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Palladium-catalyzed intramolecular allylation of aldehydes through in situ generation of allylsilanes

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Dedicated to Professor Hans-Günther (Hagga) Schmalz in celebration of his outstanding career and on the occasion of his retirement

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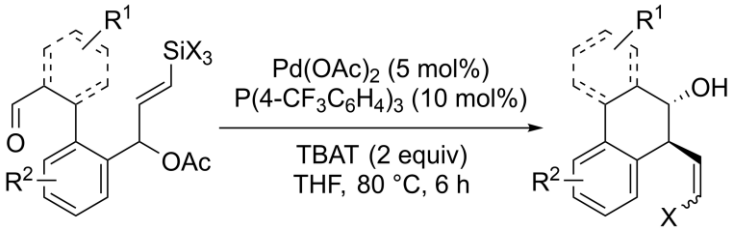
Abstract

9,10-Dihydrophenanthren-9-ol derivatives serve as key scaffolds in various natural products; however, their production has been relatively underexplored thus far. This study presents a novel general method for synthesizing dihydrophenanthrene-9-ol derivatives. The palladium-catalyzed reaction of silylated allyl acetates with tethered aldehydes in the presence of tetrabutylammonium difluorotriphenylsilicate (TBAT) induces a 1,2-shift of the substituent on silicon to yield α,γ-disubstituted allylsilanes in situ, which subsequently undergo intramolecular Hosomi–Sakurai type allylation of aldehydes to afford synthetically useful 9,10-dihydrophenanthren-9-ol derivatives. Overall, the introduction of a triarylsilyl group into the substrates proves crucial for enhancing the 1,2-shift of the substituent on silicon.

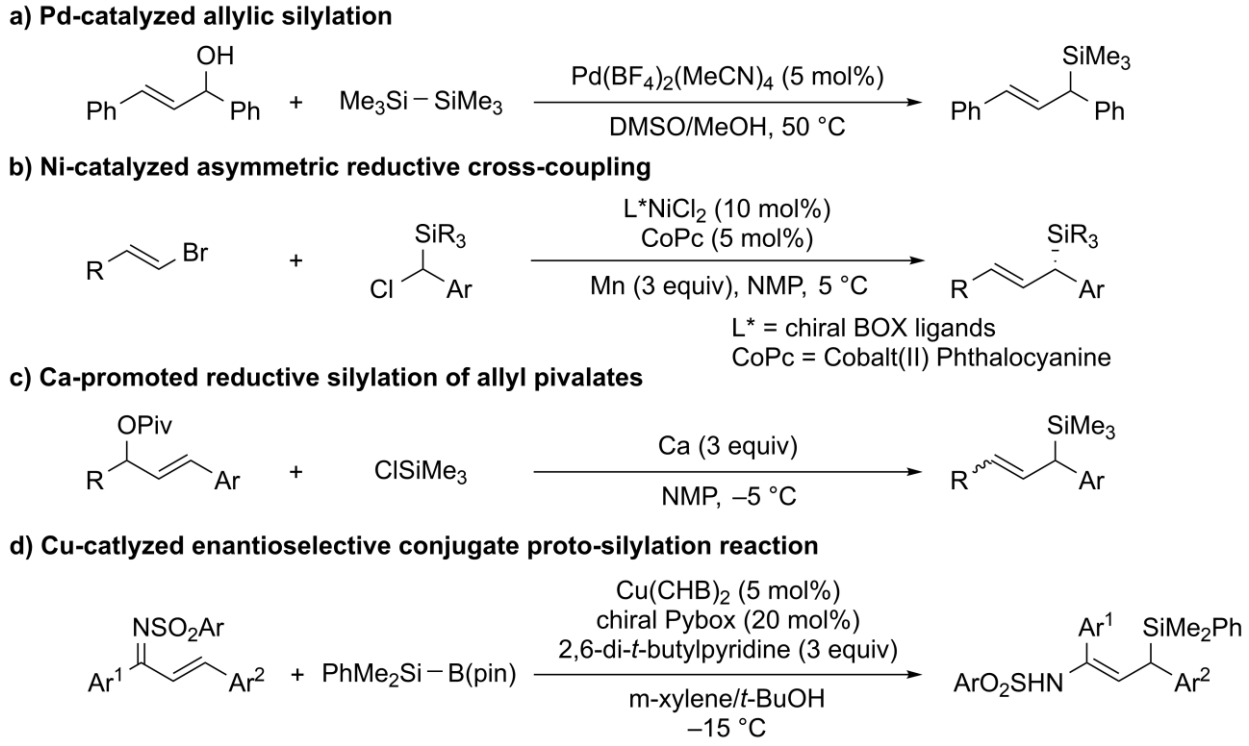


Keywords: Palladium, π-allylpalladium, allylsilanes, allylation, homoallyl alcohols, 1,2-shift

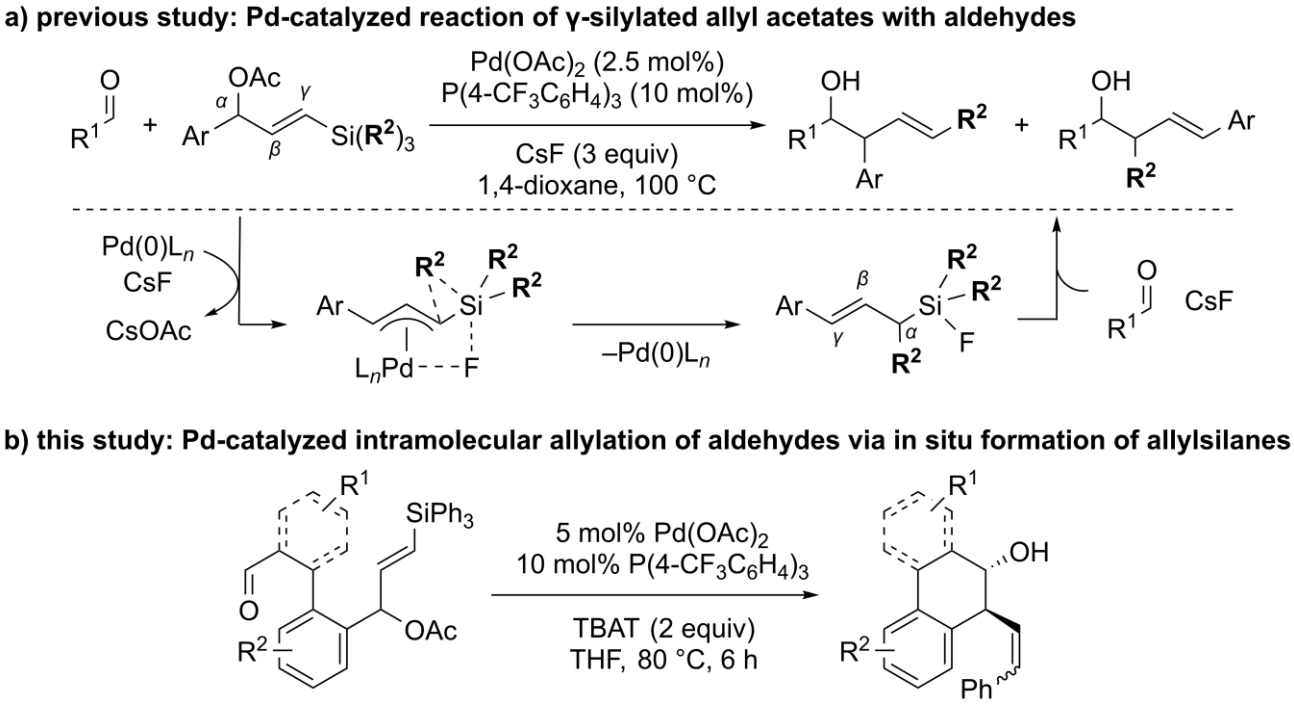
Introduction

Allylsilanes are versatile synthetic reagents and have been finding increasing application in organic synthesis such as natural product total synthesis and pharmaceuticals.[1-3] This has significantly facilitated the development of synthetic methods in this area. Specifically, Lewis acid- and Lewis base-mediated nucleophilic addition of allylsilanes to carbonyl electrophiles, known as the Hosomi–Sakurai reaction,[4-6] is a fundamental and one of the most well-studied carbon-carbon bond-forming reaction processes. In Lewis acid-mediated carbonyl allylation, allylsilanes preferentially react with the electrophile at the γ-position owing to the β-silicon effect. In contrast, fluoride-ion-mediated carbonyl allylation with allylsilanes proceeds non-regioselectively.[7] Moreover, enantioselective allylation reactions can be conducted using chiral Lewis bases[8,9] or acids.[10] Recent related studies have revealed that allylsilanes can also be employed in different reaction types, such as transition metal-catalyzed cross-coupling reactions[11,12], defluoroallylation of trifluoromethylarene via one-electron transfer pathways[13], photochemical transformations[14], photoredox/Cr-catalyzed Hosomi–Sakurai reaction[15], and α-C–H allylation of silyl ethers.[16] Thus, considerable efforts have been devoted to developing strategies for allylsilane synthesis.[17,18] However, only a few catalytic approaches for the synthesis of α,γ-diaryl-substituted allylsilanes have been reported. A representative method of α,γ-diaryl substituted allylsilanes is the Pd-catalyzed Kumada–Tamao–Corriu cross-coupling reaction of α-silylated benzylmagnesium bromide with β-bromostyrene derivatives.[19-21] In a subsequent study, Szabó et al. reported Pd-catalyzed allylic silylation of allylic alcohols with disilanes (Scheme 1a).[22] In this regard, Ni-[23] or Ni/Cu-[24] catalyzed silylation of aryl-substituted allylic alcohols has also been developed. However, these methods provided only a single synthetic example of α,γ-diphenylallylsilanes. More recently, Riesman et al. developed remarkable method for the enantioselective synthesis of α,γ-diaryl-substituted allylsilanes via Ni-catalyzed reductive cross-coupling (Scheme 1b).[25] The regioselective silylation of allyl pivalates through Ca-promoted reductive C(sp^3)–O bond cleavage has also been devised as an alternative synthesis approach (Scheme 1c).[26] Additionally, Cu-catalyzed conjugate proto-silylation of α,β-unsaturated ketimines yields α,γ-diaryl-substituted allylsilanes (Scheme 1d).[27] Another favorable approach for the synthesis of α,γ-diaryl-substituted allylsilane is the isomerization of the corresponding vinylsilanes, as the synthesis of vinylsilanes is more diverse than that of allylsilanes.[28-30] However, to the best of our knowledge, this strategy has not been fully investigated,[31] despite the existing well-developed catalytic approaches for the isomerization of allylsilanes to vinylsilanes.

