Supporting Informations
for
Total synthesis of 1-oxomiltirone and arucadiol

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General Information

All the reactions were carried out under Argon atmosphere and Oxygen atmosphere. Unless otherwise noted, all the reagents obtained from commercial sources were used without further purification. All solvents were dried by standard methods. Tetrahydrofuran were dried with sodium and benzophenone and were used immediately after distillation. Dichloromethane was dried with diphosphoruspentoxide (P₂O₅). Pentane was distilled and then dried with sodium. Analytical thin-layer chromatography (TLC) was performed on 0.25 mm Merck precoated silica gel plates (60-F₂₅₄). Column chromatography was carried out with the same kind of silica gel. The TLC plates were visualized with a UV lamp (254 nm and 366 nm) and/or with TLC visualizing solutions activated with heat, including: p-anisaldehyde solution and potassium permanganate solution. All reagents and solvents were of commercial grade and purified prior to use when necessary.

All ¹H NMR and ¹³C NMR spectra were recorded on a 400 MHz spectrometer with solvent resonances as the internal standard (¹H NMR: CDCl₃ at 7.26 ppm; ¹³C NMR: CDCl₃ at 77.16 ppm). High-resolution mass spectra (HRMS) were recorded with a Bruker TOF-Q spectrometer in the ESI mode.

Synthesis of 2-bromo-5-isopropyl-4-methoxybenzaldehyde

\[
\begin{align*}
\text{HO} & \quad \text{K₂CO₃} \quad \\ 
\text{DMF} & \quad \text{MeI} \quad \\ 
\text{1.1a} & \quad \text{CF₃COOH} \quad \text{HMTA} \quad \\ 
\text{1.1b} & \quad \text{TMEDA, n-BuLi, CH₃} \quad \text{Ether, 0°C to -78°C to rt} \quad \\ 
\text{1.1c} & \quad \text{Br}
\end{align*}
\]

1-Isopropyl-2-methoxybenzene (1.1a)

To a round bottom flask was added K₂CO₃ (10 g, 3.9 eq, 0.09 mol), 2-isopropylphenol (3 mL, 1 eq, 0.02 mol) and 20 mL of distilled DMF. The suspension was stirred for 20 min at room temperature then MeI (2.7 mL, 2 eq, 0.04 mol) at room temperature and the mixture was stirred overnight. The reaction mixture was quenched with water (60 mL) at 0°C, and then diluted with water (60 mL) and ether (50mL). The organic layer was separated and further extracted three times with ethyl ether (60 mL x 3). The combined organic layer was washed with saturated NaCl solution (60mL), dried over anhydrous MgSO₄, and filtered, and the solvent was removed at reduced pressure to yield a crude product 1.1a (3.33 g, 99%, colorless liquid); ¹H NMR (400 MHz, CDCl₃) δ 7.21 (dd, J = 7.5, 1.8 Hz, 1H), 7.16 (td, J = 7.9, 1.8 Hz, 1H), 6.93 (td, J = 7.5, 1.2 Hz, 1H), 6.85 (dd, J = 8.1, 1.2 Hz, 1H), 3.83 (s, 3H), 3.32 (sept, J = 6.9 Hz, 1H), 1.26 – 1.18 (m, 6H).
3-Isopropyl-4-methoxybenzaldehyde (1.1b)

To a round bottom flask was added 1.1a (3.33 g, 1 eq, 0.02 mol), CF₃COOH (1M, 22 mL) and HMTA (12 g, 4 eq, 0.09 mol) respectively then the mixture was heated to 80 °C for 1 h. The reaction mixture was neutralized with solid NaHCO₃ at 0 °C, and then diluted ether (50mL). The organic layer was separated and further extracted three times with ethyl ether (60 mL x 3). The combined organic layer was washed with saturated NaCl solution (60mL), dried over anhydrous MgSO₄, and filtered, and the solvent was removed at reduced pressure to yield a product. Chromatography on fresh silica gel (1:10 = ethyl acetate:hexane) afforded a product 1.1b (2.98 g, 76%, yellow liquid); ¹H NMR (400 MHz, CDCl₃) δ 9.88 (s, 1H), 7.77 (d, J = 2.2 Hz, 1H), 7.71 (dd, J = 8.4, 2.1 Hz, 1H), 6.95 (d, J = 8.4 Hz, 1H), 3.92 (s, 3H), 3.33 (sept, J = 6.9 Hz, 1H), 1.24 (d, J = 6.9 Hz, 6H).

2-Bromo-5-isopropyl-4-methoxybenzaldehyde (1.1c)

To a round bottom flask was added N, N, N′-Trimethylethylenediamine (1.3 eq), freshly distilled ether (27 mL) under A. n-BuLi (7 mL, 1.3 eq) was then added dropwise at 0 °C. The reaction mixture was stirred at this temperature for another 30 min. Compound 1.1b (2.40 g, 0.014 mol, 1 eq) in freshly distilled ether was added dropwise at 0 °C. The mixture was stirred at 0 °C for 30 min then n-BuLi (10.8 mL 2 eq) was added dropwise at 0 °C. The mixture was warmed up to rt, stirred at rt for 1 h. The reaction was cooled to –78 °C then tetrabromomethane (8.9 g, 2 eq) in freshly distilled ether was added dropwise. After addition, the reaction mixture was warmed up to rt, stirred at rt for 1 h. The reaction mixture was quenched with 1M HCl (60 mL) at 0 °C, and then diluted with water (60 mL) and ether (50 mL). The organic layer was separated and further extracted three times with ethyl ether (60 mL x 3). The combined organic layer was washed with saturated NaCl solution (60mL), dried over anhydrous MgSO₄, and filtered, and the solvent was removed at reduced pressure to yield a crude product 1.1c. Chromatography on fresh silica gel (1:20 = ethyl acetate:hexane) afforded a product 1.1c (2.98g, 91.4%, brown liquid); ¹H NMR (400 MHz, CDCl₃) δ 10.21 (s, 1H), 7.80 (d, J = 0.6 Hz, 1H), 7.03 (s, 1H), 3.91 (s, 3H), 3.30 – 3.20 (m, 1H), 1.20 (d, J = 6.9 Hz, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 191.2, 162.2, 137.6, 127.5, 126.7, 126.6, 115.1, 56.1, 26.8, 22.3.
Synthesis of 2-bromo-5-isopropyl-3,4-dimethoxybenzaldehyde

2-(5-Bromo-2,3-dimethoxyphenyl) propan-2-ol (1.2a)

To a round bottom flask containing n-BuLi was added 1,2-dimethoxybenzene (12 mL. 0.094 mol) dropwise via dropping funnel 0 °C under Argon atmosphere. The mixture was stirred for 1 h then acetone (12 mL. 0.16 mol) was added dropwise via dropping funnel at 0 °C. The reaction mixture was stirred at 0 °C for another 1 h. The reaction mixture was quenched carefully with water (60 mL) at 0 °C, and then diluted with water (60 mL) and ether (50 mL). The organic layer was separated and further extracted three times with ethyl ether (60 mL x 3). The combined organic layer was washed with saturated NaCl solution (60 mL), dried over anhydrous MgSO₄, and filtered, and the solvent was removed at reduced pressure to yield a crude product. Chromatography on fresh silica gel (1:10 = ethyl acetate: hexane) afforded a 2-(2,3-dimethoxyphenyl)propan-2-ol (8.305 g, 45%, colorless liquid); ¹H NMR (400 MHz, CDCl₃) δ 7.01 (t, J = 8.0 Hz, 1H), 6.93 (dd, J = 8.0, 1.7 Hz, 1H), 6.86 (dd, J = 8.0, 1.6 Hz, 1H), 3.99 (s, 3H), 3.87 (s, 3H), 1.60 (s, 6H).

