CHEMISTRY
AN ASIAN JOURNAL

DOI: 10.1002/asia.201200132

Palladium-Catalyzed Annulation of 1,2-Diborylalkenes and -Arenes with 1-Bromo-2-[(*Z*)-2-bromoethenyl]arenes: A Modular Approach to Multisubstituted Naphthalenes and Fused Phenanthrenes

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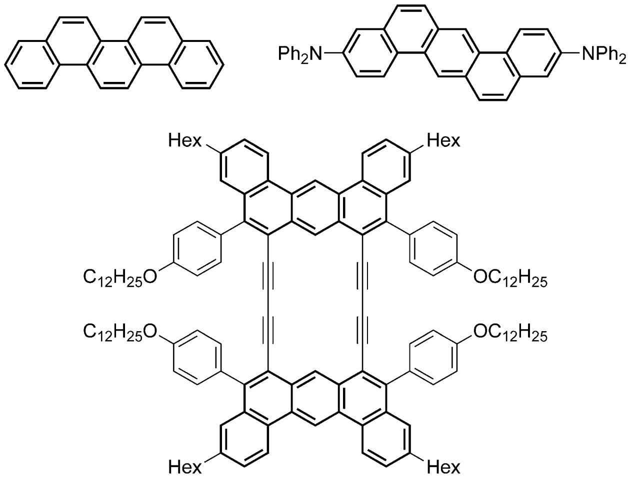
Abstract: (*Z*)-1,2-Diaryl-1,2-bis(pinacolatoboryl)ethenes underwent double-cross-coupling reactions with 1-bromo-2-[(*Z*)-2-bromoethenyl]arenes in the presence of $[Pd(PPh_3)_4]$ as a catalyst and 3 M aqueous Cs_2CO_3 as a base in THF at 80 °C. The double-coupling reaction gave multisubstituted naphthalenes in good to high yields. Annulation of 1,2-bis(pinacolatoboryl)arenes with bromo(bromoethenyl)arenes in the presence of a catalyst system that consisted of $[Pd_2(dba)_3]$ (dba = dibenzylideneacetone) and 2-dicyclohexylphosphino-2′,6′-dimethoxybiphenyl (SPhos) under the same conditions produced fused phenanthrenes in good to high yields. The first annulation coupling occurred regiospecifically at the bromoethenyl moiety. This procedure is applicable to the facile synthesis of polysubstituted anthracenes, benzothiophenes, and dibenzoanthracenes through a double annulation pathway by using the corresponding dibromobis[(*Z*)-2-bromoethenyl]benzenes as diboryl coupling partners.

Keywords: annulation · arenes · boron · cross-coupling · palladium

Introduction

Multisubstituted naphthalene moieties are often found in biologically active substances.[1] Conceptually, there are two strategies for their synthesis: 1) the incorporation of substituents into a naphthalene core and 2) the construction of a naphthalene ring by using a substituted benzene precursor. The latter strategy is more-attractive from the viewpoint of possible substitution patterns and substituent variation because functionalized naphthalene precursors are less readily available than substituted benzene derivatives and the reactive sites on a naphthalene core are primarily governed by pre-existing functional-group orientations.[2] Although a variety of synthetic approaches have been developed that use the second strategy,[3] transition-metal-catalyzed annulation/cyclization reactions based on the cross-coupling reactions of organometallic reagents and organic (pseudo)halides, which are highly efficient methods for forming $C(sp^2)-C(sp^2)$ bonds, remains unexplored for the synthesis of multisubstituted naphthalenes from functionalized benzene precursors.[4]

Polycyclic aromatic hydrocarbons (PAHs), such as picene,[5] dibenz[*a*,*h*]anthracene,[6] and dibenz[*a*,*j*]anthracene,[7] which contain fused phenanthrene groups, have recently been used as key components in functional organic materials (Scheme 1). For example, thin films of picene have exhibited excellent p-type transistor properties in air.[5a] Bis(diphenylamino)-substituted dibenz[*a*,*h*]anthracene is blue fluorescent in solution with a good



Scheme 1. Functional materials that contain benzene-fused phenanthrene moieties.

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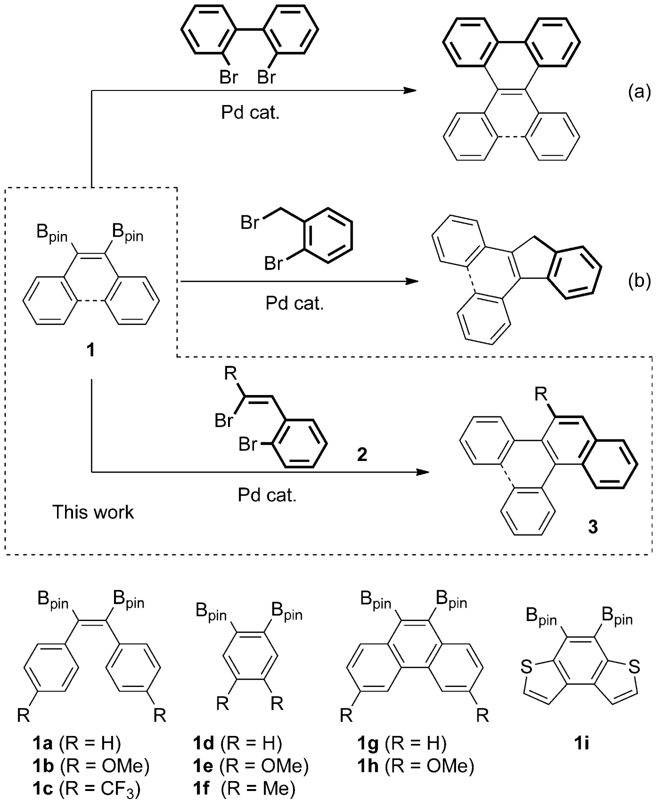
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/asia.201200132.

quantum yield and stable towards two-step oxidation.[6b] Dibenz[*a,j*]anthracene-based macrocycles have been reported to form J-aggregates in thin films and have exhibited excellent luminescence quantum efficiency in the annealed films.[7] The development of an efficient synthesis would accelerate the discovery of superior optoelectronic materials based on π-conjugated systems of fused phenanthrenes because synthetic routes to the fused phenanthrene frameworks are limited.[8]

