Arene 1,4-Diradical Formation from *o*-Dialkynylarenes

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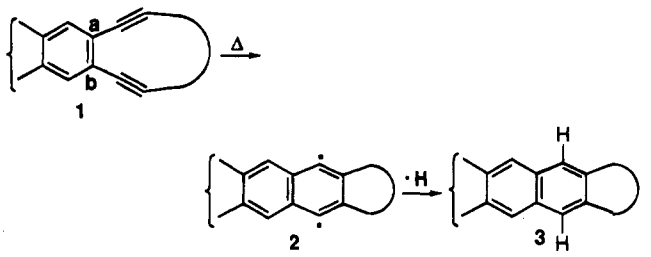
A series of 10-membered cyclic 1,5-diynes has been prepared with arene rings fused at positions C-3/C-4. The arenes include simple benzene rings, a naphthoquinone and naphthohydroquinone, and an anthraquinone and anthracene unit. Consistent with a simple picture relating the extent of double bond character in the ene part of the ene–diyne with the rate of arene-1,4-diyl formation, the hydroquinone derivatives were much less reactive compared to the corresponding quinones. Substituents such as propargylic hydroxyl or keto group have a small but significant activating effect. The parent 3,4-benzo-1,8-decadiyne shows a half-life for rearrangement of 24 h at 84 °C while the corresponding alkene, cyclodec-3-ene-1,5-diyne is reported to have a half-life of 18 h at 37 °C.

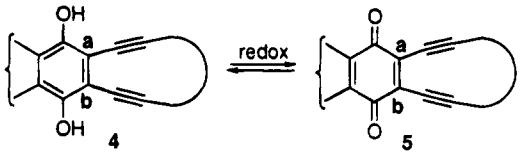
The rearrangement of 1,5-diyne–3-enes to arene-1,4-diyls[1] has taken on added significance with the discovery of natural toxins[2] which appear to function by undergoing this rearrangement under mild conditions producing DNA strand cleavage.[3] The natural structures and models have been synthesized and shown to support *in vitro* this simple mechanistic picture for the biological effects.[4] The models are important in helping us to understand the effects of the natural products and in developing applications as biochemical tools for DNA cleavage and potential antibiotics. The mechanistic hypothesis suggests an opportunity to design alternate structures which might have unique properties as triggerable DNA cleavage agents (or other biointerfering agents) and lead to significant applications in chemotherapy.

We have been interested in the design of diyne–ene with alternative triggering mechanisms and alternative frameworks for interaction with DNA. The arene–1,2-dialkynyl analogs (i.e., **1**) of the ene–diynes offer several special opportunities. Polycyclic arenes can function as DNA intercalators[5] and may position the analogous arene-1,4-diyl (i.e., **2**) for effective cleavage.[6] The reactivity of the arenediyne may depend on the olefinic character of the arene π bond (**a**–**b** in **1**) involved in the arene-1,4-diyl formation. The olefinic character may be adjustable through chemical changes, including those chemical changes which are commonly available in biological systems, such as redox potential, pH, etc.

Scheme 1



Scheme 2



A specific example is the hydroquinone/quinone couple[7] in which the two arene-1,2-diynes (i.e., **4** vs **5**) might be expected to have very different rates of rearrangement to the arene-1,4-diyl. The full double bond character in the quinone might accelerate the rearrangement.

A limited amount of structure/reactivity information for the diyne–ene rearrangement is available, largely

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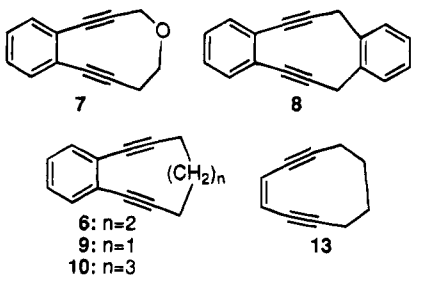
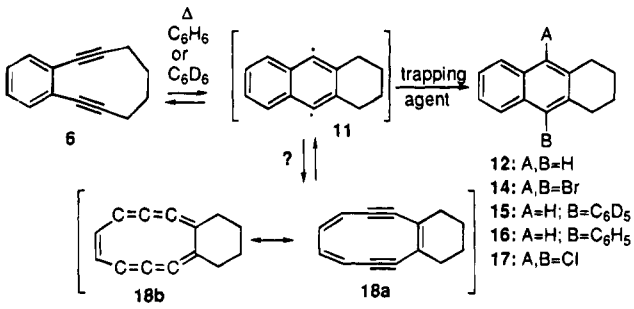
Chart 1



Scheme 3



dealing with the influence of ring size[4a,8] and strain energy changes[4a,9] on the rate of diradical formation. A series of related cyclic arene−1,2-dialkynes (**6**,[10] **7**,[11] **8**[12]) was known when we undertook this project[13] but only compound **7** had been studied in relation to the mechanism of action of the natural enediynes. Recently, the area has been active with examples of the "redox" activation of hydroquinone-1,2-diynes[4c] and a simple benzene-1,2-diyne showing DNA cleavage activity when attached to an established minor groove binder.[14]

Results and Discussion

Our first targets were the simple example, **6**, and analogs **9** and **10**; **6** had been observed previously as an intermediate in related rearrangements of polyene-diynes.[10] That work did not include evidence of arene-1,4-diyl (i.e., **11**) formation from **6**. Starting from 1,2-dibromobenzene, 1,2-bis[(trimethylsilyl)ethynyl]benzene was obtained (81% yield) in a Pd(0)-catalyzed coupling with trimethylsilylacetylene.[11,15] After cleavage of the trimethylsilyl groups, *o*-diethynylbenzene[16] was converted to the dianion and allowed to couple with 1,4-dibromobutane. The cyclic diyne **6** was obtained in 56% yield. In the same way, 1,5-diiodobutane led to **10** in 63% yield. Efforts to prepare the nine-membered ring, **9**, failed.

Both **6** and **10** are stable at 37 °C for more than 1 week in CH_2Cl_2. At elevated temperatures (84 °C), **6** was observed to rearrange, and the process showed a surprising dependence on the concentration of the trapping reagent, 1,4-cyclohexadiene (1,4-CHD), as displayed in Table 1. In all experiments, the mass balance is >90% and the naphthalene **12** is the only product detected. The dependence of the rate of arene-1,4-diyl formation on concentration of trapping agent does not seem to have been recognized in previous work and suggests that careful concentration measurements are necessary in order to compare data among experiments. The change in rate by 1 order of magnitude (Table 1) depending on the concentration of 1,4-CHD seems unlikely to be a result of changes in solvation, considering the similarity of the solvating ability of C_6H_6 compared to 1,4-CHD. Another possibility is that the arene-1,4-diyl is formed in equilibrium, and the (bimolecular) trapping step is important in the kinetic expression for the rate of disappearance of **6**. The alternate ring-opening product (**18a**) from the arene-1,4-diyl was not detected in any experiment. It was reported earlier as an assumed intermediate generated by a double elimination process and rearranged to give both **6** and **12**.[10] The formation of **6** from **18a** was rationalized in terms of a Cope rearrangement from valence tautomer **18b**, although the appearance of **12** in the same product mixture seems consistent with the formation of **11** and then **6**, from **18**. This is suggestive evidence for reversible formation of **11** from **6**. AM1 calculations[8,17] yield an energy for the singlet intermediate **11** that is 51.9 kcal/mol higher than that for the starting material, **6**. By the same method, the calculated transition state for this reaction is only 0.6 kcal/mol above **11**, which, while recognizing the limitations of semiempirical methods in dealing with singlet diradicals, suggests a high degree of reversibility for the cyclization reaction of **6** to **11**. However, other explanations of the dependence of rate on 1,4-cyclohexadiene concentration, such as a radical chain process, might also be made consistent with the observations.

Table 1. Rearrangement of 6 to 12 in 1,4-CHD

entry	1,4-CHD concn (M)	$t_{1/2}$ (h)
1	0.00	129
2	0.25	39
3	0.50	24
4	10.50 M (neat)	10.5

The original work of Bergman[1] on simple hex-3-ene-1,5-diynes demonstrated that the formation of the 1,4-diyl is reversible in the gas phase. However, reaction of 3,4-dialkylhex-3-ene-1,5-diynes in solution (reaction temperatures of 130−200 °C) shows a strong dependence of the fate of the 1,4-diyl on the concentration of 1,4-cyclohexadiene.[1b] Intramolecular H-shifts to the 1,4-diradical from the alkyl side chains as well as interaction with the solvent benzene are fast in the absence of a good H-atom source such as 1,4-cyclohexadiene. However, in a study much like that reported in Table 1, comparison of relative rates for 3,4-di-*n*-propyl-1,5-hex-3-enediyne at three concentrations of 1,4-cyclohexadiene (0, 0.19, and 0.38 M at 156 °C) revealed *no* significant variation in rate with concentration of trapping agent. Reversible formation of the 1,4-diyl was therefore excluded in those examples.[1b] To date, we are unaware of other examples which demonstrate reversible rearrangement of hex-3-ene-1,5-diynes in solution.

The rearrangement of **6** was much slower than the rearrangement of the corresponding ene−diyne **13** ($t_{1/2}$

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Table 2. Rearrangement of 6 in the Presence of CBr_4 and CCl_4

entry	condns (solvent, T (°C))	$t_{1/2}$ (h)	trapping agent[c]	product (yield, %)
1	C_6D_6, 40	18 h	CBr_4	**14** (trace); **15** (45)
2	C_6D_6, 84	6	CBr_4	**14** (23); **15** (38)
3	C_6D_6, 150	*b*	CBr_4	**14** (57)
4	C_6H_6, 84	*a*	CBr_4	**14** (23); **16** (31)
5	C_6H_6, 84	12	CCl_4	**17** (32); **15** (34); **12** (22)
6	C_6D_6, 150	*b*	CCl_4	**17** (61)

[a] The reaction was not monitored; conversion was complete after 36 h. [b] The reaction was not monitored; conversion was complete after 6 h. [c] 2.5 mol equiv.

= 18 h at 37 °C)[4a,18] and the 10-membered benzoxa diyne **7** ($t_{1/2}$ = 52 h at 37 °C).[11] The 11-membered ring analog **10** did not rearrange at a measurable rate at 84 °C and decomposed to a complex mixture at higher temperatures (150–200 °C).

Both CCl_4[19] and CBr_4 were evaluated as trapping agents (Table 2). Remarkably, reaction of **6** with CBr_4 in C_6D_6 occurred at a reasonable rate even at 23 °C and produced a mixture of bromine-containing products with no more than a trace of the expected dibromide, **14**. Reaction of the same mixture at 40 °C showed disappearance of **6** with $t_{1/2}$ = 18 h, and the major product (45% yield) was characterized as the solvent insertion product, **15** (entry 1). The same mixture at 84 °C produced **15** in 38% yield and the simple arene-1,4-diyl trapping product, **14**, in 23% yield (entry 2). Immersion of the an identical starting mixture in a bath at 150 °C produced **14** as the only identifiable product, in 57% yield (entry 3). For comparison, this experiment was repeated at 84 °C in C_6H_6, and parallel products (**14**, **16**) were obtained (entry 4). Similar results were observed with CCl_4 as trapping agent (entries 4 and 5). Slow reaction at 84 °C produced a mixture, while reaction at 150 °C gave mainly the simple 9,10-dichloride, **17**. The variation in rate and product distribution with the nature of the trapping agent (1,4-CHD, CCl_4, CBr_4) suggests more than one mechanism exists for the disappearance of **6**. It is possible that a radical chain process is initiated by the CBr_4, for example, and that H-atom or D-atom abstraction from the solvent is a chain-carrying step.

