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Syntheses of 5,6-Benzo- and 5,6-Naphtho-(1*R**,3*R**,4*S**,8*R**)-4,8-dihydroxy-3-methyl-2-oxabicyclo[2.2.2]oct-5-ene Derivatives

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A synthetic method for the title compounds has been developed for the syntheses of sarubicin A (**1**) and granaticin (**2**). Tetralones (**5**) and anthracenones (**16**) were transformed into 1-hydroxy-1-(1-hydroxyethyl) derivatives of tetralins and tetrahydroanthracenes (**8**, **18**) by the route shown in Charts 2 and 4. The diols were dehydrated to allyl alcohols (**11**, **19**) by acid treatment or by reacting their 1′-monoacetates with thionyl chloride followed by alkaline hydrolysis, the choice of procedure being dependent on the structure of the aromatic ring. *cis*-Dihydroxylation of the olefins by catalytic osmylation using trimethylamine *N*-oxide as an oxidant afforded the 1*R**,2*R**,1′*R**-triols (**12**, **20**) with 98% stereoselectivity, except in the cases of **11a** and **19b**, where the stereoselectivities were 95 and 90%, respectively. Oxidative ring closure of the triols to the corresponding oxabicycles (**13**, **21**) was achieved by reaction with *N*-bromosuccinimide under controlled conditions. The intermediate 4-bromo compounds (**14**, **15**) could be isolated in the reactions of **12c**, **d** and underwent smooth cyclization with silver perchlorate in tetrahydrofuran.

Keywords——sarubicin A; granaticin; osmylation; *N*-bromosuccinimide; 2-oxabicyclo-[2.2.2]octene

The antibiotics sarubicin A[1] (U-58,431)[2] (**1**) and granaticin (**2**)[3] isolated from *Streptomyces* cultures possess the common structural feature of a modified C-glycoside,[4] 2-oxabicyclo[2.2.2]octene ring fused to a quinone moiety, and a central aspect of our project aiming at the total syntheses of these antibiotics has been the development of synthetic methodology for building this unique system. In 1981, we introduced two approaches to the benzobicycle **13a** (Chart 1),[5] a prototype which has no substituent on the aromatic ring, and the strategy which involves oxidative cyclization of a triol intermediate (route a) has been applied to our recent total synthesis of (±)-sarubicin A.[6] This paper presents a full account of the results to date of our continuing study on the syntheses by route a of the title compounds, which are related to our target molecules.

Syntheses of 1*R**,2*R**,1′*R**-Triols of 1-Ethyl-1,2,3,4-tetrahydronaphthalenes and Anthracenes (12, 20)

Based on the idea that 1*R**,2*R**-dihydroxy-1-(1*R**-hydroxyethyl)tetralins (**12**) (Chart 2) required for the oxidative ring closure could be obtainable by osmylation of 1-(1-hydroxyethyl)-3,4-dihydronaphthalenes (**11**), methods to prepare reasonable diol precursors (**8**) have been intensively investigated. One of the two approaches starting with 1-tetralones (Chart 2) was found to be synthetically acceptable, the best route being dependent upon the nature of the substituents on the aromatic ring. As reported earlier by us,[5] 1-tetralone (**5a**) was transformed into **8a** in good overall yield by the following sequence of reactions: treatment with vinylmagnesium bromide to give **6a** (88%), Sharpless epoxidation[7] with *tert*-BuOH–VO(acac)$_2$ in refluxing *tert*-BuOH for 5 h giving **7a** (94%), and lithium aluminum

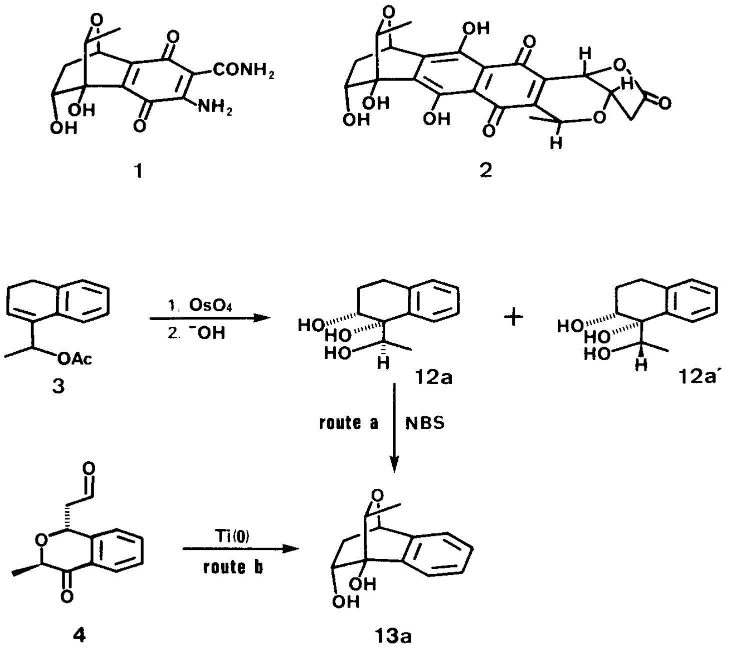
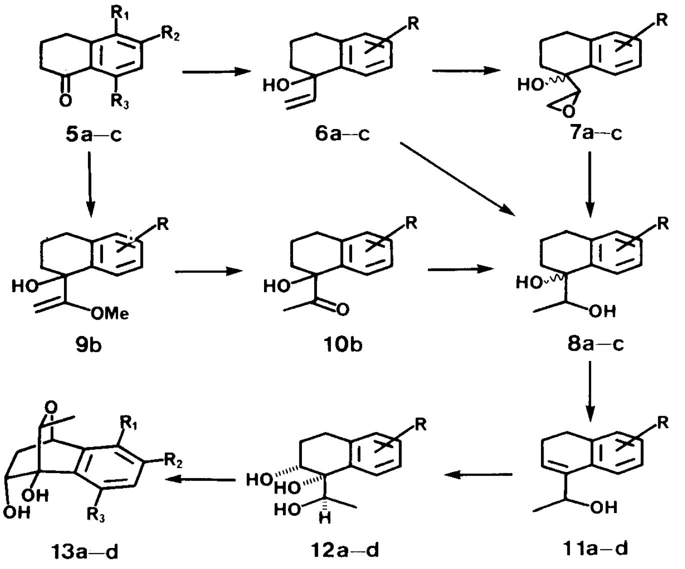


Chart 1



R =	R₁	R₂	R₃
a	H	H	H
b	OMe	H	OMe
c	OMe	Br	OMe
d	OMe	CN	OMe

Chart 2

hydride reduction (98%). However, application of this procedure to 5,8-dimethoxytetralones was not rewarding. The epoxidation of the vinyl carbinol intermediates **6b**, **c** was extremely sluggish, presumably due to steric hindrance associated with the *peri* methoxyl group, giving the corresponding epoxides **7b**, **c** in only *ca.* 35% yield even after a prolonged reaction period (24 h). Use of an acid-catalyzed acetoxymercuration–demercuration technique[8] did solve the problem encountered here; for example, **6c** could be transformed into **8c** in 73% yield. The second approach that begins with methoxyvinylation[9] was highly effective for 5,8-dimethoxy-1-tetralone (**5b**), a compound having no group sensitive to lithiated methyl vinyl ether. The subsequent steps, formation of the α-ketol (**10b**) by treatment with acid and reduction to the diol **8b** with sodium borohydride, proceeded in high yields. For dimethoxyanthracenone substrates (**16**), the latter route *via* the α-ketol (**17**) (Chart 4) was

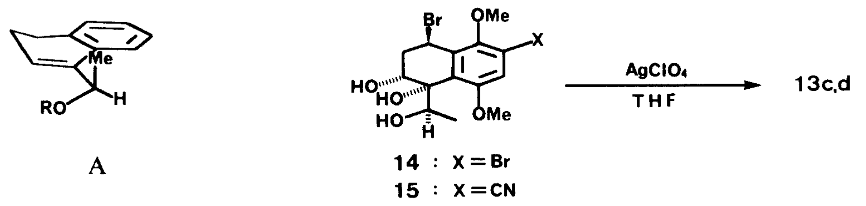


Chart 3

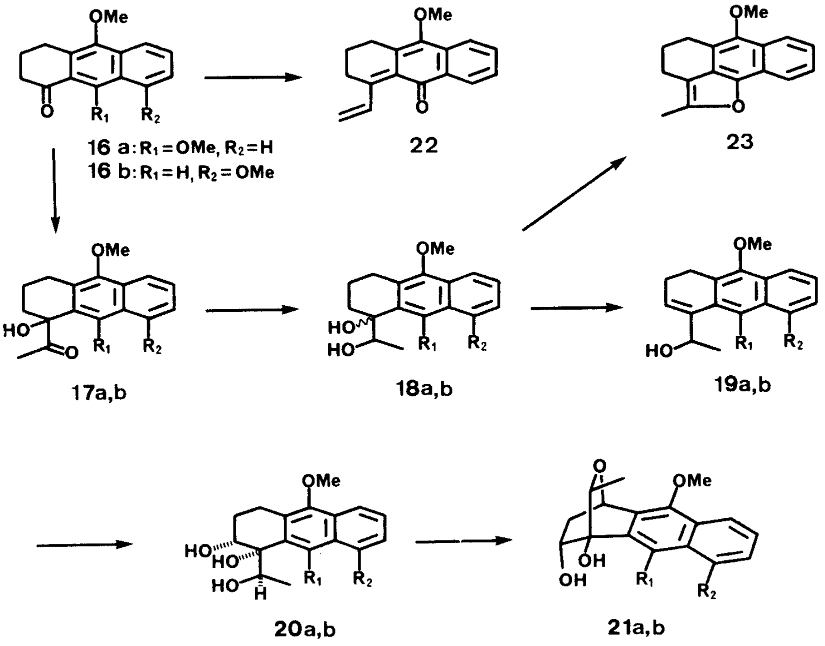


Chart 4

particularly useful. The reaction of 9,10-dimethoxyanthracenone (**16a**) with vinylmagnesium bromide afforded compound **22** as a major product, resulting from loss of methanol from the addition product.

