Kinetics. Pseudo-first-order rate constants, k_{obs}, for solvolysis of phenoxydimethylphenylsilane were determined by adding 0.6 μL of phenoxydimethylphenylsilane to 2.4 mL of a 2,2,2-trifluoroethanol (TFE) solution at 30.0 ± 0.5 °C buffered with an acetic acid–tetramethylammonium acetate buffer and at constant ionic strength of 0.05 M maintained with tetramethylammonium trifluoroacetate. The rate of solvolysis, k_{obs}, was determined by monitoring the increase in absorbance due to the formation of phenol at 280 nm as a function of time with a Shimadzu UV-160 spectrophotometer equipped with a thermostated cell holder. The spectrophotometer was interfaced to a personal computer and k_{obs} values were obtained by a nonlinear regression analysis of absorbance vs time data. Reactions were generally followed for more than three half-lives. The nonlinear regression analysis calculated the best end points. For reactions that were followed by completion the observed end points always agreed well with the calculated end points. Good pseudo-first-order kinetics were followed and semilog plots of $(A_\infty - A_t)$ were linear. Rate constants were generally reproducible within 10%.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work. We thank Chris Forester for performing some of the rate determinations and Dr. Ralph Pollack for helpful discussion.

Registry No. TFE, 75-89-8; phenoxydimethylphenylsilane, 17915-17-2; acetic acid, 64-19-7; tetramethylammonium acetate, 10581-12-1.

Supplementary Material Available: Pseudo-first-order rate constants for the trifluoroethanolysis of phenoxydimethylphenylsilane (2 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

[*abc*]-Annealated [18]Annulenes

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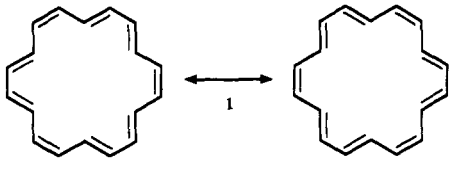
A 3-fold stereoselective cyclocondensation of the azomethines **3** and **11** yields the [18]annulenes **4** and **12**, respectively. The [*abc*]-annelation of naphthalene or phenanthrene systems, realized here for the first time, leads to nonplanar molecules consisting of "aromatic islands", which are connected by (*E*)-configured olefinic bridges. The absence of a diamagnetic ring current rules out a macrocyclic aromaticity. The NMR investigation, based on selective deuterations, is sustained by force field calculations (MMX). The disc-like compounds represent discotic mesogens of an enormous diameter. The formation of thermotropic liquid crystals can be achieved by the introduction of long flexible alkoxy chains.

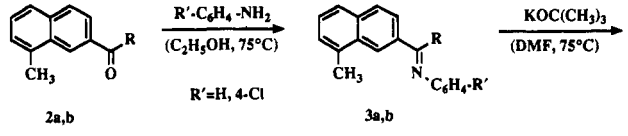
[18]Annulene[1] with the preferred conformation shown in formula **1** has two identical resonance structures. According to the VB theory, the anellation of benzene rings—from benzo[*a*]cyclooctadecene[2] up to kekulene[3]—can change the "weight" of these resonance structures. The *diatropic* or *atropic* behavior of these macrocycles is directly connected to this effect.

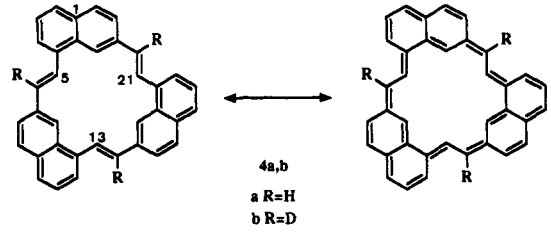


1

If radical species are disregarded, the number of common carbon atoms of [18]annulene and condensed arenes must be even. The following systems fulfill this criterion:

Scheme I





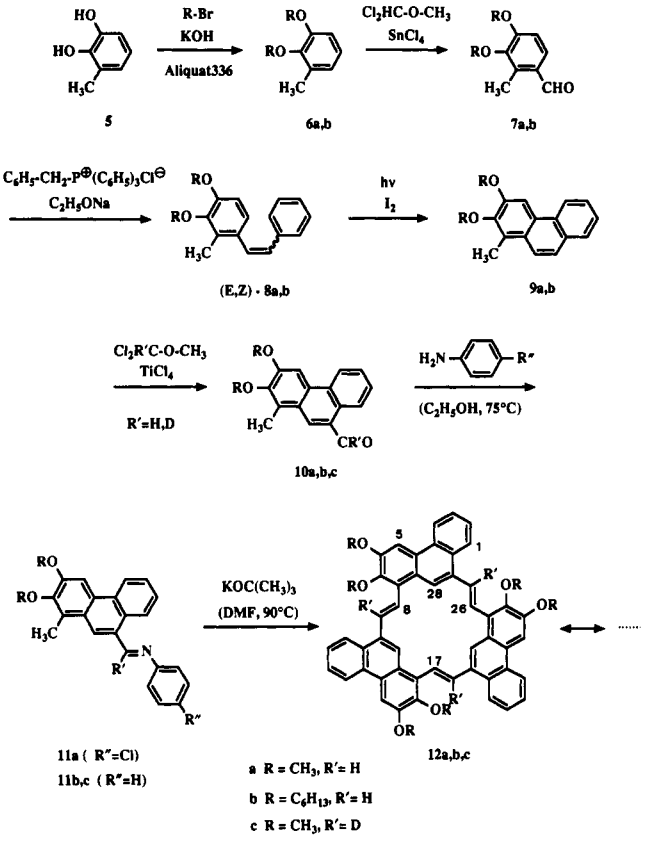
type of annelation	no. of annealated arenes	known compounds
[*a*]	1, 2, 3, ...	benzo[*a*]cyclooctadecene[2]
[*ab*]	2, 4, 6	dibenzo[*ab*,*de*]cyclooctadecene,[4b] hexa-*m*-phenylene[4a]
[*abc*]	1, 2, 3, 4	
[*abcd*]	2	
[*abcde*]	1, 2, 3	phenanthro[3,4,5,6-*abcde*]cyclooctadecene[4b] 3,6′:3,6″:3′,6-triphenanthrylene[5]

Analogous considerations are valid for other annulenes.

(1) Sondheimer, F.; Wolovsky, R.; Amiel, Y. *J. Am. Chem. Soc.* **1962**, *84*, 274.
(2) Meissner, U. E.; Gensler, A.; Staab, H. A. *Tetrahedron Lett.* **1977**, *18*, 3.
(3) Diederich, F.; Staab, H. A. *Angew. Chem.* **1978**, *90*, 383; *Angew. Chem., Int. Ed. Engl.* **1970**, *17*, 372. Staab, H. A.; Diederich, F. *Chem. Ber.* **1983**, *116*, 3487. Staab, H. A.; Diederich, F.; Krieger, C.; Schweitzer, D. *Chem. Ber.* **1983**, *116*, 3504.
(4) The anellation of benzene rings can be directly used as a probe for the assessment of the π electron structure: (a) Staab, H. A.; Binnig, F. *Chem. Ber.* **1967**, *100*, 293. (b) Staab, H. A.; Meissner, U. E.; Meissner, B. *Chem. Ber.* **1976**, *109*, 3875. (c) Cremer, D.; Günther, H. *Liebigs Ann. Chem.* **1972**, *763*, 87. (d) Ege, G.; Vogler, H. *Tetrahedron Lett.* **1975**, *31*, 569.
(5) Staab, H. A.; Bräunling, H. *Tetrahedron Lett.* **1965**, 45. Staab, H. A.; Bräunling, H.; Schneider, K. *Chem. Ber.* **1968**, *101*, 879.

