Synthesis of Higher Oxidized Metabolites of Dibenz[*a,j*]anthracene Implicated in the Mechanism of Carcinogenesis

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Higher oxidized metabolites are implicated as active carcinogenic forms of polycyclic aromatic hydrocarbons which have two or more bay or fjord molecular regions, such as dibenz[*a,j*]anthracene. These include the bis(dihydrodiols) and phenolic dihydrodiols which may potentially undergo further metabolism to the corresponding diol epoxides. The latter react with DNA resulting in mutations that lead to tumorigenesis. Prior characterization of these metabolites has been based largely on HPLC and spectroscopic evidence. This paper reports efficient syntheses of the *trans-trans*-3,4,8,9-dihydrodiol (**1**) and the 10- and 11-phenolic *trans*-3,4-dihydrodiols of dibenz[*a,j*]anthracene (**3a**,**b**). The synthetic route to **1** entails as the key steps asymmetric dihydroxylation of an appropriately substituted stilbene precursor employing a Sharpless catalyst followed by intramolecular cyclodehydrobromination catalyzed by $Pd(PPh_3)_2Cl_2$. The syntheses of **3a**,**b** proceed via sequences involving a Wittig reaction of anisaldehyde with a phosphonium salt of 2-chloro-3-methylbenzyl bromide to give a stilbene compound and then photocyclization, conversion of the product to a phosphonium salt, a second Wittig reaction and photocyclization, reductive dechlorination, and conversion of the resulting trimethoxydibenz[*a,j*]anthracenes to the phenolic dihydrodiols. A key feature of these syntheses is the effective use of chloro substituents to block photocyclization in an undesired direction. These methods are potentially applicable to the synthesis of analogous higher oxidized metabolites of other polycyclic aromatic carcinogens.

The established mechanism of carcinogenesis of polycyclic aromatic hydrocarbons (PAHs) entails activation by P-450 microsomal enzymes to form reactive diol epoxide metabolites[1,2] that combine covalently with DNA. These result in mutations that lead ultimately to tumor induction.[2,3] However, there is substantial evidence, reviewed in the preceding paper, that more polar PAH metabolites, such as bis(dihydrodiols), may also contribute to the carcinogenicity of dibenz[*a,j*]anthracene and other PAHs that possess two or more sterically crowded bay or fjord regions in the molecule. In most of these cases the structural assignments of the higher oxidized metabolites (bis(dihydrodiols), bis(diol) epoxides, and phenolic dihydrodiol and diol epoxides have been based largely on spectroscopic evidence due to their relative inaccessibility through synthesis.

To obtain more definitive evidence concerning the importance of this alternative mechanistic path relative to the better established diol epoxide pathway for PAHs with more than a single bay region, we undertook to develop convenient synthetic approaches to the higher oxidized metabolites of this class of PAHs. The synthetic compounds are urgently required as authentic standards for studies to confirm their formation metabolically as well as to determine their mutagenic and carcinogenic activities and their DNA binding properties in mammalian cells. The oxidized metabolites of dibenz[*a,j*]-anthracene were selected as specific synthetic targets because previous metabolism studies in primary cultures of mouse keratinocytes revealed the formation of substantial number of metabolites more polar than the 3,4- and 5,6-dihydrodiols of dibenz[*a,j*]anthracene.[4] The ratio of polar metabolites increased with time, and it was proposed that they were mainly the 3,4,8,9- and 3,4,10,-11-bis(dihydrodiols) (**1** and **2**)[5] plus lesser amounts of phenolic dihydrodiols, such as the 10- and 11-hydroxy-3,4-dihydrodiols (**3a**,**b**).

We now report the syntheses of the unsymmetrical 3,4,8,9-bis(dihydrodiol) **1** and the 10- and 11-phenolic *trans*-3,4- dihydrodiols (**3a**,**b**) of dibenz[*a,j*]anthracene. The stereochemistry of the dihydrodiol functions in all these compounds is trans, since it is well established that metabolism of PAHs by mammalian enzymes furnishes exclusively trans stereoisomers.[2,3] The preceding paper reported the syntheses of the terminal ring symmetrical 3,4,10,11-bis(dihydrodiol) of dibenz[*a,j*]anthracene (**2**) along with several additional suspected more highly oxidized metabolites of this hydrocarbon.[5]

Results

Synthesis of *trans*-3,4-*trans*-8,9-Tetrahydroxy-3,4,8,9-tetrahydrodibenz[*a,j*]anthracene (1). Sev-

(1) The active diol epoxide metabolites of carcinogenic PAHs contain the epoxide ring in a sterically crowded bay or fjord region which favors their resistance to epoxide hydrase and other detoxifying enzymes.[2]

(2) Harvey, R. G. *Polycyclic Aromatic Hydrocarbons: Chemistry and Carcinogenesis*; Cambridge University Press: Cambridge, England, 1991.

(3) Harvey, R. G.; Geacintov, N. E. *Acc. Chem. Res.* **1988**, *21*, 66. Harvey, R. G. *Polycyclic Hydrocarbons and Carcinogenesis*; ACS Symposium Series Monograph 283; American Chemical Society: Washington, DC, 1985. Dipple, A.; Moschel, R. C.; Bigger, C. A. H. In *Chemical Carcinogens*, 2nd ed., Searle, C. E., Ed.; ACS Monograph No. 182; American Chemical Society: Washington, DC, 1984; pp 63−84. Conney, A. H. *Cancer Res.* **1982**, *42*, 4875.

(4) Nair, R. V.; Nettikumara, A. N.; Cortez, C.; Harvey, R. G.; DiGiovanni, J. *Chem. Res. Toxicol.* **1992**, *5*, 532.

(5) Harvey, R. G.; Dai, W.; Zhang, J.-T.; Cortez, C. *J. Org. Chem.* **1998**, *63*, 8118.

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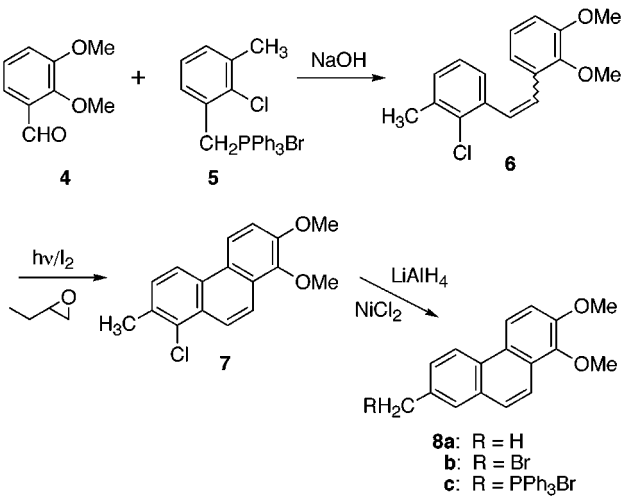
Scheme 1



eral potential synthetic routes to the unsymmetrical 3,4,8,9-bis(dihydrodiol) of dibenz[*a*,*j*]anthracene (**1**) were explored and abandoned prior to discovery of a satisfactory synthetic method. The successful approach entailed in the key steps asymmetric dihydroxylation of an appropriately substituted stilbene precursor (**9**) in the presence of a Sharpless catalyst[6] followed by intramolecular cyclodehydrobromination of the product catalyzed by $Pd(PPh_3)_2Cl_2$ (Scheme 2).[7,8]

The starting compound for this sequence was the phenanthrene derivative **8c**. It was itself synthesized via a sequence based on Wittig reaction of 2,3-dimethoxybenzaldehyde (**4**) with the phosphonium salt derivative of 2-chloro-3-methylbenzyl bromide (**5**) (Scheme 1). Phosphonium salt **5** was prepared from 2-chloro-*m*-xylene by bromination with 1 equiv of NBS and a peroxide catalyst to yield 2-chloro-3-methylbenzyl bromide followed by reaction of the latter with triphenylphosphine. Wittig reaction of **4** with **5** furnished the expected olefin (**6**) shown by the complexity of its ^{1}H NMR spectrum to be a mixture of *E*- and *Z*-isomers in approximately 1:5 ratio. The isomers were tentatively assigned on the basis of the relatively larger coupling constant exhibited by the olefinic protons of the minor *E*-isomer (δ 7.40, J = 16 Hz) versus the major *Z*-isomer (δ 6.89, J = 12 Hz). Photocyclodehydrogenation of the resulting stilbene derivative **6** took place smoothly in the presence of I_2 and epoxybutane[9] without significant displacement of chlorine to furnish 1-chloro-7,8-dimethoxy-2-methylphenanthrene (**7**) as the principal product. The chloro substituent served effectively to block the possible competing cyclization to its position. Subsequent removal of the chlorine atom was achieved by reduction with $LiAlH_4$ and $NiCl_2$ by the method of Ashby and Lin.[10] This reaction took place smoothly at room temperature in anhydrous THF to furnish 2,3-dimethoxy-7-methylphenanthrene (**8a**) in 94% yield. The ^{1}H NMR spectrum of **8a** was fully consistent with this assignment. Bromination of **8a** with *N*-bromosuccinimide in the presence of benzoyl peroxide in refluxing CCl_4 gave 2-bromomethyl-7,8-dimethoxyphenanthrene (**8b**) which in turn underwent reaction with PPh_3 to provide the corresponding phosphonium salt **8c**.

The latter salt was the starting compound for the synthesis of the key compounds **9** and **10** (Scheme 2). Wittig reaction of **8c** with 2-bromobenzaldehyde provided the expected olefin (**9**) shown by its ^{1}H NMR spectrum to be a mixture of *E*- and *Z*-isomers. This mixture was converted to the *E*-isomer by heating with a crystal of iodine for 1 day in refluxing heptane. Osmium tetraoxide-catalyzed asymmetric dihydroxylation of **9** in the presence of the catalyst $(DHQD)_2PHAL$ and methanesulfonamide (the Sharpless AD-mix-β reagent[6]) by the procedure employed previously for an analogous stilbene derivative[8] afforded stereospecifically the *cis*-dihydroxylated product (**10a**). The dihydrodiol **10a** was converted into its diacetate (**10b**) by stirring overnight with Ac_2O in pyridine in the presence of *p*-(*N*,*N*-dimethylamino)pyridine (DMAP). Intramolecular cyclodehydrobromination of **10b** catalyzed by $Pd(PPh_3)_2Cl_2$ in dimethylacetamide[7,8] provided *trans*-8,9-diacetoxy-8,9-dihydro-3,4-dimethoxydibenz[*a*,*j*]anthracene (**11a**). Analysis of the ^{1}H NMR spectrum of **11a** confirmed its structural assignment.