With a consideration of the effect of adjacent substituents on the rate of the arene-1,4-diyl formation and in order to provide points of attachment for DNA delivery agents, we developed syntheses for the functionalized analogs **19**–**21**. Selective silylation of *o*-diethynylbenzene gave **22**;[17] conversion to the alkyne anion and reaction with 4-chlorobutanal produced the adduct, **23**. After desilylation of the alkyne (**24**), silylation of the hydroxyl group (**25**), and replacement of the chloride with iodide (**26**), cyclization was initiated with lithium diisopropylamide. The hydroxyl silane **19** was obtained in 94% yield. Desilylation gave the alcohol, **20**, and oxidation produced the ketone **21**. The preparation of **20** using a different sequence of carbon–carbon coupling steps was reported recently.[15]

The hydroxyl group has a significant effect on the rate of formation of the arene-1,4-diyl. The half-life of **20** at 84 °C in C_6D_6 with 1,4-CHD at 0.5 M concentration was 4.5 h while under identical conditions **6** rearranged with a half-life of 24 h (for a summary, refer to Table 3). The

Scheme 4

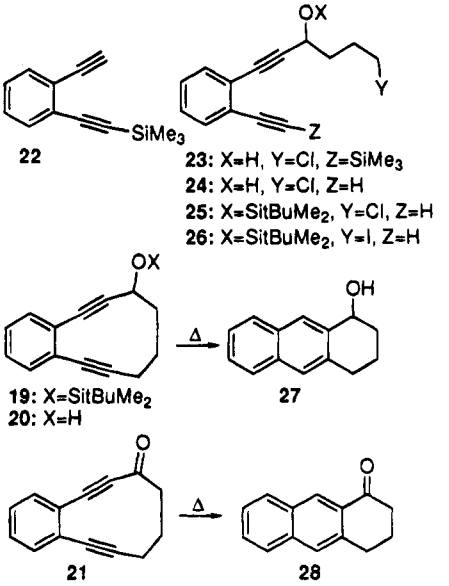
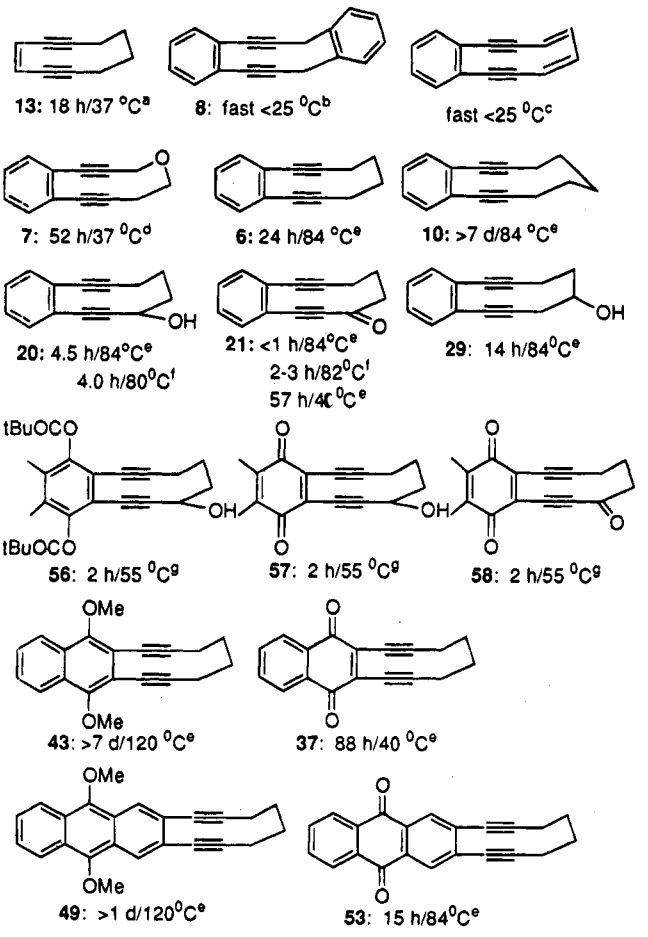


Table 3. Summary of Thermal Rearrangement Rates of the Arene–*o*-Dialkynes and Half-lives for Disappearance



[a] Reference 8. [b] Reference 12. [c] Reference 10. [d] Reference 11. [e] This work. [f] Reference 15. [g] Reference 14.

ketone **21** rearranged to **28** too rapidly to measure conveniently at 84 °C, but at 40 °C, the half-life of **21** is 57 h. These results are consistent with those reported by Boger and Zhou.[15] A related homopropargylic derivative (**29**) was prepared by reaction of the monoanion of

(18) Nicoloau, K. C.; Zuccarello, G.; Ogawa, Y.; Schweiger, E. J.; Kumazawa, T. *J. Am. Chem. Soc.* **1988**, *110*, 4866.

(19) Carbon tetrachloride was employed in the original work leading to characterization of the arene-1,4-diyl by thermal rearrangement of enediyne: see ref 1a.

Scheme 5

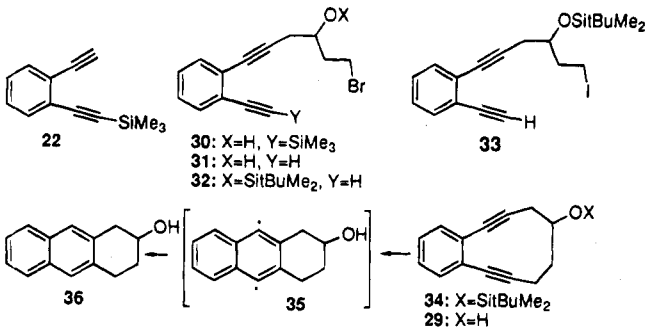
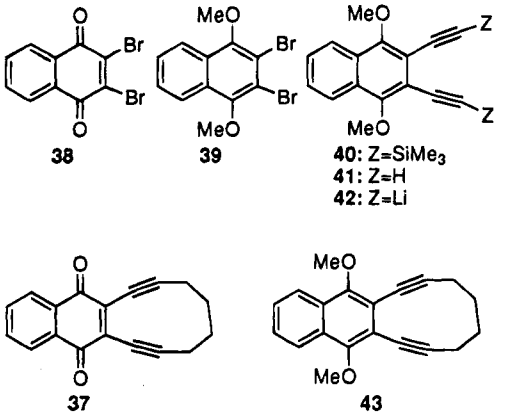


Chart 2



22 with BF_3 and then 4-bromo-1-butene oxide[20] to give the hydroxy bromide **30**. Removal of the alkynyl silyl group with fluoride (**31**, 91%) was followed by protection of the alcohol as a t-BuMe$_2$Si derivative (**32**, 93%), conversion to the corresponding iodide (**33**, 94%), ring closure promoted by treatment with LDA (to give **34**, 21%), and finally desilylation with fluoride to give the cyclic alcohol **29** (86% yield). Thermal rearrangement of **29** to give the arene-1,4-diyl (**35**) and then the naphthalene product (**36**) proceeded at 84 °C with a half-life of 14 h (0.1 M **29**; 0.5 M 1,4-CHD in C_6D_6), a rate intermediate between the parent arene **6** and the propargylic alcohol, **20** (Table 3).

Naphthalene and anthracene analogs of **6** were prepared including methoxy substituents, anticipating preparation of the corresponding quinones as well. For the synthesis of naphthoquinone **37**, benzoquinone was treated with an excess of bromine in glacial acetic acid and sodium acetate to give 2,3-dibromo-1,4-naphthoquinone (**38**).[21] Direct coupling of (trimethylsilyl)acetylene with **38** using Pd(0) failed to give the desired bis-alkyne. The quinone was reduced with dithionite, and the resulting hydroquinone was methylated with dimethyl sulfate and base[22] to provide **39**. The Pd(0)-catalyzed coupling now proceeded smoothly, giving the bis-alkyne **40** in 73% yield. After desilylation with fluoride was completed, the bis-alkyne **41** was treated with nBuLi and the dianion (**42**) was allowed to react with 1,4-diiodobutane. The cyclic ene–diyne **43** was obtained in 44% yield for the cyclization step. Finally, oxidative demethylation with cerium(IV) ammonium nitrate produced the naphthoquinone **37** in 73% yield.[23]

For the preparation of anthracene derivatives, phthalic anhydride and *o*-dibromobenzene were combined under Friedel–Crafts conditions to give 2-(3,4-dibromobenzoyl)-benzoic acid (**44**) in 92% yield. Ring closure promoted by H_2SO_4 gave 2,3-dibromo-9,10-anthraquinone (**45**).[24] Again, reduction followed by methylation allowed coupling of the dibromide (**46**) with (trimethylsilyl)acetylene using Pd(0), providing **47** in 71% yield. After removal of the silyl groups (**48**), cyclization with 1,4-diiodobutane gave the cyclic diyne **49** (62%).

The preparation of **49** and the study of its thermal rearrangements were complicated by apparent facile thermal dimerization of **47**–**49**. The dimerization of **48** was observed during NMR studies, as new signals grew into the ^{1}H NMR spectrum. However, although a systematic series of experiments was undertaken to probe for the effects of light and temperature, the formation of the new product proved unpredictable. The ^{1}H and ^{13}C NMR signals are consistent with a symmetrical structure such as **48**, and there is precedence for dimerization at the 9,10 bond.[25] The dimerization appears to be thermally highly reversible, and it has been difficult to obtain a sample of pure **50**. In addition, the dimer is reactive toward oxygen simply during exposure to air at ambient temperature, a process which can be followed conveniently in the ^{1}H NMR spectrum. The simplicity (3 arene H signals) of the spectrum from **50** deteriorates into a pattern with six different arene H signals (perhaps **51**) and then simplifies again. The final product is **52**. Related processes were observed by ^{1}H NMR for **47** and **49** but the intermediates were not fully characterized. The anthraquinone **53** was obtained by oxidative demethylation of **49** using cerium(IV) ammonium nitrate (47% yield).[25]

Thermal rearrangement of the dimethoxy derivatives **43** and **49** was not detectable at 84 °C in the presence of 1,4-CHD, and a mixture of decomposition products formed upon raising the temperature (eventually to 200 °C) in order to complete the conversion of starting materials. One of the decomposition products (low yield) from **49** was characterized as pentacenequinone (**54**), formed presumably via an oxidative-dimerization pathway as was suggested for **48**, above. In the case of naphthoquinone derivative **37**, rearrangement occurred at 84 °C with a half-life of 2–3 h and at 40 °C with a half-life of 88 h (1,4-CHD, C_6D_6); refer to Table 3. The arenediyl rearrangement product **55** was obtained in 79% yield. Anthraquinone **53** was nearly as reactive as the naphthoquinone derivative **37**, showing in 1,4-CHD/C_6D_6 a half-life of 15 h at 84 °C and giving the rearrangement product **54** (82% yield).

Table 3 summarizes the results for thermal rearrangement of the arene–1,2-dialkynes under similar conditions. None of the arene–1,2-dialkynyl derivatives with 10-membered rings in Table 3 approaches the reactivity of the simple 10-membered ring monocyclic ene–diyne **13** or the natural ene–diynes (calicheamicin, esperimicin). The parent derivative **6** is stable for many days at physiological temperature. The presence of a propargylic

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(25) Anthracene dimerization is common upon irradiation, and thermal reversal to the monomer is also well known. Formation of the 9,10 dimer thermally is unusual, and we are studying further the conditions and structures involved here (**49**, **50**, **51**, and **52**). For a review of $4\pi + 4\pi$ cycloadditions of anthracenes, see: Bouas-Laurent, H.; Desvergne, J.-P. In *Photochromism; Molecules and Systems*; Durr, H., Ed.; Elsevier: Amsterdam, 1990; p 561ff.

