JOC The Journal of Organic Chemistry

Article

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Synthesis of Phenanthrenes through Copper-Catalyzed Cross-Coupling of *N*-Tosylhydrazones with Terminal Alkynes

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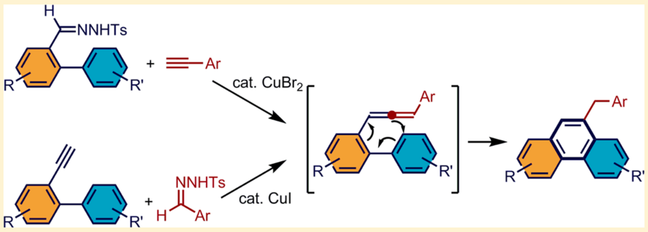
S *Supporting Information*

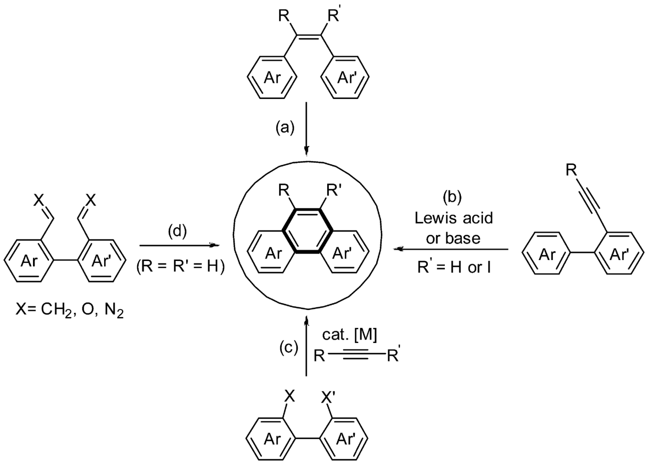
ABSTRACT: A novel protocol for the synthesis of phenanthrenes through the copper-catalyzed reaction of aromatic tosylhydrazones with terminal alkynes is explored. The reaction proceeds via the formation of an allene intermediate and subsequent six-π-electron cyclization−isomerization, affording phenanthrene derivatives in good yields. The transformation can be performed in two ways: (1) with *N*-tosylhydrazones derived from [1,1′-biphenyl]-2-carbaldehydes and terminal alkynes as the starting materials and (2) with *N*-tosylhydrazones derived from aromatic aldehydes and 2-alkynyl biphenyls as the starting materials. This new phenanthrene synthesis uses readily available starting materials and a cheap copper catalyst and has a wide range of functional group compatibility.



INTRODUCTION

Because of their versatile applications in materials science[1] and medicinal chemistry[2] as well as their wide presence in natural products,[3] phenanthrenes have attracted great attention over the years. Consequently, significant efforts have been devoted to the study of this type of compound, and a series of methodologies for phenanthrene synthesis have been developed over the past decades.[4] Among the various methods developed, a general approach is intramolecular aryl−aryl bond formation from stilbene derivatives (Scheme 1a).[5] Carbocyclization−annulation represents another useful and versatile strategy for the synthesis of phenanthrene derivatives. This strategy can be divided into two types: (1) using alkynylated biaryls as the starting materials and (2) using biphenyl derivatives and alkynes as the starting materials. The former is represented in many cyclization methods such as Lewis acid-catalyzed cyclizations, base-catalyzed cyclizations, electrophilic cyclizations, and transition-metal-catalyzed electrophilic cyclizations (Scheme 1b).[6] For the latter, various metal-catalyzed [4 + 2] cycloadditions have been documented for phenanthrene synthesis (Scheme 1c).[7] Other strategies to synthesize phenanthrenes, such as ring-closing olefin metathesis,[8] Ullman coupling−McMurry cyclization,[9] and carbene dimerization,[10] have also been reported (Scheme 1d). Despite the significant advances that have been achieved over the years, the methods developed to date suffer from at least one of the following limitations: low efficiency, poor regioselectivity, use of expensive and/or toxic reagents, poor accessibility of the starting substrates, and so on. As a result, in view of the importance of phenanthrenes and the drawbacks of the existing methods, the development of new approaches for the synthesis of functionalized phenanthrenes is highly desirable.

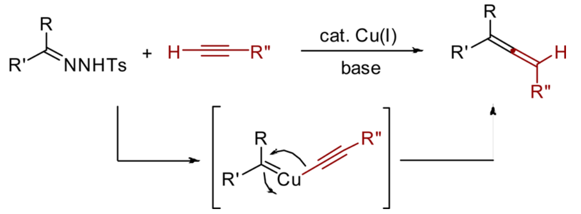
Scheme 1. General Strategies for the Synthesis of Phenanthrenes



We recently reported a method for the synthesis of allenes through Cu(I)-catalyzed cross-coupling of *N*-tosylhydrazones with terminal alkynes.[11,12] The reaction is proposed to involve a copper(I) carbene migratory insertion process (Scheme 2). Since the allene moiety is also reactive under Cu(I)-catalyzed

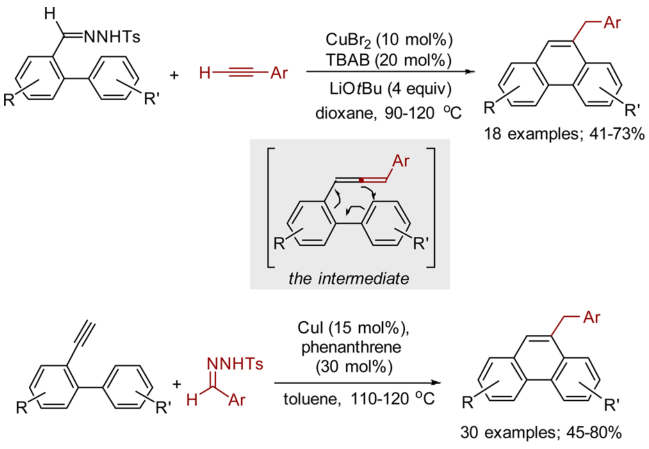
Received: July 6, 2014

Scheme 2. Cu(I)-Catalyzed Synthesis of Allenes



reaction conditions, we further developed a straightforward synthesis of benzofurans and indoles by introducing nucleophiles such as −OH and $-NH_2$ into the substrates.[12a] To further explore this coupling reaction, we conceived that the allene moiety generated from the Cu(I)-catalyzed coupling of *N*-tosylhydrazones with terminal alkynes may participate in a 6*π* cycloaddition−isomerization process to afford phenanthrenes (Scheme 3). We have previously communicated preliminary results on the synthesis of phenanthrenes by a $CuBr_2$-catalyzed coupling−cyclization cascade with terminal alkynes and *N*-tosylhydrazones derived from *o*-formyl biphenyls as the starting materials.[12b] Herein we report the details of this reaction and the further expansion of this transformation by using 2-alkynyl biphenyls and *N*-tosylhydrazones derived from aromatic aldehydes as the starting materials.

Scheme 3. Synthesis of Phenanthrenes through Copper-Catalyzed Cross-Coupling of *N*-Tosylhydrazones and Terminal Alkynes

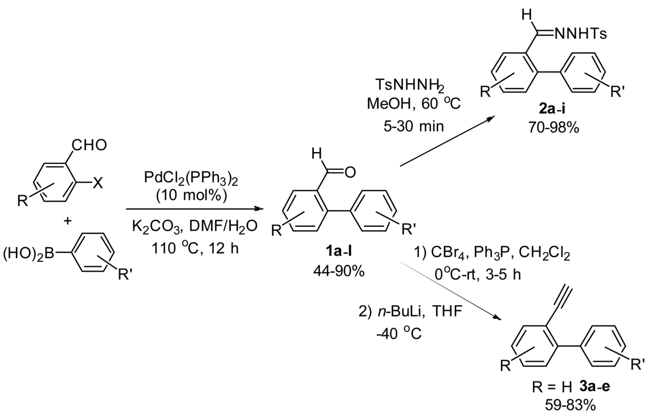


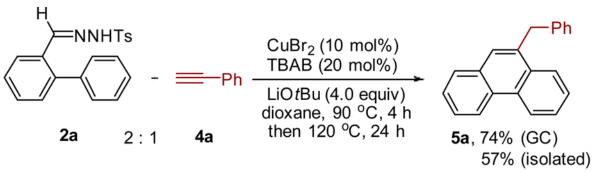
RESULTS AND DISCUSSION

As outlined in Scheme 4, *N*-tosylhydrazones **2a−i** and alkynes **3a−e** can be readily synthesized in excellent yields by a two-step transformation. Suzuki−Miyaura cross-coupling of the commercially available *α*-formyl aryl halide and arylboronic acid starting materials afforded formyl biphenyls **1a−l** in good yields. Treatment of formyl biphenyls **1a−i** with $TsNHNH_2$ in MeOH at 60 °C for 5−30 min afforded the desired *N*-tosylhydrazones **2a−i** as precipitates that could be readily separated by simple filtration. On the other hand, submitting the formyl biphenyls to the Corey−Fuchs reaction gave alkynyl biphenyls **3a−e** in good yields.

The copper-catalyzed phenanthrene synthesis was first studied by using *N*-tosylhydrazone **2a** and ethynylbenzene (**4a**) as the model substrates. Screening of the reaction conditions by inspection of the copper catalyst, the base, the additive, and the substrate ratio resulted in the optimized conditions, which can be summarized as follows: 2:1 substrate ratio (**2a**:**4a**), 10 mol % $CuBr_2$, LiO*t*Bu (4.0 equiv), and 20 mol % tetrabutylammonium bromide (TBAB) in dioxane at 90 °C for 4 h and then at 120 °C for 24 h.[12b] Under such conditions, **5a** was isolated in 74% GC yield and 57% isolated yield (eq 1).

Scheme 4. Synthesis of *N*-Tosylhydrazones 2a−i and Alkynes 3a−e





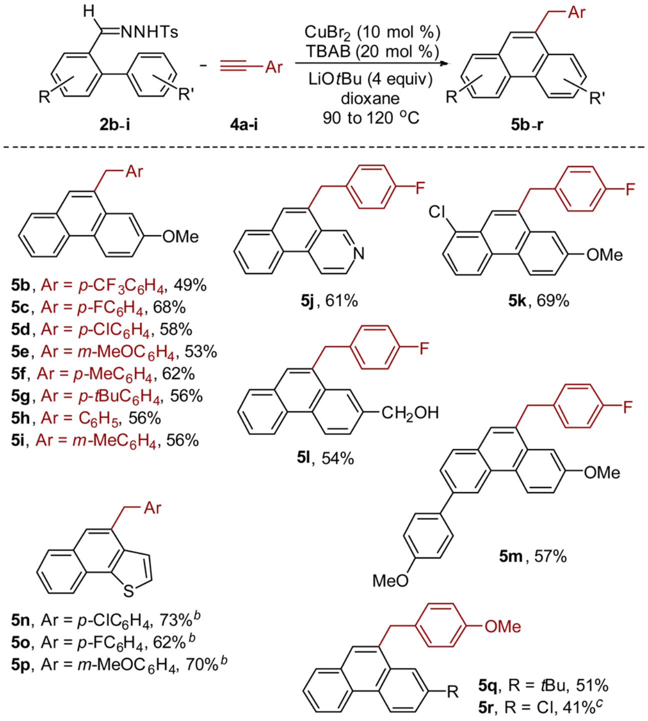
(1)

Subsequently, the scope of the reaction with a series of *N*-tosylhydrazones **2b−i** and alkynes **4a−i** was investigated under the optimized reaction conditions. As shown in Scheme 5, substituents on the aromatic ring of the alkyne do not show a significant effect on the reaction. Both electron-donating and electron-withdrawing groups, including methoxy, alkyl, halogen, and trifluoromethyl substituents, are compatible with the reaction, giving the corresponding phenanthrenes in moderately high yields. In addition, the reaction with a series of *N*-tosylhydrazones bearing a substituted phenyl ring or heteroaromatic ring also proceeded smoothly, affording the corresponding phenanthrenes in comparable yields.

Encouraged by the above results, we proceeded to study the copper-catalyzed coupling reaction using *N*-tosylhydrazones derived from aromatic aldehydes and 2-alkynyl biphenyls as the starting materials. We initially performed the experiment using CuI as the catalyst and 2-ethynylbiphenyl (**3a**) and *N*-tosylhydrazone **6** as the model substrates in the presence of LiO*t*Bu (Table 1). The reaction gave the expected phenanthrene product in 25% yield together with allene **5a′** (15%) and the recovery of significant amount of alkyne. When the reaction time was prolonged to 24 h and the temperature was raised to 120 °C, the allene byproduct was not observed, and the desired phenanthrene **5a** was obtained in 40% yield with the recovery of a small amount of alkyne **3a** (Table 1, entry 1). A study of the solvent effect indicated that toluene gave comparable results while DMF was less effective (entries 2 and 3).

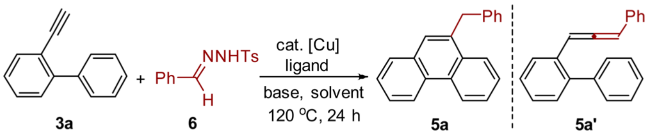
To fully convert the alkyne substrate in this reaction, some ligands were next examined, and phenanthrolines were found to be effective, affording the product in improved yield (Table 1, entries 4−7). With 3,4,7,8-tetramethyl-1,10-phenanthroline (L3) as the optimal ligand, a series of copper catalysts were

Scheme 5. Substrate Scope with *N*-Tosylhydrazones **2b−i** and Alkynes **4a−i**[a]



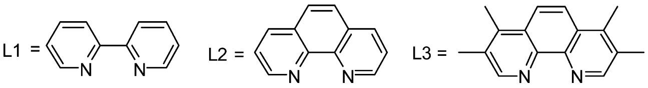
[a]Reaction conditions: *N*-tosylhydrazone **2b−i** (0.8 mmol), alkyne **4a−i** (0.4 mmol), $CuBr_2$ (10 mol %), TBAB (20 mol %), and LiO*t*Bu (1.6 mmol) in dioxane (4 mL) at 90 °C for 4 h and then at 120 °C for 24 h. Yields of products isolated by silica gel column chromatography are shown. [b]The reaction was carried out at 90 °C for 4 h and then at 120 °C for 36 h. [c]20% of the starting alkyne was recovered.