The diols **8** and **18** thus obtained were mixtures of diastereomers, the ratio being dependent on the mode of formation. The isomers could be separated by silica gel chromatography and the (1*R**,1′*R**) configuration was assigned to the more polar isomer that showed more shielded C–Me signals (0.2—0.35 ppm) in the proton nuclear magnetic resonance (^{1}H-NMR) spectra, based on the results with a pair of diastereomers of **8a**.[5] However, the separation of the isomers was of no consequence since the chiral center at C_1 was to be destroyed at the next step.

The most reliable procedure for the regioselective dehydration of diols (**8**, **18**) to allyl alcohols (**11**, **19**) consists of three steps: formation of the 1′-monoacetate, dehydration with thionyl chloride in pyridine, and alkaline hydrolysis of the acetate group. Direct dehydration under acid-catalyzed conditions was exceptionally useful for the diols having methoxyl group on the aromatic ring (*e.g.* **8b** and **18b**) that facilitate carbonium ion formation at C_1. However, it was not applicable to **18a**, since a furan derivative **23** was formed exclusively, and therefore monoacetylation before acid treatment was required to prevent this abnormal reaction.

cis-Dihydroxylation with osmium tetroxide was first attempted with 1-(1-acetoxyethyl-3,4-dihydronaphthalene (**3**) under the catalytic conditions using *N*-methylmorpholine *N*-oxide[10] or trimethylamine *N*-oxide (TMO)[11] as the second oxidant. Although no significant stereoselectivity was observed with the original protocols, use of TMO without pyridine additive produced a *ca.* 2 : 1 mixture of the desired $1R^*,2R^*,1'R^*$-triol (**12a**) and its $1'S^*$-isomer (**12'a**) in high yield after hydrolysis of the acetate group. After continued experimentation directed to improvement of the stereoselectivity of the dihydroxylation, it was found that *ca.* 95% selectivity could be secured by switching the substrate from the acetate **3** to the free alcohol **11a**. The isomer **12a** could be isolated in pure state in 53% yield by recrystallization of the diastereomeric mixture, the rather low product yield being largely a result of overoxidation—cleavage of the side chain. This dramatic change in stereoselectivity could be rationalized by consideration of the preferred conformation A of the carbinol side chain (Chart 3), in which steric interaction with the *peri* aromatic hydrogen would be minimized. In the case of the acetate (A, R = Ac), both faces of the double bond are almost equally shielded and hardly discriminable by the attacking reagent. For the alcohol (A, R = H), on the other hand, osmylation should be highly favorable from the less crowded side towards which the hydroxyl group is projecting. Assistance by the hydroxyl group in the osmate ester formation could not be excluded, though there exists no precedent in the literature to our knowledge. In accord with this argument, the catalytic osmylation of dihydronaphthalenes **11b**—**d** possessing a *peri* methoxyl group resulted in >98% stereoselectivity (^{1}H-NMR analysis) affording **12b**—**d** in good yields, whereas the stereoselectivity realized with **19b** was *ca.* 90%. Finally, since compound **19a** was very sensitive to overoxidation, it was subjected to stoichiometric osmylation in a standard manner to give **20a** in 49% yield (stereoselectivity, >98%).

Although the stereochemical assignment of the triols (**12**, **20**) prepared above was made at the next stage, it is noteworthy that, in the ^{1}H-NMR spectra of the triols where diastereomers are available, C-methyl signals of the $(1R^*,2R^*,1'R^*)$-isomers (δ 0.91 for **12a** and δ 1.02 for **20b**) appear at *ca.* 0.15 ppm higher field than those of the $(1R^*,2R^*,1'S^*)$-isomers.

Cyclization of 1*R**,2*R**,1′*R**-Triols (12, 20) to 2-Oxabicyclo[2.2.2]octenes (13, 21)

Oxidative ring closure of the triols to the oxabicycles was first attempted with **12a**. It was reacted with *N*-bromosuccinimide (NBS) in refluxing carbon tetrachloride in the presence of benzoyl peroxide and cyclohexene oxide as an acid scavenger,[12] with the expectation that the benzylic bromination product would undergo a thermal dehydrobromination to provide **13a**. The reaction did proceed as expected, but the isolated yield of 35% was unacceptably low, the major by-product being a naphthalene derivative. After extensive experimentation, improvement of the yield to 84% was accomplished by conducting the reaction at 50 °C with a lower substrate concentration (*ca.* 0.015 M) under irradiation with a sunlamp. In order to minimize the side reaction, it is imperative to interrupt the reaction as soon as the substrate has been consumed (*ca.* 15 min). Although the acid scavenger was not employed in the improved procedure for **12a**, its use for acid-sensitive substrates such as **12b** and **20b** was advantageous, giving the corresponding oxabicycles **13b** and **21b** in 83 and 88% yields, respectively. In the case of **12c**, the intermediate 4-bromide **14** could be obtained in *ca.* 65% yield by performing the reaction with NBS at 40—42 °C for a short period (*ca.* 10 min); the configuration of the bromine atom as depicted (Chart 3) was deduced by ^{1}H-NMR analysis, 4-H_{eq} being observed as a triplet with $J = 3.5$ Hz at δ 5.71. Dehydrobromination of **14** to **13c** was cleanly achieved in quantitative yield by treatment with an equivalent amount of silver perchlorate in tetrahydrofuran at room temperature.

For those triols that were hardly soluble in the solvent carbon tetrachloride, *O*-trimethylsilylation followed by the reaction with NBS was an excellent modification. The reactions carried out with **12d** and **20a** are representative. In the case of **12d**, the 4-bromo compound **15** could be isolated in 96% yield after acid-catalyzed desilylation and it was treated with silver perchlorate to give **13d** in 96% yield. On the other hand, the 4-bromo derivative of **20a** was too unstable to isolate and was therefore directly subjected to dehydrobrominative cyclization by silica gel chromatography to give **21a** in 66% overall yield.

Structures and stereochemistries of the oxabicycles prepared above were determined by mass and ^{1}H-NMR spectroscopies. Electron impact mass spectra (EI-MS) supported the presence of the epoxymethano bridge by giving a characteristic base peak ($M^+ - 44$) arising from loss of acetaldehyde from the molecular ion by a retro Diels–Alder process. In the ^{1}H-NMR spectra, observation of exceptionally shielded C-methyl signals at δ0.79—0.88 is in accordance with the assigned configuration, in which the methyl group is *syn* to the aromatic ring.

Finally, it should be mentioned that the methodology presented in this paper for the syntheses of the title compounds is considered to be more efficient than the alternative method (Chart 1, route b). Even if a highly stereoselective synthetic method for the keto-aldehyde intermediate (*e.g.* **4**) could be exploited, the next step, which is an intramolecular reductive cyclization, would not be expected to proceed satisfactorily in the sense of product yield and stereoselectivity, as we experienced with **4**.5)

Experimental

Infrared spectra (IR) were recorded on a Jasco IRA-1 grating spectrometer and were calibrated with 1601 cm^{-1} absorption of polystyrene. Proton nuclear magnetic resonance spectra (^{1}H-NMR) were taken on a JEOL PMX-60 (60 MHz) or a Varian XL-200 (200 MHz) spectrometer in deuteriochloroform unless otherwise noted. Chemical shifts are reported in parts per million (δ) downfield from internal tetramethylsilane. Resonance patterns were reported as s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet. EI-MS were obtained on a JEOL JMS-D300 spectrometer. A Büchi Kugelrohr apparatus was used for vacuum distillation and all boiling points are uncorrected. Melting points were measured with a Yanagimoto micro melting point apparatus and are uncorrected. For chromatography, the following adsorbents were used: Merck Silica gel 60, 70—230 or 230—400 mesh, for column chromatography; Merck precoated Silica gel 60 F_{254} plates for analytical thin layer chromatography (TLC). Elemental analyses were performed by the Microanalytical Laboratory of this university. Dry solvents were obtained by using standard procedures. Anhydrous magnesium sulfate was used for drying all organic solvent extracts in work-up, and removal of the solvents was performed with a rotary evaporator.

1-(1-Hydroxyethyl)-1,2,3,4-tetrahydro-1-naphthol (8a)——Vanadyl acetylacetonate (10 mg) and 93.5% *tert*-BuOOH (3.62 g, 37.4 mmol) were added to a stirred solution of **6a**13) (3.49 g, 20 mmol) in benzene (100 ml), and the mixture was heated under reflux for 5 h. It was allowed to cool to room temperature, and washed successively with 10% Na_2SO_3, water and brine, then dried. Removal of the solvent under reduced pressure afforded **7a** as a mixture of diastereomers (3.59 g, 94%), a pale yellow oil. IR (neat): 3460 cm^{-1}. ^{1}H-NMR (60 MHz, CCl_4) δ: 1.90 (4H, m, CH_2), 2.32 (1H, br s, OH), 2.6—3.1 (5H, m, CH_2 and oxirane), 7.0—7.6 (4H, m, ArH). MS *m/e*: 190 (M^+), 147 (M^+ − oxirane), 129 (147 − H_2O, base peak).