To a round bottom flask was added NaOAc (8.7 g, 2.5 eq), 2-(2,3-dimethoxyphenyl)propan-2-ol (8.3 g, 0.042 mol) and AcOH under Argon atmosphere. To this solution, bromine (4.1 mL, 1.9 eq) in AcOH was added dropwise via dropping funnel. The reaction mixture was stirred at room temperature for 30 min. After completion of reaction monitored by TLC, the reaction mixture was quenched with water (60 mL) at 0 °C, and then diluted with water (60 mL) and ether (50 mL). The organic layer was separated and further extracted three times with ethyl ether (60 mL x 3). The combined organic layer was washed with 1M Na₂S₂O₃ solution (50 mL), 10% NaHCO₃ solution (50 mL), and saturated NaCl solution (50 mL), dried over anhydrous MgSO₄, and filtered, and the solvent was removed at reduced pressure to yield a crude product. Chromatography on fresh silica gel (1:10 = ethyl acetate:hexane) afforded a
product \textit{1.2a} (10.2 g, 88\%, colorless liquid); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.10 (d, $J$ = 2.3 Hz, 1H), 6.97 (d, $J$ = 2.3 Hz, 1H), 3.94 (s, 3H), 3.86 (s, 3H), 1.58 (s, 6H).

\textbf{5-Bromo-1-isopropyl-2,3-dimethoxybenzene (1.2b)}

To a round bottom flask was added \textit{1.2a} (7.7 g, 0.03 mol) and 180 mL of freshly distilled CH$_2$Cl$_2$ under Argon atmosphere. To this solution trifluoroacetic acid (11.5 mL, 4.0 eq) and triethylsilane (17 mL, 2.9 eq) were added respectively via syringe at 0°C. The mixture was then refluxed at 80°C for 8 h. The reaction mixture was quenched with water (60 mL) at 0°C, and then diluted with water (60 mL) and ether (50 mL). The organic layer was separated and further extracted three times with ethyl ether (60 mL x 3). The combined organic layer was washed with saturated NaHCO$_3$ solution (60 mL) and saturated NaCl solution (60 mL), dried over anhydrous MgSO$_4$, and filtered, and the solvent was removed at reduced pressure to yield a crude product. Chromatography on Fresh silica gel (1:20 = ethyl acetate: hexane) afforded a product \textit{1.2b} (6.0 g, 82\%, light yellow liquid); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.96 – 6.94 (m, 1H), 6.87 (d, $J$ = 2.3 Hz, 1H), 3.84 (s, 3H), 3.79 (s, 3H), 3.30 (sept, $J$ = 7.0 Hz, 1H), 1.19 (d, $J$ = 6.9 Hz, 6H).

\textbf{3-Isopropyl-4,5-dimethoxybenzaldehyde (1.2c)}

To a round bottom flask was added \textit{1.2b} (6.0 g, 1 eq, 0.02 mol) and freshly distilled THF under argon atmosphere. To this solution n-BuLi (40 mL, 1.3 eq) was added dropwise at –78°C and the reaction mixture was stirred at this temperature for 30 min. DMF (6.1 mL, 2 eq) was then added dropwise at –78°C and the mixture was warmed up to rt, and stirred at rt for 1 h. After completion of the reaction (TLC), the reaction mixture was quenched with water (60 mL) at 0°C, and then diluted with water (60 mL) and ether (50 mL). The organic layer was separated and further extracted three times with ethyl ether (60 mL x 3). The combined organic layer was washed with saturated NaHCO$_3$ solution (50 mL) and saturated NaCl solution (50 mL), dried over anhydrous MgSO$_4$, and filtered, and the solvent was removed at reduced pressure to yield a crude product. Chromatography on fresh silica gel (1:10 = ethyl acetate: hexane) afforded a product \textit{1.2c} (3.6 g, 75\%, yellow liquid); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.89 (s, 1H), 7.39 (dd, $J$ = 1.9, 0.5 Hz, 1H), 7.30 (d, $J$ = 1.9 Hz, 1H), 3.92 (s, 3H), 3.91 (s, 3H), 3.44 – 3.35 (m, 1H), 1.25 (d, $J$ = 6.9 Hz, 6H).

\textbf{2-Bromo-5-isopropyl-3,4-dimethoxybenzaldehyde (1.2d)}

To a round bottom flask was added $N$, $N$, $N'$-Trimethylethylenediamine (2.4 g, 1.3 eq) and freshly distilled ether under Argon atmosphere. To this solution n-BuLi (19 mL, 1.3 eq) was added dropwise at 0°C and the reaction mixture was stirred at 0°C for 30 min. A solution of \textit{1.2c} (3.6 g, 1 eq) in freshly distilled ether was added dropwise at 0°C. The mixture was stirred at 0°C for 30 min. n-BuLi (30 mL, 2 eq) was added dropwise at 0°C then the mixture was warmed up to rt, stirred at
rt for 1 h. Tetrabromomethane (11.6 g, 2 eq) in freshly distilled ether was added dropwise at –78 °C. The reaction mixture was warmed up to rt, and stirred at room temperature for 1 h. The reaction mixture was quenched with 1 M HCl (60 mL) at 0 °C, and then diluted with water (60 mL) and ether (50 mL). The organic layer was separated and further extracted three times with ethyl ether (60 mL x 3). The combined organic layer was washed with saturated NaCl solution (60 mL), dried over anhydrous MgSO4, and filtered, and the solvent was removed at reduced pressure to yield a crude product. Chromatography on fresh silica gel (1:20 = ethyl acetate: hexane) afforded a product \(1.2d\) (3.583 g, 71%); \(^1\)H NMR (400 MHz, CDCl3) \(\delta\) 10.29 (s, 1H), 7.64 \((d, J = 0.5 \text{ Hz}, 1\text{H})\), 3.97 (s, 3H), 3.89 (s, 3H), 3.33 – 3.23 (m, 1H), 1.23 \((d, J = 6.9 \text{ Hz}, 6\text{H})\); \(^1^3\)C NMR (101 MHz, CDCl3) \(\delta\) 191.5, 157.1, 150.3, 142.8, 129.8, 123.3, 121.0, 61.2, 60.7, 27.3, 23.1, 22.8.

**Synthesis of 2,2-dimethylhex-5-yn-1-ol (1)**

To a round bottom flask was added 3-butyn-1-ol \(2a\) (5.1 g, 1 eq, 72.0 mmol) and freshly distilled THF and solution was cooled to -78 °C under Argon atmosphere. To this solution, \(n\)-BuLi (72 mL, 1.6 M in hexane, 2.2 eq, 160 mmol) was added at -78 °C and the mixture was stirred for 1 h then TMS-Cl (17.2 g, 2.2 eq, 160 mmol) in anhydrous THF was added at -78 °C. After 1 h, the mixture was warmed up to room temperature. After completion of the reaction (TLC), the reaction mixture was quenched with 4 N HCl (60 mL) at 0 °C, and then diluted with water (60 mL) and ether (50 mL). The organic layer was separated and further extracted three times with ethyl ether (60 mL x 3). The combined organic layer was washed with saturated NaCl solution (50 mL), dried over anhydrous MgSO4, and filtered, and the solvent was removed at reduced pressure to yield a crude product \(2b\) (10 g, 98%, light yellow liquid). This product was used for next step without further purification; \(^1\)H NMR (400 MHz, Chloroform-d) \(\delta\) 3.71 (q, \(J = 5.6 \text{ Hz}, 2\text{H})\), 2.51 (t, \(J = 6.2 \text{ Hz}, 2\text{H})\), 1.77 (t, \(J = 6.2 \text{ Hz}, 1\text{H})\), 0.16 (s, 9H).

