Benzo-Annulated Steroids: Synthesis of Octahydro-indeno-phenanthrenes by Formal [3 + 3] Cyclocondensation Reaction with 1,3-Bis[(trimethylsilyl)oxy]buta-1,3-dienes

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Octahydro-indeno-phenanthrenes, benzo-annulated steroids, were prepared by formal [3 + 3] cyclocondensation reaction of 1,3-bis[(trimethylsilyl)oxy]buta-1,3-dienes with the silyl enol ether of 16-formylestrone methyl ether.

Introduction. – Steroids are highly relevant as pharmacologically active natural products, hormones, and drugs. For example, estrone (**1**) represents a female sexual hormone. Ethynylestradiol (**2**) is used as a commercial oral contraceptivum [1]. On the other hand, the 1*H*-indenol substructure is present in various natural products. For example, the terpenoid haliclotriol A (**3**) has been isolated from the sponge *Haliclona* and exhibits antimicrobial activity [2] (*Fig.*). Octahydro-indeno-phenanthrenes, which combine the subunits of a steroid and of 1*H*-indenol have, to the best of our knowledge, not been isolated as natural products so far. However, the synthesis of such molecules has been previously reported [3][4].

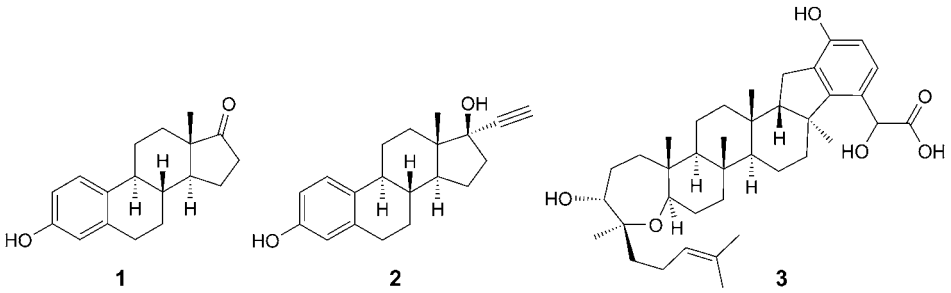
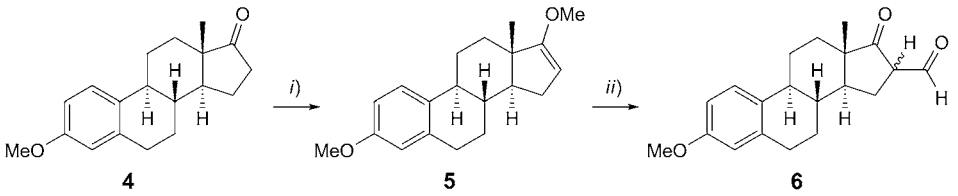


Figure. *Structure of estrone* (**1**)*, ethynylestradiol* (**2**)*, and haliclotriol A* (**3**)

Results and Discussion. – Benzo-annulated estrones have been prepared in different ways. Key step is the introduction of a functional group at C(16). For example, 16-formylestrone methyl ether (**6**) can be prepared from **4** in two steps *via* enol ether **5** (*Scheme 1*) [5]. The product, which represents a 1,3-bis-electrophile, has been used in

cyclization reactions [6]. The cyclization of steroid-derived 1,3-bis-electrophiles, such as **6**, have been scarcely reported so far. The cyclization of **6** with diethyl acetone-1,3-dicarboxylate (=diethyl 3-oxopentanedioate), which possesses two CH acidic CH_2 groups, has been reported to give the expected octahydro-indeno-phenanthrene [7]. The reaction requires harsh conditions. The direct use of non-symmetrical 1,3-dicarbonyl compounds proved to be not possible.