A solution of the epoxide **7a** (1.90 g, 10 mmol) in dry tetrahydrofuran (THF, 10 ml) was added over a 10 min period to a stirred suspension of $LiAlH_4$ (0.395 g, 10 mmol) in dry THF (10 ml) at ice-water temperature. The reaction mixture was then stirred at room temperature for 30 min and quenched by addition of water. The organic layer was separated, diluted with ether, washed with brine, dried, and concentrated under reduced pressure. The residual pale yellow oil (1.89 g, 98%) was shown to be a 3 : 2 mixture of 1*R**,1′*S**- and 1*R**,1′*R**-diols (**8a**) by integration of the methyl signals in the ^{1}H-NMR. These isomers could be separated by silica gel chromatography with hexane : AcOEt = 1 : 1 and showed the following properties. (1*R**,1′*S**) isomer: *Rf* = 0.30 (hexane : AcOEt = 3 : 1), colorless needles from hexane–$CHCl_3$, mp 77—79 °C. *Anal.* Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 75.16; H, 8.34. IR (KBr): 3400 cm^{-1}. ^{1}H-NMR (200 MHz) δ: 1.15 (3H, d, J = 6 Hz, Me), 1.7—2.2 (4H, m, 2-H and 3-H), 2.1 (2H, br, OH), 2.75 (2H, m, 4-H), 4.07 (1H, q, J = 6 Hz, 1′-H), 7.0—7.8 (4H, m, ArH). MS *m/e* (relative intensity): 174 ($M^+ - H_2O$, 10), 147 (M^+ − MeCHOH, 100), 127 (147 − H_2O, 50), 115 (20). (1*R**,1′*R**) isomer: *Rf* = 0.25 (hexane : AcOEt = 3 : 1), a colorless oil. IR (neat): 3400 cm^{-1}. ^{1}H-NMR (200 MHz) δ: 0.93 (3H, d, J = 6 Hz, Me), 2.90 (4H, m, 2-H and 3-H), 2.75 (2H, m, 4-H), 2.92 (2H, br, OH), 4.26 (1H, q, J = 6 Hz, 1′-H), 7.1—7.6 (4H, m, ArH). MS *m/e* (relative intensity): 192 (M^+, 10), 175 (M^+ − OH, 85), 129 (M^+ − MeCHOH − H_2O, 100).

1-(1-Hydroxyethyl)-5,8-dimethoxy-1,2,3,4-tetrahydro-1-naphthol (8b)——a) *Via* the Epoxide **7b**: A solution of **5b**14) (8.97 g, 43.5 mmol) in dry ether (100 ml) was added dropwise at room temperature to a stirred solution of vinylmagnesium bromide which was freshly prepared from Mg (2.12 g) and vinyl bromide (7 ml) in dry THF (110 ml) under an Ar atmosphere. After the addition was completed, stirring of the reaction mixture was continued for 1.5 h. Saturated aqueous NH_4Cl (200 ml) was slowly added, and the organic layer was separated, combined with the ether extract of the water layer, and dried. The solvent was removed under reduced pressure, and the residue was subjected to distillation to give **6b** (8.93 g, 88%) as a colorless oil, bp 120—125 °C (0.6 Torr) (mp 55—56.5 °C). *Anal.* Calcd for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74. Found: C, 71.77; H, 7.93. IR (neat): 3540 cm^{-1}. ^{1}H-NMR (60 MHz) δ: 1.87 (4H, m, CH_2), 2.5—2.8 (2H, m, CH_2), 3.80 (6H, s, OMe), 4.77 (1H, dd, *J*=17, 2 Hz, vinyl H), 4.83 (1H, s, OH), 5.05 (1H, dd, *J*=11, 2 Hz, vinyl H), 6.14 (1H, dd, *J*=17, 11 Hz, vinyl H), 6.74 (2H, s, ArH). MS *m/e*: 234 (M^+, base peak), 207 (M^+ −vinyl).

The vinyl carbinol **6b** (20.17 g) was subjected to the Sharpless epoxidation described above for **6a** except that the reaction was run for 24 h. Flash chromatography of the product with AcOEt : benzene = 1 : 6 afforded a diastereomeric mixture of the epoxide **7b** (7.31 g, 34%) as an oil and unreacted starting material (8.66 g). The diastereomers could be separated by silica gel chromatography and showed the following properties. Major isomer (less polar): mp 64—69 °C. ^{1}H-NMR (60 MHz) δ: 1.90 (4H, m, CH_2), 2.62 (2H, d, *J*=4 Hz, oxirane), 2.70 (2H, m, CH_2), 3.23 (1H, t, *J*=4 Hz, oxirane), 3.80 (3H, s, OMe), 3.87 (3H, s, OMe), 4.60 (1H, br s, OH), 6.73 (2H, s, ArH). MS *m/e*: 250 (M^+), 208 (base peak), 192, 177. Minor isomer (more polar): a colorless oil. ^{1}H-NMR (60 MHz) δ: 1.92 (4H, m, CH_2), 2.65 (2H, m, CH_2), 2.77 (2H, d, *J*=4 Hz, oxirane), 3.18 (1H, t, *J*=4 Hz, oxirane), 3.81 (3H, s, OMe), 3.87 (3H, s, OMe), 4.47 (1H, s, OH), 6.77 (2H, s, ArH). MS *m/e*: 250 (M^+), 208, 207, 192 (base peak), 177.

The oxirane **7b** (100 mg, a mixture of diastereomers) in dry THF (2 ml) was treated with $LiAlH_4$ (30 mg) at room temperature for 1 h, and the reaction mixture was worked up as described above for **7a** to give the diol **8b** (97 mg, 96%), mp 69—75 °C. The diastereomers of **8b** could be separated by preparative TLC with hexane : AcOEt = 1 : 2 and showed the following properties. Major (1*R**,1′*R**)isomer (more polar): mp 99.5—101 °C, colorless needles from iso-Pr_2O. *Anal.* Calcd for $C_{14}H_{20}O_4$: C, 66.64; H, 7.99. Found: C, 66.50; H, 8.05. IR (KBr): 3470 cm^{-1}. ^{1}H-NMR (60 MHz) δ: 0.87 (3H, d, *J*=6 Hz, C–Me), 1.4—2.2 (4H, m, CH_2), 2.4—2.9 (3H, m, CH_2 and OH), 3.80 (3H, s, OMe), 3.85 (3H, s, OMe), 4.30 (1H, br s, OH), 4.52 (1H, q, *J*=6 Hz, 1′-H), 6.76 (2H, s, ArH). MS *m/e*: 252 (M^+), 207 (M^+ −MeCHOH), 192. Minor (1*R**,1′*S**) isomer (less polar): mp 135—136 °C, colorless needles from iso-Pr_2O. *Anal.* Calcd for $C_{14}H_{20}O_4$: C, 66.64; H, 7.99. Found: C, 66.67; H, 7.99. IR (KBr): 3450 cm^{-1}. ^{1}H-NMR (60 MHz) δ: 1.23 (3H, d, *J*=6 Hz, C–Me), 1.5—2.9 (7H, m, CH_2 and OH), 3.82 (3H, s, OMe), 3.89 (3H, s, OMe), 4.28 (1H, q, *J*=6 Hz, 1′-H), 4.57 (1H, s, OH), 6.77 (2H, s, ArH). MS *m/e*: 252 (M^+), 208, 207 (M^+ −MeCHOH), 192, 177.

b) *Via* the α-Ketol **9b**: A stirred solution of methyl vinyl ether (4 ml) in dry THF (75 ml) under an Ar atmosphere was cooled to −60 °C and a pentane solution of *tert*-BuLi (2 M, 25 ml) was added during a 15 min period. The yellow solution was allowed to warm to *ca.* −10 °C in 1 h and kept at the same temperature for 1 h. The nearly colorless solution was cooled again to −60 °C and a solution of **5b** (5.11 g, 24.8 mmol) in dry THF (10 ml) was added during 30 min. The resulting pale green solution was allowed to warm to 0 °C and stirring was continued until the starting material was no longer detectable on TLC with hexane : AcOEt = 1 : 1 (*ca.* 1.5 h). This solution was treated with 20% aqueous NH_4Cl (70 ml) at room temperature for 20 min, then the bulk of the THF was removed under reduced pressure, and the residue was extracted with ether and CH_2Cl_2. Concentration of the extracts under reduced pressure afforded practically pure vinyl ether **9b** (6.9 g) as a crystalline solid. This product was dissolved in MeOH (140 ml) and treated with 2% HCl (0.6 ml) at room temperature for 3 h. The solution was then neutralized with 5% $NaHCO_3$ and concentrated under reduced pressure. The residual pale yellow solid was extracted with ether, and the extract was washed with brine, dried, and concentrated. The residue was crystallized from EtOH to give the α-ketol **10b** (5.01 g, 81%), mp 96—97.5 °C. *Anal.* Calcd for $C_{13}H_{18}O_4$: C, 67.20; H, 7.20. Found: C, 67.18; H, 7.07. IR (KBr): 3380, 1685 cm^{-1}. ^{1}H-NMR (60 MHz) δ: 2.07 (3H, s, Ac), 3.67 (3H, s, OMe), 3.77 (3H, s, OMe), 4.22 (1H, s, OH), 6.67 (2H, br s, ArH).

A stirred solution of **10b** (2.0 g, 8 mmol) in 2-propanol (80 ml) was cooled with ice-water, and a solution of $NaBH_4$ (1.5 g, 40 mmol) in water (20 ml) was added. The mixture was then stirred at room temperature until the starting material was no longer detectable on TLC with hexane : AcOEt = 1 : 1 (*ca.* 3.5 h). The reaction mixture was acidified with 10% HCl, and after being made slightly basic with $NaHCO_3$, the bulk of the 2-propanol was removed under reduced pressure. The residue was extracted with AcOEt, and the extract was washed with water and brine, dried, and concentrated under reduced pressure to give practically pure **8b** (1.9 g) as a pale yellow solid; ratio of more polar (1*R**,1′*R**) : less polar (1*R**,1′*S**) isomers = 2 : 5 as determined by ^{1}H-NMR analysis.

