Palladium-catalyzed double cross-coupling reaction of 1,2-bis(pinacolatoboryl)alkenes and -arenes with 2,2′-dibromobiaryls: annulative approach to functionalized polycyclic aromatic hydrocarbons

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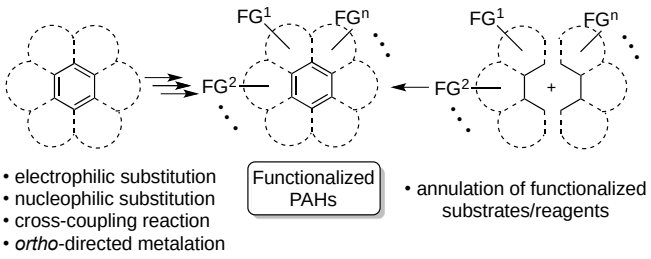
ABSTRACT

This study demonstrates that the double cross-coupling reaction of 1,2-bis(pinacolatoboryl)-alkenes and -arenes with 2,2′-dibromobiaryls proceeds smoothly with the aid of a catalytic amount of $Pd(PPh_3)_4$ in the presence of excess base to give a variety of polycyclic aromatic hydrocarbons such as phenanthrenes, [5]helicene, dithienobenzenes, triphenylenes, dibenzo-[*g*,*p*]chrysenes, and triphenyleno[1,2-*b*:4,3-*b*′]dithiophenes in good to high yields. It is noteworthy that the annulations using 2,2′-dibromooctafluorobiphenyl as an electrophile furnish the otherwise difficult to synthesize octafluorophenanthrenes and semi-fluorinated dibenzo[*g*,*p*]chrysenes in high yields.

Keywords:
Annulation
Aromatic hydrocarbons
Boron
Cross-coupling reaction
Palladium

1. Introduction

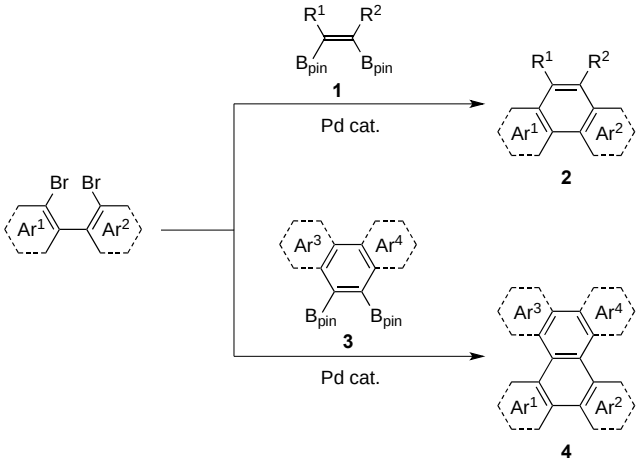
Polycyclic aromatic hydrocarbons (PAHs) have gained much attention as key components of functional organic materials such as light emitters, semiconductors, light-absorption dyes, and liquid crystals.[1] Electronic, optical, and morphological properties of organic materials based on PAHs are closely related to their molecular and electronic structures, which can be tuned by incorporation of appropriate functional groups, fusion of heteroaromatic rings, and/or bridging heteroatoms. Therefore, the development of efficient synthetic methods for producing functionalized PAHs is fundamental to the invention and modification of PAH-based functional materials, which have undisputedly contributed to the advancement of organic electronics. Conventional approaches to producing functionalized PAHs include functionalization of target polycyclic aromatic rings, electrophilic or nucleophilic substitution,[2] cross-coupling reactions,[3] and *ortho*-directed metalation.[4] With these approaches, the functional groups that can be introduced into the PAHs, as well as their substitution patterns, are strongly governed by the reactivity and regioselectivity of the parent PAH frameworks. Alternatively, annulation of functionalized substrates and reagents provides a more flexible and versatile means for producing functionalized PAHs, which may circumvent the limitations of the conventional approach, provided that appropriate precursors are readily available and ring formation is feasible with wide functional group compatibility.



Scheme 1. Synthetic Approach to Functionalized PAHs (FG: functional group).

The transition-metal-catalyzed/mediated cross-coupling reaction of organometallic reagents and organic (pseudo)halides is one of the most useful methodologies for forming bonds between sp^2 carbons stereospecifically. Hence, the double cross-coupling reaction of organodimetallic reagents and their equivalents with organic di(pseudo)halides is quite attractive as a straightforward approach to the synthesis of PAHs.[5] For example, the palladium-catalyzed reaction of 2,2′-diborylbiphenyl with 1,2-dibromobenzenes has been reported as a method for the preparation of unsymmetrical triphenylenes.[6] Copper-mediated annulation of zirconacyclopentadienes with 1,2-dihaloarenes has

been demonstrated to serve as an efficient synthetic method for polysubstituted naphthalenes, anthracenes, quinolines, and isoquinolines.[7] Double cross-coupling of [Zr(2,2′-biphenyldilyl)$_3$][Li•(THF)$_4$]$_2$ with 1,2-dihaloarenes has been shown to proceed without the aid of a transition metal complex to give triphenylenes and tetrabenz[*a*,*c*,*h*,*j*]anthracenes.[8] Palladium-catalyzed annulation of 9-stannafluorenes with 1,2-dihaloarenes has also been carried out.[9] These precedents are categorized as benzannulation of 1,4-dimetal reagents or their equivalents with 1,2-dihalogenated compounds. In sharp contrast, the double cross-coupling reaction of 1,2-dimetal reagents with 1,4-dihalides, which is the umpolung variant of the approach exemplified above, remains unexplored.[10] To this end, we implemented the palladium-catalyzed double cross-coupling reaction of 1,2-diborylalkenes **1** and -arenes **2** with 2,2′-dibromobiaryls (Scheme 2).[11] The considerations behing this approach include the fact that 1,2-diborylalkenes are readily accessbile by the platinum-catalyzed diborylation of alkynes[12] and the palladium-catalyzed cross-coupling reaction of organoboron reagents with organic halides (Suzuki–Miyaura coupling) exhibits wide functional group compatibility.[13] Indeed, the designed annulation allowed us to synthesize a variety of functionalized phenanthrenes, [5]helicene, dithienobenzenes, triphenylenes, dibenzo[*g*,*p*]-chrysenes, and triphenyleno[1,2-*b*:4,3-*b*′]dithiophenes. Reported herein are the details of the novel annulative approach to obtaining functionalized PAHs.[14]



Scheme 2. Palladium-catalyzed annulation of 1,2-diboryl reagents **1** and **3** with 2,2′-dibromobiaryls (B_{pin}: pinacolatoboryl).

2. Results and discussion

2.1. Preparation of 1,2-diborylalkenes and -arenes

Initially, 1,2-bis(pinacolatoboryl)-1-alkenes **1a**–**1j** were prepared by platinum-catalyzed diborylation of internal alkynes with bis(pinacolato)diboron using the protocol developed by Miyaura, Suzuki, and co-workers (Figure 1).[12e,12f] Subsequently, 9,10-diborylphenanthrenes **3a**–**3f** and diboryldithienobenzene **3g** were synthesized by photocyclization and *in situ* oxidation of diborylstilbenes **1a**–**1f** and diboryldithienoethene **1g** (Scheme 3).[15] Cyclization was carried out by the photo-irradiation of a toluene solution of **1** with a 400 W high-pressure mercury lamp at room temperature in the presence of iodine (1 equiv.) as an oxidant. The diborylarenes were generally obtained in moderate to high yields except for **3c**. In the case of **3c**, the reaction under the standard conditions resulted in the production of a complex mixture. It was thought that hydrogen iodide co-produced by the cyclization-oxidation sequence might have caused the protodeborylation of **3c** in which the carbon–boron bonds seemed

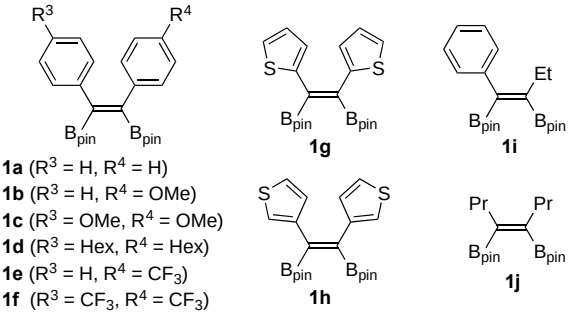
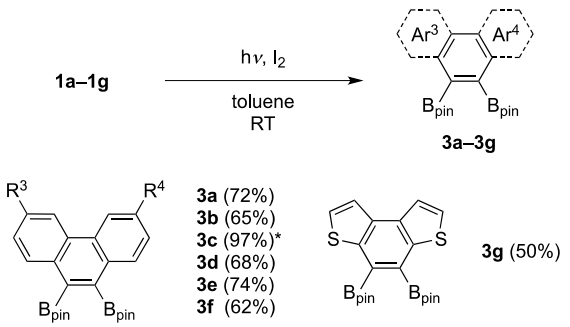


Figure 1. Molecular structures of **1**.

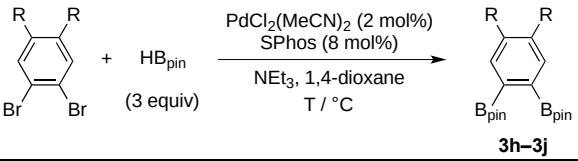


Scheme 3. Preparation of 1,2-diborylarenes **3** (in the case of **3c**, the reaction was carried out in the presence of propylene oxide).

to be more reactive toward electrophilic agents owing to the presence of two methoxy groups. Indeed, when the reaction of **1c** was effected in the presence of propylene oxide as a scavenger of hydrogen iodide, **3c** was isolated in 97% yield.[16]

Facile preparation of 1,2-diborylbenzenes was effected by applying palladium-catalyzed borylation of bromobenzenes with pinacolborane (HB_{pin}), a method which was developed by Buchwald and co-workers,[17] to 1,2-dibromobenzenes (Table 1).[18] Thus, heating a 1,4-dioxane solution of 1,2-dibromobenzenes and HB_{pin} (3 equiv.) in the presence of $PdCl_2(MeCN)_2$ (2 mol%), 2-dicyclohexylphosphino-2′,6′-dimethoxybiphenyl (SPhos; 8 mol%), and triethylamine at 110 or 80 °C gave 1,2-diborylbenzenes **3h**–**3j** in moderate to high yields.