Scheme 1. *Synthesis of 16-Formylestrone Methyl Ether* (**6**) [5]



4 **5** **6**

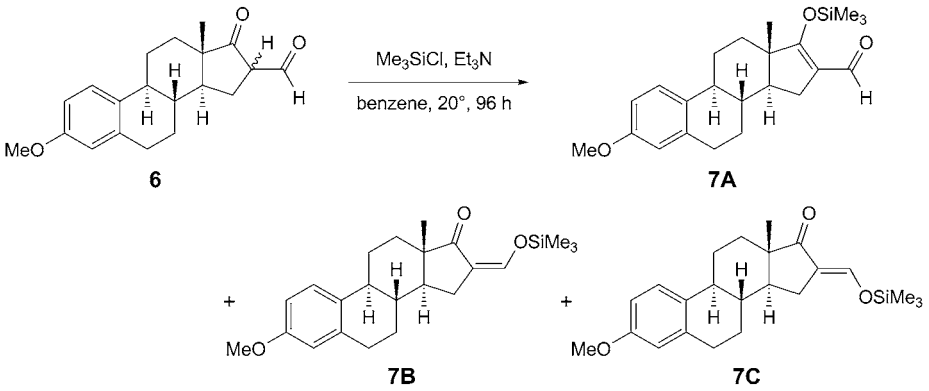
i) Me_2SO_4, KOH. *ii*) HCO_2Et, Na, benzene.

Chan and co-workers were the first to report $TiCl_4$-mediated formal [3+3] cyclocondensation reactions with 1,3-bis[(trimethylsilyl)oxy]buta-1,3-dienes, which can be regarded as masked 1,3-dicarbonyl dianions [8][9]. These dienes can be prepared in two steps from the corresponding 1,3-dicarbonyl compounds [10], and they represent important synthetic building blocks [11]. Herein, we report a new and convenient synthesis of functionalized octahydro-indeno-phenanthrenes by formal [3+3] cyclocondensations of 1,3-bis[(trimethylsilyl)oxy]buta-1,3-dienes with a silyl enol ether derived from **6**. The advantage of this methodology is based on the fact that, in contrast to the use of diethyl 3-oxopentanedioate, unsymmetrical 1,3-dicarbonyl compounds can be employed. The cyclizations proceed with very high regioselectivity.

The silylation of **6** resulted in the formation of a mixture of silyl enol ethers (*Scheme 2*). One main isomer, **7C**, and two minor isomers, **7A** and **7B**, were formed (according to ^{1}H-NMR). Separation of the isomers by distillation or chromatography was not possible (close boiling points; hydrolysis during of chromatography). Therefore, the mixture as such was used for the next step. In fact, the presence of isomers **7B** and **7C** should not cause problems during cyclization, because the configuration of the exocyclic C=C bond (isomers **7B** and **7C**) has no relevance for the cyclization/aromatization step. The presence of isomer **7A** has also no relevance for the cyclization, as it is known that 3-(silyloxy)-2-en-1-ones can undergo isomerization reactions with shift of the silyl group from one O-atom to the other under the conditions of the $TiCl_4$-mediated [3+3] cyclization [8]. This is evident from the reaction of 1,3-bis[(trimethylsilyl)oxy]buta-1,3-dienes with the 4-phenyl-4-[(trimethylsilyl)oxy]but-3-en-2-one [8].

The $TiCl_4$-mediated [3+3] cyclocondensation of 1,3-bis[(trimethylsilyl)oxy]buta-1,3-dienes **8a**–**8f** with **7** afforded the octahydro-4b*H*-indeno[2,1-*a*]phenathrene-7-carboxylates **9a**–**9f** in 21–68% yield (*Scheme 3* and *Table*). The reactions proceeded with very high regioselectivity. Only the products containing the ester group located at C(7) were observed. As side products, only hydrolyzed starting materials were observed. The structures of **9a**, **9e**, and **9f** were easily established by ^{1}H-NMR spectroscopy, which showed two *doublet*s (^3J = 8.2 Hz) for the aromatic H-atoms. The