A palladium-catalyzed double-cross-coupling reaction of 1,2-diborylalkenes and -arenes (**1**) with 2,2′-dibromobiaryl compounds has recently been developed as a straightforward route to functionalized PAHs, such as phenanthrenes, triphenylenes, dibenzo[*g,p*]chrysenes, and their thiophene analogues (Scheme 2a).[9] The application of an annulative strategy based on the double-cross-coupling reaction of **1** with 1-bromo-2-(bromomethyl)arenes as electrophiles has allowed the convenient synthesis of functionalized indenes and fused fluorenes (Scheme 2b).[10] The attention was focused on 1-bromo-2-[(*Z*)-2-bromoethenyl]arenes (**2**) as the coupling partners for enhancing the synthetic value of the palladium-catalyzed double-cross-coupling strategy by using **1** for the preparation of PAHs.[11] The dibromides (**2**) were readily obtained by transition-metal-catalyzed *trans*-selective coupling reactions[12] or by the reduction of 1-bromo-2-(2,2-dibromoethenyl)arenes[13] and the designed annulation, if feasible, could serve as a concise synthetic route to multisubstituted naphthalenes and fused phenanthrenes (Scheme 2). Herein, we report the palladium-catalyzed benzannulation of **1** with **2** leading to PAHs of type **3**.

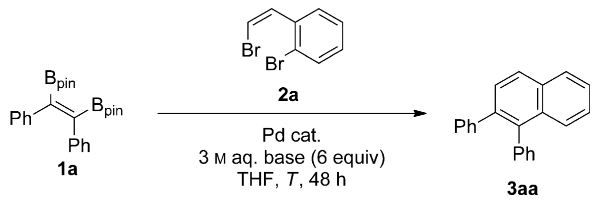


Scheme 2. The palladium-catalyzed double-cross-coupling reactions of 1,2-bis(pinacolatoboryl)alkenes and -arenes, and the molecular structures of diboryl reagents **1**.

Results and Discussion

The reaction of (*Z*)-1,2-bis(pinacolatoboryl)stilbene (**1a**)[14] and 1-bromo-2-[(*Z*)-2-bromoethenyl]benzene (**2a**) was initially examined as a model reaction. Representative results are summarized in Table 1. The reaction catalyzed by 5 mol% [Pd(PPh$_3$)$_4$] in the presence of 3 M aqueous K$_2$CO$_3$ or K$_3$PO$_4$, optimal bases in the annulation of **1a** with 2,2′-dibromobiaryls[9], in THF at 60 °C gave 1,2-diphenylnaphthalene (**3aa**) in 53 % and 59 % yield, respectively (Table 1, entries 1 and 2). The use of 3 M aqueous Cs$_2$CO$_3$ as the base (Table 1, entry 3) resulted in a slightly higher yield of **3aa**, and some oligomeric products were formed. The yield increased significantly when the molar concentration of **1a** was decreased from 0.05 M to 0.025 M in the presence of 3 M aqueous Cs$_2$CO$_3$ to suppress oligomer formation (Table 1, entry 4). Furthermore, the annulation reaction proceeded quantitatively at 80 °C (Table 1, entry 5). Under the same conditions, the amount of [Pd(PPh$_3$)$_4$] could be reduced to 2.5 mol% (Table 1, entries 6 and 7). A catalyst system that consisted of [Pd$_2$(dba)$_3$] and 2-dicyclohexylphosphino-2′,6′-

Table 1. Palladium-catalyzed double-cross-coupling reaction of **1a** with **2a**.[a]

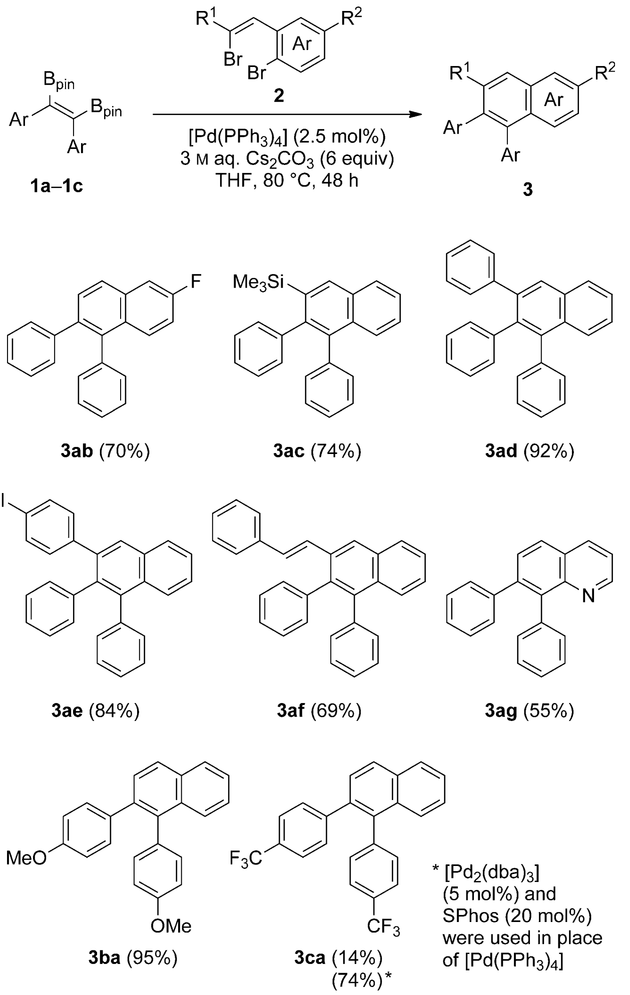


Entry	Catalyst (mol %)	Base	Concentration [M][b]	*T* [°C]	Yield [%][c]
1	[Pd(PPh$_3$)$_4$] (5.0)	K$_2$CO$_3$	0.05	60	53
2	[Pd(PPh$_3$)$_4$] (5.0)	K$_3$PO$_4$	0.05	60	59
3	[Pd(PPh$_3$)$_4$] (5.0)	Cs$_2$CO$_3$	0.05	60	62
4	[Pd(PPh$_3$)$_4$] (5.0)	Cs$_2$CO$_3$	0.025	60	85
5	[Pd(PPh$_3$)$_4$] (5.0)	Cs$_2$CO$_3$	0.025	80	99
6	[Pd(PPh$_3$)$_4$] (2.5)	Cs$_2$CO$_3$	0.025	80	99
7[d]	[Pd(PPh$_3$)$_4$] (2.5)	Cs$_2$CO$_3$	0.025	80	91[e]
8	[Pd$_2$(dba)$_3$] (5.0)/ SPhos (20)[f]	Cs$_2$CO$_3$	0.025	80	99
9	[PdCl$_2$(dppf)] (5.0)	Cs$_2$CO$_3$	0.025	80	95
10	[Pd(P*t*Bu$_3$)$_2$] (5.0)	Cs$_2$CO$_3$	0.025	80	70