0022-3263/92/1957-6847$03.00/0

Scheme II

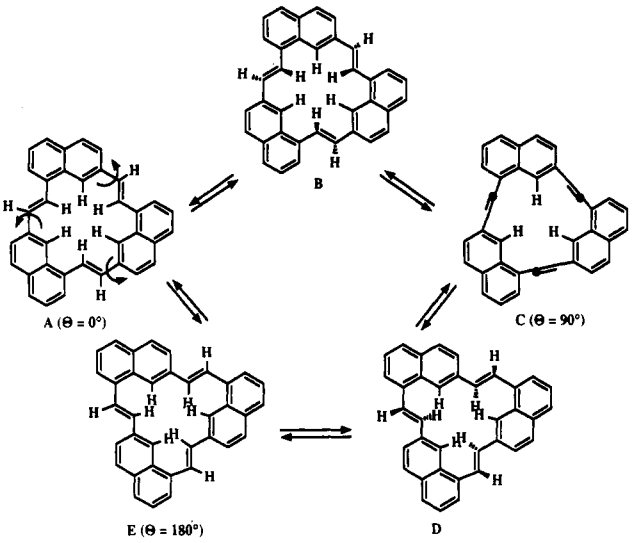


Synthesis. We report here on the [*abc*]-annelation of [18]annulene, which we were able to realize for the first time by fusing naphthalene or phenanthrene systems to the 18-membered ring (Schemes I and II). The decisive synthetic step in each case is performed by a 3-fold cyclic condensation of the corresponding methyl phenylimino arenes. The anilino group is a bulky leaving group, which leads to an extreme stereoselectivity (*E*:*Z* > 1000:1).[6] This fact is very important, as the probability for the desired cyclocondensation becomes zero by involvement of a single (*Z*)-configuration.

Whereas aldehyde **2a** is a well-known starting compound,[7] the corresponding phenanthrene system **10** has to be prepared in five steps (**5** → **10**). The additional introduction of two alkoxy groups enhances the solubility and serves finally to examine the LC properties of the annulenes **12**.

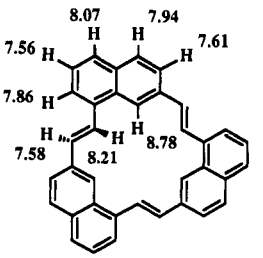
Molecular Conformations. A planar molecular geometry combined with the participation of the two resonance structures of the macrocycle mentioned at the beginning are of crucial importance for the possible diatropic behavior of **4** and **12**. In the conformation analysis one can tentatively proceed from a symmetric species with a C_3 axis. The planar conformations A and E (Scheme III), each possessing C_{3h} symmetry, ensure maximum conjugation, yet incorporate strong H–H interactions, i.e. a high steric energy. This applies especially for E. According to force field calculations[8] (MMX: Serena, PC M Version 4),

Scheme III



A and E represent transition states instead of local minima. Torsion around the angle θ, as shown by the arrows in A, leads to B (θ = 33°), the global minimum (ΔH_f = 164.3 kcal·mol^{-1}). The H–H interactions are minimized in the saddle region C (θ = 90°), but the conjugation is completely interrupted. Further torsion leads over the energetically high lying minimum D (θ = 140°, ΔH_f = 174.1 kcal·mol^{-1}), transition state E, and conformations enantiomeric to B, C, and D back to A. Of course, the rotation does not have to be synchronous in all three positions indicated in A. Flip processes are sufficient on one or two sides; additionally, the direction of the torsions can differ. The latter cases lead to C_1 conformations. As to the force field calculation, there is a minimum B′ (ΔH_f = 165.3 kcal·mol^{-1}) almost isoenergetic to B, in which two inner olefinic protons are standing upwards and one downwards. In addition, the calculation reveals that the rotation on one side is energetically somewhat more advantageous than the simultaneous rotation on two or three sides. The transformation B ⇄ A ⇄ B′ has an activation barrier $\Delta H^{\ddagger}$ = 2 kcal·mol^{-1}, the entire rotation A ⇄ E ⇄ A of about 7 kcal·mol^{-1}.

The ^{1}H-NMR spectrum of **4a** shows an AB spin pattern for the olefinic protons at δ = 8.21 and 7.58. The coupling constant ^3J of 16.0 Hz proves the (*E*)-configuration. NOE measurements by irradiation into the singlet of the inner aromatic protons at δ = 8.78 ppm lead to a positive signal in the differential spectrum at δ = 8.21 ppm. With the help of a selective introduction of deuterium in **4b** we get the assignment shown below:



The conclusions are as follows: **4** possesses C_3 symmetry either due to conformation B or to conformation B′, including fast equilibrations at all three olefinic bridges B′ ⇄ A. A conformation in which the outer olefinic protons of B are oriented inwards by torsion as in D is not populated. Finally, the resonance of the inner protons at lowest field excludes a diamagnetic ring current in the 18-mem-

(6) The corresponding condensation reaction of benzylideneaniline and methylarenes is known as Siegrist reaction: Siegrist, A. E. *Helv. Chim. Acta* **1967**, *50*, 906. Siegrist, A. E.; Meyer, H. R. *Ibid.* **1969**, *52*, 1282. Siegrist, A. E.; Liechti, P.; Meyer, H. R.; Weber, K. *Ibid.* **1969**, *52*, 2521.

(7) Nagel, D. L.; Kupper, R.; Antonson, K., Wallcave, L. *J. Org. Chem.* **1977**, *42*, 3626.

(8) Burkert, U.; Allinger, N. L. *Molecular Mechanics*; ACS Monograph 177; American Chemical Society: Washington D.C., 1982.

bered ring. **4** is therefore a system in which three aromatic "islands" are linked by three olefinic bridges with (*E*)-configurations.

Analogous NOE measurements of **12a** gave the unexpected result that irradiation of the inner aromatic proton at $\delta = 8.51$ results in a positive nuclear Overhauser effect in the high-field part of the olefinic AB system ($\delta = 8.34$ and 7.64, $^3J = 16.1$ Hz). Primarily this seems to be a hint of a conformation of type D. Although deuterium labeling of **4** shows that 6-H, 14-H, and 22-H (Scheme I) resonate at higher field than 5-H, 13-H, and 21-H, labeling of the corresponding positions of **12** gives the opposite result: 9-H, 18-H, and 27-H (Scheme II) resonate at lower field than 8-H, 17-H, and 26-H. This change may be due to the anisotropic effect of the phenanthrene moiety. That implies that **12**, like **4**, also adopts a B or B′ conformation.

It can be stated that the Kekulé structures **1** are only possible for the anellation types [*a*], [*abc*], and [*abcde*]. In contrast to the parent compound, the resonance structures **1** are not isoenergetic in condensed systems; actually, the compounds are described by benzenoid and quinoid resonance structures. The more quinoid building blocks are incorporated, the less the involvement of the corresponding resonance structure will be. Of the compounds cited in the beginning, a "macrocyclic diatropy" remains only in benzo[*a*]cyclooctadecene[2] and in phenanthro[3,4,5,6-*abcde*]cyclooctadecene.[4b] In an [*abc*]-fused annulene type with *one* condensed naphthalene a diatropic behavior of the macrocycle could be expected; however, for three fused naphthalenes the involvement of quinoid resonance structures is excluded by energetic reasons. The system adopts a nonplanar arrangement with aromatic and olefinic centers. Even in kekuléne, for which a superaromaticity[9] is postulated, essentially localized π-electron sextets are present.

Finally, another interesting property of **12b** shall be mentioned. This molecule is a real "superdisc" with a diameter of about 1.60 nm. The introduction of long flexible side chains (hexyloxy groups in **12b**) furnishes a highly mobile liquid crystalline phase, which can easily be characterized by its texture in a polarizing microscope.

