# 8-Methoxy-5-methyl-2,3-dihydro-1*H*-cyclopenta[*a*]naphthalene: synthesis and reactivity

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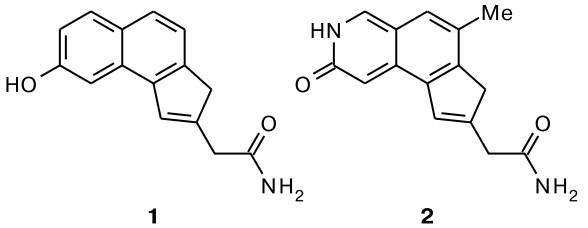
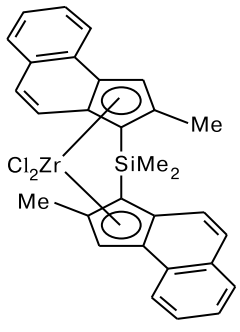
A new single-step approach to cyclopenta[*a*]naphthalenes through $TiCl_4$-catalyzed reactions of 1-trimethylsilyloxycyclopentene with arylacetaldehydes was proposed. 8-Methoxy-5-methyl-2,3-dihydro-1*H*-cyclopenta[*a*]naphthalene and its derivatives were studied in oxidation and bromination reactions, as well as in hydrolytic cleavage of the O—Me bond.

**Key words:** cyclopenta[*a*]naphthalenes, acid-catalyzed dimerization of indenes, the Darzens reaction, intramolecular electrophilic alkylation.

Cyclopenta[*a*]naphthalene derivatives are of considerable interest because of their mutagenic activity due to the presence of a planar polycyclic fragment and polar substituents.[1] In particular, cyclopentanaphthalenes **1** and **2** exhibit a strong chemotherapeutic activity by inhibiting DNA or RNA synthesis.[2] Moreover, cyclopenta[*a*]naphthalene derivatives are used as the starting ligands for the synthesis of sandwich complexes of titanium subgroup metals (*e.g.*, complex **3**); when activated by methylaluminoxane, such complexes are highly active and stereoselective catalysts for the polymerization of α-olefins.[3—7]

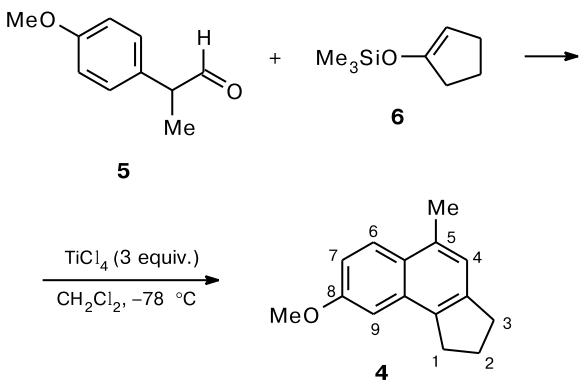



The cyclopenta[*a*]naphthalene fragment can be constructed in several ways. The most important ones involve transformations of naphthalene derivatives[8,9] according to the Nazarov reaction[10] or a standard malonic synthesis scheme.[11] Alternatively, this fragment can be synthesized by cyclization of phenylenediacetylenes on ruthenium or platinum catalysts.[12,13]

In the present work, we proposed a new general approach to cyclopenta[*a*]naphthalenes of the type **4** through $TiCl_4$-catalyzed reactions of arylacetaldehydes of the type **5** with 1-trimethylsilyloxycyclopentene (**6**). Using this approach, we obtained not easily accessible 8-methoxy-5-methyl-2,3-dihydro-1*H*-cyclopenta[*a*]naphthalene (**4**) from 2-(4-methoxyphenyl)propanal (**5**) and ether **6** (Scheme 1).

**Scheme 1**




This approach to compounds of the series **4** allows a single-step construction of their cyclopenta[*a*]naphthalene core from accessible starting reagents containing no fused aromatic fragment, which provides new scope in searching for optimum routes to polyaromatic systems. Here we also

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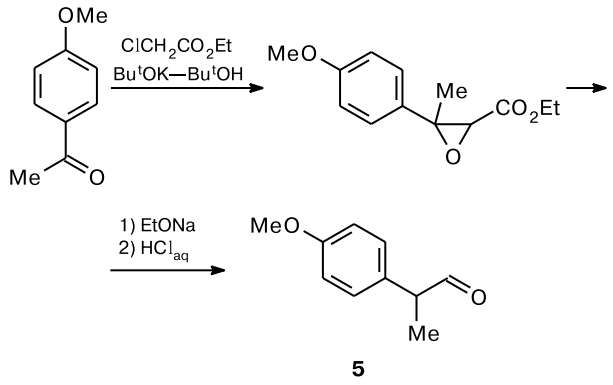
studied some aspects of the reactivities of compound **4** and its derivatives.

2-(4-Methoxyphenyl)propanal (**5**) was prepared by the Darzens reaction.[14,15] A reaction of 4-methoxyacetophenone with ethyl chloroacetate in *tert*-butanol in the presence of $Bu^tOK$ was followed by a transformation of crude intermediate glycidic ester under the action of EtONa and HCl. The yield of aldehyde **5** was 82% (Scheme 2). It should be noted that attempted purification of the glycidic ester by distillation lowers the yield of the target aldehyde **5**: it is strongly contaminated by isomeric 4-methoxypropiophenone.

**Scheme 2**




**5**

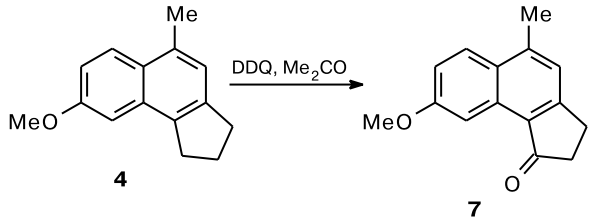
Based on the previous data,[16] we illustrated for the first time a single-step approach to the construction of the cyclopenta[*a*]naphthalene system with the synthesis of benzoindane **4** from aldehyde and 1-trimethylsilyloxycyclopentene ( ) (see Scheme 1). The yield of benzoindane (40%) is fairly acceptable for reactions of this type.

The optimization of the synthesis revealed that the yield of benzoindane remains constant in a very wide range of the concentrations of the reagents and is unaffected by scaling up to 60-fold charges. However, at insufficient dilution, the yield of benzoindane decreases substantially (from 40 to 28% when the concentration of the reaction mixture is five times higher than that specified in Experimental). Above −78 °C, the yield is much lower; the replacement of $TiCl_4$ by other Lewis acids ($SnCl_4$ and $AlCl_3$) brings about the formation of a mixture of unidentified products, the conversion of the starting substrate being virtually complete.

Because the data on the chemistry of cyclopenta[*a*]naphthalene derivatives are scarce, we used benzoindane to study the reactivity of this type of compounds, in particular, in the selective oxidation of indane with dichlorodicyanobenzoquinone (DDQ, 2 equiv.) into benzoindanone (Scheme 3).

We found that compound is oxidized in 1.5 h at room temperature in acetone in the presence of water (2—4 equiv.) to give ketone in 92% yield. With acetic

**Scheme 3**

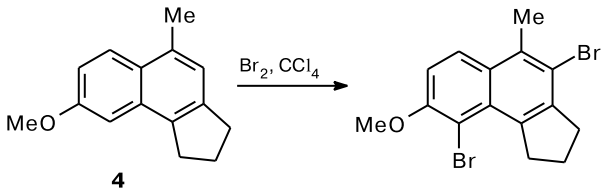



**4** **7**

acid as a solvent, the conversion of benzoindane is completed in 5 min, producing a mixture of unidentified products.

