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Synthesis of 9-Aryl-9,10-dihydrophenanthrenes by Domino [3+3] Annulation/Ring-Opening/Friedel–Crafts Alkylation Reactions of 1,3-Bis(trimethylsilyloxy)-1,3-butadienes with 3-Aroyl-5-aryl-4,5-dihydrofurans

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The reaction of 1,3-bis(trimethylsilyloxy)-1,3-butadienes with 3-benzoyl-5-aryl-4,5-dihydrofurans, available by CAN-mediated reaction of styrenes with benzoylacetones, afforded functionalized 9,10-dihydrophenanthrenes. These reactions proceed by a novel domino [3+3] cyclization/ring-opening/Friedel–Crafts alkylation process.

Introduction

Domino reactions provide a versatile tool for the facile assembly of complex molecules from simple starting materials.[1] 1,3-Bis(trimethylsilyloxy)-1,3-butadienes represent versatile building blocks for one-pot cyclizations and domino reactions.[2] We have reported cyclizations of these building blocks with oxalyl chloride,[3] 3-silyloxy- and 3-alkoxy-2-en-1-ones,[4] iminium salts,[5] benzopyrylium triflates,[6] fluorinated substrates,[7] and various other electrophiles.[8] Some years ago, we reported[9] the $TiCl_4$-mediated cyclization of 1,3-bis(trimethylsilyloxy)-1,3-butadienes with 1,1-diacylcyclopropanes. These reactions provide convenient access to 5-(2-haloethyl)salicylates and proceed by a domino [3+3] cyclization/cyclopropane opening process. Recently, we reported[10] the synthesis of 5-(2-aryl-2-haloethyl)salicylates by domino reactions of 1,3-bis(trimethylsilyloxy)-1,3-butadienes with 3-acetyl-5-aryl-4,5-dihydrofurans.

Herein, we report, for the first time, the synthesis of functionalized 9,10-dihydrophenanthrenes and phenanthrenes on the basis of the reaction of 1,3-bis(trimethylsilyloxy)-1,3-butadienes with 3-benzoyl-5-aryl-4,5-dihydrofurans. These reactions proceed by an unprecedented domino [3+3] cyclization/ring-opening/Friedel–Crafts alkylation process. All products reported herein, highly functionalized phenanthrenes, are not readily available by other methods. They represent useful synthetic intermediates, are pharmacologically relevant, and represent core structures of several natural products.

For example, the natural product juncusol,[11] isolated from the plant *Juncus roemerianus*, has been reported to possess anticancer activity (Figure 1).[12,13] The first synthesis of this compound was reported by Kende and Curran.[11] Combrestatin A-4 and several related molecules are naturally occurring *cis*-stilbenes isolated from the South African willow tree *Combretum caffrum*.[14] They are promising candidates for the development of anticancer drugs, because they act as inhibitors of tubulin polymerization. A number of structurally related oxygenated phenanthrenes have been isolated from the same tree.[15] In addition, various other phenanthrene natural products are potentially interesting as cytotoxic agents or tubulin-binding molecules.

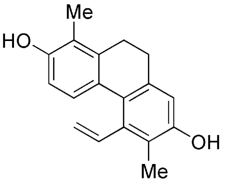

Figure 1. Structure of juncusol.

Classic synthetic approaches to phenanthrenes were developed, for example, by Pschorr and Haworth.[16] Phenanthrenes have been also prepared by oxidative cyclizations of *cis*-stilbene derivatives.[17] For example, vanadium trifluoride mediated oxidation was employed for the synthesis of the natural product (±)-tylophorine. Chan reported the synthesis of dihydrophenanthrenes by [3+3] cyclocondensation of tetralone-derived 3-silyloxy-2-alk-1-ones with 1,3-bis(silyloxy)-1,3-butadienes.[18] We reported the synthesis of cyclopenta[*def*]phenanthren-4-ones on the basis of a related approach.[19] Fürstner and co-workers developed a versatile approach to phenanthrenes that is based on transition-metal-catalyzed cycloisomerization reactions of 2-alkynylbiaryls.[20]

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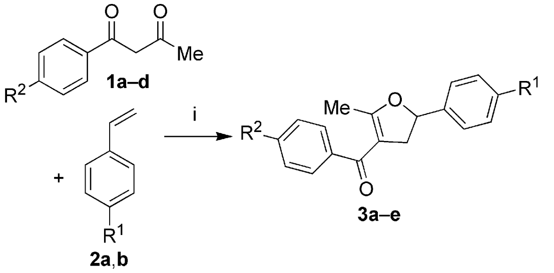
Results and Discussion

3-Aroyl-5-aryl-4,5-dihydrofurans **3a–e** were prepared by ceric ammonium nitrate (CAN)-mediated cyclization of benzoylacetones **1a–d** with styrenes **2a**,**b** (Scheme 1, Table 1). The reactions were carried out following the conditions reported for the synthesis of 3-acetyl-4,5-dihydrofurans.[21] The synthesis of 3-aroyl-5-aryl-4,5-dihydrofurans has, to the best of our knowledge, not been previously reported.



Scheme 1. Synthesis of **3a**–**e**. Reagents and conditions: (i) CAN (2.0 equiv.), CH_3CN, 20 °C, 0.5–2 h.

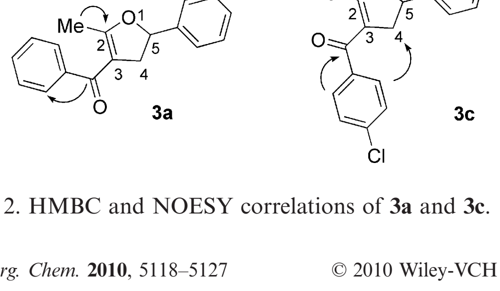
Table 1. Synthesis of **3a**–**e**.

1	2	3	R^1	R^2	% Yield of 3[a]
a	**a**	**a**	H	H	37
a	**b**	**b**	Br	H	44
b	**a**	**c**	H	Cl	45
c	**a**	**d**	H	Br	30
d	**a**	**e**	H	OMe	46

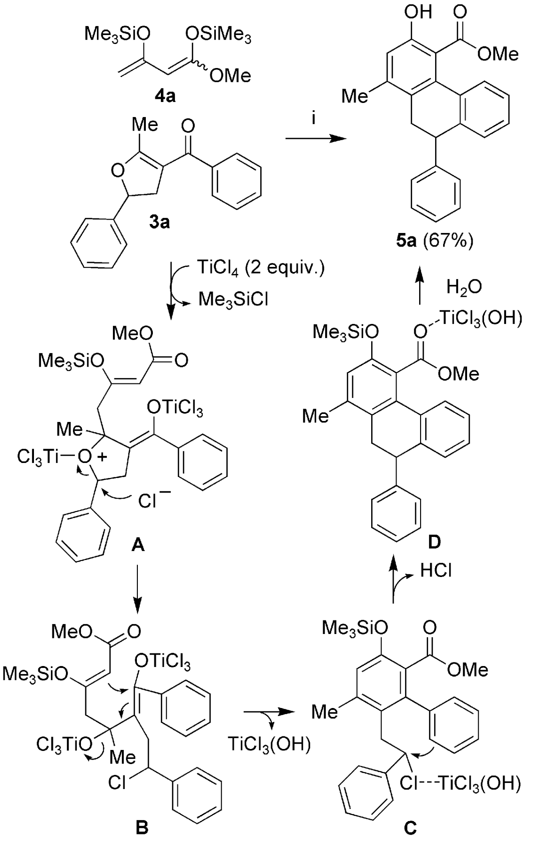
[a] Yield of isolated product.

The cyclization of benzoylacetones **1** with styrenes **2** can theoretically not only result in the formation of the 3-benzoyl-5-aryl-2-methyl-4,5-dihydrofurans **3**, but also of the isomeric products, that is, 3-acetyl-2,5-diaryl-5-phenyl-4,5-dihydrofurans. The structures of **3a** and **3c** were unambiguously proved by 2D NMR experiments (Scheme 2). The correlation of the methyl protons with carbon atom C2 and the correlation of the aromatic protons with the carbon atom of the carbonyl group (^{1}H–^{13}C HMBC) are proof of structure **3a** (Scheme 2). Similar correlations are observed for **3c**. In addition, a ^{1}H–^{1}H NOESY correlation is observed between the *ortho*-phenyl protons and the methylene protons located at carbon C4 of **3c**.

1,3-Bis(trimethylsilyloxy)-1,3-butadienes **4a–i** are readily available in one or two steps from the corresponding β-keto esters.[18,22–24] The cyclization of dihydrofuran **3a** with diene **4a** (1.5–1.7 equiv.) in the presence of $TiCl_4$ (2.0 equiv.) afforded unexpected 9-aryl-9,10-dihydrophenanthrene **5a** in 67% yield (Scheme 3).



Scheme 2. HMBC and NOESY correlations of **3a** and **3c**.



