General Synthetic Entry to Highly-Oxygenated, Angularly-Fused Polycyclic Aromatic Compounds

Sangho Koo[1] and Lanny S. Liebeskind*

Contribution from the Sanford S. Atwood Chemistry Center, Emory University, 1515 Pierce Drive, Atlanta, Georgia 30322

Received October 7, 1994[⊗]

Abstract: A convergent and efficient synthesis of highly-oxygenated, angularly-fused polycyclic aromatic compounds has been developed. Nucleophilic addition of [4-(tri-*n*-butylstannyl)phenyl]lithium to a 3,4-disubstituted-cyclobutene-1,2-dione followed by appropriate protection of the hydroxyl group and thermal rearrangement of the O-protected addition product generated a 1,4-dioxygenated-2,3-disubstituted-6-(tri-*n*-butylstannyl)naphthalene. Stille coupling of the 6-(tri-*n*-butylstannyl)naphthalene with a 4-chloro-2,3-disubstituted-2-cyclobutenone and thermolysis of the coupled product gave highly-oxygenated phenanthrenes. An isomeric series of compounds was generated from [3-(tri-*n*-butylstannyl)phenyl]lithium. Substituted phenanthrenes at higher overall levels of oxygenation were prepared by (1) thermolysis of the adduct obtained by addition of a lithiated naphthalene, generated by Sn → Li exchange from a 1,4-dioxygenated-2,3-disubstituted-6-(tri-*n*-butylstannyl)naphthalene, to a cyclobutenedione or (2) thermolysis of the double adducts generated by reaction of 2 equiv of a cyclobutenedione with either 1,4-dilithiobenzene or 1,3-dilithiobenzene. Phenanthrenes at lower levels of oxygenation were prepared by the palladium-catalyzed cross-coupling/thermolysis of 2 equivalents of a 4-chlorocyclobutenone with either 1,4-bis(tri-*n*-butylstannyl)benzene or 1,3-bis(tri-*n*-butylstannyl)benzene.

Introduction

A great diversity of linearly- and angularly-fused polycyclic aromatic compounds show various biological and/or medicinal activities.[2−15] Although synthetic routes to linear polycyclic aromatic compounds have received much attention, it is only in recent years that the biological importance of highly-oxygenated, angularly-fused polycyclic aromatic compounds has led to the exploration of general methods for their construction.[7,8,16−29] Many biologically significant angularly-fused natural products (i.e., pradimicin A, cervinomycin A_1, G-2A, and simaomicin α in Figure 1) possess a common structural feature: a phenanthrene (or dihydrophenanthrene) core wherein one terminal ring is oxygenated at either the 1- or 4-position, or at both, and the other terminal ring possesses a phenolic hydroxyl group at the 5-position oriented toward the bay region of the phenanthrene core (see structure **1** in Figure 1). Building from extensive prior experience in the construction of quinones[30−47] and phenols,[48−56] a general and in most cases efficient methodology for the synthesis of highly-oxygenated,

* Address correspondence to Professor Lanny S. Liebeskind, Sanford S. Atwood Chemistry Center, Emory University, 1515 Pierce Drive, Atlanta, Georgia 30322. Tel: (404) 727-6604. FAX: (404) 727-0845. E-mail: CHEMLL1@unix.cc.emory.edu.

⊗ Abstract published in *Advance ACS Abstracts,* March 1, 1995.

(1) Current address: Professor Sangho Koo, Department of Chemistry, Myong Ji University, Yong In, Kyung Ki Do, Korea.

(2) Harvey, R. G.; Geacintov, N. E. *Acc. Chem. Res.* **1988**, *21*, 66.
(3) Sims, P.; Grover, P. L.; Swaisland, A.; Pal, K.; Hewer, A. *Nature (London)* **1974**, *252*, 326.
(4) Arcamone, F. In *Topics in Antibiotic Chemistry*; Sammes, P. G., Ed.; Halsted Press: New York, 1978; Vol. 2.
(5) Lown, J. W. *Chem. Soc. Rev.* **1993**, *22*, 165.
(6) Remers, W. A. *The Chemistry of Antitumor Antibiotics*; Wiley Interscience: Somerset, NJ, 1979; Vol. 1.
(7) Rohr, J.; Thiericke, R. *Nat. Prod. Rep.* **1992**, 103.
(8) Kelly, T. R.; Xu, W.; Ma, Z. K.; Li, Q.; Bhushan, V. *J. Am. Chem. Soc.* **1993**, *115*, 5843.
(9) Oki, T.; Kakushima, M.; Nishio, M.; Kamei, H.; Hirano, M.; Sawada, Y.; Konishi, M. *J. Antibiot.* **1990**, *43*, 1230.
(10) Tanabe, A.; Nakashima, H.; Yoshida, O.; Yamamoto, N.; Tenmyo, O.; Oki, T. *J. Antibiot.* **1988**, *41*, 1708.
(11) Oki, T.; Konishi, M.; Tomatsu, K.; Tomita, K.; Saitoh, K.-I.; Tsunakawa, M.; Nishio, M.; Miyaki, T.; Kawaguchi, H. *J. Antibiot.* **1988**, *41*, 1701.
(12) Singh, S. B.; Pettit, G. R. *J. Org. Chem.* **1989**, *54*, 4105.
(13) Omura, S.; Nakagawa, A.; Kushida, K.; Lukacs, G. *J. Am. Chem. Soc.* **1986**, *108*, 6088.
(14) Omura, S.; Iwai, Y.; Hinotozawa, K.; Takahashi, Y.; Kato, J.; Nakagawa, A.; Hirano, A.; Shimizu, H.; Haneda, K. *J. Antibiot.* **1982**, *35*, 645.
(15) Wilton, J. H.; Cheney, D. C.; Hokanson, G. C.; French, J. C.; He, C.-H.; Clardy, J. C. *J. Org. Chem.* **1985**, *50*, 3936.
(16) Estevez, J. C.; Villaverde, M. C.; Estevez, R. J.; Castedo, L. *Tetrahedron* **1993**, *49*, 2783.
(17) Larsen, D. S.; Oshea, M. D. *Tetrahedron Lett.* **1993**, *34*, 1373.
(18) Estevez, J. C.; Estevez, R. J.; Castedo, L. *Tetrahedron Lett.* **1992**, *33*, 6883.
(19) Marks, T. M.; Morrow, G. W. *Tetrahedron Lett.* **1992**, *33*, 2269.
(20) Kraus, G. A.; Wu, Y. S. *Tetrahedron Lett.* **1991**, *32*, 3803.
(21) Parker, K.; Ruder, S. M. *J. Am. Chem. Soc.* **1989**, *111*, 5948.
(22) Kim, K.; Reibenspies, J.; Sulikowski, G. *J. Org. Chem.* **1992**, *57*, 5557.
(23) Rao, A. V. R.; Yadav, J. S.; Reddy, K. K.; Upender, V. *Tetrahedron Lett.* **1991**, *32*, 5199.
(24) Mehta, G.; Shah, S. R. *Tetrahedron Lett.* **1991**, *32*, 5195.
(25) Kelly, T. R.; Jagoe, C. T.; Li, Q. *J. Am. Chem. Soc.* **1989**, *111*, 4522.
(26) Larsen, D. S.; O'Shea, M. D. *Tetrahedron Lett.* **1993**, *34*, 1373.
(27) Valderrama, J. A.; Araya-Maturana, R.; Gonzalez, M. F.; Tapia, R.; Farina, F.; Paredes, M. C. *J. Chem. Soc., Perkin Trans. 1* **1991**, 555.
(28) Brown, P. M.; Thomson, R. H. *J. Chem. Soc., Perkin Trans. 1* **1976**, 997.
(29) Guingant, A.; Barreto, M. M. *Tetrahedron Lett.* **1987**, *38*, 3107.
(30) Liebeskind, L. S.; Riesinger, S. W. *J. Org. Chem.* **1993**, *58*, 408.
(31) Edwards, J. P.; Krysan, D. J.; Liebeskind, L. S. *J. Am. Chem. Soc.* **1993**, *115*, 9868.
(32) Liebeskind, L. S.; Granberg, K. L.; Zhang, J. *J. Org. Chem.* **1992**, *57*, 4345.
(33) Liebeskind, L. S.; Zhang, J. *J. Org. Chem.* **1991**, *56*, 6379.
(34) Liebeskind, L. S.; Foster, B. F. *J. Am. Chem. Soc.* **1990**, *112*, 8612.
(35) Liebeskind, L. S. *Tetrahedron Symposium in Print* **1989**, *45*, 3053.
(36) Lee, K. H.; Moore, H. W. *Tetrahedron Lett.* **1993**, *34*, 235.
(37) Moore, H. W.; Yerxa, B. R. *Chemtracts: Org. Chem.* **1992**, *5*, 273.
(38) Gayo, L. M.; Winters, M. P.; Moore, H. W. *J. Org. Chem.* **1992**, *57*, 6896.
(39) Xia, H. J.; Moore, H. W. *J. Org. Chem.* **1992**, *57*, 3765.
(40) Heerding, J. M.; Moore, H. W. *J. Org. Chem.* **1991**, *56*, 4048.
(41) Perri, S. T.; Moore, H. W. *J. Am. Chem. Soc.* **1990**, *112*, 1897.
(42) Enhsen, A.; Karabelas, K.; Heerding, J. M.; Moore, H. W. *J. Org. Chem.* **1990**, *55*, 1177.
(43) Perri, S. T.; Dyke, H. J.; Moore, H. W. *J. Org. Chem.* **1989**, *54*, 2032.

0002-7863/95/1517-3389$09.00/0

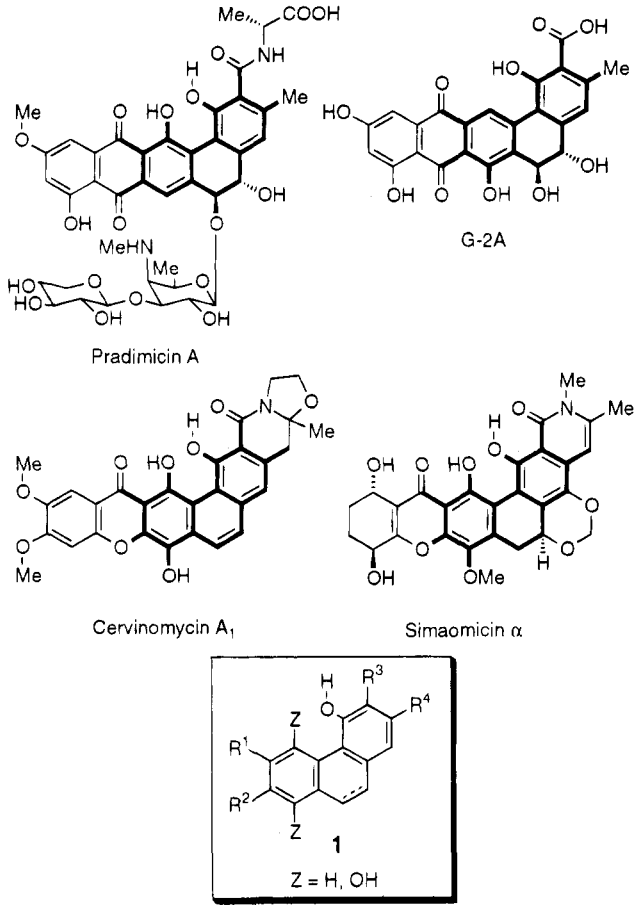
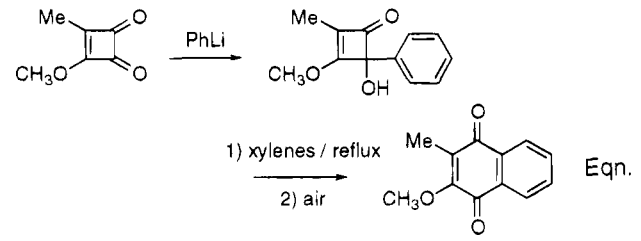


Figure 1.

angularly-fused polycyclic aromatic compounds possessing substitution pattern **1** has been developed. Details of that study are described herein.

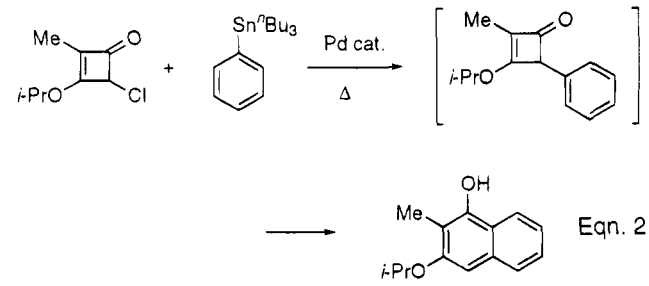
Background

The new methodology for the construction of angularly-fused, highly-oxygenated polycyclic aromatics was founded upon two general reactions that utilize the thermal reorganization of substituted cyclobutenones and are presumed to proceed through vinylketene intermediates. 1,4-Dioxygenated aromatics at either the hydroquinone or quinone oxidation state are easily generated by the 1,2-addition of aromatic nucleophiles to cyclobutenediones followed by thermal rearrangement to provide a dihydronaphthoquinone which is readily oxidized to the corresponding naphthoquinone.[57,58] This process is typified by the synthesis of 2-methoxy-3-methyl-1,4-naphthoquinone (eq 1).



Eqn. 1

Naphthol-based aromatics can be constructed utilizing a Stille cross-coupling[59,60] of a 4-chlorocyclobutenone with an aromatic tri-*n*-butylstannane followed by thermal rearrangement. The production of 3-(1-methylethoxy)-2-methylnaphthol illustrates this reaction (eq 2).[50]

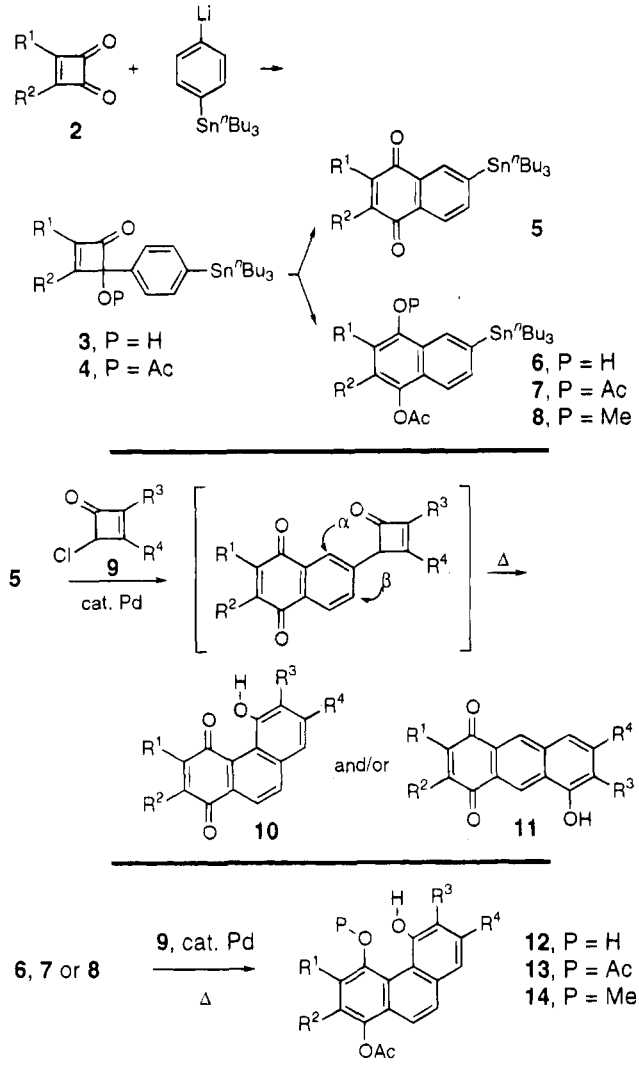


Eqn. 2

Through appropriate combination of these two benzannulation reactions a general route to the phenanthrene ring system at various levels of oxidation was envisioned (Scheme 1). Highly-regioselective addition of 4-(tri-*n*-butylstannyl)phenyllithium to a cyclobutenedione **2** should lead to the 1,2-adduct **3**. Thermolysis followed by oxidation will deliver the 6-(tri-*n*-butylstannyl)-1,4-naphthoquinone **5**. Alternatively, acetate protection of the 4-hydroxyl substituent of the cyclobutenone **3** will provide **4**, and thermolysis will give the 1-acetylated 6-(tri-*n*-butylstannyl)-1,4-naphthohydroquinone **6** which is blocked from undergoing facile oxidation to a quinone. Naphthol **6** can be further protected as the diacetate **7** or as the methyl ether **8**. In the 6-(tri-*n*-butylstannyl)naphthoquinone series, palladium-catalyzed cross-coupling of **5** with a 4-chlorocyclobutenone **9** should directly attach a 1-oxo-2-cyclobuten-4-yl moiety to the naphthoquinone core. Thermal rearrangement of the coupling product can result in either α-cyclization, leading to the desired angular ring fusion product **10**, or β-cyclization, leading to the undesired linear ring fusion product **11** (Scheme 1). The significant tendency of naphthalenes to undergo electrocyclic reactions at an α- and not at a β-position provides strong support favoring formation of the angularly-fused product,[61-65] at least in the generation of phenanthrenes **12**–**14** from the corresponding naphthohydroquinone intermediates **6**–**8**. Moreover, specific precedence exists documenting the selective formation of an angular ring fusion product by α-specific cyclization of ketenic intermediates onto naphthalenes.[40,58,66-70] By manipula-

(44) Foland, L. D.; Karlsson, J. O.; Perri, S. T.; Schwabe, R.; Xu, S. L.; Patil, S.; Moore, H. W. *J. Am. Chem. Soc.* **1989**, *111*, 975.
(45) Xu, S. L.; Moore, H. W. *J. Org. Chem.* **1989**, *54*, 6018.
(46) Foland, L. D.; Decker, O. H. W.; Moore, H. W. *J. Am. Chem. Soc.* **1989**, *111*, 989.
(47) Danheiser, R. L.; Casebier, D. S.; Loebach, J. L. *Tetrahedron Lett.* **1992**, *33*, 1149.
(48) Gurski, A.; Liebeskind, L. S. *J. Am. Chem. Soc.* **1993**, *115*, 6101.
(49) Liebeskind, L. S.; Wang, J. *J. Org. Chem.* **1993**, *58*, 3550.
(50) Krysan, D. J.; Gurski, A.; Liebeskind, L. S. *J. Am. Chem. Soc.* **1992**, *114*, 1412.
(51) Huffman, M. A.; Liebeskind, L. S. *J. Am. Chem. Soc.* **1991**, *113*, 2771.
(52) Xu, S. L.; Moore, H. W. *J. Org. Chem.* **1992**, *57*, 326.
(53) Danheiser, R. L.; Cha, D. D. *Tetrahedron Lett.* **1990**, *31*, 1527.
(54) Danheiser, R. L.; Brisbois, R. G.; Kowalczyk, J. J.; Miller, R. F. *J. Am. Chem. Soc.* **1990**, *112*, 3093.
(55) Danheiser, R. L.; Nishida, A.; Savariar, S.; Trova, M. P. *Tetrahedron Lett.* **1988**, *29*, 4917.
(56) Kowalski, C. J.; Lal, G. S. *J. Am. Chem. Soc.* **1988**, *110*, 3693.
(57) Stille, J. K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 508.
(58) Stille, J. K. *Pure Appl. Chem.* **1985**, *57*, 1771.
(59) Liebeskind, L. S.; Iyer, S.; Jewell, C. F., Jr. *J. Org. Chem.* **1986**, *51*, 3065.
(60) Moore, H. W.; Perri, S. T. *J. Org. Chem.* **1988**, *53*, 996.
(61) Claisen, L. *Chem. Ber.* **1912**, *45*, 3157.
(62) Green, J.; McHale, D. *Chem. Ind. (London)* **1964**, 1801.
(63) Green, J.; Marcinkiewicz, S.; McHale, D. *J. Chem. Soc. C* **1966**, 1422.
(64) McHale, D.; Marcinkiewicz, S.; Green, J. *J. Chem. Soc. C* **1966**, 1427.
(65) Venugopalan, B.; Balasubramanian, K. K. *Heterocycles* **1985**, *23*, 81.
(66) Iwasaki, M.; Li, J.-P.; Kobayashi, H.; Matsuzaka, Y.; Ishii, Y.; Hidai, M. *J. Org. Chem.* **1991**, *56*, 1922.
(67) Iwasaki, M.; Ishii, Y.; Hidai, M. *J. Organomet. Chem.* **1991**, *415*, 435.

Scheme 1

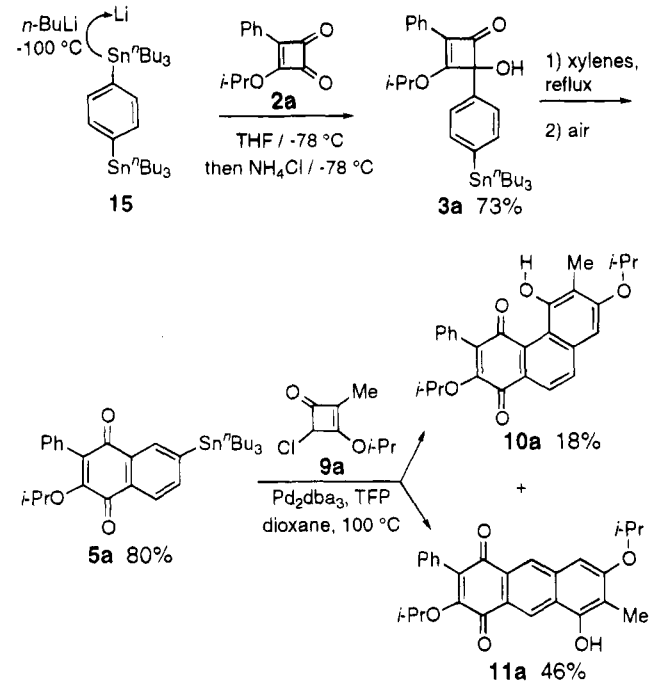


tion of reaction conditions and substrate oxidation state, the desired angularly-fused ring systems, **12**−**14**, were obtained in a general and efficient manner.