A room-temperature reaction of benzoindane with bromine (1 equiv.) in $CCl_4$ gives a mixture of dibromoindane and the starting reagent in a ratio of 1 : 1. With a double excess of bromine under the same conditions, the yield of dibromide amounts to 85%; however, ~13% of the starting benzoindane is recovered (Scheme 4).

**Scheme 4**

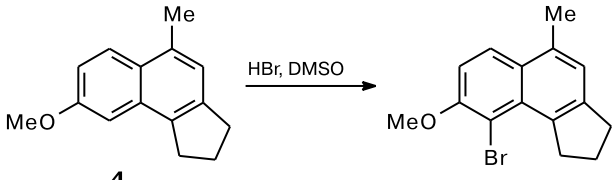



**4** **8**

The data obtained suggest that an intermediate monobromide is brominated more actively than the starting substrate. This result is rather unexpected for an introduction of a Br atom into an aromatic system should prevent its further electrophilic bromination.

Monobromide was obtained in good yield (80%) only by heating compound with a mixture of conc. HBr and DMSO (Scheme 5).

**Scheme 5**



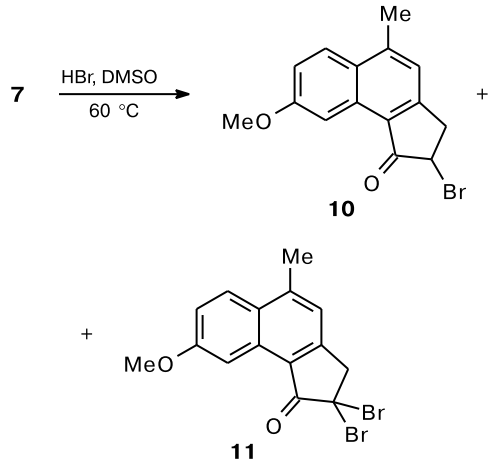

**4** **9**

Under the conditions studied, position 9 in the cyclopenta[*a*]naphthalene system is most reactive for an electrophilic attack, as in 2-methoxynaphthalene.

Attempted oxidation of bromobenzoindane with DDQ in boiling benzene into a ketone like failed: the reaction gives a mixture of unidentified products.

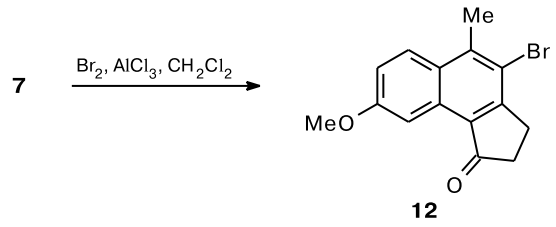
Bromination of ketone with a mixture of conc. HBr and DMSO yields bromides and and the starting substrate in a ratio of ~1 : 1 : 1 (Scheme 6).

**Scheme 6**




Bromination of compound with $Br_2$ at 0 °C in the presence of $AlCl_3$ (2 equiv.) in dichloromethane affords bromide in 81% yield (Scheme 7).

**Scheme 7**

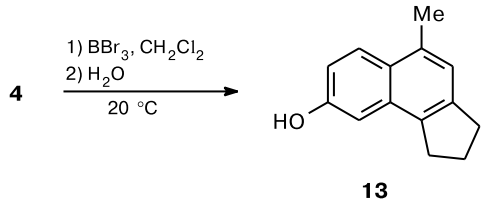



The $^1H$ NMR spectrum of dibromide in $CDCl_3$ shows signals at δ 7.94 and 7.15 due to two protons in the aromatic ring; the doublet at δ 7.94 ($J$ = 9.37 Hz) can be assigned to the H(6) proton, while the doublet at δ 7.15 ($J$ = 9.37 Hz) unambiguously relates to the H(7) proton.

In the spectrum of bromide , the singlet at δ 7.15 was unambiguously assigned to the H(4) proton. Using the spectra of bromides and , one can easily interpret the spectrum of compound as follows: the doublet at δ 8.56 ($J$ = 2.81 Hz) with a low coupling constant corresponds to the H(9) proton, the doublet at δ 7.91 ($J$ = 9.28 Hz) with a high coupling constant corresponds to the H(6) proton, and the doublet of doublets at δ 7.18 ($J_1$ = 9.28 Hz, $J_2$ = 2.81 Hz) relates to the H(7) proton.

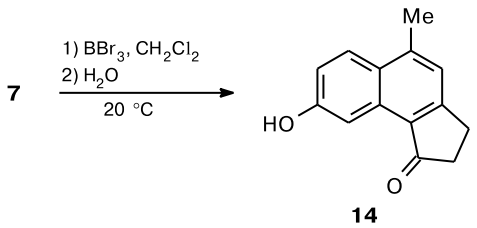
The O—Me bond in compounds and is sufficiently strong. For instance, a reaction of substrate with $BBr_3$ in dichloromethane gives the corresponding phenol in high yield (93%), and the conversion of the starting substrate is high (95%), only in 12 h (Scheme 8). Note that a sevenfold excess of $BBr_3$ is required. With one equivalent of $BBr_3$, the yield of phenol under the same conditions is only 6%. Analogous reactions of methyl phenyl ethers usually occur very rapidly even at −78 °C.[21]

**Scheme 8**



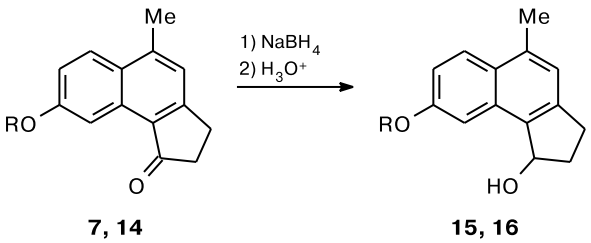

As for substrate , its room-temperature transformation into the corresponding phenol even in the presence of a tenfold excess of $BBr_3$ takes 17 h; the yield of compound does not exceed 30% and the conversion of substrate is 30%. Prolonged reflux (60 h) of the reaction mixture is required to increase the yield of phenol to 70% (Scheme 9).

**Scheme 9**




Reduction of benzoindanones and with sodium borohydride in the THF—methanol system gives benzoindanols and in quantitative yields (Scheme 10).

**Scheme 10**

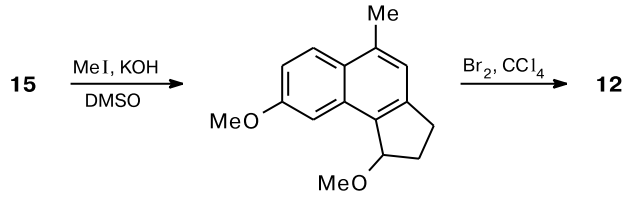



R = H (**14**, **16**), Me (**7**, **15**)

A reaction of methoxybenzoindanol with iodomethane in the KOH—DMSO system affords dimethoxybenzoindane in 95% yield (Scheme 11). Bromination of the latter with $Br_2$ (1 equiv.) in $CCl_4$ unexpectedly gives bromo ketone as a major product (47%). This compound was also obtained by electrophilic bromination of substrate in the $Br_2$—$AlCl_3$—$CH_2Cl_2$ system (see Scheme 7).