To a round bottom flask was added PPh3 (21 g, 1.1 eq, 80 mmol) and freshly distilled CH2Cl2 (240 mL) and the mixture was cooled to 0 °C. To this solution was added I2 (22.1 g, 1.2 eq, 87.1 mmol), imidazole (5.4 g, 1.2 eq, 87.1 mmol) and the reaction was warmed up to room temperature. After 30 min, alcohol \(2b\) (1 eq, 72.6 mmol) was added at room temperature and the mixture was stirred for 1 h. The reaction mixture was quenched with separated Na2S2O3 solution (50 mL) at 0 °C, and then diluted with water (60 mL) and ether (50 mL). The organic layer was separated and further extracted three times with
ethyl ether (60 mL x 3). The combined organic layer was washed with saturated NaCl solution (50 mL), dried over anhydrous MgSO₄, and filtered on silica gel by hexane, and the solvent was removed at reduced pressure to yield a product 2c (14.6 g, 80%, light yellow liquid); ¹H NMR (400 MHz, CDCl₃) δ 3.22 (t, J = 7.5 Hz, 2H), 2.79 (t, J = 7.5 Hz, 2H), 0.16 (s, 9H).

2,2-Dimethylhex-5-yn-1-ol (1)

To a round bottom flask was added diisopropylamine (6.43 g, 1.1 eq, 63.5 mmol) and freshly distilled THF and the mixture was cooled to -78 °C. To this solution, n-BuLi (40 mL, 1.6 M in hexane, 1.1 eq, 63.5 mmol) was added at -78 °C. After 30 min, ethyl isobutyrate (7.38 g, 1.1 eq, 63.5 mmol) in freshly distilled THF was added -78 °C and the reaction mixture was warmed up to 0 °C. After 30 min, the mixture was cooled to -78 °C and compound 2c (14.6 g, 1 eq, 57.8 mmol) in THF was added. The reaction mixture was then warmed up to room temperature. After completion of reaction (TLC), the reaction mixture was quenched with separated NH₄Cl solution (50 mL) at 0 °C, and then diluted with water (60 mL) and ether (50 mL). The organic layer was separated and further extracted three times with ethyl ether (60 mL x 3). The combined organic layer was washed with saturated NaCl solution (50 mL), dried over anhydrous MgSO₄, and filtered, and the solvent was removed at reduced pressure to yield a product 2d (14 g, 98%, yellow liquid). This product was used for next step without further purification; ¹H NMR (400 MHz, CDCl₃) δ 4.11 (q, J = 7.1 Hz, 2H), 2.22 – 2.14 (m, 2H), 1.84 – 1.76 (m, 2H), 1.25 (t, J = 7.1 Hz, 3H), 1.17 (s, 6H), 0.14 (s, 9H).

To a round bottom flask was added lithium aluminium hydride (3.33 g, 1.5 eq, 87.9 mmol) and freshly distilled diethylether (195 mL). The reaction was cooled to 0 °C and compound 2d (14 g, 1 eq, 58.6 mmol) dissolved in dry ether was added at 0 °C. The reaction mixture was then warmed up to room temperature. After completion of reaction (TLC), the reaction mixture was quenched with 1M HCl solution (150 mL) at 0 °C, and then diluted with water (60 mL) and ether (100 mL). The organic layer was separated and further extracted three times with ethyl ether (80 mL x 3). The combined organic layer was washed with saturated NaCl solution (80 mL), dried over anhydrous MgSO₄, and filtered, and the solvent was removed at reduced pressure to yield a product 1 (11.1 g, 94%, light yellow liquid). This product was used for next step without further purification; ¹H NMR (400 MHz, CDCl₃) δ 3.35 (s, 2H), 2.23 (t, J = 7.6 Hz, 2H), 1.55 (t, J = 7.6 Hz, 2H), 0.88 (s, 6H), 0.14 (s, 9H).

To a round bottom flask was added alcohol prepared from previous step (11.1 g, 1 eq, 55.9 mmol) and methanol (120 mL). To this solution was added K₂CO₃ (11.6 g, 1.5 eq, 83.9 mmol) at room temperature. After completion of reaction (TLC), the reaction mixture was diluted with water (60 mL) and ether (50 mL). The organic layer was separated and further extracted three times with ethyl ether (60 mL x 3). The combined organic layer was washed with saturated NaCl solution (50 mL), dried over anhydrous MgSO₄, and filtered, and the solvent was removed at reduced pressure to yield a product. Chromatography on fresh silica gel (1:4 = ethyl acetate: hexane) afforded a product 1 (4.9 g, 69%, colorless liquid); ¹H NMR (400 MHz, CDCl₃) δ 3.19 (d, J = 5.2 Hz, 2H), 2.07 – 1.99
(m, 2H), 1.80 (t, \( J = 2.7 \text{ Hz}, 1\text{H} \)), 1.44 – 1.37 (m, 2H), 0.74 (s, 6H); IR (neat) 3305 (br), 2117, 1687, 1471, 1416, 1215, 1142, 1048 cm\(^{-1}\)

**Synthesis of 1,1-dimethyl-2,3-dihydrophenanthren-4(1H)-one (7) (from 6)**

![Synthesis反应示意图](attachment:image.png)

2-(6-Hydroxy-5,5-dimethylhex-1-yn-1-yl)benzaldehyde (2)

In a sealed tube was added 2-bromobenzaldehyde (2.4 g, 1 eq, 13.1 mmol) and 1 (3.3 g, 2 eq, 26.1 mmol), freshly distilled triethylamine (26 mL), tetrabutylammonium iodide (0.5 mol%), CuI (6 mol%) and PdCl\(_2\)-PPh\(_3\) (4 mol%) respectively under Argon atmosphere. The reaction mixture was then stirred at 70 °C for 4 h. After completion of reaction (TLC), the reaction mixture was diluted with ether (50 mL), and then filtered, and the solvent was removed at reduced pressure to yield a product. Chromatography on fresh silica gel (1:4 = ethyl acetate: hexane) afforded a product 2 (2.0 g, 67%, yellow liquid); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 10.52 (d, \( J = 0.9 \text{ Hz}, 1\text{H} \)), 7.91 – 7.84 (m, 1H), 7.54 – 7.47 (m, 2H), 7.38 (dddd, \( J = 7.6, 6.5, 2.1, 0.8 \text{ Hz}, 1\text{H} \)), 3.39 (d, \( J = 5.6 \text{ Hz}, 2\text{H} \)), 2.53 – 2.45 (m, 2H), 1.73 – 1.63 (m, 2H), 0.95 (s, 6H); \(^13\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 192.3, 136.1, 133.9, 133.4, 128.1, 127.8, 127.2, 98.6, 77.5, 76.4, 71.5, 37.5, 35.4, 23.9, 14.9.