Results and Discussion

As depicted in Scheme 2, the study began with the preparation of [4-(tri-*n*-butylstannyl)phenyl]lithium, which was generated from 1,4-bis(tri-*n*-butylstannyl)benzene (**15**)[71] by Sn-Li exchange with 1 equiv of *n*-BuLi. In order to suppress the formation of 1,4-dilithiobenzene, the reaction temperature was kept below −100 °C and *n*-BuLi was added slowly. The solution of [4-(tri-*n*-butylstannyl)phenyl]lithium was then added to 3-(1-methylethoxy)-4-phenylcyclobutene-1,2-dione (**2a**) to produce the 4-hydroxycyclobutenone **3a** in 73% yield in a highly-regioselective process. Thermolysis of 4-hydroxy-4-[4′-(tri-*n*-butylstannyl)phenyl]-2-cyclobutenone **3a** produced the desired 6-(tri-*n*-butylstannyl)-1,4-naphthoquinone **5a** in 80% yield after air oxidation of the initially formed dihydroquinone. Stille coupling of **5a** and 4-chloro-3-(1-methylethoxy)-2-methyl-2-cyclobutenone (**9a**) and subsequent thermolysis of the coupling product produced two distinctly colored quinone products which

Scheme 2



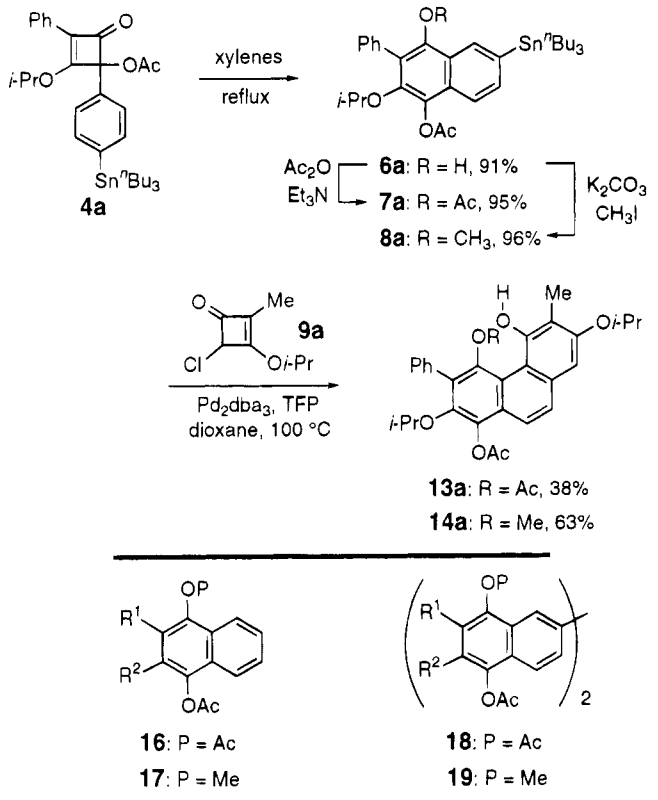
were readily separable by column chromatography. However, the desired angularly-fused 5-hydroxy-1,4-phenanthraquinone **10a** (yellow-brown) was obtained in only 18% yield; the linearly-fused 5-hydroxy-1,4-anthraquinone **11a** (red) was the major product (46% yield). The failure to obtain selectively the angularly-fused product was attributed to the use of **5a**, a substrate at the naphthoquinone oxidation state which results in the key benzannulation step occurring on an electron-deficient benzene ring (see **5** → **10** + **11**, Scheme 1) rather than on a naphthalene core. To overcome this situation a substrate at the naphthohydroquinone rather than the naphthoquinone oxidation state was studied.

To test the tandem Stille cross-coupling/benzannulation on a naphthalene core, 1,4-diacetoxy-6-(tri-*n*-butylstannyl)naphthalene **7a** was prepared (Scheme 3). Addition of [4-(tri-*n*-butylstannyl)phenyl]lithium to cyclobutenedione **2a** and then acetylation in situ with acetic anhydride formed 4-acetoxy-4-[4′-(tri-*n*-butylstannyl)phenyl]-2-cyclobutenone **4a**. Thermolysis produced 1-*O*-acetyl-6-(tri-*n*-butylstannyl)naphthohydroquinone **6a**, and simple acetylation of **6a** gave **7a**. A tandem Stille coupling and benzannulation reaction of 1,4-diacetoxy-6-(tri-*n*-butylstannyl)naphthalene **7a** and 4-chloro-2-cyclobutenone **9a** gave rise to the desired phenanthrene product **13a** in 38% yield. Because of scrambling of the acetyl group between the 4- and 5-positions of phenanthrenediol **13a**, complete acetylation was conducted prior to characterization. Although **13a** was obtained in low yield, no trace of the linearly-fused anthracene product was observed, which implied that benzannulation of the substituted naphthalene occurred regiospecifically, producing only the angularly-fused phenanthrene product. However, along with **13a** the protodestannylation product **16a** (R^1 = Ph, R^2 = *i*-PrO; 6%) and the organostannane homocoupling product **18a** (R^1 = Ph, R^2 = *i*-PrO; 22%; 44% of **7a** consumed) were also isolated. To render the process depicted in Scheme 3 practical, the consumption of organostannane starting material by palladium-mediated homocoupling must be overcome or inhibited.

Transmetalation is the rate-determining step in most Stille cross-coupling reactions.[59,60,72] If the low yield of the desired

(68) Matsuzaka, H.; Hiroe, Y.; Iwaski, M.; Ishii, Y.; Koyasu, Y.; Hidai, M. *J. Org. Chem.* **1988**, *53*, 3832.
(69) Dötz, K. H. *Pure Appl. Chem.* **1983**, *55*, 1689.
(70) Semmelhack, M. F.; Ho, S.; Cohen, D.; Steigerwald, M.; Lee, M. C.; Lee, G.; Gilbert, A. M.; Wulff, W. D.; Ball, R. G. *J. Am. Chem. Soc.* **1994**, *116*, 7108.
(71) Morgan, J.; Pinhey, J. T. *J. Chem. Soc., Perkin Trans. 1* **1990**, 715.
(72) Farina, V.; Krishnan, B. *J. Am. Chem. Soc.* **1991**, *113*, 9585.

Scheme 3

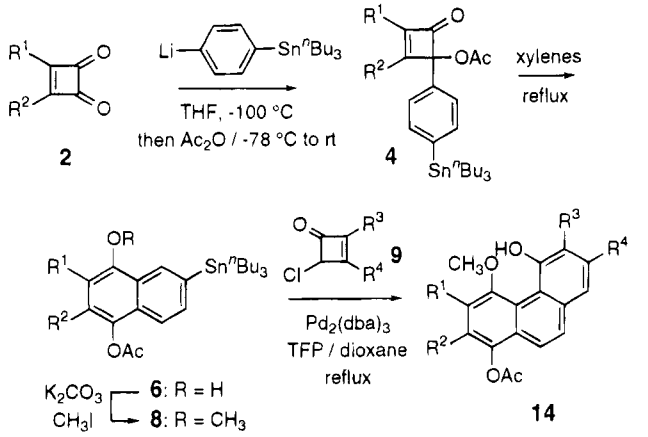


product **13a** was due to a slow transmetalation step (relative to the processes leading to protodestannylation and organostannane homocoupling), the yield could be influenced by the nature of the transferring group as well as that of the ligands used to support the palladium intermediates carrying the catalytic process.[72] To probe these factors, a limited study was conducted varying the ligands used in the cross-coupling reaction of both the acetate-protected and methyl ether protected naphthols **7a** and **8a**, with 4-chlorocyclobutenone **9a**. In this brief study, the naphthol methyl ether series **8** produced the best result; an optimum yield of the highly-oxygenated phenanthrene **14a** (63%) was obtained using tris(2-furyl)phosphine[72] as the supporting ligand (Scheme 3). Small amounts of the protodestannylation product **17a** (R^1 = Ph, R^2 = *i*-PrO; 10%) and the organostannane homocoupling product **19a** (R^1 = Ph, R^2 = *i*-PrO; 13%) were also observed in this case.

In order to demonstrate the generality of this method, variously substituted angularly-fused aromatic compounds were synthesized from four different cyclobutenediones **2a**–**d**[73,74] and three different 4-chloro-2-cyclobutenones **9a**–**c**.[50,75] The results are summarized in Table 1. To ensure monoaddition of [4-(tri-*n*-butylstannyl)phenyl]lithium to the cyclobutenedione, the nucleophile was transferred slowly via cannula into a solution of the cyclobutenedione held at −100 °C; quenching with acetic anhydride gave the 4-acetoxy-2-cyclobutenones **4a,c,d**. The addition of [4-(tri-*n*-butylstannyl)phenyl]lithium to unsymmetrically substituted cyclobutenediones took place only at the more electron-deficient carbonyl group. In the case of benzocyclobutenedione, one diastereomer of a dimeric acetal **20** (stereochemistry undefined) was obtained upon quenching the reaction mixture with acetic anhydride. To circumvent this

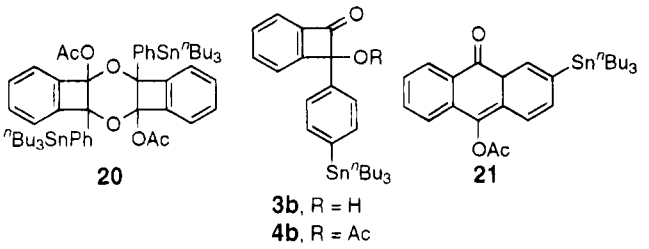
(73) Liebeskind, L. S.; Fengl, R. W.; Wirtz, K. R.; Shawe, T. T. *J. Org. Chem.* **1988**, *53*, 2482.
(74) Liebeskind, L. S.; Lescosky, L. J.; McSwain, C. M., Jr. *J. Org. Chem.* **1989**, *54*, 1435.
(75) Edwards, J. P.; Krysan, D.; Liebeskind, L. S. *J. Org. Chem.* **1993**, *58*, 3942.

Table 1. Synthesis of Highly-Oxygenated Angularly-Fused Polycyclic Aromatic Compounds



entry	2 R^1	2 R^2	compd	% 4	compd	% 6, 8	9 R^3	9 R^4	compd	% 14
1	Ph	*i*-PrO	**4a**	73	**6a, 8a**	91, 96	Me	*i*-PrO	**14a**	63
2	Ph	*i*-PrO					Et	Et	**14b**	81
3	Ph	*i*-PrO					Ph	*i*-PrO	**14c**	17
4	benzo		**4b**	49[a]	**6b, 8b**	64,[b] 51	Et	Et	**14f**	80
5	Me	Me	**4c**	50	**6c, 8c**	96, 93	Me	*i*-PrO	**14d**	51
6	Me	Me					Et	Et	**14e**	77
7	Me	*i*-PrO	**4d**	70	**6d, 8d**	94, 98	Me	*i*-PrO	**14g**	41
8	Me	*i*-PrO					Et	Et	**14h**	68

[a] Overall yield after isolation of **3b** and acetylation. [b] Isolated as the anthracenone tautomer.

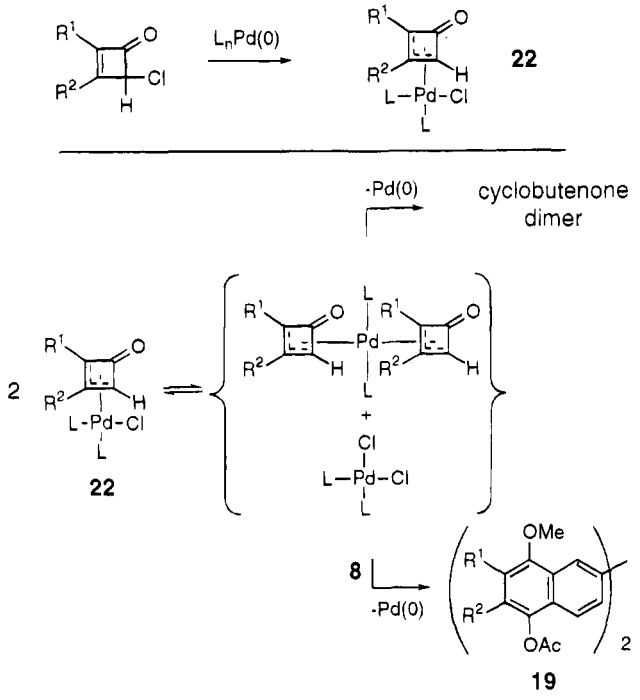


undesired process, the reaction was quenched with saturated aqueous NH_4Cl solution to cleave the dimeric acetal intermediate, and the monomeric addition product **3b** (60%) was produced. This compound was acetylated in a separate step (acetic anhydride, Et_3N, DMAP in CH_2Cl_2) and gave 2-acetoxybenzocyclobutenone **4b** (81%). In the case of 3,4-dimethylcyclobutene-1,2-dione, **2c**, a relatively low yield (50%) of the addition product **4c** was obtained, and an appreciable amount of the starting material was recovered. The highly-acidic nature of 3,4-dimethylcyclobutene-1,2-dione (**2c** is soluble in 5% NaOH solution) may have led to competitive deprotonation by the nucleophile.

Upon thermolysis in xylenes, the 4-acetoxy-2-cyclobutenones **4** produced benzannulation products. From cyclobutenones **2a**, **2c**, and **2d** were produced the 6-(tri-*n*-butylstannyl)naphthohydroquinone derivatives **6a**, **6c**, and **6d**, respectively. For these three systems, the thermolysis in refluxing xylenes was complete within 1 h. Thermolysis at lower temperature required longer reaction times and produced more of the protodestannylation product. Benzocyclobutenone **4b** underwent benzannulation at a much slower rate in refluxing xylenes (8 h) and yielded 2-(tri-*n*-butylstannyl)-9-anthracenone **21** (64%) rather than the expected hydroxyanthracene. Unreacted starting material remained (10%), even after 8 h in refluxing xylenes.

Methylation of the free OH of (tri-*n*-butylstannyl)naphthols

Scheme 4

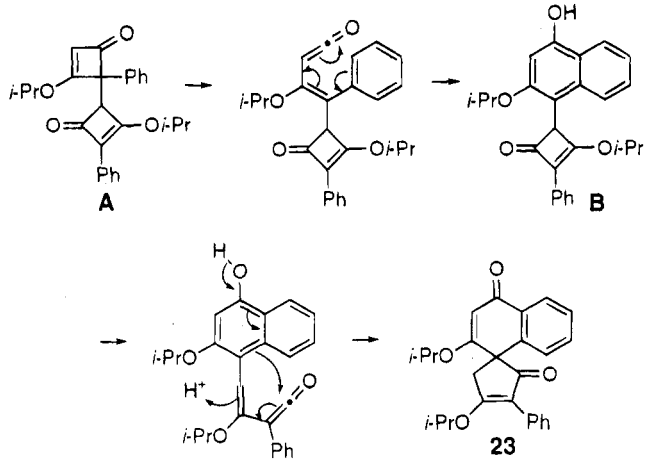


6a, **6c**, and **6d** was achieved in high yield using K_2CO_3 and CH_3I in acetone. The same method when applied to anthracenone **21** gave the desired anthracene methyl ether **8b** (51%). The major competing reaction in this case was hydrolysis of the acetoxy group and subsequent oxidation to produce 2-(tri-*n*-butylstannyl)-9,10-anthraquinone; no effort was made to improve the yield of this reaction.

The tri-*n*-butylstannyl aromatics **8** were treated with 4-chlorocyclobutenones **9a**–**c** in the presence of a catalytic amount of $Pd_2(dba)_3$ (2.5 mol %) and tris(2-furyl)phosphine (10 mol %) in dioxane at reflux. Under these conditions, the resulting cross-coupling products directly underwent benzannulation, providing the variously substituted phenanthrenes **14** shown in Table 1. 4-Chloro-2,3-diethylcyclobutenone (**9b**) consistently gave good yields (68–81%) of the cross-coupling/benzannulation products. Fair yields (41–63%) of the phenanthrene products were obtained with 4-chloro-2-methyl-3-(1-methylethoxy)-2-cyclobutenone (**9a**) although appreciable amounts of the protodestannylation products **17b** and **17c** and the organostannane homocoupling products **19b** and **19c** (in Scheme 3, $R^1 = R^2 =$ Me and $R^1 =$ Me, $R^2 = i$-PrO, respectively) were also obtained with this substrate. For reasons alluded to below, reaction of **8a** with 4-chloro-3-(1-methylethoxy)-2-phenyl-2-cyclobutenone (**9c**) was problematic, giving predominantly the homocoupling product **19a** (37%) and forming only 17% of the cross-coupling/thermolysis product **14c**.

The catalytic cycle of the Stille cross-coupling reaction is composed of oxidative addition, transmetalation, *trans*–*cis* isomerization, and reductive elimination steps.[59,60] The organostannane homocoupling side product **19** is formed by an oxidative process that must be driven by a concomitant reduction. Because the Stille cross-coupling reactions depicted in Table 1 were conducted with careful exclusion of oxygen, the formation of **19** in the quantities seen must be accompanied by the reduction of one of the reactants. On the presumption that a recalcitrant transmetalation step was the source of synthetic difficulties,[72] attention was focused on the putative (η^3-allyl)palladium intermediate **22** preceding the transmetalation (Scheme 4). If transmetalation is slow, and a fast oxidative addition delivers a *relatively* high concentration of the (η^3-allyl)-

Scheme 5



palladium **22**, two (η^3-allyl)palladium species could undergo ligand equilibration by conproportionation, producing both a bis(η^3-allyl)palladium species and L_2PdX_2. Reductive elimination of the bis(η^3-allyl)palladium would produce a cyclobutenone dimer and regenerate a source of zero-valent palladium that can reenter the cross-coupling process, while each L_2PdX_2 could react with 2 equiv of the tri-*n*-butylstannyl aromatic **8**, leading to the homocoupling product **19** and Pd(0) after reductive elimination. This mechanism features the 4-chlorocyclobutenone **9** as the oxidant that drives formation of the homocoupling product **19** and requires the formation of a cyclobutenone dimer or its synthetic descendant.

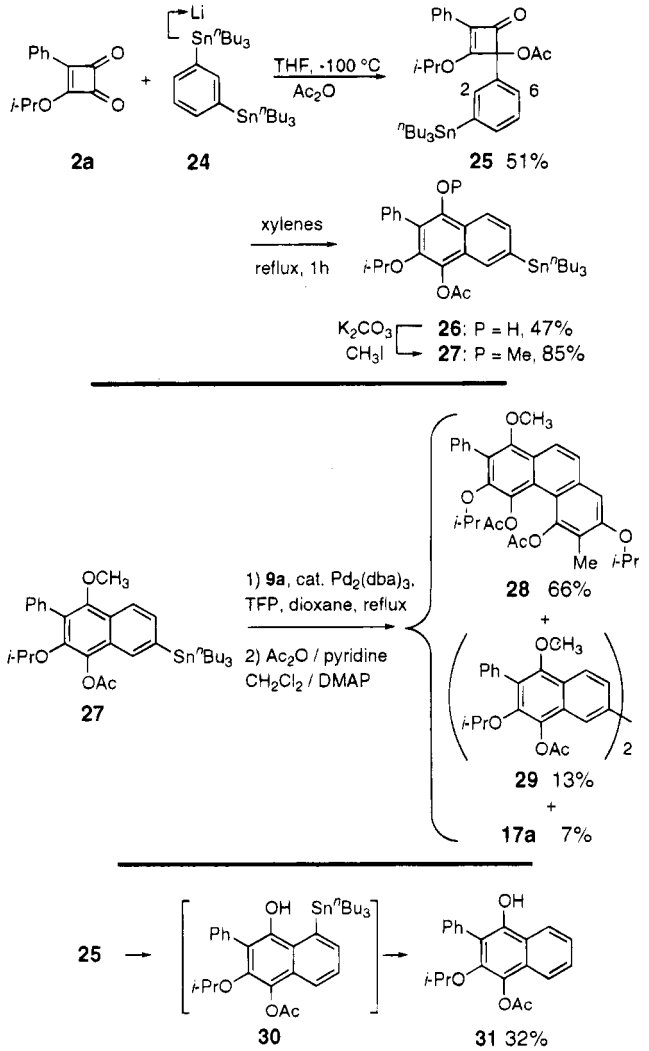
To support the mechanism proposed in Scheme 4, the reaction mixture from the Stille coupling of 6-(tri-*n*-butylstannyl)-naphthalene **8a** and 4-chloro-3-(1-methylethoxy)-2-phenyl-2-cyclobutenone (**9c**) was carefully analyzed. Indeed, a highly-polar compound was recovered from chromatography and identified by X-ray crystallography as the spiro diketo compound **23** (40%, 80% based on consumed **9c**; the supplementary material contains details of the X-ray structure determination). A probable mechanism for the formation of **23** is depicted in Scheme 5. Palladium-mediated reductive coupling of the 4-chlorocyclobutenone, as suggested in Scheme 4, could generate the unsymmetrical dimer **A**. Thermal ring opening and electrocyclization would produce the 4-(1-oxo-2-cyclobuten-4-yl)naphthol **B**. Subsequent thermal opening of the remaining cyclobutenone ring would generate a reactive vinylketene that could cyclize to generate the spirodiketone **23**. The formation of **23** requires the exclusive formation of the unsymmetrical cyclobutenone dimer **A**, a result more easily rationalized by reductive coupling through an (η^3-allyl)(η^1-allyl)palladium than a bis(η^3-allyl)palladium.

