# An Efficient Synthesis of Functionalized Helicenes

**Thomas J. Katz,*,† Longbin Liu,† Nikolaos D. Willmore,† Joseph M. Fox,† Arnold L. Rheingold,*,‡ Shuhao Shi,† Colin Nuckolls,† and Barry H. Rickman†**

*Contribution from The Department of Chemistry, Columbia University, New York, New York 10027, and Department of Chemistry and Biochemistry, University of Delaware, Newark, Delaware 19716*

*Received June 26, 1997*[⊗]

**Abstract:** [5]- and [6]helicenebisquinones can be prepared easily and in quantity by combining enol ethers of 1,4-diacetylbenzene or 2,7-diacetylnaphthalene with *p*-benzoquinone. Similar diethenyl aromatics that either have no ether functions or have them attached not to the double bonds, but to the aromatic rings, give the corresponding helicenes in only low yields and low purities. [6]Helicenebisquinone **11c** is resolved into its enantiomers. An X-ray diffraction analysis of the adduct of one of these enantiomers and L-prolinol shows the absolute stereochemistry of **11c** and the regiochemistry with which the amine adds to the quinone.

## Introduction

Helicenes, helical molecules comprised of ortho-fused aromatic rings, have been known for almost 100 years. The first, a diaza[5]helicene (3,4-diazadibenzo[*c*,*g*]phenanthrene), was prepared in 1903.[1] The parent [5]helicene was made 30 years later,[2] and [6]helicene, the first to be obtained in nonracemic form, was prepared in 1955.[3] Following the discovery that helicenes could be made by photocyclizing stilbenes,[4] many examples of helicenes whose rings are benzenes or thiophenes were prepared by this method.[5] A few others were prepared by procedures that do not use light.[1−3,6]

However before the examples described here and in earlier communications from our lab were synthesized,[7] almost all helicenes lacked reactive functionality that might be used to transform the molecules into useful materials.[8] Moreover, few had been made in appreciable amounts.[9] The problem of making helical conjugated molecules with useful functional groups easily and in quantity was, therefore, considered and a solution found that is presented here: to combine the bis-enol ethers of aryl methyl ketones with *p*-benzoquinone.[10]

The work builds on a procedure for synthesizing a [5]-helicenebisquinone, summarized in eq 1,[7b] that is significant because it is simple and because from inexpensive reagents and in appreciable amounts it provides a helicene possessing versatile reactive functionality. However, a defect of this helicene is its thermal instability. While the nonracemic material is sufficiently stable that the half-life for racemization at 25 °C is ca. 6 years, heating to only 75 °C decreases the half-life to 1 h.[7b] The next higher, [6]helicenebisquinone, **3**,[11] should be more stable to thermal racemization.[12,13] But to synthesize it by an analogous procedure requires *p*-benzoquinone to be combined with 2,7-diethenylnaphthalene (eq 2). A low yield, while inconsequential in the case of eq 1, would be a serious drawback in this case, for 2,7-diethenylnaphthalene is expensive to prepare. A low yield could similarly impede the synthesis of *derivatives* of [5]-helicenebisquinone **1** in quantity because derivatives of 1,4-diethenylbenzene are also not easily available. The experiments below surmount these problems and provide an expeditious way to prepare derivatives of [5]- and [6]helicenebisquinones in significant amounts.

## Results

**Synthesis of 3.** The synthesis of **3** according to eq 2, using **2** and 12 mol of *p*-benzoquinone either in refluxing toluene with

† Columbia University.

‡ University of Delaware.

⊗ Abstract published in *Advance ACS Abstracts,* October 15, 1997.

(1) Meisenheimer, J.; Witte, K. *Chem. Ber.* **1903**, *36*, 4153 (by the reductive cyclization of 2-nitronaphthalene).

(2) Cook, J. W. *J. Chem. Soc.* **1933**, 1592 (by a Pschorr cyclization).

(3) Newman, M. S.; Lednicer, D. *J. Am. Chem. Soc.* **1956**, *78*, 4765 (by a Friedel−Crafts acylation and the resolution of a charge-transfer complex).

(4) Flammang-Barbieux, M.; Nasielski, J.; Martin, R. H. *Tetrahedron Lett.* **1967**, 743.

(5) (a) Laarhoven, W. H.; Prinsen, W. J. *Top. Curr. Chem.* **1984**, *125*, 63. (b) Mallory, F. B.; Mallory, C. W. *Organic Reactions*; Wiley: New York, 1984; Vol. 30, p 1. (c) Meurer, K. P.; Vögtle, F. *Top. Curr. Chem.* **1985**, *127*, 1. (d) Wynberg, H. *Acc. Chem. Res.* **1971**, *4*, 65. (e) Vögtle, F. *Fascinating Molecules in Organic Chemistry*; Wiley & Sons: New York, 1992; p 156. (f) Larsen, J.; Bechgaard, K. *Acta Chem. Scand.* **1996**, *50*, 77, and references therein.

(6) See footnote 12 in ref 7b. In addition, stilbene cyclizations: (a) Staab; H. A.; Diehm, M.; Krieger, C. *Tetrahedron Lett.* **1994**, *35*, 8357. (b) Larsen, J.; Bechgaard, K. *J. Org. Chem.* **1996**, *61*, 1151. (c) Laatsch, H.; Talvitie, A.; Kral, A.; Ernst, B.-P.; Noltemeyer, M. *J. Prakt. Chem.* **1996**, *338*, 140. Biaryl couplings: (d) Tanaka, K; Suzuki, H.; Osuga, H. *J. Org. Chem.* **1997**, *62*, 4465, and references therein. (e) Pereira, D. E.; Neelima; Leonard, N. J. *Tetrahedron* **1990**, *46*, 5895. (f) Pischel, I.; Grimme, S.; Kotila, S.; Nieger, M.; Vögtle, F. *Tetrahedron Asymmetry* **1996**, *7*, 109. The trimerization of 9,10-dichlorophenanthrene: (g) Carey, J. G.; Millar, I. T. *J. Chem. Soc.* **1959**, 3144. Diels−Alder additions to tetrahydro-1,1′-binaphthyl: (h) Minuti, L.; Taticchi, A.; Marrocchi, A.; Gacs-Baitz, E. *Tetrahedron* **1997**, *53*, 6873. (i) Altman, Y.; Ginsburg, D. *J. Chem. Soc.* **1959**, 466, and references therein.

(7) (a) Yang, B.; Liu, L.; Katz, T. J.; Liberko, C. A.; Miller, L. L. *J. Am. Chem. Soc.* **1991**, *113*, 8993. (b) Liu, L.; Katz, T. J. *Tetrahedron Lett.* **1990**, *31*, 3983.

(8) For the few functionalized examples known until recently, see footnote 4 of ref 7b. In addition, pyridine-containing helicenes: (a) Reference 6a. (b) Bell, T. W.; Jousselin, *J. Am. Chem. Soc.* **1991**, *113*, 6283. (c) Deshayes, K.; Broene, R. D.; Chao, I.; Knobler, C. B.; Diederich, F. *J. Org. Chem.* **1991**, *56*, 6787. Helicenecarboxylic acid derivatives: (d) Owens, L.; Thilgen, C.; Diedrich, F.; Knobler, C. B. *Helv. Chim. Acta* **1993**, *76*, 2757. (e) Frimer, A. A.; Kinder, J. D.; Youngs, W. J.; Meador, M. A. B. *J. Org. Chem.* **1995**, *60*, 1658. A phosphine: (f) Terfort, A.; Görls, H.; Brunner, H. *Synthesis* **1997**, 79. (g) Reetz, M. T.; Beuttenmüller, E. W.; Goddard, R. *Tetrahedron Lett.* **1997**, *38*, 3211. [5]-, [6]-, [7]-, and [8]helicenebisquinones: ref 7.

