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# Reactivity of Vinyl Epoxides/Oxetanes/Cyclopropanes toward Arynes: Access to Functionalized Phenanthrenes

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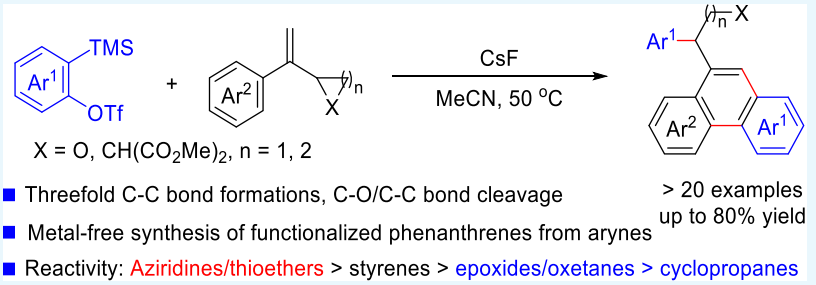


**ABSTRACT:** The reactivity of vinyl epoxides/oxetanes/cyclopropanes toward arynes has been demonstrated under mild conditions to give the corresponding phenanthrenes in moderate to good yields. This transition-metal-free cascade process involves a series of Diels−Alder reaction, ring-opening aromatization, and ene reaction. Various functionalized phenanthrenes could be synthesized utilizing the versatile hydroxy group. Interestingly, vinyl epoxides/oxiranes experience preferentially the Diels−Alder reaction toward arynes over nucleophilic attack of epoxides/oxiranes.

## INTRODUCTION

As highly electrophilic reactive intermediates, arynes have recently gained great attention in organic synthesis.[1] Because of the high strain and low-lying lowest unoccupied molecular orbital (LUMO), arynes could experience nucleophilic attack readily by various neutral nucleophiles to generate versatile zwitterions. Owing to the strong nucleophilicity of aziridines and thioethers, arynes triggered ring-opening functionalization of aziridines,[2] and cyclic thioethers[3] have been developed well. However, the reactions of arynes and weakly nucleophilic strained rings (such as epoxides,[4] oxetanes, and cyclopropanes) are less developed.

Vinyl strained rings are versatile synthetic building blocks due to the presence of a vinyl moiety and the highly strained ring.[5] Therefore, the reactivity of vinyl strained rings toward arynes has two possible pathways. Strained rings could nucleophilic attack arynes to generate the highly reactive zwitterions, followed by intramolecular annulation. Alternatively, the aryne Diels−Alder reaction[6] could trigger ring-opening of strained rings. In 2012, Saito and co-workers disclosed an elegant [6 + 2] cycloaddition reaction of vinyl azetidines and arynes to access 1-benzazocines (Scheme 1a).[7] Recently, Studer and Yudin further developed a sophisticated [5 + 2] cycloaddition reaction of vinyl aziridines and arynes that resulted in benzazepines (Scheme 1b).[8] In sharp contrast to vinyl azetidines/aziridines, we envisioned that ring-opening of vinyl epoxides/oxetanes/cyclopropanes is triggered by the aryne Diels−Alder reaction (Scheme 1c).

The phenanthrene unit constitutes a key structural motif in several pharmaceutically relevant compounds, therefore the development of efficient and practical approaches for the synthesis of phenanthrene derivatives has gained immense attention.[9] Despite the fact that palladium-catalyzed aryne annulation approaches to phenanthrenes have been developed well,[10] metal-free synthesis of phenanthrenes from arynes has been rarely studied. Recently, Wu[11] and Tiwari[12] developed elegant metal-free synthesis of phenanthrenes from $\alpha$, $\beta$-unsaturated compounds and $\beta$-bromovinylarenes with arynes, respectively. Despite the success of these synthetic approaches, the development of transition-metal-free methodology for the synthesis of phenanthrenes without versatile functional groups is still highly desirable. In continuation of our work in the developing ring-opening functionalization of vinyl strained rings and aryne chemistry,[13] we are interested in preparing phenanthrenes having hydroxy groups from arynes under transition-metal-free conditions. Significantly, various functionalized phenanthrenes would be synthesized utilizing the versatile hydroxy group.

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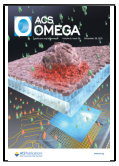


**Scheme 1. Reactivity of Vinyl Strained Rings toward Arynes**

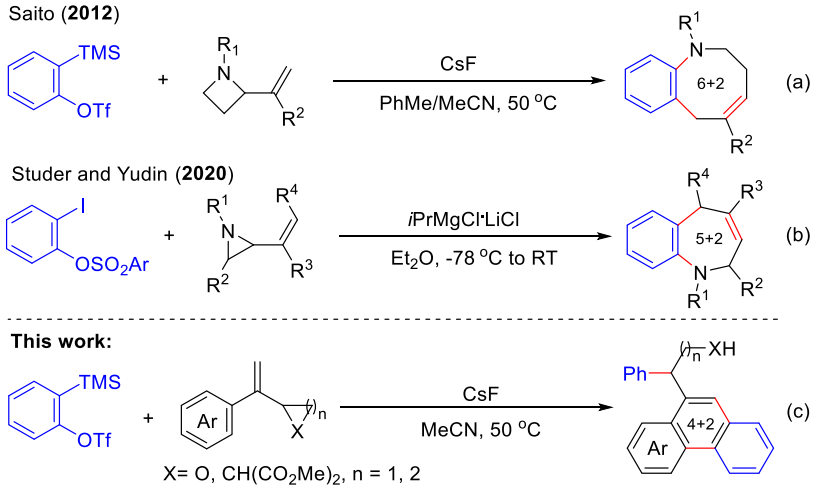
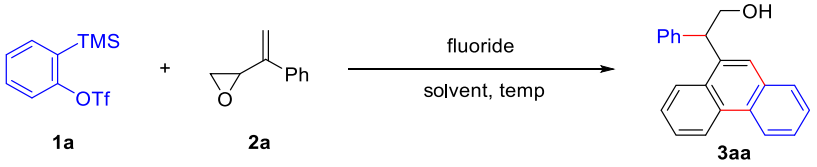



**Table 1. Reaction Optimization**[a]




| entry | fluoride (equiv) | solvent | temp (°C) | yield (%) |
|---|---|---|---|---|
| 1 | CsF | MeCN | rt | 56 |
| **2** | **CsF** | **MeCN** | **50** | **68** |
| 3 | CsF | MeCN | 80 | 61 |
| 4 | CsF | THF | 70 | 28 |
| 5 | KF | MeCN | 100 | 41 |
| 6 | TBAF | THF | rt | 20 |
| 7 | KF/18-C-6 | MeCN | rt | 50 |
| 8 | KF/18-C-6 | 1,4-dioxane | rt | 55 |
| 9 | KF/18-C-6 | 1,4-dioxane | 50 | 50 |
| 10[b] | CsF | MeCN | 50 | 68 |

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.48 mmol), fluoride source (0.8 mmol), solvent (2 mL), and 6 h; isolated yields after column chromatography. [b]**2a** (0.6 mmol) and fluoride source (1 mmol).

## RESULTS AND DISCUSSION

We began our studies with aryne precursor **1a** and 2-(1-phenylvinyl)oxirane **2a** as the benchmark substrates under various conditions (Table 1). To our delight, the desired product **3aa** was obtained in a 56% yield using CsF as a fluorine source in acetonitrile at room temperature (Table 1, entry 1). The yield of **3aa** increased to 68% along with O-Ph byproduct **3aa′** in a 15% yield when the temperature of the reaction increased to 50 °C (Table 1, entry 2). However, the yield of **3aa** declined slightly when running the reaction at 80 °C (Table 1, entry 3). The reaction was conducted in tetrahydrofuran (THF) at 70 °C, resulting in a 28% yield (Table 1, entry 4). The desired **3aa** was obtained in a 41% yield using KF as a fluoride source in MeCN at 100 °C (Table 1, entry 5). Only a 20% yield of **3aa** was obtained using tetrabutylammonium fluoride (TBAF) as a fluoride source in THF at room temperature (Table 1, entry 6). The desired **3aa** was obtained in a 50% yield using KF/18-C-6 as a fluoride source in MeCN at room temperature (Table 1, entry 7). It was found that the reaction also proceeded smoothly in 1,4-dioxane, giving the desired **3aa** in a 55% yield (Table 1, entry 8), although increasing the temperature to 50 °C did not improve the yield (Table 1, entry 9). Unfortunately, increasing the aryne precursors and fluoride sources also cannot improve the yield (Table 1, entry 10).

Having the optimal conditions in hand, the scope of the aryne precursors and vinyl epoxides/oxetanes was investigated (Scheme 2). Different arynes were tested first (**3ba**−**da**). The symmetrically disubstituted (OMe and Me) aryne precursors reacted smoothly with 2-(1-phenylvinyl)oxirane **2a**, resulting in the desired products **3ba** and **3ca** in 65 and 71% yields, respectively. In addition, the unsymmetrical (3-OMe) benzyne precursor **1d** reacted with **2a**, affording a mixture of regioisomers (>10:1 ratio) in a 45% combined yield.[14] Subsequently, the scope of vinyl epoxides was screened. To our delight, representative aryl vinyl epoxides with electron-donating (Me, OMe, and Ph) or electron-withdrawing (F, Cl, and Br) groups in the benzene ring all worked well, giving the desired products (**3ab**−**ag**) in 51−67% yields. The symmetrically trisubstituted phenyl vinyl epoxide **2h** afforded the desired product **3ah** in a 55% yield. It is worth noting that the unsymmetrical phenyl vinyl epoxide **2i** gave regioisomeric (1.5:1 ratio) product **3ai** in a 53% yield. Vinyl methyl-substituted epoxide **2j** gave two isolated diastereoisomers **3aj**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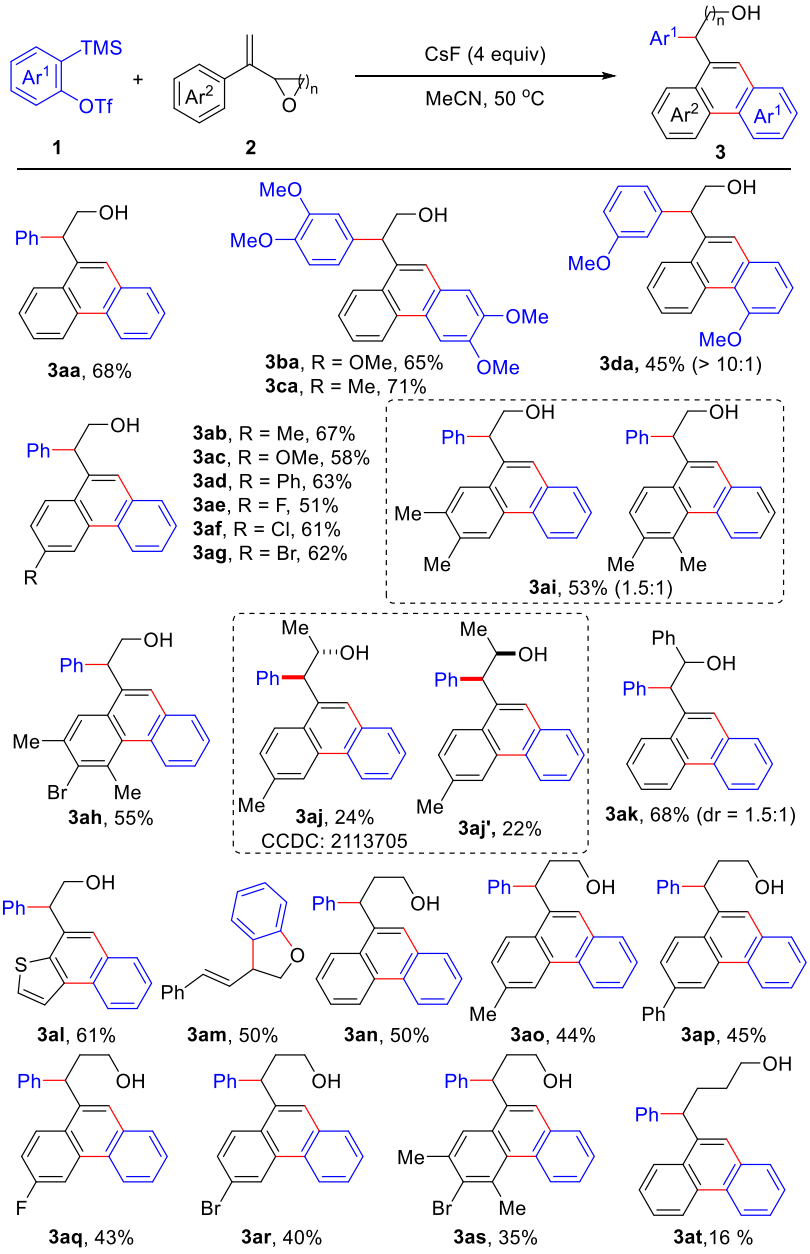
**Scheme 2. Scope of Arynes and Vinyl Epoxides/Oxetanes**[a]




[a]Reaction conditions: **1** (0.2 mmol), **2** (0.48 mmol), CsF (0.8 mmol), MeCN (2 mL), 50 °C, and 6 h; isolated yields.

and **3aj′** in 24 and 22% yields, respectively. The structure of **3aj** was confirmed unambiguously by single-crystal X-ray diffraction (XRD, CCDC 2113705). Additionally, vinyl phenyl-substituted epoxide **2k** gave the diastereoisomer **3ak** (dr = 1.5:1) in a 68% yield. Delightedly, the thienyl-substituted vinyl epoxide **2l** also worked well in this reaction, affording the desired product **3al** in a 61% yield. However, (*E*)-2-styryloxirane **2m** gave [3 + 1] cycloaddition product **3am** in a 50% yield. Encouraged by the abovementioned results, we turned to examine vinyl oxetanes. As expected, vinyl oxetanes with electron-donating (Me and Ph) or electron-withdrawing (F and Br) groups or trisubstituted groups in the aromatic ring worked well, giving the desired products (**3an**−**ar**) in moderate yields. Compared with vinyl epoxides/oxetanes, 2-(1-phenylvinyl)tetrahydrofuran **2t** only gave the desired product **3at** in a 16% yield.