By applying the tandem Stille coupling/benzannulation process to (tri-*n*-butylstannyl)naphthalene **27**, a regioisomer of the 6-(tri-*n*-butylstannyl)naphthalene **8a** used successfully above, a regioisomeric series of highly-oxygenated phenanthrenes should be accessible. Scheme 6 describes the synthesis and a cross-coupling/benzannulation reaction of (tri-*n*-butylstannyl)-naphthalene **27**. [3-(Tri-*n*-butylstannyl)phenyl]lithium was generated in situ from 1,3-bis(tri-*n*-butylstannyl)benzene (**24**).[76] The addition of [3-(tri-*n*-butylstannyl)phenyl]lithium to 3-(1-methylethoxy)-4-phenylcyclobutene-1,2-dione (**2a**) followed by acetylation of the addition product provided 4-acetoxy-4-[3′-(tri-*n*-butylstannyl)phenyl]-2-cyclobutenone **25** in 51% yield. Benzannulation of **25** can take place at either the 2- or 6-position of the phenyl ring. Thermolysis of cyclobutenone **25** produced a

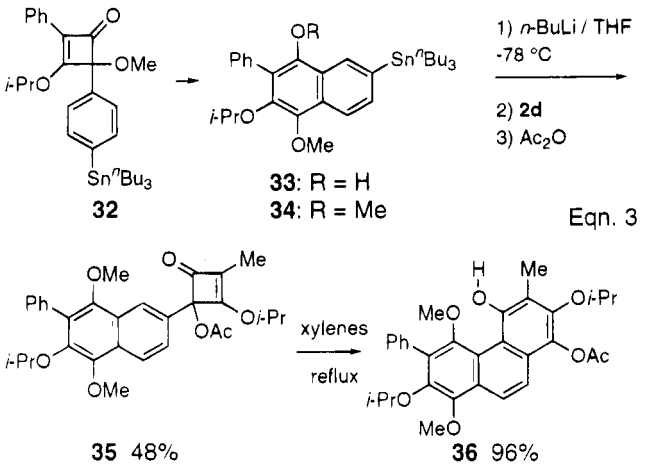
(76) Wright, M. E. *Organometallics* **1989**, *8*, 407.

3:2 mixture of the (tri-*n*-butylstannyl)naphthol **26** (47%) and the destannylated naphthol **31** (32%), the latter presumably formed partially from (tri-*n*-butylstannyl)naphthol **30** via facile protodestannylation. The regioselectivity of the benzannulation of 2,3-dimethoxy-4-hydroxy-4-(3′-substituted phenyl)-2-cyclobutenones was studied previously by Moore,[58] and selectivities of 1:1 and 10:1 favoring cyclization at C-6 were obtained for methyl and methoxy substituents, respectively. The phenolic hydroxyl group of **26** was methylated, and the resulting (tri-*n*-butylstannyl)naphthalene **27** was treated with 4-chloro-2-methyl-3-(1-methylethoxy)-2-cyclobutenone (**9a**) under cross-coupling/thermolysis conditions. After complete acetylation (because of scrambling of the acetyl group), a good yield (66%) of the anticipated product **28** was obtained along with small amounts of side products derived from protodestannylation (**17a**, 7%) and homocoupling (**29**, 13%) of naphthalene **27**.

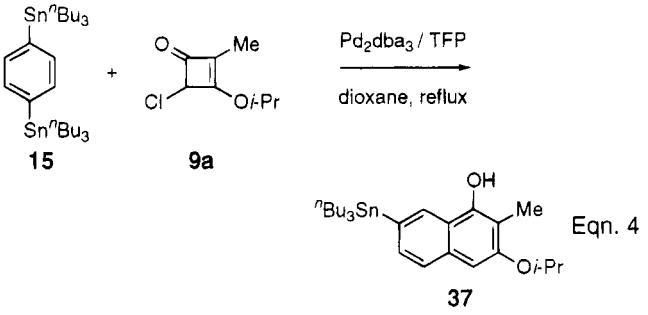
Scheme 6



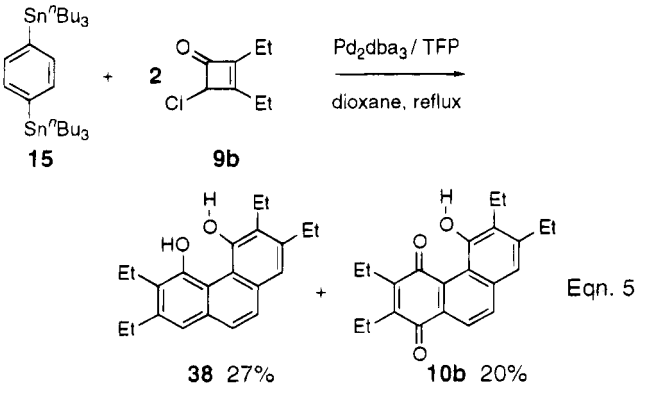
To probe a higher level of oxygen substitution in the phenanthrene synthesis, (tri-*n*-butylstannyl)naphthalene **34** was prepared by methylation of **33**, which was generated by thermolysis of **32**, (which) itself was prepared by methylation of **3a** (eq 3). (Tri-*n*-butylstannyl)naphthalene **34** was subjected to Sn → Li transmetalation with *n*-BuLi, and the reactive aryllithium reagent was then added to 3-methyl-4-(1-methylethoxy)cyclobutene-1,2-dione (**2d**). Quenching with acetic anhydride gave the 6-(1-oxo-2-cyclobuten-4-yl)naphthalene **35** (48%), which upon thermolysis gave the angularly-fused phenanthrene **36** as the only product (96%).



Having demonstrated that exchange of one of the two $SnBu_3$ groups for Li on either the 1,4- or 1,3-bis(tri-*n*-butylstannyl)-benzene (**15** or **24**) gives a reactive monolithiate that adds efficiently to a cyclobutenedione, providing after acetylation and thermolysis a (tri-*n*-butylstannyl)naphthol (**6** or **26**, Scheme 3 or Scheme 6, respectively), an alternate synthesis of (tri-*n*-butylstannyl)naphthols at a lower overall level of oxidation was sought. The palladium-catalyzed cross-coupling/benzannulation of **15** with *1 equiv* of a 4-chlorocyclobutenone was studied. 1,4-Bis(tri-*n*-butylstannyl)benzene (**15**) was treated with one equivalent of 4-chloro-2-cyclobutenone **9a** in the presence of $Pd_2(dba)_3$/TFP (2.5 and 10 mol %, respectively) in dioxane at reflux (eq 4). After 2 h, (tri-*n*-butylstannyl)naphthol **37** was obtained in

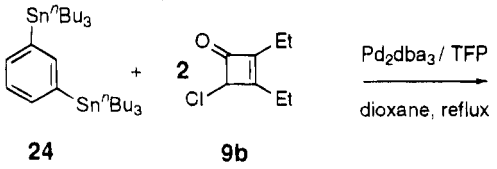


28% yield, a yield that could not be improved. Prolonged reaction time led to protodestannylation. When 1,4-bis(tri-*n*-butylstannyl)benzene (**15**) was treated under cross-coupling/benzannulation conditions with *2 equiv* of 4-chloro-2,3-diethyl-2-cyclobutenone (**9b**), 4,5-dihydroxyphenanthrene **38** (27%) and 5-hydroxy-1,4-phenanthraquinone **10b** (20%) were obtained (eq 5). A related cross-coupling/benzannulation of 1,3-bis(tri-*n*-

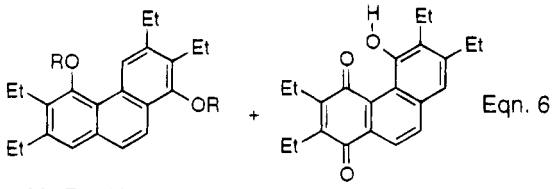


butylstannyl)benzene (**24**) with 2 equiv of 4-chloro-2,3-diethyl-2-cyclobutenone (**9b**) produced 4,8-dihydroxyphenanthrene **39**

(15%) and 5-hydroxy-1,4-phenanthraquinone **10b** (24%) (eq 6).



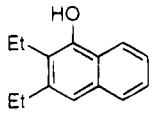
24 **9b**



39: R = H 15%
40: R = Ac 31%

10b 24%

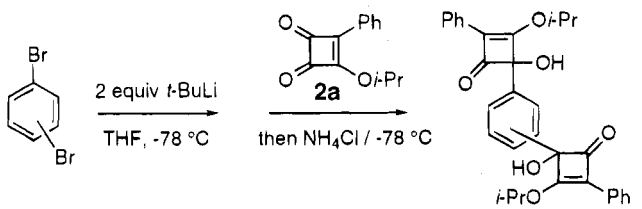
In both cases an appreciable amount of the protodestannylated naphthol **41** was observed. Apparently, facile autoxidation of

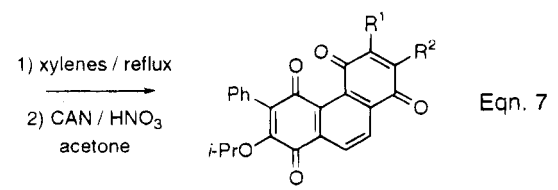


41

dihydroxyphenanthrenes **38** and **39** during workup or purification gave the phenanthraquinone **10b**. In order to produce the *same* phenanthraquinone **10b** from the regioisomeric phenanthrenediols **38** and **39**, it is clear that the oxidation of **39** must occur selectively at C-5, an oxidation possibly directed by the OH group at C-4 of **39**. Phenanthrenediol **38** was obtained in pure form, but the isomeric compound **39** could not be purified because of facile oxidation to **10b**. To prevent oxidation and allow complete characterization, crude **39** was fully acetylated producing 4,8-diacetoxy-2,3,6,7-tetraethylphenanthrene (**40**) in 31% yield.

In a final variation on phenanthrene synthesis employing double benzannulation of a central aromatic ring, both 1,4- and 1,3-dilithiobenzene were generated from the corresponding dibromobenzene by reaction with *t*-BuLi at −78 °C. Treatment of 1,4-dilithiobenzene with 2 equiv of cyclobutendione **2a**, followed by an NH_4Cl quench, thermolysis, and then oxidation, produced the symmetrical phenanthrenyl diquinone **42a** in 59% overall yield (eq 7). The isomeric unsymmetrical phenanthrenyl





42a: R^1 =Ph, R^2 = *i*-PrO 59%
42b: R^1 =*i*-PrO, R^2 = Ph 60%

diquinone **42b** was obtained (60%) when the same reaction sequence was applied to 1,3-dilithiobenzene. In both cases, exposure of the thermolysis product to air generated only partially oxidized products; oxidation with ceric ammonium nitrate was required to produce efficiently the fully oxidized phenanthrenyl diquinones **42a** and **42b**.

Conclusions

An effective and general method for the synthesis of highly-oxygenated phenanthrenes has been developed. The synthesis highlights the use of 1,4- and 1,3-bis(tri-*n*-butylstannyl)benzene as core structures from which angularly-fused polycyclic aromatic molecules are fabricated. Cyclobutenone moieties are attached to these aromatic cores either by reaction of cyclobutenediones with monolithiates, generated from the bis(tri-*n*-butylstannyl)benzene by *n*-$Bu_3Sn \rightarrow$ Li exchange, or by palladium-catalyzed cross-coupling of the bis(tri-*n*-butylstannyl)-benzene with a 4-chlorocyclobutenone. The bis(tri-*n*-butylstannyl)benzenes undergo a double palladium-catalyzed cross-coupling with 2 equiv of a 4-chlorocyclobutenone, and under the conditions of the cross-coupling (refluxing dioxane), the cross-coupling products are transformed directly into phenanthrenes. Alternatively, thermolysis of the cyclobutenedione 1,2-adducts formed via the monolithiate route induces tranformation into a tri-*n*-butylstannylated naphthalene. These organostannanes participate in palladium-catalyzed cross-coupling with 4-chlorocyclobutenones, and subsequent thermolysis provides highly-oxygenated phenanthrenes. Other variations on this synthetic scheme are also disclosed.

Experimental Section

Materials and Methods. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ with chloroform as an internal reference (7.26 ppm ^1H, 77.0 ppm ^{13}C) unless otherwise stated. Data are reported in the following order: chemical shifts (δ); multiplicities (br (broadened), s (singlet), d (doublet), t (triplet), q (quartet), hex (hextet), hept (heptet), m (multiplet)); coupling constants (J, Hz); integration. For ^{13}C spectra, the number of coincident carbon signals are given (no. of C). Infrared spectra were recorded using sodium chloride plates (liquid) or potassium chloride cells (solution). Peaks are reported (cm^{-1}) with the following relative intensities: s (strong, 67−100%), m (medium 40−67%), w (weak 20−40%), and br (broad).

Analytical thin-layer chromatography (TLC) was performed on Merck silica gel plates with F-254 indicator. Visualization was accomplished by UV light, iodine vapor, phosphomolybdic acid in ethanol, or ceric ammonium sulfate in sulfuric acid. Solvents for extraction and chromatography were reagent grade and were used as received. Flash chromatography was performed with 32−63 mm silica gel (Woelm). Solvents used as reaction media were distilled immediately before use: Et_2O, THF, and toluene were distilled from Na/benzophenone ketyl; CH_2Cl_2, diisopropylamine, and CH_3CN were distilled from CaH_2; Et_3N was distilled from KOH; DMF was dried over $MgSO_4$, filtered, and distilled under reduced pressure. Unless noted otherwise, all reactions were performed under a dry argon atmosphere in oven- and/or flame-dried glassware. "Brine" refers to a saturated aqueous solution of NaCl.

For the ^1H and ^{13}C NMR spectra of organostannanes, those peaks which show satellite resonances due to coupling with ^{117}Sn and ^{119}Sn isotopes are marked with an asterisk ("").*

Preparation of Starting Materials. 3-(1-Methylethoxy)-4-phenyl-3-cyclobutene-1,2-dione (**2a**),[73] benzocyclobutenedione (**2b**),[77] 3,4-dimethylcyclobutene-1,2-dione (**2c**),[73] and 3-methyl-4-(1-methylethoxy)cyclobutene-1,2-dione (**2d**)[73] were prepared by literature procedures.

(77) South, M. S.; Liebeskind, L. S. *J. Org. Chem.* **1982**, *47*, 3815.

1,4-Bis(tri-*n*-butylstannyl)benzene (15).[78] To a stirred solution of 1,4-dibromobenzene (4.13 g, 17.5 mmol) in THF (150 mL) at −78 °C was added a 1.4 M solution of *t*-BuLi in pentane (50.0 mL, 70.0 mmol). The resulting greenish-brown suspension was stirred vigorously at that temperature for 1 h, at which point *n*-Bu_3SnCl (14.2 mL, 52.5 mmol) was added. The reaction mixture was slowly warmed to and stirred at room temperature overnight and was then quenched with saturated aqueous NH_4Cl solution (40 mL). The solution was extracted with Et_2O (200 mL), washed with brine (2 × 30 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude oil was purified by vacuum distillation to give **15** as a clear oil (7.70 g, 11.7 mmol, 67%): bp 242−243 °C/1.8 mmHg (lit.[78] bp 206−210 °C/0.04 mmHg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41 (s, 4H),* 1.68−1.40 (m, 12H),* 1.33 (hex, *J* = 7.3 Hz, 12H), 1.04 (t, *J* = 8.1 Hz, 12H),* 0.89 (t, *J* = 7.2 Hz, 18H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 141.5 (4C), 136.2 (2C),* 29.2 (3C),* 27.5 (3C),* 13.7 (3C), 9.6 (3C)*; IR (neat, cm^{-1}) 3036 (m), 2957 (s), 2925 (s), 2872 (s), 2853 (s), 1463 (s).

1,3-Bis(tri-*n*-butylstannyl)benzene (24).[76] To a stirred solution of 1,3-dibromobenzene (15.00 g, 63.58 mmol) in THF (200 mL) at −78 °C was added a 1.7 M solution of *t*-BuLi in pentane (150 mL, 254 mmol) in several portions. The resulting greenish-brown suspension was stirred vigorously for 1 h at −78 °C, and then *n*-Bu_3SnCl (52 mL, 191 mmol) was added. The reaction mixture was slowly warmed to and stirred at room temperature overnight and was then quenched with saturated aqueous NH_4Cl solution (50 mL). The organic phase was extracted with Et_2O (200 mL), washed with brine (2 × 50 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude oil was purified by vacuum distillation to give 1,3-bis(tri-*n*-butylstannyl)benzene (**24**) as a clear oil (24.08 g, 36.70 mmol, 58%): R_f 0.81 (100% hexanes); bp 215−216 °C/1.8 mmHg; ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.54 (s, 1H),* 7.47−7.31 (m, 2H),* 7.31−7.20 (m, 1H), 1.65−1.46 (m, 12H),* 1.33 (hex, *J* = 7.2 Hz, 12H), 1.04 (dd, *J* = 8.3, 7.9 Hz, 12H), 0.89 (t, *J* = 7.2 Hz, 18H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 144.9,* 141.4, 136.1 (2C),* 127.8 (2C),* 29.2 (6C),* 27.4 (6C),* 13.7 (6C), 9.6 (6C)*; IR (neat, cm^{-1}) 2957 (s), 2926 (s), 2871 (s), 2855 (s), 1460 (s). Anal. Calcd for $C_{30}H_{58}Sn_2$: C, 54.92; H, 8.90. Found: C, 55.01; H, 8.96.

Nucleophilic Addition of 3- or 4-(Tri-*n*-butylstannyl)phenyllithium to Cyclobutenediones. Synthesis of Cyclobutenones 3a,b, 4a−d, and 25. General Comments. A solution of *n*-BuLi in hexanes was slowly added to a stirred solution of the bis(tri-*n*-butylstannyl)-benzene in THF at −100 °C (liquid N_2 in Et_2O bath). The resulting light yellow solution was slowly warmed to −20 °C (~1 h) and then cooled back to −100 °C. Then, one of two procedures was followed. Either a THF solution of the cyclobutenedione was added in one portion to the solution of (tri-*n*-butylstannyl)phenyllithium, and the reaction mixture was then stirred vigorously at −78 °C for 1 h, or the solution of (tri-*n*-butylstannyl)phenyllithium was transferred via cannula into a solution of the cyclobutenedione in THF held at −100 °C, and the reaction mixture was then stirred at −78 °C for 1 h. In either case, the reaction mixture was quenched with either acetic anhydride (to generate compounds **4**) or saturated aqueous NH_4Cl solution (to generate compounds **3**) as indicated below. The mixture was then warmed to room temperature, diluted with Et_2O, washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by SiO_2 flash chromatography.

4-Hydroxy-3-(1-methylethoxy)-2-phenyl-4-[4′-(tri-*n*-butylstannyl)-phenyl]-2-cyclobuten-1-one (3a). A solution of 3-(1-methylethoxy)-4-phenyl-3-cyclobutene-1,2-dione (**2a**) (216 mg, 1.00 mmol) in THF (5 mL) was added in one portion to a stirred solution of [4-(tri-*n*-butylstannyl)phenyl]lithium in THF (15 mL) at −100 °C (from 875 mg, 1.33 mmol of **15** and 1.1 mL, 1.00 mmol of a 0.95 M solution of *n*-BuLi in hexanes). After 1 h at −78 °C and a quench with saturated aqueous NH_4Cl solution (10 mL), workup and flash chromatography (SiO_2, 3 × 20 cm, 15−33% EtOAc/hexanes) afforded 4-hydroxy-cyclobutenone **3a** (420 mg, 0.72 mmol, 72%) as a clear oil: R_f 0.43 (1:3 ethyl acetate/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.84−7.78 (m, 2H), 7.48 (s, 4H),* 7.42−7.35 (m, 2H), 7.34−7.28 (m, 1H), 4.83 (hept, *J* = 6.0 Hz, 1H), 3.44 (br s, 1H), 1.56−1.43 (m, 6H), 1.46 (d, *J* = 6.0 Hz, 3H), 1.38−1.23 (m, 6H), 1.11 (d, *J* = 6.0 Hz, 3H), 1.04 (t, *J* = 8.1 Hz, 6H),* 0.87 (t, *J* = 7.2 Hz, 9H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 189.0, 180.6, 142.0, 136.7 (4C),* 128.8, 128.4 (2C), 127.9, 127.0 (2C), 125.6, 125.1,* 93.7, 79.6, 29.1 (3C),* 27.4 (3C),* 23.1, 22.5, 13.7 (3C), 9.6 (3C)*; IR (neat, cm^{-1}) 3367 (br s), 1741 (s), 1623 (s), 1596 (s), 1492 (s). Anal. Calcd for $C_{31}H_{44}O_3Sn$: C, 63.83; H, 7.60. Found: C, 63.65; H, 7.58.

4-Acetoxy-3-(1-methylethoxy)-2-phenyl-4-[4′-(tri-*n*-butylstannyl)-phenyl]-2-cyclobuten-1-one (4a). A solution of 3-(1-methylethoxy)-4-phenyl-3-cyclobutene-1,2-dione (**2a**) (865 mg, 4.00 mmol) in THF (10 mL) was added in one portion to a stirred solution of [4-(tri-*n*-butylstannyl)phenyl]lithium in THF (100 mL) at −100 °C (generated from 3.40 g, 5.20 mmol of **15** and 3.9 mL, 4.20 mmol of a 1.07 M solution of *n*-BuLi in hexanes). After 1 h at −78 °C and a quench with acetic anhydride (0.6 mL, 6.0 mmol), workup and flash chromatography (SiO_2, 5 × 15 cm, 15% EtOAc/hexanes) afforded acetoxy-cyclobutenone **4a** (1.82 g, 2.9 mmol, 73%) as a clear oil: R_f 0.45 (1:3 ethyl acetate/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.86−7.79 (m, 2H), 7.49 (A of ABq, *J* = 8.1 Hz, 2H),* 7.43 (B of ABq, *J* = 8.1 Hz, 2H), 7.43−7.35 (m, 2H), 7.34−7.26 (m, 1H), 4.72 (hept, *J* = 6.3 Hz, 1H), 2.24 (s, 3H), 1.59−1.45 (m, 6H),* 1.40 (d, *J* = 6.3 Hz, 3H), 1.31 (hex, *J* = 7.2 Hz, 6H), 1.14 (d, *J* = 6.3 Hz, 3H), 1.04 (t, *J* = 8.1 Hz, 6H),* 0.87 (t, *J* = 7.5 Hz, 9H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 182.3, 175.0, 169.3, 143.1, 136.8 (2C),* 134.2, 128.7, 128.4 (2C), 128.2, 127.2 (2C), 127.0, 124.6 (2C),* 97.2, 79.4, 29.1 (3C),* 27.3 (3C),* 23.0, 22.6, 21.4, 13.7 (3C), 9.6 (3C)*; IR (neat, cm^{-1}) 1752 (s), 1631 (s), 1596 (s), 1491 (s). Anal. Calcd for $C_{33}H_{46}O_4Sn$: C, 63.38; H, 7.41. Found: C, 63.30; H, 7.39.

