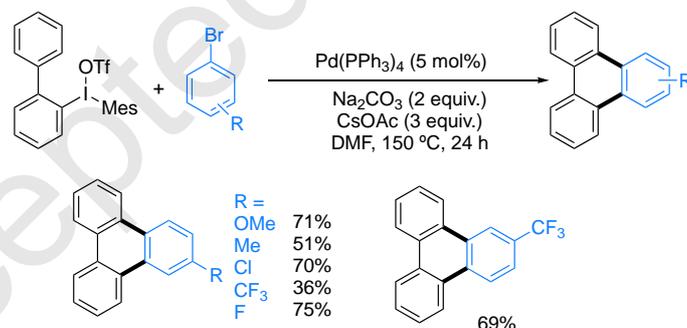
In 2018, Han, Wang and co-workers employed a similar strategy for the synthesis of triphenylene derivatives, albeit they used diaryliodonium salts as the “benzyne precursors” instead of *ortho*-bromobenzyl alcohols or *ortho*-(trimethylsilyl)phenyl triflates (Scheme 43).<sup>83</sup> A broad range of 2-bromobiphenyls substituted at *ortho*-, *meta*-, or *para*- positions (*e.g.*, methyl, methoxy, halogens, nitro, cyano, ester, trifluoromethyl, formyl or acyl groups) was well tolerated by the optimized reaction conditions with diphenyliodonium allowing the formation of triphenylenes in moderate to high yields. Other symmetrical diaryliodonium salts were

successfully employed; nevertheless, the electron-poor diaryliodonium salts often gave lower yields.



Scheme 43. Synthesis of Triphenylenes through Palladium-Catalyzed Annulation of *ortho*-Bromobiphenyls with Diaryliodonium Salts

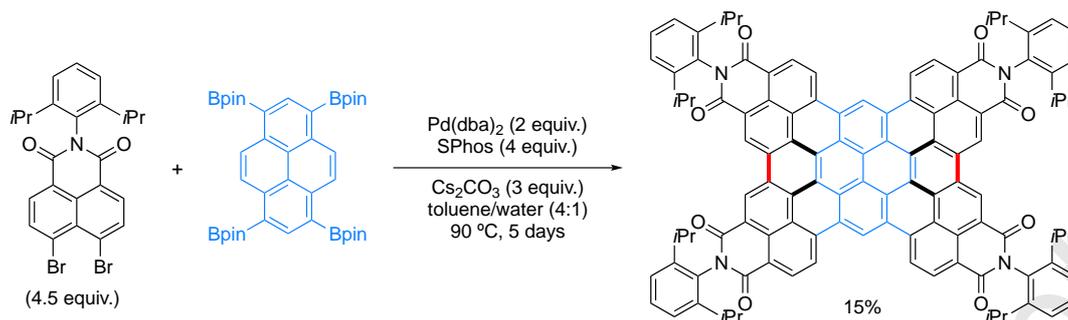
The authors also investigated the reverse reaction starting from 1,1'-biphenylmesityl iodonium triflates in the presence of aryl bromides (Scheme 44).<sup>83</sup> Several bromobenzene derivatives bearing both electron-donating (4-methoxy, 4-methyl and 3,4-dimethyl) and electron-withdrawing (4-chloro, 4-fluoro, 4-trifluoromethyl, 3-trifluoromethyl) groups were employed in this diarylation reaction to give the corresponding triphenylenes in moderate to good yields.



Scheme 44. Synthesis of Triphenylenes through Palladium-Catalyzed Annulation of 1,1'-Biphenylmesityl Iodonium Triflates with Bromobenzenes

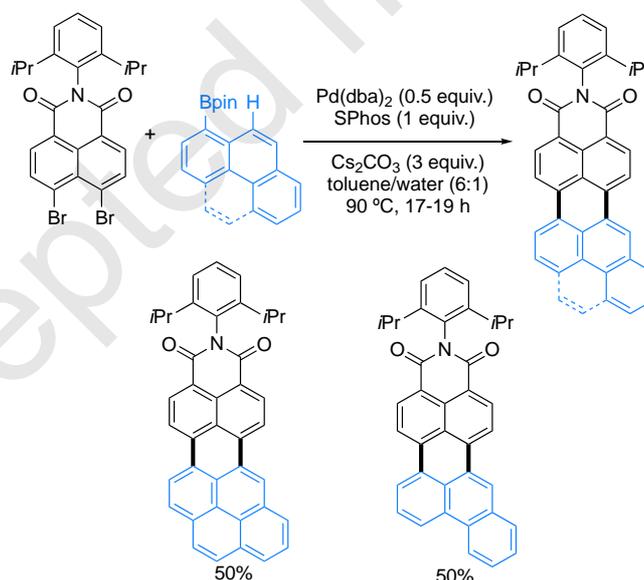
In 2016, Würthner and co-workers reported the one-pot synthesis of an electron-poor nanographene containing dicarboximide groups at the corner (Scheme 45).<sup>84</sup> The synthetic strategy involved palladium-promoted Suzuki–Miyaura cross-coupling followed by intramolecular C–H bond arylation and oxidative dehydrogenation at adjacent naphthalimide moieties to synthesize an electron-poor nanographene with 64 sp<sup>2</sup>-hybridized carbon atoms in one-pot starting from *N*-(2,6-diisopropylphenyl)-4,5-dibromo-1,8-naphthalimide and a

tetrasubstituted pyrene boronic acid ester. However, stoichiometric amount of palladium was used, and the desired PAH was obtained in only 15% yield.



Scheme 45. Palladium-Catalyzed One-Pot Synthesis of an Electron-Poor Nanographene

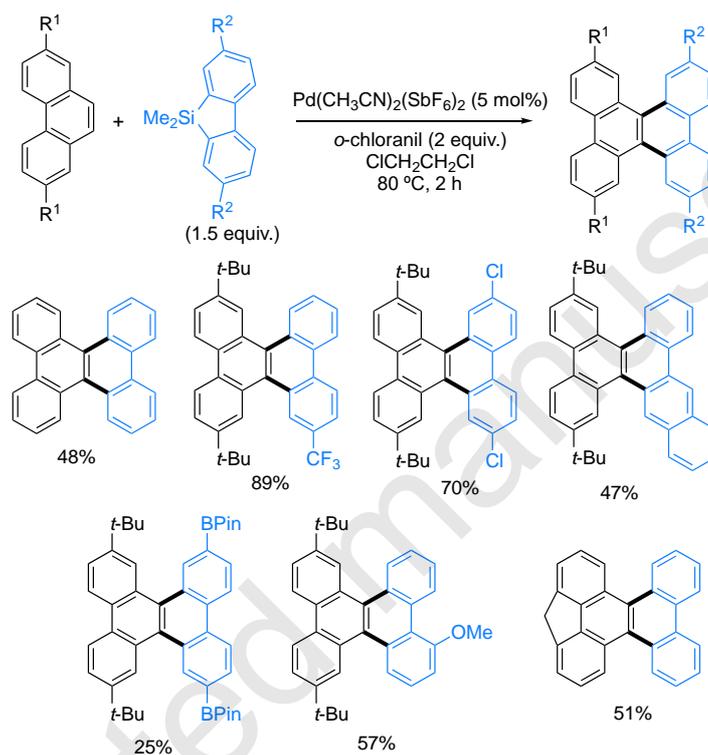
Later, the same group employed this annulation reaction of dibromonaphthalimide with different aryl boronate esters involving Suzuki–Miyaura cross-coupling in concert with C–H arylation to afford a series of 6-membered ring annulated electron-poor PAHs (Scheme 46).<sup>40</sup> The reaction from dibromonaphthalimide and 1-pyrene boronate ester or 1-phenanthrene boronate ester in the presence of  $\text{Cs}_2\text{CO}_3$  as base and 50 mol% palladium catalyst led exclusively to the formation of 6-membered ring annulated polycyclic aromatic dicarboximides in 50% yields. Interestingly the change of the base to DBU afforded the 5-membered ring annulated products (for more details see Scheme 17).



Scheme 46. Synthesis of Polycyclic Aromatic Dicarboximides by Palladium-Catalyzed C–C coupling Reactions of Dibromonaphthalimide with Different Aryl Boronic Acid Pinacol Esters

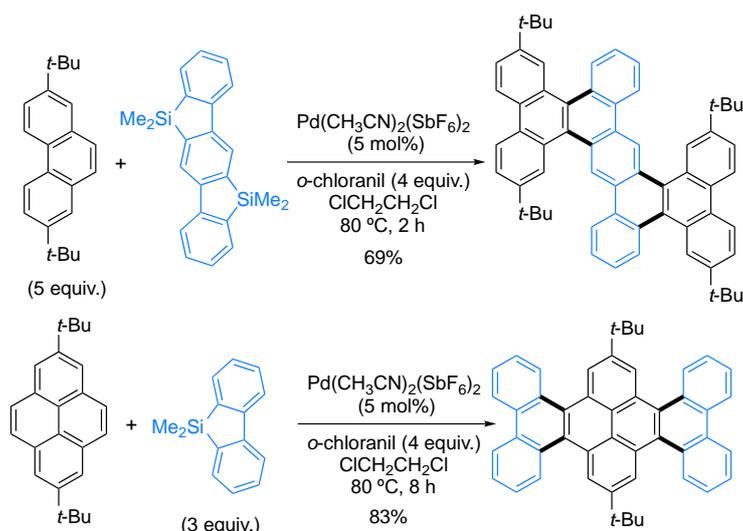
In 2015, Itami's group developed an annulative  $\pi$ -extension reactions, called APEX, of polycyclic aromatic hydrocarbons using silicon-bridged aromatics as  $\pi$ -extending agents (Scheme 47).<sup>85</sup> They applied their catalytic system for late-stage arylation of PAHs,<sup>86</sup> namely, Pd salts in the presence of 2 equivalents of *o*-chloranil, to the double C–H bond arylation of

triphenylenes leading to the formation of dibenzo[*g,p*]chrysene derivatives in one-pot. The authors demonstrated that the reaction is operative with structurally and electronically diverse silicon-bridged aromatics allowing the formation of the desired dibenzo[*g,p*]chrysenes in good-to-excellent yields with a completed K-region selectivity. Notably, the reaction was tolerant to C–Cl and C–BR<sub>2</sub> bonds allowing further transformations. They also shown that 2,20-bis(trimethylsilyl)-1,10-biphenyl and dimethyldibenzogermole were much less efficient  $\pi$ -extending agents, whereas dimethyldibenzostannole is not reactive.



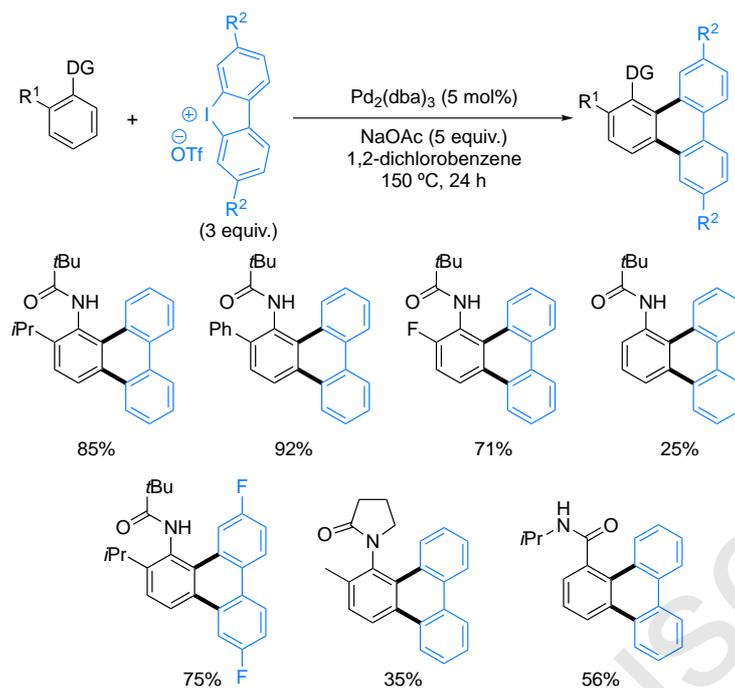
Scheme 47. Pd-catalyzed Annulative  $\pi$ -Extension Reactions of K-Region of Triphenylenes

In addition, they demonstrated the utility of this methodology by synthesizing a variety of nanographene ( $\pi$ -extended PAH) structures using a double annulative  $\pi$ -extension reaction from triphenylene or pyrene derivatives (Scheme 48).<sup>85</sup>



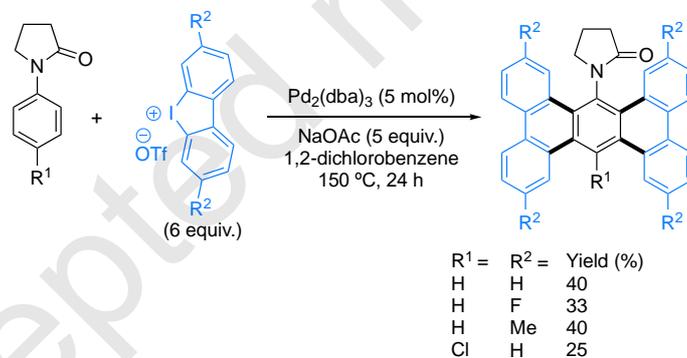
Scheme 48. Pd-catalyzed Double Annulative  $\pi$ -Extension Reactions of K-Region of Triphenylenes and Pyrenes

A similar strategy was later employed by Park, Hong *et al.* using diphenyleneiodonium salts as  $\pi$ -extending agents for the synthesis of triphenylene derivatives through palladium catalyzed 2- or even 4-fold C–H arylations (Scheme 49, and Scheme 50).<sup>87</sup> *Ortho*-substituted pivanilides undergo two-fold C–H arylation at C2 and C3 positions in the presence of  $\text{Pd}_2(\text{dba})_3$  as catalyst and NaOAc as base in 1,2-dichlorobenzene to afford triphenylene derivatives in good to high yields. When pivanilide was not substituted, a lower yield was observed. Benzamides and 1-phenylpyrrolidin-2-ones were also suitable substrates for this directed C–H bond functionalization leading to triphenylene derivatives in good yields. In addition, fluoro or methyl substituted diphenyleneiodonium salts displayed similar reactivity. On the other hand, the authors demonstrated the utility of these *N*-substituted triphenylenes by the incorporation of some of them into a graphene-based alcohol field effect transistor (FET) sensor for application as a chemical gas sensor and they showed a rapid and reversible response.



Scheme 49. Synthesis of Triphenylene Derivatives *via* Palladium-Catalyzed Two-Fold C–H Bond Arylation

Interestingly, when the reaction was performed from 1-phenylpyrrolidin-2-one in the presence of 6 equivalents of diphenyleneiodonium salts, a four-fold C–H bond arylation occurred to afford phenanthro[9,10-*b*]triphenylene derivatives in high yields (Scheme 50).<sup>87</sup>



Scheme 50. Synthesis of Phenanthro[9,10-*b*]triphenylene Derivatives *via* Palladium-Catalyzed Four-Fold C–H Bond Arylation

The authors proposed that bench-stable hypervalent iodine such as cyclic diaryliodonium salt undergoes successive single-electron reductions by Pd(0) to form X-Pd(II)-aryl complex **A**. Subsequently, cyclopalladation of the arene bearing a directing group affords **C**, which can undergo reductive elimination to give the triaryl iodide **D**. In the other cycle, oxidative addition, concerted metalation–deprotonation, and subsequent reductive elimination, regenerates Pd(0) and affords the desired triphenylene (Figure 8).<sup>87</sup>

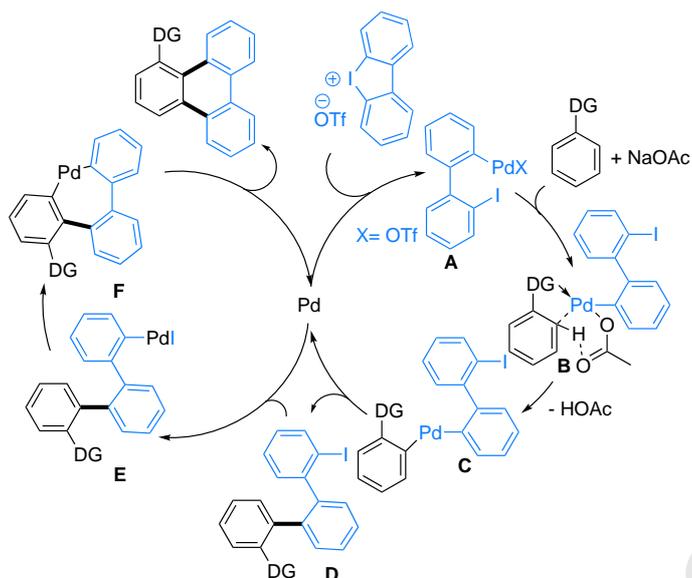
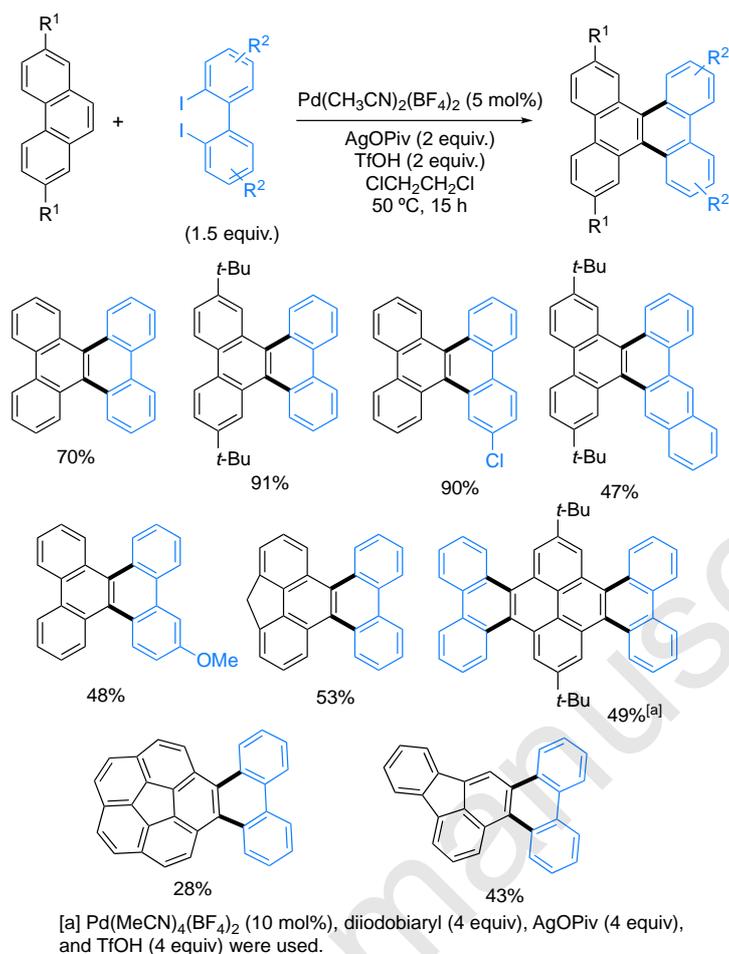


