$CHCl_3$). **4d**: oil; $[\alpha]_D^{20}$ +135° (*c* 1.2, $CHCl_3$). ^1H NMR chemical shifts of **3b–d** and **4b–d** were nearly identical with those described for **1b–d** and **2b–d** in ref 4.

General Procedure for CCL-Catalyzed Transesterification of Compounds 1a–4a. All conditions but the solvent (methylene chloride–acetone, 4:1) were the same as in the above procedure with PPL.

General Procedure for PFL-Catalyzed Transesterification of Compounds 1a–4a. All conditions but temperature (25 °C) were the same as in the above procedure with PPL.

Regioselective Synthesis of Substituted Rubrenes

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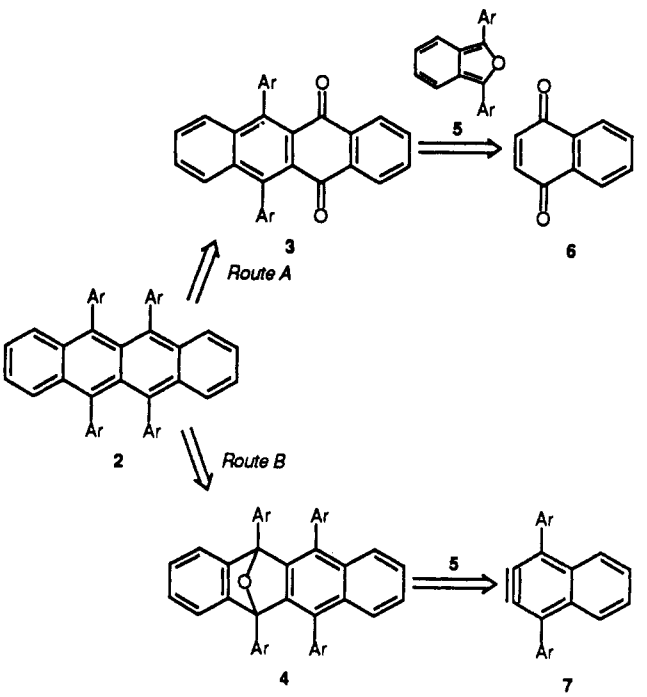
Received September 8, 1989

The development of two complementary synthetic routes to 5,6,11,12-tetraphenylnaphthacene (rubrene) derivatives is described. In one approach, selective nucleophilic addition of aryllithiums to diarylnaphthacenequinones (**13**, **14**, **16**), followed by HI aromatization of the corresponding diols, allows for the convenient preparation of a wide variety of selectively functionalized rubrenes. Symmetrically and unsymmetrically di- and tetrasubstituted rubrenes have been prepared, as well as several "end-capped" versions. In a second route, cycloaddition of 1,3-diphenylisobenzofuran with the naphthyne **7** (Ar = Ph) followed by Lewis acid mediated deoxygenation of the resultant oxo-bridged adduct gives rubrene in a particularly convergent manner. Elaboration through the use of substituted isobenzofurans (i.e. **9–11**) allows for the analogous preparation of substituted rubrenes (**45–47**).

Introduction

The polycyclic aromatic hydrocarbon rubrene (**1**; 5,6,11,12-tetraphenylnaphthacene) has been studied extensively for its wide varity of interesting properties, including electrochemiluminescence,[1a] enhanced chemiluminescence,[1b] fluorescence,[1c] photoconductivity,[1d] photooxidation,[1e] and others.[2] Rubrene and related polyaromatics have also proven to be particularly valuable tools for the trapping of singlet oxygen in a variety of chemical processes.[3] This well-studied hydrocarbon appeared to have considerable potential as the basis of a new host for small organic molecules if the shallow hydrophobic cleft formed by the intersecting aryl rings could be appropriately functionalized with complementary binding groups. Structural investigations[4] show that the phenyl rings of **1** are approximately perpendicular to the planar naphthacene core and thus provide a number of potential sites

Scheme I



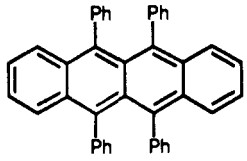
(1) For recent representative examples, see the following. (a) Electrochemiluminescence: Engstrom, R. C.; Johnson, K. W.; DesJarlais, S. *Anal. Chem.* **1987**, *59*, 670. Itoh, K.; Honda, K.; Sukigara, M. *J. Electroanal. Chem.* **1980**, *110*, 277. Dunnet, J. S.; Voivnov, M. *J. Electroanal. Chem.* **1978**, *89*, 181. Dunnet, J. S.; Voivnov, M. *J. Chem. Soc., Faraday Trans. 1* **1977**, *73*, 853. Yeh, L.-S. R.; Bard, A. J. *Chem. Phys. Lett.* **1976**, *44*, 339. Keszthelyi, C. P.; Tokel-Takvoryan, N. E.; Bard, A. J. *Anal. Chem.* **1975**, *47*, 249. Maloy, J. T.; Bard, A. J. *J. Am. Chem. Soc.* **1971**, *93*, 5968. Pighin, A. *Can. J. Chem.* **1973**, *51*, 3467. Maricle, D. L.; Maurer, A. *J. Am. Chem. Soc.* **1967**, *89*, 188. (b) Enhanced chemiluminescence: Larena, A.; Martinez-Urreaga, J. *Spectrosc. Lett.* **1985**, *18*, 463. Adam, W.; Cueto, O.; Yany, F. *J. Am. Chem. Soc.* **1978**, *100*, 2587. Adam, W.; Cancio, E. M.; Rodriguez, O. *Photochem. Photobiol.* **1978**, *27*, 617. (c) Fluorescence: Yee, W. A.; Kuzmin, V. A.; Kliger, D. S.; Hammond, G. S.; Twarowski, A. J. *J. Am. Chem. Soc.* **1979**, *101*, 5104. Liu, D. K. K.; Faulkner, L. R. *J. Am. Chem. Soc.* **1977**, *99*, 4594. Wilson, T. *J. Am. Chem. Soc.* **1969**, *91*, 2387. (d) Photoconductivity: Frankevich, E. L.; Tribel, M. M.; Sokolik, I. A. *Phys. Status Solidi B* **1976**, *77*, 265. Romanets, R. G.; Prock, A.; Zahradnik, R. *J. Chem. Phys.* **1970**, *53*, 4093; (e) Photooxidation: Yamada, M.; Isao, I.; Kurado, H. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 1057. Gsponer, H. E.; Previtali, C. M.; Garcia, N. A. *J. Photochem.* **1987**, *36*, 247. Caminade, A. M.; Khatib, F. E.; Koenig, M.; Aubry, J. M. *Can. J. Chem.* **1985**, *63*, 3203. Aubry, J. M.; Rigaudy, J.; Cuong, N. K. *Photochem. Photobiol.* **1981**, *33*, 149 and 155. Herkstroeter, W. G.; Merkel, P. B. J. *Photochemistry* **1981**, *16*, 331. Turro, N. J.; Chow, M.-F.; Kanfer, S.; Jacobs, M. *Tetrahedron Lett.* **1981**, 3. Harada, Y.; Takahashi, T.; Fujisawa, S.; Kajiwara, T. *Chem. Phys. Lett.* **1979**, *62*, 283.

(2) A CAS Online literature search of rubrene revealed 206 references (1967 to date) dealing with the aforementioned subjects (footnotes 1–5) as well as other miscellaneous topics.

(3) (a) Moureu, C.; Dufraisse, C.; Dean, P. M. *C. R. Acad. Sci.* **1926**, *182*, 1440. (b) *Ibid.* **1926**, *182*, 1584. (c) Wasserman, H. H.; Scheffer, J. R.; Cooper, J. L. *J. Am. Chem. Soc.* **1972**, *94*, 4991.

(4) For a crystal structure of rubrene, see: Akopyan, Z. A.; Avoyan, R. L.; Struchkov, Y. T. *Zh. Strukt. Khim.* **1962**, *3*, 602. Other references dealing with structural or conformational aspects of rubrene include: (a) Fagan, P. J.; Ward, M. D.; Caspar, J. V.; Calabrese, J. C.; Krusic, P. J. *J. Am. Chem. Soc.* **1988**, *110*, 2981. (b) Bulgarovskaya, I. V.; Vozzhennikov, V. M.; Aleksandrov, S. B.; Bel'skii, V. K. In *Elektron. Org. Mater.*; Ovchinnikov, A. A., Ed.; Nauka: Moscow, 1985; pp 211–3. (c) Takahashi, T.; Harada, Y.; Sato, N.; Seki, K.; Inokuchi, H.; Fujisawa, S. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 380. (d) Storek, W.; Sauer, J.; Stoesser, R. *Z. Naturforsch., A* **1979**, *34A*, 1334. (e) Henn, D. E.; Williams, W. G.; Gibbons, D. J. *J. Appl. Crystallogr.* **1971**, *4*, 256. (f) Tinland, B. *J. Mol. Struct.* **1969**, *4*, 330. (g) Nakashimi, T. T.; Offen, H. W. *J. Chem. Phys.* **1968**, *48*, 4817. Rotational barriers of related tetra- and diphenylnaphthalene systems have also been investigated. See: (a) Clough, R. L.; Roberts, J. D. *J. Org. Chem.* **1978**, *43*, 1328. (b) Clough, R. L.; Kung, W. J.; Marsh, R. E.; Roberts, J. D. *J. Org. Chem.* **1976**, *41*, 3603.

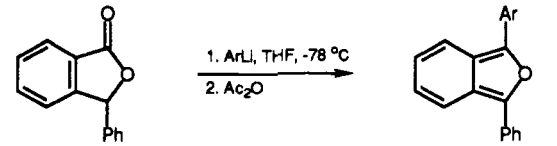
for anchoring binding groups. However, none of the reports of the preparation of functionalized rubrenes[5] dealt with the problem of selective functionalization at one or more specific sites on the pendant aryl rings.



Rubrene (1)

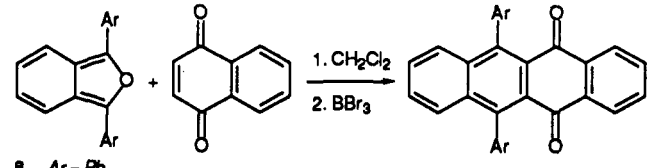
In order to achieve the desired degree of functionalization in a highly selective fashion, two complementary approaches to the rubrene skeleton have been developed, both of which meet the specific criterion of allowing the introduction of specifically substituted aryl groups in a concise and controlled manner. These two approaches are illustrated retrosynthetically in Scheme I. In one case (route A) the initial disconnection of two pendant aryl groups leaves a diarylnaphthacenequinone (**3**), which is further simplified to a 1,3-diarylisobenzofurandiene (**5**) and naphthoquinone (**6**). While the prototype of route A was introduced by Dufraisse[6] many years ago as a synthetic approach to rubrene itself, it has not since been employed for the preparation of substituted rubrenes.[7] An alternative disconnection of the target (route B) utilizes the same diene (**5**) in a cycloaddition with a naphthyne intermediate (**7**), providing a particularly convergent route to the rubrene skeleton. One attribute of both of these approaches is that aryl-substituted isobenzofuran dienes are easily obtained from commercial sources (Ar = Ph) or by short synthetic routes.[8]

Synthesis of 1,3-Diarylisobenzofurans. The preparation of 1,3-diarylisobenzofurans and their subsequent use as highly reactive Diels–Alder dienes is well documented.[8] In general, furans in which one of the phenyl substituents has been replaced by a functionalized aryl moiety are easily prepared from 3-phenylphthalide.[9] Specifically, addition of the appropriate aryllithium (prepared by halogen–metal exchange of the corresponding aryl halide with *n*-butyllithium) to the phthalide followed by quenching of the reaction mixture at −78 °C with acetic anhydride and heating at reflux for a brief period affords the 1-aryl-3-phenylisobenzofurans **8**–**11**. We have found that acetic anhydride results in higher yields of the furan than does the standard acetic acid quench.[10] This method also lends itself to the synthesis of diarylfurans from 3-arylphthalides, which are easily constructed by zinc/acetic acid reduction[11] of the corresponding aroylbenzoic acids.[12]



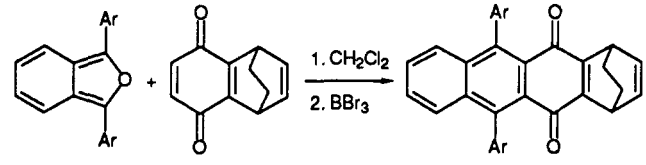
8 Ar = Ph
9 Ar = 3-ClC$_6$H$_4$
10 Ar = 3-BrC$_6$H$_4$
11 Ar = 2-pyridyl

Nucleophilic Addition to Diarylnaphthacenequinones (Route A). As illustrated by Dufraisse[6] and by Badger,[5d] naphthacenequinones serve as important intermediates in the synthesis of rubrenes. However, nucleophilic addition of dissimilar aryl groups to naphthacenequinones, which would provide selectively substituted rubrenes if carried through the rest of the sequence, has not been previously reported. Further, the sequential addition of different aryllithiums to aryl-substituted naphthacenequinones would lead to rubrenes bearing functionality on all four aryl groups. The preparation of naphthacenequinones required for this reaction is a very convenient, three-reaction, one-pot sequence consisting of an initial Diels–Alder cycloaddition of an isobenzofuran (**8** or **12**) with the appropriate dienophile (1,4-naphthoquinone or **15**[13]), followed by dehydration and subsequent oxidation of the semiquinone. Although the oxo-bridged intermediate can be isolated, cycloreversion to starting material is a considerable problem which has been eliminated by in situ aromatization.