[a] Reaction conditions: **1a** (0.06 mmol), **2a** (0.05 mmol), [Pd] catalyst, 3 M aqueous base (0.30 mmol), THF, 48 h; [b] approximate molar concentration of **2a**; [c] yield estimated by ^{1}H NMR spectroscopy by using 1,3,5-trimethoxybenzene as an internal standard; [d] reaction conditions: **1a** (1.2 mmol), **2a** (1.0 mmol), [Pd(PPh$_3$)$_4$] (25 μmol), 3 M aqueous Cs$_2$CO$_3$ (6.0 mmol), THF (40 mL), 80 °C, 48 h; [e] yield of isolated product; [f] SPhos = 2-dicyclohexylphosphino-2′,6′-dimethoxybiphenyl.

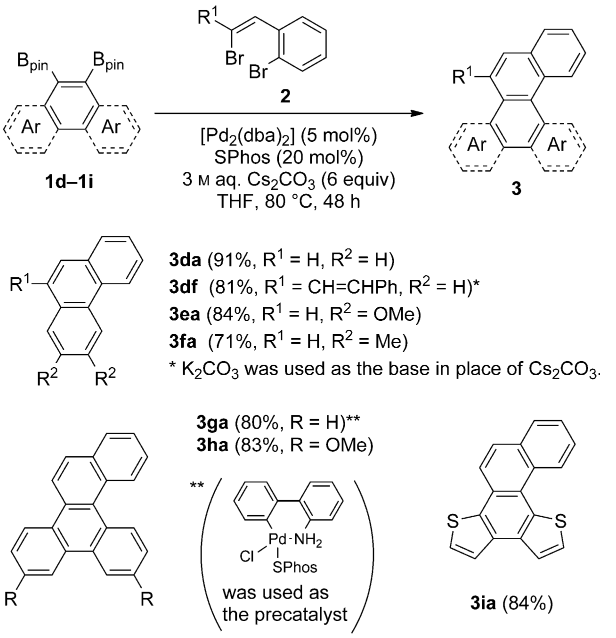
dimethoxybiphenyl (SPhos) was also effective (Table 1, entry 8).[15] [$PdCl_2$(dppf)] (dppf = 1,1′-bis(diphenylphosphino)ferrocene) exhibited similar catalytic activity, but [Pd($PtBu_3$)$_2$] was less effective (Table 1, entries 9 and 10).

The scope of the annulation reactions of diborylalkenes **1a**–**1c**[14] with various dibromides (**2**) was studied under the optimized conditions shown in Table 1, entry 7 and Scheme 3. Fluoro-substituted bromo(2-bromoethenyl)benzene **2b** reacted with **1a** to give **3ab** in 70% yield. The double-cross-coupling reaction with **2c**, in which a sterically demanding trimethylsilyl group was substituted at the geminal position of the bromine atom on an ethenyl moiety, proceeded smoothly to produce **3ac** in 74% yield. Triarylated naphthalenes **3ad** and **3ae** were obtained in high yields from the reactions of **1a** with dibromostyrenes **3d** and **3e**, respectively. The production of **3ae** in high yield indicated that the chlorine moiety tolerated the reaction conditions. Styryl-substituted bromo(bromoethenyl)benzene **2f** underwent annulation to give **3af** in 69% yield, which implied that an alkenylpalladium complex that was generated by the oxidative addition of the bromine–ethenyl bond in **2** to a palladium(0) atom preferentially underwent smooth transmetalation with **1** (for details of the catalytic cycle, see below) over a double-bond isomerization in the styryl moiety (1,3-migration of a palladium atom). The synthesis of quinoline **3ag** was achieved by using bromo(2-bromoethenyl)pyridine **2g** as the coupling partner for **1a**. Dimethoxy-substituted diborylstilbene (**1b**) was reacted with **2a** to give **3ba** in excellent yield. On the other hand, under the same conditions, the reaction of trifluoromethyl-substituted diborylstilbene **1c** with **2a** resulted in a low yield (14%) of compound **3ca**. Most of **1c** and **2a** were recovered; therefore, the low yield was ascribed to the low reactivity of **1c** in the first coupling reaction, which might have originated from the electron-withdrawing effect of the trifluoromethyl group. However, the yield of **3ca** was increased to 74% on replacing [Pd(PPh_3)$_4$] with a catalyst system that consisted of [$Pd_2(dba)_3$] and SPhos.



Scheme 3. The palladium-catalyzed double-cross-coupling reaction of 1,2-diborylalkenes **1a**–**1c** with **2**.

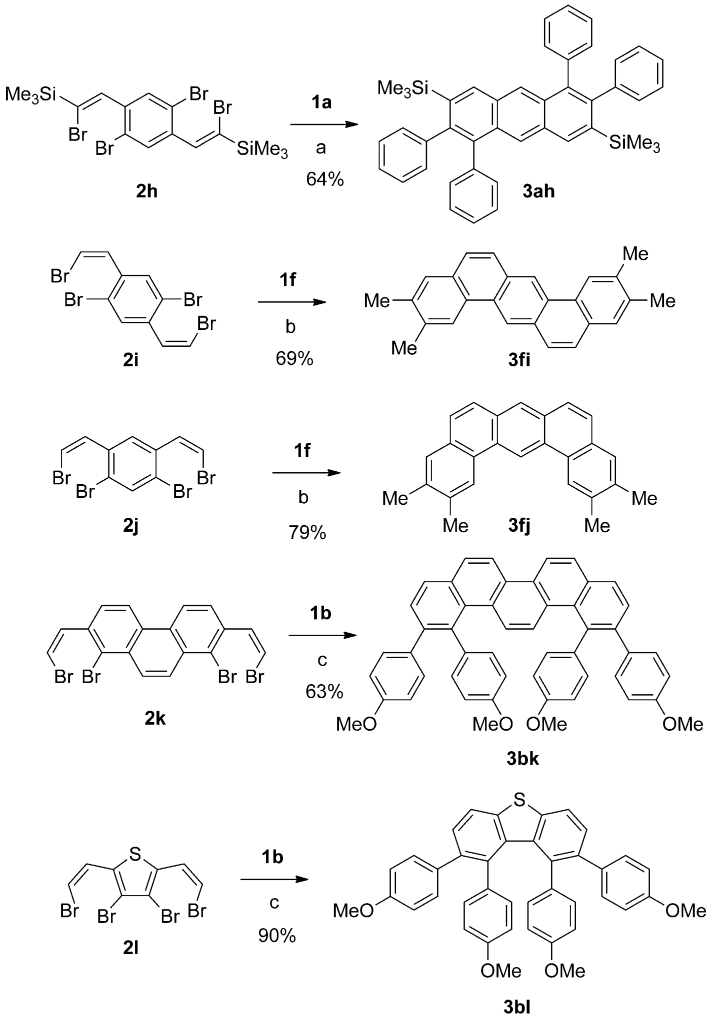
Next, the double-cross-coupling reaction of 1,2-diborylarenes **1d**–**1i**[9,10,16] with **2** was scrutinized with the aim of establishing a new synthetic method for the formation of fused phenanthrenes. The conditions that were used in the reactions of diborylalkenes **1a**–**1c** were applied to the reaction between **1d** and **2a**. The expected product (**3da**) was only obtained in 42% yield. On the other hand, annulation by using the [$Pd_2(dba)_3$]/SPhos catalyst system was quite effective, thereby yielding **3da** in 91% yield (Scheme 4). The scope of the annulation reaction using **1d**–**1i** was confirmed with the aid of a catalyst system that consisted of [$Pd_2(dba)_3$] and SPhos. Diborylbenzene **1d** reacted with **2f** to give 9-styrylphenanthrene **3df** in 81% yield. The double-cross-coupling reactions of dimethoxy- and dimethyl-substituted diborylbenzenes **1e** and **1f** with **2a** also proceeded efficiently