It was envisioned that compound **11a** might be converted to the 3,4,8,9-bis(dihydrodiol) of dibenz[*a*,*j*]anthracene (**1**) via demethylation and reduction with $NaBH_4/O_2$.[11,12] However, attempts to remove selectively the protective methyl groups of **11a** with BBr_3 or other reagents failed due to competing secondary reactions, principally elimination of acetic acid from the 8,9-positions. Conversion of **11a** to **1** was accomplished via an alternative synthetic route involving deacetylation with NaOMe in MeOH−THF to generate 3,4-dimethoxy-*trans*-8,9-dihydroxy-8,9-dihydrodibenz[*a*,*j*]anthracene (**11b**), oxidation with DDQ in moist THF to the quinone (**12a**), demethylation with BBr_3 to the A-ring hydroquinone (**12b**), and then reduction with $NaBH_4/O_2$ to the 3,4,8,9-bis(dihydrodiol) **1** in good overall yield.[11−13] Reductions of the hydroquinone and quinone functions both took place with trans-stereospecificity in accord with previous findings for reductions of this type.[12−14] The NMR spectrum of **12b** was consistent with its structural assignment. However, **12b** darkened in air, and in view of the well-known sensitivity of PAH hydroquinones to autoxidation, no attempts were made to characterize it further.

Synthesis of *trans*-3,4-Dihydroxy-3,4-dihydro-10-hydroxydibenz[*a*,*j*]anthracene (3a). The synthetic route to the 10-phenol derivative of the dibenz[*a*,*j*]-anthracene *trans*-3,4-dihydrodiol (**3a**) involved two separate photocyclization steps (Scheme 3). Wittig reaction of *o*-anisaldehyde with the phosphonium salt derivative **5** of 2-chloro-3-methylbenzyl bromide gave the expected stilbene derivative (**13**) shown by its ^{1}H NMR spectrum to be a mixture of *E*- and *Z*-isomers in approximately 1:5

(6) Sharpless, K. B.; Amberg, W.; Bennani, Y. L.; Crispino, G. A.; Hartung, J.; Jeong, K.-S.; Kwong, H.-L.; Morikawa, K.; Wang, Z.-M.; Xu, D.; Zhang, X.-L. *J. Org. Chem.* **1992**, *57*, 2768 and references cited therein.

(7) (a) Deshpande, P. P.; Martin, O. R.; *Tetrahedron Lett.* **1990**, *31*, 6313. (b) Ames, D. E.; Opalko, A. *Tetrahedron* **1984**, *40*, 1919. (c) Bringmann, G.; Keller, P. A.; Rölfing, K. *Synlett* **1994**, 423.

(8) Tang, X.-Q.; Harvey, R. G. *Tetrahedron Lett.* **1995**, *36*, 6037.

(9) Epoxybutane serves to prevent competing reactions by scavenging the HI produced: Liu, L.; Yang, B.; Katz, T. J.; Poindexter, M. K. *J. Org. Chem.* **1991**, *56*, 3769.

(10) Ashby, E. C.; Lin, J. J. *J. Org. Chem.* **1978**, *43*, 1263.

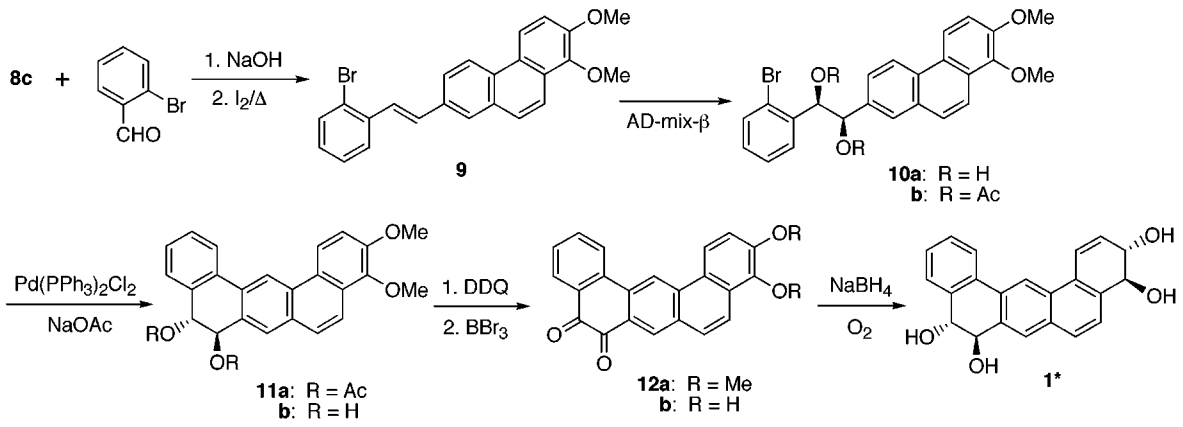
(11) Dai, W.; Abu-Shqara, E.; Harvey, R. G. *J. Org. Chem.* **1995**, *60*, 4905. Platt, K.; Oesch, F. *Synthesis* **1982**, 459.

(12) Reference 2, chapter 13, pp 306−329.

(13) In reductions of this type, O_2 serves to oxidize hydroquinones to quinones which undergo reduction with the hydride reagent to dihydrodiols plus variable amounts of hydroquinones which are then recycled.

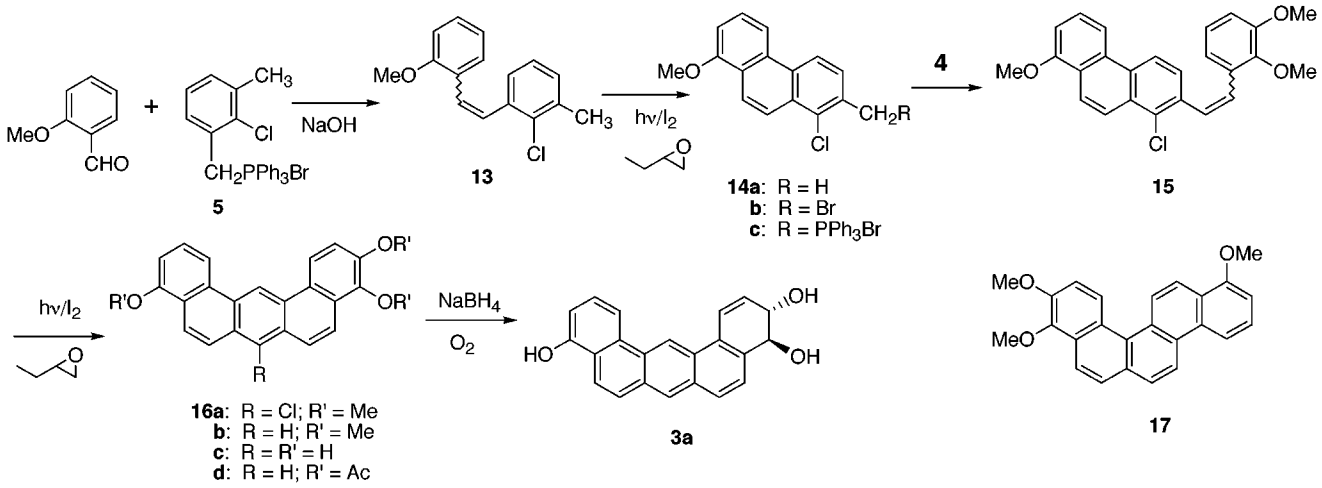
(14) Harvey, R. G.; Goh, S. H.; Cortez, C. *J. Am. Chem. Soc.* **1975**, *97*, 3468.

Scheme 2[a]



[a] Asterisk indicates mixtures of bis(*trans*) isomers.

Scheme 3



ratio. The isomeric assignments were tentatively based on the larger coupling constant of the olefinic protons of the minor *E*-isomer (δ 7.44, $J = 16$ Hz) relative to that of the major *Z*-isomer (δ 6.77, $J = 12$ Hz). Separation of the isomers was unnecessary, since interconversion of *E*- and *Z*-isomers is known to take place readily during photocyclization.[15] Oxidative photoreaction of **13** in the presence of I_2 and epoxybutane[9] gave 1-chloro-8-methoxy-2-methylphenanthrene (**14a**) as the major product. As in the synthesis of **1**, the chloro group effectively blocked the alternate mode of cyclization.

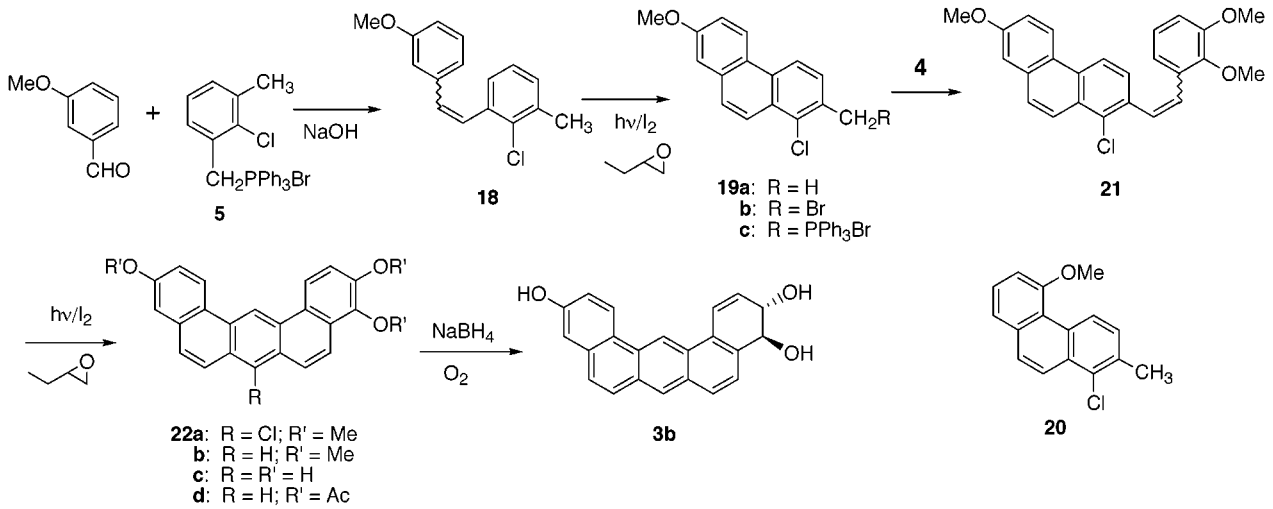
The next stage in this synthesis entailed conversion of the phenanthrene derivative **14a** to the phosphonium salt **14c**. Bromination of **14a** with NBS in the presence of benzoyl peroxide gave 2-bromomethyl-1-chloro-8-methoxyphenanthrene (**14b**) which in turn underwent reaction with triphenylphosphine to furnish **14c**. Wittig reaction of **14c** with 2,3-dimethoxybenzaldehyde (**4**) provided the expected olefin (**15**). In this case, the Z-isomer was strongly predominant, only traces of the *E*-isomer being detectable. Photocyclization of **15** in the presence of I_2 and epoxybutane took place with partial displacement of the choro protecting group to furnish 7-chloro-3,4,10-trimethoxydibenz[*a,j*]anthracene (**16a**) (42% based on conversion of **15**) and 1,9,10-trimethoxybenzo[*c*]chrysene (**17**) (35%) as the principal products. The ^{1}H NMR spectrum of the former ressembled that of 7-chloro-3,4,11-trimethoxydibenz[*a,j*]anthracene,[5] exhibiting a characteristic singlet at low field (δ 9.77) which is assigned to the sterically crowded meso region H_{12} proton. The ^{1}H NMR spectrum of **17** ressembled that of the closely related 1,2,9,10-tetramethoxybenzo[*c*]chrysene whose synthesis was described in the preceding paper,[5] exhibiting characteristic low-field doublets at δ 8.98 and 8.82 assigned to the H_{12} and H_{13} protons, respectively, in the sterically crowded fjord region of the benzo[*c*]chrysene ring system.