To further understand the ring-opening reaction, we conducted some essential control experiments. The vinyl donor−acceptor cyclopropane **4a** could react smoothly with **1a** under the standard conditions resulted in the desired ring-opening product **5aa** in an 80% yield (Scheme 3a). In sharp contrast, vinyl cyclopropane **4b** afforded the products **5ab1**, **5ab2**, and **5ab3** in 48, 17, and 30% yields, respectively (Scheme 3b). These two results indicated that the ring strain of cyclopropane and polarity of the C−C bond is indispensable in this ring-opening reaction. Unfortunately, the reaction of **1a** and vinyl thiirane **4c** was very messy even at room temperature (Scheme 3c).[3] Due to the strong nucleophilicity of thiirane, the sulfonium yield formation might contend with the Diels−Alder reaction. Similar to vinyl thiirane, vinyl aziridine **4d** also gave a very messy reaction by the same token (Scheme 3d).[2] It is worth noting that no valuable product was detected by GC−



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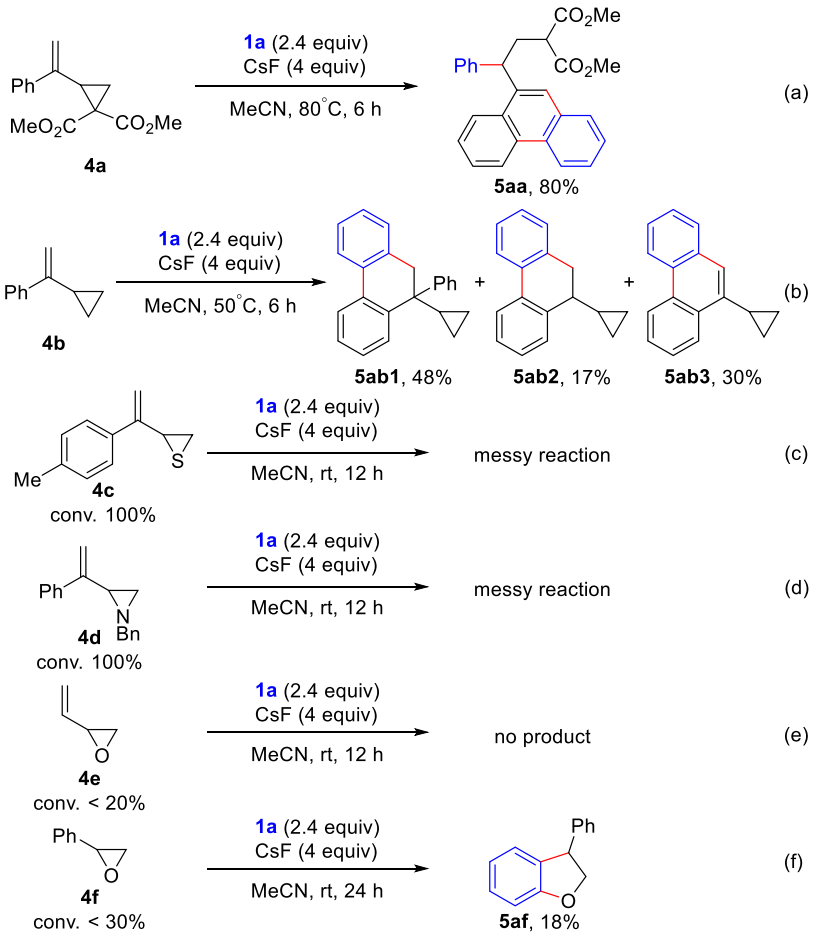
**Scheme 3. Control Experiments**




MS in the reaction of vinyl oxirane **4e** and **1a** (Scheme 3e). The result indicated that the aryl group was necessary for the Diels–Alder reaction. Different from thiirane and aziridine, epoxide **4e** displayed low reactivity toward arynes. Only an 18% yield of **5af** was detected by the crude $^1$H NMR,[4] and the conversion of epoxide **4f** was less than 30% (Scheme 3f). Based on the abovementioned experimental results, the reactivity toward arynes is aziridines/thioethers > styrenes > epoxides/oxetanes > cyclopropanes.

To prove the practicality of this approach, we executed the large-scale synthesis and further synthetic application for functionalized phenanthrenes (Scheme 4). When the reaction was scaled up to 5 mmol, 776 mg of **3aa** was obtained in a 52% yield. Then, a series of transformations of **3aa** were conducted utilizing the versatile hydroxy group. Surprisingly, **3aa** would transform into benzoyl phenanthrene **6** in an 85% yield in the presence of $Cs_2CO_3$ in dimethyl sulfoxide (DMSO) at 150 °C. As a ubiquitous nucleophile, a hydroxy group could react with various electrophiles to the corresponding functionalized phenanthrenes. For example, **3aa** reacted with propargyl bromide with the assistance of NaH in THF at 45 °C, affording the product **7** in an 88% yield. In addition, **3aa** was easily protected by benzoyl chloride (BzCl) and 4-methylbenzenesulfonyl chloride (TsCl) to yield the corresponding **8** and **9** in 93 and 85% yields, respectively. In addition, **9** would further transform using the OTs as a good leaving group. With the help of NaH, **9** could generate the styryl phenanthrene **10** in a 90% yield in THF at 60 °C. In addition, typical nucleophiles ($BnNH_2$ and $NaN_3$) could react with **9** to give the corresponding functionalized phenanthrenes **11** and **12** in 62 and 78% yields, respectively.

Based on the abovementioned experimental results, a plausible reaction mechanism is proposed in Scheme 5. Initially, aryl vinyl epoxides/cyclopropanes **2** reacted with *in situ*-generated arynes to yield the key intermediate **A** via the Diels–Alder reaction. Owing to the ring strain and polarity of the C–O/C–C bond (X = O or $C(CO_2Me)_2$), **A** readily experience ring-opening romanization, resulting in the corresponding intermediate **B**, which would further react with arynes to the final product **3** through the ene reaction. In the case of vinyl cyclopropane (X = $CH_2$), **A** not only could react with aryne to generate **5ab1** through the ene reaction but also generate the corresponding **5ab2** and **5ab3** through 1,3-hydrogen transfer and oxidative aromatization, respectively.

## CONCLUSIONS

In summary, we have developed a transition-metal-free procedure for the synthesis of phenanthrene from vinyl epoxides/oxetanes/cyclopropanes with arynes under mild conditions. This unique cascade reaction appeared to combine the Diels–Alder reaction, ring-opening romanization, and ene reaction. In addition, various functionalized phenanthrenes could be synthesized utilizing the versatile hydroxy group. Interestingly, vinyl epoxides/oxiranes experience preferentially the Diels–Alder reaction toward arynes over nucleophilic attack of epoxides/oxiranes. Further efforts are ongoing in our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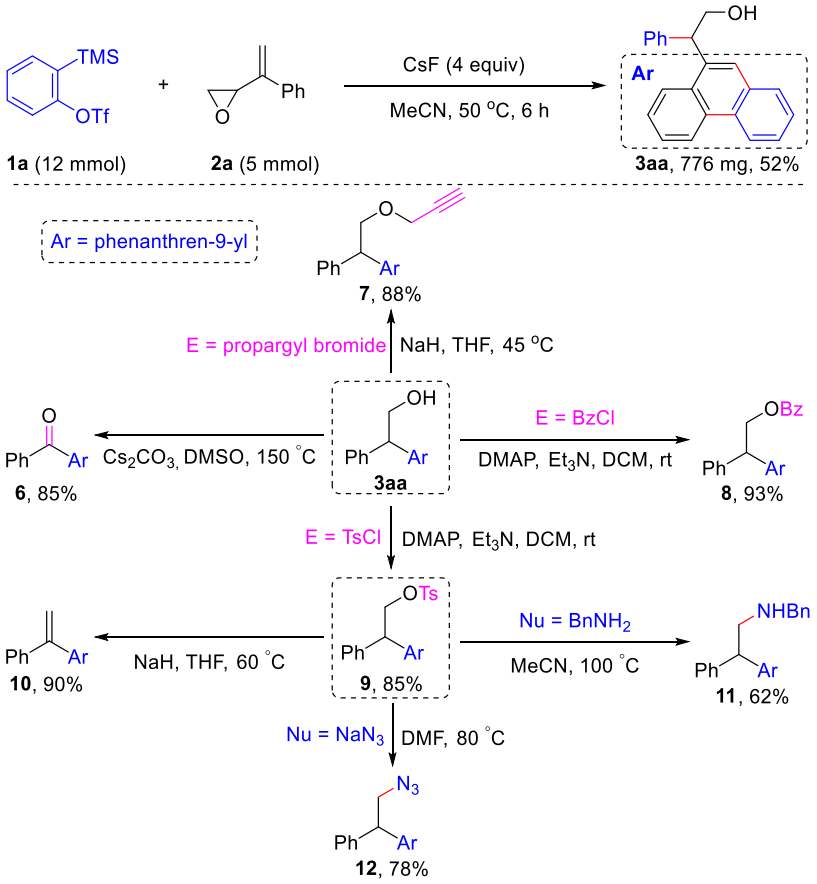
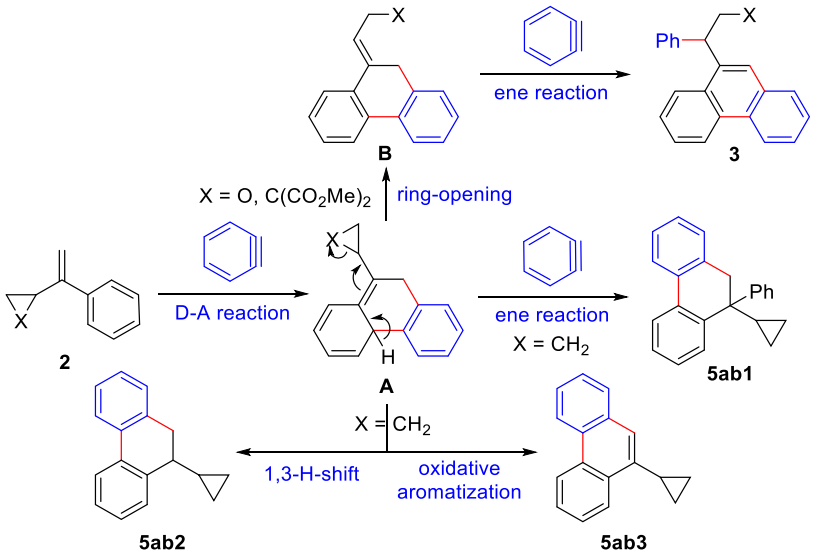
**Scheme 4. Larger Synthesis and Synthetic Application for Functionalized Phenanthrenes**




**Scheme 5. Plausible Mechanism**




laboratory to explore other ring-opening functionalization of vinyl strained rings.