6-Bromo-1-(1-hydroxyethyl)-5,8-dimethoxy-1,2,3,4-tetrahydro-1-naphthol (8c)——A solution of 98.5% $Hg(OAc)_2$ (3.47 g, 10.7 mmol) in water (10 ml) and 7% $HClO_4$ (0.15 ml) were added to a stirred solution of **6c**15) (3.19 g, 10.2 mmol) in THF (10 ml) at room temperature. The resulting yellow suspension became homogeneous in *ca.* 10 min. The mixture was stirred for 2 h, then 6 N NaOH (5 ml) was introduced followed by dropwise addition of a solution of $NaBH_4$ (210 mg) in 3 N NaOH (10 ml) under cooling with ice-water. The mixture was then stirred at room temperature for 2 h, and extracted with CH_2Cl_2. The extract was dried and concentrated under reduced pressure. The residue was subjected to flash chromatography (silica gel, 40 g; solvent, hexane : AcOEt = 1 : 1) to give the diastereomers of **8c**, a less polar isomer (828 mg, 24.5%) and a more polar isomer (1.633 g, 48.4%). Analytical samples were obtained by recrystallization from AcOEt–iso-Pr_2O. Major (1*R**,1′*R**) isomer: mp 156—157.5 °C. *Anal.* Calcd for $C_{14}H_{19}BrO_4$: C, 50.76; H, 5.74. Found: C, 50.71; H, 5.72. ^{1}H-NMR (200 MHz) δ: 0.95 (3H, d, *J*=6.5 Hz, C–Me), 1.45—1.7 (1H, m), 1.75—2.1 (3H, m), 2.43 (1H, ddd, *J*=17, 10, 4 Hz), 2.83 (1H, br, OH), 2.95 (1H, dtd, *J*=17, 4.5, 2 Hz), 3.74 (3H, s, OMe), 3.84 (3H, s, OMe), 4.09 (1H, br s, OH), 4.50 (1H, q, *J*=6.5 Hz, 1′-H), 6.95 (1H, s, ArH). MS *m/e*: 314, 312 (M^+-H_2O), 287, 285 (M^+ − MeCHOH, base peak). Minor (1*R**,1′*S**) isomer: mp 97—99 °C. *Anal.* Calcd for $C_{14}H_{19}BrO_4$: C, 50.76; H, 5.74. Found: C, 51.00; H, 5.85. ^{1}H-NMR (200 MHz) δ: 1.25 (3H, d, J = 6.5 Hz, C–Me), 1.45 (1H, br, OH), 1.55—2.2 (4H, m), 2.60 (1H, ddd, J = 17, 8.5, 5 Hz), 2.95 (1H, dt, J = 17, 6 Hz), 3.78 (3H, s, OMe), 3.90 (3H, s, OMe), 4.25 (1H, br s, OH), 4.39 (1H, q, J = 6.5 Hz, 1′-H), 7.00 (1H, s, ArH). MS *m/e*: 314, 312 (M^+ − MeCHOH, base peak).

1-(1-Hydroxyethyl)-9,10-dimethoxy-1,2,3,4-tetrahydro-1-anthracenol (18a)——A stirred mixture of methyl vinyl ether (20% v/v solution in THF, 3.0 ml, *ca.* 10 mmol) and dry THF (15 ml) was cooled to −65 °C under an Ar atmosphere and *tert*-BuLi (2 M in pentane, 4 ml) was added during a 5 min period. The mixture was allowed to warm to −5 °C slowly, and stirring at this temperature was continued for 20 min to give a pale yellow solution of the lithiated product. After being cooled to −65 °C again, it was treated with a solution of **16a**$^{16)}$ (900 mg, 3.52 mmol) in dry THF (10 ml), and then allowed to warm to 0 °C. The reaction mixture was treated with 20% aqueous NH_4Cl (10 ml) and the bulk of the THF was removed under reduced pressure. The residue was extracted with ether, and the extract was washed with brine, dried, and concentrated under reduced pressure. The residue was dissolved in MeOH (25 ml) at room temperature, and after addition of 2% HCl (3 drops) the solution was set aside for 30 min. It was then neutralized with 5% $NaHCO_3$ and concentrated under reduced pressure without heating. The residue was extracted with AcOEt, and the extract was washed with brine, dried, and concentrated. The solid residue was crystallized from iso-Pr_2O to give **17a** (745 mg, 76%) as colorless needles, mp 144—145 °C. *Anal.* Calcd for $C_{18}H_{20}O_4$: C, 71.98; H, 6.71. Found: C, 71.68; H, 6.77. IR (KBr): 3400, 1700 cm^{-1}. ^{1}H-NMR (200 MHz) δ: 1.65—2.0 (2H, m, CH_2), 2.14 (3H, s, Ac), 2.6—2.85 (2H, m, CH_2), 3.2—3.55 (2H, m, CH_2), 3.86 (3H, s, OMe), 3.93 (3H, s, OMe), 4.68 (1H, s, OH), 7.4—7.7 (2H, m, ArH), 7.95—8.2 (2H, m, ArH). MS *m/e*: 300 (M^+), 257 (M^+ − Ac), 242 (257 − Me), 227, 43 (base peak).

A stirred solution of **17a** (300 mg, 1 mmol) in 2-propanol (20 ml) at room temperature was treated with $NaBH_4$ (300 mg, 8 mmol) in water (3 ml). After 2.5 h, 10% NaOH (6 ml) was added and the mixture was stirred at room temperature overnight. It was diluted with AcOEt (50 ml), washed with brine, dried, and concentrated under reduced pressure to give a diastereomeric mixture (ratio = *ca.* 8 : 1) of **18a** as a solid. The major (1*R**,1′*S**) isomer was obtained by recrystallization from AcOEt–iso-Pr_2O, mp 119—120.5 °C. *Anal.* Calcd for $C_{18}H_{22}O_4$: C, 71.50; H, 7.33. Found: C, 71.63; H, 7.27. IR (KBr): 3450 cm^{-1}. ^{1}H-NMR (200 MHz) δ: 1.12 (3H, d, J = 6 Hz, C–Me), 1.7—2.2 (4H, m, 2-H and 3-H), 2.58 (1H, d, J = 8 Hz, OH), 2.62—2.82 (1H, m, 4-H), 3.14 (1H, ddd, J = 18, 6, 1.5 Hz, 4-H), 3.88 (3H, s, OMe), 4.06 (4H, s and m, OMe and 1′-H), 4.55 (1H, s, OH), 7.50 (2H, m, ArH), 8.05 (2H, m, ArH). MS *m/e*: 302 (M^+), 284 (M^+-H_2O), 257 (M^+ − MeCHOH, base peak).

1-(1-Hydroxyethyl)-8,10-dimethoxy-1,2,3,4-tetrahydro-1-anthracenol (18b)——As described above for **16a**, the reaction of **16b**$^{17)}$ with lithiated methyl vinyl ether followed by acid-catalyzed hydrolysis of the condensation product afforded **17b** (2.09 g) as colorless needles from AcOEt–hexane, mp 129—130 °C. *Anal.* Calcd for $C_{18}H_{20}O_4$: C, 71.88; H, 6.71. Found: C, 71.87; H, 6.74. ^{1}H-NMR (60 MHz) δ: 2.10 (3H, s, Ac), 3.92 (6H, s, OMe), 4.62 (1H, s, OH). MS *m/e*: 300 (M^+), 283, 258, 257, 197, 43 (base peak). Reduction of **17b** (2.05 g) with $NaBH_4$ (2.0 g) in 2-propanol afforded **18b** in quantitative yield as a *ca.* 2 : 1 mixture of diastereomers which could not be crystallized. ^{1}H-NMR (60 MHz) δ: (major isomer) 1.17 (d, J = 6.5 Hz, C–Me), 3.83 (s, OMe), 3.92 (s, OMe), 4.17 (q, J = 6.5 Hz, 1′-H), 6.66 (d, J = 8 Hz, ArH), 7.30 (t, J = 8 Hz, ArH), 7.55 (d, J = 8 Hz, ArH), 8.33 (s, ArH); (minor isomer) 0.93 (d, J = 6.5 Hz, C–Me), 4.33 (q, J = 6.5 Hz, 1′-H), 8.13 (s, ArH), others being overlapped with the signals due to the major isomer. MS *m/e*: 302 (M^+), 284, 266, 257, 251, 254 (base peak).

1-(3,4-Dihydro-1-naphthyl)ethanol (11a)——Acetic anhydride (8.5 ml, 90 mmol) was added to a stirred solution of **8a** (a mixture of diastereomers, 5.77 g, 30 mmol) in dry pyridine (15 ml) at room temperature. After continued stirring for 15 h, the mixture was treated with water (30 ml) to decompose excess acetic anhydride and extracted with ether. The ether extract was washed with dilute HCl and brine, dried, and concentrated to give the 1′-monoacetate (7 g) as a pale yellow oil. IR (neat): 3470, 1730 cm^{-1}. ^{1}H-NMR (60 MHz) δ: 0.95, 1.21 (d, J = 6 Hz, Me), 1.84, 2.02 (s, OAc), 5.18, 5.35 (q, J = 6 Hz, 1′-H). This acetate was dissolved in dry pyridine (8 ml) and cooled with ice-water. Purified $SOCl_2$ (3.2 ml, 45 mmol) was slowly added to the stirred solution and, after continued stirring at room temperature for 10 min, the mixture was treated with cold water (40 ml) and extracted with ether. The extract was washed with brine, dried, and concentrated under reduced pressure to give **3** (6.26 g) as a pale yellow oil. IR (neat): 1740 cm^{-1}. ^{1}H-NMR (60 MHz, CCl_4) δ: 1.44 (3H, d, J = 6 Hz, Me), 2.00 (3H, s, OAc), 2.15—2.9 (4H, m, CH_2), 5.82 (1H, q, J = 6 Hz, 1′-H), 6.07 (1H, t, J = 5 Hz, 2-H), 7.0—7.3 (4H, m, ArH). Saponification of **3** with 5% methanolic NaOH in the usual manner afforded **11a** in quantitative yield, and this product was purified by silica gel chromatography with AcOEt : hexane = 1 : 4, bp 114—116 °C (0.06 Torr). *Anal.* Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82.35; H, 7.90. IR (neat): 3350 cm^{-1}. ^{1}H-NMR (200 MHz) δ: 1.44 (3H, d, J = 6 Hz, Me), 1.75 (1H, br, OH), 2.28 (2H, m, 3-H), 2.74 (2H, t, J = 8 Hz, 4-H), 4.90 (1H, q, J = 6 Hz, 1′-H), 6.18 (1H, t, J = 5 Hz, 2-H), 7.1—7.5 (4H, m, ArH). MS *m/e* (relative intensity): 174 (M^+, 60), 129 (M^+ − MeCHOH, 100), 115 (40), 91 (30).

