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Synthesis of Multisubstituted Triphenylenes and Phenanthrenes by Cascade Reaction of *o*-Iodobiphenyls or (*Z*)-*β*-Halostyrenes with *o*-Bromobenzyl Alcohols through Two Sequential C–C Bond Formations Catalyzed by a Palladium Complex

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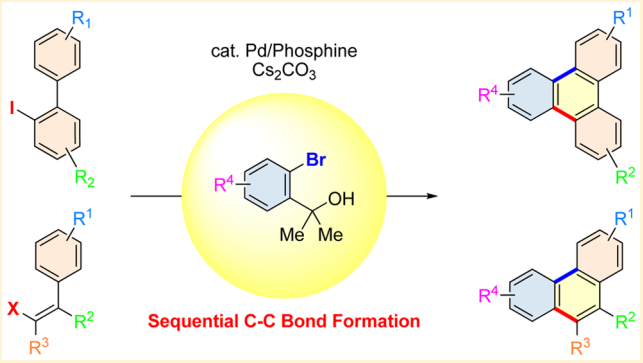
Supporting Information

ABSTRACT: *o*-Bromobenzyl alcohol has been developed as a novel annulating reagent, bearing both nucleophilic and electrophilic substituents, for the facile synthesis of polycyclic aromatic hydrocarbons. A palladium/electron-deficient phosphine catalyst efficiently coupled *o*-iodobiphenyls or (*Z*)-*β*-halostyrenes with *o*-bromobenzyl alcohols to afford triphenylenes and phenanthrenes, respectively. The present cascade reaction proceeded through deacetonative cross-coupling and sequential intramolecular cyclization. An array of experimental data suggest that the reaction mechanism involves the equilibrium of 1,4-palladium migration.



INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) have characteristic optical and electrochemical properties because of their extended *π*-conjugated systems, which are some of the most reliable molecular features for controlling several key behaviors of organic materials.[1] Among them, acene-type PAHs, in which aromatic rings are arranged linearly, are widely regarded as promising materials (Figure 1, left).[2] However, the problem remains that acene-type molecules are unstable when exposed to air and light, which gives them a short lifespan as organic functional materials.[3] In sharp contrast, phenacene-type PAHs with aromatic rings arranged in an armchair manner have attracted much interest as the next generation of practical organic materials because of their stability (Figure 1, right).[4,5]

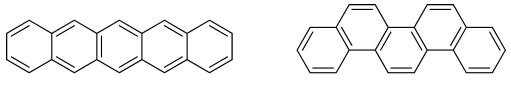


Figure 1. Acene- and phenacene-type molecules.

Because a common route to highly substituted phenacene-type PAHs has yet to be established, developing synthetic methods for phenacenes is desirable from the viewpoint of fundamental studies on functional organic materials. Until recently, although the conventional oxidative cyclization of *o*-terphenyls or stilbenes has been applied to the construction of triphenylene and phenanthrene skeletons, the substrate scope has been quite limited due to the harsh reaction conditions.[6] Moreover, the preparation of starting materials often requires multistep syntheses, leading to low overall yields of the target molecules. Although several synthetic methods have been reported for triphenylenes[7,8] and phenanthrenes[9,10] in the past two decades, a general and convenient synthesis has been continuously sought to facilitate access to these compounds for use in materials science. Among these efforts, the synthetic method using *in situ* generated arynes developed by Larock and co-workers represents a reliable strategy for the construction of PAHs.[8b,e] The palladium-catalyzed annulation of *o*-iodobiphenyls with arynes proceeds under mild conditions, affording various triphenylene derivatives. Moreover, (*Z*)-*β*-iodostyrenes undergo annulation with arynes to yield the corresponding phenanthrenes in good yields. However, preparation of the aryne precursors, *o*-trialkylsilylaryl triflates, requires bothersome treatment: *O*-silylation of *o*-bromophenols, metal–halogen exchange, *O*- to *C*- silyl migration, and entrapment of the phenoxide with triflic anhydride.[11] Furthermore, the regioselectivity of the reaction with substituted arynes is totally uncontrollable.

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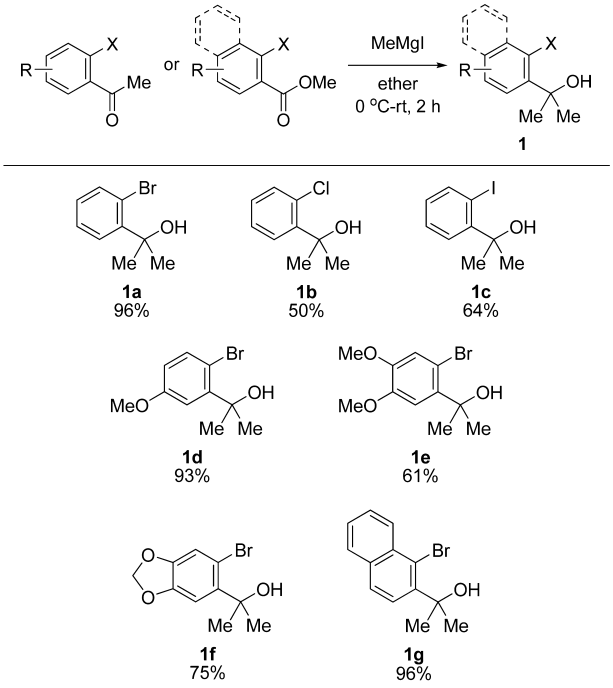
We report here the development of *o*-bromobenzyl alcohols as novel annulating reagents for the synthesis of triphenylenes and phenanthrenes.[12] We show that the palladium/electron-deficient phosphine-catalyzed cascade reaction of *o*-iodobiphenyls or (*Z*)-*β*-halostyrenes with *o*-bromobenzyl alcohols provides multisubstituted triphenylenes and phenanthrenes, respectively. The present reaction involves deacetonative cross-coupling and subsequent intramolecular cyclization, which constructs two C−C bonds sequentially.

RESULTS AND DISCUSSION

Preparation of *o*-Halobenzyl Alcohols. We first designed *o*-halobenzyl alcohols as novel annulating reagents that have both nucleophilic and electrophilic moieties.[13] In marked contrast to conventional organometallic annulating reagents, *o*-halobenzyl alcohols are quite stable on the benchtop and can be stored for at least several months. Furthermore, the present annulating reagents can be prepared by a single-step synthesis from commercially available acetophenone derivatives or benzoic esters, as treatment of *o*-haloacetophenone derivatives or methyl *o*-halobenzoates with methylmagnesium iodide gives the target tertiary alcohols **1** in good yields. As shown in Table 1, a series of *o*-halobenzyl alcohols **1a**−**1g** were

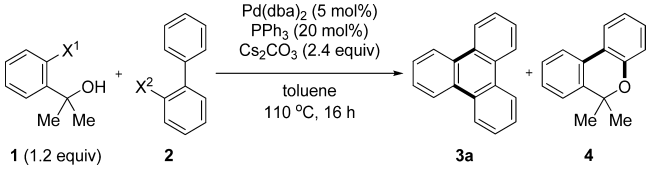
Table 1. Preparation of *o*-Halobenzyl Alcohols 1



uneventfully obtained by Grignard reaction with methylmagnesium iodide. Although any alkyl groups can be installed on the annulating reagents **1**, a methyl group may be ideal because the acetone formed can easily be removed from the reaction mixture.

Synthesis of Triphenylenes. We initiated a program to develop a synthetic method for triphenylene (**3a**) by the palladium-catalyzed annulation of *o*-halobiphenyls **2** with *o*-halobenzyl alcohols **1**. Initial screening of the leaving groups of **1** and **2** was conducted as shown in Table 2. In a typical reaction, **1** and **2** (1.2 equiv) were treated with $Pd(dba)_2$ (5 mol %), PPh_3 (20 mol %), and Cs_2CO_3 (2.4 equiv) in toluene

Table 2. Palladium-Catalyzed Annulation of *o*-Halobiphenyls 2 with *o*-Halobenzyl Alcohols 1



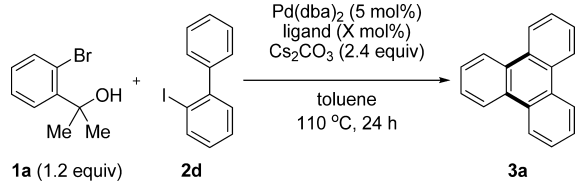
entry	X^1	X^2	yield (%)[a] 3a	4
1	Br (**1a**)	Br (**2a**)	15	<1
2	Cl (**1b**)	Br (**2a**)	<1	0
3	I (**1c**)	Br (**2a**)	2	33
4	Br (**1a**)	OTf (**2b**)	0	<1
5	Br (**1a**)	Cl (**2c**)	0	0
6	Br (**1a**)	I (**2d**)	26	0

[a]Determined by ^{1}H NMR analysis of the crude mixture, using bromoform as an internal standard.

at reflux. The combination of *o*-bromobenzyl alcohol **1a** and *o*-bromobiphenyl (**2a**) gave the target product **3a** in 15% yield (entry 1). Benzochromene **4** was found to be the major byproduct of this reaction, generated by the homocoupling of **1**.[13a,c] When *o*-chlorobenzyl alcohol **1b** was reacted with **2a**, only a trace amount of **3a** was obtained and most of the unreacted **1b** and **2a** were recovered (entry 2). The use of *o*-iodobenzyl alcohol **1c** gave a complex mixture including 2% of **3a** and 33% of **4** (entry 3). The reaction of *o*-biphenylyl triflate (**2b**) or the corresponding chloride **2c** with **1a** did not proceed, probably due to the low reactivity of **2b** and **2c** (entries 4 and 5). Finally, the reaction of *o*-iodobiphenyl (**2d**) with **1a** was found to be optimal, yielding **3a** in 26% yield (entry 6). As described later, the reaction may proceed by utilizing the different reaction rates for oxidative addition of iodides and bromides.

It is additionally notable that the choice of the phosphine ligand has a significant effect on the efficiency of the reaction (Table 3). In the absence of a phosphine ligand, almost no reaction proceeded (entry 2). The yield of **3a** slightly increased with the electron-deficient phosphine (entry 3), while the

Table 3. Ligand Screening



entry	ligand	X (mol %)	yield (%)[a]
1	PPh_3	20	44
2	none		<1
3	$P[3,5\text{-}(CF_3)_2C_6H_3]_3$	20	47
4	$P(4\text{-}MeOC_6H_4)_3$	20	35
5	$P(OPh)_3$	20	5
6	P^nBu_3	20	0
7	DPPE	10	<1
8	DPPP	10	0
9	DPPF	10	0

[a]Determined by ^{1}H NMR analysis of the crude mixture, using bromoform as an internal standard.

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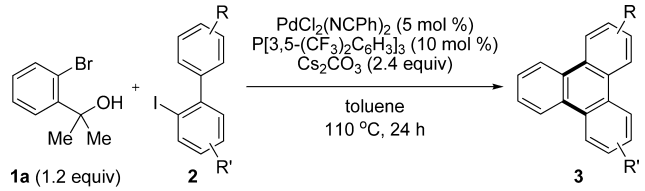
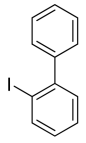
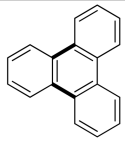
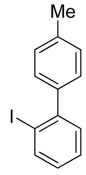
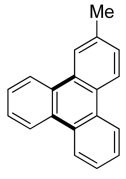
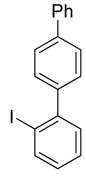
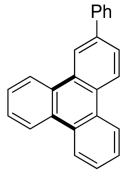
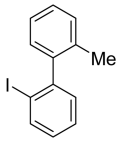
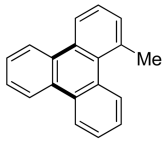
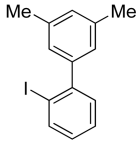
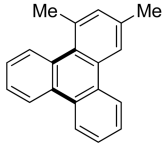
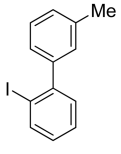
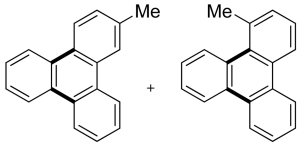
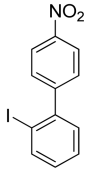
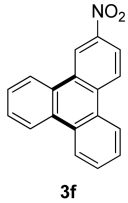
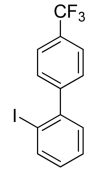
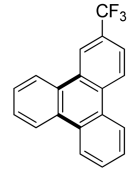
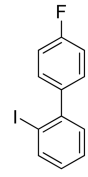
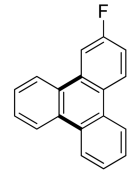
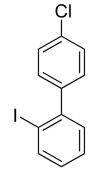
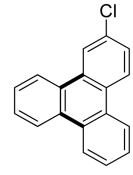
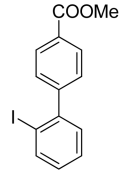
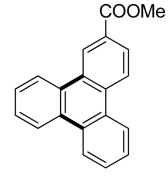
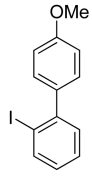
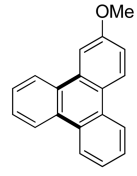
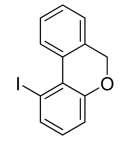
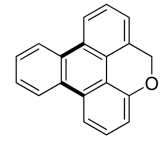
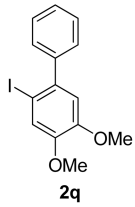
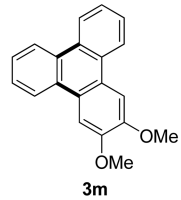
Table 4. Reactions of *o*-Bromobenzyl Alcohol 1a with *o*-Iodobiphenyls 2



entry	2	3	yield (%)[a]
1	 **2d**	 **3a**	81
2	 **2e**	 **3b**	65
3	 **2f**	 **3c**	47
4	 **2g**	 **3d**	38
5	 **2h**	 **3e**	28
6	 **2i**	 **3b** + **3d** **3b**:**3d** = 4:1[b]	62[c]
7	 **2j**	 **3f**	92
8	 **2k**	 **3g**	92
9	 **2l**	 **3h**	81
10	 **2m**	 **3i**	50
11	 **2n**	 **3j**	72
12	 **2o**	 **3k**	50
13	 **2p**	 **3l**	23
14	 **2q**	 **3m**	61

[a]Isolated yields based on **2** after silica gel column chromatography. [b]Determined by ^{1}H NMR analysis. [c]Combined yield of two regioisomers.

