Oxidative β-Cleavage of Fused Cyclobutanols Leading to Hydrofuran-Fused Polycyclic Aromatic Compounds

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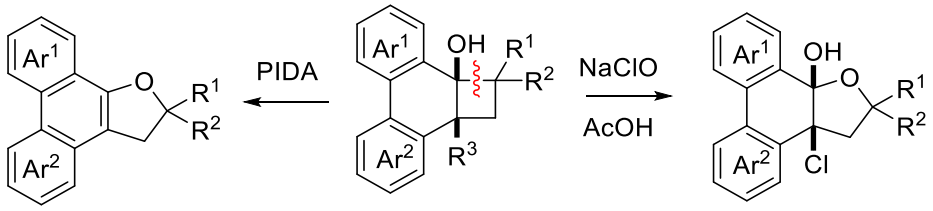
Graphic Abstract



Abstract

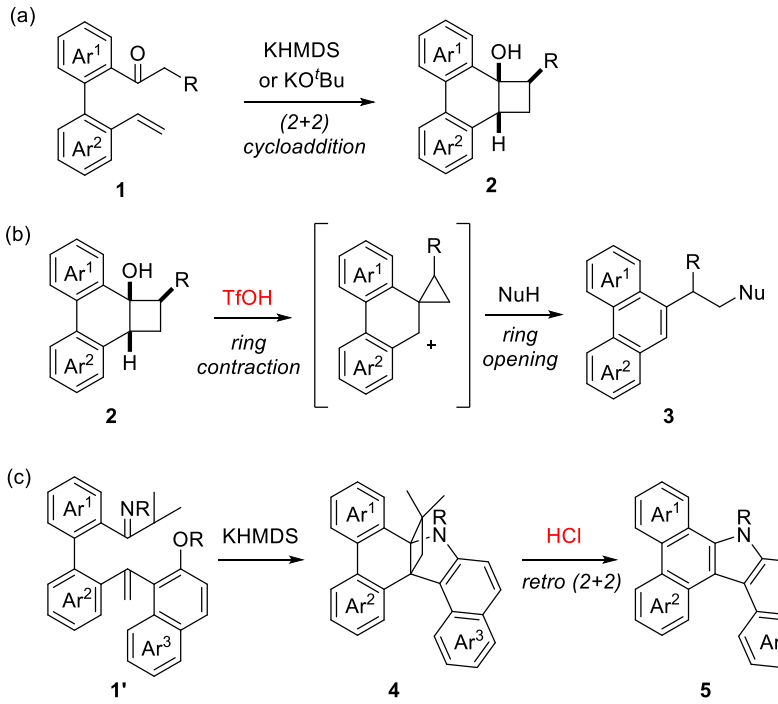
Treatment of aryl-fused bicyclo[4.2.0]octanols with an oxidant such as phenyliodine diacetate (PIDA) or hypochlorous acid gave dihydrofuran-containing polycyclic aromatic compounds by selective β-cleavage of the cyclobutanol moiety. Mechanistic studies suggest that the oxygen atom of the hydrofuran ring is incorporated from the hydroxy group of the substrate via intramolecular addition. The oxidative transformation should serve as a new method to prepare functionalized polycyclic aromatic compounds.

Introduction

Polycyclic aromatic hydrocarbons (PAHs) exhibit unique optical and electronic characteristics. PAHs have been applied to electronic devices such as organic light-emitting diodes (OLEDs), organic photovoltaics (OPVs), and organic field-effect transistors (OFETs).[1] PAHs are toxic compounds that show carcinogenic and mutagenic effects.[2] On the other hand, they have potential as medicinal compounds displaying antitumor activity.[3] The size and geometry of the aromatic skeletons and incorporation of heteroatoms into the π-system affect the properties of PAHs. Because introducing functional groups or substituents at peripheral positions can control the properties, a variety of synthetic methods have been reported to prepare functionalized/substituted PAHs.[4]

We previously reported an intramolecular (2 + 2) cycloaddition of 2-acyl-2'-alkenyl-1,1'-biaryls **1** to furnish diareno-fused bicyclo[4.2.0]octanols **2**. This reaction is promoted by a potassium base such as KO^{t}Bu and KHMDS (Scheme 1a).[5] We also demonstrated that an acid-treatment of **2** provides substituted polyaromatic compounds **3** by a domino ring contraction–opening reaction (Scheme 1b).[5,6] During our extensive studies, we found that an acid-promoted retro (2 + 2) cycloaddition of azapropellanes **4** furnishes π-extended carbazoles **5** (Scheme 1c).[7] The promotion of these reactions should be driven by alleviating the strain of the cyclobutane rings.[8] Oxidative carbon-carbon bond cleaving reactions are valuable synthetic tools, which yield structurally diverse organic molecules. In particular, cyclobutanols are representative substrates for bond cleaving reactions at the β-bond of the hydroxy group. The selectivity of the breaking

β-bond is actively researched.[9,10] However, most of studies have been done on the oxidative β-cleavage of monocyclic cyclobutanols. The examples for fused cyclobutanols are limited.[10b,d,f,h] We envisage that an oxidative β-cleavage reaction of diareno-fused bicyclo[4.2.0]octanols **2** gives substituted polyaromatic compounds **A** or cyclic biaryl compounds **B**, depending on the breaking C–C bonds (Figure 1). Herein, we describe the synthesis of dihydrofuran-fused PAHs by oxidation of **2** with an unusual regioselective bond cleavage and their further functionalization.



Scheme 1. Previous works: (a) Potassium base promoted intramolecular (2 + 2) cycloaddition, (b) domino reaction of cyclobutanols **2** giving substituted PAHs **3**, (c) retro (2 + 2) cycloaddition of azapropellanes **4** giving tribenzocarbazoles **5**.

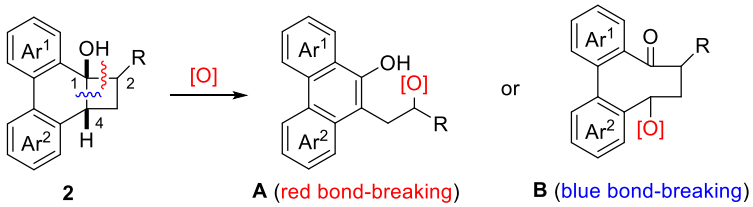


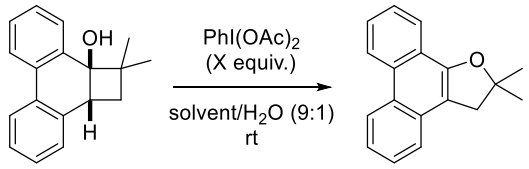
Figure 1. This work: Oxidative β-cleavage of diareno-bicylo[4.2.0]octanols **2**. **A**; A compound resulted in the C(1)–C(2) bond cleavage, **B**; A compound resulted in the C(1)–C(4) bond cleavage.