## EXPERIMENTAL SECTION

**General Information.** All reagents purchased from commercial sources were used as received. The silica gel for column chromatography was supplied as 300−400 meshes. The $^{1}H$ and $^{13}C$ NMR spectra are referenced to the residual solvent signals (7.26 ppm for $^{1}H$ and 77.0 ppm for $^{13}C$ in $CDCl_3$). The high-resolution mass spectrometry (HRMS) spectra were recorded on a Bruker MicroTOF Q II spectrometer. Vinyl cyclopropane **4a**[15] and **4b**,[13a] vinyl thiirane **4c**,[16] and vinyl aziridine **4d**[17] were synthesized according to the literature.

**General Procedures for the Synthesis of Vinyl Epoxides 2a−l and Vinyl Tetrahydrofuran 2t.** To a 100 mL flame-dried round flask with a stir bar, methyltriphenylphosphonium bromide (2.32 g, 6.5 mmol) and dry THF (30



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mL) were added. The reaction solution was protected by argon, and cooled to −78 °C, and *n*-BuLi (2.6 mL, 6.5 mmol) was added slowly in 30 min. Then, acyl epoxides (5.0 mmol) in THF (5 mL) were added slowly, and the reaction was monitored by thin layer chromatography (TLC). The reaction mixture was quenched with saturated $NH_4Cl$ and the mixture was extracted with $CH_2Cl_2$. The organic layers were dried over $MgSO_4$ and filtered. The solvent was evaporated in vacuo and the residue was purified by column chromatography (50:1 PE/EA) to afford the corresponding vinyl epoxides.

*2-(1-Phenylvinyl)oxirane (**2a**).*[13a] Slightly yellow oil. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.48−7.44 (m, 2 H), 7.39−7.31(m, 3 H), 5.45 (d, $J$ = 0.8 Hz, 1 H), 5.38 (s, 1 H), 3.70−3.67 (m, 1 H), 3.05 (dd, $J$ = 5.9, 4.1 Hz, 1 H), 2.64 (dd, $J$ = 6.0, 2.6 Hz, 1 H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 144.6, 137.9, 128.4, 128.0, 126.2, 112.6, 52.3, 49.5.

*2-(1-(p-Tolyl)vinyl)oxirane (**2b**).*[18] Slightly yellow oil. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.36 (d, $J$ = 8.1 Hz, 2 H), 7.18 (d, $J$ = 8.0 Hz, 2 H), 5.42 (s, 1 H), 5.34 (s, 1 H), 3.68 (t, $J$ = 3.0 Hz, 1 H), 3.04 (dd, $J$ = 5.9, 4.1 Hz, 1 H), 2.63 (dd, $J$ = 6.0, 2.6 Hz, 1 H), 2.37 (s, 3 H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 144.4, 137.9, 135.1, 129.1, 126.0, 111.7, 52.4, 49.5, 21.1.

*2-(1-(4-Methoxyphenyl)vinyl)oxirane (**2c**).* Slightly yellow oil. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.44−7.36 (m, 2 H), 6.93−6.85 (m, 2 H), 5.37 (s, 1 H), 5.29 (s, 1 H), 3.82 (s, 3 H), 3.66 (t, $J$ = 3.2 Hz, 1 H), 3.04 (dd, $J$ = 5.9, 4.1 Hz, 1 H), 2.63 (dd, $J$ = 6.0, 2.6 Hz, 1 H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 159.6, 144.0, 130.5, 127.3, 113.8, 110.9, 55.2, 52.4, 49.3. HRMS (ESI) $m/z$: $[M + Na]^+$ calcd for 199.0730 $C_{11}H_{12}O_2Na$, found 199.0732.

*2-(1-([1,1′-Biphenyl]-4-yl)vinyl)oxirane (**2d**).* White solid. mp 90.4−92.7 °C. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.60 (dd, $J$ = 8.2, 2.1 Hz, 4 H), 7.55 (d, $J$ = 8.4 Hz, 2 H), 7.45 (t, $J$ = 7.6 Hz, 2 H), 7.37 (d, $J$ = 7.4 Hz, 1 H), 5.51 (s, 1 H), 5.41 (s, 1 H), 3.73 (t, $J$ = 3.1 Hz, 1 H), 3.08 (dd, $J$ = 5.9, 4.1 Hz, 1 H), 2.68 (dd, $J$ = 5.9, 2.6 Hz, 1 H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 144.1, 140.9, 140.6, 136.8, 128.8, 127.4, 127.2, 127.0, 126.6, 112.6, 52.3, 49.5. HRMS (ESI) $m/z$: $[M + H]^+$ calcd for 223.1117 $C_{16}H_{15}O$, found 223.1108.

*2-(1-(4-Fluorophenyl)vinyl)oxirane (**2e**).* Slightly yellow oil. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.47−7.38 (m, 2 H), 7.09−7.00 (m, 2 H), 5.40 (s, 1 H), 5.37 (s, 1 H), 3.64 (t, $J$ = 3.2 Hz, 1 H), 3.03 (dd, $J$ = 5.8, 4.1 Hz, 1 H), 2.61 (dd, $J$ = 5.9, 2.6 Hz, 1 H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 162.6 (d, $^1J_{C-F}$ = 247.2 Hz), 143.6, 133.9 (d, $^4J_{C-F}$ = 3.4 Hz), 127.9 (d, $^3J_{C-F}$ = 8.0 Hz), 115.2 (d, $^2J_{C-F}$ = 21.5 Hz), 112.9 (d, $^5J_{C-F}$ = 1.2 Hz), 52.3, 49.1. $^{19}$F NMR (376 MHz, $CDCl_3$) $\delta$ −114.06. GC−MS (EI) $m/z$: 164.1, 149.0, 135.1, 133.1, 109.1.

*2-(1-(4-Chlorophenyl)vinyl)oxirane (**2f**).* Slightly yellow oil. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.38 (d, $J$ = 8.6 Hz, 2 H), 7.32 (d, $J$ = 8.6 Hz, 2 H), 5.44 (s, 1 H), 5.40 (s, 1 H), 3.64 (t, $J$ = 3.2 Hz, 1 H), 3.04 (dd, $J$ = 5.8, 4.1 Hz, 1 H), 2.61 (dd, $J$ = 5.9, 2.6 Hz, 1 H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 143.6, 136.3, 134.0, 128.6, 127.6, 113.5, 52.2, 49.2. GC−MS (EI) $m/z$: 180.0, 165.0, 151.0, 145.1, 125.1, 115.1.

*2-(1-(4-Bromophenyl)vinyl)oxirane (**2g**).* Slightly yellow oil. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.51−7.45 (m, 2 H), 7.35−7.29 (m, 2 H), 5.44 (s, 1 H), 5.40 (s, 1 H), 3.64 (t, $J$ = 3.1 Hz, 1 H), 3.03 (dd, $J$ = 5.8, 4.1 Hz, 1 H), 2.61 (dd, $J$ = 5.9, 2.6 Hz, 1 H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 143.6, 136.3, 133.9, 128.6, 127.6, 113.5, 52.2, 49.2. GC−MS (EI) $m/z$: 223.9, 194.9, 168.9, 145.1, 125.1, 115.1.

*2-(1-(4-Bromo-3,5-dimethylphenyl)vinyl)oxirane (**2h**).* Slightly yellow oil. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.15 (s, 2 H), 5.42 (s, 1 H), 5.37 (s, 1 H), 3.64 (t, $J$ = 3.2 Hz, 1 H), 3.04 (dd, $J$ = 5.8, 4.1 Hz, 1 H), 2.62 (dd, $J$ = 5.9, 2.6 Hz, 1 H), 2.43 (s, 6 H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 143.9, 138.3, 136.4, 127.3, 126.0, 113.0, 52.2, 49.4, 23.9. HRMS (ESI) $m/z$: $[M + Na]^+$ calcd for 275.0042 $C_{12}H_{13}OBrNa$, found 275.0041.

*2-(1-(3,4-Dimethylphenyl)vinyl)oxirane (**2i**).* Slightly yellow oil. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.25 (s, 1 H), 7.21 (d, $J$ = 7.8 Hz, 1 H), 7.13 (d, $J$ = 7.8 Hz, 1 H), 5.41 (d, $J$ = 0.6 Hz, 1 H), 5.32 (s, 1 H), 3.68 (t, $J$ = 3.1 Hz, 1 H), 3.05 (dd, $J$ = 6.0, 4.1 Hz, 1 H), 2.64 (dd, $J$ = 6.0, 2.6 Hz, 1 H), 2.30 (s, 3 H), 2.28 (s, 3 H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 144.5, 136.6, 135.6, 129.7, 127.3, 123.5, 111.5, 52.4, 49.6, 19.8, 19.4. HRMS (ESI) $m/z$: $[M + Na]^+$ calcd for 197.0937 $C_{12}H_{14}ONa$, found 197.0935.

*2-Methyl-3-(1-(p-tolyl)vinyl)oxirane (**2j**).* Slightly yellow oil. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.34 (d, $J$ = 8.0 Hz, 2 H), 7.18 (d, $J$ = 8.0 Hz, 2 H), 5.39 (s, 1 H), 5.31 (d, $J$ = 9.7 Hz, 1 H), 3.39 (s, 1 H), 2.90−2.85 (m, 1 H), 2.37 (s, 3 H), 1.46 (d, $J$ = 5.2 Hz, 3 H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 144.3, 137.8, 135.3, 129.1, 125.9, 111.1, 59.4, 57.6, 21.1, 17.7. GC−MS (EI) $m/z$: 174.1, 159.1, 145.1, 131.1, 128.1, 115.1.

*2-Phenyl-3-(1-phenylvinyl)oxirane (**2k**).* White solid. mp 36.5−37.7 °C. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.55−7.30 (m, 10 H), 5.58 (d, $J$ = 0.5 Hz, 1 H), 5.54 (s, 1 H), 3.78 (s, 1 H), 3.75 (s, 1 H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 144.0, 137.7, 137.0, 128.6, 128.5, 128.3, 128.1, 126.0, 125.6, 112.0, 62.5, 61.5. HRMS (ESI) $m/z$: $[M + Na]^+$ calcd for 245.0937 $C_{16}H_{14}ONa$, found 245.0929.

*2-(1-(Thiophen-2-yl)vinyl)oxirane (**2l**).* Slightly yellow oil. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.23 (d, $J$ = 5.1 Hz, 1 H), 7.16 (d, $J$ = 3.5 Hz, 1 H), 7.02 (dd, $J$ = 4.9, 3.8 Hz, 1 H), 5.48 (s, 1 H), 5.29 (s, 1 H), 3.80−3.66 (m, 1 H), 3.02 (dd, $J$ = 5.8, 4.1 Hz, 1 H), 2.69 (dd, $J$ = 5.9, 2.6 Hz, 1 H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 140.9, 138.3, 127.3, 124.8, 123.9, 111.2, 51.9, 48.9. GC−MS (EI) $m/z$: 152.1, 135.1, 123.1, 109.0, 97.0.

*2-(1-Phenylvinyl)tetrahydrofuran (**2t**).*[20] Slightly yellow oil. $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.45−7.27 (m, 5 H), 5.37 (t, $J$ = 1.4 Hz, 1 H), 5.30 (s, 1 H), 4.86 (t, $J$ = 6.9 Hz, 1 H), 4.07−3.97 (m, 1 H), 3.97−3.82 (m, 1 H), 2.18−2.03 (m, 1 H), 1.99−1.85 (m, 2 H), 1.73−1.55 (m, 1 H). $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 149.6, 139.9, 128.2, 127.4, 126.7, 111.6, 80.1, 68.4, 31.7, 25.5.

**General Procedures for the Synthesis of Vinyl Epoxide 2m.** To a 100 mL flame-dried round flask with a stir bar, NaH (60% purity, 44 mg, 1.1 mmol) and dry THF (2 mL) were added, followed by NaI (14 mg, 10 mol %). The reaction solution was cooled to 0 °C, then (*E*)-1-chloro-3-phenylprop-2-en-1-ol (182 mg, 1 mmol) in THF (1 mL) was added slowly over 30 min to the abovementioned solution. The reaction was monitored by TLC. Then, the reaction mixture was quenched with saturated $NH_4Cl$ and the mixture was extracted with EtOAc. The organic layers were dried over $MgSO_4$ and filtered. The solvent was evaporated in vacuo and the residue was purified by column chromatography (50:1 PE/EA) to afford the desired (*E*)-2-styryloxirane (**2m**)[19] as a slightly yellow oil: $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.43−7.26 (m, 5 H), 6.82 (d, $J$ = 16.0 Hz, 1 H), 5.88 (dd, $J$ = 16.0, 8.0 Hz, 1 H), 3.60−3.47 (m, 1 H), 3.11−3.02 (m, 1 H), 2.78 (dd, $J$ = 5.2, 2.6 Hz, 1 H). $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 136.0, 134.5, 128.6, 128.0, 126.9, 126.4, 52.6, 49.2.