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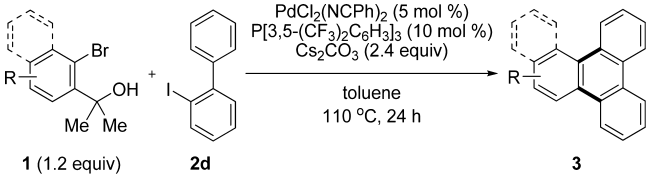
electron-rich phosphine dropped the yield (entry 4). Strong electron-donating ability of the phosphines would not control the reaction sequence of bromide **1a** and iodide **2d** with palladium. Extensive screening of the ligands including phosphite and trialkylphosphine gave the negative results (entries 5 and 6). Similar poor yields were observed with some bidentate phosphines such as DPPE (1,2-bis(diphenylphosphino)ethane), DPPP (1,3-bis(diphenylphosphino)propane), and DPPF (1,1′-bis(diphenylphosphino)ferrocene) (entries 7−9).

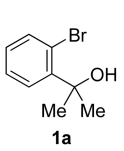
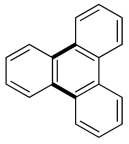
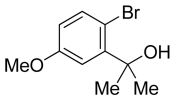
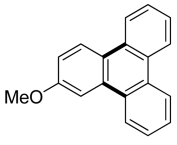
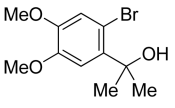
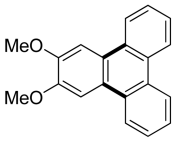
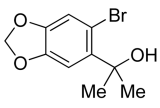
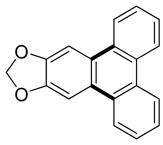
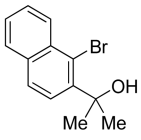
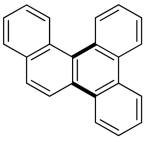
After exploring the effect of various conditions on the reaction of **1a** with **2d**,[14] we found the optimum conditions: $PdCl_2(NCPh)_2$ (5 mol %), $P[3,5\text{-}(CF_3)_2C_6H_3]_3$ (10 mol %), and Cs_2CO_3 (2.4 equiv) in toluene. Under these reaction conditions, **3a** was obtained in 81% yield (Table 4, entry 1). With the optimized conditions in hand, we performed the annulation of various *o*-iodobiphenyls **2** with **1a**. First of all, several substitution patterns of **2** were systematically investigated. In addition to nonsubstituted substrate **2d** (entry 1), not surprisingly, *o*-iodobiphenyls **2e** and **2f** with a methyl or phenyl group at the 4′-position underwent annulation with **1a** to provide the corresponding triphenylenes **3b** and **3c** (entries 2 and 3). However, substituents at the 2′- or 3′-position on **1** slightly suppressed the formation of triphenylenes **3d** and **3e** (entries 4 and 5) by retarding the intramolecular direct arylation step due to steric congestion. Although the reaction of 2-iodo-3′-methylbiphenyl (**2i**) proceeded well, a mixture of regioisomers **3b** and **3d** was formed because of two possible reaction sites (entry 6). Conceivably, the reaction occurred preferentially at the less-hindered C−H bond of **2i** to afford **3b** as the major product. Various functional groups were found to be compatible under the mild reaction conditions, but their electronic effects on **2** affected yields to some extent. For example, the substrates **2j**−**2n** with an electron-withdrawing nitro, trifluoromethyl, fluoro, chloro, or methoxycarbonyl group reacted effectively with **1a** to furnish triphenylenes **3f**−**3j** in moderate to good yields (entries 7−11). In contrast, the reaction of *o*-iodobiphenyl **2o** bearing an electron-donating methoxy group resulted in a slightly decreased yield (entry 12). The effect of a linker that restricted the rotation along the biaryl axis prevented the cyclization to form triphenylene **3l** (entry 13), probably due to the possible formation of a highly strained 7-membered palladacycle intermediate. The substituents at the 4- and 5-positions of **2q** did not interfere with the annulation with **1a** to yield the product **3m** in 61% yield (entry 14).

Various *o*-bromobenzyl alcohols **1** were then subjected to the annulation of **2d** (Table 5). The functional groups on substrate **1** did not impair the efficiency of the reaction, which provided the corresponding triphenylenes **3k**, **3m**, and **3n** in good yields (entries 2−4). The substrate does not have to be benzyl alcohol. Indeed, the naphthalene-containing tertiary alcohol **1g** converted **2d** into benzochrysene **3o** in 31% yield (entry 5). The utility of the present synthetic method was clearly demonstrated by the single-step synthesis of highly fused PAHs.

Scheme 1 shows a plausible reaction mechanism for the palladium-catalyzed annulation of *o*-iodobiphenyl (**2d**) with *o*-bromobenzyl alcohol **1a**, which is in good agreement with present and previous experimental observations. Initially, oxidative addition of **2d** to Pd(0) affords arylpalladium iodide **A** because of the faster oxidative addition of aryl iodide to Pd(0) than the bromide **1a**. The electron-deficient phosphine ligand would help the palladium to distinguish the different

Table 5. Reactions of Various *o*-Bromobenzyl Alcohols 1 with *o*-Iodobiphenyl (2d)



entry	1	3	yield (%)[a]
1	 **1a**	 **3a**	81
2	 **1d**	 **3k**	82
3	 **1e**	 **3m**	63
4	 **1f**	 **3n**	55
5	 **1g**	 **3o**	31

[a]Isolated yields based on **2d** after silica gel column chromatography.

reactivities of **1a** and **2d**. The subsequent ligand exchange between **A** and **1a** in the presence of cesium carbonate yields aryl(alkoxy)palladium intermediate **B**. Deacetonative *β*-carbon elimination[8a,15] generating diarylpalladium species **C**, followed by reductive elimination, gives the *o*-bromoterphenyl intermediate **5a**, regenerating the starting Pd(0) species. The formation of intermediate **5a** was unambiguously confirmed by NMR and GC-MS analyses. The generated **5a** again undergoes oxidative addition to Pd(0). Cyclopalladation of *o*-terphenylpalladium bromide **D** through C−H bond cleavage affords a 7-membered palladacycle intermediate **E**.[16] Final productive reductive elimination provides the desired triphenylenes **3a** along with the regeneration of the starting Pd(0) complex. At the early stage of the reaction, intermediate **5a** was accumulated prior to the formation of the product **3a**, which suggests that intramolecular cyclization could be a rate-determining step. This hypothesis was supported by the fact that the reactions of the sterically congested substrates **2g** and **2h**, or the substrate **2p** via a strained palladacycle intermediate, resulted in low yields (Table 4, entries 3, 5, and 13). It is of note that the same

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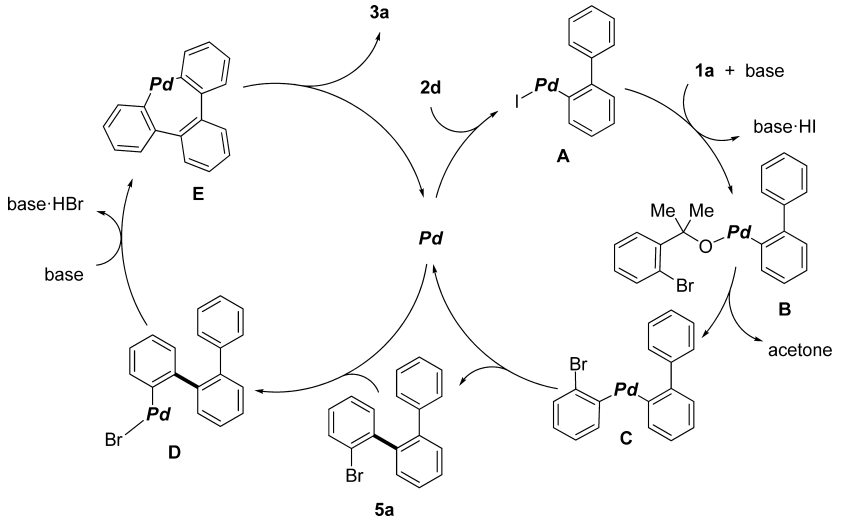
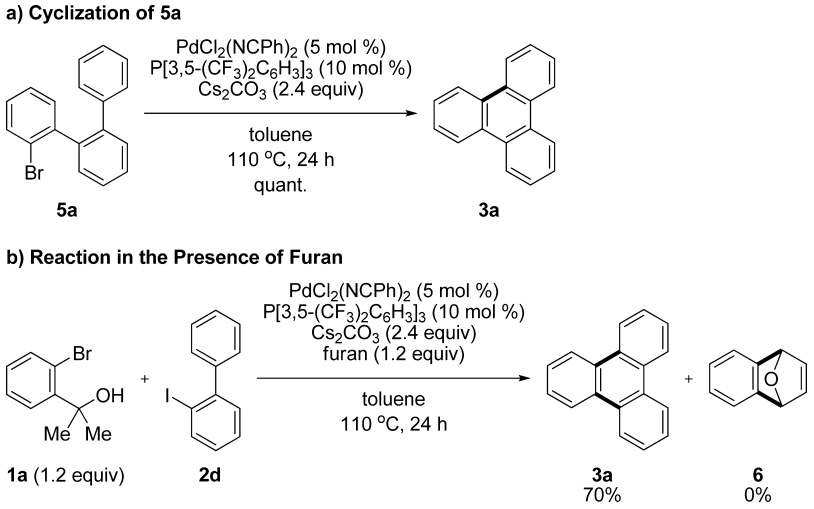
Scheme 1. A Plausible Reaction Mechanism for Triphenylene Synthesis



Scheme 2. Control Experiments



starting Pd(0) complex effectively catalyzes two different reactions, deacetonative coupling and intramolecular cyclization.

The proposed mechanism shown in Scheme 1 was confirmed by the cyclization of *o*-bromoterphenyl **5a** under the identical reaction conditions, which gave the target triphenylene **3a** quantitatively (Scheme 2a). However, the reaction mechanism involving the aryne intermediate generated from **1a** cannot be completely ruled out at this stage. We only know that the reaction of **1a** with **2d** in the presence of furan that would trap the formed aryne with a Diels–Alder reaction did not provide the adduct **6**, but triphenylene **3a** in 70% yield (Scheme 2b).[17]

Although several synthetic methods for triphenylenes have been reported, access to various substituted triphenylenes bearing several different functional groups is still challenging and highly desirable. We could successfully prepare multisubstituted triphenylenes **3** and **3′** by the annulation of substituted *o*-iodobiphenyls **2** with methoxy-bearing *o*-bromobenzyl alcohol **1d** (Table 6). The reactions of the electronically diverse substrates **2j** and **2o** proceeded smoothly to afford a 1:1 mixture of regioisomers **3** and **3′** in 82% and 48% combined yields, respectively (entries 1 and 2). On the other hand, the substrate **2h**, congested at the reaction site, reacted with **1d**, albeit in low yield, predominantly providing triphenylene **3r** (entry 3). However, the selectivity was reversed to give triphenylene **3s′** as the major product when 2-iodo-3,5-dimethoxybiphenyl (**2q**) was employed (entry 4).

A plausible mechanism for the unexpected formation of the **3′** regioisomers is shown in Scheme 3. Triphenylene **3** may be obtained by the reaction of **1d** with the generated arylpalladium iodide **F** via intermediate **5**. Considering the detailed studies by Larock and co-workers, we propose that 1,4-palladium migration from the palladium complex **F** forms arylpalladium iodide **F′** via a 5-membered palladacycle intermediate.[18] Subsequently, the palladium complex **F′** couples with **1d** to yield the intermediate **5′**, from which an intramolecular cyclization proceeds to afford triphenylene **3′**. In the case of substrates **2j** and **2o**, bearing nitro and methoxy groups, a 1:1 mixture of **3** and **3′** regioisomers was obtained probably because of the rapid equilibrium of 1,4-palladium migration, which suggests that the electronic properties of *o*-iodobiphenyls **1** did not influence the regioselectivity of the reaction. Even at 90 °C, the ratio of regioisomers **3p** and **3p′** was not changed, while the product yield was decreased to 8%. This result indicates that 1,4-palladium migration is rather faster than the reaction of **1d** with **F**.