Experimental Section

All melting points are uncorrected. Infrared (IR) absorption spectra were recorded on a Beckman Acculab 4 spectrophotometer in pure phase or in KBr. ^{1}H- and ^{13}C-NMR spectra were measured on Bruker AM 400 or AC 200 spectrometers with $CDCl_3$ as a solvent unless otherwise noted, using TMS as internal standard. Electron impact mass spectra (MS-EI, 70 eV) were obtained with a Varian CH 7A mass spectrometer. Field desorption (MS-FD) and high resolution electron impact (HRMS) mass spectra were measured on a Finnigan MAT 95 spectrometer. UV spectra were taken on a Zeiss MCS 320/340 UV–vis spectrophotometer. Fluorescence spectra were recorded on a Hitachi F-4000 fluorescence spectrophotometer. E. Merck silica gel 60 (70–230 mesh ASTM) was used for column chromatography. The photoreactions were carried out with a Hanovia 450-W Hg medium-pressure lamp with a Vycor filter.

1-Methyl-7-naphthaldehyde-*formyl-d* (2b). The reaction was carried out under the conditions described for **2a**[7] using DMF-d_7. Starting with 5.20 g (23.5 mmol) of 7-bromo-1-methylnaphthalene, 3.18 g (85%) of colorless crystals were obtained: mp 53 °C; IR (KBr) 3040, 2100, 2060, 1670, 1610, 1190, 810, 730 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.75 (s, 3 H, CH_3), 7.40 (d, 1 H, 2-H), 7.52 (t, 1 H, 3-H), 7.74 (d, 1 H, 4-H), 7.91 (d, 1 H, 5-H), 7.94 (d, 1 H, 6-H), 8.47 (s, 1 H, 8-H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 192.1 (t, $J = 27.0$ Hz, CDO), 136.8, 136.3, 133.8, 132.0, 130.6, 129.7, 128.9, 127.8, 126.5, 122.7, 19.2; MS-EI *m/z* 171 (100, M$^{\bullet+}$), 169 (50), 142 (21), 141 (50), 139 (17), 116 (14), 115 (27); HRMS *m/z* calcd for $C_{12}H_9DO$ 171.0794, obsd 171.0786.[10]

(*E*)-*N*-(4-Chlorophenyl)-1-methyl-7-naphthaldimine (3a). A solution of 6.10 g (35.9 mmol) of **2a**[7] and 4.58 g (35.9 mmol) of 4-chloroaniline in 50 mL of ethanol was stirred at 75 °C for 3 h. After being allowed to stand overnight at 5 °C 8.95 g (89%), colorless crystals were obtained: mp 88 °C; IR (KBr) 3040, 1600, 1570, 1470, 1180, 1080, 875, 840, 835, 745 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.75 (s, 3 H, CH_3), 7.21 (m, 2 H, ArH), 7.38 (m, 3 H, 2-H, ArH), 7.45 (t, 1 H, 3-H), 7.73 (d, 1 H, 4-H), 7.90 (d, 1 H, 5-H), 8.15 (m, 1 H, 6-H), 8.32 (s, 1 H, 8-H), 8.95 (s, 1 H, CHN); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 160.9 (CHN), 150.6, 135.3 (2 C), 133.5, 132.3, 131.4, 129.3, 129.2 (2 C), 127.8, 127.4 (2C), 126.3, 123.5, 122.2 (2C), 19.3; MS-EI *m/z* 281/279 (33/100, M$^{\bullet+}$, Cl pattern), 141 (24), 115 (17), 111 (21). Anal. Calcd for $C_{18}H_{14}NCl$: C, 77.29; H, 5.01; N, 5.01; Cl, 12.69. Found: C, 77.28; H, 4.97; N, 5.03; Cl, 12.72.

(*E*)-*N*-Phenyl-1-methyl-7-naphthaldimine-*imino-d* (3b). A solution of 2.82 g (16.5 mmol) of **2b** and 1.53 g (16.5 mmol) of aniline in 20 mL of ethanol was stirred at 75 °C for 3 h. The solvent was removed under reduced pressure, and the residue was dried for 5 h at 50 °C and 0.1 Torr to give 4.00 g (99%) of **3b** as a viscous pale yellow oil: IR (pure) 3050, 2160, 1600, 1570, 1480, 1185, 840, 800, 750, 690 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.76 (s, 3 H, CH_3), 7.23–7.31 (m, 3 H, ArH), 7.37 (d, 1 H, 2-H), 7.40–7.47 (m, 3 H, 3-H, ArH), 7.73 (d, 1 H, 4-H), 7.91 (d, 1 H, 5-H), 8.18 (m, 1 H, 6-H), 8.34 (s, 1 H, 8-H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 160.4 (t, $J = 24.0$ Hz, CDN), 152.2, 135.3 (2 C), 133.7, 132.3, 129.3, 129.1 (2 C), 127.6, 127.4, 127.3, 126.4, 125.9, 123.6, 120.9 (2 C), 19.3; MS-EI *m/z* 246 (100, M$^{\bullet+}$), 245 (23), 244 (34), 142 (10), 141 (10), 115 (9), 105 (11), 93 (53), 77 (40), 66 (18), 65 (11), 51 (9); HRMS calcd for $C_{18}H_{14}DN$ 246.1267, obsd 246.1256.

(5*E*,13*E*,21*E*)-1,23:7,9:15,17-Triethenotribenzo[*a*,*g*,*m*]-cyclooctadecene (4a). A solution of 1.20 g (10.5 mmol) of potassium *tert*-butoxide in 200 mL of DMF (which was freshly distilled under reduced pressure after refluxing with CaH_2) was heated under nitrogen to 75 °C. **3a** (1.50 g, 5.4 mmol) dissolved in 100 mL of DMF was added dropwise over 2 h to the stirred solution. The reaction was completed by stirring for additional 2 h at 90 °C. The dark mixture was cooled to 5 °C, and 200 mL of water was added slowly to yield a brown residue which was filtered off and washed with water. The residue was stirred in 200 mL of methanol for 3 h and then isolated again. This procedure was repeated with 50 mL of acetone and 30 mL of dichloromethane to leave 60 mg (7%) of **4a** as yellow needles: mp >330 °C; IR (KBr) 3040, 960, 825, 740 cm^{-1}; UV ($CHCl_3$) λ_{max} 291 (ϵ 41 000), 351 (ϵ 54 000) nm; fluorescence λ_{max} 480 nm; ^{1}H NMR ($CDCl_3$, 400 MHz) see text;[11] HRMS calcd (M$^{\bullet+}$) 456.1878, obsd 456.1829. Anal. Calcd for $C_{36}H_{24}$: C, 94.74; H, 5.26. Found: C, 94.98; H, 5.82.

(5*E*,13*E*,21*E*)-6,14,22-Trideuterio-1,23:7,9:15,17-triethenotribenzo[*a*,*g*,*m*]cyclooctadecene (4b).[12] The synthesis was performed as described for **4a** using 1.50 g (6.1 mmol) of **3b** and 1.37 g (12.2 mmol) of potassium *tert*-butoxide: yield 0.39 g (42%) of **4b** as a yellow powder; mp >330 °C; IR (KBr) 3040, 2240 (w), 1500, 1080, 880, 830, 745 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.55 (t, 3 H, 3-H, 11-H, 19-H), 7.61 (m, 3 H, ArH), 7.86 (d, 3 H, 4-H, 12-H, 20-H), 7.94 (d, 3 H, ArH), 8.06 (m, 3 H, 2-H, 10-H, 18-H), 8.20 (s, 3 H, olef H), 8.77 (s, 3 H, 8-H, 16-H, 24-H); MS-FD *m/z* 459 (100, M$^{\bullet+}$); HRMS calcd for $C_{36}H_{21}D_3$ 459.2066, obsd 459.2064.

