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An efficient one-pot approach to phenanthrene derivatives using a catalyzed tandem Ullmann-pinacol coupling reaction

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ABSTRACT

In the presence of catalyst $(Ph_3P)_2NiCl_2$ and reductant Zn, the Ullmann reactions of *ortho*-halo aryl aldehydes generate biaryl-dialdehydes and zinc halides. Subsequently, ZnX_2 can catalyze the intramolecular pinacol coupling reaction of biaryl-dialdehydes to form 9,10-dihydrophenanthrene-9,10-diols. One-pot synthesis of 9-phenanthrols can be achieved using this strategy.

1. Introduction

The phenanthrenes constitute a significant class of organic compounds abundantly distributed in nature.[1] They are useful intermediates for natural product synthesis[2] and exhibit a broad spectrum of biological activities such as antimalarial,[3] anticancer,[4] anti-HIV,[5] antimicrobial,[1f,6] and emetic activity.[7] These compounds also serve as a common structural motif in materials science based on their photochemical, photoconducting, optoelectrical, and electroluminescent properties.[8] For the last several decades, numerous methods have been developed for the construction of phenanthrene derivatives,[2] such as the photochemical cyclizations of stilbenes,[9] the radical cyclizations,[10] the Pd-catalyzed cocyclizations of arynes with alkenes or alkynes,[11] the metal-catalyzed cycloaddition of 2,2′-dihalobiphenyl with alkynes,[12] and the carbocyclization of alkynylated biaryl derivatives,[13] a *o*-metalation followed by a catalyzed cyclization,[1d] the McMurry coupling,[14] the ring-closing metathesis,[15] and the base-mediated condensations.[16] Besides these, facile one-pot approaches have been realized via a Suzuki–Miyaura coupling/aldol condensation cascade reaction,[17] or the tandem Ullmann-pinacol couplings developed by our group and Scherf's group independently.[18] In the preliminary letter, we have reported that *o*-carbonyl aryl halides can be coupled to form *trans*-9,10-dihydrophenanthrene-9,10-diols (phenanthrenediols) by a one-pot method, using $(Ph_3P)_2NiCl_2$ as a catalyst and zinc powder as a reductant, but this tandem sequence failed when the benzaldehydes bearing electron-donating substituents.[18a] It is meaningful to overcome this shortcoming, because most of the natural phenanthrenes are electron-rich. In this paper, we present our continuous research on this tandem Ullmann-pinacol coupling and its applications to the reactions of electron-rich benzaldehydes. We also constructed 9-phenanthrols using this one-pot method.

2. Results and discussion

Numerous Lewis acids, served as catalyst in many chemical transformations, are metal salts. However, these salts generated in reactions are usually discarded as wastes and in fact they can be reused into a lot of synthetic reactions. Can the salt engendered in the reaction in situ catalyze a subsequent reaction? To the best of our knowledge, there is no example on this strategy although other types of 'one-pot' reactions have been reported extensively in the literature.[19] We noted that the metal halides produced from the Ullmann reactions[20] of aryl halides are promoters for the pinacol couplings[21] (Scheme 1), which we have focused on for a long time.[22]

Envisioning a tandem Ullmann-pinacol could be achieved, the homocoupling experiment of *o*-bromobenzaldehyde (**1a**) was firstly investigated under the classical Ullmann reaction conditions[23] with some modifications (Table 1).

As expected, the reaction of **1a** catalyzed by $(Ph_3P)_2NiCl_2$ led to phenanthrenediol **3a** in good yield (Table 1, entry 1). The influences of the amount of zinc power and reaction temperature were then investigated. As shown above, more reductant and higher reaction

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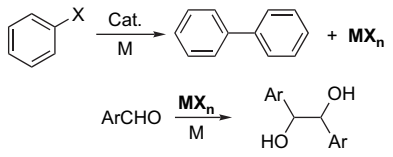
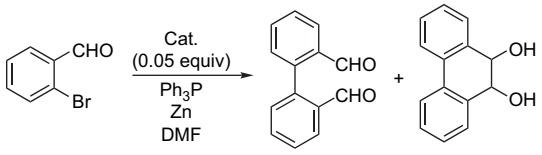


Scheme 1. MX_n produced from Ullmann reaction is a promoter for pinacol coupling.

temperature were not beneficial, but less zinc powder and lower temperature seriously retarded the reaction (Table 1, entries 2–5). The stoichiometry of triphenylphosphine was also investigated. The results suggested that this ligand had few influence on this tandem reaction although the reaction time should be prolonged to 7 h if no additional ligand was added (Table 1, entry 6). Finally, the reaction catalyzed by palladium complex was examined, but the yield of **3a** was inferior to that done by zinc salt (Table 1, entry 7).