8 Ar = Ph
12 Ar = 4-MeOC$_6$H$_4$

13 Ar = Ph
14 Ar = 4-MeOC$_6$H$_4$



15 **16**

Following this procedure with the naphthacenequinones **13**, **14**, and **16** selectively affords a variety of substituted rubrene derivatives in which the positional selectivity is determined simply by the choice of aryllithium employed in the addition step (Table I). Symmetrically substituted rubrenes (entries 1–7) are made by nucleophilic addition of 2 equiv of an aryllithium[14] to the appropriate na-

(5) For previous routes to rubrene derivatives in which substitution of the side aryl rings has been studied, see: (a) Neth. Appl. NL 85 01,277; *Chem. Abstr.* **1987**, *106*, 32637m. (b) Rauhut, M. M.; Mohan, A. G. Eur. Pat. Appl. EP 59,323; *Chem. Abstr.* **1983**, *98*, 53462g. (c) Biehl, R.; Dinse, K. P.; Moebius, K.; Plato, M.; Kurreck, H.; Mennenga, U. *Tetrahedron* **1973**, *29*, 363. (d) Badger, G. M.; Pearce, R. S.; Rodela, H. J.; Walker, I. S. *J. Chem. Soc.* **1954**, 3151. (e) Perronnet, J. *Ann. Chim.* **1959**, *4*, 365. (f) Dufraisse, C.; Etienne, A.; Valls, J. *C. R. Acad. Sci.* **1954**, *239*, 1101. (g) Bertin, D. *C. R. Acad. Sci.* **1950**, *230*, 1356. (h) Dufraisse, C.; Robin, J.; Bertin, D. *C. R. Acad. Sci.* **1949**, *229*, 5. (i) Robin, J. *Ann. Chim.* **1931**, *16*, 421. (j) Dufraisse, C.; Willemart, A. *C. R. Acad. Sci.* **1928**, *187*, 226. For analogues selectively functionalized on the naphthacene core with respect to the side aryl rings, see: (k) Rigaudy, J.; Cuong, N. K. *C. R. Acad. Sci.* **1962**, *254*, 4184. (l) Dufraisse, C.; Mathieu, J.; Valls, J. *C. R. Acad. Sci.* **1958**, *246*, 661.

(6) (a) Dufraisse, C.; Compagnon, P. *C. R. Acad. Sci.* **1938**, *207*, 585. (b) Dufraisse, C.; Velluz, L. *C. R. Acad. Sci.* **1935**, *201*, 1394. Also see: Allen, C. F. H.; Gilman, L. *J. Am. Chem. Soc.* **1936**, *58*, 937.

(7) The preparation of tetramethylrubrene by this method has been reported. See ref 5d.

(8) For reviews of isobenzofuran chemistry, see: (a) Rodrigo, R. *Tetrahedron* **1988**, *44*, 2093. (b) Rickborn, B. In *Advances in Theoretically Interesting Molecules*; Thummel, R. P., Ed.; JAI Press; Greenwich, CT, 1988. (c) Friedrichsen, W. *Adv. Heterocycl. Chem.* **1980**, *26*, 135.

(9) Newman, M. S. *J. Org. Chem.* **1961**, *26*, 2630.

(10) For example, see: (a) Allen, C. F. H.; VanAllan, J. A. *J. Am. Chem. Soc.* **1948**, *70*, 2069. (b) Cava, M. P.; Mitchell, M. J.; Deanna, A. A. *J. Org. Chem.* **1960**, *25*, 1481. For a report in which Ac_2O has been employed in a similar manner, see: Potts, K. T.; Elliot, A. *J. Org. Prep. Proc. Int.* **1972**, *4*, 269.

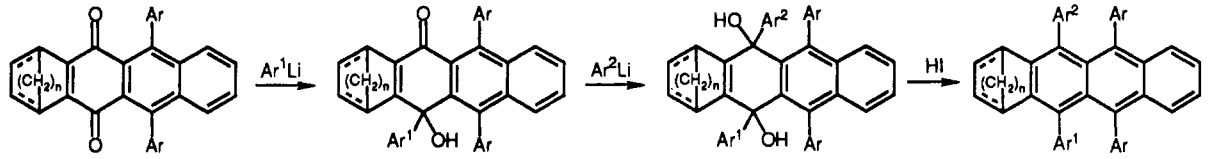
(11) Hauser, C. R.; Tetenbaum, M. T.; Hoffenberg, D. S. *J. Org. Chem.* **1958**, *23*, 861.

(12) Parham, W. E.; Piccirilli, R. M. *J. Org. Chem.* **1976**, *41*, 1268.

(13) Diels, O.; Alder, K. *Chem. Ber.* **1929**, *62*, 2337.

(14) All aryllithiums were prepared from the corresponding arylbromide by halogen–metal exchange with *n*-BuLi immediately prior to use.

Table I. Preparation of Rubrene Analogues via Nucleophilic Addition to Substituted Naphthacenequinones (Route A)



A

entry	quinone	Ar	n	Ar^1	A	yield,[b] %	Ar^2	diol	yield, %	rubrene	yield,[b] %
1	13	Ph	0	4-$MeOC_6H_4$	*a*	–	4-$MeOC_6H_4$	**17**	64	**28**	95
2	13	Ph	0	4-MeC_6H_4	*a*	–	4-MeC_6H_4	**18**	53	**29**	74
3	13	Ph	0	3-$MeOC_6H_4$	*a*	–	3-$MeOC_6H_4$	**19**	76	**30**	79
4	13	Ph	0	3-$HOCH_2C_6H_4$	*a*	–	3-$HOCH_2C_6H_4$	**20**	90	**31**	63
5	13	Ph	0	3-(2,5-dimethyl-pyrrol-1-yl)C_6H_4	*a*	–	3-(2,5-dimethylpyrrol-1-yl)C_6H_4	**21**	52	**32**	64
6	14	4-$MeOC_6H_4$	0	4-$MeOC_6H_4$	*a*	–	4-$MeOC_6H_4$	**22**	57	**33**	77
7	16	Ph	2	Ph	*a*	–	Ph	**23**	41	**34**	82
8	13	Ph	0	2-$MeOC_6H_4$	**24**	81	3-$MeOC_6H_4$	*a*	–	**35**	70
9	16	Ph	2	Ph	**25**	59	3-$MeOC_6H_4$	*a*	–	**36**	65
10	14	4-$MeOC_6H_4$	0	3-$MeOC_6H_4$	**26**	88	Ph	**27**	69	**37**	73
11	16	Ph	2	Ph	**25**	59	2-$MeOC_6H_4$	*a*	–	**38, 39**[c]	67

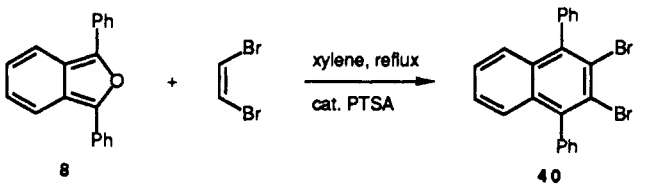
[a] Not isolated. [b] Based on purified product. [c] Two rotameric forms were isolated (see ref 7 for a discussion).

phthacenequinone, giving the diol.[15] Aromatization by standard methods[16] provides the naphthacene. This approach is also useful for the selective preparation of unsymmetrically substituted rubrenes (i.e. $Ar^1 \neq Ar^2$, entries 8–11). For example, slow addition of a slight excess of 2-lithioanisole to a dilute solution of the quinone **13** (Table I, entry 8) in THF at −78 °C gives the monoaddition product **24** as the major isolated product (81%). Addition of an excess of a second aryllithium then yields the diol, with subsequent aromatization, giving the unsymmetrically tetrasubstituted naphthacene **36** in 57% overall yield from the quinone.

In addition to aryl-substituted naphthacenes, several "end-capped" analogues (Table I, entires 7, 9, 11) were prepared from the quinone **16**, in which one of the terminal aromatic rings of the fused naphthacene core is replaced by a bridged bicyclic moiety. Addition of the indicated aryllithiums followed by HI aromatization[16] gives the 1,4-ethanonaphthacenes as shown.[17] This bicyclic end-cap provides additional potential sites for the eventual attachment of complementary binding groups in rubrene-derived hosts. Note that this particular route provides a level of regiochemical control for the aryl substituents relative to the bicyclic ring that is not possible for the alternative [4 + 2] cycloaddition of a substituted rubrene with a dienophile.[18] While these derivatives are structurally similar to the corresponding naphthacenes in terms of their respective aryl groups' substitution patterns,[7] they are much less prone to undergo photooxidation. For example, while tetraarylnaphthacenes spontaneously form peroxy-bridged species when exposed to air, no such tendency is noted for the end-capped analogues, which as a result possess an indefinite shelf-life when stored as a solid.

Several attributes of naphthacenequinones as rubrene percursors are particularly noteworthy. Aryl functionality can be introduced either by the use of 1,3-diarylisobenzofurans, or by the selective nucleophilic addition of aryllithiums to naphthacene quinones by employing the latter approach, in which aryl-functionalized isobenzofurans afford quinone intermediates, the synthesis of rubrene analogues possessing functionality on all four peri aryl rings is possible. For example, tetra-4-anisoylrubrene **33** (Table I, entry 6) is conveniently prepared by addition of 4-lithioanisole to quinone **14** to yield the corresponding diol, which is subsequently aromatized. Elaboration to more diversely substituted derivatives is also possible by the selective addition of dissimilar aryllithiums to quinone **14**, as illustrated by entry 10. Another significant feature of the methodology includes the commercial availability of many aryllithium precursors in the form of the corresponding aryl halides. Ortho, meta, and para aryl-substituted rubrene derivatives are readily accessible from such aryl halides (see Table I for examples of each). Examples of substituents that can be introduced include alkyl (entry 2), ether (e.g. entry 1), protected amine (entry 5), and benzylic alcohol groups (entry 4).

Naphthyne Cycloaddition Approach (Route B). Although an aryne cycloaddition strategy for the preparation of tetraarylnaphthacenes is a hitherto unexplored route, its convergent nature was particularly appealing because coupling of an aryl-functionalized furan with the corresponding naphthalenes would provide the desired carbon skeleton is a single step. Simple removal of the oxo bridge would then liberate the naphthacene. Initial work thus centered around the efficient preparation of the requisite naphthyne precursor, which was prepared from 1,3-diphenylisobenzofuran **8** by [4 + 2] cycloaddition with dibromoethylene in xylene at 140 °C followed by acid-catalyzed dehydration of oxo-bridged adduct to give **40** in 67% yield.[19]



8 **40**

(15) Only a single diol product was isolated in most cases for which the relative syn or anti stereochemistry was not determined.

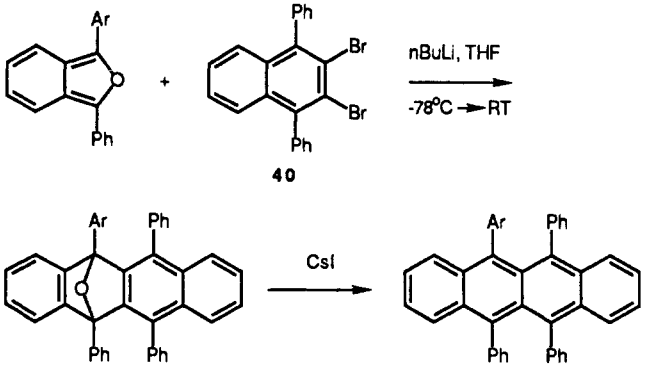
(16) (a) Rio, G. *Ann. Chim.* **1954**, *9*, 187. (b) *Ibid.* **1954**, *9*, 207.