Scheme 4. The palladium-catalyzed double-cross-coupling reaction of 1,2-diborylarenes **1d**–**1i** with **2**.

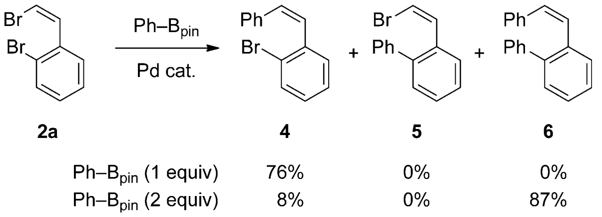
to give **3ea** and **3fa** in good to high yields, respectively. Benzo[*g*]chrysenes **3ga** and **3ha** were synthesized in high yields from diborylphenanthrenes **1g** and **1h**, respectively. Furthermore, diboryldithienobenzene **1i** was applicable to the present annulation conditions, thereby giving rise to **3ia** in 84% yield.

To further demonstrate the high synthetic value of the double-cross-coupling strategy, a double annulation was carried out by using dibromobis(2-bromoethenyl)arenes **2h**–**2l** as the coupling partners of **1** (Scheme 5). The reaction of 1,4-dibromo-2,5-bis(2-bromo-2-silylethenyl)benzene **2h** with **1a** was efficiently catalyzed by [Pd(PPh$_3$)$_4$] in the presence of 3 M aqueous Cs$_2$CO$_3$ in THF at 80 °C in a similar manner to the reaction of **2c** to give multisubstituted anthracene **3ah** in 64% yield. Each annulation reaction was roughly estimated to proceed in 80% yield. Dibenzo[*a*,*h*]anthracene **3fi** and dibenzo[*a*,*j*]anthracene **3fj** were synthesized in good yields from the reactions of **1f** with 1,4-dibromo-2,5-bis(bromoethenyl)benzene **2i** and 1,3-dibromo-4,6-bis(bromoethenyl)benzene **2j**, respectively. Thus, the fusion mode of two benzene rings onto anthracene was easily tuned by changing the substitution pattern of the two bromine atoms and the two bromoethenyl moieties on the benzene ring. Moreover, the double annulation of 1,8-dibromo-2,7-bis(bromoethenyl)phenanthrene (**2k**) and 3,4-dibromo-2,5-bis(bromoethenyl)thiophene (**2l**) with **1b** gave 1,2,11,12-tetraarylated picene **3bk** and 3,4,5,6-tetraarylated benzothiophene **3bl**, respectively, in good-to-excellent yields. The substitution patterns in these PAHs are difficult to obtain by other synthetic methods.



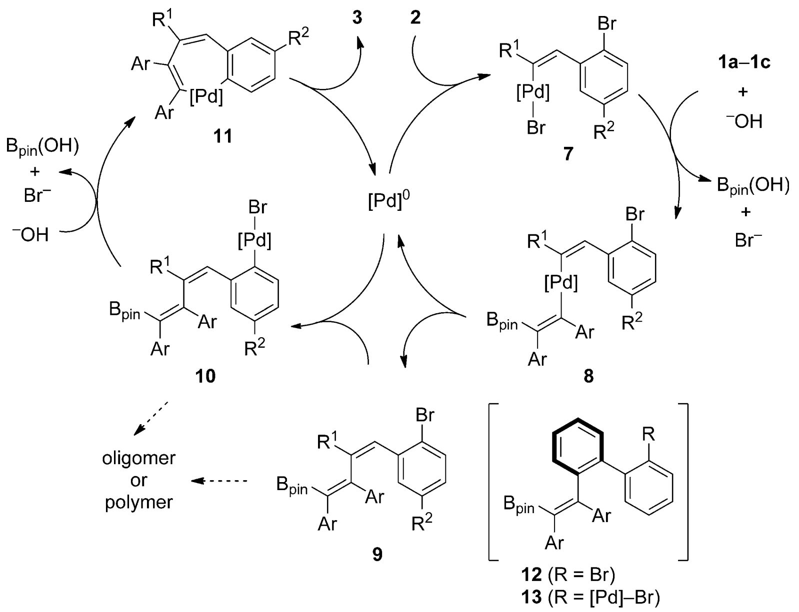
Scheme 5. The palladium-catalyzed double-annulation reaction of dibromobis(bromoethenyl)arenes Reagents and reaction conditions: a) **1a** (2.4 equiv), **2h** (1 equiv), [Pd(PPh$_3$)$_4$] (2.5 mol%), 3 M aqueous Cs$_2$CO$_3$ (12 equiv), THF, 80°C; b) **1f** (2.4 equiv), **2i** or **2j** (1 equiv), [Pd$_2$(dba)$_3$] (5 mol%), SPhos (20 mol%), 3 M aqueous Cs$_2$CO$_3$ (12 equiv), THF, 60°C; c) **1b** (2.4 equiv), **2k** or **2l** (1 equiv), [Pd$_2$(dba)$_3$] (5 mol%), SPhos (40 mol%), 3 M aqueous Cs$_2$CO$_3$ (12 equiv), THF, 80°C.

