JOC The Journal of Organic Chemistry

Freie Universität Berlin

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J. Org. Chem., **Just Accepted Manuscript** • Publication Date (Web): 18 May 2017

ACS Publications

The Journal of Organic Chemistry is published by the American Chemical Society.
1155 Sixteenth Street N.W., Washington, DC 20036

Phenanthrene Synthesis by Palladium-Catalyzed Benzannulation with *o*-Bromobenzyl Alcohols through Multiple Carbon–Carbon Bond Formations

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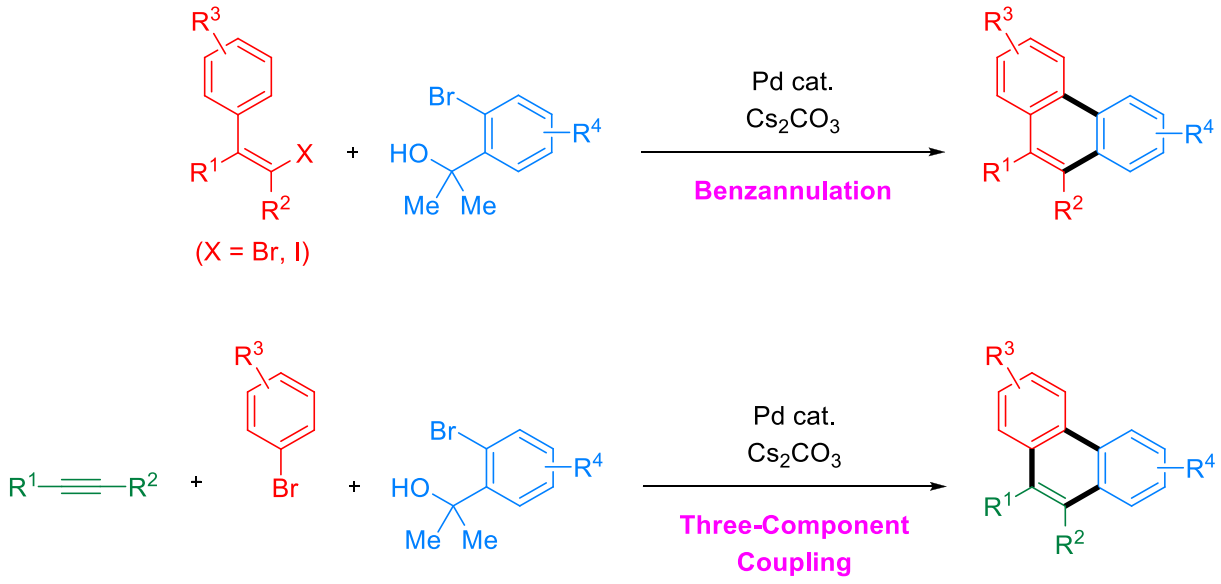


Abstract: A palladium-catalyzed benzannulation with *o*-bromobenzyl alcohols enabled the facile construction of phenanthrene skeletons via the sequential multiple carbon–carbon bond formations. A variety of multi-substituted phenanthrenes were synthesized by the reaction of (*Z*)-*β*-halostyrenes with *o*-bromobenzyl alcohols as well as by the three-component coupling of alkynes, aryl bromides, and *o*-

bromobenzyl alcohols. The electron-deficient phosphine ligand played an important role to control the sequential oxidative addition of two different organic halides employed, which realized the selective formation of the desired phenanthrenes in good yields. This synthetic protocol was also applicable to the synthesis of the highly-fused polycyclic aromatic hydrocarbons such as tetraphenes.

Introduction

Phenanthrenes have attracted much attention in the fields of materials science and medicinal chemistry because of their unique physical properties and bioactivities. For instance, phenanthrene skeletons are often incorporated in various organic functional materials, such as organic light-emitting diodes and photoluminescence materials.[1] Besides, phenanthrene derivatives are frequently found in bioactive molecules, such as halofantrine and aristolochic acid.[2] Therefore, their synthetic methods have been well studied from old times.[3] Although Mallory cyclization of stilbene derivatives represents one of the most reliable methods, there are significant drawbacks.[4] Oxidative cyclization of electron-rich stilbenes proceeded well while the reaction of electro-poor substrates suffered from low yields. In addition, the reaction required harsh reaction conditions, which led to low tolerance for functionalities. Recently, transition-metal-catalyzed reactions have realized the phenanthrene synthesis under milder reaction conditions (Figure 1). For example, cycloisomerization of *o*-alkynylbiphenyls[5] and olefin metathesis of 2,2'-divinylbiphenyls[6] were well established for the efficient synthesis of phenanthrenes. Moreover, several research groups reported the annulation of biphenyl derivatives with alkynes.[7] Furthermore, sequential cross-coupling protocol has been developed to construct phenanthrene skeletons.[8] Benzannulation with arynes were also applied to phenanthrene synthesis.[9] The reaction of (*Z*)-*β*-iodostyrenes afforded the desired phenanthrenes in good yields. These synthetic methods have the potential to expand the substrate scope significantly, but the starting substrates are difficult to prepare in most cases, which resulted in the low overall yields of the target phenanthrenes.

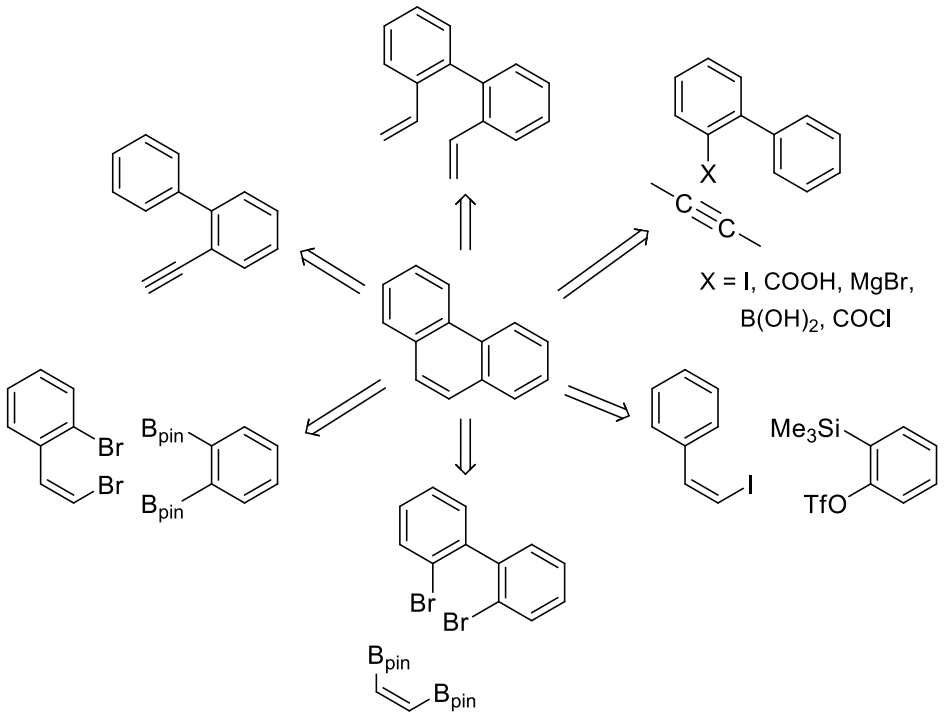


Figure 1. Conventional Synthesis of Phenanthrenes by Transition-Metal Catalysts

On the other hand, multi-component coupling has emerged in recent years as a powerful synthetic method to construct the complex molecules from commercially available or easily accessible starting materials in a single step.[10] The reaction could avoid the bothering sequential multistep synthesis to improve the total yields, which has made a significant contribution to combinatorial chemistry, diversity-orientated synthesis, and high-throughput screening. Thus, the phenanthrene synthesis by multi-component coupling is highly desirable.

We recently demonstrated that *o*-bromobenzyl alcohols could be utilized as the ideal annulating reagents for benzannulation of aryl halides. Both a nucleophilic hydroxymethyl moiety and an electrophilic bromo moiety in *o*-bromobenzyl alcohols resulted in the selective synthesis of the highly-fused polycyclic aromatic hydrocarbons. In addition, the annulating reagents we developed are quite stable in air and light, which can indeed be stored for several months. Moreover, *ortho*-substituted benzyl alcohols are known to promote β-carbon elimination,[11] which is one of the key elementary steps in palladium-catalyzed benzannulation of aryl halides. The reaction of *o*-iodobiphenyls with *o*-

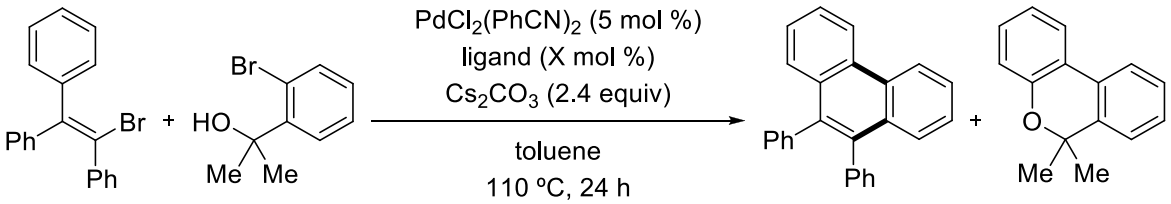
bromobenzyl alcohols provided a series of multisubstituted triphenylenes.[12,13] We herein report the facile construction of phenanthrene skeletons by palladium-catalyzed benzannulation of (*Z*)-*β*-halostyrenes with *o*-bromobenzyl alcohols.[14] Moreover, the optimized reaction conditions found to be applied to the three-component coupling of aryl bromides, alkynes, and *o*-bromobenzyl alcohols. It is of note that all of the reactants are commercially available or prepared in a single step. The present palladium catalysis achieved the sequential multiple carbon–carbon bond formations.

Results and Discussion

Benzannulation of (*Z*)-*β*-Halostyrenes with *o*-Bromobenzyl Alcohols. Prior to investigating the three-component coupling, we examined the benzannulation of (*Z*)-*β*-halostyrenes **1** with *o*-bromobenzyl alcohols **2**. This is because the possible alkenylpalladium intermediate generated from **1** might also be readily formed by the reaction of aryl halides with alkynes.[15] 1-Bromo-1,2,2-triphenylethene (**1a**) and *o*-bromobenzyl alcohol **2a** were subjected to the various palladium-catalyzed conditions (Table 1). In the presence of palladium/phosphine catalysts, the expected benzannulation proceeded to give the desired phenanthrene **3a**, while no reaction occurred without the catalyst. The precise optimization of reaction conditions revealed that the choice of phosphine ligands was crucial. The major byproduct in the reaction was the homo-coupled product of **2a**, benzochromene **4**.[11a,c] Oxidative addition of **2a** prior to **1a** resulted in the undesired formation of **4**. On the other hand, the reaction of 1-iodo-1,2,2-triphenylethene with **2a** afforded **3a** in a lower yield along with undetermined complex mixture. The catalytic activity of palladium species against **1a** and **2a** has to be controlled for selective formation of phenanthrene **3a**. The reaction gave **3a** in 7% yield without any ligand (entry 1), whereas the yield was improved with PPh_3 (entry 2). The electron-donating ligands, such as P(4-$MeOC_6H_4)_3$ and XPhos (2-dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl), gave the lower yields, in which highly active palladiums for oxidative addition might not distinguish the reactivity between alkenyl bromide **1a** and aryl bromide **2a** (entry 3 and 4). However, the desired product **3a** was obtained

in a satisfactory yield when the electron-deficient $P(4\text{-}CF_3C_6H_4)_3$ was used (entry 5). The reaction yielding **3a** was retarded by applying too electron-poor ligand (entry 6). The bidentate ligands, such as Xantophos (4,5-bis(diphenylphosphino)-9,9-dimethylxanthene) and DPPF (1,1'-bis(diphenylphosphino)ferrocene), were found to be ineffective (entries 7 and 8). The strong coordination of the bidentate ligands would block the reaction cite of palladium to retard the course of the reaction such as oxidative addition and migratory insertion steps.

Table 1. Ligand Screening for Palladium-Catalyzed Benzannulation of 1-Bromo-1,2,2-triphenylethene (**1a**) with *o*-Bromobenzyl Alcohol **2a**[a]



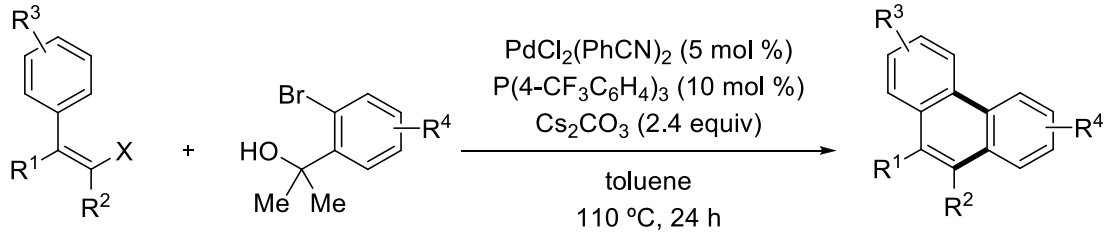
1a **2a** **3a** **4**

entry	ligand	X (mol %)	NMR yield[b]	
			3a (%)[c]	**4** (%)[d]
1	none	-	4	15
2	PPh_3	10	66	0
3	$P(4\text{-}MeOC_6H_4)_3$	10	57	22
4	XPhos	10	21	38
5	$P(4\text{-}CF_3C_6H_4)_3$	10	82	13
6	$P[3,5\text{-}(CF_3)_2C_6H_3]_3$	10	60	19
7	Xantophos	5	49	31
8	DPPF	5	30	31

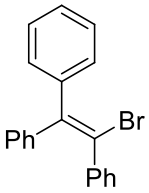
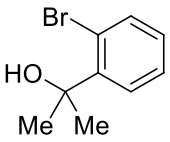
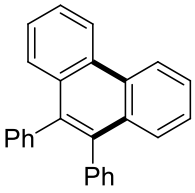
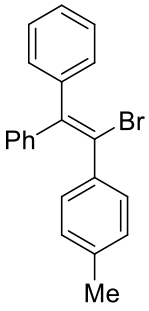
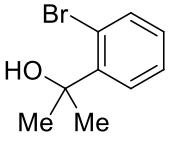
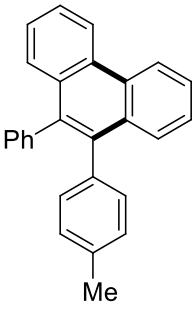
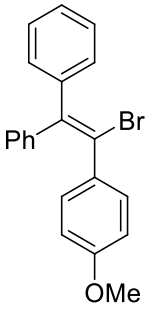
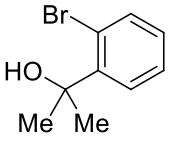
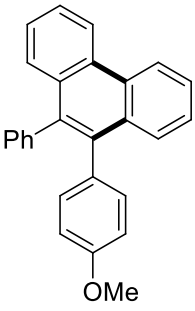
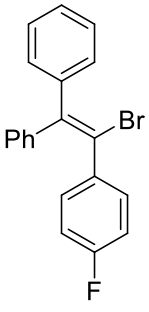
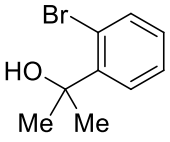
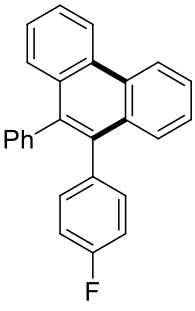
[a]**1a** (0.25 mmol), **2a** (0.30 mmol), $PdCl_2(PhCN)_2$ (0.0125 mmol), ligand, Cs_2CO_3 (0.60 mmol) in toluene (1 mL) at 110 ºC for 24 h. [b]Determined by ^1H NMR analysis of the crude mixture, using dibenzyl ether as an internal standard. [c]Based on **1a**. [d]Based on **2a**.