Table 1.
Preparation of 1,2-diborylbenzenes **3h**–**3j**[a]



Entry	R	*T* (°C)	*t* (h)	**3**	Isolated yield (%)
1	H	110	24	**3h**	51
2	OMe	80	16	**3i**	64
3	Me	110	19	**3j**	81

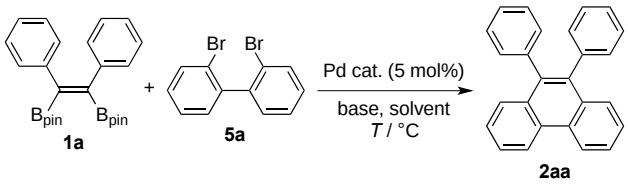
[a] Conditions: 1,2-dibromobenzene (1 equiv.), pinacolborane (HB_{pin}, 3 equiv.), $PdCl_2(MeCN)_2$ (2 mol%), 2-dicyclohexylphosphino-2′,6′-dimethoxybiphenyl (SPhos, 8 mol%), 1,4-dioxane, 80 or 100 °C.

2.2. Double cross-coupling reaction of 1,2-diborylalkenes

(*Z*)-1,2-Bis(pinacolatoboryl)stilbene (**1a**) was selected as a model 1,2-diborylalkene and 2,2′-dibromobiphenyl (**5a**) as the coupling partner. The reaction conditions were optimized via extensive screening with respect to the palladium source, base, solvent, and temperature. The screening results are summarized in Table 2. When the double cross-coupling reaction was attempted using $PdCl_2(dppf)$ as a catalyst and Cs_2CO_3, KOAc, or CsF as a base in THF at 60 °C, none or only trace amounts of the

desired product (**2aa**) formed with quantitative recovery of **1a** and **5a** (entries 1–3). A slight increase in the GC yield (10%) was observed when K_2CO_3 was used as the base (entry 4). Furthermore, it was found that the addition of water in conjunction with K_2CO_3 was quite effective in improving the yield (entries 5–7).[19] Thus, the GC yield increased from 10% to 40% when 50 equiv. of water was added to the reaction mixture with 6 equiv. of K_2CO_3 (entry 6). Other palladium catalysts such as $Pd(P^tBu_3)_2$, $Pd(OAc)_2/PCy_3$, and $Pd(PPh_3)_4$ were also examined in the presence of K_2CO_3 (6 equiv.)/H_2O (50 equiv.) in THF (0.05 M) at 60 °C for 24 h (entries 8–10). Gratifyingly, the desired **2aa** was produced in 89% GC yield and isolated in 80% yield when the double cross-coupling reaction was conducted using $Pd(PPh_3)_4$ as the catalyst.[20] Screening of other solvents such as DME, 1,4-dioxane, toluene, MeOH, and DMF revealed that THF was the most effective in promoting the annulation (entries 10–15). The temperature effect was also studied (entries 10 and 16–19) and 60 °C was confirmed to be the most effective reaction temperature. Therefore, the reaction conditions of entry 10 were considered to be optimal and applicable to a gram-scale synthesis of **2aa** (entry 20). Under the reaction conditions employed, neither oligomers nor polymers were detected in any of the cases.

Table 2.
Double cross-coupling reaction of 1,2-diborylstilbene **1a** with 2,2′-dibromobiphenyl (**5a**)[a]

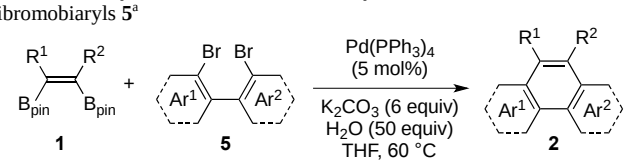


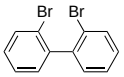
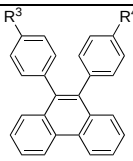
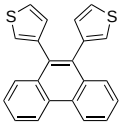
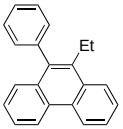
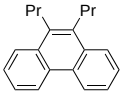
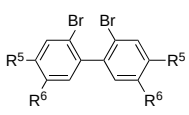
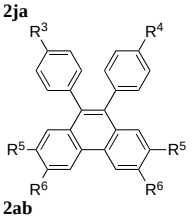
Entry	Pd cat.	Base (equiv.)	Solvent	*T* (°C)	Yield (%)[b]
1	$PdCl_2(dppf)$	Cs_2CO_3 (6)	THF	60	2
2	$PdCl_2(dppf)$	KOAc (6)	THF	60	0
3	$PdCl_2(dppf)$	CsF (6)	THF	60	4
4	$PdCl_2(dppf)$	K_2CO_3 (6)	THF	60	10
5	$PdCl_2(dppf)$	K_2CO_3 (6)/H_2O (6)	THF	60	18
6	$PdCl_2(dppf)$	K_2CO_3 (6)/H_2O (50)	THF	60	40
7	$PdCl_2(dppf)$	K_2CO_3 (6)/H_2O (100)	THF	60	31
8	$Pd(P^tBu_3)_2$	K_2CO_3 (6)/H_2O (50)	THF	60	42
9	$Pd(OAc)_2/PCy_3$	K_2CO_3 (6)/H_2O (50)	THF	60	40
10[c]	$Pd(PPh_3)_4$	K_2CO_3 (6)/H_2O (50)	THF	60	89 (80)[d]
11	$Pd(PPh_3)_4$	K_2CO_3 (6)/H_2O (50)	DME	60	64
12	$Pd(PPh_3)_4$	K_2CO_3 (6)/H_2O (50)	dioxane	60	66
13	$Pd(PPh_3)_4$	K_2CO_3 (6)/H_2O (50)	toluene	60	23
14	$Pd(PPh_3)_4$	K_2CO_3 (6)/H_2O (50)	MeOH	60	0
15	$Pd(PPh_3)_4$	K_2CO_3 (6)/H_2O (50)	DMF	60	26
16[c]	$Pd(PPh_3)_4$	K_2CO_3 (6)/H_2O (50)	THF	RT	3
17[c]	$Pd(PPh_3)_4$	K_2CO_3 (6)/H_2O (50)	THF	40	8
18[c]	$Pd(PPh_3)_4$	K_2CO_3 (6)/H_2O (50)	DME	80	80
19[c]	$Pd(PPh_3)_4$	K_2CO_3 (6)/H_2O (50)	dioxane	100	78
20[e]	$Pd(PPh_3)_4$	K_2CO_3 (6)/H_2O (50)	THF	60	(82)

[a] Reaction conditions: **1a** (0.05 mmol), **5a** (0.06 mmol), Pd cat. (2.5 μmol), base, solvent (1 mL), 48 h.
[b] Yield was calculated from GC analysis using *n*-dodecane as an internal standard. The value in parentheses is isolated yield.
[c] Reaction conditions: **1a** (0.06 mmol), **5a** (0.05 mmol), $Pd(PPh_3)_4$ (2.5 μmol), base, solvent (1 mL), 48 h.
[d] Reaction conditions: **1a** (1.2 mmol), **5a** (1.0 mmol), $Pd(PPh_3)_4$ (50 μmol), K_2CO_3 (6.0 mmol), H_2O (50 mmol), THF (20 mL), 60 °C, 48 h.
[e] Reaction conditions: **1a** (2.16 g, 6.0 mmol), **5a** (1.56 g, 5.0 mmol), $Pd(PPh_3)_4$ (0.30 g, 0.25 mmol), K_2CO_3 (4.10 g, 30 mmol), H_2O (4.5 mL, 250 mmol), THF (100 mL), 60 °C, 48 h.

The scope of the aromatic annulation of 1,2-diborylalkenes **1** and 2,2′-dibromobiaryls **5** is summarized in Table 3.[21] Methoxy- and dimethoxy-substituted diborylstilbenes **1b** and **1c** were coupled with **5a** to give **2ba** and **2ca**, respectively, in high yields (entries 1 and 2), whereas dihexyl-substituted diborylstilbene **1d** gave **2da** in 32% yield (entry 3). Trifluoromethyl-substituted diborylstilbene **1e** reacted with **5a** to give **2ea** in a good yield (entry 4). In addition to diborylstilbenes, diboryldithienylethene **1h**, 1,2-diboryl-1-phenylbut-1-ene **1i**, and 4,5-diboryloct-4-ene **1j** underwent the double cross-coupling reaction with **5a**, giving rise to **2ha**, **2ia**, and **2ja**, respectively (entries 5–7), in good to excellent yields, respectively, although a slight modification of the base was necessary for **1j** and **1i**. Substituted dibromobiphenyls **5b**–**5e** were also amenable to the annulation to give the corresponding symmetrical and unsymmetrical 9,10-diarylphenanthrenes in moderate to high yields (entries 8–14). Octafluorophenanthrenes **2ah**, **2ch**, and **2hh**, which were difficult to prepare by other synthetic methods, were obtained in good to high yields by the reaction of **1** with 2,2′-dibromo-3,3′,4,4′,5,5′,6,6′-octafluorobiphenyl (**5h**) (entries 15–17). When dibrominated binaphthyl **5i**, bithiophene **5j**, and bi(benzothiophene) **5k** reacted with **1**, [5]helicene **2ai** and dithienobenzenes **2aj** and **2jk** were isolated in 32–84% yields (entries 18–20).[22] The latter two examples clearly illustrate that the fusion mode of heterocycles onto a core aromatic ring can be easily controlled by the judicious selection of the starting 2,2′-dibromobi(heteroaryl)s.