The selective formation of such an unexpected product should be studied in detail in special investigations.

**Scheme 11**




**17**

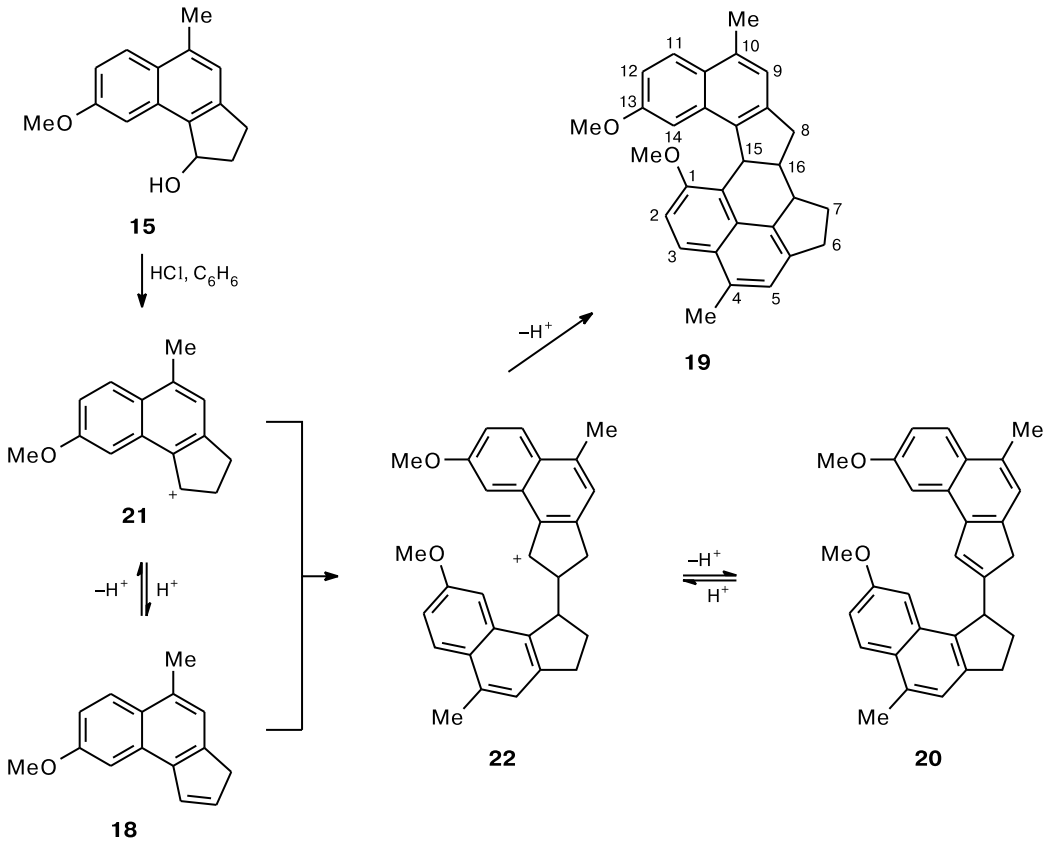
Reflux of indanol in benzene in the presence of a catalytic amount of conc. HCl using a Dean—Stark trap gives, through acid-catalyzed dimerization of indene , products and in 27 and 50% yields, respectively (Scheme 12).

The structures of compounds and were determined by X-ray diffraction and confirmed by NMR spectroscopy. In the $^1$H NMR spectrum of dimer , signals at δ 3.94 and 3.65 are due to two nonequivalent methoxy groups, signals at δ 2.70 and 2.64 are due to two nonequivalent methyl groups in the aromatic rings, and a singlet at δ 7.06 can be assigned to the sole olefinic proton in the indenyl fragment. Therefore, no acid-catalyzed migration of the double bond of the indenyl fragment occurs under the conditions studied.

Compound is produced *via* a standard acid-catalyzed indene dimerization. The unexpected structure of dimer results from an intramolecular electrophilic alkylation of compound at the *ortho*-position relative to the methoxy group. Some possible pathways of the formation of dimers and are shown in Scheme 12.

Structure (Fig. 1) includes two flattened moieties; the mean-square deviations for the planes of the naphthalene fragments and the directly bound C(8), C(10), C(23), and C(25) atoms are 0.083 Å for the C(1)...C(8), C(10)...C(13) moiety and 0.037 Å for the C(16)...C(23), C(25)...C(28) moiety. The angle between the planes of these moieties is 78.50(4)°. The deviation of the C(9) atom from the plane of the flattened moiety C(1)...C(8), C(10)...C(13) is 0.715(3) Å and the deviation of the C(24) atom from the plane of the second flattened moiety C(16)...C(23), C(25)...C(28) is 0.411(3) Å. The molecule is conformationally strained since the bond angles are far from their idealized values for the optical centers (C(9), C(10), and C(25)), through which both moieties are joined. The bond angles are smaller (C(11)—C(10)—C(9),

**Scheme 12**



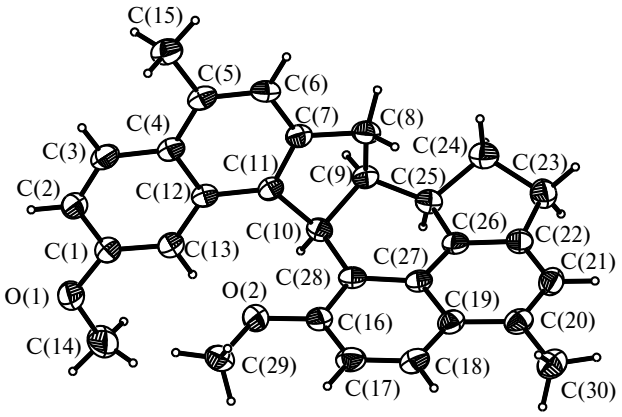



**Fig. 1.** ORTEP diagram for compound **19** with atomic thermal displacement ellipsoids (50% probability).

98.9(2)°) and greater than their idealized values (C(9)—C(25)—C(24), 120.0(2)°).

In contrast to compound , structure (Fig. 2) does not have the C(10)—C(28) bond but has the C(9)=C(10) double bond; the latter structure is conformationally more flexible and less strained. In particular, the bond angles deviate less from the idealized tetrahedral values (the largest deviation is 116.1° for the angle C(9)—C(25)—C(24)). The relative orientations of two flattened moieties C(1)...C(8), C(10)...C(13) and C(16)...C(23), C(25)...C(28) (the mean-square deviations are 0.024 and 0.021 Å, respectively) linked by the C(9)—C(25) bond seems to be determined by the steric effects of the nearest H atoms (the shortest distance is 2.38 Å between H(8B) and H(24B), which corresponds to the sum of the van der Waals radii) and the packing effect. The angle between the planes of the moieties (83.96(5)°) approximates to that in structure .

The crystal structures of both compounds are made up of separate molecules linking by no specific intermolecular interactions.

In boiling toluene in the presence of a catalytic amount of TsOH, indanol undergoes rapid (<1 min) and nearly complete dehydration leading to compound (Scheme 13).