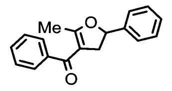
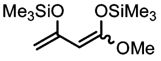
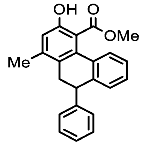
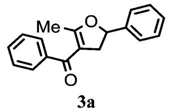
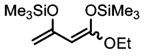
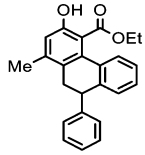
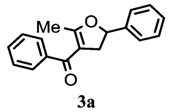
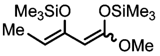
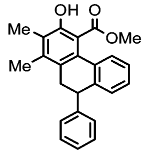
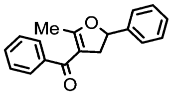
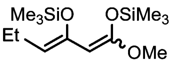
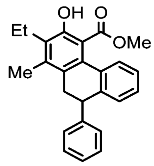
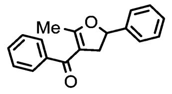
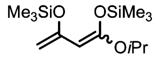
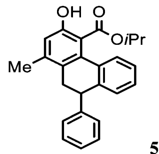
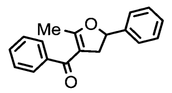
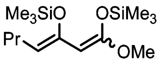
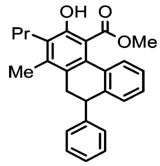
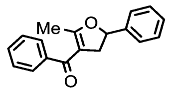
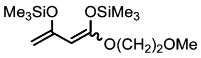
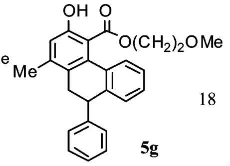
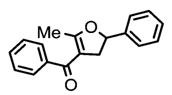
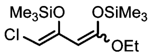
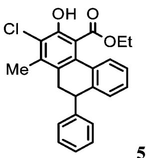
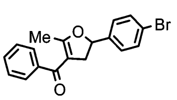
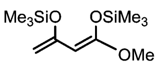
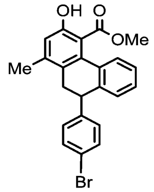
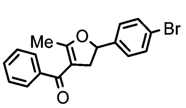
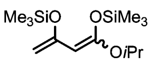
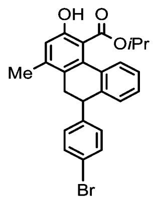
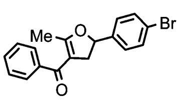
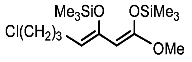
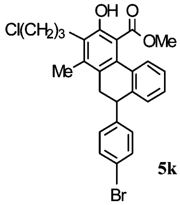
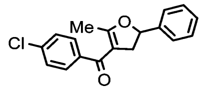
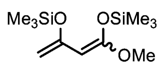
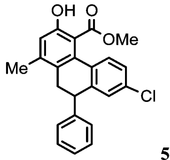
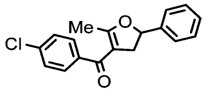
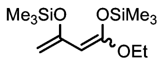
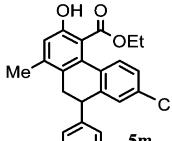
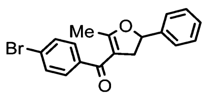
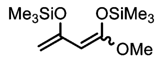
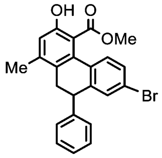
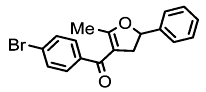
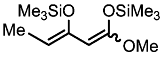
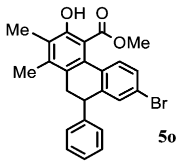
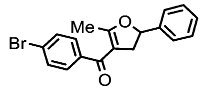
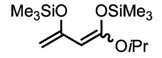
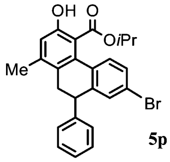
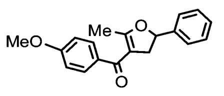
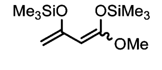
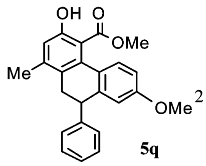
Scheme 3. Possible mechanism for the formation of **5a**. Reagents and conditions: (i) $TiCl_4$ (2.0 equiv.), CH_2Cl_2, –78→20 °C.

The formation of this product can be explained by $TiCl_4$-mediated attack of the terminal carbon atom of **4a** to **3a** to give intermediate **A**, ring cleavage (intermediate **B**), recyclization (intermediate **C**), and subsequent intramolecular Friedel–Crafts alkylation to give intermediate **D**. The addition of hydrochloric acid (aqueous workup) afforded **5a**.

The cyclization of dihydrofurans **3a–e** with dienes **4a–i** afforded 9-aryl-9,10dihydrophenanthrenes **5a–q** (Table 2). The best yields were obtained in the reactions of the simple, unsubstituted dienes **4a**,**b**,**e** with **3a**. The yields decrease for dienes containing a substituent located at carbon C4 and for dihydrofurans containing substituents attached to the phenyl groups.

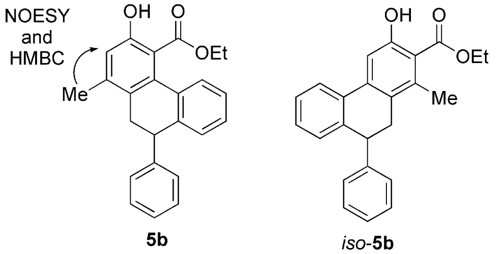
The cyclization of dienes **4** with dihydrofurans **3** can theoretically result in the formation of two regioisomeric products. The regioselectivity depends on whether the first attack of the diene occurs at the double bond or at the benzoyl group of **3**. The structure of 9,10-dihydrophenanthrene **5b** was established by 2D NMR studies (Scheme 4). A ^{1}H–^{1}H NOESY correlation was observed between the aromatic proton adjacent to the hydroxy group and the protons of the methyl group. In addition, a diagnostic ^{1}H–^{13}C

Table 2. Synthesis of **5a**–**q**.

3	4	5	% Yield of 5[a]
 **3a**	 **4a**	 **5a**	67
 **3a**	 **4b**	 **5b**	53
 **3a**	 **4c**	 **5c**	30
 **3a**	 **4d**	 **5d**	31
 **3a**	 **4e**	 **5e**	80
 **3a**	 **4f**	 **5f**	41
 **3a**	 **4g**	 **5g**	18
 **3a**	 **4h**	 **5h**	18
 **3b**	 **4a**	 **5i**	39
 **3b**	 **4e**	 **5j**	44
 **3b**	 **4i**	 **5k**	20
 **3c**	 **4a**	 **5l**	51
 **3c**	 **4b**	 **5m**	52
 **3d**	 **4a**	 **5n**	48
 **3d**	 **4c**	 **5o**	37
 **3d**	 **4e**	 **5p**	40
 **3e**	 **4a**	 **5q**	21

[a] Yield of isolated product.

HMBC correlation was observed between the carbon atom of the methyl group and the neighboring aromatic proton. Therefore, the regioisomeric product *iso*-**5b** is not present. Similar correlations were observed for **5i** and **5l**. The regioselectivity follows a general pattern, which is observed for the reaction of 1,3-bis(silyloxy)-1,3-butadienes with simple 3-alkoxy-2-alken-1-ones.[4,18,25] These cyclizations proceed by regioselective conjugate addition of the terminal carbon atom of the diene to the C=C of the enone. In contrast, the cyclizations of 1,3-bis(silyloxy)-1,3-butadienes with simple 3,3-(alkylthio)-2-alken-1-ones proceed by attack of the diene to the carbonyl group.[26] The exact explanation for the regioselectivity is unclear at present. It can be anticipated that the reaction of the enone with $TiCl_4$ results in the formation of an allylic cation. The regioselectivity is influenced by the substitution pattern of this cation by steric and electronic effects (electron density of the different carbon atoms of the allylic system).



Scheme 4. NOESY and HMBC correlation of observed product **5b** and structure of its regioisomer *iso*-**5b**, which is not observed.

The structure of **5a** was independently confirmed by X-ray crystal structure analysis (Figure 2).[27] The biaryl unit is twisted out of plane. The hydrogen atoms located at carbon atoms C11 and C12 adopt an ap orientation to each other.

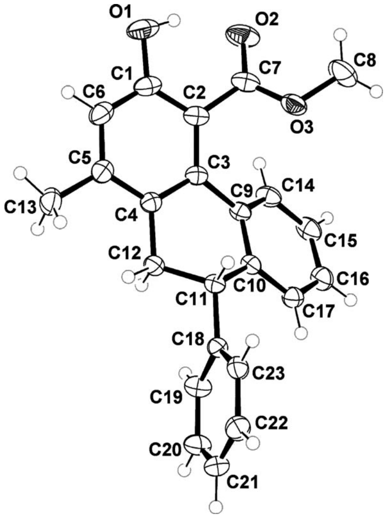
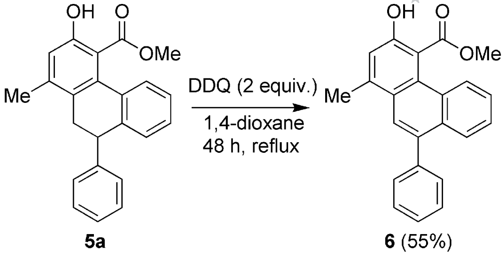


Figure 2. Crystal structure of **5a**.

Some key synthetic transformations of 9,10-dihydrophenanthrenes **5** were next studied. Compound **5a** could be successfully transformed into phenanthrene **6** by treatment with DDQ (55%; Scheme 5). The structure of **6** was independently confirmed by X-ray crystal structure analysis (Figure 3).[27] As expected, the molecule is flat.

Dihydrophenanthrene **5a** was transformed into its triflate **7**, which was converted into derivative **8** by Suzuki–Miyaura reaction (Scheme 6).

Dihydrophenanthrene **5k**, containing a chloroethyl group located at carbon atom C3, was transformed into chromane **9** by base-mediated intramolecular Williamson reaction (Scheme 7).



Scheme 5. Synthesis of **6**.

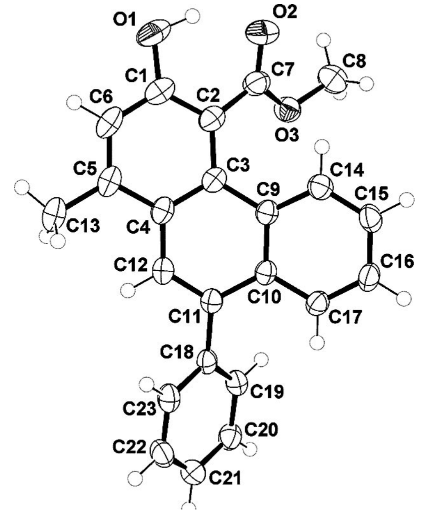
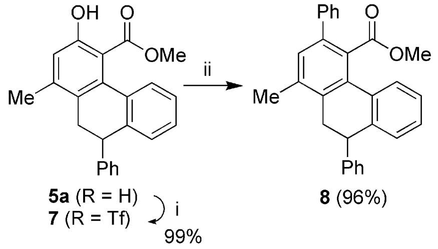
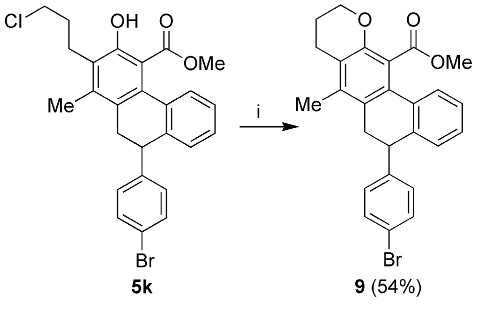


Figure 3. Crystal structure analysis of **6**.