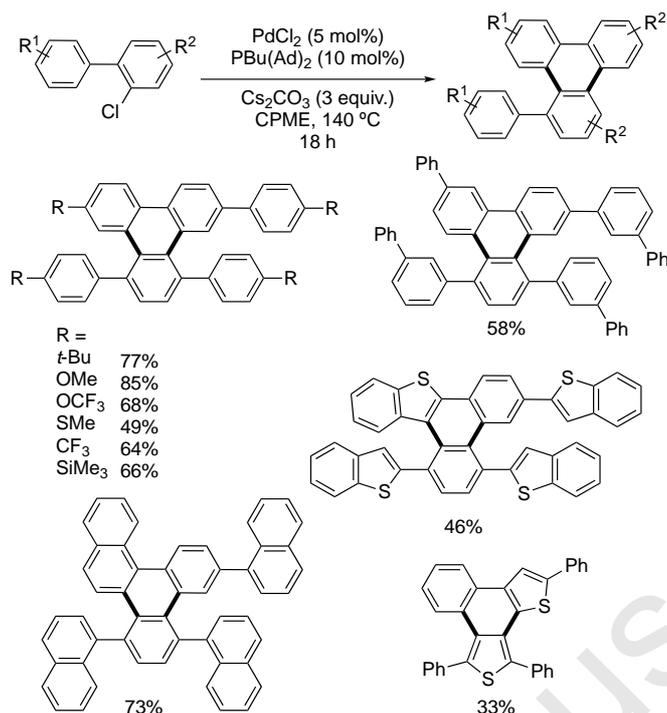
Figure 8. Proposed 2-Fold C-H Bond Arylation Mechanism in the Synthesis of Triphenylene Derivatives.

In 2017, Ito, Itami and co-workers developed a new generation of palladium-catalyzed annulative  $\pi$ -extension reaction by using diiodobiaryls as  $\pi$ -extending agents (Scheme 51).<sup>88</sup> They found that the use of  $\text{Pd}(\text{MeCN})_4(\text{BF}_4)_2$  (5 mol%) associated with 2 equivalents of both AgOPiv and TfOH effectively catalyzes the annulative  $\pi$ -extension reaction of triphenylenes with 2,2-diiodobiaryls to form the corresponding dibenzo[*g,p*]chrysene derivatives in good yields. They also performed the double annulative  $\pi$ -extension of 2,7-di-*tert*-butylpyrene to generate the hexabenzotetracene in one-step. The reaction also proceeded in moderate yields with other PAHs such as corannulene and fluoranthene.



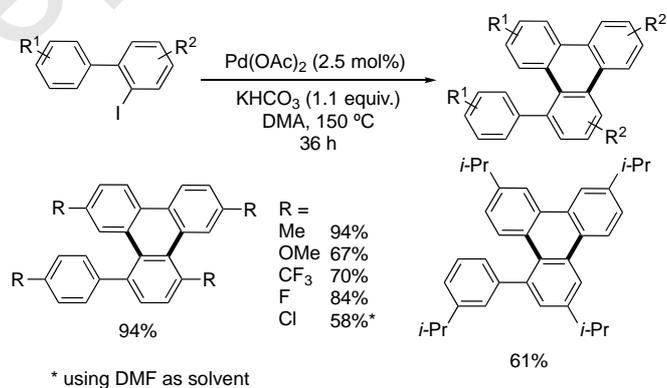
Scheme 51. Pd-catalyzed Double Annulative  $\pi$ -Extension Reactions of K-Region of Triphenylenes with Diiodobiaryls

In 2018, Murakami, Itami and co-workers reported a simple and elegant method for the preparation of triphenylene-cored fused aromatics from readily available chloroarenes *via* palladium-catalyzed annulative dimerization through double C–H bond arylation (Scheme 52).<sup>89</sup> The best reaction conditions turned out to be 5 mol%  $\text{PdCl}_2$  associated with 10 mol%  $\text{PBu}(\text{Ad})_2$  (Bu, *n*-butyl; Ad, 1-adamantyl) in the presence of 3 equivalents of  $\text{Cs}_2\text{CO}_3$  in cyclopentyl methyl ether (CPME) at 140 °C for 18 hours. The reaction tolerated a broad range of functional groups (*e.g.*, alkyl, ether, thioether, trifluoromethyl, trimethylsilyl, and ester). Moreover, this reaction had been employed for the preparation of more  $\pi$ -extended systems using chlorobenzene derivatives bearing two naphthalene rings. The synthesis of sulfur-analogs PAHs using a benzothiophene-substituted derivative or a chlorothiophene derivative was also reported. Interestingly, these partially fused aromatics can be transformed into fully fused small graphene nanoribbons through Scholl reaction using a stoichiometric amount of  $\text{FeCl}_3$ .



Scheme 52. Synthesis of Triphenylenes *via* Pd-Catalyzed Annulative Dimerization of Substituted Chlorophenylenes

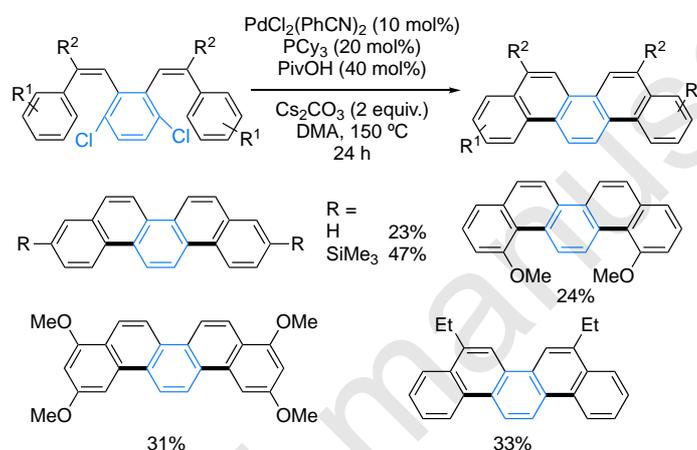
The same year, the group of Shi also reported the synthesis of triphenylene derivatives *via* palladium-catalyzed annulative dimerization, but they employed *ortho*-iodobiaryl compounds as starting materials instead of *ortho*-chlorobiaryl compounds (Scheme 53).<sup>90</sup> They developed a phosphine-free catalytic system using 2.5 mol% of  $\text{Pd(OAc)}_2$  in the presence of 1.1 equivalent of  $\text{KHCO}_3$  in DMA at 150 °C. However, the reaction was unsuccessful from *ortho*-bromobiaryls and *ortho*-triflatebiaryls. The reaction tolerated a wide range of substituents on the biphenyl motifs, including C–Cl bonds, which have been later used to introduce aromatic rings by Suzuki coupling. Similarly to Murakami and Itami, they also employed Scholl reaction using 7 equivalents of  $\text{FeCl}_3$  to prepare graphene nanoribbon segments.



Scheme 53. Synthesis of Triphenylenes *via* Pd-Catalyzed Annulative Dimerization of Substituted *Ortho*-Iodobiaryl Compounds

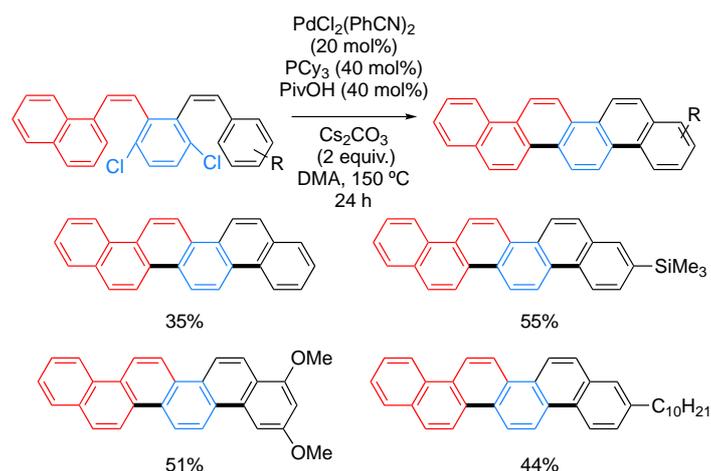
### 2.3.3. Synthesis of Phenacene Derivatives

In 2013, Nishihara and co-workers described the synthesis of picenes, also called [5]phenacenes, through palladium-catalyzed cross-coupling reaction/annulation sequences (Scheme 54).<sup>91, 92</sup> The picene precursors were prepared by two-fold Suzuki-Miyaura coupling reaction of 1,4-dichloro-2,3-diiodobenzene with the stereo defined (*Z*)-alkenylboronates bearing various substituents using PEPPSI-IPr catalyst. Then, Pd-catalyzed double intramolecular C–H arylation was performed using *in-situ* generated PdCl<sub>2</sub>(PCy<sub>3</sub>)<sub>2</sub> from PdCl<sub>2</sub>(PhCN)<sub>2</sub> and PCy<sub>3</sub> in the presence of pivalic acid as the additive and Cs<sub>2</sub>CO<sub>3</sub> as base in DMA at 150 °C to afford picene derivatives in moderate yields.



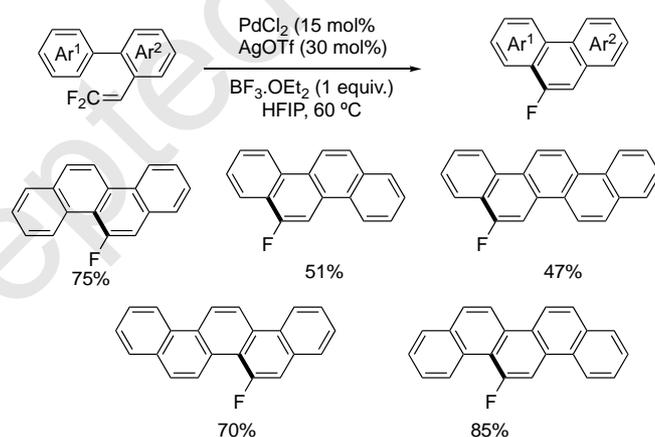
Scheme 54. Synthesis of Substituted Picenes through Palladium-Catalyzed Cross-Coupling Reaction/Annulation Sequences

The same year, they applied this synthetic scheme to the synthesis of fulminene, also called [6]phenacenes (Scheme 55).<sup>93</sup> The fulminene precursors were prepared from 1,4-dichloro-2,3-diiodobenzene *via* two successive Suzuki-Miyaura coupling reactions: i) with (*Z*)-2-(1-naphthyl)-ethenylboronate using PdCl<sub>2</sub>(dppf) as catalyst and ii) with the stereo defined (*Z*)-alkenylboronates using Pd-PEPPSI-IPr catalyst. The intramolecular cyclization through two-fold C–H arylation was performed under standard concerted-metalation deprotonation conditions using 20 mol% of PdCl<sub>2</sub>(PCy<sub>3</sub>)<sub>2</sub> and PivOH as proton shuttle, affording the desired fulminenes in moderate to good yields.



Scheme 55. Synthesis of Substituted [6]Phenacenes through Palladium-Catalyzed Intramolecular C–H Bond Arylations

In 2015, Ichikawa *et al.* reported the palladium(II)-catalyzed cyclization of 2,2-difluorovinylated biaryls following a Friedel–Crafts-type mechanism for the straightforward synthesis of pinpoint-fluorinated phenacenes (Scheme 56).<sup>94</sup> The fluorinated phenacene precursors were prepared by: (i) by a Wittig-type difluoromethylenation of biaryl carbaldehydes or (ii) by a palladium-catalyzed difluorovinylolation of biaryl triflates or halides. The electrophilic activation of 1,1-difluoro-1-alkenes was achieved using a cationic palladium(II) catalyst *in-situ* generated by the action of AgOTf on PdCl<sub>2</sub> and BF<sub>3</sub>-assisted  $\beta$ -fluorine elimination leading to the fluorinated phenacenes. Such protocol has been used for the preparation of [4]-, [5]- and [6]-phenacenes.



Scheme 56. Synthesis of Fluorinated Phenacenes by Palladium(II)/BF<sub>3</sub>-Promoted Tandem Cyclization of 2,2-Difluorovinylated Biaryls – Friedel–Crafts-Type Reaction

The reported mechanism for the phenacene synthesis is depicted in Figure 9Figure 5. 2-(2,2-Difluorovinyl)-1,1'-biphenyl coordinates to the cationic palladium(II) center to form the  $\pi$  complex **A**. This promotes a Friedel–Crafts-type ring closure, providing the cyclic alkylpalladium intermediate **B** that in turn undergoes a BF<sub>3</sub>-assisted  $\beta$ -fluorine elimination to give the desired phenacenes.

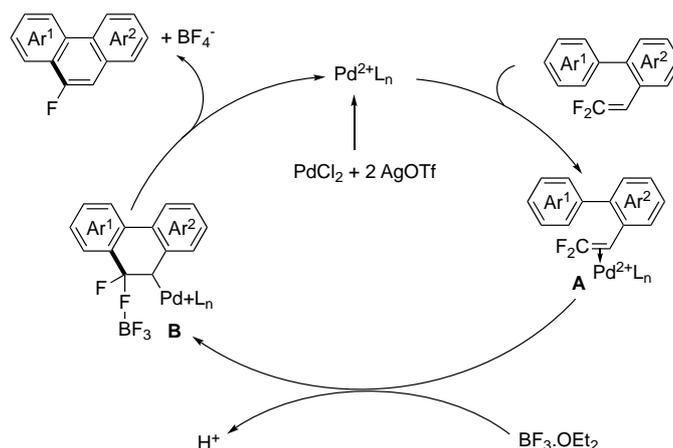
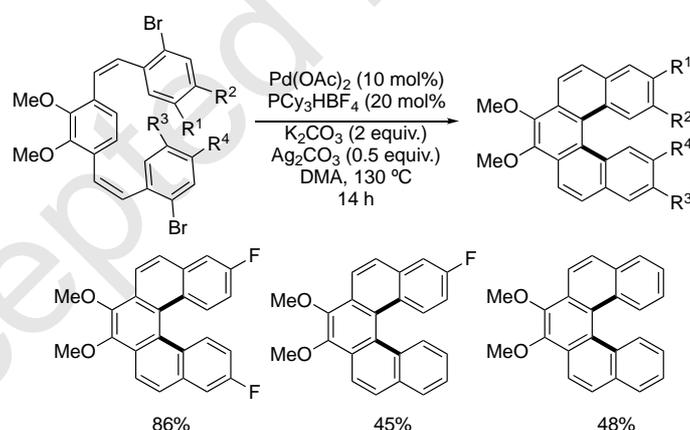


Figure 9. Proposed Catalytic Cycle for Fluorophenacene Synthesis

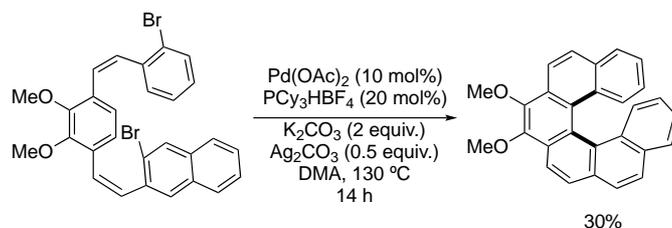
### 2.3.4. Synthesis of Helicene and Circulene Derivatives

In 2007, Kamikawa *et al.* developed a novel approach to helicene synthesis, which involved palladium-catalyzed double C–H bond arylation reaction of (*Z,Z*)-bis(stilbene)s (Scheme 57).<sup>95</sup> To avoid the formation of phenanthrene derivatives, which could be formed by a single C–H bond arylation reaction and dehalogenation, Ag<sub>2</sub>CO<sub>3</sub> was used as additive in the presence of Pd(OAc)<sub>2</sub>/PCy<sub>3</sub> as catalyst and K<sub>2</sub>CO<sub>3</sub> as base in DMA. Noteworthy, iodo-substituted (*Z,Z*)-bis-stilbenes lead to lower yields in favor of [5]helicenes than the corresponding aryl bromide derivatives.