1-(5,8-Dimethoxy-3,4-dihydro-1-naphthyl)ethanol (11b)——The diol **8b** (a mixture of diastereomers, 2.17 g) was dissolved in MeOH (40 ml) and treated with 12 N HCl (12 drops) at room temperature for 3 h. The solution was neutralized by addition of 5% $NaHCO_3$, and the bulk of the MeOH was removed under reduced pressure. The residue was extracted with ether, and the extract was washed with water and brine, then dried, and concentrated to give crude **11b** (1.94 g). This product was subjected to chromatography (silica gel, 20 g; solvent, benzene : AcOEt = 19 : 1 to 4 : 1) to give pure **11b** (1.69 g, 91%) as a crystalline solid. An analytical sample was obtained by recrystallization from hexane–iso-Pr_2O, mp 69.5—70 °C. *Anal.* Calcd for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74. Found: C, 71.79; H, 7.84. ^1H-NMR (60 MHz) δ: 1.32 (3H, d, $J=6$ Hz, C–Me), 1.9—2.2 (2H, m, CH_2), 2.5—2.8 (2H, m, CH_2), 3.22 (1H, br s, OH), 3.82 (3H, s, OMe), 3.85 (3H, s, OMe), 4.97 (1H, q, $J=6$ Hz, 1′-H), 6.31 (1H, t, $J=5$ Hz, 2-H), 6.81 (2H, s, ArH). MS *m/e*: 234 (M^+, base peak).

1-(6-Bromo-5,8-dimethoxy-3,4-dihydro-1-naphthyl)ethanol (11c)——Trifluoroacetic acid (0.47 ml) was added to a stirred solution of **8c** (major isomer, 1.41 g) in CH_2Cl_2 (47 ml) at room temperature. After continued stirring for 1 h, the solution was washed with 5% $NaHCO_3$, then dried, and the solvent was removed under reduced pressure. The residual oil was subjected to chromatography (silica gel, 35 g; solvent, hexane : AcOEt = 2 : 1) to afford **11c** (1.13 g, 85%), bp 125 °C (0.06 Torr) (mp 91—92.5 °C). *Anal.* Calcd for $C_{14}H_{17}BrO_3$: C, 53.67; H, 5.43. Found: C, 53.80; H, 5.44. IR (neat): 3450 cm^{-1}. ^1H-NMR (200 MHz) δ: 1.33 (3H, d, $J=6$ Hz, C–Me), 2.13 (2H, m, 3-H), 2.71 (2H, m, 4-H), 2.90 (1H, br, OH), 3.74 (3H, s, OMe), 3.85 (3H, s, OMe), 5.00 (1H, q, $J=6$ Hz, 1′-H), 6.36 (1H, t, $J=5$ Hz, 2-H), 7.01 (1H, s, ArH). MS *m/e* (relative intensity): 312, 314 (M^+, 100), 297, 299 (M^+-Me, 55), 233 (5), 218 (25), 190 (85). Exact mass Calcd for $C_{14}H_{17}BrO_3$: 312.0360, 314.0342. Found: 312.0313, 314.0347.

1-(6-Cyano-5,8-dimethoxy-3,4-dihydro-1-naphthyl)ethanol (11d)——A stirred solution of **11c** (313 mg, 1 mmol) and CuCN (134 mg, 1.5 mmol) in dry *N*-methyl-2-pyrrolidinone (1 ml) was heated at 150 °C for 3 h. The resulting dark solution was cooled to room temperature and treated with NaCN (150 mg) in water (5 ml) for 30 min. The mixture was extracted with AcOEt, and the extract was dried and concentrated under reduced pressure. The residue was subjected to silica gel chromatography with AcOEt : hexane = 3 : 2 to give **11d** (122 mg, 47%) as a colorless oil. IR (neat): 3450, 2240 cm^{-1}. ^1H-NMR (200 MHz) δ: 1.33 (3H, d, $J=6$ Hz, C–Me), 2.15 (2H, m, 3-H), 2.68 (3H, m, 4-H and OH), 3.87 (3H, s, OMe), 3.89 (3H, s, OMe), 5.05 (1H, q, $J=6$ Hz, 1′-H), 6.52 (1H, t, $J=5$ Hz, 2-H), 6.99 (1H, s, ArH). MS *m/e* (relative intensity): 259 (M^+, 100), 244 (M^+-Me, 65), 216 (60), 43 (95). Exact mass Calcd for $C_{15}H_{17}NO_3$: 259.1206. Found: 259.1205.

1-(9,10-Dimethoxy-3,4-dihydro-1-anthracenyl)ethanol (19a)——A stirred solution of **18a** (a mixture of diastereomers, 300 mg, 1 mmol) in dry CH_2Cl_2 (2 ml) at room temperature was treated successively with triethylamine (0.28 ml, 2 mmol), acetic anhydride (0.19 ml, 2 mmol) and 4-dimethylaminopyridine (5 mg). After continued stirring at room temperature for 1 h, ether (20 ml) and crushed ice were introduced into the reaction mixture. The organic layer was separated, washed with water, 5% $NaHCO_3$ and brine, and dried. Removal of the solvent under reduced pressure afforded the 1′-monoacetate as a pale yellow oil in quantitative yield. A stirred solution of the acetate (200 mg, 0.58 mmol) in CH_2Cl_2 (10 ml) was cooled with ice-water and F_3CCOOH (0.06 ml, 0.78 mmol) was added. Stirring of the mixture was continued for 30 min at the same temperature and then for 1 h at room temperature. The resulting dark solution was diluted with CH_2Cl_2 (10 ml), washed with 5% $NaHCO_3$ and brine, and dried. Removal of the solvent afforded a brown oil (172 mg), which was subjected to chromatography (silica gel, 10 g; solvent, AcOEt : hexane = 1 : 5), giving the dehydration product (110 mg, 58% or 84% based on the reacted material). ^1H-NMR (60 MHz) δ: 1.35 (3H, d, $J=6$ Hz, C–Me), 2.12 (3H, s, OAc), 3.85 (6H, s, OMe), 6.2—6.8 (2H, m, 1′-H and 2-H). This product was subjected to saponification with 1% methanolic KOH (5 ml) in the usual manner, and the crude product was purified by chromatography (silica gel, 8 g; solvent, AcOEt : hexane = 1 : 2) to give **19a** (84 mg, 88%), which was crystallized from AcOEt, mp 105.5—106 °C. *Anal.* Calcd for $C_{18}H_{20}O_3$: C, 76.03; H, 7.09. Found: C, 75.87; H, 7.05. ^1H-NMR (200 MHz) δ: 1.42 (3H, d, $J=6.5$ Hz, C–Me), 2.17—2.32 (2H, m, 3-H), 2.75 (1H, br, OH), 2.86 (2H, t, $J=7$ Hz, 4-H), 3.84 (3H, s, OMe), 3.87 (3H, s, OMe), 5.16—5.32 (1H, br, 1′-H), 6.47 (1H, td, $J=5$, 1.5 Hz, 2-H), 7.45—7.55 (2H, m, ArH), 8.05—8.15 (2H, m, ArH). MS *m/e*: 284 (M^+, base peak).

1-(8,10-Dimethoxy-3,4-dihydro-1-anthracenyl)ethanol (19b)——Trifluoroacetic acid (0.58 ml, 7.55 mmol) was added to a stirred solution of **18b** (1.80 g, 6.29 mmol) in dry CH_2Cl_2 (70 ml) at room temperature. After 2 h, the dark-colored solution was washed with 5% $NaHCO_3$ and brine, then dried, and concentrated under reduced pressure to give **19b** (1.2 g, 71%) as a pale yellow oil. This was used for the next step without further purification. ^1H-NMR (200 MHz) δ: 1.51 (3H, d, $J=6$ Hz, C–Me), 1.87 (1H, br s, OH), 2.33 (2H, td, $J=7.5$, 4 Hz, 3-H), 2.94 (2H, t, $J=7.5$ Hz, 4-H), 3.86 (3H, s, OMe), 3.97 (3H, s, OMe), 5.13 (1H, q, $J=6$ Hz, 1′-H), 6.31 (1H, t, $J=4$ Hz, 2-H), 6.76 (1H, d, $J=8$ Hz, 7-H), 7.36 (1H, t, $J=8$ Hz, 6-H), 7.64 (1H, d, $J=8$ Hz, 5-H), 8.03 (1H, s, 9-H). MS *m/e*: 284 (M^+, base peak).