2-Hydroxy-2-[4′-(tri-*n*-butylstannyl)phenyl]benzocyclobutenone (3b). A solution of [4-(tri-*n*-butylstannyl)phenyl]lithium in THF (30 mL) (generated from 1.94 g, 2.95 mmol of **15** and 2.0 mL, 2.50 mmol of a 1.24 M solution of *n*-BuLi in hexanes) was added by cannula to a solution of benzocyclobutenedione **2b** (300 mg, 2.27 mmol) in THF (30 mL). The resulting mixture was stirred at −78 °C for 1 h, then quenched with saturated aqueous NH_4Cl solution (10 mL). Workup and flash chromatography (SiO_2, 3 × 15 cm; 15% EtOAc/hexanes) gave hydroxycyclobutenone **3b** as an off-white solid (676 mg,1.35 mmol, 60%): R_f 0.28 (25% EtOAc/hexanes); mp 65−68 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.87−7.79 (m, 1H), 7.75−7.65 (m, 1H), 7.65−7.55 (m, 2H), 7.47 (A of ABq, *J* = 7.8 Hz, 2H),* 7.39 (B of ABq, *J* = 7.8 Hz, 2H), 3.12 (s, 1H), 1.65−1.40 (m, 6H),* 1.31 (hex, *J* = 7.2 Hz, 6H), 1.03 (dd, *J* = 8.4, 7.8 Hz, 6H),* 0.87 (t, *J* = 7.2 Hz, 9H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 191.8, 159.6, 147.9, 142.4, 138.1, 136.5 (2C),* 136.2, 131.4, 125.5 (2C),* 123.4, 122.4, 96.6, 29.0 (3C),* 27.3 (3C),* 13.6 (3C), 9.5 (3C)*; IR (CH_2Cl_2, cm^{-1}) 3569 (m), 3442 (br w), 1770 (s), 1588 (m). Anal. Calcd for $C_{26}H_{36}O_2Sn$: C, 62.55; H, 7.26. Found: C, 62.43; H, 7.29.

2-Acetoxy-2-[4′-(tri-*n*-butylstannyl)phenyl]benzocyclobutenone (4b) and 2-Hydroxy-2-[4′-(tri-*n*-butylstannyl)phenyl]benzocyclobutenone Dimer, Diacetate (20). A solution of [4-(tri-*n*-butylstannyl)-phenyl]lithium in THF (30 mL) (generated from 1.94 g, 2.95 mmol of **15** and 2.4 mL, 2.54 mmol of a 1.06 M solution of *n*-BuLi in hexanes) was added by cannula to a solution of benzocyclobutenedione **2b** (300 mg, 2.27 mmol) in THF (30 mL). The resulting mixture was stirred at −78 °C for 1 h and then quenched with acetic anhydride (0.32 mL, 3.41 mmol). Workup and flash chromatography (SiO_2, 3 × 15 cm; 15% EtOAc/hexanes) gave cyclobutenone **4b** as a light yellow oil (425 mg, 0.79 mmol, 35%) and dimeric hydroxycyclobutenone acetal **20** as a white solid (200 mg, 0.18 mmol, 16%). The latter was further purified by recrystallization (pentanes at −78 °C). Data for **4b**: R_f 0.47 (25% EtOAc/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.5 Hz, 1H), 7.74 (dd, *J* = 7.2, 6.9 Hz, 1H), 7.65 (dd, *J* = 7.5, 7.2 Hz, 1H), 7.59 (d, *J* = 7.5 Hz, 1H), 7.45 (A of ABq, *J* = 7.8 Hz, 2H),* 7.32 (B of ABq, *J* = 7.8 Hz, 2H), 2.11 (s, 3H), 1.65−1.40 (m, 6H),* 1.31 (hex, *J* = 7.2 Hz, 6H), 1.02 (dd, *J* = 8.4, 7.8 Hz, 6H),* 0.87 (t, *J* = 7.2 Hz, 9H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 184.9, 169.3, 155.4, 148.5, 142.6, 136.3 (2C),* 136.1, 135.2, 131.9, 126.8, 125.8 (2C),* 122.3, 99.0, 28.9 (3C),* 27.2 (3C),* 20.9, 13.5 (3C), 9.4 (3C)*; IR (neat, cm^{-1}) 1779 (s), 1746 (s), 1581 (m), 1465 (m). Anal. Calcd for $C_{28}H_{38}O_3Sn$: C, 62.13; H, 7.07. Found: C, 62.39; H, .7.11. Data for **20**: R_f 0.45 (25% EtOAc/hexanes); mp 126−127 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.84−7.74 (m, 1H), 7.70−7.56 (m, 3H), 7.56−7.45 (m, 2H),* 7.45−7.26 (m, 6H), 7.13−7.03 (m, 1H), 7.02−6.90 (m, 2H), 5.10 (d, *J* =

(78) Moerlein, S. M. *J. Organomet. Chem.* **1987**, *319*, 29.

7.5 Hz, 1H), 2.12 (s, 3H), 2.03 (s, 3H), 1.70−1.41 (m, 12H),* 1.41−1.22 (m, 12H), 1.22−0.95 (m, 12H),* 0.88 (t, J = 7.2 Hz, 9H), 0.87 (t, J = 7.2 Hz, 9H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 169.5, 168.5, 147.7, 145.2, 145.0, 143.1, 141.9, 141.4, 137.4, 135.9 (2C),* 135.5 (2C),* 134.7, 132.2, 131.1, 130.8, 130.7, 126.9, 126.5 (2C),* 126.2 (3C),* 124.0, 121.7, 112.7, 108.1, 94.5, 93.6, 28.9 (6C),* 27.2 (6C),* 21.4, 20.8, 13.5 (6C), 9.5 (3C),* 9.4 (3C)*; IR (CH_2Cl_2, cm^{-1}) 1756 (m), 1738 (m), 1465 (m). Anal. Calcd for $C_{56}H_{76}O_6Sn_2$: C, 62.13; H, 7.07. Found: C, 61.91; H, 7.12.

4-Acetoxy-2,3-dimethyl-4-[4′-(tri-*n*-butylstannyl)phenyl]-2-cyclobutenone (4c). A solution of [4-(tri-*n*-butylstannyl)phenyl]lithium in THF (20 mL) (generated from 1.71 g, 2.60 mmol of **15** and 1.8 mL, 2.20 mmol of a 1.21 M solution of *n*-BuLi in hexanes) was added by cannula to a solution of 3,4-dimethylcyclobutene-1,2-dione (**2c**) (220 mg, 2.00 mmol) in THF (20 mL). The resulting mixture was stirred at −78 °C for 1 h and then quenched with acetic anhydride (0.38 mL, 4.00 mmol). Workup and flash chromatography (SiO_2, 3 × 15 cm; 100% hexanes and then 15% EtOAc/hexanes) gave cyclobutenone **4c** as a clear oil (520 mg, 1.00 mmol, 50%): R_f 0.46 (25% EtOAc/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45 (A of ABq, J = 8.3 Hz, 2H),* 7.25 (B of ABq, J = 8.3 Hz, 2H), 2.28 (s, 3H), 2.14 (s, 3H), 1.85 (s, 3H), 1.66−1.40 (m, 6H),* 1.32 (hex, J = 7.2 Hz, 6H), 1.03 (dd, J = 8.4, 8.1 Hz, 6H),* 0.88 (t, J = 7.2 Hz, 9H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 186.9, 173.7, 169.5, 152.6, 142.1, 136.4 (2C),* 134.8, 124.4 (2C),* 99.3, 28.9 (3C),* 27.2 (3C),* 21.0, 13.4 (3C), 12.7, 9.4 (3C),* 7.6; IR (neat, cm^{-1}) 1778 (s), 1749 (s), 1638 (s), 1465 (m). Anal. Calcd for $C_{26}H_{40}O_3Sn$: C, 60.14; H, 7.76. Found: C, 60.23; H, 7.78.

4-Acetoxy-2-methyl-3-(1-methylethoxy)-4-[4′-(tri-*n*-butylstannyl)-phenyl]-2-cyclobutenone (4d). A solution of [4-(tri-*n*-butylstannyl)-phenyl]lithium in THF (40 mL) (generated from 5.53 g, 8.43 mmol of **15** and 7.0 mL, 7.14 mmol of a 1.02 M solution of *n*-BuLi in hexanes) was added by cannula to a solution of 3-methyl-4-(1-methylethoxy)-cyclobutene-1,2-dione (**2d**) (1.00 g, 6.49 mmol) in THF (30 mL). The resulting mixture was stirred at −78 °C for 1.5 h and quenched with acetic anhydride (0.92 mL, 9.74 mmol). Workup and flash chromatography (SiO_2, 30 × 180 cm, 100% hexanes and then 33% EtOAc/hexanes) gave cyclobutenone **4d** as a pale yellow oil (2.56 g, 4.54 mmol, 70%): R_f 0.21 (25% EtOAc/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46 (A of ABq, J = 7.7 Hz, 2H),* 7.41 (B of ABq, J = 7.7 Hz, 2H), 4.82 (hept, J = 6.3 Hz, 1H), 2.12 (s, 3H), 1.84 (s, 3H), 1.67−1.43 (m, 6H),* 1.46 (d, J = 6.0 Hz, 3H), 1.40 (d, J = 6.3 Hz, 3H), 1.31 (hex, J = 7.2 Hz, 6H), 1.03 (dd, J = 8.1, 8.1 Hz, 6H),* 0.88 (t, J = 7.2 Hz, 9H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 185.5, 176.4, 168.9, 142.2, 136.2 (2C),* 134.3,* 124.8 (2C),* 123.2, 94.9, 76.7, 28.7 (3C),* 27.0 (3C),* 22.2, 22.0, 21.0, 13.3,(3C), 9.2 (3C),* 7.1; IR (neat, cm^{-1}) 1775 (s), 1763 (s), 1747 (s), 1626 (s), 1464 (m), 1456 (m). Anal. Calcd for $C_{28}H_{44}O_4Sn$: C, 59.70; H, 7.87. Found: C, 59.80; H, 7.84.

4-Acetoxy-3-(1-methylethoxy)-2-phenyl-4-[3′-(tri-*n*-butylstannyl)-phenyl]-2-cyclobuten-1-one (25). A solution of [3-(tri-*n*-butylstannyl)-phenyl]lithium in THF (50 mL) (generated from 3.94 g, 6.01 mmol of **24** and 4.5 mL, 4.86 mmol of a 1.07 M solution of *n*-BuLi in hexanes) was added by cannula to a solution of cyclobutenedione **2a** (1.00 g, 4.62 mmol) in THF (50 mL). The resulting mixture was stirred at −78 °C for 1 h and quenched with acetic anhydride (0.65 mL, 6.93 mmol). Workup and flash chromatography (SiO_2, 3 × 15 cm; 5%−15% EtOAc/hexanes) gave cyclobutenone **25** as a clear oil (1.48 g, 2.37 mmol, 51%): R_f 0.47 (25% EtOAc/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81 (d, J = 7.2 Hz, 2H), 7.56 (s, 1H),* 7.47−7.28 (m, 6H), 4.71 (hept, J = 6.0 Hz, 1H), 2.24 (s, 3H), 1.64−1.40 (m, 6H),* 1.40 (d, J = 6.0 Hz, 3H), 1.28 (hex, J = 7.2 Hz, 6H), 1.13 (d, J = 6.0 Hz, 3H), 1.02 (dd, J = 8.7, 7.5 Hz, 6H),* 0.84 (t, J = 7.2 Hz, 9H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 182.0, 174.8, 169.1, 142.6, 136.6,* 133.7,* 132.7,* 128.3 (3C), 128.0 (2C),* 127.0 (2C), 126.8, 124.9, 97.1, 79.1, 28.9 (3C),* 27.1 (3C),* 22.8, 22.4, 21.2, 13.5 (3C), 9.5 (3C)*; IR (neat, cm^{-1}) 1754 (s), 1636 (s), 1599 (s), 1496 (s), 1462 (m). Anal. Calcd for $C_{33}H_{46}O_4Sn$: C, 63.38; H, 7.41. Found: C, 63.47; H, 7.46.

Thermolysis of 4-[3′- or 4′-(Tri-*n*-butylstannyl)phenyl]-2-cyclobutenones. Synthesis of (Tri-*n*-butylstannyl)naphthoquinone 5a, (Tri-*n*-butylstannyl)naphthalenes 6a,c,d, 26, and Anthracenone 21. 2-(1-Methylethoxy)-3-phenyl-6-(tri-*n*-butylstannyl)-1,4-naphthoquinone (5a). A solution of 4-hydroxy-4-[4′-(tri-*n*-butylstannyl)-phenyl]-2-cyclobutenone **3a** (400 mg, 0.69 mmol) in xylenes (15 mL) was heated at reflux for 1 h and then cooled to room temperature. The solvent was evaporated under reduced pressure, and the crude yellow oil was exposed to air. Standing overnight, the yellow oil transformed into a yellow solid which was purified by flash chromatography (SiO_2, 3 × 20 cm, 10% EtOAc/hexanes) to provide (tri-*n*-butylstannyl)-naphthoquinone **5a** as a yellow solid (322 mg, 0.55 mmol, 80%): mp 60−62 °C; R_f 0.65 (1:3 ethyl acetate/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.23 (s, 1H),* 8.00 (A of ABq, J = 7.4 Hz, 1H), 7.86 (B of ABq, J = 7.4 Hz, 1H),* 7.47−7.34 (m, 5H), 4.72 (hept, J = 6.0 Hz, 1H), 1.61−1.47 (m, 6H),* 1.33 (hex, J = 7.2 Hz, 6H), 1.18−1.07 (m, 6H),* 1.13 (d, J = 5.7 Hz, 6H), 0.88 (t, J = 7.2 Hz, 9H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 185.6, 183.0, 156.0, 152.4, 141.5, 134.1, 134.0,* 131.2, 131.1, 130.6 (2C), 130.1, 128.2, 127.5 (2C),* 124.4, 76.6, 29.0 (3C),* 27.3 (3C),* 22.7 (2C), 13.7 (3C), 9.9 (3C)*; IR (CH_2Cl_2, cm^{-1}) 1669 (s), 1590 (m), 1575 (m), 1466 (m). Anal. Calcd for $C_{31}H_{42}O_3Sn$: C, 64.05; H, 7.28. Found: C, 64.12; H, 7.33.

1-Acetoxy-4-hydroxy-2-(1-methylethoxy)-3-phenyl-6-(tri-*n*-butylstannyl)naphthalene (6a). A solution of 4-acetoxy-4-[4′-(tri-*n*-butylstannyl)phenyl]-2-cyclobutenone **4a** (1.61 g, 2.60 mmol) in xylenes (25 mL) was heated at reflux for 1.5 h and then cooled to room temperature. The solvent was evaporated under reduced pressure, and the crude yellow oil was purified by flash chromatography (SiO_2, 4 × 18 cm, 5% EtOAc/hexanes) to provide (tri-*n*-butylstannyl)naphthol **6a** as an off-white solid (1.46 g, 2.30 mmol, 91%): mp 83−84 °C; R_f 0.53 (1:3 ethyl acetate/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.33 (s, 1H),* 7.67 (A of ABq, J = 8.3 Hz, 1H), 7.62 (B of ABq, J = 8.3 Hz, 1H),* 7.60−7.49 (m, 4H), 7.49−7.42 (m, 1H), 5.61 (s, 1H), 3.82 (hept, J = 6.3 Hz, 1H), 2.45 (s, 3H), 1.58−1.51 (m, 6H),* 1.35 (hex, J = 7.2 Hz, 6H), 1.12 (t, J = 8.1 Hz, 6H),* 0.95 (d, J = 6.3 Hz, 3H), 0.91 (d, J = 6.3 Hz, 3H), 0.90 (t, J = 7.2 Hz, 9H); ^{13}C NMR# (75.5 MHz, $CDCl_3$) δ 169.2, 146.8, 144.3, 138.2, 134.7,* 132.8, 132.4, 131.1 (2C), 129.4 (2C), 128.4, 127.4, 121.2,* 119.3,* 118.1, 76.2, 29.2 (3C),* 27.4 (3C),* 22.3 (2C), 20.7, 13.7 (3C), 9.8 (3C)*; IR (CH_2Cl_2, cm^{-1}) 3534 (m), 1762 (s), 1630 (m), 1554 (m), 1465 (m), 1454 (m), 1436 (m). Anal. Calcd for $C_{33}H_{46}O_4Sn$: C, 63.38; H, 7.41. Found: C, 63.43; H, 7.40. (# = One less carbon observed, presumably due to coincident absorptions.)

10-Acetoxy-2-(tri-*n*-butylstannyl)anthracen-9-one (21). A solution of benzocyclobutenone **4b** (540 mg, 1.00 mmol) in xylenes (10 mL) was heated at reflux for 8 h. The crude product was purified by flash chromatography (SiO_2, 3 × 15 cm; 15% EtOAc/hexanes) to give, along with unreacted starting material (56 mg, 0.10 mmol, 10%), 2-(tri-*n*-butylstannyl)anthracen-9-one **21** as a yellow oil (344 mg, 0.64 mmol, 64%): R_f 0.49 (25% EtOAc/hexanes); ^{1}H NMR (360 MHz, $CDCl_3$) δ 8.40 (s, 1H),* 8.31 (d, J = 7.6 Hz, 1H), 7.76 (d, J = 7.6 Hz, 1H),* 7.68−7.60 (m, 1H), 7.60−7.52 (m, 2H), 7.52−7.45 (m, 1H), 7.22 (s, 1H), 2.18 (s, 3H), 1.67−1.44 (m, 6H), 1.34 (hex, J = 7.2 Hz, 6H), 1.12 (dd, J = 8.3, 7.9 Hz, 6H),* 0.89 (t, J = 7.2 Hz, 9H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 183.5, 170.8, 144.0, 141.5,* 138.7, 138.3, 135.1,* 133.2, 131.8, 130.4, 128.9, 128.3, 127.5,* 127.3, 66.6, 28.9,* 27.2 (3C),* 21.0 (3C),* 13.5 (3C), 9.6 (3C)*; IR (neat, cm^{-1}) 1738 (s), 1680 (s), 1602 (m), 1584 (m), 1460 (m). Anal. Calcd for $C_{28}H_{38}O_3Sn$: C, 62.13; H, 7.07. Found: C, 62.23; H, 7.15.

1-Acetoxy-2,3-dimethyl-4-hydroxy-6-(tri-*n*-butylstannyl)naphthalene (6c). A solution of cyclobutenone **4c** (1.70 g, 3.27 mmol) in xylenes (30 mL) was heated at reflux for 45 min. The crude product was purified by flash chromatography (SiO_2, 3 × 15 cm; 20% EtOAc/hexanes) to give (tri-*n*-butylstannyl)naphthalene **6c** as an off-white solid (1.64 g, 3.15 mmol, 96%): R_f 0.46 (25% EtOAc/hexanes); mp 95−97 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.15 (s, 1H),* 7.57 (A of ABq, J = 8.0 Hz, 1H), 7.53 (B of ABq, J = 8.0 Hz, 1H),* 5.40 (s, 1H), 2.50 (s, 3H), 2.16 (s, 3H), 1.96 (s, 3H), 1.70−1.42 (m, 6H),* 1.35 (hex, J = 7.2 Hz, 6H), 1.12 (dd, J = 8.4, 7.8 Hz, 6H),* 0.90 (t, J = 7.2 Hz, 9H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 170.7, 146.3, 138.2, 137.3, 133.3,* 130.0,* 126.6, 125.3, 123.6, 119.2,* 117.5, 29.1 (3C),* 27.4 (3C),* 20.7, 13.7 (3C), 13.5, 11.7, 9.7 (3C)*; IR (CH_2Cl_2, cm^{-1}) 3598 (m), 3449 (br w), 1758 (s), 1740 (m), 1661 (w), 1562 (w), 1462 (m). Anal. Calcd for $C_{26}H_{40}O_3Sn$: C, 60.14; H, 7.76. Found: C, 60.10; H, 7.80.