Table 1
Coupling reactions of *o*-bromobenzaldehyde[a]

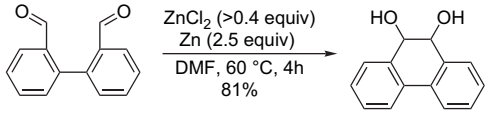


1a **2** **3a**

Entry	PPh_3 (equiv)	Zn (equiv)	Temp (°C)	Time (h)	Yield of **2**[b] (%)	Yield of **3a**[b] (%)
1	0.28	3	60	5	—[c]	81
2	0.28	3	70	5	—[c]	81
3	0.28	3	50	10	38	34
4	0.28	2	60	10	25	62
5	0.28	4	60	5	—[c]	84
6	—	3	60	7	—[c]	81
7[d]	—	3	60	7	—[c]	59

[a] Reaction conditions: $(Ph_3P)_2NiCl_2$ (0.05 equiv), PPh_3, Zn and *o*-bromobenzaldehyde were stirred in dry DMF (0.15 ml) under N_2 atmosphere.
[b] Isolated yield.
[c] Not obtained.
[d] $Pd(PPh_3)_4$ was used instead of $(Ph_3P)_2NiCl_2$, benzaldehyde was isolated with 38% yield.

To support our hypothesis of the reaction mechanism, the reaction of biphenyl-2,2′-dialdehyde (**2**) was conducted under the similar conditions to 2-bromobenzaldehyde. But dialdehyde **2** was recovered completely and no diol product was obtained. On the other hand, the dialdehyde **2** was smoothly converted to phenanthrenediol **3a** catalyzed by $ZnCl_2$ (Scheme 2).



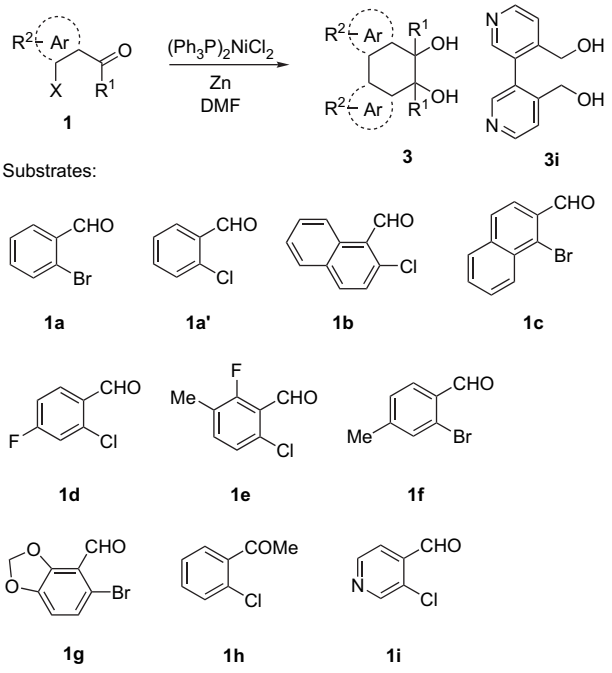
2 **3a**

Scheme 2.

We then investigated the reactions of many *ortho*-carbonyl-substituted aryl halides (Table 2).

Comparable yield of phenanthrenediol was obtained when the bromide **1a** was replaced with the less reactive chloride **1a′** though the reaction time was longer (Table 2. entries 1 and 2). In the case of naphthalene derivatives **1b** and **1c**, the cascade reaction also proceeded smoothly (Table 2. entries 3 and 4). Other substituted *o*-halobenzaldehyes were also investigated. For electron-poor **1d**, the reaction was carried out smoothly (Table 2, entry 5). The

Table 2
Scope of the $(Ph_3P)_2NiCl_2$-catalyzed tandem Ullmann-pinacol coupling[a]