Results and Discussion

We initially examined the oxidation of **2a** with phenyliodine diacetate (PIDA), which has been used by Fujioka and Kita's group for β-cleavage of monocyclic cyclobutanols to give γ-hydroxyketones.[10d] It was proposed that the reaction proceeds through a cationic pathway. When using the standard reaction in the literature in 1,1,1,3,3,3-hexafluoropropane-2-ol (HFIP) and H_2O (9 : 1 v/v), **2a** was fully consumed within 1 h to afford **6a** in 15% yield (Table 1, entry 1). ^{1}H and ^{13}C $\{^{1}H\}$ NMR spectra confirmed that **6a** had a phenanthrol[9,10-*b*]furan skeleton. We attributed the low yield of **6a** to the overoxidation of the electron-rich phenanthrene ring. Adding PIDA portionwise into the solution of **2a** over 15 min increased the yield of **6a** to 40% (entry 2). With 1.1 equivalents of PIDA, the yield of **2a** was increased into 66% (entry 3).

To suppress the reactivity of PIDA, the solvent was screened. Substituting acidic HFIP as a co-solvent with CH_2Cl_2 or CH_3CN of H_2O dramatically improved the yield of **6a** to 82% and 97%, respectively (entries 4 and 5). A high yield of **6a** was also achieved with 1.1 equivalents of PIDA in CH_3CN–H_2O (entry 6). The transformation of **2a** into **6a** resulted in the cleavage of the C(1)–C(2) bond (type A in Figure 1) followed by C–O bond formation. However, 8-membered biphenyl product (type B**)**, which would be produced by C(1)–C(4) bond cleavage, was not observed. Oxidative β-cleavage reaction of fused cyclobutanols usually gave medium-sized ring products by breaking the transannular bond (type B).[10b,d,f,h] To the best of our knowledge, this is the first case of type A regioselectivity in the oxidative β-cleavage of fused cyclobutanols.

Table 1. Optimization of the reaction conditions of PIDA-oxidation of **2a**[a,b]



2a **6a**

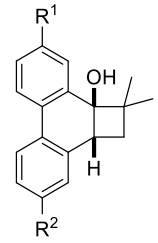
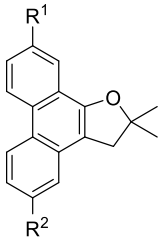
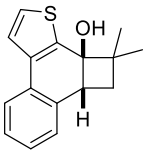
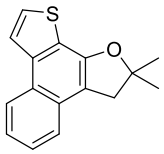
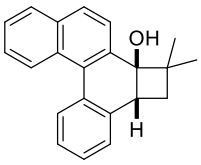
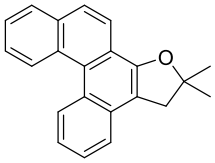
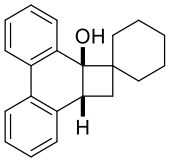
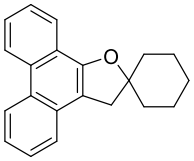
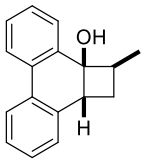
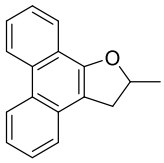
Entry	X	Solvent	Time (h)	%yield of **6a**
1	2.0	HFIP	1	15
2[c]	2.0	HFIP	0.2	40
3	1.1	HFIP	1	66
4	2.0	CH_2Cl_2	1	82
5	2.0	CH_3CN	1	97
6	1.1	CH_3CN	1	83

[a]All reactions were carried out using 0.10 mmol scale of **2a** (0.10 M). [b]Isolated yield.

[c]PIDA was added portionwise over 15 min.

With the optimized conditions (entry 5 in Table 1) in hand, we then examined the substrate scope of the diareno-fused bicyclo[4.2.0]octanols (Table 2). Compounds **2b-c** and **2d**, which have electron-withdrawing and -donating groups on the aromatic ring, respectively, afforded desired phenanthrene-fused dihydrofurans **6b–d** in moderate to high yields (entries 1–3). Substrates bearing heteroaromatic or π-extended rings were applicable to this transformation to furnish dihydrofurans **6e** and **6f** in high yields (entries 4 and 5). Spirocyclic product **6g** was also obtained in high yield from **2g** (entry 6). In contrast, monomethyl substrate **2h** gave a complex mixture of unidentified products (entry 7).

Table 2. Substrate scope of the reaction of **2** with PIDA[a,b]

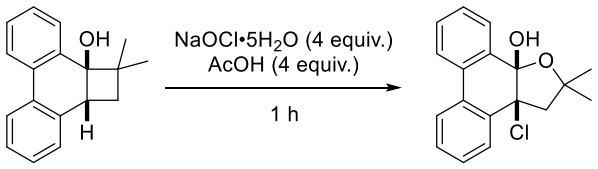
Entry	Substrates	Products		%yield of **6**
1	 **2b** (R^1 = Cl, R^2 = H)		**6b**	62
2	**2c** (R^1 = H, R^2 = Cl)		**6c**	81
3	**2d** (R^1 = MeO, R^2 = H)		**6d**	91
4	 **2e**		**6e**	99
5	 **2f**		**6f**	59
6	 **2g**		**6g**	97
7	 **2h**		**6h**	complex mixture

[a]All reactions were carried out using 0.10 mmol of **2** (0.10 M). PIDA (1.1 equiv.), CH_3CN/H_2O (9:1 v/v), rt. [b]Isolated yield.

Next, we investigated oxidative β-cleavage using hypochlorous acid (HClO), which Singleton's group employed in the radical mediated oxidative cleavage of monocyclic cyclobutanols.[10g] Treating **2a** with 4 equivalents of $NaOCl{\cdot}5H_2O$[11] and AcOH, which produced HClO *in situ* in CH_2Cl_2 at 0 °C, gave chlorinated compound **7a** in 41% yield (Table 3, entry 1). The structure of **7a** was determined by X-ray crystallographic analysis. Increasing the reaction temperature of the HClO-oxidation of **2a** improved the yield of **7a** up to 81% yield (entries 2 and 3). The reaction with a stoichiometric amount of the oxidant resulted in a poor yield of **7a** (entry 4). Solvent screening revealed that toluene and CH_3CN gave lower yields of **7a** (entries

5 and 6). **7a** should be formed by the β-cleavage of the cyclobutane ring of **2a** followed by further chlorinative dearomatization (oxidation)[12] of *in situ* generated **6a**. In fact, when oxidation of **6a** was conducted under the same conditions as entry 3, **7a** was obtained in 66% yield.

Table 3. Optimization of the reaction conditions to hemiacetal **7a**[a,b]



2a **7a**

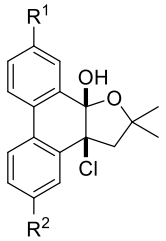
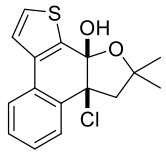
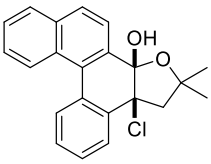
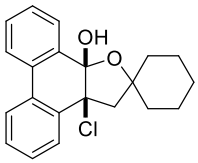
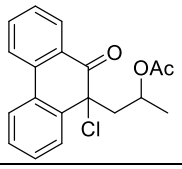
Entry	Solvent	Temp (°C)	% yield of **7a**
1	CH_2Cl_2	0	41
2	CH_2Cl_2	rt	66
3	CH_2Cl_2	40	81
4[c]	CH_2Cl_2	40	25
5	toluene	40	17
6	CH_3CN	40	43

[a]All reactions were carried out using 0.20 mmol of **2a** (0.10 M). [b]Isolated yield. [c]$NaOCl{\cdot}5H_2O$ (1.0 equiv.) and AcOH (1.0 equiv.) were used.