1-Acetoxy-4-hydroxy-3-methyl-2-(1-methylethoxy)-6-(tri-*n*-butylstannyl)naphthalene (6d). A solution of cyclobutenone **4d** (500 mg, 0.89 mmol) in xylenes (15 mL) was heated at reflux for 30 min. The

crude product was purified by flash chromatography (SiO_2, 3 × 15 cm; 15% EtOAc/hexanes) to give (tri-*n*-butylstannyl)naphthalene **6d** as a white solid (470 mg, 0.83 mmol, 94%): R_f 0.41 (25% EtOAc/hexanes); mp 111−112 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.15 (s, 1H),* 7.61 (A of ABq, J = 8.1 Hz, 1H), 7.53 (B of ABq, J = 8.1 Hz, 1H),* 5.15 (s, 1H), 4.35 (hept, J = 6.0 Hz, 1H), 2.43 (s, 3H), 2.30 (s, 3H), 1.72−1.45 (m, 6H),* 1.34 (hex, J = 7.5 Hz, 6H), 1.31 (d, J = 6.0 Hz, 6H), 1.11 (dd, J = 8.4, 7.8 Hz, 6H),* 0.89 (t, J = 7.5 Hz, 9H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 169.7, 147.6, 145.6, 137.5, 133.5,* 131.7, 129.7,* 125.9, 121.4,* 118.9,* 114.3, 76.0, 29.1 (3C),* 27.3 (3C),* 22.5 (2C), 20.6, 13.6 (3C), 9.7, 9.6 (3C)*; IR (CH_2Cl_2, cm^{-1}) 3593 (m), 1762 (s), 1631 (m), 1563 (m), 1458 (m), 1435 (m). Anal. Calcd for $C_{28}H_{44}O_4Sn$: C, 59.70; H, 7.87. Found: C, 59.80; H, 7.93.

4-Acetoxy-1-hydroxy-3-(1-methylethoxy)-2-phenyl-6-(tri-*n*-butylstannyl)naphthalene (26). A solution of 4-[3′-(tri-*n*-butylstannyl)-phenyl]-2-cyclobutenone **25** (1.05 g, 1.68 mmol) in xylenes (20 mL) was heated at reflux for 1 h. The crude product was purified by flash chromatography (SiO_2, 3 × 15 cm, 10% EtOAc/hexanes) to give (tri-*n*-butylstannyl)naphthalene **26** (492 mg, 0.79 mmol, 47%) and 4-acetoxy-3-(1-methylethoxy)-2-phenyl-1-naphthol (**31**) (181 mg, 0.54 mmol, 32%) as clear oils. Data for **26**: R_f 0.58 (25% EtOAc/hexanes); ^{1}H NMR (360 MHz, $CDCl_3$) δ 8.14 (d, J = 7.9 Hz, 1H), 7.82 (s, 1H),* 7.57−7.40 (m, 6H), 5.58 (s, 1H), 3.82 (hept, J = 6.1 Hz, 1H), 2.45 (s, 3H), 1.68−1.47 (m, 6H),* 1.36 (hex, J = 7.2 Hz, 6H), 1.12 (dd, J = 9.4, 6.8 Hz, 6H),* 0.94 (d, J = 6.1 Hz, 6H), 0.91 (t, J = 7.2 Hz, 9H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 168.8, 146.9, 144.1, 141.4, 132.7, 131.9 (2C),* 130.9 (2C), 129.1 (2C), 128.4,* 128.1, 126.8,* 121.4, 121.3, 118.0, 76.0, 29.0 (3C),* 27.3 (3C),* 22.1 (2C), 20.4, 13.5 (3C), 9.6 (3C)*; IR (neat, cm^{-1}) 3541 (s), 1773 (s), 1628 (s), 1579 (s). Anal. Calcd for $C_{33}H_{46}O_4Sn$: C, 63.38; H, 7.41. Found: C, 63.28; H, 7.36. Data for **31**: R_f 0.40 (25% EtOAc/hexanes); ^{1}H NMR (360 MHz, $CDCl_3$) δ 8.24 (d, J = 8.4 Hz, 1H), 7.74 (d, J = 8.4 Hz, 1H), 7.57−7.40 (m, 7H), 5.66 (s, 1H), 3.83 (hept, J = 6.3 Hz, 1H), 2.45 (s, 3H), 0.95 (d, J = 6.0 Hz, 6H).

Synthesis of the Cross-Coupling Precursors 7, 8, and 27. 1,4-Diacetoxy-2-(1-methylethoxy)-3-phenyl-6-(tri-*n*-butylstannyl)naphthalene (7a). To a stirred solution of (tri-*n*-butylstannyl)naphthol **6a** (486 mg, 0.78 mmol) in CH_2Cl_2 were added Et_3N (0.3 mL, 2.34 mmol), acetic anhydride (0.1 mL, 1.17 mmol), and 4-(dimethylamino)pyridine (10 mg, 0.08 mmol). The reaction mixture was stirred vigorously for 17 h at room temperature and poured into 120 mL of CH_2Cl_2. This solution was washed with saturated aqueous $NaHCO_3$ solution (2 × 20 mL) and brine (2 × 20 mL), dried over $MgSO_4$, filtered, and concentrated under reduced pressure to afford 549 mg of crude material. The crude product was purified by flash chromatography (SiO_2, 4 × 18 cm, 15% EtOAc/hexanes) to provide the 1,4-diacetoxy-6-(tri-*n*-butylstannyl)naphthalene **7a** (496 mg, 0.74 mmol, 95%) as a clear oil: R_f 0.53 (1:3 ethyl acetate/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82 (s, 1H),* 7.73 (A of ABq, J = 8.3 Hz, 1H), 7.60 (B of ABq, J = 8.3 Hz, 1H),* 7.48−7.32 (m, 5H), 3.80 (hept, J = 6.0 Hz, 1H), 2.46 (s, 3H), 2.12 (s, 3H), 1.62−1.49 (m, 6H),* 1.34 (hex, J = 7.5 Hz, 6H), 1.09 (t, J = 8.1 Hz, 6H),* 0.94 (d, J = 6.3 Hz, 6H), 0.89 (t, J = 7.5 Hz, 9H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 169.1, 168.6, 144.7, 142.2, 140.0, 137.4, 134.5,* 133.8, 130.3 (2C), 130.0, 128.7, 128.0 (2C), 127.7, 127.4, 124.0,* 120.0,* 76.6, 29.2 (3C),* 27.5 (3C),* 22.3 (2C), 20.7, 20.4, 13.7 (3C), 9.9 (3C)*; IR (neat, cm^{-1}) 1774 (s), 1628 (m), 1584 (m), 1464 (s), 1424 (s). Anal. Calcd for $C_{35}H_{48}O_5Sn$: C, 62.99; H, 7.24. Found: C, 63.09; H, 7.29.

1-Acetoxy-4-methoxy-2-(1-methylethoxy)-3-phenyl-6-(tri-*n*-butylstannyl)naphthalene (8a). To a stirred mixture of (tri-*n*-butylstannyl)-naphthol **6a** (1.42 g, 2.3 mmol) and K_2CO_3 (941 mg, 6.9 mmol) in acetone (50 mL) was added iodomethane (1.63 g, 11.5 mmol). The reaction mixture was stirred vigorously for 19 h at room temperature then filtered through Celite. The filtrate was concentrated under reduced pressure leaving a yellow oil which was purified by flash chromatography (SiO_2, 4 × 18 cm, 7% EtOAc/hexanes) to provide 1-acetoxy-4-methoxy-6-(tri-*n*-butylstannyl)naphthalene **8a** as a clear oil (1.41 g, 2.2 mmol, 96%): R_f 0.56 (1:3 ethyl acetate/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.25 (s, 1H),* 7.71 (A of ABq, J = 8.1 Hz, 1H), 7.60 (B of ABq, J = 8.1 Hz, 1H),* 7.62−7.53 (m, 2H), 7.50−7.33 (m, 3H), 3.76 (hept, J = 6.0 Hz, 1H), 3.48 (s, 3H), 2.46 (s, 3H), 1.65−1.50 (m, 6H),* 1.35 (hex, J = 7.2 Hz, 6H), 1.12 (t, J = 8.1 Hz, 6H),* 0.93 (d, J = 6.0 Hz, 6H), 0.89 (t, J = 7.2 Hz, 9H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 168.9, 151.7, 144.9, 139.0, 135.7, 134.4,* 134.2, 131.1 (3C), 127.9 (2C), 127.7, 127.6, 127.3, 125.3,* 119.8,* 76.2, 61.1, 29.2 (3C),* 27.4 (3C),* 22.3 (2C), 20.7, 13.8 (3C), 9.8 (3C)*; IR (neat, cm^{-1}) 1775 (s), 1617 (m), 1463 (m), 1446 (m). Anal. Calcd for $C_{34}H_{48}O_4Sn$: C, 63.87; H, 7.56. Found: C, 63.62; H, 7.62.

10-Acetoxy-9-methoxy-2-(tri-*n*-butylstannyl)anthracene (8b). Anthracenone **21** (720 mg, 1.33 mmol) was treated with K_2CO_3 (552 mg, 3.99 mmol) and CH_3I (0.41 mL, 6.65 mmol) in acetone (30 mL) at room temperature for 16 h. Workup as for **8a** and flash chromatography (SiO_2, 3 × 15 cm; 10% EtOAc/hexanes) gave 2-(tri-*n*-butylstannyl)-9,10-anthraquinone (77 mg, 0.16 mmol, 12%) and the (tri-*n*-butylstannyl)anthracene **8b** as a pale yellow oil (375 mg, 0.68 mmol, 51%). Data for 2-(tri-*n*-butylstannyl)-9,10-anthraquinone: R_f 0.57 (25% EtOAc/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.42 (s, 1H),* 8.32−8.28 (m, 2H), 8.19 (d, J = 7.5 Hz, 1H), 7.92 (d, J = 7.5 Hz, 1H),* 7.82−7.76 (m, 2H), 1.70−1.51 (m, 6H),* 1.35 (hex, J = 7.5 Hz, 6H), 1.15 (dd, J = 8.4, 7.8 Hz, 6H),* 0.89 (t, J = 7.5 Hz, 9H); IR (CH_2Cl_2, cm^{-1}) 1672 (s), 1571 (m). Data for **8b**: R_f 0.51 (25% EtOAc/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.43 (s, 1H),* 8.37−8.28 (m, 1H), 7.97−7.88 (m, 1H), 7.88−7.82 (m, 1H), 7.67−7.54 (m, 1H),* 7.54−7.45 (m, 2H), 4.16 (s, 3H), 2.63 (s, 3H), 1.77−1.47 (m, 6H),* 1.37 (hex, J = 7.5 Hz, 6H), 1.16 (dd, J = 8.4, 7.8 Hz, 6H),* 0.91 (t, J = 7.5 Hz, 9H); ^{13}C NMR# (75.5 MHz, $CDCl_3$) δ 169.5, 149.9, 139.6, 138.0, 133.1,* 131.0,* 126.1, 125.1, 124.4, 124.3, 124.0, 122.5, 121.5, 120.1,* 63.1, 29.1 (3C),* 27.3 (3C),* 20.5, 13.6 (3C), 9.7 (3C)*; IR (neat, cm^{-1}) 1764 (s), 1609 (w), 1462 (m), 1450 (m). Anal. Calcd for $C_{29}H_{40}O_3Sn$: C, 62.73; H, 7.26. Found: C, 62.89; H, 7.29. (# = one less carbon observed, presumably due to coincident absorptions.)

1-Acetoxy-2,3-dimethyl-4-methoxy-6-(tri-*n*-butylstannyl)naphthalene (8c). (Tri-*n*-butylstannyl)naphthalene **6c** (717 mg, 1.38 mmol) was treated with K_2CO_3 (573 mg, 4.14 mmol) and CH_3I (0.43 mL, 6.90 mmol) in acetone (30 mL) at room temperature for 24 h. Workup as for **8a** and flash chromatography (SiO_2, 3 × 15 cm, 10% EtOAc/hexanes) gave the (tri-*n*-butylstannyl)naphthalene **8c** as a pale yellow oil (682 mg, 1.28 mmol, 93%): R_f 0.59 (25% EtOAc/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.17 (s, 1H),* 7.62 (A of ABq, J = 8.1 Hz, 1H), 7.53 (B of ABq, J = 8.1 Hz, 1H),* 3.89 (s, 3H), 2.48 (s, 3H), 2.39 (s, 3H), 2.23 (s, 3H), 1.73−1.47 (m, 6H),* 1.35 (hex, J = 7.2 Hz, 6H), 1.12 (dd, J = 8.4, 7.8 Hz, 6H),* 0.89 (t, J = 7.2 Hz, 9H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 169.3, 151.1, 140.4, 139.2, 133.2, 130.4, 127.0, 126.4, 126.3, 126.0, 119.8, 61.4, 29.1 (3C),* 27.4 (3C),* 20.6, 13.7 (3C), 13.5 12.8, 9.7 (3C)*; IR (neat, cm^{-1}) 1764 (s), 1585 (w), 1463 (m), 1456 (m). Anal. Calcd for $C_{27}H_{42}O_3Sn$: C, 60.81; H, 7.93. Found: C, 60.68; H, 7.91.

1-Acetoxy-4-methoxy-3-methyl-2-(1-methylethoxy)-6-(tri-*n*-butylstannyl)naphthalene (8d). (Tri-*n*-butylstannyl)naphthalene **6d** (470 mg, 0.83 mmol) was treated with K_2CO_3 (339 mg, 2.45 mmol) and CH_3I (0.26 mL, 4.10 mmol) in acetone (20 mL) at room temperature for 15 h. Workup as for **8a** and flash chromatography (SiO_2, 3 × 15 cm, 15% EtOAc/hexanes) gave (tri-*n*-butylstannyl)naphthalene **8d** as a clear oil (471 mg, 0.82 mmol, 98%): R_f 0.53 (25% EtOAc/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.15 (s, 1H),* 7.66 (A of ABq, J = 8.1 Hz, 1H), 7.53 (B of ABq, J = 8.1 Hz, 1H),* 4.39 (hept, J = 7.5 Hz, 1H), 3.91 (s, 3H), 2.45 (s, 3H), 2.39 (s, 3H), 1.70−1.47 (m, 6H),* 1.35 (hex, J = 7.2 Hz, 6H), 1.32 (d, J = 6.3 Hz, 6H), 1.12 (dd, J = 8.4, 7.8 Hz, 6H),* 0.89 (t, J = 7.2 Hz, 9H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 168.4, 152.0, 145.9, 138.3, 134.8, 133.3,* 130.2,* 126.5, 124.7, 123.4, 119.5,* 75.8, 61.0, 29.0 (3C),* 27.2 (3C),* 22.5 (2C), 20.4, 13.5 (3C), 10.5, 9.6 (3C)*; IR (neat, cm^{-1}) 1777 (s), 1623 (m), 1585 (m), 1557 (m), 1463 (m), 1452 (s). Anal. Calcd for $C_{29}H_{46}O_4Sn$: C, 60.33; H, 8.03. Found: C, 60.44; H, 8.09.

4-Acetoxy-1-methoxy-3-(1-methylethoxy)-2-phenyl-6-(tri-*n*-butylstannyl)naphthalene (27). (Tri-*n*-butylstannyl)naphthalene **26** (650 mg, 1.04 mmol) was treated with K_2CO_3 (431 mg, 3.12 mmol) and CH_3I (0.32 mL, 5.20 mmol) in acetone (30 mL) at room temperature for 18 h. Workup as for **8a** and flash chromatography (SiO_2, 30 × 150 cm, 5% EtOAc/hexanes) gave methoxystannylnaphthalene **27** as an off-white solid (565 mg, 0.88 mmol, 85%): R_f 0.64 (25% EtOAc/hexanes); mp 83−84 °C; ^{1}H NMR (360 MHz, $CDCl_3$) δ 8.07 (d, J = 8.3 Hz, 1H), 7.87 (s, 1H),* 7.63−7.52 (m, 3H), 7.49−7.40 (m, 2H), 7.40−7.32 (m, 1H), 3.76 (hept, J = 6.1 Hz, 1H), 3.47 (s, 3H), 2.47 (s,

3H), 1.68−1.50 (m, 6H),* 1.36 (hex, J = 7.2 Hz, 6H), 1.13 (dd, J = 8.3, 7.9 Hz, 6H),* 0.94 (d, J = 6.5 Hz, 6H), 0.91 (t, J = 7.2 Hz, 9H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 168.6, 151.8, 144.6, 141.3, 135.2, 134.0, 132.6,* 131.0 (2C), 128.9,* 127.8 (2C), 127.6, 127.2, 127.0, 125.5, 121.4, 76.0, 61.0, 29.1 (3C),* 27.3 (3C),* 22.1 (2C), 20.5, 13.6 (3C), 9.7 (3C); IR (CH_2Cl_2, cm^{-1}) 1764 (s), 1618 (m), 1579 (m), 1480 (m), 1463 (s), 1447 (s). Anal. Calcd for $C_{34}H_{48}O_4Sn$: C, 63.87; H, 7.56. Found: C, 64.02; H, 7.54.

Cross-Coupling of (Tri-*n*-butylstannyl)naphthalenes with 4-Chlorocyclobutenones and Thermolysis. General Procedures. A catalytic amount of tris(2-furyl)phosphine and $Pd_2(dba)_3$ were added to a stirred solution of the (tri-*n*-butylstannyl)naphthalene (or (tri-*n*-butylstannyl)anthracene) and the 4-chloro-2-cyclobutenone in dioxane. The initial purple suspension was stirred at room temperature for 15 min, and the resulting homogeneous solution was then heated at reflux for the designated amount of time. The reaction mixture was cooled to room temperature, diluted with Et_2O, washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude brown oil was dissolved in acetonitrile (150 mL) and washed with hexanes (3 × 30 mL). The hexane layer was back-extracted with acetonitrile (50 mL), and the combined acetonitrile layers were concentrated under reduced pressure. The crude product was purified by flash chromatography.

2,7-Bis(1-methylethoxy)-5-hydroxy-6-methyl-3-phenyl-1,4-phenanthraquinone (10a) and 3,7-bis(1-methylethoxy)-5-hydroxy-6-methyl-2-phenyl-1,4-anthraquinone (11a). According to the general procedure, 6-(tri-*n*-butylstannyl)-1,4-naphthoquinone **5a** (600 mg, 1.03 mmol) and chlorocyclobutenone **9a** (216 mg, 1.24 mmol) in dioxane (5 mL) were treated with tris(2-furyl)phosphine (24 mg, 0.10 mmol) and Pd_2dba_3 (25 mg, 0.03 mmol). After heating at reflux for 17 h, the solution was cooled to room temperature and subjected to workup. Flash chromatography (SiO_2, 3 × 20 cm, 20% EtOAc/hexanes) gave the 1,4-phenanthraquinone **10a** (79 mg, 0.18 mmol, 18%) and the 1,4-anthraquinone **11a** (206 mg, 0.48 mmol, 46%) as yellow-brown and red solids, respectively. Each compound was further purified by recrystallization (**10a** from Et_2O/hexanes; **11a** from CH_2Cl_2/hexanes). Data for **10a**: mp 155 °C; R_f 0.53 (1:3 ethyl acetate/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 11.20 (s, 1H), 8.05 (A of ABq, J = 8.4 Hz, 1H), 7.96 (B of ABq, J = 8.4 Hz, 1H), 7.55−7.30 (m, 5H), 6.79 (s, 1H), 4.87 (hept, J = 6.0 Hz, 1H), 4.75 (hept, J = 6.0 Hz, 1H), 2.31 (s, 3H), 1.44 (d, J = 6.0 Hz, 6H), 1.18 (d, J = 6.0 Hz, 6H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 193.1, 182.2, 158.2, 154.5, 153.2, 137.8, 135.0, 134.3, 131.6, 130.6 (2C), 130.1, 128.5, 127.8 (2C), 121.2, 119.1, 116.7, 101.3, 101.2, 76.6, 70.2, 22.9, 22.7, 22.2, 22.0, 10.2; IR (CH_2Cl_2, cm^{-1}) 3080 (br w), 1663 (s), 1611 (s), 1581 (m), 1505 (m), 1465 (m). Anal. Calcd for $C_{27}H_{26}O_5$: C, 75.33; H, 6.08. Found: C, 75.09; H, 6.14. Data for **11a**: mp 250 °C; R_f 0.32 (1:3 ethyl acetate/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.07 (s, 1H), 8.39 (s, 1H), 7.52−7.33 (m, 5H), 6.95 (s, 1H), 6.36 (s, 1H), 4.79 (hept, J = 6.3 Hz, 2H), 2.35 (s, 3H), 1.45 (d, J = 6.0 Hz, 6H), 1.16 (d, J = 6.3 Hz, 6H); ^{13}C NMR# (75.5 MHz, $CDCl_3$) δ 184.8, 158.6, 157.7, 152.2, 135.3, 131.6, 130.6 (2C), 130.4, 128.8, 128.2, 127.6 (2C), 126.8, 125.2, 123.4, 121.2, 114.2, 102.0, 76.6, 70.6, 22.7 (2C), 22.0 (2C), 9.0; IR (CH_2Cl_2, cm^{-1}) 3588 (w), 1667 (s), 1620 (s), 1591 (s), 1455 (m). Anal. Calcd for $C_{27}H_{26}O_5$: C, 75.33; H, 6.08. Found: C, 74.12; H, 6.13. HRMS Calcd for $C_{27}H_{26}O_5$ + Li: 431.1866. Found: 431.1858. (# = One less carbon observed, presumably due to coincident absorptions.)