Scheme 6. Synthesis of **8**. Reagents and conditions: (i) pyridine, Tf_2O, CH_2Cl_2, $-78 \rightarrow 0$ °C 4 h; (ii) $PhB(OH)_2$, $Pd(PPh_3)_4$ (3–5 mol-%), K_3PO_4 (1.6 equiv.), 1,4dioxane, 101 °C, 4–20 h.



Scheme 7. Synthesis of **9**. Reagents and conditions: (i) NaH (1.5 equiv.), NBu_4I (2.2 equiv.), DMF, 20 °C, 20 h.

Conclusions

In conclusion, we have reported a new synthesis of functionalized 9,10-dihydrophenanthrenes by reaction of 1,3-bis(trimethylsilyloxy)-1,3-butadienes with 3-benzoyl-5-aryl-4,5-dihydrofurans. These reactions proceed by a novel domino [3+3] cyclization/ring-opening/Friedel–Crafts alkylation process.

Experimental Section

General Methods: ^{1}H NMR: Bruker: AM 250, Bruker ARX 300, Bruker ARX 500; δ = 0.00 ppm for tetramethylsilane; δ = 2.04 ppm for [D$_6$]acetone; δ = 7.26 ppm for (CDCl$_3$); δ = 2.50 ppm for [D$_6$]DMSO; characterization of the signal multiplicities: s = singlet, d = doublet, dd = double of doublet, ddd = doublet of a double doublet,t = triplet, q = quartet, quint = quintet, sext = sextet, sept = septet, m = multiplet, br. = broad. Spectra were evaluated according to first-order rule. All coupling constants are indicated as *J*. ^{13}C NMR: Bruker AM 250 (62.9 MHz), Bruker ARX 300 (75 MHz), Bruker ARX 500 (125 MHz); δ = 29.84 ± 0.01 ppm and 206.26 ± 0.13 ppm for (CD$_3$)$_2$CO; δ = 128.00 ppm for [D$_6$]benzene; δ = 77.00 ppm for CDCl$_3$. The multiplicity of the carbon atoms was determined by the DEPT 135 and APT techniques (APT = attached-proton test) and quoted as CH$_3$, CH$_2$, CH and C for primary, secondary, tertiary and quaternary carbon atoms, respectively. Characterization of the signal multiplicities: q = quartet; the multiplicity of the signals was determined by the DEPT recording technology and/or the APT recording technology. MS: AMD MS40, AMD 402 (AMD Intectra), Varian MAT CH 7, MAT 731. HRMS: Finnigan MAT 95 or Varian MAT 311; Bruker FT CIR, AMD 402 (AMD Intectra). IR: Bruker IFS 66 (FT IR), Nicolet 205 FT IR; Nicolet Protege 460, Nicolet 360 Smart Orbit (ATR); KBr, KAP, Nujol, and ATR; abbreviations for signals: w = weak, m = medium, s = strong, br. = broad. Elementary analysis: LECO CHNS-932, Thermoquest Flash EA 1112. X-ray crystal structure analysis: Bruker X8Apex diffractometer with CCD camera (Mo-K_α und graphite monochromator, λ = 0.71073 Å). Melting points: Micro heating table HMK 67/1825 Kuestner (Büchi apparatus). Column chromatography: Chromatography was performed on Merck silica gel 60 (0.063–0.200 mm, 70–230 mesh) as normal and/or on mesh silica gel 60 (0.040–0.063 mm, 200–400 mesh) as flash chromatography. All solvents were distilled before use. TLC: Merck DC finished foils silica gel 60 F254 on aluminum foil and Macherey finished foils Alugram® Sil G/UV254. Detection under UV light with 254 nm and/or 366 nm without dipping reagent, as well as with anisaldehyde/sulfuric acid reagent (1 mL anisaldehyde in 100 mL of stock solution of 85% methanol, 14% acetic acid and 1% sulfuric acid). Chemicals and workup technique: All solvents for were distilled according to standard methods. All reactions were carried out under an inert gas with oxygen and humidity exclusion. All of the chemicals are standard, commercially available from Merck®, Aldrich®, Arcos® and others.

General Procedure for the Synthesis of Dihydrofurans 3: Ceric ammonium nitrate (2.0 equiv.) was dissolved in acetonitrile. To the mixture was added an acetonitrile solution (10 mL) of **1** (1.0 equiv.) and **2** (4.4 equiv.), and the solution was stirred at 20 °C until the reaction was complete (TLC control). To the mixture was added water (250 mL), and the mixture was extracted with diethyl ether (3 × 100 mL). The combined organic layer was washed with water (300 mL), dried (Na$_2$SO$_4$), and filtered. The solvent of the filtrate was removed in vacuo. The residue was purified by chromatography (silica gel, heptanes/EtOAc).

(2-Methyl-5-phenyl-4,5-dihydro-furan-3-yl)phenylmethanone (3a): Starting with **1a** (0.800 g, 4.93 mmol), **2a** (2.49 mL, 21.70 mmol), and CAN (5.408 g, 9.87 mmol) in acetonitrile (100 mL), **3a** was isolated by chromatography (heptane/EtOAc, 50:1) as a yellow oil (0.480 g, 37%). R_f = 0.46 (heptane/EtOAc, 1:1). ^{1}H NMR (250 MHz, CDCl$_3$): δ = 1.89–1.96 (m, 3 H, CH$_3$), 3.07–3.23 (m, 1 H, H^a), 3.42–3.58 (m, 1 H, H^b), 5.54–5.74 (m, 1 H, H^x), 7.31–7.49 (m, 8 H, Ph), 7.56–7.64 (m, 2 H, Ph) ppm. ^{13}C NMR (62.9 MHz, CDCl$_3$): δ = 15.5 (CH$_3$), 39.4 (CH$_2$), 83.4 (*C*HCH$_2$), 112.3, 140.8, 141.0, 168.3 (C$_{\text{Ph,olefin}}$), 125.7, 127.8, 128.4, 128.7, 131.0 (CH$_{\text{Ar}}$), 193.0 (CO) ppm. IR (ATR): $\tilde{\nu}$ = 1597 (m), 1447 (m), 1386 (m), 1360 (m), 1266 (m), 1217 (s), 1106 (m), 1071 (m), 968 (m), 888 (s) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 264 (41) [M]$^+$, 221 (20), 105 (100), 77 (52). HRMS (EI): calcd. for C$_{18}$H$_{16}$O$_2$ [M]$^+$ 264.11427; found 264.11448.

[5-(4-Bromophenyl)-2-methyl-4,5-dihydrofuran-3-yl]phenylmethanone (3b): Starting with **1a** (1.000 g, 6.16 mmol), **2d** (3.55 mL, 27.13 mmol), and CAN (6.760 g, 12.33 mmol) in acetonitrile (100 mL), **3b** was isolated by chromatography (heptane/EtOAc, 200:1) as a yellow oil (0.931 g, 44%). R_f = 0.60 (heptane/EtOAc, 1:1). ^{1}H NMR (250 MHz, CDCl$_3$): δ = 1.91–1.96 (m, 3 H, CH$_3$), 3.05–3.18 (m, 1 H, H^a), 3.45–3.60 (m, 1 H, H^b), 5.57–5.69 (m, 1 H, H^x), 7.237.31 (m, 2 H, Ph/Ar), 7.41–7.66 (m, 7 H, Ph/Ar) ppm. ^{13}C NMR (62.9 MHz, CDCl$_3$): δ = 15.4 (CH$_3$), 39.3 (CH$_2$), 82.6 (*C*HCH$_2$), 112.2, 122.2, 140.1, 140.6, 168.3 (C$_{\text{Ar,olefin}}$), 127.4, 127.8, 128.3, 131.2, 131.8 (CH$_{\text{Ph,Ar}}$), 192.9 (CO) ppm. IR (ATR): $\tilde{\nu}$ = 2926 (w), 1720 (m), 1595 (s), 1488 (m), 1446 (m), 1385 (m), 1270 (m), 1216 (s), 1070 (m), 966 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 344 (6) [M$^+$, ^{81}Br], 342 (8) [M$^+$, ^{79}Br], 183 (8), 105 (100), 77 (35). HRMS (EI): calcd. for C$_{18}$H$_{15}$BrO$_2$ [M$^+$, ^{79}Br] 342.02449; found 342.02499.

(4-Chlorophenyl)(2-methyl-5-phenyl-4,5-dihydrofuran-3-yl)methanone (3c): Starting with **1b** (1.200 g, 6.10 mmol), **2a** (3.09 mL, 26.85 mmol), and CAN (6.691 g, 12.21 mmol) in acetonitrile (100 mL), **3c** was isolated by chromatography(heptane/EtOAc, 200:1) as a yellow oil (0.828 g, 45%). R_f = 0.54 (heptane/EtOAc, 1:1). ^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.94–1.99 (m, 3 H, CH$_3$), 3.07–3.19 (m, 1 H, H^a), 3.41–3.54 (m, 1 H, H^b), 5.60–5.70 (m, 1 H, H^x), 7.327.43 (m, 7 H, Ph/Ar), 7.50–7.58 (m, 2 H, Ph/Ar) ppm. ^{13}C NMR (62.9 MHz, CDCl$_3$): δ = 15.6 (CH$_3$), 39.3 (CH$_2$), 83.5 (*C*HCH$_2$), 112.1, 137.3, 139.1, 140.8, 168.9 (C$_{\text{Ar,olefin}}$), 125.7, 128.3, 128.6, 128.7, 129.3 (CH$_{\text{Ar}}$), 191.5 (CO) ppm. IR (ATR): $\tilde{\nu}$ = 3032 (w), 2922 (w), 1587 (s), 1487 (m), 1383 (m), 1266 (m), 1217 (s), 1087 (s), 967 (m), 890 (s) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 300 (21) [M$^+$, ^{37}Cl], 298 (63) [M$^+$, ^{35}Cl], 255 (20), 139 (100), 111 (46). HRMS (EI): calcd. for C$_{18}$H$_{15}$ClO$_2$ [M$^+$, ^{35}Cl] 298.07485; found 298.07551.