1 **3** **3i**

1a **1a'** **1b** **1c**

1d **1e** **1f**

1g **1h** **1i**

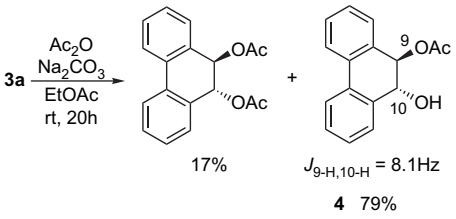
Entry	Substrate	Time (h)	Temp (°C)	Product	Yield[b] (%)
1	**1a**	7	60	**3a**	81
2	**1a′**	10	60	**3a**	76
3	**1b**	12	60	**3b**	71
4	**1c**	9	60	**3c**	63
5	**1d**	12	60	**3d**	73
6	**1e**	12	70	**3e**	79
7[c]	**1f**	12	70	**3f**	70
8[c]	**1g**	15	70	**3g**	77
9	**1h**	24	60	**3h**[d]	19
10	**1i**	12	60	**3i**	45

[a] Reaction conditions: $(Ph_3P)_2NiCl_2$ (0.05 equiv), Zn (3 equiv), and aldehyde (0.3 mmol) were stirred in dry DMF (0.15 ml) under N_2 atmosphere.
[b] Isolated yield.
[c] $(Ph_3P)_2NiCl_2$ (0.1 equiv) was used.
[d] The main product was 1,1′-(biphenyl-2,2′-diyl)diethanone (54% yield).

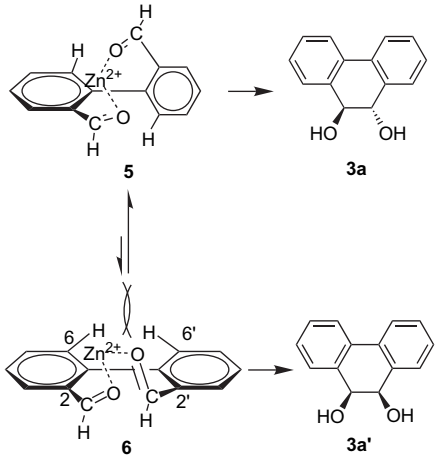
reaction temperature should be raised to 70 °C if there were electron-donating groups on the phenyl group (Table 2, entries 6–8). The necessity of raising the reaction temperature might result from the low reactivities of the electron-rich benzaldehydes in the pinacol couplings. For example, if the reaction of **1g** was conducted at 60 °C, no diol **3g** was obtained even the reaction time was prolonged to 24 h; the main product was the dialdehyde intermediate. When the reaction temperature was raised to 70 °C, the reactivity of this dialdehyde intermediate was greatly increased, which led to diol product **3g** with a good yield. For ketone **1h**, the yield of diol **3h** was low (Table 2. entry 9), presumably because of the lower reactivity of ketone and the increased steric hindrance of the methyl groups that was an obstacle to the subsequent pinacol reaction. When heterocyclic **1i** was examined, a consecutive Ullmann reaction/reduction occurred instead of an Ullmann-pinacol coupling (Table 2, entry 10).

Interestingly, all the phenanthrenediols were obtained stereoselectively. A trans-structure of **3a** was further determined by its monoacetate (Scheme 3).

The coupling constant of the two benzylic hydrogens in the central ring is 8.1 Hz for our product **4**, *trans*-10-hydroxy-9,10-dihydrophenanthren-9-yl acetate, and 3.8 Hz for its cis-counterpart.[24]



Scheme 3. Monoacetate phenanthrenediol **3a**.

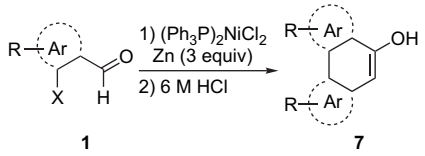


Scheme 4. Possible reaction mechanism about the trans-selectivity.

A possible reaction mechanism of this trans-selectivity is illustrated in Scheme 4.

We assumed that both the carbonyls should coordinate to Zn^{2+} to form an intermediate like **5** or **6** in the reaction. This coordination would bring the two carbonyls together and lead to a subsequent intramolecular coupling. However, in the reaction of heterocyclic **1i**, the co-coordination of Zn^{2+} with both carbonyls might be disturbed by the nitrogen atoms on the heterocycles, and no pinacol product was obtained. Among two transition states, **5** would be more favorable. Because the two phenyls would have to be nearly coplanar to form the alternative intermediate **6**, in which severe steric hindrance between the hydrogens at the 6- and 6′-position would be present. Therefore a diastereoselective reaction to **3a** was achieved.