Our recent studies on silylated *π*-allylpalladium species derived from readily available silylated allyl acetates have yielded advances in *π*-allylpalladium-mediated carbon-carbon bond-forming reactions, thereby expanding the conventional scope of *π*-allylpalladium chemistry.[32-35] In line with our continued interest in silylated *π*-allylpalladium-mediated transformation, we have discovered a novel method for in situ generation of α,γ-diaryl substituted allylsilanes **B** via silylated π-allylpalladium species, wherein a 1,2-shift of the substituent on silicon to the allylic carbon is induced in the hypervalent organosilicate species (Scheme 2a).[34,36] Although these α,γ-diaryl-substituted allylsilanes **B** cannot be isolatable, noteworthy feature of this reaction system is a one-pot Hosomi–Sakurai type reaction can be conducted in the presence of aldehydes. However, as the nucleophilic allylation of aldehydes occurs at both the α-and γ-positions of the in situ generated allylsilanes, the synthetic potential of this is limited by regioselectivity issues. To address this limitation, we herein report the intramolecular allylation of aldehydes, as part of which the carbonyl allylation reaction proceeds selectively at the γ-position of the in situ generated allylsilanes to yield synthetically useful 9,10-dihydrophenanthren-9-ol derivatives (Scheme 2b).



Scheme 1. Synthetic pathways for α,γ-diary substituted allylsilanes.



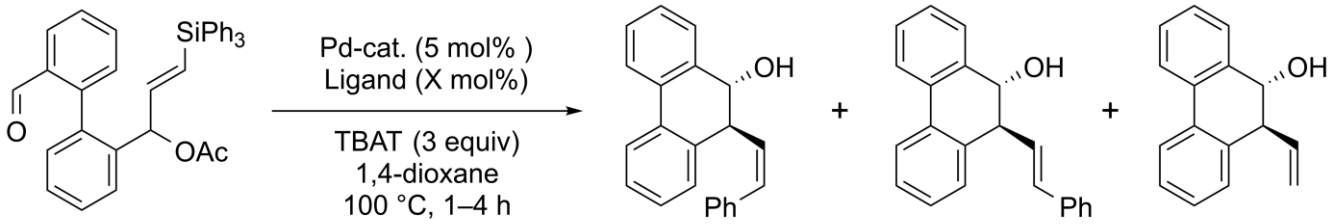
Scheme 2. Focuses of our previous and current studies.

Notably, dihydronaphthalene derivatives constitute a key class of natural products exhibiting a wide range of biological activities. However, only four representative methods for 9,10-dihydrophenanthren-9-ol derivatives synthesis have been reported thus far.[37-40] Therefore, the development novel strategies for synthesizing 9,10-dihydrophenanthren-9-ol derivatives remains of significant interest.

Results and Discussion

Initially, γ-triphenylsilyl-substituted allyl acetate–aldehyde **1a** tethered by biphenyl was employed as the model substrate to optimize the reaction conditions (Table 1). Pd-catalyzed intramolecular allylation was achieved using 5 mol % $Pd(OAc)_2$, 10 mol % Ph_3P, and tetrabutylammonium difluorotriphenylsilicate (TBAT)[41-44] in 1,4-dioxane at 100 °C for 1 h, yielding the desired products (*Z*)-**2a** (*anti*/*syn* = 3/1) and (*E*)-**2a** *(anti*/*syn* = >20/1) in 56% and 3% yields, respectively (entry 1). Trace amounts of the byproduct *anti*-**3a** were also obtained; however, the mechanism governing its formation is currently unclear. Notably, alkene isomerization of *anti*-(*Z*)-**2a** to *anti*-(*E*)-**2a** was not observed with increasing reaction time. Although both electron-rich and electron-deficient monophosphine ligands afforded the desired products in similar yields (entries 2 and 3),

Table 1. Optimization of the reaction conditions[a]



1a (*Z*)-**2a** (*E*)-**2a** *anti*-**3a**

Entry	Pd-cat.	Ligand (X mol %)	(*Z*)-**2a** (%, *anti*/*syn*)	(*E*)-**2a** (%, *anti*/*syn*)	*anti*-**3a** (%)
1	$Pd(OAc)_2$	Ph_3P (10)	56, 3:1	3, >20:1	trace
2	$Pd(OAc)_2$	$(4\text{-}MeOC_6H_4)_3P$ (10)	61, 3:1	5, >20:1	trace
3	$Pd(OAc)_2$	$(4\text{-}CF_3C_6H_4)_3P$ (10)	64, 3.8:1	6, >20:1	trace
4	$Pd(OAc)_2$	$(3,4,5\text{-}F_3C_6H_2)_3P$ (10)	42, 3.6:1	2, >20:1	trace
5	$Pd(OAc)_2$	BINAP (5)[h]	44, 3.3:1	17, >20:1	trace
6	$Pd(OAc)_2$	Xantphos (5)[i]	36, 3.2:1	14, >20:1	trace
7[b]	$Pd_2(dba)_3$	$(4\text{-}CF_3C_6H_4)_3P$ (10)	5, >20:1	0	0
8[c]	$[PdCl(allyl)]_2$	$(4\text{-}CF_3C_6H_4)_3P$ (10)	7, 7.6:1	28, >20:1	trace
9[d]	$Pd(OAc)_2$	$(4\text{-}CF_3C_6H_4)_3P$ (10)	63, 3.5:1	7, >20:1	trace
10[e]	$Pd(OAc)_2$	$(4\text{-}CF_3C_6H_4)_3P$ (10)	58, 3.5:1	5, >20:1	trace
11[f]	$Pd(OAc)_2$	$(4\text{-}CF_3C_6H_4)_3P$ (10)	0	0	0
12[d,g]	$Pd(OAc)_2$	$(4\text{-}CF_3C_6H_4)_3P$ (10)	69, 3:1	11, >20:1	trace

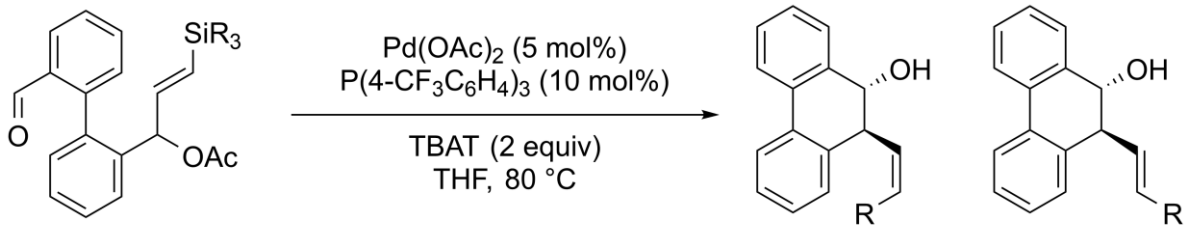
[a] Conditions: **1a** (0.3 mmol), Pd-cat. (5 mol %), ligand (X mol %) and TBAT (3 equiv) in anhydrous 1,4-dioxane (2 mL) at 100 °C in an oil-bath under Ar atmosphere. [b] $Pd_2(dba)_3$ (2.5 mol %) was used. [c] $[PdCl(allyl)]_2$ (2.5 mol %) was used. [d] TBAT (2 equiv) was used. [e] TBAT (1.5 equiv) was used. [f] CsF (3 equiv) was used instead of TBAT. [g] Reaction was performed in THF at 80 °C in an oil-bath. [h] BINAP = 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl. [i] Xantphos = 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene.

a more electron-deficient monophosphine ligand, such as $(3,4,5\text{-}F_3C_6H_2)_3P$, reduced the yield of **2a** (entry 4). Subsequently, the effect of the bisphosphine ligands on the palladium catalyst was evaluated. Ultimately, the reaction employing BINAP and Xantphos was not promoted when compared to that using monophosphine ligands (entries 5 and 6). Among the Pd sources tested, $Pd(OAc)_2$ afforded **2a** in highest yield (entries 3, 7, and 8). Although the quantity of TBAT could be reduced to 2 equiv without significant losses in catalytic activity,

further reduction to 1.5 equiv resulted in marginally reduced yields (entries 3, 9, and 10). Another fluoride source, such as CsF, was entirely ineffective (entry 11). Nevertheless, the best result was obtained when the $Pd(OAc)_2$/(*p*-CF_3-C_6H_4)$_3$P catalyst system was employed in THF at 80 °C in an oil-bath, affording (*Z*)-**2a** (*anti*/*syn* = 3/1) and (*E*)-**2a** (*anti*/*syn* = >20/1) in 69% and 11% yields, respectively (entry 12).