(9) In part the reason is that for the photocyclizations, the solutions must be very dilute. See footnote 3 in reference 7b.

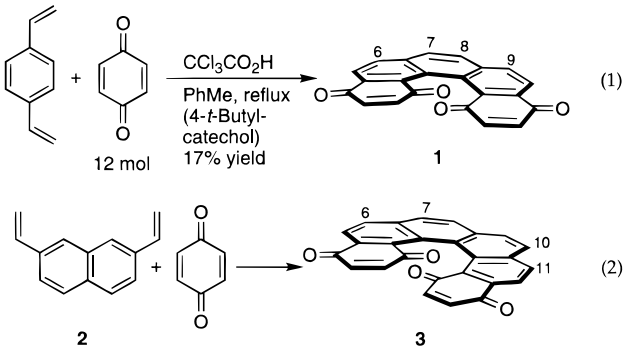
(10) Preliminary communication: Willmore, N. D.; Liu, L.; Katz, T. J. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1093.

(11) The [6]helicenebisquinone **3** was prepared previously by procedures that used photocyclization as a key step.[7a]

(12) The barrier to racemization is considerably higher for [6]helicene than for [5]helicene.[5a,13]

(13) Janke, R. H.; Haufe, G.; Würthwein, E.-U.; Borkent, J. H. *J. Am. Chem. Soc.* **1996**, *118*, 6031, and references therein.

S0002-7863(97)02132-X CCC: $14.00 

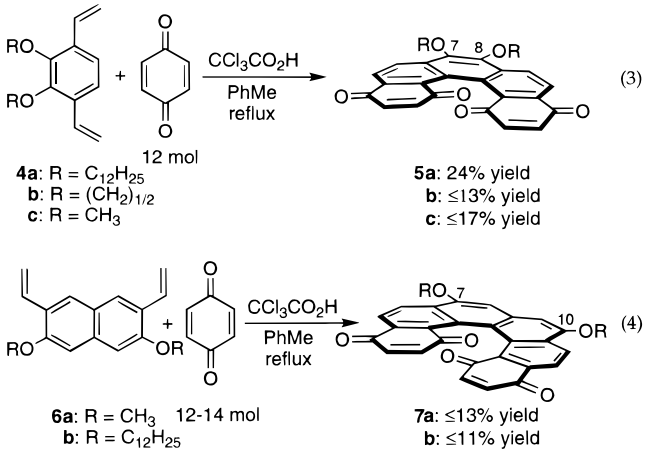



(1)

(2)

trichloroacetic acid catalyst[14] (for 39 h) or in acetonitrile at 100 °C (for 3.5 d),[15] does indeed proceed in very low yield. The procedure that Bachmann and Deno[16] and later Davies and Porter[17] used to combine ethenylnaphthalenes with *p*-benzoquinone, heating in acetic acid, worked much better. However, even then the combination of **2** and *p*-benzoquinone for 12 h gave **3** in only 6% yield.

**Synthesis of 7,8-Disubstituted Derivatives of 1 and of 7,10-Disubstituted Derivatives of 3.** Similarly, while **5a**−**c**, 7,8-dialkoxy-derivatives of **1** could be prepared according to eq 3, by refluxing *p*-benzoquinone and trichloroacetic acid in toluene with 2,3-dialkoxy-1,4-diethenylbenzenes **4a**−**c**,[18] the yields differed little from the yield of **1** according to eq 1: for **5a**, 24%; and for **5b** and **5c**, which were not fully purified, ≤13% and ≤17%, respectively. The results of similar experiments (eq 4) giving 7,10-dialkoxy-derivatives of **3** were about the same. The yields of the [6]helicenes, **7a** and **7b** (the latter not

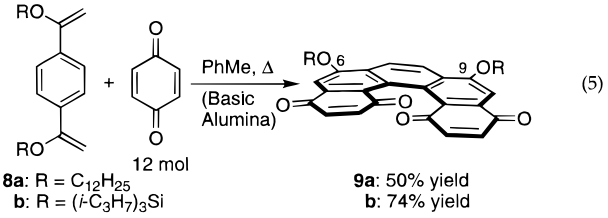



(3)

(4)

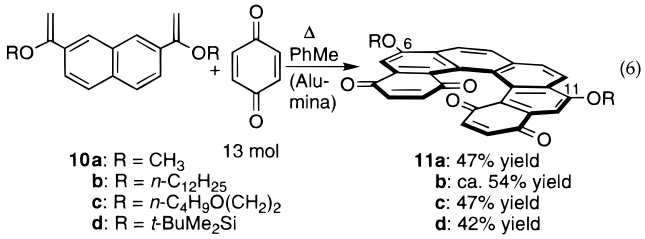
obtained pure), were just as unsatisfactory as those of the [5]-helicenes in eq 3.[18]

**Synthesis of 6,9-Disubstituted Derivatives of 1 and of 6,11-Disubstituted Derivatives of 3.** The way to obtain derivatives of the [5]- and [6]helicenebisquinones **1** and **3** in good yield is to start with alkoxy-substituted diethenyl aromatics that are the enol ethers of aryl methyl ketones. Equations 5 and 6 show examples. These procedures are so efficient and easy to carry out, the yields sufficiently high, and as will be shown below, the required enol ethers so easy to prepare, that using only conventional laboratory glassware, the amount of [6]-




(5)

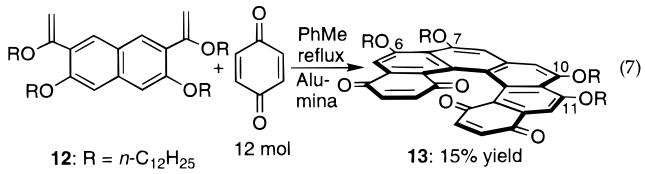
helicene **11c** that could be made quickly was 32 g. Similarly,




(6)

by using only 250 mL flasks, 14 g of the [5]helicene **9b** was made easily from 5 g of 1,4-diacetylbenzene.

**Synthesis of a 6,7,10,11-Tetraalkoxy-Derivative of 3.** The beneficial effect of alkoxyls on the ethenyl groups is lost if alkoxyls are also present on the aromatic rings adjacent to the ethenyl groups. As eq 7 shows, while **12**[18] does give the tetraalkoxy-substituted helicenebisquinone **13**, the yield is more like those in eq 4 than like those in eq 6.




(7)

**Resolution of the Enantiomers of 11c.** The enantiomers of **11c** were resolved by first converting the racemic mixture into the diastereomeric tetrakis-*N*-(tolylsulfonyl)proline esters **14** (Scheme 1).[19] The diastereomers were then separated by chromatography (95 and 93% yields) and reconverted into **11c**, now enantiomerically pure, by combining each ester with $LiAlH_4$, which removed the *N*-(tolylsulfonyl)proline groups, and oxidizing the resulting bis-hydroquinones with chloranil. In the case of each enantiomer, the yield for the two steps was 94%.