(4-Bromophenyl)(2-methyl-5-phenyl-4,5-dihydrofuran-3-yl)methanone (3d): Starting with **1c** (1.500 g, 6.22 mmol), **2a** (3.15 mL, 27.38 mmol), and CAN (6.822 g, 12.44 mmol) in acetonitrile (100 mL), **3a** was isolated by chromatography(heptane/EtOAc, 200:1) as a yellow oil (0.631 g, 30%). R_f = 0.63 (heptane/EtOAc, 1:1). ^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.93–1.99 (m, 3 H, CH$_3$), 3.07–3.18 (m, 1 H, H^a), 3.41–3.53 (m, 1 H, H^b), 5.60–5.71 (m, 1 H, H^x), 7.327.41 (m, 5 H, Ph/Ar), 7.44–7.50 (m, 2 H, Ph/Ar) 7.52–7.60 (m, 2 H, Ph/Ar) ppm. ^{13}C NMR (62.9 MHz, CDCl$_3$): δ = 15.6 (CH$_3$), 39.3 (CH$_2$), 83.5 (*C*HCH$_2$), 112.0, 139.5, 140.8, 169.0 (C$_{\text{Ar,olefin}}$), 125.7, 128.3, 128.7, 129.4, 131.5 (CH$_{\text{Ar}}$), 191.5 (CO) ppm. IR (ATR): $\tilde{\nu}$ = 1583 (s), 1482 (m), 1393 (m), 1359 (m), 1265 (m), 1217 (s), 1067 (m), 1010 (m), 888 (s), 750 (s) cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 344 (26) [M^+, ^{81}Br], 342 (30) [M^+, ^{79}Br], 220 (40), 185 (95), 43 (100). HRMS (EI): calcd. for $C_{18}H_{15}BrO_2$ [M^+, ^{79}Br] 342.02404; found 342.02499.

(4-Methoxyphenyl)(2-methyl-5-phenyl-4,5-dihydrofuran-3-yl)-methanone (3e): Starting with **1d** (1.500 g, 7.80 mmol), **2a** (3.95 mL, 34.34 mmol), and CAN (8.557 g, 15.61 mmol) in acetonitrile (100 mL), **3a** was isolated by chromatography (heptane/EtOAc, 100:1) as a yellow oil (1.051 g, 46%). R_f = 0.27 (heptane/EtOAc, 1:1). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.94–1.99 (m, 3 H, CH_3), 3.10–3.23 (m, 1 H, H^a), 3.43–3.55 (m, 1 H, H^b), 3.85 (s, 3 H, OCH_3), 5.58–5.68 (m, 1 H, H^x), 6.86–6.96 (m, 2 H, Ar), 7.33–7.43 (m, 5 H, Ph) 7.59–7.67 (m, 2 H, Ar) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 15.5 (CH_3), 39.8 (CH_2), 55.5 (OCH_3), 83.2 (*C*HCH_2), 112.0, 133.2, 141.2, 162.2, 167.2 ($C_{Ar,olefin}$), 113.5, 125.8, 128.2, 128.7, 130.3 ($CH_{Ar,Ph}$), 191.8 (CO) ppm. IR (ATR): $\tilde{\nu}$ = 2956 (w), 2930 (w), 1596 (s), 1508 (m), 1344 (m), 1247 (s), 1209 (s), 1155 (m), 1025 (m), 976 (m) cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 294 (50) $[M]^+$, 186 (21), 171 (51), 135 (100). HRMS (EI): calcd. for $C_{19}H_{18}O_3$ $[M]^+$ 294.12535; found 294.12505.

General Procedure for the Synthesis of 5a–q: To a dichloromethane solution (50 mL) of **3** (1.0 equiv.) was added **4a**–**i** (1.5–1.7 equiv.) at –78 °C under an argon atmosphere. To the mixture was added $TiCl_4$ (2.0 equiv.). The temperature of the solution was warmed to 20 °C over 16 h with stirring. To the mixture was added hydrochloric acid (10%, 50 mL). The mixture was stirred for 10 min and subsequently extracted with dichloromethane (3 × 50 mL). The combined organic layer was dried (Na_2SO_4) and filtered, and the filtrate was concentrated in vacuo. The residue was purified by chromatography (silica gel, heptanes/EtOAc).

Methyl 3-Hydroxy-1-methyl-9-phenyl-9,10-dihydrophenanthrene-4-carboxylate (5a): Starting with **3a** (0.159 g, 0.60 mmol), **4a** (0.235 g, 0.90 mmol), and $TiCl_4$ (0.13 mL, 1.20 mmol), **5a** was isolated by chromatography (heptane/EtOAc, 50:1) as a colorless solid (0.139 g, 67%). M.p. 149–150 °C. R_f = 0.62 (heptane/EtOAc, 1:1). ^1H NMR (300 MHz, $CDCl_3$): δ = 2.25 (br. s, 3 H, CH_3), 2.84–3.04 (m, 2 H, CH_2CH), 3.67 (s, 3 H, OCH_3), 4.08–4.18 (m, 1 H, CH_2CH), 6.78 (s, 1 H, Ar), 6.85–6.94 (m, 1 H, Ph/Ar), 7.10–7.38 (m, 8 H, Ph/Ar), 9.53 (s, 1 H, OH) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 20.3 (CH_3), 32.6, (CH_2), 44.5 (*C*HCH_2), 51.7 (OCH_3), 109.1, 128.9, 134.5, 136.4, 140.3, 142.1, 142.4, 158.3 ($C_{Ph,Ar}$), 117.7, 125.6, 126.7, 126.7, 127.5, 128.5, 128.6, 129.1 ($CH_{Ph,Ar}$), 172.0 (*C*O-OCH_3) ppm. IR (ATR): $\tilde{\nu}$ = 3031 (w), 2950 (w), 1659 (s), 1604 (m), 1434 (m), 1320 (m), 1225 (m), 1068 (m), 974 (m), 862 (m) cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 344 (69) $[M]^+$, 312 (100), 284 (24), 269 (31), 241 (22). HRMS (EI): calcd. for $C_{23}H_{20}O_3$ $[M]^+$ 344.14026; found 344.14070. $C_{23}H_{20}O_3$ (344.14): calcd. C 80.21, H 5.85; found C 80.10, H 5.83.

Ethyl 3-Hydroxy-1-methyl-9-phenyl-9,10-dihydrophenanthrene-4-carboxylate (5b): Starting with **3a** (0.160 g, 0.61 mmol), **4b** (0.282 g, 1.03 mmol) and $TiCl_4$ (0.13 mL, 1.21 mmol), **5b** was isolated by chromatography (heptane/EtOAc, 50:1) as a colorless solid (0.115 g, 53%). M.p. 130–131 °C. R_f = 0.48 (heptane/EtOAc, 1:1). ^1H NMR (250 MHz, $CDCl_3$): δ = 1.03 (t, ^3J = 7.2 Hz, 3 H, CH_3CH_2), 2.24 (s, 3 H, CH_3), 2.96 (d, $^3J_{H^{ab},H^x}$ = 7.0 Hz, 2 H, H^a,H^b), 4.07–4.29 (m, $^3J_{H^{ab},H^x}$ = 7.0 Hz, 1 H, H^x, 2 H, CH_3CH_2), 6.75 (s, 1 H, Ar), 6.90–6.99 (m, 1 H, Ph/Ar), 7.13–7.35 (m, 8 H, Ph/Ar), 9.62 (s, 1 H, OH) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 13.5, 20.3 (CH_3), 32.7, 61.2 (CH_2), 44.3 (*C*HCH_2), 109.3, 134.8, 136.9, 140.0, 142.0, 142.5, 158.3 ($C_{Ph,Ar}$), 117.6, 125.5, 126.5, 126.8, 127.5, 128.3, 128.5, 129.6 ($CH_{Ph,Ar}$), 171.5 (*C*$OOCH_2CH_3$) ppm. IR (ATR): $\tilde{\nu}$ = 2963 (w), 2886 (w), 1659 (s), 1452 (m), 1371 (m), 1311 (m), 1224 (s), 1205 (m), 1064 (m), 1005 (m) cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 358 (44) $[M]^+$, 312 (100), 284 (10), 269 (10). HRMS (EI): calcd. for $C_{24}H_{22}O_3$ $[M]^+$ 358.15604; found 358.15635.

Methyl 3-Hydroxy-1,2-dimethyl-9-phenyl-9,10-dihydrophenanthrene-4-carboxylate (5c): Starting with **3a** (0.131 g, 0.50 mmol), **4c** (0.204 g, 0.74 mmol), and $TiCl_4$ (0.11 mL, 0.99 mmol), **5c** was isolated by chromatography (heptane/EtOAc, 50:1) as a yellow solid (0.051 g, 30%). M.p. 136–138 °C. R_f = 0.85 (heptane/EtOAc, 1:1). ^1H NMR (250 MHz, $CDCl_3$): δ = 2.22, 2.24 (s, 3 H, CH_3), 2.87–3.10 (m, 2 H, CH_2CH), 3.67 (s, 3 H, OCH_3), 4.07–4.17 (m, 1 H, CH_2CH), 6.83–6.93 (m, 1 H, Ph/Ar), 7.07–7.38 (m, 8 H, Ph/Ar), 9.86 (s, 1 H, OH) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 12.3, 16.3 (CH_3), 33.5 (CH_2), 44.7 (*C*HCH_2), 51.7 (OCH_3), 108.5, 124.2, 128.6, 133.8, 134.9, 140.0, 140.2, 142.6, 156.4 ($C_{Ph,Ar}$), 125.5, 126.5, 126.6, 127.1, 128.4, 128.7, 128.9 ($CH_{Ph,Ar}$), 172.7 (*C*$OOCH_3$) ppm. IR (ATR): $\tilde{\nu}$ = 2961 (w), 2928 (w), 1652 (m), 1597 (m), 1434 (m), 1322 (m), 1260 (m), 1078 (m), 1011 (s), 907 (m) cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 358 (75) $[M]^+$, 326 (100), 298 (42), 235 (66), 105 (49). HRMS (EI): calcd. for $C_{24}H_{22}O_3$ [M^+, ^{35}Cl] 358.155854; found 358.15635.