With the optimized reaction conditions in hand, we explored the reaction scope using various silyl groups (Table 2). The effects of substituent on the silyl groups were also investigated. The efficiency of this transformation was found to be highly dependent on the substituents on the silyl group. For example, the reaction of substrate **1b** with a tris(*p*-fluorophenyl)silyl group proceeded smoothly at 80 °C to give the corresponding products (*Z*)-**2b** (*anti*/*syn* = 4.5/1) and (*E*)-**2b** (*anti*/*syn* = >20/1) in 62% and 9% yields, respectively (entry 1). By contrast, in the case of using substrate **2c** bearing an electron-donating group on the silyl group, such as the tris(*p*-methoxyphenyl)silyl group, a longer reaction time was required to achieve complete conversion to **2c**, and a lower yield of **2c** was observed (entry 2). Substrate **2d**, bearing a 2-thienyl group, was also suitable this reaction, affording *anti*-(*Z*)-**2d** and *anti*-(*E*)-**2d** in 11% and 23% yields, respectively (entry 3). The use of a trimethylsilyl group resulted in no reaction (entry 4); this was in contrast to the use of aryl substituents on the silyl groups and the results of our previous study.[34] The formation of silicate intermediates in this reaction was enhanced when electron-withdrawing substituents were attached to silicon. Notably, the coupling reaction of **1b**–**e** with TBAT was not observed in all cases.[45,46]

Table 2. Reaction scope based on silyl groups[a]

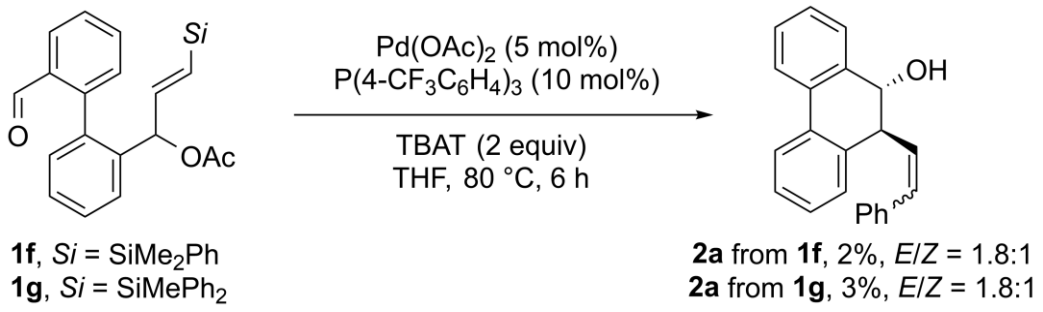


1 (*Z*)-**2** (*E*)-**2**

Entry	**1**	Time (h)	(*Z*)-**2** (%, *anti*/*syn*)	(*E*)-**2** (%, *anti*/*syn*)
1	**1b** (R = 4-FC_6H_4)	1	**2b**, 62, 4.5:1	**2b**, 9, >20:1
2	**1c** (R = 4-$MeOC_6H_4$)	2.5	**2c**, 37, 3.7:1	**2c**, 5, >20:1
3	**1d** (R = 2-thienyl)	21	**2d**, 11, >20:1	**2d**, 23, >20:1
4	**1e** (R = Me)	12	0	0

[a] Conditions: **1** (0.3 mmol), $Pd(OAc)_2$ (5 mol %), P(4-$CF_3C_6H_4$)$_3$ (10 mol %) and TBAT (2 equiv) in anhydrous THF (2 mL) at 80 °C in an oil bath under Ar atmosphere.

On the basis of this result (table 2, entry 4), the selective migration of substituents on the silyl group was investigated (Scheme 3). Although an exclusive preference for phenyl group migration over methyl group migration was observed in substrates **1f** and **1g** respectively bearing $SiMe_2Ph$ and $SiMePh_2$ groups, the desired product *anti*-**2a** was obtained in low yields. These experiments revealed that both the Lewis-acidic silyl group and the migratory ability of the substituents on the silicon atom were responsible for the success of this reaction.

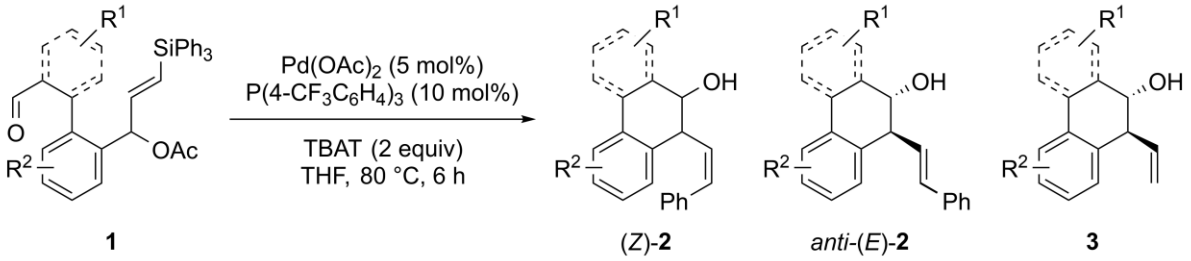


1f, *Si* = $SiMe_2Ph$
1g, *Si* = $SiMePh_2$

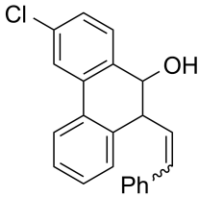
2a from **1f**, 2%, *E*/*Z* = 1.8:1
2a from **1g**, 3%, *E*/*Z* = 1.8:1

Scheme 3. Effects of varying allylsilane **1**.

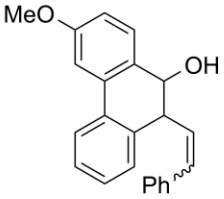
Table 3. Substrate scope[a]



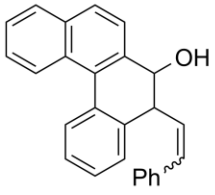
1 (*Z*)-**2** *anti*-(*E*)-**2** **3**



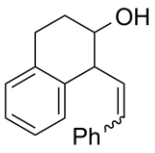
anti-(*Z*)-**2h**: 32%
syn-(*Z*)-**2h**: 13%
anti-(*E*)-**2h**: 4%
3h: 9%



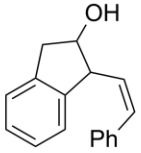
anti-(*Z*)-**2i**: 38%
syn-(*Z*)-**2i**: 15%
anti-(*E*)-**2i**: trace
3i: 0%



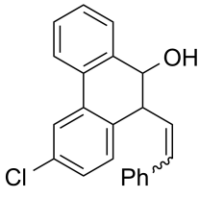
anti-(*Z*)-**2j**: 16%
syn-(*Z*)-**2j**: trace
anti-(*E*)-**2j**: 9%
3j: trace



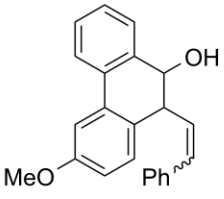
anti-(*Z*)-**2k**: 45%
syn-(*Z*)-**2k**: 0%
anti-(*E*)-**2k**: 5%
syn-(*E*)-**2k**: 1%
3k: 0%



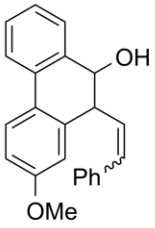
2l: 0%
3l: 0%



anti-(*Z*)-**2m**: 43%
syn-(*Z*)-**2m**: 11%
anti-(*E*)-**2m**: 3%
3m: 5%



anti-(*Z*)-**2n**: 33%
syn-(*Z*)-**2n**: 12%
anti-(*E*)-**2n**: trace
3n: 0%



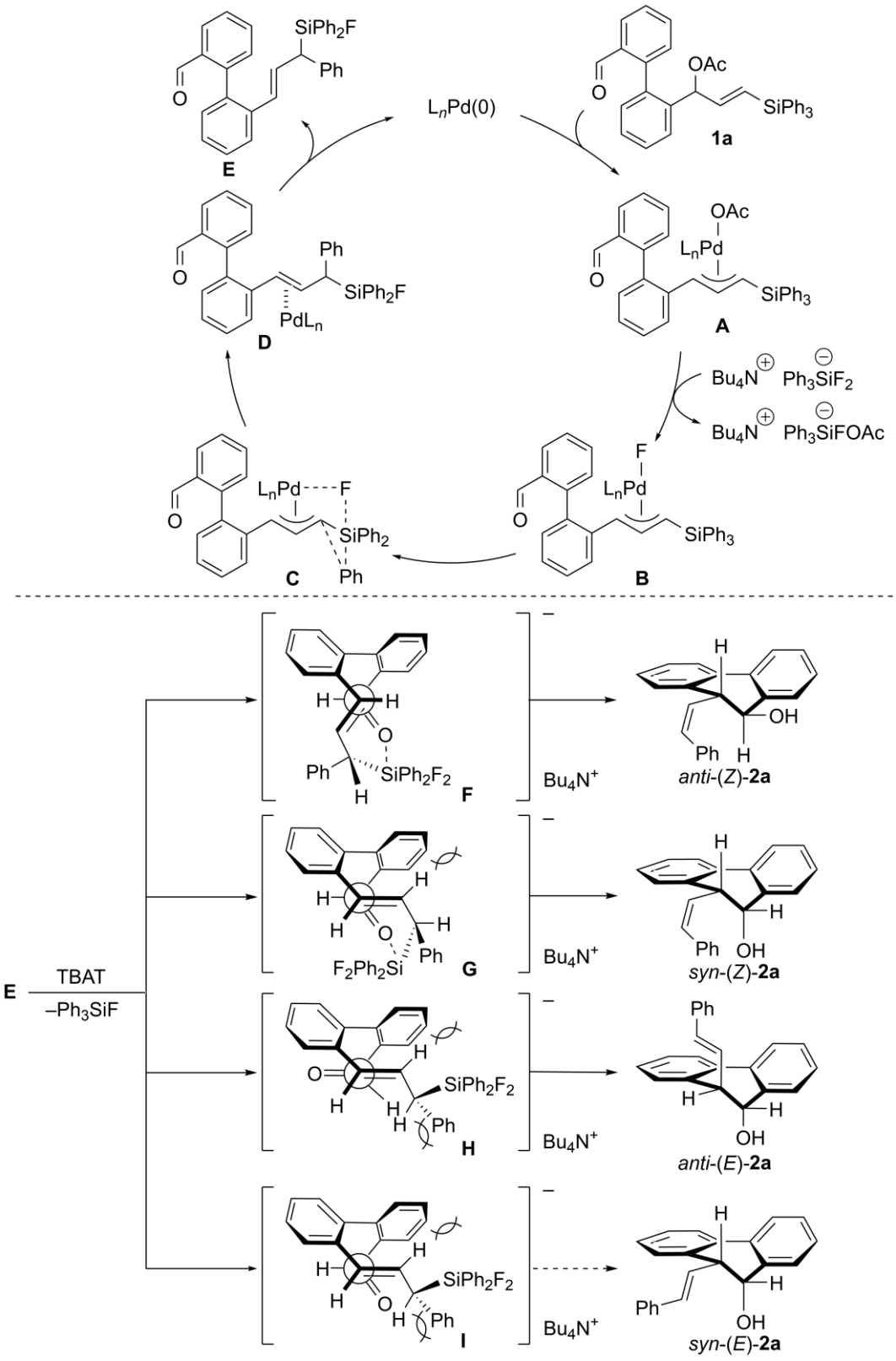
anti-(*Z*)-**2o**: 33%
syn-(*Z*)-**2o**: 12%
anti-(*E*)-**2o**: trace
3o: 0%