**Properties of 11c.** Helicenequinone **11c** is a red, seemingly noncrystalline solid melting at 163−164 °C. It dissolves easily in a number of solvents—$CH_2Cl_2$, $CHCl_3$, $CCl_4$, EtOAc, DMSO, DMF, THF, benzene, and $CH_3CN$—and in benzene at room temperature the solubility for the racemic material was measured to be 260 g/L. In other solvents, such as EtOH and MeOH, it is only slightly soluble, and in $H_2O$, $Et_2O$, hexanes, pentane, and petroleum ether, it is insoluble. The specific rotations measured for the nonracemic materials were $[\alpha]_D$ +2249 (*c* 0.0105, $CH_3CN$) and $[\alpha]_D$ −2247 (*c* 0.0110, $CH_3CN$). The CD and UV-vis spectra of the dextrorotatory enantiomer are displayed in Figure 1. The optically active quinone does not racemize at an appreciable rate unless it is heated vigorously. In 1,2,4-trichlorobenzene at 190°C, the half-life for this process is 67 min.

**Absolute Configuration of 11c and the Addition of Prolinol to it.** (*S*)-(+)-2-(Hydroxymethyl)pyrrolidine ("prolinol")[20] combines with **11c** as summarized in eq 8,[21] giving in 82% yield a single structural isomer, shown below to be **15**. If

(14) (a) Manning, W. B.; Wilbur, D. J. *J. Org. Chem.* **1980**, *45*, 733. (b) Manning, W. B.; Kelly, T. P.; Muschik, G. M. *J. Org. Chem.* **1980**, *45*, 2535. (c) Muschik, G. M.; Kelly, T. P.; Manning, W. B. *J. Org. Chem.* **1982**, *47*, 4709. (d) Wasserman, A. *J. Chem. Soc.* **1942**, 618.

(15) Blatter, K.; Schlüter, A.-D.; Wegner, G. *J. Org. Chem.* **1989**, *54*, 2396.

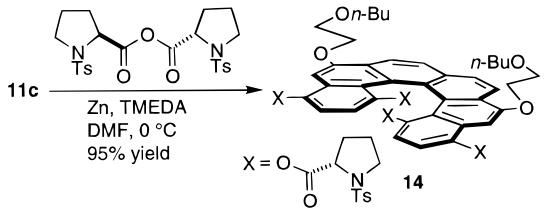
(16) Bachmann, W. E.; Deno, N. C. *J. Am. Chem. Soc.* **1949**, *71*, 3062.

(17) Davies, W.; Porter, Q. N. *J. Chem. Soc.* **1957**, 4967.

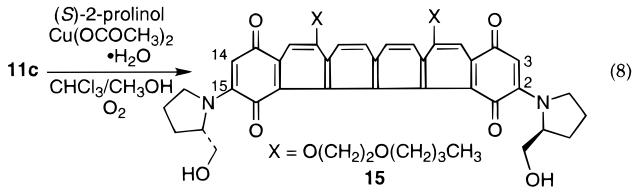
(18) The Supporting Information describes how **4a**−**c**, **6a**,**b**, and **12** were prepared.

(19) Zinc, acetic anhydride or benzoyl chloride, and pyridine or other tertiary amines convert quinones into hydroquinone esters: (a) Fieser, L. F.; Campbell, W. P.; Fry, E. M.; Gates, Jr., M. D. *J. Am. Chem. Soc.* **1939**, *61*, 3216. (b) Gaertner, R. *J. Org. Chem.* **1959**, *24*, 61.

**Scheme 1**

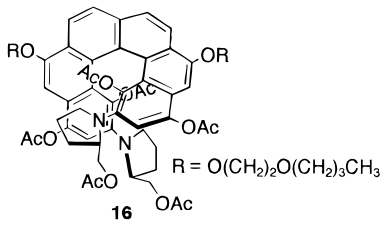



**11c** is racemic, it gives **15** as a mixture of diastereomers, which can be separated by chromatography. The levorotatory diastereomer—its CD spectrum is almost a perfect mirror image of the CD spectrum of the dextrorotatory diasteromer[22]—was reduced with zinc in acetic anhydride and triethylamine. The structure of the resulting hexaacetate **16** was determined by X-ray diffraction analysis.[23] This analysis not only demonstrates that the amines are attached to carbons 2 and 15 (rather than to




(8)

carbons 3 and 14), but since the absolute configuration is known of the prolinol that was added to **11c**, it also shows the absolute configuration of (−)-**15** and therefore of the helicenebisquinone **11c** from which it was prepared. Since (−)-**11c** with (*S*)-prolinol gives (−)-**15**, the experiments show that (−)-**11c** has the (*M*)-configuration.




Two further experiments were performed to analyze the strikingly high regiospecificity with which prolinol adds to **11c**. In one, the amine that was added to **11c** was not prolinol, but pyrrolidine, because it cannot give rise to stereoisomers. Only one adduct could be detected, and it was isolated in 92% yield. Moreover, $^1$H NMR analysis of the region of the spectrum characteristic of quinone hydrogen resonances showed that it was >95% pure and could not have contained more than 2% of any other isomer. The NMR analysis also showed that the structure formed is symmetrical, and by analogy with **15**, it is presumably the 2,15-*N*-pyrrolidinyl derivative. In the second experiment, pyrrolidine was added to **3**, and in this case the product was a mixture of 2.3 parts of a symmetrical adduct (possibly the 3,14-derivative) to 1 part of the unsymmetrical one. The implication is that the alkoxyls, not the ring system, are the origin of the high regiospecificity.

**Preparation of 2.** The 2,7-diethenylnaphthalene needed to test whether [6]helicenebisquinone **3** could be prepared accord-

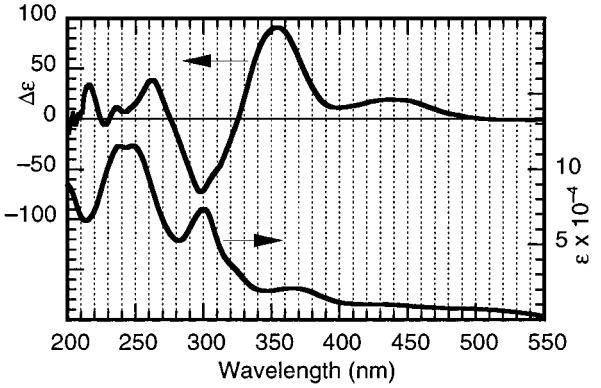
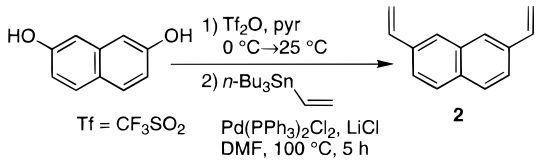



**Figure 1.** (a) CD (scale at left) and (b) UV-vis (scale at right) spectra of a $1.01 \times 10^{-5}$ M solution of (+)-**11c** in $CH_3CN$.

**Scheme 2**




ing to eq 2 was made from available 2,7-dihydroxynaphthalene by the Stille coupling procedure summarized in Scheme 2.[24] An alternative, also carried out, was to convert 2,7-dibromonaphthalene[25] to the dialdehyde[26] by treating it with *n*-BuLi and then with DMF,[27] and to transform the dialdehyde into the diethenylnaphthalene by a Wittig reaction.

**Synthesis of 8a and 8b.** The former was synthesized in 49% yield from didodecyl terephthalate and Tebbe's reagent,[28] prepared *in situ*.[29] The latter was synthesized in 93% yield by combining triisopropylsilyl triflate and triethylamine in $CH_2Cl_2$[30] with 1,4-diacetylbenzene.