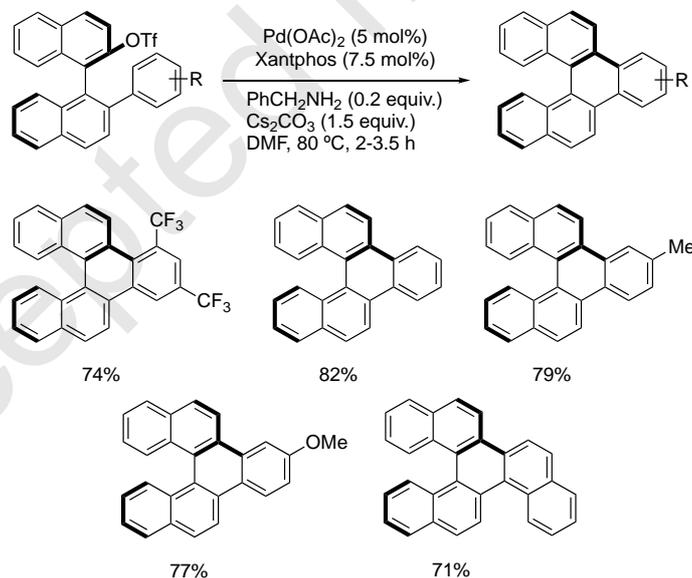
Scheme 57. Synthesis of [5]Helicene Derivatives through Palladium-Catalyzed Intramolecular C–H Bond Arylations

This synthetic scheme was also applied to the formation of [6]helicenes (Scheme 58).<sup>95</sup> Despite the sterically hindered substrate, [6]helicene was isolated in 30% yield. The authors explained the low yield by the formation of other products resulting from debromination reaction and single C–H arylation. However, this methodology could not be transferred to the synthesis of [7]helicenes.



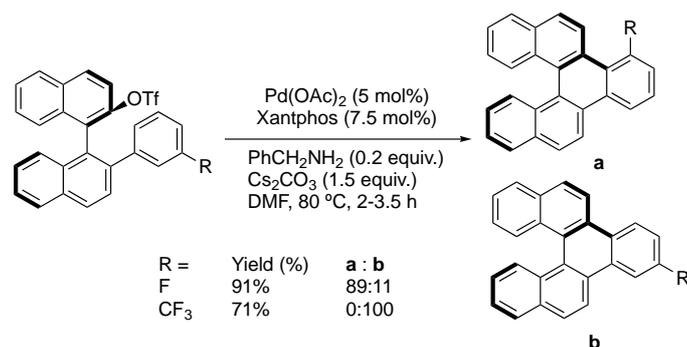
Scheme 58. Synthesis of a [6]Helicene Derivative through Palladium-Catalyzed Intramolecular C–H Bond Arylation

In 2016, during their investigations on palladium-catalyzed amination of binaphthyl-2-triflates, Slaughter and co-worker discovered that 2'-arylbinaphthyl-2-triflates undergo palladium-catalyzed intramolecular C–H arylation allowing the preparation of [5]helicene derivatives (Scheme 59).<sup>96</sup> Palladium associated with Xantphos in DMF in the presence of Cs<sub>2</sub>CO<sub>3</sub> as base were identified as the best reaction conditions. However, the presence of 0.2 equivalent of benzylamine was required. The authors suggested that the amine is required for efficient reduction of Pd(II) into catalytically active Pd(0), which is consistent with previous studies involving aliphatic or benzylic amines as reducing agents *via*  $\beta$ -hydrogen elimination from Pd–amido intermediates.<sup>97</sup> The intramolecular C–H bond arylation was not sensitive to the electronic properties of the 2'-aryl group of the binaphthyl triflate, as electron-donating unsubstituted, or electron-withdrawing substituents allowed the synthesis of [5]helicene derivatives in high yields.



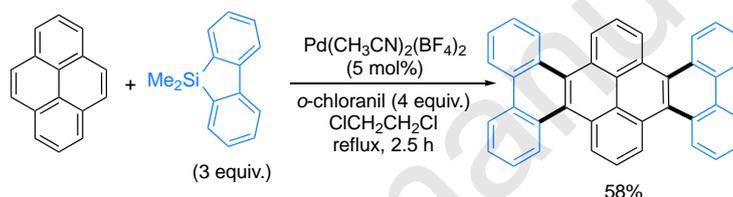
Scheme 59. Synthesis of [5]Helicenes *via* Palladium-Catalyzed Intramolecular Arylation of Triflates

In line with CMD mechanism, the authors observed that when the 2'-aryl group of the binaphthyl triflate contains a *meta*-fluoro substituent, arylation at the more acidic *ortho*-CH bond adjacent to the fluorine was favored;<sup>70-73</sup> whereas, when a *meta*-CF<sub>3</sub> group was present, the regioselectivity was driven by steric factors (Scheme 60).<sup>96</sup>



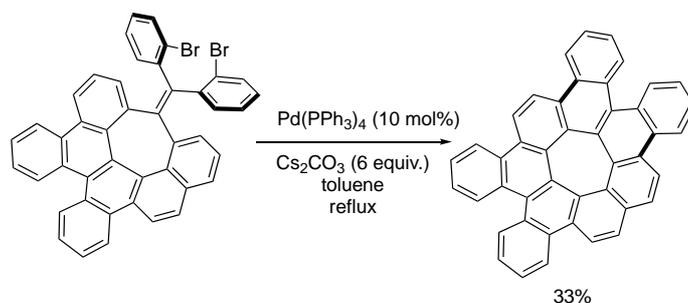
Scheme 60. Regioselectivities of Intramolecular C–H Arylations of Binaphthyl Triflates with *meta*-Substituted 2'-Aryl Groups

In 2016, Itami and co-workers employed palladium-catalyzed double C–H/C–Si coupling with pyrene and 5,5-dimethyldibenzo[*b,d*]silole to generate an unsubstituted hexabenzo[*a,c,fg,j,l,op*]tetracene in one step (Scheme 61).<sup>98</sup> They shown that in contrast to the *tert*-butyl-substituted analog, unsubstituted hexabenzo[*a,c,fg,j,l,op*]tetracene showed a helically twisted conformation in the solid state.



Scheme 61. Synthesis of a Helically Twisted Tetracene *via* Pd-Catalyzed Annulative  $\pi$ -Extension Reaction

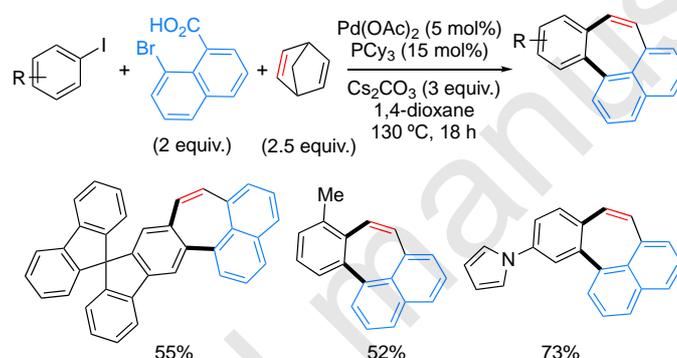
The [*n*]-circulenes are a specific class of PAHs, which contains a central *n*-membered ring surrounded with *n* fused benzenoid rings. The shape of [*n*]-circulenes varies depending on the value of *n* as demonstrated by [5]-, [6]-, and [7]-circulenes, which display a bowl shape, flat disk, and saddle, respectively. In 2017, Miao's group reported the first example of benzannulated [7]circulene structure with the synthesis of tetrabenzo[7]circulene (Scheme 62).<sup>99</sup> They employed Pd-catalyzed two-fold intramolecular C–H bond arylation as the final step using 10 mol% Pd(PPh<sub>3</sub>)<sub>4</sub> catalyst associated with Cs<sub>2</sub>CO<sub>3</sub> as base. Based on DFT calculations, they have shown that the most stable conformers of the tetrabenzo[7]circulene are two enantiomers with C<sub>2</sub> symmetry with a twisted-saddle shape close to the C<sub>2</sub> symmetry.



Scheme 62. Synthesis of a Tetrabenzo[7]circulene *via* Pd-Catalyzed Two-Fold Intramolecular C–H Bond Arylation

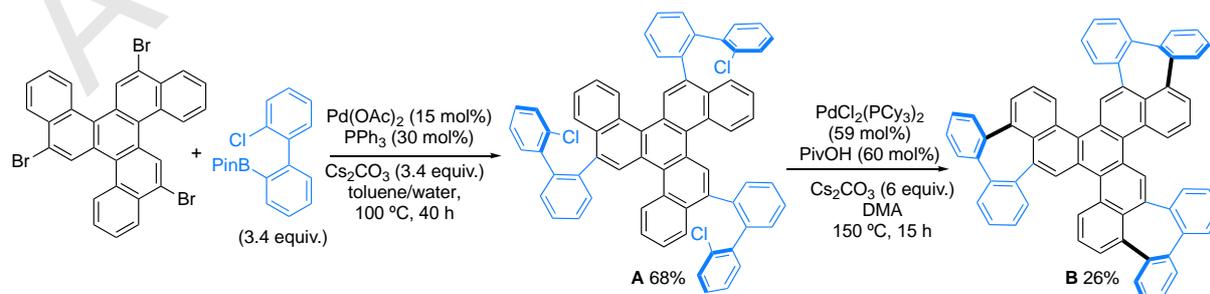
## 2.4. Formation of 7- and 8-Membered Rings by Pd-Catalyzed C–H Bond Arylation

In 2017, during their investigations on the synthesis of phenanthrene derivatives *via* palladium-catalyzed three-component cross-coupling of aryl halides, 2-haloarylcarboxylic acids, and norbornadiene, Kwong and co-workers discovered that the use of 8-bromo-1-naphthoic acid as 2-haloarylcarboxylic acid source allowed the one-pot synthesis of unique heteroatom-fused heptagonal polyaromatics (Scheme 63).<sup>100</sup> Notably, such 7-membered ring PAHs or similar one are challenging to synthesize by traditional methods due to multi-steps synthetic approaches. This  $\pi$ -extension reaction involves oxidative addition of C–I bond to Pd(0), norbornadiene insertion followed by an *ortho*-phenyl C–H bond activation *via* a Catellani process, then oxidative addition of C–Br bond and subsequent decarboxylation of the carboxyl group lead to the formation of the desired products after retro-Diels-Alder reaction.



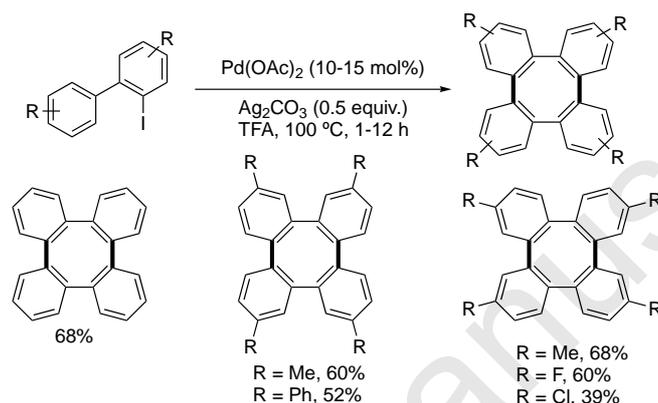
Scheme 63. Synthesis of Heptagon-Embedded Aromatic Compounds through Palladium-Catalyzed  $\pi$ -Extension Reaction

In 2018, Segawa, Itami and co-workers reported the first example of formation of a 7-membered ring in a PAH by Pd-catalyzed intramolecular C–H bond arylation with the synthesis of propeller-shaped polycyclic aromatic hydrocarbons containing 7-membered rings (Scheme 64).<sup>101</sup> They employed their previous conditions allowing an orthogonal reaction of coupling of arylboronic acids with bromoarenes without the cleavage of the C–Cl bond to produce the key intermediate **A**. In a second step, 59 mol% PdCl<sub>2</sub>(PCy<sub>3</sub>)<sub>2</sub> promoted a threefold cyclization to deliver the PAH **B** *via* the formation of three 7-membered rings.



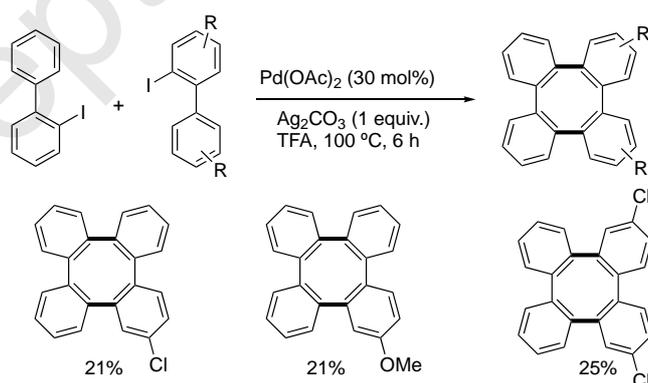
Scheme 64. Synthesis of Propeller-Shaped Polycyclic Aromatic Hydrocarbons Containing 7-Membered Rings *via* Palladium-Catalyzed Intramolecular C–H Bond Arylations

In 2016, Zhang and co-workers described an elegant approach for the synthesis of tetraphenylenes (8-membered ring) *via* palladium-catalyzed C–H bond arylation (Scheme 65).<sup>102</sup> The homocoupling of 2-iodobiphenyl derivatives was performed using phosphine-free Pd(OAc)<sub>2</sub> in the presence of 0.5 equivalents of Ag<sub>2</sub>CO<sub>3</sub> in TFA at 100 °C. Substrates bearing two *meta*- methyl, or phenyl groups underwent dimerization in good yields. 2-Iodobiphenyl derivatives *para*-substituted by methyl, fluoro or chloro groups also lead to the formation of tetraphenylenes in good yields. However, the reaction was not operative with substrates bearing ester, carbonyl, nitro, methoxy or bromo substituents.



Scheme 65. Synthesis of Symmetrical Tetraphenylenes *via* Palladium-Catalyzed C–H Bond Arylations

They also prepared unsymmetrical tetraphenylenes *via* the cross-coupling of two different 2-iodobiphenyls (Scheme 66).<sup>102</sup> The reaction of an equimolar ratio of 2-iodobiphenyl and 2-iodobiphenyl derivatives containing chloro or methoxy substituents lead to the formation of the desired unsymmetrical PAHs, albeit in low yields due to the competitive formation of homo-coupling products.

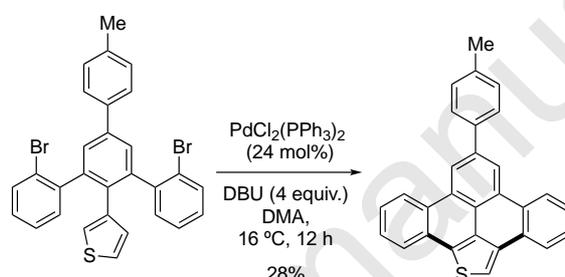


Scheme 66. Synthesis of Unsymmetrical Tetraphenylenes *via* Palladium-Catalyzed C–H Bond Arylations

### 3. Preparation of Sulfur-Containing PCHs through Palladium-Catalyzed C–H Bond Arylation

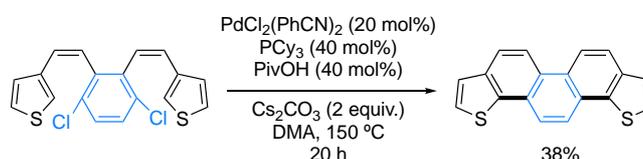
#### 3.1. Formation of Fully Unsaturated 6-Membered Rings Fused with a Thiophene Core

Höger *et al.* were the first to employ Pd-catalyzed intramolecular C–H bond arylation of thiophene for the preparation of sulfur-analogs PAHs in 2004 (Scheme 67).<sup>67</sup> During their investigations on the synthesis of dibenzo[*fg,op*]naphthacenes (Scheme 35), they replaced a phenyl ring by a thiophene ring. From this thiophene bearing a 2,5-dibromophenyl group at C3 position, C2 and C4 intramolecular direct arylations occurred using PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> as catalyst and DBU as base. Notably, the key intermediate was prepared in moderate yield from dihalo-2,4,6-triarylpyrylium salt and sodium 3-thienylacetate.

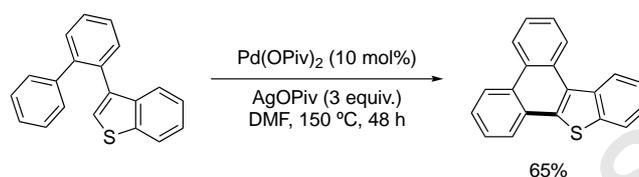


Scheme 67. Synthesis of a Benzo[11,12]tetraceno[5,6-*bc*]thiophene Derivative using Pd-Catalyzed Two-Fold C–H Intramolecular Bond Arylation

In 2013, a collaborative work from Nishihara and Kubozono groups led to the development of a new picene-type molecule by incorporating of thiophene unit (Scheme 68).<sup>103</sup> They employed their previous conditions for the synthesis of picene derivatives (Scheme 54),<sup>91, 92</sup> namely, PdCl<sub>2</sub>(PhCN)<sub>2</sub> and PCy<sub>3</sub> in the presence of pivalic acid as the additive and Cs<sub>2</sub>CO<sub>3</sub> as base in DMA at 150 °C. The intramolecular arylations regioselectively occurred at the C2-position of the thiophene unit, which is more reactive than the C4-position. The thio-picene precursor was prepared by twofold Suzuki-Miyaura coupling reaction of 1,4-dichloro-2,3-diiodobenzene with the stereodefined (*Z*)-(2-(thiophen-3-yl)vinyl)boronic acid, derived from stereoselective hydroboration of 3-ethynylthiophene, using Pd-PEPPSI-IPr catalyst. This phenanthro[1,2-*b*:8,7-*b'*]dithiophene can be used in organic field-effect transistors (OFETs) and FET devices were fabricated with these thin films, and showed field-effect mobility as high as 10<sup>-1</sup> cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>.

