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# Total Synthesis of Phenanthro-Quinolizidine Alkaloids: (±)-Cryptopleurine, (±)-Boehmeriasin A, (±)-Boehmeriasin B and (±)-Hydroxycryptopleurine

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**Keywords:** Alkaloids / Total synthesis / Structure elucidation / Natural products / Nitrogen heterocycles

The first synthesis of (±)-boehmeriasin A and B and a concise synthesis of (±)-cryptopleurine and (±)-hydroxycryptopleurine are described. The piperidine ring of these alkaloids was constructed by the coupling of the phenanthrene ring with 2-bromopyridine through a nucleophilic substitution reaction and subsequent reduction of the resulting pyridyl ketone. The first crystal structure of a phenanthro-quinolizidine alkaloid is also reported.


## Introduction

Phenanthro-quinolizidine alkaloids are a small group of alkaloids existing in the *Lauraceae*, *Vitaceae* and *Urticaceae* family of plants. Only five of these alkaloids have been isolated.[1–3] Cryptopleurine (**1**; Figure 1),[1] which was isolated by Lande from the bark of *Cryptocarya pleurosperma* in 1948,[1a] is the representative member of these alkaloids. It has been shown to possess unique and interesting biological properties including vesicant,[1a] antimicrobial,[4] antiviral[5] and anticancer activities.[6] Boehmeriasin A (**2**; Figure 1), boehmeriasin B (**3**; Figure 1) and hydroxycryptopleurine (**4**; Figure 1) are new members of this alkaloid family.[2,3] Boehmeriasin A and B were isolated from the Asian medicinal plant *Boehmeria siamensis* after bioactivity-guided fractionation by Luo et al. in 2003.[2] In assays for cytotoxicity against 12 cancer cell lines, boehmeriasin A proved to be one-to-two orders of magnitude more active than Taxol (a plant anti-tumour agent) in most cases, with $GI_{50}$ values in the range 0.2–5 ng/mL for all but one cell line. Boehmeriasin B showed lower activity.[2,7] Although hydroxycryptopleurine was synthesized in the last century,[8] it has recently been isolated from the roots of *Boehmeria pannosa* by Lee and co-workers who elucidated its structure, including the absolute configuration, by spectroscopic methods.[3] Hydroxycryptopleurine potently inhibits the hypoxia-induced expression of a reporter gene under the control of a hypoxia response element with $IC_{50}$ values of 48.1 nM. Furthermore, it suppresses the accumulation of the HIF-1R protein in a dose-dependent manner.[3]

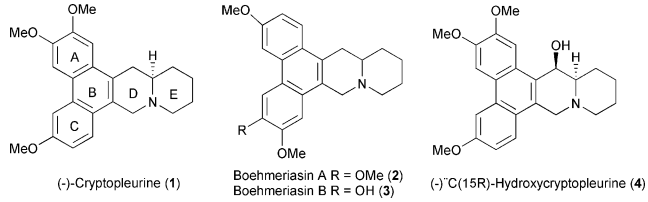


Figure 1. Chemical structures of compounds **1**–**4**.

Because of their important biological activity coupled with their low natural abundance and unusual phenanthro[9,10-*b*]quinolizidine skeleton, these phenanthro-quinolizidine alkaloids have attracted the attention of numerous synthetic research groups in recent years. There has been a number of impressive efforts towards the synthesis of these alkaloids for the purpose of fundamental research and drug development.[9] However, boehmeriasin A and B have not been synthesized until now and more efficient and general approaches to these alkaloids would still be desirable. Herein, we wish to report the first synthesis of (±)-boehmeriasin A and B, a concise synthesis of (±)-cryptopleurine and (±)-hydroxycryptopleurine and the first crystal structure of a phenanthro-quinolizidine alkaloid.

## Results and Discussion

The construction of the phenanthrene and quinolizidine rings is key to the synthesis of phenanthro-quinolizidine alkaloids. Our group has previously constructed the phenanthrene ring efficiently by using $FeCl_3$ as an oxidative coupling reagent.[10] Our synthetic plan then focused on the construction of the quinolizidine ring. Coupling of an aromatic moiety with a pyridine derivative followed by saturation of the heteroaromatic unit has been widely used in the preparation of arylpiperidine derivatives.[11,12] In this work,

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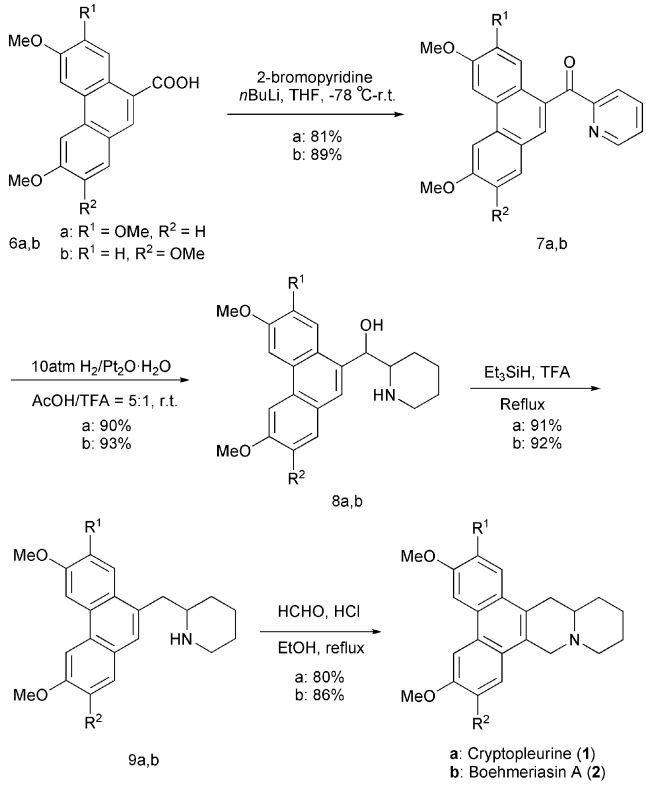
we employed this strategy in our synthesis of phenanthroquinolizidine alkaloids.