(17) For entries 9 and 11, the monoaddition product was isolated and purified then subjected to the appropriate aryllithium, giving the diol which was not isolated but aromatized directly.

(18) Aubry, J. M.; Rigaudy, J.; Coung, N. K. *Photochem. Photobiol.* **1981**, *33*, 149.

(19) For a similar example of this relatively unusual Diels–Alder reaction, see: Lown, J. W.; Matsumoto, K. *Can. J. Chem.* **1971**, *49*, 3443.

Table II. Preparation of Rubrene and Rubrene Analogues via Aryne Cycloaddition (Route B)



entry	furan	Ar	epoxy compd	yield,[a] %	naphthacene	yield,[a] %
1	8	Ph	41	99	1	88
2	9	3-ClC_6H_4	42	70	45	70
3	10	3-BrC_6H_4	43	71	46	75
4	11	2-pyridyl	44	74	47	83

[a] Based on purified product.

Treatment of **40** with *n*-butyllithium initially results in halogen–metal exchange, followed by elimination of LiBr to give the naphthyne.[20] Trapping of this reactive intermediate in situ with the substituted isobenzofurans **8–11** gives the corresponding oxo-bridged adducts in good yields (Table II). In a typical reaction, the alkyllithium is added to a THF solution containing both the dibromonaphthalene and the substituted isobenzofuran at −78 °C, followed by slow warming of the reaction mixture to room temperature. The aryne formation (signified by a dramatic color change from yellow-brown to colorless at approximately −40 °C) and ensuing cycloaddition allows convergent formation of the desired carbon skeleton in a single step, as well as avoiding the aforementioned cycloreversion problem encountered in the classical procedures.

The final step in the sequence, removal of the oxo bridge, proved to be extremely troublesome, proceeding in unacceptably low yields (<15%) with a variety of standard reagents such as HI,[16] zinc and acetic acid,[21] lithium naphthalenide,[22] methanolic HCl,[23] potassium hydroxide in dimethyl sulfoxide,[24] low valent metal species (iron, tungsten, or vanadium),[25] enneacarbonyldiiron,[26] metal hydrides (LAH and $AlCl_3$),[27] lithium amalgam,[28] and sammarium diiodide.[29] Considering alternative procedures, it seemed possible that this aromatization might be effected by a Lewis acid mediated version of the standard HI method, i.e., cleavage of the C–O bond to give a triply benzylic cation, trapping with iodide, and subsequent reductive elimination of the oxygen substituent and I_2. After exploring various combinations of Lewis acids and iodide nucleophiles, it was found that aluminum tribromide slowly added to a cold (−78 °C) chloroform slurry of the oxo-bridged naphthacene and a large excess of cesium iodide, followed by warming to room temperature, and quenching with sodium metabisulfite gives the fused aromatic product in optimal yields of 70–88% (see Table II).

This methodology gives rubrene itself as well as several aryl-substituted derivatives (Table II). For example, cycloaddition of diphenylisobenzofuran with the naphthyne generated from **40**, followed by Lewis acid mediated reductive aromatization, gives rubrene as the characteristic brilliant red solid in 87% overall yield. Likewise, several aryl derivatives (3-chlorophenyl, 3-bromophenyl, and 2-pyridyl, **45–47**), were prepared by coupling the naphthyne derived from **40** with the appropriate diarylisobenzofuran. Potentially, the scope of the reaction sequence could be expanded to include even more highly substituted analogues by simply employing 1,4-diarylnaphthalenes (**40**, Ph = Ar), which are prepared from easily obtainable diarylisobenzofurans.[30]

In conclusion, two complementary methods for the construction of rubrene and specifically substituted rubrene derivatives have been developed. In one, diarylnaphthacenequinones serve as key intermediates for the introduction of aryl functionality. In a second approach, cycloaddition of arylisobenzofurans with substituted naphthynes provides a new and convergent route to the rubrene skeleton in which the entire carbon framework is assembled in a single step. Both routes allow the convenient and regioselective construction of highly functionalized, unsymmetrically substituted rubrene and are currently being utilized to prepare derivatives with deeper, longer, and more highly functionalized clefts capable of specific binding to small molecules.

Experimental Section

General Experimental Details. Tetrahydrofuran (THF) and Et_2O were distilled either from CaH_2/Deperox or potassium and benzophenone. The molarities indicated for organolithium reagents were established by titration with 2,5-dimethoxybenzyl alcohol.[31] Hydriodic acid was purchased from Aldrich Chemical Co. as a 57% aqueous solution stabilized with phosphorous acid. ^1H NMR and ^{13}C NMR were measured at 300 and 75, and 500 and 125.5 MHz, respectively, with a Nicolet QE-300 spectrometer or a Nicolet GN-500 spectrometer. ^1H NMR chemical shifts are reported as δ values in parts per million (ppm) relative to either tetramethylsilane (0.0 ppm) or chloroform (7.26 ppm). Data is reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = mutliplet, b = broad), coupling constants (hertz), and integration. Carbon-13 chemical shifts are reported in ppm relative to $CDCl_3$ (76.9 ppm). Infrared spectra (IR) were recorded on a Perkin-Elmer 283 or 281 spectrometer. Low-resolution mass spectra (LRMS), electron impact (EI) and chemical ionization (CI), were recorded on a Finnigan 4000 spectrometer. High-resolution mass (HRMS) spectra were measured on a VG Analytical 7070E spectrometer. Combustion analyses were performed by Gailbraith Laboratories, Inc. (Knoxville, TN). Flash chromatography[32] was performed using Alfa silica gel (58 μm). Radial chromatography was performed on a Harrison Model 7924 Chromatotron (Harrison Research, Palo Alto, CA) using 1-, 2-, or 4-mm plates (as indicated) coated with

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Merck silica gel 60 PF254 containing $CaSO_4 \cdot 0.5H_2O$ binder. Analytical thin-layer chromatography (TLC) was performed using 0.25 mm E. Merck precoated silica gel plates (60-F254). Starting materials were azeotropically dried prior to reaction as required, and all air- and/or moisture-sensitive reactions were conducted in flame- and/or oven-dried glassware under an anhydrous argon atmosphere with standard precautions taken to exclude moisture. Melting points were taken an a Thomas-Hoover melting point apparatus and are uncorrected.

Representative Procedure for the Preparation of Aryl-Substituted Diphenylisobenzofurans. 1-(3-Chlorophenyl)-3-phenylisobenzofuran (9). A solution containing 1-chloro-3-iodobenzene (5.00 g, 21.0 mmol) in THF (50 mL) was cooled to −78 °C, and *n*-BuLi (13.1 mL of a 1.6 M solution in hexanes, 21.0 mmol) was added dropwise, maintaining the temperature below −60 °C. The solution was stirred at −78 °C for 2 h followed by dropwise addition of a solution of 3-phenylphthalide[11] (4.00 g, 19.0 mmol) in THF (25 mL) over a 45-min period. The deep red solution was stirred for another 15 min at −78 °C, after which acetic anhydride (2.0 mL, 21.2 mmol) was added followed by warming of the solution to room temperature and then heating at reflux for 10 min. Water (50 mL) was added to the bright yellow solution, and the organic layer was separated, dried ($MgSO_4$), and concentrated in vacuo to give an orange oil, which was purified by flash chromatography (SiO_2, cyclohexane) to give 3.12 g of chromatographically pure **9** as a golden-yellow oil. Crystallization from ethanol–benzene yielded 2.62 g (45%) of **9** as fine bright yellow needles: mp 91–93 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 7.90–7.96 (m, 3 H), 7.79–7.87 (m, 3 H), 7.50 (app t, J = 7.8 Hz, 2 H), 7.40 (app t, J = 7.9 Hz, 1 H), 7.32 (app t, J = 7.4 Hz, 1 H), 7.22–7.25 (m, 1 H), 7.01–7.09 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.5, 142.0, 134.9, 133.2, 131.3, 130.1, 123.0, 127.3, 126.6, 125.8, 125.2, 125.0, 124.4, 124.3, 122.7, 122.5, 120.4, 120.3, 119.8, 119.7; IR (KBr) 3040, 1585, 1490, 1455, 1110, 770, 740, 675, 650 cm^{-1}; HRMS (EI) calcd for $C_{20}H_{13}ClO$ 304.0655, found 304.0662.

1-(3-Bromophenyl)-3-phenylisobenzofuran (10). Halogen–metal exchange of 1,3-dibromobenzene (5.00 g, 21.0 mmol) with *n*-BuLi (13.1 mL of a 1.6 M solution in hexanes, 21.0 mmol) in THF (50 mL) at −60 °C followed by addition of the newly formed aryllithium to a solution of 3-phenylphthalide (4.00 g, 19.0 mmol) in THF (50 mL) at −78 °C gave 1.82 g (30%) of **10** as an orange powder after purification by flash chromatography and recrystallization from ethanol–toluene: ^1H NMR (300 MHz, $CDCl_3$) δ 7.91–7.98 (m, 3 H), 7.83–7.88 (m, 3 H), 7.47 (app t, J = 7.4 Hz, 1 H), 7.38 (app t, J = 7.9 Hz, 1 H), 7.37 (app t, J = 7.4 Hz, 1 H), 7.31 (app t, J = 7.4 Hz, 1 H), 7.19–7.23 (m, 1 H), 6.97–7.05 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.8, 142.1, 134.9, 133.2, 131.3, 130.2, 129.0, 127.2, 126.6, 125.7, 125.3, 124.9, 124.43, 124.37, 122.8, 122.5, 120.4, 120.3, 119.7, 119.7; IR (KBr) 3050, 1590, 1495, 1460, 1120, 780, 680 cm^{-1}; LRMS (CI, isobutane) m/e (relative intensity) 349 (MH^+, 100), 352 (18), 351 (92), 350 (39), 348 (14), 327 (38), 288 (15), 287 (80), 271 (49), 270 (21), 267 (19), 251 (18); HRMS (EI) calcd for $C_{20}H_{13}BrO$ 348.0149, found 348.0151.

1-(2-Pyridyl)-3-phenylisobenzofuran (11). Halogen–metal exchange of 2-bromopyridine (8.25 g, 52.2 mmol) with *n*-BuLi (34.3 mL of a 1.52 M solution in hexanes, 52.2 mmol) in THF (150 mL) below −50 °C for 1 h followed by addition of the newly formed aryllithium to a solution of 3-phenylphthalide (10.00 g, 47.6 mmol) in THF (100 mL) gave 5.68 g (44%) of **11** as fine bright yellow crystals after initial purification by flash chromatography (alumina, 9:1 cyclohexane–ethyl acetate) followed by recrystallization from ethanol–H_2O to give fine yellow crystals: mp 92–93 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 8.23 (d, J = 3.7 Hz, 1 H), 7.97 (dd, J = 7.2, 3.1 Hz, 2 H), 7.80–7.85 (m, 3 H), 7.37–7.45 (m, 5 H), 7.31 (dd, J = 7.2, 3.1 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.9, 145.9, 143.2, 135.9, 134.7, 133.0, 132.0, 131.2, 130.8, 130.24, 128.4, 127.4, 126.2, 125.7, 123.2, 123.2, 122.9, 120.2, 119.6; IR (KBr) 3070, 3055, 1575, 1475, 1390, 1320, 1110, 790, 650 cm^{-1}; LRMS (CI, isobutane) m/e (relative intensity) 272 (MH^+, 100), 273 (14), 271 (44); HRMS (EI) calcd for $C_{19}H_{13}NO$ 271.0997, found 271.1005.