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**General Procedures for the Synthesis of Vinyl Oxetanes 2n−t.**[21] To a 25 mL screw-capped test tube with a stir bar, vinyl epoxides (1 mmol), *t*-BuOH (5 mL), and trimethylsulfoxonium iodide (440 mg, 2 mmol) were added. Then, *t*-BuOK (224 mg, 2 mmol) was added to the abovementioned solution. The mixture was stirred at 50 °C for 12 h. Most of the reaction mixture was evaporated, and the residue was purified by column chromatography (50:1 PE/EA) to afford the corresponding vinyl oxetanes.

*2-(1-Phenylvinyl)oxetane (**2n**).*[20] Slightly yellow oil. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.41−7.27 (m, 5 H), 5.70 (t, $J$ = 7.5 Hz, 1 H), 5.60 (s, 1 H), 5.57 (s, 1 H), 4.82−4.76 (m, 1 H), 4.60−4.55 (m, 1 H), 2.98−2.90 (m, 1 H), 2.55−2.46 (m, 1 H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 148.8, 137.5, 128.4, 127.8, 125.9, 110.9, 81.8, 68.0, 29.0.

*2-(1-(p-Tolyl)vinyl)oxetane (**2o**).* Slightly yellow oil. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.24 (d, $J$ = 8.1 Hz, 2 H), 7.15 (d, $J$ = 8.1 Hz, 2 H), 5.68 (t, $J$ = 7.5 Hz, 1 H), 5.53 (s, 1 H), 5.52 (s, 1 H), 4.84−4.74 (m, 1 H), 4.59−4.54 (m, 1 H), 3.00−2.87 (m, 1 H), 2.52−2.44 (m, 1 H), 2.35 (s, 3 H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 148.6, 137.5, 134.5, 129.1, 125.7, 109.9, 81.8, 68.0, 29.0, 21.0. HRMS (ESI) $m/z$: $[M + Na]^+$ calcd for 197.0937 $C_{12}H_{14}ONa$, found 197.0937.

*2-(1-([1,1′-Biphenyl]-4-yl)vinyl)oxetane (**2p**).* White solid. mp 89.8−92.4 °C. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.67−7.57 (m, 4 H), 7.52−7.43 (m, 4 H), 7.38 (t, $J$ = 7.3 Hz, 1 H), 5.77 (t, $J$ = 7.5 Hz, 1 H), 5.65 (s, 2 H), 4.71−4.66 (m, 1 H), 4.68−4.55 (m, 1 H), 3.10−2.80 (m, 1 H), 2.66−2.46 (m, 1 H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 148.4, 140.6, 140.5, 136.4, 128.7, 127.3, 127.1, 126.9, 126.2, 110.8, 81.7, 68.1, 29.0. HRMS (ESI) $m/z$: $[M + Na]^+$ calcd for 259.1093 $C_{17}H_{16}ONa$, found 259.1090.

*2-(1-(4-Fluorophenyl)vinyl)oxetane (**2q**).* Slightly yellow oil. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.39−7.28 (m, 2 H), 7.08−6.98 (m, 2 H), 5.64 (t, $J$ = 7.5 Hz, 1 H), 5.54 (s, 1 H), 5.48 (s, 1 H), 4.83−4.72 (m, 1 H), 4.59−4.49 (m, 1 H), 3.01−2.82 (m, 1 H), 2.60−2.38 (m, 1 H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 162.5 (d, $^1J_{C-F}$ = 246.9 Hz), 147.9, 133.7 (d, $^4J_{C-F}$ = 3.4 Hz), 127.7 (d, $^3J_{C-F}$ = 7.9 Hz), 115.3 (d, $^2J_{C-F}$ = 21.3 Hz), 111.1, 81.8, 68.0, 28.8. $^{19}$F NMR (376 MHz, $CDCl_3$) $\delta$ −114.42. GC−MS (EI) $m/z$: 178.1, 150.1, 133.1, 121.1, 101.1.

*2-(1-(4-Bromophenyl)vinyl)oxetane (**2r**).* White solid. mp 46.7−48.9 °C. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.45 (d, $J$ = 8.5 Hz, 2 H), 7.21 (d, $J$ = 8.5 Hz, 2 H), 5.63 (t, $J$ = 7.5 Hz, 1 H), 5.57 (s, 1 H), 5.53 (s, 1 H), 4.79−4.74 (m, 1 H), 4.60−4.48 (m, 1 H), 2.99−2.84 (m, 1 H), 2.55−2.39 (m, 1 H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 147.9, 136.5, 131.5, 127.6, 121.8, 111.7, 81.6, 68.0, 28.7. HRMS (ESI) $m/z$: $[M + Na]^+$ calcd for 260.9885 $C_{11}H_{11}OBrNa$, found 260.9884.

*2-(1-(4-Bromo-3,5-dimethylphenyl)vinyl)oxetane (**2s**).* Slightly yellow oil. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.05 (s, 2 H), 5.64 (t, $J$ = 7.4 Hz, 1 H), 5.54 (s, 1 H), 5.50 (s, 1 H), 4.79−4.74 (m, 1 H), 4.57−4.52 (m, 1 H), 2.97−2.84 (m, 1 H), 2.54−2.35 (m, 7 H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 148.3, 138.3, 136.2, 127.0, 125.8, 111.3, 81.7, 68.0, 28.8, 24.0. HRMS (ESI) $m/z$: $[M + Na]^+$ calcd for 289.0198 $C_{13}H_{15}OBrNa$, found 289.0196.

**General Procedures for the Synthesis of Phenanthrenes 3aa−da, 3ab−at, 5aa, 5ab1, 5ab2, and 5ab3.** To a 10 mL flame-dried screw-capped test tube with a stir bar, aryne precursor **1** (0.48 mmol, 2.4 equiv), vinyl epoxides/oxetanes **2** (0.2 mmol), and MeCN (2 mL) were added. Then, CsF (70 mg, 1.2 mmol, 4 equiv) was added to the abovementioned solution. The mixture was stirred at 50 °C for 6 h. Most of the reaction mixture was evaporated, and the residue was purified by column chromatography (10:1 PE/EA) to afford the desired phenanthrenes **3**.

*2-(Phenanthren-9-yl)-2-phenylethan-1-ol (**3aa**).* Overall, 41 mg of **3aa** was obtained from **1a** (143 mg, 0.48 mmol) and **2a** (29 mg, 0.2 mmol) in a 68% yield; purified by column chromatography (10:1 PE/EA); white solid. mp 106.9−107.8 °C. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.73 (d, $J$ = 8.2 Hz, 1 H), 8.68 (d, $J$ = 7.9 Hz, 1 H), 8.09 (d, $J$ = 8.2 Hz, 1 H), 7.92 (d, $J$ = 7.4 Hz, 1 H), 7.80 (s, 1 H), 7.71−7.57 (m, 3 H), 7.54 (t, $J$ = 7.5 Hz, 1 H), 7.37 (d, $J$ = 7.4 Hz, 2 H), 7.31 (t, $J$ = 7.3 Hz, 2 H), 7.23 (t, $J$ = 7.1 Hz, 1 H), 4.99 (t, $J$ = 6.6 Hz, 1 H), 4.50−4.40 (m, 1 H), 4.39−4.28 (m, 1 H), 1.74 (s, 1 H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 141.2, 134.8, 131.3, 131.1, 131.0, 129.8, 129.4, 128.7, 128.6, 128.44, 128.39, 126.9, 126.73, 126.69, 126.6, 126.3, 125.3, 124.5, 123.2, 122.4, 66.1, 49.3. HRMS (ESI) $m/z$: $[M + Na]^+$ calcd for 321.1250 $C_{22}H_{18}ONa$, found 321.1244.

*9-(2-Phenoxy-1-phenylethyl)phenanthrene (**3aa′**).* Overall, 11 mg of **3aa′** was obtained from **1a** (143 mg, 0.48 mmol) and **2a** (29 mg, 0.2 mmol) in a 15% yield; purified by column chromatography (100:1 PE/EA); white solid. mp 50.4−52.8 °C $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.75 (d, $J$ = 8.1 Hz, 1 H), 8.69 (d, $J$ = 8.2 Hz, 1 H), 8.11 (d, $J$ = 8.2 Hz, 1 H), 7.87 (d, $J$ = 7.8 Hz, 1 H), 7.73 (s, 1 H), 7.68−7.57 (m, 3 H), 7.57−7.51 (m, 1 H), 7.39 (d, $J$ = 7.3 Hz, 2 H), 7.33−7.27 (m, 4 H), 7.23 (t, $J$ = 7.3 Hz, 1 H), 7.00−6.92 (m, 3 H), 5.30 (t, $J$ = 7.0 Hz, 1 H), 4.75 (dd, $J$ = 9.6, 7.1 Hz. 1 H), 4.63 (dd, $J$ = 9.6, 6.9 Hz, 1 H). $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 158.7, 141.4, 134.8, 131.4, 131.04, 130.96, 129.9, 129.5, 128.8, 128.59, 128.55, 126.8, 126.71, 126.68, 126.5, 126.2, 126.0, 124.5, 123.2, 122.4, 120.9, 114.8, 70.7, 46.5. HRMS (ESI) $m/z$: $[M + Na]^+$ calcd for 397.1563 $C_{28}H_{22}ONa$, found 397.1562.

*2-(2,3-Dimethoxyphenanthren-9-yl)-2-(3,4-dimethoxyphenyl)ethan-1-ol (**3ba**).* Overall, 54 mg of **3ba** was obtained from **1b** (172 mg, 0.48 mmol) and **2a** (29 mg, 0.2 mmol) in a 65% yield; purified by column chromatography (10:1 PE/EA); white solid. mp 203.1−204.7 °C. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.59 (d, $J$ = 8.3 Hz, 1 H), 8.10 (d, $J$ = 8.3 Hz, 1 H), 8.00 (s, 1 H), 7.68 (s, 1 H), 7.61 (t, $J$ = 7.5 Hz, 1 H), 7.51 (t, $J$ = 7.5 Hz, 1 H), 7.27 (s, 1 H), 6.91 (d, $J$ = 9.5 Hz, 2 H), 6.82 (d, $J$ = 8.0 Hz, 1 H), 4.94 (t, $J$ = 6.4 Hz, 1 H), 4.47−4.36 (m, 1 H), 4.36−4.26 (m, 1 H), 4.13 (s, 3 H), 4.06 (s, 3 H), 3.85 (s, 3 H), 3.81 (s, 3 H), 1.89 (s, 1 H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 149.4, 149.3, 149.1, 147.8, 133.8, 133.2, 130.4, 130.3, 126.4, 125.9, 125.6, 124.5, 124.4, 124.3, 122.6, 120.4, 111.8, 111.2, 108.4, 103.0, 66.1, 56.0, 55.9, 55.8, 55.7, 48.7. HRMS (ESI) $m/z$: $[M + Na]^+$ calcd for 441.1672 $C_{26}H_{26}O_5Na$, found 441.1668.

*2-(2,3-Dimethylphenanthren-9-yl)-2-(3,4-dimethylphenyl)ethan-1-ol (**3ca**).* White solid. Overall, 50 mg of **3ca** was obtained from **1c** (157 mg, 0.48 mmol) and **2a** (29 mg, 0.2 mmol) in a 71% yield; purified by column chromatography (10:1 PE/EA); mp 132.7−134.3 °C. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.70 (d, $J$ = 8.2 Hz, 1 H), 8.43 (s, 1 H), 8.09 (d, $J$ = 8.2 Hz, 1 H), 7.71 (d, $J$ = 9.9 Hz, 2 H), 7.59 (t, $J$ = 7.4 Hz, 1 H), 7.51 (t, $J$ = 7.5 Hz, 1 H), 7.16−7.02 (m, 3 H), 4.91 (t, $J$ = 6.8 Hz, 1 H), 4.47−4.34 (m, 1 H), 4.35−4.23 (m, 1 H), 2.55 (s, 3 H), 2.50 (s, 3 H), 2.22 (s, 3 H), 2.20 (s, 3 H), 1.75 (s, 1 H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 138.6, 136.9, 136.0, 135.8, 135.1, 134.0, 131.0, 130.8, 130.0, 129.6, 128.7, 128.2, 126.2, 126.0, 125.8, 124.6, 124.4, 122.9, 122.7,


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66.3, 48.9, 20.6, 19.9, 19.8, 19.3. HRMS (ESI) $m/z$: $[M + Na]^+$ calcd for 377.1876 $C_{26}H_{26}O_5Na$, found 377.1876.