To gain a mechanistic insight, **2a** was treated with one molar equivalent of phenylboronic pinacol ester (Ph–B$_{pin}$) in the presence of [Pd(PPh$_3$)$_4$] (2.5 mol%) and 3 M aqueous Cs$_2$CO$_3$ (6 equiv) in THF at 80 °C (Scheme 6). The sole product was *cis*-stilbene derivative **4**, which was obtained in 76% yield. The reaction with two molar equivalents of Ph–B$_{pin}$ gave diphenylated product **6** in 87% yield along with the mono-coupled product (**4**) in 8% yield. In either case, no formation of bromoethenyl-substituted biphenyl **5** was observed. These results clearly indicated that the first coupling reaction took place chemoselectively with the alkenyl C–Br functionality, which was consistent with the precedents for the palladium-catalyzed amination/carbonylation of bromo(2-bromoethenyl)arenes.[16]



Scheme 6. Cross-coupling reaction of **2a** with Ph–B$_{pin}$. Reaction conditions: [Pd(PPh$_3$)$_4$] (2.5 mol%), 3 M aqueous Cs$_2$CO$_3$ (6 equiv), THF, 80°C, 48 h.

A plausible catalytic cycle for this annulation reaction is shown in Scheme 7 (based on the results shown in Scheme 6), with diborylstilbenes **1a**–**1c** representing the 1,2-diboryl reagents. The oxidative addition of an alkenyl C–Br bond of **2** to a palladium(0) complex took place selectively to give alkenylpalladium bromide **7**. Diboryl reagents **1** and **7** underwent transmetalation with the aid of a hydroxide ion to generate a bis(alkenyl)palladium complex (**8**). Reductive elimination of the alkenyl groups of **8** gave the initial coupling product (**9**) and a palladium(0) complex. Oxidative addition of **9** to a palladium(0) complex produced arylpalladium bromide (**10**), which underwent intramolecular transmetalation, thereby giving rise to a seven-membered palladacycle (**11**). Finally, the annulated product (**3**) was released from **11** through reductive elimination along with the regeneration of a palladium(0) complex. In this annulation reac-



Scheme 7. Plausible catalytic cycle.

tion, oligomeric/polymeric products were observed in some cases. In other words, intermolecular cross-coupling reactions of **9** and/or **10** occurred. These results were in stark contrast to the fact that no oligomers/polymers formed in the annulation of **1** with 2,2′-dibromobiaryls (Scheme 2a); moreover, intermolecular reactions of **12** and **13** were completely suppressed (Scheme 7).[9] Based on these differences, the by-production of oligomers/polymers may be ascribed to less steric hindrance around the B_{pin} and Br ([Pd]Br) groups of **9** and **10**.

Conclusions

We have developed a palladium-catalyzed double cross-coupling reaction of 1,2-diaryl-1,2-diborylethenes and 1,2-diborylarenes with 1-bromo-2-[(*Z*)-2-bromoethenyl]arenes, which gives naphthalene and phenanthrene derivatives in good to high yields. Annulation proceeds via intermolecular coupling of the diboryl reagents with the bromoethenyl moiety and the subsequent intramolecular coupling of the remaining boron functionality and bromoarene moiety. The straightforward and high-yielding synthesis of extended PAHs such as dibenzoanthracenes and picene derivatives was also demonstrated by carrying out a double annulation using dibromobis(bromoethenyl)arenes as the coupling partners of the diboryl reagents.

Experimental Section

General

Melting points were determined by using a Yanagimoto Micro Point Apparatus. ^{1}H NMR spectra were measured on Varian Mercury 300 (300 MHz) and 400 (400 MHz) spectrometers. The ^{1}H NMR chemical shifts are expressed in parts per million downfield of tetramethylsilane (TMS) as an internal standard (δ=0 ppm) or $CHCl_3$ (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 Varian Mercury 300 (75 MHz) and 400 (100 MHz) spectrometers with TMS as an internal standard (δ=0 ppm) or $CHCl_3$ (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 shifts are given in parts per million downfield of an internal standard. IR spectra were recorded on a Shimadzu FTIR-8400 spectrometer. GCMS analysis was performed on a JEOL JMS-700 spectrometer by electron ionization at 70 eV. Elemental analysis was carried out on a YANAKO MT2 CHN CORDER machine at the Elemental Analysis Center of Kyoto University. TLC analysis were performed by means of Merck Kieselgel 60 F_{254} and column chromatography was carried out by using Merck Kieselgel 60 (230–400 mesh). Preparative HPLC was carried out with a Japan Analytical Industry Co., Ltd, LC-908 chromatograph by using a JAIGEL-1H and −2H GPC columns. THF 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.

*Representative Procedure for the Palladium-Catalyzed Double-Cross-Coupling Reaction of **1** with **2***

$[Pd(PPh_3)_4]$ (58 mg, 0.05 mmol), **1a** (0.52 g, 1.2 mmol), **2a** (0.26 g, 1.0 mmol), and 3 M aqueous Cs_2CO_3 (2.0 mL, 6.0 mmol) was added to a Schlenk tube (80 mL). The tube was then capped with a rubber septum, evacuated, and purged with argon. The evacuation–purge operation was repeated twice. THF (40 mL) was added to the mixture at RT. The mixture was stirred at room temperature for 5 min and heated at 80 °C for 48 h, before cooling to RT and diluting 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 (3× 40 mL). The combined organic layer was washed with saturated aqueous NaCl solution (20 mL), dried over anhydrous $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (*n*-hexane) to give 1,2-diphenylnaphthalene as a colorless solid (**3aa**; 0.28 g, 99 % yield).