Table 3
One-pot syntheses of 9-phenanthrols[a]



Entry	Substrate	Product	Yield[b] (%)
1	**1a**	**7a**	56
2	**1b**	**7b**	63
3	**1c**	**7c**	—[c]
4	**1d**	**7d**	70
5	**1e**	**7e**	90
6	**1f**	**7f**	50
7	**1g**	**7g**	32

[a] Reaction conditions: after the reactions of Ullmann-pinacol couplings were completed (Table 2, footnote a), the mixtures were cooled with ice bath following addition of 1.2 ml of 6 M HCl, then the reactions were heated at 100 °C for 2 h under N_2 atmosphere.
[b] Isolated yield.
[c] Pure product was not obtained.

As an application, the one-pot approach to 9-phenanthrols can be easily achieved using this tandem reaction followed by dehydration under acidic conditions (Table 3).

9-Phenanthrols are key intermediates in the synthesis of some natural products, such as gymnopusin[1d] and steganone.[25] But tedious steps are usually required to prepare these compounds.[26] Apparently, phenanthrenediols can be dehydrated to furnish 9-phenanthrols under acidic conditions. We added hydrochloric acid to the mixtures when the conversions to diols were completed. After preliminary investigation, we found that 6 M HCl was suitable, because less concentrated hydrochloric acid leads to incomplete reaction and higher concentration of acid makes the reaction too drastic. In this way, 9-phenanthrols were easily synthesized from the *o*-halobenzaldehydes in one-pot.

3. Conclusion

In summary, we have developed a tandem $(Ph_3P)_2NiCl_2$-catalyzed Ullmann reaction/ZnX_2-mediated pinacol coupling. This is an unprecedented tandem catalysis, in which the catalyst of the sequential step is a salt produced in situ in the previous step. Phenanthrenediols and 9-phenanthrols can be conveniently constructed by this one-pot method using this cascade coupling. These facile approaches to phenanthrenes would be expected to provide important references to synthetic chemistry, pharmaceutical, and materials science.

4. Experimental section

4.1. General

All reactions were conducted in oven-dried glassware. NMR spectra were measured on a Bruker 300 MHz spectrometer. Chemical shifts were reported in parts per million relative to internal tetramethylsilane. High resolution mass spectroscopy (HRMS) was performed on a Micromass GCT mass spectrometer. Column chromatography was carried out on silica gel (200–400 mesh) using petroleum ether (60–90 °C) and EtOAc as eluents. Compounds **1b**[27] and **1c**[28] were prepared according to the procedures described in the literature. All solvents were purified before use. Other reagents were purchased from vendors and used without further purification. N_2 was used without further purification.

4.2. Synthesis of phenanthrenediols (3a–i): general procedures

$(Ph_3P)_2NiCl_2$ (10 mg, 0.015 mmol), zinc powder (59 mg, 0.90 mmol), and the aldehyde (0.3 mmol) were stirred in DMF (0.15 ml) at 60 °C or 70 °C under N_2 atmosphere for the time indicated in Table 2. The reaction was quenched with ice bath; the mixture was diluted with 2 ml 1 M HCl and 5 ml CH_2Cl_2. The mixture was stirred for several minutes, and then filtered to remove the unreacted zinc powder. The phases were separated and the aqueous phase was extracted twice with CH_2Cl_2. The combined organic extracts were dried over $MgSO_4$ and concentrated. Purification of the residue by column chromatography gave the products.

*4.2.1. 9,10-Dihydrophenanthrene-9,10-diol[29] (**3a**)*

Yield: 81%. ^1H NMR (300 MHz, $CDCl_3$): δ 7.76 (dd, J=6.2, 2.8 Hz, 2H), 7.67 (dd, J=9.4, 3.1 Hz, 2H), 7.42–7.36 (m, 4H), 4.76 (s, 2H), 1.65 (br, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 136.2, 132.6, 128.6, 128.5, 125.3, 123.9, 74.2. HRMS calcd for $C_{14}H_{12}O_2$ (M^+) 212.0837, found 212.0838.