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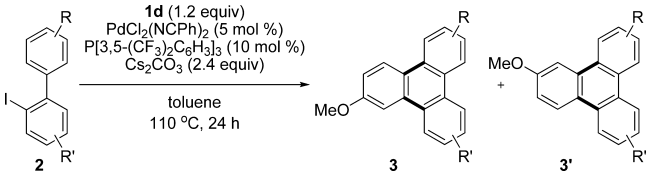
Table 6. Synthesis of Multisubstituted Triphenylenes



entry	2	3 + 3'	3:3'[a]	yield (%)[b]
1	2j	3p + 3p'	1:1	82
2	2o	3q + 3q'	1:1	48
3	2h	3r + 3r'	9:1	28
4	2q	3s + 3s'	1:2	54

[a]Determined by ^{1}H NMR analysis. [b]Isolated combined yields of two regioisomers based on **2** after silica gel column chromatography.

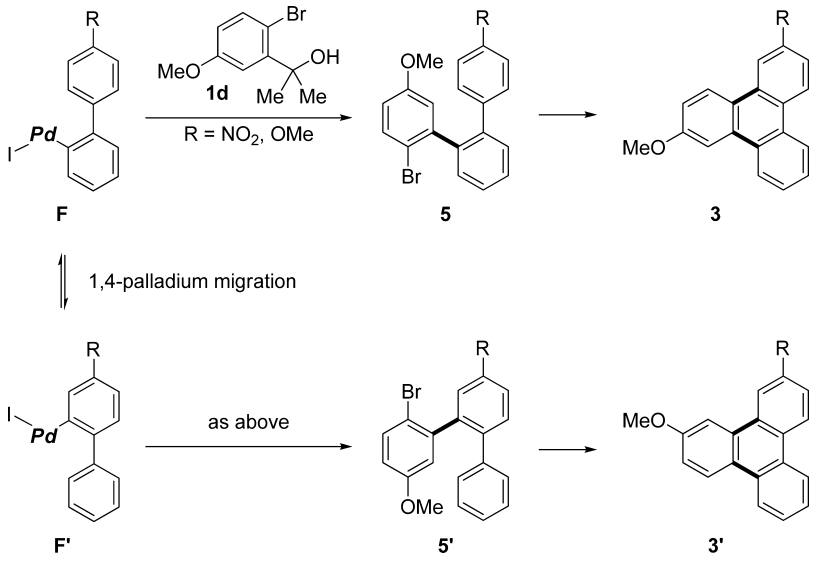
In the reaction of *o*-iodobiphenyl **2h**, the predominant formation of triphenylene **3r** was observed, which can be explained by the steric factor (Scheme 4). During 1,4-palladium migration, the arylpalladium species **G** would be favored. The other intermediate **G′** has steric repulsion between a methyl group and palladium, which would render the intermediate **G′** disfavored. The arylpalladium complex **G** smoothly reacts with *o*-benzyl alcohol **1d** to yield triphenylene **3r** as the main product. The interesting preferential formation of triphenylene **3s′** observed in the reaction of **1d** with **2q** would be also explained by the above-mentioned steric factor in 1,4-palladium migration.

Synthesis of Phenanthrenes. The successful triphenylene synthesis led us to examine palladium-catalyzed annulation of *o*-halostyrenes **7** with *o*-bromobenzyl alcohols **1** to afford the corresponding phenanthrenes. Thus, *o*-bromobenzyl alcohol **1a** was treated with *o*-iodostyrene (**7a**) under the identical conditions required to obtain triphenylene (Scheme 5). Unfortunately, our initial attempts gave none of the desired phenanthrene (**8a**), although the starting material **7a** was completely consumed. We assumed that the reactive terminal alkene would undergo undesired reactions such as oligomerization and polymerization,[19] although no byproducts were identified. In addition, the reaction of *o*-bromostyrene did not afford **8a**. Even with *o*-iodo-*α*-methylstyrene (**7b**) suppressing the interaction between alkene and palladium, only 9% yield of product **8b** was observed by ^{1}H NMR analysis. In spite of further optimization of the catalytic system, a satisfactory yield of **8b** was not realized.[14]

Because of the extra high reactivity and limited availability of *o*-iodostyrenes, we then turned our attention to the annulation of (*Z*)-*β*-iodostyrenes for the facile synthesis of phenanthrenes. To our delight, 1-iodo-1,2,2-triphenylethene (**9a**) smoothly underwent annulation with *o*-bromobenzyl alcohol **1a** under $PdCl_2(NCPh)_2/P(p\text{-}CF_3C_6H_4)_3$ catalysis to form the desired phenanthrene **8c** in 28% NMR yield (Table 7, entry 1). Since the starting iodide **9a** was consumed, the less-reactive alkenyl bromide **9b** was then investigated. The sequential C−C bond formation proceeded well to afford **8c** in 81% yield (entry 2). Finally, the yield was improved to 99% by using 1.4 equiv of **1a** and prolonging the reaction time to 24 h (entries 3 and 4).

With the identified optimal conditions in hand, we aimed at defining the scope of (*Z*)-*β*-halostyrene derivatives **9**. As summarized in Table 8, we were delighted to find that a wide range of substrates having diverse functional groups and various substitution patterns were readily transformed to the

Scheme 3. Aryl-to-Aryl 1,4-Palladium Migration



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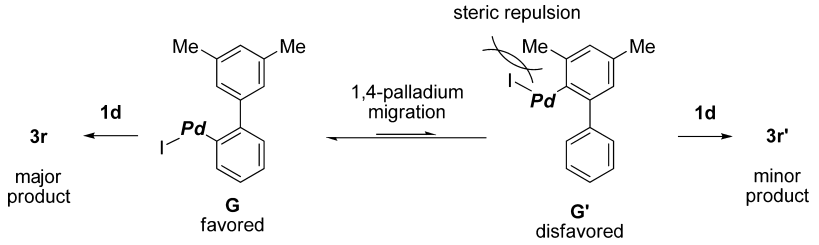
Scheme 4. Preferred Equilibrium in 1,4-Palladium Migration Determined by Steric Factor



Scheme 5. Palladium-Catalyzed Annulation of *o*-Halostyrenes 7 with *o*-Bromobenzyl Alcohol 1a

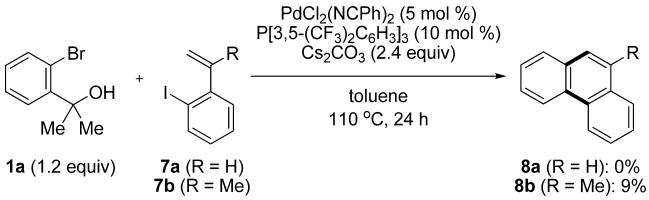
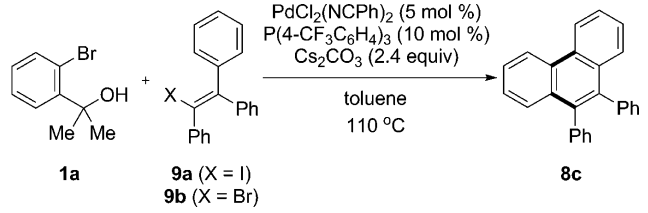


Table 7. Palladium-Catalyzed Annulation of 1-Halo-1,2,2-triphenylethenes 9 with *o*-Bromobenzyl Alcohol 1a[a]



entry	9	1a (equiv)	time (h)	yield (%)[a]
1	**9a**	1.2	12	28
2	**9b**	1.2	12	81
3	**9b**	1.2	24	85
4	**9b**	1.4	24	99 (88)

[a]Yields were determined by the ^{1}H NMR analysis of a crude mixture using dibenzyl ether as an internal standard. An isolated yield based on **9** after silica gel column chromatography is shown in parentheses.

corresponding phenanthrenes. For example, both electron-donating and -withdrawing functional groups were equally tolerated under the reaction conditions, affording the desired products **8c**–**8g** in good yields (entries 1–5). The present synthetic method was successfully applied to the synthesis of highly functionalized phenanthrene **8h**, starting from (*Z*)-*β*-bromostyrene **9g** bearing one methoxy and two fluoro groups (entry 6). Moreover, alkenyl bromides **9h** and **9k** substituted with alkyl groups were also found to be competent coupling partners, providing products **8i** and **8j** in moderate yields (entries 7 and 10). It is of note that the reactions of the corresponding alkenyl iodides **9i** and **9l** gave slightly higher yields of products **8i** and **8j** (entries 8 and 11). Electron-donating alkyl groups on the substrates may retard oxidative addition to palladium. On the other hand, the reaction of the corresponding triflate **9j** afforded no product **8i**, in which a significant amount of **9j** was consumed (entry 9). The relatively less-hindered cationic palladium species generated from **9j** would undergo the polymerization. Substituents R^2 and R^3 on substrate **9** proved to be essential for the efficient synthesis of phenanthrenes,[14] as they can interrupt the undesired interaction with palladium.[19]

As a small variant of this reaction, the effect of substituents on the phenyl ring at the *β*-position to the bromo group in **9** was examined in the reaction with **1a** (Table 9). The methoxy-substituted alkenyl bromide **9m** served as a substrate to produce the expected product **8e** in 70% yield along with phenanthrene **8e′**, which may be formed by annulation on the other side (entry 1). In addition, the reaction of electron-deficient **9n** and **9o** also gave a mixture of isomers **8** and **8′** (entries 2 and 3). These results clearly suggest that alkenylpalladium **H** formed by oxidative addition of **9** would undergo *E*/*Z* isomerization[20] to provide stereoisomer **H′**, from which the reaction with **1a** afforded the minor product **8′** (Scheme 6). The phenanthrenes **8** and **8′** were unambiguously determined by spectroscopic analysis, while the dibenzofulvene derivatives which would be possibly formed by C–H arylation were not detected in each case probably because of highly strained skeletons.[21a–c]

As shown in Table 10, annulation of **9b** with several annulating reagents **1** proceeded smoothly to provide various products **8**. In addition to nonsubstituted *o*-bromobenzyl alcohol **1a** giving rise to **8c**, the annulating reagents **1e**, having two methoxy groups, and **1f**, containing an acetal skeleton, coupled with **9b** to give the corresponding phenanthrenes **8l** and **8m** in good yields, respectively (entries 1–3). Notably, *o*-bromobenzyl alcohol **1d**, bearing one methoxy group, was employed for the annulation with **9b** to afford the expected phenanthrene **8n** in only 14% yield, while the regioisomer **8e′** was mainly formed in a 1:5 ratio (entry 4). Moreover, the reaction with naphthalene-containing tertiary alcohol **1g** did not give benzophenanthrene **8o**, but chrysene derivative **8o′** was obtained in 74% yield as a single product (entry 5).

The unexpected predominant formation of phenanthrene **8e′** can be rationalized as illustrated in Scheme 7. After oxidative addition of alkenyl bromide **9b**, the alkenylpalladium complex **I** reacts with *o*-bromobenzyl alcohol **1d** to afford the expected phenanthrene **8n**. On the other hand, 1,4-palladium migration from **I** forms arylpalladium complex **I′**, which reacts with **1d** to afford **8e′**.[21] During 1,4-palladium migration, thermodynamically more stable **I′** may be preferred.[22,23] The exclusive formation of phenanthrene **8o′** strongly supports the 1,4-palladium migration of alkenylpalladium to arylpalladium.

To gain more insight into the possible equilibrium in 1,4-palladium migration, the reaction of methoxy-substituted *o*-bromobenzyl alcohol **1d** with aryl bromide **7c** was investigated under the identical reaction conditions (Scheme 8). Consequently, phenanthrene **8e′** was obtained (55% yield) as the main product, which is consistent with the annulation of **9b** with **1d**. This observation obviously shows that equilibrium may be rapidly achieved in 1,4-palladium migration. Further modification of the catalyst system to control the *E*/*Z* isomerization and 1,4-palladium migration was essential for a selective synthesis.