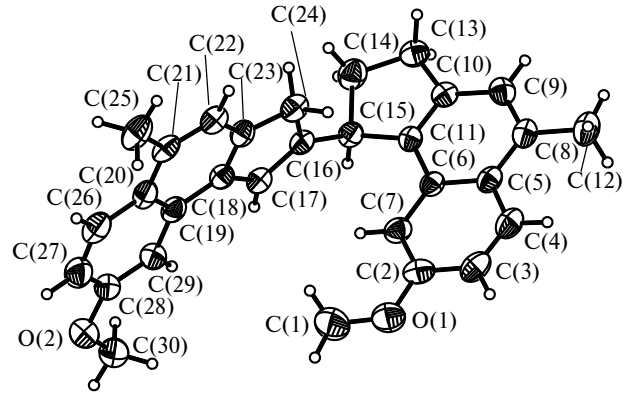
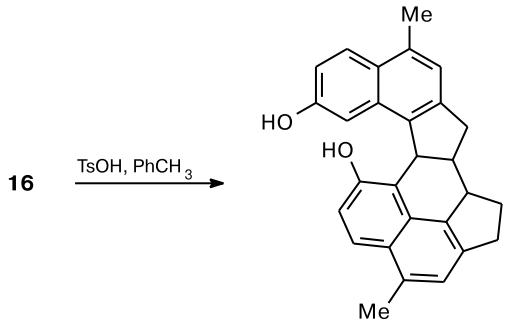



**Fig. 2.** ORTEP diagram for compound **20** with atomic thermal displacement ellipsoids (50% probability).

**Scheme 13**




**23**

According to NMR data, the carbon cores in compounds and are identical. The only substantial difference in their $^1$H NMR spectra is that the spectrum of compound in $CDCl_3$ shows two singlets at δ 4.03 and 3.12 (two nonequivalent methoxy groups), while the spectrum of compound in DMSO-$d_6$ does not contain such signals; instead, it shows two broadened singlets at δ 9.48 and 9.21 due to two nonequivalent hydroxy groups of the aromatic ring. Interestingly, the signals for the methoxy groups in the spectrum of compound in $CDCl_3$ have very different chemical shifts. The upfield shift of one signal is probably associated with the fact that the methoxy group near the H atom of the opposite aromatic ring is not coplanar. Since the OH groups in compound are less bulky substituents, this effect is much less pronounced.

To sum up, we developed a new, simple and efficient approach to not easily accessible 8-methoxy-5-methyl-2,3-dihydro-1*H*-cyclopenta[*a*]naphthalene ( ). The key step of the synthesis involves acid-catalyzed condensation of 1-trimethylsilyloxycyclopentene with 2-(4-methoxyphenyl)propanal ( ). In addition, we optimized the Darzens synthesis of arylacetaldehydes and studied some aspects of the reactivity of compound and its derivatives. The results obtained will undoubtedly be useful for further investigations of the reactivity of cyclopenta[*a*]naphthalene derivatives.

All experiments involving moisture- and oxygen-sensitive compounds were carried out in an inert (argon) atmosphere using standard Schlenk equipment. Solvents were purified according to standard procedures. Dichloromethane was distilled over $P_4O_{10}$. Chlorotrimethylsilane (Acros), *tert*-butanol (Acros), $TiCl_4$ (Aldrich), $Bu^tOK$ (Acros), and other reagents were used as purchased, unless otherwise specified. $^1$H and $^{13}$C NMR spectra were recorded on a Bruker AM-400 spectrometer (400 and 100 MHz, respectively). The signals of chloroform ($\delta_H$ 7.28 and $\delta_C$ 77.1) served as the internal standards. The course of the reactions was monitored, and the purity of the products was checked,

by TLC (Silufol UV-254). Preparative column chromatography was carried out with $SiO_2$ (Merck, 40/60) as a stationary phase. Elemental analysis was performed on a CHN-O-Rapid Analyzer instrument (Heracus).

1-Trimethylsilyloxycyclopentene (**6**) was prepared according to a known procedure.[17]

**2-(4-Methoxyphenyl)propanal (5).** A solution of $Bu^tOK$ (36 g, 320 mmol) in anhydrous $Bu^tOH$ (300 mL) was added dropwise at room temperature for 2 h to a vigorously stirred mixture of 4-methoxyacetophenone (47.1 g, 314 mmol) and ethyl chloroacetate (38.5 g, 314 mmol). After the addition of $Bu^tOK$ was completed, the reaction mixture was stirred for an additional 2 h. Then the solvent was removed in water aspirator vacuum and the residue was dissolved in $Et_2O$ (120 mL). The solution was washed with cold water (3×100 mL) and cold brine (2×100 mL) and dried over $Na_2SO_4$. The solvent was removed and the residue was mixed with a solution of EtONa (21.3 g) in anhydrous EtOH (150 mL). Water (7.36 mL) was added with slight cooling and stirring to the resulting mixture, whereupon the solvent was removed in a rotary evaporator (bath temperature 45 °C). The residue was mixed with water (150 mL). Concentrated HCl (28 mL) was carefully added through a reflux condenser to the solution. After the gas evolution ceased, the reaction mixture was heated at 80 °C for 1 h. On cooling, the product was extracted with benzene (2×100 mL). The organic extracts were dried over $Na_2SO_4$, the solvent was removed in water aspirator vacuum, and the product was distilled in oil pump vacuum. The yield of compound **5** was 42.3 g (257.5 mmol, 82%), b.p. = 87—88 °C (1 Torr). $^1$H NMR ($CDCl_3$), δ: 9.63 (d, 1 H, —COH, $J$ = 1.71 Hz); 7.12 (d, 2 H, H(2), H(6), $J$ = 8.79 Hz); 6.90 (d, 2 H, H(3), H(5), $J$ = 8.79 Hz); 3.78 (s, 3 H, OMe); 3.55 (dq, 1 H, C<u>H</u>—Me, $J_1$ = 7.08 Hz, $J_2$ = 1.71 Hz); 1.40 (d, 3 H, C<u>H</u>$_3$—CH, $J$ = 7.08 Hz).

**8-Methoxy-5-methyl-2,3-dihydro-1*H*-cyclopenta[*a*]naphthalene (4).** A solution of $TiCl_4$ (8.65 g, 45.6 mmol) in $CH_2Cl_2$ (40 mL) was added dropwise at −78 °C for 30 min to a solution of 2-(4-methoxyphenyl)propanal (**5**) (2.5 g, 15.23 mmol) and 1-trimethylsilyloxycyclopentene (**6**) (2.85 g, 18.23 mmol) in $CH_2Cl_2$ (150 mL). The mixture was stirred at −78 °C for 1.5 h and then at ambient temperature for an additional 12 h and poured onto ice (100 g). The organic layer was separated, washed with water (100 mL) and aqueous $K_2CO_3$ (200 mL), dried over $Na_2SO_4$, and concentrated in water aspirator vacuum. The product was additionally purified by column chromatography on silica gel with dichloromethane—hexane (1 : 3) as an eluent; $R_f$ = 0.3. The yield of compound **4** was 1.3 g (6.07 mmol, 39.8%). Found (%): C, 84.85; H, 7.59. $C_{15}H_{16}O$. Calculated (%): C, 84.87; H, 7.60. $^1$H NMR ($CDCl_3$), δ: 7.91 (d, 1 H, H(6), $J$ = 9.22 Hz); 7.14 (s, 1 H, H(4)); 7.14 (dd, 1 H, H(7), $J_1$ = 9.22 Hz, $J_2$ = 2.64 Hz); 7.08 (d, 1 H, H(9), $J$ = 2.64 Hz); 3.95 (s, 3 H, OMe); 3.19 (t, 2 H, α-$CH_2$, $J$ = 7.5 Hz); 3.08 (t, 2 H, β-$CH_2$, $J$ = 7.5 Hz); 2.65 (s, 3 H, Me); 2.24 (m, 2 H, $CH_2$). $^{13}$C NMR ($CDCl_3$), δ: 157.44, 141.27, 136.36, 132.73, 131.70, 126.85, 126.33, 121.89, 116.50, 103.46, 55.25, 33.92, 31.15, 24.40, 19.55.