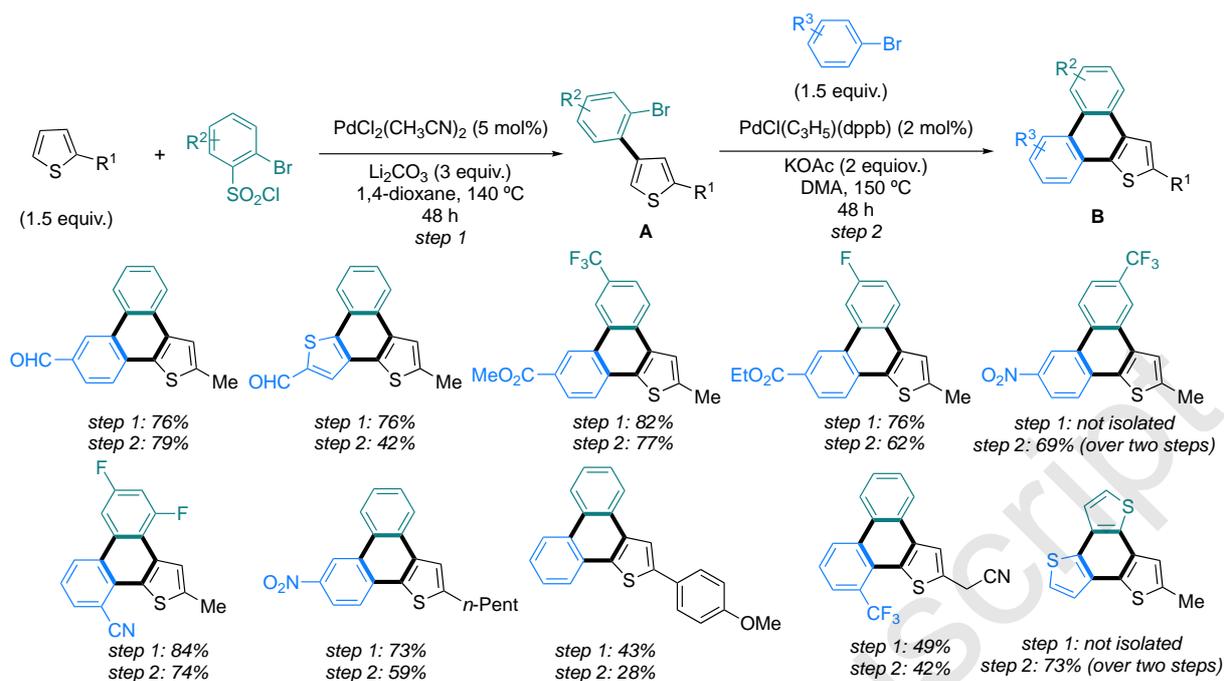


In 2015, Pd-catalyzed oxidative C–H/C–H coupling reaction was employed by Kanai, Kuninobu and co-workers for the preparation of heteroatom-containing  $\pi$ -conjugated systems.<sup>104</sup> Benzo[*b*]phenanthro[9,10-*d*]thiophene was prepared from benzothiophene substituted by an *ortho*-biphenyl group at C3 position by the action of 10 mol% Pd(OPiv)<sub>2</sub> in the presence of 3 equivalents of AgOPiv in DMF at 150 °C (Scheme 69). However, one of the major limitations of this methodology remains the access to the biphenyl-substituted heteroaromatics.



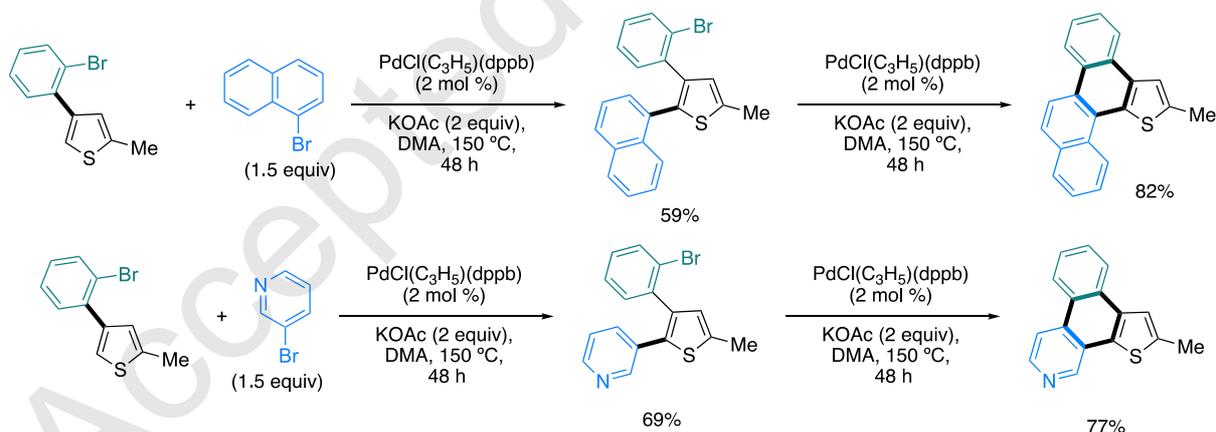
Scheme 69. Synthesis of a Benzo[*b*]phenanthro[9,10-*d*]thiophene through Palladium-Catalyzed C–H/C–H Bond Coupling

In 2016, our group achieved the synthesis of widely substituted sulfur-analogs PAHs in two-steps from thiophene derivatives using orthogonal Pd-catalyzed three-fold C–H bond arylations (Scheme 70).<sup>105</sup> To introduce a 2-bromoaryl group at the C4 position of thiophenes, we employed our previous conditions for the  $\beta$ -arylation of thiophenes with arylsulfonyl chlorides.<sup>106</sup> In the presence of 2-bromoarylsulfonyl chlorides, C2-substituted thiophenes were regioselectively arylated using 5 mol% PdCl<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub> as catalyst and Li<sub>2</sub>CO<sub>3</sub> as base in 1,4-dioxane without the cleavage of the C–Br bond. Then, in the presence of an activated aryl bromide, C5 arylation followed by an intramolecular cyclization occurred using a diphosphine palladium catalyst [i.e., PdCl(C<sub>3</sub>H<sub>5</sub>)(dppb)] leading to the corresponding sulfur-analogs PAHs in good to high yields. This procedure was tolerant toward a wide range of functional groups such as alkyl, ester, formyl, ketone, fluoro, trifluoromethyl, methoxy, and nitrile. We also applied this synthetic scheme to 2-methylthiophene, 2-bromothiophene-2-sulfonyl chloride and 3-bromothiophene for the synthesis of a benzo[1,2-*b*:3,4-*b'*:5,6-*b''*]trithiophene derivative in only two operations. Similar compounds found many applications as a core unit in electronic devices, especially in solar cells.<sup>107-112</sup>



Scheme 70. Synthesis of Sulfur-Analogs of PAH in Two-Pots Procedure *via* Three Palladium-Catalyzed C–H Bond Arylations

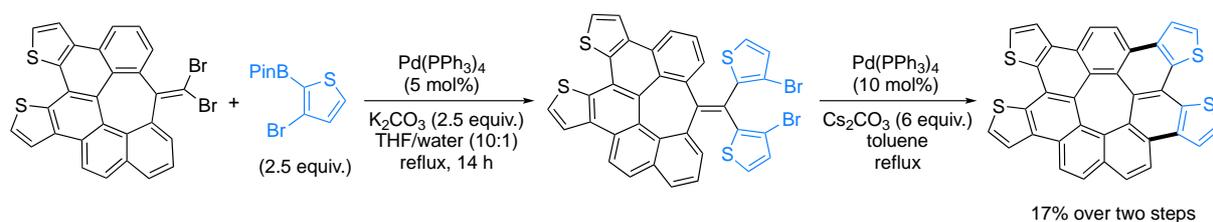
However, with some specific aryl bromides, such as 1-bromonaphthalene and 3-bromopyridine, the C4-arylated intermediates should be isolated before to perform the cyclization reaction procedure to afford the  $\pi$ -extended chryseno[5,6-*b*]thiophene and benzo[*f*]thieno[3,2-*h*]isoquinoline. Notably, the intramolecular C–H bond arylation on the pyridine unit regioselectively occurred at the C4-position.



Scheme 71. Synthesis of Sulfur Analogs of PAH in Three-Pots Procedure *via* Three Palladium-Catalyzed C–H Bond Arylations

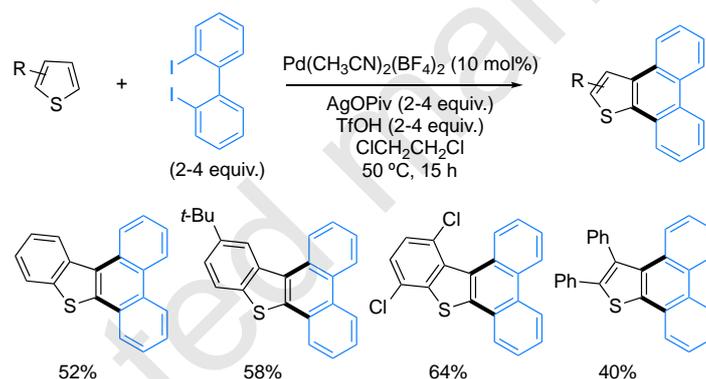
During their investigations on the preparation of tetrabenzo[7]circulene *via* Pd-catalyzed intramolecular C–H bond arylation (Scheme 62),<sup>99</sup> Miao and co-workers also applied their strategy to the synthesis of thiophene-annulated [7]-circulenes by replacing 2-bromophenylboronic acid with 3-bromothiophene-2-boronic acid pinacol ester (Scheme 72).<sup>99</sup> The reaction was operated in a two-pots procedure without the isolation of the intermediate generated by a two-fold Suzuki coupling. Then, after C–H bond cyclization using 10 mol%

$\text{Pd}(\text{PPh}_3)_4$  catalyst associated with  $\text{Cs}_2\text{CO}_3$  as base, the tetrathieno[7]circulene was isolated in 17% yield over two steps.



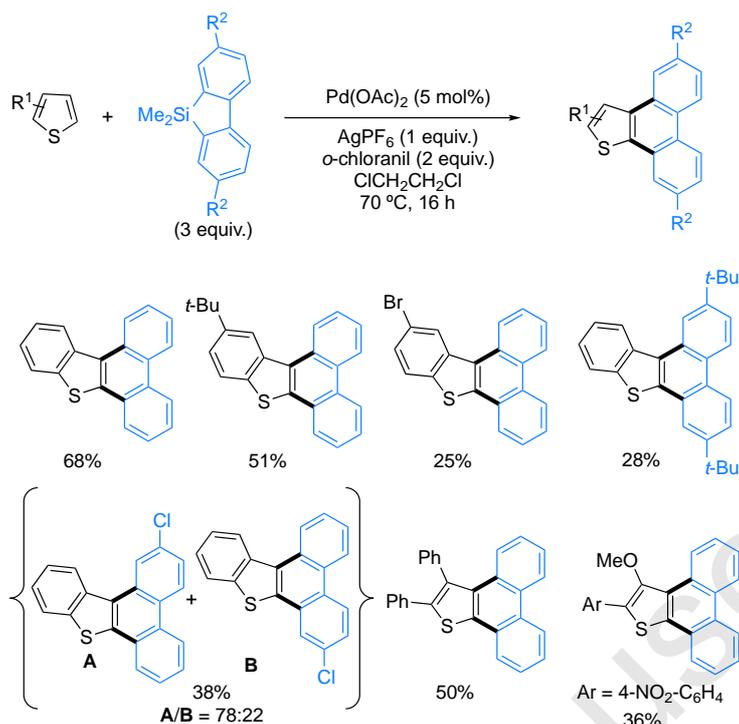
Scheme 72. Synthesis of a Tetrathieno[7]circulene *via* Palladium-Catalyzed Intramolecular C–H Bond Arylations

In 2017, during their investigation on the palladium-catalyzed annulative  $\pi$ -extension reaction of triphenylenes using diiodobiaryls as  $\pi$ -extending agents (Scheme 51),<sup>88</sup> Itami and co-workers shown that the reaction can be efficiently applied to benzothiophenes and 2,3-diphenylthiophene to produce sulfur-analogs of PAHs in one step (Scheme 73).<sup>88</sup> However, only 2,2'-diiodo-1,1'-biphenyl has been employed as the  $\pi$ -extending agent in such couplings. This limitation might be due to their access and also to the fact that with unsymmetrical diiodobiaryls, a mixtures of regioisomers should be obtained.



Scheme 73. Palladium-Catalyzed Annulative  $\pi$ -Extension Reaction of Benzothiophenes and 2,3-Diphenylthiophene

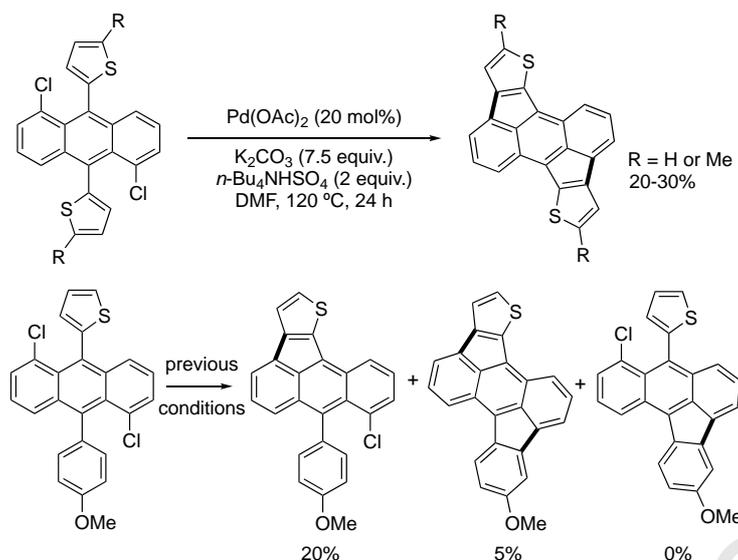
Dibenzosiloles have also been employed as  $\pi$ -extending agents not only of the formation of tetracenes (Scheme 61),<sup>98</sup> but also for the synthesis of sulfur analogs of PAHs *via* double C–H bond arylation of (benzo)thiophenes as demonstrated by Itami, Ito *et al.* (Scheme 74).<sup>113</sup> They found that the optimized conditions for the preparation of benzo[*b*]phenanthro[9,10-*d*]thiophenes were 5 mol%  $\text{Pd}(\text{OAc})_2$  as catalyst, 1 equivalent of  $\text{AgPF}_6$  and 2 equivalents of *o*-chloranil in 1,2-dichloroethane at 70 °C. Benzo[*b*]thiophenes substituted at the C5 position by an electron-donating group exhibited a higher reactivity than the electron-deficient benzo[*b*]thiophenes. However, the reaction conditions were tolerant towards the C–Br bonds allowing further derivatizations. Other dibenzosiloles were also evaluated, but the reaction was limited to the symmetrical one, as a mixture of regioisomers was obtained when an unsymmetrical dibenzosilole was employed.



Scheme 74. Annulative  $\pi$ -Extension of (Benzo)Thiophenes with Dibenzosiloles using Palladium/o-Chloranil Catalysis

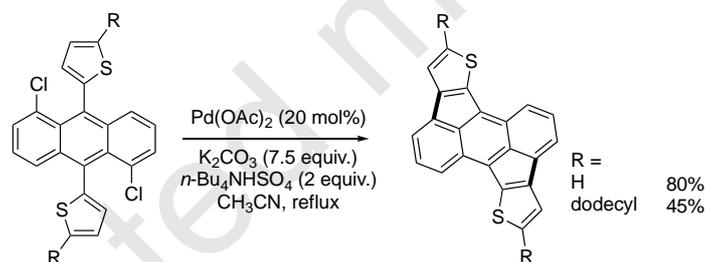
### 3.2. Formation of Fully Unsaturated 5-Membered Rings Fused with a Thiazole Core

The synthesis of PAHs containing fully unsaturated 5-membered rings fused externally to 6-membered rings such as fluoranthene derivatives, through Pd-catalyzed 5-membered ring intramolecular C–H bond arylation, has been widely studied in the literature; while the preparation PCHs analogs containing fully unsaturated 5-membered rings fused externally to 5-membered ring heterocycles remained quite scarce. The first example of the use of Pd-catalyzed intramolecular C–H bond arylation for the preparation of heterocyclic analogs of rubicene was reported in 1999 by Dehaen's group (Scheme 75).<sup>31</sup> The ring closure of the 1,5-dichloro-9,10-diarylanthracenes to the corresponding thiophene rubicene analogs was performed using Pd(OAc)<sub>2</sub> as catalyst with K<sub>2</sub>CO<sub>3</sub> as base and tetrabutylammonium hydrogensulfate as stabilizing agent in DMF at 120 °C. However, the desired PCHs were obtained in very low yields, probably due to polymer formation, decomposition, as well as the formation of benzofluoranthene analogs (mono-cyclization). The intermolecular competitive reaction showed that reaction occurred preferentially on the thiophene ring rather than on the aryl ring.



Scheme 75. Synthesis of Emeraldicene Derivatives through Pd-Catalyzed Intramolecular C–H Bond Arylation

Later Wudl and co-workers reinvestigated the formation of emeraldicene and found that reaction occurred in low yields due to the formation of mono- and bis-dehalogenation products. They were able to perform the Pd-catalyzed 5-membered ring cyclization in 45-80% yields by replacing DMF solvent with  $\text{CH}_3\text{CN}$  (Scheme 76).<sup>114</sup> Indeed, they postulated that the hydridic formyl hydrogen from DMF could act as a reducing agent under these conditions.