2,3-Bis(hexyloxy)toluene (6b).[13] To a stirred solution of 12.40 g (0.10 mol) of 3-methylcatechol in 40 mL of dimethoxyethane was added 24.00 g (0.25 mol) of potassium hydroxide. After the addition of 41.25 g (0.25 mol) of 1-bromohexane and 4.00 g of Aliquat 336, the mixture was refluxed for 18 h. The solution was filtered and evaporated to leave a dark yellow oil which was purified by column chromatography (15 × 10 cm silica gel, di-

(9) Cioslowski, J.; O'Connor, P. B.; Fleischmann, E. D. *J. Am. Chem. Soc.* **1991**, *113*, 1086.

(10) For some less stable (air-sensitive) compounds high-resolution mass spectra have been measured instead of an elemental analysis.

(11) The solubility of **4a** in normal NMR solvents is less than 0.1 mg/mL; therefore, a ^{13}C NMR spectrum was not obtained.

(12) The deuterium content in **2b**, **3b**, **10c**, and **11c** is over 98%. A D/H exchange with the medium occurs only in the condensation reactions **3b** → **4b** and **11c** → **12c**. The degree grows with the reaction time. The final D/H ratio is about 3:1.

(13) In principle, 2,3-dimethoxytoluene can be generated in the same way; however, it is a commercially available compound.

chloromethane) to yield 28.40 g (97%) of **6b** as a pale yellow liquid: IR (pure) 3040, 3000, 2960, 2900, 1590, 1500, 1480, 1390, 1320, 1280, 1230, 1100, 780, 750 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.90 (t, 6 H, CH_3), 1.33 (m, 8 H, CH_2), 1.48 (m, 4 H, CH_2), 1.78 (m, 4 H, CH_2), 2.26 (s, 3 H, CH_3), 3.92 (t, 2 H, OCH_2), 3.94 (t, 2 H, OCH_2), 6.72, 6.73 (2 d, 2 H, 4-H, 6-H), 6.89 (t, 1 H, 5-H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 152.3, 146.9, 132.1, 123.2, 122.6, 111.2, 72.7, 68.6, 31.8, 31.6, 30.4, 29.4, 25.9, 25.8, 22.6 (2 C), 16.0, 14.0 (2 C); MS-EI m/z 292 (15, $M^{\bullet+}$), 208 (14), 124 (100, $M^{\bullet+} - 2C_6H_{12}$), 123 (8), 85 (12), 57 (10), 55 (12), 43 (52). Anal. Calcd for $C_{19}H_{32}O_2$: C, 78.08; H, 10.96. Found: C, 78.01; H, 10.99.

3,4-Dimethoxy-2-methylbenzaldehyde (7a). A solution of 15.22 g (0.10 mol) of **6a** in 30 mL of dichloromethane was cooled to 0 °C, and 33.80 g (0.13 mol) of tin tetrachloride was added dropwise within 20 min. The solution was stirred for 1 h at 0 °C, and 14.95 g (0.13 mol) of dichloromethyl methyl ether was added slowly. The dark red mixture was stirred for 1 h at 0 °C and was then allowed to reach room temperature while hydrogen chloride evolved. The solution was poured on 200 mL of crushed ice and stirred again for 1 h. The organic layer was separated and the aqueous layer was extracted with dichloromethane (3 × 50 mL). The combined organic layers were washed with water, saturated aqueous $NaHCO_3$ solution, and again with water prior to drying with Na_2SO_4. The solvent was removed under reduced pressure, and the residue was distilled at 104 °C (0.5 Torr) to give 17.10 g (95%) of **7a** containing 10% of the two other regioisomers. The solid obtained was recrystallized from methanol: mp 50 °C; IR (KBr) 2940, 2850, 2720, 1680, 1595, 1565, 1485, 1460, 1445, 1285, 1255, 1100, 1085, 1010, 965, 810, 775, 695, 630 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz)[14] δ 2.55 (s, 3 H, CH_3), 3.77 (s, 3 H, 3-OCH_3), 3.91 (s, 3 H, 4-OCH_3), 6.85 (d, J = 8.4 Hz, 1 H, 5-H), 7.54 (d, J = 8.4 Hz, 1 H, 6-H), 10.06 (s, 1 H, CHO); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 191.3 (CHO), 157.4, 147.6, 134.8, 129.8, 128.6, 109.2, 60.3, 55.8, 11.1; MS-EI m/z 180 (100, $M^{\bullet+}$), 179 (28), 165 (53), 137 (23), 121 (9), 94 (11), 93 (15), 91 (20), 79 (11), 77 (18), 66 (14), 65 (24), 51 (19). Anal. Calcd for $C_{10}H_{12}O_3$: C, 66.67; H, 6.67. Found: C, 66.63; H, 6.67.

3,4-Bis(hexyloxy)-2-methylbenzaldehyde (7b). A solution of 27.10 g (92.8 mmol) of **6b** in 30 mL of dichloromethane was cooled to 0 °C, and 36.25 g (139.0 mmol) of tin tetrachloride was added dropwise over 20 min. The solution was stirred for 1 h at 0 °C, and 16.00 g (139.0 mmol) of dichloromethyl methyl ether was added slowly. The dark red mixture was stirred for 1 h at 0 °C and was then allowed to reach room temperature while HCl gas evolved. The solution was poured on 200 mL of crushed ice and stirred for 1 h. The organic layer was separated, and the aqueous layer was extracted with dichloromethane (3 × 50 mL). The combined organic layers were washed with water, saturated aqueous $NaHCO_3$ solution, and again with water prior to drying with Na_2SO_4. The solvent was removed under reduced pressure to leave 28.3 g of raw product which was purified by column chromatography (10 × 40 cm silica gel, petroleum ether containing 10% ether). After the isolation of 1.56 g (5%) of 2,3-bis(hexyloxy)-4-methylbenzaldehyde and 2.20 g (7%) of 3,4-bis(hexyloxy)-5-methylbenzaldehyde, 20.82 g (70%) of **7b** was obtained as colorless oil: IR (pure) 2940, 2900, 2840, 2710, 1670, 1575, 1555, 1480, 1450, 1435, 1370, 1260, 1240, 1230, 1060, 800 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 0.88 (t, 6 H, CH_3), 1.32 (m, 8 H, CH_2), 1.45 (m, 4 H, CH_2), 1.78 (m, 4 H, CH_2), 2.55 (s, 3 H, CH_3), 3.86 (t, 2 H, OCH_2), 4.00 (t, 2 H, OCH_2), 6.81 (d, J = 8.4 Hz, 1 H, 5-H), 7.50 (d, J = 8.4 Hz, 1 H, 6-H), 10.05 (s, 1 H, CHO); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 191.4 (CHO), 157.0, 146.8, 134.9, 129.7, 128.2, 109.8, 73.0, 68.5, 31.7, 31.5, 30.2, 29.1, 25.7 (2 C), 22.6, 22.5, 14.0, 13.9, 11.3; EI-MS m/z 320 (20, $M^{\bullet+}$), 236 (18), 152 (100, $M^{\bullet+} - 2C_6H_{12}$), 151 (18), 85 (11), 57 (20), 55 (17), 43 (73). Anal. Calcd for $C_{20}H_{32}O_3$: C, 75.00; H, 10.00. Found: C, 74.82; H, 9.86.