**8-Methoxy-5-methyl-2,3-dihydro-1*H*-cyclopenta[*a*]naphthalen-1-one (7).** A solution of DDQ (5.55 g, 24.45 mmol) in acetone (75 mL) was added at room temperature to a solution of indane **4** (2.36 g, 11.12 mmol) and water (6 mL) in acetone (180 mL). The reaction mixture was stirred for 24 h, concentrated in water aspirator vacuum, and mixed with dichloromethane (100 mL). The resulting green solution with a gray precipitate was filtered and concentrated in water aspirator vacuum. Indanone **7** was additionally purified by column chromatography on silica gel with $CH_2Cl_2$ as an eluent. The yield of compound **7** was 2.31 g (10.23 mmol, 92%). Found (%): C, 79.64; H, 6.24. $C_{15}H_{14}O_2$. Calculated (%): C, 79.62; H, 6.24. $^1$H NMR ($CDCl_3$), δ: 8.61 (d, 1 H, H(9), $J$ = 2.83 Hz); 7.89 (d, 1 H, H(6), $J$ = 9.25 Hz); 7.19 (dd, 1 H, H(7), $J_1$ = 9.25 Hz, $J_2$ = 2.83 Hz); 7.18 (s, 1 H, H(4)); 3.98 (s, 3 H, OMe); 3.10 (m, 2 H, C<u>H</u>$_2$CO); 2.73 (m, 2 H, $CH_2$); 2.69 (s, 3 H, Me). $^{13}$C NMR ($CDCl_3$), δ: 207.09, 159.87, 158.82, 143.17, 131.20, 128.53, 126.80, 125.63, 122.45, 118.37, 102.94, 55.38, 36.68, 25.76, 20.31.

**4,9-Dibromo-8-methoxy-5-methyl-2,3-dihydro-1*H*-cyclopenta[*a*]naphthalene (8).** Bromine (7.53 g, 47.1 mmol) in $CCl_4$ (50 mL) was added dropwise at room temperature for 1 h to a solution of indane **4** (5.00 g, 23.55 mmol) in $CCl_4$ (200 mL). After the addition of $Br_2$ was completed, the reaction mixture was stirred for an additional 30 min and mixed with a saturated solution of $Na_2SO_3$ (200 mL). The aqueous solution was washed with $CH_2Cl_2$ (100 mL), the combined organic extracts were dried over $Na_2SO_4$, and the solvent was removed in water aspirator vacuum. The product was recrystallized from hexane (200 mL). The yield of compound **8** was 7.37 g (19.92 mmol, 85%). Found (%): C, 48.69; H, 3.80. $C_{15}H_{14}Br_2O$. Calculated (%): C, 48.68; H, 3.81. $^1$H NMR ($CDCl_3$), δ: 7.94 (d, 1 H, H(6), $J$ = 9.37 Hz); 7.15 (d, 1 H, H(5), $J$ = 9.37 Hz); 3.99 (s, 3 H, OMe); 3.99 (m, 2 H, α-$CH_2$); 3.08 (t, 2 H, β-$CH_2$, $J$ = 7.62 Hz); 2.73 (s, 3 H, Me); 2.08 (m, 2 H, $CH_2$). $^{13}$C NMR ($CDCl_3$), δ: 154.12, 144.62, 137.79, 132.15, 130.56, 129.88, 126.28, 121.00, 112.15, 107.62, 56.99, 38.48, 36.63, 23.41, 19.54.

**9-Bromo-8-methoxy-5-methyl-2,3-dihydro-1*H*-cyclopenta[*a*]naphthalene (9).** Concentrated HBr (50 mL) was added dropwise at 56—57 °C for 15 min to a solution of indane **4** (5.00 g, 23.55 mmol) in DMSO (300 mL). The reaction mixture was stirred for 5.5 h and then poured into water (500 mL). The product was extracted with $CH_2Cl_2$ (3×200 mL). The combined organic extracts were washed with water (4×300 mL), dried over $Na_2SO_4$, and concentrated in water aspirator vacuum. The product was additionally purified by column chromatography with dichloromethane—hexane (1 : 10) as an eluent. The yield of compound **9** was 5.49 g (18.64 mmol, 79%). Found (%): C, 61.88; H, 5.20. $C_{15}H_{15}BrO$. Calculated (%): C, 61.87; H, 5.19. $^1$H NMR ($CDCl_3$), δ: 7.95 (d, 1 H, H(6), $J$ = 9.37 Hz); 7.18 (d, 1 H, H(7), $J$ = 9.37 Hz); 7.15 (s, 1 H, H(4)); 4.00 (s, 3 H, OMe); 3.89 (t, 2 H, α-$CH_2$, $J$ = 7.32 Hz); 2.98 (t, 2 H, α-$CH_2$, $J$ = 7.62 Hz); 2.62 (s, 3 H, Me); 2.10 (m, 2 H, $CH_2$). $^{13}$C NMR ($CDCl_3$), δ: 154.17, 144.52, 136.60, 133.26, 131.80, 129.09, 125.88, 123.37, 111.53, 107.62, 57.05, 36.90, 33.67, 24.78, 20.29. In addition, the starting indane **4** (910 mg) was recovered by column chromatography.

**2-Bromo-8-methoxy-5-methyl-2,3-dihydro-1*H*-cyclopenta[*a*]naphthalen-1-one (10)** and **2,2-dibromo-8-methoxy-5-methyl-2,3-dihydro-1*H*-cyclopenta[*a*]naphthalen-1-one (11).** Concentrated HBr (12 mL) was added dropwise at 56—57 °C for 15 min to a solution of indanone **7** (1.00 g, 4.42 mmol) in DMSO (30 mL). The reaction mixture was stirred for 5.5 h and then poured into water (100 mL). The product was extracted with $CH_2Cl_2$ (3×50 mL). The combined organic extracts were washed with water (2×50 mL), dried over $Na_2SO_4$, and concentrated in water aspirator vacuum. Bromoindanones **10** and **11** were additionally purified by column chromatography with dichloromethane as an eluent. The yield of compound **10** was 431 mg (1.41 mmol, 32%). The yield of compound **11** was 577 mg (1.50 mmol, 34%). In addition, the starting indanone **7** (0.3 g) was recovered.

<u>Compound **11**</u>. Found (%): C, 46.93; H, 3.18. $C_{15}H_{12}Br_2O_2$. Calculated (%): C, 46.91; H, 3.15. $^1$H NMR ($CDCl_3$), δ: 8.56

(d, 1 H, H(9), $J$ = 2.50 Hz); 7.96 (d, 1 H, H(6), $J$ = 9.36 Hz); 7.26 (dd, 1 H, H(7), $J_1$ = 9.36 Hz, $J_2$ = 2.50 Hz); 7.11 (s, 1 H, H(4)); 4.33 (s, 2 H, $CH_2$); 4.01 (s, 3 H, OMe); 2.76 (s, 3 H, Me). $^{13}$C NMR ($CDCl_3$), δ: 200.78, 161.36, 147.47, 146.32, 130.21, 126.81, 125.94, 121.57, 121.00, 120.17, 103.57, 102.08, 56.02, 52.79, 21.14.