Under the optimal conditions (Table 3, entry 3), the HClO-oxidation of various *tert*-cyclobutanols **2** was conducted (Table 4). Compounds **2b**, **2c** and **2f** respectively afforded hemiacetals **7b**, **7c**, and **7f** in good yields (entries 1, 2, and 5). In contrast, the reactions of compounds **2d** and **2e**, which have an electron-rich aromatic ring, gave a complex mixture of unidentified products (entries 3 and 4). We speculated that the different reaction scope using HClO from using PIDA might be caused by the reaction mechanism difference in the bond-cleavage. Spirocyclic product **7g** was also obtained in high yield from **2g** (entry 6). The reaction of monomethyl substrate **2h** with HClO, followed by acetylation, afforded keto-acetate **8h** in

67 % yield as a 1 : 0.17 diastereomer mixture (entry 7). It was difficult to isolate **7h** itself, because **7h** exists as a mixture of the acetal form and a ring-opened keto-alcohol tautomer in a solution.

Table 4. Oxidation of various cyclobutanols **2** with $NaOCl{\cdot}5H_2O$/AcOH [a,b]

Entry	Substrates	Products		%yield of **7**
1	**2b** (R^1 = Cl, R^2 = H)		**7b**	63
2	**2c** (R^1 = H, R^2 = Cl)		**7c**	74
3	**2d** (R^1 = MeO, R^2 = H)		**7d**	0
4	**2e**		**7e**	0
5	**2f**		**7f**	64
6[c]	**2g**		**7g**	53
7[d]	**2h**		**8h**	67 (dr = 1 : 0.17)

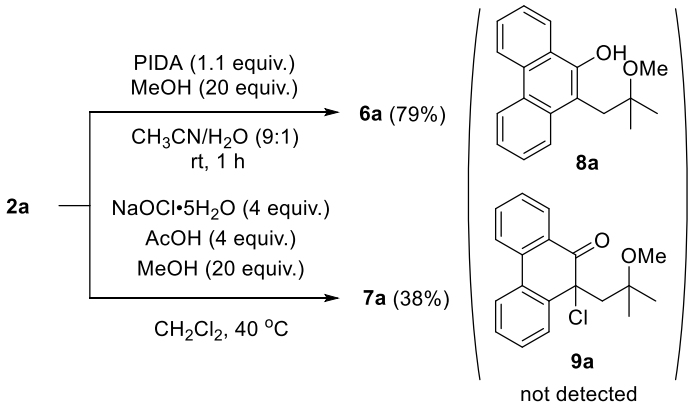
[a]All reactions were carried out on a 0.10 mmol scale (0.050 M). $NaOCl{\cdot}5H_2O$ (4.0 equiv.), AcOH (4.0 equiv.), CH_2Cl_2, 40 °C. [b]Isolated yield. [c]$NaOCl{\cdot}5H_2O$ (10 equiv.), AcOH (10 equiv.). [d]After the oxidation of **2h** with $NaOCl{\cdot}5H_2O$/AcOH (8.0 equiv.), acetylation of the crude mixture of **7h** with Ac_2O (3.0 equiv.) and DMAP (10 mol%) was carried out at ambient temperature for 16 h.

Previously, it was reported that oxidative β-cleavage of cyclobutanols usually gives acyclic γ-functionalized ketones, which are formed by the addition of an external nucleophile to the ring-opening intermediate.[9] In contrast, oxidation of **2** afforded **6** or **7** with a hydrofuran ring. We speculated that the

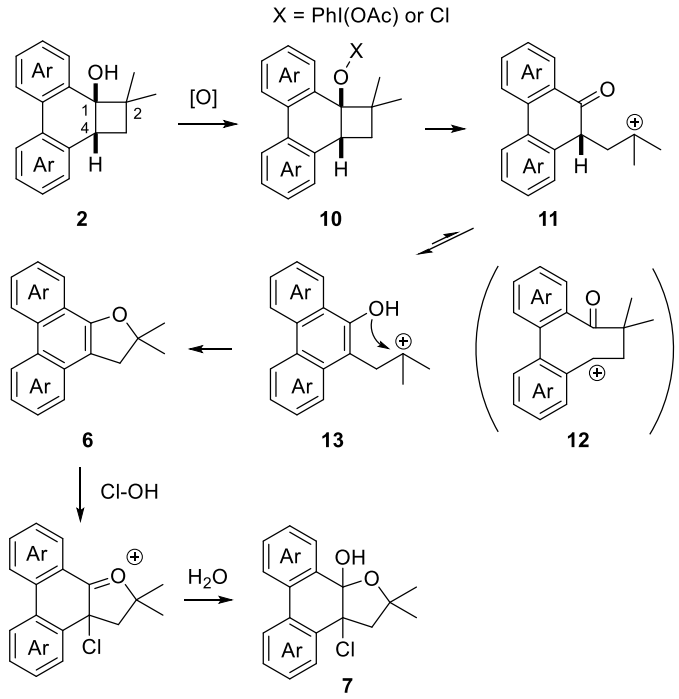
furan ring was formed by intramolecular addition of the oxygen atom derived from the hydroxy group of **2** prior to an intermolecular trap by an external reagent. This hypothesis was also supported by the following control experiments. In the presence of MeOH (20 equiv.) as an external nucleophile, neither compound **8a** nor **9a**, which could be formed by the electrophilic addition of MeOH, were detected in the oxidation of **2a** with PIDA or NaOCl·5H_2O/AcOH, respectively (Scheme 2).

Scheme 3 summarizes a plausible mechanism. First, the reaction of cyclobutanol **2** with PIDA or HClO, which is generated from NaOCl·5H_2O/AcOH, gives intermediate **10**. Then cleavage of the C(1)–C(2) bond selectively occurs to provide tertiary-cationic intermediate **11**. This cleavage is driven by the release of the cyclobutane ring strain. The formation of benzyl-cationic intermediate **12** by the cleavage of C(1)–C(4) bond is unfavorable due to the strain of the sp^2-rich 8-membered ring. Keto-type intermediate **11** readily tautomerizes into phenol intermediate **13** followed by an intramolecular attack on the tertiary cation to give dihydrofuran **6**. The higher nucleophilicity of the phenolic hydroxy group of **13** than that of the carbonyl oxygen of **11** is the rationale for the formation of the furan ring. In the reaction using HClO, phenanthrofuran **6** was further chlorinated to give **7**.

Scheme 2. Oxidative reactions of **2a** in the presence of MeOH.



Scheme 3. Plausible reaction mechanism.



Conclusions

We demonstrate that oxidative β-cleavage of dibenzo-fused bicyclo[4.2.0]octanols by PIDA gives dihydrophenanthro[9,10-*b*]furans in an unusual regioselective manner. We also show that oxidation of the alcohols by NaClO/AcOH affords higher oxidized products. This method provides various furan-fused polyaromatic compounds in good yields. These oxidative transformations should serve as a new way to prepare functionalized polycyclic aromatic compounds.