Table 1. Optimization of the Reaction Conditions with Phenylacetylene **3a** and *N*-Tosylhydrazone **6**[a]



entry	catalyst	ligand	base	solvent	yield of **5a** (%)[b]
1	CuI	none	LiO*t*Bu	dioxane	40
2	CuI	none	LiO*t*Bu	toluene	42
3	CuI	none	LiO*t*Bu	DMF	29
4	CuI	PPh_3	LiO*t*Bu	toluene	51
5	CuI	L1	LiO*t*Bu	toluene	48
6	CuI	L2	LiO*t*Bu	toluene	62
7	**CuI**	**L3**	**LiO*t*Bu**	**toluene**	**64 (55)**[c]
8	$Cu(MeCN)_4PF_6$	L3	LiO*t*Bu	toluene	52
9	CuBr	L3	LiO*t*Bu	toluene	58
10	CuCl	L3	LiO*t*Bu	toluene	46
11	$CuOTf{\cdot}C_6H_6$	L3	LiO*t*Bu	toluene	25
12	$CuBr_2$	L3	LiO*t*Bu	toluene	60
13	$Cu(OTf)_2$	L3	LiO*t*Bu	toluene	35
14	CuI	L3	NaH	toluene	47
15	CuI	L3	KOH	toluene	25
16	CuI	L3	Cs_2CO_3	toluene	21

[a]Reaction conditions: **3a** (0.2 mmol), **6** (0.5 mmol), base (4.5 equiv), copper catalyst (15 mol %), and ligand (30 mol %) in the solvent solvents (1.5 mL). [b]Isolated yields by silica gel column chromatography. [c]The yield in the parentheses refers to the scale-up reaction with 5 mmol alkyne **3a**.



investigated (entries 7−13), and the CuI was found to be the most effective (entry 7). Notably, $CuBr_2$ also afforded the product **5a** in comparable yield (entry 12), but allene **5a′** was isolated as a byproduct.

Subsequently, we examined the effect of the base. A series of bases including NaH, KOH, and Cs_2CO_3 were examined, but they were all found to be less efficient than LiO*t*Bu (Table 1, entries 14−16). We also studied the effects of phase-transfer catalysts, including TBAB, TBAI (n-Bu_4NI), and TBAC (n-Bu_4NCl). The reactions also proceeded in the presence of these additives; however, no distinguishable effect was noticed. Finally, under the optimized conditions (entry 7), a gram-scale experiment was carried out and afforded the product in 55% yield.

Following the optimization of the reaction conditions, the scope of the reaction was then studied with a series of *N*-tosylhydrazones (**7a−s**) and alkynes (**3a−e**). The results are collected in Table 2 and Scheme 6. First of all, the reaction was not significantly affected by substituents on the aromatic ring of the *N*-tosylhydrazone (Table 2). Substrates possessing either electron-donating groups (entries 1−3, 9, and 12) or electron-withdrawing groups (entries 4−8, 10, and 11) all reacted smoothly. The aromatic tosylhydrazones bearing various substituents, including alkyloxy, allyloxy, alkyl, halogen, and trifluoromethyl groups, reacted efficiently to afford the corresponding phenanthrenes in moderately good yields. Tosylhydrazones possessing heterocycles, including pyridine and thiophene, also gave the corresponding phenanthrene products in moderate yields (entries 18 and 19). However, the reaction of aliphatic tosylhydrazones with alkynes resulted in mixtures of allenes (as major products) and phenanthrenes (as minor products).

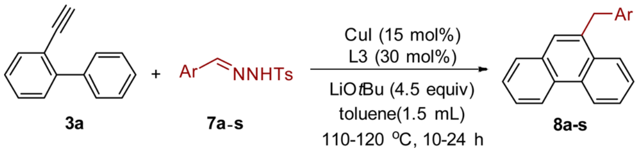
Next, the scope of alkynes was explored. Under the optimized reaction conditions, alkynes possessing alkyl, alkoxy, and thioalkyl substituents on the aromatic ring (**3b−e**) were used as the substrates for the reaction with aromatic tosylhydrazones (Scheme 6). The reactions all proceeded smoothly, giving the corresponding phenanthrenes in moderate yields with good functional group tolerance. For the reactions with 2-ethynyl-3′-methoxy-1,1′-biphenyl (**3c**) and (2′-ethynyl-[1,1′-biphenyl]-3-yl)(methyl)sulfane (**3d**), the cyclization occurred exclusively at the sterically favored position to give the corresponding products **9d−f** and **9g−i**. The structure of one of the phenanthrene products, **9g**, was confirmed by X-ray crystallography (see the Supporting Information).

Since the transformation of aldehydes to the corresponding tosylhydrazones is highly efficient, a one-pot process starting directly from the aldehydes was then carried out. The one-pot procedure afforded similar results as the stepwise transformation (Scheme 7). This result considerably simplifies the preparation of phenanthrenes by this coupling reaction.

■ CONCLUSION

A convenient and highly efficient synthetic approach for phenanthrene derivatives has been developed. The reaction employs readily available *N*-tosylhydrazones and terminal alkynes as the staring materials. Mechanistically, the reaction

Table 2. Substrate Scope of N-Tosylhydrazones[a]



entry	7, Ar	8, yield (%)[b]
1	**7a**, *m*-MeC_6H_4	**8a**, 62
2	**7b**, *p*-MeC_6H_4	**8b**, 74
3	**7c**, *p*-$tBuC_6H_4$	**8c**, 65
4	**7d**, *p*-BrC_6H_4	**8d**, 59
5	**7e**, *m*-BrC_6H_4	**8e**, 70
6	**7f**, *p*-ClC_6H_4	**8f**, 65
7	**7g**, *p*-FC_6H_4	**8g**, 67
8	**7h**, *p*-NCC_6H_4	**8h**, 61
9	**7i**, *p*-$MeOC_6H_4$	**8i**, 71
10	**7j**, *p*-$F_3CC_6H_4$	**8j**, 80
11	**7k**, *m*-$O_2NC_6H_4$	**8k**, 48[c]
12	**7l**, *p*-$Me_2NC_6H_4$	**8l**, 53
13	**7m**, *m,p*-$Cl_2C_6H_3$	**8m**, 66
14	**7n**, *m,m*-$(MeO)_2C_6H_3$	**8n**, 60
15	**7o**, *o*-Cl-*p*-$F_3CC_6H_3$	**8o**, 69 (59)[d]
16	**7p**, *o*-alloxy-C_6H_4	**8p**, 70
17	**7q**, *m,p*-$(OCH_2O)C_6H_3$	**8q**, 63
18	**7r**, 2-thiophenyl	**8r**, 54
19	**7s**, 3-pyridinyl	**8s**, 72

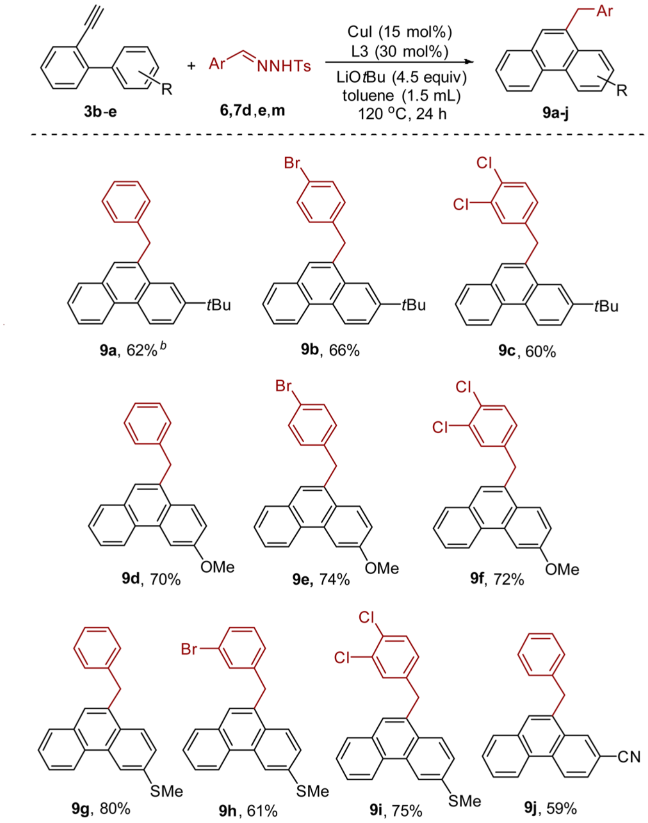
[a] Reaction conditions: alkyne **3a** (0.2 mmol), *N*-tosylhydrazone **7a−s** (2.5 equiv), CuI (15 mol %), L3 (30 mol %), and LiO*t*Bu (4.5 equiv) in toluene (1.5 mL) at 120 °C for 24 h. [b] Yields of products isolated by silica gel column chromatography. [c] The reaction was carried out at 110 °C for 10 h. [d] The yield in parentheses refers to the scaled-up reaction with 5 mmol of alkyne.

involves a cascade of CuI-catalyzed coupling−allenylation−six-π-electron cyclization−aromatization. This method has the following advantages: (1) easy preparation of the *N*-tosylhydrazone starting materials from the corresponding readily available aromatic aldehydes; (2) the use of an inexpensive copper catalyst; (3) easy operation and good functional group tolerance. With these advantages, we expect that this new protocol for phenanthrene synthesis will find wide applications in organic synthesis and related areas.

■ EXPERIMENTAL SECTION

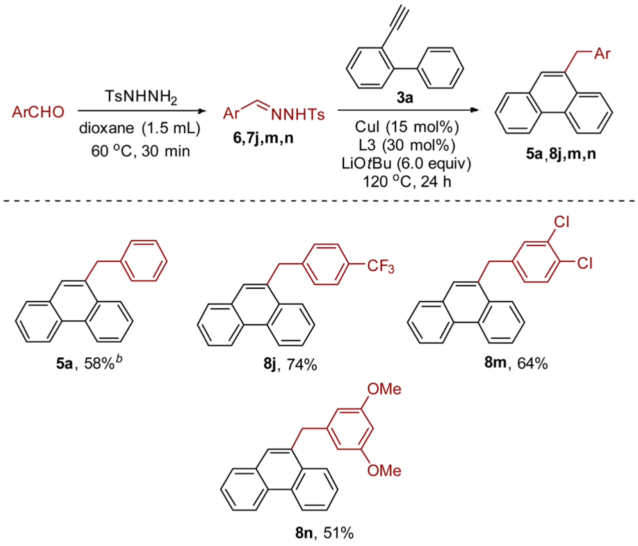
General Methods. Except for the scale-up experiments, all of the reactions were performed under a nitrogen atmosphere in a 20 mL Schlenk tube. For the scale-up experiments, the reactions were carried out in round-bottom flask. Dioxane was dried over Na before use. For chromatographic purification, 200−300 mesh silica gel was employed. Chemical shifts for ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra are reported relative to the chemical shift of tetramethylsilane (TMS). IR spectra are reported in wavenumbers (cm^{-1}). For HRMS measurements, the mass analyzer was an FT-ICR instrument. *N*-Tosylhydrazones **2a−i**, **6**, and **7a−s** were prepared according to the literature procedure.[13] Unless otherwise noted, materials purchased from commercial suppliers were used as received without further purification.

Scheme 6. Substrate Scope of Alkynes[a]



[a] Reaction conditions: alkyne **3b−e** (0.2 mmol), *N*-tosylhydrazone **6**, **7d**, **7e**, or **7m** (2.8 equiv), CuI (15 mol %), L3 (30 mol %), and LiO*t*Bu (4.5 equiv) in toluene (1.5 mL) at 120 °C for 24 h. [b] Yields of products isolated by silica gel column chromatography are shown.

Scheme 7. One-Pot Preparation of Phenanthrenes[a]



[a] Reaction conditions: aldehyde (2.5 equiv), $TsNHNH_2$ (2.5 equiv), alkyne (0.2 mmol), CuI (15 mol %), L3 (30 mol %), and LiO*t*Bu (6.0 equiv) in dioxane (1.5 mL) at 120 °C for 24 h. [b] Yields of products isolated by silica gel column chromatography are shown.

General Experimental Procedure for the Preparation of 1a−l by Suzuki−Miyaura Cross-Coupling. Under a nitrogen atmosphere, α-formyl aryl halide (10 mmol), arylboronic acid (12 mmol), K_2CO_3 (30 mmol), and $PdCl_2(PPh_3)_2$ (5 mol %, 350 mg) were suspended in DMF/H_2O (15 mL/1.5 mL). The resulting solution was stirred at 110 °C for 12 h. After cooling to room temperature, the reaction mixture was filtered through a short path of silica gel. The mixture was extracted with EtOAc/Et_2O (1:1) several times. The combined organic layers were washed with saturated NaCl three times and dried over anhydrous $MgSO_4$. The reaction mixture was then concentrated under vacuum, and the crude residue was purified by silica gel column chromatography (petroleum ether/EtOAc) to afford the coupling product.