*4.2.2. 13,14-Dihydropicene-13,14-diol (**3b**)*

Yield: 71%. ^{1}H NMR (300 MHz, acetone-d_6): δ 8.41 (d, J=8.4 Hz, 2H), 8.21 (d, J=8.7 Hz, 2H), 8.02 (d, J=8.7 Hz, 2H), 7.95 (d, J=7.8 Hz, 2H), 7.64–7.51 (m, 4H), 5.69 (s, 2H), 3.13 (s, 2H). ^{13}C NMR (75 MHz, acetone-d_6): δ 134.3, 133.9, 132.1, 131.5, 129.8, 129.2, 127.5, 126.6, 124.8, 123.5, 67.9. HRMS calcd for $C_{22}H_{16}O_2$ (M^+) 312.1150, found 312.1148.

*4.2.3. 3,4-Dihydro-dibenzo[c,g]phenanthrene-3,4-diol[30] (**3c**)*

Yield: 63%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.00 (d, J=8.4 Hz, 2H), 7.95–7.91 (m, 4H), 7.56 (d, J=8.4 Hz, 2H), 7.46 (t, J=7.5 Hz, 2H), 7.27 (t, J=6.6 Hz, 2H), 4.73 (s, 2H), 2.61 (br, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 136.2, 133.8, 130.2, 129.1, 129.1, 128.5, 127.6, 125.6, 125.4, 121.4, 75.0. HRMS calcd for $C_{22}H_{16}O_2$ (M^+) 312.1150, found 312.1157.

*4.2.4. 3,6-Difluoro-9,10-dihydrophenanthrene-9,10-diol (**3d**)*

Yield: 73%. ^{1}H NMR (300 MHz, acetone-d_6): δ 7.71 (dd, J=8.4, 6.0 Hz, 2H), 7.60 (dd, J=10.3, 2.5 Hz, 2H), 7.13 (td, J=8.6, 2.5 Hz, 2H), 4.60 (s, 2H), 3.12 (s, 2H). ^{13}C NMR (75 MHz, acetone-d_6): δ 163.7 (d, J=241.0 Hz), 135.1 (d, J=2.9 Hz), 134.7 (dd, J=8.0, 2.3 Hz), 129.0 (d, J=8.4 Hz), 115.6 (d, J=21.5 Hz), 111.2 (d, J=23.1 Hz), 73.4. HRMS calcd for $C_{14}H_{10}O_2F_2$ (M^+) 248.0649, found 248.0654.

*4.2.5. 1,8-Difluoro-2,7-dimethyl-9,10-dihydrophenanthrene-9,10-diol (**3e**)*

Yield: 79%. ^{1}H NMR (300 MHz, acetone-d_6): δ 7.51 (d, J=8.1 Hz, 2H), 7.24 (t, J=7.8 Hz, 2H), 5.04 (s, 2H), 3.04 (s, 2H), 2.27 (s, 6H). ^{13}C NMR (75 MHz, acetone-d_6): δ 160.9 (d, J=244.2 Hz), 133.6, 131.8 (d, J=5.6 Hz), 125.7 (d, J=18.6 Hz), 123.3 (d, J=13.7 Hz), 120.2 (d, J=2.9 Hz), 67.4, 14.6 (d, J=4.2 Hz). HRMS calcd for $C_{16}H_{14}O_2F_2$ (M^+) 276.0962, found 276.0966.

*4.2.6. 3,6-Dimethyl-9,10-dihydrophenanthrene-9,10-diol (**3f**)*

Yield: 63%. ^{1}H NMR (300 MHz, acetone-d_6): δ 7.62 (s, 2H), 7.56 (d, J=7.8 Hz, 2H), 7.14 (d, J=7.2 Hz, 2H), 4.55 (s, 2H), 3.03 (s, 2H), 2.37 (s, 6H). ^{13}C NMR (75 MHz, acetone-d_6): δ 137.9, 136.0, 133.4, 129.2, 126.5, 124.7, 74.1, 21.3. HRMS calcd for $C_{16}H_{16}O_2$ (M^+) 240.1150, found 240.1152.

*4.2.7. 11,12-Dihydro-1,3,8,10-tetraoxa-dicyclopenta-[a,i]phenanthrene-11,12-diol (**3g**)*

Yield: 77%. ^{1}H NMR (300 MHz, acetone-d_6): δ 7.30 (d, J=8.4 Hz, 2H), 6.82 (d, J=8.1 Hz, 2H), 6.03 (s, 4H), 4.99 (s, 2H), 3.04 (s, 2H). ^{13}C NMR (75 MHz, acetone-d_6): δ 148.1, 147.6, 128.5, 118.4, 117.6, 108.7, 102.3, 65.4. HRMS calcd for $C_{16}H_{12}O_6$ (M^+) 300.0634, found 300.0640.