At the outset, we selected cryptopleurine (**1**) and its positional isomer boehmeriasin A (**2**), which possess the basic structural element of interest, as optimal targets to test our methodology. Phenanthrene-9-carboxylic acids **6a** and **6b** as starting materials were conveniently prepared according to our previously reported procedure.[10b] 2-Bromopyridine was then treated with *n*BuLi at –78 °C to afford 2-lithiopyridine. The latter reacted smoothly with **6a** and **6b** to give pyridyl ketones **7a** and **7b** in 81 and 89% yields, respectively (Scheme 1). The saturation of the pyridine ring has usually been carried out by catalytic hydrogenation reactions in the presence of Pt,[13] $PtO_2$,[11e,14] Raney nickel[15] or Pd/C.[11d,12,16] Initially, Pd/C was selected as the catalyst to obtain the desired methylenepiperdine compounds **9a** and **9b** from **7a** and **7b** directly by the procedure reported by Agai and co-workers.[12] However, this method was not successful and the desired products **8a** and **8b** were not obtained. Then we turned our attention to $PtO_2$, which is more active than Pd/C and more widely used in the reduction of pyridines. By using $PtO_2$ as the catalyst, the hydrogenation of **7a** and **7b** proceeded smoothly in acetic acid and trifluoroacetic acid (TFA) at 10 atm to give **8a** and **8b** in 90 and 93% yields, respectively. Due to its poor solubility, the $^1$H NMR spectrum of **8b** in hot [$D_6$]DMSO was obtained, but its $^{13}$C NMR spectrum could not be obtained. The reduction of **8a** and **8b** in $Et_3SiH$/TFA[17] at reflux afforded **9a** and **9b** in 91 and 92% yields, respectively. Having successfully constructed the quinuolizidine ring of the phenanthroquinuolizidine alkaloids, we then converted quinuolizidine **9a** and **9b** into cryptopleurine and boehmeriasin A in 80 and 86% yields, respectively, by using the previously reported reaction conditions (formaldehyde, HCl, EtOH, reflux).[9b,9d]




Scheme 1. Synthesis of (±)-cryptopleurine (**1**) and (±)-boehmeriasin A (**2**).

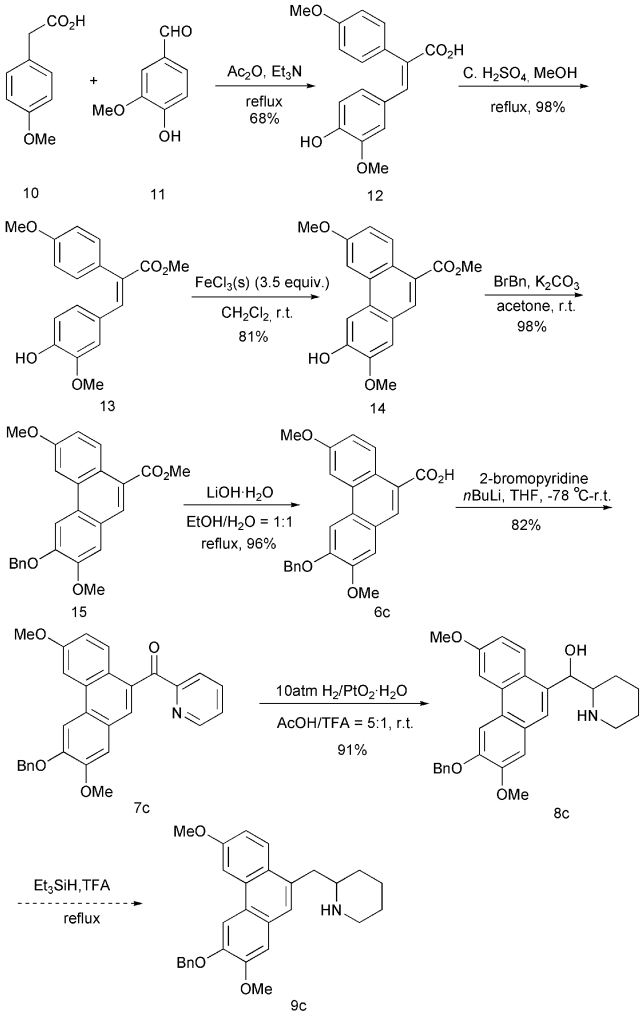
Having accomplished the synthesis of (±)-cryptopleurine (**1**) and (±)-boehmeriasin A (**2**), we then turned our attention to the preparation of boehmeriasin B (**3**). Phenanthrene-9-carboxylic acid **6c** was synthesized by employing homoanisic acid (**10**) and vanillin (**11**) as the starting materials (Scheme 2). Acrylate **13** was obtained by the conventional two steps previously reported in the literature.[10b,18] Oxidative coupling of the acrylate **13** using $FeCl_3$ (3.5 equiv.)[10] gave phenanthrene-9-carboxylate **14** in 81% yield. Then phenol protection and ester hydrolysis proceeded sequentially in 98 and 96% yields, respectively, to give **6c**. Acid **6c** was treated with 2-lithiopyridine to afford the desired ketone **7c** in 82% yield. The catalytic hydrogenation of **7c** proceeded smoothly under the same conditions as used for the preparation of **8a** and **8b** to give **8c** in 91% yield. Unfortunately, reduction of **8c** using the $Et_3SiH$/TFA system failed to afford the desired product **9c**.

Then we used Gribble′s method[19] as an alterative to study the reduction of the pyridyl ketone **7c** (Scheme 3). To our disappointment, when ketone **7c** was treated with $NaBH_4$/TFA following the procedure reported by Gribble and co-workers,[19] compound **16**, in which the benzyl group has also been removed, was obtained in only 8% yield. Most of ketone **7c** was transformed into two rearrangement products **17** and **18** in 68 and 5% yields, respectively. Owing to their poor solubility as well as the $^1$H NMR chemical shifts of the pyridine ring overlapping with those of the phenanthrene and benzene rings, we transformed **17** into the corresponding piperidine **19** by catalytic hydrogenation to deduce the position of the benzyl group. According to the H,H-COSY spectrum of compound **19**, the position of the benzyl group in **17** was confirmed to be at C5. Thus, the position of the benzyl group in **18** was proposed to be at C4. The formation of **17** and **18** could be explained by the formation of the benzyl cation and subsequent Friedel–Crafts alkylation of the phenanthrene ring.