Scheme 2



Scheme 3

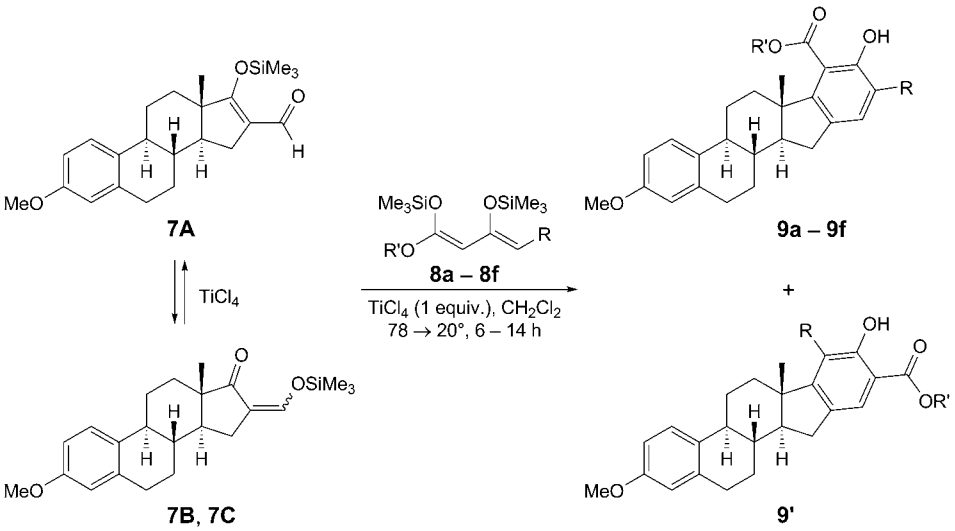


Table. *Synthesis of the Octahydro-4b*H*-indeno[2,1-*a*]phenanthrene-7-carboxylates* **9a**–**9f**

Product	R	R′	Yield [%][a])
9a	H	Me	42
9b	Me	Me	68
9c	Pr	Me	63
9d	$Cl(CH_2)_3$	Me	35
9e	H	^{i}Pr	21
9f	H	Bn	21

[a]) Yields of isolated product.

signals for the isomeric products **9′** were not observed. The products **9a**–**9c** were obtained in good yields. Products **9d**–**9f** were isolated in relatively low yields. This might be due to decomposition of the diene during the reaction. Nevertheless, for all reactions, only one regioisomer was obtained.

The products are presumably formed as follows. Under the reaction conditions, equilibrium between **7A**, **7B**, and **7C** is established. For this assumption, we have no experimental evidence, but it can be considered in analogy to a mechanism suggested by *Chan* and *Brownbridge* in [8]. Subsequently, the terminal C-atom of the diene, with the higher electron density, undergoes a $TiCl_4$-mediated attack at the exocyclic C=C bond of enones **7B** and **7C** and, finally, cyclization takes place by attack of the central C-atom of the diene at the C=O group, followed by aromatization during the aqueous workup.

In conclusion, we accomplished the synthesis of octahydro-indeno-phenanthrenes, benzo-annulated steroids, by formal [3 + 3] cyclocondensation reactions of 1,3-bis[(trimethylsilyl)oxy]buta-1,3-dienes with the silyl enol ether of 16-formylestrone methyl ether (**6**). The reactions proceed in good yields for dienes derived from methyl acetoacetate and chain-extended homologs. The yields decrease for other ester groups (Bn, ^{i}Pr) and for functionalized derivatives.