Table 3.
Palladium-catalyzed annulation of 1,2-diborylalkenes **1** and 2,2′-dibromobiaryls **5**[a]



Entry	1	5	2	Yield (%)[b]
				
1	**1b**	**5a**	**2ba**	81
2	**1c**	**5a**	**2ca**	92
3	**1d**	**5a**	**2da**	32
4	**1e**	**5a**	**2ea**	77
				
5	**1h**	**5a**	**2ha**	71
				
6	**1i**	**5a**	**2ia**	99[c] (8)[d]
				
7	**1j**	**5a**	**2ja**	81[e] (28)[d]
				
8	**1a**	**5b** (R^5 = H, R^6 = OMe)	**2ab**	20
9	**1a**	**5c** (R^5, R^6 = OMe)	**2ac**	82
10	**1c**	**5c**	**2cc**	68
11	**1a**	**5d** (R^5, R^6 = Me)	**2ad**	85

12	**1a**	**5e** (R^5, R^7, R^8 = H)	**2ae**	40[f]
13	**1a**	**5f** (R^5 = OMe, R^7, R^8 = H)	**2af**	80[f]
14	**1a**	**5g** (R^5 = OMe, R^7, R^8 = F)	**2ag**	79[f]
15	**1a**	**5h**	**2ah**	65
16	**1c**	**5h**	**2ch**	85
17	**1h**	**5h**	**2hh**	90
18	**1a**	**5i**	**2ai**	32
19	**1a**	**5j**	**2aj**	84
20	**1j**	**5k**	**2jk**	57[g]

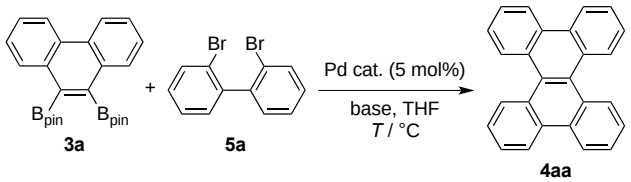
[a] Reaction conditions: **1** (1.2 mmol), **5** (1.0 mmol), $Pd(PPh_3)_4$ (50 μmol), K_2CO_3 (6.0 mmol), H_2O (50 mmol), THF (20 mL), 60 °C, 48 h.
[b] Yield of isolated product.
[c] 3 M aq K_3PO_4 (6 equiv.) was used in place of K_2CO_3/H_2O.
[d] Reaction conditions: **1** (0.06 mmol), **5** (0.05 mmol), $Pd(PPh_3)_4$ (2.5 μmol), K_2CO_3 (0.3 mmol), H_2O (2.5 mmol), THF (1 mL), 60 °C, 48 h.
[e] 3 M aq NaOH (6 equiv.) was used in place of K_2CO_3/H_2O.
[f] Reaction conditions: **1** (0.6 mmol), **5** (0.5 mmol), $Pd(PPh_3)_4$ (25 μmol), K_2CO_3 (3.0 mmol), H_2O (25 mmol), THF (10 mL), 60 °C, 48 h.
[g] $PdCl_2(dppf)$ (5 mol%) and 3 M aq K_3PO_4 (6 equiv.) were used in place of $Pd(PPh_3)_4$ and K_2CO_3/H_2O, respectively.

2.3. Double cross-coupling reaction of 1,2-diborylarenes

To extend the applicability of the present approach, we further studied the double cross-coupling reaction of 1,2-diborylarenes **3** with **5**. First, the reaction conditions were optimized using 9,10-bis(pinacolatoboryl)phenanthrene (**3a**) and **5a**. The results are summarized in Table 4. When the reaction of **3a** with **5a** was effected under the optimal conditions for **1**, dibenzo[*g*,*p*]chrysene (**4aa**), the desired annulation product was obtained in moderate yield (entry 1). Neither the change in the reaction temperatures from 60 °C to room temperature, 80, or 100 °C nor the use of $Pd(PtBu_3)_2$ or $PdCl_2(dppf)$ as a palladium catalyst was effective in improving the yield (entries 2–6). Screening of various 3 M aqueous bases such as K_2CO_3, NaOH, KOH, Cs_2CO_3, and K_3PO_4 indicated that aqueous K_3PO_4 was the most effective base for the production of **4aa** (entries 7–12). Thus, the optimized conditions for the double cross-coupling reaction of **3** and **5** were determined to be those that employed 5 mol% of $Pd(PPh_3)_4$ and 6 equivalents of 3 M aqueous K_3PO_4 in THF at 60 °C for 48 h.

The scope of the annulation reaction of **3** with **5** is shown in Table 5. Methoxy-, dimethoxy-, dihexyl-, trifluoromethyl- and bis(trifluoromethyl)-substituted diborylphenanthrenes **3b**–**3f** reacted with various derivatives of **5** to give a variety of symmetric and unsymmetrical dibenzo[*g*,*p*]chrysenes **4** in moderate to good yields (entries 1–5, 10, and 12–15). The annulation using **5h** proceeded smoothly to give octafluorodibenzo[*g*,*p*]chrysenes **4ah**, **4bh**, **4ch**, **4dh**, and **4eh** in good to excellent yields (entries 16–20). It should be noted that multi-substituted dibenzo[*g*,*p*]chrysenes are not readily accessible by the conventional methods.[23] Triphenyleno[1,2-*b*:4,3-*b*′]dithiophenes **4ga** and **4gh** were produced in 54% and 81% yield by the reaction of diboryldithienobenzene **3g** with **5a** and **5h**, respectively (entries 6 and 21). Diborylbenzenes **2h**–**2j** were also amenable to this annulation; triphenylenes **4ha**, **4ia**, **4ja**, **4hb**, **4hh**, **4ih**, and **4jh** were produced in good to high yields (entries 7–9, 11, and 22–24). Dibromobithiophene **5j** served as the coupling partner of **3a** and **3h** to give **4aj** and **4hj**, respectively (entries 25 and 26).

Table 4.
Double cross-coupling reaction of 9,10-diborylphenanthrene **3a** with **5a**[a]

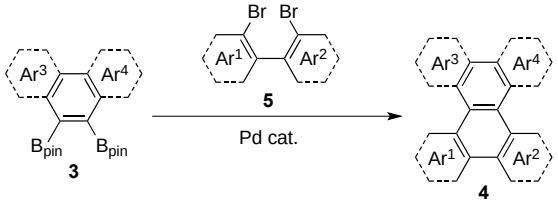


3a **5a** **4aa**

Entry	Pd cat.	Base (equiv.)	*T* (°C)	Yield (%)[b]
1[c]	$Pd(PPh_3)_4$	K_2CO_3 (6)/H_2O (50)	60	68
2	$Pd(PPh_3)_4$	K_2CO_3 (6)/H_2O (50)	RT	0
3	$Pd(PPh_3)_4$	K_2CO_3 (6)/H_2O (50)	80	66
4	$Pd(PPh_3)_4$	K_2CO_3 (6)/H_2O (50)	100	49
5	$Pd(PtBu_3)_2$	K_2CO_3 (6)/H_2O (50)	60	20
6	$PdCl_2(dppf)$	K_2CO_3 (6)/H_2O (50)	60	39
7	$Pd(PPh_3)_4$	3 M aq. K_2CO_3 (6)	60	74
8	$Pd(PPh_3)_4$	3 M aq. NaOH (6)	60	30
9	$Pd(PPh_3)_4$	3 M aq. KOH (6)	60	19
10	$Pd(PPh_3)_4$	3 M aq. Cs_2CO_3 (6)	60	97
11	$Pd(PPh_3)_4$	3 M aq. K_3PO_4 (6)	60	96 (>99)
12[c]	$Pd(PPh_3)_4$	3 M aq. K_3PO_4 (6)	60	(80)

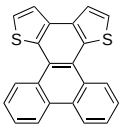
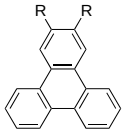
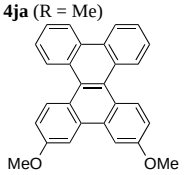
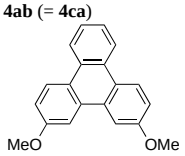
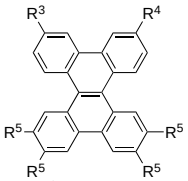
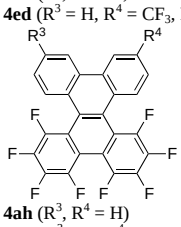
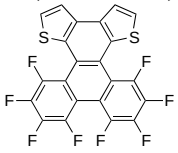
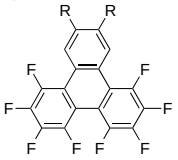
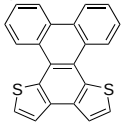
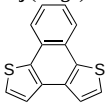
[a] Reaction conditions: **3a** (0.06 mmol), **5a** (0.05 mmol), Pd cat., base, THF (1 mL), 48 h.
[b] Yield was calculated from GC analysis using *n*-dodecane as an internal standard. The value in parentheses is isolated yield.
[c] Reaction conditions: **3a** (1.2 mmol), **5a** (1.0 mmol), $Pd(PPh_3)_4$ (50 μmol), 3 M aq. K_3PO_4 (6.0 mmol), THF (20 mL), 60 °C, 48 h.

Table 5.
Palladium-catalyzed annulation of 1,2-diborylarenes **3** and 2,2′-dibromobiaryls **5**[a]



3 **4**

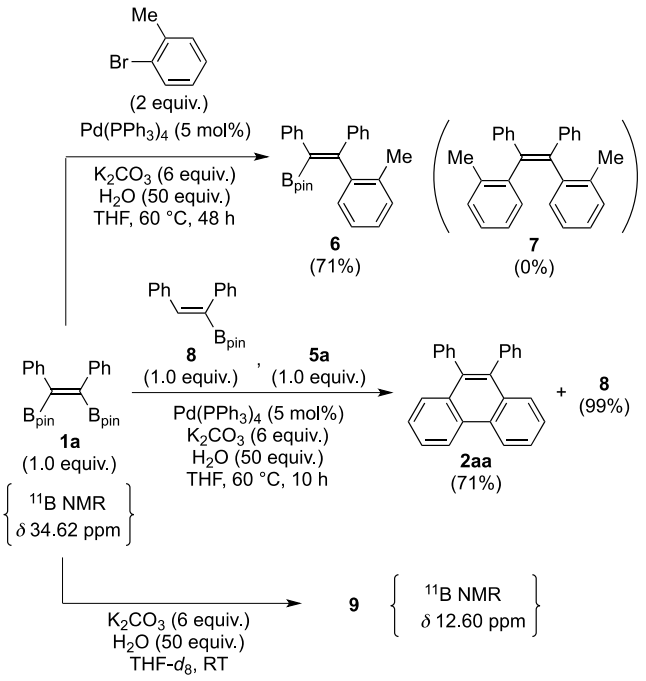
Entry	**3**	**5**	**4**	Yield (%)[b]
1	**3b**	**5a**	**4ba** (R^3 = H, R^4 = OMe)	61
2	**3c**	**5a**	**4ca** (R^3, R^4 = OMe)	64
3	**3d**	**5a**	**4da** (R^3, R^4 = Hex)	64
4[c]	**3e**	**5a**	**4ea** (R^3 = H, R^4 = CF_3)	66
5	**3f**	**5a**	**4fa** (R^3, R^4 = CF_3)	53

				
6	**3g**	**5a**	**4ga**	54
				
7[d]	**3h**	**5a**	**4ha** (R = H)	82
8[e]	**3i**	**5a**	**4ia** (R = OMe)	58
9[d]	**3j**	**5a**	**4ja** (R = Me)	65
				