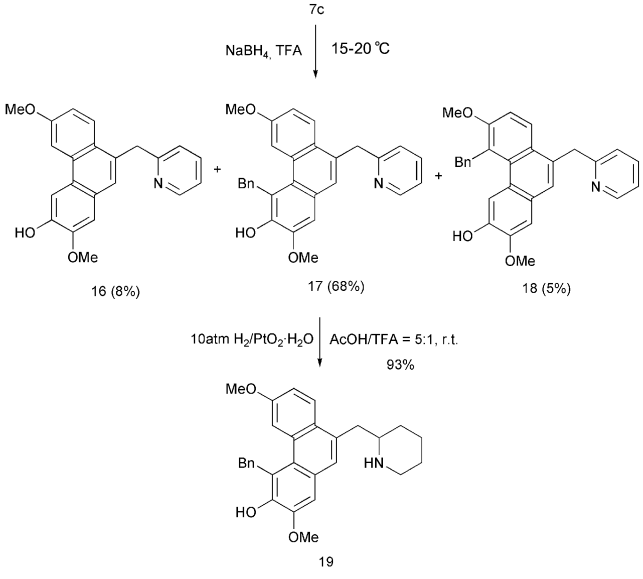
To avoid the rearrangement, the benzyl group should be removed before this step. When ketone **7c** was treated with 1 atm of hydrogen in the presence of 10% Pd/C, the desired deprotection and carbonyl reduction product **20** was obtained in 98% yield (Scheme 4). Then alcohol **20** was reduced smoothly to **16** in 82% yield by using Gribble's method.[19] Analogous to the preparation of cryptopleurine (**1**) and boehmeriasin A (**2**), catalytic hydrogenation (94%) of the pyridine compound **16** and then Pictet–Spengler cyclomethylenation (87%) of the resulting product **21** gave (±)-boehmeriasin B (**3**).

(±)-Hydroxycryptopleurine (**4**) was synthesized in 71% yield from intermediate **8a** by the Pictet–Spengler cyclomethylenation reaction (Scheme 5).[9b,9d] Its constitution was confirmed by X-ray diffraction (Figure 2). Although the crystal structures of the phenanthroindolizidine alka-

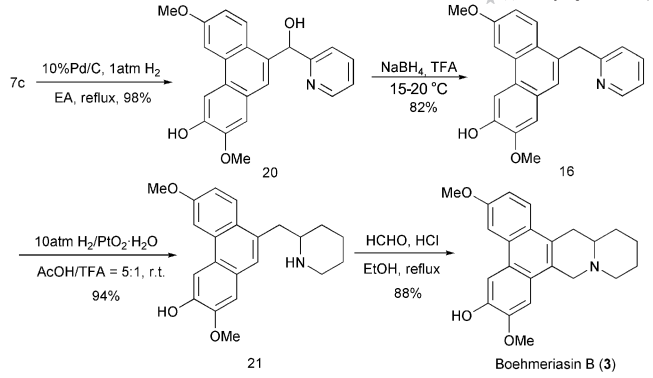
  




Scheme 2. Preparation of **7c** and the synthetic approach towards (±)-boehmeriasin B (**3**).

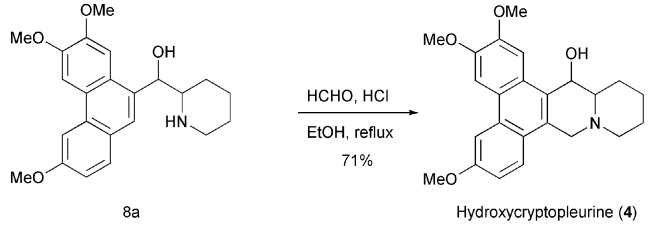



Scheme 3. Reduction of **7c** with $NaBH_4$/TFA.




Scheme 4. Synthesis of (±)-boehmeriasin B (**3**).

loids antofine and tylophorine methiodide monohydrate have previously been reported,[20] this is the first crystal structure of phenanthro-quinolizidine alkaloids. Figure 2 shows the structural formula and the numbering scheme adopted for the molecule of hydroxycryptopleurine. The hydroxy group at C6 is *trans* to the hydrogen at C5. The phenanthrene ring shows slight deviations from planarity. The non-coplanarity of the fused aromatic ring system arises from steric interactions and prevents delocalization of the π electrons.[20b] The conformation of the D ring corresponds to the atoms C6, C7, C20 and C21 lying in nearly one plane, with N above and C5 below the plane, and the four-atom plane of the D ring is nearly coplanar with ring B. The conformation of the E ring can be described as "chair"-like.




Scheme 5. Synthesis of (±)-hydroxycryptopleurine (**4**).

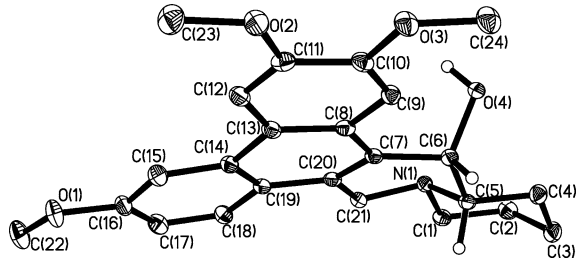



Figure 2. Molecular structure of (±)-hydroxycryptopleurine (**4**) from a single-crystal X-ray structure determination. The enantiomer and solvent molecules have been omitted for clarity.

## Conclusions

The first synthesis of (±)-boehmeriasin A and B and a concise synthesis of (±)-cryptopleurine and (±)-hydroxy-

cryptopleurine have been accomplished in high overall yields (65, 54, 53 and 52%, respectively) in three, four or five steps from phenanthrene-9-carboxylic acid. The concise and facile synthetic strategy described herein provides a practical synthetic approach to phenanthro-quinolizidine alkaloids and provides a variety of analogues readily available for biological evaluation. The first crystal structure of a phenanthro-quinolizidine alkaloid has also been revealed.

