

## ***Supporting Information***

# **Microwave Promoted Radical Addition/Cyclization of Biaryl Vinyl Ketones with Diacyl Peroxides in Water Under Metal-Free Conditions**

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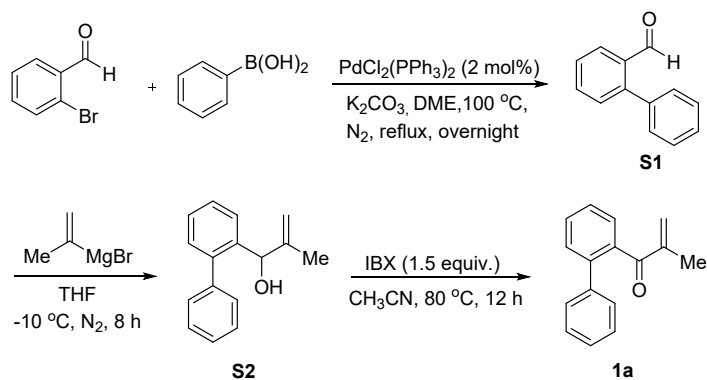
## 1. General information

All materials were obtained from commercial suppliers or prepared according to standard procedures in literature unless otherwise noted. Analytical thin layer chromatography (TLC) was performed on precoated silica gel 60 F<sub>254</sub> plates, and compounds were visualized by exposure to UV light. Flash column chromatography was performed with silica gel (300-400 meshes). NMR spectra were recorded on a 600 MHz spectrometer at ambient temperature, and chemical shifts were given in dimensionless  $\delta$  values and were frequency referenced relative to TMS in <sup>1</sup>H, <sup>13</sup>C and <sup>19</sup>F NMR spectroscopy. The peak patterns are indicated as follows: **s**, singlet; **d**, doublet; **t**, triplet; **q**, quartet; **m**, multiplet; **td**, triplet of doublet; **dd**, doublet of doublet. The coupling constants, *J*, are reported in Hertz (Hz). HRMS data were recorded on a Thermo scientific Q exactive and Agilent technologies 6540 UHD ESI-TOF mass spectrometer. All MW reactions were carried out under microwave irradiation conditions and air atmosphere in a Discover SP (CEM) microwave reactor.



## 2. Experimental section

### 2.1 General procedure to prepare 1a



**The synthesis of compound S1:** Under N<sub>2</sub> atmosphere, a flame-dried 250 mL round-bottom flask was charged with phenylboronic acid (1.2 equiv., 2.60 g, 19.2 mmol), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (0.02 equiv., 0.224 g, 0.32 mmol) and K<sub>2</sub>CO<sub>3</sub> (2.0 equiv., 4.42 g, 32 mmol) in dry DME (20 mL). And then 2-bromobenzaldehyde (2.96 g, 16 mmol) was added and the mixture was kept for stirring in a preheated oil bath at 100 °C for 12 h. The organic phase was separated and the aqueous phase was extracted with EtOAc (15 mL × 3). The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and evaporated under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 50:1) to afford the product **S1** in 91% yield as a white solid.

**The synthesis of compound S2:** A solution of **S1** (2.7 g, 15.0 mmol) in anhydrous THF (15 mL) was cooled to -10 °C under nitrogen atmosphere. Isopropenyl magnesium bromide (15 mL, 15.0 mmol, 1.0 mol/L) was added and the resulting mixture was stirred over 8 h. The reaction mixture was quenched with saturated ammonium chloride (10 mL), followed by extraction with EtOAc (3×15 mL). The combined organic extracts were washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub> filtered and concentrated. The residue was purified by silica gel column chromatography (petroleum ether: ethyl acetate = 20:1) to give the product as a yellow oil (72% yield).

**The synthesis of compound 1a:** To an oven-dried round-bottom flask **S2** (2.24 g, 10.0 mmol), IBX (1.5 equiv., 4.2 g, 15.0 mmol) and CH<sub>3</sub>CN (30 mL) were added. The reaction mixture was stirred at 80 °C for 12 h. Concentration of the reaction mixture in vacuo followed by silica gel chromatography eluting with petroleum ether: ethyl acetate = 9:1 (V/V) afforded the product **1a** as a white solid (92% yield).

## 2.2 General procedure to prepare diacyl peroxide

### 2.2.1 Preparation of aryl diacyl peroxides<sup>1</sup>

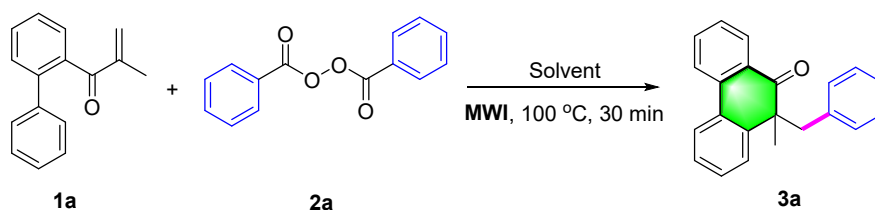
In a round-bottomed flask, the solution of aryl acid chloride (30 mmol) in diethyl ether (7 mL) was cooled to 0 °C in an ice-bath. Then, hydrogen peroxide (1.669 g, 35 wt.% in H<sub>2</sub>O, 17.2 mmol) was added dropwise over 10 minutes to the cold solution. Then an aqueous solution of NaOH (1.517 g, 37.9 mmol, dissolved in 10 mL of water) was added dropwise over 20 minutes. The resulting white precipitate was collected by filtration. After washing with water (3×5 mL) and diethyl ether (3×5 mL), the solid was crystallized from a cold acetone/water mixture (v/v = 1/3) to give the pure aryl peroxide.

## 2.2.2 Preparation of alkyl diacyl peroxides<sup>2</sup>

In a round-bottomed flask, the solution of pyridine (3.16 mL, 40 mmol) in diethyl ether (10 mL) was cooled to -10 °C in an ice-bath. Then, hydrogen peroxide (1.25 mL, 35 wt.% in H<sub>2</sub>O, 11.0 mmol) was added dropwise over 10 minutes to the cold solution. The acid chloride (20.0 mmol) was added dropwise, maintaining the temperature between -5 and -10 °C. The mixture was stirred for additional 8 hours at 0 °C and then carefully neutralized with a chilled 10% sulfuric acid solution. The reaction mixture was followed by extraction. The aqueous phase was extracted with EtOAc (10 mL × 2). The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated. The residue was purified by flash chromatography (ethyl acetate/petroleum ether = 1/20~1/15) to afford the desired product.

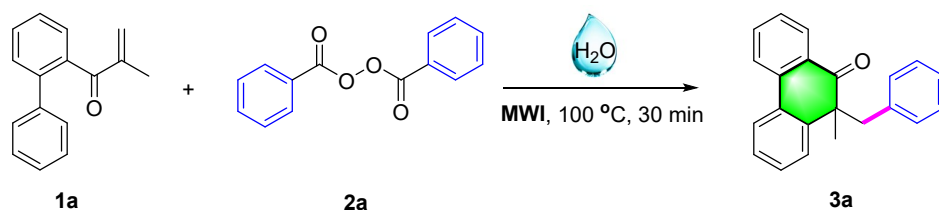
## 2.3 The optimization of reaction conditions

Table S1. Screening solvents<sup>[a]</sup>



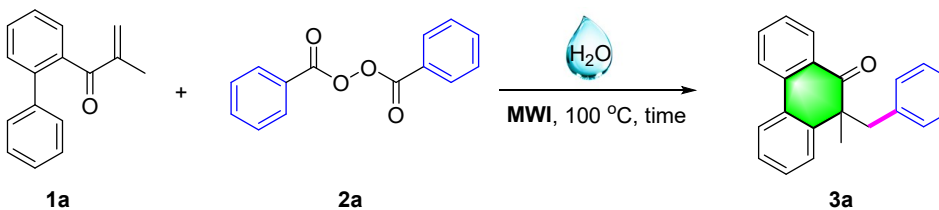
Entry	Solvent	Yield <b>3a</b> (%) <sup>[b]</sup>
1	CH <sub>3</sub> CN	59
2	Acetone	47
3	DMF	0
4	DCE	30
5	H <sub>2</sub> O	83
6 <sup>[c]</sup>	H <sub>2</sub> O	trace
7	THF	0
8	1,4-Dioxane	0
9	Toluene	0
10	EtOH	trace

<sup>[a]</sup>All reactions were carried out with **1a** (0.2 mmol), **2a** (0.3 mmol) and solvent (2 mL) at 100 °C under microwave irradiation for 30 min. <sup>[b]</sup>Isolated yield. <sup>[c]</sup>In an oil bath for 12 h.

**Table S2. Screening the loading of 2a<sup>[a]</sup>**

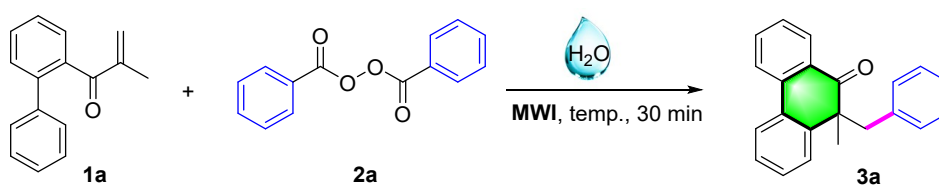
Entry	2a (x equiv.)	Yield 3a (%) <sup>[b]</sup>
1	1.0	63
2	1.5	83
3	2.0	81
4	2.5	76

<sup>[a]</sup>All reactions were carried out with **1a** (0.2 mmol), **2a** (x equiv.) and H<sub>2</sub>O (2 mL) at 100 °C under microwave irradiation for 30 min. <sup>[b]</sup>Isolated yield.

**Table S3. Screening reaction time<sup>[a]</sup>**

Entry	Time (min)	Yield 3a (%) <sup>[b]</sup>
1	25	76
2	30	83
3	35	82
4	60	80

<sup>[a]</sup>All reactions were carried out with **1a** (0.2 mmol), **2a** (0.3 mmol) and H<sub>2</sub>O (2 mL) at 100 °C under microwave irradiation. <sup>[b]</sup>Isolated yield.