10	**3a**	**5b**	**4ab** (= **4ca**)	31
				
11[d,f]	**3h**	**5b**	**4hb**	33
				
12[g]	**3a**	**5c**	**4ac** (R^3, R^4 = H, R^5 = OMe)	54
13	**3f**	**5c**	**4fc** (R^3, R^4 = CF_3, R^5 = OMe)	40
14	**3a**	**5d**	**4ad** (R^3, R^4 = H, R^5 = Me)	47
15	**3e**	**5d**	**4ed** (R^3 = H, R^4 = CF_3, R^5 = Me)	56
				
16	**3a**	**5h**	**4ah** (R^3, R^4 = H)	63
17	**3b**	**5h**	**4bh** (R^3 = H, R^4 = OMe)	80
18	**3c**	**5h**	**4ch** (R^3, R^4 = OMe)	94
19	**3d**	**5h**	**4dh** (R^3, R^4 = Hex)	82
20[h]	**3e**	**5h**	**4eh** (R^3 = H, R^4 = CF_3)	96
				
21	**3g**	**5h**	**4gh**	81
				
22[d]	**3h**	**5h**	**4hh** (R = H)	85
23[d]	**3i**	**5h**	**4ih** (R = OMe)	42
24[d]	**3j**	**5h**	**4jh** (R = Me)	76
				
25	**3a**	**5j**	**4aj** (= **4ga**)	88
				
26[d,i]	**3h**	**5j**	**4hj**	37

[a] Reaction conditions: **3** (0.06 mmol), **5** (0.05 mmol), $Pd(PPh_3)_4$ (2.5 μmol), 3 M aq. K_3PO_4 (0.3 mmol), THF (1 mL), 60 °C, 48 h.
[b] Yield of isolated product.
[c] Cs_2CO_3 (6 equiv.) and H_2O (50 equiv.) were used in place of 3 M aq. K_3PO_4.
[d] Reaction conditions: **2** (1.2 mmol), **3** (1.0 mmol), $Pd(PPh_3)_4$ (50 μmol), K_2CO_3 (6.0 mmol), H_2O (50 mmol), THF (20 mL), 60 °C, 48 h.
[e] The reaction was carried out for 42 h.
[f] The reaction was carried out for 73 h.
[g] 6 M aq K_3PO_4 (12 equiv.) was used in place of 3 M aq. K_3PO_4 at 80 °C.
[h] K_2CO_3 (6 equiv.) and H_2O (50 equiv.) were used in place of 3 M aq. K_3PO_4.
[i] The reaction was carried out for 27 h.

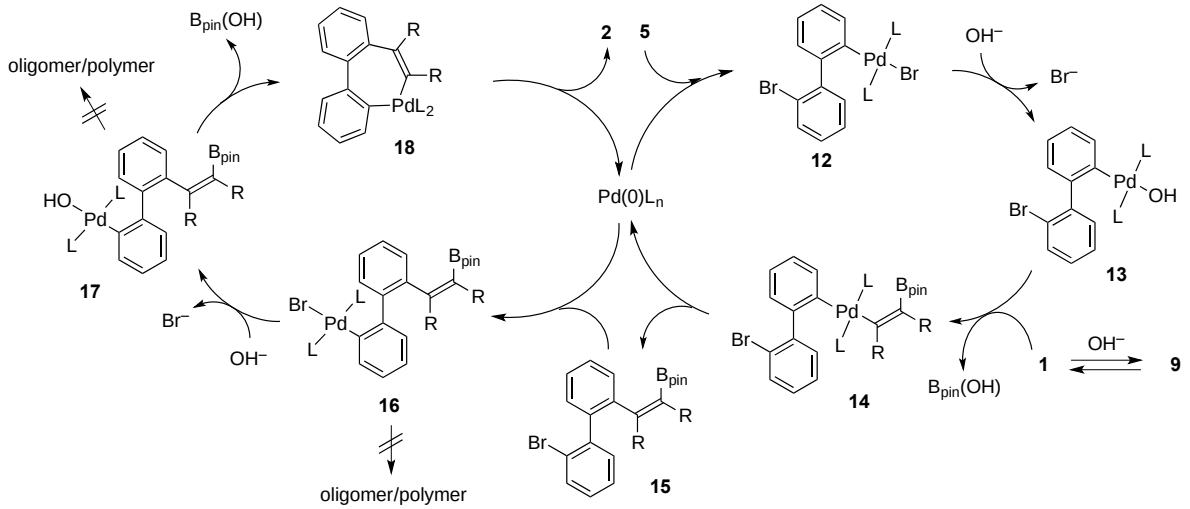
2.4. Mechanistic consideration

In order to gain mechanistic insight into the annulation reaction, the coupling reaction of **1a** with *o*-bromotoluene (2 equiv) was effected under the optimized conditions for the annulation using **1** (Scheme 4). The sole product was the mono-coupled product **6**, which was isolated in 71% yield. No formation of the di-coupled product **7** was observed. This result indicates that it is difficult for the *intermolecular* cross-coupling reaction of 1,2,2-trisubstituted ethenylboronates such as **6** with *ortho*-substituted bromobenzenes such as *o*-bromotoluene and 2,2′-dibromobiphenyl (**5a**) to occur under the employed conditions. Next, the coupling reaction of **1a** (1 equiv.) with **5a** (1 equiv.) was carried out in the presence of 1 equiv. of mono-borylstilbene **8** (Scheme 4). Unexpectedly, **2aa** was isolated in 71% yield as a sole coupling product with quantitative recovery of **8**, which implied that **1a** was much more reactive than **8** under the reaction conditions.

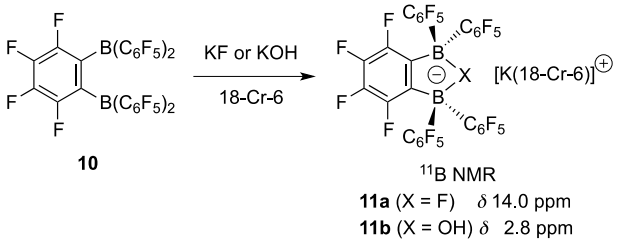


Scheme 4. Experiments performed using **1a** for elucidation of the mechanism.

Moreover, we monitored the reaction of **1a** and K_2CO_3 (6 equiv.)/H_2O (50 equiv.) in THF-d_8 by ^{11}B NMR and found that **1a** was converted into a new species **9** under the basic conditions; the addition of the base resulted in the disappearance of the ^{11}B NMR peak of **1a** at 34.62 ppm and the emergence of a single new peak at 12.60 ppm (Scheme 4). Because the borate generated by the treatment of 1,2-bis(pinacolatoboryl)octane (^{11}B NMR: δ 33.4 ppm) with KOH (3 equiv.) in dioxane-d_8 has been reported to show two singlet peaks at 34.0 and 10.5 ppm in the ^{11}B NMR spectrum,[24] the appearance of only one singlet peak at 12.60 ppm suggests that **9** is a symmetrical pinacolatoborate complex.[25] Piers and co-workers have reported that treatment of 1,2-diboryl-3,4,5,6-tetrafluorobenzene **10** with KF and KOH in the presence



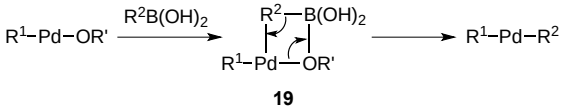
Scheme 6. Plausible catalytic cycle of the annulation.



Scheme 5. Formation of bridged borate complex **11** from 1,2-diborylbenzene **10** and potassium fluoride/hydroxide.

of 18-crown-6 produces borates **11**, in which the two boryl groups are bridged by F and OH, respectively (Scheme 5).[26] Therefore, it was likely that **9** formed a hydroxide-bridged borate structure similar to **11**.

The transition metal-catalyzed cross-coupling reaction of organometallic reagents with organic (pseudo)halides proceeds via a sequence of oxidative addition–transmetalation–reductive elimination steps. While the oxidative addition and reductive elimination processes are reasonably understood, the transmetalation step is a topic of debate.[27] In the case of the coupling reaction of organoboron reagents, in which the addition of a base is necessary for transmetalation, two mechanisms are generally proposed.[28] One involves the formation of a borate complex from an organoboronic acid or boronate with a base, and the subsequent substitution of a (pseudo)halide ion of a palladium(II) (pseudo)halide complex by a carbonaceous substituent of the borate (mechanism A). The other mechanism proposes that a palladium(II) (pseudo)halide complex is first converted into an alkoxo- or hydroxopalladium(II) complex by ligand exchange with a base, and then, a neutral organoboron reagent undergoes transmetalation with the palladium(II) complex (mechanism B). Very recently, the Carrow and Hartwig, and Amatore, Jutand, and Duc research groups independently demonstrated that mechanism B was operative in the reaction of arylpalladium halides and arylboronic acids in the presence of hydroxide ions.[29] Moreover, the transmetalation in the coupling reaction of boronic esters has also been suggested to occur through mechanism B. Based on mechanism B, a plausible catalytic cycle for the present annulation is shown in Scheme 6. Oxidative addition of **5** to a palladium(0) complex should generate a palladium(II) bromide complex **12**, which then reacts with a hydroxide ion to produce a palladium(II) hydroxo complex **13**. Transmetalation of **1** (which is in equilibrium with **9**) with **13** should give an alkenylpalladium(II) complex **14**. Successive reductive elimination would provide the mono-coupled product **15** and regenerate a palladium(0) complex. Similarly, oxidative addition of **15** followed by bromide–hydroxide exchange would generate an arylpalladium(II) hydroxo complex **17**. Intramolecular transmetalation of **17** followed by reductive elimination should result in the production of **2** and regeneration of a palladium(0) catalyst. The fact that no oligomeric/polymeric product formed in the reaction of **1a** with **5a** can be explained by assuming that the *intermolecular* reaction of **16** and/or **17** is restricted under the experimental conditions. This assumption is well supported by the result of the reaction of **1a** with *ortho*-bromotoluene shown in Scheme 4. In comparison, in mechanism B, migration of the carbonaceous group of a boron reagent to a palladium atom is proposed to proceed via a four-centered transition state **19** (Scheme 7).[30] Based on the transition state and the high Lewis acidic nature of 1,2-diboryl compounds as exemplified by **10**,[31] the reactivity difference between **1** and **8** in the annulation illustrated in Scheme 4 may be rationalized by assuming that the hydroxide-binding ability of **1** is much higher than that of **8** owing to the bifunctionality.