Experimental Section

General Information. For reactions that require heating, oil bath was used as a heat source. Column chromatography was performed on Kanto Kagaku Silica Gel 60 N (spherical, neutral) 100-210 μm. Reactions and chromatography fractions were analyzed by thin-layer chromatography (TLC) carried out on Wako Silicagel 70 F_{254} TLC Plate-Wako with visualization by ultraviolet (UV) irradiation at 254 nm, phosphomolybdic acid, anisaldehyde, ninhydrin, and/or potassium permanganate staining. NMR was

recorded on a JEOL JNM-LA (500 MHz for ^{1}H and 126 MHz for ^{13}C $\{^{1}H\}$) or a JEOL JNM ECZ600R (600 MHz for ^{1}H and 151 MHz for ^{13}C $\{^{1}H\}$) and measured in $CDCl_3$ unless otherwise mentioned. Chemical shifts and coupling constants are presented in ppm δ relative to tetramethylsilane (0.0 ppm) or C_6D_5H (7.16 ppm) and Hz, respectively. Chloroform-d_1 (δ 77.0 ppm) was used as an internal standard for ^{13}C $\{^{1}H\}$ NMR. Abbreviations are as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. IR spectra were recorded on a Shimadzu IRAffinity-1 and the wave numbers of maximum absorption peaks of them are presented in cm^{-1}. High-resolution mass spectra (HRMS) were recorded on a JEOL MS700 spectrometer (FAB) or a SHIMADZU LCMS-IT-TOF fitted with an ESI. Melting points were determined on YANACO micro melting point apparatus. X-ray single crystal diffraction analyses were performed on a Rigaku XtaLAB P200 apparatus. All reagents were purchased from chemical companies and used as received. Dehydrated solvents were purchased for the reactions and used without further desiccation unless otherwise mentioned.

Preparation of Substrates 2. Synthesis of substrates **2** was carried out in accordance with the reported procedure.[5] Compound **2h** was known.[5]

(2aR*,10bR*)-2,2-Dimethyl-1,10b-dihydrocyclobuta[l]phenanthren-2a(2H)-ol (2a). White solids, Mp. 122–124 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.46 (dd, *J* = 7.4, 1.7 Hz, 1H), 7.40 (ddd, *J* = 7.4, 7.4, 1.7 Hz, 1H), 7.36 (ddd, *J* = 7.4, 7.4, 1.5 Hz, 1H), 7.29 (ddd, *J* = 7.6, 7.6, 1.5 Hz, 1H), 7.24 (ddd, *J* = 7.4, 7.4, 1.1 Hz, 1H), 7.15 (dd, *J* = 7.2, 1.1 Hz, 1H), 3.72 (dd, *J* = 9.7, 9.7 Hz, 1H), 2.14 (brs, 1H), 2.05 (dd, *J* = 10.3, 9.7 Hz, 1H), 1.47 (s, 3H), 1.19 (dd, *J* = 10.3, 9.7 Hz, 1H), 0.84 (s, 3H); $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 136.5, 135.8, 132.3, 130.6, 130.1, 128.3, 128.2, 127.9, 127.6, 126.8, 123.4, 122.6, 74.1, 45.7, 43.8, 38.6, 26.8, 24.2; IR (neat) 3406, 2963, 752, cm^{-1}; HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{18}H_{18}ONa$ 273.1250; Found 273.1247.

(2aR*,10bR*)-4-Chloro-2,2-dimethyl-1,10b-dihydrocyclobuta[l]phenanthren-2a(2H)-ol (2b). Colorless oil, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.6 Hz, 1H), 7.84 (d, *J* = 7.2 Hz, 1H), 7.41 (d, *J* = 2.3 Hz, 1H), 7.32 (dd, *J* = 8.6, 2.3 Hz, 1H), 7.27 (td, *J* = 7.2, 1.4 Hz, 1H), 7.23 (td, *J* = 7.2, 1.4 Hz, 1H),

7.11 (dd, *J* = 7.2, 1.1 Hz, 1H), 3.65 (dd, *J* = 9.6, 9.5 Hz, 1H), 2.25 (brs, 1H), 2.05 (dd, *J* = 10.7, 9.6 Hz, 1H), 1.42 (s, 3H), 1.17 (dd, *J* = 10.7, 9.6 Hz, 1H), 0.83 (s, 3H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 137.5, 136.3, 133.1, 130.9, 129.8, 129.7, 128.33, 128.28, 128.2, 126.9, 124.1, 123.3, 74.0, 45.6, 43.7, 38.7, 26.6, 24.1; IR (neat) 3390, 2967, 1447, 764 cm^{-1}; HRMS (FAB) *m/z*: $[M + Na]^+$ Calcd for $C_{18}H_{17}ClONa$ 307.0866; Found 307.0871.

(2aR*,10bR*)-9-Chloro-2,2-dimethyl-1,10b-dihydrocyclobuta[l]phenanthren-2a(2H)-ol (2c). Colorless oil, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (dd, *J* = 7.5, 2.0 Hz, 1H), 7.85 (d, *J* = 8.6 Hz, 1H), 7.47-7.45 (m, 1H), 7.40 (td, *J* = 7.2, 2.0 Hz, 1H), 7.37 (td, *J* = 7.2, 1.7 Hz, 1H), 7.24 (dd, *J* = 8.6, 2.3 Hz, 1H), 7.14 (d, *J* = 2.3 Hz, 1H), 3.67 (dd, *J* = 10.0, 9.5 Hz, 1H), 2.14 (brs, 1H), 2.06 (dd, *J* = 10.0, 10.0 Hz, 1H), 1.46 (s, 3H), 1.18 (dd, *J* = 10.0, 9.5 Hz, 1H), 0.83 (s, 3H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 138.3, 135.5, 133.3, 131.2, 130.1, 129.2, 128.2, 127.9, 127.8, 126.8, 124.8, 122.4, 74.0, 45.8, 43.4, 38.4, 26.6, 24.1; IR (neat) 3395, 2963, 1443, 764 cm^{-1}; HRMS (FAB) *m/z*: $[M + Na]^+$ Calcd for $C_{18}H_{17}ClONa$ 307.0866; Found 307.0862.

(2aR*,10bR*)-4-Methoxy-2,2-dimethyl-1,10b-dihydrocyclobuta[l]phenanthren-2a(2H)-ol (2d). White solids, Mp. 93–95 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, *J* = 9.7 Hz, 1H), 7.80 (d, *J* = 7.5 Hz, 1H), 7.22 (td, *J* = 7.1, 1.4 Hz, 1H), 7.15 (td, *J* = 7.3, 1.1 Hz, 1H), 7.07 (dd, *J* = 7.5, 1.1 Hz, 1H), 6.92–6.89 (m, 2H), 3.80 (s, 3H), 3.62 (dd, *J* = 9.7, 9.7 Hz, 1H), 2.31 (brs, 1H), 2.01 (dd, *J* = 10.7, 9.7 Hz, 1H), 1.41 (s, 3H), 1.16 (t, *J* = 10.7, 9.7 Hz, 1H), 0.83 (s, 3H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 158.9, 137.4, 135.6, 130.6, 128.1, 126.9, 126.7, 125.3, 124.0, 122.7, 114.9, 113.8, 74.3, 55.3, 45.5, 43.7, 38.5, 26.9, 24.2; IR (neat) 3410, 2959, 1485, 768 cm^{-1}; HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{19}H_{20}O_2Na$ 303.1356; Found 303.1356.