6-(2-(1,3-Dioxan-2-yl)phenyl)-2,2-dimethylhex-5-yn-1-ol (3)

To a round bottom flask was added 2 (2.0 g, 1 eq, 8.8 mmol), 1,3-propanediol (2 eq), p-TsOH (1.5 mol%) and benzene. The reaction mixture was stirred at 120 °C under reflux using a Dean-Stark apparatus during 1.5 h. The mixture was then cooled to 0 °C and quenched with separated NaHCO\(_3\) solution (50 mL) at 0 °C, and then diluted with water (60 mL) and ether (50 mL). The organic layer was separated and further extracted three times with ethyl ether (60 mL x 3). The combined organic layer was washed with saturated NaCl solution (50 mL), dried over anhydrous MgSO\(_4\), and filtered, and the solvent was removed at reduced pressure to yield a product 3 (2.5 g, 98%, brown liquid); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.53 (dd, \( J = 7.7, 1.5 \text{ Hz}, 1\text{H} \)), 7.20 (td, \( J = 7.6, 1.6 \text{ Hz}, 1\text{H} \)), 7.18 – 7.11 (m, 2H), 5.77 (s, 1H), 4.17 (ddt, \( J = 10.4, 5.1, 1.4 \text{ Hz}, 2\text{H} \)), 3.96 – 3.86 (m, 2H), 3.30 (d, \( J = 6.1 \text{ Hz}, 2\text{H} \)), 2.37 (dd, \( J = 8.2, 7.3 \text{ Hz}, 2\text{H} \)), 2.28 – 2.06 (m, 1H), 1.58 (dd, \( J = 8.3, 7.3 \text{ Hz}, 2\text{H} \)), 1.35 (dtt, \( J = 13.5, 2.7, 1.4 \text{ Hz}, 1\text{H} \)), 0.85 (s, 6H); \(^13\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 139.7, 132.2, 128.7, 128.1, 126.0, 122.3, 100.4, 95.3, 77.9, 71.3, 67.8, 37.7, 35.4, 25.9, 24.0, 14.9.
6-(2-(1,3-Dioxan-2-yl) phenyl)-2,2-dimethylhex-5-ynal (4)

To a round bottom flask was added DMSO (0.4 g, 3 eq, 4.9 mmol), freshly distilled DCM and cooled to -78 °C. To this solution, oxalyl chloride (0.3 g, 1.5 eq, 2.5 mmol) in anhydrous DCM was added. The mixture was stirred at this temperature for 40 min, and a solution of 3 (0.47 g, 1 eq, 1.6 mmol) in anhydrous DCM was added at -78 °C. After 1.5 h, the mixture was warmed up to room temperature and triethylamine (1.0 g, 6 eq, 9.9 mmol) in anhydrous DCM was added. The reaction mixture was diluted with water (60 mL) and ether (60 mL). The organic layer was separated and further extracted three times with ethyl ether (60 mL x 3). The combined organic layer was washed with saturated NaCl solution (60 mL), dried over anhydrous MgSO₄, and filtered, and the solvent was removed at reduced pressure to yield a product. Chromatography on fresh silica gel (1:4 = ethyl acetate: hexane) afforded a product 4 (0.4 g, 88%, yellow liquid); ¹H NMR (400 MHz, CDCl₃) δ 9.55 (s, 1H), 7.64 (dd, J = 7.8, 1.5 Hz, 1H), 7.37 (dd, J = 7.5, 1.5 Hz, 1H), 7.32 (dd, J = 7.5, 1.5 Hz, 1H), 7.25 – 7.23 (m, 1H), 5.85 (s, 1H), 4.27 (dd, J = 12.1, 4.9, 1.4 Hz, 2H), 4.07 – 3.99 (m, 2H), 2.49 – 2.40 (m, 2H), 2.25 (dt, J = 12.9, 5.1 Hz, 1H), 1.90 (dd, J = 8.4, 7.1 Hz, 2H), 1.49 – 1.41 (m, 1H), 1.14 (s, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 205.5, 139.7, 132.2, 128.7, 128.3, 126.0, 122.0, 100.3, 93.7, 78.8, 77.5, 67.8, 45.9, 36.4, 26.0, 21.5, 15.3.

2-(2-(5,5-dimethylhepta-1,6-diyne-1-yl)phenyl)-1,3-dioxane (5)

To a round bottom flask was added PPh₃ (0.83 g, 3 eq, 3.17 mmol), anhydrous DCM (5 mL) and cooled to 0 °C. After 30 min, a solution of CBr₄ (0.53 g, 1.5 eq, 1.58 mmol) in anhydrous DCM was added and the reaction was stirred for 40 min. To this mixture, a solution of 4 (0.30 g, 1 eq, 1.25 mmol) in anhydrous DCM was added. After completion of the reaction, diethyl ether (10 mL) was added and the suspension was filtered on silica gel. The filtrate was concentrated under reduced pressure. Chromatography on fresh silica gel (1:20 = ethyl acetate: hexane) afforded a dibromide product 5 (0.33 g, 71%, orange liquid); ¹H NMR (400 MHz, CDCl₃) δ 7.64 (dd, J = 7.7, 1.5 Hz, 1H), 7.39 (dd, J = 7.5, 1.5 Hz, 1H), 7.31 (td, J = 7.6, 1.5 Hz, 1H), 7.28 – 7.24 (m, 1H), 6.58 (s, 1H), 5.88 (s, 1H), 4.28 (dd, J = 11.9, 5.0, 1.3 Hz, 2H), 4.02 (td, J = 12.3, 2.4 Hz, 2H), 2.53 – 2.43 (m, 2H), 2.35 – 2.21 (m, 1H), 1.99 – 1.89 (m, 2H), 1.46 (ddt, J = 13.7, 2.9, 1.5 Hz, 1H), 1.25 (s, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 145.4, 139.7, 132.2, 128.7, 128.1, 126.0, 122.3, 100.4, 94.5, 86.4, 78.2, 77.5, 67.8, 40.8, 39.2, 27.3, 26.0, 15.7.