Scheme 6

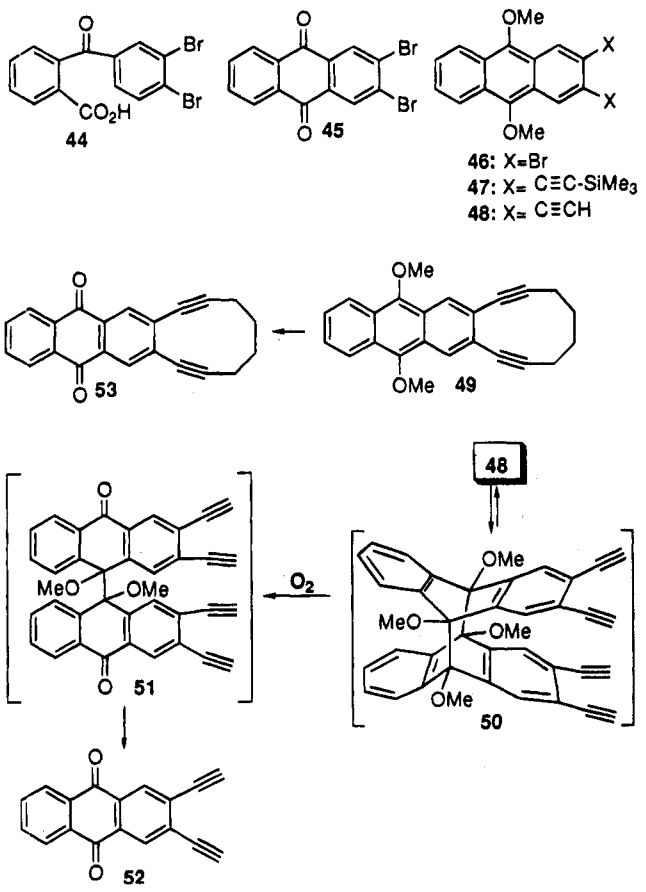
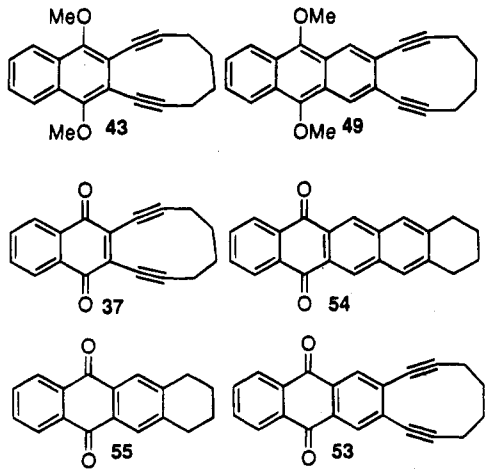


Chart 3



hydroxyl group (compare **6** and **20**) increases the rate of rearrangement by a factor of 5 or so and allows detectable DNA cleavage activity, albeit at high concentration. It is unlikely that diradical generation under these elevated temperatures can be the basis for design of cytotoxic agents. With the propargylic keto group (compare **6** and **21**), the rate is again increased by a factor of ca. 5 and is easily detectable at 40 °C.

While the hydroquinone derivatives, including benzene **56**, naphthalene **43**, and anthracene **53**, structures are strongly stabilized with respect to 1,4-diyl formation, the corresponding quinones are among the more reactive cyclic arene−1,2-dialkynes with half-lives for rearrangement in the range of a few hours at 50 °C (**37**, **53**, **57**, **58**). The large difference in reactivity between the hydroquinones and the corresponding quinones offers the basis for a redox trigger for activation of arene-1,4-diyl formation which is currently under study.

Experimental Section

General. ^{1}H NMR (270 MHz) and ^{13}C NMR (68 MHz) spectra were measured on a JEOL GX-270 instrument. All NMR spectra were recorded in $CDCl_3$ as solvent. Chemical shifts are recorded in parts per million on the δ scale referred to tetramethylsilane as zero, and coupling constants are given in hertz. IR spectra were determined on a Nicolet FT-IR spectrometer. Mass spectra were taken on a Kratos MS-80 spectrometer. Commercially available reagents were purified prior to use if necessary. THF was dried by distillation from sodium benzophenone ketyl under argon before use. Acetone was distilled from K_2CO_3 at atmospheric pressure; $(i\text{-}Pr)_2NH$, Et_3N, and lutidine were dried by distillation from CaH_2. Hexamethylphosphoric triamide (HMPA) was distilled from CaH_2 at reduced pressure. n-BuLi and EtMgBr (Aldrich Chemical Co.) were used as received.

Preparation of 3,4-Benzocyclodec-3-ene-1,5-diyne (6). To a solution of 1,2-diethynylbenzene[17] (0.500 g, 3.97 mmol) in dry THF (50 mL) cooled at −78 °C under argon was added a solution of n-BuLi (2.1 mol equiv, in hexane) over a period of 30 min. After the reaction mixture had been stirred for an additional 1 h at −78 °C, 1,4-diiodobutane (1.240 g, 4.00 mmol) was added dropwise over a period of 15 min. The reaction mixture was allowed to warm to 23 °C and allowed to stir for an additional 48 h. It was then quenched with saturated aqueous NH_4Cl solution and extracted with ether, and the ether solution was washed with water, dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was chromatographed (silica gel/hexane) to provide **6** as a colorless solid (0.342 g, 48%), mp 72−73 °C (recrystallized from pentane) (lit.[10] mp 73.0−74.5 °C). IR (KBr): 2938, 2924, 2209, 1466, 1449, 1444, 1328, 759 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$): δ 7.35 (2H, dd, J = 5.6, 3.6 Hz), 7.23 (2H, dd, J = 5.6, 3.6 Hz), 2.47−2.51 (4H, m, $2CH_2$), 1.96−2.02 (4H, m, $2CH_2$). ^{13}C NMR (68 MHz, $CDCl_3$): δ 129.51 (2C), 128.08 (2CH), 127.23 (2CH), 99.94 (2*C*≡C), 82.26 (2*C*≡C), 28.60 ($2CH_2$), 21.49 ($2CH_2$). Mass spectrum *m/z*: 180 (M^+). HRMS: calcd for $C_{14}H_{12}$ 180.0936, found 180.0933.

Preparation of 3,4-Benzocycloundec-3-ene-1,5-diyne (10). To a solution of 1,2-diethynylbenzene[17] (0.500 g, 3.97 mmol) in 50 mL of dry THF under argon and cooled at −78 °C was added 2.1 mol equiv of n-BuLi (hexane solution) over a period of 30 min. After the reaction mixture was stirred for an additional 1 h at −78 °C, 1,4-diiodobutane (1.240 g, 4.00 mmol) was added dropwise over a period of 15 min. The reaction mixture was allowed to warm to 23 °C and allowed to stir for an additional 48 h. It was then quenched with saturated aqueous NH_4Cl solution and diluted with ether, and the ether solution was washed with water, dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was chromatographed (silica gel/hexane) to give **10** as a colorless solid (0.489 g, 63%), mp 49−51 °C (hexane). IR (KBr): 2939, 2921, 2855, 2220, 1472, 1445, 752 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$): δ 7.30 (2H, dd, J = 5.6, 3.6 Hz), 7.16 (2H, dd, J = 5.6, 3.6 Hz), 2.50 (4H, t, J = 6.27 Hz), 2.05 (2H, J = 6.93−7.25 Hz), 1.62 (4H, q, J = 6.93, 6.24, 6.60 Hz). ^{13}C NMR (67.9 MHz, $CDCl_3$): δ 129.41 (2CH), 128.25 (2C), 127.22 (2CH), 95.43 (2*C*≡C), 82.34 (2C≡*C*), 24.57 ($2CH_2$), 24.17 (CH_2), 18.71 ($2CH_2$). Mass spectrum *m/z*: 194 (M^+, 90), 165 (100).

Preparation of 6-Chloro-1-([2′-[(trimethylsilyl)ethynyl]phenyl]hex-1-yn-3-ol (23). To a solution of **22**[17] (0.250 g, 1.25 mmol) in 30 mL of THF was added dropwise 1.2 mol equiv of n-BuLi (solution in hexane) at −78 °C over 15 min. The reaction mixture was stirred for an additional 1 h. Then $Cl(CH_2)_3CHO$ (0.156 g, 1.5 mmol) was added dropwise over a period of 10 min. The mixture was stirred and allowed to warm slowly until it reached −50 °C after about 3 h. It was quenched with saturated aqueous ammonium chloride and diluted with ether, and the ether solution was washed with water, dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was chromatographed (silica gel,

hexane/ethyl acetate, 5/1) to give **23** as a colorless oil (0.320 g, 80%). R_f (hexane/ethyl acetate; 2/1): 0.46. IR (neat): 3377, 2958, 2158, 1477, 1249, 863, 844 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$): δ 7.43–7.46 (1H, m, 1ArH), 7.38–7.41 (1H, m, 1ArH), 7.22–7.27 (2H, m, 2ArH), 4.68 (1H, t, J = 5.9 Hz, CHO), 3.61 (2H, t, J = 6.2 Hz, CH_2Cl), 1.94–2.06 (4H, m, $2CH_2$, OH), 0.25 (9H, s, $3CH_3$). ^{13}C-NMR (68 MHz, $CDCl_3$): δ 132.34 (CH), 131.85 (CH), 128.17 (CH), 128.14 (CH),125.62 (C), 124.98 (C), 103.25 (C≡), 98.55 (C≡), 93.40 (C≡), 83.92 (CH≡), 62.27 (CHO), 44.69 (CH_2Cl), 34.97 (CH_2), 28.34 (CH_2), −0.01 ($3CH_3$). Mass spectrum m/z: 304 (M^+, 49), 73 (100).

Preparation of 6-Chloro-1-(2′-ethynylphenyl)hex-1-yn-3-ol (24). Compound **23** (0.212 g, 0.63 mmol) was dissolved in THF (5 mL), and then 1 mol equiv of n-Bu_4NF in THF solution (0.63 mL, 1.0 M) was added at 0 °C. The reaction mixture was stirred for 30 min at 0 °C. The solvents were evaporated, and the residue was purified by column chromatography (silica gel, hexane/ethyl acetate; 4/1) to give as a colorless oil **24** (0.140 g, 95%). R_f (hexane/ethyl acetate, 2/1): 0.31. IR (neat): 3286, 2957, 2229, 2106, 1478, 1442, 760, 650 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$): δ 7.46–7.50 (1H, m, 1ArH), 7.40–7.44 (1H, m, 1ArH), 7.25–7.31 (2H, m, 2ArH), 4.70 (1H, t, J = 6.2 Hz, CHO), 3.62 (2H, t, J = 6.6 Hz, CH_2Cl), 3.29 (1H, s, C≡CH), 1.91–2.11 (4H, m, $2CH_2$). ^{13}C NMR (68 MHz, $CDCl_3$): δ 132.56 (CH), 131.91 (CH), 128.52 (CH), 128.21 (CH), 125.31 (C), 124.64 (C), 93.49 (C≡), 83.67 (C≡), 82.07 (C≡), 81.20 (CH≡), 62.26 (CHO), 44.74 (CH_2Cl), 34.87 (CH_2), 28.25 (CH_2). Mass spectrum m/z: 232 (M^+, 7), 127 (100).