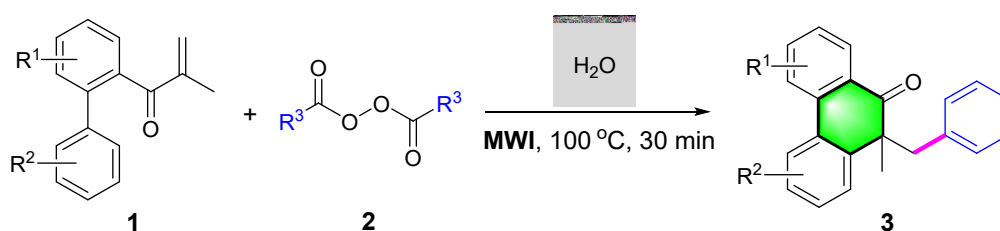
**Table S4. Screening reaction temperature<sup>[a]</sup>**

Entry	Temp. (°C)	Yield 3a (%) <sup>[b]</sup>
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1	50	41
2	70	64
3	90	80
4	100	83
5	120	72

<sup>[a]</sup>All reactions were carried out with **1a** (0.2 mmol), BPO (0.3 mmol) and H<sub>2</sub>O (2 mL) under microwave irradiation for 30 min. <sup>[b]</sup>Isolated yield.

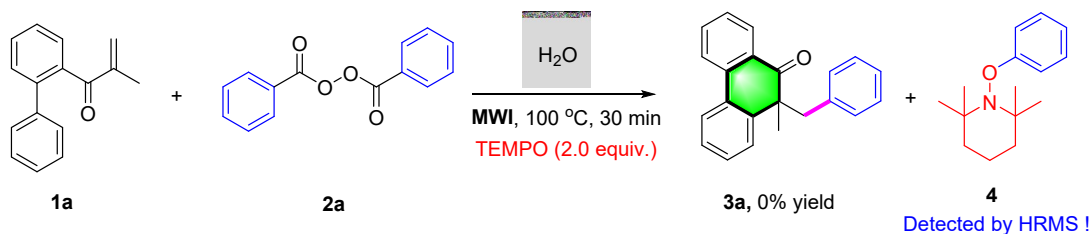
## 2.4 General procedure for the radical addition/cyclization reaction



A 10 mL oven-dried reaction vessel equipped with a magnetic stirrer bar was charged with biaryl vinyl ketone (**1**, 0.2 mmol), diacyl peroxides (**2**, 0.3 mmol) and H<sub>2</sub>O (2 mL). The reaction vessel was placed in a Discover SP (CEM) microwave reactor, and the reaction mixture was irradiated at 150 W and 100 °C for 30 min. The reaction mixture was extracted with EtOAc (10 mL × 2). The combined organic extracts were washed with brine and dried over Na<sub>2</sub>SO<sub>4</sub>. The organic solvent was removed under reduced pressure and the residue was purified by flash chromatography to give the desired product **3**.

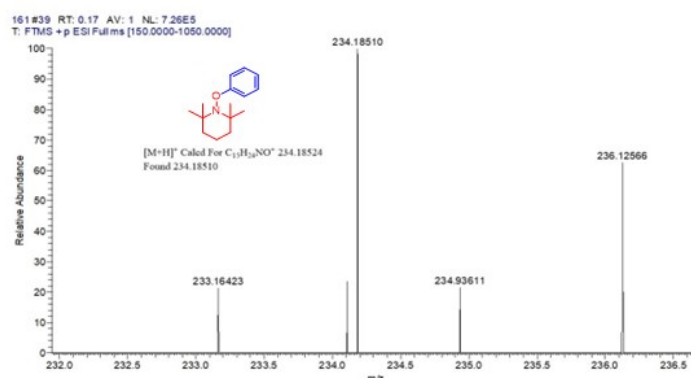
## 2.5 Mechanistic studies

### Radical Trapping experiments (Trapped with TEMPO)

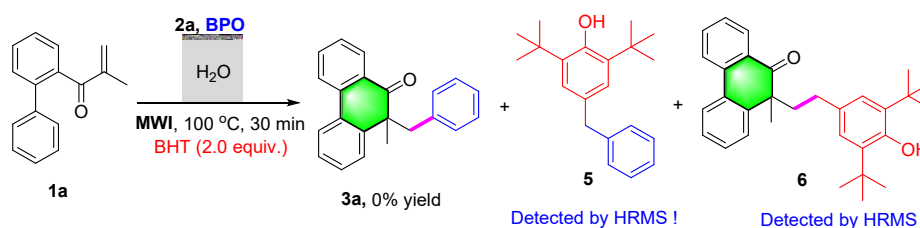


A 10 mL oven-dried reaction vessel equipped with a magnetic stirrer bar was charged with 2-methyl-1-(2-phenylphenyl)prop-2-en-1-one (**1a**, 0.2 mmol), BPO (**2a**, 0.3 mmol), TEMPO (62.5 mg, 0.4 mmol) and H<sub>2</sub>O (2 mL). The reaction vessel was placed in a Discover SP (CEM) microwave reactor, and the reaction mixture was

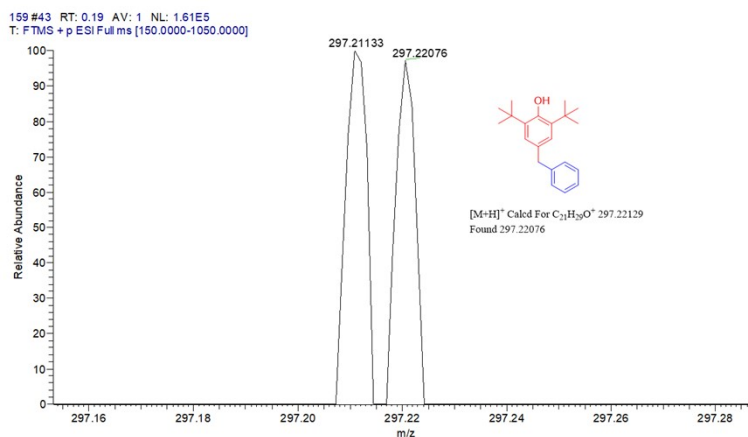
irradiated at 150 W and 100 °C for 30 min. In the reaction mixture, no desired product **3a** was detected, while an adduct of TEMPO with a phenyl radical was formed, which was detected by HRMS.

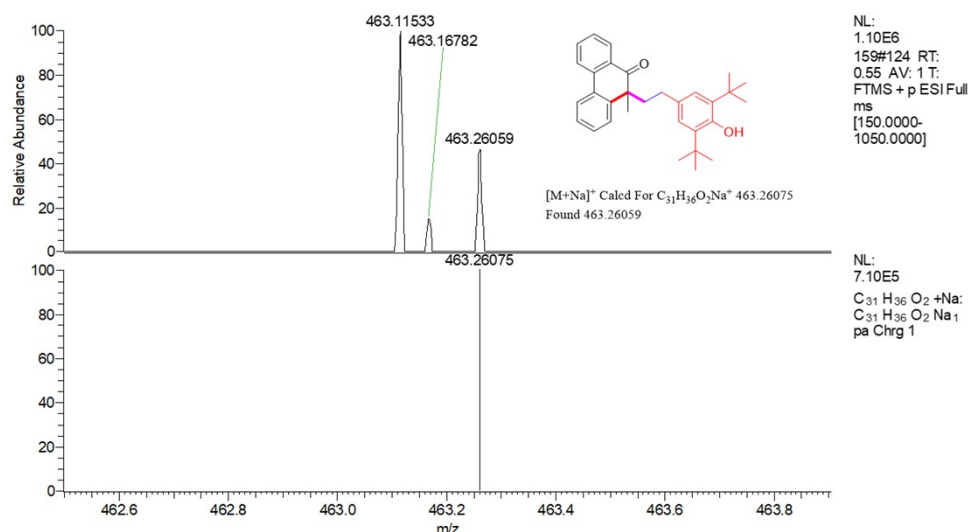


### Radical Trapping experiments (Trapped with BHT)

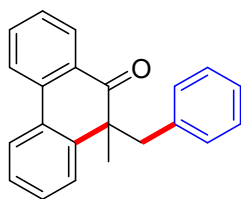


A 10 mL oven-dried reaction vessel equipped with a magnetic stirrer bar was charged with 2-methyl-1-(2-phenylphenyl)prop-2-en-1-one (**1a**, 0.2 mmol), BPO (**2a**, 0.3 mmol), BHT (88.2 mg, 0.4 mmol) and H<sub>2</sub>O (2 mL). The reaction vessel was placed in a Discover SP (CEM) microwave reactor, and the reaction mixture was irradiated at 150 W and 100 °C for 30 min. After the reaction, no **3a** was detected in the reaction mixture, while **5** and **6** were detected by HPLC/HRMS.

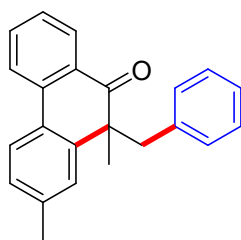




### 3. Characterization data for the products



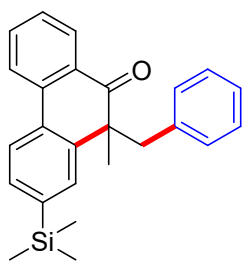
**10-Benzyl-10-methylphenanthren-9(10H)-one (3a).** Purification by column chromatography (EtOAc/PE, V/V = 1:50) afforded **3a**. Yellow oil, 48.3 mg, 81% yield.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.06 (d,  $J = 7.7$  Hz, 1H), 7.93 (d,  $J = 7.4$  Hz, 1H), 7.90 (d,  $J = 8.0$  Hz, 1H), 7.61–7.58 (m, 1H), 7.40–7.33 (m, 4H), 7.01–6.99 (m, 1H), 6.98–6.96 (m, 2H), 6.62 (d,  $J = 7.4$  Hz, 2H), 3.23 (d,  $J = 13.3$  Hz, 1H), 3.01 (d,  $J = 13.3$  Hz, 1H), 1.66 (s, 3H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$ : 202.2, 141.6, 137.0, 136.2, 134.1, 130.0, 129.9, 129.5, 128.6, 128.0, 127.6, 127.5, 127.4, 127.1, 126.3, 123.7, 122.7, 52.4, 49.5, 22.9. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd For  $\text{C}_{22}\text{H}_{19}\text{O}^+$  299.1430; Found 299.1429.