To a round bottom flask was added prepared dibromide (0.33 g, 1 eq, 0.75 mmol) in anhydrous THF (2.5 mL). The solution was cooled to -78 °C and n-BuLi (1.6 M in hexane, 3 eq, 2.26 mmol) was added during 40 min. After completion of reaction (TLC), the reaction mixture was quenched with saturated NH₄Cl solution (50 mL) at 0 °C, and then diluted with water (20 mL) and ether (60 mL). The organic layer was separated and further extracted three times with ethyl ether (60 mL x 3). The combined organic layer was washed with saturated NaCl solution (60 mL), dried over anhydrous MgSO₄, and filtered, and the solvent was removed at reduced pressure to yield a product 5 (0.22 g, 97% yield, yellow liquid); ¹H NMR (400 MHz, CDCl₃) δ 7.64 (dd, J = 7.7, 1.4 Hz, 1H), 7.38 (dt, J = 7.7, 2.4 Hz, 1H), 7.31 (td, J = 7.7, 1.4 Hz, 1H), 7.26 – 7.22 (m, 1H), 5.88 (d, J = 2.2 Hz, 1H), 4.37 – 4.21 (m, 2H), 4.02 (td, J = 12.4, 2.4 Hz, 2H), 2.67 – 2.60 (m, 2H), 2.33 – 2.19 (m, 1H), 2.15 (d, J = 0.7 Hz, 1H), 1.85 – 1.77 (m, 2H), 1.46 – 1.41 (m, 1H), 1.28 (d, J = 0.7 Hz, 6H);
To a round bottom flask was added alkyne 5 in acetone (5.5 mL) and cooling to 0 °C. A solution of 6N HCl (5.2 mL, 40 eq, 31.1 mmol) was added at 0 °C and the mixture was then stirred at room temperature. After completion of reaction (TLC), the reaction mixture was quenched with saturated NaHCO₃ solution (25 mL) at 0 °C, and then diluted with water (20 mL) and ether (40 mL). The organic layer was separated and further extracted three times with ethyl ether (30 mL x 3). The combined organic layer was washed with saturated NaCl solution (50 mL), dried over anhydrous MgSO₄, and filtered, and the solvent was removed at reduced pressure to yield a product. Chromatography on fresh silica gel (1:20 = ethyl acetate: hexane) afforded a product 6 (0.17 g, 95%, yellow liquid); ¹H NMR (400 MHz, CDCl₃) δ 10.57 – 10.49 (m, 1H), 7.94 – 7.87 (m, 1H), 7.54 – 7.46 (m, 2H), 7.44 – 7.34 (m, 1H), 2.73 – 2.61 (m, 2H), 2.15 (s, 1H), 1.82 – 1.75 (m, 2H), 1.28 (s, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 192.2, 136.1, 133.8, 133.3, 128.0, 127.9, 127.0, 98.0, 90.4, 76.4, 69.1, 41.9, 31.1, 29.0, 16.1.

**General procedure for cyclization with AuBr₃ or Cu(OTf)₂.**

**1,1-dimethyl-2,3-dihydrophenanthren-4(1H)-one (7)**

In a seal tube was added 6 (29.3 mg, 0.13 mmol), AuBr₃ (3 mol%) and dry 1,2-dichloroethane 0.4 mL under Argon atmosphere. The mixture was then stirred at 120 °C for 30 min. The solvent was removed under reduced pressure to give crude products which were purified by flash silica gel chromatography using a mixture of ethyl acetate: hexane (1:10) to furnish 7 (26.7 mg, 91%, yellow liquid).

In a seal tube was added 6 (1 eq, 51.9 mg, 0.23 mmol), Cu(OTf)₂ (10 mol%) and dry 1,2-dichloroethane 0.4 mL under Argon atmosphere. The mixture was then stirred at 120 °C for 30 min. The solvent was removed under reduced pressure to give crude products which were purified by flash silica gel chromatography using a mixture of ethyl acetate: hexane (1:10) to furnish 7 (43.1 mg, 83% yield, yellow liquid); ¹H NMR (400 MHz, CDCl₃) δ 9.27 (dd, J = 8.8, 1.0 Hz, 1H), 7.98 (d, J = 8.7 Hz, 1H), 7.85 – 7.78 (m, 1H), 7.61 (ddd, J = 8.6, 6.8, 1.5 Hz, 1H), 7.54 (d, J = 8.7 Hz, 1H), 7.49 (ddd, J = 8.1, 6.8, 1.2 Hz, 1H), 2.86 (dd, J = 7.4, 6.4 Hz, 2H), 2.17 – 2.03 (m, 2H), 1.46 (s, 7H); ¹³C NMR (101 MHz, CDCl₃) δ 200.9, 153.6, 134.5, 132.5, 131.0, 128.8, 128.1, 127.0, 126.7, 126.1, 123.8, 37.4, 37.0, 35.3, 30.0.

**Synthesis of 1,1-dimethyl-2,3-dihydrophenanthren-4(1H)-one (7) (from 4)**
2-(2-(5,5-Dimethylhept-6-en-1-yn-1-yl)phenyl)-1,3-dioxane (5b)

To a round bottom flask was added MePPh₃⁺Br⁻ (2.10 g, 1.2 eq, 5.87 mmol), anhydrous THF (10 mL). The solution was cooled to 0 °C and n-BuLi (2.5M in hexane, 1.5 eq, 7.34 mmol) was added during 30 min at room temperature. The solution was cooled to 0 °C and 4 (1.40 g, 1 eq, 4.89 mmol) in anhydrous THF was added during 1 h at room temperature. The reaction mixture was quenched with separated NH₄Cl solution (30 mL) at 0 °C, and then diluted with water (10 mL) and ether (30 mL). The organic layer was separated and further extracted three times with ethyl ether (30 mL x 3). The combined organic layer was washed with saturated NaCl solution (50 mL), dried over anhydrous MgSO₄, and filtered on silica gel by hexane, and the solvent was removed at reduced pressure to yield a product 5b (941 mg, 68%, red-yellow liquid); ¹H NMR (400 MHz, CDCl₃) δ 7.63 (dd, J = 7.7, 1.6 Hz, 1H), 7.37 (dd, J = 7.7, 1.4 Hz, 1H), 7.30 (td, J = 7.6, 1.7 Hz, 1H), 7.25 – 7.21 (m, 1H), 5.87 (s, 1H), 5.79 (dd, J = 17.4, 10.8 Hz, 1H), 5.03 – 4.89 (m, 2H), 4.34 – 4.23 (m, 2H), 4.06 – 3.96 (m, 2H), 2.45 – 2.33 (m, 2H), 2.31 – 2.11 (m, 1H), 1.74 – 1.65 (m, 2H), 1.45 (ddt, J = 13.5, 2.6, 1.4 Hz, 1H), 1.06 (s, 6H).

2-(5,5-Dimethylhept-6-en-1-yn-1-yl)benzaldehyde (6.1)

To a round bottom flask was added alkyne 5b in acetone (23 mL) and cooling to 0 °C. A solution of 6N HCl (22.1 mL, 40 eq, 132 mmol) was added at 0 °C and the mixture was then stirred at room temperature. After completion of reaction (TLC), the reaction mixture was quenched with saturated NaHCO₃ solution (25 mL) at 0 °C, and then diluted with water (20 mL) and ether (40 mL). The organic layer was separated and further extracted three times with ethyl ether (30 mL x 3). The combined organic layer was washed with saturated NaCl solution (50 mL), dried over anhydrous MgSO₄, and filtered, and the solvent was removed at reduced pressure to yield a product. Chromatography on fresh silica gel (1:10 = ethyl acetate: hexane) afforded a product 6.1 (443 mg, 59.2%, yellow liquid); ¹H NMR (400 MHz, CDCl₃) δ 10.53 (d, J = 0.8 Hz, 1H), 7.88 (ddd, J = 7.8, 1.4, 0.7 Hz, 1H), 7.55 – 7.45 (m, 2H), 7.41 – 7.34 (m, 1H), 5.77 (dd, J = 17.4, 10.8 Hz, 1H), 5.03 – 4.89 (m, 2H), 2.45 – 2.34 (m, 2H), 1.73 – 1.65 (m, 2H), 1.05 (s, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 192.4, 147.1, 136.1, 133.8, 133.3, 128.1, 128.0, 127.1, 111.7, 98.8, 76.2, 41.4, 36.8, 26.6, 15.4.