Dechlorination of **16a** by treatment with $LiAlH_4$ and $NiCl_2$ took place smoothly at room temperature in anhydrous THF to furnish 3,4,10-trimethoxydibenz[*a,j*]-anthracene (**16b**). The ^{1}H NMR spectrum of **16b** exhibited two singlets in the aromatic region at δ 8.25 and 9.79 assigned to the H_7 and H_{14} meso region protons, respectively, as well as other proton resonances consistent with structural assignment as a dibenz[*a,j*]anthracene derivative.

Conversion of trimethoxydibenz[*a,j*]anthracene (**16b**) to *trans*-3,4-dihydroxy-3,4-dihydro-10-hydroxydibenz[*a,j*]-anthracene (**3a**) was accomplished via initial demethylation with BBr_3 to 3,4,10-trihydroxydibenz[*a,j*]anthracene (**16c**). In view of the air sensitivity of **16c**, it was isolated and characterized as its triacetate (**16d**). Reduction of **16d** with $NaBH_4$ and O_2 bubbling through the solution took place smoothly with concurrent deacetylation to

(15) Mallory, F. B.; Mallory, C. W. *Org. React.* **1984**, *30*, 1.

Scheme 4



provide the target phenolic *trans*-dihydrodiol **3a** stereospecifically.[11]

Synthesis of *trans*-3,4-Dihydroxy-3,4-dihydro-11-hydroxydibenz[*a,j*]anthracene (3b). Synthesis of the 11-phenol derivative of the *trans*-3,4-dihydrodiol of dibenz[*a,j*]anthracene (**3b**) was accomplished by a modification of the route employed for the synthesis of the 10-phenol derivative (**3a**) (Scheme 4).

Wittig reaction of 3-methoxybenzaldehyde with the phosphonium salt **5** in the presence of NaOH and a catalytic amount of 18-crown-6 afforded a stilbene derivative (**18**) shown by its ^{1}H NMR spectrum to be a mixture of *E*- and *Z*-isomers in approximately 1:5 ratio. Photocyclization of **18** under the conditions employed for similar photoreactions took place with only minimal displacement of chlorine to furnish the 1-chloro-7-methoxy-2-methylphenanthrene isomer (**19a**) arising from cyclization to the position para to the methoxy group of **18**. This structural assignment was supported by its ^{1}H NMR spectrum which exhibited a characteristic singlet peak at δ 7.19 for the aromatic proton adjacent to the methoxy group along with other appropriate resonances. The alternative isomer, 1-chloro-5-methoxy-2-methylphenanthrene (**20**), anticipated to be formed by cyclization at the position ortho to the methoxy group of **18**, was not detected. Bromination of **19a** with NBS and benzoyl peroxide gave 2-bromomethyl-1-chloro-7-methoxyphenanthrene (**19b**) which reacted with triphenylphosphine to furnish the phosphonium salt **19c**.

Wittig reaction of **19c** with 2,3-dimethoxybenzaldehyde (**4**) provided the expected stilbene (**21**) mainly as the *Z*-isomer. Photoreaction of **21** under the conditions employed for previous examples afforded 7-chloro-3,4,-11-trimethoxydibenz[*a,j*]anthracene (**22a**) as the principal product. Dechlorination of **22a** by treatment with $LiAlH_4$ and $NiCl_2$ furnished 3,4,11-trimethoxydibenz[*a,j*]-anthracene (**22b**). The ^{1}H NMR spectrum of **22b** was consistent with structural assignment as a dibenz[*a,j*]-anthracene derivative, exhibiting characteristic singlets in the aromatic region at δ 8.30 and 9.78 for the H_7 and H_{14} meso region protons, respectively, and other characteristic proton resonances.

The conversion of 3,4,11-trimethoxydibenz[*a,j*]anthracene (**22b**) to *trans*-3,4-dihydroxy-3,4-dihydro-10-hydroxydibenz[*a,j*]anthracene (**3b**) was accomplished via an initial demethylation with BBr_3 to 3,4,10-trihydroxydibenz[*a,j*]anthracene (**22c**). In view of its air sensitivity, **22c** was isolated and characterized as its triacetate (**22d**). Reduction of **22d** with $NaBH_4$ and O_2 bubbling through the solution took place smoothly and trans-stereospecifically[12] with concurrent deacetylation to provide the target phenolic dihydrodiol **3b**.

Discussion

Although there is a substantial evidence that diol epoxide metabolites are the principal active forms of most carcinogenic alternant PAHs,[2,3] recent studies on the metabolic activation of PAHs with more than one bay or fjord molecular region, such as dibenz[*a,j*]anthracene, suggest that bis(dihydrodiols) and the corresponding mono- or diepoxides, and possibly also phenolic dihydrodiols and diol epoxides, may also play a role in carcinogenicity.[4,5] In this paper we report efficient syntheses of the unsymmetrical bis-3,4,8,9-dihydrodiol (**1**) and the 10- and 11-phenolic *trans*-3,4-dihydrodiols dibenz[*a,j*]-anthracene (**3a**,**b**). The accompanying paper describes syntheses of the symmetrical 3,4,10,11-bis(dihydrodiol) (**2**) and several higher oxidized derivatives of dibenz[*a,j*]-anthracene. The synthesis of these compounds completes the preparation of all of the higher oxidized metabolites of dibenz[*a,j*]anthracene suspected of playing a role in the carcinogenicity of this PAH.

Although the synthesis of **1** from precursors **4** and **5** requires 13 steps, good yields are obtained in all but one step, and the overall yield of **1** is a respectable 17%. The lowest yield step is palladium-catalyzed cyclization of **10b** which provides **11a** in 60% yield. The alternative benzo[*c*]chrysene structure which could arise by reaction at the alternative ring position is not formed. The assignment of structure **11a** was unequivocally supported by its ^{1}H NMR spectrum which exhibited characteristic singlets in the aromatic region at δ 7.97 and 9.04 for the H_7 and H_{14} meso region protons. Other proton resonances were also consistent with the dibenz[*a,j*]anthracene structure. The preference for the formation of the dibenz[*a,j*]anthracene ring system is likely to be, at least partially, a consequence of greater steric hindrance in the more crowded fjord region of the benzo[*c*]chrysene structure.[15,16]

(16) Harvey, R. G. *Polycyclic Aromatic Hydrocarbons*; Wiley-VCH: New York, 1997.

It is notable that the photochemical cyclizations of all of the chloro-substituted compounds, except **15**, exhibit strong preference for reaction at the unsubstituted site rather than the chloro-substituted position. The preceding paper contains an additional example of the use of a chloro substituent to direct cyclization to a desired site.[5] The effectiveness of choro substituents for this purpose is surprising in view of previous observations that indicate that chloro substituents undergo relatively facile displacement in these types of photocyclizations.[15] This difference may partially derive from differences in the structures and electronic properties of the polycyclic aromatic ring systems employed.

As a consequence of the mode of synthesis, all the dihydrodiol derivatives of dibenz[*a*,*j*]anthracene whose syntheses are reported herein (**1**, **3a**,**b**) are racemic. It is likely, on the basis of precedent,[8] that the asymmetry of the two chiral centers of **10b** were preserved during cyclization to **11**. However, attempts to convert **11** directly to the 3,4,8,9-bis(dihydrodiol) (**1**) via demethylation with BBr_3 were not successful. Thus, it was necessary to explore an alternative approach which unfortunately led to loss of asymmetry. This method entails oxidation to the quinone (**12a**). It should be pointed out that the use of racemic mixtures is not disadvantageous in preliminary biological studies, since it is convenient to assay the mixture of isomers for activity prior to attempting their time-consuming separation. If significant biological activity is found, the isomers may be resolved by methods devised earlier for separation of other PAH dihydrodiol isomers, such as resolution on a chiral column.[12] They can then be tested individually for activity.

The 3,4,8,9-bis(dihydrodiol) **1** and the 10- and 11-phenolic derivatives of dibenz[*a*,*j*]anthracene (**3a**,**b**) have been submitted for metabolism, mutagenicity, and for other biological studies to elucidate the possible role of these higher oxidized metabolites in the mechanism of carcinogenesis of dibenz[*a*,*j*]anthracene.

Experimental Section

Materials and Methods. *m*-Chloroperbenzoic acid (Aldrich) was purified by washing with pH 7.4 phosphate buffer and drying under reduced pressure. THF was freshly distilled from sodium benzophenone ketyl. 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) was purified by recrystallization from benzene. *N*-Bromosuccinimide (NBS) was recrystallized from water. The ^{1}H NMR spectra were recorded on 300 or 500 MHz spectrometers in $CDCl_3$ with tetramethylsilane as internal standard unless stated otherwise. Integration was consistent with all the molecular structural assignments. The ^{13}C NMR spectra were recorded on a 125 MHz spectrometer in THF-d_8. Mass spectra (MS) and HRMS were performed by University of Illinois at Urbana-Champaign School of Chemical Sciences. TLC was carried out on silica gel sheets with fluorescence indicator.