(1*R,2*R**)-1-[(*R**)-1-Hydroxyethyl]-1,2,3,4-tetrahydro-1,2-naphthalenediol (12a)**——a) From **3** (Acetate of **11a**): Trimethylamine *N*-oxide dihydrate (346 mg, 3.1 mmol) and OsO_4 (3 mg) were added to a stirred solution of **3** (436 mg, 2 mmol) in *tert*-BuOH (4 ml) and water (1.2 ml), and the mixture was heated under reflux. After 2.5 h, additional amine oxide (104 mg) was introduced and refluxing was continued for 1 h. The dark-colored reaction mixture was allowed to cool to room temperature, and after treatment with $NaHSO_3$ (520 mg, 5 mmol) for 10 min, it was extracted with ether. The extract was washed with brine, dried, and concentrated under reduced pressure to give an oil (485 mg), which was a mixture of 1′- and 2-monoacetates of **12a** and **12′a** on the basis of the 200 MHz ^1H-NMR spectrum. Treatment of the acetate mixture (430 mg) in MeOH (2.5 ml) with K_2CO_3 (790 mg) at room temperature afforded a mixture of **12a** and **12′a** (320 mg) (ratio = *ca.* 2 : 1 as determined by integration of the Me signals in the ^1H-NMR spectrum), which was separated by silica gel chromatography with $CHCl_3$: MeOH = 20 : 1. Both isomers were crystallized from CCl_4. 1*R**,2*R**,1′*R**-Triol (**12a**): colorless needles, mp 94—95 °C, *Rf*=0.35 ($CHCl_3$: MeOH=20:1). *Anal.* Calcd for $C_{12}H_{16}O_3$: C, 69.21; H, 7.74. Found: C, 69.46; H, 7.70. IR (KBr): 3400 cm^{-1}. ^{1}H-NMR (200 MHz) δ: 0.94 (3H, d, *J*=6 Hz, Me), 1.92 (2H, m, 3-H), 2.80 (2H, m, 4-H), 3.90 (3H, br, OH), 4.23 (1H, dd, *J*=8, 6 Hz, 2-H), 4.36 (1H, q, *J*=6 Hz, 1′-H), 7.0—7.5 (4H, m, ArH). MS *m/e* (relative intensity): 263 (M^+ − MeCHOH, 45), 145 (263 − H_2O, 65), 117 (100), 91 (30). 1*R**,2*R**,1′*S**-Triol (**12′a**): colorless needles, mp 97—98 °C, *Rf*=0.25 ($CHCl_3$: MeOH=20:1). *Anal.* Calcd for $C_{12}H_{16}O_3$: C, 69.21; H, 7.74. Found: C, 68.92; H, 7.86. IR (KBr): 3370 cm^{-1}. ^{1}H-NMR (60 MHz) δ: 1.07 (3H, d, *J*=6 Hz, Me), 1.6—2.2 (2H, m, 3-H), 2.65—2.9 (2H, m, 4-H), 3.13 (3H, br s, OH), 3.87 (1H, q, *J*=6 Hz, 1′-H), 4.07 (1H, dd, *J*=6, 4 Hz, 2-H), 6.95—7.85 (4H, m, ArH).

b) From **11a**: Osmium tetroxide (10 mg) was added to a stirred solution of **11a** (1.25 g, 7.18 mmol) and trimethylamine *N*-oxide dihydrate (1.60 g, 14.4 mmol) in *tert*-BuOH (15. ml) and water (4.3 ml). After being heated under reflux for 1 h, the mixture was cooled and treated with 20% $NaHSO_3$. The product (1.35 g) isolated by extraction with AcOEt was revealed by ^{1}H-NMR to be a *ca.* 95:5 mixture of **12a** and **12′a**, which was subjected to chromatography (silica gel, 100 g; solvent, hexane : AcOEt = 1:2) to remove by-products. Crystallization from CCl_4 afforded pure **12a** in 53% yield.

(1*R,2*R**)-1-[(*R**)-1-Hydroxyethyl]-5,8-dimethoxy-1,2,3,4-tetrahydro-1,2-naphthalenediol (12b)**——Catalytic osmylation of **11b** (1.34 g) according to the procedure described for **11a** except that the reaction was run at 50 °C for 8 h afforded **12b** (869 mg) after crystallization from AcOEt, mp 151—154 °C. An analytical sample was obtained by recrystallization from benzene, mp 156—157 °C. *Anal.* Calcd for $C_{14}H_{20}O_5$: C, 62.67; H, 7.51. Found: C, 62.88; H, 7.72. IR (KBr): 3380 cm^{-1}. ^{1}H-NMR (60 MHz) δ: 1.00 (3H, d, *J*=6 Hz, C–Me), 1.85—2.15 (2H, m, 3-H), 2.6—2.95 (2H, m, 4-H), 3.00 (1H, br s, OH), 3.30 (1H, br s, OH), 3.84 (3H, s, OMe), 3.91 (3H, s, OMe), 4.23 (1H, t, *J*=5 Hz, 2-H), 4.50 (1H, q, *J*=6 Hz, 1′-H), 5.08 (1H, br s, OH), 6.82 (2H, s, ArH). MS *m/e*: 268 (M^+), 223 (M^+ − MeCHOH), 207 (base peak).

(1*R,2*R**)-6-Bromo-1-[(*R**)-1-hydroxyethyl]-5,8-dimethoxy-1,2,3,4-tetrahydro-1,2-naphthalenediol (12c)**——Catalytic osmylation of **11c** (313 mg, 1 mmol) with OsO_4 (*ca.* 0.5 mg) and $Me_3N(O) \cdot 2H_2O$ (222 mg, 2 mmol) in *tert*-BuOH (3.5 ml) and water (1 ml) at 70 °C for 2 h afforded **12c** (270 mg, 78%) after chromatography (silica gel, 10 g; solvent, AcOEt), mp 125—127 °C. An analytical sample was obtained by recrystallization from hexane–$CHCl_3$ as colorless needles, mp 135 °C. *Anal.* Calcd for $C_{14}H_{19}BrO_5$: C, 48.43; H, 5.52. Found: C, 48.26; H, 5.36. IR (KBr): 3350 cm^{-1}. ^{1}H-NMR (200 MHz) δ: 1.00 (3H, d, *J*=6 Hz, C–Me), 2.00 (2H, m, 3-H), 2.75 (1H, dt, *J*=18, 6 Hz, 4-H), 3.01 (1H, dt, *J*=18, 7 Hz, 4-H), 3.10 (2H, br, OH), 3.78 (3H, s, OMe), 3.88 (3H, s, OMe), 4.23 (1H, dd, *J*=7, 6 Hz, 2-H), 4.54 (1H, q, *J*=6 Hz, 1′-H), 4.82 (1H, br, OH), 6.99 (1H, s, ArH). MS *m/e* (relative intensity): 301, 303 (M^+ − MeCHOH, 45), 283, 285 (100), 255, 257 (25), 176 (40).

(1*R,2*R**)-6-Cyano-1-[(*R**)-1-hydroxyethyl]-5,8-dimethoxy-1,2,3,4-tetrahydro-1,2-naphthalenediol (12d)**——Osmium tetroxide (1 mg) and water (1 ml) were added to a stirred solution of **11d** (311 mg, 1.2 mmol) and $Me_3N(O) \cdot 2H_2O$ (222 mg, 2 mmol) in *tert*-BuOH (2 ml), and the mixture was heated at 80 °C. After 3 h, when TLC (AcOEt) showed the presence of a very small amount of **11b** in the mixture, $Me_3N(O) \cdot 2H_2O$ (111 mg, 1 mmol), *tert*-BuOH (1 ml), water (0.5 ml) and OsO_4 (*ca.* 0.5 mg) were added and heating was continued for 1.5 h. Usual work-up of the reaction mixture afforded a brown oily mass (347 mg), essentially pure **12d** as judged by TLC and ^{1}H-NMR. This product subjected to chromatography (silica gel, 7 g; solvent, AcOEt : MeOH=95:5) to give a pale yellow solid (285 mg, 81%). An analytical sample was obtained by recrystallization from $CHCl_3$–CCl_4 as colorless needles, mp 155 °C. *Anal.* Calcd for $C_{15}H_{19}NO_5$: C, 61.42; H, 6.53; N, 4.78. Found: C, 61.03; H, 6.38; N, 4.74. IR (nujol): 3380, 2240 cm^{-1}. ^{1}H-NMR (200 MHz) δ: 1.04 (3H, d, *J*=6 Hz, C–Me), 2.02 (2H, m, 3-H), 2.70 (1H, br, OH), 2.75 (1H, dt, *J*=18, 7 Hz, 4-H), 2.92 (1H, dt, *J*=18, 7 Hz, 4-H), 3.27 (1H, br, OH), 3.94 (3H, s, OMe), 3.99 (3H, s, OMe), 4.24 (1H, t, *J*=5 Hz, 2-H), 4.50 (1H, q, *J*=6 Hz, 1′-H), 4.90 (1H, br, OH), 6.97 (1H, s, ArH). MS *m/e*: 293 (M^+), 248, 230, 202 (base peak).

(1*R,2*R**)-1-[(*R**)-1-Hydroxyethyl]-9,10-dimethoxy-1,2,3,4-tetrahydro-1,2-anthracenediol (20a)**——Osmium tetroxide (66 mg, 0.26 mmol) was added to a stirred solution of **19a** (60 mg, 0.21 mmol) in dry THF (3 ml) and pyridine (33 mg, 0.42 mmol), and the mixture was stirred at room temperature overnight. The reaction mixture was diluted with EtOH, and H_2S gas was bubbled through it for 15 min. The precipitate was removed by filtration and the filtrate was concentrated under reduced pressure. The residue was subjected to preparative TLC with AcOEt : hexane=2:1 to afford **20a** (33 mg, 49%), mp 140—141 °C. *Anal.* Calcd for $C_{18}H_{22}O_5$: C, 67.97; H, 6.97. Found: C, 67.70; H, 7.06. IR ($CHCl_3$): 3480 cm^{-1}. ^{1}H-NMR (200 MHz) δ: 0.99 (3H, d, *J*=6.5 Hz, C–Me), 1.85—2.05 (2H, m, 3-H), 2.62 (1H, br d, *J*=3.5 Hz, 1′-OH), 2.77 (1H, ddd, *J*=17.5, 8, 6.5 Hz, 4-H), 3.21 (1H, dt, *J*=17.5, 6.3 Hz, 4-H), 3.43 (1H, br d, *J*=1.5 Hz, 2-OH), 3.84 (3H, s, OMe), 4.03 (3H, s, OMe), 4.23 (1H, ddd, *J*=6, 4, 1.5 Hz, 2-H), 4.73 (1H, qd, *J*=6.5, 3.5 Hz, 1′-H), 4.84 (1H, s, 1-OH), 7.4—7.55 (2H, m, ArH), 8.0—8.1 (2H, m, ArH). MS *m/e*: 318 (M^+) 273, 255, 227, 199 (base peak).