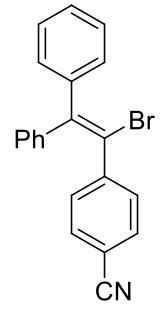
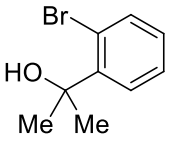
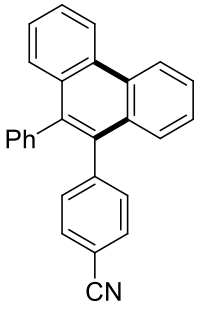
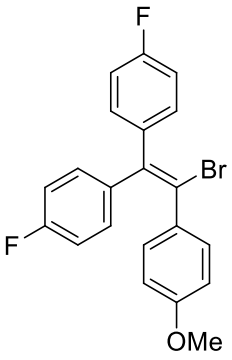
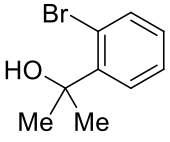
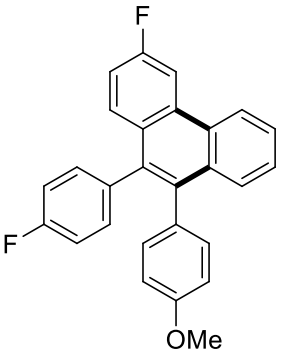
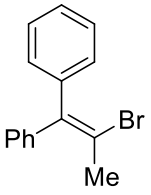
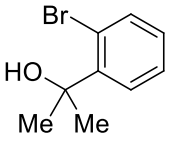
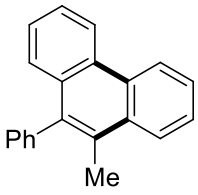
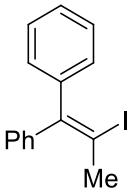
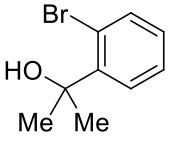
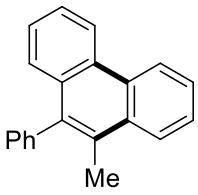
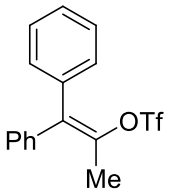
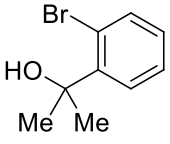
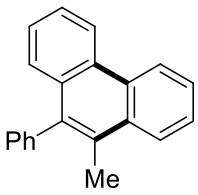
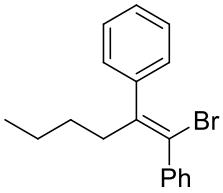
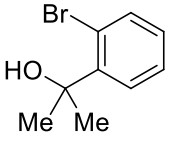
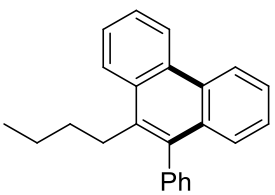
After the further fine modification of the reaction conditions, the yield of **3a** was slightly increased when 1.4 equivalent of **2a** was employed (Table 2, entry 1). Under the optimized reaction conditions in hand, a variety of (*Z*)-*β*-halostyrenes **1** were transformed to the corresponding multisubstituted phenanthrenes **3** in good yields. The results were summarized in Table 2. Electron-rich alkenyl bromides **1b** and **1c** underwent benzannulation with **2a** to provide the products **3b** and **3c** in excellent yields (entries 2 and 3). In addition, the reactions of electron-poor alkenyl bromides **1d** and **1e** proceeded as well, giving phenanthrenes **3d** and **3e** in 95% and 65% yields, respectively (entries 4 and 5). The complexly-functionalized alkenyl bromide **1f** was also applicable to the present reaction to afford phenanthrene **3f** substituted by two fluoro and one methoxy groups with functionalities remained intact (entry 6). Substituents on alkenyl bromide **1** did not have to be aryl groups. Methyl-substituted alkenyl bromide **1g** smoothly reacted with **2a**, yielding alkyl-substituted phenanthrene **3g** (entry 7). Notably, the corresponding iodide **1h** gave the better results than **1g**, while the reaction of triflate **1i** gave no product (entries 8 and 9). An electron-donating alkyl group on **1g** might prevent the smooth oxidative addition to palladium. Furthermore, *β*-alkyl-substituted alkenyl halides **1j** and **1k** were amenable to the reaction, in which the similar trend between bromide **1j** and iodide **1k** was observed (entries 10 and 11). As a result of investigation with respect to the scope of *o*-bromobenzyl alcohol **2**, the benzannulation of **1a** was achieved by using the functionalized annulating reagents **2b** and **2c** (entries 12 and 13). Although the broad scope of substrates **1** and **2** clearly demonstrated high generality of the present benzannulation, the preparation of (*Z*)-*β*-halostyrenes **1** needed several synthetic steps, which resulted in low total yields of the desired phenanthrenes **3**.

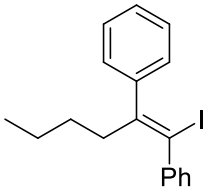
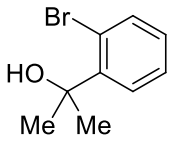
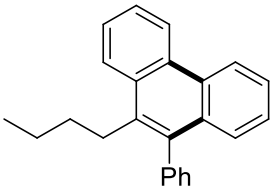
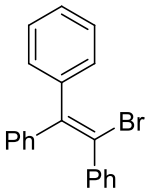
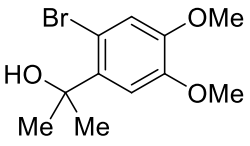
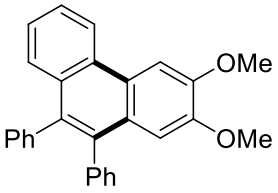
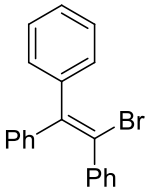
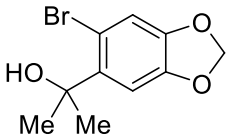
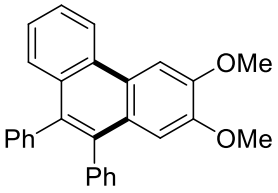
Table 2. Palladium-Catalyzed Benzannulation of (*Z*)-*β*-Halostyrenes **1** with *o*-Bromobenzyl Alcohols **2**[a,b]



1 (X = Br or I) **2** **3**

entry	**1**	**2**	**3**	yield (%)[b]
1	 **1a**	 **2a**	 **3a**	87
2	 **1b**	 **2a**	 **3b**	100
3	 **1c**	 **2a**	 **3c**	97
4	 **1d**	 **2a**	 **3d**	95

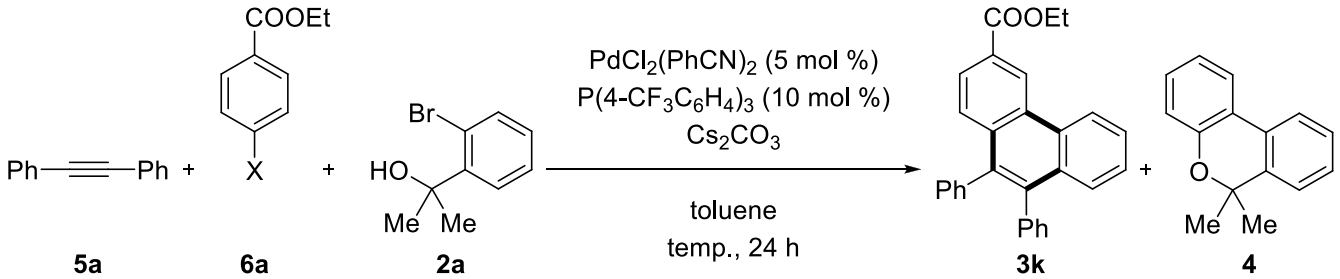
5	 **1e**	 **2a**	 **3e**	68
6	 **1f**	 **2a**	 **3f**	71
7	 **1g**	 **2a**	 **3g**	41
8	 **1h**	 **2a**	 **3g**	69
9	 **1i**	 **2a**	 **3g**	0
10	 **1j**	 **2a**	 **3h**	41

11	 **1k**	 **2a**	 **3h**	59
12	 **1a**	 **2b**	 **3i**	89
13	 **1a**	 **2c**	 **3i**	74

[a]**1** (1 equiv), **2** (1.4 equiv), $PdCl_2(PhCN)_2$ (5 mol %), $P(4\text{-}CF_3C_6H_4)_3$ (10 mol %), Cs_2CO_3 (2.4 equiv) in toluene (0.25 M) at 110 ºC for 24 h. [b]Based on **1** after silica gel column chromatography.

Three-Component Coupling of Alkynes, Aryl Bromides, and *o*-Bromobenzyl Alcohols. The promising results of benzannulation of (*Z*)-*β*-halostyrenes **1** with *o*-bromobenzyl alcohols **2** led us to examine three-component coupling of alkynes **5**, aryl bromides **6**, and *o*-bromobenzyl alcohols **2** for the efficient synthesis of multisubstituted phenanthrenes (Table 3). Under the identical reaction conditions, treatment of diphenylacetylene (**5a**), ethyl 4-iodobenzoate (**6a**), and *o*-bromobenzyl alcohol **2a** gave the desired phenanthrene **3k** in 17% yield, while most of **6a** was consumed (entry 1). We then conducted the reaction of less reactive ethyl 4-bromobenzoate (**6b**) with **5a** and **2a**. As we expected, the yield of **3k** was improved to 41% (entry 2). Since **2a** was totally consumed in the reaction of aryl bromide **6b**, 2 equivalents of **2a** was subjected to the reaction. Although the product yield was slightly improved, a significant amount of byproduct **4** was formed (entry 3). In order to accelerate oxidative addition, the amount of **6b** was increased to 2-fold excess, giving **3k** in 66% yield (entry 4). The continuous efforts to improve the product yields revealed that **3k** was isolated in 83% yield when the reaction with **6b** (4 equiv) was performed in the presence of Cs_2CO_3 (2 equiv) at 120 ºC (entries 5–7).[16]

Table 3. Palladium-Catalyzed Three-Component Coupling of Diphenylacetylene (**5a**), Ethyl 4-Halobenzoate **6a** or **6b**, and *o*-Bromobenzyl Alcohols **2a**[a]



5a **6a** (X = I) or **6b** (X = Br) **2a** **3k** **4**

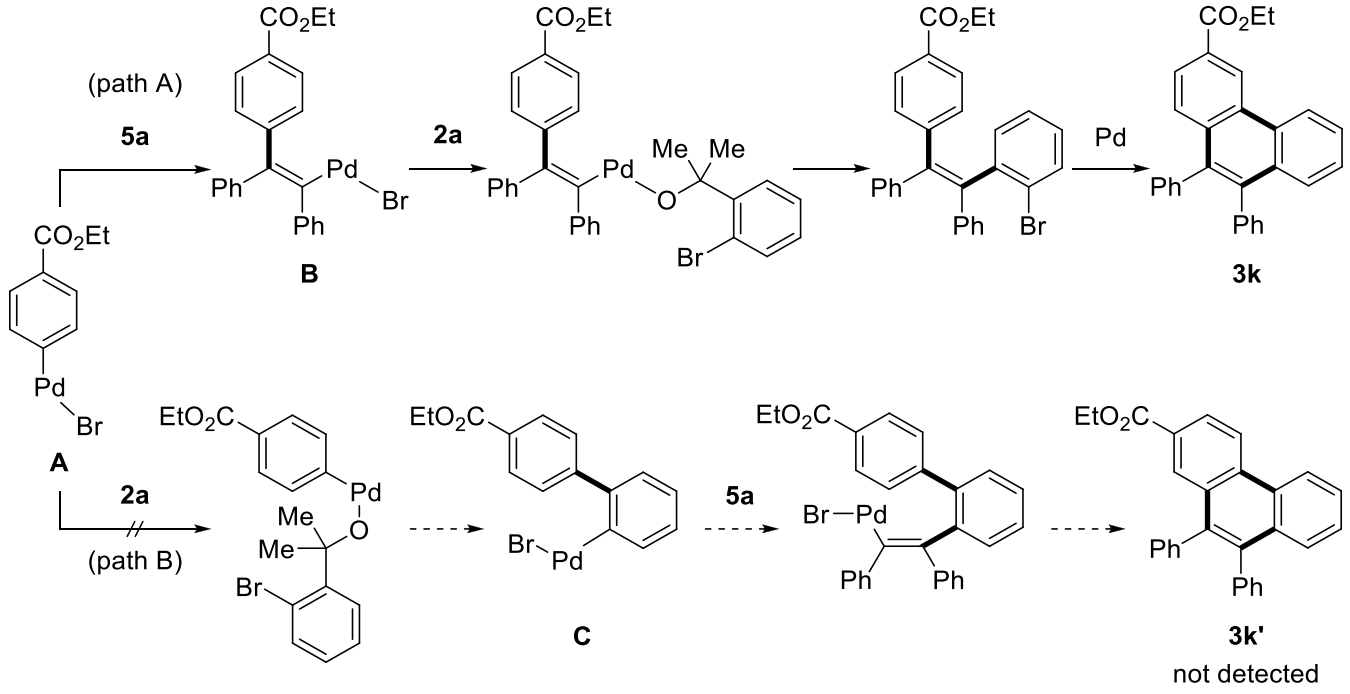
entry	X (**6**)	**6** (equiv)	**2a** (equiv)	Cs_2CO_3 (equiv)	temp. (ºC)	NMR yield[b]	
						3k (%)[c]	**4** (%)[d]
1	I (**6a**)	1	1	2.4	110	17	0
2	Br (**6b**)	1	1	2.4	110	41	50
3	Br (**6b**)	1	2	2.4	110	45	60
4	Br (**6b**)	2	2	2.4	110	66	51
5	Br (**6b**)	2	2	2.4	120	74	56
6	Br (**6b**)	4	2	2.4	120	83	54
7	Br (**6b**)	4	2	2.0	120	95 (83)	42

[a]**5a** (0.25 mmol), **6**, **2a**, $PdCl_2(PhCN)_2$ (0.0125 mmol), $P(4\text{-}CF_3C_6H_4)_3$ (0.025 mmol), Cs_2CO_3 in toluene (1 mL) for 24 h. [b]Determined by ^1H NMR analysis of the crude mixture, using dibromomethane as an internal standard. An isolated yield was shown in parentheses, based on **4a** after silica gel column chromatography. [c]Based on **5a**. [d]Based on **2a**.

The spectroscopic data for the product **3k** was exactly consistent with the literature data, indicating that triple carbon–carbon bond formations proceeded in a sequential manner. Namely, the formed arylpalladium bromide **A** reacts with alkyne **5a**, providing the corresponding alkenylpalladium species **B**, followed by the reaction with **2a** to yield the expected phenanthrene **3k** (Scheme 1, path A). The other possible pathway initiated by the reaction of **A** with **2a** can completely be ruled out (path B)

because the following reaction of the resulting palladium intermediate **C** with alkyne **5a** provides the regioisomer **3k'**.