*4.2.8. 9,10-Dimethyl-9,10-dihydrophenanthrene-9,10-diol (**3h**)*

Yield: 19%. ^{1}H NMR (300 MHz, acetone-d_6): δ 7.78–7.72 (m, 4H), 7.34–7.29 (m, 4H), 3.04 (s, 2H), 1.24 (s, 6H). ^{13}C NMR (75 MHz, acetone-d_6): δ 144.8, 132.7, 128.8, 128.0, 125.1, 124.0, 77.3, 25.0. HRMS calcd for $C_{16}H_{16}O_2$ (M^+) 240.1150, found 240.1153.

*4.2.9. 3,3′-Bipyridine-4,4′-diyldimethanol (**3i**)*

Yield: 45%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.48 (s, 4H), 7.55 (d, J=4.5 Hz, 2H), 4.81 (s, 4H), 2.96 (br, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 148.7, 148.1, 147.8, 129.8, 122.1, 61.3. HRMS calcd for $C_{12}H_{12}N_2O_2$ (M^+) 216.0899, found 216.0897.

4.3. Synthesis of *trans*-10-hydroxy-9,10-dihydrophenanthren-9-yl acetate (4)

To a suspension of **3a** (11 mg, 0.05 mmol) and Na_2CO_3 (16 mg, 0.15 mmol) in EtOAc (0.5 ml), Ac_2O (14 μl, 0.15 mmol) was added at room temperature. After the reaction was completed (monitored by TLC), the mixture was poured into 2 ml of cold H_2O and the phases were separated. The aqueous phase was extracted with EtOAc. The combined organic extracts were dried and concentrated. Purification of the residue by flash chromatography gave **4** (10 mg, 0.04 mmol, 79% yield) as white solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.75 (m, 2H), 7.55 (d, J=7.2 Hz, 1H), 7.41–7.22 (m, 5H), 6.02 (d, J=8.1 Hz, 1H), 4.82 (d, J=8.1 Hz, 1H), 2.48 (s, 1H), 2.11 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.3, 135.5, 133.1, 132.3, 132.0, 129.2, 128.9, 128.5, 128.1, 127.6, 127.1, 123.9, 123.8, 74.5, 71.1, 21.1. HRMS calcd for $C_{16}H_{14}O_3$ (M^+) 254.0943, found 254.0949.

4.4. Synthesis of 9-phenanthrols (7a–g): general procedure

$(Ph_3P)_2NiCl_2$ (10 mg, 0.015 mmol), zinc powder (59 mg, 0.90 mmol), and the aldehyde (0.3 mmol) were stirred in DMF (0.15 ml) at 60 °C or 70 °C under N_2 atmosphere for the time indicated in Table 2. The mixture was quenched by an ice bath, 1.2 ml 6 M HCl was added. The reaction was then continued at 100 °C for 2 h under N_2 atmosphere. Conventional work-up led to the 9-phenanthrols.

*4.4.1. Phenanthren-9-ol[31] (**7a**)*

Yield: 56%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.68 (d, J=7.8 Hz, 1H), 8.61 (dd, J=7.8, 1.8 Hz, 1H), 8.32 (d, J=8.4 Hz, 1H), 7.73–7.63 (m, 3H), 7.56–7.48 (m, 2H), 7.03 (s, 1H), 5.28 (br, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 149.9, 132.8, 130.3, 128.8, 128.7, 127.2, 127.0, 126.9, 126.4, 124.2, 122.8, 122.7, 122.6, 106.2. HRMS calcd for $C_{14}H_{10}O$ (M^+) 194.0732, found 194.0728.

*4.4.2. Picen-13-ol (**7b**)*

Yield: 63%. ^{1}H NMR (300 MHz, acetone-d_6): δ 10.07 (d, J=8.4 Hz, 1H), 8.90 (d, J=9.0 Hz, 1H), 8.80–8.75 (m, 2H), 8.54 (s, 1H), 8.10–7.99 (m, 3H), 7.88 (d, J=9.0 Hz, 1H), 7.73–7.62 (m, 4H). ^{13}C NMR (75 MHz, acetone-d_6): δ 156.3, 154.6, 133.5, 133.3, 132.2, 131.7, 130.7, 130.1, 130.0, 129.4, 129.2, 128.9, 127.5, 127.2, 126.9, 125.2, 124.0, 123.7, 122.7, 122.6, 121.2, 106.3. HRMS calcd for $C_{22}H_{14}O$ (M^+) 294.1045, found 294.1048.