Methyl 2-Ethyl-3-hydroxy-1-methyl-9-phenyl-9,10-dihydrophenanthrene-4-carboxylate (5d): Starting with **3a** (0.158 g, 0.60 mmol), **4d** (0.259 g, 0.90 mmol), and $TiCl_4$ (0.13 mL, 1.20 mmol), **5d** was isolated by chromatography (heptane/EtOAc, 50:1) as a colorless solid (0.068 g, 31%). M.p. 134–135 °C. R_f = 0.80 (heptane/EtOAc, 1:1). ^1H NMR (250 MHz, $CDCl_3$): δ = 1.14 (t, ^3J = 7.5 Hz, 3 H, CH_3CH_2), 2.25 (s, 3 H, CH_3), 2.69–2.84 (m, ^3J = 7.5 Hz, 2 H, CH_3CH_2), 2.85–3.10 (m, 2 H, CH_2CH), 3.66 (s, 3 H, OCH_3), 4.06–4.18 (m, 1 H, CH_2CH), 6.81–6.90 (m, 1 H, Ph/Ar), 7.07–7.39 (m, 8 H, Ph/Ar), 9.82 (s, 1 H, OH) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 13.5, 15.7 (CH_3), 19.9, 33.5 (CH_2), 44.8 (*C*HCH_2), 51.7 (OCH_3), 108.6, 129.0, 130.2, 133.9, 134.9, 139.5, 140.0, 142.6, 156.3 ($C_{Ph,Ar}$), 125.5, 126.5, 126.6, 127.1, 128.5, 128.7, 128.9 ($CH_{Ph,Ar}$), 172.7 (*C*$OOCH_3$) ppm. IR (ATR): $\tilde{\nu}$ = 2972 (w), 2878 (w), 1668 (s), 1592 (m), 1434 (m), 1400 (m), 1302 (m), 1202 (s), 1102 (m), 942 (m) cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 372 (79) $[M]^+$, 340 (100), 325 (48), 312 (41), 249 (28). HRMS (ESI): calcd. for $C_{25}H_{23}O_3$ $[M - H]^-$ 371.16527; found 371.16485.

Isopropyl 3-Hydroxy-1-methyl-9-phenyl-9,10-dihydrophenanthrene-4-carboxylate (5e): Starting with **3a** (0.142 g, 0.54 mmol), **4i** (0.233 g, 0.81 mmol), and $TiCl_4$ (0.12 mL, 1.08 mmol), **5e** was isolated by chromatography (heptane/EtOAc, 50:1) as a yellow solid (0.161 g, 80%). M.p. 132–134 °C. R_f = 0.70 (heptane/EtOAc, 1:1). ^1H NMR (250 MHz, $CDCl_3$): δ = 1.09 (d, ^3J = 6.2 Hz, 3 H, CH_3CH), 1.13 (d, ^3J = 6.2 Hz, 3 H, CH_3CH), 2.23 (s, 3 H, CH_3), 2.87–3.09 (m, 2 H, CH_2CH), 4.11–4.27 (m, 1 H, CH_2CH), 5.13 (sept., ^3J = 6.2 Hz, CH_3CHCH_3), 6.74 (s, 1 H, Ar), 6.92–7.05 (m, 1 H, Ph/Ar), 7.14–7.33 (m, 8 H, Ph/Ar), 9.75 (s, 1 H, OH) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 20.2, 21.3, 21.3 (CH_3), 32.8, (CH_2), 44.1 (*C*HCH_2), 69.4 (CH), 109.7, 128.3, 134.9, 136.9, 139.6, 141.8, 144.5, 158.4 ($C_{Ph,Ar}$), 117.5, 125.9, 126.4, 126.9, 127.5, 128.2, 128.5, 130.1 ($CH_{Ph,Ar}$), 170.9 (*C*OO) ppm. IR (ATR): $\tilde{\nu}$ = 2981 (w), 2964 (w), 1651 (s), 1568 (m), 1447 (m), 1369 (m), 1309 (s), 1177 (s), 1101 (s), 1061 (s) cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 372 (46) $[M]^+$, 312 (100), 284 (21), 269 (23), 241 (17). HRMS (ESI): calcd. for $C_{25}H_{24}NaO_3$ $[M + Na]^+$ 395.16177; found 395.16141. $C_{25}H_{24}O_3$ (372.17): calcd. C 80.62, H 6.49; found C 79.72, H 6.49.

Methyl 3-Hydroxy-1-methyl-9-phenyl-2-propyl-9,10-dihydrophenanthrene-4-carboxylate (5f): Starting with **3a** (0.130 g, 0.49 mmol), **4j** (0.223 g, 0.74 mmol), and $TiCl_4$ (0.11 mL, 0.98 mmol), **5f** was isolated by chromatography (heptane/EtOAc, 100:1) as a colorless oil (0.078 g, 41%). R_f = 0.69 (heptane/EtOAc, 1:1). ^1H NMR

(250 MHz, $CDCl_3$): δ = 1.00 (t, ^3J = 7.3 Hz, 3 H, CH_3), 1.49–1.60 (m, 2 H, CH_2), 2.24 (s, 3 H, CH_3), 2.64–2.78 (m, 2 H, CH_2), 2.83–3.10 (m, 2 H, $C\mathit{H}_2CH$), 3.66 (s, 3 H, OCH_3), 4.05–4.18 (m, 1 H, $CH_2C\mathit{H}$), 6.82–6.89 (m, 1 H, Ph/Ar), 7.06–7.38 (m, 8 H, Ph/Ar), 9.81 (s, 1 H, OH) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 14.4, 16.0 (CH_3), 22.5, 28.7, 33.5 (CH_2), 44.7 ($\mathit{C}HCH_2$), 51.7 (OCH_3), 108.5, 128.9, 133.9, 134.9, 139.8, 140.0, 142.6, 156.5 ($C_{Ph,Ar}$), 125.5, 126.4, 126.6, 127.1, 128.4, 128.7, 128.8 ($CH_{Ph,Ar}$), 172.7 ($\mathit{C}OOCH_3$) ppm. IR (ATR): $\tilde{\nu}$ = 2954 (m), 2870 (m), 1662 (s), 1595 (m), 1434 (m), 1314 (m), 1205 (s), 1108 (m), 1040 (m), 980 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 386 (11) $[M]^+$, 358 (18), 183 (75), 79 (100). HRMS (EI): calcd. for $C_{26}H_{26}O_3$ $[M]^+$ 386.18718; found 386.18765.

Ethyl 3-Hydroxy-1-methyl-9-phenyl-9,10-dihydrophenanthrene-4-carboxylate (5g): Starting with **3a** (0.160 g, 0.61 mmol), **4l** (0.277 g, 0.91 mmol), and $TiCl_4$ (0.13 mL, 1.21 mmol), **5g** was isolated by chromatography (heptane/EtOAc, 100:1) as a yellow oil (0.043 g, 18%). R_f = 0.54 (heptane/EtOAc, 1:1). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.22 (s, 3 H, CH_3), 2.95 (d, ^3J = 6.9 Hz, 2 H, $C\mathit{H}_2CH$), 3.13 (s, 3 H, OCH_3), 3.33 (t, ^3J = 4.8 Hz, 2 H, CH_2), 4.11–4.37 (m, ^3J = 6.9 Hz, 1 H, $CH_2C\mathit{H}$, ^3J = 4.8 Hz, 2 H, CH_2), 6.74 (br. s, 1 H, Ar), 6.89–7.00 (m, 1 H, Ph/Ar), 7.11–7.34 (m, 8 H, Ph/Ar), 9.46 (s, 1 H, OH) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 20.2 (CH_3), 32.6, 64.0, 69.5 (CH_2), 44.2 ($\mathit{C}HCH_2$), 58.7 (OCH_3), 109.2, 128.6, 134.7, 136.9, 140.0, 142.1, 142.4, 158.2 ($C_{Ph,Ar}$), 117.6, 125.7, 126.5 126.9, 127.5, 128.3, 128.5, 129.4 ($CH_{Ph,Ar}$), 171.1 ($\mathit{C}OO$) ppm. IR (ATR): $\tilde{\nu}$ = 2923 (w), 2880 (w), 1661 (s), 1601 (m), 1569 (m), 1447 (m), 1375 (m), 1197 (s), 1125 (s), 1064 (s) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 388 (26) $[M]^+$, 312 (100), 269 (8), 241 (8). HRMS (EI): calcd. for $C_{25}H_{24}O_4$ $[M]^+$ 388.16606; found 388.16691. $C_{25}H_{24}O_4$ (388.17): calcd. C 77.30, H 6.23; found C 77.16, H 6.48.

Ethyl 2-Chloro-3-hydroxy-1-methyl-9-phenyl-9,10-dihydrophenanthrene-4-carboxylate (5h): Starting with **3a** (0.178 g, 0.67 mmol), **4m** (0.353 g, 1.15 mmol), and $TiCl_4$ (0.15 mL, 1.35 mmol), **5h** was isolated by chromatography (heptane/EtOAc, 200:1) as a yellow solid (0.048 g, 18%). M.p. 54–54 °C. R_f = 0.53 (heptane/EtOAc, 1:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.05 (t, ^3J = 7.2 Hz, 3 H, $C\mathit{H}_3CH_2$), 2.37 (s, 3 H, CH_3), 2.96–3.12 (m, 2 H, $C\mathit{H}_2CH$), 4.09–4.32 (m, 2 H, $CH_3C\mathit{H}_2$, 1 H $CH_2C\mathit{H}$), 6.92–7.04 (m, 1 H, Ph/Ar), 7.13–7.35 (m, 8 H, Ph/Ar), 9.96 (s, 1 H, OH) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 13.4, 17.1 (CH_3), 33.8, 61.6 (CH_2), 44.1 ($\mathit{C}HCH_2$), 110.6, 121.7, 129.1, 34.3, 135.0, 139.2, 139.7, 142.1, 153.9 ($C_{Ph,Ar}$), 125.9, 126.6, 127.0, 127.9 128.4, 128.4, 129.3, ($CH_{Ph,Ar}$), 171.2 ($\mathit{C}OOCH_2CH_3$) ppm. IR (ATR): $\tilde{\nu}$ = 2980 (w), 2936 (w), 1660 (s), 1594 (m), 1445 (m), 1371 (m), 1293 (m), 1219 (s), 1193 (s), 1012 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 394 (6) $[M^+, {}^{37}Cl]$, 392 (19) $[M^+, {}^{35}Cl]$, 346 (100), 239 (21), 44 (26). HRMS (EI): calcd. for $C_{24}H_{21}ClO_3$ $[M^+, {}^{35}Cl]$ 392.11804; found 392.11737.