Experimental Part

General. Reactions were carried out under inert atmosphere (Ar 4.6) to simultaneously exclude O_2 and H_2O when appropriate. Pressure tubes were used to avoid condenser. Solvents for reactions were dried and distilled by standard methods, or purchased from *Merck®*, *Aldrich®*, *Acros Organics®*, and others, whenever exclusion of H_2O was desired. Solvents for liquid chromatography and extraction were always distilled prior to use and partly reused after fractional distillation (heptane, AcOEt). TLC: *Merck Kieselgel 60 F_{254}* on aluminium foil from *Macherey-Nagel*, detection under UV light at 254 nm and 365 nm, as colorizing reagent, the following mixtures were used: 1–2/100 *p*-anisaldehyde or vanillin, 10/100 glacial AcOH, 5/100 H_2SO_4, 83–84/100 MeOH. Column Chromatography (CC): *Merck* silica gel *60* or *Macherey-Nagel* silica gel *60* (0.063–0.200 mm, 70–230 mesh). The finer *Merck* silica gel *60* (0.040–0.063 mm, 230–400 mesh) was chosen when appropriate. M.p.: *Micro heating table HMK 67/1825 Kuestner* (*Büchi*), *Leitz Labolux 12 Pol* with heating table *Mettler FP 90*; uncorrected. IR Spectra: *Nicolet 205* FT-IR, *Nicolet Protége 460* FT-IR; $\tilde{\nu}$ in cm^{-1}. NMR Spectroscopy: *Bruker AC 250*, *Bruker ARX 300*, *Bruker ARX 500*. For characterization 1D-^{1}H-NMR, H-decoupled ^{13}C-NMR, and DEPT 135 spectra were collected. If necessary other techniques (NOESY, COSY, HMQC, and HMBC) were applied as well. All NMR spectra presented in this work were recorded in (D_6)DMSO and $CDCl_3$ soln. All chemical shifts were given in ppm. References (^{1}H-NMR): TMS (δ 0.00) or residual $CHCl_3$ (δ 7.26) were taken as internal standard. References (^{13}C-NMR): TMS (δ 0.0) or residual $CHCl_3$ (δ 77.0) were taken as internal standard. More complex coupling patterns are represented by combinations of the respective symbols. For example, *td* indicates a *triplet* of *doublet*s with the larger coupling constant associated with the first symbol (here: *triplet*). Coupling constants are given in Hz. MS: *AMD MS40*, *Varian MAT CH 7*, *MAT 731* (EI, 70 eV), *Intecta AMD 402* (EI, 70 eV and CI), *Finnigan MAT 95* (CI, 200 eV); in *m*/*z* (rel. %). HR-MS: *Varian MAT 311*, *Intecta AMD 402*; in *m*/*z*. Elemental Analysis: *LECO CHNS-932 Thermoquest Flash EA 1112*.

General Procedure (*GP*) *for the Synthesis of Octahydro-indeno-phenanthrenes* **9a**–**9f**. *3-Methoxy-16-[(trimethylsilyloxy)methylidene]estra-1,3,5(10)-trien-17-one* (**7**; 1.0 mmol) and the corresponding *1,3-bis[(trimethylsilyl)oxy]buta-1,3-dienes* **8a**–**8f** (1.1–2.0 mmol) were dissolved in 2 ml of dry CH_2Cl_2, and the mixture was cooled to −78° under Ar. After addition of $TiCl_4$ (1.0 mmol), the mixture was warmed to 20° and stirred for 20 h. Subsequently, 10% aq. HCl was added, followed by repeated extraction with

CH_2Cl_2. The combined org. layers were dried (Na_2SO_4) and evaporated under reduced pressure. The product was obtained after CC (heptane/AcOEt).

(16Z)-3-Methoxy-16-{[(trimethylsilyl)oxy]methylidene}estra-1(10),2,4-trien-17-one (**7B**). A soln. of *3-methoxy-17-oxoestra-1(10),2,4-triene-16-carbaldehyde* (**6**; 2.760 g, 8.83 mmol) and Et_3N (1.6 ml, 11.45 mmol) in benzene (20.7 ml) was stirred at 20° for 30 min. Then, addition of Me_3SiCl (1.67 ml, 13.1 mmol) followed. The mixture was stirred at 20° for 4 d. Thereafter, the precipitated $Et_3N \cdot HCl$ was removed by filtration under Ar and washed with pentane. All solvents of the clear soln. were removed under reduced pressure. Thus, compound **7** was obtained as a pale-yellow solid (2.838 g, 84%). To avoid decomposition, it had to be stored under Ar at low temp. Due to its instability, no analyses, except ^{1}H-NMR, could be performed. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.31–7.28 (*m*, H–C(19)); 7.10 (*d*, $^3J = 8.6$, H–C(1)); 6.61 (*dd*, $^3J = 8.6$, $^4J = 2.7$, H–C(2)); 6.54 (*d*, $^4J = 2.7$, H–C(4)); 3.67 (*s*, MeO); 2.86–2.53 (*m*, 3 H, CH and/or CH_2); 2.32–2.12 (*m*, 2 H, CH and/or CH_2); 2.02–1.81 (*m*, 3 H, CH and/or CH_2); 1.55–1.29 (*m*, 5 H, CH and/or CH_2); 0.81 (*s*, 3 H, H–C(18)); 0.17 (*s*, Me_3SiO).