(*E*,*Z*)-1-(3,4-Dimethoxy-2-methylphenyl)-2-phenylethene (8a). A solution of 1.29 g (56.0 mmol) of sodium in 50 mL of absolute ethanol was added quickly under argon at room temperature to a stirred solution of 21.70 g (56.0 mmol) of (phenylmethyl)triphenylphosphonium chloride in 200 mL of absolute ethanol. The mixture was stirred for 10 min, becoming light yellow and turbid; 10.07 g (56.0 mmol) of **7a** dissolved in 50 mL of absolute ethanol was added dropwise. The mixture was stirred for an additional 2 h, becoming colorless but still turbid. The solvent was removed completely in vacuo, 300 mL of hexane was added, and the mixture was refluxed for 10 min. The warm solution was filtered to remove $(C_6H_5)_3PO$; 4.06 g (29%) of colorless crystals of (*E*)-**8a** was gained by evaporating and cooling, mp 82 °C. The mother liquor was chromatographed (10 × 15 cm silica gel, petroleum ether–ether, 9/1) to yield 3.57 g (25%) of (*Z*)-**8a** as a colorless oil and 2.82 g of unreacted **7a**. (*E*)-**8a**: IR (KBr) 2990, 2960, 2940, 2840, 1590, 1490, 1450, 1300, 1280, 1220, 1085, 1010, 970, 810, 770, 730, 710 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.36 (s, 3 H, CH_3), 3.81 (s, 3 H, OCH_3), 3.88 (s, 3 H, OCH_3), 6.79 (d, J = 8.7 Hz, 1 H, ArH), 6.89 (d, J = 16.2 Hz, 1 H, olef H), 7.25 (t, 1 H, ArH), 7.28 (d, J = 16.2 Hz, 1 H, olef H), 7.34 (d, J = 8.7 Hz, 1 H, ArH), 7.36 (t, 2 H, ArH), 7.51 (d, 2 H, ArH); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 152.3, 147.2, 137.9, 130.4, 130.2, 128.8, 128.6 (2 C), 127.3, 126.5, 126.3 (2 C), 121.3, 109.8, 60.2, 55.7, 12.0; MS-EI m/z 254 (100, $M^{\bullet+}$), 239 (10), 209 (41), 181 (11), 179 (18), 165 (12), 153 (12), 127 (6), 115 (6), 89 (5), 77 (5). Anal. Calcd for $C_{17}H_{18}O_2$: C, 80.31; H, 7.09. Found: C, 80.27; H, 7.01. (*Z*)-**8a**: IR 3000, 2930, 2840, 1590, 1490, 1450, 1290, 1270, 1230, 1085, 1010, 810, 790, 700 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 2.20 (s, 3 H, CH_3), 3.79 (s, 3 H, OCH_3), 3.83 (s, 3 H, OCH_3), 6.56 (s, 2 H, olef H), 6.62 (d, J = 8.4 Hz, 1 H, ArH), 6.87 (d, J = 8.4 Hz, 1 H, ArH), 7.14 (m, 5 H, ArH); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 151.7, 147.3, 137.1, 130.5, 130.3, 130.1, 129.1, 128.8 (2 C), 128.0 (2 C), 126.8, 124.4, 109.4, 60.2, 55.5, 12.7.

(*E*,*Z*)-1-(3,4-Bis(hexyloxy)-2-methylphenyl)-2-phenylethene (8b). A solution of 0.87 g (37.5 mmol) of sodium in 30 mL of absolute ethanol was added quickly to a stirred solution of 14.57 g (37.5 mmol) of (phenylmethyl)triphenylphosphonium chloride in 150 mL of absolute ethanol under argon at room temperature. The mixture was stirred for 10 min, becoming light yellow and turbid; 12.00 g (37.5 mmol) of **7b** diluted in 50 mL of absolute ethanol was added dropwise. After stirring for 3 h the mixture became colorless but was still turbid. The solvent was removed completely in vacuo, 200 mL of hexane was added, and the mixture was refluxed for 10 min. The cold solution was filtered to remove $(C_6H_5)_3PO$ and evaporated to leave a brownish oil which was purified by chromatography (10 × 15 cm silica gel, ether–petroleum ether, 1/10). The stereoisomers of **8b** could be obtained in pure form as colorless oils by taking many small fractions. The bulk product, 12.4 g (84%) of an (*E*)/(*Z*) mixture, was used for the next reaction step. (*E*,*Z*)-**8b**: MS-EI m/z 394 (100, $M^{\bullet+}$), 310 (15), 227 (13), 226 (80), 225 (16), 179 (15), 165 (10), 57 (16), 55 (15), 43 (75), 41 (20). Anal. Calcd for $C_{27}H_{38}O_2$: C, 82.23; H, 9.64. Found: C, 82.17; H, 9.70. (*E*)-**8b**: IR (pure) 3020, 2940, 2900, 2840, 1590, 1480, 1455, 1370, 1280, 1260, 1200, 1060, 955, 795, 740, 690 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.91 (t, 6 H, CH_3), 1.35 (m, 8 H, CH_2), 1.50 (m, 4 H, CH_2), 1.80 (m, 4 H, CH_2), 2.34 (s, 3 H, CH_3), 3.90 (t, 2 H, OCH_2), 3.98 (t, 2 H, OCH_2), 6.76 (d, J = 8.6 Hz, 1 H, ArH), 6.87 (d, J = 16.1 Hz, 1 H, olef H), 7.23 (t, 1 H, ArH), 7.27 (d, J = 16.1 Hz, 1 H, olef H), 7.29 (d, J = 8.6 Hz, 1 H, ArH), 7.34 (t, 2 H, ArH), 7.49 (d, 2 H, ArH); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 151.9, 146.7, 138.0, 130.4, 130.1, 128.6 (2 C), 128.5, 127.2, 126.8, 126.3 (2 C), 120.9, 110.9, 72.9, 68.6, 31.8, 31.6, 30.4, 29.4, 25.8 (2 C), 22.7, 22.6, 14.0 (2 C), 12.2. (*Z*)-**8b**: IR 3020, 2940, 2900, 2840, 1590, 1480, 1460, 1440, 1370, 1290, 1260, 1210, 1070, 800, 780, 690 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 0.90 (t, 6 H, CH_3), 1.33 (m, 8 H, CH_2), 1.49 (m, 4 H, CH_2), 1.78 (m, 4 H, CH_2), 2.17 (s, 3 H, CH_3), 3.92 (m, 4 H, OCH_2), 6.51 (d, J = 12.3 Hz, 1 H, olef H), 6.59 (d, J = 12.3 Hz, 1 H, olef H), 6.59 (d, J = 8.4 Hz, 1 H, ArH), 6.81 (d, J = 8.4 Hz, 1 H, ArH), 7.11 (m, 5 H, ArH); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 151.4, 146.8, 137.3, 130.6, 130.4, 130.0, 129.5, 128.9 (2 C), 128.0 (2 C), 126.8, 124.1, 110.7, 72.8, 68.4, 31.8, 31.6, 30.4, 29.5, 25.9 (2 C), 22.7, 22.6, 14.1, 14.0, 12.9.

2,3-Dimethoxy-1-methylphenanthrene (9a). A solution of 3.00 g (11.8 mmol) of (*E*,*Z*)-**8a** and 1.79 g (7.1 mmol) of iodine in 2 L of dry cyclohexane was irradiated with the Vycor-filtered light of a 450-W Hg medium-pressure lamp for 47 h. The reaction was controlled by taking 20-mL samples every 6 h for ^1H NMR measurements. The solution was washed with diluted $Na_2S_2O_3$ to destroy excess iodine, dried with Na_2SO_4, and evaporated to leave a gray solid. The residue was dissolved in ether and chromatographed (7 × 5 cm Al_2O_3). A second chromatography

(14) The correlation of the signals was proved by NOE measurements.

(3 × 50 cm silica gel, dichloromethane) and recrystallization from ethanol gave 2.00 g (67%) of **9a**: mp 117–118 °C; IR 3040, 3010, 2980, 2940, 2920, 2800, 1590, 1490, 1470, 1450, 1440, 1410, 1380, 1260, 1230, 1200, 1110, 1070, 1010, 835, 810, 790, 750, 740 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz)[13] δ 2.66 (s, 3 H, CH_3), 3.90 (s, 3 H, OCH_3), 4.08 (s, 3 H, OCH_3), 7.55 (m, 1 H, 7-H), 7.61 (m, 1 H, 6-H), 7.67 (d, J = 9.1 Hz, 1 H, 9-H), 7.86 (d, J = 9.1 Hz, 1 H, 10-H), 7.87 (m, 1 H, 8-H), 7.95 (s, 1 H, 4-H), 8.57 (d, 1 H, 5-H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 152.4, 147.3, 131.7, 130.0, 128.6, 127.5, 127.4, 126.7, 126.1, 126.0, 124.8, 122.8, 122.6, 102.0, 66.7, 55.7, 11.6; MS-EI m/z 252 (100, $M^{\bullet+}$), 237 (25), 209 (13), 194 (15), 179 (12), 178 (11), 165 (27), 105 (12), 77 (12). Anal. Calcd for $C_{17}H_{16}O_2$: C, 80.95; H, 6.35. Found: C, 80.94; H, 6.35.

