Synthesis of Spiro Polycyclic Aromatic Hydrocarbons by Intramolecular Palladium-Catalyzed Arylation

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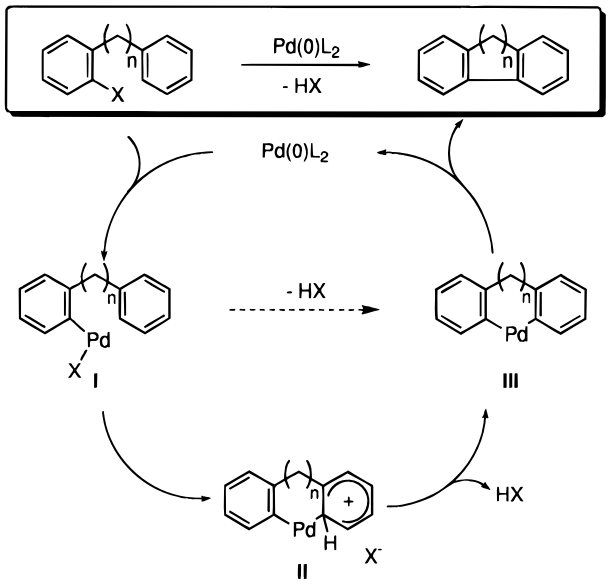
The palladium-catalyzed intramolecular arylation reaction has been applied to the synthesis of the spiro polycyclic aromatic hydrocarbons and planar polycyclic aromatic hydrocarbons by formation of a six-membered ring. The reaction proceeds more readily with aryl bromides substituted with electron-withdrawing groups by using palladium acetate in *N*,*N*-dimethylformamide as the solvent. For the less reactive *p*-methoxyaryl derivatives the use of LiI as an additive was shown to give the best results. The results obtained in the cyclization of nitro derivatives **21** and **23** suggest that the second step of the cyclization reaction is not an electrophilic substitution reaction.

Introduction

The palladium-catalyzed intramolecular arylation reaction offers one of the conceptually most simple solutions for the synthesis of carbo- and heterocycles from the corresponding halides (X = Br, I) (Scheme 1).[1,2] The utility of this process has been recently extended by Rice using aryl triflates as the substrates for the formation of a five-membered ring in the synthesis of carbocycles (X = OTf).[3,4] The reaction has usually been carried out with $Pd(OAc)_2$ or $Pd(PPh_3)_2Cl_2$ as the catalyst in polar solvents (DMF or DMA) at relatively high temperatures (120−170 °C) in the presence of a base to trap HX. However, despite the synthetic potential of this reaction, very little is known about its mechanism. A simplified mechanistic hypothesis for the arylation reaction is outlined in Scheme 1 (ligands L on Pd are removed for clarity). The initially formed arylpalladium(II) complex $[PdAr(L)_nX]$ **I** (L = phosphine or solvent molecule, $n = 1$ or 2)[5] may react with the aryl ring as an electrophile to form **II**,[1a,6,7] followed by a proton loss to form $[PdArAr'(L)_n]$ **III**. Finally, reductive elimination of **III** would give rise to the biaryl product and the reactive Pd(0) species. However, the fact that the reaction tolerates both strongly electron-withdrawing and electron-releasing groups is difficult to reconcile with this working mechanistic hypothesis.[1b,8]

Scheme 1



We wished to demonstrate the formation of six-membered rings by using the palladium-catalyzed arylation reaction as a prelude to the synthesis of more complex polycyclic aromatic hydrocarbons related to the

[⊗] Abstract published in *Advance ACS Abstracts,* February 15, 1997.

(1) Synthesis of heterocycles by palladium-catalyzed arylation: (a) Ames, D. E.; Bull, D. *Tetrahedron* **1982**, *38*, 383. (b) Ames, D. E.; Opalko, A. *Synthesis* **1983**, 234. (c) Ames, D. E.; Opalko, A. *Tetrahedron* **1984**, *40*, 1919. (d) Kuroda, T.; Suzuki, F. *Tetrahedron Lett.* **1991**, *32*, 6915. (e) Kozikowski, A. P.; Ma, D. *Tetrahedron Lett.* **1991**, *32*, 3317.

(2) Application of the palladium-catalyzed arylation to the synthesis of biaryls: (a) Bringmann, G.; Walter, R.; Weirich, R. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 977. (b) Stadlbauer, W.; Laschober, R.; Kappe, T. *Liebigs Ann. Chem.* **1990**, 531. (c) Deshpande, P. P.; Martin, O. R. *Tetrahedron Lett.* **1990**, *31*, 6313. (d) Hosoya, T.; Takashiro, E.; Matsumoto, T.; Suzuki, K. *J. Am. Chem. Soc.* **1994**, *116*, 1004. (e) Bringmann, G.; Keller, P. A.; Rölfing, K. *Synlett* **1994**, 423.

(3) Synthesis of carbocycles by palladium-catalyzed arylation: (a) Rice, J. E.; Cai, Z.-W.; He, Z.-M.; LaVoie, E. J. *J. Org. Chem.* **1995**, *60*, 8101. (b) Rice, J. E.; Cai, Z.-W. *J. Org. Chem.* **1993**, *58*, 1415. (c) Rice, J. E.; Cai, Z.-W. *Tetrahedron Lett.* **1992**, *33*, 1675.

(4) For the intermolecular palladium-catalyzed arylation, see: (a) Akita, Y.; Inoue, A.; Yamamoto, K.; Ohta, A.; Kurihara, T.; Shimizu, M. *Heterocycles* **1985**, *23*, 2327. (b) Aoyagi, Y.; Inoue, A.; Koizumi, I.; Hashimoto, R.; Tokunaga, K.; Gohma, K.; Komatsu, J.; Sekine, K.; Miyafuji, A.; Kunoh, J.; Honma, R.; Akita, Y.; Ohta, A. *Heterocycles* **1992**, *33*, 257. (c) Dyker, G. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1023. (d) Dyker, G. *J. Org. Chem.* **1993**, *58*, 6426. (e) Dyker, G. *Chem. Ber.* **1994**, *127*, 739.

(5) Pd(0) may coordinate with the added halide to form reactive anionic species: (a) Amatore, C.; Azzabi, M.; Jutand, A. *J. Am. Chem. Soc.* **1991**, *113*, 1670. (b) Amatore, C.; Azzabi, M.; Jutand, A. *J. Am. Chem. Soc.* **1991**, *113*, 8375. (c) Amatore, C.; Jutand, A.; Suarez, A. *J. Am. Chem. Soc.* **1993**, *115*, 9531. (d) Amatore, C.; Carré, E.; Jutand, A.; M'Barki, M. A.; Meyer, G. *Organometallics* **1995**, *14*, 5605. (e) Amatore, C.; Carré, E.; Jutand, A.; Tanaka, H.; Ren, Q.; Torii, S. *Chem. Eur. J.* **1996**, *2*, 957.

(6) Farina, V. In *Comprehensive Organometallic Chemistry II;* Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, 1995; Vol. 12, Chapter 3.4, pp 228−229.

(7) (a) An electrophilic pathway has been shown to operate in somewhat related palladation reactions: Canty, A. J. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, 1995; Vol. 9, Chapter 5 and references cited therein. (b) The synthesis of palladacycles by intramolecular palladation of an aryl ring has been demonstrated to proceed by electrophilic substitution: Catellani, M.; Chiusoli, G. P. *J. Organomet. Chem.* **1992**, *425*, 151.