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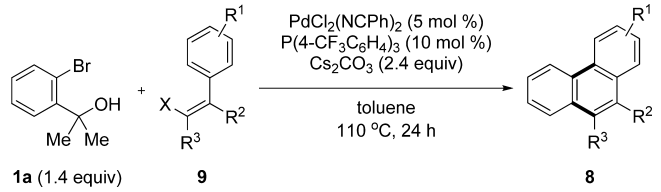
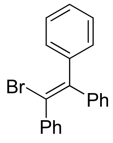
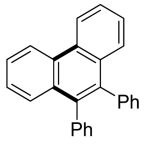
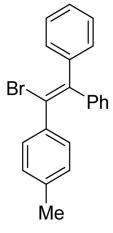
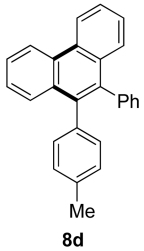
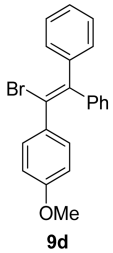
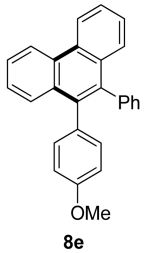
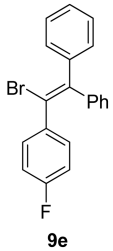
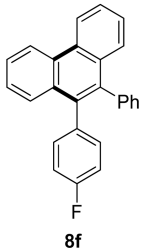
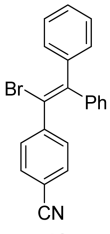
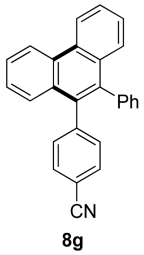
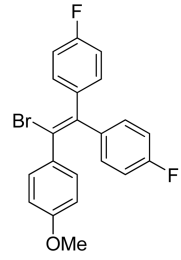
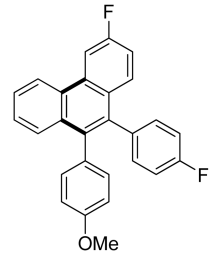
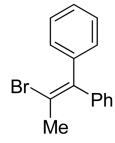
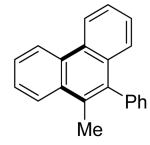
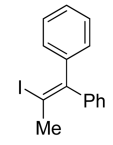
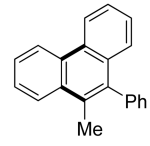
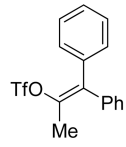
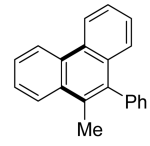
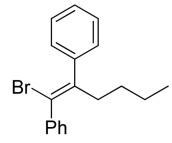
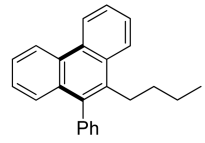
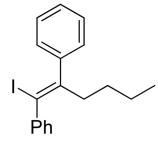
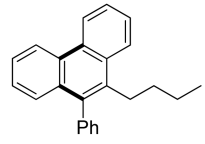
Table 8. Palladium-Catalyzed Annulation of (*Z*)-*β*-Halostyrenes 9 with *o*-Bromobenzyl Alcohol 1a



entry	9	8	yield (%)[a]
1	 **9b**	 **8c**	88
2	 **9c**	 **8d**	100
3	 **9d**	 **8e**	97
4	 **9e**	 **8f**	95
5	 **9f**	 **8g**	68
6	 **9g**	 **8h**	71
7	 **9h**	 **8i**	41
8	 **9i**	 **8i**	69
9	 **9j**	 **8i**	0
10	 **9k**	 **8j**	41
11	 **9l**	 **8j**	59

[a]Isolated yields based on **9** after silica gel column chromatography.

On the basis of the obtained results, we assume that the reaction of **1a** with **9b** proceeds as illustrated in Scheme 9. First, oxidative addition of **9b** to the starting Pd(0) provides the alkenylpalladium species **J**. In general, oxidative addition of alkenyl bromides occurred faster than that of aryl bromides.[10s,24] The following 1,4-palladium migration from **J** occurs smoothly to afford the thermodynamically more stable arylpalladium intermediate **K**. As is the case with triphenylene synthesis (Scheme 1), ligand exchange, *β*-carbon elimination, and reductive elimination proceed sequentially to yield aryl bromide **10** via the intermediates **L** and **M**, along with the regeneration of the Pd(0) complex. Next, the formed aryl bromide **10** again undergoes oxidative addition to Pd(0), affording the arylpalladium complex **N**. Finally, intramolecular migratory insertion of the alkene, followed by base-assisted *trans*-*β*-hydrogen elimination[25] from intermediate **O**, provides the desired phenanthrene **8c** to accomplish the catalytic cycle. The possible intermediate **10** was not detected even in the early

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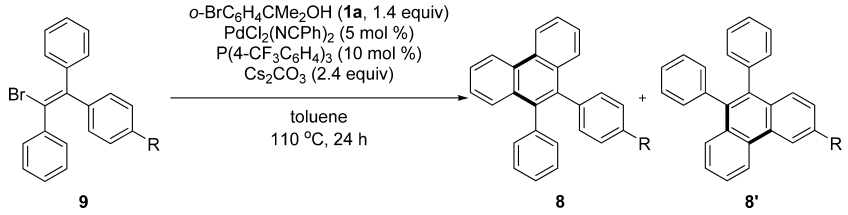
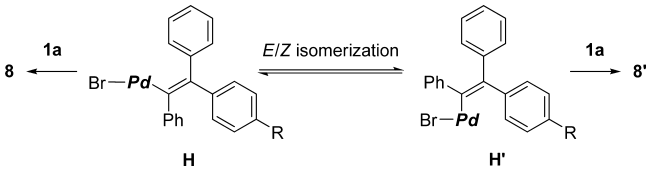
Table 9. Palladium-Catalyzed Annulation of (*Z*)-*β*-Halostyrenes 9m−9o with *o*-Bromobenzyl Alcohol 1a



				yield (%)[a]	
entry	R	9	product	8	8′
1	OMe	9m	8e + 8e′	70[b]	24[b]
2	F	9n	8f + 8f′	63[b]	32[b]
3	CF_3	9o	8k + 8k′	70	13

[a]Isolated yields based on **9** after silica gel column chromatography. [b]Determined by ^{1}H NMR analysis and the combined yields of two isomers.

Scheme 6. *E*/*Z* Isomerization of Alkenylpalladium Species



stage of the reaction, which suggests that the deacetonative coupling of *o*-bromobenzyl alcohols **1** with (*Z*)-*β*-halostyrenes **9** would be the rate-limiting step. This observation is opposite to the triphenylene synthesis, in which the intramolecular cyclization is slower than the deacetonative coupling.

To demonstrate the synthetic potential of the products, oxidative cyclization of **8d** was explored. Treatment of **8d** with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) in the presence of methanesulfonic acid gave the corresponding cyclized product **11** in 50% yield (Scheme 10).[26] The obtained dibenzochrysene derivative **11** is well-known to have attractive fluorescence properties, high quantum yields, small Stokes shifts, and long-lived excited states.[27]

CONCLUSIONS

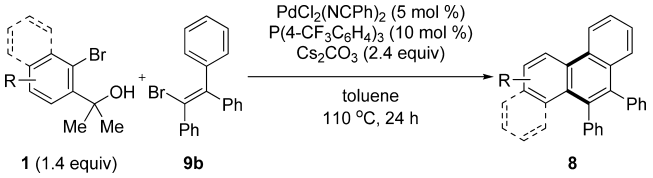
In summary, the facile synthesis of phenacene-type PAHs was achieved by palladium-catalyzed sequential C−C bond formation. We have developed *o*-bromobenzyl alcohol as a new annulating reagent, which facilitates the annulation of *o*-iodobiphenyls and (*Z*)-*β*-halostyrenes to provide triphenylenes and phenanthrenes, respectively. This protocol can allow us to access a variety of highly fused *π*-conjugated molecules bearing an array of functional groups. Mechanistic studies have provided some evidence supporting the equilibrium of 1,4-palladium migration, which explains the formation of regioisomers and the selectivity. Further application of palladium-catalyzed annulation to the synthesis of other phenacene-type molecules and the development of more reactive catalysts are currently underway in our laboratory.

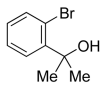
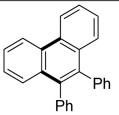
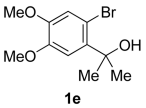
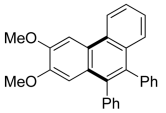
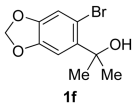
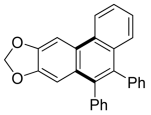
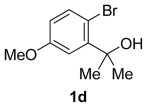
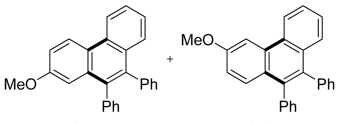
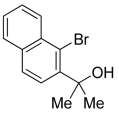
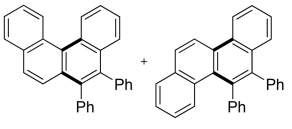
EXPERIMENTAL SECTION

Chemicals. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification.

A Typical Procedure for Preparation of *o*-Halobenzyl Alcohols 1: Synthesis of 2-(*o*-bromophenyl)-2-propanol (1a) (Table 1). Under an argon atmosphere, methylmagnesium iodide (1.0 M ethereal solution, 24 mL, 24 mmol) was placed in a 100 mL reaction flask. Ethyl *o*-bromobenzoate (1.6 mL, 10 mmol) in ether (20 mL) was added dropwise to the Grignard reagent at 0 °C. The mixture was warmed to room temperature. After being stirred for 2 h, saturated ammonium chloride solution (30 mL) was added at 0 °C. The product was extracted with ethyl acetate (20 mL × 3). The organic layers were then washed with brine and dried over anhydrous sodium sulfate. After volatiles were evaporated, silica gel column chromatography (hexane/ethyl acetate = 5:1) yielded **1a** (2.02g, 9.4 mmol, 94% yield).

Table 10. Palladium-Catalyzed Annulation of 1-Bromo-1,2,2-triphenylethene (9b) with *o*-Bromobenzyl Alcohols 1



entry	1	8	yield (%)[a]
1	 1a	 8c	88
2	 1e	 8l	89
3	 1f	 8m	74
4	 1d	 8n:8e′ = 1:5[b]	85[c]
5	 1g	 8o not detected	60

[a]Isolated yields based on **2** after silica gel column chromatography. [b]Determined by ^{1}H NMR analysis. [c]Combined yield of two regioisomers.

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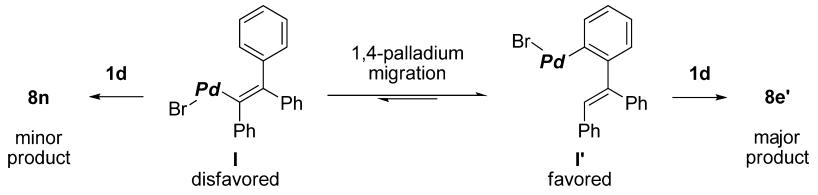
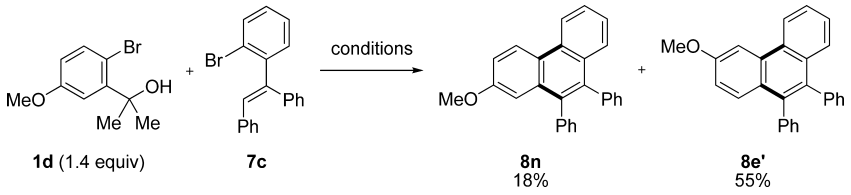
Scheme 7. Alkenyl-to-Aryl 1,4-Palladium Migration

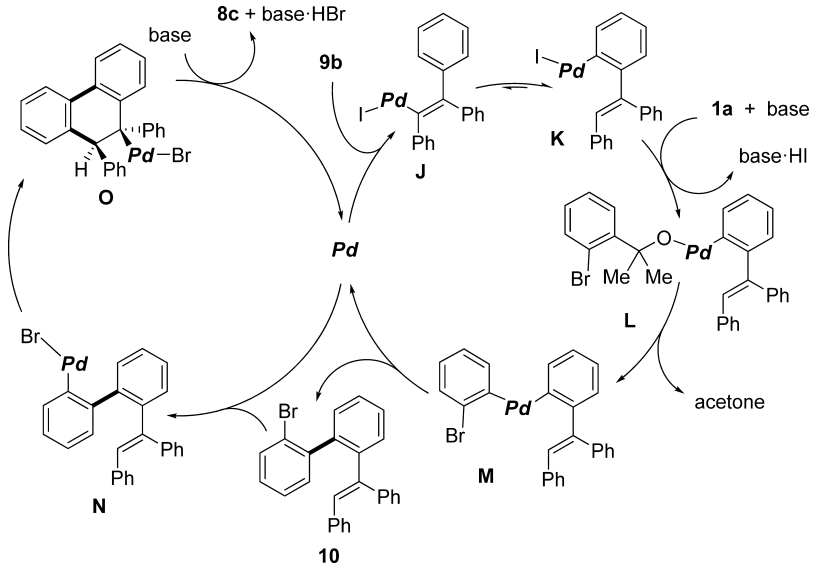


Scheme 8. A Control Experiment[a]

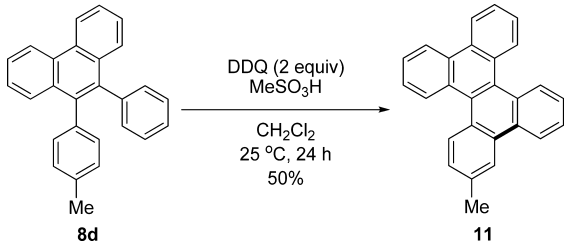


[a]Conditions: $PdCl_2(NCPh)_2$ (5 mol %), $P(4\text{-}CF_3C_6H_4)_3$ (10 mol %), Cs_2CO_3 (2.4 equiv), toluene, 110 °C, 24 h.

Scheme 9. A Plausible Reaction Mechanism for Phenanthrene Synthesis



Scheme 10. Oxidative Cyclization of 8d



A colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$, rt): δ 1.75 (s, 6H), 7.10 (dt, J = 8.1, 1.5 Hz, 1H), 7.30 (dt, J = 8.1, 1.5 Hz, 1H), 7.58 (dd, J = 8.1, 1.5 Hz, 1H), 7.67 (dd, J = 8.1, 1.5 Hz, 1H).

o-Halobenzyl alcohols **1b–1g** were prepared according to the above-mentioned procedure. Spectroscopic data of **1a**,[13a] **1b**,[28] **1c**,[29] **1d**,[30] **1e**,[13a] and **1f**[13a] can be found in the literature.