Methyl 9-(4-Bromophenyl)-3-hydroxy-1-methyl-9,10-dihydrophenanthrene-4-carboxylate (5i): Starting with **3b** (0.164 g, 0.48 mmol), **4a** (0.187 g, 0.72 mmol), and $TiCl_4$ (0.10 mL, 0.96 mmol), **5i** was isolated by chromatography (heptane/EtOAc, 100:1) as a yellow solid (0.079 g, 39%). M.p. 193–194 °C. R_f = 0.56 (heptane/EtOAc, 1:1). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.24 (br. s, 3 H, CH_3), 2.81–3.00 (m, 2 H, $C\mathit{H}_2CH$), 3.67 (s, 3 H, OCH_3), 4.04–4.16 (m, 1 H, $CH_2C\mathit{H}$), 6.77 (br. s, 1 H, Ar), 6.88–6.95 (m, 1 H, Ph/Ar), 7.07–7.27 (m, 5 H, Ph/Ar), 7.37–7.45 (m, 2 H, Ph/Ar), 9.51 (s, 1 H, OH) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 20.3 (CH_3), 32.6 (CH_2), 43.8 ($\mathit{C}HCH_2$), 51.7 (OCH_3), 109.1, 120.4, 128.3, 134.6, 136.6, 139.4, 141.4, 142.1, 158.3 ($C_{Ph,Ar}$), 117.8, 125.9, 126.8, 127.7, 129.3, 130.2, 131.5 ($CH_{Ph,Ar}$), 171.9 ($\mathit{C}OOCH_3$) ppm. IR (ATR): $\tilde{\nu}$ = 2947 (w), 2884 (w), 1668 (s), 1568 (m), 1486 (m), 1433 (s), 1312 (m), 1177 (s), 1064 (s), 1008 (s) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 424 (48) $[M^+, {}^{81}Br]$, 422 (39) $[M^+, {}^{79}Br]$, 390 (100), 283 (39), 239 (25). HRMS (ESI): calcd. for $C_{23}H_{18}BrO_3$ $[M - H]^-$ 421.04448; found 421.04412.

Isopropyl 9-(4-Bromophenyl)-3-hydroxy-1-methyl-9,10-dihydrophenanthrene-4-carboxylate (5j): Starting with **3b** (0.131 g, 0.38 mmol), **4i** (0.143 g, 0.50 mmol), and $TiCl_4$ (0.08 mL, 0.76 mmol), **5j** was isolated by chromatography (heptane/EtOAc, 100:1) as a colorless solid (0.076 g, 44%). M.p. 162–164 °C. R_f = 0.67 (heptane/EtOAc, 1:1). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.09 (d, ^3J = 6.2 Hz, 3 H, $C\mathit{H}_3CH$), 1.11 (d, ^3J = 6.2 Hz, 3 H, $C\mathit{H}_3CH$), 2.21 (br. s, 3 H, CH_3), 2.85–3.04 (m, 2 H, $C\mathit{H}_2CH$), 4.07–4.24 (m, 1 H, $CH_2C\mathit{H}$), 5.12 (sept., ^3J = 6.2 Hz, 1 H, $CH_3C\mathit{H}CH_3$), 6.72 (br. s, 1 H, Ar), 6.97–7.12 (m, 3 H, Ph/Ar), 7.17–7.39 (m, 5 H, Ph/Ar), 9.72 (s, 1 H, OH) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 20.2, 21.2, 21.4 (CH_3), 32.8 (CH_2), 43.4, 69.5 (CH), 109.6, 120.2, 134.9, 136.8, 138.8, 141.6, 141.8, 158.4 ($C_{Ph,Ar}$), 117.7, 126.2, 126.9, 127.6, 130.1, 130.2, 131.2 ($CH_{Ph,Ar}$), 170.8 ($\mathit{C}OO$) ppm. IR (ATR): $\tilde{\nu}$ = 2980 (w), 2934 (w), 1657 (s), 1569 (m), 1487 (m), 1450 (m), 1366 (m), 1221 (m), 1101 (s), 1009 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 452 (25) $[M^+, {}^{81}Br]$, 450 (25) $[M^+, {}^{79}Br]$, 392 (100), 312 (7), 283 (16). HRMS (EI): calcd. for $C_{25}H_{23}BrO_3$ $[M^+, {}^{79}Br]$ 450.08138; found 450.08251.

Methyl 9-(4-Bromophenyl)-2-(3-chloropropyl)-3-hydroxy-9,10-dihydrophenanthrene-4-carboxylate (5k): Starting with **3b** (0.185 g, 0.54 mmol), **4k** (0.309 g, 0.92 mmol), and $TiCl_4$ (0.12 mL, 1.08 mmol), **5k** was isolated by chromatography (heptane/EtOAc, 100:1) as a colorless solid (0.055 g, 20%). M.p. 172–174 °C. R_f = 0.60 (heptane/EtOAc, 1:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.93–2.06 (m, 2 H, CH_2), 2.25 (s, 3 H, CH_3), 2.82–3.04 (m, 4 H, $2CH_2$), 3.61 (t, ^3J = 6.6 Hz, 2 H, CH_2), 3.66 (s, OCH_3), 4.05–4.15 (m, 1 H, CH), 6.87–6.96 (m, 1 H, Ar), 7.07–7.23 (m, ^3J = 8.4 Hz, 5 H, Ar), 7.38–7.45 (m, ^3J = 8.4 Hz, 2 H, CH_2), 9.84 (s, OH) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 15.9 (CH_3), 24.2, 32.2, 33.5, 45.1 (CH_2), 44.2 ($\mathit{C}HCH_2$) 51.8 (OCH_3), 108.6, 120.4, 127.2, 128.4, 134.4, 134.7, 139.2, 140.0, 141.5, 156.2 (C_{Ar}), 125.8, 126.6, 127.4, 129.0, 130.3, 131.3 (CH_{Ar}), 172.4 ($\mathit{C}OOCH_3$) ppm. IR (ATR): $\tilde{\nu}$ = 2954 (w), 2915 (w), 1658 (m), 1485 (m), 1434 (m), 1324 (m), 1210 (m), 1010 (m), 988 (m), 767 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 500 (27) $[M^+, {}^{37}Cl/{}^{79}Br, {}^{35}Cl/{}^{81}Br]$, 462 (76), 433 (100), 405 (47). HRMS (EI): calcd. for $C_{18}H_{18}BrClO_3$ $[M^+, {}^{35}Cl, {}^{81}Br]$ 500.05714; found 500.05790.

Methyl 7-Chloro-3-hydroxy-1-methyl-9-phenyl-9,10-dihydrophenanthrene-4-carboxylate (5l): Starting with **3c** (0.195 g, 0.65 mmol), **4a** (0.255 g, 0.98 mmol), and $TiCl_4$ (0.14 mL, 1.31 mmol), **5l** was isolated by chromatography (heptane/EtOAc, 200:1) as a colorless solid (0.125 g, 51%). M.p. 166–167 °C. R_f = 0.54 (heptane/EtOAc, 1:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.25 (s, 3 H, CH_3), 2.85–2.99 (m, 2 H, $C\mathit{H}_2CH$), 3.69 (s, 3 H, OCH_3), 4.05–4.12 (m, 1 H, $CH_2C\mathit{H}$), 6.79 (s, 1 H, Ar),6.87 (br. s, 1 H, Ar), 7.06 (d, ^3J = 8.4 Hz, 1 H, Ph/Ar), 7.16–7.19 (m, ^3J = 8.4 Hz, 1 H, Ph/Ar), 7.22–7.37 (m, 5 H, Ph/Ar), 9.60 (s, 1 H, OH) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 20.3 (CH_3), 32.5 (CH_2), 44.5 ($\mathit{C}HCH_2$), 51.8 (OCH_3), 108.9, 128.8, 133.1, 133.4, 135.6, 141.4, 142.2, 142.3, 158.6 ($C_{Ph,Ar}$), 118.1, 125.7, 126.8, 127.0, 128.5, 128.7, 130.4 ($CH_{Ph,Ar}$), 171.7 ($\mathit{C}OOCH_3$) ppm. IR (ATR): $\tilde{\nu}$ = 2947 (w), 2884 (w), 1658 (s), 1599 (m), 1433 (m), 1348 (m), 1219 (s), 1132 (m), 1063 (m), 949 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 380 (13) $[M^+, {}^{37}Cl]$, 378 (37) $[M^+, {}^{35}Cl]$, 346 (100), 255 (12). HRMS (EI): calcd. for $C_{23}H_{19}ClO_3$ $[M^+, {}^{35}Cl]$ 378.10286; found 378.10172. $C_{23}H_{19}ClO_3$ (378.10): calcd. C 72.92, H 5.06; found C 72.63, H 5.20.