Preparation of 6-Chloro-1-(2′-ethynylphenyl)-3-[(*tert*-butyldimethylsilyl)oxy]hex-1-yne (25). To a solution of compound **24** (0.138 g, 0.60 mmol) in CH_2Cl_2 (5 mL) was added 1,6-dimethylpyridine (0.107 g, 0.90 mmol). Then *tert*-butyldimethylsilyl triflate (TBDMS-Tf, 0.206 g, 0.78 mmol) was added all at once at 0 °C, and the reaction mixture was stirred for 0.5 h at 0 °C. The reaction was quenched with water and diluted with CH_2Cl_2. The dichloromethane solution was washed with water, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. Chromatography of the residue (silica gel, hexane/ethyl acetate; 20/1) gave **25** as an oil (0.195 g, 94%). R_f (hexane/ethyl acetate, 20/1): 0.32. IR (neat): 3305, 2955, 2929, 2856, 2229, 2109, 1470, 1339, 1093, 838, 778, 651 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$): δ 7.44–7.47 (1H, m, 1ArH), 7.37–7.40 (1H, m, 1ArH), 7.21–7.28 (2H, m, 2ArH), 4.66 (1H, t, J = 5.93 Hz, CHO), 3.59 (2H, t, J = 6.2 Hz, CH_2Cl), 3.25 (1H, s, C≡CH), 1.99–2.04 (2H, m, CH_2), 1.88–1.93 (2H, m, CH_2), 0.89 (9H, s, $3CH_3$), 0.16 (3H, s, CH_3), 0.13 (3H, s, CH_3). ^{13}C NMR (68 MHz, $CDCl_3$): m δ 132.54 (CH), 131.94 (CH), 128.42 (CH), 127.90 (CH),125.87 (C), 124.52 (C), 94.34 (C≡), 82.83 (C≡), 82.13 (C≡), 80.99 (CH≡), 62.79 (CHO), 44.98 (CH_2Cl), 35.79 (CH_2), 28.39 (CH_2), 25.80 (CH_3), 18.20 (C), −4.35 (CH_3), −5.00 (CH_3). Mass spectrum m/z: 346 (M^+, 0), 289 (M^+ − t-Bu, 45), 247 (100).

Preparation of 1-(2′-Ethynylphenyl)-6-iodo-3-[(*tert*-butyldimethylsilyl)oxy]hex-1-yne (26). A mixture of compound **25** (0.173 g, 0.50 mmol) and 25 mol equiv of NaI (1.787 g, 12.5 mmol) was stirred for 48 h in dry acetone under argon at 50 °C. Then the solvent was removed under aspirator vacuum, and the residue was partitioned between CH_2Cl_2 and water. The organic phase was dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo; the residue was purified by column chromatography (silica gel, hexane/ethyl acetate, 20/1) to give **26** as a colorless liquid (0.212 g, 93%). R_f (hexane/ethyl acetate, 20/1): 0.33. IR (neat): 3230, 2953, 2926, 2856, 2227, 2109, 1476, 1253, 1089, 837, 756 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$): δ 7.45–7.48 (1H, m, 1ArH), 7.38–7.42 (1H, m, 1ArH), 7.23–7.29 (2H, m, 2ArH), 4.67 (1H, t, J = 5.94 Hz, CHO), 3.29 (1H, s, C≡CH), 3.25 (2H, t, J = 7.2 Hz, CH_2Cl), 2.05–2.13 (2H, m, CH_2), 1.83–1.91 (2H, m, CH_2), 0.91 (9H, s, $3CH_3$), 0.18 (3H, s, CH_3), 0.15 (3H, s, CH_3). ^{13}C NMR (68 MHz, $CDCl_3$): δ 132.53 (CH), 131.93 (CH), 128.40 (CH), 127.89 (CH),125.83 (C), 124.51 (C), 94.31 (C≡), 82.85 (C≡), 82.13 (C≡), 81.05 (CH≡), 62.47 (CHO), 39.23 (CH_2), 29.28 (CH_2), 25.80 (CH_3), 18.19 (C), 6.64 (CH_2I), −4.34 (CH_3), −4.98 (CH_3). Mass spectrum m/z: 438 (M^+, 0), 381 (M^+ − t-Bu, 45), 339 (100).

Preparation of 7-[(*tert*-Butyldimethylsilyl)oxy]-3,4-benzocyclodec-3-ene-1,5-diyne (19). To a solution of **26** (0.212 g, 0.48 mmol) in 15 mL of dry THF at −78 °C was added dropwise over 10 min a solution of lithium diisopropylamide (LDA, 1.2 mol equiv). The reaction mixture was stirred for an additional 1 h at −78 °C. Then HMPA (15 mol equiv, 1.3 mL) was added all at once. The reaction mixture was allowed to warm to 23 °C and was stirred at this temperature for 24 h. The mixture was poured into saturated aqueous NaCl solution and extracted with ether. The organic solution was washed with water, dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. Chromatography over silica gel (hexane/ethyl acetate, 20/1) gave **19** as a colorless liquid (0.140 g, 94%). R_f (hexane/ethyl acetate; 20/1): 0.36. IR (neat): 2952, 2929, 2856, 2223, 1469, 1343, 1253, 1090, 837, 779 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$): δ 7.31–7.35 (1H, m, 1ArH), 7.25–7.29 (1H, m, 1ArH), 7.17–7.23 (2H, m, 2ArH), 4.60 (1H, dd, J = 7.5, 2.6 Hz, CHO), 2.40–2.46 (2H, m, CH_2), 2.12–2.21 (2H, m, CH_2), 1.99–2.05 (1H, m, C*H*H), 1.75–1.79 (1H, m, CH*H*), 0.90 (9H, s, $3CH_3$), 0.15 (3H, s, CH_3), 0.13 (3H, s, CH_3). ^{13}C NMR (68 MHz, $CDCl_3$): δ 129.73 (C), 128.87 (CH), 128.69 (C), 127.98 (CH),127.93 (CH), 127.16 (CH), 100.39 (C≡), 99.47 (C), 84.15 (C≡), 82.03 (C≡), 63.74 (CHO), 38.79 (CH_2), 25.81 (CH_3), 23.59 (CH_2), 21.26 (CH_2) 18.20 (C), −4.44 (CH_3), −4.88 (CH_3). Mass spectrum m/z: 310 (M^+, 5), 253 (M^+ − t-Bu, 30), 235 (100).

Preparation of 3,4-benzocyclodec-3-ene-1,5-diyn-7-ol (20). To a solution of **19** (0.123 g, 0.396 mmol) in THF (3 mL) was added (n-$Bu)_4NF$ in THF solution (1.0 M, 1.0 mol equiv) at 0 °C. The mixture was stirred for 30 min at 0 °C. Then the solvents were removed at aspirator vacuum and the residue was purified by column chromatography (silica gel; hexane/ethyl acetate, 3/1) to give **20** (0.071 g, 91%) as a colorless oil. R_f (hexane/ethyl acetate, 3/1): 0.24. IR (neat): 3420, 2955, 2223, 1468, 1449, 1376, 1332 1079, 1036, 756 cm^{-1}. ^1H NMR (270 MHz, C_6D_6): δ 7.23–7.30 (2H, m, 2ArH), 6.79–6.85 (2H, m, 2ArH), 4.30 (1H, d, J = 2.6, Hz, CHO), 2.02–2.06 (2H, m, CH_2), 1.65–1.92 (3H, m, CH_2, OH), 1.31–1.34 (2H, m, CH_2). ^{13}C NMR (68 MHz, $CDCl_3$): δ 129.75 (C), 128.87 (CH), 128.23 (CH), 128.14 (C),128.05 (CH), 127.26 (CH), 100.33 (C≡), 98.62 (C≡), 85.10 (C≡), 82.01 (C≡), 63.30 (CHO), 38.00 (CH_2), 23.69 (CH_2), 21.24 (CH_2). Mass spectrum m/z: 196 (M^+, 78), 139 (100).

Preparation of 3,4-benzocyclodec-3-ene-1,5-diyn-7-one (21). A mixture of compound **20** (0.042 g, 0.210 mmol) and $BaMnO_4$ (0.510 g, 2.00 mmol)[26] in CH_2Cl_2 (4 mL) was stirred for 4 h at 23 °C. The reaction mixture was filtered through Celite, and the solvent was removed at aspirator vacuum. The residue was purified by column chromatography (silica gel; hexane/ethyl acetate, 10/1) to give **21** as a white solid (0.032 g, 79%). Recrystallization from hexane/chloroform produced colorless crystals with mp 57–58 °C. IR (KBr): 2950, 2194, 1683, 1463, 1118, 1092, 975, 768 cm^{-1}. ^1H NMR (270 MHz, C_6D_6): δ 7.36 (1H, d, J = 7.26 Hz, 1ArH), 7.22–7.29 (3H, m, 3ArH), 2.75 (2H, dt, J = 5.67, 2.61 Hz, CH_2), 2.47 (2H, dt, J = 5.6, 2.6 Hz, CH_2), 2.00–2.08 (2H, m, CH_2). ^{13}C NMR (68 MHz, $CDCl_3$): δ 187.82 (CO), 131.47 (C), 130.87 (CH), 130.79 (CH), 129.39 (CH), 127.63 (CH), 125.37 (C), 100.53 (C≡), 95.40 (C≡), 94.20 (C≡), 81.87 (C≡), 46.40 (CH_2), 25.41 (CH_2), 21.98 (CH_2). Mass spectrum m/z: 194 (M^+, 61), 165 (100).

Preparation of 1-Bromo-6-[2′-[(trimethylsilyl)ethynyl]-phenyl]hex-5-yn-3-ol (30). To a solution of **22** (0.495 g, 2.50 mmol) in 50 mL of dry THF was added a solution of n-BuLi in hexane (1.1 mol equiv) at −78 °C dropwise over a period of 15 min. The reaction mixture was stirred for an additional 1 h. Then $BF_3{\cdot}Et_2O$ (0.457 g, 3.22 mmol) was added at this temperature. After 15 min, 4-bromo-1,2-epoxybutane (0.378 g, 2.50 mmol) was added, and the reaction mixture was stirred for 1 h at −78 °C and then quenched with a saturated aqueous solution of NH_4Cl. The mixture was extracted with ether,

(26) Adapted from procedures reported by: (a) Garigipati, R. S.; Freyer, A. J.; Whittle, R. R.; Weinreb, S. M. *J. Am. Chem. Soc.* **1984**, *106*, 7861. (b) Firouzabadi, H.; Ghaderi, E. *Tetrahedron Lett.* **1978**, 839.

(27) Latham, H. G.; May, E. L.; Mossetiz, E. *J. Am Chem. Soc.* **1948**, *70*, 1079.