**Synthesis of 10a−d.** Like **8a**, **10b** could be synthesized from the ester (in this case didodecylnaphthalene-2,7-dicarboxylate) and Tebbe's reagent, although the yield was only 10%. The yields of the other three dienes, **10a**, **10c**, and **10d**, were all excellent (78−92%). They were prepared from 2,7-diacetylnaphthalene (**18**), which itself was prepared as shown in Scheme 3. Thus the conversion[31] of 2,7-dibromonaphthalene into 2,7-bis(trimethylsilyl)naphthalene (**17**) makes possible the silyl-directed Friedel−Crafts reaction[25b,32] that is displayed. This approach is advantageous because chlorotrimethylsilane reacts only slowly with *n*-BuLi,[33] which means that the dibromonaphthalene and chlorotrimethylsilane can be combined *before* *n*-BuLi is added.

(20) Enders, D.; Fey, P.; Kipphardt, H. *Org. Prep. Proc., Int.* **1985**, *17*, 1.

(21) (a) Baltzly, R.; Lorz, E. *J. Am. Chem. Soc.* **1948**, *70*, 861, and references cited therein. (b) Crosby, A. H.; Lutz, R. E. *J. Am. Chem. Soc.* **1956**, *78*, 1233. (c) Luly, J. R.; Rapoport, H. *J. Org. Chem.* **1981**, *46*, 2745.

(22) Willmore, N. D. Ph.D. Dissertation, Columbia University, 1994.

(23) $C_{60}H_{70}N_2O_{16}$ (formula weight 1075.231), monoclinic, $P2_1$, orange crystal, $a = 9.721(2)$ Å, $b = 21.389(6)$ Å, $c = 13.604(3)$ Å, $\beta = 98.49(2)°$, $Z = 2$, $R$ (obs data) = 7.76%, $wR = 10.24\%$, $R$ (all data) = 9.88%, $wR = 10.85\%$, GOF = 1.71.

(24) The preparation was repeated after the preliminary communication[10] by Takeuchi, M.; Tuihiji, T.; Nishimura, J. *J. Org. Chem.* **1993**, *58*, 7388.

(25) (a) Porzi, G.; Concilio, C. *J. Organomet. Chem.* **1977**, *128*, 95. (b) Katz, T. J.; Sudhakar, A.; Teasley, M. F.; Gilbert, A. M.; Geiger, W. E.; Robben, M. P.; Wuensch, M.; Ward, M. D. *J. Am. Chem. Soc.* **1993**, *115*, 3182.

(26) (a) Wood, J. H.; Stanfield, J. A. *J. Am. Chem. Soc.* **1942**, *64*, 2343. (b) Davy, J. R.; Iskander, M. N.; Reiss, J. A. *Aust. J. Chem.* **1979**, *32*, 1067. (c) Ried, W.; Bodem, H.; Ludwig, U.; Neidhardt, H. *Chem. Ber.* **1958**, *91*, 2479.

(27) (a) Yang, B. V. Ph.D. Dissertation, Columbia University, 1987, p 105. (b) Yamamoto, K.; Sonobe, H.; Matsubara, H.; Sato, M.; Okamoto, S.; Kitaura, K. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 69. (c) Osuka, A.; Yamada, H.; Maruyama, K.; Mataga, N.; Asahi, T.; Ohkouchi, M.; Okada, T.; Yamazaki, I.; Nishimura, Y. *J. Am. Chem. Soc.* **1993**, *115*, 9439.

(28) Tebbe, F. N.; Parshall, G. W.; Reddy, G. S. *J. Am. Chem. Soc.* **1978**, *100*, 3611.

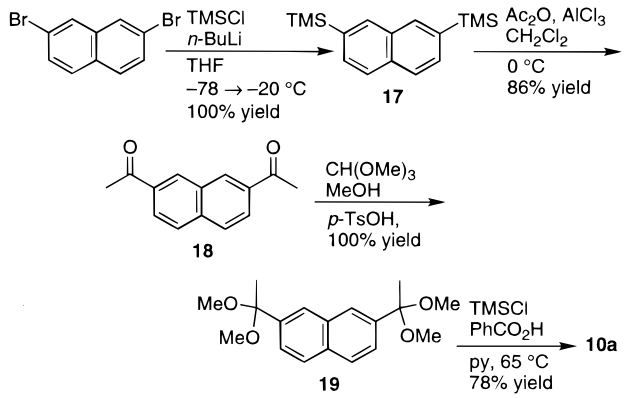
(29) Cannizzo, L. F.; Grubbs, R. H. *J. Org. Chem.* **1985**, *50*, 2386.

(30) Corey, E. J.; Cho, H.; Rücker, C.; Hua, D. H. *Tetrahedron Lett.* **1981**, *22*, 3455.

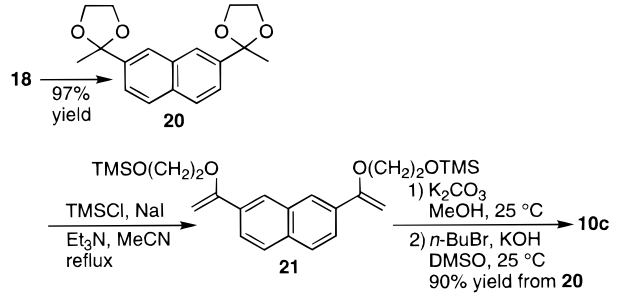
(31) Häbich, D.; Effenberger, F. *Synthesis* **1979**, 841.

(32) (a) Dey, K.; Eaborn, C.; Walton, D. R. M. *Organomet. Chem. Synth.* **1970/71**, *1*, 151. (b) Eaborn, C. *J. Organomet. Chem.* **1975**, *100*, 43. (c) Sudhakar, A.; Katz, T. J. *J. Am. Chem. Soc.* **1986**, *108*, 179. (d) Bennetau, B.; Dunogues, J. *Synlett* **1993**, 171.

**Scheme 3**




**Scheme 4**

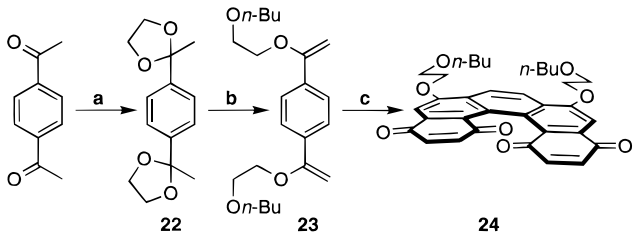



The bis(trimethylsilyl)naphthalene is formed in quantitative yield, surmounting difficulties (due in part to the organolithium combining with bromobutane) that are encountered when 2,7-dilithionaphthalene is prepared before an electrophile can be added to it.[25a]

2,7-Diacetylnaphthalene can be converted into the silyl enol ether **10d**—the yield was 88%—by refluxing it in acetonitrile with $Et_3N$, *t*-$BuMe_2SiCl$, and NaI. The diketone can also be transformed into bis(methyl enol ether) **10a** by eliminating methanol from its bis(dimethylacetal) **19**. One way to do this that works well (the yield was 89%) is to combine **19** with TMSOTf (Tf = triflate) and $(i\text{-Pr})_2EtN$ in $CH_3CN$ at room temperature.[34] However, an even better way, because it does not require TMSOTf, which is expensive, is a modification of a procedure of Newman and Vander Zwan, who eliminated methanol from two acetals by heating them at 110−120 °C with succinic anhydride, benzoic acid, and pyridine in diglyme.[35] The modified procedure uses chlorotrimethylsilane, benzoic acid, and pyridine; at 65 °C, it gives a yield of 78%.