(8) Additionally, products derived from a 1,5-hydrogen abstraction, characteristic of radical intermediates, have also been observed in the reaction of some aryl triflates.[3b]

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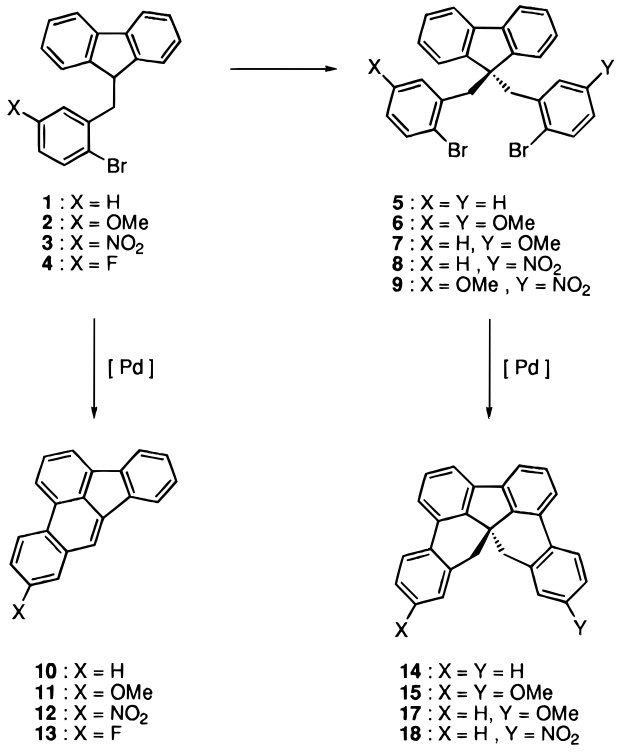
Scheme 2

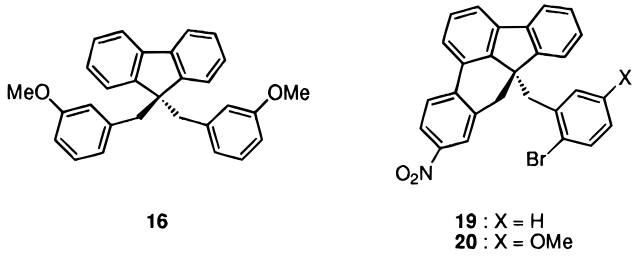


corannulenes.[9] Although the synthesis of six-membered heterocycles has been reported,[1,2] only a few carbocycles of this size have been prepared by using this reaction.[2e] We also wished to test the mechanistic proposal of Scheme 1 by determining the effect of substituents on the aromatic nucleus on the reaction. Herein, we report the successful application of the palladium-catalyzed arylation for the construction of spiro polycyclic hydrocarbons related to the helicenes, the synthesis of some planar polycyclic aromatic hydrocarbons, as well as some observations that may be of some relevance to the mechanism of this reaction.

Results and Discussion

Alkylation of the lithium anion of fluorene with an *o*-bromobenzyl bromide gave derivatives **1**−**4** (Scheme 2). Further reaction of the anions of **1**−**3** with a second equiv of the appropriate *o*-bromobenzyl bromide gave dibenzylated derivatives **5**−**9** in 51−71% yield. The cyclization of **1** with $Pd(OAc)_2$ (5 mol %), K_2CO_3 (8 equiv), and Bu_4NBr (3 equiv) (standard conditions)[10] in DMF (130 °C, 48 h) proceeded with concomitant dehydrogenation to afford benz[*e*]acephenanthrylene (**10**) in 52% yield.[11] The cyclization of methoxy derivative **2** was very sluggish under these conditions. However, replacing Bu_4NBr with LiI (2.5 equiv) led to **11** in 50% yield (130 °C, 4 d). In contrast, the cyclization of *p*-nitroaryl derivative **3** proceeded readily at 70 °C under the standard conditions in DMF to give **12** in 57% yield after 48 h. Similarly, fluoro derivative **13** was obtained in 65% yield from **4**. This straightforward synthesis of benz[*e*]acephenanthrylenes (benzo[*b*]fluoranthenes) proceeds in just two steps from readily available materials and could be easily applied for the preparation of substituted derivatives.[12] It should be stressed that in all cases, and in contrast with alternative procedures,[12a−c] a single regioisomer was obtained in the cyclization.

Dibenzylated fluorene **5** gave spiro derivative **14** in 68% yield under the standard conditions (130 °C, 24 h) (Scheme 2). The reaction of dimethoxy derivative **6** under these conditions failed to give spiro **15**. Instead, reduced fluorene **16** was isolated as the only product in 35% yield.[13] The use of LiI as the additive (DMF, 135 °C, 5 d) allowed for the formation of **15**, albeit in only 30% yield. However, no cyclization was observed in the presence of LiBr or LiCl as the additives. Reaction of unsymmetrically substituted **7** under these conditions gave **17** as the only product (62% yield). On the other hand, the cyclization of **8** furnished **18** (53% yield) under the standard conditions at 95 °C. Interestingly, by performing the reaction at 70 °C for 48 h in the presence of only 0.5 equiv of $BnMe_3NBr$, dihydrobenz[*e*]acephenanthrylene **19** was obtained as the only product (isolated in 47% yield). Under these conditions, methoxy nitro derivative **9** yielded **20** (67% yield). The selective cyclization of the *p*-nitroaryl bromides of **8** and **9** is consistent with the more facile oxidative addition of aryl halides substituted with electron-withdrawing groups.[1a,14] Additionally, the faster cyclization of substrates bearing a *p*-nitro substituent suggests that the oxidative addition is the rate-determining step of the palladium-catalyzed arylation.



16 **19** : X = H
20 : X = OMe

Alternatively, the selective cyclization of *p*-nitroaryl substrates may be due to the higher electrophilicity of the derived palladium(II) complexes **I** toward the second aryl ring (Scheme 1). In order to determine if the second step of the reaction is an electrophilic substitution process, we prepared two substrates bearing a nitro group ortho to the position attacked by the palladium(II). Thus, benzylation of 2-nitrofluorene afforded **21** (75% yield), which was cyclized at 70 °C in DMF under the standard conditions but with only 0.5 equiv of $BnMe_3NBr$ to give **22** in 53% yield (eq 1). On the other hand, reaction of

(9) Rabideau, P. W.; Sygula, A. *Acc. Chem. Res.* **1996**, *29*, 235.

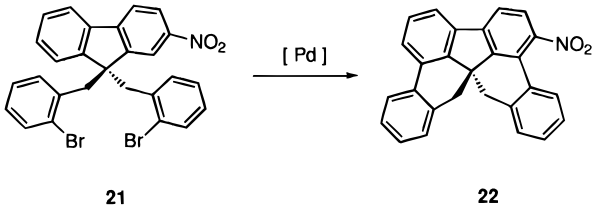
(10) Standard conditions refer to the use of $Pd(OAc)_2$ (5−12 mol%), K_2CO_3 (2−8 equiv), and Bu_4NBr or $BnMe_3NBr$ (2−3 equiv).

(11) Either no cyclization of **2** or very low yields were observed in the presence of PPh_3 or $AsPh_3$. Reaction with $Pd(CH_3CN)_2Cl_2$ as the catalyst gave **10** in 30% yield. The use of DBU, 1,8-bis(dimethylamino)-naphthalene, and *N*-methylimidazole as the base and/or ligand for Pd gave only recovered starting material.

(12) Benz[*e*]acephenanthrylenes are an important class of environmental carcinogens. For recent syntheses, see: (a) Cho, B. P.; Zhou, L. *Tetrahedron Lett.* **1996**, *37*, 1535. (b) Cho, B. P. *Tetrahedron Lett.* **1995**, *36*, 2403. (c) Tanga, M. J.; Bupp, J. E. *J. Org. Chem.* **1993**, *58*, 4173. (d) Cho, B. P.; Kim, M.; Harvey, R. G. *J. Org. Chem.* **1993**, *58*, 5788. (e) Cho, B. P.; Harvey, R. G. *J. Org. Chem.* **1987**, *52*, 5668. (f) Amin, S.; Huie, K.; Hussain, N.; Balanikas, G.; Carmella, S. G.; Hecht, S. *J. Org. Chem.* **1986**, *51*, 1206. (g) Amin, S.; Huie, K.; Hussain, N.; Balanikas, G.; Hecht, S. S. *J. Org. Chem.* **1985**, *50*, 1948.

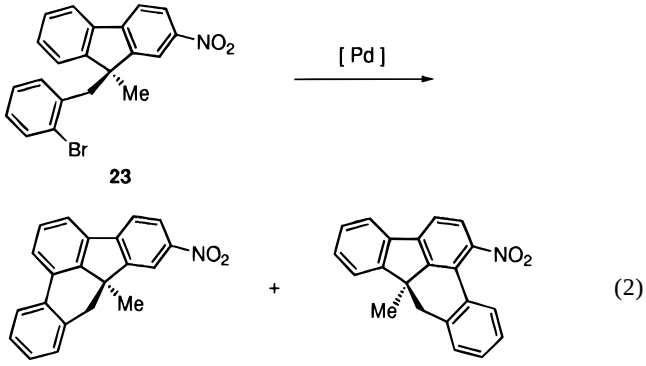
(13) For the formation of reduced products under palladium-catalyzed conditions, see: Saá, J. M.; Dopico, M.; Martorell, G.; García-Raso, A. *J. Org. Chem.* **1990**, *55*, 991 and references cited therein.