Compound **10**. Found (%): C, 59.06; H, 4.30. $C_{15}H_{13}BrO_2$. Calculated (%): C, 59.04; H, 4.29. $^1$H NMR ($CDCl_3$), δ: 8.54 (s, 1 H, H(9)); 7.91 (d, 1 H, H(6), $J$ = 9.33 Hz); 7.26 (d, 1 H, H(7), $J$ = 9.20 Hz); 7.14 (s, 1 H, H(4)); 4.72 (d, 1 H, CHBr, $J$ = 7.00 Hz); 4.00 (s, 3 H, OMe); 3.83 (dd, 1 H, CHH, $J_1$ = = 18.66 Hz, $J_2$ = 7.00 Hz); 3.43 (d, 1 H, CHH, $J$ = 18.66 Hz); 2.72 (s, 3 H, Me). $^{13}$C NMR ($CDCl_3$), δ: 199.89, 160.93, 155.33, 145.88, 131.90, 127.64, 126.48, 125.81, 122.30, 119.59, 103.48, 55.96, 45.51, 38.38, 21.02.

**9-Bromo-8-methoxy-5-methyl-2,3-dihydro-1*H*-cyclopenta[*a*]naphthalen-1-one (12).** *A*. Aluminum trichloride (2.35 g, 17.62 mmol) was added at −20 °C to a solution of indanone **7** (2.00 g, 8.84 mmol) in anhydrous dichloromethane (30 mL). The temperature was raised to 0 °C and bromine (1.41 g, 8.84 mmol, 0.452 mL) in dichloromethane (10 mL) was added dropwise for 30 min. The reaction mixture was warmed to ambient temperature, left for ~12 h, and poured into water (100 mL). The product was extracted with $CH_2Cl_2$ (3×40 mL). The combined organic extracts were washed with water (2×50 mL), dried over $Na_2SO_4$, and concentrated in water aspirator vacuum. Bromoindanone **12** was additionally purified by column chromatography with dichloromethane as an eluent. The yield of compound **12** was 2.19 g (7.16 mmol, 81%). Found (%): C, 59.05; H, 4.30. $C_{15}H_{13}BrO_2$. Calculated (%): C, 59.04; H, 4.29. $^1$H NMR ($CDCl_3$), δ: 8.56 (d, 1 H, H(9), $J$ = 2.81 Hz); 7.91 (d, 1 H, H(6), $J$ = 9.28 Hz); 7.18 (dd, 1 H, H(7), $J_1$ = 9.28 Hz, $J_2$ = 2.81 Hz); 3.97 (s, 3 H, OMe); 3.08 (m, 2 H, C$H_2$CO); 2.80 (s, 3 H, Me); 2.75 (m, 2 H, $CH_2$). $^{13}$C NMR ($CDCl_3$), δ: 201.82, 159.97, 158.13, 141.95, 140.63, 130.08, 129.93, 126.14, 125.17, 119.47, 102.93, 55.57, 36.79, 28.32, 19.71.

*B*. Bromine (0.758 g, 4.75 mmol, 0.243 mL) in tetrachloromethane (10 mL) was added dropwise at 0 °C for 30 min to a solution of methoxyindane **17** (1.15 g, 4.75 mmol) in anhydrous tetrachloromethane (30 mL). The reaction mixture was warmed to ambient temperature, left for ~12 h, and poured into water (100 mL). The product was extracted with $CH_2Cl_2$ (3×40 mL). The combined organic extracts were washed with water (2×50 mL), dried over $Na_2SO_4$, and concentrated in water aspirator vacuum. Bromoindanone **12** was additionally purified by column chromatography with dichloromethane as an eluent. The yield of compound **12** was 0.680 g (2.23 mmol, 47%). The spectroscopic characteristics of the products obtained according to methods *A* and *B* are similar.

**5-Methyl-2,3-dihydro-1*H*-cyclopenta[*a*]naphthalen-8-ol (13).** Boron tribromide (1.75 g, 7.00 mmol) was added dropwise at −80 °C to a solution of methoxy indane **4** (0.212 g, 1.00 mmol) in anhydrous dichloromethane (11.5 mL). The reaction mixture was warmed to ambient temperature, left for ~12 h, and poured into water (50 mL). The product was extracted with $CH_2Cl_2$ (3×30 mL). The combined organic extracts were washed with water (2×40 mL), dried over $Na_2SO_4$, and concentrated in water aspirator vacuum. Product **13** was additionally purified by column chromatography with dichloromethane as an eluent. The yield was 0.184 g (0.93 mmol, 93%). Found (%): C, 84.83; H, 7.11. $C_{14}H_{14}O$. Calculated (%): C, 84.81; H, 7.12. $^1$H NMR ($CDCl_3$), δ: 7.90 (d, 1 H, H(6), $J$ = 9.10 Hz); 7.11 (s, 1 H, H(4)); 7.10 (d, 1 H, H(9), $J$ = 2.53 Hz); 7.05 (dd, 1 H, H(7), $J_1$ = 9.10 Hz, $J_2$ = 2.53 Hz); 4.87 (s, 1 H, OH); 3.13 (t, 2 H, α-$CH_2$, $J$ = 7.58 Hz); 3.04 (t, 2 H, β-$CH_2$, $J$ = 7.58 Hz); 2.63 (s, 3 H, Me); 2.20 (m, 2 H, $CH_2$).

**8-Hydroxy-5-methyl-2,3-dihydro-1*H*-cyclopenta[*a*]naphthalen-1-one (14).** Boron tribromide (2.50 g, 10.00 mmol) was added dropwise at −80 °C to a solution of methoxy indanone **7** (0.226 g, 1.00 mmol) in anhydrous dichloromethane (11.5 mL). The reaction mixture was warmed to ambient temperature, refluxed for 60 h, and then poured into water (50 mL). The product was extracted with $CH_2Cl_2$ (3×30 mL). The combined organic extracts were washed with water (2×40 mL), dried over $Na_2SO_4$, and concentrated in water aspirator vacuum. Product **14** was additionally purified by column chromatography with dichloromethane—diethyl ether (50 : 1) as an eluent. The yield was 0.148 g (0.70 mmol, 70%). Found (%): C, 79.20; H, 5.70. $C_{14}H_{12}O_2$. Calculated (%): C, 79.22; H, 5.70. $^1$H NMR (DMSO-$d_6$), δ: 10.09 (s, 1 H, OH); 8.42 (d, 1 H, H(9), $J$ = 2.81 Hz); 7.94 (d, 1 H, H(6), $J$ = 9.05 Hz); 7.25 (s, 1 H, H(4)); 7.12 (dd, 1 H, H(6), $J_1$ = 9.05 Hz, $J_2$ = 2.81 Hz); 3.08 (m, 2 H, $CH_2$CO); 2.66 (s, 3 H, Me); 2.65 (m, 2 H, $CH_2$). With an increase in the reflux time to 96 h, the yield of product **14** amounts to 99%.