Caution! Dibenz[*a*,*j*]anthracene is a weak carcinogen in animal assays. It and its dihydrodiol and diol epoxide metabolites and their higher oxidized derivatives are potentially hazardous and should be handled with care in accordance with "NIH Guidlines for the Laboratory Use of Chemical Carcinogens".

2-Chloro-3-methylbenzyl Bromide. A solution of 2-chloro-*m*-xylene (20.0 g, 142 mmol), NBS (25.6 g, 144 mmol), and benzyol peroxide (0.58 g, 2.39 mmol) in 300 mL of CCl_4 was heated at reflux for 6 h. The reaction mixture was cooled to room temperature, and filtered, and the CCl_4 was removed under reduced pressure. Distillation of the product gave 2-chloro-3-methylbenzyl bromide (24.6 g, 84%) as a colorless liquid, bp 78−80 °C/0.6 mmHg (lit.[17] 75−79 °C/0.2 mmHg): ^{1}H NMR δ 7.28 (d, J = 7.5 Hz, 1H), 7.20 (d, J = 7.5 Hz, 1H), 7.14 (t, J = 7.5, 7.0 Hz, 1H), 4.62 (s, 2H), 2.40 (s, 3H).

(2-Chloro-3-methylbenzyl)triphenylphosphonium Bromide (5). A solution of 2-chloro-3-methylbenzyl bromide (18.10 g, 82.5 mmol) and PPh_3 (21.60 g, 82.5 mmol) in 200 mL of toluene was heated at reflux for 6 h. The usual workup afforded **5** (37.17 g, 94%) as a white solid, mp 250−252 °C (recrystallized from CH_2Cl_2−EtOAc): ^{1}H NMR δ 7.71−7.61 (m,15H), 7.39 (d, J = 7.5 Hz, 1H), 7.16 (d, J = 7.0 Hz, 1H), 7.03 (t, J = 7.0, 7.5 Hz, 1H), 5.57 (d, J = 13.5 Hz, 2H), 2.15 (s, 3H); MS (FAB) m/e 481 (M^+ + 1, 30); 401 (M^+ − Br, 100) (based on Br, 79, Cl, 35, and P, 31). Anal. Calcd for $C_{26}H_{23}$-BrClP: C, 64.82; H, 4.81; Br, 16.59; Cl, 7.36. Found: C, 64.91; H, 4.85; Br, 16.51; Cl, 7.33.

1-Chloro-2-methyl-1′,2′-dimethoxystilbene (6). 1,2-Dimethoxybenzaldehyde (2.68 g, 16.13 mmol), (2-chloro-3-methylbenzyl)triphenylphosphonium bromide (8.08 g, 16.77 mmol), and a catalytic amount of 18-crown-6 were dissolved in 350 mL of CH_2Cl_2, and 40 mL of 50% NaOH aqueous solution was added. The reaction mixture was stirred for 5 h until TLC indicated the absence of the starting aldehyde. The usual workup and chromatography on a column of silica gel eluted with hexane/EtOAc (98:2) afforded a mixture of *Z*- and *E*-isomers of **6** (*Z*:*E* = 5 from NMR; *Z*-isomer, δ 6.89, J = 12 Hz; *E*-isomer, δ 7.40, J = 16 Hz) as white solid, (4.42 g, 95%). This mixture of olefins was used for photocyclization. *Z*-isomer, mp 60−61 °C (EtOAc−hexane): ^{1}H NMR δ 7.09 (d, J = 7.3 Hz, 1H), 6.99 (d, J = 6.9 Hz, 1H), 6.91 (d, J = 7.6 Hz, 1H), 6.89 (d, J = 12 Hz, 1H), 6.79 (d, J = 12 Hz, 1H), 6.76−6.75 (m, 2H), 6.58 (m, 1H), 3.87 (s, 3H), 3.86 (s, 3H), 2.41 (s, 3H). Anal. Calcd for $C_{17}H_{17}ClO_2$: C, 70.71; H, 5.93; Cl, 12.28. Found: C, 70.69; H, 5.90; Cl, 12.19.

1-Chloro-7,8-dimethoxy-2-methyl-phenanthrene (7). Argon was bubbled through a stirred solution of **6** (1.0 g, 3.46 mmol) and I_2 (1.30 g, 5.12 mmol) in 700 mL of Et_2O−cyclohexane (1:1) for 30 min before 10 mL of 1,2-epoxybutane was added. The solution was irradiated by UV light generated from Hanovia 400-W medium-pressure lamp with a Vycor filter, and the argon flow was maintained throughout the procedure. After 2 h, NMR analysis showed the absence of the starting material. Solvent was evaporated and CH_2Cl_2 was added. The organic layer was washed with an aqueous solution of NaS_2O_3 and brine and dried over Na_2SO_4. Purification of the crude product by chromatography on a silica gel column eluted with hexanes−EtOAc (96:4) afforded **7** (0.90 g, 91%) as a white solid, mp 145.5−146.5 °C (EtOAc−hexane): ^{1}H NMR δ 8.39 (d, J = 8.0 Hz, 1H), 8.35 (d, J = 8.5 Hz, 1H), 8.25 (d, J = 9.5 Hz, 1H), 8.16 (d, J = 9.5 Hz, 1H), 7.47 (t, J = 8.0 Hz, 1H), 7.36 (d, J = 8.5 Hz, 1H), 4.05 (s, 6H), 2.64 (s, 3H). Anal. Calcd for $C_{17}H_{15}ClO_2$: C, 71.21; H, 5.27; Cl, 12.36. Found: C, 71.30; H, 5.29; Cl, 12.27.

2,3-Dimethoxy-7-methylphenanthrene (8a). To a stirred suspension of **7** (670 mg, 2.34 mmol) in 200 mL of freshly distilled THF was added 1.50 g of $NiCl_2$ (11.57 mmol). Stirring was continued for 30 min and then 24 mL of a solution of $LiAlH_4$ in THF (1.0 M) was added dropwise and stirring was continued for another 5 h at room temperature. Reaction was quenched by addition of 0.2 mL of water. After being stirred an additional 20 min, the solution was dried over $MgSO_4$, concentrated to a small volume, and chromatographed on a column of silica gel eluted with hexane−CH_2Cl_2 (6:4) to yield **8a** (556.8 mg, 94%) as a white solid, mp 106−108 °C (EtOAc−hexane): ^{1}H NMR δ 8.48 (d, J = 8.4 Hz, 1H), 8.39 (d, J = 8.7 Hz, 1H), 8.07 (d, J = 9.9 Hz, 1H), 7.68 (d, J = 9.9 Hz, 1H), 7.65 (s, 1H), 7.46 (d, J = 8.4 Hz, 1H), 7.37 (d, J = 8.4 Hz, 1H), 4.03 (s, 3H), 4.01 (s, 3H), 2.54 (s, 3H). Anal. Calcd for $C_{17}H_{16}O_2$: C, 80.93; H, 6.39. Found: C, 80.95; H, 6.48.

2-(Bromomethyl)-7,8-dimethoxyphenanthrene (8b). A solution of **8a** (2.40 g, 9.51 mmol), NBS (1.76 g, 9.89 mmol), and benzoyl peroxide (41.2 mg, 0.17 mmol) in 300 mL of CCl_4

(17) Bedard, T. C.; Corey, J. Y.; Lange, L. D.; Rah, N. P. *J. Organomet. Chem.* **1991**, *401*, 261.

was heated at reflux for 2 days. Then the reaction mixture was cooled to room temperature, filtered, and then evaporated to dryness. Chromatography of the product on a silica gel column eluted with hexanes−EtOAc (96:4) furnished **8b** (2.23 g, 71%) as a white solid, mp 150−152 °C (EtOAc−hexane): ^{1}H NMR δ 8.57 (d, J = 8.5 Hz, 1H), 8.41 (d, J = 10 Hz, 1H), 8.11 (d, J = 8.5 Hz, 1H), 7.86 (s 1H), 7.71 (d, J = 10 Hz, 1H), 7.66 (d, J = 8.5 Hz, 1H), 7.39 (d, J = 10 Hz, 1H), 4.71 (s, 2H), 4.03 (s, 3H), 4.02 (s, 3H). Anal. Calcd for $C_{17}H_{15}BrO_2$: C, 61.65; H, 4.57; Br, 24.13. Found: C, 61.58; H, 4.59; Br, 24.21.

2-(7,8-Dimethoxyphenanthryl)methyltriphenylphosphonium Bromide (8c). A solution of **8b** (220 mg, 0.664 mmol) and PPh_3 (175 mg, 0.667 mmol) in 10 mL of toluene was heated at reflux overnight. Conventional workup afforded **8c** (379.3 mg, 96%) as white solid, mp 263−265 °C: ^{1}H NMR δ 8.30 (d, J = 8.7 Hz, 1H), 8.26 (d, J = 8.7 Hz, 1H), 8.00 (d, J = 9.9 Hz, 1H), 7.82 (d, J = 7.2 Hz, 1H), 7.78−7.45 (m, 16H), 7.39 (d, J = 9.6 Hz, 1H), 7.33 (d, J = 9.6 Hz, 1H), 5.68 (d, J = 15 Hz, 2H), 4.01 (s, 3H), 3.98 (s, 3H).