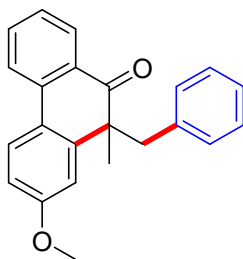
**10-Benzyl-2,10-dimethylphenanthren-9(10H)-one (3b).** Purification by column chromatography (EtOAc/PE, V/V = 1:50) afforded **3b**. Yellow oil, 51.9 mg, 83% yield.



$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.03 (d,  $J = 7.7$  Hz, 1H), 7.87 (d,  $J = 8.0$  Hz, 1H), 7.82 (d,  $J = 8.0$  Hz, 1H), 7.57 (t,  $J = 7.6$  Hz, 1H), 7.35 (t,  $J = 7.4$  Hz, 1H), 7.17 (d,  $J = 8.0$  Hz, 1H), 7.12 (s, 1H), 7.03–6.98 (m, 3H), 6.63 (d,  $J = 7.4$  Hz, 2H), 3.19 (d,  $J = 13.3$  Hz, 1H), 3.00 (d,  $J = 13.3$  Hz, 1H), 2.38 (s, 3H), 1.64 (s, 3H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$ : 202.3, 141.5, 138.5, 137.2, 136.3, 134.1, 130.0, 129.2, 129.0, 128.2, 127.9, 127.5, 127.32, 127.25, 126.3, 123.6, 122.5, 52.3, 49.5, 22.8, 21.4. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd For  $\text{C}_{23}\text{H}_{21}\text{O}^+$  313.1587; Found 313.1584.

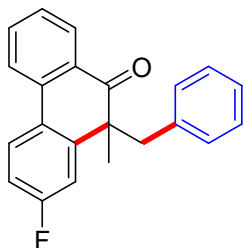


**10-Benzyl-10-methyl-2-(trimethylsilyl)phenanthren-9(10H)-one (3c).** Purification by column chromatography (EtOAc/PE, V/V = 1:50) afforded **3c**. Yellow oil, 60.7 mg, 80% yield.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.08 (dd,  $J = 7.74, 1.2$  Hz, 1H), 7.94 (d,  $J = 7.92$  Hz, 1H), 7.92 (d,  $J = 7.8$  Hz, 1H), 7.64–7.61 (m, 1H), 7.48 (dd,  $J = 7.74, 1.02$  Hz, 1H), 7.40 (t,  $J = 7.8$  Hz, 1H), 7.28 (s, 1H), 7.07–7.04 (m, 1H), 7.01 (t,  $J = 7.56$  Hz, 2H), 6.63 (d,  $J = 7.08$  Hz, 2H), 3.19 (d,  $J = 13.2$  Hz, 1H), 2.98 (d,  $J = 13.2$  Hz, 1H), 1.67 (s, 3H), 0.25 (s, 9H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$ : 202.5, 140.9, 140.0, 137.0, 136.3, 134.1, 132.7, 132.0, 130.20, 130.16, 129.4, 128.1, 127.7, 127.4, 126.3, 122.83, 122.77, 52.4, 48.9, 22.1, -1.3. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd For  $\text{C}_{25}\text{H}_{27}\text{OSi}^+$  371.1826; Found 371.1824.

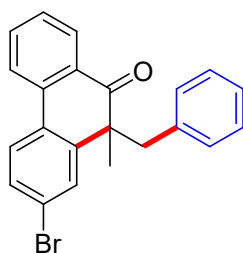


**10-Benzyl-2-methoxy-10-methylphenanthren-9(10H)-one (3d).** Purification by column chromatography (EtOAc/PE, V/V = 1:50) afforded **3d**. Yellow oil, 50.5 mg, 77% yield.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.02 (d,  $J = 7.7$  Hz, 1H), 7.85 (d,  $J = 8.8$  Hz, 1H), 7.79 (d,  $J = 8.0$  Hz, 1H), 7.55 (t,  $J = 7.6$  Hz, 1H), 7.31 (t,  $J = 7.4$  Hz, 1H), 7.03–7.00 (m,

3H), 6.89 (d,  $J = 8.7$  Hz, 1H), 6.78 (s, 1H), 6.65 (d,  $J = 7.4$  Hz, 2H), 3.78 (s, 3H), 3.19 (d,  $J = 13.3$  Hz, 1H), 2.97 (d,  $J = 13.3$  Hz, 1H), 1.62 (s, 3H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$ : 202.2, 159.8, 143.5, 137.2, 136.2, 134.2, 130.0, 128.6, 127.6, 127.4, 127.0, 126.4, 125.2, 122.9, 122.2, 113.1, 112.7, 55.3, 52.6, 49.4, 22.9. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd For  $\text{C}_{23}\text{H}_{21}\text{O}_2^+$  329.1536; Found 329.1537.

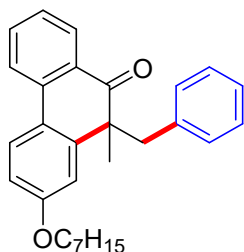


**10-Benzyl-2-fluoro-10-methylphenanthren-9(10H)-one (3e).** Purification by column chromatography (EtOAc/PE, V/V = 1:50) afforded **3e**. Yellow oil, 43.6 mg, 69% yield.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.04 (d,  $J = 7.7$  Hz, 1H), 7.90–7.88 (m, 1H), 7.79 (d,  $J = 8.0$  Hz, 1H), 7.58 (t,  $J = 7.6$  Hz, 1H), 7.38–7.36 (m, 1H), 7.07–7.04 (m, 1H), 7.02–6.97 (m, 4H), 6.62 (d,  $J = 7.5$  Hz, 2H), 3.22 (d,  $J = 13.3$  Hz, 1H), 2.96 (d,  $J = 13.3$  Hz, 1H), 1.63 (s, 3H).  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ )  $\delta$ : -112.5.  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$ : 201.5, 162.9 (d,  $J_{\text{C-F}} = 247.1$  Hz), 144.3 (d,  $J_{\text{C-F}} = 7.3$  Hz), 136.3, 135.7, 134.3, 129.9, 129.0, 127.9, 127.7, 127.5, 126.5, 125.6 (d,  $J_{\text{C-F}} = 8.6$  Hz), 122.6, 114.5, 114.4 (d,  $J_{\text{C-F}} = 4.2$  Hz), 114.3, 52.5, 49.5, 22.9. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd For  $\text{C}_{22}\text{H}_{18}\text{FO}^+$  317.1336; Found 317.1341.

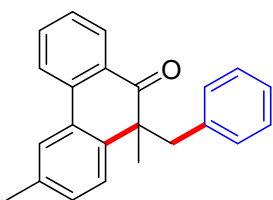


**10-Benzyl-2-bromo-10-methylphenanthren-9(10H)-one (3f).** Purification by column chromatography (EtOAc/PE, V/V = 1:50) afforded **3f**. Yellow oil, 62.4 mg, 83% yield.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.04 (d,  $J = 7.7$  Hz, 1H), 7.81 (d,  $J = 8.0$  Hz, 1H), 7.76 (d,  $J = 8.4$  Hz, 1H), 7.58 (t,  $J = 7.6$  Hz, 1H), 7.47 (d,  $J = 8.5$  Hz, 1H), 7.43 (s, 1H), 7.40 (t,  $J = 7.4$  Hz, 1H), 7.03–6.98 (m, 3H), 6.61 (d,  $J = 7.5$  Hz, 2H), 3.19 (d,  $J = 13.3$  Hz, 1H), 2.95 (d,  $J = 13.3$  Hz, 1H), 1.63 (s, 3H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$ : 201.1,

143.7, 136.1, 135.7, 134.3, 130.6, 130.3, 129.9, 129.3, 129.1, 128.4, 127.7, 127.5, 126.6, 125.2, 122.9, 122.7, 52.4, 49.4, 22.7. HRMS (ESI)  $m/z$ :  $[M+H]^+$  Calcd For  $C_{22}H_{18}BrO^+$  377.0536; Found 377.0531.

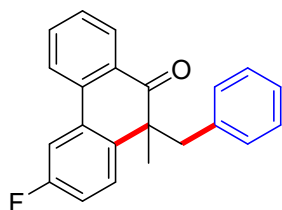


**10-benzyl-2-(heptyloxy)-10-methylphenanthren-9(10H)-one (3g).** Purification by column chromatography (EtOAc/PE, V/V = 1:50) afforded **3g**. Colorless oil, 71.0 mg, 83% yield.  $^1H$  NMR (600 MHz,  $CDCl_3$ )  $\delta$ : 8.01 (d,  $J = 7.74$  Hz, 1H), 7.82 (d,  $J = 8.82$  Hz, 1H), 7.77 (d,  $J = 7.98$  Hz, 1H), 7.54–7.51 (m, 1H), 7.30–7.27 (m, 1H), 7.02–6.97 (m, 3H), 6.87 (dd,  $J = 8.7, 2.64$  Hz, 1H), 6.79 (d,  $J = 2.4$  Hz, 1H), 6.65 (d,  $J = 7.02$  Hz, 2H), 3.97–3.93 (m, 1H), 3.89–3.86 (m, 1H), 3.18 (d,  $J = 13.26$  Hz, 1H), 2.97 (d,  $J = 13.26$  Hz, 1H), 1.80–1.75 (m, 2H), 1.62 (s, 3H), 1.48–1.42 (m, 2H), 1.39–1.35 (m, 2H), 1.34–1.30 (m, 4H), 0.91 (t,  $J = 6.42$  Hz, 3H).  $^{13}C$  NMR (150 MHz,  $CDCl_3$ )  $\delta$ : 202.2, 159.5, 143.4, 137.3, 136.2, 134.1, 130.0, 128.6, 127.6, 127.4, 126.9, 126.3, 125.1, 122.7, 122.1, 113.6, 113.2, 68.0, 52.5, 49.5, 31.8, 29.2, 29.0, 26.0, 22.9, 22.6, 14.1. HRMS (ESI) $m/z$ :  $[M+H]^+$  Calcd For  $C_{29}H_{33}O_2^+$  413.2475; Found 413.2477.