*Methyl (4bS,6aS,11aS,11bS)-5,6,6a,11,11a,11b,12,13-Octahydro-8-hydroxy-2-methoxy-6a-methyl-4b*H-*indeno[2,1-*a*]phenanthrene-7-carboxylate* (**9a**). According to *GP*, with **7** (384 mg, 1.00 mmol) and **8a** (287 mg, 1.10 mmol). CC (heptane/AcOEt 100:1 → 30:1), afforded **9a** (138 mg, 42%). Pale-yellow solid. M.p. 168–170°. IR (ATR): 3428*s*, 3045*w*, 3006*w*, 2972*w*, 2922*w*, 1705*s*, 1495*s*, 1278*s*, 1257*s*, 1201*m*, 1132*m*, 1095*m*. ^{1}H-NMR (250 MHz, $CDCl_3$): 9.83 (*s*, OH); 7.28 (*d*, $^3J(9,10) = 8.2$, H–C(9) or H–C(10)); 7.21 (*d*, $^3J(3,4) = 8.5$, H–C(4)); 6.79 (*d*, $^3J(9,10) = 8.2$, H–C(9) or H–C(10)); 6.73 (*dd*, $^3J(3,4) = 8.5$, $^4J(1,3) = 2.8$, H–C(3)); 6.66 (*d*, $^4J(1,3) = 2.6$, H–C(1)); 3.97, 3.79 (2*s*, 2 MeO); 2.99–2.23 (*m*, 8 H, CH, CH_2); 1.79–1.51 (*m*, 5 H, CH, CH_2); 1.17 (*s*, Me). ^{13}C-NMR (75 MHz, $CDCl_3$): 170.8 (C=O); 158.5, 157.5, 154.5, 137.8, 135.2, 132.6 (C); 130.9, 126.0, 114.8, 113.8, 111.5 (CH); 110.9 (C); 57.8, 55.2 (MeO); 51.7 (CH); 48.9 (C); 43.7, 37.6 (CH); 34.7, 31.4, 29.7, 27.6, 26.8 (CH_2); 15.6 (Me). EI-MS (70 eV): 392 (M^+, 89), 361 (31), 360 (100), 345 (49), 180 (24), 173 (44). HR-EI-MS: 392.198797 (M^+, $C_{25}H_{28}O_4^+$; calc. 392.19821).

*Methyl (4bS,6aS,11aS,11bS)-5,6,6a,11,11a,11b,12,13-Octahydro-8-hydroxy-2-methoxy-6a,9-dimethyl-4b*H-*indeno[2,1-*a*]phenanthrene-7-carboxylate* (**9b**). According to *GP*, with **7** (384 mg, 1.00 mmol) and **8b** (302 mg, 1.10 mmol). CC (heptane/AcOEt 100:1 → 30:1) furnished **9b** (275 mg, 68%). Colorless solid. M.p. 169–170°. IR (ATR): 3058*w*, 2992*w*, 2973*w*, 2955*w*, 1663*s*, 1614*m*, 1575*m*, 1498*m*, 1445*s*, 1254*s*, 1199*s*, 1175*m*, 1151*s*, 1044*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 10.21 (*s*, OH); 7.23 (*d*, $^3J(3,4) = 8.7$, H–C(4)); 7.21 (*s*, H–C(10)); 6.76 (*dd*, $^3J(3,4) = 8.5$, $^4J(1,3) = 2.7$, H–C(3)); 6.69 (*d*, $^4J(1,3) = 2.6$, H–C(1)); 3.99, 3.81 (2*s*, 2 MeO); 3.00–2.28 (*m*, 7 H, CH, CH_2); 2.26 (*s*, *Me*–Ar); 2.07–1.97 (*m*, 1 H, CH or CH_2); 1.81–1.48 (*m*, 5 H, CH, CH_2); 1.18 (*s*, Me). ^{13}C-NMR (75 MHz, $CDCl_3$): 171.3 (C=O); 157.4, 156.7, 151.7, 137.7, 134.3, 132.6 (6*s*, 6 C_q), 132.1, 125.9 (2*s*, 2 arom. CH); 123.6 (C_q); 113.8, 111.4 (2*s*, 2 arom. CH); 110.1 (C_q); 57.8, 55.1 (2*s*, 2 MeO); 51.6 (CH); 48.8 (C_q); 43.7, 37.6 (2*s*, 2 CH); 34.8, 31.4, 29.7, 27.6, 26.8 (5*s*, 5 CH_2); 16.0 (*Me*–Ar); 15.6 (Me). EI-MS (70 eV): 406 (40, M^+), 375 (28), 374 (100), 359 (47), 173 (35), 105 (26). HR-MS (ESI-TOF/MS): 407.22174 ($[M+H]^+$, $C_{26}H_{31}O_4^+$; calc. 407.22169). Anal. calc. for $C_{26}H_{30}O_4$ (406.51): C 76.82, H 7.44; found: C 76.35, H 7.50.