1-(2-Bromophenyl)-2-[2-(7,8-dimethoxyphenanthryl)]-ethene (9). The phosphonium salt **8c** (379.3 mg, 0.639 mmol), 2-bromobenzaldehyde (119 mg, 0.643 mmol), and a catalytic amount of 18-crown-6 were dissolved in 15 mL of CH_2Cl_2, and 1.8 mL of a 50% aqueous solution of NaOH was added. The reaction mixture was stirred overnight. The usual workup followed by chromatography on a column of silica gel eluted with hexane−CH_2Cl_2 (6:4) gave **9** (246.5 mg, 92%) as a mixture of *E*- and *Z*-isomers which was converted to the *E*-isomer by refluxing in heptane in the presence of a crystal of I_2 for 1 day (96% recovery). *Z*-isomer, white solid, mp 111−113 °C (CH_2Cl_2−hexane): ^{1}H NMR δ 8.35 (d, J = 9.5 Hz, 1H), 8.32 (d, J = 9.5 Hz, 1H), 8.04 (d, J = 9.5 Hz, 1H), 7.66 (s, 1H), 7.63 (d, J = 10 Hz, 1H), 7.58 (d, J = 9.5 Hz, 1H), 7.37 (d, J = 10 Hz, 1H), 7.33 (d, J = 8.5 Hz, 1H), 7.24 (d, J = 7.5 Hz, 1H), 7.12 (t, J = 7.5 Hz, 1H), 7.06 (t, J = 7.5 Hz, 1H), 6.89 (d, J = 12.0 Hz, 1H), 6.73 (d, J = 12.0 Hz, 1H), 4.02 (s, 3H), 4.00 (s, 3H). Anal. Calcd for $C_{24}H_{19}BrO_2$: C, 68.74; H, 4.57; Br, 19.06. Found: C, 68.69; H, 4.61; Br, 18.94. *E*-isomer, white solid, mp 157−159 °C (EtOAc−hexane): ^{1}H NMR: δ 8.59 (d, J = 9.0 Hz, 1H), 8.42 (d, J = 9.5 Hz, 1H), 8.11 (d, J = 9.5 Hz, 1H), 7.95 (s, 1H), 7.89 (d, J = 9.0 Hz, 1H), 7.76 (d, J = 9.5, Hz, 1H), 7.74 (d, J = 8.0 Hz, 1H), 7.65 (d, J = 16.5 Hz, 1H), 7.62 (d, J = 7.5 Hz, 1H), 7.40 (d, J = 9.0 Hz, 1H), 7.35 (t, J = 7.5 Hz, 1H), 7.25 (d, J = 16 Hz, 1H), 7.15 (t, J = 7.5 Hz, 1H), 4.02 (s, 3H), 4.00 (s, 3H). Anal. Calcd for $C_{24}H_{19}BrO_2$: C, 68.74; H, 4.57; Br, 19.06. Found: C, 68.84; H, 4.63; Br, 19.12.

1-(2-Bromophenyl)-1,2-dihydroxy-2-(7,8-dimethoxyphenanthryl)ethane (10a). A solution of **9** (1.4 g, 3.34 mmol), AD-mix-β (5.0 g), and $CH_3SO_2NH_2$ (320 mg, 3.36 mmol) in 65 mL of *t*-BuOH−H_2O (1:1) was stirred for 24 h at room temperature. Then Na_2SO_3 (5.57 g) and KOH (1.78 g) were added, and the reaction mixture was stirred for another 3 h. The solution was diluted with EtOAc, and the organic layer was washed with water and dried over Na_2SO_4. The solution was concentrated to a small volume and chromatographed on a silica gel column eluted with EtOAc−hexane (2:8) to furnish **10a** (1.41 g, 93%) as a white solid, mp 161−163 °C: ^{1}H NMR δ 8.51 (d, J = 8.6 Hz, 1H), 8.38 (d, J = 9.0 Hz, 1H), 8.07 (d, J = 9.1 Hz, 1H), 7.84 (s, 1H), 7.68 (d, J = 9.1 Hz, 1H), 7.66 (d, J = 8.5 Hz, 1H), 7.60 (d, J = 8.5 Hz, 1H), 7.48 (d, J = 8.0 Hz, 1H), 7.38 (t, J = 7.5 Hz, 1H), 7.36 (d, J = 9.1 Hz, 1H), 7.16 (t, J = 7.6 Hz, 1H), 5.35 (t, J = 4.4 Hz, 1H), 5.10 (t, J = 4.4 Hz, 1H), 4.03 (s, 3H), 4.01 (s, 3H). Anal. Calcd for $C_{24}H_{21}BrO_4$: C, 63.59; H, 4.67; Br, 17.63. Found: C, 63.66; H, 4.70; Br, 17.71.

1-(2-Bromophenyl)-1,2-diacetoxy-2-(7,8-dimethoxyphenanthryl)]ethane (10b). A solution of **10a** (92.3 mg, 0.204 mmol) and DMAP (5 mg) in 160 μL of Ac_2O and 3 mL of pyridine was stirred overnight at room temperature. Conventional workup gave **10b** (108.6 mg, 94%) as a white solid, mp 130−132 °C: ^{1}H NMR δ 8.49 (d, J = 8.5 Hz, 1H), 8.38 (d, J = 8.5 Hz, 1H), 8.09 (d, J = 10 Hz, 1H), 7.78 (s, 1H), 7.68 (d, J = 8.5 Hz, 1H), 7.56 (d, J = 7.5 Hz, 1H), 7.47 (d, J = 7.5 Hz, 1H), 7.45 (d, J = 8.5 Hz, 1H), 7.37 (d, J = 9.5 Hz, 1H), 7.30 (t, J = 7.5 Hz, 1H), 7.13 (t, J = 7.5 Hz, 1H), 6.61 (d, J = 4.5 Hz, 1H), 6.43 (d, J = 5.0 Hz, 1H), 4.03 (s, 3H), 4.01 (s, 3H), 2.10 (s, 3H), 2.04 (s, 3H). Anal. Calcd for $C_{28}H_{25}BrO_6$: C, 62.58; H, 4.69; Br, 14.87. Found: C, 62.59; H, 4.71; Br, 14.99.

***trans*-8,9-Diacetoxy-8,9-dihydro-3,4-dimethoxydibenz-[*a*,*j*]anthracene (11a).** A suspension of **10b** (554 mg, 1.03 mmol), $Pd(PPh_3)_2Cl_2$ (35 mg, 0.0499 mmol), and NaOAc (160.7 mg, 1.96 mmol) in 6.5 mL of *N*,*N*-dimethylacetamide was heated for 1 day at 140 °C. After being cooled to room temperature, the reaction mixture was diluted with EtOAc, washed with water, and dried over Na_2SO_4. The solution was concentrated and chromatographed on a silica gel column eluted with hexanes−EtOAc (7:3) to provide **11a** (282 mg, 60%) as a white solid, mp 254−256 °C (triturated with EtOAc): ^{1}H NMR δ 9.04 (s, 1H), 8.54 (d, J = 10 Hz, 1H), 8.16 (d, J = 7.0 Hz, 1H), 8.12 (d, J = 10 Hz, 1H), 7.97 (s, 1H), 7.75 (d, J = 10 Hz, 1H), 7.57 (t, J = 7.5, 8.5 Hz, 1H), 7.55 (d, J = 7.5 Hz, 1H), 7.42 (d, J = 9.5 Hz, 1H), 7.40 (t, J = 8.0 Hz, 1H), 6.28 (d, J = 5.0 Hz, 1H), 6.16 (d, J = 5.0 Hz, 1H), 4.06 (s, 3H), 4.03 (s, 3H), 2.03 (s, 3H), 1.98 (s, 3H). Anal. Calcd for $C_{28}H_{24}O_6$: C, 73.67; H, 5.30. Found: C, 73.77; H, 5.27.

***trans*-8,9-Dihydroxy-8,9-dihydro-3,4-dimethoxydibenz-[*a*,*j*]anthracene (11b).** A solution of **11a** (210 mg, 0.46 mmol) and MeONa (75 mg, 1.39 mmol) in MeOH (75 mL) and THF (30 mL) was heated at reflux for 15 min. The usual workup gave **11b** (155 mg, 95%) as a yellow solid, mp 206−208 °C: ^{1}H NMR δ 8.90 (s, 1H), 8.50 (d, J = 9.0 Hz, 1H), 8.09 (s, 1H), 8.07 (d, J = 9.2 Hz, 1H), 8.04 (d, J = 7.6 Hz, 1H), 7.75 (d, J = 8.9 Hz, 1H), 7.73 (d, J = 7.2 Hz, 1H), 7.50 (t, J = 6.6, 7.7 Hz, 1H), 7.44 (t, J = 7.4 Hz, 1H), 7.39 (d, J = 9.0 Hz, 1H), 4.92 (d, J = 10 Hz, 1H), 4.83 (d, J = 10 Hz, 1H), 4.04 (s, 3H), 4.03 (s, 3H). Anal. Calcd for $C_{24}H_{20}O_4$: C, 77.40; H, 5.41. Found: C, 77.39; H, 5.47.

3,4-Dimethoxydibenz[*a*,*j*]anthracene-8,9-dione (12a). A solution of **11b** (150 mg, 0.40 mmol) and DDQ (602 mg, 2.65 mmol) in 70 mL of wet THF (1% H_2O) was stirred for 2 days at room temperature. After removal of about 50% of the solvent under vacuum, water was added. The orange solid was collected and purified by column chromatography on Florisil to yield **12a** (136 mg, 92%), mp 289−291 °C: ^{1}H NMR δ 9.17 (s, 1H), 8.73 (s, 1H), 8.55 (d, J = 9.1 Hz, 1H), 8.34 (d, J = 8.1 Hz, 1H), 8.27 (dd, J = 8.0, 1.6 Hz, 1H), 8.18 (d, J = 9.2, 1H), 7.82 (t, J = 7.2 Hz, 1H), 7.80 (d, J = 9.0 Hz, 1H), 7.51 (t, J = 7.2, 8.0 Hz, 1H), 7.46 (d, J = 9.2 Hz, 1H), 4.08 (s, 3H), 4.04 (s, 3H); MS *m*/*e* 368 (M^+, 100). HRMS calcd for $C_{24}H_{16}O_4$ 368.1049, found 368.1050. Anal. Calcd for $C_{24}H_{16}O_2$: C, 78.25; H, 4.38. Found: C, 77.59; H, 4.40.

***trans*-3,4-*trans*-8,9-Tetrahydroxy-3,4,8,9-tetrahydrodibenz[*a*,*j*]anthracene (1).** Compound **11b** (120 mg, 0.326 mmol) was dissolved in 200 mL of CH_2Cl_2, and 6.4 mL of BBr_3 in CH_2Cl_2 (1.0 M) was added dropwise at 0 °C. The solution was stirred for 1.5 h at room temperature, and then reaction was quenched by addition of 0.2 mL of water. The solvent was removed under reduced pressure, and then EtOAc was added and the organic layer was washed with water, dried over Na_2SO_4, and evaporated to dryness, minimizing contact with air. The ^{1}H NMR spectrum of the air-sensitive residue confirmed demethylation to be complete and was consistent with assignment as **12b**: ^{1}H NMR (acetone-d_6) δ 9.47 (s, 1H), 8.71 (d, J = 8.0 Hz, 1H), 8.65 (s, 1H), 8.55 (d, J = 8.8 Hz, 1H), 8.24 (d, J = 9.1 Hz, 1H), 8.13 (d, J = 7.9 Hz, 1H), 7.88 (d, J = 9.2 Hz, 1H), 7.85 (t, J = 8.4 Hz, 1H), 7.56 (t, J = 7.5 Hz, 1H), 7.40 (d, J = 8.8 Hz, 1H).