The last bis(enol ether), **10c**, was also synthesized from an acetal, in this case the bisdioxolane **20** (Scheme 4). While once again the combination of TMSOTf and $(i\text{-Pr})_2EtN$ in $CH_3CN$ at room temperature transformed the acetal into enol ether **21**, the less expensive method used to make the methyl enol ether **10a** failed. But if in the procedure that does work, the TMSOTf is replaced by TMSCl plus NaI[36] and the $(i\text{-Pr})_2EtN$ is replaced by the less expensive $Et_3N$, the conversion to **21** takes place in a yield that is excellent, although it was not measured for the product is contaminated by a trimethylsilyl-containing impurity. The silyl groups were removed by treatment with $K_2CO_3$ in methanol, and the resulting diol was butylated to give **10c**. The yield from the diketone was 87%. More important is the scale on which the transformations can be carried out easily. With flasks no larger than 2 L and no chromatographic procedures, 40 g of **20** could be transformed into 49 g of **10c**, an amount that could be converted—but this time with the aid of chromatographic purification—into 32 g of **11c**.

**Scheme 5**[a]




[a] Reagents and conditions: (a) $(HOCH_2)_2$, *p*-TsOH·$H_2O$, 100% yield. (b) (i) TMSCl, NaI, $Et_3N$, $CH_3CN$, reflux; (ii) $K_2CO_3$, MeOH, 25 °C; (iii) *n*-BuBr, KOH, DMSO. (c) *p*-benzoquinone (13 mol), PhH, reflux. Total yield from 1,4-diacetylbenzene: 31%.

The generality of the method in Scheme 4 is such that it could be applied without modification to prepare the lower homologue, **24**. Scheme 5 shows the steps that converted 16 g of 1,4-diacetylbenzene into 14 g of **24**, a 31% yield overall.

## Discussion

The experiments in eqs 5 and 6, showing that combinations of enol ethers of appropriate aryl methyl ketones and *p*-benzoquinone give helicenes, are significant for the following reasons. (1) They produce helicenes with functional groups, quinones, that compared to the cyano, carboalkoxy, halogen, and ether functions of other helicenes[8] should be more useful for transforming the molecules into desirable materials. (2) The scale on which the preparations can be carried out is hundreds of times greater than is easily possible by the procedures used in the past.[37] Thus while we found that photocyclizations were effective key steps in previous syntheses of **2** and of its 5-, 7-, and 8-ring homologues,[7a,27a,38] they also limited the amounts of these helicenebisquinones that could be prepared to <100 mg. (3) The starting materials required, the enol ethers of aryl methyl ketones, are easy to obtain. (4) The yields, 52 ± 8%, are good, especially considering that the transformations comprise six tandem chemical reactions—two Diels−Alder additions and four dehydrogenations. (5) From simple materials they quickly give complex structures whose syntheses by procedures previously known[7a] would be lengthy.

In contrast, as in eqs 1−4, while diethenylbenzenes that are not enol ethers of aryl methyl ketones combine with *p*-benzoquinone to give the corresponding helicenes, the yields are poor. These results accord with those previously reported in which ethenylbenzenes were combined with dienophiles.[39] In particular, Zander and Franke,[40] as well as Blatter, Schlüter, and Wegner,[15] prepared complex ring systems by combining

(33) (a) Bey, A. E.; Weyenberg, D. R. *J. Org. Chem.* **1966**, *31*, 2036. For previous applications, see (b) Cooke, Jr., M. P. *J. Org. Chem.* **1986**, *51*, 951, and references therein. (c) Kobayashi, T.; Pannell, K. H. *Organometallics* **1991**, *10*, 1960.

(34) Gassman, P. G.; Burns, S. J. *J. Org. Chem.* **1988**, *53*, 5574.

(35) Newman, M. S.; Vander Zwan, M. C. *J. Org. Chem.* **1973**, *38*, 2910.

(36) TMSI plus $(TMS)_2NH$ in $CHCl_3$ or $CH_2Cl_2$ eliminates methanol from dimethyl acetals: (a) Miller, R. D.; McKean, D. R. *Tetrahedron Lett.* **1982**, *23*, 323. In other procedures, TMSI can be replaced as a reagent by TMSCl plus NaI: (b) Morita, T.; Okamoto, Y.; Sakurai, H. *J. Chem. Soc., Chem. Commun.* **1978**, 874. (c) Morita, T.; Okamoto, Y.; Sakurai, H. *Tetrahedron Lett.* **1978**, 2523. (d) Morita, T.; Yoshida, S.; Okamoto, Y.; Sakurai, H. *Synthesis* **1979**, 379. (e) Olah, G. A.; Narang, S. C.; Balaram Gupta, B. G.; Malhotra, R. *J. Org. Chem.* **1979**, *44*, 1247.

(37) Newman and Lednicer's classic synthesis[3] requires much effort, and the syntheses employing stilbene photocyclizations much solvent.[9] The syntheses of the parent helicenes provide some orientation. Of the 44 summarized in the reviews by Laarhoven and Prinsen and by Mallory and Mallory,[5a,b] only 14 specify the amounts of reagents used and the amounts of products obtained, and in these, the average yield per photocyclization was ≤66 mg and the average amount of solvent 1.2 L.

(38) Liu, L. Ph.D. Dissertation, Columbia University, 1991.

(39) For an extensive review see Wagner-Jauregg, T. *Synthesis* **1980**, 769.

(40) Zander, M.; Franke, W. H. *Chem. Ber.* **1974**, *107*, 727.

2,6-diethenylnaphthalenes (rather than the 2,7-derivatives in eqs 2, 4, 6, and 7) with *p*-benzoquinones, but their yields were similar to those recorded here. The experiments in eqs 3 and 4 also relate to many previously carried out in which alkoxy-substituted styrenes were combined with benzoquinones.[14ab,41] In all of these, the presence of electron-donating substituents on the benzene rings failed to increase the yields significantly.

There is another difference between the experiments in eqs 3 and 4 and those in eqs 5 and 6. Trichloroacetic acid, added to the former as a catalyst,[14a−c] could not be used for the reactions of the enol ethers. When it was added to a mixture of **8a** and *p*-benzoquinone in hot toluene (cf eq 5), the main product isolated was 1,4-diacetylbenzene. However, when it was omitted, **9a** was obtained, but in only ca. 26% yield and in low purity. Although it was not investigated further, when basic alumina was added to the reaction mixture, both the yield (50%) and the purity of **9a** were high.

Before the experiments described were undertaken, Diels−Alder reactions, although known to work superbly with enol ethers of *ethenyl* methyl ketones,[42] were limited to only two examples of enol ethers of *aryl* methyl ketones. Kita et al. found that the cyclic dimethylsilyl ethers of two 2-hydroxyacetophenones add to dienophiles.[43,44] During the course of the work reported here, experiments were also carried out in our laboratory in which the enol and thioenol ethers of the simplest aryl methyl ketone, acetophenone, were combined with *p*-benzoquinone, and they were found to proceed well.[45]

Kita et al. also found that the bis-trimethylsilyl ether of 2-hydroxyacetophenone's enol failed to give adducts, which they attributed to a steric interaction between the two ether functions.[43a] The observation in eq 7, that ortho-alkoxyl functions nullify the beneficial effects the enols exert, agrees with that result.