(1*R,2*R**)-1-[(*R**)-1-Hydroxyethyl]-8,10-dimethoxy-1,2,3,4-tetrahydro-1,2-anthracenediol (20b)**——Catalytic osmylation of **19b** (480 mg) was carried out by the procedure described for **11a** except that the reaction was run at 60 °C for 2 h. The crude product, which was found by ^{1}H-NMR to be a 9:1 mixture of **20b** and its 1′-epimer (δ for C–Me: 1.02 and 1.16), was crystallized from AcOEt–hexane to give pure **20b** (100 mg). The mother liquor was subjected to chromatography (silica gel, 20 g; solvent, AcOEt : hexane=10:1), and the eluate provided a solid product (370 mg), which was recrystallized from AcOEt–hexane to give an additional amount of **20b** (167 mg). Further purification to remove a trace amount of colored material was done by recrystallization from EtOH: colorless needles, mp 156.5—157 °C. *Anal.* Calcd for $C_{18}H_{22}O_5$: C, 67.91; H, 6.96. Found: C, 67.64; H, 6.99. ^{1}H-NMR (200 MHz) δ: 1.02 (3H, d, J=6.5 Hz, C–Me), 1.85—2.1 (2H, m, 3-H), 2.77 (1H, ddd, J=17.5, 9.5, 6 Hz, 4-H), 3.10 (1H, br, OH), 3.21 (1H, dt, J=17.5, 5.5 Hz, 4-H), 3.71 (1H, br s, OH), 3.86 (3H, s, OMe), 3.95 (3H, s, OMe), 4.34 (1H, dd, J=9, 4 Hz, 2-H), 4.50 (1H, q, J=6.5 Hz, 1′-H), 6.74 (1H, d, J=8 Hz, 7-H), 7.37 (1H, t, J=8 Hz, 6-H), 7.60 (1H, d, J=8 Hz, 5-H), 8.21 (1H, s, 9-H).

(1*R,2*R**,4*S**,10*R**)-10-Methyl-1,2,3,4-tetrahydro-4,1-(epoxymethano)naphthalene-1,2-diol (13a)**——A solution of **12a** (104 mg, 0.5 mmol) in CCl_4 (30 ml) was maintained at 35 °C, and *N*-bromosuccinimide (NBS) (recrystallized from water and powdered, 116 mg, 0.65 mmol) was added. The suspension was stirred and heated to 50 °C with a sunlamp under constant bubbling with N_2 gas. After continued heating at 50 °C for 15 min, the reaction mixture was cooled with ice-water and filtered to remove precipitated succinimide, and the pale yellow filtrate was concentrated at room temperature under reduced pressure. The residual brown oil was subjected to chromatography (silica gel, 15 g; solvent, AcOEt) to give **13a** as a pale yellow solid (86.9 mg, 84%). An analytical sample was obtained by recrystallization from CCl_4, mp 161—162 °C. *Anal.* Calcd for $C_{12}H_{14}O_3$: C, 69.88; H, 6.84. Found: 69.57; H, 6.79. IR (KBr): 3340 cm^{-1}. ^{1}H-NMR (200 MHz) δ: 0.79 (3H, d, J=6 Hz, Me), 1.48 (1H, dt, J=14, 2 Hz, 3-H), 2.88 (1H, ddd, J=14, 8, 4 Hz, 3-H), 3.92 (1H, q, J=6 Hz, 10-H), 4.06 (1H, dd, J=8, 2 Hz, 2-H), 4.82 (1H, dd, J=4, 2 Hz, 4-H), 7.29 (1H, d, J=7 Hz, ArH), 7.61 (1H, d, J=7 Hz, ArH), 7.40 (1H, t, J=7 Hz, ArH), 7.49 (1H, t, J=7 Hz, ArH). MS *m/e*: 206.0965 (M$^+$, Calcd 206.0942), 162.0678 (M$^+$ − MeCHO, Calcd 162.0680, base peak).

(1*R,2*R**,4*S**,10*R**)-5,8-Dimethoxy-10-methyl-1,2,3,4-tetrahydro-4,1-(epoxymethano)naphthalene-1,2-diol (13b)**——*N*-Bromosuccinimide (72 mg, 0.4 mmol), cyclohexene oxide (84 mg, 0.86 mmol) and benzoyl peroxide (4 mg) were added to a stirred solution of **12b** (90 mg, 0.336 mmol) in dry CCl_4 (15 ml). The mixture was heated at 55 °C for 1 h, resulting in precipitation of succinimide and disappearance of **12b** of TLC with hexane : AcOEt = 1 : 5. The pale yellow mixture was cooled with ice-water and filtered. The filtrate was concentrated under reduced pressure to give a red-brown oil, which was vigorously stirred with water (30 ml) for 10 min to remove remaining succinimide and then extracted with $CHCl_3$. The extract was washed with 5% $Na_2S_2O_3$, dried, and concentrated. The residual oil was subjected to chromatography (silica gel, 35 g; solvent, CH_2Cl_2 : MeOH = 50 : 1) to give **13b** (74.5 mg, 83%) as colorless crystals. An analytical sample was obtained by recrystallization from benzene–hexane as colorless needles, mp 152—152.5 °C. *Anal.* Calcd for $C_{14}H_{18}O_5$: C, 63.14; H, 6.81. Found: C, 63.09; H, 6.75. IR (KBr): 3480 cm^{-1}. ^{1}H-NMR (200 MHz) δ: 0.88 (3H, d, J=6 Hz, C–Me), 1.47 (1H, dt, J=14, 2 Hz, 3-H), 2.53 (1H, br s, OH), 2.71 (1H, ddd, J=14, 9, 4 Hz, 3-H), 3.78 (1H, q, J=6 Hz, 10-H), 3.82 (3H, s, OMe), 3.92 (3H, s, OMe), 4.00 (1H, dd, J=9, 2 Hz, 2-H), 5.22 (1H, dd, J=4, 2 Hz, 4-H), 6.08 (1H, s, OH), 6.81 (1H, d, J=8 Hz, ArH), 6.92 (1H, d, J=8 Hz, ArH). MS *m/e*: 266 (M$^+$), 222 (M$^+$ − MeCHO, base peak).

(1*R,2*R**,4*S**,10*R**)-6-Bromo-5,8-dimethoxy-10-methyl-1,2,3,4-tetrahydro-4,1-(epoxymethano)naphthalene-1,2-diol (13c)**——NBS (210 mg, 1.18 mmol) and azobisisobutyronitrile (AIBN) (*ca.* 5 mg) were added at 40 °C to a stirred solution of **12c** (316 mg, 0.91 mmol) in CCl_4 (55 ml). After continued stirring at 40—42 °C for 10 min, the reaction mixture was cooled with ice-water and filtered. The filtrate was concentrated under reduced pressure, and the residual pale yellow oil was subjected to chromatography (silica gel, 25 g; solvent, AcOEt) to give, in order of elution, the bromide **14** (270 mg), a 2 : 3 mixture of **14** and **12c** (by ^{1}H-NMR) (72 mg), and **12c** (15 mg). Recrystallization of **14** from AcOEt–iso-Pr_2O afforded colorless needles, mp 124—125.5 °C (dec.). *Anal.* Calcd for $C_{14}H_{18}Br_2O_5$: C, 39.44; H, 4.23. Found: C, 39.71; H, 4.24. ^{1}H-NMR (200 MHz) δ: 1.07 (3H, d, J=6.5 Hz, C–Me), 2.05 (1H, ddd, J=14, 12, 4 Hz, 3-H), 2.40 (1H, dt, J=14, 4 Hz, 3-H), 3.08 (3H, br, OH), 3.87 (3H, s, OMe), 4.01 (3H, s, OMe), 4.91 (1H, dd, J=12, 4 Hz, 2-H), 5.16 (1H, q, J=6.5 Hz, 1′-H), 5.71 (1H, t, J=4 Hz, 4-H), 7.09 (1H, s, ArH).

A solution of **14** (42.6 mg, 0.1 mmol) in THF (5 ml) was treated with $AgClO_4$ (23 mg, 0.11 mmol) in THF (0.5 ml) at room temperature for 10 min. The reaction mixture was filtered to remove precipitated AgBr, and the filtrate was concentrated under reduced pressure to about half the initial volume, then diluted with AcOEt. The organic solution was washed with brine and 5% $NaHCO_3$, dried, and concentrated under reduced pressure to give a pale yellow oil (35.0 mg), essentially pure **13c** as judged by TLC with AcOEt and 200 MHz ^{1}H-NMR spectroscopy. Silica gel chromatography of the product to remove a trace amount of less polar impurities afforded pure **13c** as a colorless oil. ^{1}H-NMR (200 MHz) δ: 0.86 (3H, d, J=6.5 Hz, C–Me), 1.47 (1H, dt, J=14.5, 1.5 Hz, 3-H), 2.73 (1H, ddd, J=14.5, 9, 3.5 Hz, 3-H), 3.76 (1H, q, J=6.5 Hz, 10-H), 3.81 (3H, s, OMe), 3.91 (3H, s, OMe), 3.99 (1H, dd, J=9, 1.5 Hz, 2-H), 5.07 (1H, dd, J=3.5, 1.5 Hz, 4-H), 5.74 (1H, s, OH), 7.13 (1H, s, ArH). MS *m/e*: 346, 344 (M$^+$), 302, 300 (M$^+$ − MeCHO, base peak).