*Methyl (4bS,6aS,11aS,11bS)-5,6,6a,11,11a,11b,12,13-Octahydro-8-hydroxy-2-methoxy-6a-methyl-9-propyl-4b*H-*indeno[2,1-*a*]phenanthrene-7-carboxylate* (**9c**). According to *GP*, with **7** (384 mg, 1.00 mmol) and **8c** (333 mg, 1.10 mmol). CC (heptane/AcOEt 100:1 → 30:1) gave **9c** (272 mg, 63%). Colorless solid. M.p. 125–127°. IR (ATR): 3049*w*, 2991*w*, 2952*w*, 1671*s*, 1608*m*, 1501*m*, 1463*w*, 1443*w*, 1422*m*, 1312*m*, 1278*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 10.12 (*s*, OH); 7.21 (*d*, $^3J(3,4) = 8.6$, H–C(4)); 7.18 (*s*, H–C(10)); 6.73 (*dd*, $^3J(3,4) = 8.6$, $^4J(1,3) = 2.8$, H–C(3)); 6.66 (*d*, $^4J(1,3) = 2.7$, H–C(1)); 3.97, 3.79 (2*s*, 2 MeO); 2.98–2.26 (*m*, 9 H, CH, CH_2); 2.05–1.95 (*m*, 1 H, CH or CH_2); 1.81–1.52 (*m*, 7 H, CH, CH_2); 1.16 (*s*, Me); 0.98 (*t*, $^3J = 7.3$, *Me*CH_2CH_2). ^{13}C-NMR (75 MHz, $CDCl_3$): 171.4 (C=O); 157.5, 156.5, 151.7, 137.8, 134.3, 132.7 (C); 131.4 (CH); 128.1 (C); 126.0, 113.8, 111.5 (CH); 110.3 (C); 57.9, 55.2 (MeO); 51.6 (CH); 48.8 (C); 43.8, 37.6 (CH); 34.8, 32.2, 31.5, 29.7, 27.7, 26.8, 22.7 (CH_2); 15.7 (Me); 14.1 (*Me*CH_2CH_2). EI-MS (70 eV): 434 (38, M^+), 402 (100), 387 (37), 374 (18), 173 (30), 147 (15). HR-MS (ESI-TOF/MS): 435.25292 ($[M+H]^+$, $C_{28}H_{35}O_4^+$; calc. 435.25299). Anal. calc. for $C_{28}H_{34}O_4$ (434.57): C 77.39, H 7.89; found: C 77.09, H 8.04.

*Methyl (4bS,6aS,11aS,11bS)-9-(3-Chloropropyl)-5,6,6a,11,11a,11b,12,13-octahydro-8-hydroxy-2-methoxy-6a-methyl-4b*H-*indeno[2,1-*a*]phenanthrene-7-carboxylate* (**9d**). According to *GP*, with **7** (384 mg,