[a] Conditions: **1** (0.3 mmol), $Pd(OAc)_2$ (5 mol%), $P(4\text{-}CF_3C_6H_4)_3$ (10 mol%) and TBAT (2 equiv) in anhydrous THF (2 mL) at 80 °C in an oil-bath for 6 h under Ar atmosphere.

Next, the substrate generality of the intramolecular allylation reaction was explored (Table 3). First, various aldehydes were evaluated. 4-Chlorobenzaldehyde at the aryl linkage was observed to be compatible with this transformation, producing *anti*-(*Z*)-**2h**, *syn*-(*Z*)-**2h**, and *anti*-(*E*)-**2h** in 32%, 13%, and 4% isolated yields, respectively. Additionally, byproduct **3h** was obtained in 9% yield. The use of **1i** possessing a 4-methoxybenzaldehyde substructure on the aryl linkage yielded results similar to those in the case of **1h**, with *anti*-(*Z*)-**2i** and *syn*-(*Z*)-**2i** being produced in 38% and 15% yields, respectively. Notably, the reaction proceeded irrespective of the electronic properties of the aromatic aldehyde on the aryl linkages.

However, **1j**, bearing a naphthaldehyde, did not undergo this reaction and afforded the desired product **2j** in low yield as a mixture of diastereomers, presumably because of the steric hindrance of the naphthyl group. The reaction was tolerated by the aliphatic aldehyde to give *anti*-(*Z*)-**2k** and (*E*)-**2k** in 45% and 6% yields, respectively. On the other hand, this system could not be applied to five-membered carbocycles. Subsequently, the effects of substituents on the bottom aromatic ring were also evaluated. Both electron-withdrawing and electron-donating groups, such as chloro and methoxy groups, produced *anti*-(*E*)-**2m**–**o** as the major product in 33–43% yields and *syn*-(*Z*)- **2m**–**o** as a minor product in 11–12% yields.

Considering the results of our previous study,[34] we propose a tentative reaction mechanism using substrate **1a** as depicted in Scheme 4. π-Allylpalladium complex **A** is formed through the oxidative addition of **1a** to L_nPd(0). Ligand exchange of **A** with TBAT occurs to form π-allylPd(L_n)F complex **B**. Subsequently, the 1,2-shift of the phenyl group proceeds through **C**, producing allylsilane species **E** and L_nPd(0). To explain the observed *anti-Z*-selectivity of the main products, a hypervalent allylsilicate generated by **E** and TBAT is proposed, in which the Lewis acidity-enhanced silicon intramolecularly coordinates to the aldehyde to form a cyclic transition state **F**. On the other hand, transition state **G** increases steric congestion by a gauche interaction between the hydrogen atom and benzene ring of the biaryl group, which leads to generation of *syn*-(*Z*)-**2a** as a minor product. Additionally, in the case of the antiperiplanar arrangement **H**, the steric repulsion between the hydrogen atom and benzene ring of the biaryl group, as well as the steric repulsion between the hydrogen atom and phenyl group on the allylsilane, render the transition state **H** less favorable. Furthermore, because synclinal mode **I** suffers from two steric repulsions between the hydrogen atom and phenyl group, as well as between the carbonyl oxygen atom and phenyl group, the reaction may not proceed through synclinal mode **I**.



Scheme 4. Proposed reaction mechanism.

Conclusions

In conclusion, we have developed a novel Pd-mediated one-pot synthetic approach for 9,10-dihydrophenanthren-9-ol derivatives. The Pd-catalyzed reaction of properly designed γ-silylated allyl acetates bearing a formyl group in the presence of TBAT induces a 1,2-shift of the substituent on silicon atom to produce allylsilanes *in situ*, which then undergo intramolecular Hosomi–Sakurai type allylation of aldehydes to afford 9,10-dihydrophenanthren-9-ol derivatives. Further investigations to elucidate the reaction mechanism, including the stereoselectivity of this process, and to develop diastereoselective carbonyl allylations are currently underway.

Experimental Section

General. Unless otherwise noted, the reactions were carried out in flame-dried glassware under argon atmosphere. NMR spectra were recorded on Bruker AVANCE NEO 400 spectrometer. Chemical shifts (δ) are reported in ppm from the solvent resonance or tetramethylsilane (TMS) as the internal standard ($CDCl_3$: 7.26 ppm, TMS: 0.00 ppm). Peak multiplicities are designated by the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad and coupling constants (J) are provided in Hz. ^{13}C NMR spectra were recorded on Bruker AVANCE NEO 400 (100 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from the solvent resonance as the internal standard ($CDCl_3$: 77.16 ppm). Some reported spectra in $CDCl_3$ include minor solvent impurities of water (^1H NMR δ 1.56 ppm) and/or silicone grease (^1H NMR δ 0.07 ppm, ^{13}C NMR δ 1.19 ppm), which do not impact product assignments.[47] Melting points were measured using open glass capillaries in a Büchi B545 apparatus. Infrared (IR) spectra were recorded on a JASCO FT/IR- 4100 spectrometer. Flash chromatography was performed with Fuji Silysia PSQ100B (100 μm) and KANTO silica gel 60N (63-210 μm). Analytical thin layer chromatography (TLC) was performed on Merck precoated TLC plates (silica gel 60 GF254, 0.25 mm). High-resolution mass (HRMS) spectral data were obtained on an Agilent 6546 LC/Q-TOF or a JEOL MStation JMS-700 mass spectrometer.

General procedure for palladium-catalyzed intramolecular allylation of aldehydes (GP-1). A 10 mL two-neck round-bottom flask was charged with $Pd(OAc)_2$ (5 mol %), $P(4\text{-}CF_3C_6H_4)_3$ (10 mol %), and THF (1.0 mL) under an argon atmosphere. The mixture was stirred in a preheated oil-bath at 80 °C for 0.5 h, cooled to room temperature, and then transferred into another 10 mL two-neck round-bottom flask charged with TBAT (2 equiv) and **1** (1 equiv) in THF (1.0 mL). The reaction mixture was stirred in an oil-bath at 80 °C. Upon completion of the reaction, the mixture was filtered through a pad of Celite using diethyl ether (10 mL) as the washing solvent. The filtrate was subsequently washed with saturated NH_4Cl (2 × 20 mL) and brine (2 × 20 mL). The combined organic layers were dried over $MgSO_4$ and then concentrated. Diethyl ether (10 mL) was added to this residue, and the precipitate was removed using Celite pad and concentrated. This procedure was repeated at least twice to remove the TBAT contents. After concentration, the crude products were purified by silica gel column chromatography to yield desired product **2**.

General procedure for TBS protection of alcohols (GP-2). A flame-dried round-bottomed flask was cooled under argon atmosphere and charged with **2** (1.0 equiv) and dry CH_2Cl_2 (0.14 M). Imidazole (4.0 equiv) was added in one portion, and the solution cooled to 0 °C in an ice/water bath. Then, *tert*-butylchlorodimethylsilane (3.0 equiv) was added portionwise, the flask fitted with a rubber septum, and the

solution allowed to warm to rt. The mixture was stirred at rt for overnight, at which point the reaction was quenched with saturated NH_4Cl (aq.) and stirred for 10 min at rt. The resulting aqueous layer was extracted with CH_2Cl_2. The organic extracts were washed with water and brine. The organic extracts were combined, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography to afford the TBS ether.

***anti*-10-[(*Z*)-2-Phenylethenyl]-9,10-dihydrophenanthren-9-ol (*anti*-(*Z*)-2a)**. Following GP-1 (0.30 mmol scale reaction), *anti*-(*Z*): white amorphous, 46.5 mg, 52%, R_f = 0.41, EtOAc/hex = 3/7, *syn*-(*Z*): white amorphous, 14.4 mg, 17%, R_f = 0.41, EtOAc/hex = 3/7.