(7bR*,9aR*)-9,9-Dimethyl-8,9-dihydrocyclobuta[3,4]naphtho[2,1-b]thiophen-9a(7bH)-ol (2e). Colorless solids, Mp. 75–77°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (d, *J* = 7.7 Hz, 1H), 7.47 (d, *J* = 5.3 Hz, 1H), 7.42 (d, *J* = 5.3 Hz, 1H), 7.26 (td, *J* = 7.5, 1.4 Hz, 1H), 7.19 (td, *J* = 7.5, 1.4 Hz, 1H), 7.15 (dd, *J* = 7.5, 1.7Hz, 1H), 3.79 (dd, *J* = 10.0, 10.0 Hz, 1H), 2.28 (brs, 1H), 2.03 (dd, *J* = 10.6, 10.0 Hz, 1H), 1.46 (s, 3H), 1.27 (dd, *J* = 10.6, 10.0 Hz, 1H), 1.07 (s, 3H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 138.2, 136.3, 135.3,

129.3, 127.6, 127.2, 126.81, 126.78, 123.5, 122.2, 74.1, 46.2, 45.5, 38.1, 26.6, 24.0; IR (neat) 3426, 2963, 748, 718 cm^{-1}; HRMS (ESI) *m/z*: $[M - H_2O + H]^+$ Calcd for $C_{16}H_{15}S$ 239.0889; Found 239.0890.

(2aR*,12bR*)-2,2-Dimethyl-1,12b-dihydrobenzo[c]cyclobuta[a]phenanthren-2a(2H)-ol (2f). White solids, Mp. 114–116 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 8.64–8.62 (m, 1H), 7.97 (d, *J* = 7.7 Hz, 1H), 7.85–7.83 (m, 1H), 7.72 (d, *J* = 8.6 Hz, 1H), 7.51–7.47 (m, 3H), 7.25–7.16 (m, 3H), 3.71 (dd, *J* = 10.2, 10.0 Hz, 1H), 2.44 (brs, 1H), 1.88 (dd, *J* = 10.5, 10.0 Hz, 1H), 1.46 (s, 3H), 1.23 (dd, *J* = 10.5, 10.2 Hz, 1H), 0.56 (s, 3H); ^{13}C {^1H} NMR (126 MHz, $CDCl_3$) δ 136.8, 134.1, 133.5, 131.8, 131.1, 129.8, 129.7, 128.8, 128.2, 127.4, 127.3, 127.11, 127.07, 126.3, 125.6, 125.4, 74.9, 46.5, 45.6, 36.3, 26.0, 24.2; IR (neat) 3387, 2967, 745 cm^{-1}; HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{22}H_{20}ONa$ 323.1406; Found 323.1408.

(2aR*,10bR*)-2,2a-Dihydro-10bH-spiro[cyclobuta[l]phenanthrene-1,1'-cyclohexan]-10b-ol (2g). White solids, Mp. 120–122 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 8.01 (dd, *J* = 7.7, 1.4, 1H), 7.93 (d, *J* = 7.7 Hz, 1H), 7.47 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.38 (td, *J* = 7.5, 1.7 Hz, 1H), 7.34 (td, *J* = 7.5, 1.4 Hz, 1H), 7.29 (td, *J* = 7.7, 1.4 Hz, 1H), 7.24 (td, *J* = 7.2, 1.4 Hz, 1H), 7.14 (dd, *J* = 7.5, 1.7 Hz, 1H), 3.66 (dd, *J* =10.3, 9.5 Hz, 1H), 2.31 (dd, *J* = 10.6, 10.3 Hz, 1H), 2.15–2.14 (m, 2H), 1.76–1.71 (m, 2H), 1.59 (m, 1H), 1.52–1.42 (m, 2H), 1.29 (td, *J* = 12.9, 3.4, 1H), 1.14 (qdd, *J* = 12.7, 3.4, 3.4 Hz, 1H), 1.14 (dd, *J* = 10.6, 9.5 Hz, 1H), 1.02 (qdd, *J* = 12.9, 2.9, 2.9 Hz, 1H), 0.93 (m, 1H); ^{13}C {^1H} NMR (126 MHz, $CDCl_3$) δ 136.8, 135.4, 132.3, 130.6, 130.1, 128.3, 128.1, 127.9, 127.4, 126.8, 123.4, 122.5, 74.9, 49.9, 43.3, 36.3, 35.5, 31.6, 26.1, 22.7, 22.2; IR (neat) 3368, 2924, 1447, 748 cm^{-1}; HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{21}H_{22}ONa$ 313.1563; Found 313.1565.

General Procedure for Oxidative β-Cleavage of 2a–h with PIDA. To a solution of cyclobutanol **2a–h** (0.10 mmol) in CH_3CN/H_2O (9:1, 1.0 mL) was added PIDA (0.11 mmol) at ambient temperature under Ar atmosphere, and the resulting solution was stirred for 1 h. After the completion of the reaction, the solvent was removed under reduced pressure. The residue was purified by column chromatography (hexanes/EtOAc) to give dihydrofuran **6a–h**.

2,2-Dimethyl-2,3-dihydrophenanthro[9,10-b]furan (6a). The reaction was conducted according to the

general procedure with cyclobutanol **2a** (25.0 mg, 0.10 mmol), and PIDA (64 mg, 0.20 mmol). Purification by silica gel column chromatography (hexanes/EtOAc: 10:1) afforded compound **6a** (24.5 mg, 97% yield) as white solids. Mp. 121–122 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.69 (d, *J* = 7.7 Hz, 1H), 8.65 (d, *J* = 8.3 Hz, 1H), 8.09 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.67–7.57 (m, 4H), 7.51–7.48 (m, 1H), 3.37 (s, 2H), 1.65 (s, 6H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 152.1, 131.2, 130.6, 126.9, 126.6, 126.34, 126.29, 123.23, 123.16, 122.98, 122.96, 122.5, 122.2, 113.3, 87.6, 42.6, 28.8; IR (neat) 2970, 1359, 752 cm^{-1}; HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{17}O$ 249.1274; Found 249.1264.

Oxidation of 2a with PIDA in a preparative scale: To a solution of cyclobutanol **2a** (501 mg, 2.0 mmol) in CH_3CN/H_2O (9:1, 20 mL) was added PIDA (709 mg, 2.2 mmol) at ambient temperature under Ar atmosphere, and the resulting solution was stirred for 1 h. After the completion of the reaction, the solvent was removed under reduced pressure. The residue was purified by column chromatography (hexanes/EtOAc: 10 : 1) to afford dihydrofuran **6a** (426 mg, 86% yield) as white solids.

10-Chloro-2,2-dimethyl-2,3-dihydrophenanthro[9,10-b]furan (6b). The reaction was conducted according to the general procedure with cyclobutanol **2b** (28.4 mg, 0.10 mmol), and PIDA (35 mg, 0.11 mmol). Purification by silica gel column chromatography (hexanes/EtOAc: 10:1) afforded compound **6b** (17.5 mg, 62% yield) as white solids. Mp. 88–90 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.58 (d, *J* = 8.9 Hz, 1H), 8.57 (d, *J* = 8.0 Hz, 1H), 8.06 (d, *J* = 2.3 Hz, 1H), 7.61–7.59 (m, 2H), 7.57 (dd, *J* = 8.9, 2.3 Hz, 1H), 7.49 (ddd, *J* = 8.5, 5.6, 2.9, 1H), 3.36 (s, 2H), 1.64 (s, 6H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 151.1, 132.4, 130.5, 129.5, 127.2, 126.8, 126.2, 124.7, 123.6, 123.4, 123.2, 123.1, 121.6, 114.7, 88.0, 42.6, 28.8; IR (neat) 2970, 752 cm^{-1}; HRMS (FAB) *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{16}ClO$ 283.0890; Found 283.0892.