A suspension of **12b** and $NaBH_4$ (680 mg,18.0 mmol) in 150 mL of EtOH was stirred at room temperature with O_2 bubbling through the solution for 24 h. Following removal of EtOH under vacuum, water was added, and the aqueous suspension was extracted with EtOAc−THF. The combined organic extracts were washed with brine, dried over Na_2SO_4, and evaporated to dryness. The crude **1** was purified by chromatograpy on Florisil to furnish pure **1** (85 mg,76%) as a white solid, mp 225−227 °C: ^{1}H NMR (DMSO-d_6) δ 8.54 (d, J = 7.7 Hz, 1H), 8.15 (dd, J = 6.5, 7.3 Hz, 1 H), 8.02 (d, J = 2.0 Hz, 1H), 7.82 (d, J = 8.4 Hz, 1H), 7.71 (d, J = 8.3 Hz, 1 H), 7.63 (d, J = 7.2 Hz, 1H), 7.49−7.35 (m, 3H), 6.14 (d, J = 10 Hz, 1H), 5.75 (dd, J = 5.0, 5.0 Hz, exchangeable with D_2O, 1H),

5.67 (dd, J = 5.0, 5.15 Hz, exchangeable with D_2O, 1H), 5.56 (dd, J = 4.8, 4.85 Hz, exchangeable with D_2O, 1H), 5.23 (dd, J = 1.5, 5.1 Hz, exchangeable with D_2O, 1H), 4.70−4.67 (br, 1H, after addition of D_2O changed to doublet, J = 11.0 Hz), 4.56 (br, 1H, after addition of D_2O changed to doublet, J = 8.6 Hz), 4.49 (br, 1H, after addition of D_2O changed to doublet, J = 9.50 Hz), 4.34−4.32 (br, 1H, after addition of D_2O changed to doublet, J = 8.8 Hz); ^{13}C NMR (THF-d_8) δ 74.31, 74.40, 74.45, 74.54, 76.42, 76.46, 118.11, 122.66, 124.13, 124.54, 124.60, 125.24, 125.29, 126.11, 126.12, 127.84, 128.29, 128.59, 128.72, 132.56, 132.61, 133.82, 133.86, 133.91, 134.55, 134.57, 136.98, 139.86; MS *m/e* 346 (M^+, 50), 328 ($M^+ - H_2O$, 100); HRMS calcd for $C_{22}H_{18}O_4$ 346.1218, found 346.1214; UV (EtOH) λ_{max} (ϵ) 207.3 (1.21×10^5), 252.3 (5.47×10^4), 276.2 (5.92×10^4), 334.6 (2.23×10^4) nm. HPLC on a reverse phase ZORBAX ODS column (9.4 × 25 cm) eluted with a linear gradient of 50% aqueous MeOH to 100% MeOH (in 15 min) with a flow rate of 4.0 mL/min showed the product to be a mixture of two isomers with retention times 6.3 and 6.6 min, respectively.

Compound **1** was further characterized by conversion to its tetraacetate with Ac_2O and pyridine. **1**-tetraacetate, mp 201−204 °C (dec): ^{1}H NMR δ 8.60 (s, 1H), 8.06 (d, J = 7.7 Hz, 1H), 7.97 (d, J = 2.8 Hz, 1 H), 7.81 (d, J = 8.4 Hz, 1 H), 7.59 (d, J = 10.2 Hz, 1 H), 7.51−7.54 (m, 2H), 7.48 (dd, J = 8.4, 3.3 Hz, 1H), 7.40 (t, J = 7.5 Hz, 1H), 6.29−6.32 (m, 2H), 6.24 (d, J = 4.9 Hz, 1H), 6.12 (dd, J = 1.6, 4.8 Hz, 1H), 5.64 (m, 1H), 2.13 (s, 1.5 H), 2.12 (s, 1.5 H), , 2.060 (s, 1.5 H), 2.058 (s, 1.5 H), 2.00 (s, 1.5 H), 1.99 (s, 1.5 H), 1.964 (s, 1.5 H), 1.962 (s, 1.5 H); MS *m/e* 514 (M^+, 11), 310 (100); HRMS calcd for $C_{30}H_{26}O_8$ 514.1628, found 514.1637.

1-Chloro-2-methyl-1′-methoxystilbene (13). Reaction of *o*-anisaldehyde (4.05 g, 29.0 mmol) with **5** (14.60 g, 30.3 mmol) by the procedure employed for preparation of **6** (16 h) gave **13**. Purification by chromatography on a column of silica gel eluted with hexanes−EtOAc (98:2) afforded a mixture of *Z*- and *E*-isomers of **13** (*Z*/*E* = 5 by NMR; *Z*-isomer, δ 6.77, J = 12 Hz; *E*-isomer, δ 7.44, J = 16 Hz) as a white solid (7.51 g, 98%). This mixture was used for photocyclization. *Z*-isomer, mp 75.5−76.5 °C (EtOAc−hexane): ^{1}H NMR δ 7.17 (t, J = 7.0, 8.5 Hz, 1H), 7.06 (d, J = 7.0 Hz, 1H), 6.97−6.99 (m, 2H), 6.89 (d, J = 7.5 Hz, 1H), 6.86 (d, J = 8.5 Hz, 1H), 6.84 (d, J = 12 Hz, 1H), 6.77 (d, J = 12 Hz, 1H), 6.68 (t, J = 7.0, 7.5 Hz, 1H), 3.83 (s, 3H), 2.41 (s, 3H); MS *m/e* 258 (M^+, 100) (based on Cl, 35). Anal. Calcd for $C_{16}H_{15}ClO$: C, 74.27; H, 5.84; Cl, 13.70. Found: C, 74.37; H, 5.91; Cl, 13.57.

1-Chloro-2-methyl-8-methoxyphenanthrene (14a). Photocyclization of **13** (1.03 g, 3.98 mmol) in the presence of I_2 and 1,2-epoxybutane by the procedure employed for preparation of **7** (10 h) gave crude **14a**. This was purified by chromatography on a silica gel column eluted with hexanes−EtOAc (96:4). Pure **14a** (0.91 g, 92%) was obtained as a white solid, mp 151−152 °C (EtOAc−hexane): ^{1}H NMR δ 8.48 (d, J = 8.5 Hz, 1H), 8.32 (d, J = 9.5 Hz, 1H), 8.26 (d, J = 9.5 Hz, 1H), 8.21 (d, J = 8.0 Hz, 1H), 7.57 (t, J = 8.0 Hz, 1H), 7.49 (d, J = 8.5 Hz, 1H), 7.01 (d, J = 8.0 Hz, 1H), 4.07 (s, 3H), 2.66 (s, 3H); MS *m/e* 256 (M^+, 100 based on Cl, 35). Anal. Calcd for $C_{16}H_{13}ClO$: C, 74.85; H, 5.10; Cl, 13.81. Found: C, 74.72; H, 5.17; Cl, 13.82.

2-Bromomethyl-1-chloro-8-methoxyphenanthrene (14b). Bromination of **14a** (1.10 g, 4.28 mmol) with NBS (0.76 g, 4.27 mmol) by the procedure employed for the preparation of **8b** (reaction time 16 h) gave **14b** (1.23 g, 87%) as a yellow solid, mp 161−163 °C (EtOAc−hexane): ^{1}H NMR δ 8.57 (d, J = 8.5 Hz, 1H), 8.36 (d, J = 9.0 Hz, 1H), 8.26 (d, J = 9.5 Hz, 1H), 8.21 (d, J = 8.5 Hz, 1H), 7.66 (d, J = 8.5 Hz, 1H), 7.60 (t, J = 8.0 Hz, 1H), 7.05 (d, J = 7.5 Hz, 1H), 4.88 (s, 2H), 4.08 (s, 3H); MS *m/e* 336 (M^+ + 2, 27); 255 (M^+ − Br, 100, based on Br, 79, and, Cl, 35). Anal. Calcd for $C_{16}H_{12}BrClO$, C, 57.26; H, 3.60; Br, 23.81; Cl, 10.56. Found, C, 57.09; H, 3.56; Br, 23.93; Cl, 10.62.

2-(1-Chloro-8-methoxyphenanthrylmethyl)triphenylphosphonium Bromide (14c). Reaction of **14b** (0.76 g, 2.26 mmol) with PPh_3 (0.60 g, 2.29 mmol) by the procedure employed for preparation of **8c** furnished **14c** (1.35 g, 91%) as a white solid, mp 289−290 °C (darkening): ^{1}H NMR δ 8.48 (d, J = 8.5 Hz, 1H), 8.29 (d, J = 9.5 Hz, 1H), 8.16 (d, J = 8.5 Hz, 1H), 7.89 (d, J = 9.5 Hz, 1H), 7.86 (d, J = 8.5 Hz, 1H), 7.60−7.80 (m, 16H), 7.06 (d, J = 8.5 Hz, 1H), 5.95 (d, J = 13.5 Hz, 2H), 4.05 (s, 3H); MS (FAB) 517 (M^+ − Br, 100, based on Br, 79, Cl, 35, and P, 31). Anal. Calcd for $C_{34}H_{27}BrClOP$: C, 68.30; H, 4.55; Br, 13.36; Cl, 5.93. Found: C, 68.04; H, 4.53; Br, 13.46; Cl, 5.97.

1-(1-Chloro-8-methoxy-2-phenanthryl)-2-(2′,3′-dimethoxyphenyl)ethene (15). Wittig reaction of **14c** (0.80 g, 1.34 mmol) with 2,3-dimethoxybenzaldehyde (0.22 g, 1.32 mmol) was carried out by the procedure employed for preparation of **9** and worked up in similar manner. Compound **15** (0.48 g, 90%) was obtained as a white solid consisting principally of the *Z*-isomer with only traces of the *E*-isomer. *Z*-isomer, white solid, mp 160−162 °C (EtOAc−hexane): ^{1}H NMR δ 8.35 (d, J = 9.5 Hz, 1H), 8.32 (d, J = 8.0 Hz, 1H), 8.30 (d, J = 9.5 Hz, 1H), 8.14 (d, J = 8.5 Hz, 1H), 7.55 (t, J = 8.0 Hz, 1H), 7.39 (d, J = 8.5 Hz, 1H), 7.03 (d, J = 2.5 Hz, 2H), 7.01 (d, J = 7.5 Hz, 1H), 6.77 (dd, J = 1.5, 8.0 Hz, 1H), 6.71 (t, J = 8.0 Hz, 1H), 6.59 (dd, J = 1.5, 8.0 Hz, 1H), 4.05 (s, 3H), 3.92 (s, 3H), 3.87 (s, 3H); MS *m/e* 404 (M^+, 15), 256 (100, based on Cl, 35). Anal. Calcd for $C_{25}H_{21}ClO_3$: C, 74.16; H, 5.23; Cl, 8.76. Found: C, 74.05; H, 5.28; Cl, 8.75.