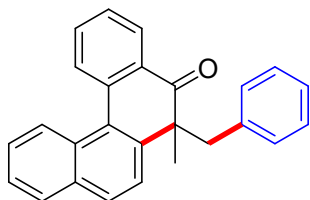


**10-Benzyl-3,10-dimethylphenanthren-9(10H)-one (3h).** Purification by column chromatography (EtOAc/PE, V/V = 1:50) afforded **3h**. Yellow oil, 39.4 mg, 63% yield.  $^1H$  NMR (600 MHz,  $CDCl_3$ )  $\delta$ : 8.03 (d,  $J = 7.7$  Hz, 1H), 7.89 (d,  $J = 8.0$  Hz, 1H), 7.73 (s, 1H), 7.57 (t,  $J = 7.5$  Hz, 1H), 7.36 (t,  $J = 7.4$  Hz, 1H), 7.21 (d,  $J = 8.0$  Hz, 1H), 7.14 (d,  $J = 8.0$  Hz, 1H), 7.02–6.96 (m, 3H), 6.63 (d,  $J = 7.4$  Hz, 2H), 3.20 (d,  $J = 13.3$  Hz, 1H), 2.98 (d,  $J = 13.3$  Hz, 1H), 2.42 (s, 3H), 1.61 (s, 3H).  $^{13}C$  NMR (150 MHz,  $CDCl_3$ )  $\delta$ : 202.5, 138.6, 137.1, 136.6, 136.4, 134.0, 129.9, 129.7, 129.6, 129.5, 127.9, 127.6, 127.44, 127.37, 126.3, 124.3, 122.7, 52.0, 49.4, 23.1, 21.3. HRMS (ESI)  $m/z$ :  $[M+H]^+$

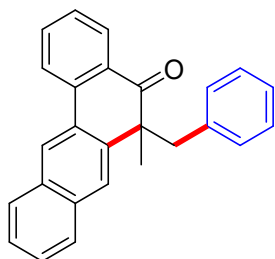
Calcd For C<sub>23</sub>H<sub>21</sub>O<sup>+</sup> 313.1587; Found 313.1584.



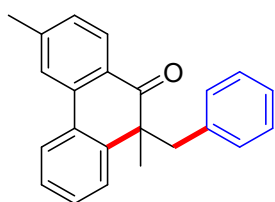
**10-Benzyl-3-fluoro-10-methylphenanthren-9(10H)-one (3i).** Purification by column chromatography (EtOAc/PE, V/V = 1:50) afforded **3i**. Colorless oil, 44.3 mg, 70% yield. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ: 8.07 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.79 (d, *J* = 7.8 Hz, 1H), 7.62–7.58 (m, 2H), 7.43–7.41 (m, 1H), 7.27–7.25 (m, 1H), 7.03–7.01 (m, 2H), 6.98 (t, *J* = 7.8 Hz, 2H), 6.60 (d, *J* = 7.2 Hz, 2H), 3.22 (d, *J* = 13.2 Hz, 1H), 2.96 (d, *J* = 13.2 Hz, 1H), 1.65 (s, 3H). <sup>19</sup>F NMR (564 MHz, CDCl<sub>3</sub>) δ: -115.4. <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ: 201.7, 162.0 (d, *J*<sub>C-F</sub> = 243.5 Hz), 137.2 (d, *J*<sub>C-F</sub> = 3.0 Hz), 135.94, 135.90 (d, *J*<sub>C-F</sub> = 2.0 Hz), 134.2, 132.2 (d, *J*<sub>C-F</sub> = 7.3 Hz), 129.9, 129.6, 129.4 (d, *J*<sub>C-F</sub> = 7.8 Hz), 128.7, 127.7, 127.5, 126.4, 122.9, 115.4 (d, *J*<sub>C-F</sub> = 21.0 Hz), 110.2 (d, *J*<sub>C-F</sub> = 22.7 Hz), 52.0, 49.5, 23.1. HRMS (ESI)m/z: [M+H]<sup>+</sup> Calcd For C<sub>22</sub>H<sub>18</sub>FO<sup>+</sup> 317.1336; Found 317.1336.



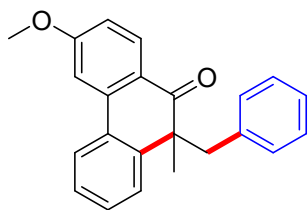
**6-Benzyl-6-methylbenzo[c]phenanthren-5(6H)-one (3j).** Purification by column chromatography (EtOAc/PE, V/V = 1:50) afforded **3j**. Colorless oil, 54.3 mg, 78% yield. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ: 8.51–8.50 (m, 1H), 7.98 (t, *J* = 8.1 Hz, 2H), 7.89–7.87 (m, 1H), 7.81 (d, *J* = 8.5 Hz, 1H), 7.62 (t, *J* = 7.6 Hz, 1H), 7.52–7.50 (m, 2H), 7.45 (t, *J* = 7.5 Hz, 1H), 7.39 (d, *J* = 8.6 Hz, 1H), 7.04–7.02 (m, 1H), 6.99–6.97 (m, 2H), 6.64 (d, *J* = 7.5 Hz, 2H), 3.11 (d, *J* = 13.4 Hz, 1H), 2.98 (d, *J* = 13.4 Hz, 1H), 1.65 (s, 3H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ: 202.9, 137.7, 136.6, 136.1, 133.6, 132.7, 132.1, 129.9, 129.6, 128.90, 128.85, 128.5, 127.7, 127.5, 127.3, 126.5, 126.4, 125.7, 124.3, 53.0, 48.3, 21.0. HRMS (ESI) m/z: [M+H]<sup>+</sup> Calcd For C<sub>26</sub>H<sub>21</sub>O<sup>+</sup> 349.1587; Found 349.1585.



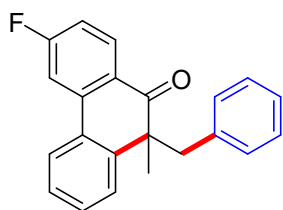
**6-Benzyl-6-methyltetraphen-5(6H)-one (3k).** Purification by column chromatography (EtOAc/PE, V/V = 1:50) afforded **3k**. Colorless oil, 43.2 mg, 62% yield.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.72 (d,  $J = 8.8$  Hz, 1H), 8.10 (d,  $J = 7.7$  Hz, 1H), 8.02 (d,  $J = 8.7$  Hz, 1H), 7.92 (d,  $J = 8.0$  Hz, 1H), 7.88 (d,  $J = 8.1$  Hz, 1H), 7.85 (d,  $J = 8.8$  Hz, 1H), 7.64 (d,  $J = 7.1$  Hz, 1H), 7.62–7.53 (m, 2H), 7.36 (t,  $J = 7.5$  Hz, 1H), 6.79 (t,  $J = 7.3$  Hz, 1H), 6.72 (d,  $J = 7.3$  Hz, 2H), 6.70 (d,  $J = 7.6$  Hz, 2H), 4.09 (d,  $J = 13.3$  Hz, 1H), 3.72 (d,  $J = 13.3$  Hz, 1H), 2.09 (s, 3H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$ : 203.2, 137.9, 137.7, 136.8, 134.7, 134.4, 131.9, 129.8, 129.2, 128.8, 128.7, 128.5, 127.9, 127.5, 127.2, 126.9, 126.0, 125.8, 125.7, 123.9, 121.4, 53.3, 47.3, 27.2. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd For  $\text{C}_{26}\text{H}_{21}\text{O}^+$  349.1587; Found 349.1587.



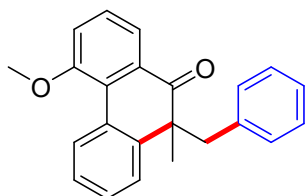
**10-Benzyl-6,10-dimethylphenanthren-9(10H)-one (3l).** Purification by column chromatography (EtOAc/PE, V/V = 1:50) afforded **3l**. Yellow oil, 52.4 mg, 84% yield.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.96 (d,  $J = 7.9$  Hz, 1H), 7.93 (d,  $J = 7.5$  Hz, 1H), 7.70 (s, 1H), 7.35–7.33 (m, 1H), 7.31–7.30 (m, 2H), 7.19 (d,  $J = 7.9$  Hz, 1H), 7.01–6.99 (m, 1H), 6.89–6.95 (m, 2H), 6.61 (d,  $J = 7.6$  Hz, 2H), 3.24 (d,  $J = 13.3$  Hz, 1H), 2.99 (d,  $J = 13.3$  Hz, 1H), 2.44 (s, 3H) 1.63 (s, 3H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$ : 201.8, 144.8, 141.9, 137.0, 136.4, 130.0, 129.9, 129.1, 128.5, 127.8, 127.6, 127.4, 127.2, 127.0, 126.2, 123.6, 123.2, 52.2, 49.3, 23.3, 22.1. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd For  $\text{C}_{23}\text{H}_{21}\text{O}^+$  313.1587; Found 313.1585.



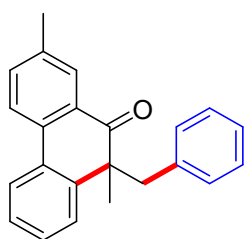
**10-Benzyl-6-methoxy-10-methylphenanthren-9(10H)-one (3m).** Purification by column chromatography (EtOAc/PE, V/V = 1:50) afforded **3m**. Yellow oil, 59.0 mg, 90% yield.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.84 (t,  $J = 8.6$  Hz, 2H), 7.53 (d,  $J = 1.7$  Hz, 1H), 7.34–7.28 (m, 3H), 7.16 (dd,  $J = 8.7, 1.68$  Hz, 1H), 7.02–6.96 (m, 3H), 6.62 (d,  $J = 7.6$  Hz, 2H), 3.90 (s, 3H), 3.25 (d,  $J = 13.3$  Hz, 1H), 3.01 (d,  $J = 13.3$  Hz, 1H), 1.64 (s, 3H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$ : 202.2, 159.4, 140.7, 136.3, 130.6, 130.4, 130.0, 129.9, 127.7, 127.5, 127.4, 127.1, 126.3, 124.5, 123.1, 122.3, 109.4, 55.6, 52.4, 49.3, 23.4. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd For  $\text{C}_{23}\text{H}_{21}\text{O}_2^+$  329.1536; Found 329.1533.