Scheme 7. Structure of the proposed transition state **19** in mechanism B.

3. Conclusion

This study demonstrates that the palladium-catalyzed double cross-coupling reaction of 1,2-diborylalkenes and -arenes with 2,2′-dibromobiaryls serves as a new and versatile synthetic approach to obtaining functionalized PAHs. This methodology efficiently produces a variety of functionalized phenanthrenes, dibenzo[*g*,*p*]chrysenes, triphenylenes, and their heteroaromatic analogues, which have attracted attention in recent years as versatile modules for the development of π-conjugated materials such as luminescent polymers, thin-field effect transistors, and molecular wires.[32] As such, the present study represents a fundamental contribution to the exploration and development of novel functional organic materials based on PAHs.

4. Experimental section

4.1. General

Melting points were determined using a Yanagimoto Micro Point Apparatus. ^{1}H NMR spectra measured on a Varian Mercury 300 (300 MHz) and 400 (400 MHz) spectrometers. The chemical shifts of ^{1}H NMR are expressed in parts per million downfield relative to the internal tetramethylsilane (δ = 0 ppm) or chloroform (δ = 7.26 ppm). Splitting patterns are indicated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. ^{13}C NMR spectra were measured on a Varian Mercury 300 (75 MHz) and 400 (100 MHz) spectrometers with tetramethylsilane as an internal standard (δ = 0 ppm) or chloroform (δ = 77.0 ppm). ^{19}F NMR spectra were measured on a Varian Mercury 300 (282 MHz) spectrometer with $CFCl_3$ as an internal standard (δ = 0 ppm). Chemical shift values are given in parts per million downfield relative to the internal standard. Infrared spectra (IR) were recorded on a Shimadzu FTIR-8400 spectrometer. GC-MS analyses were performed with a JEOL JMS-700 spectrometer by electron ionization at 70 eV. Elemental analyses were carried out with a YANAKO MT2 CHN CORDER machine at Elemental Analysis Center of Kyoto University. TLC analyses were performed by means of Merck Kieselgel 60 F_{254} and column chromatography was carried out using Merck Kieselgel 60 (230–400 mesh). Preparative HPLC was carried out with a Japan Analytical Industry Co., Ltd, LC-908 chromatograph using a JAIGEL-1H and -2H GPC columns. Tetrahydrofuran was passed through two packed columns of neutral alumina and copper oxide under a nitrogen atmosphere before use. All reactions were carried out under an argon atmosphere.

*4.2. Preparation of 1,2-Diborylalkenes **1***

vic-Diborylalkenes **1** were prepared according to the reported procedure of platinum-catalyzed diborylation of alkynes with bis(pinacolato)diboron.[12e,12f,14]

*4.3. General Procedures for Preparation of 1,2-Diborylarenes **3** by Photo-cyclization of 1,2-Diborylalkenes **1** and Subsequent in situ Oxidation*

Preparation of **3** except for **3c**: A stirred toluene (1 L) solution of **1** (4.0 mmol) and I_2 (1.02 g, 4.0 mmol) was purged with argon for 30 min. The resulting solution was irradiated with a 400 W high-pressure mercury lamp at room temperature for 12 h. The organic layer was washed with saturated aq $Na_2S_2O_3$ solution and saturated aq NaCl solution, and then dried over anhydrous $MgSO_4$. Removal of organic solvent by rotary evaporator followed by recrystallization from hexane gave **3** as a colorless solid. *4,5-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-benzo[1,2-b:4,3-b']dithiophene (**3g**)*: Yield: 50%, colorless solid. Mp: 230.4–233.7 °C. TLC: R_f 0.35 (hexane/AcOEt 4:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.46 (s, 24H), 7.59 (d, 2H, *J* = 5.5 Hz), 7.68 (d, 2H, *J* = 5.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 25.1, 84.4, 116.3, 121.2, 127.9, 135.0, 141.1. IR (KBr): ν = 2978, 1472, 1446, 1391, 1380, 1371, 1321, 1260, 1214, 1181, 1167, 1144, 1109, 849, 737 cm^{-1}. MS (FAB) *m/z*: 444 (32, M^+ + 2), 443 (73, M^+ + 1), (100, M^+), 301 (100). Anal. Calcd for: $C_{22}H_{28}B_2O_4S_2$: C, 59.75; H, 6.38. Found: C, 59.74; H, 6.26.

Preparation of **3c**: A stirred toluene (500 mL) solution of **1c** (0.98 g, 2.0 mmol) and I_2 (0.51 g, 2.0 mmol) was purged with argon for 30 min before the addition of propylene oxide (1.40 mL, 20 mmol). The resulting solution was irradiated with a 400 W high-pressure mercury lamp at room temperature for 6 h. The organic layer was washed with an aq $Na_2S_2O_3$ solution and saturated aq NaCl solution, and then dried over anhydrous $MgSO_4$. Removal of organic solvent by rotary evaporator followed by recrystallization from diethyl ether gave **3c** (0.95 g, 97% yield) as a colorless solid.

*4.4. General Procedure for Preparation of 1,2-Diborylarenes **3h**–**3j** by Palladium-catalyzed Borylation of 1,2-Dibromoarenes with Pinacolborane*

To a Schlenk tube (20 mL) were added $PdCl_2(MeCN)_2$ (26 mg, 0.10 mmol) and 2-dicyclohexylphosphino-2′,6′-dimethoxy-biphenyl (SPhos, 0.16 g, 0.40 mmol). The Schlenk tube was capped with a rubber septum and then evacuated and purged with argon. The evacuation–purge operation was repeated twice. To the tube was added 1,4-dioxane (6.0 mL), 1,2-dibromobenzene (1.63 g, 0.82 mL, 5.0 mmol), NEt_3 (3.04 g, 4.18 mL, 30.0 mmol), and pinacolborane (2.18 mL, 1.92 g, 15.0 mmol) in this order with syringes, respectively, through the septum. The reaction mixture was heated at 110 °C and the progress of the reaction was monitored by gas chromatography. After the complete consumption of the dibromide was confirmed, the reaction mixture was then allowed to cool to room temperature. The resulting solution was filtered through a thin pad of Celite with EtOAc as the eluent. The organic solvent was removed under reduced pressure to give the crude product which was purified by column chromatography on silica gel followed by recrystallization from hexane at –20 °C, giving rise to 1,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (**3h**, 0.83 g, 51%) as a colorless solid. Mp: 107.1–107.6 °C. TLC: R_f 0.20 (hexane/AcOEt 15:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.38 (s, 24H), 7.34–7.40 (m, 2H), 7.62–7.67 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 25.0, 83.8, 129.0, 133.3. IR (KBr): ν = 3050, 2978, 2934, 1593, 1562, 1495, 1379, 1371, 1344, 1329, 1306, 1271, 1165, 1146, 1105, 1053, 963, 858, 752, 683, 671 cm^{-1}. MS (EI) *m/z*: 331 (7, M^+ + 1), 330 (30, M^+), 329 (15, M^+ – 1), 315 (52), 272 (90), 189 (100). Anal. Calcd for $C_{18}H_{28}B_2O_4$: C, 65.51; H, 8.55. Found: C, 65.42; H, 8.52.

*1,2-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3,4-dimethoxybenzene (**3i**)*: Purified by silica gel column chromatography (hexane/AcOEt 20:1–2:1). Yield: 64%, colorless solid. Mp: 118.0–118.6 °C. TLC: R_f 0.35 (hexane/AcOEt 4:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.37 (s, 24H), 3.92 (s, 6H), 7.15 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 25.0, 55.8, 83.7, 116.1, 149.5. IR (KBr): ν = 2978, 2945, 1587, 1557, 1479, 1445, 1416, 1385, 1360, 1317, 1254, 1196, 1173, 1140, 1119, 1046, 1034, 1005, 964, 880, 860, 762, 748, 692, 610 cm^{-1}. MS (EI) *m/z*: 392 (3, M^+ + 2), 391 (23, M^+ + 1), 390 (100, M^+). Anal. Calcd for $C_{20}H_{32}B_2O_6$: C, 61.58; H, 8.27. Found: C, 61.36; H, 8.51.

*1,2-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3,4-dimethylbenzene (**3j**)*: Purified by silica gel column chromatography (hexane/AcOEt 15:1). Yield: 81%, colorless solid. Mp: 134.1–134.9 °C. TLC: R_f 0.22 (hexane/AcOEt 15:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.37 (s, 24H), 2.25 (s, 6H), 7.41 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.9, 25.0, 83.6, 134.8, 137.5. IR (KBr): ν = 2978, 2930, 1601, 1547, 1514, 1445, 1416, 1371, 1360, 1317, 1273, 1215, 1140, 1119, 1011, 980, 964, 860, 683, 667 cm^{-1}. MS (EI) *m/z*: 360 (3, M^+ + 2), 359 (21, M^+ + 1), 358 (100, M^+). Anal. Calcd for $C_{20}H_{32}B_2O_4$: C, 66.86; H, 9.08. Found: C, 67.08; H, 9.01.

4.5. Representative Procedure for Preparation of Unsymmetrical 2,2′-Dibromobiphenyls:

A Schlenk tube (250 mL) was charged with 1,2-dibromo-benzene (2.26 g, 9.6 mmol), 3,4-dimethoxyphenylboronic acid (1.46 g, 8.0 mmol), $Pd(PPh_3)_4$ (92 mg, 0.080 mmol), benzene (64 mL), EtOH (19 mL), and 2 M aq Na_2CO_3 solution (12 mL, 24 mmol). The reaction mixture was heated at reflux for 24 h.

After cooled to room temperature, the mixture was diluted with water (50 mL) and the aqueous layer was extracted with AcOEt (50 mL × 3). The combined organic solvent was washed with saturated aq NaCl solution (50 mL), dried over anhydrous $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (hexane/AcOEt 7:1) to give 2-bromo-3′,4′-dimethoxybiphenyl (1.34 g, 57%) as a colorless oil. A Schlenk tube (80 mL) was charged with 2-bromo-3′,4′-dimethoxybiphenyl (1.20 g, 4.1 mmol) and acetic acid (8.7 mL). To the solution was added bromine (0.25 mL, 4.9 mmol) at room temperature. The resulting mixture was stirred overnight before quenching with saturated aq $Na_2S_2O_3$ solution (50 mL). The aqueous layer was extracted with CH_2Cl_2 (50 mL × 3). The combined organic layer was washed with saturated aq NaCl solution (50 mL), dried over anhydrous $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (hexane/AcOEt 7:1) to produce 2,2′-dibromo-4,5-dimethoxybiphenyl (**5f**, 1.44 g, 95%) as a colorless solid.