(14) Stille, J. K. In *The Chemistry of the Metal−Carbon Bond*; Hartley, F. R., Patai, S., Eds.; Wiley: Chichester, 1985; Vol. 2, Chapter 9.



21 **22** (1)

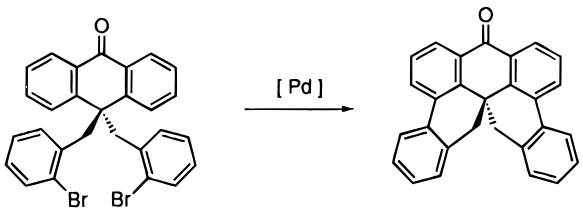
the potassium anion of 9-methyl-2-nitrofluorene[15] with *o*-bromobenzyl bromide afforded **23**, which reacted under similar conditions at 100 °C to give a 2:1 mixture of **24** and **25** in 62% yield (eq 2). The observed ratio probably



23 **24** **25** (2)

reflects the steric influence of the nitro group. These results are not easily reconciled with a cyclization proceeding by a rate-determining electrophilic attack of an arylpalladium(II) complex **I** onto the aryl ring to form an arenium cation.[16] The somewhat related alkylation of aryl substrates by a cationic benzylpalladium complex has been demonstrated to proceed in a low-coordinating solvent such as $CDCl_3$ by an electrophilic substitution pathway.[17] However, a different reaction course was observed in a coordinating solvent.[17] Although further mechanistic work is clearly necessary to clarify this point, the result with **23** suggests that the second step of the intramolecular arylation reaction (see Scheme 1) is not an electrophilic substitution reaction. An attractive mechanistic alternative, suggested by the required presence of carbonate as the base, is the formation of intermediate **III** from **I** (X = carbonate) by an intramolecular aromatic C−H activation.[18,19]

The intramolecular arylation reaction was also applied for the cyclization of **26** readily prepared by alkylation of anthrone. The palladium-catalyzed cyclization of **26** proceeded under the standard conditions (140 °C, 36 h) to give **27** in 80% yield (eq 3).



26 **27** (3)

In contrast with the successful cyclizations of the above substrates, acenaphthene derivative **28**, prepared by Wittig olefination of acenaphthenequinone[20] followed by catalytic hydrogenation, led only to traces of cyclized product **30** (Scheme 3). The crude reaction mixtures showed that **28** suffered dehydrogenation and reductive elimination of the bromide as the major decomposition pathways. Interestingly, the reaction of its methyl enol ether **29** with $Pd(OAc)_2$ proceeded with concomitant demethylation and oxidation to give known 4*H*-cyclopenta[*def*]chrysen-4-one (**30**).[21] The oxidation observed in this process is reminiscent of that observed in the oxidation of silyl enol ethers by $Pd(OAc)_2$ to give enones.[22]

This work demonstrates that the palladium-catalyzed intramolecular reaction can be applied for the formation of six-membered ring carbocycles. The reaction proceeds more readily with aryl bromides substituted with electron-withdrawing groups. For the less reactive *p*-methoxyaryl derivatives the use of LiI as an additive was shown to give the best results. The rate enhancement observed in the presence of LiI is a likely manifestation of the known iodide catalysis effect on the oxidative addition step. The ready construction of spiro derivatives **14**−**18**, **22**, and **27** should allow for the synthesis of chiral trans-chelating ligands based on these chiral hexacyclic scaffolds. Progress on the application of this reaction for the synthesis of more complex substrates is underway.

Experimental Section

Solvents were purified and dried using standard procedures. "Usual workup" means extraction with the stated solvent, washing with 10% aqueous HCl, drying (Na_2SO_4 or $MgSO_4$), filtration, and evaporation. Chromatography purifications were carried out using flash grade silica gel. All reactions were carried out under an Ar atmosphere.

The following compounds were prepared according to the published procedures: 1-bromo-2-(bromomethyl)-4-methoxybenzene,[23] 1-bromo-2-(bromomethyl)-4-nitrobenzene,[24] 9-methyl-2-nitrofluorene,[15] and 1-bromo-2-(bromomethyl)-4-fluorobenzene.[25]

General Procedures for the Synthesis of 1-8, 21, and 23: Method A. Fluorene was deprotonated with BuLi (1 equiv) in THF (−78 °C, 3 h) followed by addition of a solution of the corresponding *o*-bromobenzyl bromide (0.8 equiv) in THF. Usual workup and chromatographic purification (EtOAc−hexane mixtures) led to pure compounds. **Method B.** Deprotonation of **1** with a suspension of NaH (60%) (1 equiv) in DMF (2 mL) at 23 °C was followed by addition of a solution of the

(15) Klemm, L. M.; Huber, E.; Klopfenstein, C. E. *J. Org. Chem.* **1964**, *29*, 1960.

(16) The palladium-catalyzed synthesis of dibenzofurans from 2-bromophenyl ethers has been shown to take place in the presence of a para or meta nitro group.[1b]

(17) Gretz, E.; Sen, A. *J. Am. Chem. Soc.* **1986**, *108*, 6038.

(18) This reaction may proceed by coordination of the second arene to Pd(II) in a η^2 fashion: (a) Li, C.-S.; Jou, D.-C.; Cheng, C.-H. *Organometallics* **1993**, *12*, 3945. (b) Li, C.-S.; Cheng, C.-H.; Liao, F.-L.; Wang, S.-L. *J. Chem. Soc., Chem. Commun.* **1991**, 710. (c) Ossor, H.; Pfeffer, M.; Jastrzebski, J. T. B. H.; Stam, C. H. *Inorg. Chem.* **1987**, *26*, 1169.

(19) Reaction of Ag_2CO_3 with (diphosphine)platinum dichloride complexes led to (diphosphine)platinum carbonate complexes: (a) Andrews, M. A.; Gould, G. L.; Voss, E. J. *Inorg. Chem.* **1996**, *35*, 5740. (b) Andrews, M. A.; Gould, G. L.; Klooster, W. T.; Koening, K. S.; Voss, E. J. *Inorg. Chem.* **1996**, *35*, 5478 and references cited therein. (c) For the formation of bis(triphenylphosphino)carbonatopalladium: Nyman, C. J.; Wymore, C. E.; Wilkinson, G. *J. Chem. Soc. A* **1968**, 561.

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(21) (a) Lee-Ruff, E.; Kruk, H.; Katz, M. *J. Org. Chem.* **1984**, *49*, 553. (b) Harvey, R. G.; Abu-shqara, E.; Yang, C. *J. Org. Chem.* **1992**, *57*, 6313.

(22) Ito, Y.; Hirao, T.; Saegusa, T. *J. Org. Chem.* **1978**, *43*, 1011.

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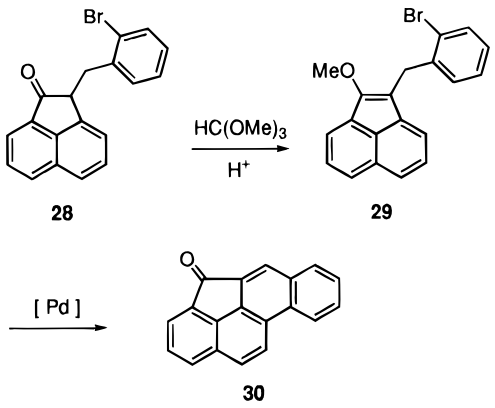
(24) Lisitsyn, V. N.; Lugovskaya, E. K. *Zh. Org. Khim.* **1974**, *10*, 92.

(25) Carson, J. R.; Almond, H. R.; Brannan, M. D.; Carmosin, R. J.; Flaim, S. F.; Gill, A.; Gleason, M. M.; Keely, S. L.; Ludovici, D. W.; Pitis, P. M.; Rebarchak, M. C.; Villani, F. J. *J. Med. Chem.* **1988**, *31*, 630.

Scheme 3



corresponding *o*-bromobenzyl bromide (1 equiv) in DMF. (See the Supporting Information for details and characterization data).