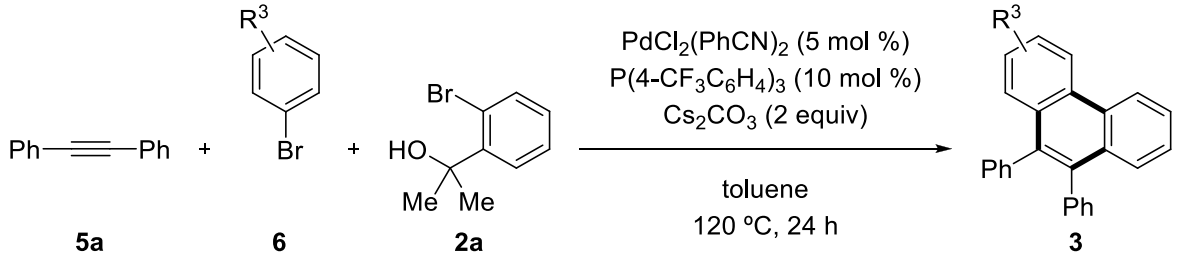
Scheme 1. Selective Synthesis of Phenanthrenes through Sequential C–C Bond Formations



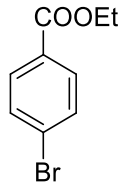
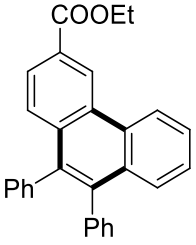
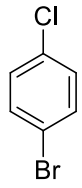
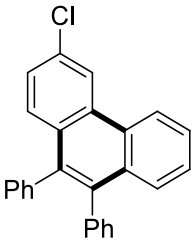
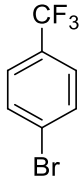
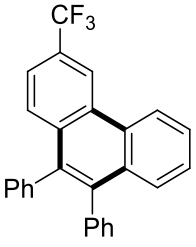
We then turned our attention to examine the substrate scope of the present three-component coupling. A wide range of aryl bromides **6** were subjected to the reaction with diphenylacetylene (**5a**) and *o*-bromobenzyl alcohol **2a** (Table 4). The reactions of electron-deficient aryl bromides **6b**–**6d**, bearing ethoxycarbonyl, chloro, or trifluoromethyl group, provided the corresponding phenanthrenes **3k**–**3m** in good yields (entries 1–3). In contrast, electron-donating 4-bromoanisole (**6e**) reacted with **5a** and **2a**, giving the product **3n** in modest yield (entry 4). The desired three-component coupling might be retarded by the competing oxidative addition of **2a** that leads to the formation of byproduct **4**. The yield of **3n** was not improved even when 4-iodoanisole was used or the amount of **6e** was increased. It is notable that site-selective benzannulation proceeded by employing 2-bromonaphtharene (**6f**) which has two different reaction sites. The bulky palladium would avoid the steric repulsion at 1-position of **6f**. Benzannulation occurred at the less hindered position to afford the tetraphene **3o** in 68% yield as a sole

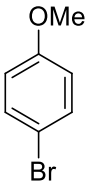
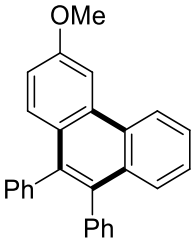
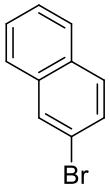
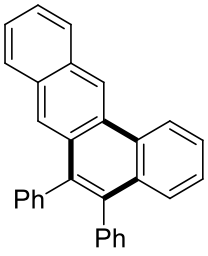
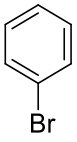
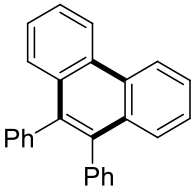
product (entry 5). This example strongly showed the utility of the present protocol for the synthesis of highly-fused PAHs. In the case of bromobenzene (**6g**), the reaction was not complete with 4 equivalents of **6g**. The reaction was conducted in a solvent amount of **6g** (0.50 mL, 18 equiv) instead of toluene, furnishing the product **3a** in 86% yield (entry 6).

Table 4. Scope of Aryl Bromides **6** in Reactions of Diphenylacetylene (**5a**) with *o*-Bromobenzyl Alcohol **2a**[a]



5a **6** **2a** **3**

entry	**6**	**3**	yield (%)[b]
1	 **6b**	 **3k**	83
2[c]	 **6c**	 **3l**	82
3[c]	 **6d**	 **3m**	60

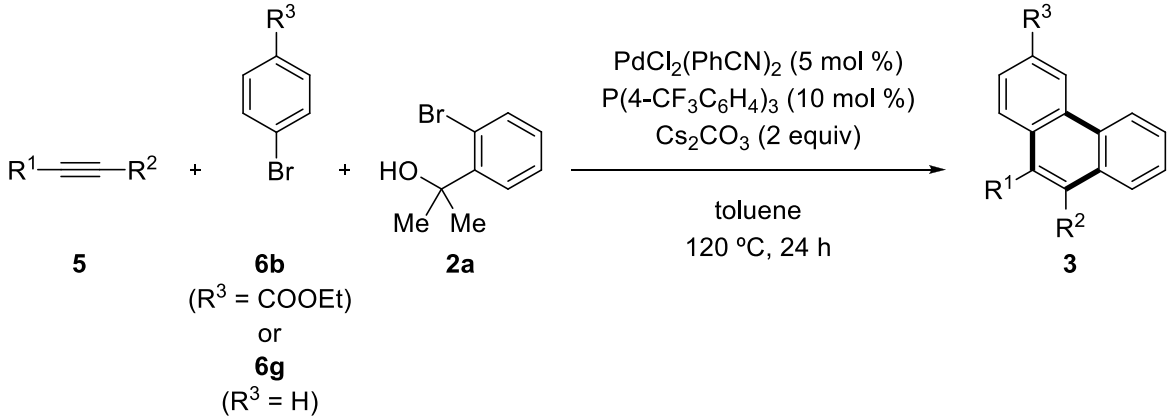
4	 **6e**	 **3n**	39
5	 **6f**	 **3o**	68
6[d]	 **6g**	 **3a**	86

[a]**5a** (0.25 mmol), **6** (1.0 mmol), **2a** (0.50 mmol), $PdCl_2(PhCN)_2$ (0.0125 mmol), $P(4\text{-}CF_3C_6H_4)_3$ (0.025 mmol), Cs_2CO_3 (0.50 mmol) in toluene (1 mL) at 120 ºC for 24 h. [b]Based on **1a** after silica gel column chromatography. [c]**6** (8 equiv). [d]**6g** (0.5 mL, 18 equiv) was used as solvent instead of toluene.

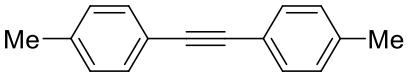
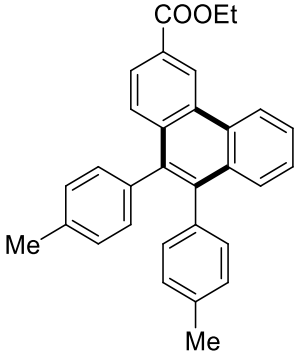
We then investigated the scope of the alkynes **5** in the three-component coupling (Table5). The electronic properties of diarylacetylenes **5b**–**5d** had only little influence on the reaction efficiency to afford the corresponding phenanthrenes **3p**–**3r** in moderate to good yields (entries 1–3). In addition, the sterically bulky **5e** could also be effectively converted into **3s** in 54% yield (entry 4). Moreover, the electronically-biased unsymmetrical alkynes **5f**–**5h** underwent the benzannulation with **6g** and **2a** to give the products **3c**, **3d**, and **3t**, respectively (entries 5–7). Although several reactions of unsymmetrical diarylacetylenes with **6b** and **2a** were conducted, poor regioselectivity was observed only in the reaction of **5h**, providing a 2:1 mixture of regioisomers **3u** and **3u'** in 61% combined yields (entry 8). However, the reaction of methylphenylacetylene (**5i**) with **6b** and **2a** proceeded with high regioselectivity, furnishing a 10:1 mixture of regioisomers **3v** and **3v'** in 54% combined yield (entry 9). The regioselectivity can be rationalized as follows. During a migratory insertion step of alkyne **5h** to an

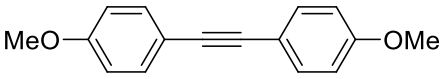
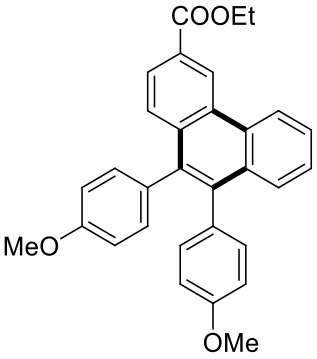
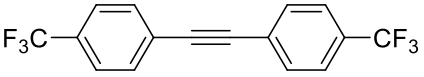
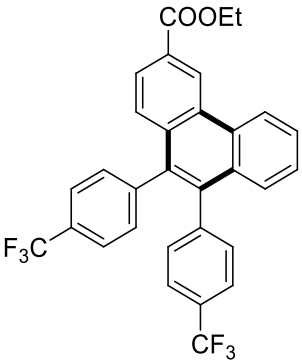
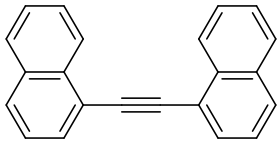
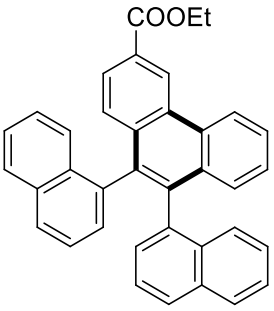
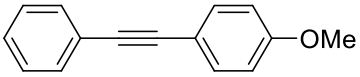
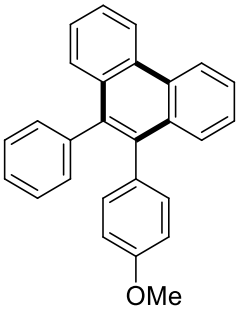
Ar–Pd bond, the palladium might favor to be located at the benzylic position to generate the relatively stable alkenyl palladium species. The electronically-biased unsymmetrical alkynes increased the selectivity of the reaction. On the other hand, the reaction of dialkylacetylenes and terminal alkynes gave poor results. The reaction of 4-octyne gave no product, which would retard the migratory insertion step. While the reaction of phenylacetylene affords the product in at most 15% NMR yield, but the attempted isolation resulted in failure due to the contamination of unidentified byproducts.

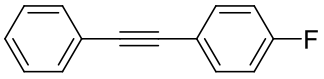
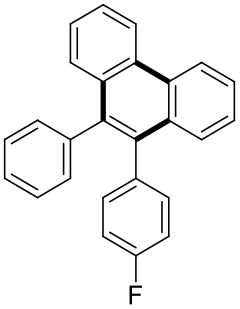
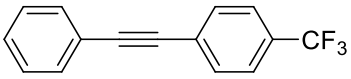
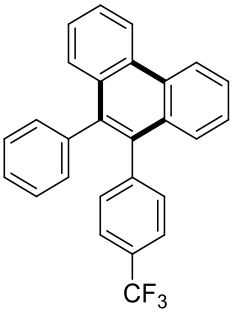
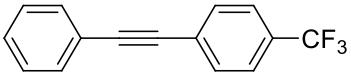
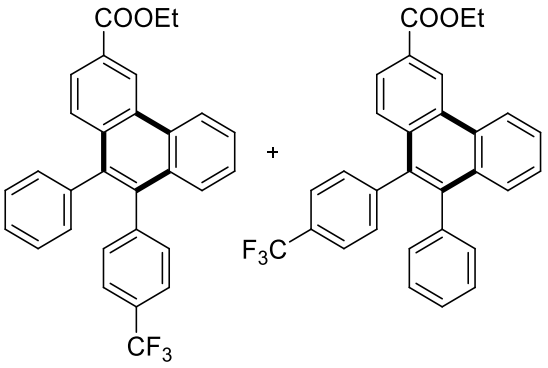
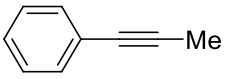
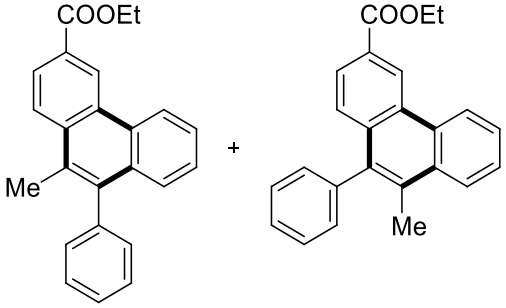
Table 5. Scope of Alkynes **5** in Reactions of Aryl Bromide **6b** or **6g** with *o*-Bromobenzyl Alcohol **2a**[a]



5 **6b** (R^3 = COOEt) or **6g** (R^3 = H) **2a** **3**

entry	5	6	3	yield (%)[b]
1	 **5b**	**6b**	 **3p**	75

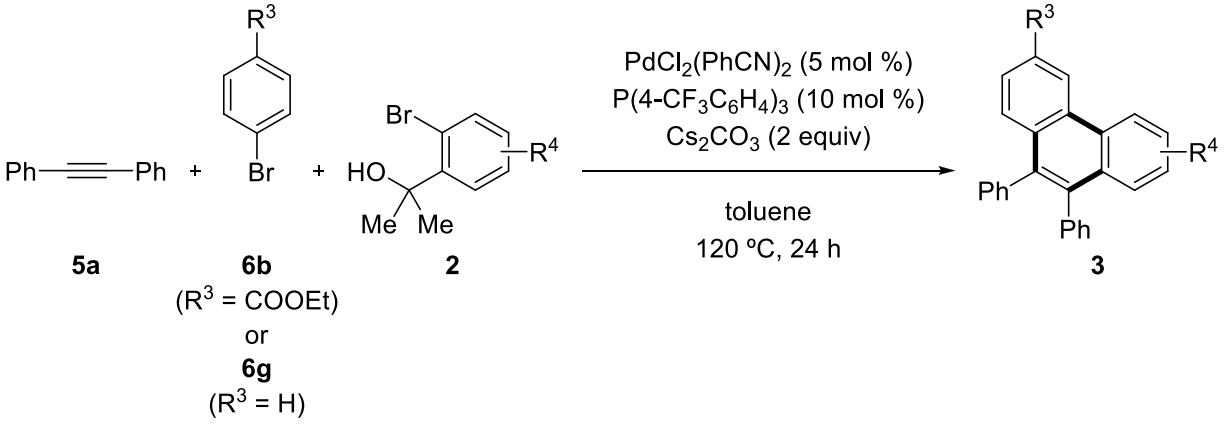
2	 **5c**	**6b**	 **3q**	62
3	 **5d**	**6b**	 **3r**	54
4	 **5e**	**6b**	 **3s**	54
5[c]	 **5f**	**6g**	 **3c**	88

6[c]	 **5g**	**6g**	 **3d**	64
7[c]	 **5h**	**6g**	 **3t**	55
8	 **5h**	**6b**	 **3u** : **3u'** = 2 : 1[d]	61[e]
9	 **5i**	**6b**	 **3v** : **3v'** = 10 : 1[d]	54[e]

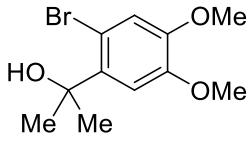
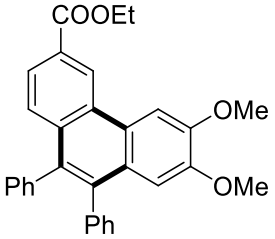
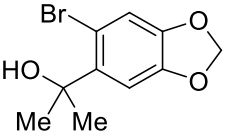
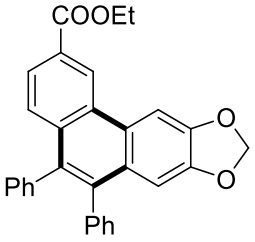
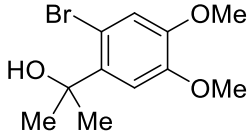
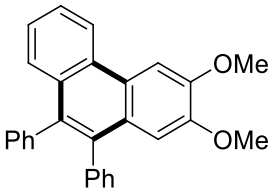
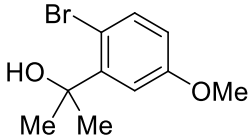
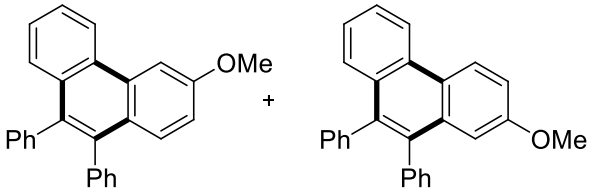
[a]**5** (0.25 mmol), **6b** (1.0 mmol), **2a** (0.50 mmol), $PdCl_2(PhCN)_2$ (0.0125 mmol), $P(4\text{-}CF_3C_6H_4)_3$ (0.025 mmol), Cs_2CO_3 (0.50 mmol) in toluene (1 mL) at 120 ºC for 24 h. [b]Based on **5** after silica gel column chromatography. [c]**6g** (0.5 mL, 18 equiv) was used as solvent instead of toluene. [d]Determined by ^1H NMR analyses. [e]Combined yields of two regioisomers.