2,7-Bis(1-methylethoxy)-5-hydroxy-6-methyl-3-phenyl-1,4-diacetoxyphenanthrene (13a). According to the general procedure, 1,4-diacetoxy-6-(tri-*n*-butylstannyl)naphthalene **7a** (450 mg, 0.67 mmol) and chlorocyclobutenone **9a** (141 mg, 0.81 mmol) in dioxane (10 mL) were treated with tris(2-furyl)phosphine (16 mg, 0.07 mmol) and Pd_2dba_3 (15 mg, 0.02 mmol). After heating at reflux for 23 h, the solution was cooled to room temperature and subjected to workup. The crude product (535 mg) was purified by flash chromatography (SiO_2, 4 × 15 cm, 20−40% EtOAc/hexanes) to elute first 1,4-diacetoxy-2-(1-methylethoxy)-3-phenylnaphthalene (**16a**) (15 mg, 0.04 mmol, 6%, clear oil) and then a mixture of 2,7-bis(1-methylethoxy)-5-hydroxy-6-methyl-3-phenyl-1,4-diacetoxyphenanthrene **13a** and its 1,5-diacetate regioisomer (131 mg, 0.25 mmol, 38%, white solid), and finally 6,6′-bisnaphthalene **18a** (111 mg, 0.15 mmol, 22%, white solid). Data for **16a**: R_f 0.32 (25% EtOAc in hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81 (d, J = 8.4 Hz, 1H), 7.74 (d, J = 8.1 Hz, 1H), 7.58−7.32 (m, 7H), 3.84 (hept, J = 6.0 Hz, 1H), 2.49 (s, 3H), 0.97 (s, 3H), 0.95 (s, 3H). Data for **18a**: mp > 250 °C (CH_2Cl_2/hexanes); R_f 0.10 (1:3 ethyl acetate/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.91 (A of ABq, J = 9.0 Hz, 2H), 7.90 (s, 2H), 7.82 (B of ABq, J = 9.0 Hz, 2H), 7.50−7.34 (m, 10H), 3.84 (hept, J = 6.3 Hz, 2H), 2.49 (s, 6H), 2.14 (s, 6H), 0.96 (d, J = 6.3 Hz, 12H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 169.2 (2C), 168.5 (2C), 145.1 (2C), 142.7 (2C), 138.8 (2C), 137.5 (2C), 133.5 (2C), 130.2 (4C), 129.6 (2C), 128.0 (4C), 127.8 (2C), 127.2 (2C), 126.8 (2C), 124.8 (2C), 122.0 (2C), 120.6 (2C), 76.7 (2C), 22.3 (4C), 20.7 (2C), 20.4 (2C); IR (CH_2Cl_2, cm^{-1}) 2307 (w), 1769 (s), 1713 (w), 1607 (w). Anal. Calcd for $C_{46}H_{42}O_{10}$: C, 73.20; H, 5.61. Found: C, 72.56; H, 5.65. HRMS calcd for $C_{46}H_{42}O_{10}$ + Li: 761.2938. Found: 761.2945. To facilitate characterization of **13a**, the regioisomeric mixture of diacetoxyphenanthrenes (**13a** and the 1,5-diacetoxy isomer) was converted to the 1,4,5-triacetoxyphenanthrene: A stirred solution of a ~1:1 mixture of isomers in CH_2Cl_2 (10 mL) was treated with triethylamine (102 mg, 0.14 mL, 1.00 mmol), acetic anhydride (51 mg, 0.05 mL, 0.50 mmol), and a catalytic amount of DMAP (5 mg). The reaction mixture was stirred for 22 h at room temperature under a nitrogen atmosphere. The solvent was removed under reduced pressure, and the crude material was purified by flash chromatography (SiO_2, 2 × 18 cm; 40% EtOAc/hexanes) to give 2,7-bis(1-methylethoxy)-6-methyl-3-phenyl-1,4,5-triacetoxyphenanthrene (**13a**, 5-acetate) (112 mg, 0.20 mmol, 80%): mp 104−106 °C (CH_2Cl_2/hexanes); R_f 0.18 (1:3 ethyl acetate/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59 (A of ABq, J = 9.0 Hz, 1H), 7.56 (B of ABq, J = 9.0 Hz, 1H), 7.48−7.33 (m, 5H), 7.09 (s, 1H), 4.72 (hept, J = 6.0 Hz, 1H), 3.83 (hept, J = 6.0 Hz, 1H), 2.46 (s, 3H), 2.42 (s, 3H), 2.19 (s, 3H), 1.83 (br s, 3H), 1.44 (d, J = 6.0 Hz, 6H), 0.96 (br s, 6H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 168.4, 168.1, 167.9, 155.6, 146.0 (2C), 145.4, 137.7, 134.5, 132.9, 130.7 (2C), 130.0, 128.2, 127.9 (2C), 127.5, 126.7, 121.7, 119.4, 119.3, 115.8, 107.1, 76.8, 70.5, 22.4 (2C), 22.2 (2C), 21.1, 20.7, 20.4, 10.7 (br); IR (CH_2Cl_2, cm^{-1}) 1765 (br s), 1612 (m), 1448 (m), 1437 (m). Anal. Calcd for $C_{33}H_{34}O_8$ + CH_2Cl_2: C, 63.46; H, 5.64. Found: C, 63.93; H, 5.73. HRMS calcd for $C_{33}H_{34}O_8$ + Li: 565.2414. Found: 565.2418.

1-Acetoxy-2,7-bis(1-methylethoxy)-5-hydroxy-4-methoxy-6-methyl-3-phenylphenanthrene (14a). According to the general procedure, 1-acetoxy-4-methoxy-6-(tri-*n*-butylstannyl)naphthalene **8a** (500 mg, 0.78 mmol) and chlorocyclobutenone **9a** (164 mg, 0.94 mmol) in dioxane (5 mL) were treated with tris(2-furyl)phosphine (18 mg, 0.08 mmol) and Pd_2dba_3 (18 mg, 0.02 mmol). After heating at reflux for 24 h, the solution was cooled to room temperature and subjected to workup. The crude product (576 mg) was purified by flash chromatography (SiO_2, 4 × 18 cm, 17−25% EtOAc/hexanes) to provide 1-acetoxy-4-methoxy-2-(1-methylethoxy)-3-phenylnaphthalene (**17a**) as a clear oil (27 mg, 0.08 mmol, 10%), 1-acetoxy-4-methoxyphenanthrene **14a** as a white solid (241 mg, 0.49 mmol, 63%), and 6,6′-bis[1-acetoxy-4-methoxy-2-(1-methylethoxy)-3-phenylnaphthalene] (**19a**) as a white solid (70 mg, 0.10 mmol, 13%). The solid products were further purified by recrystallization (**14a** from Et_2O /hexanes; **19a** from CH_2Cl_2/hexanes). Data for **17a**: R_f 0.49 (1:3 ethyl acetate/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.15 (d, J = 7.8 Hz, 1H), 7.79 (d, J = 7.8 Hz, 1H), 7.34−7.68 (m, 7H), 3.76 (hept, J = 6.0 Hz, 1H), 3.47 (s, 3H), 2.47 (s, 3H), 0.94 (d, J = 6.0 Hz, 6H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 168.8, 151.9, 145.0, 135.7, 134.0, 131.0 (2C), 128.4, 127.9 (2C), 127.7, 127.3, 127.0, 125.7, 125.3, 122.8, 120.9, 76.2, 61.1, 22.2 (2C), 20.7; IR (neat, cm^{-1}) 3140 (br w), 1770 (s), 1624 (m), 1593 (s), 1563 (m), 1495 (m), 1454 (s), 1420 (s). HRMS calcd for $C_{22}H_{22}O_4$ + Li: 357.1678. Found: 357.1666. Data for **14a**: mp 201 °C; R_f 0.39 (1:3 ethyl acetate/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.6 (S, 1H), 7.70−7.36 (m, 7H), 6.90 (s, 1H), 4.75 (hept, J = 6.0 Hz, 1H), 3.76 (hept, J = 6.0 Hz, 1H), 3.26 (s, 3H), 2.50 (s, 3H), 2.40 (s, 3H), 1.45 (d, J = 6.0 Hz, 6H), 0.96 (d, J = 6.0 Hz, 6H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 168.8, 156.3, 153.2, 149.0, 144.9, 137.6, 133.8, 132.8, 131.4 (2C), 129.6 (2C), 127.9 (2C), 127.6, 126.7, 119.7, 118.1, 116.7, 112.8, 102.8, 76.5, 70.2, 61.6, 22.3 (2C), 22.2 (2C), 20.8, 10.1; IR (CH_2Cl_2, cm^{-1}) 3148 (br m), 1767 (s), 1609 (s), 1549 (m), 1506 (m), 1463 (s), 1419 (s). Anal. Calcd for $C_{30}H_{32}O_6$: C, 73.75; H, 6.60. Found: C, 73.88; H, 6.61. Data for **19a**: mp > 250 °C; R_f 0.26 (1:3 ethyl acetate/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.44 (s, 2H), 7.89 (A of ABq,

J = 9.0 Hz, 2H), 7.89 (B of ABq, J = 9.0 Hz, 2H), 7.67−7.53 (m, 4H), 7.53−7.33 (m, 6H), 3.79 (hept, J = 6.0 Hz, 2H), 3.49 (s, 6H), 2.48 (s, 6H), 0.95 (d, J = 6.0 Hz, 12H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 168.9 (2C), 152.2 (2C), 145.2 (2C), 138.1 (2C), 135.8 (2C), 134.0 (2C), 131.0 (4C), 128.4 (2C), 128.0 (4C), 127.5 (2C), 127.0 (2C), 126.9 (2C), 126.1 (2C), 121.8 (2C), 121.1 (2C), 76.3 (2C), 61.3 (2C), 22.3 (4C), 20.8 (2C); IR (CH_2Cl_2, cm^{-1}) 2306 (w), 1765 (s), 1597 (m), 1421 (m). Anal. Calcd for $C_{44}H_{42}O_8$: C, 75.63; H, 6.05. Found: C, 74.93; H, 6.12. HRMS calcd for $C_{44}H_{42}O_8$ + Li: 705.3040. Found: 705.3040.

1-Acetoxy-6,7-diethyl-5-hydroxy-4-methoxy-2-(1-methylethoxy)-3-phenylphenanthrene (14b). According to the general procedure, (tri-*n*-butylstannyl)naphthalene **8a** (700 mg, 1.09 mmol) and 4-chloro-2,3-diethyl-2-cyclobutenone (**9b**) (207 mg, 1.31 mmol) in dioxane (10 mL) were treated with tris(2-furyl)phosphine (25 mg, 0.109 mmol) and $Pd_2(dba)_3$ (25 mg, 0.027 mmol). After heating at reflux for 20 h, the solution was cooled to room temperature and subjected to workup. The crude product was purified by flash chromatography (SiO_2, 3 × 18 cm, 15%−25% EtOAc/hexanes) to give hydroxyphenanthrene **14b** (417 mg, 0.88 mmol, 81%) as an off-white solid which was further purified by recrystallization (CH_2Cl_2 and hexanes): R_f 0.53 (25% EtOAc/hexanes); mp 185−186 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.39 (s, 1H), 7.63 (d, J = 8.7 Hz, 2H), 7.63 (A of ABq, J = 8.9 Hz, 1H), 7.53 (B of ABq, J = 8.9 Hz, 1H), 7.51−7.35 (m, 3H), 7.29 (s, 1H), 3.75 (hept, J = 6.0 Hz, 1H), 3.25 (s, 3H), 2.99 (q, J = 7.2 Hz, 2H), 2.88 (q, J = 7.5 Hz, 2H), 2.50 (s, 3H), 1.37 (t, J = 7.5 Hz, 3H), 1.25 (t, J = 7.2 Hz, 3H), 0.95 (d, J = 6.0 Hz, 6H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 168.7, 151.7, 149.4, 145.4, 142.5, 137.5, 133.6, 132.3, 131.3 (2C), 130.5, 129.7, 129.4, 127.8 (2C), 127.5, 127.3, 119.5, 119.4, 117.6, 116.4, 76.4, 61.5, 25.9, 22.1 (2C), 20.6, 20.5, 15.1, 14.4; IR (CH_2Cl_2, cm^{-1}) 3153 (br m), 1769 (s), 1609 (m), 1542 (w), 1455 (m), 1416 (s). Anal. Calcd for $C_{30}H_{32}O_5$: C, 76.25; H, 6.82. Found: C, 76.01; H, 6.86.

1-Acetoxy-2,7-bis(1-methylethoxy)-3,6-diphenyl-5-hydroxy-4-methoxyphenanthrene (14c) and 3-(1-Methylethoxy)-1-oxo-1,4-dihydronaphthalene-4-spiro-5′-[2-phenyl-3-(1-methylethoxy)-2-cyclopentenone] (23). According to the general procedure, (tri-*n*-butylstannyl)naphthalene **8a** (620 mg, 0.97 mmol) and 4-chloro-2-phenyl-3-(1-methylethoxy)-2-cyclobutenone (**9c**) (241 mg, 1.02 mmol) in dioxane (10 mL) were treated with tris(2-furyl)phosphine (23 mg, 0.097 mmol) and $Pd_2(dba)_3$ (22 mg, 0.020 mmol). After heating at reflux for 22 h, the solution was cooled to room temperature and subjected to workup. The crude product was purified by flash chromatography (SiO_2, 3 × 15 cm, 12%-25% EtOAc/hexanes) to give phenanthrene **14c** as a light brown solid (92 mg, 0.17 mmol, 17%), 6,6′-bis[1-acetoxy-4-methoxy-2-(1-methylethoxy)-3-phenylnaphthalene] (**19a**) as a pale yellow solid (249 mg, 0.36 mmol, 74%, see above for characterization of this product), and 3-(1-methylethoxy)-1-oxo-1,4-dihydronaphthalene-4-spiro-5′-[2-phenyl-3-(1-methylethoxy)-2-cyclopentenone] (**23**) (59 mg, 0.15 mmol, 79%) as a white solid. The solid products were further purified by recrystallization (CH_2Cl_2 and hexanes). Data for **14c**: R_f 0.34 (25% EtOAc/hexanes); mp 186−188 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.50 (s, 1H), 7.68−7.53 (m, 4H), 7.52−7.30 (m, 8H), 7.00 (s, 1H), 4.63 (hept, J = 6.0 Hz, 1H), 3.73 (hept, J = 6.3 Hz, 1H), 3.27 (s, 3H), 2.51 (s, 3H), 1.28 (d, J = 6.0 Hz, 6H), 0.94 (d, J = 6.3 Hz, 6H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 168.7, 155.4, 152.7, 148.8, 145.0, 137.6, 135.9, 134.2, 133.4, 131.3 (2C), 131.0 (2C), 129.8, 129.3, 127.8 (2C), 127.5, 127.4 (2C), 126.6, 126.3, 121.6, 119.8, 119.0, 113.3, 104.0, 76.4, 70.6, 61.4, 22.1 (2C), 22.0 (2C), 20.7; IR (CH_2Cl_2, cm^{-1}) 3119 (br, w), 1769 (m), 1601 (m), 1462 (m), 1420 (m). HRMS calcd for $C_{35}H_{34}O_6$: 551.2434. Found: 551.2431. Anal. Calcd for $C_{35}H_{34}O_6$: C, 76.35; H, 6.22. Found: C, 75.24; H, 6.20. Data for **23**: R_f 0.06 (25% EtOAc/hexanes); mp 200−202 °C (decomposed); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.21 (dd, J = 7.8, 1.2 Hz, 1H), 7.81 (dd, J = 8.1, 0.9 Hz, 2H), 7.55−7.34 (m, 4H), 7.33−7.20 (m, 2H), 5.98 (s, 1H), 4.84 (hept, J = 6.0 Hz, 1H), 4.60 (hept, J = 6.0 Hz, 1H), 3.52 (A of ABq, J = 17.7 Hz, 1H), 3.12 (B of ABq, J = 17.7 Hz, 1H), 1.51 (d, J = 6.0 Hz, 3H), 1.49 (d, J = 6.0 Hz, 3H), 1.33 (d, J = 6.3 Hz, 3H), 1.27 (d, J = 6.3 Hz, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 197.3, 185.4, 184.1, 170.7, 141.3, 132.6, 131.1, 130.5, 127.9 (2C), 127.8 (2C), 127.4, 127.0, 126.2, 124.2, 117.2, 104.8, 74.3, 71.4, 56.6, 40.4, 22.9, 22.8, 21.3, 20.9; IR (CH_2Cl_2, cm^{-1}) 1704 (m), 1644 (s), 1618 (s), 1595 (s), 1575 (m) Anal. Calcd for $C_{26}H_{26}O_4$: C, 77.59; H, 6.51. Found: C, 77.47; H, 6.57.

1-Acetoxy-5-hydroxy-4-methoxy-7-(1-methylethoxy)-2,3,6-trimethylphenanthrene (14d). According to the general procedure, (tri-*n*-butylstannyl)naphthalene **8c** (650 mg, 1.22 mmol) and 4-chloro-2-methyl-3-(1-methylethoxy)-2-cyclobutenone (**9a**) (255 mg, 1.46 mmol) in dioxane (10 mL) were treated with tris(2-furyl)phosphine (28 mg, 0.122 mmol) and $Pd_2(dba)_3$ (28 mg, 0.031 mmol). After heating at reflux for 15 h, the solution was cooled to room temperature and subjected to workup. The crude product was purified by flash chromatography (SiO_2, 3 × 15 cm, 20%−25% EtOAc/hexanes) to give the protodestannylation product 1-acetoxy-2,3-dimethyl-4-methoxynaphthalene (**17b**) as a yellow oil (24 mg, 0.098 mmol, 8%), hydroxyphenanthrene **14d** as a white solid (236 mg, 0.62 mmol, 51%), and the homocoupling product 6,6′-bis(1-acetoxy-2,3-dimethyl-4-methoxynaphthalene) (**19d**) as an off-white solid (101 mg, 0.21 mmol, 34%). The two solid products were further purified by recrystallization (CH_2Cl_2 and hexanes). Data for **17b**: R_f 0.47 (25% EtOAc/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.12−8.03 (m, 1H), 7.73−7.65 (m, 1H), 7.50−7.40 (m, 2h), 3.89 (s, 3H), 2.49 (s, 3H), 2.39 (s, 3H), 2.23 (s, 3H). Data for **14d**: R_f 0.42 (25% EtOAc/hexanes); mp 151−152 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.56 (s, 1H), 7.51 (A of ABq, J = 9.0 Hz, 1H), 7.45 (B of ABq, J = 9.0 Hz, 1H), 6.86 (s, 1H), 4.73 (hept, J = 6.0 Hz, 1H), 3.61 (s, 3H), 2.50 (s, 3H), 2.47 (s, 3H), 2.38 (s, 3H), 2.26 (s, 3H), 1.44 (d, J = 6.0 Hz, 6H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 169.2, 156.2, 153.4, 149.3, 141.9, 132.8, 128.8, 128.4, 126.8, 124.7, 121.1, 118.3, 116.0, 112.2, 102.3, 70.0, 61.3, 22.3 (2C), 20.6, 13.4, 13.1, 10.0; IR (CH_2Cl_2, cm^{-1}) 3141 (br m), 1760 (s), 1602 (m), 1554 (w), 1513 (w). Anal. Calcd for $C_{23}H_{26}O_5$: C, 72.23; H, 6.85. Found: C, 71.98; H, 6.90. Data for **19d**: R_f 0.24 (25% EtOAc/hexanes); mp 199−201 °C; ^{1}H NMR (360 MHz, $CDCl_3$) δ 8.36 (s, 2H), 7.84 (d of A of ABq, J = 1.4, 8.6 Hz, 2H), 7.81 (B of ABq, J = 8.6 Hz, 2H), 3.93 (s, 6H), 2.52 (s, 6H), 2.43 (s, 6H), 2.26 (s, 6H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 169.3 (2C), 151.6 (2C), 140.5 (2C), 138.3 (2C), 127.4 (2C), 127.2 (4C), 125.8 (2C), 125.4 (2C), 121.8 (2C), 120.4 (2C), 61.5 (2C), 20.6 (2C), 13.5 (2C), 13.0 (2C); IR (CH_2Cl_2, cm^{-1}) 1759 (s), 1605 (w), 1451 (w). Anal. Calcd for $C_{30}H_{30}O_6$: C, 74.06; H, 6.21. Found: C, 73.39; H, 6.20.

1-Acetoxy-6,7-diethyl-2,3-dimethyl-5-hydroxy-4-methoxyphenanthrene (14e). According to the general procedure, (tri-*n*-butylstannyl)-naphthalene **8c** (820 mg, 1.54 mmol) and 4-chloro-2,3-diethyl-2-cyclobutenone (**9b**) (400 mg, 2.52 mmol) in dioxane (15 mL) were treated with tris(2-furyl)phosphine (36 mg, 0.154 mmol) and $Pd_2(dba)_3$ (35 mg, 0.039 mmol). After heating at reflux for 15 h, the solution was cooled to room temperature and subjected to workup. The crude product was purified by flash chromatography (SiO_2, 30 × 150 cm, 15% EtOAc/hexanes) to give hydroxyphenanthrene **14e** as a white solid (434 mg, 1.18 mmol, 77%) which was further purified by recrystallization (CH_2Cl_2 and hexanes). Data for **14e**: R_f 0.41 (25% EtOAc/hexanes); mp 148−150 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.41 (s, 1H), 7.55 (A of ABq, J = 9.0 Hz, 1H), 7.45 (B of ABq, J = 9.0 Hz, 1H), 7.26 (s, 1H), 3.61 (s, 3H), 2.99 (q, J = 7.5 Hz, 2H), 2.87 (q, J = 7.5 Hz, 2H), 2.50 (s, 3H), 2.48 (s, 3H), 2.27 (s, 3H), 1.36 (t, J = 7.5 Hz, 3H), 1.26 (t, J = 7.5 Hz, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 169.2, 152.0, 149.7, 142.5, 141.8, 132.4, 130.0, 128.7, 128.6, 127.6, 125.4, 121.0, 119.0, 117.9, 115.9, 61.3, 25.9, 20.6, 20.5, 15.2, 14.4, 13.5, 13.1; IR (CH_2Cl_2, cm^{-1}) 3142 (br s), 2306 (m), 1759 (s), 1613 (m), 1601 (m), 1547 (m), 1452 (s), 1420 (s). Anal. Calcd for $C_{23}H_{26}O_4$: C, 75.39; H, 7.15. Found: C, 75.25; H, 7.21.