*6-Fluoro-1,2-diphenylnaphthalene (**3ab**)*

Yield: 70 %; colorless solid; R_f=0.13 (*n*-hexane/EtOAc, 40:1); m.p.: 133.1–134.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.12–7.22 (m, 8H), 7.28–7.34 (m, 3H), 7.53 (dd, J=9.5, 2.6 Hz, 1H), 7.61 (d, J=8.6 Hz, 1H), 7.67 (dd, J=9.5, 5.5 Hz, 1H), 7.87 ppm (d, J=8.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=110.7 (d, J(C,F)=20.7 Hz), 116.2 (d, J(C,F)=24.5 Hz), 126.1, 126.7 (d, J=5.4 Hz), 126.8, 127.5, 127.8, 129.3, 129.4 (d, J=8.4 Hz), 129.6, 129.9, 133.5 (d, J=8.4 Hz), 137.6 (d, J=13.0), 138.6, 141.5, 159.1, 161.5 ppm; ^{19}F NMR (282 MHz, $CDCl_3$): δ=−116.2 ppm; IR (KBr): $\tilde{\nu}$=1541, 1506, 873, 702, 579 cm^{-1}; MS (EI): m/z (%): 300 (3) $[M+2]^+$, 299 (23) $[M+1]^+$, 298 (100) $[M]^+$, 283 (10); elemental analysis calcd (%) for $C_{22}H_{15}F$: C 88.56, H 5.07; found: C 88.51, H 5.14.

*(3,4-Diphenylnaphthalen-2-yl)trimethylsilane (**3ac**)*

Yield: 74%; colorless solid; $R_f=0.20$ (*n*-hexane); m.p.: 161.3–162.1°C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=0.04$ (s, 9H), 7.04–7.22 (m, 10H), 7.35–7.52 (m, 3H), 7.92 (d, $J=8.1$ Hz, 1H), 8.15 ppm (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=0.8$, 125.5, 126.1, 126.2, 126.5, 126.8, 127.3, 127.9, 130.9, 131.7, 132.7, 134.8, 137.4, 137.8, 139.2, 142.2, 143.6 ppm; IR (KBr): $\tilde{\nu}=1246$, 893, 848, 837, 752, 700 cm^{-1}; MS (FAB): *m/z* 354 (6) $[M+2]^+$, 353 (23) $[M+1]^+$, 352 (73) $[M]^+$, 337 (100), 321 (45); elemental analysis calcd (%) for $C_{25}H_{24}Si$: C 85.17, H 6.86; found: C 85.05, H 6.88.

*3-(4-Chlorophenyl)-1,2-diphenylnaphthalene (**3ae**)*

Yield: 84%; colorless solid; $R_f=0.45$ (*n*-hexane/EtOAc, 40:1); m.p.: 197.8–198.4°C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=6.82$–6.90 (m, 2H), 6.94–7.00 (m, 3H), 7.08–7.18 (m, 6H), 7.20–7.28 (m, 3H), 7.38–7.44 (m, 1H), 7.50–7.55 (m, 1H), 7.59 (d, $J=8.4$ Hz, 1H), 7.92 (s, 1H), 7.94 ppm (d, $J=8.1$ Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=126.1$, 126.4, 126.6, 126.7, 127.1, 127.3, 127.8, 128.0, 128.1, 128.9, 131.4, 131.5, 131.6, 132.3, 132.6, 132.8, 138.0, 138.7, 139.4, 169.6, 139.9, 140.6 ppm; IR (KBr): $\tilde{\nu}=$ 1489, 1090, 1013, 893, 827, 750, 698 cm^{-1}; MS (EI): *m/z* 394 (2) $[M+4]^+$, 393 (10) $[M+3]^+$, 392 (35) $[M+2]^+$, 391 (32) $[M+1]^+$, 390 (100) $[M]^+$; HRMS (EI): calcd for $C_{28}H_{19}Cl$: 390.1175 $[M]^+$; found: 390.1186.

*(E)-1,2-Diphenyl-3-styrylnaphthalene (**3af**)*

Yield: 69%; orange solid; $R_f=0.13$ (*n*-hexane); m.p.: 193.5–194.5°C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=6.94$ (d, $J=16.0$ Hz, 1H), 7.07–7.38 (m, 17H), 7.48–7.52 (m, 2H), 7.96 (d, $J=8.4$ Hz, 1H), 8.26 ppm (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=123.8$, 126.0, 126.37, 126.44, 126.5, 126.8, 127.4, 127.47, 127.51, 127.9, 128.3, 128.6, 129.8, 131.0, 131.1, 132.2, 132.9, 134.8, 137.6, 138.5, 139.0, 139.2, 139.6 ppm; IR (KBr): $\tilde{\nu}=1597$, 1489, 1447, 1375, 1323, 1260, 1074, 1028, 963, 887, 845, 762, 747, 702, 691 cm^{-1}; MS (EI): *m/z* (%): 383 (32) $[M+1]^+$, 382 (100) $[M]^+$; HRMS (EI): calcd for $C_{30}H_{22}$: 382.1722 $[M]^+$; found: 382.1730.

*7,8-Diphenylquinoline (**3ag**)*

Yield: 55%; colorless solid; $R_f=0.43$ (*n*-hexane/EtOAc, 4:1); m.p.: 145.8–146.5°C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=7.12$–7.32 (m, 10H), 7.40 (dd, $J=8.2$, 4.2 Hz, 1H), 7.66 (d, $J=8.4$ Hz, 1H), 7.89 (d, $J=$ 8.4 Hz, 1H), 8.21 (dd, $J=8.2$, 1.6 Hz, 1H), 8.94 ppm (dd, $J=4.2$, 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=120.6$, 126.4, 126.6, 127.1, 127.3, 127.5, 127.6, 129.0, 129.9, 131.7, 135.7, 137.9, 138.8, 141.4, 141.8, 146.8, 150.4 ppm; IR (KBr): $\tilde{\nu}=3055$, 1489, 835, 761, 754, 704 cm^{-1}; MS (EI): *m/z* (%): 238 (1) $[M+2]^+$, 282 (10) $[M+1]^+$, 281 (57) $[M]^+$, 280 (100) $[M-1]^+$, 204 (11); elemental analysis calcd (%) for $C_{21}H_{15}N$: C 89.65, H 5.37; found: C 89.56, H 5.46.

*1,2-Bis(4-methoxyphenyl)naphthalene (**3ba**)*

Yield: 95%; colorless solid; $R_f=0.13$ (*n*-hexane/EtOAc, 40:1); m.p.: 162.4–162.8°C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=3.78$ (s, 3H), 3.84 (s, 3H), 6.72–6.78 (m, 2H), 6.84–6.89 (m, 2H), 7.06–7.14 (m, 4H), 7.36–7.42 (m, 1H), 7.44–7.49 (m, 1H), 7.55 (d, $J=8.6$ Hz, 1H), 7.69 (d, $J=$ 8.4 Hz, 1H), 7.86–7.92 ppm (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=$ 55.19, 55.23, 113.0, 113.3, 125.3, 126.0, 126.6, 127.2, 127.7, 128.3, 131.0, 131.2, 132.2, 132.5, 132.9, 134.4, 136.9, 137.9, 157.7, 158.0 ppm; IR (KBr): $\tilde{\nu}=1608$, 1514, 1242, 1179, 1032, 819, 748 cm^{-1}; MS (EI): *m/z* (%): 342 (6) $[M+2]^+$, 341 (41) $[M+1]^+$, 340 (100) $[M]^+$, 309 (3); elemental analysis calcd (%) for $C_{24}H_{20}O_2$: C 84.68, H 5.92; found: C 84.39, H 5.76.