5-Chloro-2,2-dimethyl-2,3-dihydrophenanthro[9,10-b]furan (6c). The reaction was conducted according to the general procedure with cyclobutanol **2c** (28.4 mg, 0.10 mmol), and PIDA (35 mg, 0.11 mmol). Purification by silica gel column chromatography (hexanes/EtOAc: 10:1) afforded compound **6c** (22.8 mg, 81% yield) as white solids. Mp. 99–101 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.59 (d, *J* = 7.6 Hz, 1H), 8.53 (d, *J* = 9.0 Hz, 1H), 8.08 (d, *J* = 7.6 Hz, 1H), 7.65 (ddd, *J* = 8.3, 6.9, 1.4 Hz, 1H), 7.62 (dd, *J* = 7.6, 6.9 Hz, 1H), 7.56 (d, *J* = 2.1 Hz, 1H), 7.41 (dd, *J* = 9.0, 2.1 Hz, 1H), 3.32 (s, 2H), 1.64 (s, 6H); ^{13}C

{^{1}H} NMR (151 MHz, $CDCl_3$) δ 153.1, 132.9, 131.8, 130.8, 126.8, 126.5, 124.9, 124.8, 123.4, 122.9, 122.4, 122.3, 122.1, 112.5, 88.0, 42.4, 28.7; IR (neat) 764 cm^{-1}; HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{16}ClO$ 283.0884; Found 283.0882.

10-Methoxy-2,2-dimethyl-2,3-dihydrophenanthro[9,10-b]furan (6d). The reaction was conducted according to the general procedure with cyclobutanol **2d** (28.0 mg, 0.10 mmol), and PIDA (35 mg, 0.11 mmol). Purification by silica gel column chromatography (hexanes/EtOAc: 10:1) afforded compound **6d** (25.3 mg, 91% yield) as white solids. Mp. 121–122 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.57 (d, *J* = 9.2 Hz, 1H), 8.55 (d, *J* = 8.3 Hz, 1H), 7.59 (dd, *J* = 7.9, 1.0 Hz, 1H), 7.52 (ddd, *J* = 8.0, 6.9, 1.2 Hz, 1H), 7.47 (ddd, *J* = 8.3, 6.9, 1.4 Hz, 1H), 7.42 (d, *J* = 2.9 Hz, 1H), 7.26 (dd, *J* = 9.2, 2.9 Hz, 1H), 4.00 (s, 3H), 3.37 (s, 2H), 1.65 (s, 6H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 158.3, 151.7, 129.4, 126.8, 125.9, 125.5, 124.7, 123.6, 123.3, 122.9, 122.7, 117.2, 113.8, 102.0, 87.5, 55.5, 42.7, 28.8; IR (neat) 2966, 752 cm^{-1}; HRMS (FAB) *m/z*: $[M + H]^+$ Calcd for $C_{19}H_{19}O_2$ 279.1385; Found 279.1380.

2,2-Dimethyl-2,3-dihydrothieno[2',3':3,4]naphtho[2,1-b]furan (6e). The reaction was conducted according to the general procedure with cyclobutanol **2e** (25.6 mg, 0.10 mmol), and PIDA (35 mg, 0.11 mmol). Purification by silica gel column chromatography (hexanes/EtOAc: 10:1) afforded compound **6e** (25.2 mg, 99% yield) as white solids. Mp. 127–128 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.32 (d, *J* = 8.3 Hz, 1H), 8.00 (d, *J* = 5.2 Hz, 1H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.55 (d, *J* = 5.4 Hz, 1H), 7.52 (dd, *J* = 6.9, 1.2 Hz, 1H), 7.45 (ddd, *J* = 8.3, 6.9, 1.2 Hz, 1H), 3.39 (s, 2H), 1.66 (s, 6H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 150.6, 138.1, 129.6, 125.8, 125.4, 125.2, 124.3, 123.6, 123.2, 122.9, 122.5, 113.5, 89.2, 42.3, 28.7; IR (neat) 2970, 756 cm^{-1}; HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{16}H_{15}OS$ 255.0838; Found 255.0839.

2,2-Dimethyl-1,2-dihydrobenzo[3,4]phenanthro[1,2-b]furan (6f). The reaction was conducted according to the general procedure with cyclobutanol **2f** (30.0 mg, 0.10 mmol), and PIDA (35 mg, 0.11 mmol). Purification by silica gel column chromatography (hexanes/EtOAc: 10:1) afforded compound **6f** (17.6 mg, 59% yield) as a yellowish oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.10 (dd, *J* = 8.6, 8.3 Hz, 2H), 8.09 (d, *J* = 8.6 Hz, 1H), 8.02 (d, *J* = 8.0 Hz, 1H), 7.92 (d, *J* = 8.6 Hz, 1H), 7.72(d, *J* = 7.7 Hz, 1H), 7.67 (t, *J* = 7.7 Hz, 1H), 7.63–7.59 (m, 2H), 7.53–7.50 (m, 1H), 3.44 (s, 2H), 1.67 (s, 6H); ^{13}C {^{1}H} NMR (126 MHz,

$CDCl_3$) δ 152.7, 137.5, 133.4, 131.4, 130.4, 128.8, 128.7, 128.3, 128.1, 127.3, 126.5, 126.3, 126.0, 125.7, 123.0, 122.7, 120.6, 120.2, 114.9, 87.9, 42.6, 28.8; IR (neat) 2970, 760 cm^{-1}; HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{22}H_{19}O$ 299.1430; Found 299.1429.

3'H-Spiro[cyclohexane-1,2'-phenanthro[9,10-b]furan] (6g). The reaction was conducted according to the general procedure with cyclobutanol **2g** (29.0 mg, 0.10 mmol), and PIDA (35 mg, 0.11 mmol). Purification by silica gel column chromatography (hexanes/EtOAc: 10:1) afforded compound **6g** (28.0 mg, 97% yield) as colorless solids. Mp. 128–129 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 8.69 (dd, *J* = 7.3, 2.1 Hz, 1H), 8.66 (d, *J* = 8.3 Hz, 1H), 8.16–8.13 (m, 1H), 7.66 (td, *J* = 6.9, 1.7 Hz, 1H), 7.65–7.62 (m, 2H), 7.60 (td, *J* = 6.9, 1.2 Hz, 1H), 7.50 (ddd, *J* = 9.2, 8.3, 1.6 Hz, 1H), 3.31 (s, 2H), 2.05–2.01 (m, 2H), 1.98–1.92 (m, 2H), 1.84–1.79 (m, 2H), 1.65–1.53 (m, 4H); ^{13}C {^1H} NMR (126 MHz, $CDCl_3$) δ 152.1, 131.2, 130.7, 126.9, 126.5, 126.3, 126.2, 123.2, 123.0, 122.93, 122.86, 122.6, 122.2, 113.0, 89.5, 40.9, 37.6, 25.3, 23.1; IR (neat) 2931, 752 cm^{-1}; HRMS (FAB) *m/z*: $[M + H]^+$ Calcd for $C_{21}H_{21}O$ 289.1592; Found 289.1598.