(28) Japanese Patent 16,863 (1966) reported as: Iwai, I.; Ide, J. *Chem. Abstr.* **1967**, *66*, 18666u.

dried over anhydrous Na_2SO_4, filtered, and concentrated at aspirator pressure. The residue was purified by column chromatography (silica gel; hexane/ethyl acetate, 5/1) to give **30** as a colorless liquid (0.722 g, 82%). R_f (hexane/ethyl acetate, 3/1): 0.35. IR (neat): 3532, 2958, 2900, 2156, 1477, 1250, 862, 759 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$): δ 7.43–7.46 (1H, m, 1ArH), 7.35–7.39 (1H, m, 1ArH), 7.20–7.26 (2H, m, 2ArH), 4.03–4.09 (1H, m, CHO), 3.53–3.60 (2H, m, CH_2Br), 2.72 (1H, dd, J = 16.8, 4.2 Hz, C*H*H), 2.58 (1H, dd, J = 16.8, 7.2 Hz, C*H*H), 2.02–2.16 (2H, m, CH_2), 1.50–1.63 (1H, br, OH). ^{13}C NMR (68 MHz, $CDCl_3$): δ 132.44 (CH), 131.55 (CH), 128.21 (CH), 127.68 (CH),125.62 (C), 125.55 (C), 103.91 (C≡), 98.32 (C≡), 89.67 (C≡), 82.44 (CH≡), 67.82 (CHO), 39.08 (CH_2Br), 29.97 (CH_2), 28.55 (CH_2), −0.04 ($3CH_3$). Mass spectrum *m/z*: 350 (M^+, ^{81}Br, 5), 348 (M^+, ^{79}Br, 5), 197 (100).

Preparation of 1-Bromo-6-(2′-ethynylphenyl)hex-5-yn-3-ol (31). To a solution of **30** (0.628 g, 1.80 mmol) in THF (8 mL) at 0 °C was added all at once $(n\text{-}Bu)_4NF$ in THF (1.0 M, 1.2 mol equiv). The reaction mixture was stirred for 30 min at 0 °C. The solvents were removed at aspirator pressure, and the residue was purified by column chromatography (silica gel; hexane/ethyl acetate, 3/1) to give **31** as an oil (0.456 g, 91%). R_f (hexane/ethyl acetate, 3/1): 0.29. IR (neat): 3286, 2956, 2930, 2233, 2103, 1478, 1258, 1052, 735 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$): δ 7.46–7.49 (1H, m, 1ArH), 7.38–7.41 (1H, m, 1ArH), 7.21–7.31 (2H, m, 2ArH), 4.03–4.08 (1H, m, CHO), 3.53–3.60 (2H, m, CH_2Br), 3.32 (1H, s, C≡CH), 2.74 (1H, dd, J = 16.8, 4.9 Hz, C*H*H), 2.60 (1H, dd, J = 16.8, 6.6 Hz, C*H*H), 2.35 (1H, d, J = 5.3 Hz, OH), 2.02–2.20 (2H, m, CH_2). ^{13}C NMR (68 MHz, $CDCl_3$): δ 132.45 (CH), 131.53 (CH), 128.55 (CH), 127.71 (CH),126.04 (C), 124.54 (C), 89.83 (C≡), 82.73 (C≡), 82.13 (C≡), 80.79 (CH≡), 67.89 (CHO), 38.91 (CH_2Br), 30.01 (CH_2), 28.40 (CH_2). Mass spectrum *m/z*: 278 (M^+, ^{81}Br, 2), 276 (M^+, ^{79}Br, 2), 140 (100).

Preparation of 1-Bromo-3-[(*tert*-butyldimethylsilyl)oxy]-6-(2′-ethynylphenyl)hex-5-yne (32). To a solution of **31** (0.415 g, 1.50 mmol) in CH_2Cl_2 (15 mL) at 23 °C was added 1,6-dimethylpyridine (0.321 g, 2.70 mmol). To this mixture at 0 °C was added TBDMS-Tf (0.618 g, 2.34 mmol). After the mixture was stirred for 30 min, it was quenched with water and extracted with CH_2Cl_2. The organic solution was washed with water, dried over anhydrous Na_2SO_4, filtered, and chromatographed over silica gel with hexane/ethyl acetate (20/1) to give **32** as an oil (0.547 g, 93%). R_f (SiO_2; hexane/ethyl acetate, 20/1): 0.28. IR (neat): 3305, 2954, 2856, 2233, 2109, 1471, 1256, 1100, 836, 777 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$): δ 7.44–7.47 (1H, m, 1ArH), 7.36–7.39 (1H, m, 1ArH), 7.18–7.28 (2H, m, 2ArH), 4.03–4.09 (1H, m, CHO), 3.46–3.54 (2H, m, CH_2Br), 3.29 (1H, s, Cxba≡CH), 2.67 (1H, dd, J = 16.8, 4.9 Hz, C*H*H), 2.58 (1H, dd, J = 16.8, 6.6 Hz, C*H*H), 2.28–2.36 (1H, m, C*H*H), 2.11–2.21 (1H, m, C*H*H), 0.88 (9H, s, $3CH_3$), 0.11 (6H, s, $2CH_3$). ^{13}C NMR (68 MHz, $CDCl_3$): δ 132.48 (CH), 131.85 (CH), 128.40 (CH), 127.45 (CH),126.57 (C), 124.49 (C), 90.43 (Cxba≡), 82.35 (Cxba≡), 81.22 (Cxba≡), 80.84 (CHxba≡), 69.06 (CHO), 39.59 (CH_2Br), 30.27 (CH_2), 28.49 (CH_2), 25.77 (CH_3), 17.97 (CH_3), −4.44 (CH_3), −4.73 (CH_3). Mass spectrum *m/z*: 391 (M^+, 0), 335 (M^+ − t-Bu, ^{81}Br, 18), 333 (M^+ − t-Bu, ^{79}Br, 18), 73 (100).

Preparation of 3-[(*tert*-Butyldimethylsilyl)oxy]-6-(2′-ethynylphenyl)-1-iodohex-5-yne (33). A mixture of compound **32** (0.547 g, 1.40 mmol) and NaI (5.250 g, 25 mol equiv, 35.00 mmol) was stirred for 48 h in dry acetone under Ar at 50 °C. The solvent was removed at aspirator vacuum, and the residue was partitioned between CH_2Cl_2 and water. The organic phase was dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo, and the residue was purified by column chromatography (silica gel; hexane/ethyl acetate, 20/1) to give **33** as a colorless oil (0.578 g, 94%). R_f (hexane/ethyl acetate, 20/1): 0.30. IR (neat): 3220, 2953, 2856, 2236, 2106, 1478, 1255, 1098, 836, 776 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$): δ 7.44–7.47 (1H, m, 1ArH), 7.36–7.40 (1H, m, 1ArH), 7.18–7.28 (2H, m, 2ArH), 3.93–3.97 (1H, m, CHO), 3.32 (1H, s, Cxba≡CH), 3.17–3.31 (2H, m, CH_2I), 2.66 (1H, dd, J = 16.7, 4.8 Hz, C*H*H), 2.57 (1H, dd, J = 16.7, 7.5 Hz, C*H*H), 2.29–2.38 (1H, m, C*H*H), 2.09–2.19 (1H, m, C*H*H), 0.88 (9H, s, $3CH_3$), 0.11 (6H, s, $2CH_3$). ^{13}C NMR (68 MHz, $CDCl_3$): δ 132.50 (CH), 131.87 (CH), 128.40 (CH), 127.46 (CH),126.54 (C), 124.48 (C), 90.44 (Cxba≡), 82.37 (Cxba≡), 81.22 (Cxba≡), 80.89 (CHxba≡), 70.98 (CHO), 40.52 (CH_2), 28.24 (CH_2), 25.80 (CH_3), 17.98 (C), 2.78 (CH_2I), −4.37 (CH_3), −4.53 (CH_3). Mass spectrum *m/z*: 438 (M^+, 0), 381 (M^+ − t-Bu, 18), 73 (100).

Preparation of 9-[(*tert*-Butyldimethylsilyl)oxy]benzo[3,4]cyclodec-3-ene-1,5-diyne (34). To a solution of **33** (0.587 g, 1.30 mmol) in 20 mL of dry THF at −78 °C was added dropwise over 10 min a solution of LDA in THF (1.2 mol equiv). After addition was complete, the reaction mixture was stirred for an additional 1 h at −78 °C. Then HMPA (1.5 mL) was added all at once. The reaction mixture was allowed to warm to 23 °C and to stir for 24 h. The mixture was poured into saturated aqueous NaCl solution and extracted with ether; the organic layer was washed with water, dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. Chromatography over silica gel (hexane/ethyl acetate, 40/1) gave **34** as a colorless oil (0.082 g, 21%). R_f (hexane/ethyl acetate, 20/1): 0.40. IR (neat): 2953, 2929, 2855, 2214, 1469, 1254, 1076, 835, 756 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$): δ 7.27–7.30 (2H, m, 2ArH), 7.16–7.25 (2H, m, 2ArH), 3.95–4.02 (1H, m, CHO), 2.58 (2H, d, J = 7.2 Hz, CH_2), 2.58 (1H, dd, J = 16.5, 7.1 Hz, C*H*H), 2.44 (1H, dd, J = 16.5, 4.5 Hz, C*H*H), 2.18–2.30 (1H, m, C*H*H), 2.02–2.10 (1H, m, C*H*H), 0.87 (9H, s, $3CH_3$), 0.06 (6H, s, $2CH_3$). ^{13}C NMR (68 MHz, $CDCl_3$): δ 129.03 (C), 128.91 (C), 128.18 (CH), 128.03 (CH), 127.41 (CH), 127.33 (CH), 99.75 (C≡), 95.10 (C≡), 83.96 (C≡), 83.04 (C≡), 74.17 (CHO), 40.81 (CH_2), 31.02 (CH_2), 25.74 (CH_3), 19.40 (CH_2), 17.91 (C), −4.66 (CH_3), −4.69 (CH_3). Mass spectrum *m/z*: 310 (M^+, 0), 253 (M^+ − t-Bu, 100).

Preparation of Benzo[3,4]cyclodec-3-ene-1,5-diyne-8-ol (29). To a solution of **34** (0.080 g, 0.260 mmol) in THF (5 mL) at 0 °C was added 1 mol equiv of $(n\text{-}Bu)_4NF$ in THF (1.0 M). After the reaction mixture had been stirred for 30 min at 0 °C, the solvents were removed at aspirator vacuum and the residue was purified by column chromatography (silica gel; hexane/ethyl acetate, 3/1) to give as an oil **29** (0.044 g, 86%). Crystallization from hexane/chloroform produced colorless crystals of **29**, mp 83–84 °C. IR (KBr): 3362, 2957, 2905, 2218, 1469, 1429, 1060, 784, 736 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$): δ 7.18–7.32 (4H, m, 4ArH), 4.11–4.19 (1H, m, CHO), 2.58 (2H, d, J = 6.9 Hz, CH_2), 2.64 (1H, dd, J = 6.8, 3.0 Hz, C*H*H), 2.56 (1H, dd, J = 9.9, 3.0 Hz, C*H*H), 2.42 (1H, d, J = 7.8 Hz, OH), 2.23–2.30 (1H, m, C*H*H), 2.02–2.12 (1H, m, C*H*H). ^{13}C NMR (68 MHz, $CDCl_3$): δ 128.90 (C), 128.84 (C), 128.27 (CH), 128.06 (CH), 127.57 (CH), 127.41 (CH), 99.73 (Cxba≡), 94.15 (Cxba≡), 84.21 (Cxba≡), 83.45 (Cxba≡), 71.71 (CHO), 38.06 (CH_2), 30.89 (CH_2), 18.41 (CH_2). Mass spectrum *m/z*: 196 (M^+, 58), 152 (100).

Preparation of 2,3-Dibromo-1,4-naphthoquinone (38). Following a literature procedure,[23] the dibromoquinone **38** was obtained as yellow solid with mp 223–225 °C (CH_2Cl_2/acetone) (lit.[23] mp 218 °C). ^1H NMR (270 MHz, $CDCl_3$): δ 8.16 (2H, dd, J = 5.6, 3.3 Hz), 7.76 (2H, dd, J = 5.6, 3.3 Hz). ^{13}C NMR (68 MHz, $CDCl_3$): δ 175.80 (C=O), 142.55 (C), 134.49 (CH), 130.77 (C), 128.20 (CH). IR (KBr) 1675, 1265, 1125, 701. Mass spectrum *m/z*: 318 (M^+, 63, ^{81}Br, ^{81}Br), 235 (100).