Ethyl 7-Chloro-3-hydroxy-1-methyl-9-phenyl-9,10-dihydrophenanthrene-4-carboxylate (5m): Starting with **3c** (0.168 g, 0.56 mmol),

4b (0.231 g, 0.84 mmol), and $TiCl_4$ (0.12 mL, 1.13 mmol), **5a** was isolated by chromatography (heptane/EtOAc, 200:1) as a colorless solid (0.115 g, 52%). M.p. 143–145 °C. R_f = 0.63 (heptane/EtOAc, 1:1). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.09 (t, ^3J = 7.2 Hz, 3 H, CH_3CH_2), 2.24 (s, 3 H, CH_3), 2.91–2.97 (m, 2 H, CH_2CH), 4.07–4.29 (m, 1 H, CH_2CH, 2 H, CH_3CH_2), 6.77 (br. s, 1 H, Ar), 6.92 (br. s, 1 H, Ar), 7.087.37 (m, 7 H, Ph/Ar), 9.71 (s, 1 H, OH) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 13.6, 20.2 (CH_3), 32.5, 61.3 (CH_2), 44.2 ($CHCH_2$), 109.0, 128.5, 133.3, 133.3, 135.7, 141.5, 141.9, 142.1, 158.6 ($C_{Ph,Ar}$), 118.0, 125.7, 126.8, 126.9, 128.4, 128.5, 130.8 ($CH_{Ph,Ar}$), 171.2 ($COOCH_3CH_2$) ppm. IR (ATR): $\tilde{\nu}$ = 2980 (w), 2882 (w), 1657 (s), 1573 (m), 1452 (m), 1371 (m), 1313 (m), 1222 (s), 1193 (s), 1066 (m) cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 394 (11) [M^+, ^{37}Cl], 392 (31) [M^+, ^{35}Cl], 346 (100), 255 (10). HRMS (EI): calcd. for $C_{24}H_{21}ClO_3$ [M^+, ^{35}Cl] 392.11749; found 392.11737.

Methyl 7-Bromo-3-hydroxy-1-methyl-9-phenyl-9,10-dihydrophenanthrene-4-carboxylate (5n): Starting with **3d** (0.190 g, 0.55 mmol), **4a** (0.216 g, 0.83 mmol), and $TiCl_4$ (0.12 mL, 1.11 mmol), **5n** was isolated by chromatography (heptane/EtOAc, 200:1) as a colorless solid (0.112 g, 48%). M.p. 81–82 °C. R_f = 0.57 (heptane/EtOAc, 1:1). ^1H NMR (300 MHz, $CDCl_3$): δ = 2.25 (br. s, 3 H, CH_3), 2.81–3.01 (m, 2 H, CH_2CH), 3.69 (s, 3 H, OCH_3), 4.04–4.13 (m, 1 H, CH_2CH), 6.79 (br. s, 1 H, Ar), 6.99 (d, ^3J = 8.3 Hz, 1 H, Ph/Ar), 7.03 (br. s, 1 H, Ar), 7.20–7.38 (m, ^3J = 8.3 Hz, 6 H, Ph/Ar), 9.61 (s, 1 H, OH) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 20.3 (CH_3), 32.5 (CH_2), 44.4 ($CHCH_2$), 51.8 (OCH_3), 108.1, 121.7 128.8, 133.6, 135.6, 141.4, 142.3, 142.5, 158.6 ($C_{Ph,Ar}$), 118.2, 127.0, 128.5, 128.7, 129.7, 130.7 ($CH_{Ph,Ar}$), 171.7 ($COOCH_3$) ppm. IR (ATR): $\tilde{\nu}$ = 3026 (w), 2947 (w), 1662 (s), 1573 (m), 1434 (s), 1316 (m), 1221 (s), 1196 (s), 163 (s), 949 (m) cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 424 (26) [M^+, ^{81}Br], 422 (26) [M^+, ^{79}Br], 390 (100), 283 (27), 239 (34). HRMS (EI): calcd. for $C_{23}H_{19}BrO_3$ [M^+, ^{79}Br] 422.05080; found 422.05121. $C_{23}H_{19}BrO_3$ (422.05): calcd. C 65.26, H 4.52; found C 64.85, H 4.29.

Methyl 7-Bromo-3-hydroxy-1,2-dimethyl-9-phenyl-9,10-dihydrophenanthren-4-carboxylate (5o): Starting with **3d** (0.170 g, 0.50 mmol), **4c** (0.204 g, 0.74 mmol), and $TiCl_4$ (0.11 mL, 0.99 mmol), **5a** was isolated by chromatography (heptane/EtOAc, 200:1) as a colorless solid (0.080 g, 37%). M.p. 204–205 °C. R_f = 0.64 (heptane/EtOAc, 1:1). ^1H NMR (300 MHz, $CDCl_3$): δ = 2.21, 2.23 (s, 3 H, CH_3), 2.84–3.08 (m, 2 H, CH_2CH), 3.68 (s, 3 H, OCH_3), 4.02–4.13 (m, 1 H, CH_2CH), 6.96 (d, ^3J = 8.3 Hz, 1 H, Ar), 7.01 (br. s, 1 H, Ar), 7.217.38 (m, 6 H, Ph/Ar), 9.93 (s, 1 H, OH) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 12.3, 16.3 (CH_3), 33.4 (CH_2), 44.6 ($CHCH_2$), 51.8 (OCH_3), 108.2, 121.2, 124.8, 128.4, 132.8, 134.0, 140.5, 141.6, 142.2, 156.8 ($C_{Ph,Ar}$), 127.0, 128.5, 128.6, 128.6, 129.5, 130.4 ($CH_{Ph,Ar}$), 172.4 ($COOCH_3$) ppm. IR (ATR): $\tilde{\nu}$ = 2922 (w), 1651 (s), 1588 (m), 1481 (m), 1450 (m), 1429 (m), 1316 (s), 1209 (s), 1090 (s), 1009 (s) cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 438 (50) [M^+, ^{81}Br], 436 (50) [M^+, ^{79}Br], 406 (100), 378 (24), 325 (94). HRMS (EI): calcd. for $C_{24}H_{21}BrO_3$ [M^+, ^{79}Br] 436.06650; found 436.06686. $C_{24}H_{21}BrO_3$ (436.07): calcd. C 65.91, H 4.84; found C 65.80, H 5.10.

Isopropyl 7-Bromo-3-hydroxy-1-methyl-9-phenyl-9,10-dihydrophenanthrene-4-carboxylate (5p): Starting with **3d** (0.170 g, 0.50 mmol), **4i** (0.214 g, 0.74 mmol), and $TiCl_4$ (0.11 mL, 0.99 mmol), **5p** was isolated by chromatography (heptane/EtOAc, 200:1) as a colorless solid (0.086 g, 40%). M.p. 74–55 °C. R_f = 0.66 (heptane/EtOAc, 1:1). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.11 (d, ^3J = 6.2 Hz, 3 H, CH_3CH), 1.14 (d, ^3J = 6.2 Hz, 3 H, CH_3CH), 2.22 (s, 3 H, CH_3), 2.85–3.04 (m, 2 H, CH_2CH), 4.07–4.20 (m, 1 H, CH_2CH), 5.13 (sept., ^3J = 6.2 Hz, CH_3CHCH_3), 6.75 (s, 1 H, Ar), 7.04–7.42 (m, 8 H, Ph/Ar), 9.80 (s, 1 H, OH) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 20.2, 21.3, (CH_3), 32.6, (CH_2), 44.0 ($CHCH_2$), 69.7 (CH), 109.4, 121.4, 128.2, 133.9, 135.8, 141.5, 141.9, 142.0, 158.7 ($C_{Ph,Ar}$), 118.0, 126.7, 128.3, 128.4, 128.8, 129.8, 131.6, ($CH_{Ph,Ar}$), 170.6 (COO) ppm. IR (ATR): $\tilde{\nu}$ = 2978 (w), 2921 (w), 1657 (s), 1572 (m), 1451 (m), 1370 (m), 1307 (m), 1221 (s), 1101 (s), 1060 (s) cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 452 (21) [M^+, ^{81}Br], 450 (21) [M^+, ^{79}Br], 390 (100), 283 (23), 239 (32). $C_{25}H_{23}BrO_3$ (450.08): calcd. C 66.53, H 5.14; found C 66.31, H 5.29.

Methyl 3-Hydroxy-7-methoxy-1-methyl-9-phenyl-9,10-dihydrophenanthrene-4-carboxylate (5q): Starting with **3e** (0.152 g, 0.52 mmol), **4a** (0.202 g, 0.75 mmol), and $TiCl_4$ (0.11 mL, 1.03 mmol), **5q** was isolated by chromatography (heptane/EtOAc, 100:1) as a colorless solid (0.041 g, 21%). M.p. 70–71 °C. R_f = 0.79 (heptane/EtOAc, 1:1). ^1H NMR (300 MHz, $CDCl_3$): δ = 2.24 (s, 3 H, CH_3), 2.81–3.03 (m, 2 H, CH_2CH), 3.70, 3.72 (s, 3 H, OCH_3), 4.05–4.15 (m, 1 H, CH_2CH), 6.45 (d, ^4J = 2.6 Hz, 1 H, Ar), 6.72 (br. s, 1 H, Ar), 6.76 (dd, ^4J = 2.6 Hz, ^3J = 8.6 Hz, 1 H, Ar), 7.08 (d, ^3J = 8.6 Hz, 1 H, Ar), 7.20–7.38 (m, 5 H, Ph), 9.52 (s, 1 H, OH) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 20.3 (CH_3), 32.6 (CH_2), 44.8 ($CHCH_2$), 51.7, 55.1 (OCH_3), 108.7, 127.5, 128.1, 136.6, 141.9, 142.1, 142.3, 158.2, 159.2 ($C_{Ph,Ar}$), 111.2, 112.2, 116.8, 126.7, 128.5, 128.6, 130.5 ($CH_{Ph,Ar}$), 172.1 ($COOCH_3$) ppm. IR (ATR): $\tilde{\nu}$ = 2947 (w), 2836 (w), 1661 (m), 1604 (m), 1573 (m), 1494 (m), 1434 (m), 1300 (m), 1228 (s), 1034 (m) cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 374 (36) $[M]^+$, 342 (100), 314 (16), 44 (36). HRMS (EI): calcd. for $C_{24}H_{22}O_4$ $[M]^+$ 374.15149; found 374.15126. $C_{24}H_{22}O_4$ (374.15): calcd. C 76.99, H 5.92; found C 76.78, H 5.85.