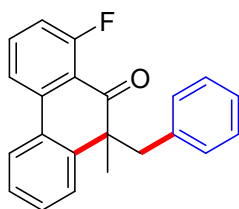
**10-Benzyl-6-fluoro-10-methylphenanthren-9(10H)-one (3n).** Purification by column chromatography (EtOAc/PE, V/V = 1:50) afforded **3n**. Yellow oil, 45.6 mg, 72% yield.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.07 (t,  $J = 7.4$  Hz, 1H), 7.80 (d,  $J = 7.2$  Hz, 1H), 7.49 (d,  $J = 10.6$  Hz, 1H), 7.38 (s, 3H), 7.04–6.98 (m, 2H), 6.94 (t,  $J = 7.2$  Hz, 2H), 6.56 (d,  $J = 7.6$  Hz, 2H), 3.25 (d,  $J = 13.3$  Hz, 1H), 2.99 (d,  $J = 13.3$  Hz, 1H), 1.67 (s, 3H).  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ )  $\delta$ : -103.7.  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$ : 200.6, 166.8 (d,  $J_{\text{C-F}} = 252.4$  Hz), 142.2, 140.0 (d,  $J_{\text{C-F}} = 8.8$  Hz), 136.0, 130.7 (d,  $J_{\text{C-F}} = 9.8$  Hz), 129.8, 129.3, 129.1 (d,  $J_{\text{C-F}} = 1.9$  Hz), 127.7, 127.4, 127.3, 126.4, 126.2, 123.8, 115.4 (d,  $J_{\text{C-F}} = 22.4$  Hz), 109.2 (d,  $J_{\text{C-F}} = 23.0$  Hz), 52.3, 49.9, 23.6. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd For  $\text{C}_{22}\text{H}_{18}\text{FO}^+$  317.1336; Found 317.1332.



**10-Benzyl-5-methoxy-10-methylphenanthren-9(10H)-one (3o).** Purification by column chromatography (EtOAc/PE, V/V = 1:50) afforded **3o**. Yellow oil, 49.9 mg, 76% yield.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.06 (d,  $J = 8.6$  Hz, 1H), 7.88–7.87 (m, 1H), 7.35–7.32 (m, 4H), 6.98 (d,  $J = 7.0$  Hz, 1H), 6.95 (t,  $J = 6.9$  Hz, 2H), 6.90 (d,  $J = 8.6$  Hz, 1H), 6.60 (d,  $J = 7.6$  Hz, 2H), 3.92 (s, 3H), 3.28 (d,  $J = 13.3$  Hz, 1H), 3.01 (d,  $J = 13.3$  Hz, 1H), 1.64 (s, 3H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$ : 200.6, 164.4, 142.3, 139.1, 136.5, 130.2, 129.9, 129.8, 128.7, 127.7, 127.3, 127.0, 126.2, 123.5, 123.3, 114.0, 107.2, 55.5, 51.9, 49.5, 24.0. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd For  $\text{C}_{23}\text{H}_{21}\text{O}_2^+$  329.1536; Found 329.1533.

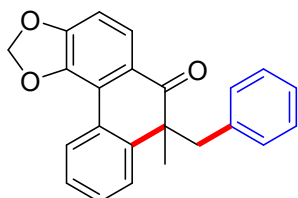


**10-Benzyl-7,10-dimethylphenanthren-9(10H)-one (3p).** Purification by column chromatography (EtOAc/PE, V/V = 1:50) afforded **3p**. Yellow oil, 49.4 mg, 79% yield.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.91 (d,  $J = 7.7$  Hz, 1H), 7.87 (s, 1H), 7.81 (d,  $J = 8.1$  Hz, 1H), 7.42 (d,  $J = 8.2$  Hz, 1H), 7.35–7.34 (m, 1H), 7.30 (d,  $J = 4.0$  Hz, 2H), 7.02–6.97 (m, 3H), 6.63 (d,  $J = 7.5$  Hz, 2H), 3.24 (d,  $J = 13.3$  Hz, 1H), 3.01 (d,  $J = 13.3$  Hz, 1H), 2.42 (s, 3H) 1.63 (s, 3H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$ : 202.5, 141.3, 138.0, 136.4, 135.1, 134.5, 130.1, 130.0, 129.3, 128.2, 127.7, 127.5, 127.4, 127.1, 126.3, 123.4, 122.8, 52.4, 49.1, 23.1, 21.1. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd For  $\text{C}_{23}\text{H}_{21}\text{O}^+$  313.1587; Found 313.1587.

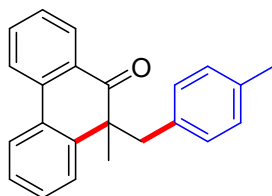


**10-Benzyl-6-fluoro-10-methylphenanthren-9(10H)-one (3q).** Purification by column chromatography (EtOAc/PE, V/V = 1:50) afforded **3q**. Yellow oil, 55.0 mg, 87% yield.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.88 (d,  $J = 7.7$  Hz, 1H), 7.67 (d,  $J = 8.0$  Hz, 1H), 7.54 (dd,  $J = 13.0, 7.9$  Hz, 1H), 7.3–7.32 (m, 2H), 7.24 (s, 1H), 7.09–7.03 (m, 4H), 6.66 (d,  $J$

= 7.4 Hz, 2H), 3.06 (d,  $J = 13.3$  Hz, 1H), 2.99 (d,  $J = 13.3$  Hz, 1H), 1.59 (s, 3H).  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ )  $\delta$ : -114.2.  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$ : 200.2, 161.3 (d,  $J_{\text{C-F}} = 261.1$  Hz), 141.3, 139.4, 135.9, 134.65, 134.58, 129.9, 129.2, 127.6, 127.4, 127.2, 126.6, 124.5, 118.84, 118.81, 116.0 (d,  $J_{\text{C-F}} = 21.7$  Hz), 53.5, 49.1, 20.0 HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd For  $\text{C}_{22}\text{H}_{18}\text{FO}^+$  317.1336; Found 317.1335.

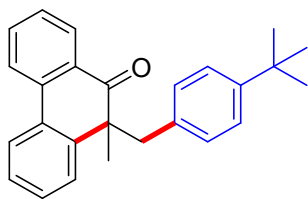


**7-Benzyl-7-methylphenanthro[3,4-d][1,3]dioxol-6(7H)-one (3r).** Purification by column chromatography (EtOAc/PE, V/V = 1:50) afforded **3r**. Colorless oil, 49.2 mg, 72% yield.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.75–7.74 (m, 1H), 7.50 (s, 1H), 7.36–7.32 (m, 3H), 7.29 (s, 1H), 7.01–6.94 (m, 3H), 6.59 (d,  $J = 7.5$  Hz, 2H), 6.04 (d,  $J = 6.5$  Hz, 2H), 3.28 (d,  $J = 13.3$  Hz, 1H), 3.01 (d,  $J = 13.3$  Hz, 1H), 1.64 (s, 3H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$ : 200.4, 153.1, 147.9, 141.6, 136.4, 134.3, 129.9, 129.8, 128.1, 127.5, 127.4, 127.0, 126.3, 125.1, 123.2, 106.4, 102.3, 101.9, 52.0, 49.7, 24.2. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd For  $\text{C}_{23}\text{H}_{19}\text{O}_3^+$  343.1329; Found 343.1324.

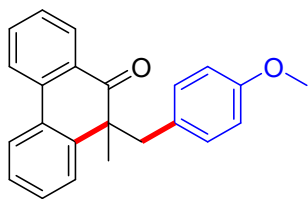


**10-Methyl-10-(4-methylbenzyl)phenanthren-9(10H)-one (3s).** Purification by column chromatography (EtOAc/PE, V/V = 1:50) afforded **3s**. Yellow oil, 50.0 mg, 80% yield.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.06 (d,  $J = 7.7$  Hz, 1H), 7.94 (dd,  $J = 13.8, 7.7$  Hz, 2H), 7.62 (t,  $J = 7.6$  Hz, 1H), 7.41–7.31 (m, 4H), 6.81 (d,  $J = 7.6$  Hz, 2H), 6.52 (d,  $J = 7.6$  Hz, 2H), 3.17 (d,  $J = 13.4$  Hz, 1H), 2.96 (d,  $J = 13.3$  Hz, 1H), 2.18 (s, 3H), 1.63 (s, 3H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$ : 202.3, 141.7, 137.0, 135.8, 134.0, 133.1, 130.0, 129.8, 129.5, 128.6, 128.1, 128.0, 127.6, 127.5, 127.1, 123.7, 122.8, 52.5, 48.9, 22.5, 20.9. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd For  $\text{C}_{23}\text{H}_{21}\text{O}^+$  313.1587; Found 313.1584.

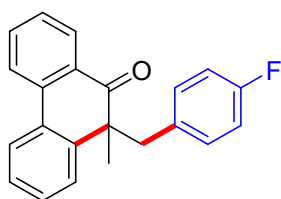




**10-(4-(tert-butyl)benzyl)-10-methylphenanthren-9(10H)-one (3t).** Purification by column chromatography (EtOAc/PE, V/V = 1:50) afforded **3t**. Colorless oil, 58.8 mg, 83% yield.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.02 (d,  $J = 7.7$  Hz, 1H), 7.92 (d,  $J = 7.9$  Hz, 1H), 7.85 (d,  $J = 8.0$  Hz, 1H), 7.56 (t,  $J = 7.5$  Hz, 1H), 7.37–7.34 (m, 4H), 6.97 (d,  $J = 7.7$  Hz, 2H), 6.52 (d,  $J = 7.8$  Hz, 2H), 3.15 (d,  $J = 13.3$  Hz, 1H), 2.97 (d,  $J = 13.3$  Hz, 1H), 1.66 (s, 3H), 1.17 (s, 9H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$ : 202.3, 149.1, 141.8, 137.1, 133.9, 133.0, 130.3, 129.8, 129.5, 128.7, 127.9, 127.5, 127.4, 127.1, 124.2, 123.7, 122.7, 52.5, 49.4, 34.2, 31.2, 22.6. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd For  $\text{C}_{26}\text{H}_{27}\text{O}^+$  355.2056; Found 355.2053.