2-Bromo-3',4'-dimethoxybiphenyl: TLC: R_f 0.19 (hexane/AcOEt 7:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.92 (s, 3H), 3.94 (s, 3H), 6.91–6.98 (m, 3H), 7.16–7.22 (m, 1H), 7.32–7.37 (m, 2H), 7.66 (dd, *J* = 8.0, 0.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.86, 55.93, 110.5, 112.7, 121.5, 122.7, 127.2, 128.3, 131.2, 132.9, 133.6, 142.1, 148.0, 148.3. IR (KBr): ν = 1518, 1244, 1026, 754, cm^{-1}. MS (EI) *m/z*: 296 (2, M^+ + 4), 295 (16, M^+ + 3), 294 (96, M^+ + 2), 293 (16, M^+ + 1), 292 (100, M^+). HRMS Calcd for $C_{14}H_{13}BrO_2$: M^+ 292.0099. Found: 292.0091. Anal. Calcd for $C_{14}H_{13}BrO_2$: C, 57.36; H, 4.47. Found: C, 57.62; H, 4.46.

*2,2′-Dibromo-4,5-dimethoxybiphenyl (**5f**)*: Mp: 109.9–110.8 °C. TLC: R_f 0.28 (hexane/AcOEt 7:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.86 (s, 3H), 3.93 (s, 3H), 6.75 (s, 1H), 7.12 (s, 1H), 7.26 (dd, *J* = 8.0, 7.6 Hz, 1H), 7.26 (d, *J* = 7.6 Hz, 1H), 7.37 (dd, *J* = 7.6, 7.6 Hz, 1H), 7.67 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 56.1, 56.2, 113.36, 113.40, 114.9, 123.8, 126.9, 129.1, 131.3, 132.4, 133.9, 141.7, 147.8, 148.9. IR (KBr): ν = 1474, 1254, 1209, 1022, 773 cm^{-1}. MS (EI) *m/z*: 376 (1, M^+ + 6), 375 (9, M^+ + 5), 374 (49, M^+ + 4), 372 (100, M^+ + 2), 370 (50, M^+). HRMS Calcd for $C_{14}H_{12}Br_2O_2$: M^+ 369.9204. Found: 369.9202. Anal. Calcd for $C_{14}H_{12}Br_2O_2$: C, 45.20; H, 3.25. Found: C, 44.97; H, 3.23.

2-Bromo-3'-methoxybiphenyl: Purified by silica gel column chromatography (hexane/AcOEt 30:1). Yield: 97%, colorless oil. TLC: R_f 0.22 (hexane/AcOEt 30:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.86 (s, 3H), 6.93–6.96 (m, 2H), 7.00 (dd, *J* = 7.6, 2.4 Hz, 1H), 7.19–7.23 (m, 1H), 7.33–7.38 (m, 3H), 7.68 (d, *J* = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.3, 113.1, 114.9, 121.7, 122.4, 127.2, 128.6, 128.8, 131.0, 133.0, 142.2, 158.9. IR (KBr): ν = 1603, 1582, 1468, 1416, 1319, 1302, 1252, 1211, 1179, 1049, 1018, 860, 783, 754, 698, 660 cm^{-1}. MS (EI) *m/z*: 266 (2, M^+ + 4), 265 (25, M^+ + 3), 264 (99, M^+ + 2), 263 (27, M^+ + 1), 262 (100, M^+). HRMS Calcd for $C_{14}H_{11}BrO$: 261.9993. Found: *m/z* 261.9985.

*2,2'-Dibromo-5-methoxybiphenyl (**5e**)*: Purified by silica gel column chromatography (hexane/AcOEt 30:1). Yield: 94%, colorless oil. TLC: R_f 0.22 (hexane/AcOEt 30:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.82 (s, 3H), 6.79–6.84 (m, 2H), 7.24–7.28 (m, 2H), 7.38 (dd, *J* = 7.6, 7.6 Hz, 1H), 7.54 (d, *J* = 8.4 Hz), 7.67 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.6, 113.8, 115.3, 116.2, 123.2, 127.0, 129.3, 130.7, 132.4, 133.0, 141.8, 142.6, 158.3. IR (KBr): ν = 1597, 1586, 1568, 1462, 1439, 1393, 1300, 1221, 1179, 1049, 1026, 756 cm^{-1}. MS (EI) *m/z*: 345 (17, M^+ + 5), 344 (98, M^+ + 4), 342 (100, M^+ + 2), 340 (97, M^+). HRMS Calcd for $C_{13}H_{10}Br_2O$: 339.9098. Found: *m/z* 339.9100.

2-Bromo-4,5-difluoro-3',4'-dimethoxybiphenyl: Purified by silica gel column chromatography (hexane/AcOEt 7:1). Yield: 53%, colorless solid. Mp: 84.7–85.6 °C. TLC: R_f 0.25 (hexane/AcOEt 7:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.92 (s, 3H), 3.94 (s, 3H), 6.89–6.94 (m, 3H), 7.18 (dd, *J* = 10.8, 8.4 Hz, 1H), 7.46 (dd, *J* = 9.6, 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.92, 56.96, 55.99, 56.03, 110.6, 112.5, 115.5, 116.2 (dd, *J* = 6.8, 3.8 Hz), 118.9, 120.6 (dd, *J* = 231.8, 22.9 Hz), 121.6, 131.8, 139 (dd, *J* = 6.1, 6.1 Hz), 148.2, 148.8, 149.0 (d, *J* = 248.6 Hz); ^{19}F NMR (282 MHz, CDCl3): δ –137.9 (m), –139.2 (m). IR (KBr): ν = 1736, 1599, 1580, 1483, 1387, 1288, 1263, 1244, 1163, 1047, 779 cm^{-1}. MS (EI) *m/z*: 332 (2, M^+ + 4), 331 (15, M^+ + 3), 330 (98, M^+ + 2), 328 (100, M^+). Anal. Calcd for $C_{14}H_{11}BrF_2O_2$: C, 51.09; H, 3.37. Found: C, 51.29; H, 3.43.

*2,2'-Dibromo-4,5-difluoro-4',5'-dimethoxybiphenyl (**5g**)*: Purified by silica gel column chromatography (hexane/AcOEt 7:1). Yield: 99%, colorless solid. Mp: 69.9–70.8 °C. TLC: R_f 0.25 (hexane/AcOEt 7:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.87 (s, 3H), 3.93 (s, 3H), 6.70 (s, 1H), 7.11 (s, 1H), 7.12 (dd, *J* = 8.0, 10.4 Hz, 1H), 7.49 (dd, *J* = 7.6, 9.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 56.20, 56.24, 113.2, 113.4, 115.0, 117.7 (dd, *J* = 3.8, 7.6 Hz), 119.8 (d, *J* = 18.3 Hz), 121.3 (d, *J* = 19.8 Hz), 132.1, 138.3 (dd, *J* = 4.5, 4.5 Hz), 147.96, 148.02 (dd, *J* = 13.8, 38.1 Hz), 149.4, 150.5 (dd, *J* = 13.7, 54.9 Hz); ^{19}F NMR (282 MHz, $CDCl_3$): δ –139.0, –136.2. IR (KBr): ν = 1599, 1487, 1440, 1402, 1362, 1329, 1294, 1252, 1213, 1167, 1034, 978, 883, 858, 779, 629, 602 cm^{-1}. MS (EI) *m/z*: 411 (9, M^+ + 5), 410 (32, M^+ + 4), 408 (100, M^+ + 2), 406 (51, M^+). HRMS Calcd for $C_{14}H_{10}Br_2F_2O_2$: 405.9016. Found: *m/z* 405.9018.

*4.6. Typical Procedure for Annulation of 1,2-Diborylalkenes **1** with 2,2′-Dibromobiaryls **5***

To a Schlenk tube (80 mL) were added $Pd(PPh_3)_4$ (58 mg, 0.05 mmol), **1a** (0.52 g, 1.2 mmol), and **3a** (0.31 g, 1.0 mmol) and K_2CO_3 (0.83 g, 6.0 mmol). The tube was then capped with a rubber septum, evacuated, and purged with argon. The evacuation–purge operation was repeated twice. THF (20 mL) and H_2O (0.90 mL, 50 mmol) was added to the mixture at room temperature. The solution was stirred at room temperature for 5 min and then heated at 60 °C for 48 h. The mixture was allowed to cool to room temperature, and diluted with EtOAc (20 mL). The resulting solution was washed with saturated aqueous NH_4Cl solution (20 mL), and the aqueous layer was extracted with EtOAc (40 mL × 3). The combined organic layer was washed with saturated aq NaCl solution (20 mL), dried over anhydrous $MgSO_4$, and concentrated *in vacuo*. Recrystallization of the crude product from MeOH gave **4aa** (0.26 g, 80% yield) as a colorless solid.

*9,10-Bis(4-hexylphenyl)phenanthrene (**2da**)*: Purified by silica gel column chromatography (hexane/AcOEt 40:1). Yield: 32%, colorless solid. Mp: 98.8–99.4 °C. TLC: R_f 0.35 (hexane/AcOEt 40:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.91 (t, *J* = 6.4 Hz, 6H), 1.27–1.33 (m, 12H), 1.59 (m, 4H), 7.03 (s, 8H), 7.48 (m, 2H), 7.63 (d, *J* = 7.2 Hz, 2H), 7.65 (m, 2H), 8.80 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.3, 22.8, 28.9, 31.0, 31.4, 31.8, 35.7, 122.3, 126.0, 126.3, 127.4, 127.8, 129.8, 130.7, 131.9, 136.6, 137.2, 140.6. IR (KBr): ν = 1506, 1487, 1466, 1447, 1117, 1020, 773, 758, 725, 635 cm^{-1}. MS (EI) *m/z*: 501 (1, M^+ + 3), 500 (8, M^+ + 2), 499 (41, M^+ + 1), 498 (100, M^+). HRMS Calcd for $C_{38}H_{42}$: M^+, 498.3287. Found: *m/z* 498.3290.