Preparation of Diarylnaphthacenequinones. 6,11-Diphenyl-5,12-naphthacenequinone (13). A one-pot synthesis was developed based on the work of Dufraisse.[6] 1,3-Diphenylisobenzofuran (0.17 g, 0.6 mmol) was added slowly as a solid to 1,4-naphthoquinone (0.1 g, 0.6 mmol) in CH_2Cl_2 (5 mL), and the solution was stirred at room temperature for 12 h. Additional CH_2Cl_2 (10 mL) was added, and the mixture was cooled to −78 °C followed by dropwise addition of BBr_3 (0.7 mL of a 1 M solution in CH_2Cl_2, 0.7 mmol). After 0.5 h at −78 °C, the dark reaction mixture was warmed to room temperature and then heated at reflux for 4 h and subsequently cooled to room temperature. The solution was then poured into water, and the aqueous portion was extracted with CH_2Cl_2. The combined organic extracts were washed with brine, dried ($MgSO_4$), and concentrated in vacuo to give a yellow solid, which was recrystallized from $CHCl_3$–MeOH to give 0.22 g (85%) of **13** as a bright yellow crystalline solid: mp 288–290 °C; ^1H NMR ($CDCl_3$, 500 MHz) δ 8.09 (dd, J = 5.8, 3.33 Hz, 2 H), 7.67 (dd, J = 5.9, 2.6 Hz, 2 H), 7.56–7.61 (m, 8 H), 7.51 (dd, J = 6.6, 3.3 Hz, 2 H), 7.33–7.34 (m, 4 H); ^{13}C NMR ($CDCl_3$, 125.5 MHz) δ 184.1, 143.8, 140.1, 135.4, 134.8, 133.5, 128.7, 128.6, 128.5, 128.2, 127.4, 127.0, 126.8; IR ($CHCl_3$) 3080, 3020, 1685, 1604, 1385, 1345 cm^{-1}; LRMS (CI, isobutane) m/e (relative intensity) 411 (MH^+, 100); HRMS (EI) calcd for M^+ $C_{30}H_{18}O_2$ 410.1307, found 410.1279.

6,11-Bis(4-methoxyphenyl)-5,12-naphthacenequinone (14). To 4-bromoanisole (1.5 mL, 12.4 mmol) stirring in THF (15 mL) at −78 °C was added *n*-BuLi (4.5 mL of a 2.65 M solution in hexanes, 11.5 mmol) dropwise. The solution was allowed to stir for 0.5 h before being transferred dropwise by canula to a solution of 3-(4-methoxyphenyl)phthalide[33] (2.1 g, 8.9 mmol) stirring at −78 °C in THF (15 mL). The resultant burgundy solution was allowed to stir for 15 min before the addition of acetic anhydride (2.3 mL, 25 mmol). The mixture was subsequently warmed to room temperature and then heated at reflux for 10 min, cooled, and quenched with H_2O. The aqueous layer extracted with Et_2O, and the combined organic extracts were washed with brine and then dried ($MgSO_4$). Removal of the solvent in vacuo gave the desired isobenzofuran as an air-sensitive bright yellow solid which was immediately dissolved in CH_2Cl_2 (20 mL). Commercially available 1,4-naphthoquinone (1.4 g, 8.9 mmol) was added in one portion to the crude phthalide solution which was subsequently heated at reflux for 0.5 h and then cooled to −78 °C, and BBr_3 (10 mL of a 1 M solution in CH_2Cl_2, 10 mmol) was added dropwise. The dark reaction mixture was allowed to warm to room temperature and then heated at reflux for 3 h before quenching by slow addition of water. The aqueous portion was then extracted with CH_2Cl_2, and the combined organic extracts were washed with brine and dried ($MgSO_4$). Removal of the solvent in vacuo gave a crude brown solid, which was recrystallized from $CHCl_3$–MeOH to give 1.25 g (30% for the five-step, two-plot process) of quinone **14** as yellow crystals: mp 285–286 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 8.08 (dd, J = 5.8, 3.3 Hz, 2 H), 7.62–7.67 (m, 6 H), 7.50 (dd, J = 6.6, 3.3 Hz, 2 H), 7.21–7.23 (m, 4 H), 7.12–7.14 (m, 4 H), 3.96 (s, 6 H); ^{13}C NMR (125.5 MHz, $CDCl_3$) δ 184.5, 158.6, 135.9, 135.0, 133.5, 132.1, 129.8, 128.8, 128.7, 127.9, 126.8, 113.8, 55.2; IR (KBr) 3000, 2840, 1675, 1610, 1510, 1370, 1338, 1287, 1260, 1245, 1176, 1033, 993, 830, 730 cm^{-1}; LRMS (EI, 70 eV) m/e (relative intensity) 470 (M^+, 32), 455 ($M^+ - CH_3$, 6), 439 (6), 326 (10), 219 (67), 198 (45), 183 (40), 169 (100), 162 (84), 150 (74), 55 (44); HRMS (EI) calcd for $C_{32}H_{22}O_4$ require 470.1518, found 470.1498. Anal. Calcd for $C_{32}H_{22}O_4$: C, 81.67; H, 4.52. Found: C, 81.33; H, 4.60.

1,4-Dihydro-6,11-diphenyl-1,4-ethano-5,12-naphthacenequinone (16). To dienophile **15**[13] (1.88 g, 10 mmol) in CH_2Cl_2 (25 mL) was added a solution of 1,3-diphenylisobenzofuran in CH_2Cl_2 (25 mL), and the reaction was allowed to stir for 12 h at 0 °C in the dark. An additional amount of CH_2Cl_2 (150 mL) was added, and the reaction mixture was cooled to −78 °C before the dropwise addition of BBr_3 (10 mL of a 1 M solution in CH_2Cl_2, 10 mmol). The resulting dark solution was stirred at −78 °C for 0.5 h, warmed to room temperature, and subsequently heated at reflux. After 3 h, the green reaction mixture was cooled to room temperature and poured into water (100 mL). The aqueous portion was then extracted with Et_2O, and the combined organic extracts were washed with brine, dried ($MgSO_4$), and concentrated in vacuo. Flash chromatography (SiO_2, 4.8:0.2 hexanes–ethyl acetate) gave 1.82 g (42%) of quinone **16** as a bright yellow solid: mp 285–288 °C, evolution of gas noted from 160 to 190 °C; ^1H

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NMR ($CDCl_3$, 300 MHz) δ 7.48–7.60 (m, 10 H), 7.32 (d, J = 9.0 Hz, 2 H), 6.34 (dd, J = 4.4, 3.3 Hz, 2 H), 4.38 (s, 2 H), 1.30–1.45 (m, 4 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 182.7, 152.4, 140.7, 136.0, 134.6, 129.6, 129.4, 129.3, 129.8, 128.9, 128.6, 128.0, 127.7, 35.0, 25.5; IR ($CDCl_3$) 3035, 1660, 1590, 1430 cm^{-1}; LRMS (CI, isobutane) m/e (relative intensity) 439 (MH^+, 78), 411 ($MH^+ - C_2H_4$, 48), 271 (32), 85 (100), 81 (93), 71 (86); HRMS (EI) calcd for $M^+ - C_2H_4$ 410.1307, found 410.1306.

Representative Procedure for the Preparation of Symmetrically Substituted Naphthacenediols. 5,12-Dihydro-5,12-bis(4-methoxyphenyl)-6,11-diphenyl-5,12-naphthacenediol (17). To a solution of 4-bromoanisole (1.25 mL, 10 mmol) stirring in THF (10 mL) at −78 °C was added n-BuLi (3.47 mL of a 2.74 M solution in hexanes, 9.5 mmol) dropwise. The mixture was allowed to stir at this temperature for 15 min before being transferred by canula to a solution of quinone **1o** stirring in THF (10 mL) at −78 °C. The resulting dark reaction mixture was then allowed to warm to room temperature slowly over a 12-h period and then quenched by pouring into an aqueous solution of saturated NH_4Cl. The aqueous portion was subsequently extracted with Et_2O, and the combined organic extracts were dried ($MgSO_4$) and then concentrated in vacuo. The resulting solid was washed thoroughly with 4:1 hexanes–Et_2O to give 0.4 g (64%) of diol **17** as a tan solid. An analytical sample was prepared by recrystallization from Et_2O to give an off-white solid: mp 175–177 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 7.24–7.29 (m, 5 H), 7.14–7.17 (m, 4 H), 6.93–6.96 (m, 11 H), 6.56 (d, J = 8.7 Hz, 4 H), 6.29 (d, J = 7.6 Hz, 2 H), 3.75 (s, 6 H), 3.68 (s, 2 H); ^{13}C NMR (125.5 MHz, $CDCl_3$) δ 157.4, 142.1, 140.0, 137.8, 136.9, 134.3, 131.6, 131.1, 129.2, 128.5, 127.3, 126.96, 126.90, 126.5, 126.0, 125.9, 113.0, 75.0, 65.8; IR ($CDCl_3$) 3460 (b), 3070, 2962, 1612, 1510, 1350, 1277, 1039, 830 cm^{-1}; LRMS (CI, isobutane) m/e (relative intensity) 609 ($MH^+ - H_2O$, 3), 135 (100), 109 (70); HRMS (EI) calcd for $C_{26}H_{34}O_4$ 621.2457, found 626.2456.

5,12-Dihydro-5,12-bis(4-methylphenyl)-6,11-diphenyl-5,12-naphthacenediol (18). Halogen–metal exchange of 4-bromotoluene (1.2 g, 7.0 mmol) and n-BuLi (2.4 mL of a 2.74 M solution in hexanes, 6.5 mmol) in THF at −78 °C for 1 h, followed by addition of the newly formed aryllithium to quinone **13** (410 mg, 1.0 mmol) gave 316 mg (53%) of diol **18** as a tan solid after purification by radial chromatography (SiO_2, 4 mm, 9:1 hexanes-Et_2O): mp >300 dec; ^1H NMR (500 MHz, $CDCl_3$) δ 6.78–7.22 (m, 24 H), 6.18 (d, J = 7.2 Hz, 2 H), 4.30 (s, 2 H), 2.29 (s, 6 H); ^{13}C NMR (125.5 MHz, $CDCl_3$) δ 146.6, 140.5, 139.7, 137.5, 136.9, 434.7, 134.7, 134.2, 131.5, 131.2, 128.4, 128.0, 127.2, 126.7, 126.4, 125.80, 125.77, 125.6, 75.0, 20.8; IR ($CDCl_3$) 3450 (b), 3040, 2935, 1609, 1498, 1448, 1290, 1018, 819 cm^{-1}; LRMS (CI, isobutane), m/e (relative intensity) 577 ($MH^+ - 2H_2O$, 4), 119 (30), 93 (37), 81 (100); HRMS (EI) calcd for $C_{44}H_{24}O_2$ 594.2559, found 594.2547.

5,12-Dihydro-5,12-bis(3-methoxyphenyl)-6,11-diphenyl-5,12-naphthacenediol (19). Halogen–metal exchange of 3-bromoanisole (0.57 mL, 4.5 mmol) and n-BuLi (1.45 mL of a 2.74 M solution in hexanes, 4.0 mmol) in THF at −78 °C for 0.5 h followed by slow addition of the newly formed aryllithium to quinone **13** gave 0.48 g (76%) of diol **19** as a white solid after thorough washing of the crude solid with 4:1 hexanes–Et_2O: mp 175–178 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 7.13–7.17 (m, 6 H), 6.55–6.99 (m, 18 H), 6.17 (d, J = 7.5 Hz, 2 H), 4.49 (s, 2 H), 3.69 (s, 6 H); ^{13}C NMR (125.5 MHz, $CDCl_3$) δ 158.8, 151.0, 140.7, 139.6, 137.0 136.6, 134.2, 131.6, 131.5, 128.5, 128.4, 127.4, 126.8, 126.48, 126.46, 125.9, 125.8, 118.9, 111.6, 110.6, 74.9, 54.8; IR ($CDCl_3$) 3430, 3064, 2943, 1600, 1485, 1254, 1041, 783; LRMS (EI, 70 eV) m/e (relative intensity) 626 (M^+, 1), 608 ($M^+ - H_2O$, 3), 519 ($M^+ - C_6H_4OCH_3$, 6), 135 (57), 77 (100); HRMS (EI) calcd for $C_{44}H_{34}O_4$ 626.2457, found 626.2477.