Preparation of 2,3-Dibromo-1,4-dimethoxynaphthalene (39). To a stirred solution of **38** (1.300 g, 4.10 mmol) in ether/THF (70 mL each) was added dropwise over 10 min a solution of sodium dithionite (3.200 g, 15.00 mmol) in 40 mL of water. After the heterogeneous mixture was heated at reflux for 4 h, the organic layer was separated. With the organic layer at 0 °C, NaH (60%, 0.416 g, 10.25 mmol) was added, followed after 30 min by Me_2SO_4 (1.300 g, 10.25 mmol). The mixture was stirred for 15 h at 23 °C. It was poured into water, and the resulting mixture was extracted with ether. The organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by column chromatography (silica gel; hexane/ethyl acetate, 15/1) to give **39** as a colorless solid (1.007 g, 85%), mp 123–125 °C (hexane) (lit.[29] mp 123–125 °C). ^1H NMR (270 MHz, $CDCl_3$): δ 8.10 (2H, dd, J = 6.3, 3.3 Hz), 7.58 (2H, dd, J =

(29) Kabuto, K.; Imuta, M.; Kempter, E. S.; Ziffer, H. *J. Org. Chem.* **1978**, *43*, 2357.

6.6, 3.3 Hz), 3.98 (6H, s, $2CH_3$). ^{13}C NMR (68 MHz, $CDCl_3$): δ 151.10 (2C), 128.15 (2C), 127.36 (2CH), 122.69 (2CH), 116.12 ($2CH_3$), 61.41 ($2CH_3$). IR (KBr): 2968, 2937, 1553, 1456, 1441, 1354, 1079, 984, 761. Mass spectrum *m/z*: 348 (M^+, 63, ^{81}Br, ^{81}Br), 331 (100).

Preparation of 2,3-Bis[(trimethylsilyl)ethynyl]-1,4-dimethoxynaphthalene (40). To a mixture of (trimethylsilyl)acetylene (0.392 g, 4.00 mmol) and **39** (0.188 g, 0.54 mmol) in dry piperidine (15 mL) was added tetrakis(triphenylphosphine)palladium(0) (0.024 g, 0.02 mmol) and copper(I) iodide (0.008 g, 0.04 mmol). The mixture was stirred at 100 °C under argon for 15 h. The solvent was then removed under reduced pressure, and the residue was extracted into benzene. The organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. Purification on silica gel by flash chromatography with hexane/ethyl acetate (20/1) gave **40** as a yellow solid (0.162 g, 73%), mp 75–77 °C (hexane/chloroform). ^1H NMR (270 MHz, $CDCl_3$): δ 8.09 (2H, dd, J = 6.6, 3.3 Hz), 7.51 (2H, dd, J = 6.6, 3.3 Hz), 4.08 (6H, s, $2CH_3$), 0.32 (18H, s, 6 $SiCH_3$). ^{13}C NMR (68 MHz, $CDCl_3$): δ 155.46 (2C), 128.68 (2C), 127.48 (CH), 122.56 (2CH), 133.61 (2C), 103.73 (C≡C), 99.505 (C≡C), 61.41 ($2CH_3$), −0.02 (2 $SiCH_3$). IR (KBr): 2960, 2932, 2151, 1454, 1356, 1249, 1055, 853, 842, 760 cm^{-1}. Mass spectrum *m/z*: 380 (M^+, 100).

Preparation of 2,3-Diethynyl-1,4-dimethoxynaphthalene (41). A solution of **40** (0.162 g, 0.40 mmol), KF (0.200 g, 3.45 mmol), and water (1 mL) in dimethylformamide (10 mL) was stirred at 23 °C for 4 h and then poured onto ice (20 g). The mixture was then was extracted with CH_2Cl_2, and the organic solution was washed with water, dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by column chromatography (silica gel; hexane/ethyl acetate, 20/1) to give **41** (0.081 g, 87%), mp 101–102 °C (hexane/chloroform). ^1H NMR (270 MHz, $CDCl_3$): δ 8.11 (2H, dd, J = 6.6, 3.3 Hz), 7.56 (2H, dd, J = 6.6, 3.3 Hz), 4.07 (6H, s, $2CH_3$), 3.61 (2H, s, C≡C*H*). ^{13}C NMR (68 MHz, $CDCl_3$): δ 155.81 (2C), 128.74 (2C), 127.71 (2CH), 122.58 (2CH), 112.82 (2C), 85.80 (C≡*C*H), 78.24 (*C*≡CH), 61.79 ($2OCH_3$). IR (KBr): 3281, 3266, 1574, 1458, 1355, 1094, 770 cm^{-1}. Mass spectrum *m/z*: 236 (M^+, 100). HRMS: calcd for $C_{16}H_{12}O_2$ 236.08378, found 236.0834.

Preparation of 1,4-Dimethoxynaphtho[3,4-*b*]cyclodec-3-ene-1,3-diyne (43). Compound **41** (0.062 g, 0.26 mmol) was dissolved in 10 mL of dry THF and cooled to −78 °C. n-BuLi (2.1 mol equiv) was added over a period of 30 min. The reaction mixture was stirred for an additional 1 h at −78 °C. Then 1,4-diiodobutane (0.090 g, 0.29 mmol) was added dropwise over a period of 15 min. The mixture was allowed to warm to 23 °C and stirred for 48 h. The mixture was quenched with water and extracted with ether. The organic solution was dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was chromatographed over silica gel with hexane/ethyl acetate (10/1) to give **43** as a white solid (0.033 g, 44%), mp 145–146 °C (hexane/chloroform). ^1H NMR (270 MHz, $CDCl_3$): δ 8.09 (2H, dd, J = 6.3, 3.3 Hz), 7.50 (2H, dd, J = 6.3, 3.3 Hz), 4.12 (6H, $2CH_3$), 2.01–2.55 (4H, m, $2CH_2$), 1.96–2.01 (4H, m, $2CH_2$). ^{13}C NMR (68 MHz, $CDCl_3$): δ 151.73 (2C), 128.12 (2C), 126.78 (2CH), 122.53 (2CH), 116.18 (2C), 103.54 (C≡C), 78.82 (C≡C), 61.65 ($2CH_3$), 28.47 ($4CH_2$), 21.95 ($2CH_2$). IR (KBr): 2947, 2914, 2217, 1587, 1455, 1440, 1353, 1074, 999, 774 cm^{-1}. Mass spectrum *m/z*: 290 (M^+, 24). HRMS: calcd for $C_{20}H_{18}O_2$ 290.1307, found 290.1304.

Preparation of 1,4-Dihydro-1,4-dioxonaphtho[3,4-*b*]-cyclodec-3-ene-1,5-diyne (37). To a solution of **43** (0.072 g, 0.25 mmol) in CH_3CN (3 mL) was added a solution on CAN [cerium(IV) ammonium nitrate] (1.100 g, 2.00 mmol) in water (3 mL).[25] After being stirred for 30 min at 23 °C, the mixture was extracted with CH_2Cl_2. The organic solution was concentrated in vacuo to give **37** as a yellow-brown solid (0.051 g, 73%), mp > 300 °C (darkens above 100 °C). ^1H NMR (270 MHz, $CDCl_3$): δ 8.07 (2H, dd, J = 5.6, 3.3 Hz), 7.71 (2H, dd, J = 5.6, 3.3 Hz), 2.54–2.58 (4H, m, $2CH_2$), 1.94–1.98 (4H, m, $2CH_2$). ^{13}C NMR (68 MHz, $CDCl_3$): δ 180.61 (2C=O), 139.51 (2C), 133.99 (2CH), 131.59 (2C), 126.89 (2CH), 116.26 (2C≡*C*), 80.13 (2C≡*C*), 28.19 ($4CH_2$), 22.53 ($2CH_2$). IR (KBr): 2942, 2932, 2190, 1666, 1595, 1369, 1323, 1301, 1204, 1006, 712 cm^{-1}. Mass spectrum *m/z*: 262 (M^+, 2.93), 260 (M^+, 100).

Preparation of 2-(3,4-Dibromobenzoyl)benzoic Acid (44). To 20.00 g (84.77 mmol) of *o*-dibromobenzene was added 6.28 g (47.00 mmol) of dry aluminum chloride. Then 3.14 g (21.19 mmol) of phthalic anhydride was added slowly, and the reaction mixture was heated to 90 °C for 1.5 h (until HCl evolution ceased). The solution was poured into ice-cold 1.0 M HCl solution and filtered. The residue was dissolved in 100 mL of 1 M of NaOH. The water layer was separated and poured into cold dilute sulfuric acid. The colorless precipitate was filtered and recrystallized from ethanol to give **44** (7.500 g, 92%), mp 186–188 °C (ethanol). ^1H NMR (270 MHz, acetone-d_6): δ 7.4–7.95 (m, 7H, ArH), 8.08 (s, 1H, COOH). IR (KBr) 3429, 3064, 2096, 2879, 2842, 2677, 2554, 1676, 1571, 1425, 1301, 1286, 941, 930, 773 cm^{-1}. Mass spectrum *m/z*: 386 (M^+, 5, ^{81}Br, ^{81}Br).

Preparation of 2,3-Dibromo-9,10-anthraquinone (45). Compound **44** (3.00 g, 7.82 mmol) was added to a mixture of 96% sulfuric acid and 4.46 g (24%) of oleum. The solution was heated to 115 °C for 90 min, poured into ice–water, and filtered. The filtrate was recrystallized from acetone/CH_2Cl_2 (1/1) to give **45** as a light yellow solid (1.96 g, 69%), mp 279–281 °C (acetone/CH_2Cl_2) (lit.[23] 278–279 °C). ^1H NMR (270 MHz, $CDCl_3$): δ 8.51 (2H, s, ArH), 8.30 (2H, dd, J = 5.93, 3.3 Hz), 7.82 (2H, dd, J = 5.93, 3.3 Hz). IR (KBr) 1676, 1327, 1298, 1282, 1269, 71 cm^{-1}. ^{13}C NMR (68 MHz, $CDCl_3$): δ 181.49 (2C=O), 134.63 (2CH), 133.11 (2C), 132.75 (2C), 132.48 (2CH), 132.18 (2C), 127.48 (2CH). Mass spectrum *m/z*: 368 (M^+, 33, ^{81}Br, ^{81}Br).

Preparation of 2,3-Dibromo-9,10-dimethoxyanthracene (46). To a stirred solution of **45** (2.000 g, 5.47 mmol) in ether/THF (100 mL each) was added dropwise a solution of sodium dithionite (2.860 g, 16.40 mmol) diluted in 50 mL of water. After being heated under reflux for 4 h, the organic layer was separated and cooled to 0 °C. Then NaH (60%, 0.570 g, 13.67 mmol) was added, and the mixture was stirred for 30 min. Dimethyl sulfate (1.733 g, 13.67 mmol) was added, and the mixture was stirred for 15 h at 23 °C. The reaction was quenched with water and extracted with ether. The organic solution was dried over Na_2SO_4 and filtered, and the solvents were removed in vacuo. The residue was purified by column chromatography (silica gel, hexane/ethyl acetate, 15/1) to give **46** as a yellow solid (1.780 g, 83%), mp 159–161 °C (hexane/chloroform). ^1H NMR (270 MHz, $CDCl_3$): δ 8.57 (2H, s, 2CH), 8.24 (2H, dd, J = 6.6, 3.3 Hz), 7.52 (2H, dd, J = 6.6, 3.3 Hz), 4.08 (6H, s, $2CH_3$). ^{13}C NMR (68 MHz, $CDCl_3$): δ 147.75 (2C), 127.24 (2CH), 126.21 (2CH), 125.75 (2C), 124.08 (2C), 122.66 (2CH), 121.99 (2C), 63.58 ($2CH_3$). IR (KBr) 1459, 1365, 1310, 1074, 972, 876, 769, 697 cm^{-1}. Mass spectrum *m/z*: 398 (M^+, 8, ^{81}Br, ^{81}Br), 301 (100).