1.00 mmol) and **8d** (674 mg, 2.00 mmol). CC (heptane/AcOEt 100:1 → 15:1) gave **9d** (164 mg, 35%). Colorless solid. M.p. 132–134°. IR (ATR): 3049*w*, 3024*w*, 2991*w*, 2931*m*, 2906*m*, 2850*m*, 1674*s*, 1608*m*, 1579*m*, 1500*s*, 1453*m*, 1441*s*, 1434*s*, 1421*s*, 1355*m*, 1337*m*, 1312*s*, 1294*m*, 1279*s*, 1262*m*, 1247*m*, 1230*s*, 1198*s*, 1170*s*, 1150*s*, 1102*m*, 1044*m*, 1032*m*, 1025*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 10.20 (*s*, OH); 7.23 (*d*, $^3J(3,4) = 8.3$, H–C(4)); 7.22 (*s*, H–C(10)); 6.75 (*dd*, $^3J(3,4) = 8.5$, $^4J(1,3) = 2.7$, H–C(3)); 6.68 (*d*, $^4J(1,3) = 2.6$, H–C(1)); 3.99, 3.80 (2*s*, 2 MeO); 3.58 (*t*, $^3J = 6.6$, CH_2Cl); 2.99–2.02 (*m*, 12 H, CH, CH_2); 1.79–1.47 (*m*, 5 H, CH, CH_2); 1.18 (*s*, Me). ^{13}C-NMR (75 MHz, $CDCl_3$): 171.2 (C=O); 157.5, 156.5, 152.4, 137.7, 134.5, 132.6 (C); 131.7 (CH); 126.0 (C); 125.9, 113.7, 111.4 (CH); 110.4 (C); 57.8, 55.1 (MeO); 51.6 (CH); 48.8 (C); 44.7 (CH_2Cl); 43.7, 37.5 (CH); 34.7, 32.1, 31.5, 29.7, 27.6, 27.5, 26.8 (CH_2); 15.6 (Me). EI-MS (70 eV): 470 (21, $M(^{37}Cl)^+$), 468 (61, $M(^{35}Cl)^+$), 436 (76), 401 (85), 187 (40), 173 (100), 147 (61). HR-MS (ESI-TOF/MS): 491.19591 ($[M(^{35}Cl) + Na]^+$, $C_{28}H_{33}ClNaO_4^+$; calc. 491.19596); 493.19429 ($[M(^{37}Cl) + Na]^+$, $C_{28}H_{33}ClNaO_4^+$; calc. 493.19436). Anal. calc. for $C_{28}H_{33}ClO_4$ (469.01): C 71.70, H 7.09; found: C 71.47, H 7.22.

*1-Methylethyl (4b*S*,6a*S*,11a*S*,11b*S*)-5,6,6a,11,11a,11b,12,13-Octahydro-8-hydroxy-2-methoxy-6a-methyl-4b*H*-indeno[2,1-*a*]phenanthrene-7-carboxylate* (**9e**). According to *GP*, with **7** (384 mg, 1.00 mmol) and **8e** (577 mg, 2.00 mmol). CC (heptane/AcOEt 100:1 → 40:1) furnished **9e** (87 mg, 21%). Colorless oil. IR (ATR): 3406*w*, 2978*m*, 2929*m*, 2858*m*, 1657*s*, 1600*m*, 1497*m*, 1454*m*, 1373*m*, 1300*m*, 1275*s*, *1255s*, 1237*m*, 1224*s*, 1210*s*, 1200*s*, 1179*s*, 1161*m*, 1142*m*, 1095*s*, 1050*m*, 1035*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 9.95 (*s*, OH); 7.27 (*d*, $^3J(9,10) = 8.2$, H–C(9) or H–C(10)); 7.23 (*d*, $^3J(3,4) = 8.6$, H–C(4)); 6.79 (*d*, $^3J(9,10) = 8.2$, H–C(9) or H–C(10)); 6.74 (*dd*, $^3J(3,4) = 8.5$, $^4J(1,3) = 2.8$, H–C(3)); 6.67 (*d*, $^4J(1,3) = 2.7$, H–C(1)); 5.36 (*sept.*, $^3J = 6.3$, Me_2CH); 3.80 (*s*, MeO); 2.99–2.28 (*m*, 7 H, CH, CH_2); 2.05–1.95 (*m*, CH or CH_2); 1.83–1.54 (*m*, 5 H, CH, CH_2); 1.52 (*d*, $^3J = 6.3$, 3 H, Me_2CH); 1.41 (*d*, $^3J = 6.3$, 3 H, Me_2CH); 1.21 (*s*, Me). ^{13}C-NMR (63 MHz, $CDCl_3$): 169.8 (C=O); 158.5, 157.5, 154.2, 137.8, 135.1, 132.6 (C); 130.5, 125.9, 114.8, 113.8 (CH); 111.9 (C); 111.4 (CH); 70.3 (Me_2CH); 57.9, 55.1 (CH); 48.7 (C); 43.7, 37.6 (CH); 34.7, 31.4, 29.7, 27.7, 26.4 (CH_2); 22.0, 21.8 (Me_2CH); 15.4 (Me). EI-MS (70 eV): 420 (36, M^+), 360 (100), 345 (29), 173 (27), 171 (16), 147 (13). HR-MS (ESI-TOF/MS): 443.21896 ($[M + Na]^+$, $C_{27}H_{32}NaO_4^+$; calc. 443.21928).