*Biphenyl-2-carbaldehyde (**1a**).*[14] Colorless liquid (910 mg, 50%); R_f = 0.5 (petroleum ether/EtOAc = 30:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.98 (s, 1H), 8.02 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.62 (dt, *J* = 7.6, 1.2 Hz, 1H), 7.42−7.50 (m, 6H), 7.36−7.38 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.3, 145.9, 133.7, 133.6, 133.5, 130.7, 130.0, 128.3, 128.0, 127.7, 127.5.

*4′-tert-Butylbiphenyl-2-carbaldehyde (**1b**).*[15] Colorless liquid (1.53 g, 64%); R_f = 0.55 (petroleum ether/EtOAc = 30:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.90 (s, 1H), 7.90 (d, *J* = 7.6 Hz, 1H), 7.47−7.50 (m, 1H), 7.36−7.38 (m, 2H), 7.31−7.33 (m, 2H), 7.18−7.20 (m, 2H), 1.26 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.5, 151.1, 145.9, 134.6, 133.7, 133.4, 130.7, 129.8, 127.4, 127.4, 125.3, 34.6, 31.2.

*2,4-Bis(4′-methoxyphenyl)benzaldehyde (**1c**).* White powder (1.75 g, 55%); mp 101−102 °C; R_f = 0.35 (petroleum ether/EtOAc = 10:1); IR (film) 2917, 2848, 1682, 1597, 1517, 1251, 1177, 1028, 824, 730, 676 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.00 (s, 1H), 8.06 (d, *J* = 8.4 Hz, 1H), 7.60−7.66 (m, 4H), 7.36 (d, *J* = 8.4 Hz, 2H), 7.01 (t, *J* = 8.4 Hz, 4H), 3.88 (s, 3H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.2, 160.1, 159.7, 146.2, 145.8, 132.0, 131.9, 131.2, 130.2, 128.7, 128.5, 128.3, 125.5, 114.4, 113.9, 55.4, 55.3; EI-MS *m*/*z* (relative intensity) 319 [(M + H)$^+$, 35], 318 (M$^+$, 100), 303 (16), 287 (26), 275 (27), 259 (9), 247 (15), 231 (14), 215 (22), 202 (28), 189 (9), 182 (22), 159 (8), 139 (12), 132 (10), 84 (8), 72 (7), 59 (13), 43 (40); HRMS (ESI) calcd for $C_{21}H_{19}O_3$ [(M + H)$^+$] 319.1329, found 319.1330.

*4′-Methoxybiphenyl-2-carbaldehyde (**1d**).*[16] White powder (1.51 g, 71%); mp 51−52 °C; R_f = 0.5 (petroleum ether/EtOAc = 30:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.0 (s, 1H), 7.99 (d, *J* = 7.6 Hz, 1H), 7.60 (dt, *J* = 7.6, 1.2 Hz, 1H), 7.40−7.46 (m, 2H), 7.29 (d, *J* = 7.6 Hz, 2H), 6.99 (d, *J* = 8.4 Hz, 2H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.5, 159.6, 145.5, 133.6, 133.4, 131.2, 130.7, 129.9, 127.5, 127.2, 113.8, 55.2.

*3-Chloro-4′-methoxybiphenyl-2-carbaldehyde (**1e**).* Greenish liquid (1.09 g, 44%); R_f = 0.5 (petroleum ether/EtOAc = 10:1); IR (film) 2961, 2916, 1698, 1607, 1513, 1249, 1179, 1049, 1025, 836, 794, 663 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.0 (s, 1H), 7.45−7.46 (m, 2H), 7.31 (dd, *J* = 6.4, 2.4 Hz, 1H), 7.22−7.26 (m, 3H), 6.97 (d, *J* = 8.8 Hz, 2H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.3, 158.8, 145.3, 133.2, 131.6, 130.9, 129.9, 129.0, 128.7, 128.5, 113.0, 54.3; EI-MS *m*/*z* (relative intensity) 248 (M$^+$, ^{37}Cl, 90), 246 (M$^+$, 90), 231 (12), 215 (28), 203 (30), 183 (18), 175 (45), 168 (33), 152 (27), 140 (33), 139 (100), 115 (14), 84 (28), 75 (8), 63 (12), 58 (22), 43 (84); HRMS (ESI) calcd for $C_{14}H_{12}ClO_2$ [(M + H)$^+$] 247.0520, found 247.0514.

*2-(Thiophen-2-yl)benzaldehyde (**1f**).*[17] Colorless liquid (1.13 g, 60%); R_f = 0.4 (petroleum ether/EtOAc = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.18 (s, 1H), 8.00 (d, *J* = 7.6 Hz, 1H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.50−7.55 (m, 3H), 7.14−7.16 (m, 1H), 7.07−7.08 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.1, 133.5, 133.4, 131.3, 129.5, 128.8, 128.5, 128.2, 127.8, 127.3.

*4′-Chlorobiphenyl-2-carbaldehyde (**1g**).*[17] Colorless liquid (1.58 g, 73%); R_f = 0.3 (petroleum ether/EtOAc = 60:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.96 (s, 1H), 8.02 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.64 (dt, *J* = 7.6, 1.2 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.39−7.45 (m, 3H), 7.30−7.32 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.8, 144.4, 136.2, 134.4, 133.6, 133.6, 131.2, 130.6, 128.6, 128.1, 127.8.

*4′-(Hydroxymethyl)biphenyl-2-carbaldehyde (**1h**).*[18] Colorless liquid (1.28 g, 60%); R_f = 0.2 (petroleum ether/EtOAc = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.96 (s, 1H), 8.02 (d, *J* = 8.0 Hz, 1H), 7.62−7.65 (dt, *J* = 7.6, 0.8 Hz, 1H), 7.42−7.48 (m, 2H), 7.35−7.37 (m, 2H), 4.78 (s, 2H), 2.34 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.4, 145.6, 140.9, 136.9, 133.6, 133.6 (peak overlaps), 130.7, 130.2, 127.7, 127.6 (peak overlaps), 126.9, 64.7.

*2-(Pyridin-4-yl)benzaldehyde (**1i**).*[19] Solid powder (1.17 g, 64%); mp 67−68 °C; R_f = 0.2 (petroleum ether/EtOAc = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.98 (s, 1H), 8.72−8.73 (d, *J* = 6.0 Hz, 2H), 8.07 (d, *J* = 7.6 Hz, 1H), 7.71 (dt, *J* = 7.6, 1.6 Hz, 1H), 7.59 (t, *J* = 7.6 Hz, 1H), 7.43 (d, *J* = 7.6 Hz, 1H), 7.32−7.34 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.1, 149.8, 145.8, 142.7, 133.9, 133.4, 130.3, 129.0, 128.4, 124.7.

*3′-Methoxybiphenyl-2-carbaldehyde (**1j**).*[6c] Colorless liquid (1.90 g, 90%); R_f = 0.43 (petroleum ether/EtOAc = 100:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.99 (s, 1H), 8.01 (dd, *J* = 0.9, 7.8 Hz, 1H), 7.62 (dt, *J* = 1.3, 7.5 Hz, 1H), 7.44−7.50 (m, 2H), 7.37 (t, *J* = 7.9 Hz, 1H), 6.92−6.99 (m, 3H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.3, 159.5, 145.8, 139.1, 133.7, 133.4, 130.5, 129.4, 127.8, 127.4, 122.7, 115.6, 113.6, 55.3.

*3′-(Methylthio)biphenyl-2-carbaldehyde (**1k**).* Colorless liquid (1.73 g, 76%); R_f = 0.45 (petroleum ether/EtOAc = 100:1); IR (film) 3052, 2919, 2846, 1692, 1597, 1258, 1195, 1022, 909, 962, 654 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.98 (s, 1H), 8.02 (dd, *J* = 0.9, 7.8 Hz, 1H), 7.63 (dt, *J* = 1.3, 7.5 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 1H), 7.43 (d, *J* = 7.6 Hz, 1H), 7.37 (t, *J* = 7.6 Hz, 1H), 7.31 (d, *J* = 8.1 Hz, 1H), 7.24 (s, 1H), 7.12 (d, *J* = 7.4 Hz, 1H), 2.50 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.1, 145.3, 139.2, 138.4, 133.7, 133.5, 130.6, 128.6, 127.9, 127.5, 127.4, 126.7, 125.8, 15.5; EI-MS *m*/*z* (relative intensity) 228 (M$^+$, 100), 213 (5), 200 (30), 181 (35), 167 (30), 152 (70), 139 (10), 115 (8); HRMS (ESI) calcd for $C_{14}H_{12}OSNa$ [(M + Na)$^+$] 251.0501, found 251.0500.

*2′-Formylbiphenyl-4-carbonitrile (**1l**).*[20] White powder (1.65 g, 80%); mp 98−99 °C; R_f = 0.40 (petroleum ether/EtOAc = 100:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.95 (s, 1H), 8.05 (d, *J* = 7.7 Hz, 1H), 7.78 (d, *J* = 8.1 Hz, 2H), 7.70 (dt, *J* = 1.2, 7.5 Hz, 1H), 7.59 (t, *J* = 7.6 Hz, 1H), 7.51 (d, *J* = 8.1 Hz, 2H), 7.42 (d, *J* = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.1, 143.4, 142.7, 133.8, 133.5, 132.1, 130.6, 130.5, 128.9, 128.6, 118.4, 112.0.

General Procedure for the Preparation of *N*-Tosylhydrazones 2a−i. A solution of $TsNHNH_2$ (5 mmol) in methanol (5 mL) was stirred and heated to 60 °C until the $TsNHNH_2$ was completely dissolved. Then the aldehyde **1a**−**i** was dropped into the solution slowly. After approximately 5−30 min, the crude product was obtained as a precipitate. The precipitate was washed with petroleum ether and then dried in vacuo to afford the pure product. The reaction provided *N*-tosylhydrazones **2a**−**i** in 70−99% yield.

*N′-(Biphenyl-2-ylmethylene)-4-methylbenzenesulfonohydrazide (**2a**).*[21] White powder (1.72 g, 98%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.82−7.84 (d, *J* = 8.4 Hz, 2H), 7.79 (s, 1H), 7.68 (s, 1H), 7.25−7.43 (m, 8H), 7.17−7.20 (m, 2H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.9, 144.2, 142.4, 139.1, 135.3, 130.5, 130.1, 129.7, 129.6, 128.3, 127.9, 127.6, 127.6, 126.3, 21.6.

*N′-((4′-tert-Butylbiphenyl-2-yl)methylene)-4-methylbenzenesulfonohydrazide (**2b**).* White powder (1.95 g, 96%); mp 138−139 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93−7.96 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.83−7.85 (d, *J* = 8.4 Hz, 2H), 7.79 (s, 1H), 7.72 (s, 1H), 7.37−7.41 (m, 3H), 7.26−7.35 (m, 4H), 7.12−7.14 (d, *J* = 8.4 Hz, 2H), 2.41 (s, 3H), 1.35 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.6, 147.2, 144.1, 142.3, 136.1, 135.4, 130.5, 130.1, 130.0, 129.6, 129.4, 127.9, 127.4, 126.2, 125.3, 34.6, 31.3, 21.6; IR (film) 3196, 2962, 1703, 1363, 1167, 1049, 945, 813, 678, 667 cm^{-1}; EI-MS *m*/*z* (relative intensity) 236 (M$^+$, 6), 222 (28), 207 (78), 179 (36), 165 (64), 152 (12), 139 (16), 124 (12), 107 (10), 91 (75), 65 (36), 57 (100); HRMS (ESI) calcd for $C_{24}H_{27}N_2O_2S$ [(M + H)$^+$] 407.1788, found 407.1793.

*4-Methyl-N′-(2,4-bis(4′-methoxyphenyl)phenylmethylene)-benzenesulfonohydrazide (**2c**).* White powder (2.19 g, 90%); mp 112−113 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.4 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 3H), 7.73 (s, 1H), 7.51−7.55 (m, 3H), 7.44−7.44 (d, *J* = 1.6 Hz, 1H), 7.31 (d, *J* = 8.4 Hz, 2H), 7.16 (d, *J* = 8.4 Hz, 2H), 6.92−6.97 (m, 4H), 3.84 (s, 6H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6, 159.3, 147.3, 144.1, 142.6, 142.3, 135.4, 132.5, 131.5, 130.8, 129.6, 128.9, 128.2, 128.1, 127.9, 126.8, 125.5, 114.3, 113.8, 60.4, 55.3, 21.6; IR (film) 2923, 1681, 1597, 1517, 1250, 1167, 1029, 824, 704, 661 cm^{-1}; EI-MS *m*/*z* (relative intensity) 486 (M$^+$, 8), 320 (6), 303 (100), 287 (38), 272 (14), 259 (12), 228 (14), 215 (24), 189 (8), 165 (6), 156 (16), 139 (22), 108 (8), 91 (78), 65 (42); HRMS (ESI) calcd for $C_{28}H_{27}N_2O_4S$ [(M + H)$^+$] 487.1686, found 487.1676.

*N′-((4′-Methoxybiphenyl-2-yl)methylene)-4-methylbenzenesulfonohydrazide (**2d**).* White powder (1.7 g, 89%); mp 144−145 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.6 Hz, 1H), 7.83−7.86 (m, 3H), 7.71 (s, 1H), 7.24−7.40 (m, 5H), 7.11 (d, *J* = 8.4 Hz, 2H), 6.90 (d, *J* = 8.4 Hz, 2H), 3.82 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3, 147.5, 144.3, 142.2, 135.5, 131.6, 131.0, 130.7, 130.3, 130.2, 129.8, 128.1, 127.4, 126.5, 114.0, 55.5, 21.7; IR (film) 3192, 1701, 1514, 1246, 1166, 1036, 943, 883, 764, 664 cm^{-1}; EI-MS *m/z* (relative intensity) 380 (M^+, 14), 225 (10), 210 (10), 196 (100), 181 (88), 165 (48), 153 (92), 139 (22), 124 (14), 115 (12), 91 (74), 77 (22), 65 (38); HRMS (ESI) calcd for $C_{21}H_{21}N_2O_3S$ [$(M + H)^+$] 381.1267, found 381.1268.