^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.77-7.68 (m, 2H), 7.59-7.50 (m, 1H), 7.40-7.16 (m, 10H), 6.84 (d, *J* = 11.6 Hz, 1H), 5.56 (dd, *J* = 11.6, 10.4 Hz, 1H), 4.66 (dd, *J* = 8.8, 4.0 Hz, 1H), 4.18 (t, *J* = 10.0 Hz, 1H), 1.95 (d, *J* = 5.2 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 137.6, 136.7, 135.7, 134.4, 133.4, 132.8, 130.8, 128.62, 128.61, 128.50, 128.48, 128.33, 128.29, 128.0, 127.5, 125.9, 124.1, 123.9, 72.4, 46.6; IR (ATR, cm^{-1}) 3372, 3052, 2961, 2920, 2874, 2851, 1693, 1598, 1565, 1196, 998; HRMS (ESI-TOF) *m/z*: $[M\text{-}OH]^+$ Calcd for $C_{22}H_{17}^+$: 281.1325, found: 281.1320.

***syn*-10-[(*Z*)-2-Phenylethenyl]-9,10-dihydrophenanthren-9-ol (*syn*-(*Z*)-2a).** ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.77-7.68 (m, 2H), 7.59-7.50 (m, 2H), 7.40-7.16 (m, 9H), 6.77 (d, *J* = 11.6 Hz, 1H), 5.86 (t, *J* = 11.2 Hz, 1H), 4.73 (dd, *J* = 7.6, 4.0 Hz, 1H), 4.20 (dd, *J* = 10.8, 4.0 Hz, 1H), 1.67 (d, *J* = 8.4 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 137.5, 137.0, 135.60, 134.50, 134.48, 133.2, 133.0, 130.2, 129.00, 128.95, 128.55, 128.2, 128.1, 127.9, 127.3, 127.2, 124.2, 71.8, 44.1.

***anti*-10-[(*E*)-2-Phenylethenyl]-9,10-dihydrophenanthren-9-ol (*anti*-(*E*)-2a).** Following GP-1 (0.30 mmol scale reaction), yellow oil, 9.8 mg, 11%, R_f = 0.41, EtOAc/hex = 3/7.

^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.86-7.82 (m, 2H), 7.57 (dd, *J* = 0.8, 7.2 Hz, 1H), 7.49-7.20 (m, 10H), 6.57 (d, *J* = 15.6 Hz, 1H), 6.15 (dd, *J* = 8.8, 16.0 Hz, 1H), 4.77 (d, *J* = 6.8 Hz, 1H), 3.85 (dd, *J* =8.0, 8.8 Hz, 1H), 1.90 (bs, 1H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 136.8, 136.7, 135.7, 134.2, 133.0, 132.8, 129.4, 128.9, 128.77, 128.69, 128.39, 128.36, 128.0, 127.8, 127.3, 126.5, 124.1, 124.0, 72.0, 51.6; HRMS (ESI-TOF) *m/z*: $[M\text{-}OH]^+$ Calcd for $C_{22}H_{17}^+$: 281.1325, found: 281.1327.

***anti*-10-[(*Z*)-2-(4-Fluorophenyl)ethenyl]-9,10-dihydrophenanthren-9-ol (*anti*-(*Z*)-2b).** Following GP-1 (0.30 mmol scale reaction), *anti*-(*Z*): yellow oil, 46.8 mg, 51%, R_f = 0.47, EtOAc/hex = 3/7, *syn*-(*Z*): yellow oil, 10.1 mg, 11%, R_f = 0.47, EtOAc/hex = 3/7.

^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.85-7.77 (m, 2H), 7.62 (d, *J* = 7.2 Hz, 1H), 7.44-7.29 (m, 7H), 7.02-6.97 (m, 2H), 6.88 (d, *J* = 11.6 Hz, 1H), 5.66 (dd, *J* = 11.2, 10.4 Hz, 1H), 4.75 (d, *J* = 9.2 Hz, 1H), 4.20 (t, *J* = 10.0 Hz, 1H), 1.95-1.65 (br, 1H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 162.2 (d, *J* = 246.0 Hz), 137.52, 135.5, 133.5, 133.3 (2C), 132.8, 132.7 (d, *J* = 3.9 Hz), 130.8, 130.3 (d, *J* = 7.6 Hz), 128.5, 128.4 (2C), 128.1, 125.9, 124.2, 124.0, 115.5 (d, *J* = 21.0 Hz), 72.4, 46.4.

***syn*-10-[(*Z*)-2-(4-Fluorophenyl)ethenyl]-9,10-dihydrophenanthren-9-ol (*syn*-(*Z*)-2b)**

^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.85-7.77 (m, 2H), 7.48-7.29 (m, 8H), 7.02-6.97 (m, 2H), 6.80 (d, *J* = 12.0 Hz, 1H), 5.93 (t, *J* = 11.2 Hz, 1H), 4.83 (d, *J* = 4.0 Hz, 1H), 4.22 (dd, *J* = 10.4, 4.0 Hz, 1H), 1.95-1.65 (br, 1H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 162.0 (d, *J* = 245.0 Hz), 137.48, 133.2, 133.01 (d, *J* = 3.4 Hz), 132.97, 132.3, 130.2 (d, *J* = 7.6 Hz), 129.1, 129.0, 128.8, 128.0, 127.1, 124.3, 115.5 (d, *J* = 20.9 Hz), 71.7, 44.1; HRMS-EI: *m/z*: $[M]^+$ calcd for $C_{22}H_{17}FO$: 316.1263, found 316.1262.

***anti*-10-[(*E*)-2-(4-Fluorophenyl)ethenyl]-9,10-dihydrophenanthren-9-ol (*anti*-(*E*)-2b).** Following GP-1 (0.30 mmol scale reaction), colorless oil, 8.3 mg, 9%, R_f = 0.40, EtOAc/hex = 3/7.

^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.84 (t, *J* = 8.4 Hz, 2H), 7.56 (d, *J* = 7.6 Hz, 1H), 7.44 (dt, *J* = 7.6, 1.2 Hz, 1H), 7.41-7.27 (m, 6H), 7.00-6.92 (tm, *J* = 8.8 Hz, 2H), 6.51 (d, *J* = 15.6 Hz, 1H), 6.04 (dd, *J* = 15.6, 8.8 Hz, 1H), 4.76 (d, *J* =

7.2 Hz, 1H), 3.84 (t, *J* = 8.0 Hz, 1H), 2.00-1.50 (bs, 1H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 162.5 (d, *J* = 196.5 Hz), 136.5, 135.6, 133.0 (d, *J* = 2.3 Hz), 132.9, 132.85, 132.78, 129.4, 129.0, 128.6, 128.43, 128.40, 128.1 (d, *J* = 3.4 Hz), 127.98, 127.5, 124.11, 124.06, 115.6 (d, *J* = 17.3 Hz), 72.1, 51.6; HRMS-EI: *m/z*: $[M]^+$ calcd for $C_{22}H_{17}FO$: 316.1263, found 316.1251.

10-[(*Z*)-2-(4-Methoxyphenyl)ethenyl]-9,10-dihydrophenanthren-9-ol (2c). Following GP-1 (0.30 mmol scale reaction), *anti*-(*Z*): yellow oil, 29.6 mg, 30%, R_f = 0.41, EtOAc/hex = 3/7, *syn*-(*Z*): yellow oil, 6.9 mg, 7%, R_f = 0.41, EtOAc/hex = 3/7. ***anti*-(*Z*)-2c**, ***syn*-(*Z*)-2c**, and ***anti*-(*E*)-2c** were isolated as an inseparable mixture. The above data was assigned after TBS protection of the alcohol.

***anti*-*tert*-Butyldimethyl({10-[(*Z*)-2-(4-methylphenyl)ethenyl]-9,10-dihydrophenanthren-9-yl}oxy)silane.** Following GP-2 (0.11 mmol scale reaction as a mixture of ***anti*-(*Z*)-2c**, ***syn*-(*Z*)-2c**, and ***anti*-(*E*)-2c**), colorless oil, 100%, R_f 0.69, EtOAc/hex = 3/7. Title compound was obtained as a mixture of *anti*-(*Z*) and *anti*-(*E*) isomers, and *syn*-(*Z*) isomer was not isolated.

^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.80 (d, *J* = 8.4 Hz, 1H), 7.73 (d, *J* = 7.6 Hz, 1H), 7.53 (d, *J* = 7.2 Hz, 1H), 7.41-7.27 (m, 7H), 6.83 (d, *J* = 8.8 Hz, 2H), 6.76 (d, *J* = 11.2 Hz, 1H), 5.55 (t, *J* = 10.8 Hz, 1H), 4.78 (d, *J* = 8.0 Hz, 1H), 4.24 (t, *J* = 10.0 Hz, 1H), 3.78 (s, 3H), 0.92 (s, 9H), 0.16 (s, 3H), 0.03 (s, 3H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 158.7, 139.2, 137.3, 133.8, 133.6, 132.3, 130.7, 130.0, 129.9, 128.27, 128.1, 127.97, 127.7, 127.6, 125.8, 124.01, 123.8, 113.8, 73.2, 55.4, 46.4, 26.1,18.3, -3.7, -4.1; HRMS-EI: *m/z*: $[M\text{-OTBS}]^+$ calcd for $C_{23}H_{19}O$: 311.1430, found 311.1440.

***anti*-10-[(*E*)-2-(4-Methoxyphenyl)ethenyl]-9,10-dihydrophenanthren-9-ol (*anti*-(*E*)-2c).** Following GP-1 (0.30 mmol scale reaction), yellow oil, 4.9 mg, 5%, R_f = 0.38, EtOAc/hex = 3/7.

The above data was assigned after TBS protection of the alcohol.