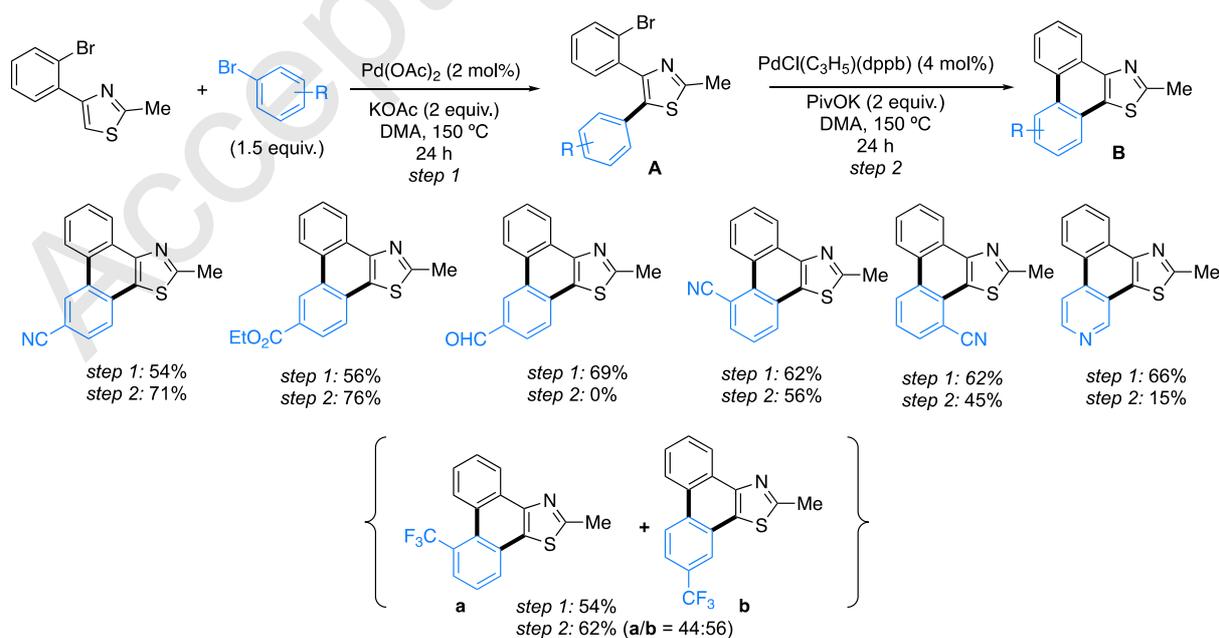


Scheme 76. Synthesis of Emeraldicene Derivatives through Pd-Catalyzed Intramolecular C–H Bond Arylation in  $\text{CH}_3\text{CN}$

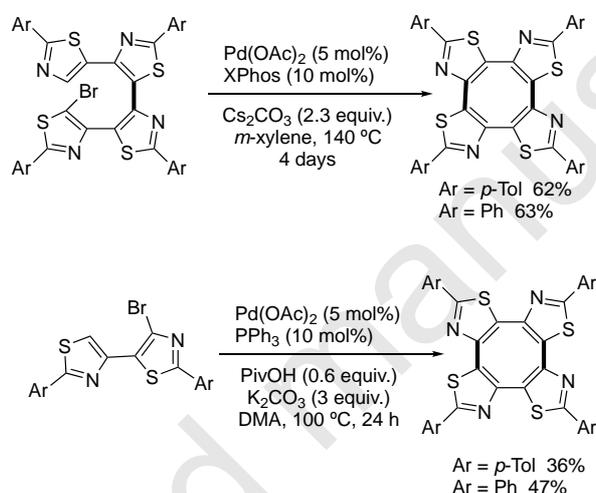
### 3.3. Formation of Fully Unsaturated 6-Membered Rings Fused with a Thiazole Core

Among the diverse PCHs containing a heterocycle, the synthesis of phenanthroid-fused thiazoles is underdeveloped. Although thiazoles display a high reactivity in Pd-catalyzed C–H bond arylation with high regioselectivity in favor of C5 position, this behavior has been poorly employed in intramolecular fashion to prepare thiazole-PAHs. To date, there are only two examples. In 2017, our group reported the first synthesis of phenanthrothiazoles through Pd-catalyzed successive direct arylations including a C–H bond cyclization reaction (Scheme 77).<sup>115</sup> We found that the use of phosphine-free palladium catalyst [i.e.,  $\text{Pd}(\text{OAc})_2$ ] allowed

the chemoselective C5-arylation of the thiazole unit of 4-(2-bromophenyl)-2-methylthiazole with activated aryl bromides without cleavage of the C–Br bond of the 2-bromophenyl group at the C4 position of the thiazole ring. Then, in the presence of a more active diphosphine-palladium catalyst [i.e., PdCl(C<sub>3</sub>H<sub>5</sub>(dppb))], intramolecular 6-membered ring C–H bond arylation afforded the phenanthrothiazoles in moderate to good yields. Diverse aryl bromides bearing an electron-withdrawing group at *para* or *ortho* positions have been successfully employed in this two-pots procedure. The cyclization of 3-(4-(2-bromophenyl)-2-methylthiazol-5-yl)benzonitrile, containing a *meta*-substituent on the benzonitrile unit, lead to a single regioisomer in 56% yield resulting from the cyclization at the most sterically hindered *ortho*-position of the cyano group. In contrast, the *meta*-substituted 4-(2-bromophenyl)-2-methyl-5-(3-(trifluoromethyl)phenyl)thiazole gave a mixture of the two phenanthrothiazole regioisomers **a** and **b** in 44:56 ratio. The major product **b** results from the functionalization of the less sterically hindered C–H bond (at the *para* position of the CF<sub>3</sub>). This methodology has also been employed for the preparation of a hybrid structure enclosing two heteroaromatics, namely, thiazole and pyridine. After the introduction of 3-pyridinyl group at the C5 position of thiazole, 2-methylbenzo[*f*]thiazolo[4,5-*h*]isoquinoline has been obtained through cyclization of the C–H bond at C4 position of the pyridine unit.



The same year, Yamaguchi and co-workers achieved the synthesis of cyclic thiazole tetramers with a head-to-tail connection using palladium-catalyzed C–H bond annulation reaction (Scheme 78).<sup>116</sup> The head-to-tail cyclic tetramers were prepared using two different routes, both employing a Pd-catalyzed C4–H bond arylation of thiazole rings: i) intramolecular ring closure of acyclic thiazole tetramers under high-dilution conditions (Scheme 78, top); ii) C–H dimerization–annulation of thiazole dimers (Scheme 78, bottom). Although the final ring-closing of the route (i) proceeded in better yield, this procedure is less convenient than the dimerization–annulation strategy owing to the preparation of the bromo acyclic thiazole tetramer, which required three additional steps.

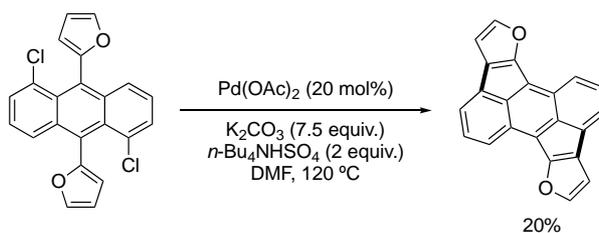


Scheme 78. Synthesis of Highly Flexible  $\pi$ -Expanded Cyclooctatetraenes using Pd-Catalyzed C–H Bond Annulation of Thiazoles

## 4. Preparation of Oxygen-Containing PCHs through Palladium-Catalyzed C–H Bond Arylation

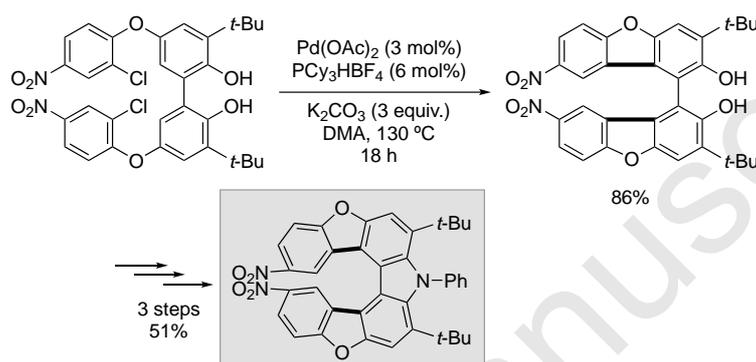
### 4.1. Formation of 5-Membered Rings by Pd-Catalyzed C–H Bond Arylation

A single example of furan PCH analogs of rubicene was prepared by Dehaen group using Pd-catalyzed intramolecular C–H bond arylation of 1,5-dichloro-9,10-difurananthracenes in low yield (Scheme 79).<sup>31</sup>



Scheme 79. Synthesis of a Furan PCH Analog of Rubicene via Pd-Catalyzed Intramolecular C–H Bond Arylation

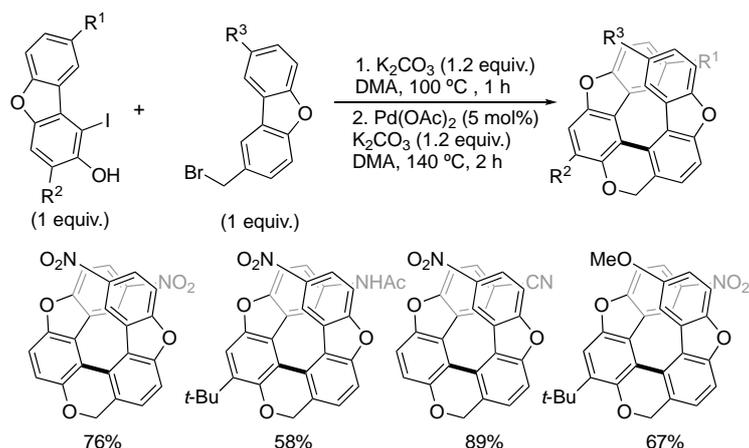
In 2012, Dehaen and co-workers achieved the synthesis of a functionalized dioxaza[7]helicene using palladium-catalyzed intramolecular arylation as the key step (Scheme 80).<sup>117</sup> The C–H bond arylation was conducted using standard conditions, namely Pd(OAc)<sub>2</sub> associated with PCy<sub>3</sub> in DMA in the presence of K<sub>2</sub>CO<sub>3</sub>. The bulky *tert*-butyl substituents controlled both the nucleophilic aromatic substitution and the regioselectivity of C–H arylation towards the less sterically hindered position. Post functionalization including a double Buchwald–Hartwig amination lead to the formation of the desired 2,13-dinitro-dioxaza[7]helicene in a racemic form.



Scheme 80. Synthesis of a Functionalized Dioxaza[7]helicene Using Palladium-Catalyzed Intramolecular C–H Bond Arylations

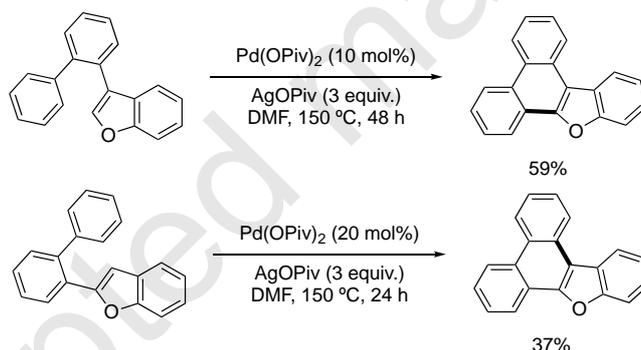
#### 4.2. Formation of 6-Membered Rings by Pd-Catalyzed C-H Bond Arylation

In their continuous efforts on palladium-catalyzed C–H bond arylations of sterically more demanding structures, Dehaen *et al.* reported the one-pot synthesis of trioxa[7]helicenes (Scheme 81).<sup>118</sup> Firstly, an *in-situ* generation of the ether bond from 1-iododibenzo[*b,d*]furan-2-ol and 2-(bromomethyl)dibenzo[*b,d*]furan was conducted followed by the addition of palladium catalyst to achieve the intramolecular 6-membered ring C–H bond arylation allowing the formation of trioxa[7]helicenes in one-pot. Notably, the linearly fused isomers, namely [5]helicenes, was only formed in trace amounts even though it is less sterically strained than its helical counterpart.



Scheme 81. Synthesis of Substituted Trioxa[7]helicenes using Palladium-Catalyzed Intramolecular C–H Bond Arylations

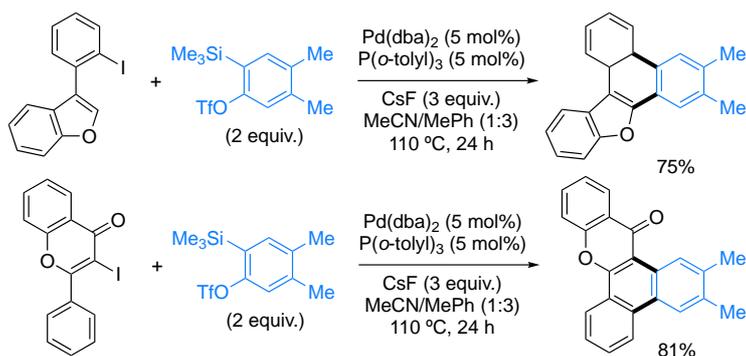
In 2015, Kanai, Kuninobu and co-workers reported the synthesis of a phenanthro[9,10-*b*]benzofuran *via* Pd-catalyzed oxidative C–H/C–H coupling reaction using  $Pd(OPiv)_2$  in the presence of 3 equivalents of  $AgOPiv$  in DMF at 150 °C (Scheme 82).<sup>104</sup> When the reaction was performed from a benzofuran bearing an *o*-biphenyl unit at C3 position, the oxidative C2 arylation occurred in 59% yield, while the reverse reaction (i.e., *o*-biphenyl unit at C2 position and the oxidative arylation at C3 position) the reaction was more sluggish.



Scheme 82. Synthesis of a Phenanthro[9,10-*b*]benzofuran through Palladium-Catalyzed C–H/C–H Bond Coupling

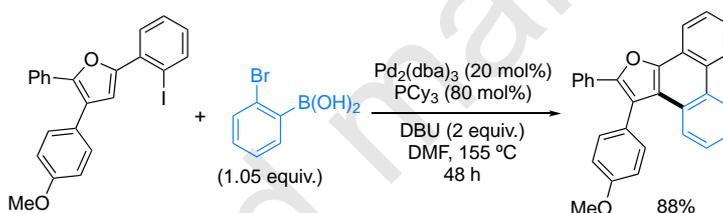
### 4.3. Annulation Through Pd-Catalyzed C-H Bond Arylation

During the synthesis of fused polycyclic aromatics using palladium-catalyzed annulation of arynes with 2-halobiaryls (Scheme 39),<sup>77</sup> Larock and co-workers shown that the reaction is also operative with 3-(2-iodophenyl)benzofuran and 3-iodo-2-phenyl-4H-chromen-4-one to afford the benzofuran and chromone PCH congeners in good yields (Scheme 83).<sup>77, 78</sup>



Scheme 83. Synthesis of Benzofuran and Chromone Fused PAHs by Palladium-Catalyzed Annulation of Arynes

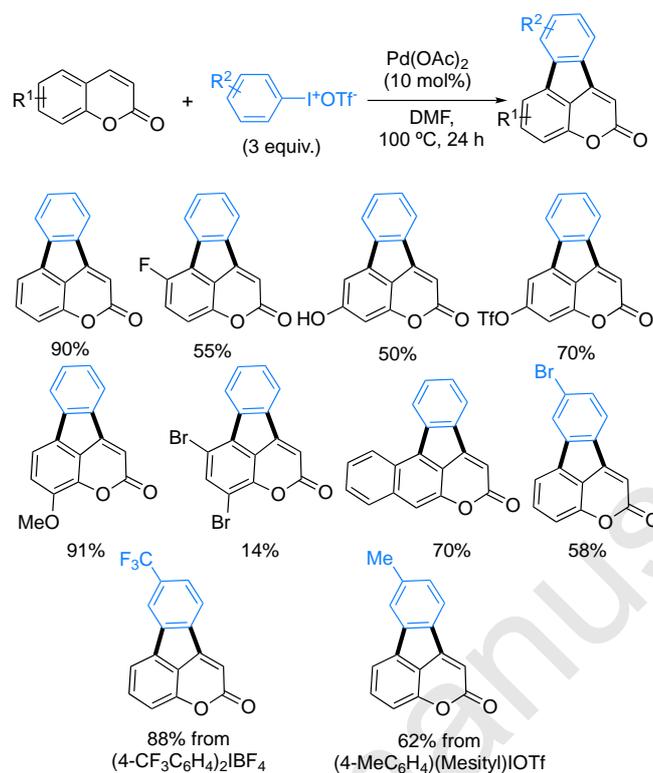
In 2014, during their investigations on the synthesis of multisubstituted furans *via* Pd-catalyzed condensation of *N*-aryl imines and alkynylbenziodoxolones, Yoshikai and co-workers achieved the synthesis of 2-(2-iodoaryl)furan derivatives. They show that functionalized furan derivative are versatile building block for the synthesis of furan-PCHs (Scheme 84).<sup>119</sup> From 2-(2-iodoaryl)furan and 2-bromophenylboronic acid, domino Suzuki–Miyaura coupling/intramolecular C–H bond arylation occurred using 20 mol% Pd<sub>2</sub>(dba)<sub>3</sub> associated with 80 mol% of PCy<sub>3</sub> in the presence of DBU as to afford a phenanthro[9,10-*b*]furan derivative.