*2-(4-Methoxyphenanthren-9-yl)-2-(3-methoxyphenyl)-ethan-1-ol (**3da**)*. White solid. Overall, 32 mg of **3da** was obtained from **1d** (157 mg, 0.48 mmol) and **2a** (29 mg, 0.2 mmol) in a 45% yield; purified by column chromatography (10:1 PE/EA); mp 125.5−127.0 °C. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 9.76 (d, $J$ = 8.4 Hz, 1 H), 8.09 (d, $J$ = 8.1 Hz, 1 H), 7.76 (s, 1 H), 7.64−7.49 (m, 4 H), 7.22 (t, $J$ = 7.9 Hz, 1 H), 7.19−7.12 (m, 1 H), 6.96 (d, $J$ = 7.6 Hz, 1 H), 6.90 (s, 1 H), 6.76 (dd, $J$ = 8.2, 2.3 Hz, 1 H), 4.95 (t, $J$ = 6.7 Hz, 1 H), 4.32 (dd, $J$ = 11.0, 6.7 Hz, 1 H), 4.22 (dd, $J$ = 11.0, 6.7 Hz, 1 H), 4.13 (s, 3 H), 3.73 (s, 3 H), 1.77 (s, 1 H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 159.9, 158.5, 142.9, 135.1, 133.8, 131.6, 131.2, 129.7, 129.0, 126.7, 126.00, 125.98, 125.8, 123.8, 121.7, 120.9, 120.3, 114.7, 111.8, 108.5, 66.2, 55.8, 55.1, 49.3. HRMS (ESI) $m/z$: $[M + Na]^+$ calcd for 381.1461 $C_{24}H_{22}O_3Na$, found 381.1452.

*2-(6-Methylphenanthren-9-yl)-2-phenylethan-1-ol (**3ab**)*. Overall, 42 mg of **3ab** was obtained from **1a** (143 mg, 0.48 mmol) and **2b** (32 mg, 0.2 mmol) in a 67% yield; purified by column chromatography (10:1 PE/EA); white solid. mp 142.3−144.4 °C. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.70 (d, $J$ = 7.9 Hz, 1 H), 8.55 (s, 1 H), 8.00 (d, $J$ = 8.5 Hz, 1 H), 7.93 (d, $J$ = 7.3 Hz, 1 H), 7.75 (s, 1 H), 7.69−7.60 (m, 2 H), 7.40−7.36 (m, 3 H), 7.32 (t, $J$ = 7.5 Hz, 2 H), 7.26−7.22 (d, $J$ = 7.1 Hz, 1 H), 4.97 (t, $J$ = 6.7 Hz, 1 H), 4.43 (dd, $J$ = 11.1, 6.9 Hz, 1 H), 4.32 (dd, $J$ = 11.1, 6.7 Hz, 1 H), 2.60 (s, 3 H), 1.96 (s, 1 H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 141.3, 135.9, 134.7, 131.5, 131.1, 129.6, 129.0, 128.7, 128.6, 128.4, 128.4, 126.8, 126.6, 126.3, 124.3, 124.3, 122.9, 122.4, 66.1, 49.3, 21.8. HRMS (ESI) $m/z$: $[M + Na]^+$ calcd for 335.1406 $C_{23}H_{20}ONa$, found 335.1404.

*2-(6-Methoxyphenanthren-9-yl)-2-phenylethan-1-ol (**3ac**)*. Overall, 38 mg of **3ac** was obtained from **1a** (143 mg, 0.48 mmol) and **2c** (35 mg, 0.2 mmol) in a 58% yield; purified by column chromatography (10:1 PE/EA); white solid. mp 45.7−46.5 °C. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.63−8.55 (m, 1 H), 8.09 (d, $J$ = 2.4 Hz, 1 H), 7.99 (d, $J$ = 9.1 Hz, 1 H), 7.89 (dd, $J$ = 9.7, 7.4 Hz, 1 H), 7.67 (s, 1 H), 7.66−7.57 (m, 2 H), 7.35 (d, $J$ = 7.3 Hz, 2 H), 7.30 (t, $J$ = 7.5 Hz, 2 H), 7.22 (t, $J$ = 7.1 Hz, 1 H), 7.17 (dd, $J$ = 9.1, 2.5 Hz, 1 H), 4.94 (t, $J$ = 6.8 Hz, 1 H), 4.43 (dd, $J$ = 11.0, 7.0 Hz, 1 H), 4.31 (dd, $J$ = 11.0, 6.7 Hz, 1 H), 3.98 (s, 3 H), 1.79 (s, 1 H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 158.0, 141.2, 134.7, 132.6, 131.9, 129.4, 128.8, 128.7, 128.4, 126.9, 126.8, 126.2, 126.1, 125.7, 122.9, 122.5, 116.3, 104.7, 66.2, 55.4, 49.4. HRMS (ESI) $m/z$: $[M + Na]^+$ calcd for 351.1356 $C_{23}H_{20}O_2Na$, found 351.1353.

*2-Phenyl-2-(6-phenylphenanthren-9-yl)ethan-1-ol (**3ad**)*. Overall, 47 mg of **3ad** was obtained from **1a** (143 mg, 0.48 mmol) and **2d** (44 mg, 0.2 mmol) in a 63% yield; purified by column chromatography (10:1 PE/EA); white solid. mp 82.7−84.3 °C. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.83 (s, 1 H), 8.66 (d, $J$ = 7.9 Hz, 1 H), 8.05 (d, $J$ = 8.6 Hz, 1 H), 7.83 (d, $J$ = 7.4 Hz, 1 H), 7.77−7.62 (m, 4 H), 7.62−7.48 (m, 2 H), 7.41 (t, $J$ = 7.3 Hz, 2 H), 7.36−7.26 (m, 3 H), 7.22 (t, $J$ = 7.3 Hz, 2 H), 7.13 (m, 1 H), 4.90 (t, $J$ = 6.4 Hz, 1 H), 4.41−4.30 (m, 1 H), 4.30−4.16 (m, 1 H), 1.74 (s, 1 H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 141.2, 141.1, 138.9, 134.70, 131.67, 131.3, 130.3, 123.0, 128.9, 128.8, 128.7, 128.5, 127. 5, 127.0, 126.9, 126.7, 126.0, 125.4, 125.0, 122.5, 121.5, 66.2, 49.4. HRMS (ESI) $m/z$: $[M + Na]^+$ calcd for 397.1563 $C_{28}H_{20}ONa$, found 397.1559.

*2-(6-Fluorophenanthren-9-yl)-2-phenylethan-1-ol (**3ae**)*. New compound. Overall, 32 mg of **3ae** was obtained from **1a** (143 mg, 0.48 mmol) and **2e** (33 mg, 0.2 mmol) in a 51% yield; purified by column chromatography (10:1 PE/EA); white solid. mp 140.9−143.5 °C. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.58−8.47 (m, 1 H), 8.31 (dd, $J$ = 11.0, 2.1 Hz, 1 H), 8.09−7.99 (m, 1 H), 7.96−7.87 (m, 1 H), 7.77 (s, 1 H), 7.70−7.61 (m, 2 H), 7.42−7.21 (m, 6 H), 4.92 (t, $J$ = 6.6 Hz, 1 H), 4.49−4.37 (m, 1 H), 4.38−4.26 (m, 1 H), 1.74 (s, 1 H). $^{19}$F NMR (376 MHz, $CDCl_3$) $\delta$ -114.17. $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 161.2 (d, $^1J_{C-F}$ = 246.0 Hz), 141.0, 134.5, 132.9 (d, $^3J_{C-F}$ = 8.1 Hz), 131.8, 129.3, 129.2, 128.8, 128.7, 128.4, 127.8 (d, $^4J_{C-F}$ = 1.4 Hz), 127.4, 127.1, 126.8 (d, $^3J_{C-F}$ = 8.8 Hz), 126.7, 124.5 (d, $^4J_{C-F}$ = 2.1 Hz), 122.6, 115.5 (d, $^2J_{C-F}$ = 23.3 Hz), 108.2 (d, $^2J_{C-F}$ = 21.9 Hz), 66.1, 49.5. HRMS (ESI) $m/z$: $[M + Na]^+$ calcd for 339.1156 $C_{22}H_{17}OFNa$, found 339.1160.

*2-(6-Chlorophenanthren-9-yl)-2-phenylethan-1-ol (**3af**)*. Overall, 41 mg of **3af** was obtained from **1a** (143 mg, 0.48 mmol) and **2f** (36 mg, 0.2 mmol) in a 61% yield; purified by column chromatography (10:1 PE/EA); white solid. mp 156.7−158.1 °C. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.60 (s, 1 H), 8.51 (d, $J$ = 6.3 Hz, 1 H), 7.92 (d, $J$ = 8.7 Hz, 1 H), 7.86 (d, $J$ = 5.9 Hz, 1 H), 7.75 (s, 1 H), 7.60 (s, 2 H), 7.40 (d, $J$ = 8.6 Hz, 1 H), 7.33−7.12 (m, 5 H), 4.85 (s, 1 H), 4.43−4.32 (m, 1 H), 4.32−4.21 (m, 1 H), 1.64 (s, 1 H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 140.9, 134.5, 132.5, 132.3, 131.7, 129.5, 128.8, 128.7, 128.4, 127.4, 127.1, 126.9, 126.1, 125.5, 122.8, 122.5, 66.1, 49.4. HRMS (ESI) $m/z$: $[M + Na]^+$ calcd for 335.0860 $C_{22}H_{17}OClNa$, found 335.0854.

*2-(6-Bromophenanthren-9-yl)-2-phenylethan-1-ol (**3ag**)*. Overall, 47 mg of **3ag** was obtained from **1a** (143 mg, 0.48 mmol) and **2g** (45 mg, 0.2 mmol) in a 62% yield; purified by column chromatography (10:1 PE/EA); white solid. mp 154.7−156.3 °C. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.73 (s, 1 H), 8.46 (d, $J$ = 7.5 Hz, 1 H), 7.80 (d, $J$ = 8.6 Hz, 2 H), 7.72 (s, 1 H), 7.61−7.51 (m, 2 H), 7.49 (d, $J$ = 8.8 Hz, 1 H), 7.24−7.10 (m, 5 H), 4.79 (t, $J$ = 6.5 Hz, 1 H), 4.39−4.27 (m, 1 H), 4.26−4.15 (m, 1 H), 1.65 (s, 1 H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 140.9, 134.5, 132.5, 132.3, 131.7, 129.5, 128.8, 128.7, 128.4, 127.4, 127.1, 126.9, 126.1, 125.5, 122. 8, 122.5, 66.1, 49.4. HRMS (ESI) $m/z$: $[M + Na]^+$ calcd for 339.0355 $C_{22}H_{17}OBrNa$, found 339.0341.

*2-(6-Bromo-5,7-dimethylphenanthren-9-yl)-2-phenylethan-1-ol (**3ah**)*. Overall, 44 mg of **3ah** was obtained from **1a** (143 mg, 0.48 mmol) and **2h** (50 mg, 0.2 mmol) in a 55% yield; purified by column chromatography (10:1 PE/EA); white solid. mp 146.3−147.7 °C. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.57−8.46 (m, 1 H), 7.93−7.85 (m, 1 H), 7.81 (s, 1 H), 7.73 (s, 1 H), 7.61−7.53 (m, 2 H), 7.37−7.28 (m, 4 H), 7.25−7.20 (m, 1 H), 4.90 (t, $J$ = 6.7 Hz, 1 H), 4.45−4.36 (m, 1 H), 4.35−4.27 (m, 1 H), 3.12 (s, 3 H), 2.54 (s, 3 H), 1.66 (t, $J$ = 5.8 Hz, 1 H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 141.1, 135.9, 135.2, 134.1, 132.6, 131.3, 130.9, 130.2, 130.0, 128.9, 128.4, 128.3, 128.0, 127.0, 126.6, 125.9, 125.1, 123.3, 66.3, 49.3, 27.2, 25.1. HRMS (ESI) $m/z$: $[M + Na]^+$ calcd for 427.0668 $C_{24}H_{21}OBrNa$, found 427.0662.