***anti*-*tert*-Butyldimethyl({10-[(*E*)-2-(4-methylphenyl)ethenyl]-9,10-dihydrophenanthren-9-yl}oxy)silane**

^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.82 (d, *J* = 6.8 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.47 (d, *J* = 7.6 Hz, 1H), 7.42-7.28 (m, 7H), 6.83 (d, *J* = 8.8 Hz, 2H), 6.45 (d, *J* = 16.0 Hz, 1H), 5.94 (dd, *J* = 16.0, 8.8 Hz, 1H), 4.78 (d, *J* = 8.0 Hz, 1H), 3.80 (s, 3H), 3.75 (t, *J* = 8.8 Hz, 1H), 0.84 (s, 9H), 0.06 (s, 3H), -0.03 (s, 3H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 159.1, 138.2, 137.4, 133.7, 133.4, 132.7, 130.2, 128.9, 128.28, 128.01, 127.8, 127.5 (2C), 127.3, 127.0, 124.02, 123.7, 114.0, 73.0, 55.39, 52.3, 26.0, 18.2, -4.0, -4.2; IR (ATR, cm^{-1}) 3066, 2953, 2927, 2890, 1607, 1248, 1077, 1005.

10-[(*Z*)-2-(Thiophen-2-yl)ethenyl]-9,10-dihydrophenanthren-9-ol ((*Z*)-2d)

Following GP-1 (0.30 mmol scale reaction), orange oil, 10.0 mg, 11%, R_f = 0.40, EtOAc/hex = 3/7).

The above data was assigned after TBS protection of the alcohol.

***anti*-*tert*-Butyldimethyl({10-[(*Z*)-2-(thiophen-2-yl)ethenyl]-9,10-dihydrophenanthren-9-yl}oxy)silane**

Following GP-2 (0.033 mmol scale reaction as a mixture of ***anti*-(*Z*)-2d**, ***anti*-(*E*)-2d**), orange oil, 100%, R_f 0.61, EtOAc/hex = 1/4. Title compound was obtained as a mixture of *anti*-(*Z*) and *anti*-(*E*) isomers.

^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.83-7.76 (m, 2H), 7.48 (d, *J* = 5.6 Hz, 1H), 7.42-7.22 (m, 6H), 7.06 (d, *J* = 3.6 Hz, 1H), 6.99 (dd, *J* = 4.8, 3.6 Hz, 1H), 6.75 (d, *J* = 11.2 Hz, 1H), 5.43 (dd, *J* = 11.2, 10.8 Hz, 1H), 4.79 (d, *J* = 8.0 Hz, 1H), 4.51 (dd, *J* = 10.4, 7.6 Hz, 1H), 0.91 (s, 9H), 0.15 (s, 3H), -0.04 (s, 3H); Characteristic peaks: ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 73.0, 47.5, 25.8, 18.4, -3.8, -4.1; HRMS-EI: $[M\text{-OTBS}]^+$ calcd for $C_{20}H_{15}OS^+$: 303.0844, found 303.0844.

10-[(*E*)-2-(thiophen-2-yl)ethenyl]-9,10-dihydrophenanthren-9-ol (*anti*-(*E*)-2d)

Following GP-1 (0.30 mmol scale reaction), orange oil, 21.0 mg, 23%, R_f = 0.40, EtOAc/hex = 3/7.

The above data was assigned after TBS protection of the alcohol.

***anti*-*tert*-Butyldimethyl({10-[(*E*)-2-(thiophen-2-yl)ethenyl]-9,10-dihydrophenanthren-9-yl}oxy)silane**

^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.82 (d, *J* = 8.0 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.48 (d, *J* = 5.6 Hz, 1H), 7.42-7.23 (m, 5H), 7.12 (d, *J* = 5.2 Hz, 1H), 6.94 (dd, *J* = 5.2, 4.0 Hz, 1H), 6.89 (d, *J* = 2.8 Hz, 1H), 6.61 (d, *J* = 15.6 Hz, 1H),

5.97 (dd, *J* = 15.6, 8.8 Hz, 1H), 4.79 (d, *J* = 8.0 Hz, 1H), 3.73 (t, *J* = 8.8 Hz, 1H), 0.86 (s, 9H), 0.10 (s, 3H), 0.08 (s, 3H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 142.5, 138.2, 136.9, 133.6, 133.5, 129.4, 128.8, 128.3 (2C), 128.1, 127.8, 127.7, 127.4, 125.2, 124.1, 123.9, 123.8, 72.8, 52.1, 26.0, 18.2, -4.0, -4.2.

***anti*-6-Chloro-10-[(*Z*)-2-phenylethenyl]-9,10-dihydrophenanthren-9-ol (*anti*-(*Z*)-2h)**

Following GP-1 (0.506 mmol scale reaction), *anti*-(*Z*): white amorphous, 53.7 mg, 32%, R_f = 0.51, EtOAc/hex = 3/7, *syn*-(*Z*): white amorphous, 21.8 mg, 13%, R_f = 0.51, EtOAc/hex = 3/7.)

^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.79-7.76 (dm, *J* = 7.6 Hz, 1H), 7.74 (d, *J* = 2.0 Hz, 1H), 7.56 (dd, *J* = 8.4, 0.8 Hz, 1H), 7.44-7.20 (m, 9H), 6.97 (d, *J* = 11.6 Hz, 1H), 5.65 (dd, *J* = 11.6, 10.4 Hz, 1H), 4.71 (dd, *J* = 9.6, 4.4 Hz, 1H), 4.22 (t, *J* = 10.0 Hz, 1H), 2.05 (d, *J* = 4.8 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 136.5, 136.1, 135.85, 135.1, 134.6, 134.4, 132.4, 130.3, 129.0, 128.7, 128.6, 128.52, 128.2, 128.05, 127.6, 127.4, 124.27, 124.0, 72.0, 46.5; IR (ATR, cm^{-1}) 3343, 3022, 2956, 2923, 2871, 2852, 1695, 1595, 1558, 1193, 1082, 997; HRMS (ESI-TOF) *m/z*: [M-OH]$^+$ Calcd for $C_{22}H_{16}Cl^+$: 315.0936, found: 315.0936.

***syn*-6-Chloro-10-[(*Z*)-2-phenylethenyl]-9,10-dihydrophenanthren-9-ol (*syn*-(*Z*)-2h)**

^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.44-7.20 (m, 12H), 6.85 (d, *J* = 12.0 Hz, 1H), 5.86 (t, *J* = 11.2 Hz, 1H), 4.83 (dd, *J* = 8.0, 4.0 Hz, 1H), 4.30-4.25 (ddm, *J* = 10.4, 4.0 Hz, 1H), 1.75 (d, *J* = 8.8 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 136.9, 136.0, 135.9, 134.93, 134.8, 133.8, 132.1, 129.2, 129.1, 128.50, 128.4, 128.1, 124.33, 124.0, 71.1, 44.0.

***anti*-6-Chloro-10-[(*E*)-2-phenylethenyl]-9,10-dihydrophenanthren-9-ol (*anti*-(*E*)-2h)**

Following GP-1 (0.30 mmol scale reaction), white amorphous, 3.9 mg, 4%, R_f = 0.51, EtOAc/hex = 3/7.

^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.82-7.76 (m, 2H), 7.52 (d, *J* = 8.4 Hz, 1H), 7.43-7.20 (m, 9H), 6.57 (d, *J* = 15.6 Hz, 1H), 6.13 (dd, *J* = 15.6, 8.8 Hz, 1H), 4.73 (dd, *J* = 7.6, 4.8 Hz, 1H), 3.82 (t, *J* = 7.6 Hz, 1H), 2.09 (d, *J* = 4.8 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 136.6, 135.9, 135.2, 134.8, 134.73, 134.66, 131.9, 129.4, 129.1, 128.8, 128.6, 128.23, 128.23, 128.19, 128.0, 126.5, 124.19, 124.16, 71.5, 51.6; HRMS (ESI-TOF) *m/z*: [M-OH]$^+$ Calcd for $C_{22}H_{16}Cl^+$: 315.0936, found: 315.0935.

***anti- tert*-Butyldimethyl({6-Chloro-10-ethenyl-9,10-dihydrophenanthren-9-yl}oxy)silane (3h)**

Following GP-1 (0.30 mmol scale reaction), white solid, 11.0 mg, 9%, R_f = 0.52, EtOAc/hex = 3/7.

The above data was assigned after TBS protection of the alcohol.

^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.74 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.72 (d, *J* = 2.0 Hz, 1H), 7.38-7.22 (m, 5H), 5.64 (ddd, *J* = 16.8, 10.0, 8.0 Hz, 1H), 5.13-5.01 (m, 2H), 4.67 (d, *J* = 6.0 Hz, 1H), 3.62 (dd, *J* = 7.6, 7.2 Hz, 1H), 0.80 (s, 9H), 0.08 (s, 3H), -0.09 (s, 3H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 137.5, 136.9, 135.9, 135.6, 134.3, 132.1, 129.2, 129.1, 128.6, 127.6, 127.5, 124.2, 123.8, 118.1, 72.4, 52.7, 25.9, 18.2, -4.0, -4.2; IR (ATR, cm^{-1}) 3077, 2949, 1593, 1560, 1192, 1095, 1083, 1021; HRMS (ESI-TOF) *m/z* : [M-OTBS]$^+$ Calcd for $C_{16}H_{12}Cl^+$: 239.0623 , found: 239.0621.

***anti*-6-Methoxy-10-[(*Z*)-2-phenylethenyl]-9,10-dihydrophenanthren-9-ol (*anti*-(*Z*)-2i)**

Following GP-1 (0.165 mmol scale reaction), *anti*-(*Z*): yellow amorphous, 20.4 mg, 38%, R_f = 0.34, EtOAc/hex = 3/7, *syn*-(*Z*): yellow amorphous, 8.1 mg, 15%, R_f = 0.34, EtOAc/hex = 3/7.