7-Chloro-3,4,10-trimethoxydibenz[*a*, *j*]anthracene (16a). Photocyclization of **15** (205 mg, 0.506 mmol) by the procedure employed for preparation of **7** and **14a** and flash chromatography on a silica gel column eluted with hexane−CH_2Cl_2 (6:4) gave initially **17** (56 mg, 30%) as a yellow solid, mp 154−155 °C: ^{1}H NMR δ 8.98 (d, J = 9.5 Hz, 1H), 8.82 (d, J = 9.3 Hz, 1H), 8.76 (d, J = 8.7 Hz, 1H), 8.41 (d, J = 8.0 Hz, 1H), 8.39 (d, J = 9.2 Hz, 1H), 8.27 (d, J = 8.9 Hz, 1H), 8.01 (d, J = 8.6 Hz, 1H), 7.88 (d, J = 8.9 Hz, 1H), 7.64 (t, J = 8.1 Hz, 1H), 7.43 (d, J = 9.3 Hz, 1H), 7.06 (d, J = 7.8 Hz, 1H), 4.10 (s, 3H), 4.09 (s, 3H), 4.08 (s, 3H). Anal. Calcd for $C_{25}H_{20}O_3$: C, 81.50; H, 5.47. Found: C, 81.24; H, 5.56. Further elution gave **16a** (74 mg, 36%) as a yellow solid, mp 283−284 °C (CH_2Cl_2−hexane): ^{1}H NMR δ 9.77 (s, 1H), 8.60 (d, J = 9.0 Hz, 1H), 8.46 (d, J = 8.5 Hz, 1H), 8.33 (d, J = 9.5 Hz, 1H), 8.32 (d, J = 9.5 Hz, 1H), 8.25 (d, J = 9.5 Hz, 1H), 8.13 (d, J = 9.0 Hz, 1H), 7.58 (t, J = 8.0 Hz, 1H), 7.36 (d, J = 9.0 Hz, 1H), 7.03 (d, J = 8.0 Hz, 1H), 4.03 (s, 6H), 4.01 (s, 3H); MS *m/e* 402 (M^+, 100, based on Cl, 35); HRMS Calcd for $C_{25}H_{19}ClO_3$ 402.1023, found 402.1023. Anal. Calcd for $C_{25}H_{19}ClO_3$: C, 74.52; H, 4.75; Cl, 8.80. Found: C, 73.95; H, 4.80; Cl, 8.73.

3,4,10-Trimethoxydibenz[*a*, *j*]anthracene (16b). Dechlorination of **16a** (121 mg, 0.30 mmol) by the procedure employed for preparation of **8a** afforded **16b** (96.5 mg, 92%) as a white solid, mp 242−243 °C (EtOAC−hexane): ^{1}H NMR δ 9.79 (s, 1H), 8.62 (d, J = 8.5 Hz, 1H), 8.50 (d, J = 8.0 Hz, 1H), 8.25 (s, 1H), 8.15 (d, J = 9.0 Hz, 1H), 8.02 (d, J = 9.0 Hz, 1H), 7.78 (m, 2H), 7.59 (t, J = 8.0 Hz, 1H), 7.34 (d, J = 8.5 Hz, 1H), 7.01 (d, J = 8.0 Hz, 1H), 4.02 (s, 6H), 4.01 (s, 3H); MS *m/e* 368 (M^+, 100). Anal. Calcd for $C_{25}H_{20}O_3$: C, 81.50; H, 5.47. Found: C, 81.39; H, 5.52.

3,4,10-Trihydroxydibenz[*a*, *j*]anthracene (16c). Demethylation of **16b** (102 mg, 0.28 mmol) with BBr_3 by the procedure employed for the preparation of **12b** provided **16c** (81 mg, 90%): ^{1}H NMR (CD_3COCD_3): δ 10.02 (s, 1H), 8.66 (d, J = 8.1 Hz, 1H), 8.60 (d, J = 8.7 Hz, 1H), 8.40 (s, 1H), 8.19 (d, J = 8.4 Hz, 1H), 8.16 (d, J = 7.2 Hz, 1H), 7.86 (d, J = 6.3 Hz, 1H), 7.84 (d, J = 9.0 Hz, 1H), 7.53 (t, J = 7.8, 8.1 Hz, 1H), 7.36 (d, J = 8.7 Hz, 1H), 7.14 (d, J = 7.5 Hz, 1H). In the view of the air sensitivity of **16c**, its exposure to air was kept to a minimum, and it was isolated and characterized as its diacetate.

3,4,10-Triacetoxydibenz[*a*, *j*]anthracene (16d). A solution of **16c** (80.7 mg) in 0.5 mL of Ac_2O and 2.0 mL of pyridine was stirred overnight at room temperature. The usual workup gave **16d** (95.2 mg, 85%) as a white solid, mp 255−257 °C (CH_2Cl_2−hexane): ^{1}H NMR δ 9.76 (s, 1H), 8.74 (d, J = 8.5 Hz, 2H), 8.22 (s, 1H), 7.79 (m, 2H), 7.72 (d, J = 9.0 Hz, 1H), 7.65 (m, 2H), 7.51 (d, J = 9.0 Hz, 1H), 7.36 (d, J = 7.5 Hz, 1H), 2.49 (s, 3H), 2.48 (s, 3H), 2.37 (s, 3H); MS *m/e* 452 (M^+, 40), 326 (100). Anal. Calcd for $C_{28}H_{20}O_6$: C, 74.33; H, 4.46. Found, C, 74.21; H, 4.46.

***trans*-3,4,-Dihydroxy-3,4-dihydro-10-hydroxydibenz-[*a, j*]anthracene (3a).** Reduction of **16d** (42.0 mg, 0.093 mmol) with $NaBH_4/O_2$ in EtOH was carried out by the procedure employed for the preparation of **1** (reaction time 3 days). Compound **3a** (23.7 mg, 78%) was obtained as a yellow solid, mp 270−272 °C: ^{1}H NMR (CD_3COCD_3) δ 9.59 (s, 1H), 9.05 (s, 0.6 H, exchangeable with D_2O), 8.58 (d, J = 8.0 Hz, 1H), 8.45 (s, 1H), 8.11 (d, J = 9.5 Hz, 1H), 8.04 (d, J = 8.0 Hz, 1H), 7.92 (d, J = 8.5 Hz, 1H), 7.80 (d, J = 9.0 Hz, 1H), 7.69 (dd, J = 2.5, 10.0 Hz, 1H), 7.49 (t, J = 8.0 Hz, 1H), 7.12 (d, J = 8.0 Hz, 1H), 6.29 (dd, J = 2.5, 10.0 Hz, 1H), 4.92 (dd, J = 5.5, 12 Hz, 1H), 4.69 (d, J = 5.5 Hz, 0.6 H, exchangeable with D_2O), 4.54 (dd, J = 5.5, 12 Hz, 1H), 4.35 (d, J = 5.5 Hz, 0.6 H, exchangeable with D_2O); ^{13}C NMR (THF-d_8) δ 74.48, 76.60, 112.04, 115.05, 117.71, 121.78, 122.78, 124.23, 125.97, 127.78, 127.82, 127.85, 128.60, 128.72, 128.96, 130.00, 131.32, 132.73, 133.23, 134.72, 136.73, 155.15; MS *m/e* 328 (M^+, 35), 310 ($M^+ - H_2O$, 100); HRMS calcd for $C_{22}H_{16}O_3$ 328.1099, found 328.1100; UV (EtOH) λ_{max} (ϵ) 249 (5.25×10^4), 295 (4.35×10^4), 320 (1.83×10^4) nm.

1-Chloro-2-methyl-2′-methoxystilbene (18). Reaction of *m*-anisaldehyde (4.02 g, 29.5 mmol) with **5** (14.20 g, 29.5 mmol) by the procedure employed for preparation of **6** (16 h) gave **18** as a mixture of *Z*- and *E*-isomers (*Z*/*E* = 5 by NMR; *Z*-isomer, δ 6.65, J = 12 Hz; *E*-isomer, δ 7.57, J = 16 Hz) as a colorless oil (7.30 g, 96%). This mixture was used directly for photocyclization. *Z*-isomer, colorless oil: ^{1}H NMR δ 7.10 (d, J = 8.0 Hz, 1H), 7.08 (s, 1H), 7.06 (d, J = 8.0 Hz, 1H), 6.96 (t, J = 7.5 Hz, 1H), 6.75 (d, J = 7.5 Hz, 1H), 6.68−6.72 (m, 3H), 6.65 (d, J = 12 Hz, 1H), 3.61 (s, 3H), 2.41 (s, 3H); MS *m/e* 258 (M^+, 100 based on Cl, 35). Anal. Calcd for $C_{16}H_{15}ClO$: C, 74.27; H, 5.84; Cl, 13.70. Found: C, 74.30; H, 5.83; Cl, 13.80.

1-Chloro-2-methyl-7-methoxyphenanthrene (19a). Photocyclization of **18** (1.00 g, 3.46 mmol) by the procedure employed for preparation of **14a** (10 h) provided **19a** (0.80 g, 81%) as a white solid, mp 170−171.5 °C (EtOAc−hexane): ^{1}H NMR δ 8.45 (d, J = 9.0 Hz, 1H), 8.32 (d, J = 8.0 Hz, 1H), 8.18 (d, J = 9.0 Hz, 1H), 7.68 (d, J = 9.0 Hz, 1H), 7.40 (d, J = 8.0 Hz, 1H), 7.22, (d, J = 9.0 Hz, 1H), 7.19 (s, 1H), 3.96 (s, 3H), 2.60 (s, 3H); MS *m/e* 256 (M^+, 100) (based on Cl, 35). Anal. Calcd for $C_{16}H_{13}ClO$: C, 74.85; H, 5.10; Cl, 13.81. Found: C, 74.72; H, 5.14; Cl, 13.76.