1-Bromo-2-(1-hydroxy-2-propyl)naphthalene (1g). The title compound was obtained as a colorless liquid (530 mg, 0.200 mmol, 96%). IR (neat) 3424, 2974, 1497, 1315, 1165, 955, 818, 746 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 1.89 (s, 6H), 3.08 (s, 1H), 7.50–7.54 (m, 1H), 7.58–7.62 (m, 1H), 7.80–7.87 (m, 3H), 7.45–7.47 (d, J = 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.1, 74.6, 121.1, 124.8, 126.6, 127.6, 127.7, 128.0, 128.0, 133.2, 133.8, 144.4. Calcd for $C_{13}H_{13}BrO$: C, 58.89; H, 4.94%. Found: C, 58.91; H, 4.75%.

o-Halobiphenyls **2a**, **2c**, and **2d** were obtained from commercial suppliers. Compounds **2b**,[31] **2e–2i**,[32] **2j**,[33] **2k–2o**,[30] **2p**,[34] and **2q**[30] were prepared by literature procedures. Spectroscopic data of **2b**[35] and **2g**[8e] can be found in the literature.

2-Iodo-4′-methylbiphenyl (2e).[32] The title compound was obtained as a white solid (412 mg, 1.40 mmol, 56%). Mp = 35 °C. IR (KBr): 3049, 1460, 1001, 818, 754 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 2.42 (s, 3H), 7.02 (td, J = 7.6, 1.8 Hz, 1H), 7.24 (s, 4H), 7.29 (dd, J = 7.6, 1.8 Hz, 1H), 7.38 (td, J = 7.6, 1.2 Hz, 1H), 7.95 (dd, J = 7.6, 1.2 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, rt): δ 21.3, 98.8, 128.1, 128.6, 128.6, 129.1, 130.1, 137.4, 139.4, 141.3, 146.6. Calcd for $C_{13}H_{11}I$: C, 53.09; H, 3.77%. Found: C, 53.10; H, 3.64%.

2-Iodo-4′-phenylbiphenyl (2f).[32] The title compound was obtained as a white solid (482 mg, 1.35 mmol, 27%). Mp = 97 °C. IR (KBr): 3028, 1460, 997, 843, 754 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 7.05 (td, J = 7.6, 1.9 Hz, 1H), 7.34–7.49 (m, 7H), 7.66–7.68 (m, 4H), 7.98 (d, J = 7.6 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, rt): δ 98.7, 126.8, 127.3, 127.6, 128.3, 128.9, 129.0, 129.9, 130.3, 139.7, 140.6, 140.8, 143.2, 146.4. Calcd for $C_{18}H_{13}I$: C, 60.69; H, 3.68%. Found: C, 60.67; H, 3.66%.

2-Iodo-3′,5′-dimethylbiphenyl (2h). The title compound was obtained as a colorless liquid (388 mg, 1.26 mmol, 50%). IR (neat):

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2914, 1603, 1460, 1014, 851, 756 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, rt): δ 2.38 (s, 6H), 6.96−7.04 (m, 4H), 7.29 (dd, J = 7.6, 1.9 Hz, 1H), 7.37 (td, J = 7.6, 1.2 Hz, 1H), 7.94 (dd, J = 7.6, 1.2 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, rt): δ 21.5, 98.8, 127.2, 128.1, 128.7, 129.3, 130.2, 137.5, 139.5, 144.2, 147.0. Calcd for $C_{14}H_{13}I$: C, 54.57; H, 4.25%. Found: C, 54.93; H, 4.34%.

2-Iodo-3′-methylbiphenyl (2i). The title compound was obtained as a colorless liquid (53.4 mg, 0.182 mmol, 12%). IR (neat): 3049, 1584, 1460, 1012, 754 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, rt): δ 2.42 (s, 3H), 7.03 (td, J = 7.7, 1.8, 1H), 7.14−7.23 (m, 3H), 7.29−7.41 (m, 3H), 7.96 (dd, J = 7.7, 1.1 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.6, 98.8, 126.5, 127.9, 128.2, 128.5, 128.8, 130.1, 130.2, 137.7, 139.6, 144.3, 146.9. Calcd for $C_{13}H_{11}I$: C, 53.09; H, 3.77%. Found: C, 53.35; H, 3.82%.

2-Iodo-4′-nitrobiphenyl (2j). The title compound was obtained as a white solid (130 mg, 0.400 mmol, 30%). Mp = 103 °C. IR (KBr): 3080, 1597, 1506, 1350, 854, 768 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, rt): δ 7.11 (td, J = 7.6, 1.7 Hz, 1H), 7.29 (dd, J = 7.6, 1.7 Hz, 1H), 7.44 (td, J = 7.6, 1.1 Hz, 1H), 7.51−7.54 (m, 2H), 7.99 (dd, J = 7.6, 1.1 Hz, 1H), 8.28−8.32 (m, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, rt): δ 97.5, 123.5, 128.6, 129.9, 130.0, 130.5, 140.0, 144.5, 147.4, 150.5. Calcd for $C_{12}H_8INO_2$: C, 44.33; H, 2.48; N, 4.31%. Found: C, 44.38; H, 2.40; N, 4.14%.

2-Iodo-4′-(trifluoromethyl)biphenyl (2k). The title compound was obtained as a colorless liquid (135 mg, 0.389 mmol, 30%). IR (neat): 3051, 1618, 1325, 1128, 840, 760 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, rt): δ 7.08 (td, J = 7.6, 1.7 Hz, 1H), 7.28 (dd, J = 7.6, 1.7 Hz, 1H), 7.42 (td, J = 7.6, 1.2 Hz, 1H), 7.47 (d, J = 8.0 Hz, 2H), 7.69 (d, J = 8.0 Hz, 2H), 7.98 (dd, J = 7.6, 1.2 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, rt): δ 98.0, 124.2 (q, $^1J_{C\text{-}F}$ = 270 Hz), 125.0 (q, $^3J_{C\text{-}F}$ = 3.7 Hz), 128.4, 129.6, 129.9, 129.9 (q, $^2J_{C\text{-}F}$ = 32.4 Hz) 130.1 139.8, 145.4, 147.7; $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$, rt): δ −62.6. Calcd for $C_{13}H_8F_3I$: C, 44.85; H, 2.32%. Found: C, 45.25; H, 2.33%.

4′-Fluoro-2-iodobiphenyl (2l). The title compound was obtained as a colorless liquid (457 mg, 1.53 mmol, 79%). IR (neat): 3049, 1605, 1512, 1460, 1222, 1001, 835, 758 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, rt): δ 7.04 (td, J = 7.6, 1.6 Hz, 1H), 7.09−7.13 (m, 2H), 7.27−7.33 (m, 3H), 7.39 (td, J = 7.6, 1.2 Hz, 1H), 7.95 (dd, J = 7.6, 1.2 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, rt): δ 98.9, 115.1 (d, $^2J_{C\text{-}F}$ = 21.4 Hz), 128.3, 129.1, 130.2, 131.1 (d, $^3J_{C\text{-}F}$ = 8.2 Hz), 139.7, 140.3 (d, $^4J_{C\text{-}F}$ = 3.3 Hz), 145.8, 162.5 (d, $^1J_{C\text{-}F}$ = 245 Hz); $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$, rt): δ −114.6. Calcd for $C_{12}H_8FI$: C, 48.35; H, 2.70%. Found: C, 48.46; H, 2.64%.

4′-Chloro-2-iodobiphenyl (2m). The title compound was obtained as a colorless liquid (302 mg, 0.960 mmol, 48%). IR (neat): 3049, 1595, 1494, 1458, 1092, 1016, 827, 756 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, rt): δ 7.05 (td, J = 7.7, 1.6 Hz, 1H), 7.26−7.30 (m, 3H), 7.37−7.42 (m, 3H), 7.96 (dd, J = 7.7, 1.2 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, rt): δ 98.5, 128.36, 128.38, 129.2, 130.1, 130.8, 133.9, 139.8, 142.7, 145.6. Calcd for $C_{12}H_8ClI$: C, 45.82; H, 2.56%. Found: C, 45.90; H, 2.54%.

2-Iodo-4′-methoxycarbonylbiphenyl (2n). The title compound was obtained as a colorless liquid (114 mg, 0.337 mmol, 57%). IR (neat): 3051, 2949, 1726, 1610, 1435, 1279, 1113, 754 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, rt): δ 3.95 (s, 3H), 7.07 (td, J = 7.8, 1.6 Hz, 1H), 7.29 (dd, J = 7.8, 1.6 Hz, 1H), 7.39−7.43 (m, 3H), 7.97 (dd, J = 7.8, 0.8 Hz, 1H), 8.09−8.11 (m, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, rt): δ 52.3, 97.9, 128.4, 129.4, 129.48, 129.52, 129.6, 130.0, 139.8, 145.8, 148.7, 167.0. HRMS (FAB+) Calcd for $C_{14}H_{12}IO_2$: 338.9882. Found: 338.9861 $[M + H]^+$.

2-Iodo-4′-methoxybiphenyl (2o). The title compound was obtained as a white solid (270 mg, 0.869 mmol, 35%). Mp = 48 °C. IR (KBr): 3435, 2835, 1609, 1458, 1242, 1034, 827, 760 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, rt): δ 3.87 (s, 3H), 6.95−6.97 (m, 2H), 7.01 (td, J = 7.6, 1.8 Hz, 1H), 7.27−7.31 (m, 3H), 7.37 (td, J = 7.6, 1.2 Hz, 1H), 7.95 (dd, J = 7.6, 1.2 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, rt): δ 55.3, 99.2, 113.3, 128.1, 128.5, 130.2, 130.4, 136.7, 139.5, 146.2, 159.1. Calcd for $C_{13}H_{11}IO$: C, 50.35; H, 3.58%. Found: C, 50.20; H, 3.34%.

1-Iodo-6*H*-dibenzo[*b*,*d*]pyran (2p). The title compound was obtained as a brown liquid (52.7 mg, 0.171 mmol, 11%). IR (neat): 2851, 1585, 1423, 1247, 1013, 845, 783 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, rt): δ 4.95 (s, 2H), 6.90 (t, J = 7.9 Hz, 1H), 7.04 (dd, J = 7.5, 1.2, 1H), 7.22 (m, 1H), 7.34 (td, J = 7.5, 1.2, 1H), 7.44 (td, J = 7.5, 1.2 Hz, 1H), 7.68 (dd, J = 7.5, 1.2 Hz, 1H), 8.54 (d, J = 7.9 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, rt): δ 69.5, 91.9, 118.0, 124.9, 126.1, 126.9, 127.5, 128.1, 130.1, 130.5, 133.4, 136.1, 156.7. HRMS (FAB+) Calcd for $C_{13}H_9IO$: 307.9698. Found: 307.9712 $[M^+]$.

2-Iodo-5,6-dimethoxybiphenyl (2q). The title compound was obtained as a white solid (107 mg, 0.315 mmol, 13%). Mp = 110 °C. IR (KBr): 2961, 1487, 1206, 1018, 858, 766 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, rt): δ 3.86 (s, 3H), 3.91 (s, 3H), 6.83 (s, 1H), 7.34−7.43 (m, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, rt): δ 56.1, 56.4, 86.4, 113.1, 121.8, 127.6, 128.1, 129.6, 139.4, 144.2, 148.8, 149.2. Calcd for $C_{14}H_{13}IO_2$: C, 49.43; H, 3.85%. Found: C, 49.48; H, 3.72%.

A Typical Procedure for Annulation of *o*-Iodobiphenyls 2 with *o*-Bromobenzyl Alcohols 1: Synthesis of Triphenylene (3a) (Table 4, entry 1). Under an argon atmosphere, cesium carbonate (390 mg, 1.2 mmol), bis(benzonitrile)dichloropalladium (9.6 mg, 0.025 mmol), and tris{3,5-bis(trifluoromethyl)phenyl}-phosphine (34 mg, 0.050 mmol) were placed in a 20 mL Schlenk tube. A solution of *o*-iodobiphenyl (**2d**, 140 mg, 0.50 mmol) and 2-(*o*-bromophenyl)-2-propanol (**1a**, 130 mg, 0.60 mmol) in toluene (2.0 mL) was added. The resulting mixture was stirred at 110 °C for 24 h. The mixture was then cooled to room temperature. Hydrochloric acid (1 M, 6 mL) was added, and the product was extracted with ethyl acetate (10 mL × 3). The organic layers were then washed with brine and dried over anhydrous sodium sulfate. After the volatiles were evaporated, silica gel column purification with hexane as an eluent afforded triphenylene **3a** (92.4 mg, 0.405 mmol, 81% yield). White solid. ^1H NMR (300 MHz, $CDCl_3$, rt): δ 7.66−7.69 (m, 6H), 8.66−8.69 (m, 6H).

Spectroscopic data of **3a**,[36] **3b**,[8b] **3e**−**3f**,[8e] **3k**,[8b] **3m**,[8b] **3o**,[37] **3q**,[38] **3q′**,[8f] and **3s**[8e] can be found in the literature.

2-Methyltriphenylene (3b). The reaction of **1a** with **2e** provided the title compound as a white solid (39.5 mg, 0.163 mmol, 65%). ^1H NMR (300 MHz, $CDCl_3$, rt): δ 2.62 (s, 3H), 7.50 (d, J = 8.4 Hz, 1H), 7.62−7.67 (m, 4H), 8.45 (s, 1H), 8.55 (d, J = 8.4 Hz, 1H), 8.61−8.67 (m, 4H).