^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.77-7.68 (m, 2H), 7.40-7.20 (m, 8H), 7.19 (dd, J = 2.8, 0.4 Hz, 1H), 7.00-6.90 (m, 2H), 5.70 (dd, *J* = 11.6, 10.4 Hz, 1H), 4.71 (dd, *J* = 9.6, 5.2 Hz, 1H), 4.22 (t, *J* = 10.0 Hz, 1H), 3.87 (s, 3H), 2.03 (d, *J* = 5.2 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 160.0, 139.4, 136.7, 134.74, 134.68, 133.6, 130.8, 128.61, 128.3, 128.0, 127.5, 127.4, 125.58, 125.4, 123.46, 114.3, 110.7, 72.5, 55.6, 46.7; IR (ATR, cm^{-1}) 3426, 3053, 2922, 1615, 1585, 1565, 1156, 1107; HRMS (ESI-TOF) *m/z*: [M-OH]$^+$ Calcd for $C_{23}H_{19}O^+$: 311.1341, found: 311.1436.

***syn*-6-Methoxy-10-[(*Z*)-2-phenylethenyl]-9,10-dihydrophenanthren-9-ol (*syn*-(*Z*)-2i)**

^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.77-7.68 (m, 2H), 7.40-7.20 (m, 8H), 7.05 (d, *J* = 2.8 Hz, 1H), 7.00-6.90 (m, 1H), 6.84 (d, *J* = 11.6 Hz, 1H), 5.88 (t, *J* = 11.2 Hz, 1H), 4.82 (dd, *J* = 8.8, 4.4 Hz, 1H), 4.29 (dd, *J* = 10.8, 4.4 Hz, 1H), 3.87 (s, 3H), 1.80 (d, *J* = 9.2 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 159.9, 139.3, 137.0, 134.9, 133.5, 133.2,

130.8, 128.91, 128.90, 128.57, 127.9, 127.6, 127.3, 125.7, 125.55, 123.51, 114.5, 112.0, 71.9, 55.6, 44.2; HRMS (ESI-TOF) *m/z*: $[M\text{-}OH]^+$ Calcd for $C_{23}H_{19}O^+$: 311.1341, found: 311.1436.

***anti*-5-[(*Z*)-2-Phenylethenyl]-5,6-dihydrobenzo[*c*]phenanthren-6-ol (*anti*-(*Z*)-2j)**

Following GP-1 (0.30 mmol scale reaction), white amorphous, 16.8 mg, 16%, R_f = 0.44, EtOAc/Hex = 3/7.

^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.60-8.55 (dm, *J* = 8.0 Hz, 1H), 8.01 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.93-7.84 (m, 2H), 7.80 (d, *J* = 8.4 Hz, 1H), 7.56-7.43 (m, 4H), 7.40-7.32 (m, 3H), 7.30-7.25 (m, 2H), 7.23-7.17 (m, 1H), 6.99 (d, *J* = 11.2 Hz, 1H), 5.75 (t, *J* = 11.2 Hz, 1H), 4.74 (dd, *J* = 9.6, 4.8 Hz, 1H), 4.21 (t, *J* = 9.6 Hz, 1H), 2.07 (d, *J* = 5.2 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 137.0, 136.9, 136.7, 135.1, 134.5, 133.2, 130.4, 129.9, 129.6, 129.2, 128.9, 128.7, 128.59, 128.56, 128.0, 127.8, 127.5, 127.1, 126.5, 125.8, 125.7, 123.1, 73.3, 46.8; IR (ATR, cm^{-1}) 3270, 3023, 2919, 2850, 1690, 1590, 1117, 997.

***anti*-5-[(*E*)-2-Phenylethenyl]-5,6-dihydrobenzo[*c*]phenanthren-6-ol (*anti*-(*E*)-2j)**

Following GP-1 (0.30 mmol scale reaction), white amorphous, 9.4 mg, 9%, R_f = 0.44, EtOAc/Hex = 3/7.

^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.62-8.55 (m, 1H), 8.05-8.00 (dm, *J* = 8.0 Hz, 1H), 7.95-7.90 (m, 1H), 7.87 (d, *J* = 8.4 Hz, 1H), 7.76 (d, *J* = 8.4 Hz, 1H), 7.57-7.20 (m, 10H), 6.66 (d, *J* = 16.0 Hz, 1H), 6.22 (dd, *J* = 16.0, 8.8 Hz, 1H), 4.77 (d, *J* = 7.2 Hz, 1H), 3.83 (t, *J* = 8.4 Hz, 1H), 2.24-2.10 (bs, 1H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 137.3, 136.8, 135.9, 134.9, 134.7, 132.8, 130.1, 129.7, 129.2, 128.9, 128.71, 128.67, 128.3, 127.9, 127.8, 127.1, 126.50, 126.48, 125.9, 125.8, 124.3, 72.7, 51.9; HRMS (ESI-TOF) *m/z*: $[M\text{-}OH]^+$ Calcd for $C_{26}H_{19}^+$: 331.1482, found: 331.1482.

***anti*-1-[(*Z*)-2-Phenylethenyl]-1,2,3,4-tetrahydtonaphthalen-2-ol (*anti*-(*Z*)-2k)**

Following GP-1 (0.30 mmol scale reaction), colorless oil, 32.5 mg, 45%, R_f = 0.40, EtOAc/hex = 3/7.

^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.45 (d, *J* = 7.2 Hz, 2H), 7.36-7.32 (tm, *J* = 7.2 Hz, 2H), 7.28-7.24 (m, 2H), 7.18-7.10 (m, 3H), 6.95 (d, *J* = 11.6 Hz, 1H), 5.63 (dd, *J* = 11.6, 10.4 Hz, 1H), 4.05 (t, *J* = 10.4 Hz, 1H), 3.84 (ddt, *J* = 10.4, 8.8, 3.2 Hz, 1H), 2.96 (dd, *J* = 8.4, 4.4 Hz, 2H), 2.25-2.16 (m, 1H), 1.90 (d, *J* = 2.8 Hz, 1H), 1.87-1.79 (m, 1H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 136.8, 136.4, 135.8, 134.1, 132.8, 129.1, 128.9, 128.6 (2C), 127.5, 126.7, 126.3, 72.1, 47.5, 30.2, 28.2; IR (ATR, cm^{-1}) 3374, 3020, 2864, 2853, 1717, 1599, 1576, 1116, 1028.

***anti*-1-[(*E*)-2-Phenylethenyl]-1,2,3,4-tetrahydtonaphthalen-2-ol (*anti*-(*E*)-2k)**

Following GP-1 (0.3 mmol scale reaction), *anti*-(*E*): colorless oil, 3.8 mg, 5%, R_f = 0.40, EtOAc/hex = 3/7, *syn*-(*E*): colorless oil, 0.85 mg, 1%, R_f = 0.40, EtOAc/hex = 3/7.

^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.46-7.37 (m, 2H), 7.37-7.30 (m, 2H), 7.30-7.25 (m, 1H), 7.25-7.10 (m, 4H), 6.67 (d, *J* = 16.0 Hz, 1H), 6.17 (dd, *J* = 15.6, 9.2 Hz, 1H), 3.86 (ddd, *J* = 10.4, 8.4, 3.2 Hz, 1H), 3.50 (t, *J* = 8.8 Hz, 1H), 3.08-2.88 (m, 2H), 2.29-2.21 (m, 1H), 2.15-2.05 (bs, 1H), 1.94-1.81 (m, 1H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 136.8, 136.3, 135.8, 134.8, 130.8, 129.6, 128.9, 128.8, 127.9, 126.69, 126.50, 126.2, 71.0, 53.2, 29.5, 27.9.

***syn*-1-[(*E*)-2-Phenylethenyl]-1,2,3,4-tetrahydtonaphthalen-2-ol (*syn*-(*E*)-2k)**

^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.46-7.37 (m, 2H), 7.37-7.30 (m, 2H), 7.30-7.25 (m, 2H), 7.25-7.10 (m, 3H), 6.56 (d, *J* = 16.0 Hz, 1H), 6.35 (dd, *J* = 15.6, 8.8 Hz, 1H), 4.21-4.13 (bs, 1H), 3.80 (dd, *J* = 8.8, 5.2 Hz, 1H), 3.08-2.88 (m, 2H), 2.06-1.95 (m, 2H), 1.75-1.73 (bs, 1H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 137.0, 135.6, 133.8, 130.5, 129.4, 129.0, 128.7, 127.7, 126.74, 126.55, 126.1, 69.9, 49.3, 28.6, 27.4; HRMS (ESI-TOF) *m/z*: $[M\text{-}OH]^+$ Calcd for $C_{18}H_{17}^+$: 233.1325, found: 233.1326.

***anti*-3-Chloro-10-[(*Z*)-2-phenylethenyl]-9,10-dihydrophenanthren-9-ol (*anti*-(*Z*)-2m)**

Following GP-1 (0.3 mmol scale reaction), *anti*-(*Z*): white amorphous, 42.4 mg, 43%, R_f = 0.33, EtOAc/hex = 1/4, *syn*-(*Z*): white amorphous, 10.8 mg, 11%, R_f = 0.33, EtOAc/hex = 1/4.

^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.76-7.66 (m, 2H), 7.58-7.54 (m, 1H), 7.43-7.14 (m, 9H), 6.87 (d, *J* = 11.6 Hz, 1H), 5.55 (dd, *J* = 11.6, 10.4 Hz, 1H), 4.68 (d, *J* = 9.2 Hz, 1H), 4.20-4.10 (m, 1H), 2.10-1.92 (bs, 1H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 137.7, 136.5, 135.2, 134.8, 133.9, 133.8, 131.7, 130.2, 129.9, 128.97, 128.7, 128.64, 128.58, 128.1,

127.6, 126.1, 124.25, 124.0, 72.2, 46.0; IR (ATR, cm^{-1}) 3367, 3021, 2954, 2927, 2873, 2853, 1695, 1593, 1559, 1117, 1024, 997; HRMS (ESI-TOF) *m/z*: $[M\text{-}OH]^+$ Calcd for $C_{22}H_{16}Cl^+$: 315.0936, found: 315.0929.