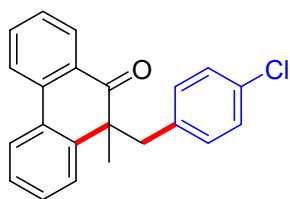


**10-(4-methoxybenzyl)-10-methylphenanthren-9(10H)-one (3u).** Purification by column chromatography (EtOAc/PE, V/V = 1:50) afforded **3u**. Colorless oil, 54.6 mg, 78% yield.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.04 (d,  $J = 7.7$  Hz, 1H), 7.92 (dd,  $J = 13.8$ , 7.7 Hz, 2H), 7.60 (t,  $J = 7.6$  Hz, 1H), 7.40–7.31 (m, 4H), 6.80 (d,  $J = 7.6$  Hz, 2H), 6.52 (d,  $J = 7.6$  Hz, 2H), 3.15 (d,  $J = 13.4$  Hz, 1H), 2.95 (d,  $J = 13.3$  Hz, 1H), 2.17 (s, 3H), 1.62 (s, 3H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$ : 202.3, 141.7, 137.0, 135.8, 134.0, 133.1, 130.0, 129.8, 129.5, 128.6, 128.1, 128.0, 127.6, 127.5, 127.1, 123.7, 122.8, 52.5, 48.9, 22.5, 20.9. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{Na}]^+$  Calcd For  $\text{C}_{23}\text{H}_{20}\text{O}_2\text{Na}^+$  351.13555; Found 351.13501.

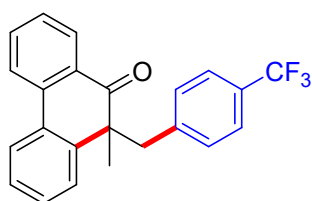


**10-(4-fluorobenzyl)-10-methylphenanthren-9(10H)-one (3v).** Purification by column

chromatography (EtOAc/PE, V/V = 1:50) afforded **3v**. Colorless oil, 51.2 mg, 81% yield.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.03 (d,  $J = 7.7$  Hz, 1H), 7.93–7.92 (m, 1H), 7.88 (d,  $J = 8.0$  Hz, 1H), 7.59 (t,  $J = 7.6$  Hz, 1H), 7.39–7.36 (m, 4H), 6.63 (t,  $J = 8.3$  Hz, 2H), 6.55–6.53 (m, 2H), 3.22 (d,  $J = 13.3$  Hz, 1H), 2.97 (d,  $J = 13.4$  Hz, 1H), 1.65 (s, 3H).  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ )  $\delta$ : -116.7.  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$ : 202.1, 161.5 (d,  $J_{\text{C-F}} = 243.0$  Hz), 141.4, 140.0, 134.3, 131.9 (d,  $J_{\text{C-F}} = 3.1$  Hz), 131.2 (d,  $J_{\text{C-F}} = 8.2$  Hz), 130.1, 129.4, 128.7, 127.51, 127.49, 127.3, 123.7, 122.8, 114.2, 114.1, 52.3, 48.8, 23.3. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd For  $\text{C}_{22}\text{H}_{18}\text{FO}^+$  317.1336; Found 317.1330.

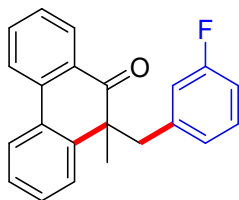


**10-(4-chlorobenzyl)-10-methylphenanthren-9(10H)-one (3w)**. Purification by column chromatography (EtOAc/PE, V/V = 1:50) afforded **3w**. Colorless oil, 59.2 mg, 89% yield.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.04 (d,  $J = 7.7$  Hz, 1H), 7.94 (d,  $J = 7.0$  Hz, 1H), 7.90 (d,  $J = 8.0$  Hz, 1H), 7.61 (t,  $J = 7.5$  Hz, 1H), 7.40–7.36 (m, 4H), 6.92 (d,  $J = 7.6$  Hz, 2H), 6.53 (d,  $J = 7.7$  Hz, 2H), 3.23 (d,  $J = 13.4$  Hz, 1H), 2.97 (d,  $J = 13.4$  Hz, 1H), 1.65 (s, 3H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$ : 201.9, 141.2, 137.0, 134.8, 134.3, 132.2, 131.1, 130.0, 129.3, 128.7, 128.1, 127.6, 127.5, 127.4, 127.3, 123.8, 122.8, 52.2, 48.6, 23.5. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd For  $\text{C}_{22}\text{H}_{18}\text{ClO}^+$  333.1041; Found 333.1040.

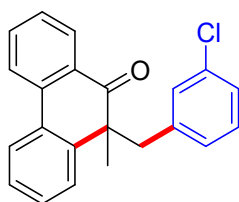


**10-methyl-10-(4-(trifluoromethyl)benzyl)phenanthren-9(10H)-one (3x)**. Purification by column chromatography (EtOAc/PE, V/V = 1:50) afforded **3x**. Colorless oil, 50.5 mg, 69% yield.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.03 (d,  $J = 7.7$  Hz, 1H), 7.93–7.91 (m, 1H), 7.85 (d,  $J = 8.0$  Hz, 1H), 7.58 (t,  $J = 7.6$  Hz, 1H), 7.38–7.36 (m, 4H), 7.18 (d,  $J = 7.9$  Hz, 2H), 6.69 (d,  $J = 7.9$  Hz, 2H), 3.33 (d,  $J = 13.3$  Hz, 1H), 3.06 (d,  $J = 13.3$  Hz, 1H), 1.67 (s, 3H).  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ )  $\delta$ : -62.5.  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$ : 201.7, 141.0, 140.4, 136.9, 134.4, 130.1, 130.0, 129.3, 128.8, 128.5 (d,  $J_{\text{C-F}} = 32.4$

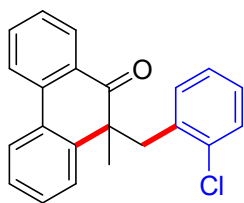
Hz), 128.1, 127.5, 127.4, 127.3, 124.2 (q,  $J_{C-F} = 3.5$  Hz), 124.1 (q,  $J_{C-F} = 270.6$  Hz), 123.8, 122.8, 52.1, 48.9, 23.9. HRMS (ESI)  $m/z$ :  $[M+H]^+$  Calcd For  $C_{23}H_{18}F_3O^+$  367.1304; Found 367.1307.



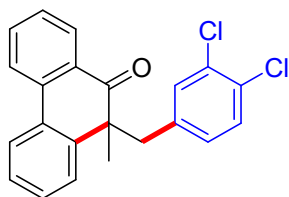
**10-(3-fluorobenzyl)-10-methylphenanthren-9(10H)-one (3y).** Purification by column chromatography (EtOAc/PE, V/V = 1:50) afforded **3y**. Colorless oil, 51.8 mg, 82% yield.  $^1H$  NMR (600 MHz,  $CDCl_3$ )  $\delta$ : 8.05 (d,  $J = 7.8$  Hz, 1H), 7.95–7.93 (m, 1H), 7.90 (d,  $J = 8.0$  Hz, 1H), 7.59 (t,  $J = 7.5$  Hz, 1H), 7.39–7.36 (m, 4H), 6.91 (dd,  $J = 14.5, 7.1$  Hz, 1H), 6.68 (t,  $J = 8.4$  Hz, 1H), 6.40 (d,  $J = 7.6$  Hz, 1H), 6.30 (d,  $J = 10.1$  Hz, 1H), 3.26 (d,  $J = 13.3$  Hz, 1H), 3.00 (d,  $J = 13.3$  Hz, 1H), 1.65 (s, 3H).  $^{19}F$  NMR (564 MHz,  $CDCl_3$ )  $\delta$ : -114.4.  $^{13}C$  NMR (150 MHz,  $CDCl_3$ )  $\delta$ : 201.9, 162.0 (d,  $J_{C-F} = 243.6$  Hz), 141.2, 138.8 (d,  $J_{C-F} = 7.5$  Hz), 137.0, 134.3, 130.0, 129.4, 128.8, 128.7, 128.1, 127.6, 127.3 (d,  $J_{C-F} = 8.6$  Hz), 125.6, 125.5, 123.8, 122.8, 116.6 (d,  $J_{C-F} = 21.4$  Hz), 113.2 (d,  $J = 20.7$  Hz), 52.2, 48.9, 23.6. HRMS (ESI)  $m/z$ :  $[M+H]^+$  Calcd For  $C_{22}H_{18}FO^+$  317.1336; Found 317.1335.



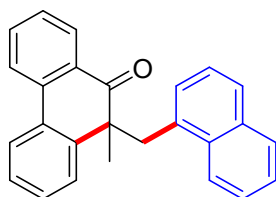
**10-(3-chlorobenzyl)-10-methylphenanthren-9(10H)-one (3z).** Purification by column chromatography (EtOAc/PE, V/V = 1:50) afforded **3z**. Yellow oil, 57.1 mg, 86% yield.  $^1H$  NMR (600 MHz,  $CDCl_3$ )  $\delta$ : 8.04 (d,  $J = 7.7$  Hz, 1H), 7.93 (d,  $J = 7.4$  Hz, 1H), 7.88 (d,  $J = 8.0$  Hz, 1H), 7.59 (t,  $J = 7.5$  Hz, 1H), 7.39–7.34 (m, 4H), 6.96 (d,  $J = 7.9$  Hz, 1H), 6.86 (t,  $J = 7.7$  Hz, 1H), 6.56 (s, 1H), 6.46 (d,  $J = 7.6$  Hz, 1H), 3.20 (d,  $J = 13.3$  Hz, 1H), 2.95 (d,  $J = 13.3$  Hz, 1H), 1.66 (s, 3H).  $^{13}C$  NMR (150 MHz,  $CDCl_3$ )  $\delta$ : 201.8, 141.1, 138.2, 136.9, 134.3, 133.1, 130.1, 129.9, 129.4, 128.8, 128.6, 128.4, 128.1, 128.0, 127.5, 127.4, 126.5, 123.8, 122.7, 52.2, 49.1, 23.2. HRMS (ESI)  $m/z$ :  $[M+H]^+$  Calcd For  $C_{22}H_{18}ClO^+$  333.1041; Found 333.1040.