2-Phenyltriphenylene (3c). The reaction of **1a** with **2f** provided the title compound as a white solid (35.8 mg, 0.118 mmol, 47%). Mp = 182 °C. IR (KBr): 3053, 1491, 746 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, rt): δ 7.41−7.46 (m, 1H), 7.52−7.57 (m, 2H), 7.65−7.72 (m, 4H), 7.81−7.84 (m, 2H), 7.91 (dd, J = 8.4, 1.8 Hz, 1H), 8.66−8.78 (m, 5H), 8.87 (d, J = 1.8 Hz, 1H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, rt): δ 121.9, 123.46, 123.48, 123.48, 123.53, 124.0, 126.5, 127.4, 127.4, 127.4, 127.5, 127.6, 127.7, 129.0, 129.1, 129.7, 129.92, 129.94, 130.2, 130.2, 140.0, 141.3. HRMS (FAB+) Calcd for $C_{24}H_{17}$: 305.1330. Found: 305.1331 $[M + H]^+$.

1-Methyltriphenylene (3d). The reaction of **1a** with **2g** provided the title compound as a white solid (23.0 mg, 0.095 mmol, 38%). Mp = 96 °C. IR (KBr): 2947, 1431, 752 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, rt): δ 3.07 (s, 3H), 7.53−7.68 (m, 6H), 8.53−8.67 (m, 5H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, rt): δ 26.8, 121.2, 123.1, 123.4, 123.8, 125.7, 126.4, 126.7, 127.2, 127.4, 128.6, 130.0, 130.5, 130.5, 130.8, 131.1, 131.4, 131.8, 135.5. Calcd for $C_{19}H_{14}$: C, 94.18; H, 5.82%. Found: C, 93.93; H, 5.88%.

1,3-Dimethyltriphenylene (3e). The reaction of **1a** with **2h** provided the title compound as a white solid (17.9 mg, 0.070 mmol, 28%). ^1H NMR (300 MHz, $CDCl_3$, rt): δ 2.58 (s, 3H), 3.03 (s, 3H), 7.35 (s, 1H), 7.54−7.65 (m, 4H), 8.34 (s, 1H), 8.57−8.65 (m, 4H).

2-Nitrotriphenylene (3f). The reaction of **1a** with **2j** provided the title compound as a light-yellow solid (62.9 mg, 0.230 mmol, 92%). ^1H NMR (300 MHz, $CDCl_3$, rt): δ 7.70−7.81 (m, 4H), 8.42 (dd, J = 9.0, 2.4 Hz, 1H), 8.63−8.75 (m, 5H), 9.51 (d, J = 2.4 Hz, 1H).

2-Trifluoromethyltriphenylene (3g). The reaction of **1a** with **2k** provided the title compound as a white solid (68.1 mg, 0.230 mmol, 92%). Mp = 110 °C. IR (KBr): 1325, 1115, 754 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, rt): δ 7.66 (m, 4H), 7.84 (d, J = 8.6 Hz, 1H), 8.61−8.66

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(m, 4H), 8.71 (d, J = 8.6 Hz, 1H), 8.87 (s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, rt): δ 120.78 (q, $^3J_{C\text{-}F}$ = 4.3 Hz), 123.3 (q, $^3J_{C\text{-}F}$ = 3.0 Hz), 123.5, 123.56, 123.58, 123.9, 124.2, 124.8 (q, $^1J_{C\text{-}F}$ = 271 Hz), 127.67, 127.75, 128.2, 128.4, 128.9, 129.0 (q, $^2J_{C\text{-}F}$ = 32 Hz), 129.1, 129.8, 130.2, 130.6, 132.4 (q, $^4J_{C\text{-}F}$ = 1.3 Hz); $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$, rt): δ −62.2. Calcd for $C_{19}H_{11}F_3$: C, 77.02; H, 3.74%. Found: C, 77.05; H, 3.52%.

2-Fluorotriphenylene (3h). The reaction of **2l** with **1a** provided the title compound as a white solid (49.9 mg, 0.203 mmol, 81%). Mp = 188 °C. IR (KBr): 1616, 1501, 1435, 1192, 758 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, rt): δ 7.34−7.42 (m, 1H), 7.65−7.70 (m, 4H), 8.27 (dd, J = 11, 2.6 Hz, 1H), 8.51−8.68 (m, 5H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, rt): δ 108.9 (d, $^2J_{C\text{-}F}$ = 22.4 Hz), 115.6 (d, $^2J_{C\text{-}F}$ = 22.4 Hz), 123.2, 123.50, 123.51, 123.6, 125.6 (d, $^3J_{C\text{-}F}$ = 8.7 Hz), 126.4 (d, $^4J_{C\text{-}F}$ = 2.0 Hz), 127.2, 127.4, 127.6, 128.0, 129.1 (d, $^4J_{C\text{-}F}$ = 3.3 Hz), 129.4, 129.5, 130.3, 131.9 (d, $^3J_{C\text{-}F}$ = 8.7 Hz), 162.3 (d, $^1J_{C\text{-}F}$ = 224 Hz); $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$, rt): δ −114.3. HRMS (FAB+) Calcd for $C_{18}H_{11}F$: 246.0845. Found: 246.0843 [M^+].

2-Chlorotriphenylene (3i). The reaction of **1a** with **2m** provided the title compound as a white solid (32.8 mg, 0.125 mmol, 50%). Mp = 146 °C. IR (KBr): 1597, 1493, 1429, 1101, 756 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, rt): δ 6.59 (dd, J = 8.8, 2.0 Hz, 1H), 7.63−7.71 (m, 4H), 8.54−8.59 (m, 4H), 8.62−8.65 (m, 2H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, rt): δ 123.2, 123.4, 123.50, 123.50, 123.52, 125.1, 127.56, 127.57, 127.58, 127.64, 128.0, 128.3, 128.8, 129.2, 129.8, 130.3, 131.4, 133.5. HRMS (FAB+) Calcd for $C_{18}H_{11}Cl$: 262.0549. Found: 262.0563 [M^+].

2-Methoxycarbonyltriphenylene (3j). The reaction of **1a** with **2n** provided the title compound as a white solid (51.5 mg, 0.180 mmol, 72%). Mp = 171 °C. IR (KBr): 2951, 1716, 1612, 1431, 1261, 1109, 746 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, rt): δ 4.04 (s, 3H), 7.69−7.73 (m, 4H), 8.27 (dd, J = 8.8, 1.6 Hz, 1H), 8.65−8.71 (m, 4H), 8.75−8.77 (m, 1H), 9.37 (d, J = 1.6 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, rt): δ 52.5, 123.5, 123.6, 123.7, 123.8, 124.2, 125.7, 127.5, 127.6, 127.7, 127.9, 128.5, 128.6, 129.2, 129.67, 129.73, 130.1, 130.9, 133.4, 167.4. HRMS (FAB+) Calcd for $C_{20}H_{14}O_2$: 286.0994. Found: 286.1019 [M^+].

2-Methoxytriphenylene (3k). The reaction of **1a** with **2o** provided the title compound as a white solid (32.3 mg, 0.125 mmol, 50%). The reaction of **1d** with **2d** provided the title compound (53.0 mg, 0.205 mmol, 82%). ^1H NMR (300 MHz, $CDCl_3$, rt): δ 4.04 (s, 3H), 7.29 (dd, J = 9.0, 2.7 Hz, 1H), 7.56−7.91 (m, 4H), 8.06 (d, J = 2.7 Hz, 1H), 8.55−8.68 (m, 5H).

2*H*-Phenanthro[1,10,9-*cde*]chromene (3l). The reaction of **1a** with **2p** provided the title compound as a white solid (14.7 mg, 0.058 mmol, 23%). Mp = 122 °C. IR (KBr): 2926, 1597, 1412, 1236, 748 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, rt): δ 5.55 (s, 2H), 7.13 (dd, J = 8.4, 1.8 Hz, 1H), 7.32 (dd, J = 8.4, 1.8 Hz, 1H), 7.53−7.69 (m, 4H), 8.17 (d, J = 8.4 Hz, 1H), 8.48 (d, J = 8.4 Hz, 1H), 8.60−8.64 (m, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, rt): δ 68.2, 113.6, 115.9, 116.9, 122.0, 122.3, 123.3, 123.6, 124.1, 127.5, 127.52, 127.54, 127.6, 128.6, 129.2, 129.5, 129.95, 130.02, 153.5. HRMS (FAB+) Calcd for $C_{19}H_{12}O$: 256.0888. Found: 256.0877 [M^+].

2,3-Dimethoxytriphenylene (3m). The reaction of **1a** with **2q** provided the title compound as a white solid (44.0 mg, 0.153 mmol, 61%). The reaction of **1e** with **2d** provided the title compound (45.4 mg, 0.157 mmol, 63%). ^1H NMR (300 MHz, $CDCl_3$, rt): δ 4.14 (s, 6H), 7.62−7.67 (m, 4H), 8.02 (s, 2H), 8.50−8.53 (m, 2H), 8.66−8.69 (m, 2H).

Triphenyleno[2,3-*d*]-1,3-dioxole (3n). The reaction of **1f** with **2d** provided the title compound as a white solid (37.4 mg, 0.137 mmol, 55%). Mp = 260 °C. IR (KBr): 2910, 1502, 1229, 1041, 752 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, rt): δ 6.14 (s, 2H), 7.60−7.66 (m, 4H), 8.03 (s, 2H), 8.44−8.47 (m, 2H), 8.65−8.67 (m, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, rt): δ 101.7, 102.1, 123.2, 123.5, 125.9, 126.6, 127.3, 129.3, 129.9, 148.4. HRMS (FAB+) Calcd for $C_{19}H_{12}O_2$: 272.0837. Found: 272.0854 [M^+].

Benzo[*g*]chrycene (3o). The reaction of **1g** with **2d** provided the title compound as a white solid (21.6 mg, 0.078 mmol, 31%). ^1H NMR (400 MHz, $CDCl_3$, rt): δ 7.60−7.73 (m, 6H), 8.00−8.04 (m, 2H), 8.61 (d, J = 9.2 Hz, 1H), 8.65−8.67 (m, 1H), 8.71−8.76 (m, 2H), 8.92 (dd, J = 8.0, 1.6 Hz, 1H), 8.96 (d, J = 8.0 Hz, 1H).

2-Methoxy-6-nitrotriphenylene (3p) and 3-Methoxy-6-nitrotriphenylene (3p′). The reaction of **2j** with **2d** provided a 1:1 mixture of isomers **3p** and **3p′** as a yellow solid (62.2 mg, 0.205 mmol, 82%). IR (KBr): 1614, 1516, 1340, 1229, 741 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, rt): δ 4.05 (s, 3H (minor)), 4.07 (s, 3H (major)), 7.32−7.37 (m, 1H (major), 1H (minor)), 7.63−7.77 (m, 2H (major), 2H (minor)), 8.00−8.03 (m, 1H (major), 1H (minor)), 8.34 (dd, J = 9.0, 2.4 Hz, 1H (minor)), 8.41 (dd, J = 9.0, 2.4 Hz, 1H (major)), 8.55−8.73 (m, 4H (major), 4H (minor)), 9.37−9.40 (m, 1H (major), 1H (minor)); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, rt): δ 55.5, 55.6, 105.5, 105.6, 116.2, 117.1, 118.2, 118.8, 119.6, 120.6, 122.3, 122.8, 123.4, 123.8, 124.04, 124.04, 124.1, 124.2, 124.9, 125.0, 126.6, 126.8, 127.7, 128.3, 128.8, 129.1, 129.2, 129.7, 129.9, 130.4, 131.0, 131.5, 132.9, 134.4, 145.8, 146.1, 159.1, 159.7. HRMS (FAB+) Calcd for $C_{19}H_{13}NO_3$: 303.0895. Found: 303.0920 [M^+].

2,6-Dimethoxytriphenylene (3q) and 3,6-Dimethoxytriphenylene (3q′). The reaction of **1d** with **2o** provided a 1:1 mixture of isomers **3q** and **3q′** as a white solid (34.6 mg, 0.120 mmol, 48%). ^1H NMR (600 MHz, $CDCl_3$, rt): δ 4.03 (s, 3H (**3q**)), 4.03 (s, 6H (**3q′**)), 4.04 (s, 3H (**3q**)), 7.23 (dd, J = 9.0, 2.4 Hz, 1H (**3q**)), 7.28−7.30 (m, 1H (**3q**), 2H (**3q′**)), 7.57−7.64 (m, 2H (**3q**), 2H (**3q′**)), 7.96−7.97 (m, 1H (**3q**), 2H (**3q′**)), 8.05 (d, J = 2.4 Hz, 1H (**3q**)), 8.49−8.58 (m, 4H (**3q**), 4H (**3q′**)).

2-Methoxy-5,7-dimethyltriphenylene (3r) and 3-Methoxy-5,7-dimethyltriphenylene (3r′). The reaction of **1d** with **2h** provided a 9:1 mixture of isomers **3r** and **3r′** as a white solid (20.0 mg, 0.070 mmol, 28%). IR (KBr): 2920, 1609, 1449, 1219, 1043, 760 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, rt): δ 2.56 (s, 3H (minor)), 2.57 (s, 3H (major)), 3.00 (s, 3H (minor)), 3.05 (s, 3H (major)), 3.98(s, 3H (major)), 4.03 (s, 3H (minor)), 7.17−7.26 (m, 1H (major), 1H (minor)), 7.33 (s, 1H (major), 1H (minor)), 7.53−7.60 (m, 2H (major), 2H (minor)), 8.06−8.07 (m, 1H (major), 1H (minor)), 8.33 (s, 1H (major), 1H (minor)), 8.48−8.58 (m, 3H (major), 3H (minor)); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, rt): δ 21.6, 21.7, 26.8, 29.8, 55.6, 55.6, 106.3, 112.0, 113.7, 114.2, 116.1, 121.4, 121.6, 122.6, 123.2, 123.8, 124.7, 124.8, 126.3, 127.0, 127.2, 127.4, 128.0, 129.5, 129.8, 129.9, 130.3, 130.5, 131.9, 132.37, 132.38, 132.43, 133.2, 133.3, 134.6, 135.0, 135.28, 135.29, 136.0, 136.0, 157.6, 157.9. HRMS (FAB+) Calcd for $C_{21}H_{18}O$: 286.1358. Found: 286.1357 [M^+].