9-[(2-Bromo-5-methoxyphenyl)methyl]-9-[(2-bromo-5-nitrophenyl)methyl]fluorene (9). Benzylation of **2** according to method B gave **9** as a pale yellow solid (63%): mp ($CHCl_3$−Et_2O) 168−170 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.61 (dd, J = 8.7, 2.8 Hz, 1H), 7.58−7.51 (m, 4H), 7.42 (d, J = 8.8 Hz, 1H), 7.35−7.27 (m, 4H), 7.23 (d, J = 8.8 Hz, 1H), 7.14 (d, J = 2.7 Hz, 1H), 6.45 (dd, J = 8.8, 3.1 Hz, 1H), 6.01 (d, J = 3.1 Hz, 1H), 3.79 (s, 2H), 3.68 (s, 2H), 3.29 (s, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz; DEPT) δ 157.73 (1C, s, Ar), 147.01 (2C, s, Ar), 145.88 (1C, s, Ar), 140.74 (2C, s, Ar), 138.61 (1C, s, Ar), 137.19 (1C, s, Ar), 133.07 (1C, d, ArH), 132.90 (1C, d, ArH), 127.94 (2C, d, ArH), 126.98 (2C, d, ArH), 124.74 (1C, d, ArH), 124.68 (2C, d, ArH), 122.08 (1C, d, ArH), 119.93 (2C, d, ArH), 116.15 (1C, s, Ar), 115.30 (1C, d, ArH), 114.68 (1C, d, ArH), 56.18 (1C, s, $Ar_2C(CH_2)_2$), 54.80 (1C, q, CH_3O), 43.36 (2C, t, $ArCH_2C$) (one carbon signal overlaps); EI-MS m/z 579, 577 (M^+, 29, 16), 380, 378 (100), 252 (100). Anal. Calcd for $C_{28}H_{21}Br_2NO_3$: C, 58.06; H, 3.65; N, 2.42. Found: C, 57.68; H, 3.55; N, 2.56.

Benz[*e*]acephenanthrylene (10).[3b] A suspension of **1** (200 mg, 0.60 mmol), K_2CO_3 (662 mg, 4.80 mmol), Bu_4NBr (560 mg, 1.8 mmol), and $Pd(OAc)_2$ (7 mg, 5 mol %, 0.03 mmol) in DMF (8 mL) was heated at 130 °C for 48 h. After the usual workup (Et_2O), the residue was chromatographed (hexane) to give **10** as a white solid (80 mg, 52%):[26] mp 162−164 °C (lit. mp[4b] 168 °C); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.67 (dd, J = 7.5, 2.2 Hz, 1H), 8.46 (d, J = 8.1 Hz, 1H), 8.23 (s, 1H), 8.10−7.90 (m, 4H), 7.80−7.60 (m, 3H), 7.46−7.41 (m, 2H); ^{13}C NMR ($CDCl_3$, 50 MHz; DEPT) δ 140.63 (1C, s, Ar), 138.49 (1C, s, Ar), 136.91 (1C, s, Ar), 135.00 (1C, s, Ar), 133.96 (1C, s, Ar), 132.00 (1C, s, Ar), 130.65 (1C, s, Ar), 130.14 (1C, d, ArH), 129.24 (1C, s, Ar), 128.10 (1C, d, ArH), 128.01 (1C, d, ArH), 127.37 (1C, d, ArH), 126.94 (1C, d, ArH), 126.69 (1C, d, ArH), 123.08 (1C, d, ArH), 121.87 (1C, d, ArH), 121.57 (1C, d, ArH), 121.45 (1C, d, ArH), 121.31 (1C, d, ArH), 119.48 (1C, d, ArH).

10-Methoxybenz[*e*]acephenanthrylene (11).[12f] A suspension of **2** (300 mg, 0.82 mmol), $Pd(OAc)_2$ (19 mg, 10 mol %, 0.08 mmol), K_2CO_3 (227 mg, 1.6 mmol), and LiI (281 mg, 2.05 mmol) in DMF (5 mL) was stirred at 130 °C for 4 d. After the usual workup (Et_2O) the residue was suspended in hexane and filtered to give **11** as a white solid (116 mg, 50%):[27] mp 194−196 °C (lit.[12f] mp 198−199 °C); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.55 (d, J = 8.9 Hz, 1H), 8.37 (d, J = 8.9 Hz, 1H), 8.17 (s, 1H), 8.01−7.89 (m, 3H), 7.74 (dd, J = 8.1, 7.1 Hz, 1H), 7.46−7.36 (m, 4H), 4.00 (s, 3H).

10-Nitrobenz[*e*]acephenanthrylene (12). A suspension of **3** (160 mg, 0.42 mmol), $Pd(OAc)_2$ (13 mg, 11 mol %, 0.06 mmol), K_2CO_3 (440 mg, 3.2 mmol), and Bu_4NBr (270 mg, 0.84 mmol) in DMF (10 mL) was stirred at 70 °C for 48 h. After the usual workup (Et_2O), the residue was chromatographed (10:1 hexane−CH_2Cl_2) to give **12** as a yellow solid (70 mg, 57%): mp 192−194 °C; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.90 (d, J = 2.2 Hz, 1H), 8.74 (d, J = 9.2 Hz, 1H), 8.46 (d, J = 8.1 Hz, 1H), 8.44 (d, J = 9.2 Hz, 1H), 8.29 (s, 1H), 8.10−7.90 (m, 3H), 7.83 (dd, J = 8.1, 7.0 Hz, 1H), 7.52−7.42 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz, 50 °C; DEPT) δ 146.05 (1C, s, Ar), 140.53 (1C, s, Ar), 137.64 (1C, s, Ar), 137.41 (1C, s, Ar), 137.24 (1C, s, Ar), 134.32 (1C, s, Ar), 133.44 (1C, s, Ar), 133.37 (1C, s, Ar), 129.04 (1C, d, ArH), 128.96 (1C, d, ArH), 127.88 (1C, d, ArH), 126.47 (1C, s, Ar), 125.37 (1C, d, ArH), 124.05 (1C, d, ArH), 122.25 (1C, d, ArH), 122.10 (1C, d, ArH), 121.47 (1C, d, ArH), 121.08 (1C, d, ArH), 120.78 (1C, d, ArH), 120.38 (1C, d, ArH); EI-MS m/z 297 (M^+, 100). Anal. Calcd for $C_{20}H_{11}NO_2 \cdot 0.5H_2O$: C, 78.42; H, 3.95; N, 4.57. Found: C, 78.42; H, 3.71; N, 4.57. (The presence of water was confirmed by ^{1}H NMR.)

10-Fluorobenz[*e*]acephenanthrylene (13). A suspension of **4** (240 mg, 0.68 mmol), K_2CO_3 (281 mg, 2 mmol), $BnMe_3NBr$ (81 mg, 0.35 mmol), and $Pd(OAc)_2$ (16 mg, 0.07 mmol) in DMF (5 mL) was stirred at 120 °C for 48 h. After the usual workup (Et_2O), the residue was chromatographed (100:1 hexane−EtOAc) to give **13** as a white solid (120 mg, 65%): mp 138−140 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.59 (dd, J = 9.0, 5.5 Hz, 1H), 8.35 (d, J = 8.0 Hz, 1H), 8.10 (s, 1 H), 8.03−7.90 (m, 3H), 7.74 (dd, J = 8.2, 7.1 Hz, 1H), 7.65 (dd, J = 9.8, 2.7 Hz, 1H), 7.46−7.38 (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz; DEPT) δ 161.28 [1C, d, $^1J(^{13}C-^{19}F)$ = 245.6 Hz, Ar], 140.72 (1C, Ar), 138.13 (1C, Ar), 136.98 (1C, Ar), 136.14 (1C, Ar), 135.34 [1C, d, $^3J(^{13}C-^{19}F)$ = 8.7 Hz, Ar], 131.54 (1C, Ar), 128.43 (1C, ArH), 128.34 (1C, ArH), 127.45 (1C, ArH), 127.13 (1C, Ar), 127.07 (1C, Ar), 124.93 [1C, d, $^3J(^{13}C-^{19}F)$ = 8.8 Hz, ArH], 121.99 (1C, ArH), 121.32 (1C, ArH), 121.29 (1C, ArH), 120.32 [1C, d, $^4J(^{13}C-^{19}F)$ = 3.0 Hz, ArH], 119.22 (1C, ArH), 115.50 [1C, d, $^2J(^{13}C-^{19}F)$ = 23.6 Hz, ArH], 114.21 [1C, d, $^2J(^{13}C-^{19}F)$ = 20.8 Hz, ArH]; EI-MS m/z 270 (M^+, 100). Anal. Calcd for $C_{20}H_{11}F$: C, 88.87; H, 4.10. Found: C, 88.72; H, 4.22.