Scheme 84. Synthesis of a phenanthro[9,10-*b*]furan derivative using Palladium-Catalyzed Domino Suzuki–Miyaura Coupling/Intramolecular C–H Bond Arylation

In 2015, Han, Wang and co-worker developed a palladium-catalyzed diarylation of coumarins by using diaryliodonium salts for the synthesis of 4,5-benzocoumarin derivatives (Scheme 85).<sup>120</sup> They found that annulation of coumarins occurred with diaryliodoniums in the presence of 10 mol% Pd(OAc)<sub>2</sub> in DMF. This one-pot reaction involved the difunctionalization of diaryliodoniums *via* C–I and vicinal C–H bond activations. Notably, when the reaction was carried out in the presence of iodobenzene or even 1,2-diiodobenzene instead of diaryliodoniums, no reaction occurred. The reaction tolerated many different substituents on the coumarine unit (6-, 7-, or 8-positions) including halogens, alkoxy, phenyl, and methyl groups. Symmetrical and unsymmetrical diaryliodonium salts bearing a wide variety of functionalities, e.g., halogens, methyl, methoxy- or trifluoromethyl- substituents on the aromatic ring were efficiently coupled to give the corresponding 4,5-benzocoumarins in good to high yields. Based on the structure of the final product, the authors showed that the carbon

site of the C–I bond attacked the 4-position of coumarin. As expected, the unsymmetrical tolyl-mesityl iodonium reagents transferred the less sterically hindered group.



Scheme 85. Synthesis of 4,5-Benzocoumarins *via* Palladium-Catalyzed C–I and Vicinal C–H Dual Activation of Diaryliodonium Salts for Diarylations

The authors proposed the mechanism depicted in the Figure 10.<sup>120</sup> The reaction started by the cleavage of the hypervalent iodine–aryl bond to generate palladium species **A**. The authors also mentioned that iodonium species could act as Lewis acids in association with an activation of the carbonyl group of coumarin. In the coordinating DMF solvent, an oxidative attack at C4 position with a synergetic activation of the vicinal C–H bond of coumarin formed arylpalladacycle **B**, followed by a reductive elimination affording the arylated intermediate **C**. Then, palladium(IV) complex **D** was formed by a second oxidative addition of **C** using  $[\text{Ph}_2\text{I}]\text{OTf}$  in concert with the C–H bond activation at *ortho*-position of the phenyl unit. Finally, a reductive elimination regenerates the catalyst **A** with the formation of annulated coumarin.

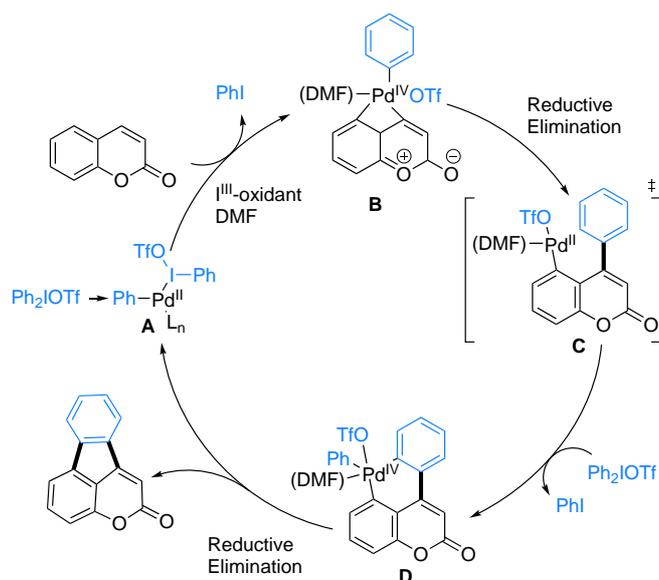
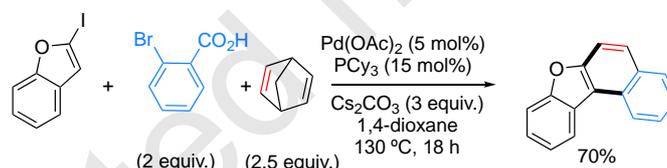


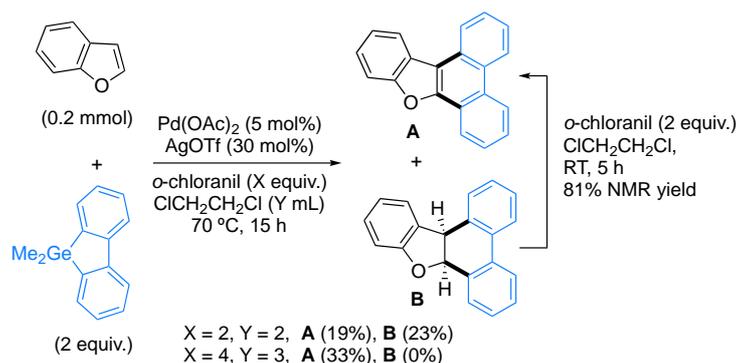
Figure 10. Proposed Mechanism for Palladium-Catalyzed C–I and Vicinal C–H Dual Activation of Diaryliodonium Salts for Diarylation

In 2017, during their investigations on the synthesis of phenanthrene derivatives *via* palladium-catalyzed three-components cross-coupling of aryl halides, 2-haloarylcaboxylic acids, and norbornadiene (Scheme 63),<sup>100</sup> Kwong *et al.* reported one example of synthesis of large PCH containing a benzofuran unit using 2-iodobenzofuran and 2-bromobenzoic acid as the coupling partners (Scheme 86).<sup>100</sup>



Scheme 86. Synthesis of a Naphtho[2,1-*b*]benzofuran through Palladium-Catalyzed Three-Components Cross-Coupling

In 2018 Itami, Ito *et al.* succeeded to prepare a phenanthro[9,10-*b*]benzofuran from benzofuran using their previous Pd-catalyzed annulative  $\pi$ -extension reaction, albeit dibenzosilole was replaced by dimethyldibenzogermole (Scheme 87).<sup>113</sup> In addition to the previous reaction conditions with benzothiophene (see, Scheme 74), AgOTf has been employed. However, the reaction was more sluggish, and the desired phenanthro[9,10-*b*]benzofuran was obtained in only 18% yield along with 23% of the *cis*-dehydrogenated product, which can be further converted into the desired PAH using 2 equiv. of *o*-chloranil in 1,2-dichloroethane at room temperature. Notably, when the annulative  $\pi$ -extension reaction was performed with an increased amount of *o*-chloranil (4 equivalents), the authors observed only the formation phenanthro[9,10-*b*]benzofuran in 33% yield.

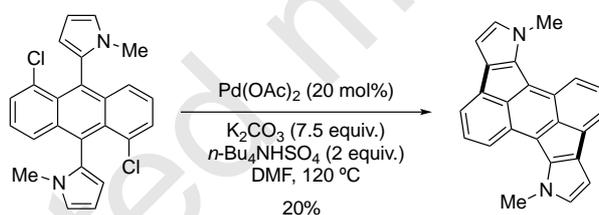


Scheme 87. Annulative  $\pi$ -Extension of Benzofuran with Dimethyldibenzogermole using Palladium/*o*-Chloranil Catalysis

## 5. Preparation of Nitrogen-Containing PCHs through Palladium-Catalyzed C–H Bond Arylation

### 5.1. Formation of 5-Membered Rings by Pd-Catalyzed C–H Bond Arylation

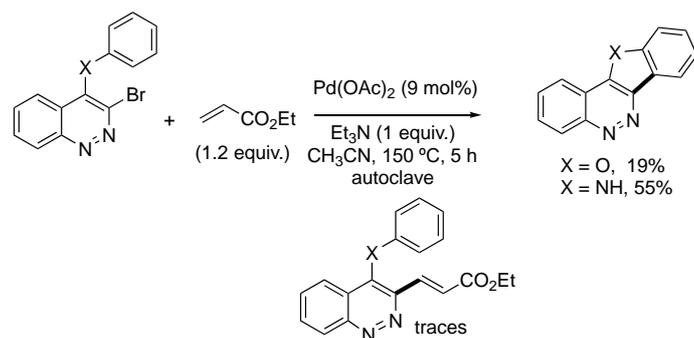
In 1999, among other PCH analogs of rubicene Dehaen's group shown one example of the preparation of a rubicene containing pyrrole rings using Pd-catalyzed intramolecular C–H bond arylation of 1,5-dichloro-9,10-di(*N*-methyl)pyrroleanthracene. However, the product was obtained in a low yield (Scheme 88).<sup>31</sup>



Scheme 88. Synthesis of a Pyrrole PCH Analog of Rubicene via Pd-Catalyzed Intramolecular C–H Bond Arylation

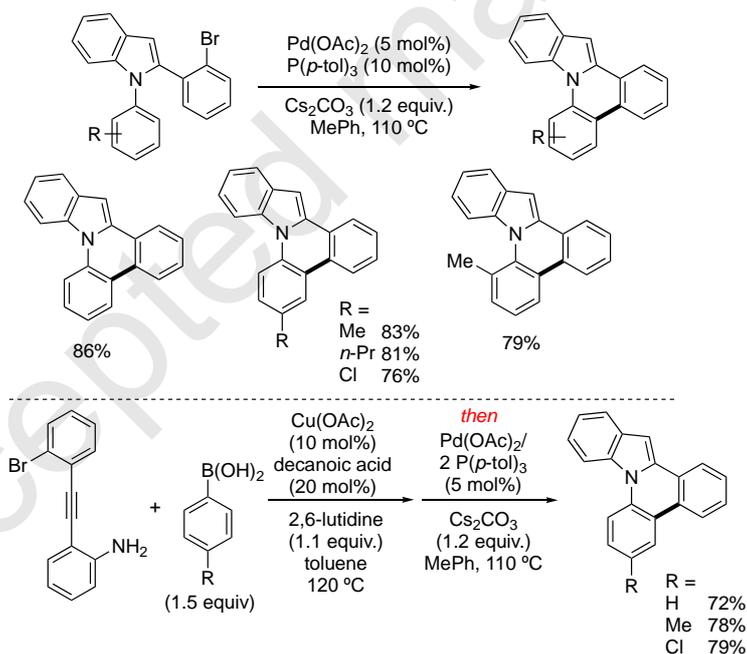
### 5.2. Formation of 6-Membered Rings by Pd-Catalyzed C–H Bond Arylation

One of the first examples of Pd-catalyzed intramolecular C–H bond arylation for the synthesis of nitrogen-analogs PAHs was reported by Ames *et al.* in 1982.<sup>121</sup> During their investigations on Heck reaction with 3-halogenocinnolines, they observed that the reaction between 3-bromo-4-phenoxy-cinnoline or 3-bromo-4-phenylaminocinnoline and ethyl acrylate in the presence of Pd(OAc)<sub>2</sub> associated with Et<sub>3</sub>N in acetonitrile at 150 °C under autoclave conditions, did not lead to the formation of the Heck-type products, but to the formation of the cyclized products benzofurocinnoline and indolocinnoline in 19% and 55% yield, respectively (Scheme 89). Notably, in the absence of acrylate, the condensed heterocycles were not obtained. The authors suggested that acrylate is required for the reduction of Pd(II) into Pd(0).



Scheme 89. Pd-Catalyzed Intramolecular C–H bond Arylation of 3-Halogenocinnolines

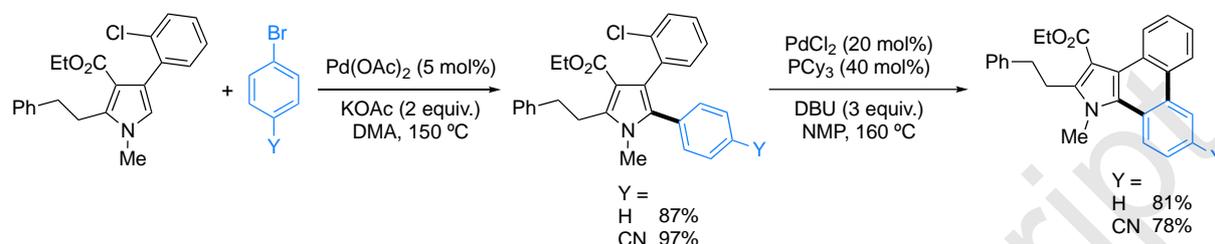
In 2014, indolo[1,2-*f*]phenanthridine derivatives have been synthesized through Pd-catalyzed intramolecular C–H arylation of *o*-brominated indoles (Scheme 90).<sup>122</sup> *o*-Brominated indole precursors were synthesized through a copper-mediated domino reaction between 2-alkynylanilines and boronic acids. Then, classical conditions for intramolecular direct C–H arylation, namely 5 mol% Pd(OAc)<sub>2</sub> associated with 10 mol% P(*p*-tol)<sub>3</sub> in the presence of Cs<sub>2</sub>CO<sub>3</sub> as base in toluene at 110 °C, were employed. Interestingly, the authors also achieved the tandem synthesis of indolo[1,2-*f*]phenanthridines *via* two-steps reaction in one pot from alkynylanilines and boronic acids (Scheme 90, bottom).



Scheme 90. Synthesis of Indolo[1,2-*f*]phenanthridines *via* Pd-Catalyzed Intramolecular C–H Arylation

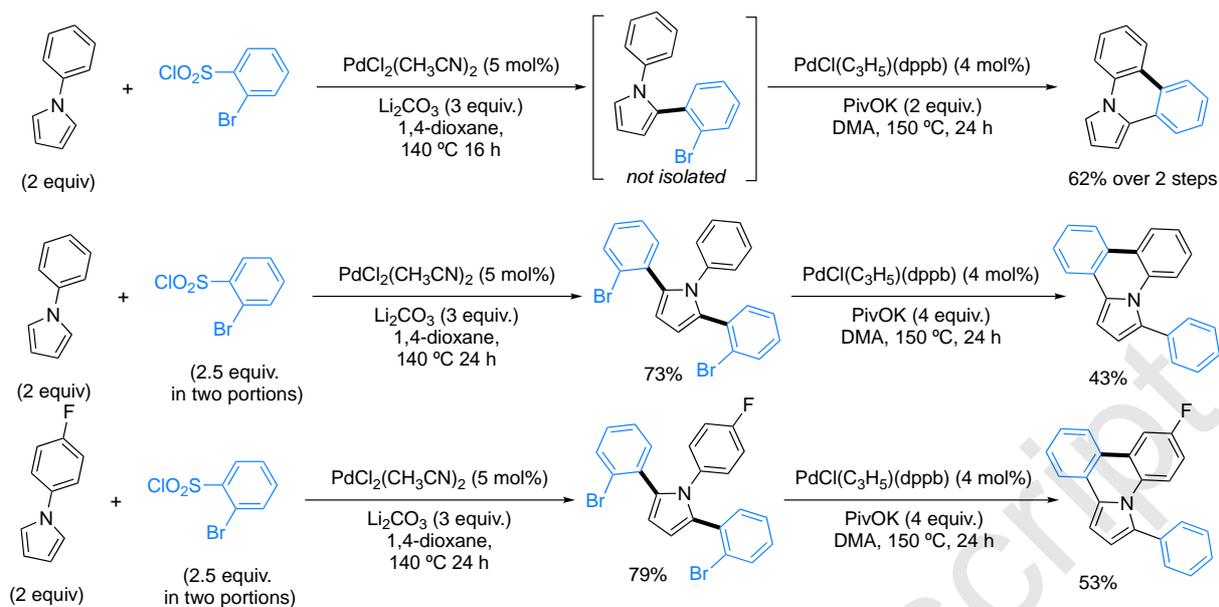
In 2014, Lee and co-workers reported two examples of Pd-catalyzed intramolecular C–H bond arylations of pyrrole derivatives to generate pyrrolophenanthrene derivatives (Scheme 91).<sup>123</sup> Using a standard catalytic system [i.e., Pd(OAc)<sub>2</sub>/KOAc/DMA] for the C5-arylation of pyrroles, the authors succeeded to arylate a 2,3,4-trisubstituted pyrroles bearing an *o*-chlorophenyl with bromobenzene and 4-bromobenzonitrile leading to the precursors of the

synthesis of pyrrolophenanthrene derivatives *via* intramolecular C–H bond arylation. Notably, they did not observe the tandem one-pot intermolecular – intramolecular C–H bond arylations owing the challenging activation of C–Cl bond, with which the use of more reactive palladium catalysts is required. Indeed, in the presence of PdCl<sub>2</sub> associate with PCy<sub>3</sub> in the presence of DBU in NMP, intramolecular C–H bond arylation occurred in high yields.



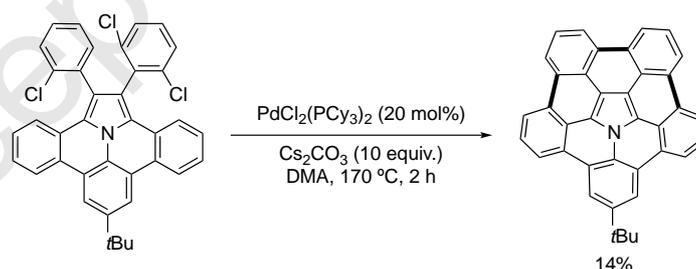
Scheme 91. Synthesis of Pyrrolophenanthrene Derivatives *via* Pd-Catalyzed Intramolecular C–H Arylations

In 2015, our group also investigated the synthesis of pyrrolophenanthrene derivatives *via* successive C–H bond arylations (Scheme 92).<sup>124</sup> Firstly, C2-arylation of 1-phenylpyrrole using Pd-catalyzed desulfitative C–H bond arylation with 2-bromobenzenesulfonyl chloride was achieved using PdCl<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub> in the presence of Li<sub>2</sub>CO<sub>3</sub> in 1,4-dioxane.<sup>125</sup> Then, Pd-catalyzed intramolecular C–H bond arylation was performed using 2 mol% PdCl(C<sub>3</sub>H<sub>5</sub>)(dppb) as catalyst, PivOK as base in DMA (Scheme 92, top). 2,5-Bis(2-bromophenyl)-1-phenylpyrrole has been prepared using of 2.5 equivalents of 2-bromobenzenesulfonyl chloride, but two-fold intramolecular C–H bond arylations leading to the formation of benzo[7,8]indolizino[6,5,4,3-*def*]phenanthridine was not achieved. We observed the formation of pyrrolo[1,2,*f*]phenanthridine owing the hydrogenolysis of the second C–Br bond instead of the intramolecular direct arylation due to a too congested structure (Scheme 92, middle). Similar results were observed with 1-(4-fluorophenyl)pyrrole, which afforded the 6-membered-ring fused polycyclic derivative in two steps in 53% yield (Scheme 92, bottom).