2,3,6-Trimethoxytriphenylene (3s) and 2,3,7-Trimethoxytriphenylene (3s′). The reaction of **1d** with **2q** provided a 1:2 mixture of isomers **3s** and **3s′** as a white solid (43.0 mg, 0.135 mmol, 54%). IR (KBr): 2957, 1614, 1512, 1267, 1202, 1043, 1016, 845, 756 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$, rt): δ 4.01 (s, 3H (minor)), 4.02 (s, 3H (major)), 4.09 (s, 3H (minor)), 4.10 (s, 3H (major)), 4.10 (s, 3H (major)), 4.11 (s, 3H (minor)), 7.21 (dd, J = 8.7, 2.7 Hz, 1H (minor)), 7.25 (dd, J = 9.0, 2.4 Hz, 1H (major)), 7.57−7.65 (m, 2H (major), 2H (minor)), 7.81−7.83 (m, 1H (major), 2H (minor)), 7.92 (s, 1H (major)), 7.93 (s, 1H (minor)), 8.02 (d, J = 2.4 Hz, 1H (major)), 8.36 (d, J = 9.0 Hz, 1H (major)), 8.42−8.46 (m, 1H (major), 1H (minor)), 8.51−8.56 (m, 1H (major), 2H (minor)); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, rt): δ 55.57, 55.61, 56.01, 56.03, 56.05, 56.07, 104.1, 104.55, 104.57, 104.60, 105.6, 106.0, 114.2, 116.0, 122.8, 122.9, 123.0, 123.3, 123.5, 123.7, 123.8, 124.41, 124.42, 124.43, 124.7, 125.1, 126.13, 126.15, 126.4, 127.2, 128.5, 128.9, 129.3, 130.0, 130.6, 131.0, 148.7, 149.3, 149.5, 149.6, 158.3, 158.8. HRMS (FAB+) Calcd for $C_{21}H_{18}O_3$: 318.1256. Found: 318.1247 [M^+].

6,6-Dimethyl-6*H*-dibenzo[*b*,*d*]pyran (4). A colorless liquid. ^1H NMR (400 MHz, $CDCl_3$, rt): δ 1.64 (s, 6H), 6.95 (dd, J = 8.0, 1.2 Hz, 1H), 7.03 (dt, J = 7.6, 1.2 Hz, 1H), 7.21−7.26 (m, 2H), 7.28−7.37 (m, 2H), 7.73 (d, J = 7.6 Hz, 2H).

Spectroscopic data of **4** can be found in the literature.[39]

o-Bromoterphenyl **5a** was prepared by literature procedures.[40]

2-(2-Bromophenyl)biphenyl (5a). The title compound was obtained as a colorless liquid (204 mg, 0.660 mmol, 66%). IR (neat): 3055, 1462, 1423, 1026, 748, 700 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, rt): δ 7.06−7.09 (m, 2H), 7.13−7.21 (m, 6H), 7.33−7.35 (m, 1H), 7.40−7.54 (m, 4H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, rt): δ

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124.0, 126.7, 126.9, 127.0, 127.8, 128.3, 128.5, 129.6, 130.2, 130.9, 132.3, 132.6, 139.8, 141.1, 141.2, 142.5. Calcd for $C_{18}H_{13}Br$: C, 69.92; H, 4.24%. Found: C, 69.77; H, 4.30%.

o-Iodostyrenes **7a**[41] and **7b**[42] were prepared by literature procedures and showed the identical spectroscopic data reported in the literature.

Preparation of (*E*/*Z*)-1-(2-Bromophenyl)-1,2-diphenylethene ((*E*/*Z*)-7c).[43] Under an argon atmosphere, benzyltriphenylphosphonium bromide (2.69 g, 6.2 mmol) and potassium *tert*-butoxide (696 mg, 6.2 mmol) were placed in a 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, which was washed with ethyl acetate. The reaction mixture was poured into water (12 mL), and 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 (*E*/*Z*)-**7c** (183 mg, 0.546 mmol, 55%) as a 1:1 mixture of *E*/*Z* isomers.

A colorless liquid. 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%.

Preparation of 1-Iodo-1,2,2-triphenylethene (9a).[44] Under an argon atmosphere, magnesium turnings (134 mg, 5.5 mmol) were placed in a 100 mL reaction flask. A solution of 1-bromo-1,2,2-triphenylethene (1.68 g, 5.0 mmol) in THF (34 mL) was added. The mixture was stirred at reflux for 2 h. After the reaction mixture was cooled to room temperature, iodine (1.52 g, 6.0 mmol) was added. After being stirred for 30 min at room temperature, the product was extracted with diethyl ether (40 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 = 40:1), afforded **9a** (1.81 g, 4.74 mmol, 95%).

Pale yellow solid. Mp 118−120 °C. IR (KBr): 3073 (w), 1595 (w), 1441 (m) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, rt): δ 6.94−6.97 (m, 2H), 7.01−7.05 (m, 3H), 7.09−7.18 (m, 3H), 7.27−7.42 (m, 7H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, rt): δ 101.7, 127.3, 128.0, 128.1, 128.2, 128.4, 128.8, 129.7, 130.6, 130.7, 140.7, 145.0, 147.6, 150.4. Calcd for $C_{20}H_{15}I$: C, 62.84; H, 3.94%. Found: C, 62.89; H, 3.82%.

(*Z*)-β-Halostyrenes **9b**,[42] **9h**,[42,45] **9i**,[46] and **9j**[47] were prepared by literature procedures. Spectroscopic data of **9b**,[48] **9c**,[49] **9d**,[50] **9h**,[51] **9i**,[52] and **9j**[53] can be found in the literature.

Preparation of 1-Bromo-1-(4-fluorophenyl)-2,2-diphenylethene (9e).[54] 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 a 50 mL of Schlenk tube. THF (4.9 mL), diethyl 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 **9e** (157 mg, 0.444 mmol, 44%).

Orange solid. Mp 113−114 °C. 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, $^2J_{C\text{-}F}$ = 21.9 Hz), 121.0, 127.3, 127.8, 128.1, 128.4, 129.6, 130.4, 132.3 (d, $^3J_{C\text{-}F}$ = 8.1 Hz), 137.3 (d, $^4J_{C\text{-}F}$ = 3.5 Hz), 141.0, 143.7, 144.1, 162.1 (d, $^1J_{C\text{-}F}$ = 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%.

(*Z*)-β-Halostyrenes **9c**, **9d**, **9f**, and **9g** were prepared according to the above-mentioned procedure.

1-Bromo-1-(4-methylphenyl)-2,2-diphenylethene (9c). The title compound was obtained as a white solid (112 mg, 0.306 mmol, 31%). ^1H NMR (400 MHz, $CDCl_3$, rt): δ 2.29 (s, 3H), 6.96−7.00 (m, 4H), 7.07−7.10 (m, 3H), 7.21 (d, J = 8.0 Hz, 2H), 7.29−7.34 (m, 1H), 7.35−7.41 (m, 4H).

1-Bromo-1-(4-methoxyphenyl)-2,2-diphenylethene (9d). The title compound was obtained as a white solid (144 mg, 0.413 mmol, 41%). ^1H NMR (400 MHz, $CDCl_3$, rt): δ 3.77 (s, 3H), 6.70 (d, J = 7.6 Hz, 2H), 6.95−6.98 (m, 2H), 7.07−7.09 (m, 3H), 7.25 (d, J = 7.6 Hz, 2H), 7.30−7.33 (m, 1H), 7.35−7.40 (m, 4H).

1-Bromo-1-(4-cyanophenyl)-2,2-diphenylethene (9f). The title compound was obtained as a pale yellow solid (90.3 mg, 0.251 mmol, 50%). Mp 162−163 °C. 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 (9g). The title compound was obtained as a pale yellow solid (79.9 mg, 0.199 mmol, 40%). Mp 80−82 °C. 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, J = 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, $^2J_{C\text{-}F}$ = 21.2 Hz), 115.4 (d, $^2J_{C\text{-}F}$ = 21.3 Hz), 123.0, 131.6 (d, $^3J_{C\text{-}F}$ = 8.0 Hz), 131.8, 132.2 (d, $^3J_{C\text{-}F}$ = 8.0 Hz), 133.2, 137.3 (d, $^4J_{C\text{-}F}$ = 3.5 Hz), 139.8 (d, $^4J_{C\text{-}F}$ = 3.5 Hz), 140.7, 159.4, 161.7 (d, $^1J_{C\text{-}F}$ = 246 Hz), 162.2 (d, $^1J_{C\text{-}F}$ = 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 (9k).[55] Under an argon atmosphere, diphenylacetylene (891 mg, 5.0 mmol) was placed in a 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 °C. The reaction mixture was stirred for 2 h. 1,2-Dibromoethane (0.57 mL, 6.6 mmol) was added at −78 °C, and the reaction mixture was stirred for an additional 30 min. After being cooled to 0 °C, 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. After the volatiles were evaporated in vacuo, the product was chromatographed on silica gel (hexane) to afford **9k** (537 mg, 1.70 mmol, 34%).

White solid. Mp 50−51 °C. 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 (9l).[56] Under an argon atmosphere, lithium granules (694 mg, 100 mmol) were placed in a 50 mL Schlenk tube. THF (24 mL) and trimethylstannyl chloride (1.99 g, 10 mmol) were added. The reaction mixture was vigorously stirred at 0 °C for 12 h. The resulting dark green solution was transferred via a syringe to a 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 °C. After the reaction mixture was stirred at 0 °C for 3 h, 1-iodobutane (1.14 mL, 10 mmol) was added at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred for an 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).

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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) afforded **9l** (1.66 g, 4.59 mmol, 51%).

White solid. Mp 67−68 °C. 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%.

Preparation of (*E*)-1-Bromo-2-(4-methoxyphenyl)-1,2-diphenylethene (9m).[43] Under an argon atmosphere, lithium granules (174 mg, 25 mmol) were placed in a 50 mL Schlenk tube. THF (7.5 mL) and trimethylstannyl chloride (498 mg, 2.5 mmol) were added, and the reaction mixture was vigorously stirred at 0 °C for 12 h. The resulting dark green solution was transferred via a syringe to a 50 mL Schlenk tube, and the volatiles were removed in vacuo. Hexane (4 mL) and diphenylacetylene (401 mg, 2.25 mmol) were added at 0 °C. After the reaction mixture was vigorously stirred at 0 °C for 3 h, zinc chloride (0.50 M THF solution, 5 mL, 2.5 mmol) was added, and the reaction mixture was allowed to warm to room temperature. After stirring for 30 min, 4-iodoanisole (553 mg, 2.36 mmol), tris(dibenzylideneacetone)dipalladium(0)-chloroform (116 mg, 0.1125 mmol), and SPhos (185 mg, 0.45 mmol) were added at 0 °C. The reaction mixture was then allowed to warm gradually to room temperature with continuous stirring over 12 h. The reaction mixture was poured into water (20 mL) and extracted with dichloromethane (40 mL × 3). The combined organic layers were washed with brine (10 mL) and dried over sodium sulfate. The volatiles were removed in vacuo. Under an argon atmosphere, the crude product was placed in a 50 mL Schlenk tube. Dichloromethane (25 mL) and *N*-bromosuccinimide (712 mg, 4.0 mmol) were then added. After being stirred at room temperature for 2 h, the reaction mixture was poured into saturated sodium thiosulfate 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/ethyl acetate = 10:1) afforded **9m** (248 mg, 0.679 mmol, 30%).

White solid. Mp 94−95 °C. IR (KBr): 3055 (w), 2951 (w), 1508 (m), 1254 (s), 1032 (s) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, rt): δ 3.71 (s, 3H), 6.60 (d, J = 7.6 Hz, 2H), 6.87 (d, J = 7.6 Hz, 2H), 7.15−7.23 (m, 3H), 7.31−7.42 (m, 7H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, rt): δ 55.2, 113.4, 121.2, 127.6, 127.9, 128.2, 128.3, 129.7, 130.5, 131.8, 133.5, 141.5, 143.2, 144.2, 158.6. Calcd for $C_{21}H_{17}BrO$: C, 69.05; H, 4.69%. Found: C, 68.94; H, 4.34%.

(*Z*)-β-Halostyrenes **9n** and **9o** were prepared according to the above procedure.

(*E*)-1-Bromo-2-(4-fluorophenyl)-1,2-diphenylethene (9n). The title compound was obtained as a pale yellow solid (404 mg, 1.14 mmol, 51%). Mp 88−89 °C. IR (KBr): 3055 (w), 1603 (w), 1504 (m) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, rt): δ 6.76 (t, J = 7.6 Hz, 2H), 6.92 (dd, J = 7.6, 5.2 Hz, 2H), 7.18−7.22 (m, 3H), 7.30−7.42 (m, 7H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, rt): δ 115.0 (d, $^2J_{C\text{-}F}$ = 21.4 Hz), 122.4 (d, $^5J_{C\text{-}F}$ = 1.1 Hz), 127.9, 128.2, 128.3, 128.4, 129.6, 130.4, 132.2 (d, $^3J_{C\text{-}F}$ = 8.0 Hz), 137.1 (d, $^4J_{C\text{-}F}$ = 3.5 Hz), 141.1, 142.6, 143.7, 161.7 (d, $^1J_{C\text{-}F}$ = 246 Hz); $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$, rt): δ −114. 6. Calcd for $C_{20}H_{14}BrF$: C, 68.01; H, 3.99%. Found: C, 68.02; H, 3.85%.