Methyl 3-Hydroxy-1-methyl-9-phenylphenanthrene-4-carboxylate (6): To a 1,4-dioxane solution (7 mL per 1 mmol **5a**) of **5a** (1.0 equiv.) was added DDQ (2.0 equiv.), and the solution was stirred for 48 h at 101 °C. To the mixture was added diethyl ether (50 mL), and the mixture was filtered. The solvent of the filtrate was removed in vacuo. The residue was purified by chromatography (silica gel, heptanes/EtOAc). Starting with **5a** (0.254 g, 0.74 mmol) and DDQ (0.335 g, 1.48 mmol), **6** was isolated by chromatography (heptane/EtOAc, 30:1) as a yellow solid (0.139 g, 55%). M.p. 55–57 °C. R_f = 0.59 (heptane/EtOAc, 1:1). ^1H NMR (300 MHz, $CDCl_3$): δ = 2.70 (d, ^4J = 0.8 Hz, 3 H, CH_3), 3.84 (s, 3 H, OCH_3), 7.15 (d, ^4J = 0.8 Hz, 1 H, Ar), 7.42–7.61 (m, 8 H, Ph/Ar), 7.85–7.93 (m, 1 H, Ph/Ar), 7.95–8.03 (m, 1 H, Ph/Ar), 9.87 (s, 1 H, OH) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 20.2 (CH_3), 51.3 (OCH_3), 106.5, 125.7, 129.5, 130.2, 132.0, 137.2, 140.7, 142.5, 159.2 ($C_{Ph,Ar}$), 119.1, 122.5, 124.3, 126.2, 126.7, 127.4, 128.4, 129.2, 130.1 ($CH_{Ph,Ar}$), 172.5 ($COOCH_3$) ppm. IR (ATR): $\tilde{\nu}$ = 2954 (w), 2916 (w), 1659 (m), 1574 (m), 1429 (m), 1333 (m), 1220 (s), 1072 (m), 1009 (m), 976 (m) cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 342 (15) $[M]^+$, 310 (100), 284 (30), 252 (36), 239 (14). HRMS (EI): calcd. for $C_{23}H_{18}O_3$ $[M]^+$ 342.12556; found 342.12505.

Methyl 1-Methyl-9-phenyl-3-trifluoromethansulfonyloxy-9,10-dihydrophenanthrene-4-carboxylate (7): To a dichloromethane solution (10 mL per 1 mmol of **5a**) of **5a** (1.0 equiv.) was added pyridine (2.0 equiv.) at –78 °C and Tf_2O (1.2 equiv.). The temperature of the solution was warmed to 0 °C over 4 h with stirring. The mixture was purified by chromatography (dichloromethane) without aqueous workup. Starting with **5a** (0.300 g, 0.87 mmol), Tf_2O (0.17 mL, 1.05 mmol), and pyridine (0.14 mL, 1.74 mmol), **7** was isolated by chromatography (CH_2Cl_2) as a colorless solid (0.409 g, 99%). M.p. 238–240 °C. R_f = 0.95 (CH_2Cl_2). ^1H NMR (300 MHz, $CDCl_3$): δ = 2.33 (s, 3 H, CH_3), 2.96–3.15 (m, 2 H, CH_2CH), 3.86 (s, 3 H, OCH_3), 4.08–4.19 (m, 1 H, CH_2CH), 6.85–6.95 (m, 1 H, Ph/Ar), 7.06 (s, 1 H, Ar), 7.15–7.39 (m, 7 H, Ph/Ar), 7.41–7.50 (m, 1 H, Ph/Ar) ppm. ^{13}C NMR (75.5 MHz, CDCl$_3$): δ = 20.2 (CH$_3$), 33.1 (CH$_2$), 44.1 (*C*HCH$_2$), 52.7 (OCH$_3$), 118.5 (^1J = 320.1 Hz, CF$_3$), 121.5, 126.6, 126.8, 126.9, 127.5, 128.5, 128.7, 128.8 (CH$_{\text{Ph,Ar}}$), 122.4, 132.6, 135.7, 137.0, 139.4, 141.0, 141.7, 145.3 (C$_{\text{Ph,Ar}}$), 166.8 (*C*OOCH$_3$) ppm. ^{19}F NMR (282 MHz, CDCl$_3$): δ = –73.8 (CF$_3$) ppm. IR (ATR): $\tilde{\nu}$ = 1730 (s), 1603 (w), 1658 (s), 1421 (s), 1277 (m), 1203 (s), 1137 (s), 1025 (m), 973 (m), 903 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 476 (100) [M]$^+$, 445 (12), 311 (92), 283 (74), 239 (21). HRMS (EI): calcd. for $C_{24}H_{19}F_3SO_5$ [M]$^+$ 476.08978; found 476.08998.

1-Methyl-3,9-diphenyl-9,10-dihydrophenanthrene-4-carboxylate (8): To a 1,4-dioxane solution (2.5 mL/mmol **7**) of **7** (1.0 equiv.) was added phenylboronic acid (1.3 equiv.), K$_3$PO$_4$ (1.6 equiv.), and the catalyst (3 mol-%). The mixture was heated for 21 h at 101 °C. The mixture was allowed to cool to 20 °C and an aqueous solution of NH$_4$Cl (20 mL) was added. The organic and the aqueous layer were separated, and the latter was extracted with diethyl ether (3 × 20 mL). The combined organic layer was dried (Na$_2$SO$_4$), filtered, and concentrated in vacuo. Starting with **7** (0.190 g, 0.40 mmol), phenylboronic acid (0.063 g, 0.52 mmol), K$_3$PO$_4$ (0.135 g, 0.64 mmol), and Pd(PPh$_3$)$_4$ (0.014 mL, 0.01 mmol), **8** was isolated by chromatography (heptane/EtOAc, 100:1) as a colorless solid (0.150 g, 96%). M.p. 83–84 °C. R_f = 0.74 (heptane/EtOAc, 1:1). ^{1}H NMR (300 MHz, CDCl$_3$): δ = 2.34 (s, 3 H, CH$_3$), 2.97–3.20 (m, 2 H, C*H$_2$*CH), 3.55 (s, 3 H, OCH$_3$), 4.12–4.20 (m, 1 H, CH$_2$C*H*), 6.81–6.89 (m, 1 H, Ph/Ar), 7.09–7.45 (m, 13 H, Ph/Ar), 7.55 (m, 1 H, Ph/Ar) ppm. ^{13}C NMR (62.9 MHz, CDCl$_3$): δ = 20.0 (CH$_3$), 33.3, (CH$_2$), 44.6 (*C*HCH$_2$), 51.9 (OCH$_3$), 126.4, 126.5, 126.7, 127.1, 127.2, 127.7, 128.1, 128.3, 128.6, 128.7, 131.0 (CH$_{\text{Ph,Ar}}$), 128.5, 132.9, 133.9, 135.9, 134.4, 139.1, 140.9, 141.4, 142.5 (C$_{\text{Ph,Ar}}$), 171.2 (*C*OOCH$_3$) ppm. IR (ATR): $\tilde{\nu}$ = 3026 (w), 2945 (w), 1725 (s), 1598 (m), 1494 (m), 1447 (m), 1267 (m), 1238 (m), 1195 (m), 1129 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 404 (100) [M]$^+$, 373 (23), 345 (13), 295 (10), 252 (20). HRMS (EI): calcd. for $C_{29}H_{24}O_2$ [M]$^+$ 404.17745; found 404.17708.

Methyl 5-(4-Bromophenyl)-5,7a,8,9,10,11a-hexahydro-6*H*-11-oxabenzo[*a*]anthracene-12-carboxylate (9): To a solution of **5k** (1.0 equiv.) in DMF (20 mL per 1 mmol of **5k**) was added TBAI (2.2 equiv.) under an argon atmosphere. The mixture was cooled to –78 °C and NaH (60% dispersion in mineral oil, 1.5 equiv.) was added at 0 °C. After stirring for 20 h at 20 °C, ethyl acetate (5 mL) and ice-cold water (5 mL) were added, and the mixture was subsequently neutralized by addition of hydrochloric acid (10%). The mixture was extracted with EtOAc (3 × 20 mL). The combined organic layer was dried (Na$_2$SO$_4$) and filtered, and the filtrate was concentrated in vacuo. The residue was purified by chromatography. Starting with **5k** (0.050 g, 0.10 mmol), sodium hydride (0.006 g, 0.15 mmol), and TBAI (0.081 g, 0.22 mmol), **9** was obtained as a colorless solid (0.025 g, 54%). M.p. 88–90 °C. R_f = 0.74 (heptane/EtOAc, 1:1). ^{1}H NMR (300 MHz, CDCl$_3$): δ = 2.002.10 (m, 2 H, CH$_2$), 2.12 (s, 3 H, CH$_3$), 2.68 (t, ^3J = 6.6 Hz, 2 H, CH$_2$), 2.88–3.08 (m, 2 H, CH$_2$), 3.79 (s, 3 H, OCH$_3$), 4.00–4.08 (m, 1 H, CH), 4.10–4.23 (m, 2 H, CH$_2$), 6.83–6.90 (m, 1 H, Ar), 7.02–7.10 (m, ^3J = 8.4 Hz, 2 H, Ar), 7.12–7.27 (m, 2 H, Ar), 7.37–7.44 (m, ^3J = 8.4 Hz, 2 H, Ar), 7.52–7.58 (m, 1 H, Ar) ppm. ^{13}C NMR (75.5 MHz, CDCl$_3$): δ = 15.1 (CH$_3$), 22.3, 23.4, 33.3, 66.1 (CH$_2$), 44.4 (*C*HCH$_2$), 52.4 (OCH$_3$), 118.0, 120.3, 121.2, 127.2, 131.2, 134.2, 136.1, 140.2, 141.9, 151.3 (C$_{\text{Ar}}$), 126.1, 126.9, 127.1, 127.6, 130.3, 131.5 (CH$_{\text{Ar}}$), 170.1 (*C*OOCH$_3$) ppm. IR (ATR): $\tilde{\nu}$ = 2946 (w), 2874 (w), 1727 (s), 1562 (w), 1485 (m), 1408 (m), 1282 (s), 1203 (s), 1068 (s), 1009 (s) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 464 (97) [M$^+$, ^{81}Br], 462 (100) [M$^+$, ^{79}Br], 431 (16), 403 (42), 252 (9). HRMS (EI): calcd. for $C_{23}H_{19}BrO_3$ [M$^+$, ^{81}Br] 464.08046; found 464.08104.

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[27] CCDC-767218 (for **5a**) and -767219 (for **6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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