*9,10-Di(thiophen-3-yl)phenanthrene (**2ha**)*: Purified by recrystallization from MeOH. Yield: 71%, colorless solid. Mp: 228.2–228.9 °C. TLC: R_f 0.26 (hexane/EtOAc 40:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.94 (bs, 2H), 7.01 (bs, 2H), 7.53 (dd, *J* =

8.4, 7.2 Hz 2H), 7.68 (dd, *J* = 8.4, 7.2 Hz, 2H), 8.23 (d, *J* = 8.4 Hz), 8.79 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 122.4, 124.3, 126.5, 126.6, 127.5, 129.9, 130.2, 131.7, 133.0, 139.3. IR (KBr): ν = 1487, 1447, 1418, 1304, 1076, 1045, 845, 835, 781, 763, 741, 727, 675, 648 cm^{-1}. MS (EI) *m/z*: 345 (2, M^+ + 3), 344 (12, M^+ + 2), 343 (26, M^+ + 1), 342 (100, M^+). Anal. Calcd for $C_{22}H_{14}S_2$: C, 77.15; H, 4.12. Found: C, 76.95; H, 4.08.

3,6-Dimethoxy-9,10-diphenylphenanthrene (***2ab***): Purified by silica gel column chromatography (hexane/EtOAc/CH_2Cl_2 12:1:1). Yield: 20%, colorless solid. Mp: 190.0–190.9 °C. TLC: R_f 0.31 (hexane/EtOAc/CH_2Cl_2 12:1:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.05 (s, 6H), 7.14–7.27 (m, 12H), 7.52 (d, *J* = 9.2 Hz, 2H), 8.11 (d, *J* = 2.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.57, 104.29, 116.03, 126.16, 126.80, 127.35, 129.30, 130.57, 131.01, 134.57, 139.60, 157.70. IR (KBr): ν = 1613, 1516, 1464, 1362, 1225, 1203, 1038, 833, 706 cm^{-1}. MS (EI) *m/z*: 392 (5, M^+ + 2), 391 (31, M^+ + 1), 390 (100, M^+). HRMS Calcd for $C_{28}H_{22}O_2$: M^+, 390.1620. Found: *m/z* 390.1618.

2,3,6,7-Tetramethoxy-9,10-bis(4-methoxyphenyl)phenanthrene (***2cc***): Purified by recrystallization from MeOH. Yield: 68%, colorless solid. TLC: R_f 0.56 (hexane/EtOAc 2:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.74 (s, 6H), 3.81 (s. 6H), 4.16 (s, 6H), 6.80 (d, *J* = 8.0 Hz, 4H), 6.94 (s, 2H), 7.06 (d, *J* = 8.0 Hz, 4H), 7.90 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.1, 55.7, 56.2, 102.7, 108.0, 113.0, 124.0, 126.6, 131.9, 132.3, 134.7, 148.3, 148.8, 157.6. IR (KBr): ν = 1609, 1508, 1466, 1259, 1240, 1198, 1169, 1103, 1028, 860 cm^{-1}. MS (EI) *m/z*: 512 (10, M^+ + 2), 511 (60, M^+ + 1), 510 (96, M^+), 154 (100). Anal. Calcd for $C_{32}H_{30}O_6$: C, 75.28; H, 5.92. Found: C, 75.44; H, 5.90.

3-Methoxy-9,10-diphenylphenanthrene (***2ae***): Purified by silica gel column chromatography (hexane/AcOEt 20:1). Yield: 40%, colorless solid. Mp: 191.2–192.2 °C. TLC: R_f 0.32 (hexane/AcOEt 20:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.06 (s, 3H), 7.13–7.27 (m, 11H), 7.47–7.52 (m, 2H), 7.57 (d, *J* = 8.4 Hz, 1H), 7.65, (dd, *J* = 8.4, 8.4 Hz, 1H), 8.19 (d, *J* = 1.2 Hz, 1H), 8.74 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.6, 103.9, 116.3, 122.4, 125.8, 126.2, 126.3, 126.4, 126.6, 127.4 (2C), 127.7, 129.25, 129.30, 130.8, 131.1, 131.2, 132.1, 134.7, 136.9, 139.47, 139.54, 158.0. IR (KBr): ν =1616, 1501, 1493, 1437, 1429, 1238, 1209, 1034, 826, 767, 700 cm^{-1}. MS (EI) *m/z*: 362 (7, M^+ + 2), 361 (34, M^+ + 1), 360 (100, M^+). HRMS Calcd for $C_{27}H_{20}O$: M^+, 360.1514. Found: *m/z* 360.1520.

2,3-Dimethoxy-9,10-diphenylphenanthrene (***2af***): Purified by silica gel column chromatography (hexane/AcOEt 7:1). Yield: 80%, colorless solid. Mp: 213.6–214.4 °C. TLC: R_f 0.14 (hexane/AcOEt 7:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.73 (s, 3H), 4.17 (s, 3H), 6.93 (s, 1H), 7.15–7.27 (m, 10H), 7.44 (dd, *J* = 8.4, 8.4 Hz, 1H), 7.56 (d, *J* = 8.4 Hz, 1H), 7.64 (dd, *J* = 8.4, 8.4 Hz, 1H), 8.14 (s, 1H), 8.65 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.6, 56.1, 103.0, 107.9, 121.8, 124.6, 125.5, 125.9, 126.2, 126.4, 126.8, 127.4, 127.5, 127.8, 129.2, 130.7, 131.00, 131.04, 135.4, 136.3, 139.58, 139.61, 148.87, 148.94. IR (KBr): ν = 1616, 1526, 1502, 1466, 1439, 1390, 1261, 1205, 1171, 1022, 760, 704 cm^{-1}. MS (EI) *m/z*: 392 (6, M^+ + 2), 391 (31, M^+ + 1), 390 (100, M^+). Anal. Calcd for $C_{28}H_{22}O_2$: C, 86.13; H, 5.68. Found: C, 85.83; H, 5.74.

2,3-Difluoro-6,7-dimethoxy-9,10-diphenylphenanthrene (***2ag***): Purified by silica gel column chromatography (hexane/AcOEt 7:1). Yield: 79%, colorless solid. Mp: 196.0–196.9 °C. TLC: R_f 0.25 (hexane/AcOEt 7:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.73 (s, 3H), 4.15 (s, 3H), 7.09–7.15 (m, 4H), 7.18–7.32 (m, 5H), 7.85 (s, 1H), 8.29–8.34 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.6, 55.7, 56.1, 56.2, 102.9, 108.0, 109.3 (d, *J* = 17.5 Hz), 114.6 (dd, *J* = 17.5, 3.8 Hz), 123.7 (d, *J* = 3.1 Hz), 126.3 (d, *J* = 5.3 Hz), 126.59, 126.64, 126.7, 127.6 (2C), 127.7 (2C), 128.3 (d, *J* = 4.6 Hz), 130.6 (2C), 130.8 (2C), 134.5, 136.9 (d, *J* = 5.3 Hz), 138.9, 139.1, 148.9 (dd, *J* = 13.0, 24.1 Hz), 149.2, 149.3, 149.6 (dd, *J* = 13.0, 124.0 Hz); ^{19}F NMR (282 MHz, $CDCl_3$): δ –138.7, –139.2. IR (KBr): ν = 1616, 1535, 1508, 1468, 1425, 1263, 1207, 1129, 1161, 1098, 1030, 1017, 876, 723, 698, 613, 586 cm^{-1}. MS (EI) *m/z*: 426 (6, M^+ + 2), 425 (32, M^+ + 1), 426 (100, M^+). HRMS Calcd for $C_{28}H_{20}O_2F_2$: M^+, 426.1431. Found: *m/z* 426.1426.

4.7. General Procedure for Annulation of vic-Diborylarenes ***3*** *with 2,2′-Dibromobiaryls* ***5***

To a vial tube (5 mL) were added $Pd(PPh_3)_4$ (2.9 mg, 2.5 μmol), **3a** (26 mg, 0.060 mmol), **5a** (16 mg, 0.050 mmol). The tube was then capped with a rubber septum, evacuated for 5 min and purged with argon. The evacuation–purge operation was repeated twice. THF (1 mL) and 3 M aq K_3PO_4 (0.10 mL, 0.30 mmol) were added to the mixture at room temperature. The solution was stirred at room temperature for 5 min, the solution before heating at 60 °C for 48 h. The reaction mixture was diluted with dichloromethane (10 mL) and filtered through a Celite pad. The filtrate was concentrated with a rotary evaporator. The residue was purified by column chromatography on silica gel (eluent: hexane/EtOAc/CH_2Cl_2 40:1:1) followed by preparative GPC to give **4aa** (16 mg, >99% yield) as a colorless solid.

2,15-Dihexyldibenzo[g,p]chrysene (***4da***): Purified by silica gel column chromatography (hexane/AcOEt/CH_2Cl_2 40:1:1). Yield: 64%, colorless solid. Mp: 79.9–81.4 °C. TLC: R_f 0.25 (hexane/AcOEt/CH_2Cl_2 40:1:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.93 (t, 6H, *J* = 7.1 Hz), 1.30–1.52 (m, 12H), 1.76–1.88 (m, 4H), 2.92 (t, *J* = 7.6 Hz, 4H), 7.46 (dd, *J* = 8.4, 1.6 Hz, 2H), 7.58–7.70 (m, 4H), 8.48 (d, *J* = 1.6 Hz, 2H), 8.60 (d, *J* = 8.4 Hz, 2H), 8.69 (d, *J* = 7.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.3, 22.8, 29.3, 31.85, 31.93, 36.4, 122.8, 123.4, 126.1, 126.3, 126.9, 127.1, 127.2, 128.70, 128.72, 129.2, 130.5, 130.7, 141.1. IR (KBr): ν = 1613, 1458, 1433, 826, 760, 727 cm^{-1}. MS (EI) *m/z*: 498 (13, M^+ + 2), 497 (56, M^+ + 1), 496 (100, M^+), 425 (19). HRMS Calcd for $C_{38}H_{40}$: M^+, 496.3130. Found: 496.3140.