Finally, several *o*-bromobenzyl alcohols **2** were examined in the present three-component coupling (Table 6). As a result, the annulating reagents **2b** substituted by two methoxy groups and **2c** having 1,3-benzoxal skeletons found to be suitable for the benzannulation with diphenylacetylene (**5a**) and aryl bromide **6b**, giving the desired multisubstituted phenanthrenes **3w** and **3x** in 72% and 44% yields, respectively (entries 1 and 2). Moreover, phenanthrene **3i** was obtained in 67% yield from the three-component coupling of readily available reagents **5a**, **6g**, and **2b** (entry 3). Unfortunately, the reaction with *o*-bromobenzyl alcohols bearing electron-withdrawing groups did not give the desired phenanthrenes. When the difluorinated *o*-bromobenzyl alcohol was used, the corresponding product was not obtained. Instead, a considerable amount of the homocoupled product derived from *o*-bromobenzyl alcohol was formed probably because the undesired oxidative addition of *o*-bromobenzyl alcohol was accelerated. Interestingly, the benzannulation of **5a** and **6g** with unsymmetrical *o*-bromobenzyl alcohol **2d** provided an unexpected mixture of regioisomers **3n** and **3n'** in a 5:1 ratio (entry 4).

Table 6. Scope of *o*-Bromobenzyl Alcohols **2** in Reactions of Diphenylacetylene (**5a**) with Aryl Bromide **6b** or **6g**[a]



entry	6	2	3	yield (%)[b]

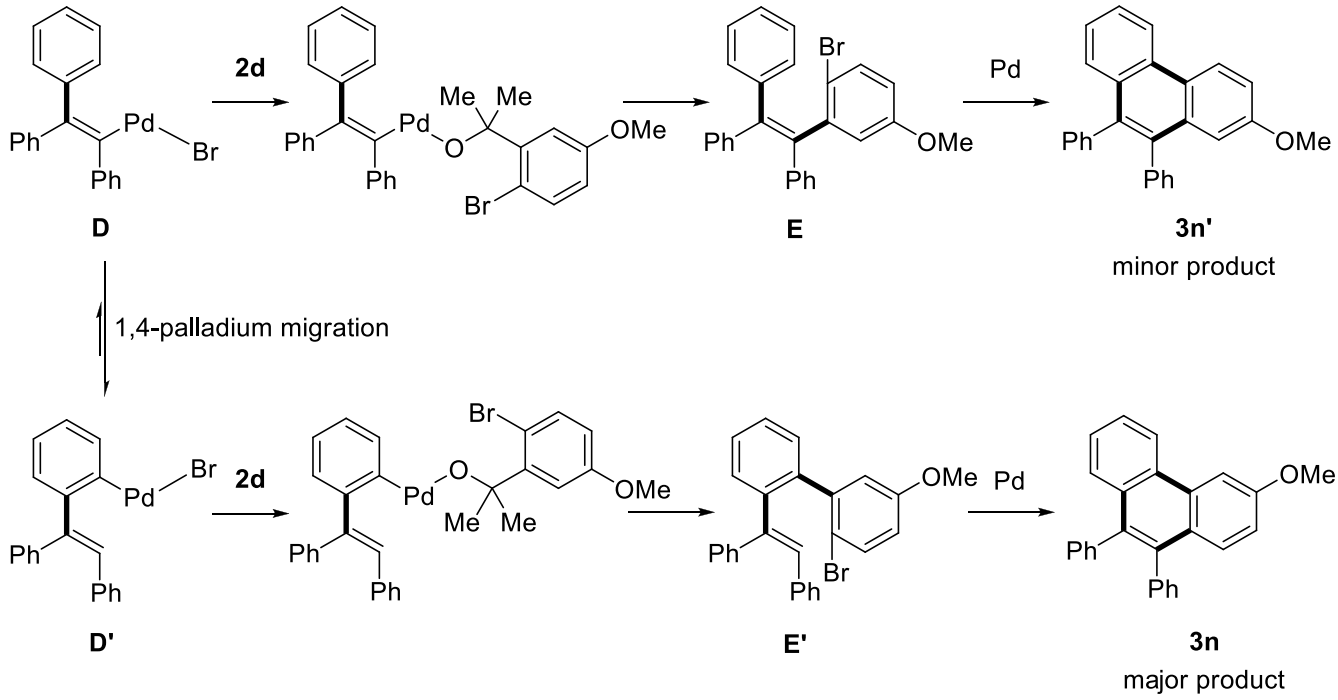
1	**6b**	 **2b**	 **3w**	72
2[c]	**6b**	 **2c**	 **3x**	54
3[d]	**6g**	 **2b**	 **3i**	67
4[d]	**6g**	 **2d**	 **3n** : **3n'** = 5 : 1[e]	34[f]

[a]**5a** (0.25 mmol), **6b** (1.0 mmol), **2** (0.50 mmol), $PdCl_2(PhCN)_2$ (0.0125 mmol), $P(4\text{-}CF_3C_6H_4)_3$ (0.025 mmol), Cs_2CO_3 (0.50 mmol) in toluene (1 mL) at 120 ºC for 24 h. [b]Based on **5a** after silica gel column chromatography. [c]0.125 mmol scale. [d]**6g** (0.5 mL, 18 equiv) was used as solvent instead of toluene. [e]Determined by ^{1}H NMR analyses. [f]Combined yields of two regioisomers.

We initially expected that phenanthrene **3n'** was solely obtained in the three-component coupling of **5a**, **6g**, and **2d**, as shown in Scheme 2. After the alkenylpalladium species **D** is generated by oxidative addition of **6g** and the subsequent migratory insertion of alkyne **5a**, the deacetonative coupling with *o*-bromobenzyl alcohol **2d** affords the intermediate **E** which leads to the formation of the desired phenanthrene **3n'**. On the other hand, prior to the reaction of **D** with **2d**, 1,4-palladium migration from **D** occurs to form arylpalladium species **D'**.[17] The reaction of **D'** with **2d** affords the regioisomer **3n** in the same fashion through the intermediate **E'**. The predominant formation of **3n** would be explained by

the isomerization of alkenylpalladium species **D** to thermodynamically stable arylpalladium species **D'**, from which the reaction with **2d** would occur.[18,19]

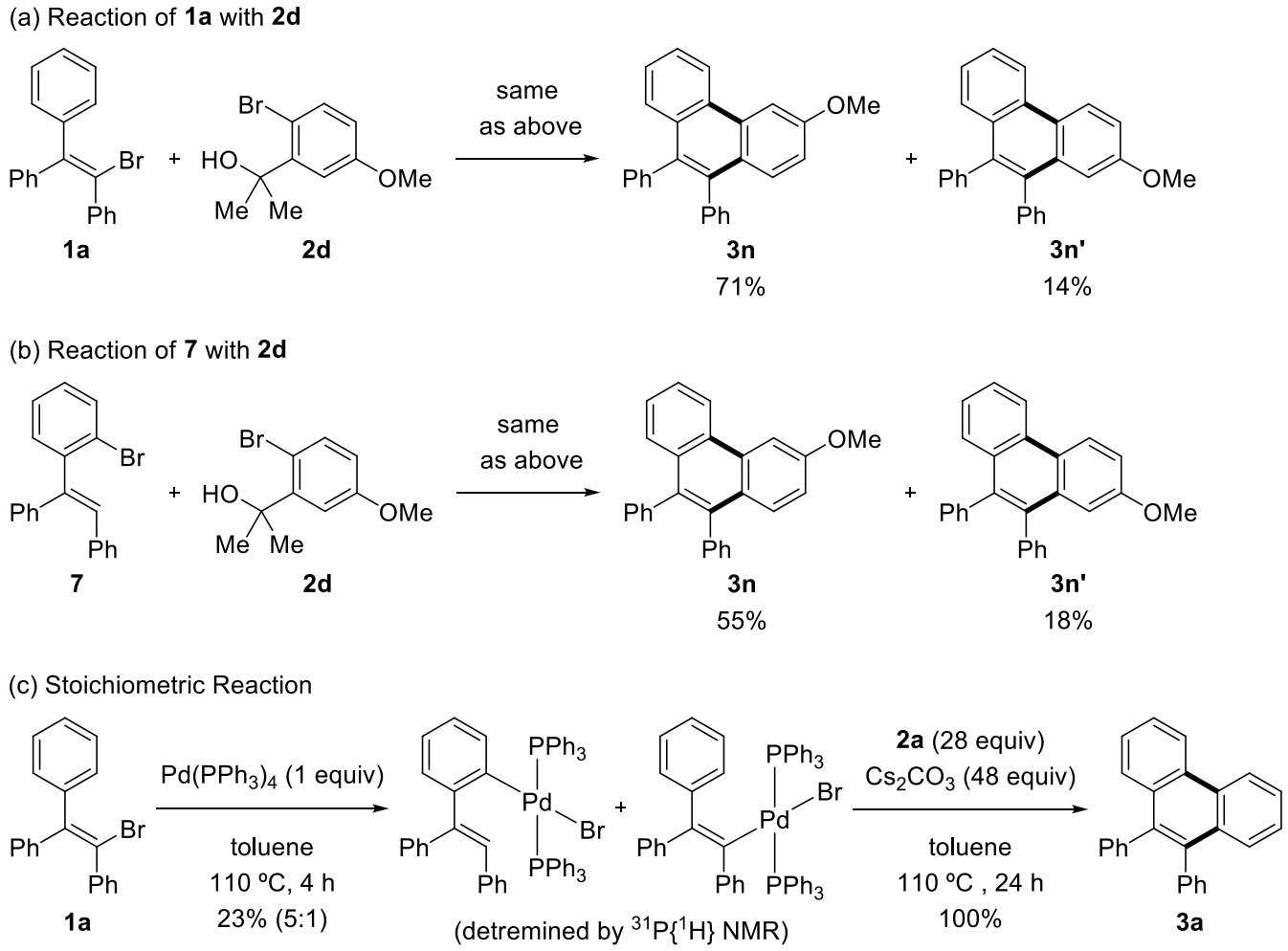
Scheme 2. 1,4-Palladium Migration from Alkenyl- to Arylplladium Species



Several control experiments were conducted to gain some mechanistic insights into the above mentioned 1,4-palladium migration in the reaction of **5a**, **6g**, and **2d**. (*Z*)-*β*-Bromostyrene **1a** which might generate the same palladium intermediate also underwent the benzannulation with **2d** to yield phenanthrene **3n** as the main product (Scheme 3a). In addition, under the identical reaction conditions, the reaction of aryl bromide **7** also gave the similar results to that of **1a** (Scheme 3b). The selectivity of the reaction of **7** with **2d** was slightly different from that of **1a** with **2d** and that of **5a** and **6g** with **2d**, which might result from the slower oxidative addition of aryl bromide **7**. Three-component coupling was lower yielding than both two-component couplings shown in Scheme 3a and 3b probably because three different carbon–carbon bond formation reactions have to be catalyzed by the single catalyst. Moreover, a stoichiometric reaction of **1a** with $Pd(PPh_3)_4$ provided the 5:1 mixture of two palladium complexes. $^{31}P\{^1H\}$ NMR spectrum of the obtained complexes shows two signals (δ 19.6 and 20.5)

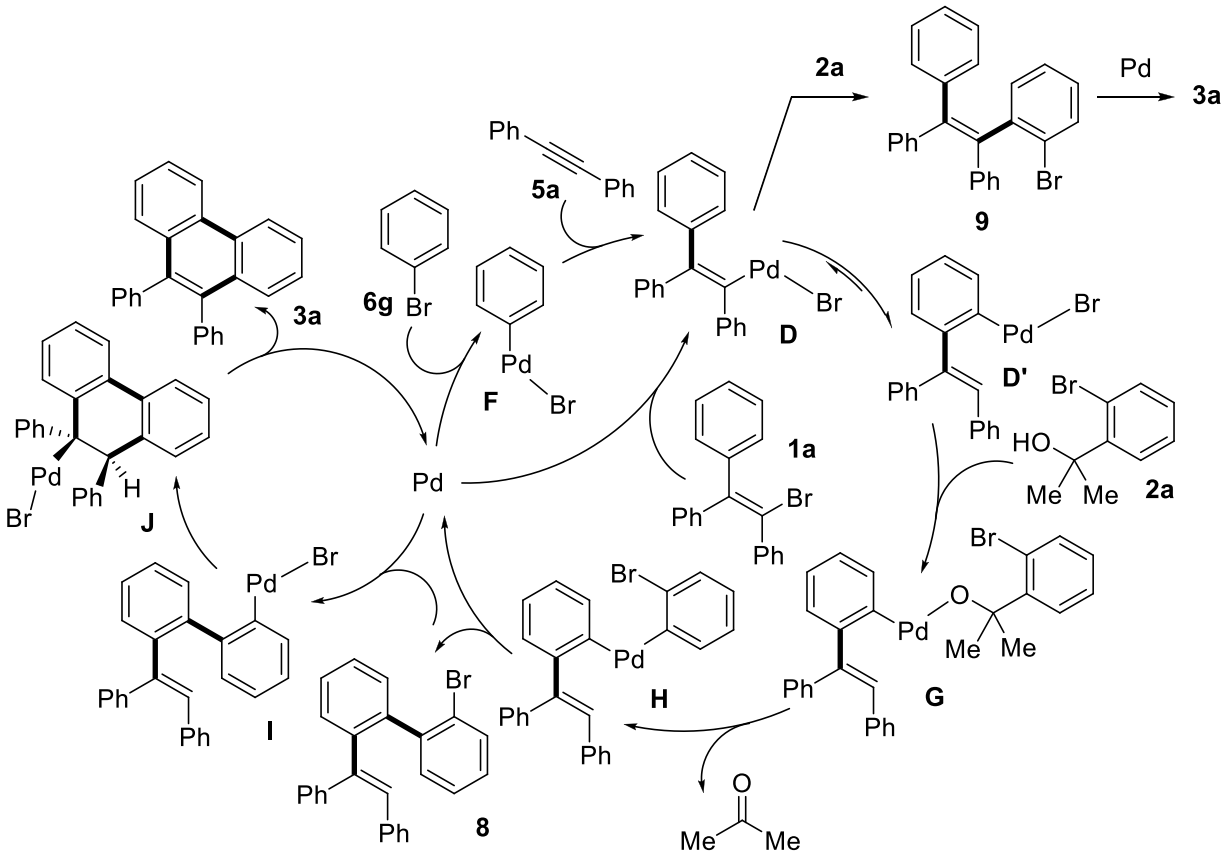
assignable to **D** and **D'** (Scheme 3c).[16] The obtained palladium complexes were treated with **2a** in the presence of cesium carbonate to yield **3a** quantitatively. These results strongly imply the existence of the rapid equilibrium in 1,4-palladium migration between **D** and **D'**. At this stage, selective synthesis of the desired phenanthrenes by the reaction with unsymmetrical *o*-bromobenzyl alcohols has yet to be achieved although several experiments of different substrates with **2d** were conducted. Further efforts to synthesize the desired phenanthrenes with a perfect selectivity by tuning the phosphine ligands are currently under investigation.