2,3-Bis(hexyloxy)-1-methylphenanthrene (9b). A solution of 6.00 g (15.2 mmol) of (*E,Z*)-**8b** and 2.60 g (10.2 mmol) of iodine in 2 L of dry cyclohexane was irradiated with the Vycor-filtered light of an 450-W Hg middle-pressure lamp for 42 h. The reaction was controlled by taking 20-mL samples every 6 h for ^1H NMR measurements. The solution was washed with diluted $Na_2S_2O_3$, dried with Na_2SO_4, and evaporated to leave a dark oil. The residue was diluted in ether and chromatographed (10 × 5 cm Al_2O_3, ether). A second column chromatography (10 × 15 cm silica gel, CH_2Cl_2) left 4.47 g (75%) of **9b** as a colorless oil: IR (pure) 3040, 2950, 2920, 2860, 1590, 1460, 1380, 1270, 1230, 1200, 1070, 810, 750 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.93 (t, 6 H, CH_3), 1.40 (m, 8 H, CH_2), 1.55 (m, 4 H, CH_2), 1.85 (m, 2 H, CH_2), 1.94 (m, 2 H, CH_2), 2.65 (s, 3 H, CH_3), 4.02 (t, 2 H, OCH_2), 4.21 (t, 2 H, OCH_2), 7.53 (m, 1 H, 7-H), 7.59 (m, 1 H, 6-H), 7.65 (d, J = 9.1 Hz, 1 H, 9-H), 7.86 (m, 2 H, 8-H, 10-H), 7.94 (s, 1 H, 4-H), 8.55 (d, 1 H, 5-H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 152.0, 146.7, 131.6, 130.0, 128.5, 127.3 (2 C), 126.3 126.0, 125.8, 124.5, 122.9, 122.6, 102.8, 73.4, 68.5, 31.8, 31.6, 30.4, 29.4, 26.0, 25.9, 22.7 (2 C), 14.0 (2 C), 11.8; MS-EI m/z 392 (56, $M^{\bullet+}$), 308 (20), 225 (18), 224 (100, $M^{\bullet+}-2C_6H_{12}$), 223 (25), 178 (11), 55 (14), 43 (57), 41 (17). Anal. Calcd for $C_{27}H_{36}O_2$: C, 82.65; H, 9.18. Found: C, 82.51; H, 9.12.

2,3-Dimethoxy-1-methylphenanthrene-9-carboxaldehyde (10a). A solution of 2.00 g (7.9 mmol) of **9a** in 30 mL of dichloromethane was cooled to 0 °C, and 2.26 g (11.9 mmol) of titanium tetrachloride was added dropwise within 20 min. The solution was stirred for 1 h at 0 °C, and 1.37 g (11.9 mmol) of dichloromethyl methyl ether was added dropwise. The dark red mixture was stirred again for 30 min at 0 °C and was then allowed to reach room temperature while HCl gas evolved. The solution was poured on 50 mL of crushed ice and stirred for 1 h. The organic layer was separated and the aqueous layer extracted with dichloromethane (3 × 30 mL). The combined organic layers were washed with water, saturated aqueous $NaHCO_3$ solution, and again with water prior to drying with Na_2SO_4. The solvent was removed under reduced pressure, and the residue was purified by column chromatography (3 × 80 cm silica gel, CH_2Cl_2) to leave 1.29 g (58%) of colorless crystals: mp 109 °C; IR (KBr) 3000, 2940, 2840, 2750, 1670, 1590, 1460, 1390, 1360, 1270, 1210, 1140, 1080, 1060, 1010, 770, 750 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.64 (s, 3 H, CH_3), 3.89 (s, 3 H, OCH_3), 4.07 (s, 3 H, OCH_3), 7.63 (m, 2 H, 6-H, 7-H), 7.77 (s, 1 H, 4-H), 8.18 (s, 1 H, 10-H), 8.45 (m, 1 H, 5-H), 9.31 (m, 1 H, 8-H), 10.24 (s, 1 H, CHO); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 193.4 (CHO), 155.2, 147.5, 137.2, 131.0, 130.1, 129.4, 128.2, 127.9, 127.7, 127.0, 125.8, 124.4, 122.6, 101.8, 60.8, 55.6, 11.5; MS-EI m/z 280 (100, $M^{\bullet+}$), 265 (21), 237 (8), 222 (5), 194 (8), 178 (7), 165 (24). Anal. Calcd for $C_{18}H_{16}O_3$: C, 77.14; H, 5.71. Found: C, 76.95; H, 5.80.

2,3-Bis(hexyloxy)-1-methylphenanthrene-9-carboxaldehyde (10b). A solution of 2.00 g (5.1 mmol) of **9b** in 15 mL of dichloromethane was cooled to 0 °C, and 1.82 g (7.0 mmol) of tin tetrachloride was added dropwise within 20 min. The solution was stirred for 1 h at 0 °C, and 0.81 g (7.0 mmol) of dichloromethyl methyl ether was added dropwise. The dark red mixture was stirred for 30 min at 0 °C and was then allowed to reach room temperature while HCl gas evolved. The solution was poured on 50 mL of crushed ice and stirred for 1 h. The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (3 × 30 mL). The combined organic layers were washed with water, saturated aqueous $NaHCO_3$ solution, and again with water prior to drying with Na_2SO_4. The solvent was removed under reduced pressure, and the residue was purified by column chromatography (3 × 80 cm silica gel, CH_2Cl_2) to leave 1.67 g (78%) of **10b** as a colorless oil: IR (pure) 2940, 2900, 2840, 2720, 1665, 1590, 1450,1380, 1360, 1270, 1210, 1180, 1070, 1050, 745 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 0.93 (t, 6 H, CH_3), 1.38 (m, 8 H, CH_2), 1.55, (m, 4 H, CH_2), 1.89 (m, 4 H, CH_2), 2.67 (s, 3 H, CH_3), 4.00 (t, 2 H, OCH_2), 4.19 (t, 2 H, OCH_2), 7.63 (m, 2 H, 6-H, 7-H), 7.81 (s, 1 H, 4-H), 8.26 (s, 1 H, 10-H), 8.48 (m, 1 H, 5-H), 9.33 (m, 1 H, 8-H), 10.27 (s, 1 H, CHO); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 193.6 (CHO), 154.9, 146.8, 137.6, 130.9, 130.1, 129.3, 127.9, 127.8, 127.5, 126.9, 125.8, 124.3, 122.6, 102.4, 73.4, 68.4, 31.7, 31.6, 30.3, 29.2, 25.9, 25.8, 22.6 (2 C), 14.1, 14.0, 11.7; MS-EI m/z 420 (71, $M^{\bullet+}$), 336 (25), 252 (100, $M^{\bullet+}-2C_6H_{12}$), 223 (8), 55 (12), 43 (69). Anal. Calcd for $C_{28}H_{36}O_3$: C, 80.00; H, 8.57. Found: C, 80.26; H, 8.67.