*Phenylmethyl (4b*S*,6a*S*,11a*S*,11b*S*)-5,6,6a,11,11a,11b,12,13-Octahydro-8-hydroxy-2-methoxy-6a-methyl-4b*H*-indeno[2,1-*a*]phenanthrene-7-carboxylate* (**9f**). According to *GP*, with **7** (384 mg, 1.00 mmol) and **8f** (673 mg, 2.00 mmol). CC (heptane/AcOEt 100:1 → 15:1) afforded **9f** (97 mg, 21%). Colorless oil, from which traces of hydrolyzed 1,3-bis[(trimethylsilyl)oxy]buta-1,3-diene could not be removed. IR (ATR): 3400*w*, 3061*w*, 3031*w*, 2928*m*, 2856*m*, 1724*m*, 1661*s*, 1600*m*, 1497*s*, 1454*s*, 1386*m*, 1333*m*, 1299*m*, 1275*s*, 1253*s*, 1236*m*, 1225*s*, 1208*s*, 1194*s*, 1177*s*, 1141*m*, 1122*s*, 1096*s*, 1050*m*, 1035*m*. ^{1}H-NMR (250 MHz, $CDCl_3$): 9.81 (*s*, OH); 7.49–7.32 (*m*, 5 H, CH_2Ph); 7.28 (*d*, $^3J(9,10) = 8.2$, H–C(9) or H–C(10)); 7.20 (*d*, $^3J(3,4) = 8.6$, H–C(4)); 6.80 (*d*, $^3J(9,10) = 8.2$, H–C(9) or H–C(10)); 6.76 (*dd*, $^3J(3,4) = 8.6$, $^4J(1,3) = 2.8$, H–C(3)); 6.67 (*d*, $^4J(1,3) = 2.7$, H–C(1)); 5.51 (*d*, $^2J = 12.1$, 1 H, PhCH_2); 5.37 (*d*, $^2J = 12.1$, 1 H, PhCH_2); 3.80 (*s*, MeO); 2.98–2.25 (*m*, 7 H, CH, CH_2); 2.02–1.92 (*m*, 1 H, CH or CH_2); 1.77–1.43 (*m*, 5 H, CH, CH_2); 1.04 (*s*, Me). ^{13}C-NMR (75 MHz, $CDCl_3$): 170.0 (C=O); 158.5, 157.4, 154.5, 137.8, 135.2, 134.4, 132.6 (C); 130.8 (CH); 129.3, 128.8 (CH); 128.6 (CH); 125.9, 114.8, 113.8, 111.4 (CH); 111.2 (C); 67.6 (PhCH_2); 57.8 (MeO); 55.1 (CH); 48.8 (C); 43.6, 37.5 (CH); 34.6, 31.4, 29.7, 27.6, 26.4 (CH_2); 15.3 (Me). EI-MS (70 eV): 468 (64, M^+), 360 (89), 345 (15), 173 (19), 147 (12), 91 (100). HR-MS (ESI-TOF/MS): 469.23745 ($[M + H]^+$), $C_{31}H_{33}O_4^+$; calc. 469.23734).

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