## Experimental Section

**General:** All non-aqueous reactions were performed under an inert atmosphere (nitrogen or argon) with rigid exclusion of moisture from reagents and all reaction vessels were oven-dried. All anhydrous solvents were dried and purified by standard techniques just before use. The melting points were determined with an X-4 binocular microscope melting-point apparatus (Beijing Tech Instruments Co., Beijing, China) and are uncorrected. High-resolution mass spectra (HRMS) were obtained with a FTICR-MS (Ionspec 7.0T) spectrometer. $^1$H NMR spectra were obtained by using a Bruker AC-P 300, AV 400, AV 600 or a Varian Mercury Plus 400 spectrometer. Chemical shifts are reported in parts per million (ppm) relative to either a tetramethylsilane internal standard or solvent signals. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br. = broad), coupling constants and integration. $^{13}$C NMR spectra were recorded using a Bruker AC-P 300 (75 MHz) or AV 400 spectrometer (100 MHz) using $CDCl_3$ or [$D_6$]DMSO as the solvent. Chemical shifts ($\delta$) are reported in parts per million measured relative to the solvent peak. IR spectra were recorded with a MAGNA-560 FTIR (Nicolet Company) spectrometer.

**(Pyridin-2-yl)(2,3,6-trimethoxyphenanthren-10-yl)methanone (7a):** *n*BuLi (32 mL, 80 mmol, 2.5 M in hexane solution) was added to a stirred solution of 2-bromopyridine (12.64 g, 80.00 mmol) at –78 °C over 20 min. The brown solution was stirred at –78 °C for 1 h and the acid **6a** (6.24 g, 20.00 mmol) was added at once. The mixture was stirred at –78 °C for 2 h and then allowed to warm to room temperature. The mixture was then hydrolysed with saturated aqueous $NH_4Cl$ and extracted with $CH_2Cl_2$. The organic layer was dried with anhydrous $Na_2SO_4$, filtered and concentrated in vacuo. Ethanol was added to the residue and the precipitate was filtered and washed with ethanol to give **7a** (6.06 g, 81%) as a bright yellow solid; m.p. 224–226 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 3.97 (s, 3 H, OMe), 4.03 (s, 3 H, OMe), 4.12 (s, 3 H, OMe), 7.17 (d, $J$ = 8 Hz, 1 H, Ar-H), 7.50 (s, 1 H, Ar-H), 7.75 (d, $J$ = 8 Hz, 1 H, Ar-H), 7.83 (s, 1 H, Ar-H), 7.90 (s, 3 H, Ar-H), 8.05 (s, 1 H, Ar-H), 8.10–8.12 (m, 1 H, Ar-H), 8.74 (s, 1 H, Ar-H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 55.5, 55.8, 55.9, 103.4, 103.9, 107.0, 116.0, 124.0, 124.8, 125.2, 126.1, 129.3, 131.9, 132.6, 133.2, 136.9, 149.1, 149.2, 149.9, 156.5, 160.3, 196.3 ppm. HRMS (ESI): calcd. for $C_{23}H_{19}NO_4$ [M + H]$^+$ 374.1387; found 374.1386.

**(Pyridin-2-yl)(2,3,6-trimethoxyphenanthren-9-yl)methanone (7b):** Ketone **7b** was synthesized from **6b** (6.24 g, 20.00 mmol) by using a procedure similar to that described for **7a** (bright-yellow solid, 6.66 g, 89%); m.p. 213–214 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 3.99 (s, 3 H, OMe), 4.01 (s, 3 H, OMe), 4.13 (s, 3 H, OMe), 7.19–7.22 (m, 2 H, Ar-H), 7.49 (s, 1 H, Ar-H), 7.80 (s, 1 H, Ar-H), 7.87 (s, 1 H, Ar-H), 7.90–7.94 (m, 2 H, Ar-H), 8.14 (d, $J$ = 6.4 Hz, 1 H, Ar-H), 8.34 (d, $J$ = 8.4 Hz, 1 H, Ar-H), 8.72 (s, 1 H, Ar-H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 55.4, 55.9, 56.0, 103.2, 104.3, 109.4, 115.7, 123.5, 124.6, 125.4, 126.2, 126.4, 128.3, 130.0, 131.3, 131.7, 136.9, 149.1, 149.6, 150.9, 156.1, 158.2, 196.3 ppm. HRMS (ESI): calcd. for $C_{23}H_{19}NO_4$ [M + H]$^+$ 374.1387; found 374.1390.

**[3-(Benzyloxy)-2,6-dimethoxyphenanthren-9-yl](pyridin-2-yl)methanone (7c):** Ketone **7c** was synthesized from **6c** (7.76 g, 20.00 mmol) by using a procedure similar to that described for **7a** (bright-yellow solid, 7.36 g, 82%); m.p. 171–172 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 3.97 (s, 3 H, OMe), 3.99 (s, 3 H, OMe), 5.40 (s, 2 H, $CH_2$), 7.17 (d, $J$ = 9.2 Hz, 1 H, Ar-H), 7.20 (s, 1 H, Ar-H), 7.34 (d, $J$ = 6 Hz, 1 H, Ar-H), 7.41 (s, 2 H, Ar-H), 7.48 (s, 1 H, Ar-H), 7.56–7.57 (m, 2 H, Ar-H), 7.70 (s, 1 H, Ar-H), 7.79 (s, 1 H, Ar-H), 7.91 (s, 2 H, Ar-H), 8.12 (d, $J$ = 6.8 Hz, 1 H, Ar-H), 8.28 (d, $J$ = 8.4 Hz, 1 H, Ar-H), 8.71 (s, 1 H, Ar-H) ppm. $^{13}$C NMR (75 MHz, [$D_6$]-DMSO): $\delta$ = 55.3, 55.9, 71.2, 103.8, 106.1, 109.7, 116.1, 123.4, 124.6, 125.6, 126.2, 126.3, 127.4, 128.1, 128.2, 128.7, 129.9, 131.5, 131.7, 136.9, 149.1, 149.9, 150.2, 156.1, 158.2, 196.3 ppm. HRMS (ESI): calcd. for $C_{29}H_{23}NO_4$ [M + H]$^+$ 450.1700; found 450.1697.