1*H*,16*H*-Phenanthro[1,10,10-*aef*]acephenanthrylene (14). A suspension of **5** (300 mg, 0.60 mmol), K_2CO_3 (0.60 g, 4.3 mmol), Bu_4NBr (360 mg, 1.1 mmol), and $Pd(OAc)_2$ (17 mg, 6 mol %, 0.08 mmol) in DMF (10 mL) was stirred at 130 °C for 24 h. After the usual workup (Et_2O), the residue was triturated with hexane and filtered to give **14** as a white solid (140 mg, 68%): mp (hexane) 219−220 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.89 (dd, J = 7.6, 1.1 Hz, 2H), 7.71 (dd, J = 7.4, 1.0 Hz, 2H), 7.59 (dd, J = 7.6, 1.0 Hz, 2H), 7.52 (t, J = 7.4 Hz, 2H), 7.40 (br t, J = 7.5 Hz, 2H), 7.29 (td, J = 7.4, 1.1 Hz, 2H), 7.17 (br d, J = 7.4 Hz, 2H), 3.21 (d, J = 14.4 Hz, 2H), 2.41 (d, J = 14.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz; DEPT) δ 147.97 (2C, s, Ar), 140.20 (2C, s, Ar), 137.08 (2C, s, Ar), 135.13 (2C, s, Ar), 134.39 (2C, s, Ar), 130.09 (2C, d, ArH), 128.94 (2C, d, ArH), 128.34 (2C, d, ArH), 127.54 (2C, d, ArH), 123.57 (2C, d, ArH), 122.01 (2C, d, ArH), 119.39 (2C, d, ArH), 45.23 (1C, s, $Ar_2C(CH_2)_2$), 34.84 (2C, t, $ArCH_2C$); EI-MS m/z 342 (M^+, 100). Anal. Calcd for $C_{27}H_{18}$: C, 94.70; H, 5.30. Found: C, 95.03; H, 5.00.

3,14-Dimethoxy-1*H*,16*H*-phenanthro[1,10,10-*aef*]acephenanthrylene (15). A suspension of **6** (200 mg, 0.35 mmol), $Pd(OAc)_2$ (8 mg, 10 mol %, 0.035 mmol), K_2CO_3 (100 mg, 0.7 mmol), and LiI (120 mg, 0.9 mmol) in DMF (5 mL) was stirred at 135 °C for 5 d. After the usual workup (Et_2O), the residue was suspended in Et_2O to give **15** as a yellow solid (42 mg, 30%): mp 238−240 °C; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.78 (d, J = 8.7 Hz, 2H), 7.66−7.59 (m, 2H), 7.50−7.43 (m, 4H), 6.91 (dd, J = 8.7, 3.0 Hz, 2H), 6.74 (d, J = 3.0 Hz, 2H), 3.80 (s, 6H), 3.07 (d, J = 14.5 Hz, 2H), 2.38 (d, J = 14.5 Hz, 2H); ^{13}C NMR ($CDCl_3$, 50 MHz; DEPT) δ 159.79 (2C, s, Ar), 147.13 (2C, s, Ar), 140.17 (2C, s, Ar), 138.85 (2C, s, Ar), 134.27 (2C, s, Ar), 128.84 (2C, d, ArH), 127.99 (2C, s, Ar), 124.51 (2C, d, ArH), 121.35 (2C, d, ArH), 118.50 (2C, d, ArH), 116.13 (2C, d, ArH), 112.17 (2C, d, ArH), 55.38 (2C, q, CH_3O), 45.26 (1C, s, $Ar_2C(CH_2)_2$), 35.24 (2C, t, $ArCH_2C$); EI-MS m/z 402 (M^+, 100). Anal. Calcd for $C_{29}H_{22}O_2$: C, 86.54; H, 5.51. Found: C, 86.38; H, 5.55.

9,9-Bis[(3-methoxyphenyl)methyl]fluorene (16). A solution of **6** (30 mg, 0.05 mmol), $Pd(OAc)_2$ (2.4 mg, 10 mol %,

(26) Alternatively, palladium-catalyzed reaction of 9-(2-bromobenzylidene)fluorene afforded **10** in 44% yield.

(27) Alternatively, palladium-catalyzed reaction of 9-(2-bromo-5-methoxybencyliden)fluorene[12f] gave **11** in 32% yield.

0.01 mmol), K_2CO_3 (56 mg, 0.4 mmol), and Bu_4NBr (25 mg, 0.08 mmol) in DMF (5 mL) was stirred at 120 °C for 36 h. After the usual workup (Et_2O), the residue was suspended in EtOAc and filtered to give **16** as a white solid (7 mg, 35%): mp 122−125 °C; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.45−7.40 (m, 4H), 7.31−7.16 (m, 4H), 6.83 (t, J = 7.1 Hz, 2H), 6.50 (dd, J = 7.1, 2.4 Hz, 2H), 6.30 (d, J = 7.1 Hz, 2H), 6.13 (d, J = 2.4 Hz, 2H), 3.44 (s, 6H), 3.35 (s, 4H); ^{13}C NMR ($CDCl_3$, 50 MHz; DEPT) δ 158.34 (2C, s, Ar), 148.19 (2C, s, Ar), 140.97 (2C, s, Ar), 138.49 (2C, s, Ar), 127.88 (2C, d, ArH), 126.98 (2C, d, ArH), 126.19 (2C, d, ArH), 124.50 (2C, d, ArH), 122.81 (2C, d, ArH), 119.76 (2C, d, ArH), 114.91 (2C, d, ArH), 112.25 (2C, d, ArH), 56.58 (1C, s, $Ar_2C(CH_2)_2$), 54.77 (2C, q, CH_3O), 43.52 (2C, t, $ArCH_2C$); EI-MS m/z 406 (M^+, 29), 285 (100). Anal. Calcd for $C_{29}H_{26}O_2$: C, 85.68; H, 6.45. Found: C, 85.30; H, 6.64.

3-Methoxy-1*H*,16*H*-phenanthro[1,10,10-*aef*]acephenanthrylene (17). A suspension of **7** (300 mg, 0.56 mmol), $Pd(OAc)_2$ (14 mg, 10 mol %, 0.06 mmol), K_2CO_3 (250 mg, 1.8 mmol), and LiI (206 mg, 1.5 mmol) in DMF (10 mL) was stirred at 130 °C for 4 d. After the usual workup (Et_2O), the residue was suspended in Et_2O and filtered to give **17** as a white solid (130 mg, 62%): mp 216−219 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.89 (dd, J = 7.5, 1.1 Hz, 1H), 7.80 (d, J = 8.4 Hz, 1H), 7.70 (dd, J = 7.4, 0.8 Hz, 1H), 7.68 (dd, J = 6.6, 1.7 Hz, 1H), 7.59−7.49 (m, 4H), 7.40 (br t, J = 7.5 Hz, 1H), 7.27 (td, J = 7.5, 1.1 Hz, 1H), 7.19 (br d, J = 2.6 Hz, 1H), 6.92 (dd, J = 8.4, 2.6 Hz, 1H), 6.74 (d, J = 2.6 Hz, 1H), 3.85 (s, 3H), 3.13 (AB system, part A, J = 14.6 Hz, 1H), 3.08 (AB system, part A, J = 14.6 Hz, 1H), 2.41 (AB system, part B, J = 14.3 Hz, 1H), 2.40 (AB system, part B, J = 14.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 50 MHz; DEPT) δ 159.74 (1C, s, Ar), 147.77 (1C, s, Ar), 147.19 (1C, s, Ar), 140.22 (1C, s, Ar), 140.01 (1C, s, Ar), 138.80 (1C, s, Ar), 137.01 (1C, s, Ar), 135.06 (1C, s, Ar), 134.27 (1C, s, Ar), 130.10 (1C, d, ArH), 128,84 (2C, d, ArH), 128.26 (1C, d, ArH), 127.89 (1C, s, Ar), 127.41 (1C, d, ArH), 124.51 (1C, d, ArH), 123.46 (1C, d, ArH), 121.82 (1C, d, ArH), 121.35 (1C, d, ArH), 119.29 (1C, d, ArH), 118.50 (1C, d, ArH), 116.07 (1C, d, ArH), 112.01 (1C, d, ArH), 55.32 (1C, q, CH_3O), 45.20 (1C, s, $Ar_2C(CH_2)_2$), 35.13 (1C, t, $ArCH_2C$), 34.81 (1C, t, $ArCH_2C$) (one carbon signal overlaps); EI-MS m/z 372 (M^+, 100).[28]