Scheme 3. Control Experiments



On the basis of the obtained results, a plausible reaction pathway for the palladium-catalyzed benzannulation of (*Z*)-*β*-halostyrene **1a** with *o*-bromobenzyl alcohol **2a** and three-component coupling of alkyne **5a**, aryl bromide **6g**, and *o*-bromobenzyl alcohol **2a** is shown in Scheme 4. Initial alkenylpalladium species **D** is generated by oxidative addition of alkenyl bromide **1a**, or oxidative addition of aryl bromide **6g** and the sequential migratory insertion[15] of alkyne **5a** to arylpalladium species **F**. The electron-deficient phosphine ligand, $P(4\text{-}CF_3C_6H_4)_3$, might suppress the reactivity of palladium for oxidative addition of **2a**, which leads to the undesired formation of benzochromene **4**.[8d,20] The formed alkenylpalladium **D** smoothly isomerizes to the relatively stable arylpalladium **D'** by 1,4-palladium migration.[17] The following ligand exchange between **D'** and *o*-bromobenzyl alcohol **2a** is facilitated by cesium carbonate to give the palladium intermediate **G**. Alkoxopalladium **G** undergoes *β*-carbon elimination[12] with the release of acetone, providing the arylpalladium **H**, followed by reductive elimination to yield aryl bromide **8** and regenerate the initial palladium species. Subsequently, the smooth oxidative addition of **8** proceeds probably through ring-walking pathway[21,22] to generate arylpalladium species **I**, which undergoes the 6-*endo*-*trig* cyclization to furnish benzylpalladium intermediate **J**. Finally, *β*-hydrogen elimination[23] from **J** releases the desired phenanthrene **3a**, with the initial palladium catalyst regenerated. The present reaction consists of two catalytic cycles; deacetonative coupling and intramolecular cyclization. The first catalytic cycle might involve the rate-determining step of the reaction because the intermediate **8** was not detected in the reaction mixture. From the results of the reaction with unsymmetrical *o*-bromobenzyl alcohol, the minor pathway to give the product **3a** is considerable, which is initiated by the reaction of **D** with **2a**. Aryl bromide **9** is generated through ligand exchange, *β*-carbon elimination, and reductive elimination. The following palladium-catalyzed intramolecular cyclization of **9** affords **3a**.

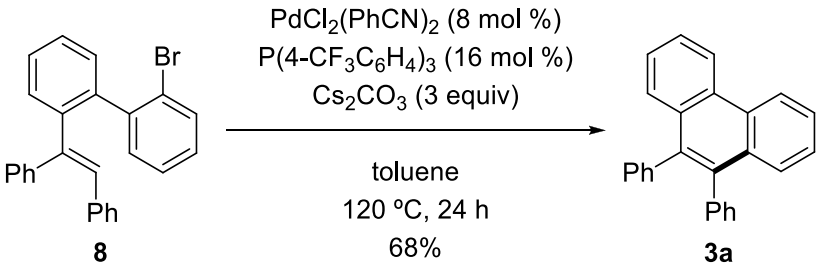
Scheme 4. A Plausible Reaction Pathway



The proposed reaction pathway shown in Scheme 4 was supported by the following experiment. The possible intermediate **8** was independently prepared and reacted under the similar reaction conditions (Scheme 5a). The desired phenanthrene **3a** was obtained in 68% yield, which clearly suggested the intermediacy of aryl bromide **8**. As an alternative reaction mechanism, the pathway through the aryne intermediate would be plausible, which might be generated from *o*-bromobenzyl alcohols. The reaction of **1a** with **2a** in the presence of furan gave **3a** in 84% yield while Diels–Alder reaction of benzyne with furan did not proceed (Scheme 5b). In addition, Diels–Alder adduct was not detected at all in the reaction of **2a** with furan (Scheme 5c). On the basis of the obtained results, the reaction pathway via aryne intermediates would be unlikely.

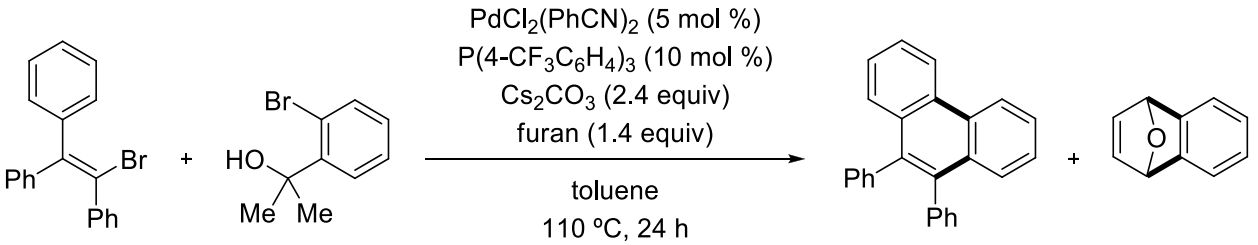
Scheme 5. Mechanistic Studies

(a) Intramolecular Cyclization of Possible Intermediate **8**



8 **3a**

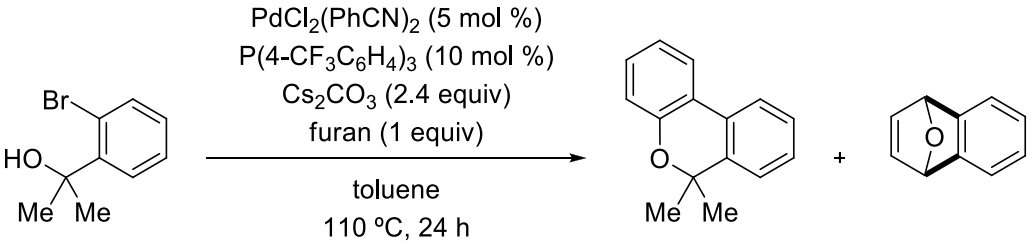
(b) Reaction of **1a** with **2a** in the Presence of Furan



1a **2a** **3a** not detected

84%

(c) Reaction of **2a** with Furan

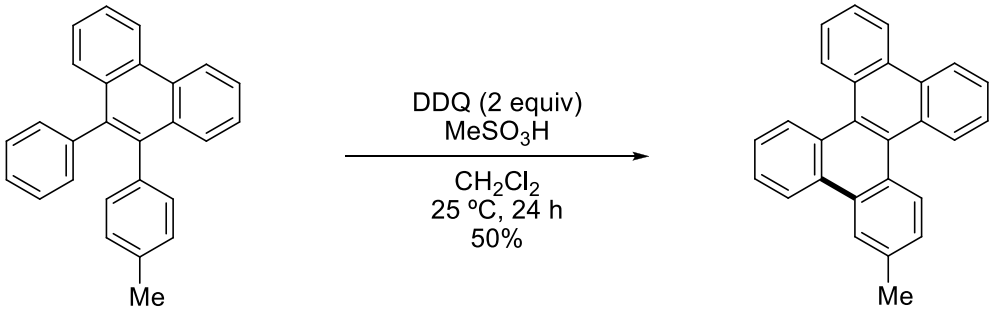


2a **4** not detected

84%

The obtained 9,10-diarylphenanthrenes **3** represent useful precursors of the highly-fused PAHs. Oxidative cyclization of **3b** by 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) in the presence of methanesulfonic acid provided dibenzochrysene **10** in 50% yield (Scheme 6).[24] The present benzannulation-oxidation sequences demonstrated a powerful synthetic method of the functionalized unsymmetrical PAHs which are difficult to be prepared by the conventional methods.

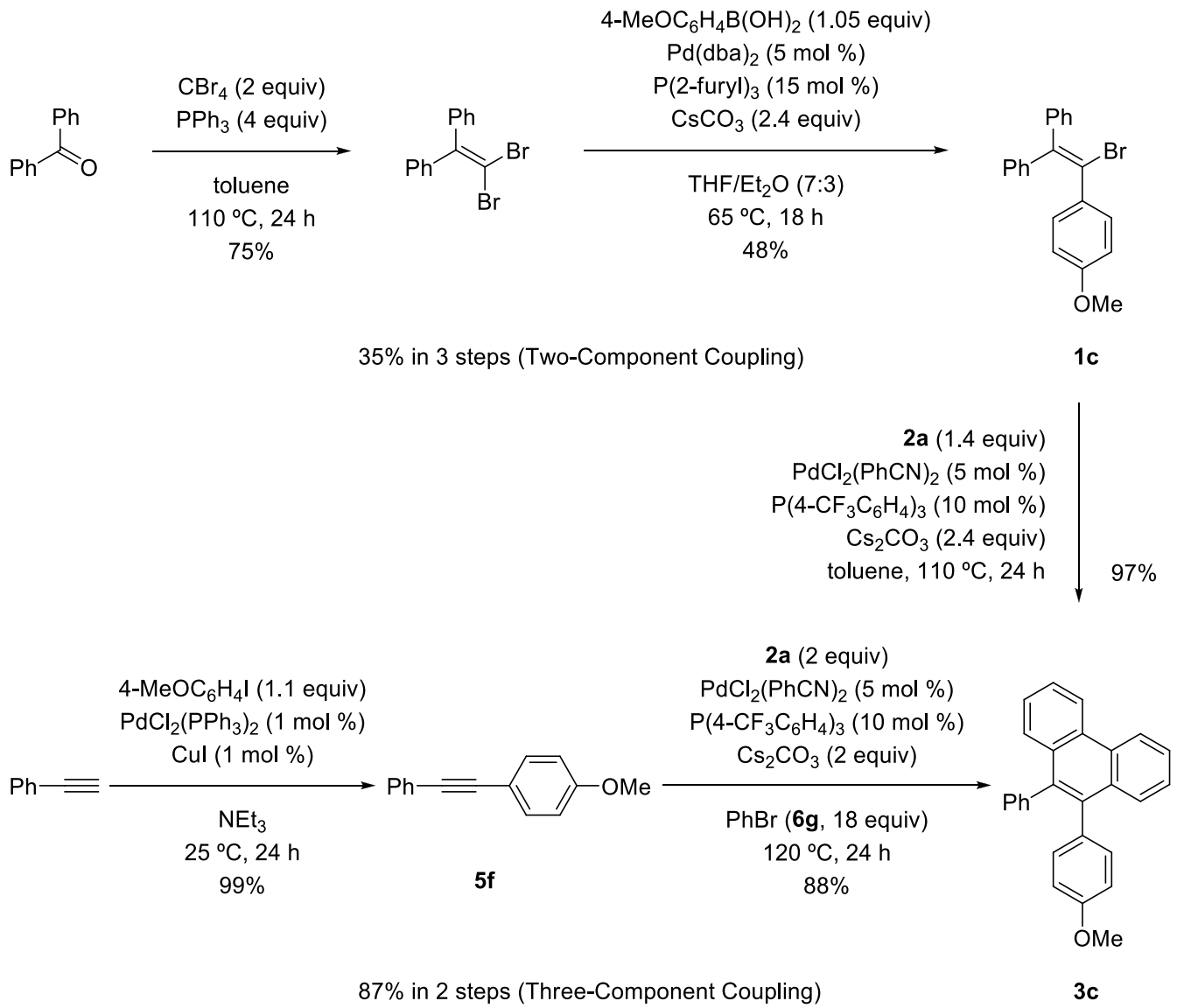
Scheme 6. Synthesis of Dibenzochrycene **10** by Oxidative Cyclization of **3b**



3b **10**

The present method by three-component coupling established the facile access to the desired phenanthrenes from the commercially available substrates, which provided dramatically improvement over two-component coupling. One example was shown in Scheme 7. When phenanthrene **3c** was synthesized by two-component coupling, the starting (*Z*)-*β*-halostyrene **1c** had to be prepared by dibromoolefination of benzophenone and the sequential cross-coupling with 4-methoxyphenylboronic acid. Although the benzannulation of **1c** with **2a** yielded **3c** in excellent yield, the overall yield was 35% yield in 3 steps. On the other hand, by using three-component coupling, **3c** was obtained in 87% overall yield in 2 steps since alkyne **5f** employed can be available from the reliable Sonogashira–Hagihara coupling of phenylacetylene with 4-iodoanisole.

Scheme 7. Synthetic Routes to Phenanthrene **3c**



Conclusions

In summary, we have developed the palladium-catalyzed benzannulation of (*Z*)-*β*-halostyrenes with *o*-bromobenzyl alcohols and three-component coupling of alkynes, aryl bromides, and *o*-bromobenzyl alcohols for the novel phenanthrene synthesis. Both reactions were efficiently catalyzed by a palladium/phosphine complex through the multiple carbon–carbon bond formations. The present protocol provided a variety of multisubstituted phenanthrenes with high functionalities, including a highly-fused tetraphene derivative. The desired phenanthrene skeletons can be constructed in a single step from the readily available starting materials, which represents the most advantageous point

distinguished from the conventional synthesis. Further investigation to apply the palladium-catalyzed benzannulation to the other PAH synthesis are ongoing in our laboratory.

Experimental Section

General. High resolution mass spectra (HRMS) were obtained by fast atom bombardment (FAB) using a double focusing magnetic sector mass spectrometer.

Chemicals. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Alkynes **5a**, **5i**, and aryl halides **6a**–**6g** were obtained from commercial suppliers. (*Z*)-*β*-Halostyrenes **1a**,[25] **1b**,[26] **1c**,[27] **1g**,[28] **1h**,[29] **1i**,[30] *o*-bromobenzyl alcohols **2a**–**2c**,[11a] **2d**,[31] benzochromene **4**,[32] alkynes **5b**,[33] **5c**,[34] **5d**,[35] **5e**,[34] **5f**,[36] **5g**,[37] **5h**,[36] and chrysene **10**[38] were known compounds.

Typical Procedure for Palladium-Catalyzed Benzannulation of (*Z*)-*β*-Halostyrenes 1 with *o*-Bromobenzyl Alcohols 2: Synthesis of 9,10-diphenylphenanthrene (**3a**) is representative. Under an argon atmosphere, cesium carbonate (196 mg, 0.60 mmol), bis(benzonitrile)dichloropalladium (4.8 mg, 0.0125 mmol), and tris(4-trifluoromethylphenyl)phosphine (11.7 mg, 0.025 mmol) were placed in a 20-mL Schlenk tube. Toluene (1.0 mL), 1-bromo-1,2,2-triphenylethene (**1a**, 83.8 mg, 0.25 mmol) and 2-(*o*-bromophenyl)-2-propanol (**2a**, 75.3 mg, 0.35 mmol) were added. The resulting mixture was stirred at 110 ºC for 24 h. The mixture was then cooled to room temperature. Hydrochloric acid (1 M, 3 mL) was added, and the product was extracted with dichloromethane (10 mL × 3). The organic layers were dried over anhydrous sodium sulfate. After the volatile was evaporated, silica gel column purification with hexane as an eluent afforded 9,10-diphenylphenanthrene (**3a**, 71.9 mg, 0.217 mmol, 87% yield).

Typical Procedure for Palladium-Catalyzed Three-Component Coupling of Aryl Bromides 5, Alkynes 6, and *o*-Bromobenzyl Alcohols 2: Synthesis of 3-ethoxycarbonyl-9,10-diphenylphenanthrene (**3k**) is representative. Under an argon atmosphere, cesium carbonate (163 mg, 0.50 mmol), bis(benzonitrile)dichloropalladium (4.8 mg, 0.0125 mmol), and tris(4-trifluoromethylphenyl)phosphine (11.7 mg, 0.025 mmol) were placed in a 20-mL Schlenk tube. Toluene (1.0 mL), diphenylacetylene (**5a**,

44.6 mg, 0.25 mmol), ethyl 4-bromobenzoate (**6a**, 229 mg, 1.0 mmol), and 2-(*o*-bromophenyl)-2-propanol (**2a**, 108 mg, 0.50 mmol) were added. The resulting mixture was stirred at 120 ºC for 24 h. The mixture was then cooled to room temperature. Hydrochloric acid (1 M, 3 mL) was added, and the product was extracted with dichloromethane (10 mL × 3). The organic layers were dried over anhydrous sodium sulfate. After the volatile was evaporated, silica gel column purification (hexane/ethyl acetate = 80:1) afforded 3-ethoxycarbonyl-9,10-diphenylphenanthrene (**3k**, 84.0 mg, 0.209 mmol, 83% yield).