1,1-Dimethyl-2,3-dihydrophenanthren-4(1H)-one (7) (from 6.1)

In a seal tube was added 6.1 (36.5 mg, 1 eq, 0.16 mmol), Cu(OTf)₂ (5 mol%) and dry 1,2-dichloroethane 0.5 mL under oxygen atmosphere. When the mixture was then stirred at 60 °C for 1.0 h, two products 7.1 and 7 were formed as a mixture. After prolonged time for 15h, 7.1 was almost converted into 7 presumably via air-oxidation. Then, the solvent was removed under reduced pressure to give the crude products containing mostly 7 which were purified by flash silica gel chromatography using a mixture of ethyl acetate: hexane (1:6) to furnish pure 7 (33.2 mg, 91%, yellow liquid).

(7.1) ¹H NMR (400 MHz, CDCl₃) δ 7.25 – 7.15 (m, 2H), 7.08 (dd, J = 7.2, 1.7 Hz, 1H), 6.98 – 6.93 (m, 1H), 6.58 (dd, J = 9.8, 2.3 Hz, 1H), 5.99 (dd, J = 9.8, 3.6 Hz, 1H), 3.74 (d, J = 7.0 Hz, 1H), 2.50 – 2.42 (m, 2H), 1.87 (ddd, J = 13.5, 9.7, 5.8 Hz, 1H), 1.73 – 1.64 (m, 1H), 1.46 (s, 1H), 1.27 (s, 3H), 1.02 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 211.8, 133.6, 133.0, 130.2, 127.8, 127.7, 127.7, 127.6, 126.3, 51.6, 47.7, 37.5, 37.3, 33.2, 27.2, 25.3.
(7) $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.27 (dd, $J = 8.8$, 1.0 Hz, 1H), 7.98 (d, $J = 8.7$ Hz, 1H), 7.85 – 7.78 (m, 1H), 7.61 (ddd, $J = 8.6$, 6.8, 1.5 Hz, 1H), 7.54 (d, $J = 8.7$ Hz, 1H), 7.49 (ddd, $J = 8.1$, 6.8, 1.2 Hz, 1H), 2.86 (t, $J = 7.4$, 6.4 Hz, 2H), 2.17 – 2.03 (m, 2H), 1.46 (s, 6H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 200.9, 153.6, 134.5, 132.5, 131.0, 128.8, 128.1, 127.0, 126.7, 126.1, 123.8, 37.4, 37.0, 35.3, 30.0.

1-Oxomiltirone from 6a

![Diagram of 1-Oxomiltirone from 6a]

2-(5,5-dimethylhepta-1,6-diyn-1-yl)-5-isopropyl-4-methoxybenzaldehyde (6a)

Compound 6a was prepared from 1.1c and alcohol 1 as following the simple model procedure. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 10.38 (s, 1H), 7.76 (s, 1H), 6.88 (s, 1H), 3.89 (s, 3H), 3.26 (sept, $J = 6.9$ Hz, 1H), 2.68 – 2.61 (m, 2H), 1.83 – 1.75 (m, 2H), 1.27 (s, 6H), 1.20 (d, $J = 7.0$ Hz, 6H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 191.3, 161.4, 138.1, 129.7, 127.7, 125.1, 113.8, 97.0, 90.5, 76.6, 69.0, 55.8, 42.0, 31.2, 29.1, 26.9, 22.4, 16.2; HRMS (ESI): exact mass calculated for [M+Na]$^+$ calculated for C$_{20}$H$_{24}$NaO$_2$: 319.1669; found 319.1672.

7-isopropyl-6-methoxy-1,1-dimethyl-2,3-dihydrophenanthren-4(1H)-one (7a)

A 5 mL seal tube was charged with 6a (58.5 mg, 0.20 mmol) and dry 1,2-dichloroethane (0.4 mL). To the solution was added AuBr$_3$ (3 mol%) under argon atmosphere at 0 oC. The resultant mixture was stirred at 120 oC for 30 min and cooled down to room temperature. The solvent was removed under reduced pressure to give crude product 7a (52.7 mg, 90%, brown liquid).

A 5 mL seal tube was charged with 6a (22.4 mg, 0.08 mmol) and dry 1,2-dichloroethane (0.4 mL). To the solution was added Cu(OTf)$_2$ (10 mol%) under argon atmosphere at 0 oC. The resultant mixture was stirred at 120 oC for 30 min and cooled down to room temperature. The solvent was removed under reduced pressure to give crude product 7a (17.9 mg, 80%, brown liquid). 7a: $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 8.88 (s, 1H), 7.89 (d, $J = 8.6$ Hz, 1H), 7.55 (s, 1H), 7.38 (d, p $J = 8.6$ Hz, 1H), 4.00 (s, 3H), 3.44 – 3.35 (m, 1H), 2.84 (t, $J = 7.4$, 6.4 Hz, 2H), 2.08 (t, $J = 7.4$, 6.4 Hz, 2H), 1.45 (s, 6H), 1.29 (d, $J = 6.8$ Hz, 6H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 201.3, 158.9, 153.7, 138.6, 134.2, 131.1, 128.2, 124.8, 124.8, 121.3, 104.8, 55.5, 43.6, 37.5, 37.1, 35.3, 30.2, 27.2, 22.7
**1-Oxomiltirone**

To a round bottom flask was added 7a (58.5 mg, 1 eq, 0.2 mmol) and anhydrous CH₂Cl₂ (15 mL) and the mixture was stirred at 0°C under Aron atmosphere. To this solution a 1.0 M solution of BBr₃ in CH₂Cl₂ (0.3 mL 1.5 eq, 0.30 mmol) was added at 0°C. The reaction was then warmed up to room temperature and stirred overnight. After completion of reaction (TLC), the reaction mixture was quenched with saturated NaHCO₃ solution (10 mL) at 0°C, and then diluted with water (10 mL) and ether (10 mL). The organic layer was separated and further extracted two times with ethyl ether (10 mL x 2). The combined organic layer was washed with saturated NaCl solution (10 mL), dried over anhydrous MgSO₄, and filtered, and the solvent was removed at reduced pressure to yield a product 8a (50 mg, 89%, brown liquid); ¹H NMR (400 MHz, CDCl₃) δ 9.26 (s, 1H), 7.93 (d, J = 8.6 Hz, 1H), 7.59 (s, 1H), 7.35 (d, J = 8.6 Hz, 1H), 3.52 – 3.42 (m, 1H), 2.96 – 2.90 (m, 2H), 2.08 (t, J = 6.8 Hz, 2H), 1.45 (s, 6H), 1.36 (d, J = 6.9 Hz, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 157.6, 155.1, 137.8, 135.5, 131.5, 128.1, 125.5, 123.9, 120.4, 109.3, 36.9, 36.8, 35.3, 30.1, 27.4, 22.7.

To a round bottom flask was added freshly prepared phenol 8a (35.5 mg, 1 eq, 0.13 mmol), Dess-martin periodinane (133 mg, 2.5 eq, 0.3 mmol) and anhydrous CH₂Cl₂ (3 mL). The solution was stirred overnight at room temperature and then diluted with ethyl acetate (4 mL) and water (5 mL). The organic layer was separated and further extracted two times with ethyl ether (5 mL x 2). The combined organic layer was washed with 1N NaOH (5 mL), saturated NaCl solution (5 mL), dried over anhydrous MgSO₄, and filtered, and the solvent was removed at reduced pressure to yield a product 1-oxomiltirone (29.8 mg, 77%, red solid); ¹H NMR (400 MHz, CDCl₃) δ 7.52 (d, J = 8.1 Hz, 1H), 7.07 (d, J = 7.1 Hz, 2H), 1.32 (s, 6H), 1.16 (d, J = 6.9 Hz, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 199.0, 183.9, 183.3, 153.9, 146.6, 138.1, 138.0, 135.6, 132.9, 132.0, 131.1, 36.7, 36.3, 35.1, 29.0, 27.1, 21.7.