3-Nitro-1*H*,16*H*-phenanthro[1,10,10-*aef*]acephenanthrylene (18). A suspension of **8** (320 mg, 0.58 mmol), K_2CO_3 (600 mg, 4.3 mmol), Bu_4NBr (360 mg, 1.1 mmol), and $Pd(OAc)_2$ (17 mg, 12 mol %, 0.08 mmol) in DMF (10 mL) was stirred at 95 °C for 48 h. After the usual workup (Et_2O), the residue was chromatographed (3:1 hexane−CH_2Cl_2) to give **18** as a white solid (120 mg, 53%): mp ($CHCl_3$−Et_2O) 221−225 °C; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.23 (dd, J = 8.1, 2.1 Hz, 1H), 7.99 (d, J = 2.1 Hz, 1H), 7.94 (d, J = 8.1 Hz, 1H), 7.85 (dd, J = 7.5, 1.6 Hz, 1H), 7.75 (dd, J = 7.0, 1.6 Hz, 1H), 7.68 (dd, J = 7.0, 1.1 Hz, 1H), 7.60−7.48 (m, 4H), 7.39 (td, J = 7.5, 1.6 Hz, 1H), 7.28 (td, J = 7.5, 1.6 Hz, 1H), 7.12 (br d, J = 7.5 Hz, 1H), 3.21 (d, J = 14.5 Hz, 1H), 2.96 (d, J = 14.5 Hz, 1H), 2.38 (d, J = 14.5 Hz, 2H); ^{13}C NMR ($CDCl_3$, 50 MHz; DEPT) δ 148.42 (1C, s, Ar), 147.40 (1C, s, Ar), 147.00 (1C, s, Ar), 141.48 (1C, s, Ar), 140.58 (1C, s, Ar), 139.56 (1C, s, Ar), 138.54 (1C, s, Ar), 136.06 (1C, s, Ar), 134.71 (1C, s, Ar), 134.37 (1C, s, Ar), 132.11 (1C, s, Ar), 129.97 (1C, d, ArH), 129.29 (1C, d, ArH), 129.21 (1C, d, ArH), 128.62 (1C, d, ArH), 127.77 (1C, d, ArH), 124.72 (1C, d, ArH), 123.93 (1C, d, ArH), 123.60 (1C, d, ArH), 123.09 (1C, d, ArH), 122.52 (1C, d, ArH), 122.35 (1C, d, ArH), 121.11 (1C, d, ArH), 119.42 (1C, d, ArH), 44.73 (1C, s, $Ar_2C(CH_2)_2$), 34.86 (1C, t, $ArCH_2C$), 34.69 (1C, t, $ArCH_2C$); EI-MS m/z 387 (M^+, 100). Anal. Calcd for $C_{27}H_{17}NO_2$: C, 83.70; H, 4.42; N, 3.62. Found: C, 83.25; H, 4.30; N, 3.56.[28]

7b,8-Dihydro-8a-[(2-bromophenyl)methyl]-10-nitrobenz[*e*]acephenanthrylene (19). A suspension of **8** (400 mg, 0.73 mmol), $Pd(OAc)_2$ (12 mg, 7 mol %, 0.05 mmol), K_2CO_3 (806 mg, 5.8 mmol), and $BnMe_3NBr$ (84 mg, 0.37 mmol) in DMF (15 mL) was stirred at 70 °C for 48 h. After the usual workup (Et_2O), the residue was chromatographed (5:1 hexane−CH_2Cl_2) to give **19** (140 mg, 41%) as a yellow solid: mp ($CHCl_3$−Et_2O) 184−185 °C; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.32 (d, J = 2.2 Hz, 1H), 8.21 (dd, J = 8.6, 2.2 Hz, 1H), 7.94 (d, J = 8.6 Hz, 1H), 7.63−7.26 (m, 7H), 7.19−7.14 (m, 1H), 6.87−6.78 (m, 2H), 6.35−6.30 (m, 1H), 3.65 (d, J = 15.1 Hz, 1H), 3.30 (d, J = 12.9 Hz, 1H), 3.05 (d, J = 12.9 Hz, 1H), 3.02 (d, J = 15.1 Hz, 1H); ^{13}C NMR ($CDCl_3$, 50 MHz; DEPT) δ 149.56 (1C, s, Ar), 147.50 (1C, s, Ar), 147.08 (1C, s, Ar), 140.97 (1C, s, Ar), 140.75 (1C, s, Ar), 139.70 (1C, s, Ar), 137.70 (1C, s, Ar), 136.11 (1C, s, Ar), 132.26 (1C, d, ArH), 131.13 (1C, d, ArH), 130.58 (1C, s, Ar), 129.10 (1C, d, ArH), 127.89 (1C, d, ArH), 127.73 (1C, d, ArH), 127.10 (1C, d, ArH), 125.99 (1C, d, ArH), 124.88 (1C, d, ArH), 124.35 (1C, d, ArH), 123.93 (1C, d, ArH), 122.88 (1C, d, ArH), 121.56 (1C, d, ArH), 120.66 (2C, d, ArH), 49.84 (1C, s, $Ar_2C(CH_2)_2$), 41.35 (1C, t, $ArCH_2C$), 37.19 (1C, t, $ArCH_2C$) (one carbon signal overlaps); EI-MS m/z 467 (M^+, 1), 252 (100).[28]

7b,8-Dihydro-8a-[(2-bromo-5-methoxyphenyl)methyl]-10-nitrobenz[*e*]acephenanthrylene (20). A suspension of **9** (210 mg, 0.36 mmol), $Pd(OAc)_2$ (6 mg, 7.5 mol %, 0.027 mmol), K_2CO_3 (397 mg, 2.88 mmol), and $BnMe_3NBr$ (41.4 mg, 0.18 mmol) in DMF (6 mL) was stirred at 70 °C for 24 h. After the usual workup (Et_2O), the residue was chromatographed (3:1 hexane−CH_2Cl_2) to give **20** (120 mg, 67%) as a white solid: mp ($CHCl_3$−Et_2O) 144−146 °C; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.30 (d, J = 2.7 Hz, 1H), 8.19 (dd, J = 8.6, 2.7 Hz, 1H), 7.93 (d, J = 8.6 Hz, 1H), 7.63−7.28 (m, 7H), 7.00 (d, J = 8.6 Hz, 1H), 6.37 (dd, J = 8.6, 3.2 Hz, 1H), 5.76 (d, J = 3.2 Hz, 1H), 3.63 (AB system, part A, J = 15.1 Hz, 1H), 3.40 (s, 3H), 3.32 (AB system, part A, J = 12.9 Hz, 1H), 2.97 (AB system, part B, J = 15.1 Hz, 1H), 2.96 (AB system, part B, J = 12.9 Hz, 1H); ^{13}C NMR ($CDCl_3$, 50 MHz; DEPT) δ 157.37 (1C, s, Ar), 149.72 (1C, s, Ar), 147.24 (1C, s, Ar), 147.03 (1C, s, Ar), 141.12 (1C, s, Ar), 140.75 (1C, s, Ar), 139.75 (1C, s, Ar), 137.70 (1C, s, Ar), 136.80 (1C, s, Ar), 132.58 (1C, d, ArH), 130.74 (1C, s, Ar), 129.15 (1C, d, ArH), 127.94 (1C, d, ArH), 127.15 (1C, d, ArH), 124.83 (1C, d, ArH), 124.25 (1C, d, ArH), 123.93 (1C, d, ArH), 122.88 (1C, d, ArH), 121.56 (1C, d, ArH), 120.77 (1C, d, ArH), 120.61 (1C, d, ArH), 116.23 (1C, s, Ar), 115.39 (1C, d, ArH), 114.97 (1C, d, ArH), 54.96 (1C, q, CH_3O), 49.90 (1C, s, $Ar_2C(CH_2)_2$), 41.62 (1C, t, $ArCH_2C$), 37.40 (1C, t, $ArCH_2C$); EI-MS m/z 499, 497 (M^+, 2), 252 (100). Anal. Calcd for $C_{28}H_{20}BrNO_3$: C, 67.48; H, 4.05; N, 2.81. Found: C, 67.48; H, 4.24; N, 2.80.