Characterization of Compounds.

Preparation of 1-Bromo-1-(4-fluorophenyl)-2,2-diphenylethene (1d)[39]: Under an argon atmosphere, 1,1-dibromo-2,2-diphenylethene (338 mg, 1.0 mmol), 4-fluorophenylboronic acid (147 mg 1.05 mmol), tri(2-furyl)phosphine (34.8 mg, 0.15 mmol), and bis(dibenzylideneacetone)palladium (28.8 mg, 0.05 mmol) were placed in 50-mL of Schlenk tube. THF (4.9 mL), ether (2.1 mL), and a solution of cesium carbonate (652 mg, 2.0 mmol) in water (2 mL) were then added. The reaction mixture was stirred at reflux for 18 h. The product was extracted with ethyl acetate (30 mL × 3). The combined organic layers were washed with brine (10 mL) and dried over anhydrous sodium sulfate. Evaporation followed by silica gel column chromatography (hexane/ethyl acetate = 80:1) afforded **1d** as orange solid (157 mg, 0.444 mmol, 44%).

M.p. 113–114 ºC. IR (KBr) 3059 (w), 1647 (w), 1491 (m) cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$, rt):δ 6.88 (t, J = 9.0 Hz, 2H), 6.96–6.99 (m, 2H), 7.08–7.13 (m, 3H), 7.30–7.41 (m, 7H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, rt): δ 115.2 (d, $^2J_{C-F}$ = 21.9 Hz), 121.0, 127.3, 127.8, 128.1, 128.4, 129.6, 130.4, 132.3 (d, $^3J_{C-F}$ = 8.1 Hz), 137.3 (d, $^4J_{C-F}$ = 3.5 Hz), 141.0, 143.7, 144.1, 162.1 (d, $^1J_{C-F}$ = 248 Hz); $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$, rt): δ –113.0. Calcd for $C_{20}H_{14}BrF$: C, 68.01; H, 3.99%. Found: C, 67.80; H, 3.91%.

1-Bromo-1-(4-cyanophenyl)-2,2-diphenylethene (1e): The title compound was obtained as light-yellow solid (90.3 mg, 0.251 mmol, 50%). M.p. 162–163 ºC. IR (KBr) 3061 (w), 2226 (w), 1682 (w), 1599 (m) cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$, rt):δ 6.93 (d, J = 8.4 Hz, 2H), 7.09–7.16 (m, 3H), 7.33–7.37 (m, 3H), 7.39–7.41 (m, 4H), 7.47 (d, J = 8.4 Hz, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, rt): δ

111.4, 118.6, 119.2, 127.8, 128.2, 128.3, 128.4, 129.5, 130.4, 131.2, 131.9, 140.4, 143.0, 145.9, 146.1. Calcd for $C_{21}H_{14}BrN$: C, 70.01; H, 3.92; N, 3.89%. Found: C, 69.81; H, 3.71; N, 3.76%.

1-Bromo-2,2-di(4-fluorophenyl)-1-(4-methoxyphenyl)ethene (1f): The title compound was obtained as light-yellow solid (79.9 mg, 0.199 mmol, 40%). M.p. 80–82 ºC. IR (KBr) 3044 (w), 2963 (w), 1655 (w), 1510 (m), 1225 (s), 1028 (s) cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$, rt): δ 3.78 (s, 3H), 6.72 (d, 9.0 Hz, 2H), 6.78 (t, J = 9.0 Hz, 2H), 6.90 (dd, J = 8.4, 5.4 Hz, 2H), 7.06 (t, J = 9.0 Hz, 2H), 7.22 (d, J = 9.0 Hz, 2H), 7.32 (dd, J = 8.4, 5.4 Hz, 2H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, rt): δ 55.4, 113.6, 115.1 (d, $^2J_{C–F}$ = 21.2 Hz), 115.4 (d, $^2J_{C–F}$ = 21.3 Hz), 123.0, 131.6 (d, $^3J_{C–F}$ = 8.0 Hz), 131.8, 132.2 (d, $^3J_{C–F}$ = 8.0 Hz), 133.2, 137.3 (d, $^4J_{C–F}$ = 3.5 Hz), 139.8 (d, $^4J_{C–F}$ = 3.5 Hz), 140.7, 159.4, 161.7 (d, $^1J_{C–F}$ = 246 Hz), 162.2 (d, $^1J_{C–F}$ = 246 Hz); $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$, rt): δ –114.5, –114.0. Calcd for $C_{21}H_{15}BrF_2O$: C, 62.86; H, 3.77%. Found: C, 63.02; H, 3.66%.

Preparation of (*Z*)-1-Bromo-1,2-diphenyl-1-hexene (1j)[40]: Under an argon atmosphere, diphenylacetylene (891 mg, 5.0 mmol) was placed in 50-mL Schlenk tube. THF (6 mL) was then added. *n*-Butyllithium (1.6 M hexane solution, 3.4 mL, 5.5 mmol) was added dropwise at –10 ºC. The reaction mixture was stirred for 2 h. 1,2-Dibromoethane (0.57 mL, 6.6 mmol) was added at –78 ºC and the reaction mixture was stirred for additional 30 min. After being cooled to 0 ºC, the reaction mixture was poured into saturated ammonium chloride solution (20 mL), and extracted with diethyl ether (40 mL × 3). The combined organic layers were washed with brine (10 mL) and dried over anhydrous sodium sulfate. The volatiles were evaporated in vacuo. The product was chromatographed on silica gel (hexane) to afford **1j** as white solid (537 mg, 1.70 mmol, 34%).

M.p. 50–51 ºC. IR (KBr) 3076 (w), 2957 (m), 1597 (w), 1443 (m) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, rt): δ 0.73 (t, J = 7.2 Hz, 3H), 1.11–1.28 (m, 4H), 2.33 (t, J = 7.2 Hz, 2H), 7.30–7.36 (m, 4H), 7.38–7.44 (m, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, rt): δ 13.9, 22.4, 30.4, 36.0, 118.9, 127.3, 128.2, 128.3, 128.4, 128.5, 129.1, 141.0, 142.7, 143.7. Calcd for $C_{18}H_{19}Br$: C, 68.58; H, 6.07%. Found: C, 68.60; H, 5.98%.

Preparation of (*Z*)-1-Iodo-1,2-diphenyl-1-hexene (1k)[41]: Under argon atmosphere, lithium granules (694 mg, 100 mmol) was placed in 50-mL Schlenk tube. THF (24 mL) and trimethylstannyl chloride (1.99 g, 10 mmol) was added and the reaction mixture was vigorously stirred at 0 ºC for 12 h. The resulting dark green solution was transferred via a syringe to 20-mL Schlenk tube and the volatiles were removed in vacuo. Hexane (18.2 mL) and diphenylacetylene (1.60 g, 9 mmol) were added at 0 ºC. After the reaction mixture was stirred at 0 ºC for 3 h, 1-iodobutane (1.14 mL, 10 mmol) was added at 0 ºC. The reaction mixture was allowed to warm to room temperature and stirred for additional 3 h. The volatiles were removed in vacuo. To the reaction mixture, were added dichloromethane (40 mL) and iodine (4.57 g, 18 mmol). After being stirred at room temperature for 2 h, the reaction mixture was poured into saturated sodium thiosulfate aqueous solution (20 mL). The product was extracted with dichloromethane (40 mL × 3). The combined organic layers were washed with brine (20 mL) and dried over sodium sulfate. After concentration in vacuo, purification by silica gel column chromatography (hexane) affords **1k** as white solid (1.66 g, 4.59 mmol, 51%).

M.p. 67–68 ºC. IR (KBr) 3051 (w), 2959 (m), 1597 (w), 1441 (m) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, rt): δ 0.71 (t, J = 7.2 Hz, 3H), 1.11–1.26 (m, 4H), 2.33 (t, J = 7.2 Hz, 2H), 7.24–7.30 (m, 2H), 7.33–7.44 (m, 8H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, rt): δ 13.9, 22.3, 30.6, 35.5, 97.6, 127.4, 127.8, 128.3, 128.36, 128.39, 128.7, 144.4, 146.2, 150.4. Calcd for $C_{18}H_{19}I$: C, 59.68; H, 5.29%. Found: C, 59.35; H, 5.16%.

9,10-Diphenylphenanthrene (3a): The reaction of **1a** with **2a** provided the title compound as white solid (71.9 mg, 0.218 mmol, 87% yield). The reaction of **5a**, **6g**, and **2a** provided the title compound as white solid (71.0 mg, 0.215 mmol, 86% yield). ^1H NMR (300 MHz, $CDCl_3$, rt): δ 7.14–7.28 (m, 10H), 7.47–7.52 (m, 2H), 7.55–7.58 (m, 2H), 7.64–7.70 (m, 2H), 8.82 (d, J = 8.4 Hz, 2H). Compound **3a** was consistent with the literature data.[42]

9-Phenyl-10-(4-methylphenyl)phenanthrene (3b): The reaction of **1b** with **2a** provided the title compound as white solid (105.2 mg, 0.305 mmol, 100%). ^1H NMR (400 MHz, $CDCl_3$, rt): δ 2.31 (s,

3H), 7.04 (s, 4H), 7.17–7.28 (m, 5H), 7.48 (t, J = 8.0 Hz, 2H), 7.53–7.59 (m, 4H), 7.66 (t, J = 8.0 Hz, 2H), 8.81 (d, J = 8.0 Hz, 2H). Compound **3b** was consistent with the literature data.[43]

9-(4-Methoxyphenyl)-10-phenylphenanthrene (3c): The reaction of **1c** with **2a** provide the title compound as white solid (69.9 mg, 0.194 mmol, 97%). The reaction of **5f**, **6g**, and **2a** provided the title compound as white solid (79.5 mg, 0.221 mmol, 88%). ^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 3.79 (s, 3H), 6.79 (d, J = 8.4 Hz, 2H), 7.07 (d, J = 8.4 Hz, 2H), 7.15–7.28 (m, 5H), 7.46–7.69 (m, 6H), 8.81 (d, J = 8.4 Hz, 2H). Compound **3c** was consistent with the literature data.[7f]

9-(4-Fluorophenyl)-10-phenylphenanthrene (3d): The reaction of **1d** with **2a** provided the title compound as white solid (66.4 mg, 0.191 mmol, 95%). The reaction of **5g**, **6g**, and **2a** provided the title compound as white solid (55.8 mg, 0.160 mmol, 64%). M.p. 254–256 ºC. IR (KBr): 3065 (w), 1506 (m) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 6.95 (t, J = 8.8 Hz, 2H), 7.10–7.16 (m, 4H), 7.20–7.29 (m, 3H), 7.48–7.57 (m, 4H), 7.66–7.71 (m, 2H), 8.82 (d, J = 8.8 Hz, 2H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, rt): δ 114.8 (d, $^2J_{C–F}$ = 21.0 Hz), 122.6, 122.7, 126.6, 126.69, 126.74, 126.8, 126.9, 127.7, 127.9, 128.0, 130.2 (2C), 131.1, 131.9, 132.0, 132.7 ($^3J_{C–F}$, J = 7.8 Hz), 135.6 (d, $^4J_{C–F}$ = 3.5 Hz), 136.2, 137.8, 139.6, 161.6 (d, $^1J_{C–F}$ = 244 Hz); ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$, rt): δ –116.1. Calcd for $C_{26}H_{17}F$: C, 89.63; H, 4.92. Found: C, 89.43; H, 4.84.

9-(4-Cyanophenyl)-10-phenylphenanthrene (3e): The reaction of **1e** with **2a** provided the title compound as white solid (48.1 mg, 0.135 mmol, 68%). M.p. 222–223 ºC. IR (KBr): 3065 (w), 2228 (m), 1607 (m) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 7.07–7.10 (m, 2H), 7.19–7.26 (m, 5H), 7.39 (d, J = 8.4 Hz, 1H), 7.47–7.55 (m, 5H), 7.68 (t, J = 8.0 Hz, 2H), 8.79 (d, J = 8.4 Hz, 1H), 8.81 (d, J = 8.4 Hz, 1H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, rt): δ 110.6, 119.1, 122.7, 122.9, 126.9, 127.0, 127.08, 127.12, 127.15, 127.2, 128.0, 128.1 (2C), 130.2, 130.3, 130.9, 131.6 (2C), 132.0, 135.4, 137.6, 138.8, 145.1. Calcd for $C_{27}H_{17}N$: C, 91.24; H, 4.82 N, 3.94%. Found: C, 90.85; H, 4.83 N, 3.88%.

3-Fluoro-9-(4-fluorophenyl)-10-(4-methoxyphenyl)phenanthrene (3f): The reaction of **1f** with **2a** provided the title compound as white solid (56.0 mg, 0.141 mmol, 71%). M.p. 231–232 ºC. IR (KBr):

3038 (w), 2938 (w), 1497 (m), 1219 (s), 1034 (s) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, rt): δ 3.81 (s, 3H), 6.81 (d, J = 8.8 Hz, 2H), 6.96 (t, J = 8.8 Hz, 2H), 7.03 (d, J = 8.8 Hz, 2H), 7.10 (dd, J = 8.8, 5.2 Hz, 2H), 7.21–7.26 (m, 1H), 7.50–7.55 (m, 2H), 7.61 (d, J = 8.4, 1H), 7.67 (t, J = 8.4 Hz, 1H), 8.40 (dd, J = 11.2, 2.4 Hz, 1H), 8.65 (d, J = 8.4 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, rt): δ 55.3, 107.8 (d, $^2J_{C-F}$ = 22.2 Hz), 113.4, 114.9 (d, $^2J_{C-F}$ = 21.1 Hz), 115.6 (d, $^2J_{C-F}$ = 23.2 Hz), 122.8, 126.7, 127.4, 128.1, 128.8 (d, $^5J_{C-F}$ = 1.3 Hz), 129.6 (d, $^4J_{C-F}$ = 4.1 Hz), 130.0 (d, $^3J_{C-F}$ = 8.8 Hz), 131.5, 131.8 (d, $^3J_{C-F}$ = 8.4 Hz), 132.1, 132.6 (d, $^3J_{C-F}$ = 7.8 Hz), 132.7, 135.5 (d, $^4J_{C-F}$ = 3.5 Hz), 136.1 (d, $^5J_{C-F}$ = 1.2 Hz), 136.7 (d, $^5J_{C-F}$ = 1.8 Hz), 158.3, 161.6 (d, $^1J_{C-F}$ = 245 Hz), 161.7 (d, $^1J_{C-F}$ = 244 Hz); $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$, rt): δ –115.9, –114.3. Calcd for $C_{27}H_{18}F_2O$: C, 81.80; H, 4.58%. Found: C, 81.68; H, 4.28%.

9-Methyl-10-phenylphenanthrene (3g): The reaction of **1h** with **2a** provided the title compound as white solid (46.0 mg, 0.171 mmol, 69%). ^1H NMR (400 MHz, $CDCl_3$, rt): δ 2.47 (s, 3H), 7.31–7.61 (m, 8H), 7.66–7.72 (m, 2H), 8.15–8.18 (m, 1H), 8.74 (d, J = 7.6 Hz, 1H), 8.78–8.80 (m, 1H). Compound **3g** was consistent with the literature data.[42]

9-Butyl-10-phenylphenanthrene (3h): The reaction of **1k** with **2a** provided the title compound was obtained as white solid (46.0 mg, 0.148 mmol, 59%). M.p. 113–114 ºC. IR (KBr): 3069 (w), 2955 (m), 1491 (m) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, rt): δ 0.81 (t, J = 7.2 Hz, 3H), 1.24–1.36 (m, 2H), 1.56–1.65 (m, 2H), 2.82–2.87 (m, 2H), 7.30–7.33 (m, 3H), 7.38–7.60 (m, 5H), 7.64–7.70 (m, 2H), 8.14–8.18 (m, 1H), 8.73 (d, J = 8.4 Hz, 1H), 8.78–8.81 (m, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, rt): δ 13.9, 23.3, 30.4, 33.2, 122.4, 123.2, 125.4, 125.8, 126.2, 126.4, 126.9, 127.2, 127.7, 128.5, 129.4, 130.4, 130.5, 131.1, 132.6, 135.0, 136.9, 140.6. HRMS (FAB+): Calcd for $C_{24}H_{22}$: 310.1722. Found: 310.1745 $[M]^+$.