*(E)-9-Styrylphenanthrene (**3df**)*

Yield: 81%; colorless solid; $R_f=0.18$ (*n*-hexane); m.p.: 116.0–117.0°C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=7.24$ (d, $J=15.2$ Hz, 1H), 7.31–7.35 (m, 1H), 7.42–7.45 (m, 1H), 7.60–7.73 (m, 6H), 7.89 (d, $J=15.2$ Hz, 1H), 7.93 (d, $J=7.6$ Hz, 1H), 7.98 (s, 1H), 8.27 (d, $J=8.0$ Hz, 1H), 8.68 (d, $J=$ 8.0 Hz, 1H), 8.68 (d, $J=8.0$ Hz, 1H), 8.76 ppm (d, $J=8.8$ Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=122.5$, 123.1, 124.55, 124.64, 126.3, 126.5, 126.67, 126.74, 126.8, 127.8, 128.7, 128.8, 130.2, 130.4, 130.8, 131.8, 132.1, 134.0, 137.6 ppm; IR (KBr): $\tilde{\nu}=1497$, 1449, 961, 737, 721, 689 cm^{-1}; MS (EI): *m/z* (%): 281 (24) $[M+1]^+$, 279 (100) $[M]^+$; HRMS (EI): calcd for $C_{22}H_{16}$: 280.1252 $[M]^+$; found: 280.1243.

*2,13-Dimethoxybenzo[g]chrysene (**3ha**)*

Yield: 83%; colorless solid; $R_f=0.13$ (*n*-hexane/EtOAc, 20:1); m.p.: 146.7–147.6°C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=4.06$ (s, 3H), 4.07 (s, 3H), 7.28 (dd, $J=9.0$, 2.8 Hz, 1H), 7.34 (dd, $J=9.0$, 2.8 Hz, 1H), 7.54–7.63 (m, 2H), 7.93 (d, $J=8.4$ Hz, 1H), 7.99 (dd, $J=8.4$, 1.6 Hz, 1H), 8.02 (d, $J=2.8$ Hz, 1H), 8.04 (d, $J=2.8$ Hz, 1H), 8.52 (d, $J=9.0$ Hz, 1H), 8.58 (d, $J=9.0$ Hz, 1H), 8.84 (d, $J=9.6$ Hz, 1H), 8.87 ppm (d, $J=9.6$ Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=55.8$, 105.9, 106.3, 114.7, 116.2, 120.8, 124.4, 124.5, 125.60, 125.65, 126.0, 126.1, 127.0, 128.3, 128.4, 130.3, 131.2, 132.2, 133.3, 158.3, 158.9 ppm; IR (KBr): $\tilde{\nu}=3055$, 3001, 2963, 2922, 2831, 1610, 1466, 1456, 1377, 1238, 1213, 1026, 835, 812, 754 cm^{-1}; MS (EI): *m/z* (%): 340 (4) $[M+2]^+$, 339 (27) $[M+1]^+$, 338 (100) $[M]^+$; HRMS (EI): calcd for $C_{24}H_{18}O_2$: 338.1307 $[M]^+$; found: 338.1305.

*Phenanthro[1,2-b:4,3-b']dithiophene (**3ia**)*

Yield: 84%; yellow solid; $R_f=0.13$ (*n*-hexane); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=7.64$–7.70 (m, 3H), 7.76 (d, $J=5.5$ Hz, 1H), 7.82–7.88 (m, 2H), 7.90–7.95 (m, 2H), 8.03 (dd, $J=7.9$, 1.3 Hz, 1H), 8.19 (d, $J=8.6$ Hz, 1H), 9.28 ppm (dd, $J=8.6$, 0.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=122.1$, 122.8, 123.3, 123.6, 125.7, 126.0, 126.10, 126.13, 127.1, 127.34, 129.2, 129.7, 132.4, 132.6, 133.5, 134.4, 136.5 ppm; IR (KBr): $\tilde{\nu}=1541$, 810, 717, 555 cm^{-1}; MS (EI): *m/z* (%): 292 (11) $[M+2]^+$, 291 (22) $[M+1]^+$, 290 (100) $[M]^+$, 245 (15); elemental analysis calcd (%) for $C_{18}H_{10}S_2$: C 74.45, H 3.47; found: C 74.38, H 3.60.

*Representative Procedure for the Double-Annulation Reaction of **1** with **2***

$[Pd(PPh_3)_4]$ (7.2 mg, 6.3 μmol), **1a** (0.26 g, 0.60 mmol), and **2h** (0.15 g, 0.25 mmol) were placed in a screw-topped test tube. The tube was then capped with a rubber septum, evacuated for 5 min, and purged with argon. The evacuation–purge cycle was repeated twice. THF (20 mL) and 3 M aqueous Cs_2CO_3 (1.0 mL, 3.0 mmol) were added to the mixture at RT. After stirring at RT for 5 min, the solution was heated at 80°C for 48 h. The reaction mixture was diluted with CH_2Cl_2 (10 mL) and filtered through a pad of celite. The filtrate was concentrated under vacuum and the residue was washed with MeOH to give 1,2,5,6-tetraphenyl-3,7-bis(-trimethylsilyl)anthracene as a yellow solid (**3ah**; 0.10 g, 64% yield). $R_f=$ 0.73 (*n*-hexane/EtOAc/CH_2Cl_2, 3:1:1); M.p.: >400°C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=0.00$ (s, 18H), 7.06–7.21 (m, 14H), 7.22–7.32 (m, 6H), 8.07 (s, 2H), 8.11 ppm (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=$ -10.0, 114.7, 115.2, 115.8, 116.4, 119.8, 119.9, 120.0, 120.2, 125.0, 126.2, 126.7, 128.4, 131.3, 131.4 ppm; IR (KBr): $\tilde{\nu}=1246$, 985, 854, 839, 698, 418 cm^{-1}; MS (EI): *m/z* (%): 629 (7) $[M+3]^+$, 628 (23) $[M+2]^+$, 627 (58) $[M+1]^+$, 626 (100) $[M]^+$, 523 (18); elemental analysis calcd (%) for $C_{44}H_{42}Si_2$: C 84.29, H 6.75; found: C 84.03, H 6.68.