2-Bromomethyl-1-chloro-7-methoxyphenanthrene (19b). Bromination of **19a** (2.23 g, 8.69 mmol) with NBS (1.55 g, 8.7 mmol) by the procedure employed for preparation of **8b** and **14b** (16 h) provided **19b** (2.34 g, 80%) as a yellow solid, mp 155−156 °C (EtOAc−hexane): ^{1}H NMR δ 8.5 (d, J = 9.0 Hz, 1H), 8.50 (d, J = 8.6 Hz, 1H), 8.27 (d, J = 9.3 Hz, 1H), 7.81 (d, J = 9.2 Hz, 1H), 7.66 (d, J = 8.6 Hz, 1H), 7.32, (dd, J = 2.7, 9.0 Hz, 1H), 7.28 (d, J = 2.6 Hz, 1H) 4.86 (s, 2H), 3.98 (s, 3H); MS *m/e* 336 ($M^+ + 2$, 15), 255 ($M^+ - Br$, 100, based on Br, 79, and Cl, 35). Anal. Calcd for $C_{16}H_{12}BrClO$: C, 57.26; H, 3.60; Br, 23.81; Cl, 10.56. Found: C, 57.22; H, 3.60; Br, 23.49; Cl, 10.42.

2-(1-Chloro-7-methoxyphenanthrylmethyl)triphenylphosphonium Bromide (19c). Reaction of **19b** (2.04 g, 6.08 mmol) with PPh_3 (1.59 g, 6.06 mmol) by the procedure employed for preparation of **8c** furnished **19c** (3.29 g, 91%) as a white solid, mp 286−288 °C: ^{1}H NMR δ 8.47 (d, J = 8.5 Hz, 1H), 8.38 (d, J = 8.5 Hz, 1H), 7.88 (d, J = 10 Hz, 1H), 7.84 (d, J = 10 Hz, 1H), 7.57−7.81 (m, 17H), 7.31 (d, J = 7.5 Hz, 1H), 5.90 (d, J = 13.5 Hz, 2H), 3.97 (s, 3H); MS (FAB) 517 ($M^+ -$ Br, 100, based on Br, 79, Cl, 35, and P, 31). Anal. Calcd for $C_{34}H_{27}BrClOP$: C, 68.30; H, 4.55; Br, 13.36; Cl, 5.93. Found: C, 68.40; H, 4.61; Br, 13.28; Cl, 5.89.

1-(1-Chloro-7-methoxy-2-phenanthryl)-2-(2′,3′-dimethoxyphenyl)ethene (21). Wittig reaction of **19c** (2.95 g, 4.93 mmol) with 2,3-dimethoxybenzaldehyde (0.82 g, 4.93 mmol) by the procedure used for preparation of **9** gave **21** (1.83 g, 92%) as a white solid consisting mainly of the *Z*-isomer with only traces of the *E*-isomer. *Z*-isomer, white solid, mp 161−163 °C (EtOAc−hexane): ^{1}H NMR δ 8.37 (d, J = 9.5 Hz, 1H), 8.22 (d, J = 9.0 Hz, 1H), 8.16 (d, J = 8.5 Hz, 1H), 7.70 (d, J = 9.5 Hz, 1H), 7.32 (d, J = 8.5 Hz, 1H), 7.19 (br, 2H), 6.95 (d, J = 3.5 Hz, 2H), 6.71 (d, J = 8.0 Hz, 1H), 6.65 (t, J = 8.0 Hz, 1H), 6.55 (d, J = 8.0 Hz, 1H), 3.92 (s, 3H), 3.88 (s, 3H), 3.84 (s, 3H); MS *m/e* 404 (M^+, 100, based on Cl, 35). Anal. Calcd for $C_{25}H_{21}ClO_3$: C, 74.16; H, 5.23, Cl, 8.76. Found: C, 74.01; H, 5.28; Cl, 8.68.

7-Chloro-3,4,11-trimethoxydibenz[*a, j*]anthracene (22a). Photocyclization of **21** (172 mg, 0.43 mmol) by the procedure employed for preparation of **14a** and **19a** (3 h) provided **22a** (77 mg, 45%) as a white solid, mp 250−252 °C (EtOAc−hexane): ^{1}H NMR δ 9.79 (s, 1H), 8.87 (d, J = 9.5 Hz, 1H), 8.70 (d, J = 9.0 Hz, 1H), 8.42 (d, J = 9.5 Hz, 1H), 8.41 (d, J = 9.5 Hz, 1H), 8.19 (d, J = 9.5 Hz, 1H), 7.79 (d, J = 9.5 Hz, 1H), 7.44 (d, J = 9.5 Hz, 1H), 7.38 (dd, J = 2.6, 9.0 Hz, 1H), 7.31 (d, J = 2.6 Hz, 1H), 4.06 (s, 3H), 4.03 (s, 3H), 4.00 (s, 3H); MS *m/e* 402 (M^+, 100, based on Cl, 35); HRMS calcd for $C_{25}H_{19}ClO_3$ 402.1023, found 402.1023.

3,4,11-Trimethoxydibenz[*a, j*]anthracene (22b). Reduction of **22a** (105 mg, 0.26 mmol) with $NiCl_2$ (170 mg, 1.31 mmol) and 2.6 mL of $LiAlH_4$ in THF (1.0 M) by the procedure employed for reduction of **16a** furnished **22b** (86.8 mg, 90%) as a white solid, mp 184−186 °C (EtOAC−hexane): ^{1}H NMR δ 9.78 (s, 1H), 8.88 (d, J = 10 Hz, 1H), 8.70 (d, J = 10 Hz, 1H), 8.30 (s, 1H), 8.08 (d, J = 8.5 Hz, 1H), 7.85 (d, J = 8.5 Hz, 2H), 7.66 (d, J = 9.5 Hz, 1H), 7.41 (d, J = 8.5 Hz, 1H), 7.36 (dd, J = 2.5, 8.5 Hz, 1H), 7.30 (d, J = 2.5 Hz, 1H), 4.07 (s, 3H), 4.05 (s, 3H), 4.00 (s, 3H); MS *m/e* 368 (M^+, 100). Anal. Calcd for $C_{25}H_{20}O_3$: C, 81.50; H, 5.47. Found: C, 81.42; H, 5.51.

3,4,11-Trihydroxydibenz[*a, j*]anthracene (22c). Demethylation of **22b** (76 mg, 0.21 mmol) with BBr_3 by the procedure employed for preparation of **12b** gave **22c** (58.5 mg, 87%) used directly in the next step: ^{1}H NMR (CD_3COCD_3) δ 9.95 (s, 1H), 9.06 (d, J = 9.0 Hz, 1H), 8.81 (s, 0.5 H, exchangeable with D_2O), 8.71 (br, 0.5 H, exchangeable with D_2O), 8.62 (d, J = 8.5 Hz, 1H), 8.38 (s, 1H), 8.14 (d, J = 9.0 Hz, 1H), 7.91 (br, 0.5 H, exchangeable with D_2O), 7.87 (d, J = 9.5 Hz, 1H), 7.84 (d, J = 9.5 Hz, 1H), 7.65 (d, J = 8.5 Hz, 1H), 7.35 (d, J = 9.0 Hz, 1H), 7.34 (d, J = 2.5 Hz, 1H), 7.31 (dd, J = 2.5, 9.0 Hz, 1H).

In the view of its air sensitivity, **22c** was isolated and characterized as its diacetate. Acetylation of **22c** (58 mg) of 0.5 mL of Ac_2O in 2.0 mL of pyridine overnight at room temperature gave **22c** diacetate (64 mg, 85%) as a white solid, mp 267−269 °C: ^{1}H NMR δ 9.90 (s, 1H), 8.99 (d, J = 10 Hz, 1H), 8.90 (d, J = 10 Hz, 1H), 8.37 (s, 1H), 7.93 (d, J = 9.5 Hz, 1H), 7.89 (d, J = 8.5 Hz, 1H), 7.76 (d, J = 8.5 Hz, 1H), 7.71 (d, J = 10 Hz, 1H), 7.66 (d, J = 2.5 Hz, 1H), 7.60 (d, J = 9.0 Hz, 1H), 7.51 (dd, J = 2.5, 10 Hz), 2.51 (s, 3H), 2.41 (s, 3H), 2.40 (s, 3H); MS, *m/e* 452 (M^+, 34), 326 (100); HRMS calcd for $C_{28}H_{20}O_6$ 452.1260, found 452.1260.

***trans*-3,4-Dihydroxy-3,4-dihydro-11-hydroxydibenz-[*a, j*]anthracene (3b).** Reduction of **22d** (55 mg, 0.167 mmol) with $NaBH_4/O_2$ in EtOH by the procedure used for preparation of **1** (3 days) afforded **3b** (40 mg, 74%) as a yellow solid, mp 263−265 °C: ^{1}H NMR (CD_3COCD_3) δ 9.49 (s, 1H), 8.96 (d, J = 8.5 Hz, 1H), 8.81 (s, 0.5 H, exchangeable with D_2O), 8.41 (s, 1H), 8.02 (d, J = 8.5 Hz, 1H), 7.89 (d, J = 9.5 Hz, 1H), 7.79 (d, J = 9.5 Hz, 1H), 7.70 (d, J = 10 Hz, 1H), 7.57 (d, J = 9.5 Hz, 1H), 7.32 (d, J = 2.5 Hz, 1H), 7.26 (dd, J = 2.5, 8.5 Hz, 1H), 6.29 (dd, J = 2.5, 10 Hz, 1H), 4.94 (dd, J = 6.0, 11 Hz, 1H), 4.69 (d, J = 5.0 Hz, 0.6 H, exchangeable with D_2O), 4.56 (d, J = 10 Hz, 1H), 4.37 (d, J = 10 Hz, 0.6H, exchangeable with D_2O); ^{13}C NMR (THF-d_8) δ 74.49, 76.64, 113.15, 116.05, 117.35, 122.85, 123.67, 124.67, 125.47, 127.57, 127.96, 128.13, 128.36, 128.72, 129.25, 130.38, 130.44, 132.03, 134.52, 134.81, 136.82, 158.04; MS *m/e* 328 (M^+, 25), 310 ($M^+ - H_2O$, 100); HRMS calcd for $C_{22}H_{16}O_3$ 328.1099, found 328.1100; UV (EtOH) λ_{max} (ϵ) 240.0 (4.53×10^4), 246.9 (5.50×10^4), 293.8 (6.45×10^4), 306.2 (7.50×10^4) nm.

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