(1*R,2*R**,4*S**,10*R**)-6-Cyano-5,8-dimethoxy-10-methyl-1,2,3,4-tetrahydro-4,1-(epoxymethano)naphthalene-1,2-diol (13d)**——Methylketene methyl trimethylsilyl acetal[18] (720 mg, 4.5 mmol) was added to a stirred solution of **12d** (147 mg, 0.5 mmol) in dry CH_2Cl_2 under an Ar atmosphere, and the mixture was heated under reflux for 20 min. Removal of any volatiles from the reaction mixture under high vacuum afforded the *O*-trimethylsilylated product as an orange oil. It was dissolved in dry CCl_4 (30 ml), and NBS (115.7 mg, 0.65 mmol) and AIBN (5 mg) were added to the solution. The mixture was heated with a sunlamp (keeping the temperature at 60—65 °C) and N_2 gas was bubbled through it. After disappearance of **12d** on TLC with AcOEt (*ca.* 50 min), the reaction mixture was cooled with ice-water, and filtered. The filtrate was concentrated under reduced pressure. The residual oil was dissolved in THF (20 ml) and treated with HCl-saturated THF (0.5 ml) at room temperature for 30 min. The solvent was evaporated off under reduced pressure to give a red-brown oil, which was subjected to chromatography (silica gel, 30 g, previously deactivated with AcOEt : MeOH = 75 : 25) with AcOEt : hexane = 97 : 3, AcOEt, and AcOEt : MeOH = 95 : 5. The bromide **15** (178 mg, 96%) was obtained as a crystalline mass (homogeneous on TLC), which was recrystallized from AcOEt to give an analytical sample: colorless prisms, mp 142—143 °C. *Anal.* Calcd for $C_{15}H_{18}BrNO_5$: C, 48.38; H, 4.88; N, 3.76. Found: C, 48.22; H, 4.97; N, 3.63. IR (KBr): 3450, 2250 cm^{-1}. ^{1}H-NMR (200 MHz) δ: 1.05 (3H, d, J = 6 Hz, C–Me), 2.07 (1H, ddd, J = 14, 12, 4 Hz, 3-H), 2.42 (1H, dt, J = 14, 4 Hz, 3-H), 3.30 (3H, br s, OH), 3.90 (3H, s, OMe), 4.22 (3H, s, OMe), 4.91 (1H, dd, J = 12, 4 Hz, 2-H), 5.20 (1H, q, J = 6 Hz, 1′-H), 5.66 (1H, t, J = 4 Hz, 4-H), 7.06 (1H, s, ArH). MS *m/e*: 371, 373 (M^+), 309, 311, 247 (M^+ − HBr − MeCHO, base peak).

A solution of the bromide **15** (55.8 mg, 0.15 mmol) in dry THF (8 ml) was stirred at room temperature and treated with $AgClO_4$ (31.1 mg, 0.15 mmol) for 20 min. The reaction mixture was filtered, and the filtrate was concentrated under reduced pressure. The residue was subjected to chromatography (silica gel, 4 g, solvent, $CHCl_3$ and $CHCl_3$: AcOEt = 95 : 5) to give **13d** (41.9 mg, 96%) as a colorless solid. An analytical sample was obtained by recrystallization from $CHCl_3$–hexane: colorless needles, mp 163.5 °C. *Anal.* Calcd for $C_{15}H_{17}NO_5$: C, 61.85; H, 5.88; N, 4.81. Found: C, 61.75; H, 5.87; N, 4.84. IR (KBr): 3560, 3500, 2240 cm^{-1}. ^{1}H-NMR (200 MHz) δ: 0.86 (3H, d, J = 6 Hz, C–Me), 1.46 (1H, dt, J = 15, 2 Hz, 3-H), 2.60 (1H, d, J = 2 Hz, OH), 2.73 (1H, ddd, J = 15, 8, 4 Hz, 3-H), 3.77 (1H, q, J = 6 Hz, 10-H), 3.95 (3H, s, OMe), 4.01 (4H, overlapped OMe and 2-H), 5.10 (1H, dd, J = 4, 2 Hz, 4-H), 5.73 (1H, s, OH), 7.10 (1H, s, ArH). MS *m/e*: 291 (M^+), 247 (M^+ − MeCHO, base peak).

(1R*,2*R,4*S**,10*R**)-9,10-Dimethoxy-12-methyl-1,2,3,4-tetrahydro-4,1-(epoxymethano)anthracene-1,2-diol (21a)**——As described above for **12d**, **20a** (16 mg, 0.05 mmol) was subjected to *O*-trimethylsilylation with methylketene methyl trimethylsilyl acetal (144 mg, 0.9 mmol), and the resulting product was dissolved in CCl_4 (3 ml) and reacted with 1.2 eq NBS at 60 °C in the presence of AIBN for 20 min. After desilylation with HCl–THF, the reaction product was isolated by preparative TLC (multidevelopment with AcOEt and AcOEt–hexane mixtures) to give **21a** (10.5 mg, 66%), mp 212—212.5 °C. *Anal.* Calcd for $C_{18}H_{20}O_5$: C, 68.34; H, 6.37. Found: C, 68.40; H, 6.44. IR ($CHCl_3$): 3480 cm^{-1}, ^{1}H-NMR (200 MHz) δ: 0.87 (3H, d, J = 6 Hz, C–Me), 1.54 (1H, dt, J = 14, 3 Hz, 3-H), 2.44 (1H, d, J = 3 Hz, OH), 2.83 (1H, ddd, J = 14, 9, 4 Hz, 3-H), 3.86 (1H, q, J = 6 Hz, 12-H), 3.93 (3H, s, OMe), 4.05 (3H, s, OMe), 4.09 (1H, dt, J = 9, 3 Hz, 2-H), 5.22 (1H, dd, J = 4, 1 Hz, 4-H), 6.02 (1H, s, OH), 7.5—7.65 (2H, m, ArH), 8.0—8.25 (2H, m, ArH). MS *m/e*: 316 (M^+), 272 (M^+ − MeCHO, base peak).

(1*R,2*R**,4*S**,10*R**)-8,10-Dimethoxy-12-methyl-1,2,3,4-tetrahydro-4,1-(epoxymethano)anthracene-1,2-diol (21b)**——Reaction of **20b** (59 mg, 0.186 mmol) in CCl_4 (18 ml) with NBS (43 mg, 0.241 mmol) in the presence of cyclohexene oxide (47 mg, 0.482 mmol) and AIBN (2 mg) at 55 °C for 10 min afforded **21b** (47 mg, 80%) as a crystalline solid after chromatography (silica gel, 7 g; solvent, AcOEt : hexane = 5 : 1). An analytical sample was obtained by recrystallization from AcOEt–iso-Pr_2O as colorless needles, mp 192.5—193 °C. *Anal.* Calcd for $C_{18}H_{20}O_5$: C, 68.34; H, 6.37. Found: C, 68.58; H, 6.48. ^{1}H-NMR (200 MHz) δ: 0.78 (3H, d, J = 6.5 Hz, C–Me), 1.39 (1H, d, J = 8 Hz, OH), 1.50 (1H, dt, J = 14.5, 2 Hz, 3-H), 2.86 (1H, s, OH), 2.93 (1H, ddd, J = 14.5, 9, 4 Hz, 3-H), 3.95 (3H, s, OMe), 3.95 (1H, q, J = 6.5 Hz, 12-H), 4.00 (3H, s, OMe), 4.09 (1H, dd, J = 8, 2 Hz, 2-H), 5.27 (1H, dd, J = 4, 2 Hz, 4-H), 6.87 (1H, dd, J = 8, 1 Hz, ArH), 7.44 (1H, dd, J = 9, 8 Hz, ArH), 7.74 (1H, dt, J = 9, 1 Hz, ArH), 8.21 (1H, s, 9-H). MS *m/e*: 316 (M^+), 272 (M^+ − MeCHO, base peak).

Reaction of 16a with Vinylmagnesium Bromide (Formation of 22)——A solution of **16a** (128 mg, 0.5 mmol) in dry THF (2 ml) was cooled with ice-water and treated with 1 M $CH_2=CHMgBr$ in THF (0.55 ml) for 1 h. The crude reaction product obtained by usual work-up showed several spots on TLC. It was subjected to chromatography (silica gel, 7 g; solvent, AcOEt : hexane = 1 : 6) and then preparative TLC with Et_2O : iso-Pr_2O : hexane : benzene = 1 : 1 : 2 : 10 to isolate the following two compounds in addition to the starting material (5 mg). **22** (26 mg): mp 99.5 °C after recrystallization from $CHCl_3$–hexane. *Anal.* Calcd for $C_{17}H_{16}O_2$: C, 80.95; H, 6.35. Found: C, 81.13; H, 6.41. IR (neat): 1675 cm^{-1}. ^{1}H-NMR (60 MHz) δ: 1.83—2.33 (2H, m, CH_2), 2.70 (2H, t, J = 6 Hz, CH_2), 3.12 (2H, t, J = 6 Hz, CH_2), 3.92 (3H, s, OMe), 5.13 (1H, dd, J = 18, 2 Hz vinyl H), 5.67 (1H, dd, J = 12, 2 Hz, vinyl H), 7.37 (1H, dd, J = 18, 12 Hz, vinyl H), 7.2—7.7 (2H, m, ArH), 7.95—8.55 (2H, m, ArH). MS *m/e*: 252 (M^+), 251 (base peak), 250, 236. 9,10-Dimethoxy-1-vinyl-1,2,3,4-tetrahydro-1-anthracenol (15 mg): a pale yellow oil. ^{1}H-NMR (60 MHz) δ: 3.87 (3H, s, OMe), 3.95 (3H, s, OMe), 4.90 (1H, dd, J = 17, 2 Hz, vinyl H), 5.13 (1H, dd, J = 11, 2 Hz, vinyl H), 5.22 (1H, s, OH), 6.30 (1H, dd, J = 17, 11 Hz, vinyl H).

Attempted Dehydration of 18a with Trifluoroacetic Acid (Formation of 23)——A solution of **18a** (25 mg) in CH_2Cl_2 (2 ml) was treated with F_3CCOOH (0.04 ml) at 0 °C for 2 h and then at room temperature for 2 h. The crude product (17 mg) obtained by usual work-up was subjected to preparative TLC with AcOEt : hexane = 1 : 12 to give **23** (9 mg) as a crystalline mass. ^{1}H-NMR (200 MHz) δ: 2.04 (2H, t, J = 6 Hz, CH_2), 2.48 (3H, s, C–Me), 2.74 (2H, t, J = 6 Hz, CH_2), 3.02 (2H, t, J = 6 Hz, CH_2), 3.96 (3H, s, OMe), 7.44 (1H, t, J = 8 Hz, ArH), 7.53 (1H, t, J = 8 Hz, ArH), 8.15 (1H, d, J = 8 Hz, ArH), 8.20 (1H, d, J = 8 Hz, ArH). MS *m/e*: 252 (M^+, base peak), 237, 43.

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