**(Piperidin-2-yl)(2,3,6-trimethoxyphenanthren-10-yl)methanol (8a):** A mixture of **7a** (3.73 g, 10.00 mmol), acetic acid (200 mL), trifluoroacetic acid (40 mL) and $PtO_2{\cdot}H_2O$ (0.10 g) was stirred under hydrogen at a pressure of 10 atm for 24 h. The mixture was filtered and the filtrate was evaporated to dryness in vacuo. The residue was treated with aqueous NaOH and extracted with $CH_2Cl_2$ (3 × 100 mL). The combined organic extracts were dried with anhydrous $Na_2SO_4$, filtered and concentrated in vacuo to give the crude product, which was recrystallized from petroleum ether and $CH_2Cl_2$ to give the amine **8a** (3.45 g, 90%) as a white solid; m.p. 123–125 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 1.18–1.26 (m, 1 H, 3-H), 1.31–1.41 (m, 2 H, 4-H), 1.52–1.62 (m, 2 H, 5-H), 1.76 (d, $J$ = 12.8 Hz, 1 H, 3-H), 2.57–2.64 (m, 1 H, 6-H), 3.03 (d, $J$ = 11.6 Hz, 1 H, 6-H), 3.09–3.13 (m, 1 H, 1-H), 4.01 (s, 3 H, OMe), 4.02 (s, 3 H, OMe), 4.10 (s, 3 H, OMe), 5.25 (d, $J$ = 5.2 Hz, 1 H, Ar-CH), 7.18 (dd, $J$ = 2.0, 8.8 Hz, 1 H, Ar-H), 7.56 (s, 1 H, Ar-H), 7.74 (s, 1 H, Ar-H), 7.77 (s, 1 H, Ar-H), 7.81 (d, $J$ = 2.0 Hz, 1 H, Ar-H), 7.89 (s, 1 H, Ar-H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 24.3, 26.3, 26.7, 47.0, 55.6, 55.9, 56.1, 60.0, 75.0, 103.9, 103.9, 105.0, 115.4, 123.6, 125.0, 125.3, 125.5, 130.4, 130.7, 131.9, 148.6, 149.1, 158.2 ppm. HRMS (ESI): calcd. for $C_{23}H_{27}NO_4$ [M + H]$^+$ 382.2013; found 382.2017.

**(Piperidin-2-yl)(2,3,6-trimethoxyphenanthren-9-yl)methanol (8b):** A mixture of **7b** (3.73 g, 10.00 mmol), acetic acid (200 mL), trifluoroacetic acid (40 mL) and $PtO_2{\cdot}H_2O$ (0.10 g) was stirred under hydrogen at a pressure of 10 atm for 24 h. The mixture was filtered and the filtrate was evaporated to dryness in vacuo. The residue was treated with aqueous NaOH and then $CH_2Cl_2$ (300 mL) was added. After shaking the mixture the organic layer formed a suspension, which was separated, and the organic phase was concentrated in vacuo to give the crude product, which was washed with $CH_2Cl_2$ to give amine **8b** (3.55 g, 93%) as a white solid; m.p. 250–253 °C. $^1$H NMR (400 MHz, [$D_6$]DMSO): $\delta$ = 1.12–1.28 (m, 3 H, 3-H, 4-H), 1.42–1.44 (m, 1 H, 5-H), 1.52–1.55 (m, 1 H, 5-H), 1.69–1.71 (m, 1 H, 3-H), 2.40–2.45 (m, 1 H, 6 H), 2.50 (s, 1 H, NH), 2.80–2.82 (m, 1 H, 6-H), 2.89–2.92 (m, 1 H, 1-H), 3.92 (s, 3 H, OMe), 4.00 (s, 3 H, OMe), 4.02 (s, 3 H, OMe), 5.10 (s, 1 H, OH), 5.31 (s, 1 H, Ar-CH), 7.24 (d, $J$ = 7.6 Hz, 1 H, Ar-H), 7.42 (s, 1 H, Ar-H), 7.69 (s, 1 H, Ar-H), 8.05 (s, 1 H, Ar-H), 8.11 (s, 1 H, Ar-H), 8.14 (d, $J$ = 8.8 Hz, 1 H, Ar-H) ppm. HRMS (ESI): calcd. for $C_{23}H_{27}NO_4$ [M + H]$^+$ 382.2013; found 382.2017.

**[3-(Benzyloxy)-2,6-dimethoxyphenanthren-9-yl](piperidin-2-yl)methanol (8c):** Methanol **8c** was synthesized from **7c** (2.32 g, 5.17 mmol) by using a procedure similar to that described for **8a** (white solid, 2.15 g, 91%); m.p. 223–225 °C. $^1$H NMR (400 MHz, [$D_6$]DMSO): $\delta$ = 1.11–1.17 (m, 1 H, 3-H), 1.23–1.29 (m, 2 H, 4-H), 1.43 (d, $J$ =

11.6 Hz, 1 H, 5-H), 1.53 (d, $J$ = 12 Hz, 1 H, 5-H), 1.70 (d, $J$ = 10.4 Hz, 1 H, 3-H), 2.42 (t, $J$ = 11.2 Hz, 1 H, 6-H), 2.80–2.82 (m, 1 H, 6-H), 2.90 (d, $J$ = 8.7 Hz, 1 H, 1-H), 3.93 (s, 3 H, OMe), 4.00 (s, 3 H, OMe), 5.10 (s, 1 H, OH), 5.30 (s, 1 H, Ar-CH), 5.40 (s, 2 H, benzyl-$CH_2$), 7.23 (dd, $J$ = 2.4, 9.2 Hz, 1 H, Ar-H), 7.36 (d, $J$ = 7.2 Hz, 1 H, Ar-H), 7.41–7.45 (m, 3 H, Ar-H), 7.58 (s, 1 H, Ar-H), 7.60 (s, 1 H, Ar-H), 7.68 (s, 1 H, Ar-H), 8.03 (d, $J$ = 2 Hz, 1 H, Ar-H), 8.14 (d, $J$ = 9.6 Hz, 1 H, Ar-H), 8.17 (s, 1 H, Ar-H) ppm. $^{13}$C NMR (75 MHz, [D$_6$]DMSO): $\delta$ = 24.3, 26.3, 26.8, 46.6, 55.4, 55.5, 60.9, 70.2, 73.5, 104.5, 106.0, 108.8, 115.2, 121.9, 123.1, 123.5, 126.0, 126.8, 127.9, 128.0, 128.4, 131.2, 135.0, 137.2, 147.7, 149.7, 157.4 ppm. HRMS (ESI): calcd. for $C_{29}H_{31}NO_4$ [M + H]$^+$ 458.2326; found 458.2326.