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**1-Oxomiltirone from 4a**

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**6-(2-(1,3-Dioxan-2-yl)-4-isopropyl-5-methoxyphenyl)-2,2-dimethylhex-5-ynal (4a)**

Compound 6.1a have been prepared from 1.1c and alcohol 1 following the simple model procedure. ¹H NMR (400 MHz, CDCl₃) δ 9.56 (s, 1H), 7.44 (s, 1H), 6.82 (s, 1H), 5.78 (s, 1H),
4.26 (ddd, \( J = 11.9, 5.0, 1.3 \) Hz, 2H), 4.05 – 3.94 (m, 2H), 3.80 (s, 3H), 3.24 (sept, \( J = 6.9 \) Hz, 1H), 2.43 (t, \( J = 8.3, 7.2 \) Hz, 2H), 2.34 – 2.17 (m, 1H), 1.89 (t, \( J = 8.3, 7.2 \) Hz, 2H), 1.43 (ddd, \( J = 12.5, 2.8, 1.6 \) Hz, 1H), 1.20 (d, \( J = 6.9 \) Hz, 6H), 1.14 (s, 6H).

2-(2-(5,5-Dimethylhept-6-en-1-yn-1-yl)-5-isopropyl-4-methoxyphenyl)-1,3-dioxane (5c)

To a round bottom flask was added \( \text{MePPh}_3^+\text{Br}^- \) (600 mg, 1.2 eq, 1.6 mmol), anhydrous THF (3 mL). The solution was cooled to 0 °C and \( n\)-BuLi (2.5 M in hexane, 1.5 eq, 2.0 mmol) was added during 30 min at room temperature. The solution was cooled to 0 °C and 4a (470 mg, 1 eq, 1.3 mmol) in anhydrous THF was added during 1 h at room temperature. The reaction mixture was quenched with separated \( \text{NH}_4\text{Cl} \) solution (30 mL) at 0 °C, and then diluted with water (10 mL) and ether (30 mL). The organic layer was separated and further extracted three times with ethyl ether (30 mL x 3). The combined organic layer was washed with saturated NaCl solution (50 mL), dried over anhydrous MgSO\(_4\), and filtered on silica gel by hexane, and the solvent was removed at reduced pressure to yield a product 5c (303 mg, 64%, red-yellow liquid); \( ^1\text{H} \) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.44 (s, 1H), 6.81 (s, 1H), 5.85 – 5.74 (m, 2H), 5.02 – 4.92 (m, 2H), 4.26 (ddd, \( J = 11.0, 5.0 \) Hz, 2H), 3.79 (td, \( J = 12.3, 2.5 \) Hz, 2H), 3.24 (sept, \( J = 6.9 \) Hz, 1H), 2.44 – 2.30 (m, 2H), 2.29 – 2.22 (m, 1H), 1.81 – 1.65 (m, 2H), 1.47 – 1.39 (m, 1H), 1.20 (d, \( J = 7.0 \) Hz, 6H), 1.05 (s, 6H). 2-(5,5-Dimethylhept-6-en-1-yn-1-yl)benzaldehyde (6.1a)

To a round bottom flask was added alkyne 5c in acetone (6 mL) and cooling to 0 °C. A solution of 6N HCl (5.7 mL, 40 eq, 34 mmol) was added at 0 °C and the mixture was then stirred at room temperature. After completion of reaction (TLC), the reaction mixture was quenched with saturated NaHCO\(_3\) solution (25 mL) at 0 °C, and then diluted with water (20 mL) and ether (40 mL). The organic layer was separated and further extracted three times with ethyl ether (30 mL x 3). The combined organic layer was washed with saturated NaCl solution (50 mL), dried over anhydrous MgSO\(_4\), and filtered, and the solvent was removed at reduced pressure to yield a product. Chromatography on fresh silica gel (1:20 = ethyl acetate: hexane) afforded a product 6.1a (199 mg, 79%, yellow liquid); \( ^1\text{H} \) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 10.37 (s, 1H), 7.76 (d, \( J = 0.6 \) Hz, 1H), 6.86 (s, 1H), 5.77 (ddd, \( J = 17.4, 10.8 \) Hz, 1H), 5.03 – 4.91 (m, 2H), 3.89 (s, 3H), 3.31 – 3.22 (m, 1H), 2.41 – 2.32 (m, 2H), 1.73 – 1.65 (m, 2H), 1.20 (d, \( J = 7.0 \) Hz, 6H), 1.05 (s, 6H); \( ^{13}\text{C} \) NMR (101 MHz, CDCl\(_3\)) \( \delta \) 191.4, 161.4, 147.2, 138.1, 129.7, 127.9, 125.1, 113.8, 111.7, 97.7, 76.4, 55.8, 41.5, 36.8, 26.9, 26.6, 22.4, 15.4. 7-isopropyl-6-methoxy-1,1-dimethyl-2,3-dihydrophenanthren-4(1H)-one (7a)

A 5 mL seal tube was charged with 6.1a (58.5 mg, 0.20 mmol) and dry 1,2-dichloroethane (0.4 mL). To the solution was added \( \text{AuBr}_3 \) (3 mol%) or \( \text{Cu(OTf)}_2 \) (10 mol%) under argon atmosphere at 0 °C. The resultant mixture was stirred at 120 °C for 30 min and cooled down to room temperature. The solvent was removed under reduced pressure to give crude products which were purified by flash silica gel chromatography using a mixture of ethyl acetate: hexane (1:6) to furnish 7a (45.2 mg, 76%, yellow liquid). 7.1a: \( ^1\text{H} \) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 6.93 (s, 1H), 6.53 (dd, \( J = 9.8, 2.4 \) Hz, 1H), 6.48 (s, 1H), 5.84 (dd, \( J = 9.8, 3.5 \) Hz, 1H), 3.80 (s, 3H), 3.27 (sept, \( J = 6.8 \) Hz, 1H), 2.64 (ddt, \( J = 5.9, 3.9, 2.4 \) Hz, 1H).
2.3 Hz, 1H), 2.49 – 2.41 (m, 2H), 1.89 (ddd, J = 13.4, 9.8, 5.8 Hz, 1H), 1.69 (dd, J = 13.6, 5.9, 2.0 Hz, 1H), 1.28 (s, 3H), 1.20 (dd, J = 15.1, 6.9 Hz, 6H), 1.04 (s, 3H); \[^{13}C\]NMR (101 MHz, CDCl\(_3\)) \(\delta\) 212.2, 156.2, 135.8, 131.4, 130.0, 126.4, 124.6, 124.3, 110.4, 55.6, 51.8, 47.8, 37.5, 37.2, 33.1, 27.1, 26.6, 25.5, 23.1, 22.5.