**8-Methoxy-5-methyl-2,3-dihydro-1*H*-cyclopenta[*a*]naphthalen-1-ol (15).** Sodium borohydride (2.94 g, 77.8 mmol) was added in small portions at 0 °C for 30 min to a solution of indanone **7** (11.00 g, 48.7 mmol) in a mixture of THF (133 mL) and MeOH (67 mL). The reaction mixture was stirred at room temperature for 1 h, poured into water (200 mL), and acidified with HCl to a weakly acidic reaction. The product was extracted with $CH_2Cl_2$ (3×200 mL). The combined organic extracts were washed with water (2×50 mL), dried over $Na_2SO_4$, and concentrated in water aspirator vacuum. The yield of compound **15** was 10.99 g (48.2 mmol, 99%). Found (%): C, 78.90; H, 7.08. $C_{15}H_{16}O_2$. Calculated (%): C, 78.92; H, 7.06. $^1$H NMR ($CDCl_3$), δ: 7.90 (d, 1 H, H(6), $J$ = 9.20 Hz); 7.46 (d, 1 H, H(9), $J$ = 2.66 Hz); 7.14 (dd, 1 H, H(7), $J_1$ = 9.20 Hz, $J_2$ = 2.66 Hz); 7.10 (s, 1 H, H(4)); 5.69 (m, 1 H, CHOH); 3.94 (s, 3 H, OMe); 3.23 (m, 1 H, CHHCHOH); 2.91 (m, 1 H, CHHCHOH); 2.65 (s, 3 H, Me); 2.55 (m, 1 H, CHH); 2.13 (m, 1 H, CHH); 1.73 (br.s, 1 H, OH). $^{13}$C NMR ($CDCl_3$), δ: 158.34, 142.47, 136.87, 136.26, 127.79, 126.81, 126.63, 122.27, 117.58, 103.48, 76.46, 55.78, 35.73, 31.28, 20.16.

**5-Methyl-2,3-dihydro-1*H*-cyclopenta[*a*]naphthalene-1,8-diol (16).** Sodium borohydride (0.700 g, 18.41 mmol) was added in small portions at 0 °C for 30 min to a solution of indanone **14** (1.503 g, 7.08 mmol) in a mixture of THF (70 mL) and MeOH (30 mL). The reaction mixture was stirred at room temperature for 1 h, poured into water (200 mL), and acidified with HCl to a weakly acidic reaction. The product was extracted with $CH_2Cl_2$ (3×100 mL). The combined organic extracts were washed with water (2×50 mL), dried over $Na_2SO_4$, and concentrated in water aspirator vacuum. The yield of compound **16** was 1.500 g (7.00 mmol, 99%). Found (%): C, 78.50; H, 6.60. $C_{14}H_{14}O_2$. Calculated (%): C, 78.48; H, 6.59. $^1$H NMR (DMSO-$d_6$), δ: 9.63 (s, 1 H, OH); 7.83 (d, 1 H, H(6), $J$ = 9.05 Hz); 7.44 (d, 1 H, H(9), $J$ = 2.50 Hz); 7.03 (dd, 1 H, H(7), $J_1$ = 9.05 Hz, $J_2$ = 2.50 Hz); 6.99 (s, 1 H, H(4)); 5.42 (dt, 1 H, CHOH, $J_1$ = 7.18 Hz, $J_2$ = = 2.81 Hz); 5.02 (d, 1 H, OH, $J$ = 7.18 Hz); 3.07 (m, 1 H, CHHCHOH); 2.76 (m, 1 H, CHHCHOH); 2.55 (s, 3 H, Me); 2.39 (m, 1 H, CHH); 1.95 (m, 1 H, CHH). $^{13}$C NMR (DMSO-$d_6$), δ: 155.97, 141.50, 140.05, 137.65, 135.09, 132.85, 128.91, 126.90, 125.79, 121.64, 117.70, 107.64, 75.06, 35.93, 31.30, 20.22.

**1,8-Dimethoxy-5-methyl-2,3-dihydro-1*H*-cyclopenta[*a*]-naphthalene (17).** Potassium hydroxide (10.8 g, 192.8 mmol) was added in one portion to a solution of indanol **15** (10.99 g, 48.2 mmol) in DMSO (100 mL). Then MeI (6.84 g, 48.2 mmol) was added dropwise for 5 min. After 70 min, an additional portion of MeI (6.84 g, 48.2 mmol) was added dropwise. The reaction mixture was stirred at room temperature for 2 h and poured into water (400 mL). The product was extracted with $CH_2Cl_2$ (3×100 mL). The combined organic extracts were washed with water (3×100 mL), dried over $Na_2SO_4$, and concentrated in water aspirator vacuum. The yield of compound **17** was 11.08 g (45.8 mmol, 95%). Found (%): C, 79.30; H, 7.50. $C_{16}H_{18}O_2$. Calculated (%): C, 79.31; H, 7.49. $^1$H NMR ($CDCl_3$), δ: 7.91 (d, 1 H, H(6), $J$ = 9.19 Hz); 7.47 (d, 1 H, H(9), $J$ = 2.66 Hz); 7.15 (dd, 1 H, H(7), $J_1$ = 9.19 Hz, $J_2$ = 2.66 Hz); 7.10 (s, 1 H, H(4)); 5.70 (m, 1 H, C<u>H</u>OMe); 3.95 (s, 3 H, OMe); 3.45 (s, 3 H, CHO<u>Me</u>); 3.23 (m, 1 H, C<u>H</u>HCHOMe); 2.91 (m, 1 H, CH<u>H</u>CHOMe); 2.67 (s, 3 H, Me); 2.57 (m, 1 H, C<u>H</u>H); 2.16 (m, 1 H, CH<u>H</u>). $^{13}$C NMR ($CDCl_3$), δ: 158.34, 142.47, 136.87, 136.26, 127.79, 126.81, 126.63, 122.27, 117.58, 103.48, 76.46, 74.23, 55.78, 35.73, 31.28, 20.16.

**1,13-Dimethoxy-4,10-dimethyl-6,7,7a,7b,8,14c-hexahydrobenzo[6,7]indeno[1,2-*a*]cyclopenta[*cd*]phenalene (19) and 8,8´-dimethoxy-5,5´-dimethyl-2,3-dihydro-1*H*,3´*H*-1,2´-bi(cyclopenta[*a*]naphthalene) (20).** Concentrated HCl (0.5 mL) was added to a boiling solution of indanol **15** (0.428 g, 2 mmol) in benzene (50 mL). The reaction mixture was refluxed using a Dean—Stark trap until the starting compound was completely consumed (TLC, hexane—dichloromethane, 1 : 1). Then the mixture was poured into saturated $NaHCO_3$ (150 mL), the organic phase was separated, and the solvent was removed in water aspirator vacuum. The reaction products were separated by column chromatography with hexane—dichloromethane (1 : 1) as an eluent. The yield of compound **19** was 0.209 g (0.497 mmol, 50%). The yield of compound **20** was 0.114 g (0.271 mmol, 27%).