7-Acetoxy-2,3-diethyl-1-hydroxy-12-methoxybenz[*a*]anthracene (14f). According to the general procedure, (tri-*n*-butylstannyl)anthracene **8b** (280 mg, 0.50 mmol) and 4-chloro-2,3-diethyl-2-cyclobutenone (**9b**) (105 mg, 0.66 mmol) in dioxane (5 mL) were treated with tris(2-furyl)phosphine (12 mg, 0.050 mmol) and $Pd_2(dba)_3$ (11 mg, 0.013 mmol). After heating at reflux for 20 h, the solution was cooled to room temperature and subjected to workup. The crude product was purified by flash chromatography (SiO_2, 3 × 15 cm, 15% EtOAc/hexanes) to give hydroxybenz[*a*]anthracene **14f** as a yellow solid (156 mg, 0.40 mmol, 80%) which was further purified by recrystallization (CH_2Cl_2 and hexanes). Data for **14f**: R_f 0.39 (25% EtOAc/hexanes); mp 155−157 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.16 (s, 1H), 8.45−8.37 (m, 1H), 7.97−7.90 (m, 1H), 7.70−7.58 (m, 2H), 7.51

(A of ABq, J = 9.3 Hz, 1H), 7.48 (B of ABq, J = 9.3 Hz, 1H), 7.23 (s, 1H), 3.82 (s, 3H), 3.01 (q, J = 7.5 Hz, 2H), 2.88 (q, J = 7.5 Hz, 2H), 2.63 (s, 3H), 1.37 (t, J = 7.5 Hz, 3H), 1.29 (t, J = 7.5 Hz, 3H); ^{13}C NMR# (75.5 MHz, $CDCl_3$) δ 169.5, 153.0, 147.5, 143.5, 138.9, 132.0, 131.1, 129.7, 126.8, 126.5, 126.3, 125.2, 124.4, 122.3, 121.3, 119.7, 118.2, 114.8, 62.5, 26.0, 20.7, 20.6, 15.3, 14.5; IR (CH_2Cl_2, cm^{-1}) 3170 (br m), 1762 (s), 1605 (w), 1577 (w). Anal. Calcd for $C_{25}H_{24}O_4$: C,77.30 ; H, 6.22. Found: C, 77.20; H, 6.22. (# = One less carbon observed, presumably due to coincident absorptions.)

1-Acetoxy-3,6-dimethyl-2,7-bis(1-methylethoxy)-5-hydroxy-4-methoxyphenanthrene (14g). According to the general procedure, (tri-*n*-butylstannyl)naphthalene **8d** (750 mg, 1.30 mmol) and 4-chloro-2-methyl-3-(1-methylethoxy)-2-cyclobutenone (**9a**) (272 mg, 1.56 mmol) in dioxane (10 mL) were treated with tris(2-furyl)phosphine (30 mg, 0.130 mmol) and $Pd_2(dba)_3$ (30 mg, 0.033 mmol). After heating at reflux for 18 h, the solution was cooled to room temperature and subjected to workup. The crude product was purified by flash chromatography (SiO_2, 3 × 15 cm, 20%−33% EtOAc/hexanes) to give the protodestannylation product 1-acetoxy-4-methoxy-3-methyl-2-(1-methylethoxy)naphthalene (**17c**) as a yellow oil (45 mg, 0.16 mmol, 12%), hydroxyphenanthrene **14g**, the cross-coupling product, as an off-white solid (226 mg, 0.53 mmol, 41%), and bisnaphthalene 6,6′-bis-[1-acetoxy-4-methoxy-3-methyl-2-(1-methylethoxy)naphthalene] (**19c**), the homocoupling product, as an off-white solid (147 mg, 0.26 mmol, 40%). The two solid products were further purified by recrystallization (CH_2Cl_2 and hexanes). Data for **17c**: R_f 0.32 (25% EtOAc/hexanes): ^{1}H NMR (300 mHz, $CDCl_3$) δ 8.09−8.01 (m, 1H), 7.77−7.69 (m, 1H), 7.49−7.40 (m, 2H), 4.40 (hept, J = 6.0 Hz, 1H), 3.91 (s, 3H), 2.45 (s, 3H), 2.40 (s, 3H), 1.33 (d, J = 6.3 Hz, 6H). Data for **14g**: R_f 0.31 (25% EtOAc/hexanes); mp 134−136 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.42 (s, 1H), 7.51 (A of ABq, J = 9.2 Hz, 1H), 7.47 (B of ABq, J = 9.2 Hz, 1H), 6.86 (s, 1H), 4.73 (hept, J = 6.0 Hz, 1H), 4.34 (hept, J = 6.0 Hz, 1H), 3.61 (s, 3H), 2.47 (s, 3H), 2.45 (s, 3H), 2.39 (s, 3H), 1.44 (d, J = 6.0 Hz, 6H), 1.33 (d, J = 6.0 Hz, 6H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 168.2, 155.9, 153.1, 149.7, 145.5, 136.7, 132.4, 128.5, 125.1, 124.8, 119.0, 117.9, 115.9, 112.0, 102.3, 76.1, 69.8, 61.0, 22.4 (2C), 22.1 (2C), 20.4, 10.7, 9.8; IR (CH_2Cl_2, cm^{-1}) 3149 (br m), 1766 (s), 1610 (s), 1554 (m), 1463 (s), 1422 (s); Anal. Calcd for $C_{25}H_{30}O_6$: C, 70.41; H, 7.09. Found: C, 70.32; H, 7.10. Data for **19c**: R_f 0.16 (25% EtOAc/hexanes); mp 194−196 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.32 (s, 2H), 7.83 (s, 4H), 4.43 (hept, J = 6.0 Hz, 2H), 3.95 (s, 6H), 2.48 (s, 6H), 2.42 (s, 6H), 1.35 (d, J = 6.0 Hz, 12H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 168.6 (2C), 152.6 (2C), 146.3 (2C), 137.8 (2C), 135.0 (2C), 126.0 (2C), 125.9 (2C), 125.5 (2C), 124.4 (2C), 121.5 (2C), 120.2 (2C), 76.0 (2C), 61.4 (2C), 22.6 (4C), 20.6 (2C), 10.7 (2C); IR (CH_2Cl_2, cm^{-1}) 1764 (s), 1629 (w), 1601 (s), 1562 (w), 1497 (w), 1451 (s), 1425 (s). Anal. Calcd for $C_{34}H_{38}O_8$: C, 71.07; H, 6.66. Found: C, 70.85; H, 6.63.

1-Acetoxy-6,7-diethyl-5-hydroxy-4-methoxy-3-methyl-2-(1-methylethoxy)phenanthrene (14h). According to the general procedure, (tri-*n*-butylstannyl)naphthalene **8d** (2.00 g, 3.46 mmol) and 4-chloro-2,3-diethyl-2-cyclobutenone (**9b**) (659 mg, 4.16 mmol) in dioxane (35 mL) were treated with tris(2-furyl)phosphine (80 mg, 0.346 mmol) and $Pd_2(dba)_3$ (79 mg, 0.087 mmol). After heating at reflux for 15 h, the solution was cooled to room temperature and subjected to workup. The crude product was purified by flash chromatography (SiO_2, 3 × 15 cm, 15%-33% EtOAc/hexanes) to give hydroxyphenanthrene **14h** as an off-white solid (971 mg, 2.37mmol, 68%) which was further purified by recrystallization (CH_2Cl_2/hexanes). Data for **14h**: R_f 0.43 (25% EtOAc/hexanes); mp 114−116 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.27 (s, 1H), 7.55 (A of ABq, J = 9.0 Hz, 1H), 7.46 (B of ABq, J = 9.0 Hz, 1H), 7.25 (s, 1H), 4.34 (hept, J = 6.0 Hz, 1H), 3.61 (s, 3H), 2.99 (q, J = 7.5 Hz, 2H), 2.87 (q, J = 7.5 Hz, 2H), 2.47 (s, 3H), 2.45 (s, 3H), 1.36 (t, J = 7.5 Hz, 3H), 1.33 (d, J = 6.0 Hz, 6H), 1.26 (t, J = 7.5 Hz, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 168.5, 151.8, 150.4, 146.2, 142.4, 136.8, 132.1, 130.1, 128.8, 126.0, 124.9, 119.2, 118.9, 117.6, 115.9, 76.3, 61.2, 25.9, 22.6 (2C), 20.7, 20.5, 15.2, 14.4, 10.8; IR (CH_2Cl_2, cm^{-1}) 3156 (br m), 1769 (s), 1608 (m), 1546 (w), 1463 (m), 1455 (m), 1422 (s). Anal. Calcd for $C_{25}H_{30}O_5$: C, 73.15; H, 7.36. Found: C, 72.61; H, 7.42. HRMS calcd for $C_{25}H_{30}O_5$ + H: 411.2174. Found: 411.2162.

4,5-Diacetoxy-3,7-bis(1-methylethoxy)-1-methoxy-6-methyl-2-phenylphenanthrene (28). According to the general procedure, (tri-*n*-butylstannyl)naphthalene **27** (510 mg, 0.80 mmol) and 4-chloro-2-methyl-3-(1-methylethoxy)-2-cyclobutenone (**9a**) (167 mg, 0.96 mmol) in dioxane (5 mL) were treated with tris(2-furyl)phosphine (19 mg, 0.080 mmol) and $Pd_2(dba)_3$ (18 mg, 0.020 mmol). After heating at reflux for 16 h, the solution was cooled to room temperature and subjected to workup. The crude product was acetylated (Ac_2O, Et_3N, DMAP in CH_2Cl_2) and purified by flash chromatography (SiO_2, 3 × 18 cm, 15%−25% EtOAc/hexanes) to give the protodestannylation product 1-acetoxy-4-methoxy-2-(1-methylethoxy)-3-phenylnaphthalene (**17a**) as a yellow oil (20 mg, 0.056 mmol, 7%, characterized above), the anticipated phenanthrene (**28**) as an off-white solid (258 mg, 0.53 mmol, 66%), and bisnaphthalene 6,6′-bis[4-acetoxy-1-methoxy-3-(1-methylethoxy)-2-phenylnaphthalene] (**29**) as a white solid (73 mg, 0.104 mmol, 26%). The products were further purified by recrystallization (CH_2Cl_2 and hexanes). Data for **28**: R_f 0.37 (25% EtOAc/hexanes); mp 233−234 °C (decomposed); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.93 (d, J = 9.0 Hz, 1H), 7.65−7.55 (m, 2H), 7.49 (d, J = 9.0 Hz, 1H), 7.50−7.33 (m, 3H), 7.09 (s, 1H), 4.75 (hept, J = 6.0 Hz, 1H), 3.90 (hept, J = 6.0 Hz, 1H), 3.50 (s, 3H), 2.36 (s, 3H), 2.35 (s, 3H), 2.21 (s, 3H), 1.45 (d, J = 6.0 Hz, 6H), 0.97 (br s, 6H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 168.3, 168.1, 155.7, 151.6, 146.9, 146.4, 137.3, 134.2, 133.6, 130.9 (2C), 127.8 (2C), 127.4, 127.2, 125.9, 124.2, 123.0, 120.8, 120.7, 115.6, 106.7, 76.1, 70.3, 61.5, 22.3 (2C), 22.1 (2C), 21.1, 21.0, 10.4; IR (CH_2Cl_2, cm^{-1}) 1758 (s), 1610 (m). Anal. Calcd for $C_{32}H_{34}O_7$: C, 72.44; H, 6.46. Found: C, 72.25; H, 6.51. Data for **29**: R_f 0.34 (25% EtOAc/hexanes); mp > 255 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.27 (d, J = 8.7 Hz, 2H), 8.02 (d, J = 1.2 Hz, 2H), 7.82 (dd, J = 8.7, 1.5 Hz, 2H), 7.68−7.57 (m, 4H), 7.53−7.36 (m, 6H), 5.30 (s, 0.67 H, CH_2Cl_2), 3.81 (hept, J = 6.0 Hz, 2H), 3.51 (s, 6H), 2.51 (s, 6H), 0.97 (d, J = 6.3 Hz, 12H); ^{13}C NMR# (75.5 MHz, $CDCl_3$) δ 168.9 (2C), 151.9 (2C), 145.5 (2C), 139.8 (2C), 136.0 (2C), 133.9 (2C), 131.0 (4C), 128.0 (2C), 127.9 (4C), 127.4 (2C), 125.3 (2C), 125.0 (2C), 123.6 (2C), 119.4 (2C), 76.2 (2C), 61.2 (2C), 22.2 (4C), 20.8 (2C); IR (CH_2Cl_2, cm^{-1}) 1765 (s), 1628 (m), 1602 (w), 1593 (w). Anal. Calcd for $C_{44}H_{42}O_8$ + 1/3 CH_2Cl_2: C, 73.23; H, 5.91. Found: C, 72.43; H, 5.86. The presence and stoichiometry of CH_2Cl_2 of crystallization were determined from the ^{1}H NMR spectrum. (# = Two less carbons observed, presumably due to coincident absorptions.)

Synthesis of Phenanthrene 36 by Addition of Cyclobutenedione 2d to the Lithiate Generated from (Tri-*n*-butylstannyl)naphthalene 34 and Thermolysis. Construction of Tri-*n*-butylstannylnaphthalene 34. 4-Methoxy-3-(1-methylethoxy)-2-phenyl-4-[4′-(tri-*n*-butylstannyl)phenyl]-2-cyclobutenone (32). To a solution of 4-hydroxy-3-(1-methylethoxy)-2-phenyl-4-[4′-(tri-*n*-butylstannyl)phenyl]-2-cyclobutenone (**3a**) (1.70 g, 2.90 mmol) in acetonitrile (100 mL) were added K_2CO_3 (2.01 g, 14.6 mmol), Ag_2O (0.72 g, 5.80 mmol), and iodomethane (1.8 mL, 29.1 mmol). The reaction mixture was stirred vigorously for 2 days at room temperature and filtered through Celite. The filtrate was concentrated under reduced pressure to give a yellow oil (1.73 g) which was purified by flash chromatography (SiO_2, 6 × 15 cm, 7% EtOAc/hexanes) to provide 4-methoxy-3-(1-methylethoxy)-2-phenyl-4-[4′-(tri-*n*-butylstannyl)phenyl]-2-cyclobutenone (**32**) as a pale-yellow oil (1.46 g, 2.5 mmol, 84%): R_f 0.63 (1:3 EtOAc/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.93−7.85 (m, 2H), 7.46 (s, 4H),* 7.46−7.37 (m, 2H), 7.36−7.27 (m, 1H), 4.79 (hept, J = 6.3 Hz, 1H), 3.64 (s, 3H), 1.58−1.42 (m, 6H),* 1.43 (d, J = 6.3 Hz, 3H), 1.30 (hex, J = 7.2 Hz, 6H), 1.07 (d, J = 6.0 Hz, 3H), 1.03 (t, J = 8.1 Hz, 6H),* 0.86 (t, J = 7.2 Hz, 9H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 186.9, 178.8, 142.2, 136.6 (2C),* 135.9, 128.6, 128.5 (2C), 128.1, 127.2, 127.1 (2C), 125.1 (2C),* 99.9, 78.9, 53.4, 29.1 (3C),* 27.3 (3C),* 23.1, 22.7, 13.7 (3C), 9.6 (3C)*; IR (neat, cm^{-1}) 1757 (s), 1630 (s), 1597 (s), 1490 (s). Anal. Calcd for $C_{32}H_{46}O_3Sn$: C, 64.34; H, 7.76. Found: C, 64.45; H, 7.82.

4-Hydroxy-1-methoxy-2-(1-methylethoxy)-3-phenyl-6-(tri-*n*-butylstannyl)naphthalene (33). A solution of 4-methoxy-3-(1-methylethoxy)-2-phenyl-4-[4′-(tri-*n*-butylstannyl)phenyl]-2-cyclobutenone (**32**) (680 mg, 1.14 mmol) in xylenes (20 mL) was heated at reflux for 5 h and then cooled to room temperature. The solvent was evaporated under reduced pressure, and the crude oil was purified by flash chromatography (SiO_2, 4 × 18 cm, 5% EtOAc/hexanes) to provide

4-hydroxy-1-methoxy-2-(1-methylethoxy)-3-phenyl-6-(tri-*n*-butylstannyl)naphthalene (**33**) as a yellow oil (486 mg, 0.81 mmol, 71%): R_f 0.66 (1:3 EtOAc/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.30 (s, 1H),* 8.04 (A of ABq, J = 8.1 Hz, 1H), 7.61 (B of ABq, J = 8.1 Hz, 1H),* 7.57−7.37 (m, 5H), 5.41 (s, 1H), 4.24 (hept, J = 6.0 Hz, 1H), 3.99 (s, 3H), 1.66−1.53 (m, 6H),* 1.36 (hex, J = 7.2 Hz, 6H), 1.13 (t, J = 8.1 Hz, 6H),* 0.99 (d, J = 6.3 Hz, 6H), 0.90 (t, J = 7.2 Hz, 9H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 144.7, 144.6, 141.3, 137.7, 134.1,* 133.6, 131.3 (2C), 130.9, 129.1 (2C), 128.8, 128.1, 121.4,* 120.3,* 119.1, 75.6, 61.0, 29.3 (3C),*, 27.5 (3C),* 22.5 (2C), 13.8 (3C), 9.8 (3C)*. Anal. Calcd for $C_{32}H_{46}O_3Sn$: C, 64.34; H, 7.76. Found: C, 63.72; H, 7.60. HRMS calcd for $C_{32}H_{46}O_3Sn$ + Li: 599.2547. Found: 599.2546.

1,4-Dimethoxy-2-(1-methylethoxy)-3-phenyl-6-(tri-*n*-butylstannyl)-naphthalene (34). To a stirred mixture of 4-hydroxy-2-(1-methylethoxy)-1-methoxy-3-phenyl-6-(tri-*n*-butylstannyl)naphthalene (**33**) (410 mg, 0.69 mmol) prepared above by thermolysis of **32**, and K_2CO_3 (285 mg, 2.06 mmol) in acetone (25 mL) was added iodomethane (0.2 mL, 3.45 mmol). The reaction mixture was stirred overnight at room temperature and then subjected to workup as described above for **8a**. The product was purified by flash chromatography (SiO_2, 3 × 12 cm, 5% EtOAc/hexanes) to provide 1,4-dimethoxy-6-stannylnaphthalene **34** (402 mg, 0.66 mmol, 95%) as a clear oil: R_f 0.70 (1:3 ethyl acetate/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.24 (s, 1H), 8.09 (A of ABq, J = 8.3 Hz, 1H), 7.61 (B of ABq, J = 8.3 Hz, 1H),* 7.56−7.32 (m, 5H), 4.12 (hept, J = 6.3 Hz, 1H), 4.04 (s, 3H), 3.48 (s, 3H), 1.66−1.53 (m, 6H),* 1.36 (hex, J = 7.5 Hz, 6H), 1.13 (t, J = 8.1 Hz, 6H),* 0.97 (d, J = 6.3 Hz, 6H), 0.89 (t, J = 7.2 Hz, 9H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 149.7, 145.2, 144.7, 138.5, 135.0, 133.7,* 131.3 (2C), 131.0, 128.9, 128.8, 127.7 (2C), 127.0, 125.5,* 120.8,* 75.8, 61.0 (2C), 29.4 (3C),* 27.6 (3C),* 22.4 (2C), 13.8 (3C), 9.9 (3C)*; IR (neat, cm^{-1}) 2958 (s), 2929 (s), 2872 (m), 2851 (s), 1611 (m), 1581 (m). Anal. Calcd for $C_{33}H_{48}O_3Sn$: C, 64.83; H, 7.91. Found: C, 65.10; H, 8.02.

6-[4-Acetoxy-2-methyl-3-(1-methylethoxy)-2-cyclobutenon-4-yl]-1,4-dimethoxy-2-(1-methylethoxy)-3-phenylnaphthalene (35). To a stirred solution of 6-(tri-*n*-butylstannyl)naphthalene **34** (670 mg, 1.12 mmol) in THF (20 mL) at −78 °C was added a solution of *n*-BuLi (1.04 M, 1.2 mL, 1.23 mmol) in hexanes. The mixture was stirred at −78 °C for 30 min. To this solution was added in one portion a solution of 3-methyl-4-(1-methylethoxy)cyclobutene-1,2-dione (**2d**) (224 mg, 1.45 mmol) in THF (5 mL). The mixture was stirred at −78 °C for 2 h and then quenched with acetic anhydride. The reaction mixture was slowly warmed to room temperature, extracted with Et_2O (150 mL), washed with brine (2 × 30 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by flash chromatography (SiO_2, 3 × 15 cm, 50% EtOAc/hexanes) to give naphthalene **35** (280 mg, 0.54 mmol, 48%), which was further purified by recrystallization (hexanes and Et_2O) to give a white solid. Data for **35**: R_f 0.68 (50% EtOAc/hexanes); mp 130−132 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.23 (d, J = 1.5 Hz, 1H), 8.14 (d, J = 9.0 Hz, 1H), 7.62 (dd, J = 8.7, 1.8 Hz, 1H), 7.55−7.33 (m, 5H), 4.89 (hept, J = 6.0 Hz, 1H), 4.13 (hept, J = 6.0 Hz, 1H), 4.01 (s, 3H), 3.46 (s, 3H), 2.15 (s, 3H), 1.88 (s, 3H), 1.49 (d, J = 6.3 Hz, 3H), 1.44 (d, J = 6.0 Hz, 3H), 0.97 (d, J = 6.0 Hz, 3H), 0.94 (d, J = 6.3 Hz, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 185.7, 176.4, 169.2, 149.8, 145.4, 144.3, 134.3, 131.7, 130.8 (2C), 129.1, 128.5, 127.5 (2C), 126.9, 125.1, 123.8, 123.4, 122.1, 119.8, 95.2, 76.9, 75.4, 61.0, 60.8, 22.4, 22.2, 22.1 (2C), 21.2, 7.5; IR (CH_2Cl_2, cm^{-1}) 1772 (s), 1751 (s), 1619 (s), 1454 (m), 1419 (w), 1400 (s). Anal. Calcd for $C_{31}H_{34}O_7$: C, 71.80; H, 6.60. Found: C, 71.79; H, 6.62.