2,3-Dimethoxy-1-methylphenanthrene-9-carboxaldehyde-*formyl*-*d* (10c). A solution of 2.52 g (10.0 mmol) of **9a** in 15 mL of dichloromethane was cooled to 0 °C, and 3.91 g (15.0 mmol) of tin tetrachloride was added dropwise over 20 min. The solution was stirred for 1 h at 0 °C, and 1.74 g (15.0 mmol) of deuteriodichloromethyl methyl ether[15] was added dropwise. The dark red mixture was again stirred for 30 min at 0 °C and was then allowed to reach room temperature while HCl gas evolved. The solution was poured on 40 mL of cold D_2O and stirred for 1 h. The organic layer was separated and the aqueous layer extracted with CH_2Cl_2 (3 × 30 mL). The combined organic layers were washed with water, saturated aqueous $NaHCO_3$ solution, and again with water prior to drying with Na_2SO_4. The solvent was removed under reduced pressure, and the residue was purified by column chromatography (3 × 80 cm silica gel, CH_2Cl_2) to leave 1.57 g (56%) of colorless crystals: mp 130–131 °C; IR (KBr) 2990, 2930, 2820, 2120, 2080, 1650, 1580, 1480, 1450, 1380, 1360, 1270, 1210, 1200, 1150, 1090, 1070, 1060, 1000, 830, 780, 770, 740, 730 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.60 (s, 3 H, CH_3), 3.87 (s, 3 H, OCH_3), 4.05 (s, 3 H, OCH_3), 7.60 (m, 2 H, 6-H, 7-H), 7.70 (s, 1 H, 4-H), 8.11 (s, 1 H, 10-H), 8.39 (m, 1 H, 5-H), 9.28 (m, 1 H, 8-H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 193.1 (t, J = 26.0 Hz, CDO), 155.1, 147.4, 137.0, 130.8, 130.0, 129.3, 128.0, 127.8, 127.6, 127.0, 125.7, 124.3, 122.5, 101.8, 60.7, 55.6, 11.4; MS-EI m/z 281 (100, $M^{\bullet+}$), 266 (24), 238 (9), 195 (9), 166 (15), 165 (12); HRMS calcd for $C_{18}H_{15}DO_3$ 281.1162, obsd 281.1196.

(*E*)-*N*-(4-Chlorophenyl)-2,3-dimethoxy-1-methylphenanthren-9-imine (11a). A solution of 1.00 g (3.6 mmol) of **10a** and 0.46 g (3.6 mmol) of 4-chloroaniline in 20 mL of ethanol was stirred at 75 °C for 4 h. The solution was allowed to stand overnight at 5 °C to yield 1.23 g (88%) pale yellow crystals: mp 141 °C; IR (KBr) 3090, 2990, 2920, 2820, 1610, 1590, 1570, 1480, 1450, 1390, 1360, 1270, 1230, 1200, 1140, 1080, 1000, 820, 780, 760 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.69 (s, 3 H, CH_3), 3.91 (s, 3 H, OCH_3), 4.08 (s, 3 H, OCH_3), 7.23 (d, 2 H, ArH), 7.38 (d, 2 H, ArH), 7.66 (m, 2 H, 6-H, 7-H), 7.88 (s, 1 H, 4-H), 8.34 (s, 1 H, 10-H), 8.58 (m, 1 H, 5-H), 8.96 (s, 1 H, CHN), 9.27 (m, 1 H, 8-H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 161.7 (CHN), 154.0, 151.3, 147.5, 131.2, 130.4, 129.7, 129.6, 129.2 (2 C), 128.7, 127.7, 126.9, 126.6, 125.5, 125.3, 123.0, 122.3 (3 C), 101.8, 60.8, 55.7, 11.6; MS-EI m/z 391/389 (37/100, $M^{\bullet+}$), 374 (8), 358 (9), 330 (6), 302 (7), 190 (5), 165 (14), 111 (9). Anal. Calcd for $C_{24}H_{20}ClNO_2$: C, 73.94; H, 5.13; N, 3.59; Cl, 9.12. Found: C, 74.01; H, 5.11; N, 3.63; Cl, 9.34.

(*E*)-*N*-Phenyl-2,3-bis(hexloxy)-1-methylphenanthren-9-imine (11b). A mixture of 1.53 g (3.6 mmol) of **10b** and 0.34 g (3.6 mmol) of aniline was stirred for 6 h at 60 °C and evaporated several times at 15 Torr to remove water. While drying at 10^{-2} Torr the greenish oil crystallized to leave 1.80 g (100%) of crystals: mp 60 °C; IR (KBr) 3080, 3050, 2920, 2850, 1620, 1580, 1480, 1450, 1370, 1270, 1080, 750, 690 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.95 (m, 6 H, CH_3), 1.41 (m, 8 H, CH_2), 1.57 (m, 4 H, CH_2), 1.86 (m, 2 H, CH_2), 1.96 (m, 2 H, CH_2), 2.72 (s, 3 H, CH_3), 4.03 (t, 2 H, OCH_2), 4.22 (t, 2 H, OCH_2), 7.27 (t, 1 H, ArH), 7.33 (d, 2 H, ArH), 7.45 (t, 2 H, ArH), 7.65 (m, 2 H, 6-H, 7-H), 7.91 (s, 1 H, 4-H), 8.41 (s, 1 H, 10-H), 8.59 (m, 1 H, 5-H), 9.05 (s, 1 H, CHN), 9.28 (m, 1 H, 8-H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 161.3 (CHN), 153.6, 153.0, 146.8, 130.4, 129.4, 129.3 (2 C), 129.1 (2 C), 128.6, 127.8, 126.7, 126.4, 125.6, 125.5, 125.2, 122.9, 120.9 (2 C), 102.6, 73.4, 68.4, 31.8, 31.6, 30.4, 29.3, 25.9, 25.8, 22.6 (2 C), 14.0 (2 C), 11.8; MS-EI m/z 495 (100, $M^{\bullet+}$), 411 (15), 410 (14), 327 (17), 326

(15) Dichlorodeuteriomethyl methyl ether was prepared according to the procedure described in Gross, H.; Rieche, A.; Höft, E.; Beyer, E. *Org. Synth.* **1967**, *47*, 47.

(42), 298 (17), 252 (9), 104 (7), 55 (7), 43 (65). Anal. Calcd for $C_{34}H_{41}NO_2$: C, 82.42; H, 8.24; N, 2.83. Found: C, 82.12; H, 8.38; N, 2.91.

(*E*)-*N*-Phenyl-2,3-dimethoxy-1-methylphenanthren-9-imine-*imino-d* (11c). A solution of 1.38 g (4.9 mmol) of **10c** and 0.46 g (4.9 mmol) of aniline in 8 mL of ethanol was stirred at 75 °C for 3 h and then allowed to stand overnight at 0 °C to yield 1.62 g (92%) of pale yellow crystals: mp 118 °C; IR (KBr) 3050, 2990, 2960, 2920, 2820, 1585, 1570, 1480, 1450, 1360, 1260, 1230, 1200, 1140, 1095, 1070, 1060, 1000, 840, 830, 775, 740, 690 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.69 (s, 3 H, CH_3), 3.91 (s, 3 H, OCH_3), 4.08 (s, 3 H, OCH_3), 7.27 (t, 1 H, ArH), 7.33 (d, 2 H, ArH), 7.45 (t, 2 H, ArH), 7.65 (m, 2 H, 6-H, 7-H), 7.87 (s, 1 H, 4-H), 8.36 (s, 1 H, 10-H), 8.56 (m, 1 H, 5-H), 9.26 (m, 1 H, 8-H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 160.9 (t, J = 25.0 Hz, CDN), 153.8, 152.9, 147.4, 130.3, 129.4, 129.3, 129.1 (2 C), 129.0, 128.6, 127.8, 126.8, 126.4, 125.6, 125.4, 125.3, 122.9, 120.9 (2 C), 101.8, 60.7, 55.6, 11.6; MS-EI m/z 356 (100, $M^{\cdot+}$), 355 (70), 354 (10), 341 (7), 325 (8), 178 (11), 77 (12); HRMS calcd for $C_{24}H_{20}DNO_2$ 356.1635, obsd 356.1660.