We elaborate here on a point made above, that the enol ethers whose combination with benzoquinone produces helicenebisquinones in good yields are themselves easy to obtain. Of the methods used to prepare them here, those that proceed from aryl methyl ketones, either by enolization and silylation (as in the examples of **8b** and **10d**) or by elimination of alcohols from acetals (as in the examples of **10a**, **10c**, and **21**), are much more effective than those that proceed from esters (as in the examples of **8a**, **10b**, and **12**). In particular, the methods we developed for preparing enol ethers from acetals and used to synthesize **10a**, **10c**, and **21** have the virtues of simplicity, low cost, and generality.[45] Moreover, the method used to prepare *tert*-butyldimethylsilyl enol ether **10d**—to combine the ketone with *t*-BuMe$_2$SiCl, NaI, and Et$_3$N in CH$_3$CN—while a variant on the now common procedure for preparing *trimethyl*silyl enol ethers[46] appears not to have been used before. Instead, such enol ethers have been made from the much more expensive *tert*-butyldimethylsilyl triflate.[47]

**Evidence for the Structures Assigned.** That the benzoquinone adducts have structures with the symmetries displayed is implied by the symmetries of the $^1$H and $^{13}$C NMR spectra. However, while two symmetrical structures are possible, those with four linearly fused rings are excluded for the products from **10** by the proton spectra exhibiting, at $\delta > 6$, two pairs of doublets and one singlet (as required by structures **11a**−**d**), not one pair of doublets and three singlets (as required by the alternative structures). For **5a** and **9a** the distinction can be made on the basis of the complexity of the OCH$_2$ resonances. In the spectra of each, the resonances are split into two sets, at $\delta$ 4.34 and 4.08 in the former and at $\delta$ 4.37 and 4.31 in the latter. The implication is that the ring-systems themselves are chiral, which eliminates the linear structures. Similar supporting evidence is found for structures **11b**−**d**. In the spectrum of **11b** the OCH$_2$ resonance at $\delta$ 4.36 is complex, and in the spectra of **11c** and **11d**, analogous resonances are so complex that they are split into two clear sets, at $\delta$ 4.48 and 4.57 in the former and at $\delta$ 0.49 and 0.41 (the SiCH$_3$ resonances) in the latter.

**Resolution and Absolute Configuration.** The best evidence for the chirality of **11c**, however, is the resolution into its optical antipodes and the X-ray diffraction analysis of its derivative **16**. The resolved helicene is sufficiently stable that it requires heating to 190 °C to bring about racemization at an appreciable rate. The half-time for racemization in 1,2,4-trichlorobenzene at this temperature is 67 min, corresponding to a rate constant for inversion of configuration of $8.6 \times 10^{-5}$ s$^{-1}$, equivalent to $\Delta G^{\ddagger} = 36.1 \pm 0.1$ kcal/mol.

This barrier is similar to that for the inversion of [6]helicene, $\Delta G^{\ddagger} = 36.9$ kcal/mol at 190 °C.[48] Although there are no calculations to provide guidance,[49] the figure seems surprisingly small considering that the introduction of methyl groups into its 1 and 14 positions raises the barrier to [6]helicene's inversion by 6.9 kcal/mol[50] and that the quinone functions in **1** raise the barrier[7b] by 3.9 kcal/mol above that of the parent [5]helicene.[51] It may be relevant that in raising the barrier to the inversion of [5]helicene, the effect of the quinone functions in **1** is considerably smaller than that of a single methyl group introduced into the 1-position.[52]

The determination of the absolute configuration of **11c** shows that the molecules with *P*-helicity give rise to a positive circular dichroism in the n→$\pi$* quinone transition (the one at 440 nm).[53] Although this is the first such assignment for a helical quinone,[53] the conclusion accords with a similar one reached for streptavaricin C, an antibiotic with an axially chiral quinone methide chromophore.[54]

**Regiochemistry of Nucleophilic Addition.** The X-ray diffraction analysis of a crystal of **16** confirmed the structure of helicenebisquinone **11c** and revealed its absolute configura-

(41) (a) Rosen, B. I.; Weber, W. P. *J. Org. Chem.* **1977**, *42*, 3463. (b) Manning, W. B.; Tomaszewski, J. E.; Muschik, G. M.; Sato, R. I. *J. Org. Chem.* **1977**, *42*, 3465. (c) Muschik, G. M.; Tomaszewski, J. E.; Sato, R. I.; Manning, W. B. *J. Org. Chem.* **1979**, *44*, 2150. (d) Manning, W. B. *Tetrahedron Lett.* **1981**, *22*, 1571. (e) Kelly, T. R.; Magee, J. A.; Weibel, F. R. *J. Am. Chem. Soc.* **1980**, *102*, 798.

(42) (a) Fringuelli, F.; Taticchi, A. *Dienes in the Diels-Alder Reaction*; Wiley: New York, 1990. (b) Danishefsky, S. *Acc. Chem. Res.* **1981**, *14*, 400, and references cited therein.

(43) (a) Kita, Y.; Yasuda, H.; Tamura, O.; Tamura, Y. *Tetrahedron Lett.* **1984,** *25*, 1813. Another example was an internal version: (b) Kita, Y.; Okunaka, R.; Honda, T.; Shindo, M.; Tamura, O. *Tetrahedron Lett.* **1989**, *30*, 3995.

(44) Related reactions are Diels−Alder additions of benzynes and methyleneisoquinolines or related structures: (a) Saá, C.; Guitian, E.; Castedo, L.; Saá, J. M. *Tetrahedron Lett.* **1985**, *26*, 4559. (b) Castedo, L.; Guitián, E.; Saá, C.; Suau, R.; Saá, J. M. *Tetrahedron Lett.* **1983**, *24*, 2107. (c) Atanes, N.; Castedo, L; Guitián, E.; Saá, C.; Saá, J. M.; Suau, R. *J. Org. Chem.* **1991**, *56*, 2984. (d) Castedo, L; Guitian, E. In *Studies in Natural Products Chemistry, Volume 3: Stereoselective Synthesis (Part B)*; Rahman, A-u., Ed.; Elsevier: New York, 1989; pp 417−454.

(45) Willmore, N. D.; Hoic, D. A.; Katz, T. J. *J. Org. Chem.* **1994**, *59*, 1889.

(46) (a) Cazeau, F.; Duboudin, F.; Moulines, F.; Babot, O.; Dunogues, J. *Tetrahedron* **1987**, *43*, 2075. A recent variant: (b) Lin, J.-M.; Liu, B.-S. *Synth. Commun.* **1997**, *27*, 739.

(47) Mander, L. N.; Sethi, S. P. *Tetrahedron Lett.* **1984**, *25*, 5953.

(48) (a) Martin, R. H.; Marchant, M.-J. *Tetrahedron Lett.* **1972**, 3707. (b) Martin, R. H.; Marchant, M. J. *Tetrahedron* **1974**, *30*, 347.

(49) Inversion barriers have been calculated for other helicenes. See reference 13.

(50) Borkent, J. H.; Laarhoven, W. H. *Tetrahedron* **1978**, *34*, 2565.

(51) Goedicke, C.; Stegemeyer, H. *Tetrahedron Lett.* **1970**, 937.

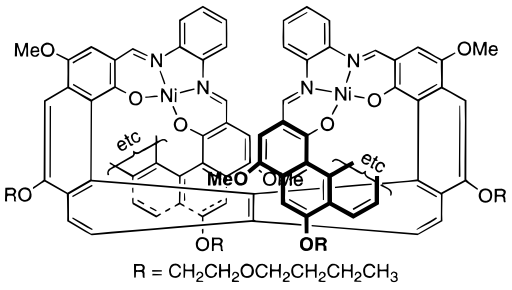
(52) Scherübl, H.; Fritzche, U.; Mannschreck, A. *Chem. Ber.* **1984**, *117*, 336.

(53) A review on the chiroptical properties and absolute configurations of chiral quinones: Smith, H. E. In *The Chemistry of Quinoid Compounds, Vol. II*; Patai, S., Rappoport, Z., Ed.; Wiley: Chichester, UK, 1988; Chapter 4.

(54) Rinehart, K. L., Jr.; Knöll, W. M. J.; Kakinuma, K.; Antosz, F. J.; Paul, I. C.; Wang, A. H.-J.; Reusser, F.; Li, L. H.; Kreuger, W. C. *J. Am. Chem. Soc.* **1975**, *97*, 196.