8-Acetoxy-1,4-dimethoxy-2,7-bis(1-methylethoxy)-5-hydroxy-6-methyl-3-phenylphenanthrene (36). A solution of naphthalene **35** (200 mg. 0.39 mmol) in xylenes (10 mL) was heated at reflux for 2.5 h. The solvent was removed under reduced pressure, and the crude product was purified by flash chromatography (SiO_2, 3 × 15 cm, 25% EtOAc/hexanes) to give phenanthrene **36** (191 mg, 0.37 mmol, 96%) which was further purified by recrystallization (hexanes and CH_2Cl_2) to give an off-white solid. Data for **36**: R_f 0.38 (25% EtOAc/hexanes); mp 193−195 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.63 (s, 1H), 8.00 (d, J = 9.3 Hz, 1H), 7.67 (d, J = 9.3 Hz, 1H), 7.62−7.52 (m, 2H), 7.52−7.36 (m, 3H), 4.41 (hept, J = 6.0 Hz, 1H), 4.10 (s, 3H), 4.08 (hept, J = 6.0 Hz, 1H), 3.26 (s, 3H), 2.46 (s, 3H), 2.43 (s, 3H), 1.35 (d, J = 6.3 Hz, 6H), 0.99 (d, J = 6.0 Hz, 6H); ^{13}C NMR# (75.5 MHz, $CDCl_3$) δ 168.9, 151.0, 147.2, 146.3, 146.0, 134.0, 132.2, 131.2 (2C), 130.8, 127.7, 127.5 (2C), 127.2, 125.2, 120.5, 120.4, 120.0, 119.0, 114.7, 75.8 (2C), 61.5, 61.1, 22.5 (2C), 22.1 (2C), 20.5, 11.5; IR (CH_2Cl_2, cm^{-1}) 3110 (br w), 1764 (m), 1605 (w), 1549 (w). Anal. Calcd for $C_{31}H_{34}O_7$: C, 71.80; H, 6.60. Found: C, 71.70; H, 6.65. (# = One less carbon observed, presumably due to coincident absorptions.)

Cross-Coupling/Thermolysis of 4-Chlorocyclobutenones with 1,4- and 1,3-bis(tri-*n*-butylstannyl)benzenes 15 and 24. 1-Hydroxy-2-methyl-3-(1-methylethoxy)-7-(tri-*n*-butylstannyl)naphthalene (37). A mixture of 4-chloro-3-(1-methylethoxy)-2-methyl-2-cyclobutenone (**9a**) (200 mg, 1.15 mmol), 1,4-bis(tri-*n*-butylstannyl)benzene (**15**) (752 mg, 1.15 mmol), tris(2-furyl)phosphine (28 mg, 0.12 mmol), and Pd_2dba_3 (27 mg, 0.03 mmol) in dioxane (10 mL) was stirred vigorously at room temperature for 10 min and then heated at reflux for 2 h. The reaction mixture was cooled to room temperature and poured into Et_2O (100 mL). The Et_2O solution was washed with saturated aqueous NH_4Cl (20 mL) and brine (2 × 20 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure to give a black oil (562 mg). The crude product was purified by flash chromatography (SiO_2, 2 × 25 cm, 5−30% EtOAc/hexanes) to afford the known protodestannylation product 1-hydroxy-2-methyl-3-(1-methylethoxy)naphthalene[50] (47 mg, 0.22 mmol, 19%) and (tri-*n*-butylstannyl)naphthalene **37** (162 mg, 0.28 mmol, 28%) as yellow oils. A small amount of 4-methylene-3-(1-methylethoxy)-2-cyclobutenone (12 mg, 0.09 mmol, 8%) was also observed. Data for 1-hydroxy-2-methyl-3-(1-methylethoxy)naphthalene:[50] R_f 0.45 (1:3 ethyl acetate/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.02 (d, J = 8.1 Hz, 1H), 7.65 (d, J = 8.1 Hz, 1H), 7.39 (t, J = 7.1 Hz, 1H), 7.31 (t, J = 7.9 Hz, 1H), 6.79 (s, 1H), 5.19 (s, 1H), 4.69 (hept, J = 6.0 Hz, 1H), 2.28 (s, 3H), 1.42 (d, J = 6.0 Hz, 6H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 154.9, 149.5, 133.1, 126.4, 125.9, 122.8, 120.9, 120.0, 110.5, 100.5, 70.2, 22.1 (2C), 8.8. Data for **37**: R_f 0.58 (1:3 ethyl acetate/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.11 (s, 1H),* 7.61 (A of ABq, J = 8.0 Hz, 1H), 7.48 (B of ABq, J = 8.0 Hz, 1H),* 6.77 (s, 1H), 5.16 (s, 1H), 4.69 (hept, J = 6.0 Hz, 1H), 2.28 (s, 3H), 1.74−1.47 (m, 6H),* 1.47−1.26 (m, 6H), 1.41 (d, J = 6.0 Hz, 6H), 1.12 (t, J = 7.8 Hz, 6H),* 0.91 (t, J = 7.2 Hz, 9H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 154.8, 149.2, 135.4, 133.3*, 132.9, 129.1,* 125.5,* 119.8, 110.2, 100.4, 70.1, 29.2 (3C),* 27.4 (3C),* 22.1 (2C), 13.7 (3C), 9.7 (3C),* 8.7; IR (neat, cm^{-1}) 3475 (w, br), 1742 (s), 1723 (s), 1629 (s), 1561 (m), 1494 (m), 1456 (s). HRMS calcd for $C_{22}H_{33}O_2Sn$ (M^+ − Bu): 449.1503. Found: 449.1500. Data for 4-methylene-3-(1-methylethoxy)-2-cyclobutenone: R_f 0.18 (1:3 EtOAc/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.93 (s, 1H), 5.04 (s, 1H), 4.80 (s, 1H), 4.58 (hept, J = 6.0 Hz, 1H), 1.44 (d, J = 6.0 Hz, 6H); IR (CH_2Cl_2, cm^{-1}) 1764 (m), 1735 (w), 1675 (w), 1600 (w), 1559 (s).

4,5-Dihydroxy-2,3,6,7-tetraethylphenanthrene (38), 5-Hydroxy-2,3,6,7-tetraethyl-1,4-phenanthraquinone (10b), and 2,3-Diethyl-1-hydroxynaphthalene (41). A mixture of 1,4-distannylbenzene **15** (1.60 g, 2.44 mmol), 4-chloro-2,3-diethyl-2-cyclobutenone (**9b**) (851 mg, 5.36 mmol), tris(2-furyl)phosphine (53 mg, 0.229 mmol), and $Pd_2(dba)_3$ (52 mg, 0.057 mmol) in dioxane (10 mL) was heated at reflux for 20 h. The reaction mixture was subjected to workup as above. The crude product was purified by flash chromatography (SiO_2, 3 × 15 cm, 5%−10% EtOAc/hexanes) to give dihydroxyphenanthrene **38** as an off-white solid (215 mg, 0.67 mmol, 27%) and 5-hydroxy-1,4-phenanthraquinone **10b** as a purple-black solid (153 mg, 0.48 mmol, 20%). A small amount of the protodestannylation product, 2,3-diethyl-1-hydroxynaphthalene (**41**), was also obtained. On the basis of TLC analysis, dihydroxyphenanthrene **38** was formed initially and was oxidized to 5-hydroxy-1,4-phenanthraquinone during the workup and purification process. The products were further purified by recrystallization (**38**, CH_2Cl_2 and hexanes; **10b**, hexanes at −78 °C). Data for **38**: R_f 0.54 (25% EtOAc/hexanes); mp 156−157 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76 (br s, 2H), 7.44 (s, 2H), 7.31 (s, 2H), 2.93 (q, J = 7.5 Hz, 4H), 2.85 (q, J = 7.5 Hz, 4H), 1.35 (t, J = 7.5 Hz, 6H), 1.26 (t, J = 7.5 Hz, 6H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 148.8 (2C), 141.1 (2C), 132.6 (2C), 128.4 (2C), 126.4 (2C), 120.7 (2C), 117.2 (2C), 25.8 (2C), 20.0 (2C), 15.3 (2C), 14.3 (2C); IR (CH_2Cl_2, cm^{-1}) 3577 (m), 3286 (br m), 1732 (w), 1617 (m), 1546 (w). Anal. Calcd for $C_{22}H_{26}O_2$: C, 81.95; H, 8.12. Found: C, 81.75; H, 8.18. Data for **10b**: R_f 0.64 (25% EtOAc/hexanes); mp 124−125 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 11.04

(s, 1H), 8.06 (A of ABq, J = 8.7 Hz, 1H), 8.03 (B of ABq, J = 8.7 Hz, 1H), 7.27 (s, 1H), 2.94 (q, J = 7.5 Hz, 2H), 2.84 (q, J = 7.5 Hz, 2H), 2.72 (q, J = 7.5 Hz, 2H), 2.65 (q, J = 7.5 Hz, 2H), 1.34 (t, J = 7.5 Hz, 3H), 1.24 (t, J = 7.5 Hz, 3H), 1.22 (t, J = 7.5 Hz, 3H), 1.18 (t, J = 7.5 Hz, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 192.7, 185.1, 151.8, 149.7, 146.0, 145.9, 136.4 (2C), 133.4, 131.8, 125.1, 121.0, 119.9, 119.5, 26.0, 21.1, 20.5, 19.8, 14.7, 13.9, 13.8 (2C); IR (CH_2Cl_2, cm^{-1}) 3689 (w), 3684 (w), 3439 (br w), 1744 (w), 1653 (s), 1640 (s), 1625 (m), 1608 (m), 1585 (m). Anal. Calcd for $C_{22}H_{24}O_3$: C, 78.55; H, 7.19. Found: C, 77.98; H, 7.23; HRMS calcd for $C_{22}H_{24}O_3$ + H: 337.1804. Found: 337.1815. Data for **41**: R_f 0.45 (25% EtOAc/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.10−8.02 (m, 1H), 7.78−7.72 (m, 1H), 7.46−7.37 (m, 2H), 7.31 (s, 1H), 5.26 (s, 1H), 2.85 (q, J = 7.5 Hz, 2H), 2.82 (q, J = 7.5 Hz, 2H), 1.34 (t, J = 7.5 Hz, 3H), 1.26 (t, J = 7.5 Hz, 3H); IR (neat, NaCl, cm^{-1}) 3496 (br s), 1755 (m), 1740 (m), 1651 (m), 1634 (m), 1596 (s), 1457 (s).

4,8-Dihydroxy-2,3,6,7-tetraethylphenanthrene (39), 5-Hydroxy-2,3,6,7-tetraethyl-1,4-phenanthraquinone (10b), and 4,8-Diacetoxy-2,3,6,7-tetraethylphenanthrene (40). A mixture of 1,3-distannylbenzene **24** (1.70 g, 2.59 mmol), 4-chloro-2,3-diethyl-2-cyclobutenone (**9b**) (904 mg, 5.70 mmol), tris(2-furyl)phosphine (60 mg, 0.259 mmol), and $Pd_2(dba)_3$ (60 mg, 0.065 mmol) in dioxane (10 mL) was heated at reflux for 16 h. The reaction mixture was subjected to workup as above. The crude product was purified by flash chromatography (SiO_2, 3 × 15 cm, 15%−25% EtOAc/hexanes) to give 4,8-dihydroxy-2,3,6,7-tetraethylphenanthrene (**39**) (R_f 0.34, 128 mg, 0.40 mmol, 15%) as a red oil and 5-hydroxy-2,3,6,7-tetraethyl-1,4-phenanthraquinone (**10b**) (R_f 0.64, 208 mg, 0.62 mmol, 24%) as a purple-black solid. A small amount of the protodestannylation product, 2,3-diethyl-1-hydroxynaphthalene (**41**), was also obtained. On the basis of TLC analysis, dihydroxyphenanthrene **39** was formed initially and was oxidized to 5-hydroxy-1,4-phenanthraquinone **10b** during the workup and purification process. Purification of 4,8-dihydroxy-2,3,6,7-tetraethylphenanthrene (**39**) was not feasible due to facile oxidation. Instead, dihydroxyphenanthrene **39** was acetylated to give pure 4,8-diacetoxy-2,3,6,7-tetraethylphenanthrene (**40**) according to the following procedure.

A mixture of 1,3-distannylbenzene **24** (1.50 g, 2.29 mmol), 4-chloro-2,3-diethyl-2-cyclobutenone (**9b**) (800 mg, 5.04 mmol), tris(2-furyl)-phosphine (53 mg, 0.229 mmol), and $Pd_2(dba)_3$ (52 mg, 0.057 mmol) in dioxane (10 mL) was heated at reflux for 18 h. The reaction mixture was subjected to workup as indicated above. The crude product was dissolved in CH_2Cl_2 (50 mL) and treated with Et_3N (1.90 mL, 13.74 mmol), acetic anhydride (0.63 mL, 6.87 mmol), and DMAP (84 mg, 0.69 mmol). The reaction mixture was stirred at room temperature for 18 h, diluted with CH_2Cl_2 (100 mL), washed with brine (3 × 30 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by flash chromatography (SiO_2, 30 × 150 cm, 12%-25% EtOAc/hexanes) to give diacetoxyphenanthrene **40** (287 mg, 0.71 mmol, 31%) as an off-white solid. An appreciable amount of the protodestannylation product, 1-acetoxy-2,3-diethylnaphthalene, was also obtained. Data for 1-acetoxy-2,3-diethylnaphthalene: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.84−7.75 (m, 1H), 7.70−7.62 (m, 1H), 7.60 (s, 1H), 7.48−7.40 (m, 2H), 2.87 (q, J = 7.5 Hz, 2H), 2.82−2.64 (br m, 2H), 2.52 (s, 3H), 1.37 (t, J = 7.5 Hz, 3H), 1.22 (t, J = 7.5 Hz, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 169.4, 144.2, 140.7, 132.8, 131.7, 127.3, 125.5, 125.4, 124.4, 120.8, 25.6, 20.5, 20.1, 14.9, 14.1. Data for **40**: R_f 0.30 (25% EtOAc/hexanes); mp 110−114 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.81 (s, 1H), 7.62 (A of ABq, J = 8.9 Hz, 1H), 7.61 (s, 1H), 7.54 (B of ABq, J = 8.9 Hz, 1H), 2.92 (q, J = 7.5 Hz, 2H), 2.88 (q, J = 7.5 Hz, 2H), 2.82−2.59 (br m, 4H), 2.55 (s, 3H), 2.51 (s, 3H), 1.40 (t, J = 7.5 Hz, 3H), 1.38 (t, J = 7.5 Hz, 3H), 1.27 (t, J = 7.5 Hz, 3H), 1.24 (t, J = 7.5 Hz, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 169.4, 169.1, 146.1, 145.1, 140.9, 134.0, 132.0, 131.8, 128.1, 126.7, 125.9, 124.3, 123.3, 121.4, 119.4, 26.7, 25.4, 21.4, 20.5 (2C), 20.2, 15.9, 14.8, 14.1 (2C); IR (CH_2Cl_2, cm^{-1}) 1760 (s), 1605 (w). HRMS calcd for $C_{26}H_{30}O_4$ + H: 407.2222. Found 407.2211. Anal. Calcd for $C_{26}H_{30}O_4$: C, 76.82; H, 7.43. Found: C, 76.21; H, 7.42.

Double Benzannulation of 1,4- and 1,3-Dilithiobenzene with Cyclobutenedione 2a. 2,7-Bis(1-methylethoxy)-3,6-diphenyl-1,4,5,8-phenanthradiquinone (42a). To a stirred solution of 1,4-dibromobenzene (436 mg, 1.85 mmol) in THF (20 mL) at −78 °C was added a solution of *t*-BuLi (1.93 M, 3.8 mL, 3.70 mmol) in pentane. The resulting solution was stirred at −78 ° for 40 min, and the cold bath was removed. After stirring for 20 min, the mixture was cooled again to −78 °C and transferred via cannula into a solution of 3-(1-methylethoxy)-4-phenyl-1,2-cyclobutenedione (**2a**) (800 mg, 3.70 mmol) in THF (10 mL) at −78 °C. The reaction mixture was stirred at −78 °C for 2 h, quenched with saturated aqueous NH_4Cl (30 mL), extracted with Et_2O (150 mL), and washed with brine (2 × 30 mL). The aqueous layer was extracted again with ethyl acetate (2 × 70 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure to afford a yellow solid (1.01 g). The crude product was suspended in xylenes (30 mL) and heated at reflux for 2 h to give a homogeneous solution. The solvent was removed under reduced pressure and the crude product (986 mg) was dissolved in acetone (50 mL). To this solution were added ceric ammonium nitrate (14.80 mmol, 8.11 g) and concentrated HNO_3 (4 mL). The mixture was stirred at room temperature for 10 min under air, extracted with Et_2O (200 mL), and washed with brine (2 × 50 mL). The aqueous layer was extracted with CH_2Cl_2 (100 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure to give an orange-colored solid (1.03 g). The crude product was purified by flash chromatography (SiO_2, 3 × 15 cm, 20% EtOAc/hexanes) to give phenanthradiquinone **42a** as a bright yellow solid (519 mg, 1.09 mmol, 59%). The product was further purified by trituration with Et_2O. Data for **42a**: R_f 0.40 (25% EtOAc/hexanes); mp 219−222 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.37 (s, 2H), 7.70−7.56 (m, 4H), 7.53−7.36 (m, 6H), 4.71 (hept, J = 6.0 Hz, 2H), 1.19 (d, J = 6.3 Hz, 12 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 185.4 (2C), 180.6 (2C), 153.9 (2C), 136.1 (2C), 135.5 (2C), 135.0 (2C), 131.0 (4C), 130.8 (2C), 129.1 (2C), 128.8 (2C), 127.8 (4C), 76.8 (2C), 22.7 (4C); IR (CH_2Cl_2, cm^{-1}) 1675 (s), 1594 (s), 1563 (w). Anal. Calcd for $C_{32}H_{26}O_6$: C, 75.88; H, 5.17. Found: C, 75.69; H, 5.06.

2,6-Bis(1-methylethoxy)-3,7-diphenyl-1,4,5,8-phenanthradiquinone (42b). To a stirred solution of 1,3-dibromobenzene (546 mg, 2.31 mmol) in THF (20 mL) at −78 °C was added a solution of *t*-BuLi (1.93 M, 4.8 mL, 9.24 mmol) in pentane. The resulting solution was stirred at −78 °C for 15 min, and the cold bath was removed. After stirring for 15 min, the mixture was cooled again to −78 °C and transferred via cannula into a solution of 3-(1-methylethoxy)-4-phenyl-1,2-cyclobutenedione (**2a**) (1.00 g, 4.62 mmol) in THF (20 mL) at −78 °C. The reaction mixture was stirred at −78 °C for 3 h, quenched with saturated aqueous NH_4Cl (30 mL), extracted with Et_2O (150 mL), and washed with brine (2 × 30 mL). The aqueous layers were extracted again with ethyl acetate (3 × 50 mL). The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure to give a yellow solid (1.28 g). The crude product was then suspended in xylenes (15 mL) and heated at reflux for 2 h to give a homogeneous solution. The solvent was removed under reduced pressure, and the crude product (986 mg) was dissolved in Et_2O (100 mL). The Et_2O solution was filtered through a short pad of silica gel. The filtrate was concentrated under reduced pressure to give a brown solid. The crude solid was dissolved in acetone (50 mL), and ceric ammonium nitrate (14.80 mmol, 8.11 g) and concentrated HNO_3 (4 mL) were added. The mixture was stirred at room temperature for 2 h under air, extracted with Et_2O (200 mL), and washed with brine (2 × 50 mL). The aqueous layer was extracted with CH_2Cl_2 (100 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure to give an orange-colored solid (1.11 g). The crude product was purified by flash chromatography (SiO_2, 3 × 15 cm, 15% EtOAc/hexanes) to give phenanthradiquinone **42b** as a bright yellow solid (660 mg, 1.39 mmol, 60%). The product was further purified by trituration with Et_2O. Data for **42b**: R_f 0.38 (25% EtOAc/hexanes); mp 181−184 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.41 (A of ABq, J = 8.1 Hz, 1H), 8.38 (B of ABq, J = 8.1 Hz, 1H), 7.63−7.54 (m, 2H), 7.53−7.35 (m, 8H), 5.16 (hept, J = 6.0 Hz, 1H), 4.75 (hept, J = 6.0 Hz, 1H), 1.32 (d, J = 6.0 Hz, 6 H), 1.19 (d, J = 6.0 Hz, 6H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 184.5, 182.4, 182.2, 180.7, 159.5, 154.3, 136.7, 135.7, 134.5, 134.3, 130.8 (3C), 130.4 (3C), 130.1, 129.9, 129.6, 129.4, 129.0, 128.2, 127.8 (2C), 127.6 (2C), 76.8, 76.3,

22.8 (2C), 22.7 (2C); IR (CH_2Cl_2, cm^{-1}) 1674 (s), 1656 (s), 1595 (s), 1562 (m). Anal. Calcd for $C_{32}H_{26}O_6$: C, 75.88; H, 5.17. Found: C, 75.49; H, 5.08.

Acknowledgment. This investigation was supported by Grant No. CA40157, awarded by the National Cancer Institute, DHHS. We acknowledge the use of a VG 70-S mass spectrometer purchased through funding from the National Institutes of Health, S10-RR-02478, and a 300 MHz NMR and 360 MHz NMR purchased through funding from the National Science Foundation, NSF CHE-85-16614 and NSF CHE-8206103, respectively. We thank Dr. Richard Yu for providing the benzocyclobutenedione used in this work. We are particularly grateful to Dr. J. Stuart McCallum and Marcus Semones for carrying out the X-ray crystal structure analysis of the molecular structure of compound **23**.

Supplementary Material Available: X-ray crystallographic determination of compound **23**, ORTEP plot, crystal data, intensity measurements, structure solution and details of refinement, non-hydrogen atomic coordinates and U_{eq}, non-hydrogen temperature factors, hydrogen atom coordinates and temperature factors, bond lengths, and bond angles (7 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS; and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

JA943301F