General Procedure for Oxidative β-Cleavage of 2a–g with $NaOCl·5H_2O$/AcOH. To a solution of cyclobutanol **2a–g** (0.10 mmol) and $NaOCl·5H_2O$ (0.40 mmol) in CH_2Cl_2 (2.0 mL) was added AcOH (0.40 mmol) at 40 °C under Ar atmosphere and the resulting solution was stirred for 1 h. After the completion of the reaction, the reaction mixture was quenched with sat. $Na_2S_2O_3$ aq. and extracted with EtOAc three times. The combined organic layers were washed with sat. $NaHCO_3$ aq. and brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified with silica gel column chromatography (hexanes/EtOAc) to give hemiacetal **7a–g**.

(3aS*,11bS*)-3a-chloro-2,2-dimethyl-3,3a-dihydrophenanthro[9,10-b]furan-11b(2H)-ol (7a). The reaction was conducted according to the general procedure with cyclobutanol **2a** (25.0 mg, 0.10 mmol), $NaOCl·5H_2O$ (132 mg, 0.40 mmol) and AcOH (46 μL, 0.40 mmol). Purification by silica gel column chromatography (hexanes/EtOAc: 10:1 to 3:1) afforded compound **7a** (24.4 mg, 81% yield) as white solids. Mp. 113–115 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 8.00 (dd, 1H, *J* = 7.7, 1.7 Hz), 7.92 (dd, 1H, *J* = 7.2, 2.0 Hz), 7.88 (dd, 1H, *J* = 7.7, 0.9 Hz), 7.74 (dd, 1H, *J* = 7.4, 1.7 Hz), 7.48 (td, 1H, *J* = 7.7, 1.4 Hz), 7.38–7.46 (m, 3H), 3.42 (brs, 1H), 2.99 (s, 2H), 1.57 (s, 3H), 0.76 (s, 3H); ^1H NMR (500 MHz,C_6D_6) δ 8.06-8.08 (m,

1H), 7.54–7.57 (m, 1H), 7.50–7.53 (m, 2H), 7.11–7.14 (m, 2H), 7.02–7.08 (m, 2H), 3.20 (s, 1H), 2.82 (d, J = 12.9 Hz, 1H), 2.64 (d, J = 12.9 Hz, 1H), 1.47 (s, 3H), 0.65 (s, 3H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 135.7, 133.7, 131.3, 130.7, 129.8, 129.1, 128.6, 128.5, 128.3, 127.0, 124.0, 123.8, 101.9, 80.7, 74.5, 51. 3, 31.2, 28.2 ; IR (neat) 3502, 2974, 756, 732 cm^{-1}; HRMS (ESI) *m/z*: [M + Na]$^+$ Calcd for $C_{18}H_{17}ClO_2Na$ 323.0809; Found 323.0808. X-ray crystallographic analysis (CCDC 2103959): Recrystallization from pentane/MeOH gave colorless platelets suitable for X-ray crystal structural analysis: orthorhombic $P2_12_12_1$; a = 10.3098(3), b = 11.4153(3), c = 12.3089.205(3); V = 1448.63(6), Z = 4, D_x = 1.379.

Oxidation of 2a* with NaOCl·5H$_2$O/AcOH *in a preparative scale: To a solution of cyclobutanol **2a** (501 mg, 2.0 mmol) and NaOCl·5H$_2$O (2.64 g, 16 mmol) in CH_2Cl_2 (40 mL) was added AcOH (1.0 mL, 16 mmol) at 40 °C under Ar atmosphere and the resulting solution was stirred for 1 h. After the completion of the reaction, the reaction mixture was quenched with sat. $Na_2S_2O_3$ aq. and extracted with EtOAc three times. The combined organic layers were washed with sat. $NaHCO_3$ aq. and brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified with silica gel column chromatography (hexanes/EtOAc: 10 : 1 to 3 : 1) to afford hemiacetal **7a** (434 mg, 72% yield) as white solids.

(3aS*,11bS*)-3a,10-Dichloro-2,2-dimethyl-3,3a-dihydrophenanthro[9,10-b]furan-11b(2H)-ol (7b). The reaction was conducted according to the general procedure with cyclobutanol **2b** (28.4 mg, 0.10 mmol), NaOCl·5H$_2$O (132 mg, 0.40 mmol) and AcOH (46 μL, 0.40 mmol). Purification by silica gel column chromatography (hexanes/EtOAc: 10:1 to 3:1) afforded compound **7b** (21.1 mg, 63% yield) as white solids. Mp. 114–116 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.01 (d, J = 2.1 Hz, 1H), 7.88–7.87 (m, 1H), 7.91 (d, J = 9.0 Hz, 1H), 7.73–7.72 (m, 1H), 7.46–7.42 (m, 3H), 3.43 (s, –OH), 3.03 (d, J = 13.1 Hz, 1H), 2.99 (d, J = 13.1 Hz, 1H), 1.56 (s, 3H), 0.78 (s, 3H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 135.8, 135.5, 134.6, 129.90, 129.86, 129.81, 129.3, 128.8, 128.4, 127.4, 125.3, 123.9, 101.4, 81.2, 74.5, 51.2, 31.2, 28.1; IR (neat): 3541, 2974, 1477, 764, 729 cm^{-1}; HRMS (ESI) *m/z*: [M + Na]$^+$ Calcd for $C_{18}H_{16}Cl_2O_2Na$ 357.0420; Found 357.0438.

(3aS*,11bS*)-3a,5-Dichloro-2,2-dimethyl-3,3a-dihydrophenanthro[9,10-b]furan-11b(2H)-ol (7c). The reaction was conducted according to the general procedure with cyclobutanol **2c** (28.4 mg, 0.10 mmol),

$NaOCl·5H_2O$ (132 mg, 0.40 mmol) and AcOH (46 μL, 0.40 mmol). Purification by silica gel column chromatography (hexanes/EtOAc: 10:1 to 3:1) afforded compound **7c** (24.8 mg, 74% yield) as white solids. Mp. 109–111 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.99 (dd, *J* = 7.4, 1.7 Hz, 1H), 7.86 (d, *J* = 8.6 Hz, 1H), 7.82 (dd, *J* = 7.7, 1.1 Hz, 1H), 7.72 (d, *J* = 2.3 Hz, 1H), 7.49 (td, *J* = 7.4, 1.7 Hz, 1H), 7.45 (td, *J* = 7.4, 1.3 Hz, 1H), 7.40 (dd, *J* = 8.6, 2.3 Hz, 1H), 3.42 (s, 1H), 2.97 (d, *J* = 13.2 Hz, 1H), 2.89 (d, *J* = 13.2 Hz, 1H), 1.57 (s, 3H), 0.84 (s, 3H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$): δ 137.8, 134.1, 133.6, 129.9, 129.4, 129.3, 129.0, 128.4, 127.2, 125.5, 123.7, 101.8, 80.6, 74.6, 51.5, 31.1, 28.4; IR (neat): 3510, 2974, 764 cm^{-1}; HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{18}H_{16}Cl_2O_2Na$ 357.0420; Found 357.0422.