**10-(2-chlorobenzyl)-10-methylphenanthren-9(10H)-one (3aa).** Purification by column chromatography (EtOAc/PE, V/V = 1:50) afforded **3aa**. Yellow oil, 52.5 mg, 79% yield.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.09 (d,  $J = 7.7$  Hz, 1H), 7.93 (t,  $J = 8.3$  Hz, 2H), 7.62 (t,  $J = 7.5$  Hz, 1H), 7.41 (t,  $J = 7.5$  Hz, 1H), 7.37–7.34 (m, 1H), 7.29–7.28 (m, 2H), 7.13 (d,  $J = 7.8$  Hz, 1H), 6.96 (t,  $J = 7.5$  Hz, 1H), 6.84 (t,  $J = 7.6$  Hz, 1H), 6.43 (d,  $J = 7.7$  Hz, 1H), 3.50 (d,  $J = 14.3$  Hz, 1H), 3.17 (d,  $J = 14.3$  Hz, 1H), 1.67 (s, 3H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$ : 201.9, 141.2, 137.1, 135.0, 134.3, 134.2, 131.4, 130.1, 129.4, 129.1, 128.9, 128.1, 127.9, 127.6, 127.3, 127.2, 125.8, 123.9, 122.7, 52.0, 43.9, 23.3. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd For  $\text{C}_{22}\text{H}_{18}\text{ClO}^+$  333.1041; Found 333.1043.

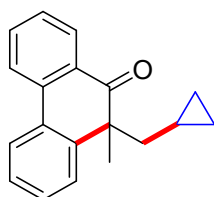


**10-(3,4-dichlorobenzyl)-10-methylphenanthren-9(10H)-one (3ab).** Purification by column chromatography (EtOAc/PE, V/V = 1:50) afforded **3ab**. Yellow oil, 59.3 mg, 81% yield.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.03 (d,  $J = 7.7$  Hz, 1H), 7.95–7.93 (m, 1H), 7.88 (d,  $J = 8.0$  Hz, 1H), 7.61 (t,  $J = 7.7$  Hz, 1H), 7.40–7.38 (m, 4H), 6.98 (d,  $J = 8.2$  Hz, 1H), 6.65 (s, 1H), 6.40 (d,  $J = 8.2$  Hz, 1H), 3.21 (d,  $J = 13.3$  Hz, 1H), 2.94 (d,  $J = 13.4$  Hz, 1H), 1.65 (s, 3H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$ : 201.6, 140.8, 136.9, 136.5, 134.4, 131.7, 131.3, 130.4, 130.1, 129.3, 129.2, 129.1, 128.9, 128.2, 127.53, 127.51, 127.3, 123.8, 122.8, 52.1, 48.4, 23.6. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd For  $\text{C}_{22}\text{H}_{17}\text{Cl}_2\text{O}^+$  367.0651; Found 367.0656.

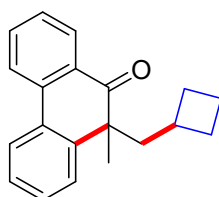


**10-methyl-10-(naphthalen-1-ylmethyl)phenanthren-9(10H)-one (3ac).** Purification

by column chromatography (EtOAc/PE, V/V = 1:50) afforded **3ac**. Yellow oil, 41.1 mg, 61% yield.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.06 (d,  $J = 7.7$  Hz, 1H), 7.91 (d,  $J = 7.9$  Hz, 1H), 7.84 (d,  $J = 8.0$  Hz, 1H), 7.65–7.64 (m, 1H), 7.54–7.52 (m, 2H), 7.43 (d,  $J = 8.4$  Hz, 1H), 7.37–7.31 (m, 6H), 7.08 (s, 1H), 6.72 (d,  $J = 8.4$  Hz, 1H), 3.38 (d,  $J = 13.3$  Hz, 1H), 3.15 (d,  $J = 13.3$  Hz, 1H), 1.69 (s, 3H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$ : 202.3, 141.5, 137.0, 134.1, 133.9, 132.8, 132.0, 130.0, 129.5, 128.8, 128.6, 128.4, 128.0, 127.63, 127.58, 127.5, 127.3, 127.2, 126.8, 125.5, 125.3, 123.8, 122.7, 52.6, 49.4, 22.8. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd For  $\text{C}_{26}\text{H}_{21}\text{O}^+$  349.1587; Found 349.1590.

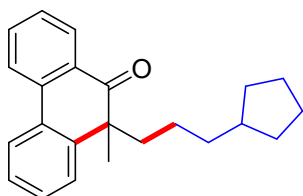


**10-(cyclopropylmethyl)-10-methylphenanthren-9(10H)-one (3ad)**. Purification by column chromatography (EtOAc/PE, V/V = 1:50) afforded **3ad**. Colorless oil, 43.0 mg, 82% yield.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.28 (dd,  $J = 7.8, 1.26$  Hz, 1H), 8.21–8.18 (m, 2H), 7.84–7.81 (m, 1H), 7.67–7.66 (m, 1H), 7.60–7.58 (m, 1H), 7.57–7.55 (m, 1H), 7.54–7.52 (m, 1H), 2.02–1.97 (m, 2H), 1.81 (s, 3H), 0.53–0.47 (m, 1H), 0.35–0.30 (m, 1H), 0.25–0.19 (m, 1H), 0.02– -0.02 (m, 1H), -0.05– -0.09 (m, 1H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$ : 203.0, 143.2, 137.2, 134.1, 129.8, 129.7, 128.8, 128.0, 127.6, 127.1, 126.9, 123.6, 122.8, 51.6, 49.3, 23.9, 7.2, 4.8, 4.4. HRMS (ESI) $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd For  $\text{C}_{19}\text{H}_{19}\text{O}^+$  263.1430; Found 263.1431.

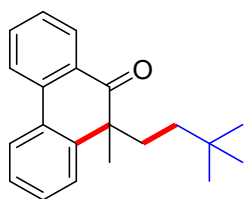


**10-(cyclobutylmethyl)-10-methylphenanthren-9(10H)-one (3ae)**. Purification by column chromatography (EtOAc/PE, V/V = 1:50) afforded **3ae**. Colorless oil, 46.4 mg, 84% yield.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.09 (dd,  $J = 12.54, 7.74$  Hz, 1H), 8.03 (d,  $J = 8.04$  Hz, 1H), 8.01–7.99 (m, 1H), 7.67–7.64 (m, 1H), 7.46–7.45 (m, 1H), 7.42–7.40 (m, 1H), 7.37–7.33 (m, 2H), 2.14 (q,  $J = 7.08$  Hz, 1H), 2.02–1.97 (m, 1H), 1.90 (q,  $J =$

6.78 Hz, 1H), 1.58–1.56 (m, 1H), 1.56 (s, 3H), 1.56–1.55 (m, 2H), 1.51–1.47 (m, 1H), 1.43–1.39 (m, 1H), 1.34–1.29 (m, 1H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ: 202.7, 143.1, 137.1, 134.2, 129.5, 129.4, 128.8, 128.0, 127.7, 127.2, 126.8, 123.6, 122.8, 51.4, 50.7, 33.2, 29.6, 29.4, 24.7, 18.7. HRMS (ESI)m/z: [M+H]<sup>+</sup> Calcd For C<sub>20</sub>H<sub>21</sub>O<sup>+</sup> 277.1587; Found 277.1588.

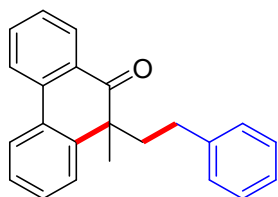


**10-(3-cyclopentylpropyl)-10-methylphenanthren-9(10H)-one (3af).** Purification by column chromatography (EtOAc/PE, V/V = 1:50) afforded **3af**. Colorless oil, 45.9 mg, 72% yield. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ: 8.03 (dd, *J* = 7.8, 1.26 Hz, 1H), 7.97–7.94 (m, 2H), 7.61–7.58 (m, 1H), 7.39 (dd, *J* = 7.74, 1.5 Hz, 1H), 7.37–7.34 (m, 1H), 7.33–7.28 (m, 2H), 2.06–2.01 (m, 1H), 1.75–1.70 (m, 1H), 1.46 (s, 3H), 1.42–1.39 (m, 2H), 1.33–1.30 (m, 2H), 1.21–1.18 (m, 2H), 1.09–0.98 (m, 2H), 0.96–0.88 (m, 1H), 0.87–0.71 (m, 4H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ: 202.8, 143.1, 137.2, 134.2, 129.7, 129.3, 129.0, 128.1, 127.6, 126.84, 126.83, 123.7, 122.8, 51.2, 42.7, 39.6, 36.3, 32.6, 32.5, 25.9, 25.1, 25.0, 24.1. HRMS (ESI) m/z: [M+H]<sup>+</sup> Calcd For C<sub>23</sub>H<sub>27</sub>O<sup>+</sup> 319.2056; Found 319.2058.

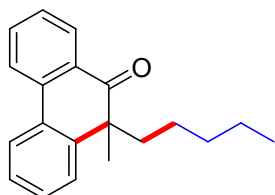


**10-(3,3-dimethylbutyl)-10-methylphenanthren-9(10H)-one (3ag).** Purification by column chromatography (EtOAc/PE, V/V = 1:50) afforded **3ag**. Colorless oil, 50.3 mg, 86% yield. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ: 8.11 (dd, *J* = 7.8, 1.14 Hz, 1H), 8.04–8.01 (m, 2H), 7.67–7.65 (m, 1H), 7.45 (dd, *J* = 7.74, 1.2 Hz, 1H), 7.43–7.38 (m, 2H), 7.38–7.35 (m, 1H), 2.15 (td, *J* = 13.02, 4.56 Hz, 1H), 1.82 (td, *J* = 13.08, 3.9 Hz, 1H), 1.52 (s, 3H), 0.89 (td, *J* = 13.08, 4.56 Hz, 1H), 0.78–0.75 (m, 1H), 0.73 (s, 9H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ: 202.7, 143.1, 137.1, 134.2, 129.7, 129.2, 129.0, 128.0,

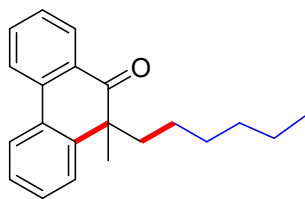
127.6, 126.80, 126.78, 123.7, 122.8, 51.0, 38.5, 37.1, 30.0, 29.0, 26.6. HRMS (ESI)  $m/z$ :  $[M+H]^+$  Calcd For  $C_{21}H_{25}O^+$  293.1900; Found 293.1899.