5,12-Dihydro-5,12-bis[3-(hydroxymethyl)phenyl]-6,11-diphenyl-5,12-naphthacenediol (20). Halogen–metal exchange of 3-bromobenzyl alcohol (0.70 mL, 5.5 mmol) and n-BuLi (3.7 mL of a 2.74 M solution in hexanes, 10.0 mmol) in THF at −40 °C for 10 min followed by addition of the newly formed aryllithium to quinone **13** gave 0.56 g (90%) of tetrol **20** as a tan solid after purification by radial chromatography (SiO_2, 2 mm, 2:2:1 Et_2O–CH_2Cl_2–hexanes): mp >250 dec; ^1H NMR (500 MHz, $CDCl_3$) δ 7.57 (d, J = 7.5 Hz, 2 H), 7.50 (t, J = 7.4 Hz, 2 H), 7.32 (t, J = 7.4 Hz, 2 H), 7.14–7.16 (m, 4 H), 6.90–6.99 (m, 14 H), 5.95 (d, J = 7.6 Hz, 2 H), 4.33 (AB q, J_{AB} = 12.7 Hz, ν_A = 4.35, ν_B = 4.32, 2 H), 3.85 (s, 2 H), 2.04 (bs, 2 H); ^{13}C NMR (125.5 MHz, $CDCl_3$) δ 131.7, 123.6, 123.3, 123.1, 121.9, 121.6, 119.1, 117.6, 116.7, 114.9, 114.6, 114.5, 114.3, 113.7, 113.4, 113.1, 112.7, 111.9, 111.4, 76.1, 68.0; IR ($CDCl_3$) 3540 (b), 3065, 2940, 2890, 1660, 1604, 1443, 1375, 1188, 1139, 1040, 792 cm^{-1}; LRMS (CI, isobutane) m/e (relative intensity) 627 (MH^+, 12), 609 ($MH^+ - H_2O$, 100), 591 ($MH^+ - 2H_2O$, 65), 91 (77); HRMS (EI) calcd for $C_{44}H_{34}O_4$ 626.2457, found 626.2427.

5,12-Dihydro-5,12-bis[3-(2,5-dimethylpyrrol-1-yl)-phenyl]-6,11-diphenyl-5,12-naphthacenediol (21). Halogen–metal exchange of 1-(3-bromophenyl)-2,5-dimethylpyrrole[34] (1.50 g, 6.0 mmol) in Et_2O (10 mL) at −20 °C for 40 min followed by addition of the newly formed aryllithium to quinone **13** (0.41 g, 1.0 mmol) gave 0.39 g (52%) of diol **21** as an off-white solid after purification by radial chromatography (SiO_2, 4 mm, 4:1 hexanes–Et_2O): mp 158–161 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 6.83–7.23 (m, 24 H), 6.37 (d, J = 7.4 Hz, 2 H), 5.9 (s, 2 H), 1.95 (s, 12 H); ^{13}C NMR (125.5 MHz, $CDCl_3$) δ 150.7, 140.8, 139.2, 138.1, 137.1, 135.8, 134.4, 131.9, 131.5, 128.5, 128.2, 127.8, 127.4, 127.0, 126.9, 126.5, 126.3, 125.3, 125.1, 124.5, 105.9, 75.0, 13.0; IR ($CDCl_3$) 3040 (b), 3072, 2936, 1608, 1490, 1448, 1401, 1334 cm^{-1}; LRMS (CI, isobutane) m/e (relative intensity) 753 (MH^+, 11), 735 ($MH^+ - H_2O$, 9), 188 (35), 172 (100), 95 (22); HRMS (EI) calcd for $C_{54}O_{44}N_2O_2$ 752.3403, found 752.3394.

5,12-Dihydro-5,6,11,12-tetrakis(4-methoxyphenyl)-5,12-naphthacenediol (22). Halogen–metal exchange of 4-bromoanisole (0.7 mL, 5.2 mol) and n-BuLi (1.98 mL of a 2.53 M solution in hexanes, 5.0 mmol) at −78 °C for 0.5 h followed by addition of the newly formed aryllithium to quinone **14** (0.47 g, 1 mmol) gave 0.4 g (57%) of diol **22** as a white solid after purification by radial chromatography (SiO_2, 2 mm, 4:1 hexanes–Et_2O): mp 262.5–264 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 7.16 (dd, J = 3.4, 3.3 Hz, 2 H), 6.91–7.01 (m, 10 H), 6.82 (dd, J = 3.7, 2.7 Hz, 2 H), 6.64 (dd, J = 8.4, 2.4 Hz, 2 H), 6.56–6.60 (m, 4 H), 6.45 (dd, J = 6.0, 2.3 Hz, 2 H), 6.10 (dd, J = 8.4, 2.4 Hz, 2 H), 4.18 (s, 2 H), 3.82 (s, 6 H), 3.75 (s, 6 H); ^{13}C NMR (125.5 MHz, $CDCl_3$) δ 157.7, 157.3, 142.2, 140.2, 137.54, 137.50, 134.7, 132.4, 132.0, 131.9, 128.4, 127.2, 126.7, 126.5, 125.8, 113.1, 112.8, 111.6, 74.9, 55.2; IR ($CDCl_3$) 3450 (b), 3010, 2760, 1611, 1510, 1350, 1180, 1040, 834 cm^{-1}; LRMS (EI, 70 eV) m/e (relative intensity) 668 ($M^+ - H_2O$, 3), 650 ($M^+ - 2H_2O$, 0.2), 560 ($M^+ - C_6H_4OCH_3$, 3), 135 (100), 77 (35); HRMS (EI) calcd for $C_{46}H_{38}O_6$ 686.2668, found 686.2648.

1,4,5,12-Tetrahydro-5,6,11,12-tetraphenyl-1,4-ethano-5,12-naphthacenediol (23). Halogen–metal exchange of bromobenzene (1.32 mL, 3.0 mmol) and n-BuLi (1.9 mL of a 1.63 M solution in hexanes, 3.0 mmol) in THF (5 mL) at −78 °C for 0.5 h followed by addition of the newly formed aryllithium to quinone **16** (0.46 g, 1 mmol) gave 0.24 g (41%) of diol **23** as a tan solid after purification by flash chromatography (SiO_2, 9:1 hexanes–ethyl acetate): mp 168–170 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 7.33–7.40 (m, 4 H), 7.06–7.25 (m, 12 H) 6.92 (dd, J = 6.6, 3.3 Hz, 2 H), 6.81 (t, J = 7.6 Hz, 2 H), 6.32 (dd, J = 4.1, 3.1 Hz, 2 H), 6.12 (d, J = 8 Hz, 2 H), 3.49 (s, 2 H), 2.98 (s, 2 H), 0.75 (d, J = 6.5 Hz, 2 H), 0.21 (dd, J = 6.0, 0.6 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.0, 140.2, 140.0, 138.2, 138.3, 136.6, 134.6, 132.4, 132.2, 128.2, 128.1, 127.9, 127.1, 126.7, 126.5, 74.9, 37.7, 26.5; IR ($CDCl_3$) 3560, 3080, 2970, 2609, 1498, 1450 cm^{-1}; LRMS (CI, isobutane) m/e (relative intensity) 577 ($MH^+ - H_2O$, 100), 548 ($MH^+ - H_2O - C_2H_4$, 3.9), 112 (13), 97 (15), 85 (17); HRMS (EI) calcd for $C_{44}H_{34}O_2$ 594.2559, found 294.2564.

Representative Procedure for the Monoaddition of Aryllithiums to Naphthacenequinones. 12-Hydroxy-12-(2-methoxyphenyl)-6,11-diphenylnaphthacen-5(12*H*)-one (24). To 2-bromoanisole (0.11 mL, 0.92 mmol) stirring in THF (15 mL) at −78 °C was added n-BuLi (0.49 mL of a 1.6 M solution in hexanes, 0.92 mmol). The reaction was allowed to stir for 0.5 h before being transferred dropwise by canula over a 45-min period into a solution of quinone **13** (0.25 g, 0.61 mmol) stirring in THF (20 mL) at −78 °C. After 2.5 h, the dark reaction mixture was poured into a saturated solution of aqueous NH_4Cl (50 mL). The aqueous portion was extracted with ethyl acetate, and the combined organic extracts were dried ($MgSO_4$) then concentrated in vacuo. The yellow-brown solid was purified by washing with 3:2

(34) Bruekelman, S. P.; Leach, S. E.; Meakins, G. D.; Tirel, M. D. *J. Chem. Soc., Perkin Trans. 1* **1984**, 2801.

hexane–Et_2O to give 256 mg (81%) of pure monoaddition product **24** as a tan solid: mp 270–271 °C; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.82 (d, J = 7.5 Hz, 1 H), 6.95–7.55 (m, 17 H), 6.85 (t, J = 7.6 Hz, 1 H), 6.61 (t, J = 7.6 Hz, 1 H), 6.46 (d, J = 8.1 Hz, 1 H), 6.03 (d, J = 7.5 Hz, 1 H), 3.72 (s, 1 H), 3.14 (s, 3 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 187.3, 155.2, 145.8, 142.2, 142.0, 141.1, 138.9, 138.4, 136.5, 136.46, 133.3, 132.3, 132.2, 131.6, 131.1, 129.08, 129.01, 129.0, 128.9, 128.8, 128.7, 128.5, 128.2, 128.12, 127.9, 127.0, 126.8, 126.0, 125.8, 121.2, 112.0, 73.7, 55.5; IR ($CHCl_3$) 3550, 2080, 3020, 2980, 1684, 1608, 1490, 1300, 1030 cm^{-1}; LRMS (CI, isobutane) m/e (relative intensity 519 (MH^+), 501 ($MH^+ - H_2O$), 85 (74), 79 (67), 71 (100); HRMS (EI) calcd for $C_{37}H_{26}O_3$ 518.1882, found 518.1862.

1,4-Dihydro-12-hydroxy-6,11,12-triphenyl-1,4-ethanonaphthacen-5(12*H*)-one (25). To bromobenzene (40 mL, 0.37 mmol) stirring in THF (1 mL) at −78 °C was added n-BuLi (0.24 mL of a 1.57 M solution in hexanes, 0.4 mmol). After 0.5 h the solution was transferred dropwise by canula over a 1-h period to quinone **16** (86 mg, 0.2 mmol) in THF (5 mL) at −78 °C. The reaction was stirred at this temperature for 3 h and then at room temperature for 12 h before an additional 2 equiv of PhLi (generated as above) was added. After 48 h, the reaction was quenched by pouring into a saturated solution of aqueous NH_4Cl. The aqueous portion was extracted with ethyl acetate, and the combined organic extracts dried ($MgSO_4$) and then concentrated in vacuo. Flash chromatography (SiO_2, 23:1 hexanes–ethyl acetate) gave 60 mg (59%) of monoaddition product **25** as a tan solid: mp 188–190 °C; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.25–7.39 (m, 10 H), 7.08–7.19 (m, 4 H), 6.93–7.02 (m, 4 H), 6.35–6.65 (m, 2 H), 5.99 (d, J = 7.6 Hz, 1 H), 4.32 (m, 2 H), 3.82 (m, 1 H), 3.29 (s, 1 H), 0.80–1.20 (m, 4 H); ^{13}C NMR ($CDCl_3$, 125.5 MHz) δ 161.6, 144.0, 142.4, 141.6, 140.4, 138.7, 138.6, 137.8, 136.2, 135.4, 133.1, 133.0, 131.6, 130.9, 129.5, 128.3, 12892, 128.1, 128.0, 127.9, 127.7, 126.9, 126.5, 126.4, 126.1, 125.8, 125.5, 74.5, 37.7, 33.9, 25.9, 24.9; IR ($CDCl_3$) 3550, 3080, 2965, 1660, 1610, 1555, 1500, 1450 cm^{-1}; LRMS (CI, isobutane) m/e (relative intensity) 517 (MH^+, 100), 501 ($MH^+ - H_2O$, 67), 489 ($MH^+ - C_2H_4$, 67), 112 (52.2), 99 (36); (HRMS) calcd for M^+ $C_{38}H_{28}O_2$ 516.2089, found 516.2093.