(3aS*,11bS*)-13b-Chloro-2,2-dimethyl-1,13b-dihydrobenzo[3,4]phenanthro[1,2-b]furan-3a(2H)-ol (7f). The reaction was conducted according to the general procedure with cyclobutanol **2f** (30.0 mg, 0.10 mmol), $NaOCl·5H_2O$ (132 mg, 0.40 mmol) and AcOH (46 μL, 0.40 mmol). Purification by silica gel column chromatography (hexanes/EtOAc: 10:1 to 3:1) afforded compound **7f** (22.5 mg, 64% yield) as white solids. Mp. 114–116 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.55 (d, *J* = 8.3 Hz, 1H), 8.39 (d, *J* = 8.6 Hz, 1H), 8.17 (s, 1H), 7.98–7.95 (m, 1H), 7.89–7.85 (m, 1H), 7.68–7.64 (m, 1H), 7.61–7.57 (m, 1H), 7.48 (dd, *J* = 9.5, 1.7 Hz, 1H), 7.46 (t, *J* = 6.4 Hz, 1H), 7.44 (dd, *J* = 9.5, 1.7 Hz, 1H), 3.49 (brs, 1H), 2.94 (s, 2H), 1.59 (s, 3H), 0.68 (s, 3H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 136.0, 132.6, 132.2, 132.0, 130.5, 130.2, 129.8, 128.6, 128.2, 128.1, 128.0, 127.3, 127.0, 126.8, 125.0, 124.5, 102.3, 80.8, 75.2, 51.2, 31.1, 28.3; IR (neat)1365, 756 cm^{-1}; HRMS (ESI) *m/z*: $[M + K]^+$ Calcd for $C_{22}H_{19}ClO_2K$ 389.0705; Found 389.0713.

(3a'S*,11b'S*)-3a'-Chloro-3',3a'-dihydro-11b'H-spiro[cyclohexane-1,2'-phenanthro[9,10-b]furan-11b'-ol (7g). The reaction was conducted according to the general procedure with cyclobutanol **2g** (29.0 mg, mmol), $NaOCl·5H_2O$ (132 mg, 0.40 mmol) and AcOH (46 μL, 0.40 mmol). Purification by silica gel column chromatography (hexanes/EtOAc: 10:1 to 3:1) afforded compound **7g** (18.1 mg, 53% yield) as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.6 Hz, 1H), 7.91 (d, *J* = 7.6 Hz, 1H), 7.87 (d, *J* = 8.3 Hz, 1H), 7.75 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.48 (td, *J* = 7.6, 1.4 Hz, 1H), 7.43 (td, *J* = 8.3, 1.4 Hz, 1H), 7.41–7.38 (m, 2H), 3.48 (brs, 1H), 2.93 (d, *J* = 13.5 Hz, 1H), 2.85 (d, *J* = 13.5 Hz, 1H), 1.99–1.93 (m, 1H), 1.90–1.89 (m, 1H), 1.78–1.75 (m, 1H), 1.51–1.48 (m, 1H), 1.40–1.36 (m, 2H), 1.27–1.24 (m, 1H),

1.18–1.15 (m, 1H), 1.07–1.03 (m, 1H), 0.91–0.88 (m, 1H); ^{13}C {^{1}H} NMR (151 MHz, $CDCl_3$) δ 136.1, 134.1, 131.2, 130.5, 129.7, 129.1, 128.6, 128.4, 128.2, 127.1, 123.9, 123.6, 101.3, 82.6, 75.7, 49.5, 40.3, 36.7, 25.1, 23.6, 23.5; IR (neat); 3507, 2932, 756, 729 cm^{-1}; HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{21}H_{21}ClO_2Na$ 363.1122; Found 363.1126.

(S*)-1-{(S* and R*)-9-chloro-10-oxo-9,10-dihydrophenanthren-9-yl}propan-2-yl acetate (8h). To a solution of cyclobutanol **2h** (49.0 mg, 0.21 mmol) and $NaOCl{\cdot}5H_2O$ (273 mg, 1.66 mmol) in CH_2Cl_2 (2.0 mL) was added AcOH (95 μL, 1.66 mmol) at 40 °C under Ar atmosphere and the resulting solution was stirred for 30 min. After the completion of the reaction, the reaction mixture was quenched with sat. $Na_2S_2O_3$ aq. and extracted with EtOAc three times. The combined organic layers were washed with sat. $NaHCO_3$ aq. and brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. And then, the crude was dissolved in CH_2Cl_2 (2.0 mL) and acetic anhydride (59 μL, 0.62 mmol) and 4-dimethylaminopyridine (2.6 mg, 0.021 mmol) successively added to the mixture at ambient temperature and the resulting solution was stirred for 16 h. After the completion of the reaction, the reaction mixture was quenched with H_2O and brine, then extracted with EtOAc three times. The combined organic layers were washed with sat. $NaHCO_3$ aq. and brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (hexane/AcOEt = 10:1 to 3:1) to afford product **8h** (45.6 mg, 67% over 2 steps) as colorless solids in a 1 : 0.17 diastereomeric ratio. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.28 (dd, *J* = 8.0, 1.4 Hz, 0.17H), 8.13 (d, *J* = 7.7, 1H), 8.06 (d, *J* = 8.6 Hz, 0.17H), 8.04–8.02 (m, 0.17H), 8.00 (d, *J* = 8.0 Hz, 1H), 7.98–7.96 (m, 1H), 7.87 (ddd, *J* = 8.6, 8.0, 7.6 Hz, 1H), 7.75–7.69 (m, 1.34H), 7.49–7.43 (m, 3.51H), 4.95 (dqd, *J* = 8.9, 6.3, 3.2 Hz, 1H), 4.47 (dqd, *J* = 11.2, 5.7, 2.9 Hz, 0.17H), 3.32 (dd, *J* = 14.0, 11.2 Hz, 0.17H), 2.85 (dd, *J* = 14.8, 8.9 Hz, 1H), 2.78 (dd, *J* = 14.8, 3.2 Hz, 1H), 2.69 (dd, *J* = 14.0, 2.9 Hz, 0.17H), 1.61 (s, 3H), 1.17 (s, 0.51H), 1.13 (d, *J* = 5.7 Hz, 0.51H), 1.12 (d, *J* = 6.3 Hz, 3H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$, signals from the minor diastereomer are marked with an asterisk) δ 192.4, 191.9*, 169.9, 169.5*, 137.6, 137.0*, 136.1, 136.0*, 135.2*, 135.1, 129.7*, 129.5, 129.2, 129.14, 129.10, 129.0*, 128.9*, 128.8, 128.7, 128.3, 127.7*, 123.9, 123.7*, 123.3*, 123.2, 69.5, 67.9*, 67.5, 66.1*, 48.9*, 47.3, 20.9, 20.5,

20.2*, 19.9* (three peaks are unidentified.); IR (neat) 1736, 1690, 1450, 1238, 729 cm^{-1}; HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{19}H_{17}ClO_3Na$ 351.0758; Found 351.0769.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: xxxxxx. ^1H, ^{13}C $\{^1H\}$ NMR spectra of new compounds and X-ray crystallography (PDF). Crystallographic data for **7a** (CCDC 2103959) (CIF).

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Notes

The authors declare no competing financial interest.

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