<u>Compound **19**</u>. $^1$H NMR ($CDCl_3$), δ: 7.86 (d, 1 H, H(3), $J$ = 9.37 Hz); 7.80 (d, 1 H, H(14), $J$ = 2.63 Hz); 7.75 (d, 1 H, H(11), $J$ = 9.38 Hz); 7.15 (s, 1 H, H(9)); 7.13 (dd, 1 H, H(12), $J_1$ = 9.38 Hz, $J_2$ = 2.64 Hz); 7.02 (d, 1 H, H(2), $J$ = 9.38 Hz); 6.95 (s, 1 H, H(5)); 5.03 (d, 1 H, $J$ = 5.56 Hz); 4.03 (s, 3 H, 13-OMe); 3.73, 3.29 (both m, 1 H each); 3.12 (s, 3 H, 1-OMe); 3.01 (m, 1 H); 2.63 (s, 3 H, 10-Me); 2.63 (m, 1 H); 2.59 (s, 3 H, 4-Me); 2.42, 2.00 (both m, 1 H each).

<u>Compound **20**</u>. $^1$H NMR ($CDCl_3$), δ: 7.92 (d, 1 H, H(6), $J$ = 9.38 Hz); 7.91 (d, 1 H, H(6´), $J$ = 9.38 Hz); 7.30 (d, 1 H, H(9), $J$ = 2.64 Hz); 7.20 (s, 2 H, H(4), H(4´)); 7.19 (d, 1 H, H(9´), $J$ = 2.64 Hz); 7.14 (dd, 1 H, H(7), $J_1$ = 9.38 Hz, $J_2$ = 2.64 Hz); 7.08 (dd, 1 H, H(7´), $J_1$ = 9.38 Hz, $J_2$ = 2.64 Hz); 7.06 (br.s, 1 H, H(1´)); 4.86 (m, 1 H, C<u>H</u>$CH_2$); 3.94 (s, 3 H, 8-OMe); 3.65 (s, 3 H, 8´-OMe); 3.45 (m, 1 H); 3.27 (m, 2 H); 3.05 (m, 1 H); 2.70 (s, 3 H, 5-Me); 2.64 (s, 3 H, 5´-Me); 2.63, 2.26 (both m, 1 H each).

**4,10-Dimethyl-6,7,7a,7b,8,14c-hexahydrobenzo[6,7]indeno-[1,2-*a*]cyclopenta[*cd*]phenalene-1,13-diol (23).** *p*-Toluenesulfonic acid monohydrate (0.59 g, 2.68 mmol) was added in one portion to a boiling solution of indanol **16** (0.5745 g, 2.6815 mmol) in toluene (50 mL). After 60 s, the solution was filtered through a short column (10 cm) with silica gel. The silica gel was washed with $CH_2Cl_2$ (200 mL). The combined solutions were concentrated in water aspirator vacuum. The product was additionally purified by column chromatography with THF—hexane (2 : 5) as an eluent. The yield of compound **23** was 0.432 g (1.102 mmol, 82%). $^1$H NMR (DMSO-$d_6$), δ: 9.48 (s, 1 H, 13-OH); 9.21 (s, 1 H, 1-OH); 7.77 (br.s, 1 H, H(14)); 7.75 (d, 1 H, H(3), $J$ = 9.05 Hz); 7.60 (d, 1 H, H(11), $J$ = 9.05 Hz); 7.04 (s, 1 H, H(9)); 7.01 (dd, 1 H, H(12), $J_1$ = 9.05 Hz, $J_2$ = 2.50 Hz); 6.85 (d, 1 H, H(2), $J$ = 9.05 Hz); 6.84 (s, 1 H, H(5)); 4.83 (d, 1 H, $J$ = 5.30 Hz); 3.60 (m, 1 H); 3.38 (s, 3 H, 10-M); 3.12, 2.94 (both m, 1 H each); 2.52 (s, 3 H, 4-Me); 2.50, 2.42, 1.87, 1.75 (all m, 1 H each). $^{13}$C NMR (DMSO-$d_6$), δ: 154.36, 154.20, 141.93, 141.00, 138.50, 135.80, 134.37, 133.09, 132.04, 131.07, 126.30, 125.91, 125.56, 124.28, 122.06, 121.12, 118.64, 117.13, 115.86, 111.15, 67.88, 49.11, 45.00, 42.82, 33.18, 31.74, 31.28, 20.18.


1. W. Vance, D. Levin, *Environ. Mutagen*, 1984, **6**, 797.
2. N. G. Kundu, *J. Med. Chem.*, 1980, **23**, 512.
3. E. Aitola, A. Puranen, H. Setala, S. Lipponen, L. Sami, *J. Polym. Sci. (A), Polym. Chem.*, 2006, **44**, 6569.
4. U. Stehling, J. Diebold, R. Kirsten, W. Roell, H. H. Brintzinger, S. Juengling, R. Muelhaupt, F. Langhauser, *Organometallics*, 1994, **13**, 964.
5. V. V. Izmer, A. Y. Lebedev, M. V. Nikulin, A. N. Ryabov, A. F. Asachenko, A. V. Lygin, D. A. Sorokin, A. Z. Voskoboynikov, *Organometallics*, 2006, **25**, 1217.
6. T. Seraidaris, B. Lofgren, *J. Polym. Sci. (A), Polym. Chem.*, 2005, **43**, 6455.
7. J. S. Moffatt, *J. Chem. Soc. (C)*, 1966, 734.
8. G. M. Badger, W. Carruthers, J. W. Cook, *J. Chem. Soc. (C)*, 1952, 4996.
9. J. R. Merchant, R. B. Upasani, *Chem. Ind.* (*London*), 1980, **11**, 466.
10. G. A. R. Kon, F. C. J. Ruþièka, *J. Chem. Soc. (C)*, 1935, 187.
11. B. P. Taduri, Y. Ran, C. Huang, R. Liu, *Org. Lett.*, 2006, **8**, 883.
12. A. Odedra, C. Wu, B. P. Taduri, Y. Ran, C. Huang, R. Liu, *J. Am. Chem. Soc.*, 2005, **127**, 3406.
13. J. Svoboda, Z. Kocfeldova, J. Paleèek, *Coll. Czech. Chem. Commun.*, 1988, **53**, 822.
14. L. F. Tietze, T. Eicher, *Reaktionen und Synthesen im organisch-chemischen Praktikum und Forschungslaboratorium*, Georg Thieme Verlag, Stuttgart—New York, 1991.
15. C. F. H. Allen, J. VanAllan, *Org. Synth.*, 1955, **3**, 733.
16. P. Di Raddo, R. G. Harvey, *Tetrahedron Lett.*, 1988, **29**, 3885.
17. E. A. A. Wallen, A. M. C. Christiaans, S. M. Saario, M. M. Forsberg, J. I. Venalainen, P. M. Hanna, M. T. Pekka, J. Gynther, *Bioorg. Med. Chem.*, 2002, **10**, 2199.
18. J. Wang, Q. Ji, J. Xu, X. Wu, Y. Xie, *Synth. Commun.*, 2005, **35**, 581.
19. G. Majetich, R. Hicks, S. Reister, *J. Org. Chem.*, 1997, **62**, 4321.
20. E. A. Braude, L. M. Jackman, R. P. Linstead, G. Lowe, *J. Chem. Soc.*, 1960, 3123.
21. J. F. W. McOmie, M. L. Watts, D. E. West, *Tetrahedron*, 1968, **24**, 2289.
22. I. V. Taidakov, I. E. Nifant´ev, M. Yu. Talanova, K. A. Lyssenko, *Izv. Akad. Nauk, Ser. Khim.*, 2004, 860 [*Russ. Chem. Bull., Int. Ed.*, 2004, **53**, 897].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