Scheme 92. Synthesis of Pyrrolophenanthrene Derivatives *via* Pd-Catalyzed Desulfative C2–H or C2,C5–H Bond Arylations Followed by Pd-Catalyzed Intramolecular C–H Arylation

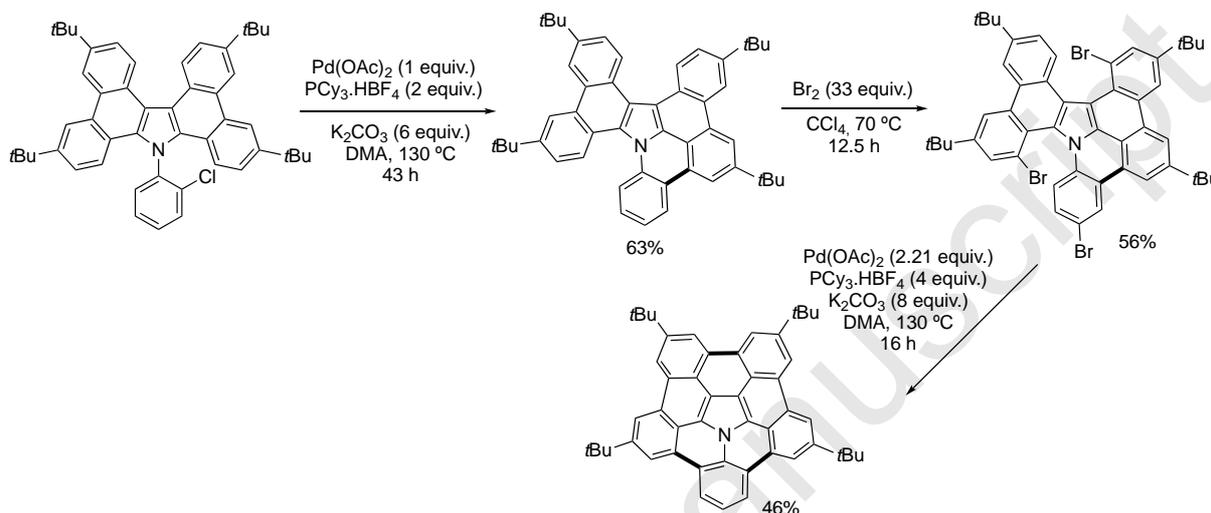
The same year, Ito, Nozaki and co-workers employed Pd-catalyzed three-fold C–H bond intramolecular arylation to synthesize a congested pyrrole ring (Scheme 93).<sup>126</sup> The trichlorinated 1,2,3,4,5-pentaarylpyrrole intermediate was heated in the presence of 20 mol% PdCl<sub>2</sub>(PCy<sub>3</sub>)<sub>2</sub> as catalyst with Cs<sub>2</sub>CO<sub>3</sub> as base in DMA at 170 °C to afford 8-*tert*-butyl-6b<sup>2</sup>-azapentabenzob[bc,ef,hi,kl,no]corannulene in 14% yield. This structure exhibited specific physical properties: *i*) a unique C<sub>s</sub> symmetry because of the introduction of a trigonal nitrogen atom, *ii*) formation of one directional bowl-in-bowl  $\pi$ -stacking in the solid state and *iii*) efficient fluorescence with longer emission wavelengths resulting from extended  $\pi$ -conjugation of 5 fused benzene rings.



Scheme 93. Synthesis of a Benzene-Fused Azacorannulene Bearing an Internal Nitrogen Atom *via* Pd-Catalyzed Three-fold Intramolecular C–H Arylation

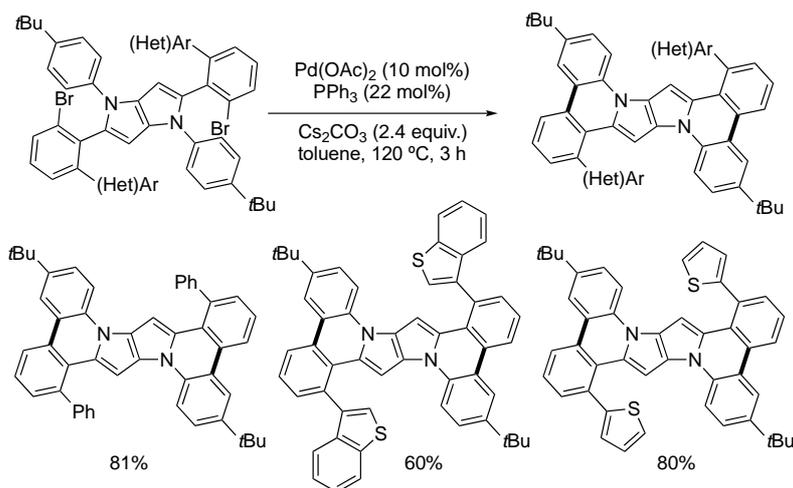
Hiroto, Shinokubo and co-workers synthesized a similar nitrogen-embedded buckybowll through successive intramolecular C–H bond arylations (Scheme 94).<sup>127</sup> From a tetrabenzocarbazole bearing an *o*-chlorophenyl group at N atom, intramolecular C–H bond arylation using a stoichiometric amount of Pd(OAc)<sub>2</sub>/tricyclohexylphosphine provided a singly fused product in 63% yield. Then, in the presence of a large excess of bromine in CCl<sub>4</sub>, the

tris-brominated product was isolated in 56% yield. Interestingly, the bromo substituents were introduced at the right position allowing cyclization reaction, which was conducted using 2 equivalents of Pd(OAc)<sub>2</sub>/PCy<sub>3</sub> allowing the formation of nitrogen-embedded bucky bowl in 46% yield. Under these reaction conditions the *N*-aryl group was also brominated, but luckily hydrogenolysis reaction occurred during the palladium-catalyzed C–H bond arylation procedure.



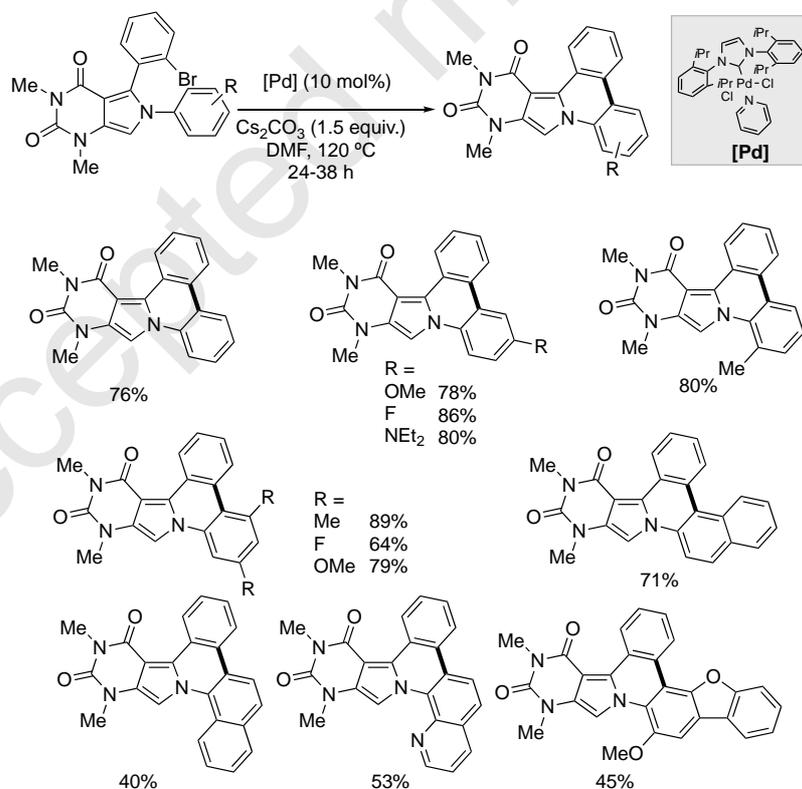
Scheme 94. Synthesis of a Nitrogen-Embedded Atom Buckybowl *via* Pd-Catalyzed Successive Intramolecular C–H Arylations

In 2016, nonplanar butterfly-shaped  $\pi$ -expanded pyrrolopyrroles have been prepared from the collaborative work of Vullev's, Kubo's and Gryko's groups using Pd-catalyzed intramolecular 6-membered ring C–H bond arylation (Scheme 95).<sup>128</sup> Two-fold cyclization reactions of tetraarylpyrrolopyrroles bearing two *o*-bromoaryl units at 2 and 5 positions were carried out using Pd(OAc)<sub>2</sub>/PPh<sub>3</sub> as the catalytic system in the presence of Cs<sub>2</sub>CO<sub>3</sub> in toluene at 120 °C. In addition,  $\pi$ -extensions on the third (hetero)aromatic were conducted using standard Scholl reaction. The incorporation of these three different heterocycles (benzene, thiophene, and benzothiophene) allowed the fine-tuning of the energy barriers and prevented structural planarity owing the overlapping of van der Waals between spatially close hydrogen atoms from different aromatic rings. This forced conformation induced interesting optical properties.



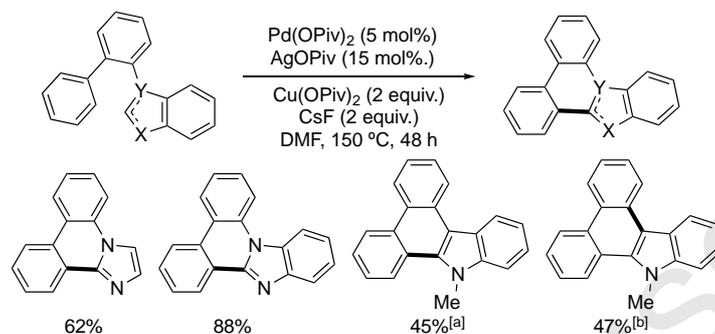
Scheme 95. Synthesis of Nonplanar Butterfly-Shaped  $\pi$ -Expanded Pyrrolopyrroles *via* Pd-Catalyzed Intramolecular C–H Arylations

In 2018, Chernysheva and co-workers employed Pd-catalyzed intramolecular C–H bond arylation for the preparation of pyrimido[5',4':3,4]pyrrolo[1,2-*f*]phenanthridine-12,14(11H,13H)-diones and related compounds (Scheme 96).<sup>129</sup> They have selected a palladium complex which contains a sterically crowded IPr NHC ligand as the catalyst with Cs<sub>2</sub>CO<sub>3</sub> as base in DMF to perform the 6-membered ring cyclization of 6-aryl-5-(2-bromophenyl)pyrrolo[3,4-*d*]pyrimidine-2,4-diones.



Scheme 96. Synthesis of pyrimido[5',4':3,4]pyrrolo[1,2-*f*]phenanthridines *via* Pd-Catalyzed Intramolecular C–H Arylations

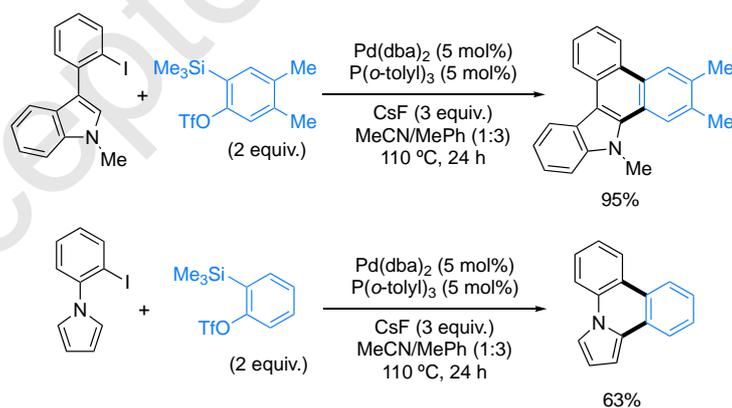
In 2015, Pd-catalyzed oxidative C–H/C–H coupling reaction was employed by Kanai, Kuninobu, and co-workers for the preparation of heteroatom-containing  $\pi$ -conjugated systems.<sup>104</sup> PCHs containing imidazole, benzoimidazole or indole units were prepared from heteroaromatics substituted by an *ortho*-biphenyl group at N1 or C3 positions by the action of 10 mol% Pd(OPiv)<sub>2</sub> in the presence of 3 equivalents of AgOPiv in DMF at 150 °C (Scheme 97).



Scheme 97. Synthesis of PCHs Containing Imidazole, Benzoimidazole or Indole units through Palladium-Catalyzed C–H/C–H Bond Couplings. [a] without CsF; [b] without CsF in PivOH instead of DMF.

### 5.3. Annulation Through Pd-Catalyzed C-H Bond Arylation

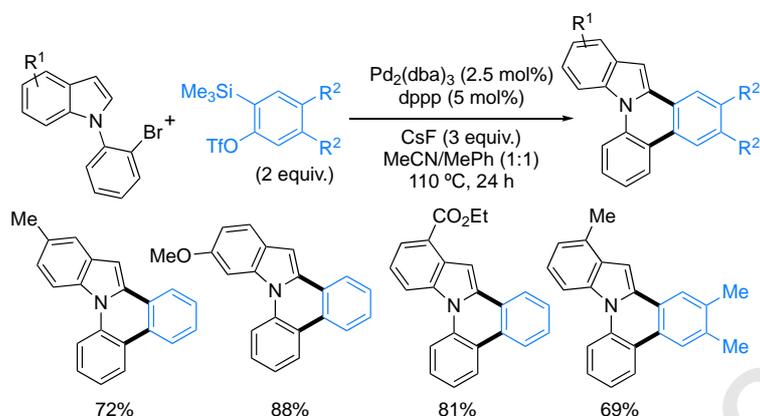
Larock and co-workers reported one application of their palladium-catalyzed annulation of arynes for the synthesis of a dibenzo[*a,c*]carbazole in 95% yield from 3-(2-iodophenyl)-1-methylindole and 4,5-dimethyl-2-(trimethylsilyl)phenyl triflate (Scheme 98, top).<sup>77</sup> Later, they also succeeded to synthesize a pyrrolo[1,2-*f*]phenanthridine in 63% yield using a similar strategy from 1-(2-iodophenyl)-pyrrole (Scheme 98, bottom).<sup>78</sup>



Scheme 98. Palladium-Catalyzed Annulation of Arynes with 3-(2-Iodophenyl)-1-methylindole or 1-(2-Iodophenyl)-pyrrole

In 2007, Zhang and co-workers picked up these reaction conditions and applied them for the synthesis of diversely substituted indolo[1,2-*f*]phenanthridine derivatives from 1-(2-bromophenyl)indole and aryne precursors (Scheme 99).<sup>130</sup> The critical factor to improve the yield was to employ dppp [1,3-bis-(diphenylphosphino)propane] as phosphine ligand.