***syn*-3-Chloro-10-[(*Z*)-2-phenylethenyl]-9,10-dihydrophenanthren-9-ol (*syn*-(*Z*)-2m)**

^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.76-7.66 (m, 2H), 7.43-7.14 (m, 10H), 6.81 (d, *J* = 11.6 Hz, 1H), 5.86 (t, *J* = 11.6 Hz, 1H), 4.78-4.72 (bs, 1H), 4.20-4.10 (m, 1H), 1.72-1.57 (bs, 1H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 137.6, 136.8, 135.0, 134.1(2C), 134.0, 131.9, 130.3, 129.2, 128.99, 128.61, 128.5, 128.4, 128.2, 127.4, 126.1, 124.29, 124.27, 71.5, 43.5.

***anti*-3-Chloro-10-[(E)-2-phenylethenyl]-9,10-dihydrophenanthren-9-ol (*anti*-(*E*)-2m)**

Following GP-1 (0.30 mmol scale reaction), yellow oil, 2.8 mg, 3%, R_f = 0.22, EtOAc/hex = 1/4.

^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.83-7.80 (m, 1H), 7.76 (d, *J* = 1.6 Hz, 1H), 7.59-7.53 (m, 1H), 7.46-7.20 (m, 4H), 6.54 (d, *J* = 16.0 Hz, 1H), 6.10 (dd, *J* = 16.0, 8.8 Hz, 1H), 4.76 (dd, *J* = 6.8, 2.4 Hz, 1H), 3.81 (t, *J* = 8.0 Hz, 1H), 2.05 (d, *J* = 4.8 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 136.71, 136.63, 134.75, 134.6, 134.2, 133.9, 131.7, 130.7, 129.1, 128.7, 128.2, 128.10, 127.96, 127.5, 126.5, 124.2, 71.9, 51.1; HRMS (ESI-TOF) *m/z*: $[M\text{-}OH]^+$ Calcd for $C_{22}H_{16}Cl^+$: 315.0936, found: 315.0939.

***anti*-3-Chloro-10-ethenyl-9,10-dihydrophenanthren-9-ol (3m)**

Following GP-1 (0.30 mmol scale reaction), yellow oil, 5.2 mg, 5%, R_f = 0.22, EtOAc/hex = 1/4.

^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.79 (d, *J* = 2.4 Hz, 1H), 7.74 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.59-7.53 (m, 1H), 7.46-7.20 (m, 9H), 5.76 (ddd, *J* = 17.2, 10.4, 8.0 Hz, 1H), 5.28-5.22 (dm, *J* = 10.4 Hz, 1H), 5.18 (dt, *J* = 17.2, 1.6 Hz, 1H), 4.68 (dd, *J* = 6.8, 3.2 Hz, 1H), 3.66 (t, *J* = 7.6 Hz, 1H), 2.01 (d, *J* = 4.0 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 136.9, 136.66, 134.73, 133.8, 130.6, 129.00, 128.98, 128.1, 127.4, 124.12, 124.09, 119.7, 71.5, 51.7; HRMS (ESI-TOF) *m/z*: $[M\text{-}OH]^+$ Calcd for $C_{16}H_{12}Cl^+$: 239.0623, found. 239.0620.

***anti*-3-Methoxy-10-[(*Z*)-2-phenylethenyl]-9,10-dihydrophenanthren-9-ol (*anti*-(*Z*)-2n)**

Following GP-1 (0.3 mmol scale reaction), *anti*-(*Z*): white amorphous, 36.1 mg, 37%, R_f = 0.42, EtOAc/hex = 3/7, *anti*-(*Z*): white amorphous, 14.7 mg, 15%, R_f = 0.42, EtOAc/hex = 3/7.

^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.66 (d, *J* = 7.6 Hz, 1H), 7.55-7.49 (dm, *J* = 7.2 Hz, 1H), 7.40-7.08 (m, 9H), 6.81 (d, *J* = 11.6 Hz, 1H), 6.76 (dd, *J* = 8.4, 2.8 Hz, 1H), 5.55 (dd, *J* = 11.6, 10.4 Hz, 1H), 4.62 (d, *J* = 9.2 Hz, 1H), 4.08 (t, *J* = 10.0 Hz, 1H), 3.78 (s, 3H), 2.05-1.90 (bs, 1H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 159.54, 137.9, 136.7, 134.6, 134.2, 132.7, 131.2, 129.5, 128.60, 128.59, 128.52, 127.8, 127.4, 125.9, 123.9, 113.4, 110.1, 72.6, 55.5, 45.9; IR (ATR, cm^{-1}) 3419, 3051, 2922, 2839, 1615, 1598, 1565, 1226, 1003.

***syn*-3-Methoxy-10-[(*Z*)-2-phenylethenyl]-9,10-dihydrophenanthren-9-ol (*syn*-(*Z*)-2n)**

^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.68 (d, *J* = 7.2 Hz, 1H), 7.55-7.49 (dm, *J* = 7.2 Hz, 1H), 7.40-7.08 (m, 10H), 6.74 (d, *J* = 10.8 Hz, 1H), 5.82 (t, *J* = 10.8 Hz, 1H), 4.73-4.65 (bs, 1H), 4.14 (dd, *J* = 10.8, 4.0 Hz, 1H), 3.78 (s, 3H), 1.80-1.68 (bs, 1H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 159.48, 137.8, 137.1, 134.3, 133.1, 132.9, 130.0, 129.3, 128.9, 128.40, 128.37, 127.7, 127.2, 124.1, 113.5, 110.2, 71.8, 55.5, 43.3; HRMS (ESI-TOF) *m/z*: $[M\text{-}OH]^+$ Calcd for $C_{23}H_{19}O^+$: 311.1341, found: 311.1440.

***anti*-3-Methoxy-10-[(*E*)-2-phenylethenyl]-9,10-dihydrophenanthren-9-ol (*anti*-(*E*)-2n)**

Following GP-1 (0.30 mmol scale reaction), yellow amorphous, 8.1 mg, 9%, R_f = 0.33, EtOAc/hex = 3/7.

^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.79 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.60-7.55 (dm, *J* = 7.6 Hz, 1H), 7.47-7.18 (m, 9H), 6.87 (dd, *J* = 8.4, 2.8 Hz, 1H), 6.55 (d, *J* = 15.6 Hz, 1H), 6.14 (dd, *J* = 16.0, 8.8 Hz, 1H), 4.74 (dd, *J* = 6.8, 4.8 Hz, 1H), 3.89 (s, 3H), 3.78 (t, *J* = 8.0 Hz, 1H), 2.10 (d, *J* = 4.8 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 159.6, 136.95, 136.88, 134.1, 134.0, 132.7, 130.3, 129.1, 128.8, 128.7, 128.5, 127.9, 127.8, 127.2, 126.5, 124.0, 113.6, 109.9, 72.2, 55.6, 51.0; HRMS (ESI-TOF) *m/z*: $[M\text{-}OH]^+$ Calcd for $C_{23}H_{19}O^+$: 311.1341, found: 311.1437.

***anti*-2-Methoxy-10-[(*Z*)-2-phenylethenyl]-9,10-dihydrophenanthren-9-ol (*anti*-(*Z*)-2o)**

Following GP-1 (0.3 mmol scale reaction), *anti*-(*Z*): white amorphous, 32.3 mg, 33%, R_f = 0.40, EtOAc/hex = 3/7, *syn*-(*Z*): white amorphous, 11.7 mg, 12%, R_f = 0.40, EtOAc/hex = 3/7.
^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.66 (d, *J* = 9.2 Hz, 1H), 7.61 (d, *J* = 7.6 Hz, 1H), 7.48 (d, *J* = 7.6 Hz, 1H), 7.32-7.17 (m, 6H), 7.16-7.10 (m, 1H), 6.85-6.76 (m, 3H), 5.53 (dd, *J* = 11.2, 10.4 Hz, 1H), 4.63 (dd, *J* = 8.8, 4.8 Hz, 1H), 4.13 (t, *J* = 9.6 Hz, 1H), 3.72(s, 3H), 1.96 (d, *J* = 5.2 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 159.8, 137.5, 136.70, 136.68, 134.3, 132.8, 130.7, 128.63, 128.60, 127.44, 127.35, 126.2, 126.04, 125.46, 123.2, 114.2, 113.1, 72.5, 55.4, 46.7; IR (ATR, cm^{-1}) 3397, 3056, 2918, 2848, 1600, 1588, 1563, 1227, 1001.

***syn*-2-Methoxy-10-[(*Z*)-2-phenylethenyl]-9,10-dihydrophenanthren-9-ol (*syn*-(*E*)-2o)**

^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.67 (d, *J* = 8.0 Hz, 1H), 7.32-7.17 (m, 7H), 7.16-7.10 (m, 2H), 6.85-6.76 (m, 3H), 5.89 (t, *J* = 10.8 Hz, 1H), 4.67 (dd, *J* = 8.0, 3.6 Hz, 1H), 4.13 (t, *J* = 9.6 Hz, 1H), 3.72(s, 3H), 1.68 (d, *J* = 5.2 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 159.9, 137.3, 137.0, 136.65, 133.5, 133.0, 129.1, 129.0, 128.55, 128.48, 127.31, 127.26, 126.01, 125.50, 123.5, 114.6, 113.0, 71.9, 55.4, 44.2; HRMS (ESI-TOF) *m/z*: $[M\text{-}OH]^+$ Calcd for $C_{23}H_{19}O^+$: 311.1341, found: 311.1432.

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Supplementary Material

Copies of ^{1}H NMR and ^{13}C NMR spectra of synthesized compounds are available in the supplementary material file associated with this manuscript.

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