*2-(6,7-Dimethylphenanthren-9-yl)-2-phenylethan-1-ol (**3ai**) and 2-(5,6-Dimethylphenanthren-9-yl)-2-phenylethan-1-ol (**3ai′**)*. Overall, 35 mg of **3ai** and **3ai′** was obtained from **1a** (143 mg, 0.48 mmol) and **2i** (35 mg, 0.2 mmol) in a 53% yield; purified by column chromatography (10:1 PE/EA); white solid. mp 129.5−131.2 °C. Major isomer (**3ai**); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.65 (d, $J$ = 8.1 Hz, 1 H), 8.48 (s,


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1 H), 7.87 (d, $J$ = 6.3 Hz, 2 H), 7.68 (s, 1 H), 7.64−7.55 (m, 2 H), 7.39 (d, $J$ = 7.4 Hz, 2 H), 7.32 (t, $J$ = 7.6 Hz, 2 H), 7.23 (t, $J$ = 6.8 Hz, 1 H), 5.00 (t, $J$ = 6.8 Hz, 1 H), 4.47−4.39 (m, 1 H), 4.32 (dd, $J$ = 10.5, 6.9 Hz, 1 H), 2.50 (s, 3 H), 2.42 (s, 3 H), 1.76 (s, 1 H). Representative peaks of minor (**3ai′**); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.62 (d), 7.85−7.79 (m), 7.68 (s), 4.94 (t), 2.93 (s), 2.51 (s), 1.80 (s). Major isomer (**3ai**); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 141.30, 135.91, 135.59, 134.41, 131.12, 129.59, 129.35, 128.76, 128.54, 128.44, 126.85, 126.33, 126.18, 124.66, 124.37, 123.54, 122.21, 66.2, 49.2, 20.5, 20.3. Representative peaks of minor (**3ai′**); 141.4, 136.3, 134.6, 133.6, 130.8, 130.3, 129.4, 128.6, 128.3, 128.2, 125.9, 124.63, 124.61, 121.6, 66.3, 49.4, 22.1, 21.4. HRMS (ESI) $m/z$: [M + Na]$^+$ calcd for 349.1563 $C_{24}H_{22}ONa$, found 348.1553.

*(1R, 2S or 1S, 2R)-1-(6-Methylphenanthren-9-yl)-1-phenylpropan-2-ol (**3aj**).* Overall, 16 mg of **3aj** was obtained from **1a** (143 mg, 0.48 mmol) and **2j** (35 mg, 0.2 mmol) in a 24% yield; purified by column chromatography (10:1 PE/EA); white solid. mp 181.7−183.4 °C. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.65 (dd, $J$ = 14.3, 7.4 Hz, 1 H), 8.50 (s, 1 H), 8.11 (d, $J$ = 8.5 Hz, 1 H), 8.02 (s, 1 H), 7.95 (dd, $J$ = 6.1, 2.9 Hz, 1 H), 7.67−7.58 (m, 2 H), 7.43−7.36 (m, 3 H), 7.23 (d, $J$ = 7.7 Hz, 2 H), 7.15 (t, $J$ = 7.3 Hz, 1 H), 4.84−4.74 (m, 1 H), 4.67 (d, $J$ = 8.8 Hz, 1 H), 2.57 (s, 3 H), 2.19 (s, 1 H), 1.32 (d, $J$ = 6.0 Hz, 3 H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 141.5, 136.1, 135.2, 131.6, 131.3, 129.6, 129.5, 128.7, 128.52, 128.50, 128.4, 126.70, 126.66, 126.5, 124.3, 123.6, 123.0, 122.4, 70.0, 55.3, 21.8, 21.2. HRMS (ESI) $m/z$: [M + Na]$^+$ calcd for 349.1563 $C_{24}H_{22}ONa$, found 349.1558.

*(1R, 2R or 1S, 2S)-1-(6-Methylphenanthren-9-yl)-1-phenylpropan-2-ol (**3aj**).* Overall, 14 mg of **3aj′** was obtained from **1a** (143 mg, 0.48 mmol) and **2j** (35 mg, 0.2 mmol) in a 22% yield; purified by column chromatography (10:1 PE/EA); white solid. mp 56.4−58.5 °C. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.68−8.61 (m, 1 H), 8.51 (s, 1 H), 8.08 (d, $J$ = 8.5 Hz, 1 H), 7.92−7.88 (m, 1 H), 7.87 (s, 1 H), 7.65−7.56 (m, 2 H), 7.49 (d, $J$ = 7.4 Hz, 2 H), 7.40 (d, $J$ = 8.4 Hz, 1 H), 7.31 (t, $J$ = 7.5 Hz, 2 H), 7.21 (t, $J$ = 7.3 Hz, 1 H), 4.85−4.74 (m, 1 H), 4.64 (d, $J$ = 7.3 Hz, 1 H), 2.58 (s, 3 H), 1.65 (s, 1 H), 1.38 (d, $J$ = 6.1 Hz, 3 H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 140.7, 136.7, 135.8, 131.7, 131.0, 129.4, 129.2, 129.0, 128.7, 128.6, 128.4, 127.0, 126.6, 126.2, 124.8, 124.2, 123.0, 122.4, 70.3, 54.2, 22.0, 21.8. HRMS (ESI) $m/z$: [M + Na]$^+$ calcd for 349.1563 $C_{24}H_{22}ONa$, found 349.1564.

*2-(Phenanthren-9-yl)-1,2-diphenylethan-1-ol (**3ak**).* Overall, 51 mg of **3ak** (including two diastereoisomers) was obtained from **1a** (143 mg, 0.48 mmol) and **2k** (44 mg, 0.2 mmol) in a 68% yield; purified by column chromatography (10:1 PE/EA); white solid. Major isomer: $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.67 (d, $J$ = 8.1 Hz, 1 H), 8.65−8.60 (m, 1 H), 8.21 (s, 1 H), 8.02 (d, $J$ = 8.3 Hz, 1 H), 7.97−7.91 (m, 1 H), 7.66−7.58 (m, 2 H), 7.56 (t, $J$ = 7.6 Hz, 1 H), 7.47 (t, $J$ = 7.2 Hz, 1 H), 7.37−7.14 (m, 10 H), 5.74 (t, $J$ = 4.8 Hz, 1 H), 5.15 (d, $J$ = 5.8 Hz, 1 H), 2.18 (d, $J$ = 4.8 Hz, 1 H). Representative peaks of the minor isomer: 8.73 (d, $J$ = 8.2 Hz), 8.24 (s), 8.12 (d, $J$ = 8.1 Hz), 7.72−7.65 (m, 2 H), 6.90 (d, $J$ = 4.2 Hz), 5.62 (d, $J$ = 9.3 Hz), 5.05 (d, $J$ = 9.3 Hz), 2.57 (s). The mixture of two isomers: $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 142.9, 141.9, 140.3, 139.2, 136.1, 134.8, 131.4, 131.2, 130.9, 130.7, 129.9, 129.7, 129.6, 128.9, 128.8, 128.7, 128.4, 128.2, 128.1, 128.0, 127.6, 127.5, 127.1, 127.1, 126.8, 126.8, 126.7, 126.64, 126.60, 126.54, 126.49, 126.46, 126.3, 126.0, 124.4, 124.3, 123.1, 122.5, 122.3, 77.1, 76.3, 55.8, 54.0. HRMS (ESI) $m/z$: [M + Na]$^+$ calcd for 397.1563 $C_{28}H_{22}ONa$, found 397.1563.

*2-(Naphtho[2,1-b]thiophen-4-yl)-2-phenylethan-1-ol (**3al**).* Overall, 37 mg of **3al** was obtained from **1a** (143 mg, 0.48 mmol) and **2l** (30 mg, 0.2 mmol) in a 61% yield; purified by column chromatography (10:1 PE/EA); white solid. mp 107.3−109.6 °C. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.31 (d, $J$ = 8.0 Hz, 1 H), 8.02−7.94 (m, 2 H), 7.77 (s, 1 H), 7.64−7.50 (m, 3 H), 7.40 (d, $J$ = 7.2 Hz, 2 H), 7.33 (t, $J$ = 7.4 Hz, 2 H), 7.29−7.22 (m, 1 H), 4.63 (t, $J$ = 6.9 Hz, 1 H), 4.46 (dd, $J$ = 11.0, 7.0 Hz, 1 H), 4.36 (dd, $J$ = 11.0, 6.9 Hz, 1 H), 1.80 (s, 1 H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 139.8, 138.7, 136.5, 133.5, 131.4, 128.7, 128.6, 128.52, 128.51, 127.2, 126.3, 125.8, 125.5, 123.4, 122.3, 122.2, 65.4, 52.6. HRMS (ESI) $m/z$: [M + Na]$^+$ calcd for 327.0814 $C_{20}H_{16}OSNa$, found 327.0810.

*(E)-3-Styryl-2,3-dihydrobenzofuran (**3am**).*[22] Overall, 22 mg of **3am** was obtained from **1a** (143 mg, 0.48 mmol) and **2m** (29 mg, 0.2 mmol) in a 50% yield; purified by column chromatography (100:1 PE/EA); white solid. mp 70.8−72.9 °C $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 7.40 (d, $J$ = 7.3 Hz, 2 H), 7.33 (t, $J$ = 7.6 Hz, 2 H), 7.29−7.23 (m, 1 H), 7.18 (t, $J$ = 7.4 Hz, 2 H), 6.91 (t, $J$ = 7.4 Hz, 1 H), 6.86 (d, $J$ = 7.9 Hz, 1 H), 6.58 (d, $J$ = 15.7 Hz, 1 H), 6.32−6.20 (m, 1 H), 4.86−4.73 (m,1 H), 4.38−4.24 (m, 2 H). $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$159.9, 136.7, 131.8, 129.4, 129.3, 128.6, 127.6, 126.3, 125.0, 120.7, 109.7, 76.5, 46.4.

*3-(Phenanthren-9-yl)-3-phenylpropan-1-ol (**3an**).* Overall, 31 mg of **3an** was obtained from **1a** (143 mg, 0.48 mmol) and **2n** (32 mg, 0.2 mmol) in a 50% yield; purified by column chromatography (10:1 PE/EA); white solid. mp 33.8−35.0 °C. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.69 (d, $J$ = 8.2 Hz, 1 H), 8.65−8.61 (m, 1 H), 8.18 (d, $J$ = 8.1 Hz, 1 H), 7.90−7.85 (m, 1 H), 7.74 (s, 1 H), 7.65−7.48 (m, 4 H), 7.34 (d, $J$ = 7.3 Hz, 2 H), 7.23 (d, $J$ = 9.1 Hz, 2 H), 7.15 (t, $J$ = 7.3 Hz, 1 H), 4.98−4.91 (m, 1 H), 3.78−3.66 (m, 2 H), 2.58−2.80 (m, 1 H), 2.46−2.37 (m, 1 H), 1.53 (s, 1 H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 144.0, 137.9, 131.5, 131.1, 130.9, 129.7, 128.52, 128.50, 128.1, 126.63, 126.59, 126.34, 126.32, 126.1, 125.1, 124.6, 123.1, 122.4, 60.9, 42.5, 38.7. HRMS (ESI) $m/z$: [M + Na]$^+$ calcd for 335.1406 $C_{23}H_{20}ONa$, found 335.1405.

*3-(6-Methylphenanthren-9-yl)-3-phenylpropan-1-ol (**3ao**).* Overall, 29 mg of **3ao** was obtained from **1a** (143 mg, 0.48 mmol) and **2o** (35 mg, 0.2 mmol) in a 44% yield; purified by column chromatography (10:1 PE/EA); white solid. mp 89.0−90.2 °C. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.65 (d, $J$ = 8.1 Hz, 1 H), 8.50 (s, 1 H), 8.08 (d, $J$ = 8.5 Hz, 1 H), 7.91−7.84 (m, 1 H), 7.70 (s, 1 H), 7.66−7.55 (m, 2 H), 7.40−7.32 (m, 3 H), 7.29−7.23 (m, 3 H), 7.17 (t, $J$ = 7.2 Hz, 1 H), 4.95 (t, $J$ = 7.5 Hz, 1 H), 3.84−3.66 (m, 2 H), 2.65−2.51 (m, 4 H), 2.49−2.40 (m, 1 H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 144.2, 137.8, 135.8, 131.7, 131.0, 129.5, 129.0, 128.52, 128.48, 128.3, 128.1, 126.5, 126.3, 126.1, 124.5, 124.2, 122.9, 122.4, 61.1, 42.6, 38.7, 21.8. HRMS (ESI) $m/z$: [M + Na]$^+$ calcd for 349.1563 $C_{24}H_{20}ONa$, found 349.1558.