**Hydroxycryptopleurine (4):** A 37% formaldehyde solution (25 mL) was added dropwise over 10 min to a solution of piperidine **8a** (1.53 g, 4.00 mmol) in ethanol (100 mL) and then conc. HCl (2.5 mL) was added. The reaction mixture was heated at reflux for 2 d in the dark. The reaction mixture was evaporated under reduced pressure to remove most of the ethanol. The residue was filtered and washed with ethyl acetate to give a white solid. The solid was dissolved with $CH_2Cl_2$ and washed with aqueous NaOH. The organic layer was dried with anhydrous $MgSO_4$, filtered and concentrated in vacuo to afford the hydroxycryptopleurine (**4**; 1.12 g, 71%) as a yellow powder; m.p. 232–234 °C (ref.[3] 201–203 °C; ref.[8a] 236–237 °C (isomer A), 208–209 °C (isomer B); ref.[8b] 203–205 °C).

**2-[(2,3,6-Trimethoxyphenanthren-10-yl)methyl]piperidine (9a):** A mixture of **8a** (1.53 g, 4.00 mmol), trifluoroacetic acid (60 mL) and triethylsilane (0.58 g, 5.00 mmol) was heated at reflux for 8 h. The reaction mixture was concentrated to dryness under reduced pressure. The residue was treated with aqueous NaOH and extracted with $CH_2Cl_2$ (3 × 100 mL). The combined organic layer was dried with anhydrous $Na_2SO_4$, filtered and concentrated in vacuo. Purification of the residue by flash column chromatography on silica gel ($CH_2Cl_2$/MeOH, 10:1) afforded the amine **9a** (1.33 g, 91%) as a white solid; m.p. 147–148 °C (ref.[9a] 110–116 °C; ref.[9b] 136–137 °C; ref.[9d] 147–148 °C; ref.[9e] 122–123 °C).

**2-[(2,3,6-Trimethoxyphenanthren-9-yl)methyl]piperidine (9b):** Piperidine **9b** was synthesized from **8b** (3.35 g, 8.79 mmol) by using a procedure similar to that described for **9a** (white solid, 3.21 g, 92%); m.p. 177–179 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 1.30–1.44 (m, 2 H, 3-H, 4-H), 1.54–1.60 (m, 2 H, 5-H), 1.78–1.84 (m, 2 H, 3-H, 4-H), 2.51–2.57 (m, 1 H, 1-H), 2.69 (br., 1 H, NH), 2.98 (s, 1 H, 6-H), 3.06–3.14 (m, 2 H, Ar$CH_2$), 3.22–3.25 (m, 1 H, 6-H), 4.01 (s, 3 H, OMe), 4.08 (s, 3 H, OMe), 4.11 (s, 3 H, OMe), 7.18 (d, $J$ = 8.4 Hz, 1 H, Ar-H), 7.44 (s, 1 H, Ar-H), 7.49 (s, 1 H, Ar-H), 7.73 (d, $J$ = 8.4 Hz, 1 H, Ar-H), 7.83 (s, 1 H, Ar-H), 7.92 (s, 1 H, Ar-H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 24.9, 26.2, 33.3, 41.4, 47.1, 55.4, 55.7, 56.0, 56.8, 103.4, 104.5, 108.0, 114.9, 123.6, 124.7, 125.2, 126.2, 127.3, 131.2, 131.7, 148.8, 149.6, 157.8 ppm. HRMS (ESI): calcd. for $C_{23}H_{27}NO_3$ [M + H]$^+$ 366.2064; found 366.2064.

**Cryptopleurine (1):** Cryptopleurine (**1**) was synthesized from **9a** (1.22 g, 3.34 mmol) as a white solid (1.00 g, 80%) by using a procedure similar to that described for the synthesis of hydroxycryptopleurine (**4**); m.p. 204–206 °C (ref.[3] 198–201 °C).

**Boehmeriasin A (2):** Boehmeriasin A (**2**) was synthesized from **9b** (1.65 g, 4.52 mmol) as a white solid (1.47 g, 86%) by using a procedure similar to that described for the synthesis of hydroxycryptopleurine (**4**); m.p. 222–223 °C (ref.[2] 216–218 °C).

**Reduction of Diaryl Ketone 7c in Sodium Borohydride/Trifluoroacetic Acid Media:** Solid sodium borohydride (0.76 g, 20.00 mmol) was added over 30 min to a stirred trifluoroacetic acid (20 mL) at 15–20 °C under nitrogen. Ketone **7c** (0.90 g, 2.00 mmol) was added in portions to this mixture at 15–20 °C over 15 min. The mixture was stirred under nitrogen at 20 °C for 12 h and then another portion of sodium borohydride (0.38 g, 10.00 mmol) was added. Stirring was continued for another 12 h. The reaction mixture was diluted with water, basified with $NaHCO_3$ (solid) and extracted with $CH_2Cl_2$ (3 × 100 mL). The combined organic extracts were washed with water, dried with $Na_2SO_4$, filtered and concentrated in vacuo. Compounds **16**, **17** and **18** were isolated by column chromatography on silica gel (petroleum ether/EtOAc, 1:1).