7a: \(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 8.88 (s, 1H), 7.89 (d, J = 8.6 Hz, 1H), 7.55 (s, 1H), 7.38 (d, J = 8.6 Hz, 1H), 4.00 (s, 3H), 3.44 – 3.35 (m, 1H), 2.84 (t, J = 7.4, 6.4 Hz, 2H), 2.08 (t, J = 7.4, 6.4 Hz, 2H), 1.45 (s, 6H), 1.29 (d, J = 6.9 Hz, 6H); \[^{13}C\]NMR (101 MHz, CDCl\(_3\)) \(\delta\) 201.3, 158.9, 153.7, 138.6, 134.2, 131.1, 128.2, 124.8, 124.8, 121.3, 104.8, 55.5, 43.6, 37.5, 37.1, 35.3, 30.2, 27.2, 22.7.

**Arucadiol from 6b**

2-(5,5-Dimethylhepta-1,6-diy-1-yl)-5-isopropyl-4-methoxybenzaldehyde (6b)

Compound 6b have been prepared from 1.2d and alcohol 1 following the simple model procedure. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 10.39 (s, 1H), 7.57 (s, 1H), 3.94 (d, J = 5.1 Hz, 6H), 3.28 (sept, J = 6.9 Hz, 1H), 2.74 – 2.66 (m, 2H), 1.87 – 1.77 (m, 2H), 1.27 (s, 6H), 1.21 (d, J = 6.9 Hz, 6H); \[^{13}C\]NMR (101 MHz, CDCl\(_3\)) \(\delta\) 192.0, 156.0, 154.0, 143.3, 132.3, 121.1, 120.9, 101.6, 90.4, 72.1, 69.0, 61.2, 61.0, 41.9, 31.1, 29.1, 27.4, 23.1, 16.4; HRMS (ESI): exact mass calculated for [M+Na]^+ calculated for C\(_{21}\)H\(_{26}\)NaO\(_3\): 349.1774; found 349.1775.

7-isopropyl-5,6-dimethoxy-1,1-dimethyl-2,3-dihydrophenanthren-4 (1H)-one (7b)

(a) AuBr\(_3\)-catalyzed cyclization

In a seal tube was added 6b (21.9 mg, 1 eq, 0.07 mmol), AuBr\(_3\) (3 mol%) and dry 1,2-dichloroethane 0.5 mL under Argon atmosphere. The mixture was then stirred at 120 °C for 30 min The solvent was removed under reduced pressure to give crude products which were purified by flash silica gel chromatography using a mixture of ethyl acetate: hexane (1:6) to furnish 7.1b and 7b (1:1 ratio) in 90%, respectively. The product 7b is yellow liquid (7b's TLC Rf is 1:10=0.3; 7.1b's TLC Rf is 1:10=0.7).

7.1b: \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.63 (d, J = 8.3 Hz, 1H), 7.45 (s, 1H), 7.24 (d, J = 8.3 Hz, 1H), 3.98 (s, 3H), 3.96 (s, 3H), 3.53 (t, J = 7.2 Hz, 2H), 3.41 (sept, J = 6.9 Hz, 1H), 2.06 (t, J = 7.3 Hz, 2H), 1.34 (s, 3H), 1.32 (d, 6H); \[^{13}C\]NMR (101 MHz, CDCl\(_3\)) \(\delta\) 149.7, 149.1, 148.2, 141.5, 135.4, 131.4, 127.0, 125.5, 120.9, 120.3, 60.8, 60.8, 43.6, 41.4, 31.4, 29.9, 29.0, 27.5, 23.7; HRMS (ESI): exact mass calculated for [M+Na]^+ calculated for C\(_{20}\)H\(_{26}\)NaO\(_2\): 321.1830 found 321.1833

7b: \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.78 (d, J = 8.6 Hz, 1H), 7.38 (s, 1H), 7.33 (d, J = 8.6 Hz, 1H), 3.91 (s,3H), 3.88 (s, 3H), 3.43 – 3.35 (m, 1H), 2.93 (t, J = 7.2 Hz, 2H), 2.11 (t, J = 7.2 Hz, 2H), 1.37 (s, 6H), 1.30 (d, J = 6.9 Hz, 6H); \[^{13}C\]NMR (101 MHz, CDCl\(_3\)) \(\delta\) 200.1, 151.4, 150.4, 148.0, 143.3, 132.0, 131.0, 130.0, 124.4, 121.6, 120.1, 60.7, 59.7, 36.80, 36.78, 35.3, 28.8, 27.5, 23.6.
(b) Cu(OTf)₂-catalyzed cyclization
In a seal tube was added 6b (15.9 mg, 1 eq, 0.05 mmol), Cu(OTf)₂ (10 mol%) and dry 1,2-dichloroethane 0.4 mL under Aron atmosphere. The mixture was then stirred at 120 °C for 30 min. The reaction was concentrated under reduced pressure and crude compound was by flash chromatography (ethyl acetate/hexane=1/6) to give unique product 7b (15 mg, 95%, yellow liquid).

5,6-Dihydroxy-7-isopropyl-1,1-dimethyl-2,3-dihydrophenanthren-4(1H)-one: arucadiol
To a round bottom flask was added 7b (11.6 mg, 1 eq, 0.04 mmol) and anhydrous CH₂Cl₂ (15 mL) and the mixture was stirred at 0 °C under Aron atmosphere. To this solution BBr₃ (1.0 M in CH₂Cl₂, 0.3 mL, 1.5 eq, 0.30 mmol) was added at 0 °C. The reaction was then warmed up to room temperature and stirred overnight. After completion of reaction (TLC), the reaction mixture was quenched with saturated NaHCO₃ solution (10 mL) at 0 °C, and then diluted with water (10 mL) and ether (10 mL). The organic layer was separated and further extracted two times with ethyl ether (10 mL x 2). The combined organic layer was washed with saturated NaCl solution (10 mL), dried over anhydrous MgSO₄, and filtered, and the solvent was removed at reduced pressure to yield a product. Chromatography on fresh silica gel (1:6 = ethyl acetate: hexane) afforded a product arucadiol (8.1 mg, 76%, light brown liquid); ¹H NMR (400 MHz, CDCl₃) δ 10.64 (s, 1H), 7.95 (d, J = 8.6 Hz, 1H), 7.32 (d, J = 8.6 Hz, 1H), 6.88 (s, 1H), 3.48 – 3.38 (m, 1H), 2.92 (t, J = 6.9 Hz, 2H), 2.07 (t, J = 6.9 Hz, 2H), 1.34 (d, J = 6.9 Hz, 6H), 1.26 (s, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 204.5, 158.4, 145.1, 138.3, 137.8, 136.7, 128.0, 125.5, 120.5, 120.3, 118.8, 36.5, 36.2, 35.6, 31.1, 29.8, 27.8, 22.4.
Copies of NMR Spectra

(1) \(^1\)H and \(^{13}\)C NMR of 6.
(2) $^1$H and $^{13}$C NMR of 6.1.
(3) $^1$H and $^{13}$C NMR of 7.1.
(4) $^1$H and $^{13}$C NMR of 7.

![NMR Spectra](image)
(S) $^1$H and $^{13}$C NMR of 6a.
(6) $^1$H and $^{13}$C NMR of 6.1a.
(7) $^1$H and $^{13}$C NMR of 7.1a.
(8) $^1$H and $^{13}$C NMR of 7a.
(9) $^1$H and $^{13}$C NMR of 8a.
(10) $^1$H and $^{13}$C NMR of 1-oxomiltirone.
(11) $^1$H and $^{13}$C NMR of $6b$. 
(12) $^1$H and $^{13}$C NMR of 7.1b.
(13) $^1$H and $^{13}$C NMR of 7b.
(14) ¹H and ¹³C NMR of arucadiol.