*3-Phenyl-3-(6-phenylphenanthren-9-yl)propan-1-ol (**3ap**).* Overall, 35 mg of **3ap** was obtained from **1a** (143 mg, 0.48 mmol) and **2p** (47 mg, 0.2 mmol) in a 45% yield; purified by column chromatography (10:1 PE/EA); white solid. mp 69.7−72.0 °C. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.91 (d, $J$ = 1.3 Hz, 1 H), 8.75 (d, $J$ = 7.9 Hz, 1 H), 8.27 (d, $J$ = 8.7 Hz, 1 H), 7.94−7.88 (m, 1 H), 7.82−7.72 (m, 4 H), 7.68−7.59 (m, 2 H), 7.51 (t, $J$ = 7.6 Hz, 2 H), 7.43−7.37 (m, 3 H), 7.29 (t, $J$ = 7.6 Hz, 2 H), 7.19 (t, $J$ = 7.3 Hz, 1 H), 5.07−4.96 (m, 1 H), 3.86−


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3.71 (m, 2 H), 2.65−2.57 (m, 1 H), 2.52−2.44 (m, 1 H), 1.55 (s, 1 H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 144.1, 141.2, 138.8, 137.8, 131.8, 131.2, 130.3, 129.8, 128.9, 128.62, 128.58, 128.1, 127.5, 127.4, 126.8, 126.40, 126.38, 125.9, 125.2, 125.1, 122.4, 121.5, 61.0, 42.6, 38.7. HRMS (ESI) $m/z$: $[M + Na]^+$ calcd for 411.1719 $C_{29}H_{24}ONa$, found 411.1710.

*3-(6-Fluorophenanthren-9-yl)-3-phenylpropan-1-ol (**3aq**).* Overall, 28 mg of **3aq** was obtained from **1a** (143 mg, 0.48 mmol) and **2q** (36 mg, 0.2 mmol) in a 43% yield; purified by column chromatography (10:1 PE/EA); white solid. mp 91.6−93.5 °C. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.51 (dd, $J$ = 5.8, 3.4 Hz, 1 H), 8.30 (dd, $J$ = 11.0, 2.4 Hz, 1 H), 8.17 (dd, $J$ = 9.1, 5.9 Hz, 1 H), 7.90 (dd, $J$ = 5.9, 3.3 Hz, 1 H), 7.73 (s, 1 H), 7.63 (dd, $J$ = 6.0, 3.2 Hz, 2 H), 7.34 (d, $J$ = 7.4 Hz, 2 H), 7.31−7.24 (m, 3 H), 7.18 (t, $J$ = 7.2 Hz, 1 H), 5.01−4.87 (m, 1 H), 3.87−3.66 (m, 2 H), 2.61−4.52 (m, 1 H), 2.48−2.40 (m, 1 H), 1.49 (s, 1 H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 161.2 (d, $^1J_{C-F}$ = 245.7 Hz), 143.8, 137.6, 132.8 (d, $^3J_{C-F}$ = 8.1 Hz), 131.9, 129.12, 129.08, 128.58, 128.55, 128.0, 127.8 (d, $^4J_{C-F}$ = 1.4 Hz), 127.2, 126.9 (d, $^3J_{C-F}$ = 8.7 Hz), 126.44, 126.38, 124.3 (d, $^4J_{C-F}$ = 1.9 Hz), 122.6, 115.3 (d, $^2J_{C-F}$ = 23.2 Hz), 108.1 (d, $^2J_{C-F}$ = 21.9 Hz), 60.8, 42.7, 38.6. $^{19}$F NMR (376 MHz, $CDCl_3$) $\delta$ −114.53. HRMS (ESI) $m/z$: $[M + Na]^+$ calcd for 353.1312 $C_{23}H_{19}OFNa$, found 353.1304.

*3-(6-Bromophenanthren-9-yl)-3-phenylpropan-1-ol (**3ar**).* Overall, 31 mg of **3ar** was obtained from **1a** (143 mg, 0.48 mmol) and **2r** (48 mg, 0.2 mmol) in a 40% yield; purified by column chromatography (10:1 PE/EA); white solid. mp 177.2−179.1 °C. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.82 (d, $J$ = 1.8 Hz, 1 H), 8.57−8.55 (m, 1 H), 8.04 (d, $J$ = 8.9 Hz, 1 H), 7.93−7.86 (m, 1 H), 7.77 (s, 1 H), 7.68−7.57 (m, 3 H), 7.32 (d, $J$ = 7.3 Hz, 2 H), 7.30−7.23 (m, 2 H), 7.18 (t, $J$ = 7.2 Hz, 1 H), 4.93−4.89 (m, 1 H), 3.83−3.67 (m, 2 H), 2.60−2.51 (m, 1 H), 2.50−2.37 (m, 1 H), 1.50 (s, 1 H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 143.7, 137.6, 132.6, 131.9, 129.8, 129.6, 128.7, 128.62, 128.58, 128.1, 127.3, 126.7, 126.5, 126.4, 125.9, 125.5, 122.5, 120.7, 60.8, 42.5, 38.6. HRMS (ESI) $m/z$: $[M + Na]^+$ calcd for 413.0511 $C_{23}H_{19}OBrNa$, found 413.0499.

*3-(6-Bromo-5,7-dimethylphenanthren-9-yl)-3-phenylpropan-1-ol (**3as**).* Overall, 29 mg of **3as** was obtained from **1a** (143 mg, 0.48 mmol) and **2s** (53 mg, 0.2 mmol) in a 35% yield; purified by column chromatography (10:1 PE/EA); white solid. mp 33.8−35.0 °C.$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.50 (d, $J$ = 7.5 Hz, 1 H), 7.93 (s, 1 H), 7.91−7.84 (m, 1 H), 7.71 (s, 1 H), 7.61−7.50 (m, 2 H), 7.34 (d, $J$ = 7.4 Hz, 2 H), 7.30−7.23 (m, 2 H), 7.18 (t, $J$ = 7.2 Hz, 1 H), 4.95−4.84 (m, 1 H), 3.83−3.66 (m, 2 H), 3.11 (s, 3 H), 2.61−2.36 (m, 5 H), 1.55 (s, 1 H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 144.0, 137.1, 135.7, 135.0, 132.8, 131.2, 130.9, 130.0, 129.8, 128.6, 128.2, 128.03, 128.01, 126.4, 126.1, 125.7, 124.8, 123.5, 60.9, 42.5, 38.9, 27.2, 25.1. HRMS (ESI) $m/z$: $[M + Na]^+$ calcd for 441.0824 $C_{25}H_{23}ONa$, found 441.0819.

*4-(Phenanthren-9-yl)-4-phenylbutan-1-ol (**3at**).* Overall, 10 mg of **3at** was obtained from **1a** (143 mg, 0.48 mmol) and **2t** (35 mg, 0.2 mmol) in a 16% yield; purified by column chromatography (10:1 PE/EA); slightly yellow oil. $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 8.78−8.69 (m, 1 H), 8.69−8.62 (m, 1 H), 8.16 (d, $J$ = 8.0 Hz, 1 H), 7.96−7.86 (m, 1 H), 7.78 (s, 1 H), 7.70−7.50 (m, 4 H), 7.35 (d, $J$ = 7.3 Hz, 2 H), 7.31−7.21 (m, 2 H), 7.16 (t, $J$ = 7.2 Hz, 1 H), 4.72 (t, $J$ = 7.5 Hz, 1 H), 3.72 (t, $J$ = 6.5 Hz, 2 H), 2.47−2.20 (m, 2 H), 1.85−1.57 (m, 2 H). $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 144.5, 138.1, 131.6, 131.2, 130.9, 129.6, 128.5, 128.4, 128.1, 126.6, 126.5, 126.3, 126.2, 126.0, 125.0, 124.5, 123.1, 122.4, 62.9, 46.4, 32.5, 31.3. HRMS (ESI) $m/z$: $[M + H]^+$ calcd for 327.1743 $C_{24}H_{23}O$, found 327.1735.

*Dimethyl-2-(2-(phenanthren-9-yl)-2-phenylethyl)-malonate (**5aa**).* Overall, 66 mg of **5aa** was obtained from **1a** (143 mg, 0.48 mmol) and **5a** (52 mg, 0.2 mmol) in an 80% yield; purified by column chromatography (10:1 PE/EA); slightly yellow oil. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.72 (d, $J$ = 7.7 Hz, 1 H), 8.68−8.63 (m, 1 H), 8.15 (d, $J$ = 7.9 Hz, 1 H), 7.93−7.88 (m, 1 H), 7.77 (s, 1 H), 7.69−7.50 (m, 4 H), 7.41−7.31 (m, 4 H), 7.24−7.15 (m, 1 H), 4.84−4.73 (m, 1 H), 3.77 (s, 3 H), 3.67 (s, 3 H), 3.53 (t, $J$ = 7.4 Hz, 1 H), 3.02−2.73 (m, 2 H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 169.9, 169.8, 142.8, 136.8, 131.4, 130.9, 129.8, 128.7, 128.6, 128.2, 126.71, 126.70, 126.68, 126.5, 126.2, 125.1, 124.4, 123.2, 122.4, 52.7, 52.5, 49.9, 44.0, 34.8. HRMS (ESI) $m/z$: $[M + Na]^+$ calcd for 435.1567 $C_{27}H_{24}O_4Na$, found 435.1593.

*9-Cyclopropyl-9-phenyl-9,10-dihydrophenanthrene (**5ab1**).* Overall, 28 mg of **5ab1** was obtained from **1a** (143 mg, 0.48 mmol) and **4b** (29 mg, 0.2 mmol) in a 48% yield; purified by column chromatography (200:1 PE/EA); slightly yellow oil. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.91 (dd, $J$ = 7.5, 1.0 Hz, 1 H), 7.79−7.68 (m, 2 H), 7.52−7.42 (m, 2 H), 7.36−7.32 (m, 4 H), 7.31−7.27 (m, 2 H), 7.25 (d, $J$ = 7.8 Hz, 1 H), 7.19 (t, $J$ = 7.1 Hz, 1 H), 3.67−3.64 (m, 1 H), 3.22−3.18 (m, 1 H), 1.55−1.37 (m, 1 H), 0.74−0.53 (m, 2 H), 0.24−0.04 (m, 2 H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 143.6, 142.4, 135.6, 134.9, 134.3, 128.8, 128.6, 128.3, 127.4, 127.2, 127.07, 127.06, 126.8, 125.8, 124.0, 123.3, 46.0, 41.9, 20.0, 2.9, −0.3. HRMS (ESI) $m/z$: $[M + Na]^+$ calcd for 319.1457 $C_{23}H_{20}Na$, found 319.1452.

*9-Cyclopropyl-9,10-dihydrophenanthrene (**5ab2**).* Overall, 8 mg of **5ab2** was obtained from **1a** (143 mg, 0.48 mmol) and **4b** (29 mg, 0.2 mmol) in a 17% yield; purified by column chromatography (200:1 PE/EA); slightly yellow oil. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.77 (t, $J$ = 7.0 Hz, 2 H), 7.50 (d, $J$ = 7.2 Hz, 1 H), 7.39−7.27 (m, 4 H), 7.26−7.21 (m, 1 H), 3.10−3.05 (m, 1 H), 2.92−2.68 (m, 1 H), 2.05−1.99 (m, 1 H), 0.95−0.80 (m, 1 H), 0.63−0.44 (m, 2 H), 0.34−0.29 (m, 1 H), 0.27−0.21 (m, 1 H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 140.5, 136.5, 134.3, 133.9, 128.5, 127.5, 127.4, 127.2, 127.0, 126.9, 123.8, 123.5, 43.9, 35.3, 14.9, 5.0, 3.6. GC−MS (EI) $m/z$: 220.1, 205.0, 191.0, 179.1.

*9-Cyclopropylphenanthrene (**5ab3**).*[23] Overall, 13 mg of **5ab3** was obtained from **1a** (143 mg, 0.48 mmol) and **4b** (29 mg, 0.2 mmol) in a 30% yield; purified by column chromatography (200:1 PE/EA); white solid. mp 64.9−66.6 °C. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.76−8.73 (m, 1 H), 8.68 (d, $J$ = 7.9 Hz, 1 H), 8.56−8.52 (m, 1 H), 7.89−7.81 (m, 1 H), 7.75−7.66 (m, 2 H), 7.66−7.55 (m, 3 H), 2.44−2.31 (m, 1 H), 1.18−1.08 (m, 2 H), 0.91−0.81 (m, 2 H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 137.3, 132.7, 131.9, 130.4, 129.6, 128.2, 126.54, 126.46, 126.3, 126.01, 125.04, 124.5, 122.9, 122.4, 13.8, 6.2.

**Larger Synthesis of Phenanthrene 3aa.** To a 100 mL flame-dried screw-capped test tube with a stir bar, aryne precursor **1a** (3.58 g, 12 mmol), vinyl epoxide **2a** (0.73 g, 5 mmol), and MeCN (20 mL) were added. Then, CsF (3.04 g, 20 mmol) was added to the abovementioned solution. The mixture was stirred at 50 °C for 6 h. Most of the reaction mixture was evaporated, and the residue was purified by column chromatography (10:1 PE/EA) to afford the desired **3aa** (776 mg, 52% yield).