12-Hydroxy-12-(2-methoxyphenyl)-6,11-bis(4-methoxyphenyl)naphthacen-5(12*H*)-one (26). Halogen–metal exchange of 3-bromoanisole and n-BuLoi (0.3 mL of a 2.66 M solution in hexanes, 1.6 mmol) in THF (10 mL) at −78 °C for 45 min followed by slow dropwise addition of the newly formed aryllithium to quinone **14** (0.2 g, 0.4 mmol) stirring THF (20 mL) at −78 °C gave 0.22 g (88%) of monoaddition product **26** after purification by thorough washing of the crude solid with 4:1 hexane–Et_2O: mp 279–282 °C dec; ^1H NMR (300 MHZ, $CDCl_3$) δ 7.88 (dd, J = 7.8, 1.2 Hz, 1 H), 7.74 (d, J = 7.9 Hz, 1 H), 7.63–7.66 (m, 2 H), 6.98–7.53 (m, 11 H), 6.74 (t, J = 3.0 Hz, 1 H), 6.60–6.65 (m, 3 H), 6.14 (dd, J = 8.5, 2.2 Hz, 1 H), 3.95 (s, 3 H), 3.89 (s, 3 H), 3.66 (s, 3 H); ^{13}C NMR (125.5 MHz, $CDCl_3$) δ 186.8, 159.1, 158.9, 158.1, 150.5, 146.4, 141.6, 139.4, 137.0, 136.0, 133.0, 132.9, 132.4, 132.03, 132.00, 131.2, 131.0, 129.2, 129.24, 129.05, 129.00, 128.8, 128.0, 127.8, 127.5, 127.2, 126.1, 125.9, 125.8, 117.5, 113.7, 113.4, 113.3, 113.0, 111.6, 110.2, 75.0, 55.0, 54.8, 54.7; IR ($CDCl_3$) 3521, 3016, 2950, 1670, 1604, 1511, 1248, 1179, 1040, 836 cm^{-1}; LRMS (EI, 70 eV) m/e (relative intensity) 578 (M^+, 2), 560 ($MH^+ - H_2O$, 0.3), 471 ($M^+ - C_6H_4OCH_3$, 19), 92 (47), 77 (100); HRMS (EI) calcd for $C_{39}H_{30}O_5$ 578.2093, found 578.2065.

5,12-Dihydro-5-(3-methoxyphenyl)-6,11-bis(4-methoxyphenyl)-12-phenyl-5,12-naphthacenediol (27). Halogen–metal exchange of bromobenzene (62 μL, 0.6 mmol) and n-BuLi (0.2 mL of a 2.66 M solution in hexanes, 0.5 mmol) in THF (2 mL) at −78 °C for 20 min followed by addition of newly formed aryllithium to monoadduct **26** (30 mg, 52 μmol) in THF (5 mL) gave 24 mg (69%) of diol **27** as a white solid after purification by radial chromatography (SiO_2, 1 mm, 5:3 hexanes–Et_2O): mp 173–175 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 7.15–7.17 (m, 2 H), 6.89–7.06 (m, 12 H), 6.79 (m, 2 H), 6.68 (s, 1 H), 6.55–6.59 (m, 4 H), 6.37 (ddd, J = 18.2, 5.8, 2.6 Hz, 2 H), 6.08 (dd, J = 8.4, 1.9 Hz, 1 H), 5.96 (dd, J = 8.4, 2.0 Hz, 1 H), 4.41 (s, 1 H), 4.36 (s, 1 H), 3.815 and 3.810 (2 s, 6 H total), 3.71 (s, 3 H); ^{13}C NMR (125.5 MHz, $CDCl_3$) δ 158.9, 157.8, 157.7, 151.2, 149.9, 140.5, 140.2, 137.44, 137.39, 137.2, 137.1, 134.73, 134.68, 132.5, 132.4, 132.3, 131.6, 128.7, 128.6, 128.3, 127.4, 127.3, 126.6, 126.4, 125.8, 125.6, 125.4, 118.8, 113.4, 112.7, 111.8, 111.7, 111.6, 110.4, 75.1, 74.9, 55.2, 55.1, 54.7; IR ($CDCl_3$) 3446, 3038, 3013, 2928, 2823, 1609, 1508, 1494, 1467, 1452, 1250, 1379, 1034, 830 cm^{-1}; LRMS (EI, 70 eV) m/e (relative intensity) 656 (M^+, 1), 638 ($MH^+ - H_2O$, 17), 620 ($MH^+ - 2H_2O$, 2), 533 (8), 135 (50), 105 (92), 77 (100); HRMS (EI) calcd for $C_{45}H_{36}O_5$ 651.2562, found 656.2559.

Representative Procedure for the Aromatization of Naphthacenediols. 5,12-Bis(3-methoxyphenyl)-6,11-diphenylnaphthacene (30). To a solution of diol **19** (60 mg, 96 mmol) heated at reflux in Et_2O was added 1.8 mL of 57% aqueous HI. The reaction was allowed to proceed for 5 min and cooled to room temperature before addition of a saturated aqueous solution of sodium metabisulfite. The aqueous portion was extracted with Et_2O, and the combined organic extracts immediately dried ($MgSO_4$) and concentrated. *Immediate* radial chromatography (SiO_2, 1 mm, 9:1 hexanes–Et_2O) gave 45 mg (79%) of **30** as a bright red solid: mp >300 °C dec; ^1H NMR (500 MHz, $CDCl_3$) δ 7.34–7.44 (m, 4 H), 6.88–7.14 (m, 16 H), 6.68 (t, J = 6.4 Hz, 2 H), 6.43–6.48 (m, 4 H), 3.69 and 3.68 (s, total integration 6 H); ^{13}C NMR (125.5 MHz, $CDCl_3$) δ 158.3, 158.2, 142.93, 142.88, 141.6, 136.9, 136.77, 136.72, 132.4, 132.2, 132.0, 131.7, 130.2, 130.1, 129.94, 129.92, 128.9, 128.8, 127.0, 126.9, 126.5, 125.58, 125.55, 125.2, 124.8, 124.77, 117.2, 117.1, 112.2, 54.9, 54.8; IR ($CDCl_3$) 3072, 2948, 1600, 1469, 1240, 1050, 779 cm^{-1}; LRMS (EI, 70 eV) m/e (relative intensity) 592 (M^+, 14), 485 ($M^+ - C_6H_4OCH_3$, 2), 219 (68), 77 (100); HRMS (EI) calcd for $C_{44}H_{32}O_2$ 592.2402, found 592.2397.

5,12-Bis(4-methoxyphenyl)-6,11-diphenylnaphthacene (28). Diol **17** (50 mg, 80 μmol) and 57% HI (0.9 mL) in THF (10 mL) gave 45 mg (95%) of **28** as a bright red powder after *immediate* radial chromatography (SiO_2, 1 mm, 9:1 hexanes–Et_2O): mp >300 °C dec; ^1H NMR (500 MHz, $CDCl_3$) δ 7.44 (dd, J = 7.0, 3.3 Hz, 2 H), 7.36 (dd, J = 7.0, 3.3 Hz, 2 H), 7.08–7.14 (m, 12 H), 6.87 (m, 4 H), 6.78 (dd, J = 6.6, 2.0 Hz, 4 H), 3.85 (s, 6 H); ^{13}C NMR (125.5 MHz, $CDCl_3$) δ 157.6, 141.9, 136.9, 136.5, 134.2, 133.6, 131.8, 130.5, 130.1, 129.5, 127.0, 126.6, 126.5, 125.6, 124.7, 124.6, 112.8, 55.2; IR ($CDCl_3$) 3070, 2963, 1612, 1513, 1247, 1178, 1048, 892, 710 cm^{-1}; LRMS (CI, isobutane) m/e (relative intensity) 593 (MH^+, 56), 487 (9), 229 (30), 122 (59), 108 (25), 89 (100); HRMS (EI) calcd for $C_{44}H_{32}O_2$ 592.2402, found 592.2395.

5,12-Bis(4-methylphenyl)-6,11-diphenylnaphthacene (29). Diol **18** (50 mg, 80 μmol) and 57% HI (0.9 mL) in THF (10 mL) gave 35 mg (74%) of **29** as a red powder after *immediate* radial chromatography (SiO_2, 1 mm, 19:1 hexanes–Et_2O): mp >300 °C dec; ^1H NMR (500 MHz, $CDCl_3$) δ 7.43 (dd, J = 3.6, 3.3 Hz, 2 H), 7.34 (dd, J = 3.6, 3.3 Hz, 2 H), 6.99–7.25 (m, 14 H), 6.82–6.85 (m, 6 H), 6.73 (d, J = 7.8 Hz, 4 H), 2.34 (s, 6 H); ^{13}C NMR (125.5 MHz, $CDCl_3$) δ 141.8, 138.6, 136.9, 136.8, 134.9, 132.0, 131.9, 130.0, 127.8, 126.8, 126.6, 126.5, 125.8, 125.3, 124.63, 124.61, 124.58, 21.1; IR ($CDCl_3$) 3050, 1601, 1515, 1448, 1400, 1195, 1026, 819 cm^{-1}; LRMS (EI, 70 eV) m/e (relative intensity) 560 (M^+, 31), 376 (21), 234 (33), 226 (49), 219 (71), 195 (100), 188 (47); HRMS (EI) calcd for $C_{44}H_{32}$ 560.2504, found 560.2511.

5,12-Bis[3-(hydroxymethyl)phenyl]-6,11-diphenylnaphthacene (31). Diol **20** (50 mg, 80 μmol) and 57% HI (1.1 mL) in Et_2O (10 mL) gave 30 mg (63%) of **31** as a red powder after *immediate* radial chromatography (SiO_2, 1 mm, 19:1 hexanes–Et_2O): mp >300 °C dec; ^1H NMR (500 MHz, $CDCl_3$) δ 6.77–7.49 (m, 24 H), 4.55 (app d, J = 7.4 Hz, 4 H); ^{13}C NMR (125.5 MHz, $CDCl_3$) δ 142.1, 141.9, 139.4, 139.3, 136.8, 136.7, 136.6, 132.6, 132.3, 131.9, 131.6, 131.3, 130.9, 130.7, 130.26, 130.24, 130.1, 128.98, 128.96, 127.7, 127.6, 127.3, 127.2, 127.0, 126.99, 126.92, 126.4, 126.1, 125.4, 125.3, 125.0, 124.9, 124.8, 124.6, 65.33, 65.31; IR ($CDCl_3$) 3590, 3453, 3066, 3940, 1602, 1596, 1190, 1020, 800 cm^{-1}; LRMS (CI, isobutane) m/e (relative intensity) 593 (MH^+, 3), 575 ($MH^+ - H_2O$, 5), 81 (100); HRMS (EI) calcd for $C_{44}H_{32}O_2$ 592.2402, found 592.2397.

5,12-Bis[3-(2,5-dimethylpyrrol-1-yl)phenyl]-6,11-diphenylnaphthacene (32). Diol **21** (44 mg, 58 μmol) and 57% HI (2 mL) in Et_2O (10 mL) gave 27 mg (64%) of **32** as a red powder after *immediate* radial chromatography (SiO_2, 1 mm, 9:1 hexanes–Et_2O): mp >300 °C dec; ^1H NMR (500 MHz, $CDCl_3$) δ 6.83–7.36 (m, 24 H), 6.67 (t, J = 1.7 Hz, 2 H), 5.80 (s, 4 H), 2.13 (bs, 12 H); ^{13}C NMR (125.5 MHz, $CDCl_3$) 142.7, 141.6, 141.5, 138.0, 137.9, 136.5, 135.9, 132.9, 132.4, 132.38, 132.33, 131.6, 131.5, 130.9, 130.5, 130.40, 130.37, 130.3, 128.7, 128.6, 128.5, 127.74, 127.71, 127.6, 127.4, 127.2, 127.1, 126.6, 126.4, 126.34, 126.30, 126.1, 125.6, 125.4, 125.3, 125.21, 125.15, 125.0, 105.8, 105.7, 13.5, 13.2; IR ($CDCl_3$) 3060, 2964, 2930, 1601, 1466, 1395, 1210, 915, 760 cm^{-1}; LRMS

(EI, 70 eV) m/e (relative intensity) 718 (MH^+, 38), 359 (100), 273 (42), 171 (55), 57 (67); HRMS (EI) calcd for $C_{54}H_{42}N_2$ 7618.3348, found 718.3327.

5,6,11,12-Tetrakis(4-methoxyphenyl)naphthacene (33). Diol **22** (100 mg, 0.2 mmol) and 57% HI (1.1 mL) in Et_2O (30 mL) gave 73 mg (77%) of **33** as a bright red powder after *immediate* radial chromatography (SiO_2, 1 mm, 1:1 CH_2Cl_2–hexanes): mp >300 °C dec; ^1H NMR (300 MHz, $CDCl_3$) δ 7.24 (dd, J = 13.8, 6.2 Hz, 4 H), 7.12 (dd, J = 13.9, 6.5 Hz, 4 H), 6.76–6.79 (m, 8 H, 6.61–6.55 (m, 8 H), 3.86 (s, 12 H); ^{13}C NMR (125.5 MHz, $CDCl_3$) δ 157.5, 136.4, 134.4, 132.7, 130.5, 126.6, 124.6, 112.7, 55.2; IR ($CDCl_3$) 3078, 3020, 1612, 1513, 1469, 1401, 1290, 1248, 1179, 1038, 834 cm^{-1}; LRMS (EI, 70 eV) m/e (relative intensity) 652 (M^+, 7), 272 (10), 212 (19), 135 (28), 124 (25), 109 (27), 57 (100); HRMS (EI) calcd for $C_{46}H_{36}O_4$ 652.2613, found 652.2590.