6-Nitro-1*H*,16*H*-phenanthro[1,10,10-*aef*]acephenanthrylene (22). A suspension of **21** (400 mg, 0.73 mmol), K_2CO_3 (805 mg, 5.8 mmol), $BnMe_3NBr$ (84 mg, 0.37 mmol), and $Pd(OAc)_2$ (8 mg, 5.5 mol %, 0.04 mmol) in DMF (20 mL) was heated at 70 °C for 32 h. After the usual workup (Et_2O), the residue was chromatographed (4:1 hexane−CH_2Cl_2) to give **22** as a yellow solid (150 mg, 53%): mp ($CHCl_3$−Et_2O) 231−232 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.87 (dd, J = 7.6, 1.2 Hz, 1H), 7.79−7.73 (m, 3H), 7.65 (dd, J = 7.7, 0.9 Hz, 1H), 7.63−7.53 (m, 2H), 7.41 (br t, J = 7.3 Hz, 1H), 7.37−7.34 (m, 2H), 7.30 (dd, J = 7.4, 1.4 Hz, 1H), 7.22−7.20 (m, 1H), 7.08 (br d, J = 7.4 Hz, 1H), 3.08 (d, J = 14.2 Hz, 1H), 2.82 (d, J = 14.4 Hz, 1H), 2.40 (br d, J = 14.4 Hz, 1H), 2.35 (br d, J = 14.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz; DEPT) δ 150.95 (1C, s, Ar), 148.83 (1C, s, Ar), 145.89 (1C, s, Ar), 143.06 (1C, s, Ar), 138.25 (1C, s, Ar), 138.09 (1C, s, Ar), 136.07 (1C, s, Ar), 134.41 (1C, s, Ar), 134.29 (1C, s, Ar), 130.12 (1C, d, ArH), 129.97 (1C, d, ArH), 129.93 (1C, s, Ar), 129.57 (1C, d, ArH), 129.32 (1C, d, ArH), 128.63 (1C, d, ArH), 127.73 (1C, d, ArH),127.37 (1C, d, ArH), 127.17 (1C, s, Ar), 126.61 (1C, d, ArH), 124.69 (1C, d, ArH), 123.59 (1C, d, ArH), 123.07 (1C, d, ArH), 119.90 (1C, d, ArH), 119.58 (1C, d, ArH), 46.63 (1C, s, $Ar_2C(CH_2)_2$), 34.57 (1C, t, $ArCH_2C$), 33.91 (1C, t, $ArCH_2C$); EI-MS m/z 387 (M^+, 100).[28]

7b,8-Dihydro-8a-methyl-6-nitrobenz[*e*]acephenanthrylene (24) and 7b,8-Dihydro-8a-methyl-1-nitrobenz[*e*]acephenanthrylene (25). A suspension of **23** (220 mg, 0.56 mmol), K_2CO_3 (230 mg, 1.7 mmol), $BnMe_3NBr$ (130 mg, 0.56 mmol), and $Pd(OAc)_2$ (13 mg, 11 mol %, 0.06 mmol) in DMF (8 mL) was stirred at 100 °C for 24 h. After the usual workup (Et_2O), the residue was chromatographed (3:1 hexane−CH_2Cl_2) to give a 2:1 mixture of **24** and **25** (109 mg, 62%). After recrystallization ($CHCl_3$−Et_2O), **24** was obtained as a yellow solid: mp ($CHCl_3$−Et_2O) 178−179 °C; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.38 (d, J = 2.1 Hz, 1H), 8.31 (dd, J = 8.5, 2.1 Hz, 1H), 7.89−7.85 (m, 1H), 7.86 (d, J = 8.5 Hz, 1H), 7.70 (dd, J

(28) Copies of the ^{1}H and ^{13}C NMR spectra are provided as Supporting Information.

= 7.5, 0.7 Hz, 1H), 7.67 (dd, J = 6.8, 0.7 Hz, 1H), 7.49 (dd, J = 7.5, 6.8 Hz, 1H), 7.44−7.29 (m, 3H), 3.31 (AB system, part A, J = 14.7 Hz, 1H), 2.92 (AB system, part B, J = 14.7 Hz, 1H), 1.30 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz; DEPT) δ 154.23 (1C, s, Ar), 150.87 (1C, s, Ar), 147.07 (1C, s, Ar), 146.86 (1C, s, Ar), 136.01 (2C, s, Ar), 133.03 (1C, s, Ar), 132.09 (1C, s, Ar), 130.20 (1C, d, ArH), 128.95 (1C, d, ArH), 128.57 (1C, d, ArH), 127.54 (1C, d, ArH), 123.63 (1C, d, ArH), 123.55 (1C, d, ArH), 123.12 (1C, d, ArH), 120.92 (1C, d, ArH), 120.31 (1C, d, ArH), 118.63 (1C, d, ArH), 46.15 (1C, s, $Ar_2(CH_3)\mathit{C}CH_2$), 38.13 (1C, t, Ar$\mathit{C}H_2$C), 23.54 (1C, q, $\mathit{C}H_3$); EI-MS m/z 313 (M^+, 52), 252 (100). The filtrate from the recrystallization showed a 1:1 mixture of **24** and **25** that could not be separated by chromatography. **25**: ^{1}H NMR ($CDCl_3$, 200 MHz) (only distinctive signals) δ 3.19 (AB system, part A, J = 14.5 Hz, 1H), 2.87 (AB system, part B, J = 14.5 Hz, 1H), 1.13 (s, 3H). The EI-MS of the mixture of **24** and **25** was identical with that of pure **24**.[28]

10,10-Bis[(2-bromophenyl)methyl]-9(10*H*)-anthracenone (26). A solution of 9(10*H*)-anthracenone (1.00 g, 5 mmol) and 1-bromo-2-(bromomethyl)benzene (3.75 g, 15 mmol) in CH_2Cl_2 (20 mL) was treated with a solution of $BnEt_3NBr$ (250 mg) in aqueous NaOH (30%, 15 mL). The mixture was stirred for 2 h. After the usual workup (CH_2Cl_2), the residue was chromatographed (10:1 hexane−EtOAc) to give **9-[(2-bromophenyl)methoxy]-10-[(2-bromophenyl)methyl]anthracene** as a yellow solid (0.60 g, 23%): mp 146−148 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.44−8.38 (m, 2H), 8.09−8.01 (m, 3H), 7.68 (dd, J = 7.9, 1.3 Hz, 1H), 7.67 (dd, J = 8.0, 1.2 Hz, 1H), 7.53−7.43 (m, 5H), 7.30 (td, J = 7.4, 1.7 Hz, 1H), 7.04 (td, J = 7.4, 1.7 Hz, 1H), 6.93 (td, J = 7.4, 1.4 Hz, 1H), 6.43 (dd, J = 7.7, 1.6 Hz, 1H), 5.35 (s, 2H), 5.00 (s, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz; DEPT) δ 150.55 (1C, s, Ar), 139.86 (1C, s, Ar), 137.05 (1C, s, Ar), 132.67 (1C, d, ArH), 132.43 (1C, d, ArH), 131.34 (2C, s, Ar), 129.73 (1C, d, ArH), 129.39 (1C, d, ArH), 129.03 (1C, d, ArH), 127.76 (1C, d, ArH), 127.66 (1C, d, ArH), 127.51 (1C, d, ArH), 127.14 (1C, s, Ar), 126.31 (2C, d, ArH), 125.18 (2C, d, ArH), 124.94 (2C, d, ArH), 124.73 (2C, s, Ar), 124.51 (1C, s, Ar), 122.90 (2C, d, ArH), 122.30 (1C, s, Ar), 76.51 (1C, t, Ar$\mathit{C}H_2$O), 34.05 (1C, t, Ar$\mathit{C}H_2$Ar); EI-MS m/z 532, 530 (M^+, 12, 7), 363 (100), 361 (99). Anal. Calcd for $C_{28}H_{20}Br_2O$: C, 63.18; H, 3.79. Found: C, 63.13; H, 3.79. Elution with 5:1 hexane−EtOAc afforded **26** as a white solid (1.00 g, 38%): mp 189−190 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.26 (dd, J = 7.7, 1.6 Hz, 2H), 7.60−7.35 (m, 8H), 6.87 (td, J = 7.7, 1.7 Hz, 2H), 6.72 (td, J = 7.6, 1.4 Hz, 2H), 6.07 (dd, J = 7.8, 1.7 Hz, 2H), 3.85 (s, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz; DEPT) δ 183.21 (1C, s, CO), 145.27 (2C, s, Ar), 135.40 (2C, s, Ar), 133.37 (2C, d, ArH), 132.62 (2C, s, Ar), 132.56 (2C, d, ArH), 131.21 (2C, d, ArH), 127.87 (2C, d, ArH), 127.66 (2C, d, ArH), 127.35 (2C, d, ArH), 126.70 (2C, d, ArH), 126.49 (2C, d, ArH), 126.33 (2C, s, Ar), 48.10 (2C, t, Ar$\mathit{C}H_2$C), 47.27 (1C, s, $Ar_2\mathit{C}(CH_2)_2$); EI-MS m/z 532, 530 (M^+, 11, 6), 363 (100), 361 (100). Anal. Calcd for $C_{28}H_{20}Br_2O$: C, 63.18; H, 3.79. Found: C, 63.00; H, 3.89.