(*E*)-1-Bromo-2-(4-trifluoromethylphenyl)-1,2-diphenylethene (9o). The title compound was obtained as a pale yellow solid (595 mg, 1.48 mmol, 33%). Mp 119−121 °C. IR (KBr): 3055 (w), 1616 (w), 1337 (m) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, rt): δ 7.13 (d, J = 8.0 Hz, 2H), 7.25−7.28 (m, 2H), 7.35−7.48 (m, 10H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, rt): δ 124.10 (q, $^1J_{C\text{-}F}$ = 271 Hz), 124.12, 125.0 (q, $^3J_{C\text{-}F}$ = 3.8 Hz), 128.1, 128.4, 128.5, 128.6, 129.0 (q, $^2J_{C\text{-}F}$ = 32.4 Hz), 129.6, 130.3, 130.7, 140.6, 142.3, 143.2, 144.8 (q, $^4J_{C\text{-}F}$ = 1.3 Hz); $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$, rt): δ −62.8. Calcd for $C_{21}H_{14}BrF_3$: C, 62.55; H, 3.50%. Found: C, 62.50; H, 3.34%.

Typical Procedure for Palladium-Catalyzed Annulation of (*Z*)-β-Bromostyrenes 9 with *o*-Bromobenzyl Alcohols 1: Synthesis of 9,10-Diphenylphenanthrene (8c) (Table 7, entry 4). 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 (**9b**, 83.8 mg, 0.25 mmol), and 2-(*o*-bromophenyl)-2-propanol (**1a**, 75.3 mg, 0.35 mmol) were added. The resulting mixture was stirred at 110 °C 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 and the sequential bulb-to-bulb distillation afforded 9,10-diphenylphenanthrene **8c** (71.9 mg, 0.22 mmol, 88% yield).

White solid. ^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).

Spectroscopic data of **8a**,[57] **8b**,[58] **8c**,[59] **8d**,[60] **8e**,[10l] **8i**,[58] **8e′**,[10j] **8k**,[10q] **8l**,[8b] **8n**,[10r] **8o′**,[10j] and **11**[59] can be found in the literature.

9-Phenyl-10-(4-methylphenyl)phenanthrene (8d). The reaction of **1a** with **9c** provided the title compound as a 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).

9-(4-Methoxyphenyl)-10-phenylphenanthrene (8e). The reaction of **1a** with **9d** provided the title compound as a white solid (69.9 mg, 0.194 mmol, 97%). ^1H 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).

9-(4-Fluorophenyl)-10-phenylphenanthrene (8f). The reaction of **1a** with **9e** provided the title compound as a white solid (66.4 mg, 0.191 mmol, 95%). Mp 254−256 °C. IR (KBr): 3065 (w), 1506 (m) cm^{-1}. ^1H 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); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, rt): δ 114.8 (d, $^2J_{C\text{-}F}$ = 21.0 Hz), 122.6, 122.7, 126.6, 126.7, 126.7, 126.8, 126.9, 127.7, 127.9, 128.0, 130.2 (2C), 131.1, 131.9, 132.0, 132.7 ($^3J_{C\text{-}F}$, J = 7.8 Hz), 135.6 (d, $^4J_{C\text{-}F}$ = 3.5 Hz), 136.2, 137.8, 139.6, 161.6 (d, $^1J_{C\text{-}F}$ = 244 Hz); $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$, rt): δ −116.1. HRMS (FAB+): Calcd for $C_{26}H_{17}F$: 348.1314. Found: 348.1328 $[M]^+$.

9-(4-Cyanophenyl)-10-phenylphenanthrene (8g). The reaction of **1a** with **9f** provided the title compound as a white solid (48.1 mg, 0.135 mmol, 68%). Mp 222−223 °C. IR (KBr): 3065 (w), 2228 (m), 1607 (m) cm^{-1}. ^1H 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); $^{13}C\{^1H\}$ 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 (8h). The reaction of **1a** with **9g** provided the title compound as a white solid (56.0 mg, 0.141 mmol, 71%). Mp 231−232 °C. 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, $^2J_{C\text{-}F}$ = 22.2 Hz), 113.4, 114.9 (d, $^2J_{C\text{-}F}$ = 21.1 Hz), 115.6 (d, $^2J_{C\text{-}F}$ = 23.2 Hz), 122.8, 126.7, 127.4, 128.1, 128.8 (d, $^5J_{C\text{-}F}$ = 1.3 Hz), 129.6 (d, $^4J_{C\text{-}F}$ = 4.1 Hz), 130.0 (d, $^3J_{C\text{-}F}$ = 8.8 Hz), 131.5, 131.8 (d, $^3J_{C\text{-}F}$ = 8.4 Hz), 132.1, 132.6 (d, $^3J_{C\text{-}F}$ = 7.8 Hz), 132.7, 135.5 (d, $^4J_{C\text{-}F}$ = 3.5 Hz), 136.1 (d, $^5J_{C\text{-}F}$ = 1.2 Hz), 136.7 (d, $^5J_{C\text{-}F}$ = 1.8 Hz), 158.3, 161.6

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(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 (8i). The reaction of **1a** with **9i** provided the title compound as a 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).

9-Butyl-10-phenylphenanthrene (8j). The reaction of **1a** with **9l** provided the title compound as a white solid (46.0 mg, 0.148 mmol, 59%). Mp 113−114 °C. 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 $[M]^+$.

9-(4-Methoxyphenyl)-10-phenylphenanthrene (8e) and 3-Methoxy-9,10-diphenylphenanthrene (8e′). The reaction of **1a** with **9m** provided a 3:1 mixture of isomers **8e** and **8e′** as a white solid (84.9 mg, 0.236 mmol, 94%).

9-(4-Methoxyphenyl)-10-phenylphenanthrene (8e). ^1H 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), 7.15−7.29 (m, 5H), 7.46−7.69 (m, 6H), 8.81 (d, *J* = 8.0 Hz, 2H).

3-Methoxy-9,10-diphenylphenanthrene (8e′). ^1H NMR (400 MHz, $CDCl_3$, rt): δ 4.05 (s, 3H), 7.12−7.29 (m, 11H), 7.46−7.69 (m, 4H), 8.18 (d, *J* = 2.4 Hz, 1H), 8.73 (d, *J* = 8.4 Hz, 1H).

9-(4-Fluorophenyl)-10-phenylphenanthrene (8f) and 3-Fluoro-9,10-diphenylphenanthrene (8f′). The reaction of **1a** with **9n** provided a 2:1 mixture of isomers **8f** and **8f′** as a white solid (82.5 mg, 0.237 mmol, 95%). IR (KBr): 3055 (w), 1506 (m) cm^{-1}. Calcd for $C_{26}H_{17}F$: C, 89.63; H, 4.92%. Found: C, 89.41; H, 4.72%.

9-Fluorophenyl-10-phenylphenanthrene (8f). ^1H NMR (400 MHz, $CDCl_3$, rt): δ 6.96 (t, *J* = 8.8 Hz, 2H), 7.11−7.18 (m, 4H), 7.20−7.31 (m, 3H), 7.49−7.60 (m, 4H), 7.67−7.72 (m, 2H), 8.83 (d, *J* = 8.0 Hz, 2H).

3-Fluoro-9,10-diphenylphenanthrene (8f′). ^1H NMR (400 MHz, $CDCl_3$, rt): δ 7.11−7.18 (m, 4H), 7.20−7.31 (m, 7H), 7.49−7.60 (m, 3H), 7.67−7.72 (m, 1H), 8.43 (dd, *J* = 11.2, 2.8 Hz, 1H), 8.68 (d, *J* = 8.4 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, rt): δ 107.7 (d, $^2J_{C-F}$ = 22.1 Hz), 115.6 (d, $^2J_{C-F}$ = 23.1 Hz), 122.8, 126.6, 126.7, 126.8, 127.4, 127.78, 127.81, 128.1, 128.8 (d, $^5J_{C-F}$ = 1.5 Hz), 129.5 (d, $^4J_{C-F}$ = 4.1 Hz), 130.4 (d, $^3J_{C-F}$ = 8.8 Hz), 131.1, 131.2, 131.8 (d, $^3J_{C-F}$ = 8.4 Hz), 132.4, 136.6 (d, $^4J_{C-F}$ = 2.4 Hz), 137.0 (d, $^5J_{C-F}$ = 1.3 Hz), 139.4, 139.5, 161.7 (d, $^1J_{C-F}$ = 241 Hz); $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$, rt): δ −114.3.

9-Phenyl-10-[4-(trifluoromethyl)phenyl]phenanthrene (8k). The reaction of **1a** with **9o** provided the title compound as a white solid (138.5 mg, 0.348 mmol, 70%). ^1H NMR (400 MHz, $CDCl_3$, rt): δ 7.14 (d, *J* = 8.4 Hz, 2H), 7.20−7.30 (m, 5H), 7.44−7.58 (m, 6H), 7.70 (t, *J* = 8.4 Hz, 2H), 8.826 (d, *J* = 8.4 Hz, 1H), 8.834 (d, *J* = 8.4 Hz, 1H).

3-Trifluoromethyl-9,10-diphenylphenanthrene (8k′). The reaction of **1a** with **9o** provided the title compound as a white solid (26.3 mg, 0.0660 mmol, 13%). Mp.164−165 °C. IR (KBr): 3075 (w), 1489 (m) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, rt): δ 7.13−7.16 (m, 4H), 7.20−7.28 (m, 6H), 7.35−7.61 (m, 2H), 7.67 (s, 2H), 7.73 (t, *J* = 8.0 Hz, 1H), 8.82 (d, *J* = 8.0 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, $^3J_{C-F}$ = 3.3 Hz), 122.7, 124.8 (q, $^1J_{C-F}$ = 271 Hz), 126.9, 127.0, 127.2, 127.6, 127.85, 127.94, 128.2 (q, $^2J_{C-F}$ = 32 Hz), 128.3, 128.8, 129.7, 129.9, 130.9, 131.1, 132.3, 134.0, 136.8, 139.0, 139.1, 139.6; $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$, rt): δ −62.0. HRMS (FAB+): Calcd for $C_{27}H_{17}F_3$: 398.1282. Found: 398.1311 $[M]^+$.

2,3-Dimethoxy-9,10-diphenylphenanthrene (8l). The reaction of **1e** with **9b** provided the title compound as a white solid (86.4 mg, 0.221 mmol, 89%). ^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).

5,6-Diphenylphenanthro[2,3-*d*][1,3]dioxole (8m). The reaction of **1f** with **9b** provided the title compound as a orange solid (69.3 mg, 0.185 mmol, 74%). Mp 234−235 °C. 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-Methoxy-9,10-diphenylphenanthrene (8n) and 2-Methoxy-9,10-diphenylphenanthrene (8e′). The reaction of **1d** with **9b** provided a 1:5 mixture of isomers **8n** and **8e′** as a white solid (76.6 mg, 0.213 mmol, 85%). The reaction of **1d** with **7c** provided a 1:3 mixture of isomers **8n** and **8e′** as a white solid (65.9 mg, 0.183 mmol, 73%).

3-Methoxy-9,10-diphenylphenanthrene (8n). ^1H NMR (600 MHz, $CDCl_3$, rt): δ 3.72 (s, 3H), 6.95 (d, *J* = 3.0 Hz, 1H), 7.13−7.26 (m, 10H), 7.31 (dd, *J* = 9.0 Hz, 2.4 Hz, 1H), 7.42 (t, *J* = 7.2 Hz, 1H), 7.53 (d, *J* = 8.4 Hz, 1H), 7.62−7.66 (m, 1H), 8.70−8.74 (m, 2H).

2-Methoxy-9,10-diphenylphenanthrene (8e′). ^1H NMR (600 MHz, $CDCl_3$, rt): δ 4.05 (s, 3H), 7.13−7.26 (m, 11H), 7.47−7.50 (m, 2H), 7.56 (d, *J* = 8.4 Hz, 1H), 7.62−7.66 (m, 1H), 8.18 (d, *J* = 2.4 Hz, 1H), 8.70−8.74 (m, 1H).

11,12-Diphenylchrysene (8o′). The reaction of **1g** with **9b** provided the title compound as a white solid (57.4 mg, 0.151 mmol, 60%). ^1H NMR (300 MHz, $CDCl_3$, rt): δ 7.00−7.29 (m, 10H), 7.38−7.60 (m, 5H), 7.68−7.73 (m, 1H), 7.91 (dd, *J* = 8.1, 1.2 Hz, 1H), 8.04 (d, *J* = 9.0 Hz, 1H), 8.87 (t, *J* = 9.3 Hz, 2H).

2-Methyldibenzo[*g*,*p*]chrysene (11). The title compound was obtained as a 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).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b01693.

More detailed results of palladium-catalyzed reactions and ^1H, $^{13}C\{^1H\}$, and $^{19}F\{^1H\}$ NMR spectra for products (PDF)

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Notes

The authors declare no competing financial interest.

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