2-(Trifluoromethyl)dibenzo[g,p]chrysene (***4ea***): Purified by silica gel column chromatography (hexane/AcOEt/CH_2Cl_2 40:1:1). Yield: 66%, colorless solid. Mp: 176.0–180.4 °C. TLC: R_f 0.25 (hexane/AcOEt/CH_2Cl_2 40:1:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64–7.77 (m, 6H), 7.83 (dd, *J* = 8.6, 1.3 Hz, 1H), 8.60–8.76 (m, 6H), 8.80 (d, *J* = 8.6 Hz, 2H), 8.97 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 120.8 (q, *J* = 3.8 Hz), 122.3 (q, *J* = 3.8 Hz), 123.4, 123.5, 123.6, 124.4 (q, *J* = 271 Hz), 126.4, 126.6, 126.70, 126.74, 126.8, 127.0, 127.2, 127.3 (q, *J* = 8.6 Hz), 127.7, 128.8, 128.3, 128.5, 128.7, 128.75, 128.83, 128.9, 129.3, 130.1, 130.7, 131.0, 131.1; ^{19}F NMR (282 MHz, $CDCl_3$): δ –62.4. IR (KBr): ν = 2359, 2342, 2330, 1354, 1317, 1304, 1103, 756 cm^{-1}. MS (EI) *m/z*: 398 (4, M^+ + 2), 397 (29, M^+ + 1), 396 (100, M^+), 326 (22). Anal. Calcd for: $C_{27}H_{15}F_3$: C, 81.81; H, 3.81. Found: C, 81.69; H, 3.68.

2,15-Bis(trifluoromethyl)dibenzo[g,p]chrysene (***4fa***): Purified by silica gel column chromatography (hexane/AcOEt/CH_2Cl_2 40:1:1). Yield: 53%, colorless solid. Mp: 270.5–270.9 °C. TLC: R_f 0.25 (hexane/AcOEt/CH_2Cl_2 40:1:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66–7.80 (m, 4H), 7.90 (d, 2H, *J* = 8.8 Hz), 8.62 (d, 2H, *J* = 8.2 Hz), 8.74 (d, 2H, *J* = 8.2 Hz), 8.83 (d, 2H, *J* = 8.6 Hz), 8.96 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 120.7 (q, *J* = 3.8 Hz), 123.1(q, *J* = 3.1 Hz), 123.6 (q, *J* = 272 Hz), 126.9, 127.4, 127.7, 128.2, 128.3 (q, *J* = 33 Hz), 129.5, 129.6, 131.0, 131.3; ^{19}F NMR (282 MHz, $CDCl_3$): δ –62.5. IR (KBr): ν =

1622, 1356, 1327, 1310, 1273, 1120, 1080, 1034, 760, 729, 739 cm^{-1}. MS (EI) *m/z*: 466(5, M^+ + 2), 465(30, M^+ + 1), 464 (100, M^+), 394 (22). Anal. Calcd for: $C_{28}H_{14}$: C, 72.42; H, 3.04. Found: C, 72.16; H, 3.31.

*2,3,14,15-Tetramethyldibenzo[g,p]chrysene (**4ad**)*: Purified by silica gel column chromatography (hexane/AcOEt/CH_2Cl_2 40:1:1). Yield: 47%, colorless solid. Mp: 263.0–269.6 °C. TLC: R_f 0.25 (hexane/AcOEt/CH_2Cl_2 40:1:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.49 (s, 6H), 2.57 (s, 6H), 7.58–7.69 (m, 4H), 8.42 (s, 2H), 8.44 (s, 2H), 8.66–8.74 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.4, 20.5, 123.4, 123.7, 126.0, 126.2, 126.7, 127.2, 128.7, 128.9, 129.0, 129.4, 130.4, 134.9, 135.4. IR (KBr): ν = 1499, 1485, 1446, 1427, 1024, 872, 758, 729, 635 cm^{-1}. Anal. Calcd for: $C_{30}H_{24}$: C, 93.71; H, 6.29. Found: C, 93.45; H, 6.24.

*2,3,14,15-Tetramethyl-7-(trifluoromethyl)dibenzo[g,p]chrysene (**4ed**)*: Purified by silica gel column chromatography (hexane/AcOEt/CH_2Cl_2 40:1:1). Yield: 56%, colorless solid. Mp: 275.5–276.6 °C. TLC: R_f 0.35 (hexane/AcOEt/CH_2Cl_2 40:1:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.49 (s, 6H), 2.58 (s, 6H), 7.64–7.74 (m, 2H), 7.81 (dd, *J* = 8.8, 1.5 Hz, 1H), 8.34 (brs, 3H), 8.68–8.74 (m, 2H), 8.79 (d, *J* = 8.6 Hz, 1H), 8.94 (s, 1H); ^{19}F NMR (282 MHz, $CDCl_3$): δ –62.3. IR (KBr): ν = 1618, 1449, 1352, 1317, 1117, 1086, 867, 756 cm^{-1}. MS (EI) *m/z*: 454 (7, M^+ + 2), 453 (36, M^+ + 1), 452 (100, M^+), 422 (3). Anal. Calcd for: $C_{31}H_{23}F_3$: C, 82.28; H, 5.12. Found: C, 82.20; H, 5.08.

*4,5,6,7,8,9,10,11-Octafluorotriphenyleno[1,2-b:4,3-b']dithiophene (**4gh**)*: Purified by recrystallization from MeOH. Yield: 81%, colorless solid. Mp: 241.1–241.4 °C. TLC: R_f 0.30 (hexane/AcOEt/CH_2Cl_2 40:1:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (s, 4H); ^{19}F NMR (282 MHz, $CDCl_3$): δ –155.6 ~ –155.2 (m, 2F), –153.2 ~ –152.8(t, *J* = 6.5 Hz, 2F), –129.8 (bs, 2F), –123.9 (d, *J* = 8.6 Hz, 2F). IR (KBr): ν = 1518, 1481, 1074, 964, 723 cm^{-1}. MS (EI) *m/z*: 486 (12, M^+ + 2), 485 (25, M^+ + 1), 484 (100 M^+). Anal. Calcd for: $C_{22}H_4F_8S_2$: C, 54.55; H, 0.83. Found: C, 54.31; H, 0.90.

*1,2,3,4,5,6,7,8-Octafluorotriphenylene (**4hh**)*: Purified by silica gel column chromatography (hexane). Yield: 85%, colorless solid. Mp: 163.5–164.3 °C. TLC: R_f 0.43 (hexane/AcOEt 40:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (m, 2H), 8.86 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 110.1, 116.5, 126.3, 127.1 (d, *J* = 26.7 Hz), 129.2, 139.6 (d, *J* = 261.5 Hz), 140.8 (ddd, *J* = 252.4, 31.2, 13.0 Hz), 144.4 (dd, *J* = 254.7, 9.9 Hz), 145.2 (dd, *J* = 249.3, 12.2 Hz); ^{19}F NMR (282 MHz, $CDCl_3$): δ –156.2, –154.3 ~ –154.2 (m), –138.9, –130.2. IR (KBr): ν = 1636, 1613, 1597, 1518, 1476, 1435, 1364, 1335, 1092, 1084, 1034, 951, 883, 821, 772, 723, 654 cm^{-1}. MS (EI) *m/z*: 374 (2, M^+ + 2), 373 (20, M^+ + 1), 372 (100, M^+). Anal. Calcd for $C_{18}H_4F_8$: C, 58.08; H, 1.08. Found: C, 58.04; H, 1.22.

*1,2,3,4,5,6,7,8-Octafluoro-10,11-dimethoxytriphenylene (**4ih**)*: Purified by silica gel column chromatography (hexane/AcOEt 20:1). Yield: 42%, colorless solid. Mp: 225.2–226.3 °C. TLC: R_f 0.13 (hexane/AcOEt 20:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.09 (s, 6H), 8.34 (J_{H-F} = 5.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.9, 108.4 (d, *J* = 27.5 Hz), 109.7, 116.5, 120.9, 139.0 (d, *J* = 250.8 Hz), 140.7 (ddd, *J* = 251.6, 16.0, 13.0 Hz), 144.5 (dd, *J* = 248.6, 13 Hz), 144.4 (dd, *J* = 209.7, 130.4); ^{19}F NMR (282 MHz, $CDCl_3$): δ –157.8 ~ –157.7 (m), –155.0 ~ –154.8 (m), –141.1, –130.0. IR (KBr): ν = 1609, 1533, 1520, 1466, 1420, 1370, 1283, 1219, 1146, 1082, 1071, 851, 721 cm^{-1}. MS (EI) *m/z*: 434 (3, M^+ + 2), 433 (24, M^+ + 1), 432 (100, M^+). Anal. Calcd for $C_{20}H_8F_8O_2$: C, 55.57; H, 1.87. Found: C, 55.49; H, 1.97.

*1,2,3,4,5,6,7,8-Octafluoro-10,11-dimethyltriphenylene (**4jh**)*: Purified by silica gel column chromatography (hexane). Yield: 76%, colorless solid. Mp: 210.4–211.6 °C. TLC: R_f 0.36 (hexane/AcOEt 40:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.51 (s, 6H), 8.62 (J_{H-F} = 1.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.5, 109.9, 116.6, 124.3, 127.6 (d, *J* = 25.9 Hz), 138.5, 139.1 (d, *J* = 260.7 Hz), 140.7 (ddd, *J* = 251.6, 18.3, 12.9 Hz), 144.4 (d, *J* = 263.1 Hz), 144.8 (dd, *J* = 250.8, 10.7 Hz); ^{19}F NMR (282 MHz, $CDCl_3$): δ –157.4, –155.0 ~ –154.8 (m), –139.3, –130.6. IR (KBr): ν = 1638, 1611, 1520, 1481, 1474, 1443, 1072, 718 cm^{-1}. MS (EI) *m/z*: 402 (3, M^+ + 2), 401 (23, M^+ + 1), 400 (100, M^+). Anal. Calcd for $C_{20}H_8F_8$: C, 60.01; H, 2.01. Found: C, 59.84; H, 1.97.

*Naphtho[1,2-b:4,3-b']dithiophene (**4hj**)*: Purified by silica gel column chromatography (hexane). Yield: 37%, colorless solid. Mp: 172.0–172.8 °C. TLC: R_f 0.28 (hexane/AcOEt 40:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (dd, *J* = 6.4, 3.2 Hz, 2H), 7.59 (d, *J* = 5.2 Hz, 2H), 7.76 (d, *J* = 5.2 Hz, 2H), 8.19 (dd, *J* = 6.4, 3.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 122.9, 124.4, 125.3, 126.2, 126.8, 133.2, 135.3. IR (KBr): ν = 1456, 1400, 1258, 1098, 845, 752, 748, 625, 617 cm^{-1}. MS (EI) *m/z*: 243 (2, M^+ + 3), 242 (11, M^+ + 2), 241 (20, M^+ + 1), 240 (100, M^+). Anal. Calcd for $C_{14}H_8S_2$: C, 69.96; H, 3.36. Found: C, 70.01; H, 3.44.

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