*4.4.3. 3,6-Difluorophenanthren-9-ol (**7d**)*

Yield: 70%. ^{1}H NMR (300 MHz, acetone-d_6): δ 8.44–8.36 (m, 2H), 8.30 (dd, J=11.1, 2.1 Hz, 1H), 7.79–7.72 (m, 1H), 7.48 (td, J=8.6, 2.2 Hz, 1H), 7.35 (td, J=8.6, 2.4 Hz, 1H), 7.15 (s, 1H), 3.41 (br, 1H). ^{13}C NMR (75 MHz, acetone-d_6): δ 162.1 (d, J=242.8 Hz), 159.9 (d, J=238.7 Hz), 150.6, 132.8 (d, J=8.2 Hz), 130.9, 128.8 (d, J=8.2 Hz), 126.6, 125.7 (d, J=8.9 Hz), 123.7, 117.1 (d, J=22.4 Hz), 116.3 (d, J=23.7 Hz), 115.5 (d, J=23.7 Hz), 111.6 (d, J=25.1 Hz), 108.1 (dd, J=22.4, 9.1 Hz), 104.2. HRMS calcd for $C_{14}H_8OF_2$ (M^+) 230.0543, found 230.0545.

*4.4.4. 1,8-Difluoro-2,7-dimethylphenanthren-9-ol (**7e**)*

Yield: 90%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.17 (d, J=8.4 Hz, 1H), 8.01 (d, J=8.4 Hz, 1H), 7.35–7.30 (m, 2H), 7.22–7.11 (m, 1H), 7.01 (s, 1H), 2.40 (s, 3H), 2.39 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 157.7 (d, J=237.5 Hz), 156.0 (d, J=245.2 Hz), 149.2, 133.9 (d, J=19.4 Hz), 132.0, 129.9 (d, J=6.8 Hz), 128.6 (d, J=6.8 Hz), 126.9 (d, J=5.0 Hz), 122.7 (d, J=16.4 Hz), 121.4 (dd, J=33.2, 17.8 Hz), 119.4 (d, J=3.2 Hz), 117.8 (d, J=3.7 Hz), 114.0 (d, J=6.3 Hz), 101.4 (d, J=6.2 Hz), 14.5 (d, J=3.3 Hz), 14.3 (d, J=6.2 Hz). HRMS calcd for $C_{16}H_{12}OF_2$ (M^+) 258.0856, found 258.0862.

*4.4.5. 3,6-Dimethylphenanthren-9-ol (**7f**)*

Yield: 50%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.42 (s, 1H), 8.35 (s, 1H), 8.16 (d, J=8.4 Hz, 1H), 7.53 (d, J=8.1 Hz, 1H), 7.43 (d, J=8.1 Hz, 1H), 7.32 (d, J=7.8 Hz, 1H), 6.86 (s, 1H), 5.44 (s, 1H), 2.60 (s, 3H), 2.56 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 149.1, 136.8, 133.6, 131.5, 130.9, 129.8, 129.8, 128.6, 128.1, 126.7, 123.8, 122.6, 122.5, 122.3, 22.2, 22.0. HRMS calcd for $C_{16}H_{14}O$ (M^+) 222.1045, found 222.1046.

*4.4.6. 1,3,8,10-Tetraoxa-dicyclopenta[a,i]phenanthren-11-ol (**7g**)*

Yield: 32%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.08 (d, J=9.0 Hz, 1H), 7.94 (d, J=8.7 Hz, 1H), 7.21 (d, J=8.7 Hz, 1H), 7.05–6.98 (m, 2H), 6.20 (s, 2H), 6.13 (s, 2H), 6.00 (br, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 149.0, 144.8, 144.4, 142.0, 141.2, 128.2, 122.2, 118.3, 117.5, 116.5, 116.2, 110.2, 107.0, 102.1, 101.7, 99.7. HRMS calcd for $C_{16}H_{10}O_5$ (M^+) 282.0528, found 282.0528.

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