*N′-((3-Chloro-4′-methoxybiphenyl-2-yl)methylene)-4-methylbenzenesulfonohydrazide (**2e**).* White powder (1.45 g, 70%); mp 53−54 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.74 (d, *J* = 8.0 Hz, 2H), 7.64 (s, 1H), 7.26−7.29 (m, 4H), 7.16 (d, *J* = 7.6 Hz, 1H), 7.08 (d, *J* = 8.4 Hz, 2H), 6.82 (d, *J* = 8.4 Hz, 2H), 3.81 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3, 145.3, 144.2, 144.0, 135.6, 133.9, 131.7, 130.9, 129.9, 129.6, 129.4, 129.1, 129.0, 128.2, 113.8, 55.4, 21.7; IR (film) 3196, 2924, 1608, 1514, 1441, 1247, 1155, 1047, 813, 678 cm^{-1}; EI-MS *m/z* (relative intensity) 414 (M^+, 18), 386 (6), 259 (8), 233 (28), 231 (96), 215 (36), 196 (100), 181 (24), 152 (42), 139 (8), 91 (24), 65 (10); HRMS (ESI) calcd for $C_{21}H_{20}ClN_2O_3S$ [$(M + H)^+$] 415.0878, found 415.0886.

*4-Methyl-N′-(2-(thiophen-2-yl)benzylidene)benzenesulfonohydrazide (**2f**).* White powder (1.51 g, 85%); mp 139−140 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.90−7.92 (m, 2H), 7.84−7.86 (d, *J* = 8.0 Hz, 2H), 7.30−7.38 (m, 6H), 7.03−7.06 (m, 1H), 6.85−6.86 (d, *J* = 7.2 Hz, 1H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.7, 144.2, 140.2, 135.3, 134.6, 131.3, 130.8, 130.0, 129.7, 128.2, 128.1, 127.9, 127.5, 126.7, 126.5, 21.6; IR (film) 3194, 2925, 1596, 1448, 1324, 1166, 943, 762, 665 cm^{-1}; EI-MS *m/z* (relative intensity) 355 (M^+, 12), 201 (18), 185 (12), 171 (100), 156 (6), 139 (12), 129 (12), 115 (8), 91 (22); HRMS (ESI) calcd for $C_{18}H_{17}N_2O_2S_2$ [$(M + H)^+$] 357.0726, found 357.0733.

*N′-((4′-Chlorobiphenyl-2-yl)methylene)-4-methylbenzenesulfonohydrazide (**2g**).* Brown powder (1.5 g, 78%); mp 135−136 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.91−7.93 (m, 1H), 7.82 (d, *J* = 8.0 Hz, 2H), 7.69 (s, 1H), 7.29−7.41 (m, 6H), 7.21−7.23 (m, 1H), 7.10−7.13 (m, 2H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.5, 144.2, 141.0, 137.5, 135.2, 133.8, 130.9, 130.6, 130.1, 129.9, 129.6, 128.5, 128.3, 127.9, 126.4, 21.6; IR (film) 3187, 2924, 1596, 1361, 1317, 1163, 1090, 946, 814, 672 cm^{-1}; EI-MS *m/z* (relative intensity) 386 (M^+, ^{37}Cl, 4), 384 (M^+, 6), 269 (12), 267 (22), 252 (4), 229 (12), 212 (10), 199 (16), 194 (10), 165 (100), 163 (20), 139 (24), 124 (8), 107 (12), 91 (82), 84 (18), 65 (39); HRMS (ESI) calcd for $C_{20}H_{18}ClN_2O_2S$ [$(M + H)^+$] 385.0772, found 385.0775.

*N′-((4′-(Hydroxymethyl)biphenyl-2-yl)methylene)-4-methylbenzenesulfonohydrazide (**2h**).* Brown powder (1.65 g, 87%); mp 70−71 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (s, 1H), 7.94−7.96 (m, 1H), 7.83 (d, *J* = 8.0 Hz, 2H), 7.67 (s, 1H), 7.25−7.40 (m, 7H), 7.16 (d, *J* = 8.0 Hz, 2H), 4.68 (d, 2H), 2.40 (s, 3H), 1.80 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.9, 144.1, 142.0, 140.1, 138.5, 135.4, 130.7, 130.0, 129.9, 129.6, 128.2, 127.9, 127.7, 127.1, 126.2, 64.8, 21.6; IR (film) 3199, 2922, 1596, 1326, 1165, 1043, 813, 663 cm^{-1}; EI-MS *m/z* (relative intensity) 380 (M^+, 8), 214 (6), 212 (6), 196 (30), 179 (26), 167 (100), 152 (36), 139 (24), 124 (8), 107 (8), 93 (6), 91 (72), 77 (22), 65 (46); HRMS (ESI) calcd for $C_{21}H_{21}N_2O_3S$ [$(M + H)^+$] 381.1267, found 381.1275.

*4-Methyl-N′-(2-(pyridin-4-yl)benzylidene)benzenesulfonohydrazide (**2i**).* White powder (1.69 g, 96%); mp 172−173 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.37 (s, 1H), 8.64−8.66 (m, 2H), 7.82−7.84 (m, 2H), 7.73−7.75 (m, 2H), 7.48−7.52 (m, 2H), 7.41−7.43 (m, 2H), 7.34−7.36 (m, 1H), 7.27−7.28 (m, 2H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 149.6, 146.4, 144.9, 143.6, 139.0, 136.1, 130.7, 130.2, 130.0, 129.7, 128.9, 127.2, 125.4, 124.5, 21.0; IR (film) 3147, 2255, 1655, 1049, 1024, 1003, 824, 761, 666 cm^{-1}; EI-MS *m/z* (relative intensity) 351 (M^+, 10), 323 (4), 195 (8), 183 (6), 168 (100), 156 (12), 139 (52), 115 (12), 113 (6), 91 (33), 84 (16); HRMS (ESI) calcd for $C_{19}H_{18}N_3O_2S$ [$(M + H)^+$] 352.1114, found 352.1104.

General Procedure for the Preparation of 3a−e by the Corey−Fuchs Reaction. *First Step.* To a solution of aldehyde (1.0 equiv) and CBr_4 (1.5 equiv) in anhydrous DCM cooled to 0 °C (ice−water bath) was added Ph_3P (3.0 equiv) as a solid in small portions. The resultant light-yellow reaction mixture was then stirred at ambient temperature for 3−5 h. Solvent was removed in vacuo, and the residue was dissolved in petroleum ether/EtOAc (60:1). Triphenylphosphine oxide was filtered off by suction. The filtrate was concentrated under reduced pressure, and the crude *gem*-dibromide was purified by chromatography on silica gel using petroleum ether/EtOAc as the eluent.

Second Step. A well-stirred solution of the *gem*-dibromide (10 mmol) in anhydrous THF was cooled to −40 °C under an argon atmosphere. *n*-BuLi (1.6 M solution in hexanes, 2.05 equiv) was then added dropwise via syringe. The stirring was continued at −40 °C until the reaction was complete as monitored by TLC (2−3 h). After completion of the reaction, the resultant light-yellow/orange mixture was diluted with distilled water, and the stirring was continued for 0.5 h to allow the mixture to slowly reach room temperature. The layers were separated, and the aqueous layer was extracted with Et_2O. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by chromatography on silica gel using petroleum ether/EtOAc as the eluent.

*2-Ethynylbiphenyl (**3a**).*[22] Colorless liquid (1.35 g, 76%); R_f = 0.51 (petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (dd, *J* = 7.5, 13.1 Hz, 1H), 7.36−7.44 (m, 5H), 7.23−7.31 (m, 1H), 3.02 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.4, 140.2, 133.8, 129.6, 129.2, 128.9, 128.0, 127.5, 127.0, 120.4, 83.1, 80.1; IR (film) 3064, 2964, 2360, 1595, 1474, 1449, 1432, 1260, 1017, 800, 759, 699, 658 cm^{-1}.

*4′-(tert-Butyl)-2-ethynylbiphenyl (**3b**).* Colorless liquid (1.7 g, 73%); R_f = 0.55 (petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (s, 1H), 7.62 (d, *J* = 7.6 Hz, 1H), 7.37−7.41 (m, 5H), 7.23−7.31 (m, 1H), 3.03 (s, 1H), 1.36 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.5, 144.9, 139.7, 133.9, 129.6, 128.9, 127.8, 126.9, 126.8, 126.1, 124.3, 120.4, 83.4, 80.0, 34.9, 31.3; IR (film) 3078, 2960, 2362, 1595, 1472, 1364, 1240, 910, 758, 707, 688 cm^{-1}; HRMS (ESI) calcd for $C_{18}H_{19}$ [$(M + H)^+$] 235.1481, found 235.1478.

*2-Ethynyl-3′-methoxybiphenyl (**3c**).*[6c] Colorless liquid (1.73 g, 83%); R_f = 0.41 (petroleum ether/EtOAc = 60:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.6 Hz, 1H), 7.27−7.39 (m, 4H), 7.14−7.16 (m, 2H), 6.92 (dd, *J* = 1.7, 8.3 Hz, 1H), 3.84 (s, 3H), 3.05 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.1, 144.2, 141.6, 133.9, 129.5, 129.0, 128.9, 127.0, 121.7, 120.4, 114.8, 133.3, 83.1, 80.3, 55.3; IR (film) 3060, 2834, 2367, 1604, 1582, 1219, 910, 669, 657 cm^{-1}.

*(2′-Ethynylbiphenyl-3-yl)(methyl)sulfane (**3d**).* Colorless liquid (1.5 g, 67%); R_f = 0.50 (petroleum ether/EtOAc = 100:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.7 Hz, 1H), 7.49 (s, 1H), 7.24−7.40 (m, 6H), 3.05 (s, 1H), 2.51 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.9, 140.8, 138.0, 133.9, 129.5, 129.0, 128.4, 127.3, 127.2, 126.0, 125.8, 120.4, 83.0, 80.4, 15.8; IR (film) 3063, 2926, 2364, 1588, 1465, 1438, 1103, 759, 657 cm^{-1}; HRMS (ESI) calcd for $C_{15}H_{13}S$ [$(M + H)^+$] 225.0732, found 225.0733.

*2′-Ethynylbiphenyl-4-carbonitrile (**3e**).* White powder (1.2 g, 59%); mp 104−105 °C; R_f = 0.48 (petroleum ether/EtOAc = 30:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70−7.63 (m, 5H), 7.45 (t, *J* = 7.3 Hz, 1H), 7.39−7.34 (m, 2H), 3.07 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.8, 142.3, 134.0, 131.8, 129.9, 129.3, 129.2, 128.1, 120.4, 118.8, 111.3, 82.2, 81.0; IR (film) 3072, 2228, 1608, 1476, 841, 761, 733, 655 cm^{-1}; HRMS (ESI) calcd for $C_{15}H_{10}N$ [$(M + H)^+$] 204.0808, found 204.0803.

Typical Procedure for the $CuBr_2$-Catalyzed Coupling of *N*-Tosylhydrazones 2a−i and Terminal Alkynes 4a−i. $CuBr_2$ (10 mol %, 9 mg), LiO*t*Bu (1.6 mmol, 128 mg), TBAB (20 mol %, 26 mg), and *N*-tosylhydrazone **2a** (0.8 mmol, 280 mg) were suspended in dioxane (4 mL) in a 10 mL Schlenk tube under nitrogen. Phenylacetylene (**4a**) (0.4 mmol, 41 mg) was added. The resulting solution was stirred at 90 °C for 4 h, and then the temperature was raised to 120 °C for another 24 h. After cooling to room temperature, the resulting mixture was filtered through a short path of silica gel, eluting with EtOAc. The volatile compounds were removed in vacuo, and the crude residue was purified by column chromatography (SiO_2, hexane) to afford the phenanthrene product **5a**.

9-Benzylphenanthrene (**5a**).[6j] White powder (61 mg, 57%); R_f = 0.75 (petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (d, J = 8.4 Hz, 1H), 8.67 (d, J = 8.0 Hz, 1H), 8.03 (d, J = 8.4 Hz, 1H), 7.81 (d, J = 7.6 Hz, 1H), 7.55−7.63 (m, 4H), 7.32−7.36 (m, 2H), 7.25−7.28 (m, 4H), 4.49 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.2, 140.4, 134.9, 132.0, 131.5, 131.0, 128.7, 128.4, 128.1, 128.1, 126.9, 126.8, 126.4, 126.3, 125.2, 123.3, 122.6, 39.8.

10-(4-(Trifluoromethyl)benzyl)-2-methoxyphenanthrene (**5b**). White powder (72 mg, 49%); R_f = 0.45 (petroleum ether/EtOAc = 30:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, J = 9.2 Hz, 1H), 8.56 (d, J = 8.4 Hz, 1H), 7.79 (d, J = 8.0 Hz, 1H), 7.52−7.60 (m, 3H), 7.19−7.32 (m, 4H), 6.94−6.98 (m, 2H), 4.40 (s, 2H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.2, 135.8, 135.8, 135.7, 134.0, 132.6, 131.0, 130.6, 130.0, 128.2, 127.7 (q, J = 162.5 Hz), 125.5 (q, J = 5.0 Hz, CF_3), 125.1, 124.7, 121.9, 116.1, 115.4, 115.2, 106.2, 55.2, 39.2; IR (film) 2849, 1616, 1508, 1224, 827 cm^{-1}; EI-MS m/z (relative intensity) 316 (100), 299 (6), 283 (16), 270 (8), 221 (5), 141 (4); HRMS (ESI) calcd for $C_{23}H_{17}F_3NaO$ $[(M + Na)^+]$ 389.0760, found 389.0756.