(8*E*,17*E*,26*E*)-6,7,15,16,24,25-Hexamethoxytriphenanthro[8,9,10-*abc*:8,9,10-*ghi*:8,9,10-*mno*]cyclooctadecene (12a). The synthesis described for **4a** using 1.00 g (6.6 mmol) **11a** and 0.58 g (5.1 mmol) of potassium *tert*-butoxide yielded 50 mg (7%) of **12a** as yellow crystals: mp >280 °C; IR (KBr) 3060, 2920, 2820, 1580, 1470, 1450, 1410, 1380, 1270, 1230, 1200, 1080, 960, 770, 750 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz)[14] δ 4.01 (s, 9 H, 7-OCH_3, 16-OCH_3, 25-OCH_3), 4.18 (s, 9 H, 6-OCH_3, 15-OCH_3, 24-OCH_3), 7.65 (d, J = 16.1 Hz, 3 H, 8-H, 17-H, 26-H), 7.69 (m, 6 H, 2-H, 3-H, 11-H, 12-H, 20-H, 21-H), 8.09 (s, 3 H, 5-H, 14-H, 23-H), 8.34 (d, J = 16.1 Hz, 3 H, 9-H, 18-H, 27-H), 8.49 (m, 3 H, 1-H, 10-H, 19-H), 8.51 (s, 3 H, 28-H, 29-H, 30-H), 8.66 (m, 3 H, 4-H, 13-H, 22-H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 152.7, 147.6, 136.4, 133.4, 131.0, 130.0, 128.8, 127.7, 126.6, 126.4, 125.7, 125.1, 123.2, 123.1, 120.2, 103.4, 60.6, 56.0; MS-FD m/z 786 (100, $M^{\cdot+}$). Anal. Calcd for $C_{54}H_{42}O_6$: C, 82.44; H, 5.34. Found: C, 82.16; H, 5.59.

(8*E*,17*E*,26*E*)-6,7,15,16,24,25-Hexakis(hexyloxy)triphenanthro[8,9,10-*abc*:8,9,10-*ghi*:8,9,10-*mno*]cyclooctadecene (12b). A solution of 1.16 g (10.3 mmol) of potassium *tert*-butoxide in 100 mL of DMF (which was freshly distilled under reduced pressure after refluxing with CaH_2) was heated under nitrogen to 85 °C and 1.70 g (3.4 mmol) of **11b** dissolved in 120 mL of DMF was added dropwise over 90 min with vigorous stirring. The reaction was complete after an additional 2 h at 85 °C. The dark mixture was cooled to 5 °C, and 100 mL of water and 100 mL of 2 N HCl were added dropwise. After the solvent was removed a brown glutinous residue was left which was allowed to stand overnight in methanol. The methanol was removed, and the slurry was taken up in CH_2Cl_2 followed by column chromatography (3 × 100 cm silica gel, CH_2Cl_2). The first fraction contained the greenish fluorescing product which was recrystallized from acetone to yield 135 mg (10%) of green-yellow needles: mp 115 °C (clearing point 192 °C); IR (KBr) 3060, 2940, 2900, 2840, 1570, 1470, 1430, 1410, 1370, 1270, 1240, 1220, 1180, 1070, 1050, 970, 830, 770, 740 cm^{-1}; UV (hexane) λ_{max} 251 (ϵ 107 000), 331 (ϵ 63 000) nm; fluorescence λ_{max} 490 nm; ^1H NMR ($CDCl_3$, 400 MHz)[16] δ 0.89 (t, 9 H, CH_3), 1.02 (t, 9 H, CH_3), 1.28 (m, 12 H, CH_2), 1.45 (m, 18 H, CH_2), 1.65 (m, 6 H, CH_2), 1.90 (m, 6 H, CH_2), 1.99 (m, 6 H, CH_2), 4.03 (t, 6 H, 7-OCH_2, 16-OCH_2, 25-OCH_2), 4.19 (t, 6 H, 6-OCH_2, 15-OCH_2, 24-OCH_2), 7.34 (d, J = 16.1 Hz, 3 H, 8-H, 17-H, 26-H), 7.52 (t, 3 H, 2-H, 11-H, 20-H), 7.60 (t, 3 H, 3-H, 12-H, 21-H), 7.94 (s, 3 H, 5-H, 14-H, 23-H), 8.11 (d, J = 16.1 Hz, 3 H, 9-H, 18-H, 27-H), 8.19 (s, 3 H, 28-H, 29-H, 30-H), 8.40 (d, 3 H, 1-H, 10-H, 19-H), 8.54 (d, 3 H, 4-H, 13-H, 22-H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 152.1 (C-6, C-15, C-24), 146.8 (C-7, C-16, C-25), 135.9 (C-9, C-18, C-27), 132.9 (C-9a, C-18a, C-27a), 130.6 (C-9b, C-18b, C-27b), 129.8 (C-4a, C-13a, C-22a), 128.9 (C-7a, C-16a, C-25a), 127.2 (C-4b, C-13b, C-22b), 126.0 (C-3, C-12, C-21), 125.7 (C-2, C-11, C-20), 125.5 (C-28a, C-29a, C-30a), 125.4 (C-1, C-10, C-19), 123.1 (C-8, C-17, C-26), 122.8 (C-4, C-13, C-22), 119.2 (C-28, C-29, C-30), 103.7 (C-5, C-14, C-23), 73.4 (OCH_2), 68.5 (OCH_2), 32.0, 31.8, 30.7, 29.6, 26.1, 25.9, 22.7, 22.6, 14.1, 14.0; MS-FD m/z 1206.8 (100, $M^{\cdot+}$). Anal. Calcd for $C_{84}H_{102}O_6$: C, 83.58; H, 8.46. Found: C, 83.51; H, 8.52.

(8*E*,17*E*,26*E*)-9,18,27-Trideuterio-6,7,15,16,24,25-hexamethoxytriphenanthro[8,9,10-*abc*:8,9,10-*ghi*:8,9,10-*mno*]-cyclooctadecene (12c). The synthesis described for **4a** using 0.80 g (2.3 mmol) of **11c** and 1.51 g (13.5 mmol) of potassium *tert*-butoxide furnished 100 mg (17%) of crude product. (The MS-FD showed that most of this had lost under the strong basic conditions one methyl group.) **12c** was separated by column chromatography (3 × 7 cm Al_2O_3, $CHCl_3$) to leave 10 mg (2%) of yellow crystals: mp >280 °C; IR (KBr) 3060, 2920, 2820, 1590, 1490, 1460, 1430, 1390, 1290, 1270, 1250, 1220, 1100, 770, 750 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 4.00 (s, 9 H, 7-OCH_3, 16-OCH_3, 25-OCH_3), 4.18 (s, 9 H, 6-OCH_3, 15-OCH_3, 24-OCH_3), 7.62 (m, 3 H, 8-H, 17-H, 26-H), 7.68 (m, 6 H, 2-H, 3-H, 11-H, 12-H, 20-H, 21-H), 8.07 (s, 3 H, 5-H, 14-H, 23-H), 8.46 (m, 3 H, 1-H, 10-H, 19-H), 8.48 (s, 3 H, 28-H, 29-H, 30-H), 8.66 (m, 3 H, 4-H, 13-H, 22-H); MS-FD m/z 789 (100, $M^{\cdot+}$); HRMS calcd for $C_{54}H_{39}D_3O_6$ 789.3170, obsd 789.3193.

(16) The enhanced solubility of **12b** permits NMR measurements in higher concentrations (150 mg/mL). The δ values of the ^1H NMR spectrum show high-field shifts $\Delta\delta \leq 0.4$ ppm with increasing concentration.