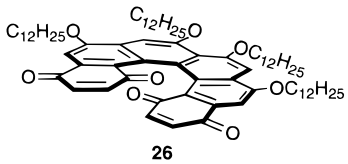
tion. It also demonstrated that prolinol adds to the quinone specifically as shown in eq 8, to carbons 2 and 15. Pyrrolidine and other amines also add to **11c** to give single adducts,[22] presumably with the same regiochemistry. This specificity accords with that observed first for the addition of aniline to 6-hydroxy- and 6-acetoxynaphthalene-1,4-diones[55] and subsequently for additions of other nucleophiles to 6-methoxynaphthalene-1,4-dione,[56] explained by Kelly et al. as a consequence of conjugation with an oxygen substituent weakening a carbonyl's electron-withdrawing effect.[57] That such specificity is not observed when pyrrolidine adds to **3** tallies with that explanation.

Both that specificity and the method developed here to synthesize helical bisquinones such as **11c** have already proven useful. The former has provided a way to convert **11c** into the bis-salicylaldehyde precursor of a helical salophen polymer (**25**).[58] The latter was applied to make the first example (**26**) of a helical conjugated molecule that spontaneously self-assembles into aggregates, the properties of which have proven to be exceptional.[59] Moreover, the methods described hold the additional promise of leading to other novel materials. We hope to describe some in future publications.




R = $CH_2CH_2OCH_2CH_2CH_2CH_3$

**25**




**26**

## Conclusions

The union of *p*-benzoquinone with bis enol ethers of aryl methyl ketones provides a way to prepare easily and in quantity helicenes functionalized with reactive groups. The experiments show how **11c** can be made not only in significant amounts, but in non-racemic form. They show that the isomer with positive circular dichroism at the n→$\pi$* transition has *P*-helicity and that amines add to the carbons $\beta$ to the external CO functions. They provide effective new methods for preparing enol ethers.

## Experimental Section

THF, benzene, and toluene were distilled from Na (or K) plus benzophenone, $CH_2Cl_2$ and $Et_3N$ from $CaH_2$. Unless otherwise specified, reactions were carried out under a $N_2$ atmosphere. *p*-Benzoquinone was purified either by subliming it at water aspirator pressure (for the preparations of **3**, **5a**−**c**, **7a**,**b**, **9a**, and **13**) or by recrystallizing it from acetone and drying in a vacuum (for the preparations of **11a**−**d** and **24**), or by slurrying it in $CH_2Cl_2$ with four times its weight of basic alumina, filtering through Celite, and drying in a vacuum (for the preparation of **9b**). Unless otherwise specified, "chromatography" refers to "flash chromatography".[60]

**[6]Helicenebisquinone (3).** 2,7-Diethenylnaphthalene (**2**, 0.90 g, 5.0 mmol), *p*-benzoquinone (6.5 g, 60 mmol), and HOAc (30 mL) were heated at 100 °C for 12 h. After the black mixture had been cooled, it was filtered, and washed with much $CH_2Cl_2$. The filtrate was washed with water, $NaHCO_3$ and $MgSO_4$ were added, solids were filtered, and after the solvent had been stripped, the residue was chromatographed (eluting with $CH_2Cl_2$−ether). The yield of red solid, mp > 280 °C, whose $^1$H NMR spectrum was identical to that of **3** prepared by Yang,[7a] was 0.20 g, 6%.

**1,4-Bis(1-(dodecyloxy)ethenyl)benzene (8a).** Following an example of Ono et al.,[61] didodecyl terephthalate was prepared by refluxing for 18 h terephthalic acid (3.32 g, 20.0 mmol), 1-bromododecane (9.6 mL, 40 mmol), and 1,8-diazabicyclo[5.4.0]undec-7-ene (6.0 mL, 40 mmol) in 30 mL of benzene. The mixture was filtered while warm and the precipitate washed with benzene. The filtrate gave 11g (100%) of the ester as a white solid. $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 8.09 (s, 4H), 4.32 (t, $J$ = 6.6 Hz, 4H), 1.75 (m), 1.25 (m), 0.87 (m, 6H).

Following Cannizzo and Grubbs,[29] titanocene dichloride (12.8 g, 50 mmol) and $AlMe_3$ (2 M, in toluene, 55 mL, 110 mmol) were combined under argon and stirred at 25 °C for 72 h. More $AlMe_3$ (20 mL, 40 mmol) was added, and stirring was continued for another 12 h. After this mixture had been cooled to −40 °C (dry ice−$CH_3CN$), the ester above (3.4 g, 20 mmol), dissolved in THF (100 mL), was added by cannula while the flask was shaken. After having been stirred and warmed overnight to 25 °C, the mixture was diluted with 50 mL of THF, cautiously shaken, and quenched at −10 °C with 40 mL of 15% aqueous NaOH, and after stirring at 25 °C, filtered through Celite (which was washed with ether). Evaporation and trituration with pentane (300 mL) gave a yellow slurry, which, after 10 mL of $Et_3N$ had been added to it, was quickly filtered through a pad of basic alumina (2 cm thick) and Celite to remove $Cp_2TiO$. The solvent was stripped and the residue treated with $CHCl_3$ (25 mL, previously shaken with $K_2CO_3$)−ether (5 mL). Cooling to −10 °C precipitated pure **8a** (5.0 g, 49% yield from terephthalic acid). Mp 63.0−64.5 °C (from $CH_2Cl_2$); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.59 (s, 2H), 4.64 (d, $J$ = 3.8 Hz, 2H), 4.19 (d, $J$ = 3.8 Hz, 2H), 3.84 (t, $J$ = 9.5 Hz, 4H), 1.80 (m, 4H), 1.27 (m, 36 H), 0.88 (t, $J$ = 9.4 Hz, 6H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 159.71, 136.60, 125.00, 82.09, 67.78, 31.92, 29.62 (br), 29.43, 29.35, 29.07, 26.30, 22.69, 14.11; IR (KBr) 2918 (vs), 2850 (vs), 1636 (s), 1586 (m), 1471 (vs), 1308 (vs), 1279 (vs), 1136 (vs), 1036 (m), 929 (w), 851 (w), 793 (vs), 718 (w), 639 cm$^{-1}$ (w).

**6,9-Bis(dodecyloxy)[5]helicenebisquinone (9a).** Diene **8a** (0.75 g, 1.5 mmol) was added to a slurry of *p*-benzoquinone (1.95 g, 18 mmol) and basic alumina (70 mg) in toluene (7 mL, previously passed through basic alumina) and refluxed for 62 h. Chromatography (eluting with $CH_2Cl_2$) gave 0.53 g (50%) of pure **9a**, a bright orange solid, mp 99.0−100.0 °C. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.38 (s, 2H), 7.54 (s, 2H), 6.88 (d, $J$ = 10 Hz, 2H), 6.77 (d, $J$ = 10 Hz, 2H), 4.37 (dt, $J$ = 6.4, 7.8 Hz, 2H) and 4.31 (dt, $J$ = 6.4, 7.8 Hz, 2H), 1.99 (m, 4H), 1.58−1.27 (m, 36 H), 0.88 (m, 6H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 186.33, 185.34, 158.50, 139.94, 136.07, 131.99, 129.67, 127.68, 127.65, 122.41, 102.66, 69.43, 31.91, 29.60 (m), 29.34, 29.02, 26.20, 22.68, 14.12; MS (EI) *m*/*z* 706 ($M^+$, 100%); HRMS (EI) calcd for $C_{46}H_{58}O_6$ 706.4233, found 706.4249; IR ($CDCl_3$) $\nu$ 2928 (vs), 2855 (s), 1668 (vs), 1654 (vs), 1587 (vs), 1552 (m), 1504 (w), 1401 (w), 1352 (w), 1299 (vs), 1236 (s), 1079 (s), 1020 cm$^{-1}$ (w); UV-vis ($CHCl_3$, $c = 1.27 \times 10^{-5}$ M) $\lambda_{max\ (nm)}$ (log $\epsilon$) 298 (4.47), 330 (4.00), 405 (3.92), 570 (3.01).