**2,6-Dimethoxy-9-[(pyridin-2-yl)methyl]phenanthren-3-ol (16):** White solid (0.055 g, 8%); m.p. 226–228 °C. $^1$H NMR (400 MHz, [D$_6$]-DMSO): $\delta$ = 3.94 (s, 6 H, OMe), 4.50 (s, 2 H, Ar$CH_2$), 7.13 (dd, $J$ = 2, 9.2 Hz, 1 H, Ar-H), 7.18 (s, 1 H, Ar-H), 7.20 (s, 1 H, Ar-H), 7.33 (s, 1 H, Ar-H), 7.50 (s, 1 H, Ar-H), 7.63 (t, $J$ = 7.6 Hz, 1 H, Ar-H), 7.87 (s, 1 H, Ar-H), 7.98 (d, $J$ = 9.2 Hz, 1 H, Ar-H), 8.01 (s, 1 H, Ar-H), 8.50 (d, $J$ = 4 Hz, 1 H, Ar-H), 9.43 (s, 1 H, OH) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 42.7, 55.3, 55.9, 104.0, 106.8, 107.5, 116.0, 121.3, 123.1, 124.8, 125.2, 125.4, 126.6, 127.0, 131.2, 131.8, 136.7, 145.5, 147.4, 149.1, 157.8, 161.0 ppm. HRMS (ESI): calcd. for $C_{22}H_{19}NO_3$ [M + H]$^+$ 346.1438; found 346.1440.

**4-Benzyl-2,6-dimethoxy-9-[(pyridin-2-yl)methyl]phenanthren-3-ol (17):** White solid (0.59 g, 68%); m.p. 219–220 °C. $^1$H NMR (400 MHz, [D$_6$]DMSO): $\delta$ = 3.81 (s, 3 H, OMe), 3.94 (s, 3 H, OMe), 4.41 (s, 2 H, benzyl-$CH_2$), 4.43 (s, 2 H, Ar$CH_2$), 6.98 (d, $J$ = 7.6 Hz, 1 H, Ar-H), 7.11–7.23 (m, 7 H, Ar-H), 7.55–7.59 (m, 2 H, Ar-H), 7.87 (s, 1 H, Ar-H), 8.02 (d, $J$ = 9.2 Hz, 1 H, Ar-H), 8.04 (s, 1 H, Ar-H), 8.47 (d, $J$ = 3.6 Hz, 1 H, Ar-H), 9.87 (s, 1 H, OH) ppm. $^{13}$C NMR (75 MHz, [D$_6$]DMSO): $\delta$ = 30.8, 42.0, 55.2, 60.2, 104.3, 107.1, 116.0, 121.3, 122.0, 122.8, 124.7, 124.7, 125.6, 126.5, 126.5, 128.1, 128.2, 128.9, 131.0, 131.2, 136.4, 141.1, 147.0, 148.8, 149.4, 157.5, 160.4 ppm. HRMS (ESI): calcd. for $C_{29}H_{25}NO_3$ [M + Na]$^+$ 458.1727; found 458.1722.

**5-Benzyl-2,6-dimethoxy-9-[(pyridin-2-yl)methyl]phenanthren-3-ol (18):** White solid (0.044 g, 5%); m.p. 236–237 °C. $^1$H NMR (400 MHz, [D$_6$]DMSO): $\delta$ = 3.16 (s, 3 H, OMe), 4.02 (s, 3 H, OMe), 4.50 (s, 2 H, benzyl-$CH_2$), 4.69 (s, 2 H, Ar$CH_2$), 7.02 (d, $J$ = 8.8 Hz, 1 H, Ar-H), 7.19–7.20 (m, 3 H, Ar-H), 7.27–7.32 (m, 4 H, Ar-H), 7.42 (s, 1 H, Ar-H), 7.57 (s, 1 H, Ar-H), 7.62 (d, $J$ = 7.6 Hz, 1 H, Ar-H), 7.67 (s, 1 H, Ar-H), 7.96 (d, $J$ = 8.8 Hz, 1 H, Ar-H), 8.50 (s, 1 H, Ar-H), 9.02 (s, 1 H, OH) ppm. $^{13}$C NMR (75 MHz, [D$_6$]-DMSO): $\delta$ = 35.1, 41.7, 54.1, 55.7, 107.3, 108.3, 115.2, 119.7, 121.3, 122.7, 124.7, 125.6, 125.8, 126.1, 126.4, 127.3, 128.0, 128.3, 130.7, 131.7, 136.5, 139.9, 145.5, 147.3, 148.9, 156.2, 160.5 ppm. HRMS (ESI): calcd. for $C_{29}H_{25}NO_3$ [M + H]$^+$ 436.1907; found 436.1899.

**4-Benzyl-2,6-dimethoxy-9-[(piperidin-2-yl)methyl]phenanthren-3-ol (19):** A mixture of **17** (0.30 g, 0.69 mmol), acetic acid (10 mL), trifluoroacetic acid (2 mL) and $PtO_2$·$H_2O$ (0.01 g) was stirred under hydrogen at a pressure of 10 atm for 24 h. The mixture was filtered and the filtrate was evaporated to dryness in vacuo. The residue was treated with saturated aqueous $NaHCO_3$ and extracted with $CH_2Cl_2$ (3 × 100 mL). The combined organic extracts were dried with $Na_2SO_4$, filtered and concentrated in vacuo to give the crude product, which was recrystallized from petroleum ether and $CH_2Cl_2$ to give the amine **19** (0.30 g, 93%) as a white solid; m.p. 176–177 °C. $^1$H NMR (400 MHz, [D$_6$]DMSO): $\delta$ = 1.14 (br., 2 H, 3-H, 4-H), 1.29–1.32 (m, 1 H, 5-H), 1.43–1.46 (m, 1 H, 5-H), 1.56–1.58 (m, 1 H, 4-H), 1.66 (br., 1 H, 3-H), 2.39 (t, $J$ = 11.6 Hz, 1 H, 2-H), 2.71–2.73 (m, 1 H, 6-H), 2.88–3.00 (m, 3 H, 6-H, Ar$CH_2$), 3.17 (s, 3 H, OMe), 4.01 (s, 3 H, OMe), 4.69 (s, 2 H, benzyl-$CH_2$), 7.09 (d, $J$ = 9.2 Hz, 1 H, Ar-H), 7.21–7.24 (m, 1 H, Ar-H), 7.27–