Preparation of 2,3-Bis[(trimethylsilyl)ethynyl]-9,10-dimethoxyanthracene (47). To a mixture of (trimethylsilyl)-acetylene (0.372 g, 3.80 mmol) and compound **46** (0.500 g, 1.26 mmol) in dry piperidine (30 mL) was added tetrakis(triphenylphosphine)palladium(0) (0.029 g, 0.02 mmol) and copper(I) iodide (0.007 g, 0.04 mmol). The reaction mixture was stirred at 65 °C under argon for 15 h. The solvent was removed under reduced pressure, and the residue was extracted into benzene. The organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. Purification on silica gel by flash chromatography with hexane/ethyl acetate (15/1) gave **47** as a yellow solid (0.387 g, 71%), mp 192–193 °C (hexane/chloroform). ^1H NMR (270 MHz, $CDCl_3$): δ 8.42 (2H, s, ArH), 8.24 (2H, dd, J = 6.9, 3.3 Hz), 7.49 (2H, dd, J = 6.9, 3.3 Hz), 4.09 (6H, s, $2CH_3$), 0.31 (18H, s, $9CH_3$). ^{13}C NMR (68 MHz, $CDCl_3$): δ 148.35 (2C), 127.77 (2CH), 126.09 (4C, 2C, 2CH), 123.19 (2C), 122.81 (2CH), 121.01 (2C), 103.83 (2C≡C), 98.23 (2C≡C), 63.64 ($2CH_3$), 0.11 ($6CH_3$). IR (KBr) 2956, 2152, 1451, 1368, 1248, 1064, 858, 842, 759 cm^{-1}. Mass spectrum *m/z*: 430 (M^+, 3.8), 319 (100).

Preparation of 2,3-Diethynyl-9,10-dimethoxyanthracene (48). A solution of **47** (0.387 g, 0.90 mmol), KF (0.078 g, 1.35 mmol), and water (2 mL) in dimethylformamide (50 mL) was stirred at 23 °C for 4 h. The mixture was poured onto ice (50 g) and extracted with CH_2Cl_2. The organic solution was

washed with water, dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by column chromatography (silica gel, hexane/ethyl acetate, 20/1) to give **48** (0.223 g, 87%), mp 136–138 °C (hexane–CH_2Cl_2). ^1H NMR (270 MHz, $CDCl_3$): δ 8.50 (2H, s), 8.28 (2H, dd, J = 7.0, 3.3 Hz), 7.54 (2H, dd, J = 7.0, 3.3 Hz), 4.11 (6H, s, $2CH_3$), 3.40 (2H, s, C≡C*H*). ^{13}C NMR (68 MHz, $CDCl_3$): δ 148.37 (2C), 128.34 (2CH), 126.28 (2CH), 126.22 (2C), 123.12 (2C), 122.80 (2CH), 119.99 (2C), 82.44 (*C*≡CH), 77.46 (OC≡*C*H), 63.61 ($2CH_3$). IR (KBr): 3287, 3274, 2099, 1451, 1363, 1317, 1081, 972, 766, 708, 615 cm^{-1}. Mass spectrum *m/z*: 286 (M^+, 41), 256 (100). HRMS: calcd for $C_{20}H_{24}O_2$ 286.0994, found 286.0996.

Preparation of 9,10-Dimethoxyanthro[3,4-*b*]cyclodec-3-ene-1,5-diyne (49). To a solution of **48** (0.452 g, 1.58 mmol) in 60 mL of dry THF at −78 °C was added 2.1 mol equiv of n-BuLi over 30 min. The reaction mixture was stirred for an additional hour at this temperature. Then 1,4-diiodobutane (0.558 g, 1.80 mmol) was added dropwise over a period of 15 min. The reaction mixture was allowed to warm to 23 °C, stirred for 48 h, and then quenched with water and extracted with ether. The organic solution was dried over Na_2SO_4, filtered, and chromatographed over silica gel with hexane/ethyl acetate (10/1) to give **49** as a yellow solid (0.333 g, 62%), mp 156–158 °C (hexane/CH_2Cl_2). ^1H NMR (270 MHz, $CDCl_3$): δ 8.25 (2H, s, 2CH), 8.24 (2H, dd, J = 6.6, 3.3 Hz), 7.48 (2H, dd, J = 6.6, 3.3 Hz), 4.08 (6H, s, $2CH_3$), 2.51–2.55 (4H, m, $2CH_2$), 1.98–2.02 (4H, m, $2CH_2$). ^{13}C NMR (68 MHz, $CDCl_3$): δ 148.30 (2C), 125.78 (2CH), 125.69 (2C), 124.64 (2C), 123.24 (2C), 122.64 (2CH), 22.36 (2CH), 100.13 (2C≡C), 82.51 (2C≡C), 63.36 ($2CH_3$), 28.49 ($2CH_2$), 21.65 ($2CH_2$). IR (KBr): 2942, 2226, 2206, 1618, 1456, 1367, 1310, 1070, 973, 768 cm^{-1}. Mass spectrum *m/z*: 340 (M^+, 45), 325 (100). HRMS: calcd for $C_{24}H_{20}O_2$ 340.1464, found 340.1463.

Preparation of 9,10-Dihydro-9,10-dioxoanthro[3,4-*b*]-cyclodec-3-ene-1,5-diyne (53). To a solution of **49** (0.115 g, 0.34 mmol) in CH_3CN (3 mL) was added a solution on CAN [cerium(IV) ammonium nitrate] (1.100 g, 2.00 mmol) in water (3 mL). After being stirred for 30 min at 23 °C, the mixture was extracted with CH_2Cl_2. The organic solution was dried, filtered, and concentrated in vacuo to give **53** as a white solid (0.049 g, 47%), mp > 300 °C (darkens above 100 °C). ^1H NMR (270 MHz, $CDCl_3$): δ 8.28 (2H, dd, J = 6.0, 3.3 Hz), 8.17 (s, 2 H), 7.77 (2H, dd, J = 6.0, 3.3 Hz), 2.49–2.51 (4H, m, $2CH_2$), 1.95–1.99 (4H, m, $2CH_2$). ^{13}C NMR (68 MHz, $CDCl_3$): δ 182.19 (2C=O), 135.18 (2C), 134.08 (2CH), 133.48 (2C), 131.81 (2C), 127.20 (2CH), 126.40 (2CH), 105.25 (2C≡C), 81.75 (2C≡*C*), 28.25 ($2CH_2$), 21.68 ($2CH_2$). IR (KBr): 3252, 2941, 2927, 2208, 1673, 1586, 1336, 1307, 1247, 938, 713. Mass spectrum *m/z*: 310 (M^+, 100). HRMS: calcd for $C_{22}H_{14}O_2$ 310.0994, found 310.0981.

Formation of Dimer 50. Dimer **50** was obtained when compound **48** was heated neat at 80 °C under argon, and recrystallization from hexane gave light yellow crystals, mp 156–158 °C. IR (KBr): 3278, 3254, 2956, 2109, 2102, 1461, 1304, 1048, 754, 633 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$): δ 7.74 (2H, s, 2ArH), 7.47 (2H, dd, J = 6.5, 3.2 Hz, 2ArH), 7.22 (2H, dd, J = 6.5, 3.2 Hz, 2ArH), 3.96 (6H, s, $2CH_3$), 3.34 (2H, s, 2CH×ba≡). ^{13}C NMR (68 MHz, $CDCl_3$): δ 138.91 (C), 137.85 (C), 127.82 (CH), 124.77 (C), 124.73 (CH), 124.41 (C), 120.92 (CH), 101.72 (C), 81.87 (C×ba≡), 81.44 (C×ba≡), 54.30 (CH_3). The EI and CI mass spectra were superimposable with monomer **48**.

Oxidative Dedimerization of 50 To Give 52. An unstable compound (**52**) was obtained when dimer **50** was heated in the presence of oxygen; it showed mp > 300 °C (darkens above 100 °C). R_f (hexane/ethyl acetate, 5/1): 0.56. IR (mull): 2106, 1674, 1587, 1332, 1315, 1290 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$): δ 8.44 (2H, s, 2ArH), 8.32 (2H, dd, J = 6.6, 3.2 Hz, 2ArH), 7.83 (2H, dd, J = 6.6, 3.2 Hz, 2ArH), 3.16 (2H, s, C≡CH). Mass spectrum *m/z*: 256 (M^+, 5), 188 (100).

Thermal Rearrangements of the Cyclic Arene–*o*-Dialkynyl Derivatives. General Procedure. The arene–*o*-dialkyne (0.1 mmol) was dissolved in 1.0 mL of deuteriobenzene in a 5-mm NMR tube. The relevant amount of 1,4-cyclohexadiene (Aldrich; redistilled) or other trapping agent was added, and the mixture was placed under argon by a series of freeze–pump–thaw cycles using an oil pump vacuum. The tube was then sealed with a flame and heated as described. The disappearance of characteristic starting material signals and the appearance of product signals were monitored by ^1H NMR. After the reaction was complete, the tube was opened and the products were isolated by chromatography.

(a) 3,4-Benzocyclodec-3-ene-1,5-diyne (6) with 1,4-CHD. The reaction mixture was heated at 84 °C (reflux of t-BuOH). Half-lives for the disappearance of **6** were 129 h (0 equiv of cyclohexadiene), 39 h (2.5 equiv of cyclohexadiene), and 24 h (5.0 equiv of cyclohexadiene). When the reaction was carried out in neat 1,4-cyclohexadiene, the $t_{1/2}$ was found to be 10.5 h. The solvents were removed in vacuo, and the residue was purified by column chromatography (silica gel–hexane) to give **12** [11% (0 equiv of 1,4-CHD), 83% (2.5 equiv of 1,4-CHD), 87% (5.0 equiv of 1,4-CHD), and 88% (neat 1,4-CHD)], mp 102–104 °C (pentane) (lit.[28] mp 103–105 °C). ^1H NMR (270 MHz, $CDCl_3$): δ 7.69 (2H, dd, J = 6.2, 3.3 Hz), 7.52 (s, 2 H), 734 (2H, dd, J = 6.2, 3.3 Hz), 2.97–2.94 (4H, m, $2CH_2$), 1.82–1.87 (m, 4H, $2CH_2$). ^{13}C NMR (68 MHz, $CDCl_3$): δ 136.21 (2C), 132.21 (2C), 126.97 (2CH), 126.62 (2CH), 124.87 (2CH), 29.78 ($2CH_2$), 23.38 ($2CH_2$). IR (KBr): 3049, 3005, 2927, 2856, 1500, 862, 742 cm^{-1}. Mass spectrum *m/z*: 182 (M^+, 100).