10-(4-Fluorobenzyl)-2-methoxyphenanthrene (**5c**). White powder (86 mg, 68%); R_f = 0.45 (petroleum ether/EtOAc = 30:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (d, J = 8.8 Hz, 1H), 8.55 (d, J = 8.4 Hz, 1H), 7.78−7.79 (d, J = 7.6 Hz, 1H), 7.49−7.61 (m, 4H), 7.18−7.30 (m, 4H), 6.94−6.98 (m, 2H), 4.39 (s, 2H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.4 (d, J = 243.0 Hz), 158.2, 135.8 (d, J = 3.1 Hz), 134.0, 132.5, 130.6, 130.1 (d, J = 7.1 Hz), 128.5, 128.2, 126.5, 126.4, 125.7, 125.1, 124.7, 121.9, 116.1, 115.3 (d, J = 21.0 Hz), 106.1, 55.2, 39.2; IR (film) 1616, 1508, 1042, 823, 749 cm^{-1}; EI-MS m/z (relative intensity) 316 (M$^+$, 100), 283 (21), 270 (10), 71 (11), 57 (16), 43 (16); HRMS (ESI) calcd for $C_{22}H_{18}FO$ $[(M + H)^+]$ 317.1336, found 317.1340.

10-(4-Chlorobenzyl)-2-methoxyphenanthrene (**5d**). White powder (77 mg, 58%); R_f = 0.45 (petroleum ether/EtOAc = 30:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, J = 8.8 Hz, 1H), 8.56 (d, J = 8.0 Hz, 1H), 7.80−7.78 (d, J = 8.0 Hz, 1H), 7.62−7.58 (m, 1H), 7.54−7.50 (m, 2H), 7.29−7.17 (m, 6H), 4.39 (s, 2H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.2, 138.7, 133.6, 132.5, 131.9, 130.6, 130.1, 130.0, 128.6, 128.3, 126.5, 125.8, 125.1, 124.7, 122.0, 116.1, 106.1, 55.3, 39.3; IR (film) 1599, 1488, 1260, 1048, 778, 749 cm^{-1}; EI-MS m/z (relative intensity) 334 (M$^+$, ^{37}Cl, 36), 332 (M$^+$, ^{35}Cl, 100), 281 (10), 266 (9), 265 (13), 252 (12), 126 (13); HRMS (ESI) calcd for $C_{22}H_{18}ClO$ $[(M + H)^+]$ 333.1041, found 333.1044.

2-Methoxy-10-(3-methoxybenzyl)phenanthrene (**5e**). White powder (70 mg, 53%); R_f = 0.35 (petroleum ether/EtOAc = 30:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (d, J = 9.2 Hz, 1H), 8.55 (d, J = 8.4 Hz, 1H), 7.79 (d, J = 7.6 Hz, 1H), 7.60−7.50 (m, 3H), 7.38−7.18 (m, 5H), 6.89−6.73 (m, 3H), 4.40 (s, 2H), 3.83 (s, 3H), 3.72 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8, 158.1, 141.8, 134.1, 132.7, 130.7, 130.0, 129.4, 128.5, 128.3, 126.3, 125.6, 125.1, 124.0, 121.9, 116.1, 114.6, 113.4, 106.2, 55.2, 55.1, 40.1; IR (film) 2971, 1633, 1460, 1058, 762 cm^{-1}; EI-MS m/z (relative intensity) 328 (M$^+$, 100), 262 (62), 252 (8), 213 (11), 176 (6), 126 (10); HRMS (ESI) calcd for $C_{23}H_{21}O_2$ $[(M + H)^+]$ 329.1536, found 329.1540; $C_{23}H_{20}NaO_2$ $[(M + Na)^+]$ 351.1356, found 351.1359.

10-(4-Methylbenzyl)-2-methoxyphenanthrene (**5f**). White powder (77 mg, 62%); R_f = 0.40 (petroleum ether/EtOAc = 30:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (d, J = 9.2 Hz, 1H), 8.55 (d, J = 8.4 Hz, 1H), 7.79 (d, J = 7.6 Hz, 1H), 7.48−7.60 (m, 3H), 7.38 (s, 1H), 7.22−7.25 (m, 1H), 7.15−7.17 (m, 2H), 7.07−7.09 (m, 2H), 4.39 (s, 2H), 3.83 (s, 3H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.1, 137.0, 135.6, 134.5, 132.8, 130.8, 130.0, 129.2, 128.6, 128.3, 128.2, 126.2, 125.6, 125.1, 124.6, 121.9, 116.1, 106.2, 55.2, 39.6, 21.0; IR (film) 1616, 1466, 1225, 1042, 748 cm^{-1}; EI-MS m/z (relative intensity) 312 (M$^+$, 100), 281 (14), 265 (14), 126 (12), 57 (25); HRMS (ESI) calcd for $C_{23}H_{21}O$ $[(M + H)^+]$ 313.1587, found 313.1588.

10-(4-tert-Butylbenzyl)-2-methoxyphenanthrene (**5g**). White powder (79 mg, 56%); R_f = 0.45 (petroleum ether/EtOAc = 30:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (d, J = 9.2 Hz, 1H), 8.54 (d, J = 8.0 Hz, 1H), 7.78 (d, J = 8.0 Hz, 1H), 7.49−7.56 (m, 3H), 7.38 (d, J = 2.4 Hz, 1H), 7.28 (m, 2H), 7.18−7.24 (m, 3H), 4.39 (s, 2H), 3.80 (s, 3H), 1.28 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.1, 149.0, 137.1, 134.4, 132.8, 130.8, 130.0, 128.4, 128.3, 128.2, 126.2, 125.6, 125.4, 125.1, 124.6, 121.9, 116.1, 106.3, 55.2, 39.5, 34.4, 31.4; IR (film) 2960, 1616, 1466, 1042, 748 cm^{-1}; EI-MS m/z (relative intensity) 354 (M$^+$, 100), 239 (24), 297 (8), 2212 (16), 169 (12), 155 (7), 131 (7); HRMS (ESI) calcd for $C_{26}H_{27}O$ $[(M + H)^+]$ 355.2056, found 355.2059; $C_{26}H_{26}NaO$ $[(M + Na)^+]$ 377.1876, found 377.1879.

10-Benzyl-2-methoxyphenanthrene (**5h**). White powder (67 mg, 56%); R_f = 0.5 (petroleum ether/EtOAc = 30:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (d, J = 8.8 Hz, 1H), 8.55 (d, J = 8.4 Hz, 1H), 7.79 (d, J = 7.6 Hz, 1H), 7.60−7.49 (m, 3H), 7.37−7.19 (m, 7H), 4.43 (s, 2H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.1, 140.1, 134.2, 132.7, 130.7, 130.0, 128.7, 128.5, 128.4, 128.2, 126.3, 126.1, 125.6, 125.0, 124.6, 121.9, 116.1, 106.1, 55.2, 40.0; IR (film) 2960, 1616, 1466, 1042, 748 cm^{-1}; EI-MS m/z (relative intensity) 298 (M$^+$, 100), 265 (18), 252 (10), 221 (7), 178 (6), 126 (7); HRMS (ESI) calcd for $C_{22}H_{19}O$ $[(M + H)^+]$ 299.1430, found 299.1434; $C_{22}H_{18}NaO$ $[(M + Na)^+]$ 321.1250, found 321.1254.

10-(3-Methylbenzyl)-2-methoxyphenanthrene (**5i**). White powder (70 mg, 56%); R_f = 0.5 (petroleum ether/EtOAc = 30:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (d, J = 9.2 Hz, 1H), 8.56 (d, J = 8.4 Hz, 1H), 7.80 (d, J = 8.0 Hz, 1H), 7.59−7.51 (m, 3H), 7.39−7.39 (m, 1H), 7.26−7.00 (m, 5H), 4.40 (s, 2H), 3.83 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.1, 140.1, 138.1, 134.4, 132.8, 130.7, 130.0, 129.5, 128.4, 128.4, 128.2, 127.0, 126.3, 125.8, 125.6, 125.1, 124.6, 121.9, 116.1, 106.2, 55.2, 40.0, 21.4; IR (film) 2920, 1615, 1224, 1042, 747 cm^{-1}; EI-MS m/z (relative intensity) 312 (M$^+$, 100), 265 (9), 149 (11), 111 (12), 97 (17), 71 (40), 57 (65); HRMS (ESI) calcd for $C_{23}H_{21}O$ $[(M + H)^+]$ 313.1587, found 313.1589.

5-(4-Fluorobenzyl)benzo[f]isoquinoline (**5j**). Slightly yellow powder (70 mg, 61%); R_f = 0.35 (petroleum ether/EtOAc = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.39 (s, 1H), 8.74 (d, J = 2.4 Hz, 1H), 8.66−8.64 (m, 1H), 8.43 (d, J = 5.2 Hz, 1H), 7.87−7.85 (m, 1H), 7.70−7.68 (m, 2H), 7.58−7.57 (m, 1H), 7.23−7.20 (m, 2H), 6.70−6.96 (m, 2H), 4.52 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.6 (d, J = 243.0 Hz), 149.9, 148.7, 145.0, 135.6, 135.1 (d, J = 3.2 Hz), 134.0, 133.3, 130.2 (d, J = 7.8 Hz), 129.0, 128.9, 128.8, 128.4, 128.1, 126.9, 123.0, 115.5 (d, J = 21.0 Hz), 38.0; IR (film) 1616, 1509, 1224, 829, 750 cm^{-1}; EI-MS m/z (relative intensity) 287 (M$^+$, 100), 257 (6), 192 (7), 142 (11), 109 (10), 57 (9); HRMS (ESI) calcd for $C_{20}H_{15}FN$ $[(M + H)^+]$ 288.1183, found 288.1180.

9-(4-Fluorobenzyl)-1-chloro-7-methoxyphenanthrene (**5k**). White powder (97 mg, 69%); R_f = 0.35 (petroleum ether/EtOAc = 30:1); IR (film) 1614, 1508, 1219, 1043, 790, cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, J = 9.2 Hz, 1H), 8.44 (d, J = 8.4 Hz, 1H), 8.06 (s, 1H), 7.59−7.57 (d, J = 8.0 Hz, 1H), 7.46 (d, J = 7.6 Hz, 1H), 7.28−7.17 (m, 4H), 6.96−6.92 (m, 2H), 4.41 (s, 2H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.4 (d, J = 243 Hz), 158.6, 135.6 (d, J = 3.2 Hz), 135.4, 132.5, 132.3, 131.6, 129.9 (d, J = 7.8 Hz), 127.8, 126.2, 126.1, 125.1, 124.8, 124.1, 120.9, 116.7, 115.3 (d, J = 21.0 Hz), 106.1, 55.2, 39.6; EI-MS m/z (relative intensity) 352 (M$^+$, ^{37}Cl, 33), 350 (M$^+$, ^{35}Cl, 100), 283 (19), 230 (24), 195 (14), 152 (12), 135 (10), 57 (14); HRMS (ESI) calcd for $C_{22}H_{17}ClFO$ $[(M + H)^+]$ 351.0946, found 351.0952.

(10-(4-Fluorobenzyl)phenanthren-2-yl)methanol (**5l**). White powder (68 mg, 54%); R_f = 0.25 (petroleum ether/EtOAc = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (d, J = 8.4 Hz, 1H), 8.64 (d, J = 8.0 Hz, 1H), 7.97 (s, 1H), 7.81−7.79 (d, J = 7.6 Hz, 1H), 7.64−7.51 (m, 4H), 7.22−7.18 (m, 2H), 6.98−6.94 (m, 2H), 4.84 (s, 2H), 4.44 (s, 2H), 1.76 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.4 (d, J = 243 Hz), 139.1, 135.7 (d, J = 3.2 Hz), 134.6, 131.7, 131.2, 130.3, 130.2 (d, J = 7.7 Hz), 129.8, 128.3, 128.1, 126.7, 126.4, 125.3, 123.6, 122.7, 122.5, 115.3 (d, J = 21 Hz), 65.5, 38.7; IR (film) 1603, 1221, 1039, 822, 749

cm^{-1}; EI-MS m/z (relative intensity) 316 (M$^+$, 100), 285 (26), 179 (15), 165 (15), 149 (14), 109 (25), 57 (33); HRMS (ESI) calcd for $C_{22}H_{17}FNaO$ $[(M + Na)^+]$ 339.1156, found 339.1157.

*10-(4-Fluorobenzyl)-2-methoxy-6-(4-methoxyphenyl)-phenanthrene **(5m)**.* White powder (96 mg, 57%); R_f = 0.25 (petroleum ether/EtOAc = 30:1); ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.70−8.68 (m, 2H), 7.84−7.82 (m, 1H), 7.73−7.69 (m, 3H), 7.54 (s, 1H), 7.31−6.94 (m, 9H), 4.40 (s, 2H), 3.88 (s, 3H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 161.4 (d, J = 244 Hz), 159.3, 158.3, 138.9, 135.8 (d, J = 3.2 Hz), 134.2, 133.8, 132.8, 130.3, 130.1 (d, J = 7.8 Hz), 129.4, 128.7, 128.5, 128.2, 125.0, 124.7, 119.8, 116.1, 115.3 (d, J = 21 Hz), 114.3, 106.2, 55.4, 55.2, 39.2; IR (film) 1608, 1247, 1221, 1045, 821 cm^{-1}; EI-MS m/z (relative intensity) 422 (M$^+$, 100), 407 (7), 350 (6), 211 (7), 149 (10), 57 (17); HRMS (ESI) calcd for $C_{29}H_{24}FO_2$ $[(M + H)^+]$ 423.1755, found 423.1763.