*2,3,9,10-Tetramethylbenzo[k]tetraphene (**3fi**)*

Purified by recrystallization from MeOH. Yield: 69%; yellow solid; $R_f=$ 0.13 (*n*-hexane); m.p.: 358.0–358.7°C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=$ 2.51 (s, 6H), 2.60 (s, 6H), 7.74–7.90 (m, 4H), 7.88 (d, $J=9.0$ Hz, 2H), 8.61 (s, 2H), 9.08 ppm (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=20.0$, 21.0, 109.7, 115.5, 118.8, 121.6, 123.2, 126.4, 128.4, 128.5, 128.7, 130.3, 130.5, 135.8, 135.9 ppm; IR (KBr): $\tilde{\nu}=1749$, 1684, 1558, 1541, 1506, 1456, 891, 667, 418 cm^{-1}; MS (EI): *m/z* (%): 336 (12) $[M+2]^+$, 335 (30) $[M+1]^+$, 334 (100) $[M]^+$; HRMS (EI): calcd for $C_{26}H_{22}$: 334.1722 $[M]^+$; found: 334.1713.

*2,3,11,12-Tetramethylbenzo[m]tetraphene (**3fj**)*

Purified by column chromatography on silica gel (*n*-hexane/EtOAc, 15:1). Yield: 79%; yellow solid; $R_f=0.50$ (*n*-hexane/EtOAc, 15:1); m.p.: 260.6–262.2°C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=2.52$ (s, 6H), 2.66 (s, 6H), 7.62–7.69 (m, 4H), 7.78 (d, $J=8.8$ Hz, 2H), 8.30 (s, 1H), 8.76 (s, 2H), 9.92 ppm (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=20.1$, 20.8, 115.5, 123.1, 125.9, 126.4, 127.1, 128.4, 128.76, 128.85, 130.3, 130.4, 135.7, 135.9 ppm; IR (KBr): $\tilde{\nu}=1749$, 1716, 1541, 1506, 1456, 889, 871, 441, 418 cm^{-1}; MS (EI): *m/z* (%): 336 (4) $[M+2]^+$, 335 (28) $[M+1]^+$, 334 (100)

[*M*]$^+$, 303 (7); HRMS (EI): calcd for $C_{26}H_{22}$: 334.1722 [*M*]$^+$; found: 334.1720.

*1,2,11,12-Tetrakis(4-methoxyphenyl)picene (**3bk**)*

Purified by recrystallization from MeOH. Yield: 63%; yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 3.79$ (s, 6H), 3.85 (s, 6H), 6.72 (d, $J = 8.0$ Hz, 8H), 6.90–6.95 (m, 8H), 7.14 (s, 2H), 7.59 (d, $J = 8.0$ Hz, 2H), 7.94–7.99 (m, 4H), 8.78 ppm (d, $J = 9.2$ Hz, 2H); IR (KBr): $\tilde{\nu} = 1608$, 1518, 1506, 1246, 1176, 1032, 827 cm^{-1}; MS (FAB): *m*/*z* (%): 704 (17) [*M*+2]$^+$, 703 (52) [*M*+1]$^+$, 702 (100) [*M*]$^+$, 351 (9); HRMS (EI): calcd for $C_{50}H_{38}O_4$: 702.2770 [*M*]$^+$; found: 702.2774.

*1,2,8,9-Tetrakis(4-methoxyphenyl)dibenzo[b,d]thiophene (**3bl**)*

Purified by column chromatography on silica gel (*n*-hexane/EtOAc, 4:1). Yield: 90%; yellow solid; $R_f = 0.36$ (*n*-hexane/EtOAc, 4:1); m.p.: > 400 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 3.66$ (s, 6H), 3.73 (s, 6H), 6.17–6.30 (m, 8H), 6.60–6.74 (m, 8H), 7.31 (d, $J = 8.4$ Hz, 2H), 7.78 ppm (d, $J = 8.4$ Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 55.0$, 55.1, 112.8, 112.9, 120.8, 129.8, 130.8, 131.0, 132.8, 134.0, 134.6, 138.0, 138.4, 139.5, 157.1, 157.6 ppm; IR (KBr): $\tilde{\nu} = 1608$, 1514, 1290, 1248, 1179, 1030, 829, 596 cm^{-1}; MS (EI): *m*/*z* (%): 611 (4) [*M*+3]$^+$, 610 (16) [*M*+2]$^+$, 609 (43) [*M*+1]$^+$, 608 (100) [*M*]$^+$. HRMS (EI): Calcd for $C_{40}H_{32}O_4S$: 608.2021 [M]$^+$; found: 608.2027.

Acknowledgements

This work was supported by a Grant-in-Aid for Creative Scientific Research (No. 16GS0209) from the Ministry of Education, Culture, Sports, Science and Technology, Japan and The Asahi Glass Foundation (M.S.).

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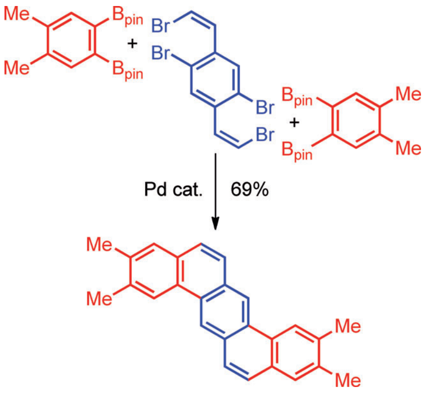
Received: February 10, 2012

A class apart: Bromo(bromoethenyl)arenes are a new class of electrophiles that successfully undergo palladium-catalyzed double-cross-coupling reactions with 1,2-diborylalkenes and -arenes. This straightforward, modular approach is suitable for the formation of multisubstituted polycyclic aromatic hydrocarbons, such as naphthalenes, anthracenes, and fused phenanthrenes.



Cross-Coupling Reactions

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Palladium-Catalyzed Annulation of 1,2-Diborylalkenes and -Arenes with 1-Bromo-2-[(*Z*)-2-bromoethenyl]arenes: A Modular Approach to Multisubstituted Naphthalenes and Fused Phenanthrenes