7.32 (m, 4 H, Ar-H), 7.41 (s, 1 H, Ar-H), 7.42 (s, 1 H, Ar-H), 7.68 (s, 1 H, Ar-H), 8.01 (d, $J$ = 9.2 Hz, 1 H, Ar-H) ppm. $^{13}$C NMR (75 MHz, [D$_6$]DMSO): $\delta$ = 24.6, 26.0, 32.6, 35.1, 40.6, 46.6, 54.1, 55.6, 56.7, 107.1, 108.3, 115.2, 119.5, 124.5, 125.7, 125.8, 126.0, 127.2, 128.1, 128.3, 130.2, 131.6, 140.0, 145.4, 147.3, 156.1 ppm. HRMS (ESI): calcd. for $C_{29}H_{31}NO_3$ [M + H]$^+$ 442.2377; found 442.2369.

**9-[Hydroxy(pyridin-2-yl)methyl]-2,6-dimethoxyphenanthren-3-ol (20):** A solution of ketone **7c** (1.34 g, 2.98 mmol) in EtOAc (1000 mL) was charged with Pd/C (0.2 g, 10 wt.%). The reaction mixture was stirred for 12 h under a balloon filled with hydrogen gas at slight reflux. The mixture was filtered and the filtrate was evaporated. The residue was washed with EtOAc twice (2 × 5 mL) to afford **20** as a white solid (1.05 g, 98%); m.p. 220–222 °C. $^1$H NMR (400 MHz, [D$_6$]DMSO): $\delta$ = 3.93 (s, 3 H, OMe), 3.94 (s, 3 H, OMe), 6.21 (s, 1 H, ArCH), 6.30 (s, 1 H, OH), 7.11 (d, $J$ = 8.8 Hz, 1 H, Ar-H), 7.21–7.24 (m, 1 H, Ar-H), 7.39 (s, 1 H, Ar-H), 7.57 (d, $J$ = 8 Hz, 1 H, Ar-H), 7.70 (s, 1 H, Ar-H), 7.73–7.77 (m, 1 H, Ar-H), 7.85 (s, 1 H, Ar-H), 7.99 (s, 1 H, Ar-H), 8.17 (d, $J$ = 8.8 Hz, 1 H, Ar-H), 8.45 (d, $J$ = 3.2 Hz, 1 H, Ar-H), 9.42 (br., 1 H, ArOH) ppm. $^{13}$C NMR (75 MHz, [D$_6$]DMSO): $\delta$ = 55.2, 55.5, 74.0, 103.7, 107.3, 108.9, 115.2, 121.0, 122.1, 122.2, 123.4, 123.9, 125.9, 126.7, 131.0, 125.0, 136.6, 146.8, 148.2, 148.8, 157.2, 163.8 ppm. HRMS (ESI): calcd. for $C_{22}H_{19}NO_4$ [M + Na]$^+$ 384.1206; found 384.1214.

**2,6-Dimethoxy-9-[(pyridin-2-yl)methyl]phenanthren-3-ol (16):** Pyridine **16** was synthesized from **20** (0.81 g, 2.24 mmol) as a white solid (0.63 g, 82%) by using a procedure similar to that described for the reduction of diaryl ketone **7c** in sodium borohydride/trifluoroacetic acid media.

**2,6-Dimethoxy-9-[(piperidin-2-yl)methyl]phenanthren-3-ol (21):** Piperidine **21** was synthesized from **16** (0.58 g, 1.68 mmol) as a white solid (0.55 g, 94%) by using a procedure similar to that described for the synthesis of **9a** except saturated aqueous $NaHCO_3$ was used to basify the evaporated residue; m.p. 155–157 °C. $^1$H NMR (400 MHz, [D$_6$]DMSO): $\delta$ = 1.17–1.27 (m, 2 H, 3-H, 4-H), 1.36–1.42 (m, 1 H, 5-H), 1.49–1.52 (m, 1 H, 5-H), 1.58–1.60 (m, 1 H, 4-H), 1.67–1.69 (m, 1 H, 3-H), 2.47–2.51 (m, 2 H, 6-H), 2.84–2.85 (m, 1 H, NH), 2.95–3.00 (m, 2 H, 2-H, ArCH$_2$), 3.11–3.15 (m, 1 H, ArCH$_2$), 3.93 (s, 3 H, OMe), 3.97 (s, 3 H, OMe), 5.76 (s, 1 H, OH), 7.21 (dd, $J$ = 2.0, 8.8 Hz, 1 H, Ar-H), 7.32 (s, 1 H, Ar-H), 7.38 (s, 1 H, Ar-H), 7.89 (d, $J$ = 2 Hz, 1 H, Ar-H), 8.02 (s, 1 H, Ar-H), 8.05 (d, $J$ = 8.8 Hz, 1 H, Ar-H) ppm. $^{13}$C NMR (75 MHz, [D$_6$]DMSO): $\delta$ = 23.94, 25.18, 31.65, 46.07, 54.86, 55.24, 55.49, 56.56, 103.93, 107.36, 108.21, 115.53, 123.66, 124.64, 124.78, 126.11, 126.17, 129.62, 131.09, 146.51, 148.81, 157.44 ppm. HRMS (ESI): calcd. for $C_{22}H_{25}NO_3$ [M + H]$^+$ 352.1907; found 352.1903.

**Boehmeriasin B (3):** Boehmeriasin B (**3**) was synthesized from **21** (0.66 g, 1.88 mmol) as a white solid (0.60 g, 88%) by using a procedure similar to that described for the synthesis of hydroxycryptopleurine (**4**) except saturated aqueous $NaHCO_3$ was used to wash the organic solvent; m.p. 228–230 °C (ref.[2] 248–250 °C).

**Supporting Information** (see also the footnote on the first page of this article): Experimental procedures, characterization data for compounds **12**–**15** and **6c**, spectroscopic data for compounds **1**–**4** and **9a**, copies of $^1$H and $^{13}$C NMR spectra for all compounds and crystallographic data for hydroxycryptopleurine (**4**).

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