*4-(4-Chlorobenzyl)naphtho[1,2-b]thiophene **(5n)**.* White powder (90 mg, 73%); R_f = 0.45 (petroleum ether/EtOAc = 60:1); ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.10 (d, J = 8.0 Hz, 1H), 7.83 (d, J = 7.6 Hz, 1H), 7.54−7.43 (m, 4H), 7.37−7.36 (m, 1H), 7.24−7.22 (m, 2H), 7.15−7.13 (m, 2H), 4.33 (s, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 138.5, 138.0, 137.2, 133.2, 132.0, 131.0, 130.1, 128.6, 128.4, 128.2, 126.2, 125.8, 125.1, 123.5, 123.2, 39.5; IR (film) 1608, 1247, 1221, 1045, 821 cm^{-1}; EI-MS m/z (relative intensity) 310 (M$^+$, ^{37}Cl, 36), 308 (100), 271 (26), 197 (27), 149 (8), 135 (12); HRMS (ESI) calcd for $C_{19}H_{14}ClS$ $[(M + H)^+]$ 309.0499, found 309.0500.

*4-(4-Fluorobenzyl)naphtho[1,2-b]thiophene **(5o)**.* White powder (72 mg, 62%); R_f = 0.45 (petroleum ether/EtOAc = 60:1); ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.10 (d, J = 7.6 Hz, 1H), 7.83 (d, J = 8.0 Hz, 1H), 7.52−7.38 (m, 5H), 7.22−6.93 (m, 4H), 4.34 (s, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 161.4 (d, J = 243 Hz), 138.0, 137.2, 135.6 (d, J = 3.2 Hz), 133.6, 131.1, 130.2 (d, J = 7.8 Hz), 128.4, 128.1, 126.2, 125.8, 125.1, 125.0, 123.5, 123.2, 115.3 (d, J = 21 Hz), 39.4; IR (film) 1508, 1221, 1157, 811, 748 cm^{-1}; EI-MS m/z (relative intensity) 292 (M$^+$, 100), 259 (7), 197 (33), 149 (30), 57 (11); HRMS (ESI) calcd for $C_{19}H_{14}FS$ $[(M + H)^+]$ 293.0795, found 293.0796.

*4-(3-Methoxybenzyl)naphtho[1,2-b]thiophene **(5p)**.* White powder (85 mg, 70%); R_f = 0.40 (petroleum ether/EtOAc = 30:1); ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.09 (d, J = 7.6 Hz, 1H), 7.83 (d, J = 7.6 Hz, 1H), 7.52−7.43 (m, 5H), 7.21−7.17 (m, 1H), 6.84−6.73 (m, 3H), 4.35 (s, 2H), 3.72 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 159.7, 141.6, 137.7, 137.4, 133.6, 131.1, 129.4, 128.4, 128.1, 126.0, 125.7, 125.1, 124.9, 123.4, 123.4, 121.3, 114.8, 111.3, 55.1, 40.2; IR (film) 1599, 1488, 1260, 1048, 778, 749 cm^{-1}; EI-MS m/z (relative intensity) 304 (M$^+$, 100), 272 (14), 258 (6), 197 (18), 152 (7); HRMS (ESI) calcd for $C_{20}H_{17}OS$ $[(M + H)^+]$ 305.0995, found 305.0999.

*10-(4-Methoxybenzyl)-2-tert-butylphenanthrene **(5q)**.* White powder (72 mg, 51%); R_f = 0.45 (petroleum ether/EtOAc = 30:1); ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.63−8.60 (m, 2H), 8.02 (s, 1H), 7.78 (d, J = 8.0 Hz, 1H), 7.69−7.66 (m, 1H), 7.59−7.52 (m, 3H), 7.21−7.19 (m, 2H), 6.83−6.81 (m, 2H), 4.41 (s, 2H), 3.75 (s, 3H), 1.36 (s, 9H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 157.9, 149.1, 135.5, 132.5, 131.6, 131.0, 129.8, 129.8, 128.6, 128.1, 127.4, 126.2, 126.0, 124.4, 122.8, 122.3, 121.0, 113.9, 55.2, 39.1, 35.0, 31.4; IR (film) 1510, 1246, 1037, 826, 748 cm^{-1}; EI-MS m/z (relative intensity) 354 (M$^+$, 100), 339 (41), 297 (12), 231 (45), 170 (8), 121 (21); HRMS (ESI) calcd for $C_{26}H_{27}O$ $[(M + H)^+]$ 355.2056, found 355.2059.

*10-(4-Methoxybenzyl)-2-chlorophenanthrene **(5r)**.* White powder (54 mg, 41%); R_f = 0.45 (petroleum ether/EtOAc = 30:1); ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.61 (d, 1H, J = 8.8 Hz), 8.57 (d, 1H, J = 8.4 Hz), 8.00 (s, 1H), 7.78 (d, J = 7.6 Hz, 1H), 7.63−7.50 (m, 4H), 7.16−7.14 (m, 2H), 6.85−6.83 (m, 2H), 4.45 (s, 2H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 158.1, 134.3, 132.6, 132.6, 131.7, 131.5, 129.8, 129.4, 129.1, 128.7, 128.4, 126.6, 124.7, 124.3, 122.3, 114.0, 55.2, 38.4; IR (film) 2922, 1511, 1036, 821, 748 cm^{-1}; EI-MS m/z (relative intensity) 334 (M$^+$, ^{37}Cl, 38), 332 (M$^+$, ^{35}Cl, 100), 297 (18), 265 (19), 252 (14), 148 (10), 121 (23), 71 (30), 43 (40); HRMS (ESI) calcd for $C_{22}H_{17}ClNaO$ $[(M + Na)^+]$ 355.0860, found 355.0864.

Typical Procedure for the CuI-Catalyzed Reaction of Terminal Alkynes 3a−e and *N*-Tosylhydrazones 6 and 7a−s. Under a nitrogen atmosphere, alkyne **3a** (35.6 mg, 0.2 mmol) was added to a mixture of CuI (5.7 mg, 15 mol %, 0.03 mmol), LiO*t*Bu (72 mg, 0.9 mmol), 3,4,7,8-tetramethyl-1,10-phenanthroline (14.2 mg, 30 mol %, 0.06 mmol), and *N*-tosylhydrazone **6** (137 mg, 0.5 mmol) in toluene (1.5 mL). The mixture was stirred at 120 °C for 24 h and monitored by TLC. After cooling to room temperature, the resulting mixture was filtered through a short path of silica gel using EtOAc as the eluent. The solvent was then removed in vacuo. The crude product was purified on a silica gel column using petroleum ether as the eluent to afford phenanthrene **5a** as a white powder (35 mg, 64% based on **3a**).

*9-(3-Methylbenzyl)phenanthrene **(8a)**.* White powder (35 mg, 62%); mp 129−130 °C; R_f = 0.48 (petroleum ether); ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.71 (dd, J = 8.2, 32.9 Hz, 2H), 8.02 (d, J = 8.1 Hz, 1H), 7.72 (d, J = 7.8 Hz, 1H), 7.68−7.51 (m, 4H), 7.28−7.23 (m, 2H), 7.19 (t, J = 7.4 Hz, 1H), 7.09 (t, J = 7.3 Hz, 1H), 6.98 (d, J = 7.5 Hz, 1H), 4.42 (s, 2H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 138.0, 136.6, 134.3, 131.8, 131.5, 130.6, 130.1, 129.7, 129.6, 128.3, 127.0, 126.7, 126.6, 126.5, 126.3, 126.2, 124.5, 123.1, 122.4, 36.6, 19.6; IR (film) 2917, 1602, 1452, 1260, 1031, 743 cm^{-1}; HRMS (EI) calcd for $C_{22}H_{19}$ $[(M + H)^+]$ 283.1481, found 283.1484.

*9-(4-Methylbenzyl)phenanthrene **(8b)**.*[23] White powder (42 mg, 74%); mp 123−124 °C; R_f = 0.55 (petroleum ether); ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.70 (dd, J = 8.1, 23.2 Hz, 2H), 8.04 (d, J = 8.1 Hz, 1H), 7.82 (d, J = 7.6 Hz, 1H), 7.65−7.52 (m, 5H), 7.14 (d, J = 8.0, 2H), 7.08 (d, J = 7.9 Hz, 2H), 4.45 (s, 2H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 137.1, 135.6, 135.0, 131.8, 131.4, 129.9, 129.2, 128.6, 128.2, 127.8, 126.6, 126.2, 126.1, 125.0, 123.1, 122.4, 39.2, 21.0; IR (film) 3022, 2962, 2913, 2356, 1794, 1493, 1260, 1022, 771 cm^{-1}.

*9-(4-(tert-Butyl)benzyl)phenanthrene **(8c)**.*[23] White powder (42 mg, 65%); mp 132−133 °C; R_f = 0.58 (petroleum ether); ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.62 (dd, J = 8.1, 24.1 Hz, 2H), 7.98 (d, J = 8.1 Hz, 1H), 7.74 (d, J = 7.7 Hz, 1H), 7.55−7.47 (m, 5H), 7.21 (d, J = 7.7 Hz, 2H), 7.10 (d, J = 8.0 Hz, 2H), 4.38 (s, 2H), 1.21 (s, 9H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 148.9, 137.1, 134.9, 131.8, 131.4, 130.8, 129.9, 128.4, 128.2, 127.8, 126.6, 126.2, 126.1, 125.4, 125.1, 123.1, 122.4, 39.0, 34.4, 31.4; IR (film) 2960, 1513, 1260, 1019, 803, 724 cm^{-1}.

*9-(4-Bromobenzyl)phenanthrene **(8d)**.* White powder (41 mg, 59%); mp 152−153 °C; R_f = 0.48 (petroleum ether); ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.70 (dd, J = 8.1, 24.1 Hz, 2H), 7.94 (d, J = 8.2 Hz, 1H), 7.82 (d, J = 7.6 Hz, 1H), 7.65−7.53 (m, 5H), 7.38 (d, J = 8.4 Hz, 2H), 7.11 (d, J = 8.4 Hz, 2H), 4.42 (s, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 139.3, 134.1, 131.9, 131.6, 131.1, 130.9, 130.5, 129.9, 128.3, 128.0, 126.7, 126.6, 126.4, 126.3, 124.8, 123.2, 122.5, 120.0, 39.0; IR (film) 2928, 2851, 2368, 1618, 1486, 1012, 799, 747 cm^{-1}; HRMS (EI) calcd for $C_{21}H_{16}Br$ $[(M + H)^+]$ 347.0430, found 347.0436.

*9-(3-Bromobenzyl)phenanthrene **(8e)**.* Colorless powder (49 mg, 70%); mp 121−122 °C; R_f = 0.45 (petroleum ether); ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.70 (dd, J = 8.2, 23.6 Hz, 2H), 7.94 (d, J = 7.6 Hz, 1H), 7.83 (d, J = 7.6 Hz, 1H), 7.65−7.53 (m, 5H), 7.40 (s, 1H), 7.33 (d, J = 7.3 Hz, 1H), 7.16−7.10 (m, 2H), 4.44 (s, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 142.7, 133.8, 131.7, 131.1, 130.9, 130.0, 129.4, 128.3, 128.2, 127.4, 126.7, 126.4, 126.3, 124.8, 123.2, 122.7, 122.5, 39.3; IR (film) 2965, 1591, 1474, 1260, 1071, 798 cm^{-1}; HRMS (EI) calcd for $C_{21}H_{16}Br$ $[(M + H)^+]$ 347.0430, found 347.0432.

*9-(4-Chlorobenzyl)phenanthrene **(8f)**.* White powder (39 mg, 65%); mp 159−160 °C; R_f = 0.44 (petroleum ether); ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.70 (dd, J = 8.2, 24.4 Hz, 2H), 7.95 (d, J = 8.1 Hz, 1H), 7.82 (d, J = 7.5 Hz, 1H), 7.65−7.53 (m, 5H), 7.24 (d, J = 8.3 Hz, 2H), 7.16 (d, J = 8.3 Hz, 2H), 4.44 (s, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 138.8, 134.2, 131.9, 131.7, 131.1, 130.9, 130.1, 128.7, 128.3, 128.0, 126.7, 126.6, 126.4, 126.3, 124.9, 123.2, 122.5, 39.0; IR (film) 2958, 2923, 2851, 2329, 1490, 1259, 702 cm^{-1}; HRMS (EI) calcd for $C_{21}H_{16}Cl$ $[(M + H)^+]$ 303.0935, found 303.0942.

*9-(4-Fluorobenzyl)phenanthrene **(8g)**.* White powder (38.5 mg, 67%); mp 153−154 °C; R_f = 0.35 (petroleum ether/EtOAc = 100:1); ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.70 (dd, J = 8.2, 24.9 Hz, 2H), 7.98 (d, J = 8.1 Hz, 1H), 7.81 (dd, J = 1.1, 7.8 Hz, 1H), 7.65−7.52 (m, 5H), 7.21−7.17 (m, 2H), 6.96 (t, J = 8.7 Hz, 2H), 4.44 (s, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 162.6, 160.2, 135.9, 135.8, 134.6, 131.7, 131.2, 130.8, 130.1, 130.0, 129.9, 128.3, 127.9, 126.7, 126.6, 126.3, 124.9, 123.2, 122.5, 115.4, 115.2, 38.8; IR (film) 3024, 2923, 2850, 2358, 1602, 1508, 1218, 1014, 743, 661 cm^{-1}; HRMS (EI) calcd for C$_{21}$H$_{16}$F [(M + H)$^+$] 287.1231, found 287.1235.