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**Synthesis of Functionalized Phenanthrene 6.** To a 25 mL flame-dried screw-capped test tube with a stir bar, **3aa** (60 mg, 0.2 mmol) and DMSO (2 mL) were added. Then, $Cs_2CO_3$ (65 mg, 0.2 mmol) was added to the abovementioned solution, and the mixture was stirred at 150 °C for 2 h. Most of the reaction mixture was evaporated, and the residue was purified by column chromatography (10:1 PE/EA) to afford the desired phenanthren-9-yl(phenyl)methanone **6**[24] (48 mg, 85% yield) as a slightly yellow oil. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.76 (dd, $J$ = 14.5, 8.4 Hz, 2 H), 8.13 (d, $J$ = 8.2 Hz, 1 H), 7.95 (t, $J$ = 8.2 Hz, 2 H), 7.90 (d, $J$ = 7.8 Hz, 1 H), 7.86 (s, 1 H), 7.79−7.56 (m, 5 H), 7.48 (t, $J$ = 7.7 Hz, 2 H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 197.9, 138.1, 135.3, 133.3, 131.2, 130.6, 130.4, 130.0, 129.5, 129.3, 129.1, 128.5, 128.3, 127.2, 127.13, 127.09, 126.6, 122.9, 122.7.

**Synthesis of Functionalized Phenanthrene 7.** To a 25 mL flame-dried screw-capped test tube with a stir bar, **3aa** (60 mg, 0.2 mmol), propargyl bromide (35 mg, 0.3 mmol), and dry THF (2 mL) were added. Then, NaH (14 mg, 0.6 mmol) was added to the abovementioned solution, and the mixture was stirred at 45 °C for 12 h. Most of the reaction mixture was evaporated, and the residue was purified by column chromatography (10:1 PE/EA) to afford the desired 9-(1-phenyl-2-(prop-2-yn-1-yloxy)ethyl)phenanthrene **7** (59 mg, 88% yield) as a slightly yellow solid. mp 81.7−83.8. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.76 (d, $J$ = 8.2 Hz, 1 H), 8.70 (d, $J$ = 7.7 Hz, 1 H), 8.15 (d, $J$ = 8.2 Hz, 1 H), 7.95 (d, $J$ = 7.4 Hz, 1 H), 7.83 (s, 1 H), 7.69−7.62 (m, 3 H), 7.57 (t, $J$ = 7.5 Hz, 1 H), 7.41 (d, $J$ = 7.5 Hz, 2 H), 7.33 (t, $J$ = 7.5 Hz, 2 H), 7.28−7.22 (m, 1 H), 5.17 (t, $J$ = 6.9 Hz, 1 H), 4.42 (t, $J$ = 8.4 Hz, 1 H), 4.35−4.21 (m, 3 H), 2.60−2.50 (m, 1 H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 141.6, 134.9, 131.5, 131.1, 130.9, 129.8, 128.6, 128.5, 126.7, 126.6, 126.4, 126.1, 125.9, 124.5, 123.1, 122.4, 79.7, 74.7, 72.8, 58.2, 46.6. HRMS (ESI) $m/z$: $[M + Na]^+$ calcd for 359.1406 $C_{25}H_{20}ONa$, found 359.1407.

**Synthesis of Functionalized Phenanthrene 8.** To a 25 mL flame-dried screw-capped test tube with a stir bar, **3aa** (60 mg, 0.2 mmol), 4-dimethylaminopyridine (5 mg, 0.04 mmol), dichloromethane (DCM) (2 mL), and $Et_3N$ (41 mg, 0.4 mmol) were added. Then, benzoyl chloride (42 mg, 0.3 mmol) was added to the abovementioned solution, and the mixture was stirred at room temperature for 2 h. Most of the reaction mixture was evaporated, and the residue was purified by column chromatography (10:1 PE/EA) to afford the desired 2-(phenanthren-9-yl)-2-phenylethyl benzoate **8** (75 mg, 93% yield) as a white solid. mp 84.6−85.4 °C. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.76 (d, $J$ = 8.1 Hz, 1 H), 8.70 (d, $J$ = 8.0 Hz, 1 H), 8.20 (d, $J$ = 8.0 Hz, 1 H), 7.98 (d, $J$ = 7.4 Hz, 2 H), 7.93 (d, $J$ = 7.4 Hz, 1 H), 7.83 (s, 1 H), 7.70−7.61 (m, 3 H), 7.60−7.56 (m, 1 H), 7.52 (t, $J$ = 7.9 Hz, 1 H). 7.44 (d, $J$ = 7.4 Hz, 2 H), 7.39 (t, $J$ = 7.7 Hz, 2 H), 7.33 (t, $J$ = 7.5 Hz, 2 H), 7.27−7.23 (m, 1 H), 5.34 (t, $J$ = 7.3 Hz, 1 H), 5.17 (dd, $J$ = 11.1, 7.1 Hz, 1 H), 5.06 (dd, $J$ = 11.1, 7.5 Hz, 1 H). $^{13}$C NMR (100 MHz, $CDCl_3$). $\delta$ $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 166.5, 140.9, 134.5, 132.9, 131.4, 131.0, 130.9, 130.5, 130.0, 129.9, 129.6, 128.8, 128.69, 128.65, 128.5, 128.3, 127.0, 126.77, 126.75, 126.6, 126.3, 125.7, 124.5, 123.2, 122.4, 67.3, 45.8. HRMS (ESI) $m/z$: $[M + Na]^+$ calcd for 425.1512 $C_{29}H_{22}O_2Na$, found 425.1511.

**Synthesis of Functionalized Phenanthrene 9.** To a 25 mL flame-dried screw-capped test tube with a stir bar, **3aa** (60 mg, 0.2 mmol), 4-dimethylaminopyridine (5 mg, 0.04 mmol), DCM (2 mL), and $Et_3N$ (41 mg, 0.4 mmol) and were added. Then, 4-methylbenzenesulfonyl chloride (57 mg, 0.3 mmol) was added to the abovementioned solution, and the mixture was stirred at room temperature for 2 h. Most of the reaction mixture was evaporated, and the residue was purified by column chromatography (10:1 PE/EA) to afford the desired 2-(phenanthren-9-yl)-2-phenylethyl 4-methylbenzenesulfonate **9** (77 mg, 85% yield) as a white solid. mp 151.7−152.8 °C. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.72 (d, $J$ = 8.2 Hz, 1 H), 8.67 (d, $J$ = 8.0 Hz, 1 H), 7.98 (d, $J$ = 8.3 Hz, 1 H), 7.81 (d, $J$ = 7.6 Hz, 1 H), 7.73−7.58 (m, 5 H), 7.57 (s, 1 H), 7.52 (t, $J$ = 7.6 Hz, 1 H), 7.34−7.21 (m, 5 H), 7.17 (d, $J$ = 7.9 Hz, 2 H), 5.18 (t, $J$ = 7.1 Hz, 1 H), 4.87 (t, $J$ = 8.8 Hz, 1 H), 4.77 (dd, $J$ = 9.6, 7.5 Hz, 1 H), 2.38 (s, 3 H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 144.5, 139.3, 133.0, 132.6, 131.0, 130.8, 130.4, 129.8, 129.6, 128.6, 128.5, 128.3, 127.6, 127.1, 126.70, 126.66, 126.6, 126.2, 125.7, 124.0, 123.1, 122.3, 71.6, 45.7, 21.4. HRMS (ESI) $m/z$: $[M + Na]^+$ calcd for 475.1338 $C_{29}H_{24}O_3SNa$, found 475.1338.

**Synthesis of Functionalized Phenanthrene 10.** To a 25 mL flame-dried screw-capped test tube with a stir bar, **9** (90 mg, 0.2 mmol) and dry THF (2 mL) were added. Then, NaH (48 mg, 2 mmol) was added to the abovementioned solution, and the mixture was stirred at 60 °C for 12 h. Most of the reaction mixture was evaporated, and the residue was purified by column chromatography (10:1 PE/EA) to afford the desired 9-(1-phenylvinyl)phenanthrene **10**[25] (50 mg, 90% yield) as a white solid. mp 128.3−130.7 °C. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.77 (dd, $J$ = 8.0, 4.9 Hz, 2 H), 7.96 (d, $J$ = 7.4 Hz, 1 H), 7.89 (d, $J$ = 8.2 Hz, 1 H), 7.82 (s, 1 H), 7.76−7.62 (m, 3 H), 7.53−7.43 (m, 3 H), 7.37−7.28 (m, 3 H), 6.10 (d, $J$ = 1.1 Hz, 1 H), 5.57 (d, $J$ = 1.1 Hz, 1 H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 148.5, 140.6, 138.3, 131.6, 131.0, 130.5, 130.3, 128.6, 128.4, 127.82, 127.75, 127.3, 126.8, 126.6, 126.54, 126.46, 126.3, 122.7, 122.5, 116.2.

**Synthesis of Functionalized Phenanthrene 11.** To a 25 mL flame-dried screw-capped test tube with a stir bar, **9** (90 mg, 0.2 mmol) and MeCN (2 mL) were added. Then, benzylamine (43 mg, 0.4 mmol) was added to the above-mentioned solution, and the mixture was stirred at 100 °C for 24 h. Most of the reaction mixture was evaporated, and the residue was purified by column chromatography (10:1 PE/EA) to afford the desired *N*-benzyl-2-(phenanthren-9-yl)-2-phenylethan-1-amine **11** (48 mg, 62% yield) as a white solid. mp 95.9−98.6 °C. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.74 (d, $J$ = 8.2 Hz, 1 H), 8.69 (d, $J$ = 7.8 Hz, 1 H), 8.17 (d, $J$ = 8.2 Hz, 1 H), 7.87 (d, $J$ = 7.2 Hz, 1 H), 7.72−7.60 (m, 4 H), 7.56 (t, $J$ = 7.5 Hz, 1 H), 7.41−7.27 (m, 9 H), 7.22 (t, $J$ = 7.1 Hz, 1 H), 5.08 (t, $J$ = 7.1 Hz, 1 H), 3.99−3.87 (m, 2 H), 3.55 (dd, $J$ = 11.7, 7.4 Hz, 1 H), 3.40 (dd, $J$ = 11.8, 7.0 Hz, 1 H), 1.80 (s, 1 H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 142.7, 140.1, 136.0, 131.4, 131.2, 131.0, 129.8, 128.6, 128.5, 128.4, 128.2, 128.1, 126.9, 126.64, 126.63, 126.6, 126.4, 126.2, 125.0, 124.5, 123.1, 122.4, 53.8, 46.8. HRMS (ESI) $m/z$: $[M + H]^+$ calcd for 388.2060 $C_{29}H_{26}N$, found 388.2056.

**Synthesis of Functionalized Phenanthrene 12.** To a 25 mL flame-dried screw-capped test tube with a stir bar, **9** (90 mg, 0.2 mmol) and MeCN (2 mL) were added. Then, $NaN_3$ (26 mg, 0.4 mmol) was added to the abovementioned solution, and the mixture was stirred at 100 °C for 24 h. Most of the reaction mixture was evaporated, and the residue was purified by column chromatography (10:1 PE/EA) to afford the desired 9-(2-azido-1-phenylethyl)phenanthrene **12** (50 mg, 78% yield) as a slightly yellow oil. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.76 (d, $J$ = 8.2 Hz, 1 H), 8.70 (d, $J$ = 8.0 Hz, 1 H),


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8.10 (d, $J$ = 8.2 Hz, 1 H), 7.98−7.91 (m, 1 H), 7.74 (s, 1 H), 7.72−7.62 (m, 3 H), 7.58 (t, $J$ = 7.2 Hz, 1 H), 7.40 (d, $J$ = 7.3 Hz, 2 H), 7.34 (t, $J$ = 7.4 Hz, 2 H), 7.31−7.26 (m, 1 H), 5.04 (t, $J$ = 7.3 Hz, 1 H), 4.16 (dd, $J$ = 12.4, 7.0 Hz, 1 H), 4.08 (dd, $J$ = 12.4, 7.7 Hz, 1 H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 141.0, 134.5, 131.2, 131.0, 130.7, 129.9, 128.8, 128.7, 128.3, 127.2, 126.80, 126.78, 126.7, 126.3, 125.5, 124.2, 123.3, 122.4, 55.7, 46.5. HRMS (ESI) $m/z$: $[M + Na]^+$ calcd for 346.1315 $C_{22}H_{17}N_3Na$, found 346.1312.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c06166.

Copies of $^1$H and $^{13}$C NMR spectra of compounds **2c−l**, **2o−s**, **3aa−da**, **3ab−at**, **3aa′**, **3aj′**, **5aa**, **5ab1−ab3**, and **6−12** (PDF)

X-ray crystal structure of **3aj** (CIF)

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### Notes

The authors declare no competing financial interest.

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