1,4-Dihydro-5,6,11,12-tetraphenyl-1,4-ethanonaphthacene (34). Diol **23** (100 mg, 0.2 mmol) and 57% HI (0.2 mL) in THF (5 mL) gave 77 mg (82%) of **34** as a yellow powder after flash chromatography (SiO_2, hexanes): mp 245 °C dec; ^1H NMR (300 MHz, $CDCl_3$) δ 7.12 (dd, J = 6.9, 3.3 Hz, 2 H), 7.05 (dd, J = 6.9, 3.3 Hz, 2 H), 6.68–7.02 (m, 12 H), 6.65–6.69 (m, 4 H), 6.35 (dd, J = 4.6, 3.2 Hz, 2 H), 3.49 (dd, J = 2.3, 1.4 Hz, 2 H), 1.20–1.40 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.8, 142.3, 141.5, 136.1, 133.0, 132.9, 132.7, 131.6, 131.3, 131.2, 127.7, 127.6, 127.0, 126.0, 125.0, 37.6, 26.0; IR ($CDCl_3$) 3170, 2940, 1609, 1500, 1449, 1388, 1033, 770 cm^{-1}; LRMS (EI, 70 eV) m/e (relative intensity) 560 (M^+, 100), 532 ($M^+ - C_2H_4$, 96), 455 (21), 378 (23), 188 (88); HRMS (EI) calcd for $C_{44}H_{32}$ 560.2504, found 560.2518.

5-(2-Methoxyphenyl)-12-(3-methoxyphenyl)-6,11-diphenylnaphthacene (35). To 3-bromoanisole (0.3 mL, 2.4 mmol) stirring in THF (5 mL) at −78 °C was added n-BuLi (1.7 mL of a 1.6 M solution in hexane, 2.7 mmol). After 1 h, this solution was transferred by canula into a solution of monoadduct **24** (0.25 g, 0.5 mmol) in THF (6 mL) stirring at −78 °C. After 2 h, an additional 5 equiv of aryllithium was added (prepared as above), and the reaction was allowed to proceed for 1 h before being quenched with HI (1.0 mL of a 57% solution in water). An aqueous solution of sodium metabisulfite was added, and the aqueous portion was extracted with CH_2Cl_2. The combined organic extracts were concentrated in vacuo and purified by flash chromatography (SiO_2, 24:1 hexanes–ether) to give 200 mg (70%) of **35** as a bright red solid: mp >300 °C dec; ^1H NMR ($CDCl_3$, 300 MHz) δ 6.58–7.40 (m, 20 H), 6.34–6.46 (m, 6 H), 3.69 (s), 3.67 (s), 3.52 (s), 3.51 (s) total integration for the four MeOAr singlets 6 H; ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 133.9, 133.8, 131.7, 130.9, 130.6, 129.4, 129.3, 128.,, 128.2, 128.0, 127.8, 127.7, 127.6, 127.4, 127.3, 127.2, 126.9, 126.7, 126.3, 126.2, 126.1, 126.0, 125.6, 125.5, 125.3, 120.6, 113.4, 112.8, 110.7, 110.2, 110.1, 105.1, 105.0, 55.8, 55.5, 54.8; IR ($CHCl_3$) 3090, 3020, 2975, 1609, 1500, 1470, 1110, 1034 cm^{-1}; LRMS (CI, isobutane) m/e (relative intensity) 593 (MH^+, 36.4), 592 (M^+, 100), 71 (100), 79 (64); HRMS (EI) calcd for $C_{44}H_{32}O_2$ 592.2402, found 529.2388.

1,4-Dihydro-5-(3-methoxyphenyl)-6,11,12-triphenyl-1,4-ethanonaphthacene (36). To 3-bromoanisole (0.35 mL, 2.8 mmol), stirring in THF (5 mL) at −78 °C, was added n-BuLi (1.5 mL of a 1.6 M solution in hexanes, 2.4 mmol) dropwise. After approximately 1 h, this mixture was transferred dropwise by canula into a solution of monoadduct **26** (0.3 g, 0.4 mmol) in THF (4 mL) at −78 °C. The reaction was quenched after 3 h by addition of HI (1 mL of a 57% aqueous solution) and extracted with CH_2Cl_2. Drying ($MgSO_4$) of the combined organic extracts and concentration of the solvent in vacuo gave a yellow residue, which was purified by flash chromatography (SiO_2, 24:1 hexanes–ethyl acetate) to give 78 mg (65%) of pure tetraaryl **36** as a bright yellow solid: mp 220 °C dec; ^1H NMR ($CDCl_3$, 300 MHz) δ 6.87–7.15 (m, 2 H), 6.72–6.76 (m, 16 H), 6.72–6.76 (m, 2 H), 6.56–6.59 (m, 1 H), 6.29–6.40 (m, 4 H), 3.68 and 3.70 (s, total integration 3 H), 3.51–3.57 (m, 2 H), 1.25–1.48 (m, 4 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 158.9, 144.1, 144.0, 142.8, 142.3, 142.2, 141.4, 136.3, 135.9, 133.2, 133.1, 133.0, 132.9, 132.5, 131.72, 131.6, 131.4, 131.28, 128.7, 127.8, 127.7, 127.5, 127.1, 127.0, 126.4, 126.3, 125.8, 125.1, 124.7, 124.3, 117.0, 112.4, 112.1, 55.6, 37.7, 26.3, 26.2, 25.9; IR (CCl_4) 3070, 3017, 2974, 2880, 1609, 1500, 1500, 1390, 1030, 7000 cm^{-1}; LRMS (EI, 70 eV) m/e (relative intensity) 590 (M^+, 62), 662 ($M^+ - C_2H_4$, 100), 485 (14), 378 (14); HRMS (EI) calcd for $C_{45}H_{34}O$ 590.2609, found 590.2603.

5-(3-Methoxyphenyl)-6,11-bis(4-methoxyphenyl)-12-phenylnaphthacene (37). Diol **27** (26 mg, 40 μmol) and 57% HI (0.6 mL) in Et_2O (10 mL) gave 18 mg (73%) of **37** as a bright red powder after *immediate* radial chromatography (SiO_2, 1 mm, 3:2 hexanes–CH_2Cl_2): mp >300 °C dec; ^1H NMR (500 MHz, $CDCl_3$) δ 6.45–7.46 (m, 25 H), 3.87 and 3.85 (s, total integration 6 H); ^{13}C NMR (125.5 MHz, $CDCl_3$) δ 158.1, 157.3, 142.9, 141.7, 136.7, 136.3, 136.2, 133.9, 133.0, 132.9, 132.6, 131.7, 131.3, 130.3, 129.2, 127.7, 126.8, 126.7, 126.4, 126.3, 126.2, 125.3, 124.45, 124.41, 117.0, 112.6, 112.5, 112.3, 111.7, 55.0, 54.8, 54.5; IR ($CDCl_3$) 3046, 2965, 2843, 1610, 1512, 1247, 1178, 1038, 839, 678 cm^{-1}; LRMS (EI 70 eV) m/e (relative intensity) 622 (M^+, 21), 515 ($M^+ - C_6H_4OCH_3$, 3), 406 (4), 311 (15), 257 (50), 212 (100), 181 (51); HRMS (EI) calcd for $C_{45}H_{34}O_3$ 622.2508, found 622.2485.

Rotameric Forms of 1,4-Dihydro-5-(2-methoxyphenyl)-6,11,12-triphenyl-1,4-ethanonaphthacene (38 and 39). To 2-bromoanisole (0.4 mL, 3.3 mmol) stirring in THF (4 mL) at −78 °C was added n-BuLi (1.94 mL of a 1.6 M solution in hexanes, 3.1 mmol) dropwise. After 45 min, this mixture was transferred dropwise by canula into a solution of monoaddition product **25** (0.2 g, 0.4 mmol) in THF (4 mL) at −78 °C. An additional 4 equiv of aryllithium (prepared as above) was added after 3 h, and the reaction was subsequently quenched after 1 h by pouring the dark mixture into a saturated solution of aqueous NH_4Cl (15 mL). The aqueous portion was extracted with ethyl acetate, and the combined organic extracts were dried ($MgSO_4$) and then concentrated in vacuo. The crude solid was purified by washing with 8:2 hexanes–Et_2O and filtering to give 155 mg (64%) of the diol as a labile white solid which was immediately carried on to the next step. Thus, to the crude product (50 mg, 8 μmol) in THF (4 mL) was added HI (0.1 mL of a 57% aqueous solution), and the solution was stirred at room temperature. After 15 min, water (5 mL) and solid sodium metabisulfite were added. Extraction of the aqueous portion with CH_2Cl_2 followed by drying ($MgSO_4$) of the combined organic extracts and concentration of the solvent in vacuo gave a yellow residue, which was purified by flash chromatography (SiO_2, 24:1 hexanes–ethyl acetate) to give two rotamers **38** and **39** in a 7:1 ratio (26 mg of a less polar isomer and 4 mg of the slightly polar isomer, 59% and 8.5%, respectively).

Higher R_f rotamer: mp >250 °C dec; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.16–7.29 (m, 2 H), 7.16–7.20 (m, 2 H), 6.65–7.18 (m, 18 H), 6.30–6.39 (m, 3 H), 3.58 (s, 3 H), 3.51 (m, 2 H), 3.32 (m, 1 H), 1.20–1.41 (m, 4 H); ^{13}C NMR ($CDCl_3$, 300 MHz) δ 157.2, 143.5, 142.9, 141.9, 141.6, 137.3, 135.8, 133.6, 133.4, 133.0, 132.4, 132.0, 131.7, 131.6, 129.0, 128.2, 128.1, 128.0, 127.7, 127.4, 126.9, 126.7, 126.5, 126.1, 125.3, 125.2, 120.7, 110.2, 54.9, 38.7, 38.1, 26.2, 25.8; IR (CCl_4) 3070, 3017, 2974, 2880, 1609, 1500, 1390, 1030, 700 cm^{-1}; LRMS (EI, 70 eV) m/e (relative intensity) 590 (M^+, 58), 562 ($M^+ - C_2H_4$, 100), 392 (13); HRMS (EI) calcd for $C_{45}H_{34}O$ 590.2609, found 590.2586.

Lower R_f rotamer: mp >250 °C dec; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.16–7.22 (m, 4 H), 6.51–7.04 (m, 18 H), 6.24–6.32 (m, 3 H), 3.53 (s, 3 H), 3.36 (m, 2 H), 1.20–1.36 (m, 4 H); ^{13}C NMR ($CDCl_3$, 125.5 MHz) δ 155.7, 142.2, 141.0, 140.4, 137.0, 135.8, 134.7, 132.7, 132.6, 132.1, 131.9, 131.1, 131.0, 130.9, 130.8, 130.5, 130.4, 129.8, 128.0, 127.9, 127.03, 127.06, 126.94, 126.89, 126.44, 126.38, 126.3, 125.9, 125.5, 125.3, 125.0, 124.2, 119.6, 109.6, 109.2, 54.0, 37.5, 36.9, 26.0, 24.4; IR (CCl_4) 3060, 2938, 1605, 1494, 1385, 1248, 1040, 907, 694 cm^{-1}; LRMS (EI, 70 eV) m/e (relative intensity) 590 (M^+, 65), 562 ($M^+ - C_2H_4$, 100), 392 (13); HRMS (EI) calcd for $C_{45}H_{34}O$ 590.2609, found 590.2616.

2,3-Dibromo-1,4-diphenylnaphthalene (40). A solution of 1,3-diphenylisobenzofuran (3.0 g, 11.1 mmol), freshly distilled 1,2-dibromoethylene (4.1 g, 22.1 mmol), and p-toluenesulfonic acid (50 mg, catalytic) in xylene (15 mL) was heated at reflux for 4 h. Addition of methanol (15 mL) to the warm solution precipitated a crude yellow-white solid, wich was recrystallized from ethanol–benzene to give 3.2 g (67%) of **40** as off-white needles: mp 215–217 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 7.65–7.71 (m, 6 H), 7.43–7.48 (m, 8 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.7, 142.7, 135.7, 133.0, 131.6, 130.7, 130.2, 128.8, 127.6, 125.4, 122.9; IR (KBr) 3070, 3055, 1150, 970, 725 cm^{-1}; LRMS (CI, isobutane) m/e (relative intensity) 437 (MH^+, 59), 441 (40), 440, (52), 439 (100), 438 (70), 436 (38), 402 (18), 400 (25), 361 (33), 360 (51), 359 (43), 358 (51), 278 (13), 99 (14); HRMS (EI) calcd for $C_{22}H_{14}Br_2$ 435.9462, found 435.9443. Anal. Calcd for $C_{22}H_{14}Br_2$: C, 60.30;

H, 3.22; Br, 36.47. Found: C, 60.14; H, 3.55; Br, 36.08.