9-(4-Cyanobenzyl)phenanthrene (***8h***). White solid (36 mg, 61%); mp 164−165 °C; R_f = 0.45 (petroleum ether/EtOAc = 30:1); ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.71 (dd, J = 8.2, 25.1 Hz, 2H), 7.85 (dd, J = 7.8, 12.2 Hz, 2H), 7.68−7.52 (m, 7H), 7.33 (d, J = 8.3 Hz, 2H), 4.53 (s, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 146.1, 133.0, 132.3, 131.5, 130.9, 130.8, 130.1, 129.4, 128.4, 128.3, 126.9, 126.8, 126.7, 126.5, 124.7, 123.3, 122.5, 118.9, 110.2, 39.7; IR (film) 2960, 2925, 2854, 2227, 1606, 1260, 1020, 800 cm^{-1}; HRMS (EI) calcd for C$_{22}$H$_{15}$NNa [(M + Na)$^+$] 316.1097, found 316.1103.

9-(4-Methoxybenzyl)phenanthrene (***8i***). Pale-white powder (42.5 mg, 71%); mp 114−115 °C; R_f = 0.32 (hexane/EtOAc = 19:1); ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.61 (dd, J = 8.1, 24.2 Hz, 2H), 7.96 (d, J = 7.8 Hz, 1H), 7.73 (d, J = 7.5 Hz, 1H), 7.57−7.45 (m, 5H), 7.10 (dd, J = 8.7, 14.8 Hz, 2H), 6.71 (dd, J = 8.7, 23.0 Hz, 2H), 4.34 (s, 2H), 3.67 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 158.0, 135.2, 132.2, 131.8, 131.4, 130.8, 130.0, 129.7, 128.2, 127.7, 126.6, 126.5, 126.2, 126.1, 125.0, 123.1, 122.4, 113.9, 55.2, 38.7; IR (film) 3027, 1603, 1410, 1261, 798, 695, 667 cm^{-1}; HRMS (EI) calcd for C$_{22}$H$_{19}$O [(M + H)$^+$] 299.1430, found 299.1432.

9-(4-(Trifluoromethyl)benzyl)phenanthrene (***8j***). White powder (54 mg, 80%); mp 126−127 °C; R_f = 0.48 (petroleum ether/EtOAc = 60:1); ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.63 (dd, J = 8.2, 24.6 Hz, 2H), 7.85 (d, J = 8.1 Hz, 1H), 7.75 (d, J = 7.6 Hz, 1H), 7.58−7.43 (m, 7H), 7.28−7.17 (m, 2H), 4.45 (s, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 144.47, 133.64, 131.6, 131.0, 130.9, 130.0, 129.0, 128.3, 128.2, 126.8, 126.7, 126.5, 126.4, 125.4 (q, J = 3.8 Hz, CF$_3$), 124.8, 123.2, 122.5, 39.4; IR (film) 2961, 2926, 2322, 1616, 1326 cm^{-1}; HRMS (EI) calcd for C$_{22}$H$_{16}$F$_3$ [(M + H)$^+$] 337.1199, found 337.1203.

9-(3-Nitrobenzyl)phenanthrene (***8k***). Pale-white solid (30 mg, 48%); mp 103−104 °C; R_f = 0.30 (EtOAc/petroleum ether = 30:1); ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.71 (dd, J = 8.2, 25.5 Hz, 2H), 8.15 (s, 1H), 8.06 (d, J = 8.1 Hz, 1H), 7.87 (dd, J = 7.9, 25.3 Hz, 2H), 7.68−7.53 (m, 6H), 7.41 (t, J = 7.9 Hz, 1H), 4.57 (s, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 148.5, 142.5, 133.8, 133.0, 131.5, 130.8, 130.1, 129.4, 128.5, 128.3, 126.9, 126.8, 126.7, 126.6, 124.6, 123.5, 123.4, 122.5, 121.5, 39.3; IR (film) 2960, 2923, 2854, 1528, 1348, 1260, 1017, 799 cm^{-1}; HRMS (EI) calcd for C$_{21}$H$_{16}$NO$_2$ [(M + H)$^+$] 314.1176, found 314.1181.

N,N-Dimethyl-4-(phenanthren-9-ylmethyl)aniline (***8l***).[24] Pale-red powder (33 mg, 53%); mp 131−132 °C; R_f = 0.32 (petroleum ether/EtOAc = 40:1); ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.69 (dd, J = 8.1, 23.4 Hz, 2H), 8.08 (d, J = 8.1 Hz, 1H), 7.81 (dd, J = 1.1, 7.8 Hz, 1H), 7.64−7.53 (m, 5H), 7.24−7.11 (m, 2H), 6.69 (d, J = 8.5 Hz, 2H), 4.40 (s, 2H), 2.90 (s, 6H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 135.6, 131.9, 131.5, 130.7, 129.8, 129.4, 128.2, 127.5, 126.5, 126.1, 126.0, 125.1, 123.0, 122.4, 113.0, 40.8, 38.6; IR (film) 2960, 2922, 2850, 1615, 1520, 1260, 1019, 800 cm^{-1}.

9-(3,4-Dichlorobenzyl)phenanthrene (***8m***). White powder (44.5 mg, 66%); mp 141−142 °C; R_f = 0.42 (petroleum ether/EtOAc = 100:1); ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.70 (dd, J = 8.2, 24.1 Hz, 2H), 7.89 (d, J = 7.8 Hz, 1H), 7.83 (dd, J = 1.0, 7.8 Hz, 1H), 7.66−7.53 (m, 5H), 7.32−7.24 (m, 2H), 7.05 (dd, J = 1.9, 8.2 Hz, 1H), 4.41 (s, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 140.6, 133.4, 132.5, 131.6, 130.9, 130.8, 130.5, 130.4, 130.2, 130.1, 128.3, 128.2, 128.1, 126.8, 126.7, 126.6, 126.5, 124.7, 123.3, 122.5, 38.8; IR (film) 2963, 2927, 2356, 1452, 1325, 1260, 1029, 727 cm^{-1}; HRMS (EI) calcd for C$_{21}$H$_{15}$Cl$_2$ [(M + H)$^+$] 337.0545, found 337.0550.

9-(3,5-Dimethoxybenzyl)phenanthrene (***8n***). Brown powder (39 mg, 60%); mp 108−109 °C; R_f = 0.35 (petroleum ether/EtOAc = 30:1); ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.69 (dd, J = 8.1, 22.4 Hz, 2H), 8.03 (d, J = 7.9 Hz, 1H), 7.82 (d, J = 7.5 Hz, 1H), 7.64−7.24 (m, 5H), 6.42 (d, J = 2.1 Hz, 2H), 6.32 (t, J = 2.1 Hz, 1H), 4.41 (s, 2H), 3.71 (s, 6H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 160.9, 142.7, 134.4, 131.8, 131.4, 130.8, 130.0, 128.3, 127.9, 126.6, 126.5, 126.2, 125.0, 123.1, 122.4, 107.1, 98.0, 55.2, 39.9; IR (film) 2958, 2927, 2851, 1723, 1595, 1461, 1205, 1155, 1067, 747 cm^{-1}; HRMS (EI) calcd for C$_{23}$H$_{21}$O$_2$ [(M + H)$^+$] 329.1536, found 329.1538.

9-(2-Chloro-4-(trifluoromethyl)benzyl)phenanthrene (***8o***). White powder (51 mg, 69%); mp 119−120 °C; R_f = 0.45 (petroleum ether/EtOAc = 60:1); ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.72 (dd, J = 8.2, 27.9 Hz, 2H), 7.89 (d, J = 8.1 Hz, 1H), 7.79 (d, J = 7.7 Hz, 1H), 7.69−7.63 (m, 2H), 7.60−7.57 (m, 3H), 7.46 (d, J = 8.3 Hz, 1H), 7.40 (s, 1H), 7.27 (s, 1H), 4.59 (s, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 139.0, 138.0, 132.3, 131.6, 130.9, 130.8, 130.1, 130.0, 128.4, 127.9, 127.5, 127.4, 126.9, 126.8, 126.6, 124.7, 124.6, 124.3, 123.3, 122.5, 36.8; IR (film) 2928, 2856, 2333, 1612, 1332, 1170, 1083, 742 cm^{-1}; HRMS (EI) calcd for C$_{22}$H$_{15}$ClF$_3$ [(M + H)$^+$] 371.0809, found 371.0808.

9-(2-(Allyloxy)benzyl)phenanthrene (***8p***). White waxy liquid (45 mg, 70%); R_f = 0.43 (petroleum ether/EtOAc = 60:1); ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.70 (dd, J = 8.1, 23.4 Hz, 2H), 8.05 (d, J = 8.1 Hz, 1H), 7.79 (d, J = 7.6 Hz, 1H), 7.64−7.52 (m, 5H), 7.19−7.15 (m, 1H), 6.92 (d, J = 8.8 Hz, 2H), 6.78 (dd, J = 5.8, 13.4 Hz, 1H), 6.13−6.03 (m, 1H), 5.44 (dd, J = 1.5, 17.3 Hz, 1H), 5.26 (dd, J = 1.4, 10.5 Hz, 1H), 4.64 (d, J = 5.0 Hz, 2H), 4.50 (s, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 156.1, 134.8, 133.5, 131.9, 131.6, 130.7, 130.1, 129.0, 128.2, 127.7, 127.2, 126.5, 126.1, 126.0, 125.1, 123.0, 122.4, 120.7, 117.1, 111.5, 68.8, 33.1; IR (film) 3033, 2962, 2927, 1726, 1560, 1490, 1451, 1260, 1019, 746 cm^{-1}; HRMS (EI) calcd for C$_{24}$H$_{21}$O [(M + H)$^+$] 325.1587, found 325.1595.

5-(Phenanthren-9-ylmethyl)benzo[d][1,3]dioxole (***8q***). Pale-white solid (39 mg, 63%); mp 127−129 °C; R_f = 0.42 (petroleum ether/EtOAc = 60:1); ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.69 (dd, J = 8.1, 23.9 Hz, 2H), 8.02 (d, J = 8.1 Hz, 1H), 7.82 (d, J = 7.4 Hz, 1H), 7.64−7.54 (m, 5H), 7.35−7.12 (m, 3H), 5.89 (s, 2H), 4.39 (s, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 147.7, 145.9, 134.8, 134.1, 131.7, 131.3, 130.8, 129.9 128.8, 128.2, 127.8, 126.6, 126.5, 126.2, 124.9, 123.1, 122.5, 121.6, 109.2, 108.2, 100.8, 39.3; IR (film) 2926, 2855, 2322, 1727, 1502, 1259, 1039, 799 cm^{-1}; HRMS (EI) calcd for C$_{22}$H$_{17}$O$_2$ [(M + H)$^+$] 313.1223, found 313.1228.

2-(Phenanthren-9-ylmethyl)thiophene (***8r***). Pale-yellow solid (29 mg, 54%); mp 134−135 °C; R_f = 0.48 (petroleum ether); ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.70 (dd, J = 8.3, 25.3 Hz, 2H), 8.09 (d, J = 8.1 Hz, 1H), 7.84 (d, J = 7.6 Hz, 1H), 7.67−7.56 (m, 4H), 7.25 (s, 1H), 7.14 (dd, J = 1.1, 5.1 Hz, 1H), 6.91 (dd, J = 3.5, 5.1 Hz, 1H), 6.82−6.81 (m, 1H), 4.65 (s, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 143.4, 134.3, 131.7, 130.9, 130.8, 130.1, 128.4, 127.5, 126.9, 126.7, 126.4, 126.3, 125.4, 124.7, 123.8, 123.2, 122.5, 34.0; IR (film) 2925, 2854, 1453, 1022, 656 cm^{-1}; HRMS (EI) calcd for C$_{19}$H$_{15}$S [(M + H)$^+$] 275.0889, found 275.0895.

3-(Phenanthren-9-ylmethyl)pyridine (***8s***). Pale-green powder (39 mg, 72%); mp 125−126 °C; R_f = 0.30 (petroleum ether/EtOAc = 1:1); ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.70 (dd, J = 8.2, 26.3 Hz, 2H), 8.64 (s, 1H), 8.47 (d, J = 4.1 Hz, 1H), 7.96 (d, J = 8.1 Hz, 1H), 7.81 (d, J = 7.9 Hz, 1H), 7.66−7.56 (m, 4H), 7.54 (s, 1H), 7.46 (d, J = 7.8 Hz, 1H), 7.16 (dd, J = 4.9, 7.7 Hz, 1H), 4.47 (s, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 150.2, 147.7, 136.1, 135.7, 133.4, 131.6, 130.9, 130.0, 128.3, 128.1, 126.8, 126.5, 126.4, 124.7, 123.4, 123.2, 122.5, 36.7; IR (film) 2925, 1725, 1422, 1260, 1026, 749 cm^{-1}; HRMS (EI) calcd for C$_{20}$H$_{16}$N [(M + H)$^+$] 270.1277, found 270.1280.

10-Benzyl-2-(tert-butyl)phenanthrene (***9a***). White powder (40 mg, 62%); mp 101−102 °C; R_f = 0.44 (petroleum ether/EtOAc = 100:1); ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.72 (d, J = 1.9 Hz, 1H), 8.70 (d, J = 8.4 Hz, 1H), 7.96 (d, J = 8.7 Hz, 1H), 7.79 (dd, J = 0.9, 7.8 Hz, 1H), 7.63−7.53 (m, 3H), 7.49 (s, 1H), 7.27−7.23 (m, 4H), 4.46 (s, 2H), 1.47 (s, 9H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 148.9, 140.4, 134.5, 132.0, 130.5, 130.1, 129.3, 128.8, 128.5, 128.3, 127.8, 127.2, 126.4, 126.1, 126.0, 124.9, 124.7, 122.3, 118.8, 39.6, 35.1, 31.5; IR (film) 3026, 2962, 1602, 1494, 1260, 1028, 802, 699 cm^{-1}; HRMS (EI) calcd for C$_{25}$H$_{25}$ [(M + H)$^+$] 325.1951, found 325.1958.