1*H*,17*H*-Dinaphtho[1,2,3-*de*:3,2,1-*fg*]anthracen-9-one (27). A suspension of **26** (200 mg, 0.37 mmol), $Pd(OAc)_2$ (10 mg, 3 mol %, 0.044 mmol), K_2CO_3 (420 mg, 3.0 mmol), and Bu_4NBr (400 mg, 1.24 mmol) in DMF (5 mL) was stirred at 140 °C for 36 h. After the usual workup (Et_2O), the residue was chromatographed (3:1 hexane−EtOAc) to give **27** as a white solid (120 mg, 88%): mp > 300 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.38 (dd, J = 7.8, 1.3 Hz, 2H), 8.05 (dd, J = 7.8, 1.3 Hz, 2H), 7.92 (br d, J = 7.8 Hz, 2H), 7.63 (t, J = 7.8 Hz, 2H), 7.41 (br t, J = 7.8 Hz, 2H), 7.22 (td, J = 7.5, 1.3 Hz, 2H), 6.75 (br d, J = 7.5 Hz, 2H), 2.95 (AB system, part A, J = 15.4 Hz, 2H), 2.67 (AB system, part B, J = 15.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz; DEPT) δ 183.17 (1C, s, CO), 143.74 (2C, s, Ar), 135.33 (2C, s, Ar), 134.78 (2C, s, Ar), 134.44 (2C, s, Ar), 129.92 (2C, s, Ar), 129.45 (2C, d, ArH), 129.02 (2C, d, ArH), 128.38 (2C, d, ArH), 127.79 (2C, d, ArH), 127.60 (2C, d, ArH), 126.54 (2C, d, ArH), 123.07 (2C, d, ArH), 37.24 (2C, t, Ar$\mathit{C}H_2$C), 35.83 (1C, s, $Ar_2\mathit{C}(CH_2)_2$); EI-MS m/z 370 (M^+, 100).[28]

2-[(2-Bromophenyl)methyl]acenaphthen-1-one (28). A mixture of acenaphthenequinone (1.0 g, 5.5 mmol) and (2-bromobenzyl)triphenylphosphonium bromide (4.2 g, 8.2 mmol) in CH_2Cl_2 (80 mL) was treated with aqueous LiOH (5 M, 10 mL) at 23 °C for 2 h. After the usual workup (CH_2Cl_2), the residue was chromatographed (4:1 hexane−EtOAc) to afford a yellow solid whose ^{1}H NMR spectrum showed several multiplets at 8.25−7.25 ppm. This solid was dissolved in EtOAc (100 mL) and stirred under hydrogen (1 atm) in the presence of Pd/C 10% (500 mg) at 23 °C for 18 h. The mixture was filtered through Celite, evaporated, and chromatographed (6:1 hexane−EtOAc) to afford **28** as a white solid (1.51 g, 82%, overall yield): mp (Et_2O) 86−88 °C; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.09 (d, J = 8.6 Hz, 1H), 8.00 (d, J = 6.3 Hz, 1H), 7.81−7.61 (m, 3H), 7.50−7.42 (m, 1H), 7.33−7.13 (m, 3H), 6.86 (d, J = 7.0 Hz, 1H), 4.22 (dd, J = 10.1, 5.5 Hz, 1H), 3.70 (dd, J = 13.3, 5.5 Hz, 1H), 3.01 (dd, J = 14.1, 10.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 204.25, 141.76, 138.38, 138.26, 132.96, 131.83, 131.55, 130.65, 128.34, 128.11, 127.92, 127.15, 124.84, 123.99, 121.57, 121.45, 50.54, 37.45 (one carbon signal overlaps); EI-MS m/z 338, 336 (M^+, 2), 257 (100). Anal. Calcd for $C_{19}H_{13}$BrO: C, 67.67; H, 3.89. Found: C, 67.63; H, 3.65.

1-[(1-Bromophenyl)methyl]-2-methoxyacenaphthylene (29). A solution of **28** (500 mg, 1.48 mmol), trimethyl orthoformate (1.62 mL, 14.8 mmol), and *p*-toluenesulfonic acid monohydrate (3 mg) in MeOH (30 mL) was stirred at 65 °C for 2 h. After being cooled to room temperature, the reaction mixture was made alkaline by addition of aqueous NaOH (50%), and the solvent was evaporated. After the usual workup (Et_2O), the residue was chromatographed (9:1 hexane−Et_2O) to afford **29** as a bright red solid (410 mg, 79%): mp (Et_2O) 66−68 °C; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.76 (d, J = 7.8 Hz, 2H), 7.65−7.48 (m, 3H), 7.41−7.33 (m, 1H), 7.28−7.23 (m, 2H), 7.19−7.01 (m, 2H), 4.17 (s, 2H), 4.15 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 157.22, 139.84, 138.32, 133.69, 132.39, 130.14, 127.83, 127.54, 127.32, 126.98, 125.29, 124.44, 122.02, 120.89, 117.28, 59.85, 30.29 (three carbon signals overlap); EI-MS m/z 352, 350 (M^+, 59), 321, 319 (40), 337, 335 (10), 255 (100). Anal. Calcd for $C_{20}H_{15}BrO$: C, 68.39; H, 4.30. Found: C, 68.71; H, 4.13.

4*H*-Cyclopenta[*def*]chrysen-4-one (30). A mixture of **29** (88 mg, 0.25 mmol), $Pd(OAc)_2$ (67 mg, 0.3 mmol), K_2CO_3 (276 mg, 2 mmol), and $BnMe_3NBr$ (174 mg, 0.75 mmol) in DMF (3 mL) was stirred for 4 days at 160 °C. After the usual workup (Et_2O), the residue was chromatographed (6:1 hexane−EtOAc) to afford **30** as a pale yellow solid with ^{1}H NMR and MS data in agreement with those reported (25 mg, 39%): mp (CH_2Cl_2) 180−181 °C (lit.[21,29] mp 204−205 °C; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.49 (d, J = 8.6 Hz, 1H), 8.33 (d, J = 9.4 Hz, 1H), 8.14 (s, 1H), 8.07−7.86 (m, 4H), 7.77−7.56 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.73, 138.38, 134.34, 134.26, 134.13, 132.56, 132.46, 131.70, 130.74, 129.00, 128.74, 127.91, 126.76, 125.03, 125.02, 123.62, 123.16, 122.30, 121.74; EI-MS m/z 254 (M^+, 100).

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Supporting Information Available: Experimental procedures and characterization data for fluorenes **1**−**8**, **21**, and **23** and copies of the NMR spectra for **17**−**19**, **22**, **24**, and **27** (17 pages). This material is contained in 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.

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(29) Recrystallized **30** showed consistently a mp of 180−181 °C, approximately 24 °C lower than that reported in ref 21. However, the ^{1}H NMR spectrum matches the reported data within experimental error.[21b]