2,3-Dimethoxy-9,10-diphenylphenanthrene (3i): The reaction of **1a** with **2b** provided the title compound as white solid (86.4 mg, 0.221 mmol, 89%). The reaction of **5a**, **6g**, and **2b** provided the title compound as white solid (65.6 mg, 0.168 mmol, 67%). ^1H NMR (400 MHz, $CDCl_3$, rt): δ 3.72 (s, 3H), 4.16 (s, 3H), 6.92 (s, 1H), 7.15–7.26 (m, 10H), 7.43 (t, J = 8.4 Hz, 1H), 7.55 (d, J = 8.4 Hz, 1H), 7.63 (t,

J = 8.4 Hz, 1H), 8.14 (s, 1H), 8.65 (d, J = 8.4 Hz, 1H). Compound **3i** was consistent with the literature data.[44]

5,6-Diphenyl-1,3-phenanthro[2,3-*d*]dioxole (3j): The reaction of **1a** with **2c** provided the title compound as orange solid (69.3 mg, 0.185 mmol, 74%). M.p. 234–235 ºC. IR (KBr): 3022 (w), 2924 (w), 1458 (m), 1244 (m), 1038 (m) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, rt): δ 6.07 (s, 2H), 6.91 (s, 1H), 7.12–7.26 (m, 10H), 7.43 (t, J = 8.4 Hz, 1H), 7.53 (d, J = 8.4 Hz, 1H), 7.62 (t, J = 8.4 Hz, 1H), 8.16 (s, 1H) 8.59 (d, J = 8.4 Hz, 1H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, rt): δ 100.8, 101.5, 105.6, 122.4, 125.9, 126.3, 126.45, 126.51, 126.7, 127.7, 127.8, 128.0, 128.5, 129.8, 131.1, 131.27, 131.29, 135.9, 137.1, 139.8, 140.0, 147.7, 148.0. HRMS (FAB+): Calcd for $C_{27}H_{18}O_2$: 374.1307. Found: 374.1318 $[M]^+$.

3-Ethoxycarbonyl-9,10-diphenylphenanthrene (3k): The reaction of **5a**, **6b**, and **2a** provided the title compound as white solid (84.0 mg, 0.209 mmol, 83%). ^1H NMR (400 MHz, $CDCl_3$, rt): δ 1.49 (t, J = 7.2 Hz, 3H), 4.50 (q, J = 7.2 Hz, 2H), 7.13–7.17 (m, 4H), 7.19–7.28 (m, 6H), 7.51–7.62 (m, 3H), 7.71–7.75 (m, 1H), 8.08 (dd, J = 8.4, 1.6 Hz, 1H), 8.92 (d, J = 8.4 Hz, 1H), 9.55 (d, J = 1.6 Hz, 1H). Compound **3k** was consistent with the literature data.[9g]

3-Chloro-9,10-diphenylphenanthrene (3l): The reaction of **5a**, **6c**, and **2a** provided the title compound as white solid (75.2 mg, 0.206 mmol, 82%). M.p. 186–187 ºC. IR (KBr): 3059 (w), 1485 (m) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, rt): δ 7.13–7.16 (m, 4H), 7.19–7.28 (m, 6H), 7.42–7.59 (m, 4H), 7.67–7.71 (m, 1H), 8.72 (d, J = 8.0 Hz, 1H), 8.77 (d, J = 2.0 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, rt): δ 122.3, 122.7, 126.76, 126.820 (2C), 127.2, 127.4, 127.79, 127.84, 128.1, 129.1, 129.6, 130.4, 131.065, 131.072, 131.3, 132.4, 132.7, 136.9, 137.6, 139.2, 139.3. Calcd for $C_{26}H_{17}Cl$: C, 85.59; H, 4.70%. Found: C, 85.56; H, 4.35%.

9,10-Diphenyl-3-(trifluoromethyl)phenanthrene (3m): The reaction of **5a**, **6d**, and **2a** provided the title compound as white solid (59.8 mg, 0.150 mmol, 60%). M.p. 165–166 ºC. IR (KBr): 3073 (w), 1489 (m) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, rt): δ 7.13–7.17 (m, 4H), 7.20–7.28 (m, 6H), 7.53–7.62 (m, 2H), 7.67 (s, 2H), 7.71–7.76 (m, 1H), 8.83 (d, J = 8.4 Hz, 1H), 9.07 (s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz,

$CDCl_3$, rt): δ 120.1 (q, $^3J_{C–F}$ = 4.3 Hz), 122.6 (q, $^3J_{C–F}$ = 3.4 Hz), 122.7, 124.8 (q, $^1J_{C–F}$ = 270.7 Hz), 126.9, 127.0, 127.2, 127.6, 127.85, 127.94, 128.2 (q, $^2J_{C–F}$ = 32.0 Hz), 128.3, 128.8, 129.7, 129.9, 130.9, 131.1, 132.3, 133.9 (q, $^4J_{C–F}$ = 1.2 Hz), 136.8, 139.0, 139.1, 139.6; $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$, rt): δ –62.0. Calcd for $C_{27}H_{17}F_3$: C, 81.39; H, 4.30%. Found: C, 81.49; H, 3.97%.

3-Methoxy-9,10-diphenylphenanthrene (3n): The reaction of **5a**, **6e**, and **2a** provided the title compound as white solid (35.5 mg, 0.0985 mmol, 39%). ^1H NMR (300 MHz, $CDCl_3$, rt): δ 4.05 (s, 3H), 7.11–7.27 (m, 11H), 7.46–7.57 (m, 3H), 7.62–7.67 (m, 1H), 8.18 (d, J = 2.4 Hz, 1H), 8.73 (d, J = 8.4 Hz, 1H). Compound **3n** was consistent with the literature data.[8c]

5,6-Diphenyltetraphene (3o): The reaction of **5a**, **6f**, and **2a** provided the title compound as white solid (64.3 mg, 0.169 mmol, 68%). ^1H NMR (400 MHz, $CDCl_3$, rt): δ 7.18–7.32 (m, 10H), 7.45–7.57 (m, 4H), 7.68–7.72 (m, 1H), 7.84 (d, J = 8.0 Hz, 1H), 8.02 (s, 1H), 8.15 (d, J = 8.0 Hz, 1H), 8.97 (d, J = 8.0 Hz, 1H), 9.30 (s, 1H). Compound **3o** was consistent with the literature data.[45]

3-Ethoxycarbonyl-9,10-di(4-methylphenyl)phenanthrene (3p): The reaction of **5b**, **6b**, and **2a** provided the title compound as white solid (80.5 mg, 0.187 mmol, 75%). M.p. 206–207 ºC. IR (KBr): 2984 (w), 1709 (s) cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$, rt): δ 1.49 (t, J = 7.8 Hz, 3H), 2.34 (s, 6H), 4.50 (q, J = 7.8 Hz, 2H), 7.02–7.08 (m, 8H), 7.50–7.53 (m, 1H), 7.58–7.61 (m, 2H), 7.69–7.72 (m, 1H), 8.07 (dd, J = 9.0, 1.2 Hz, 1H), 8.91 (d, J = 9.0 Hz, 1H), 9.53 (d, J = 1.2 Hz, 1H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, rt): δ 14.6, 21.405 (2C), 61.3, 122.8, 125.0, 126.5, 126.9, 127.1, 127.9, 128.1, 128.2, 128.5, 128.6, 129.6, 130.3, 130.8, 130.9, 132.5, 135.2, 136.203 (2C), 136.26, 136.35, 137.0, 139.8, 167.1. HRMS (FAB+): Calcd for $C_{31}H_{26}O_2$: 430.1933 Found: 430.1957 $[M]^+$.

3-Ethoxycarbonyl-9,10-di(4-methoxyphenyl)phenanthrene (3q): The reaction of **5c**, **6b**, and **2a** provided the title compound as white solid (71.5 mg, 0.155 mmol, 62%). M.p. 220–221 ºC. IR (KBr): 1717 (s), 1246 (s) cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$, rt): δ 1.48 (t, J = 7.2 Hz, 3H), 3.81 (s, 6H), 4.49 (q, J = 7.2 Hz, 2H), 6.81 (d, J = 6.6 Hz, 4H), 7.04–7.06 (m, 4H), 7.52 (t, J = 8.4 Hz, 1H), 7.61–7.64 (m, 2H), 7.71 (t, J = 8.4 Hz, 1H), 8.07 (d, J = 8.4 Hz, 1H), 8.90 (d, J = 8.4 Hz, 1H), 9.53 (s, 1H); $^{13}C\{^1H\}$

NMR (150 MHz, $CDCl_3$, rt): δ 14.6, 55.3 (2C), 61.3, 113.3, 113.4, 122.9, 125.0, 126.5, 127.0, 127.2, 127.9, 128.1, 128.2, 129.6, 130.4, 131.6, 131.7, 132.0, 132.1, 132.6, 135.3, 137.0, 139.7, 158.270 (2C), 167.1. HRMS (FAB+): Calcd for $C_{31}H_{26}O_4$: 462.1831. Found: 462.1812 $[M]^+$.

3-Ethoxycarbonyl-9,10-bis[4-(trifluoromethyl)phenyl]phenanthrene (3r): The reaction of **5d**, **6b**, and **2a** provided the title compound as white solid (72.2 mg, 0.134 mmol, 54%). M.p. 223–224 ºC. IR (KBr): 2988 (m), 1724 (s) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, rt): δ 1.49 (t, J = 7.2 Hz, 3H), 4.51 (q, J = 7.2 Hz, 2H), 7.26–7.29 (m, 4H), 7.45–7.50 (m, 2H), 7.54–7.59 (m, 5H), 7.76–7.80 (m, 1H), 8.12 (dd, J = 8.0, 1.6 Hz, 1H), 8.95 (d, J = 8.0 Hz, 1H), 9.56 (d, J = 1.6 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, rt): δ 14.6, 61.5, 123.1, 124.2 (q, $^1J_{C-F}$ = 270.7 Hz, 2C), 125.09 (q, $^3J_{C-F}$ = 3.8 Hz), 125.14 (q, $^3J_{C-F}$ = 3.6 Hz), 125.2, 127.0, 127.69, 127.72, 127.77, 127.78, 128.7, 129.51 (q, $^2J_{C-F}$ = 32.2 Hz), 129.52 (q, $^2J_{C-F}$ = 32.2 Hz), 129.9, 130.6, 131.2, 131.3, 131.4, 133.9, 135.7, 138.4, 142.6, 142.7, 166.8; $^{19}F\{^1H\}$ NMR (376 MHz, acetone-d_6, rt): δ –62.31, –62.30. Calcd for $C_{31}H_{20}F_6O_2$: C, 69.14; H, 3.74%. Found: C, 69.00; H, 3.70%.

3-Ethoxycarbonyl-9,10-di(1-naphthyl)phenanthrene (3s): The reaction of **5e**, **6b**, and **2a** provided a 4:1 mixture of conformers **3s** as white solid (67.7 mg, 0.135 mmol, 54%). M.p. 274–275 ºC. IR (KBr): 2920 (m), 1715 (s) cm^{-1}. HRMS (FAB+): Calcd for $C_{37}H_{26}O_2$: 502.1933. Found: 502.1930 $[M]^+$.

major product: ^1H NMR (600 MHz, $CDCl_3$, rt): δ 1.471 (t, J = 7.2 Hz, 3H), 4.494 (q, J = 7.2 Hz, 2H), 6.96–7.04 (m, 2H), 7.16–7.20 (m, 2H), 7.25–7.45 (m, 9H), 7.59–7.61 (m, 4H), 7.73–7.76 (m, 1H), 7.98 (dd, J = 8.4, 1.8 Hz, 1H), 9.01 (d, J = 8.4 Hz, 1H), 9.636–9.643 (m, 1H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, rt): δ 167.07, 139.4, 136.5, 136.4, 136.29, 135.3, 133.24, 133.21, 132.7, 132.2, 132.1, 130.49, 129.780 (2C), 129.6, 128.55, 128.48, 128.29, 127.95, 127.89, 127.64, 127.60, 127.473, 127.4, 127.07, 127.0, 126.760, 125.518 (2C), 125.40, 125.38, 125.143, 124.8, 124.7, 122.96, 61.363, 14.599.

minor product: ^1H NMR (600 MHz, $CDCl_3$, rt): δ 1.469 (t, J = 7.2 Hz, 3H), 4.491 (q, J = 7.2 Hz, 2H), 6.96–7.04 (m, 4H), 7.25–7.45 (m, 8H), 7.49 (d, J = 8.4 Hz, 1H), 7.59–7.61 (m, 2H), 7.73–7.76 (m, 1H), 7.78 (d, J = 8.4 Hz, 2H), 7.97 (dd, J = 8.4, 1.8 Hz, 1H), 9.01 (d, J = 8.4 Hz, 1H), 9.636–9.643 (m, 1H);

$^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$, rt): δ 167.05, 139.2, 136.9, 136.7, 136.33, 135.2, 133.18, 133.1, 133.04, 133.01, 132.6, 130.54, 129.8, 129.780 (2C), 128.45, 128.38, 128.26, 127.71, 127.66, 127.473, 127.3, 127.06, 126.83, 126.760, 126.7, 126.6, 126.085 (2C), 125.687 (2C), 125.2, 125.143 (2C), 123.00, 61.363, 14.599.

9-Phenyl-10-[4-(trifluoromethyl)phenyl]phenanthrene (3t): The reaction of **5h**, **6g**, and **2a** provided the title compound as white solid (54.5 mg, 0.137 mmol, 55%). ^{1}H NMR (600 MHz, $CDCl_3$, rt): δ 7.13–7.15 (m, 2H), 7.21–7.30 (m, 5H), 7.44–7.57 (m, 6H), 7.68–7.71 (m, 2H), 8.82–8.84 (m, 2H). Compound **3t** was consistent with the literature data.[8b]

3-Ethoxycarbonyl-10-phenyl-9-[4-(trifluoromethyl)phenyl]phenanthrene (3u) and 3-Ethoxycarbonyl-9-phenyl-10-[4-(trifluoromethyl)phenyl]phenanthrene (3u'): The reaction of **5h**, **6b**, and **2a** provided a 2:1 mixture of isomers **3u** and **3u'** as white solid (72.1 mg, 0.153 mmol, 61%). M.p. 186–187 ºC. IR (KBr): 2986 (w), 1721 (s) cm^{-1}. Calcd for $C_{30}H_{21}F_3O_2$: C, 76.59; H, 4.50%. Found: C, 76.40; H, 4.38%.