10-(4-Bromobenzyl)-2-(tert-butyl)phenanthrene (***9b***). White powder (53 mg, 66%); mp 122−123 °C; R_f = 0.44 (petroleum ether/EtOAc = 100:1); ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.70 (d, J = 10.0 Hz, 2H), 7.88 (8, J = 8.7 Hz, 1H), 7.80 (d, J = 7.6 Hz, 1H), 7.64−7.54 (m, 3H), 7.48 (s, 1H), 7.38 (d, J = 8.3 Hz, 2H), 7.11 (d, J = 8.3 Hz, 2H), 4.39 (s, 2H), 1.47 (s, 9H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 149.1, 139.4, 133.9, 131.9, 131.5, 130.5, 130.1, 129.0, 128.3, 127.3, 126.5, 126.2, 125.0, 124.6, 122.4, 119.9, 118.9, 39.0, 35.1, 31.5; IR (film) 2959, 1605, 1486, 1260, 790, 697 cm^{-1}; HRMS (EI) calcd for $C_{25}H_{24}Br$ $[(M + H)^+]$ 403.1056, found 403.1066.

*2-(tert-Butyl)-10-(3,4-dichlorobenzyl)phenanthrene (**9c**).* White powder (47 mg, 60%); mp 99−100 °C; R_f = 0.43 (petroleum ether/EtOAc = 19:1); ^1H NMR (400 MHz, $CDCl_3$) δ 8.71 (d, J = 10.3 Hz, 2H), 7.82 (t, J = 7.1 Hz, 2H), 7.65−7.55 (m, 3H), 7.49 (s, 1H), 7.32 (dd, J = 4.8, 7.3 Hz, 2H), 7.06 (dd, J = 1.3, 8.2 Hz, 1H), 4.39 (s, 2H), 1.47 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.2, 140.8, 133.2, 132.4, 131.8, 130.6, 130.5, 130.3, 130.2, 130.1, 128.8, 128.3, 128.1, 127.5, 126.6, 126.3, 125.1, 124.5, 122.4, 118.9, 38.8, 35.1, 31.5; IR (film) 2962, 1725, 1471, 1260, 1029, 800, 748 cm^{-1}; HRMS (EI) calcd for $C_{25}H_{23}Cl_2$ $[(M + H)^+]$ 393.1171, found 393.1176.

*10-Benzyl-3-methoxyphenanthrene (**9d**).* White powder (42 mg, 70%); mp 109−110 °C; R_f = 0.40 (petroleum ether/EtOAc = 60:1); ^1H NMR (400 MHz, $CDCl_3$) δ 8.58 (d, J = 7.9 Hz, 1H), 8.09 (d, J = 2.5 Hz, 1H), 7.93 (d, J = 9.0 Hz, 1H), 7.79 (dd, J = 1.4, 7.7 Hz, 1H), 7.57 (dp, J = 1.5, 7.0 Hz, 2H), 7.42 (s, 1H), 7.28−7.22 (m, 4H), 7.18 (dt, J = 2.1, 9.2 Hz, 2H), 4.45 (s, 2H), 3.99 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.0, 140.4, 134.6, 132.3, 129.4, 128.7, 128.5, 128.3, 126.7, 126.6, 126.1, 126.0, 125.8, 125.7, 122.5, 116.3, 104.6, 55.4, 39.7; IR (film) 2961, 2927, 2853, 2350, 1727, 1618, 1453, 1230, 1030, 799, 748, 663 cm^{-1}; HRMS (EI) calcd for $C_{22}H_{19}O$ $[(M + H)^+]$ 299.1430, found 299.1431.

*10-(4-Bromobenzyl)-3-methoxyphenanthrene (**9e**).* Pale-yellow powder (56 mg, 74%); mp 138−139 °C; R_f = 0.41 (petroleum ether/EtOAc = 60:1); ^1H NMR (400 MHz, $CDCl_3$) δ 8.57 (d, J = 6.6 Hz, 1H), 8.08 (d, J = 2.5 Hz, 1H), 7.84 (d, J = 9.0 Hz, 1H), 7.79 (dd, J = 1.3, 7.7 Hz, 1H), 7.62−7.54 (m, 2H), 7.39−7.23 (m, 3H), 7.16 (dd, J = 2.6, 9.0 Hz, 1H), 7.08 (d, J = 8.4 Hz, 2H), 4.36 (s, 2H), 3.98 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.1, 139.4, 133.9, 133.2, 132.6, 132.4, 132.2, 131.5, 130.4, 129.5, 128.3, 126.8, 126.4, 126.0, 125.8, 125.7, 122.5, 120.0, 116.4, 104.7, 55.4, 39.1; IR (film, cm^{-1}) 2917, 2850, 2229, 1722, 1618, 1486, 1230, 1070, 1011, 748; HRMS (EI) calcd for $C_{22}H_{18}BrO$ $[(M + H)^+]$ 377.0536, found 377.0542.

*10-(3,4-Dichlorobenzyl)-3-methoxyphenanthrene (**9f**).* White powder (53 mg, 72%); mp 99−100 °C; R_f = 0.40 (petroleum ether/EtOAc = 19:1); ^1H NMR (400 MHz, $CDCl_3$) δ 8.58 (d, J = 7.9 Hz, 1H), 8.09 (d, J = 2.5 Hz, 1H), 7.82−7.78 (m, 2H), 7.63−7.56 (m, 2H), 7.40 (s, 1H), 7.30 (dd, J = 3.2, 5.0 Hz, 2H), 7.18 (dd, J = 2.5, 9.0 Hz, 1H), 7.03 (dd, J = 1.8, 8.3 Hz, 1H), 4.36 (s, 2H), 3.99 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.2, 140.7, 133.2, 132.4, 132.1, 130.5, 130.3, 130.1, 129.6, 128.3, 128.0, 126.9, 126.2, 126.1, 126.0, 125.5, 122.4, 116.5, 104.8, 55.4, 38.8; IR (film) 2962, 2926, 1726, 1618, 1470, 1230, 1030, 803, 734, 700, 662 cm^{-1}; HRMS (EI) calcd for $C_{22}H_{17}Cl_2O$ $[(M + H)^+]$ 367.0651, found 367.0650.

*(10-Benzylphenanthren-3-yl)(methyl)sulfane (**9g**).* White solid (50 mg, 80%); mp 80−81 °C; R_f = 0.38 (petroleum ether/EtOAc = 60:1); ^1H NMR (400 MHz, $CDCl_3$) δ 8.60 (d, J = 8.0 Hz, 1H), 8.53 (d, J = 1.7 Hz, 1H), 7.91 (d, J = 8.7 Hz, 1H), 7.79 (d, J = 7.4 Hz, 1H), 7.62−7.54 (m, 2H), 7.49 (s, 1H), 7.42 (dd, J = 1.9, 8.7 Hz, 1H), 7.28−7.19 (m, 5H), 4.43 (s, 2H), 2.61 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.2, 136.5, 134.5, 132.2, 131.3, 129.1, 129.0, 128.7, 128.5, 128.3, 127.3, 126.9, 126.2, 126.1, 125.6, 125.5, 122.4, 120.3, 39.5, 16.1; IR (film) 2961, 2923, 1725, 1599, 1494, 1260, 1018, 800, 699 cm^{-1}; HRMS (EI) calcd for $C_{22}H_{19}S$ $[(M + H)^+]$ 315.1202, found 315.1209.

*(10-(3-Bromobenzyl)phenanthren-3-yl)(methyl)sulfane (**9h**).* Pale-white solid (48 mg, 61%); mp 105−106 °C; R_f = 0.38 (petroleum ether/EtOAc = 60:1); ^1H NMR (400 MHz, $CDCl_3$) δ 8.61 (d, J = 8.0 Hz, 1H), 8.54 (d, J = 1.7 Hz, 1H), 7.82 (dd, J = 5.1, 12.9 Hz, 2H), 7.64−7.56 (m, 2H), 7.49 (s, 1H), 7.44 (dd, J = 1.9, 8.6 Hz, 1H), 7.38 (s, 1H), 7.34−7.31 (m, 1H), 7.12 (d, J = 5.7 Hz, 2H), 4.40 (s, 2H), 2.63 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.6, 136.8, 133.6, 132.1, 131.6, 131.4, 130.0, 129.4, 129.2, 128.7, 128.3, 127.6, 127.3, 127.0, 126.4, 125.7, 125.3, 122.7, 122.4, 120.3, 39.2, 16.1; IR (film) 2960, 2924, 2851, 2350, 2226, 1732, 1598, 1260, 1017, 823 cm^{-1}; HRMS (EI) calcd for $C_{22}H_{18}BrS$ $[(M + H)^+]$ 393.0307, found 393.0308.

*(10-(3,4-Dichlorobenzyl)phenanthren-3-yl)(methyl)sulfane (**9i**).* Pale-white solid (57.5 mg, 75%); mp 107−108 °C; R_f = 0.37 (petroleum ether/EtOAc = 60:1); ^1H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, J = 8.1 Hz, 1H), 8.54 (d, J = 1.8 Hz, 1H), 7.82 (d, J = 7.5 Hz, 1H), 7.79 (d, J = 8.7 Hz, 1H), 7.65−7.57 (m, 2H), 7.48 (s, 1H), 7.44 (dd, J = 1.9, 8.6 Hz, 1H), 7.31 (d, J = 8.3 Hz, 2H), 7.03 (dd, J = 2.0, 8.2 Hz, 1H), 4.37 (s, 2H), 2.63 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.6, 137.0, 133.1, 132.5, 132.0, 131.4, 130.5, 130.4, 129.2, 128.5, 128.3, 128.0, 127.6, 127.1, 126.5, 125.7, 125.2, 122.5, 120.3, 38.7, 16.0; IR (film) 2961, 2927, 2862, 2368, 1724, 1598, 1470, 1260, 1031, 658 cm^{-1}; HRMS (EI) calcd for $C_{22}H_{17}Cl_2S$ $[(M + H)^+]$ 383.0423, found 383.0424.

*10-Benzylphenanthrene-2-carbonitrile (**9j**).* Reddish powder (34.5 mg, 59%); mp 117−118 °C; R_f = 0.32 (petroleum ether/EtOAc = 30:1); ^1H NMR (400 MHz, $CDCl_3$) δ 8.77 (d, J = 8.6 Hz, 1H), 8.64 (d, J = 9.1 Hz, 1H), 8.36 (d, J = 1.3 Hz, 1H), 7.85 (dd, J = 2.1, 7.1 Hz, 1H), 7.80 (dd, J = 1.5, 8.6 Hz, 1H), 7.71−7.67 (m, 2H), 7.64 (s, 1H), 7.30 (d, J = 6.8 Hz, 2H), 7.25−7.22 (m, 3H), 4.47 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.2, 134.1, 133.5, 132.7, 131.0, 130.2, 129.7, 128.9, 128.8, 128.7, 128.6, 128.5, 128.4, 128.2, 127.7, 127.1, 126.6, 124.2, 123.0, 119.4, 109.9, 39.3; IR (film) 2961, 2924, 2852, 2227, 2343, 1725, 1259, 1018, 730, 705 cm^{-1}; HRMS (EI) calcd for $C_{22}H_{16}N$ $[(M + H)^+]$ 294.1277, found 294.1280.

Typical Procedure for Scale-Up Experiments. Under a nitrogen atmosphere, alkyne **3a** (890 mg, 5 mmol) was added to a mixture of CuI (142.5 mg, 0.75 mmol), 3,4,7,8-tetramethyl-1,10-phenanthroline (354 mg, 1.5 mmol), LiO*t*Bu (1.8 g, 22.5 mmol), and *N*-tosylhydrazone **6** (3.43 g, 12.5 mmol) in dioxane (30 mL). The solution was stirred at 120 °C for 24 h. Upon completion of the reaction, the reaction mixture was cooled to room temperature and filtered through a short silica gel column, eluting with EtOAc. The solvent was removed in vacuum to leave a crude mixture, which was purified by silica gel column chromatography using petroleum ether as an eluting solvent to afford pure 9-benzylphenanthrene (**5a**) as white solid powder (735 mg, 55% based on **3a**).

Typical Procedure for the One-Pot Reaction. 4-Trifluoromethylbenzaldehyde (87 mg, 0.5 mmol) and 4-methylbenzenesulfonohydrazide ($TsNHNH_2$) (93 mg, 0.5 mmol) were suspended in dioxane (1.5 mL) in a 10 mL microwave tube, and the resulting suspension was stirred at 60 °C for 30 min. Upon completion of the reaction (as monitored by TLC), CuI (5.7 mg, 0.03 mmol), 3,4,7,8-tetramethyl-1,10-phenanthroline (14.2 mg, 0.06 mmol), and LiO*t*Bu (96 mg, 1.2 mmol) were added under nitrogen. Then alkyne **3a** (35.6 mg, 0.2 mmol) was added. The resulting mixture was stirred at 120 °C for 24 h. After cooling to room temperature, the mixture was filtered through a short silica gel column, eluting with EtOAc. The solvent was removed under vacuum, and the crude residue was purified by column chromatography on silica gel, eluting with PE/EtOAc (60:1), to afford pure 9-(4-(trifluoromethyl)benzyl)phenanthrene (**8j**) as a white powder (50 mg, 74% based on **3a**).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Copies of ^1H and ^{13}C spectra for all products and the X-ray structure and crystallographic data (CIF) for **9g**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The project was supported by National Basic Research Program (973 Program) (Grant 2012CB821600) and the National Natural Science Foundation of China (Grants 21332002 and 21272010).

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