However, as previously observed, this methodology is limited to the use of symmetrical aryne precursors. This strategy was later employed for the preparation of organic sensitizers containing an indolo[1,2-*f*]phenanthridine unit for solar cells applications.<sup>131</sup>



Scheme 99. Synthesis of Indolo[1,2-*f*]phenanthridines *via* Palladium-Catalyzed Annulation of Arynes with 1-(2-bromophenyl)-1H-indoles

In 2015, Jana and co-workers described the palladium-catalyzed one-pot synthesis of dibenzofused carbazoles from readily available 2-arylindoles and diaryliodonium salts *via* 1,4-palladium migration and 1,2-aryl shift. The authors proposed that the reaction started by an electrophilic palladation at the indolyl C3 position to generate the Pd(II) intermediate **A**. Then, 1,4-palladium migration occurred *via* the formation of palladacycle **B** to afford the Pd(II) intermediate **C**. The arylated product **D** is obtained in the presence of diaryliodonium salts *via* a Pd(IV)/Pd(II) cross-coupling. Then, a second electrophilic C3 indolyl palladation followed by 1,2-palladium and aryl migration delivers the intermediate **G**, which undergoes cross-dehydrogenative coupling *via* the palladacycle **H** to give Pd(0) species and the desired PCH. Finally, the Pd(0) species, which is generated after reductive elimination, is reoxidized into Pd(II) by a portion of hypervalent iodine(III) reagent to complete the catalytic cycle (Figure 11).<sup>132</sup>

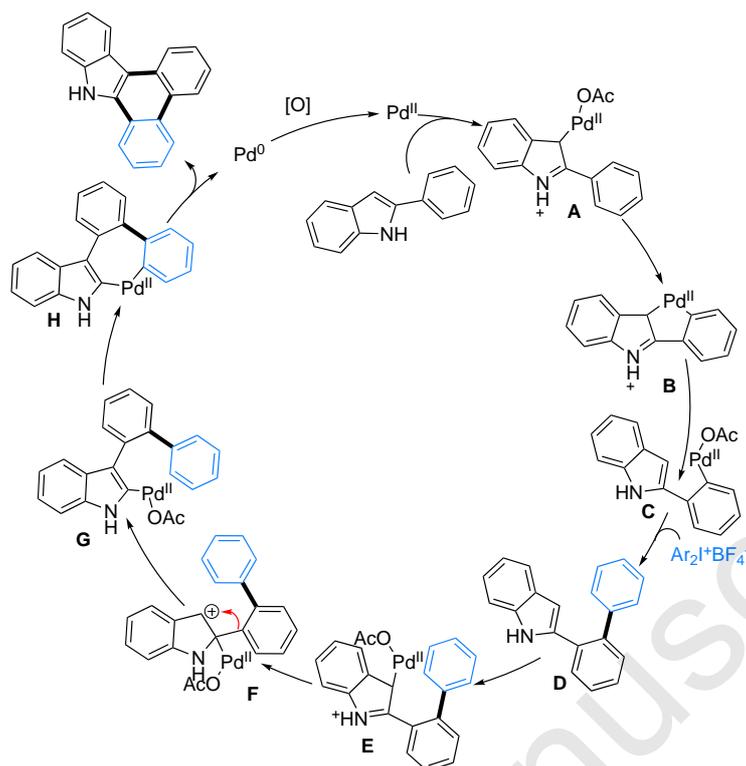
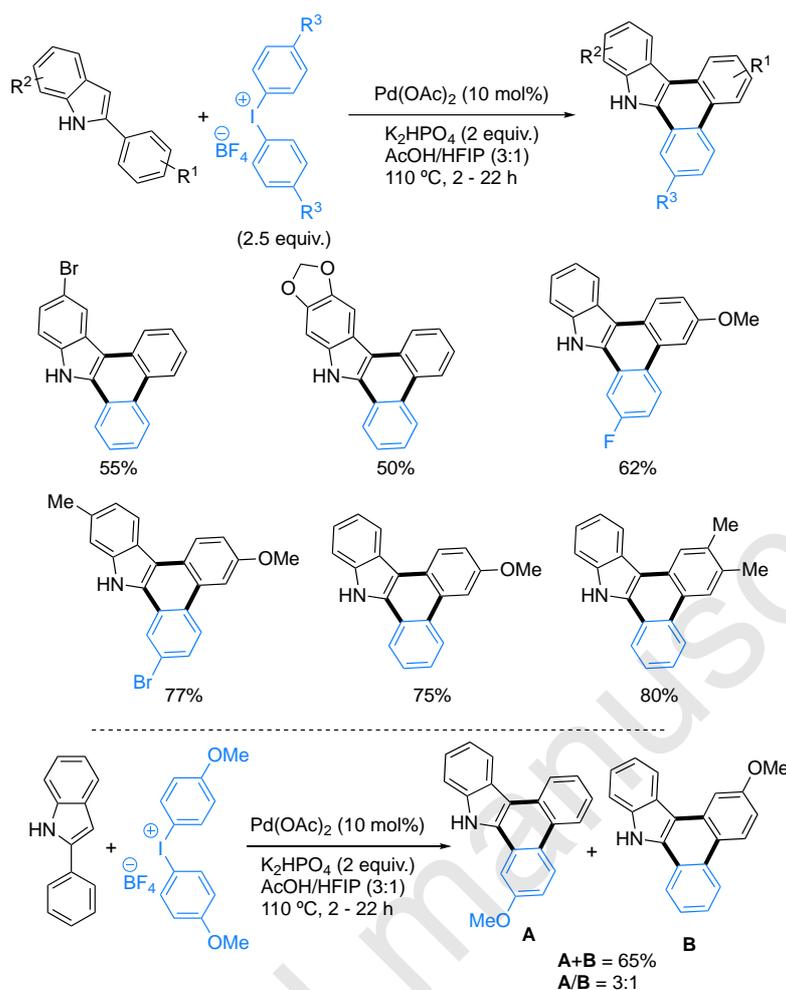


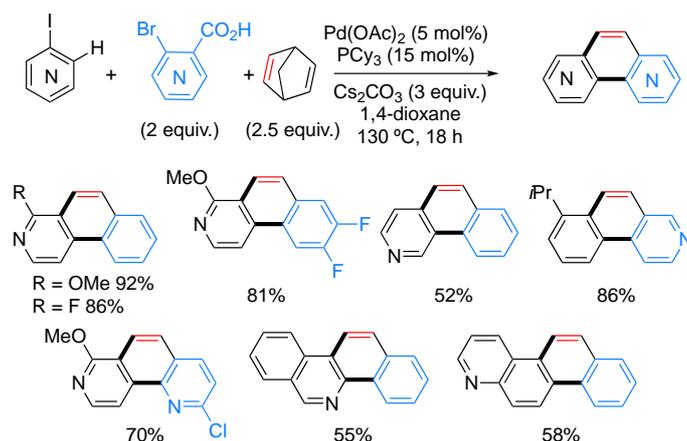
Figure 11. Proposed Mechanism of 1,4-Palladium Migration and 1,2-Aryl Shift in the Synthesis of Dibenzofused Carbazoles

The authors applied cascade reaction to diversely substituted 2-aryl indoles (Scheme 100, top).<sup>132</sup> Interestingly, the reaction tolerated halogen substituents such as bromo, chloro, and fluoro, which could be useful for further transformations to extend the  $\pi$ -system. Only non or *para*-substituted diaryliodonium salts have been employed. When diaryliodonium species was bearing more electron-rich aryls than 2-aryl indoles (2-phenyl vs. *p*-methoxyphenyl), mixtures of migratory and non-migratory products was obtained (Scheme 100, bottom). These results indicate that the aryl migration may occur through electrophilic aromatic substitution (SEAr).



Scheme 100. Access to Dibenzo[*a,c*]carbazoles through a Palladium-Catalyzed Cascade Triple C–H Arylations

Kwong *et al.* applied their palladium catalyzed three-components cross-coupling of aryl halides, 2-haloarylcarboxylic acids, and norbornadiene to the preparation of PCHs containing a pyridine (Scheme 101).<sup>100</sup> Benzoquinolines were prepared from iodopyridines and 2-bromobenzoic acid or iodobenzene and bromonicotinic acid. Phenanthrolines were obtained from the coupling of iodopyridines with 2-bromonicotinic acid. The syntheses of larger PCHs were also described using 4-iodoisoquinoline or 5-iodoquinoline.



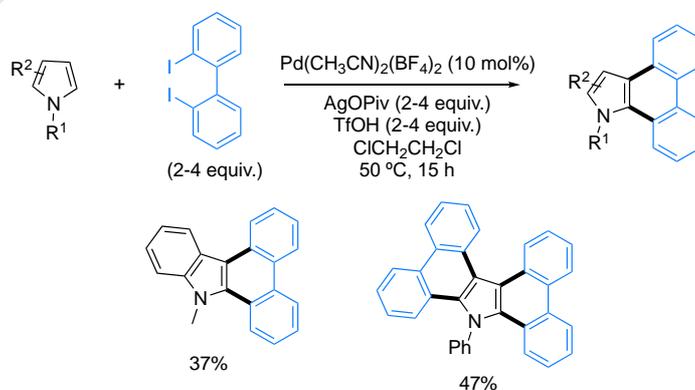
Scheme 101. Synthesis of Pyridine Containing PCHs through Palladium-Catalyzed Three-Components Cross-Couplings

During their investigations on palladium-catalyzed annulative  $\pi$ -extension reaction with dibenzosilole as annulative reagents (Scheme 74),<sup>113</sup> Itami, Ito *et al.* demonstrated that the reaction was not applicable to indole derivatives and that dibenzosilole should be replaced by dimethyldibenzogermole (Scheme 102).<sup>113</sup> Only one example has been reported, from *N*-tosylindole and dimethyldibenzogermole in the presence of 5 mol%  $\text{Pd}(\text{OAc})_2$ , 30 mol%  $\text{AgOTf}$  and 2 equivalents of *o*-chloranil, 9-tosyl-9H-dibenzo[*a,c*]carbazole was isolated in 30% yield.



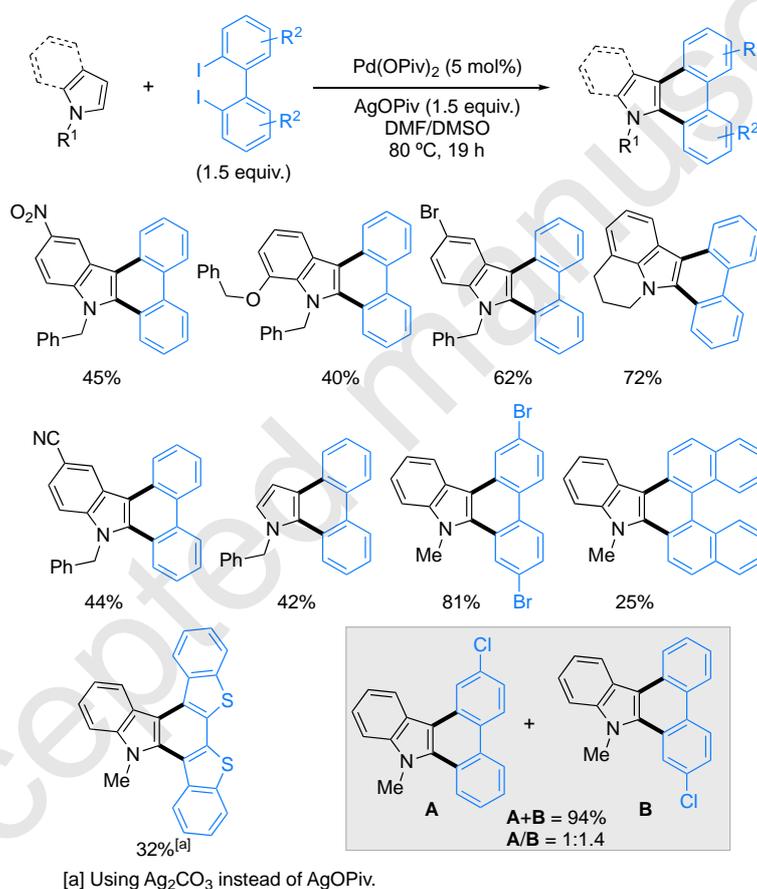
Scheme 102. Palladium-Catalyzed Annulative  $\pi$ -Extension Reaction of *N*-Tosylindole with Dimethyldibenzogermole

In the meantime, they also shown that  $\pi$ -extension reaction of *N*-methylindole could occur in better yields using 2,2'-diiodo-1,1'-biphenyl (Scheme 103).<sup>88</sup> Moreover, they performed a double annulative  $\pi$ -extension of *N*-phenylpyrrole to prepare a tetrabenzocarbazole in 47% yield.



Scheme 103. Palladium-Catalyzed Annulative  $\pi$ -Extension Reaction of *N*-Methylindole and *N*-Phenylpyrrole

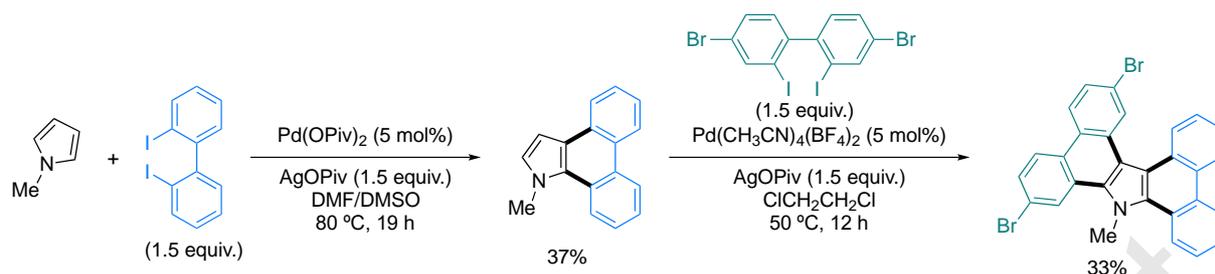
They have also reported a specific study on the palladium-catalyzed annulative  $\pi$ -extension reaction with diiodobiaryls for the preparation of nitrogen-containing PCHs (Scheme 104).<sup>133</sup> The reaction was conducted using 5 mol% of Pd(OPiv)<sub>2</sub> associated with 1.5 equivalents of AgOPiv in 7 : 3 mixture of DMF and DMSO at 80 °C, whereas TfOH was not required anymore. The reaction conditions tolerated different functionalities on indole part (e.g., NO<sub>2</sub>, OR, Br, CN). However, the *NH*-indole had to be substituted by an alkyl group, as the reaction with *N*-acetyl indole failed to deliver the PCH. Lilolidine and *N*-alkylpyrrole were successfully employed in this reaction conditions. Reactions with substituted diiodobiaryls, including a heteroaryl one, gave the expected products. However, the use of unsymmetrical diiodobiaryls led to a mixture of two regioisomers.



Scheme 104. Palladium-Catalyzed Annulative  $\pi$ -Extension Reaction of *N*-Methylindole and *N*-Phenylpyrrole

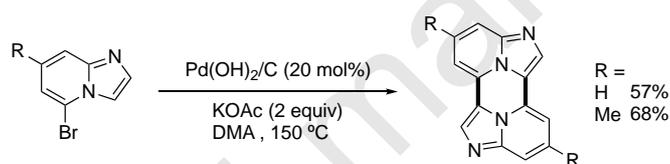
The authors demonstrated the efficiency of this technology for the construction of unsymmetrical *N*-PCHs, from simple starting materials. They employed a two-step sequence to synthesize tetrabenzocarbazole (Scheme 105).<sup>133</sup> First, reaction of *N*-methylpyrrole with 2,2'-diiodo-1,1'-biphenyl was carried out to give the corresponding dibenzo[*e,g*]indole in 37% yield. In a second step, this dibenzo[*e,g*]indole was further reacted with 4,4'-dibromo-2,2'-

diiodo-1,1'-biphenyl by using Pd(CH<sub>3</sub>CN)<sub>4</sub>(BF<sub>4</sub>)<sub>2</sub>/AgOPiv/TfOH catalytic system to give the desired tetrabenzocarbazole in 33% yield.



Scheme 105. Sequential Annulative  $\pi$ -Extension Reactions of *N*-Methylpyrrole for the Synthesis of an Unsymmetrically Substituted Tetrabenzocarbazole

In 2016, a collaborative work between Gryko's, Kozankiewicz's and Cyrański's groups offered the synthesis of a new PCH, 2,2a<sup>1.5</sup>b<sup>1.7</sup>-tetraazacyclopenta[*hi*]aceanthrylene, which is a class of seldom encountered compounds with dark lowest electronically excited singlet state. This molecule composed by two imidazo[1,2-*a*]pyridine units, was prepared by double head-to-tail direct C–H bond arylation using 20 mol% Pd(OH)<sub>2</sub>/C as catalyst in the presence of 2 equivalents of KOAc as base in DMA at 150 °C (Scheme 106).<sup>134</sup>



Scheme 106. Synthesis of Aza-Analogs of Dihydrocyclopenta[*hi*]aceanthrylene through Double Head-to-Tail Direct Arylations

## 6. Conclusion and Outlook

In the past few years, the synthesis of various planar, curved, and twisted complex  $\pi$ -conjugated polycycles has been significantly impacted by the application Pd-catalyzed C–H bond arylation. Indeed, compared to established organic synthetic methods involving multi-steps synthesis and/or harsh (FVP) conditions with stoichiometric amount of metallic salts, direct C–H bond arylation allowed preparing PAHs and PCHs in higher yields using a smaller number of steps, and with a higher functional groups tolerance. In most of the cases, intramolecular C–H functionalizations were carried out using simple palladium salts associated with inexpensive bases and allowed the straightforward synthesis of  $\pi$ -conjugated polycycles in high yields with a high degree of selectivity. The intramolecular Pd-catalyzed intramolecular C–H arylations were often performed using Pd(II) salts associated with phosphine ligands (PPh<sub>3</sub>, PCy<sub>3</sub>, SPhos, etc..) in polar solvent such as DMF or DMA. However, the nature of the phosphine may not matter. In most of the cases, its major role is to promote the reduction of Pd(II) into Pd(0), and in some cases to increase the oxidative addition rate of the deactivated (pseudo)aryl halides to

palladium. On the other hand, Pd<sub>2</sub>(bda)<sub>3</sub> can also be employed as Pd(0) source. Regarding, the nature of the base, organic bases such as DBU is often used. Until recently, the preparation of the substrates was quite challenging and remained a major drawback. Now, with the development of very selective C–H bond arylation methods exhibiting orthogonal reactivities (*i.e.*, tolerant toward C–halo bonds, such as Pd-catalyzed desulfitative arylation), the preparation of  $\pi$ -conjugated polycycles through successive C–H bond functionalizations can be achieved from simple substrates.

On the other hand, the cascade C–H bond annulation enabled the direct  $\pi$ -extension of diverse aromatics and heteroaromatics in a one-pot process. Pd-catalyzed C–H bond arylation was not only applied in the synthesis of known PAHs and PCHs but also offers the opportunity to design novel  $\pi$ -conjugated polycycles, especially geodesic PAHs or PCHs *via* the challenging formation of very strained cycles. However, many challenges remain in the application of Pd-catalyzed C–H bond intra- and/or inter-molecular arylations for the synthesis of complex  $\pi$ -conjugated polycycles. In several cases, nearly stoichiometric amount of palladium catalysts had to be employed. Therefore, the development of more efficient catalysts needed to be developed in order to provide more economically attractive procedures. Moreover, the development of more selective catalysts, as well as the discovery of new arylating sources with orthogonal reactivities, will open new ways to prepare unprecedented sophisticated  $\pi$ -conjugated polycycles such as larger polycycles or PCHs composed by different heterocycles units, which could find further applications in the preparation of innovative optoelectronic devices.

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