3-Ethoxycarbonyl-10-phenyl-9-[4-(trifluoromethyl)phenyl]phenanthrene (3u): ^{1}H NMR (600 MHz, C_6D_6, rt): δ 1.12 (t, J = 7.2 Hz, 3H), 4.26 (q, J = 7.2 Hz, 2H), 6.87 (d, J = 8.4 Hz, 2H), 6.90–6.92 (m, 3H), 6.97–7.00 (m, 2H), 7.22 (d, J = 8.4 Hz, 2H), 7.25–7.29 (m, 1H), 7.34–7.37 (m, 1H), 7.40 (dd, J = 8.4, 1.2 Hz, 1H), 7.73 (d, J = 8.4 Hz, 1H), 8.26 (dd, J = 8.4, 1.2 Hz, 1H), 8.65 (d, J = 8.4 Hz, 1H), 9.85 (d, J = 1.2 Hz, 1H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, rt): δ 14.6, 61.4, 123.1, 124.4 (q, $^{1}J_{C-F}$ = 271.2 Hz), 124.82 (q, $^{3}J_{C-F}$ = 3.8 Hz), 125.0, 126.7, 127.2, 127.4, 127.51, 128.0, 128.1, 128.2, 128.25, 129.1 (q, $^{2}J_{C-F}$ = 32.3 Hz), 129.8, 130.4, 130.9, 131.3, 131.51, 134.6, 137.3, 138.1, 138.6, 143.3 (q, $^{4}J_{C-F}$ = 1.3 Hz), 167.0; $^{19}F\{^{1}H\}$ NMR (376 MHz, acetone-d_6, rt): δ –62.20.

3-Ethoxycarbonyl-9-phenyl-10-[4-(trifluoromethyl)phenyl]phenanthrene (3u'): ^{1}H NMR (600 MHz, C_6D_6, rt): δ 1.13 (t, J = 7.2 Hz, 3H), 4.28 (q, J = 7.2 Hz, 2H), 6.88 (d, J = 8.4 Hz, 2H), 6.90–6.92 (m, 3H), 6.97–7.00 (m, 2H), 7.23 (d, J = 8.4 Hz, 2H), 7.25–7.29 (m, 1H), 7.34–7.37 (m, 1H), 7.47 (d, J = 8.4 Hz, 1H), 7.65 (dd, J = 8.4, 1.2 Hz, 1H), 8.29 (dd, J = 8.4, 1.2 Hz, 1H), 8.64 (d, J = 8.4 Hz, 1H),

9.86 (d, J = 1.2 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, rt): δ 14.6, 61.4, 122.9, 124.4 (q, $^1J_{C-F}$ = 271.2 Hz), 124.84 (q, $^3J_{C-F}$ = 3.8 Hz), 125.2, 126.8, 127.2, 127.47, 127.51, 127.6, 127.7, 128.28, 128.4, 129.1 (q, $^2J_{C-F}$ = 32.3 Hz), 129.7, 130.5, 130.8, 131.55, 131.9, 134.2, 135.5, 138.7, 140.0, 143.2 (q, $^4J_{C-F}$ = 1.3 Hz), 166.9; $^{19}F\{^1H\}$ NMR (376 MHz, acetone-d_6, rt): δ –62.19.

3-Ethoxycarbonyl-10-methyl-9-phenylphenanthrene (3v) and 3-Ethoxycarbonyl-9-phenyl-10-methylphenanthrene (3v'): The reaction of **5i**, **6b**, and **2a** provided a 10:1 mixture of isomers **3v** and **3v'** as white solid (45.6 mg, 0.134 mmol, 54%). M.p. 105–106 ºC. IR (KBr): 2974 (w), 1705 (s) cm^{-1}. Calcd for $C_{24}H_{20}O_2$: C, 84.68; H, 5.92%. Found: C, 84.36; H, 5.77%.

3-Ethoxycarbonyl-10-methyl-9-phenylphenanthrene (3v): ^1H NMR (600 MHz, $CDCl_3$, rt): δ 1.53 (t, J = 7.2 Hz, 3H), 2.47 (s, 3H), 4.53 (q, J = 7.2 Hz, 2H), 7.30–7.32 (m, 2H), 7.40–7.44 (m, 1H), 7.46–7.50 (m, 2H), 7.54 (t, J = 8.4 Hz, 2H), 7.64 (t, J = 8.4 Hz, 1H), 8.18 (d, J = 8.4 Hz, 1H), 8.28 (d, J = 8.4 Hz, 1H), 8.84 (d, J = 8.4 Hz, 1H), 9.51 (s, 1H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, rt): δ 14.622, 17.5, 61.3, 122.7, 125.3, 125.350, 126.3, 126.8, 127.0, 127.388, 127.7, 127.8, 128.6, 129.6, 129.7 (2C), 130.2, 132.6, 134.9, 139.6, 140.380, 167.123.

3-Ethoxycarbonyl-9-phenyl-10-methylphenanthrene (3v'): ^1H NMR (600 MHz, $CDCl_3$, rt): δ 1.48 (t, J = 7.2 Hz, 3H), 2.49 (s, 3H), 4.49 (q, J = 7.2 Hz, 2H), 7.30–7.32 (m, 2H), 7.40–7.44 (m, 1H), 7.54 (t, J = 8.4 Hz, 2H), 7.71–7.77 (m, 2H), 8.03–8.05 (m, 1H), 8.18 (d, J = 8.4 Hz, 1H), 8.89 (d, J = 8.4 Hz, 1H), 9.48 (s, 1H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, rt): δ 14.622, 17.7, 61.2, 123.2, 124.9, 125.350, 126.4, 126.9, 127.3, 127.388, 127.5, 127.6, 128.7, 128.9, 130.4, 132.1, 132.9, 135.2, 136.9, 140.3, 140.380, 167.123.

3-Ethoxycarbonyl-6,7-dimethoxy-9,10-diphenylphenanthrene (3w): The reaction of **5a**, **6b**, and **2b** provided the title compound as white solid (83.3 mg, 0.180 mmol, 72%). ^1H NMR (400 MHz, $CDCl_3$, rt): δ 1.47 (t, J = 7.2 Hz, 3H), 3.72 (s, 3H), 4.20 (s, 3H), 4.49 (q, J = 7.2 Hz, 2H), 6.93 (s, 1H), 7.13–7.28 (m, 10H), 7.59 (d, J = 8.8 Hz, 1H), 8.01 (dd, J = 8.8, 1.6 Hz, 1H), 8.21 (s, 1H), 9.38 (d, J = 1.6 Hz, 1H). Compound **3w** was consistent with the literature data.[9g]

3-Ethoxycarbonyl-5,6-diphenyl-1,3-phenanthro[2,3-*d*]dioxole (3x): The reaction of **5a**, **6b**, and **2c** provided the title compound as white solid (60.3 mg, 0.135 mmol, 54%). M.p. 237–238 ºC. IR (KBr): 2914 (w), 1711 (s) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, rt): δ 1.48 (t, J = 7.2 Hz, 3H), 4.49 (q, J = 7.2 Hz, 2H), 6.09 (s, 2H), 6.91 (s, 1H), 7.11–7.13 (m, 4H), 7.17–7.26 (m, 6H), 7.56 (d, J = 8.8 Hz, 1H), 8.01 (dd, J = 8.8, 1.6 Hz, 1H), 8.25 (s, 1H), 9.32 (s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, rt): δ 14.6, 61.3, 101.1, 101.7, 105.7, 125.0, 125.6, 126.7, 126.9, 127.0, 127.7, 127.8, 127.9, 128.1, 128.7, 129.2, 130.8, 131.2, 134.0, 135.6, 139.3, 139.4, 139.6, 148.1, 148.4, 167.1. HRMS (FAB+): Calcd for $C_{30}H_{22}O_4$: 446.1518. Found: 446.1500 $[M]^+$.

3-Methoxy-9,10-diphenylphenanthrene (3n) and 2-Methoxy-9,10-diphenylphenanthrene (3n'): The reaction of **5a**, **6g**, and **2d** provided a 5:1 mixture of isomers **3n** and **3n'** as white solid (12.1 mg, 0.0336 mmol, 34%). The reaction of **1a** with **2d** provided a 5:1 mixture of isomers **3n** and **3n'** as white solid (76.6 mg, 0.213 mmol, 85%). The reaction of **7** with **2d** provided a 3:1 mixture of isomers **3n** and **3n'** as white solid (65.9 mg, 0.183 mmol, 73%).

3-Methoxy-9,10-diphenylphenanthrene (3n): ^1H NMR (300 MHz, $CDCl_3$, rt): δ 4.05 (s, 3H), 7.11–7.27 (m, 11H), 7.42–7.57 (m, 3H), 7.62–7.67 (m, 1H), 8.18 (d, J = 2.4 Hz, 1H), 8.73 (d, J = 7.8 Hz, 1H). Compound **3n** was consistent with the literature data.[8c]

2-Methoxy-9,10-diphenylphenanthrene (3n'): ^1H NMR (300 MHz, $CDCl_3$, rt): δ 3.72 (s, 3H), 6.94 (d, J = 2.7 Hz, 1H), 7.11–7.27 (m, 10H), 7.29–7.32 (m, 1H), 7.42–7.57 (m, 2H), 7.62–7.67 (m, 1H), 8.69–8.74 (m, 2H). Compound **3n'** was consistent with the literature data.[7d]

Preparation of (*E*/*Z*)-1-(2-Bromophenyl)-1,2-diphenylethene ((*E*/*Z*)-7)[46]: Under an argon atmosphere, benzyltriphenylphosphonium bromide (2.69 g, 6.2 mmol) and potassium *tert*-butoxide (696 mg, 6.2 mmol) were placed in 50-mL Schlenk tube. A solution of 2-bromobenzophenone (261 mg, 1.0 mmol) in toluene (5 mL) was then added. The reaction mixture was vigorously stirred at reflux for 70 h. The mixture was filtrated through a pad of Celite. The pad was washed with ethyl acetate (20 mL × 3). The reaction mixture was poured into water (12 mL). The product was extracted with ethyl acetate (40

mL × 3). The combined organic layers were dried over anhydrous sodium sulfate. After concentration in vacuo, purification by silica gel column chromatography (hexane/ethyl acetate = 40:1) afforded a 1:1 mixture of **(*E*)-7** and **(*Z*)-7** as a colorless liquid (183 mg, 0.546 mmol, 55%).

IR (neat) 3078 (w), 3022 (m), 1599 (w), 1445 (m) cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$, rt): δ 6.69 (s, 1H), 7.01 (d, J = 8.4 Hz 1H), 7.02 (s, 1H), 7.13–7.25 (m, 17H), 7.29–7.36 (m, 8H), 7.61 (d, J = 7.8 Hz, 1H), 7.68 (d, J = 8.4 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, rt): δ 123.6, 124.6, 126.8, 127.2, 127.3, 127.5, 127.7, 128.0, 128.2, 128.27, 128.29, 128.5, 128.9, 129.2 (2C), 129.3, 129.4, 129.6, 130.2, 136.96, 137.00, 139.5, 141.1, 141.2, 141.4, 141.9, 144.9, 131.77, 131.78, 132.2, 133.4, 133.5. Calcd for $C_{20}H_{15}Br$: C, 71.65; H, 4.51%. Found: C, 72.00; H, 4.36%.

Stoichiometric Reaction of 1a with $Pd(PPh_3)_4$: Under an argon atmosphere, 1-bromo-1,2,2-triphenylethene (**1a**, 335 mg, 1.0 mmol) and tetrakis(triphenylphosphine)palladium (1.16 mg, 1.0 mmol) were placed in a 50-mL Schlenk tube. Toluene (5 mL) was then added and the reaction mixture was vigorously stirred at 110 ºC for 4 h. After the mixture was cooled to room temperature, the resulted precipitation was collected by filtration with hexane (20 mL × 3). Purification by silica gel column chromatography (hexane/ethyl acetate = 40:1) and recrystallization (ethyl acetate) afforded a 5:1 mixture of palladium complexes as yellow solid (220 mg, 0.228 mmol, 23%). $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6, rt): δ 19.6, 20.5.

Preparation of (*E*)-2-Bromo-2'-(1,2-diphenylethenyl)biphenyl (8)[8c]: Under an argon atmosphere, potassium carbonate (1.24 g, 9.0 mmol), tetrakis(triphenylphosphine)palladium (173 mg, 0.15 mmol) were placed in a 20-mL Schlenk tube. THF (6.0 mL), 2,2'-dibromobiphenyl (936 mg, 3.0 mmol), (*Z*)-2-(1,2-diphenylethenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.10 g, 3.6 mmol), and water (1.35 mL) were added. The resulting mixture was stirred at room temperature for 5 min, then at 60 ºC for 24 h. The mixture was then cooled to room temperature, diluted with dichloromethane (60 mL), and filtered through a pad of Celite. The pad was washed with dichloromethane (20 mL × 3). The filtrate was concentrated with a rotary evaporator. The residue was purified by silica gel column purification (hexane/ethyl acetate = 80:1) afforded a 1.7:1 mixture of the desired compound **8** (0.435 mmol, 15%)

and the inseparable (*E*)-2-(1,2-diphenylethenyl)biphenyl (0.256 mmol, 9%) as a colorless liquid (264 mg). IR (KBr) 3055 (m), 1439 (m), 756 (m) cm^{-1}. HRMS (FAB+): Calcd for $C_{26}H_{19}Br$: 410.0670. Found: 410.0659 $[M]^+$, Calcd for $C_{26}H_{20}$: 332.1565. Found: 332.1584 $[M]^+$.

(*E*)-2-Bromo-2'-(1,2-diphenylethenyl)biphenyl (8): ^1H NMR (600 MHz, $CDCl_3$, rt): δ 6.71 (d, J = 1.8 Hz, 1H), 6.73–6.75 (m, 2H), 6.94–7.04 (m, 8H), 7.08–7.13 (m, 3H), 7.20–7.23 (m, 1H), 7.35–7.41 (m, 2H), 7.43–7.46 (m, 1H), 7.51–7.52 (m, 1H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, rt): δ 123.7, 126.57, 126.64, 126.78, 127.3, 127.80, 127.96, 127.97, 128.2, 129.4, 129.7, 130.48, 130.7, 131.3, 131.6, 132.3, 137.5, 140.0, 140.45, 142.3, 142.7, 144.0.

(*E*)-2-(1,2-diphenylethenyl)biphenyl: ^1H NMR (600 MHz, $CDCl_3$, rt): δ 6.65 (d, J = 1.2 Hz, 1H), 6.81–6.82 (m, 2H), 6.94–7.13 (m, 9H), 7.15–7.17 (m, 2H), 7.20–7.23 (m, 2H), 7.29–7.30 (m, 1H), 7.35–7.41 (m, 2H), 7.43–7.46 (m, 1H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, rt): δ 126.5, 126.66, 126.76, 127.2, 127.657 (2C), 127.77, 128.02, 129.28, 129.30, 130.1, 130.53, 130.8, 131.2, 137.7, 140.37, 141.7, 142.0, 142.9, 143.7.

2-Methyldibenzo[*g*,*p*]chrysene (10): The title compound was obtained as white solid (16.3 mg, 0.0476 mmol, 50%). ^1H NMR (400 MHz, $CDCl_3$, rt): δ 2.66 (s, 3H), 7.47 (d, J = 8.4 Hz, 1H), 7.60–7.70 (m, 6H), 8.50 (s, 1H), 8.59 (d, J = 8.4 Hz, 1H), 8.68–8.72 (m, 6H).

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Notes. The authors declare no competing financial interest.

Acknowledgements

This work was partly supported by JST ACT-C Grant Number JPMJCR12YW, Japan, as well as a Grant-in-Aid for Scientific Research (KAKENHI) (No. 16K17901) from JSPS. The authors gratefully thank Ms. Megumi Kosaka and Mr. Motonari Kobayashi (Department of Instrumental Analysis, Advanced Science Research Center, Okayama University) for performing elemental analyses, and the SC-NMR Laboratory (Okayama University) for the NMR spectral measurements.

Associated Content

Supporting Information Available. More detailed results of palladium-catalyzed reactions and ^{1}H, $^{13}C\{^{1}H\}$, and $^{19}F\{^{1}H\}$ NMR spectra for products. This material is available free of charge via the Internet at http://pubs.acs.org.

Dedication

This work is dedicated to Professor Emeritus Koichiro Oshima on the occasion of his 70th birthday.

References and Footnotes

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