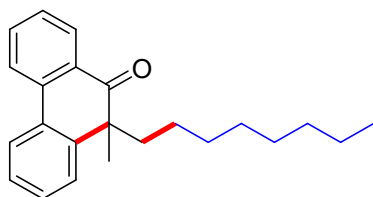
**(S)-10-methyl-10-(3-phenylpropyl)phenanthren-9(10H)-one (3ah).** Purification by column chromatography (EtOAc/PE, V/V = 1:50) afforded **3ah**. Colorless oil, 54.4 mg, 87% yield.  $^1H$  NMR (600 MHz,  $CDCl_3$ )  $\delta$ : 8.15 (dd,  $J = 7.8, 1.2$  Hz, 1H), 8.05–8.02 (m, 2H), 7.69–7.66 (m, 1H), 7.45–7.37 (m, 4H), 7.22 (t,  $J = 1.44$  Hz, 2H), 7.15 (t,  $J = 7.32$  Hz, 1H), 7.01 (d,  $J = 7.02$  Hz, 2H), 2.54–2.49 (m, 1H), 2.46–2.41 (m, 1H), 2.28–2.23 (m, 1H), 1.93–1.88 (m, 1H), 1.54 (s, 3H).  $^{13}C$  NMR (150 MHz,  $CDCl_3$ )  $\delta$ : 202.5, 142.7, 141.8, 137.1, 134.3, 129.6, 129.1, 129.0, 128.2, 128.11, 128.05, 127.6, 126.9, 126.8, 125.6, 123.7, 122.9, 51.0, 41.6, 35.9, 26.6. HRMS (ESI) $m/z$ :  $[M+H]^+$  Calcd For  $C_{23}H_{21}O^+$  313.1587; Found 313.1589.



**10-methyl-10-pentylphenanthren-9(10H)-one (3ai).** Purification by column chromatography (EtOAc/PE, V/V = 1:50) afforded **3ai**. Colorless oil, 44.0 mg, 79% yield.  $^1H$  NMR (600 MHz,  $CDCl_3$ )  $\delta$ : 8.11 (d,  $J = 7.74$  Hz, 1H), 8.03–8.00 (m, 2H), 7.65 (t,  $J = 7.5$  Hz, 1H), 7.45 (dd,  $J = 7.74, 1.44$  Hz, 1H), 7.41 (t,  $J = 7.68$  Hz, 1H), 7.38 (td,  $J = 14.76, 2.4$  Hz, 1H), 7.36–7.33 (m, 1H), 2.11 (td,  $J = 12.42, 4.68$  Hz, 1H), 1.79 (td,  $J = 12.62, 4.5$  Hz, 1H), 1.53 (s, 3H), 1.13–1.04 (m, 4H), 0.99–0.95 (m, 1H), 0.93–0.88 (m, 1H), 0.73 (t,  $J = 6.9$  Hz, 3H).  $^{13}C$  NMR (150 MHz,  $CDCl_3$ )  $\delta$ : 202.7, 143.0, 137.1, 134.2, 129.6, 129.3, 129.0, 128.0, 127.6, 126.82, 126.78, 123.7, 122.8, 51.1, 42.5, 32.0, 25.9, 24.6, 22.2, 13.9. HRMS (ESI) $m/z$ :  $[M+H]^+$  Calcd For  $C_{20}H_{23}O^+$  279.1743; Found 279.1743.

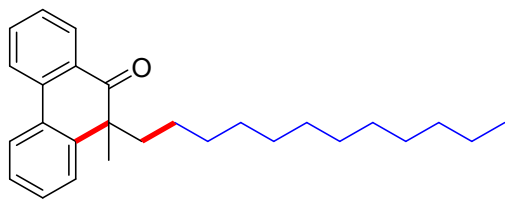


**10-hexyl-10-methylphenanthren-9(10H)-one (3aj).** Purification by column chromatography (EtOAc/PE, V/V = 1:50) afforded **3aj**. Colorless oil, 48.5 mg, 83% yield.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.03 (dd,  $J = 7.74, 1.2$  Hz, 1H), 7.97–7.94 (m, 2H), 7.61–7.58 (m, 1H), 7.39 (dd,  $J = 7.74, 1.44$  Hz, 1H), 7.36–7.34 (m, 1H), 7.33–7.28 (m, 2H), 2.06–2.01 (m, 1H), 1.75–1.70 (m, 1H), 1.46 (s, 3H), 1.08–1.03 (m, 3H), 1.02–0.98 (m, 3H), 0.93–0.87 (m, 1H), 0.83–0.80 (m, 1H), 0.70 (t,  $J = 7.08$  Hz, 3H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$ : 202.8, 143.1, 137.2, 134.2, 129.7, 129.3, 129.0, 128.1, 127.6, 126.9, 126.8, 123.7, 122.8, 51.2, 42.6, 31.4, 29.5, 26.0, 24.9, 22.5, 13.9. HRMS (ESI) $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd For  $\text{C}_{21}\text{H}_{25}\text{O}^+$  293.1900; Found 293.1900.

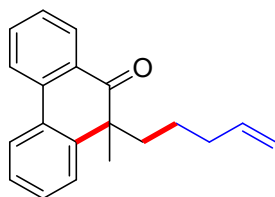


**10-methyl-10-octylphenanthren-9(10H)-one (3ak).** Purification by column chromatography (EtOAc/PE, V/V = 1:50) afforded **3ak**. Colorless oil, 52.6 mg, 82% yield.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.03 (dd,  $J = 7.8, 1.2$  Hz, 1H), 7.95–7.92 (m, 2H), 7.56–7.22 (m, 1H), 7.37 (dd,  $J = 7.74, 1.38$  Hz, 1H), 7.34–7.31 (m, 1H), 7.30 (td,  $J = 7.26, 1.38$  Hz, 1H), 7.27 (td,  $J = 7.68, 1.62$  Hz, 1H), 2.05–2.00 (m, 1H), 1.73–1.68 (m, 1H), 1.45 (s, 3H), 1.13–1.10 (m, 2H), 1.04–1.00 (m, 8H), 0.90–0.85 (m, 1H), 0.83–0.78 (m, 1H), 0.73 (t,  $J = 7.2$  Hz, 3H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$ : 202.7, 143.0, 137.1, 134.2, 129.6, 129.3, 128.9, 128.0, 127.6, 126.84, 126.79, 123.7, 122.8, 51.1, 42.6, 31.7, 29.8, 29.11, 29.08, 25.9, 24.9, 22.5, 14.0. HRMS (ESI) $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd For  $\text{C}_{23}\text{H}_{29}\text{O}^+$  321.2213; Found 321.2213.





**10-dodecyl-10-methylphenanthren-9(10H)-one (3al).** Purification by column chromatography (EtOAc/PE, V/V = 1:50) afforded **3al**. Colorless oil, 63.2 mg, 84% yield.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.11 (dd,  $J = 7.7, 1.2$  Hz, 1H), 8.02–7.99 (m, 2H), 7.65–7.63 (m, 1H), 7.46–7.44 (m, 1H), 7.42–7.39 (m, 1H), 7.39–7.33 (m, 2H), 2.13–2.08 (m, 1H), 1.82–1.77 (m, 1H), 1.53 (s, 3H), 1.28–1.08 (m, 20H), 0.87–0.85 (m, 3H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$ : 202.6, 143.0, 137.1, 134.2, 129.6, 129.3, 128.9, 128.0, 127.6, 126.83, 126.78, 123.6, 122.8, 51.1, 42.6, 31.9, 29.8, 29.54, 29.48, 29.4, 29.3, 29.2, 25.9, 24.9, 22.6, 14.1. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd For  $\text{C}_{27}\text{H}_{37}\text{O}^+$  377.28389; Found 377.28378.



**10-methyl-10-(pent-4-en-1-yl)phenanthren-9(10H)-one (3am).** Purification by column chromatography (EtOAc/PE, V/V = 1:50) afforded **3am**. Colorless oil, 33.2 mg, 60% yield.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.11 (dd,  $J = 7.8, 1.26$  Hz, 1H), 8.04–8.01 (m, 2H), 7.68–7.65 (m, 1H), 7.46 (dd,  $J = 7.8, 1.5$  Hz, 1H), 7.43–7.41 (m, 1H), 7.40–7.38 (m, 1H), 7.37–7.35 (m, 1H), 5.64–5.57 (m, 1H), 4.87–4.83 (m, 2H), 2.17–2.12 (m, 1H), 1.90–1.85 (m, 2H), 1.84–1.80 (m, 1H), 1.53 (s, 3H), 1.12–1.06 (m, 1H), 1.04–0.96 (m, 1H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$ : 202.3, 149.1, 141.8, 137.1, 133.9, 133.0, 129.5, 128.7, 127.9, 127.5, 127.4, 127.1, 124.2, 123.7, 122.7, 52.5, 49.4, 34.2, 31.2, 22.6. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd For  $\text{C}_{20}\text{H}_{21}\text{O}^+$  277.1587; Found 277.1591.

#### 4. References

1. Yu, W. Y.; Sit, W. N.; Zhou, Z.; Chan, A. S. C. *Org. Lett.* **2009**, *11*, 3174–3177.
2. Y. Li, Y. Han, H. Xiong, N. Zhu, B. Qian, C. Ye, E. A. B. Kantchev and H. Bao, *Org.*

*Lett.*, 2016, **18**, 392–395.

### 5. $^1\text{H}$ NMR, $^{13}\text{C}$ NMR and $^{19}\text{F}$ NMR spectra of the products.