Representative Procedure for Naphthyne Cycloadditions. 5,12-Dihydro-5,12-epoxy-5,6,11,12-tetraphenylnaphthacene (41). To a solution of 1,3-diphenylisobenzofuran (301 mg, 1.11 mmol) and 2,3-dibromo-1,4-diphenylnaphthalene (**40**) (503 mg, 1.15 mmol) stirring in THF (10 mL) at −78 °C was added *n*-BuLi (0.71 mL of a 1.6 M solution in hexanes, 1.14 mmol) in one portion. The solution was allowed warm to room temperature slowly and after 12 h quenched with water (10 mL). Addition of hexane (10 mL) followed by cooling the heterogeneous solution to 0 °C gave a white precipitate, which was recrystallized from ethanol–benzene to give 602 mg (99%) of **41** as white crystals: mp >300 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75–7.78 (dd, J = 6.0, 3.1 Hz, 2 H), 7.55–7.61 (m, 6 H), 6.96–7.30 (m, 20 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.0, 144.7, 136.9, 134.6, 132.1, 132.0, 131.1, 129.9, 128.7, 128.3, 127.8, 127.6, 127.0, 126.4, 126.2, 125.9, 122.6, 90.9; IR (KBr) 3065, 3040, 1595, 1460, 780, 690 cm^{-1}; LRMS (CI, isobutane) m/e (relative intensity) 549 (MH^+, 100), 550 (33), 533 (13), 532 (19), 531 (22); HRMS (EI) calcd for $C_{42}H_{28}O$ 548.2140, found 548.2125.

5,12-Dihydro-5-(3-chlorophenyl)-5,12-epoxy-6,11,12-triphenylnaphthacene (42). Addition of *n*-BuLi (1.43 mL of a 1.6 M solution in hexanes, 22.9 mmol) to a solution of **9** (700 mg, 2.30 mmol) and **40** (998 mg, 2.29 mmol) in THF (15 mL) at −78 °C gave 937 mg (70%) of **42** as white crystalline solid after recrystallization from ethanol–benzene: mp 291–294 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75 (ddd, J = 11.1, 5.1, 3.0 Hz, 2 H), 7.52–7.59 (m, 6 H), 6.94–7.33 (m, 19 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.8, 149.4, 136.8, 136.8, 134.4, 133.5, 132.2, 132.1, 132.0, 131.1, 131.0, 129.8, 129.7, 129.6, 128.7, 128.6, 128.5, 127.9, 127.7, 127.6, 127.3, 127.1, 126.4, 126.3, 126.2, 126.1; IR (KBr) 3060, 3030, 1600, 1450, 745, 705, 660 cm^{-1}; LRMS (CI, isobutane) m/e 583 (MH^+, 100), 585 (32), 584 (35); HRMS (EI) calcd for $C_{42}H_{27}ClO$ 582.1750, found 582.1735.

5,12-Dihydro-5-(3-bromophenyl)-5,12-epoxy-6,11,12-triphenylnaphthacene (43). Addition of *n*-BuLi (0.47 mL of a 1.6 M solution in hexanes, 0.75 mmol) to a solution of **10** (261 mg, 0.75 mmol) and **40** (327 mg, 0.75 mmol) in THF (10 mL) at −78 °C gave 333 mg (71%) of **43** as a white crystalline solid after recrystallization from ethanol–benzene: mp 285–286.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74 (ddd, J = 13.9, 5.4, 3.0 Hz, 2 H), 7.66 (t, J = 1.7 Hz, 1 H), 7.56–7.60 (m, 5 H), 7.14–7.33 (m, 14 H), 7.05–7.10 (m, 3 H) 6.93–6.99 (m, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.8, 149.4, 149.1, 144.3, 144.2, 141.8, 141.0, 136.8, 136.8, 134.4, 132.5, 132.2, 132.2, 132.0, 131.1, 131.1, 130.8, 129.8, 129.6, 129.5, 129.0, 128.6, 128.32, 128.1, 127.9, 127.7, 127.6, 127.3, 127.1, 126.7, 126.4, 126.3, 126.1, 125.9, 122.7, 122.6, 122.3, 121.9; IR (KBr) 3060, 3030, 1595, 1445, 755, 700, 670 cm^{-1}; HRMS (EI) calcd for $C_{42}H_{27}BrO$ 626.1245, found 626.1215.

5,12-Dihydro-5-(2-pyridyl)-5,12-epoxy-6,11,12-triphenylnaphthacene (44). Addition of *n*-BuLi (2.44 mL of a 2.35 M solution in hexanes, 5.7 mmol) to a solution of **11** (1.50 g, 5.5 mmol) and **40** (2.50 g, 5.7 mmol) in THF (50 mL) at −78 °C gave 2.46 g (74%) of **44** as a white solid after recrystallization from ethanol–benzene: mp >300 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.24 (d, J = 3.8 Hz, 1 H), 7.97 (dd, J = 7.4, 3.2 Hz, 2 H), 7.81 (ddd, J = 13.9, 5.7, 2.7 Hz, 2 H), 7.63 (t, J = 1.7 Hz, 1 H), 7.47–7.53 (m, 5 H), 7.17–7.28 (m, 11 H), 7.70–7.11 (m, 2 H), 6.97–7.03 (m, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.7, 149.5, 149.2, 144.2, 143.3, 141.7, 140.9, 136.8, 136.8, 134.4, 132.7, 132.4, 132.2, 131.1, 131.1, 130.8, 129.8, 129.6, 129.5, 129.0, 128.6, 128.3, 128.1, 127.9, 127.7, 127.6, 127.3, 127.1, 126.8, 126.4, 126.3, 126.1, 125.9, 122.7, 122.6, 122.3, 121.9; IR (KBr) 3070, 3030, 1590, 1450, 700, 680 cm^{-1}; LRMS (CI, isobutane) m/e (relative intensity) 550 (MH^+, 100), 551 (19); HRMS (EI) calcd for $C_{41}H_{27}NO$ 549.2093, found 549.2089. Anal. Calcd for $C_{41}H_{27}NO$: C, 89.58; H, 4.96; N, 2.55. Found: C, 89.29; H, 5.27; N, 2.21.

Representative Procedure for the Cesium Iodide Mediated Aromatization of Epoxy-Bridged Adducts. 5,6,11,12-Tetraphenylnaphthacene (Rubrene). To a solution of **41** (372 mg, 0.68 mmol) and cesium iodide (530 mg, 2.04 mmol) in $CHCl_3$ (10 mL) at −78 °C was added dropwise $AlBr_3$ (0.75 ml of a 1.0 M solution in dibromomethane, 0.75 mmol). The reaction warmed to room temperature before slow addition of sodium metabisulfite (5 mL of a 5% aqueous solution) at which time HBr evolution was noted. The organic layer was separated, dried ($MgSO_4$), and concentrated in vacuo to give a red solid, which was initially purified by flash chromatography (alumina, petroleum ether) and then recrystallization from ethanol–benzene to give 321 mg (88%) of rubrene as ruby-red crystals: mp >300 °C dec; The sample was spectroscopically identical in all respects (^{1}H NMR, ^{13}C NMR, mass spectrum) with an authentic sample of rubrene.

5-(3-Chlorophenyl)-6,11,12-triphenylnaphthacene (45). Addition of $AlBr_3$ (1.77 ml of a 1.0 M solution in dibromomethane, 1.77 mmol) to a solution of **42** (937 mg, 1.61 mmol) and cesium iodide (1.25 g, 4.81 mmol) in $CHCl_3$ (20 mL) gave 636 mg (70%) of **45** as ruby-red crystals after recrystallization from ethanol–benzene: mp >300 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29–7.41 (m, 6 H), 6.99–7.22 (m, 14 H), 6.83–6.88 (m, 7 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.5, 141.6, 141.4, 141.0, 138.1, 137.7, 136.6, 135.0, 133.2, 132.4, 132.3, 132.2, 132.1, 132.0, 131.6, 130.3, 130.2, 130.1, 128.9, 128.5, 128.3, 128.3, 128.2, 127.6, 127.5, 127.2, 127.0, 126.8, 126.7, 126.6, 126.6, 126.3, 126.2, 126.1, 125.8, 125.2, 125.1, 125.0, 124.9, 120.7, 119.3, 117.4; IR (KBr) 3070, 2940, 2880, 1595, 1565, 1470, 1080, 775, 695 cm^{-1}; HRMS (EI) calcd for $C_{42}H_{27}Cl$ 566.1801, found 566.1789.

5-(3-Bromophenyl)-6,11,12-triphenylnaphthacene (46). Addition of $AlBr_3$ (0.41 ml of a 1.0 M solution in dibromomethane, 0.41 mmol) to a solution of **43** (233 mg, 0.37 mmol) and cesium iodide (288 mg, 1.1 mmol) in $CHCl_3$ (7 mL) gave 169 mg (75%) of **46** as ruby-red crystals after recrystallization from ethanol–benzene: mp 294–295 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.27–7.42 (m, 6 H), 7.03–7.25 (m, 14 H), 6.84–6.92 (m, 7 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.1, 141.5, 141.34, 141.0, 138.1, 137.6, 136.8, 135.0, 133.4, 132.3, 132.2, 132.1, 132.1, 131.8, 131.7, 130.5, 130.2, 130.0, 128.7, 128.4, 128.3, 128.2, 128.1, 127.6, 127.5, 127.3, 127.1, 126.51, 126.49, 126.47, 126.45, 126.3, 126.2, 126.2, 125.8, 125.2, 125.0, 125.0, 124.9, 120.8, 119.3, 117.3; IR (KBr) 3070, 2945, 2885, 1600, 1470, 780, 650 cm^{-1}; HRMS (EI) calcd for $C_{42}H_{27}Br$ 610.1296, found 610.1257.

5-(2-Pyridyl)-6,11,12-triphenylnaphthacene (47). Addition of $AlBr_3$ (5.3 ml of a 1.0 M solution in dibromomethane, 5.3 mmol) to a solution of **44** (2.61 g, 4.8 mmol) and cesium iodide (3.74 g, 14.4 mmol) in $CHCl_3$ (50 mL) gave 2.15 g (83%) of **47** as an orange solid after purification by flash chromatography (SiO_2, 9.8:0.2 CH_2Cl_2–triethylamine): mp 298–300 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.17 (d, J = 3.8 Hz, 1 H), 7.91 (dd, J = 7.4, 3.2 Hz, 2 H), 7.87 (ddd, J = 13.9, 5.7, 2.7 Hz, 2 H), 7.63 (t, J = 1.7 Hz, 1 H), 7.47–7.53 (m, 7 H), 7.15–7.24 (m, 9 H), 7.70–7.11 (m, 2 H), 6.97–7.03 (m, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.6, 149.5, 149.2, 144.2, 143.4, 141.7, 141.1, 136.8, 136.8, 134.4, 132.7, 132.6, 132.2, 131.09, 131.08, 130.8, 129.8, 129.6, 129.7, 129.0, 128.8, 128.3, 128.1, 127.9, 127.75, 127.6, 127.3, 127.1, 126.8, 126.4, 126.2, 126.1, 125.9, 122.7, 122.6, 122.3, 121.9; IR (KBr) 3065, 3035, 1600, 1450, 700, 680 cm^{-1}; LRMS (CI, isobutane) m/e (relative intensity) 534 (MH^+, 78), 535 (28), 533 (100), 491 (23), 490 (94), 473 (12), 472 (37); HRMS (EI) calcd for $C_{41}H_{27}N$ 533.2413, found 533.2126.

Acknowledgment. We are indebted to the National Institutes of Health (NS 25401 and a Career Development Award to A.R.C.) for financial support.

Supplementary Material Available: ^{1}H NMR spectra for compounds **8–11**, **13**, **14**, and **16–47** (38 pages). Ordering information is given on any current masthead page.