(b) 3,4-Benzocyclodec-3-ene-1,5-diyne (6) with CCl_4. Compound **6** (0.018 g, 0.10 mmol) was dissolved in 1 mL of deuteriobenzene. To this solution was added CCl_4 (0.038 g, 0.25 mmol), and the mixture was placed in an NMR tube. The sample was heated at 84 °C and monitored by ^1H NMR. The $t_{1/2}$ was 12 h. After 24 h, the usual isolation procedure gave **17** (32%), **15** (34%), and **12** (22%). When the reaction was carried out at 150 °C, **13** was found as the only isolable product (61%).

Characterization of 17. Mp: 154–156 °C (hexane). ^1H NMR (270 MHz, $CDCl_3$): δ 8.27 (2H, dd, J = 6.6, 3.3 Hz), 7.54 (2H, dd, J = 6.6, 3.3 Hz), 2.99–3.04 (4H, m, $2CH_2$), 1.81–1.88 (4H, m, $2CH_2$). ^{13}C NMR (68 MHz, $CDCl_3$): δ 134.58 (2C), 130.14 (2C), 129.97 (2O*C*), 126.72 (2CH), 124.38 (2CH), 29.00 ($2CH_2$), 22.55 ($2CH_2$). IR (KBr): 2935, 2863, 1487, 1426, 1305, 1251, 909, 751 cm^{-1}. Mass spectrum *m/z*: 250 (M^+, 100, ^{35}Cl, ^{35}Cl).

Characterization of 15. Mp: 87–88 °C (hexane). ^1H NMR (270 MHz, $CDCl_3$): δ 7.74 (1H, d, J = 8.2 Hz, 1ArH), 7.59 (1H, s, 1ArH), 7.22–7.36 (3H, m, 3ArH), 3.02 (2H, t, J = 5.8 Hz, CH_2), 2.55 (2H, t, J = 5.6 Hz, CH_2), 1.73–1.82 (4H, m, $2CH_2$). ^{13}C NMR (68 MHz, $CDCl_3$): δ 139.92 (C), 138.04 (C), 136.03 (C), 133.76 (C), 131.82 (C), 131.46 (C), 130.11 (CD, t), 128.40 (CH, CD, t), 126.98 (CH), 126.86 (CD, t), 126.48 (CH), 125.93 (CH), 124.79 (CH), 30.49 (CH_2), 28.65 (CH_2), 23.45 (CH_2), 22.94 (CH_2). IR (KBr): 3049, 2927, 2856, 1500, 862, 742 cm^{-1}. Mass spectrum *m/z*: 265 (M + 2, 11.5), 264 (M + 1, 59), 263 (M^+, 100), 262 (M − 1, 15), 261 (M − 2, 8).

(c) 3,4-Benzocyclodec-3-ene-1,5-diyne (6) with CBr_4. Compound **6** (0.018 g, 0.10 mmol) was dissolved in 1 mL of deuteriobenzene, and to this solution was added CBr_4 (0.830 g, 0.25 mmol). The sample was placed in an NMR tube and heated at 84 °C. The starting material was completely converted in less than 6 h to **14** and a mixture of other products, among them **15**. The usual isolation procedure gave a mixture of **14** (20%) and **15** (45%). When the reaction was carried out at 150 °C, **14** was found as the only isolable product (57%).

Characterization of 14. Mp: 166–168 °C (hexane) (lit.[27] mp 165–166 °C). ^1H NMR (270 MHz, $CDCl_3$): δ 8.30 (2H, dd, J = 6.6, 3.3 Hz), 7.52 (2H, dd, J = 6.6, 3.3 Hz), 3.00–3.05 (4H, m, $2CH_2$), 1.82–1.87 (4H, m, $2CH_2$). ^{13}C NMR (68 MHz, $CDCl_3$): δ 137.09 (2C), 131.72 (2C), 127.30 (2CH), 127.07 (2CH), 125.25 (2C), 32.73 ($2CH_2$), 23.03 ($2CH_2$). IR (KBr): 2934, 2926, 2859, 1423, 1242, 902, 748 cm^{-1}. Mass spectrum *m/z*: 342 (M^+, 21, ^{81}Br, ^{81}Br), 180 (100).

In order to support the structure of compound **15**, the reaction was carried out in C_6H_6 instead of C_6D_6 at 84 °C which led to **14** (23%) and 1,2,3,4-tetrahydro-9-phenylanthracene **16** (31% yield), mp: 86–88 °C (hexane) (lit.[28] mp 82–84 °C). ^1H NMR (270 MHz, $CDCl_3$): δ 7.74 (1H, d, J = 8.2 Hz, 1ArH),

7.59 (1H, s, 1ArH), 7.18–7.53 (8H, m, 8ArH), 3.02 (2H, t, J = 5.8 Hz, CH_2), 2.55 (2H, t, J = 5.6 Hz, CH_2), 1.73–1.82 (4H, m, $2CH_2$).

(d) Compound 20. A sample of **20** (0.020 g, 0.102 mmol) was dissolved in 1 mL of deuteriobenzene. To this solution was added 1,4-cyclohexadiene (0.040 g, 0.500 mmol), and the sample was placed in an NMR tube. At 84 °C, the reaction was monitored by ^{1}H NMR. The $t_{1/2}$ was found to be 4.5 h. The solvents were evaporated and the residue purified by column chromatography (silica gel, hexane/ethyl acetate, 3/1) to give **27** (0.018 g, 90%), mp 84–85 °C (hexane/chloroform) (lit.[29] mp 83–84 °C). ^{1}H NMR (270 MHz, C_6D_6): δ 7.91 (1H, s, 1ArH), 7.75–7.79 (1H, m, 1ArH), 7.70–7.73 (1H, m, 1ArH), 7.55 (1H, s, 1ArH), 7.35–7.43 (2H, m, 2ArH), 4.96 (1H, dd, J = 5.61, 4.69 Hz), 2.90–3.05 (2H, m, CH_2), 1.69–2.12 (5H, m, $2CH_2$, OH).

(e) Compound 21. Compound **21** (0.020 g, 0.103 mmol) was dissolved in 1 mL of deuteriobenzene. To this solution was added 1,4-cyclohexadiene (0.040 g, 0.500 mmol), and the sample was heated in an NMR tube. The $t_{1/2}$ at 40.0 °C was found to be 57 h. The solvents were evaporated, and the residue was purified by column chromatography (silica gel, hexane/ethyl acetate, 5/1) to give **28** (0.015 g, 75%), mp 92–93 °C (hexane/chloroform) (lit. mp 90–91 °C). ^{1}H NMR (270 MHz, C_6D_6): δ 8.59 (1H, s, 1ArH), 7.93 (1H, d, J = 8.58 Hz, 1ArH), 7.77 (1H, d, J = 7.98 Hz, 1ArH), 7.67 (1H, s, 1ArH), 7.53 (1H, dt, J = 6.6, 1.3 Hz, 1ArH), 7.44 (1H, dt, J = 6.6, 1.3 Hz, 1ArH), 3.11 (2H, t, J = 5.9 Hz, CH_2), 2.74 (2H, t, J = 6.2, CH_2), 2.14–2.20 (2H, m, CH_2).

(f) Compound 29. Compound **29** (0.020 g, 0.102 mmol) was dissolved in 1 mL of deuteriobenzene. To this solution was added 1,4-cyclohexadiene (0.040 g, 0.500 mmol), and the sample was sealed in an NMR tube. The reaction mixture was heated at 84 ° C. The $t_{1/2}$ was found to be 14 h. The solvents were evaporated, and the residue was purified by column chromatography (silica gel, hexane/ethyl acetate, 3/1) to give **36** (0.017 g, 84%), mp 140–142 °C (hexane/chloroform) (lit. mp 144–146 °C).

(g) Compound 43. Compound **43** (0.029 g, 0.10 mmol) was dissolved in 1 mL of deuteriobenzene, and 1,4-cyclohexadiene (0.040 g, 0.500 mmol) was added. The sample was sealed in an NMR tube under argon. The mixture was heated at 84 °C (reflux of t-BuOH) for 16 h. There was no change. Then the sample was heated at 200 °C. At this temperature, an intractable mixture was obtained with 100% conversion with detectable cyclization product.

(h) Compound 49. Compound **49** (0.034 g, 0.10 mmol) was dissolved in 1 mL of deuteriobenzene, and 1,4-cyclohexadiene (0.040 g, 0.500 mmol) was added. The sample was sealed under argon and heated at 84 °C (reflux of t-BuOH) for 16 h. There was no change. Then the sample was heated at 200 °C. At this temperature, no cyclization products were detected after 24 h. Instead, a mixture of decomposition products was obtained, among them pentacenequinone derivative (**54**) (17%), mp 257–259 °C (hexane/chloroform). IR (KBr): 2931, 2919, 2862, 1672, 1585, 1454, 1407, 1321, 1284, 1234, 967, 716 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$): δ 8.70 (2H, s, ArH), 8.36 (2H, dd, J = 5.6, 3.3 Hz), 7.79 (2H, dd, J = 5.6, 3.3 Hz), 7.76 (2H, s, ArH), 2.98–3.01 (4H, m, $2CH_2$), 1.85–1.90 (4H, m, $2CH_2$). ^{13}C NMR (67.9 MHz, $CDCl_3$): δ 183.16 (2C=O), 140.94 (2C), 134.66 (2C), 133.96 (2CH), 133.70 (2CH), 129.09 (2CH), 128.88 (2C, 2CH), 127.41 (2CH), 29.85 ($2CH_2$), 22.88 ($2CH_2$). Mass spectrum m/z: 312 (M^+, 17.6).

(i) Cyclization of 1,2,3,4-Tetrahydro-6,11-naphthacenequinone (37). Compound **37** (0.026 g, 0.10 mmol) was dissolved in 1 mL of deuteriobenzene, and 1,4-cyclohexadiene (0.040 g, 0.500 mmol) was added. The mixture was sealed in an NMR tube under argon, and the mixture was heated at 40 °C. The reaction was monitored by ^{1}H NMR. The $t_{1/2}$ was 88 h. The usual isolation procedure gave **55** (0.027 g, 79%), mp 209–211 °C (hexane/chloroform). IR (KBr): 2932, 2861, 1677, 1590, 1333, 1290, 960, 715 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$): δ 8.27 (2H, dd, J = 5.6, 3.3 Hz), 7.96 (2H, s, CH), 7.75 (2H, dd, J = 5.6, 3.3 Hz), 2.89–2.93 (4H, m, $2CH_2$), 1.82–1.87 (4H, m, $2CH_2$). ^{13}C NMR (68 MHz, $CDCl_3$): δ 183.33 (2C=O), 144.64 (2C), 133.83 (2CH), 133.77 (2C), 131.02 (2C), 131.02 (2C), 127.93 (2C), 127.08 (2C), 29.83 ($4CH_2$), 22.56 ($2CH_2$). Mass spectrum m/z: 262 (M^+, 100). HRMS: calcd for $C_{18}H_{14}O_2$ 262.09944, found 262.0994.

(j) 1,2,3,4-Tetrahydro-7,12-pentacenequinone (54). Compound **53** (0.031 g, 0.10 mmol) was dissolved in 1 mL of deuteriobenzene, and 1,4-cyclohexadiene (0.40 g, 0.500 mmol) was added. The sample was sealed in an NMR tube and was heated at 84 °C. The reaction was monitored by ^{1}H NMR. The $t_{1/2}$ was 15 h. After 5 d, the usual isolation procedure gave **54** (0.021 g, 82%).

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Supplementary Material Available: Photocopies of the ^{1}H NMR spectra for compounds **10**, **17**, **37**, **43**, **49**, **53**, **54**, and **55** (8 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.