**Triisopropylsilyl Enol Ether of 1,4-Diacetylbenzene (8b).** (*i*-Pr)$_3$SiOSO$_2$CF$_3$ (18.9 g, 62 mmol) was added in drops to a solution at 0 °C of 1,4-diacetylbenzene (5 g, 31 mmol) and $Et_3N$ (17.1 mL, 123 mmol) in 25 mL of $CH_2Cl_2$. After it had been stirred at 0 °C for 5 min and at 25 °C for 15 min, the lower layer was discarded, and the organic layer was washed with 1 M aqueous NaOH (2×), saturated aqueous $NaHCO_3$, and $H_2O$. Drying ($K_2CO_3$/powdered 4 Å molecular sieves), filtration through Celite, and evaporation of solvent gave an oil that after chromatography on a short plug of silica slurried with

(55) Lyons, J. M.; Thomson, R. H. *J. Chem. Soc.* **1953**, 2910.
(56) Cameron, D. W.; Crossley, M. J.; Feutrill, G. I.; Griffiths, P. G. *Aust. J. Chem.* **1978**, *31*, 1335.
(57) (a) Kelly, T. R.; Gillard, J. W.; Goerner, R. N., Jr.; Lyding, J. M. *J. Am. Chem. Soc.* **1977**, *99*, 5513. (b) Kelly, T. R.; Parekh, N. D.; Trachtenberg, E. N. *J. Org. Chem.* **1982**, *47*, 5009. (c) Rozeboom, M. D.; Tegmo-Larsson, I.-M.; Houk, K. N. *J. Org. Chem.* **1981**, *46*, 2338.
(58) Dai, Y.; Katz, T. J. *J. Org. Chem.* **1997**, *62*, 1274.
(59) Nuckolls, C.; Katz, T. J.; Castellanos, L. *J. Am. Chem. Soc.* **1996**, *118*, 3767.
(60) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.
(61) Ono, N.; Yamada, T.; Saito, T.; Tanaka, K.; Kaji, A. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 2401.

50% PhH, 48% $CH_2Cl_2$, 2% $Et_3N$ (eluting with the same solvent) gave a colorless oil (14.7 g, 93%). $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.59 (s, 4H), 4.88 (d, 2H, $J$ = 1.7 Hz), 4.43 (d, 2H, $J$ = 1.7 Hz), 1.31 (m, 6H), 1.15 (d, 36H, $J$ = 7.0 Hz); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 155.9, 137.5, 125.0, 90.0, 18.1, 12.8; IR (neat) 2942, 2870, 1608, 1463, 1313, 1122, 1112, 1014 cm$^{-1}$; HRMS calcd for $C_{28}H_{51}O_2Si_2$ 475.3428, found 475.3414.

**6,9-Bis(triisopropylsiloxy)[5]helicenebisquinone (9b).** A solution of **8b** (13.0 g, 27 mmol) and *p*-benzoquinone (44 g, 410 mmol) in 100 mL of dry toluene was heated at 100 °C for 4.5 days, cooled, and filtered through Celite (which was washed with benzene). Chromatography (eluting with 3% EtOAc in benzene) gave **9b**, a rust-colored solid (12.5 g, 67%). Rechromatographing impure fractions (eluting with 3% EtOAc in benzene) gave an additional 1.3 g of **9b**, bringing the total yield to 74%. Mp 180−182 °C (from EtOH); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 8.39 (s, 2H), 7.59 (s, 2H), 6.89 (d, 2H, $J$ = 10.1 Hz), 6.79 (d, 2H, $J$ = 10.0 Hz), 1.52 (m, 6H), 1.20 (t, 36H, $J$ = 6.3 Hz); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 186.1, 184.7, 156.0, 139.9, 135.9, 131.6, 131.3, 128.3, 127.7, 122.6, 109.4, 17.8, 12.8; IR (KBr) 2937, 2864, 1659, 1581, 1429.9, 1389.2, 1285.4, 1238.7, 1068.0, 1000.0 cm$^{-1}$; HRMS calcd for $C_{40}H_{51}O_6Si_2$ 683.3224, found 683.3249. Anal. Calcd for $C_{40}H_{50}O_6Si_2$: C, 70.34; H, 7.38. Found: C, 70.69; H, 7.46.

**2,7-Naphthalenediylbis(trimethylsilane) (17).** *n*-BuLi (2.5 M, in hexanes, 160 mL, 0.400 mol) was added during 1 h to a stirred solution at −78 °C of $Me_3SiCl$ (59.9 mL, 0.472 mol) and 2,7-dibromonaphthalene (45.0 g, 0.157 mol) in THF (315 mL). The suspension was stirred for another 5 min and, when warmed to −20 °C, gave a solution that was poured into saturated aqueous $NaHCO_3$ (500 mL), extracted (3×) with hexanes, and dried ($MgSO_4$). Drying *in vacuo* gave 43.0 g (100%) of **17**, mp 79−80 °C (from hexanes). A similar experiment converted 28.1 g of 2,7-dibromonaphthalene into 25.0 g of **17** (a 93% yield). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.01 (s, 2H), 7.79 (d, $J$ = 8.3 Hz, 2H), 7.59 (dd, $J$ = 8.2, 1.1 Hz, 2H), 0.34 (s, 18H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 137.85, 133.89, 133.82, 132.39, 130.10, 126.74, −1.08; IR ($CDCl_3$) 3045, 2958, 2898, 1315, 1249, 1096, 837, 535, 476 cm$^{-1}$; MS (EI) *m/z* 272 ($M^+$), 257, 121, 73; HRMS (EI) calcd for $C_{16}H_{24}Si_2$ 272.1417, found 272.1434.

**1,1′-(2,7-Naphthalenediyl)bis(ethanone) (18).** A solution of **17** (36.5 g, 0.134 mol) and $Ac_2O$ (35.4 mL, 0.375 mol) in 160 mL of $CH_2Cl_2$ was added during 2.5 h to a slurry of $AlCl_3$ (100 g, 0.749 mol, one full bottle of Aldrich 99.99% grade[62]) in 167 mL of $CH_2Cl_2$ at 0 °C. The mixture was stirred at 0 °C for 40 min and poured onto 1 L of crushed ice. The aqueous layer was extracted (10×) with $CH_2Cl_2$, the organic layers were dried ($K_2CO_3$), and the solid left by evaporating the solvent was dried *in vacuo*, washed (3×) with hexanes, and dried again, to give 24.5 g (86%) of **18**, mp 104−105 °C. A similar experiment converted 19.9 g of **7** into 13.6 g of **18** (an 88% yield). $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 8.57 (s, 2H), 8.14 (dd, $J$ = 8.7 Hz and $J$ = 1.6 Hz, 2H), 7.93 (d, $J$ = 8.8 Hz, 2H), 2.75 (s, 6H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 197.51, 137.61, 135.28, 131.78, 131.48, 128.35, 126.48, 26.68; IR ($CDCl_3$) 1681, 1628, 1420, 1362, 1275, 1222, 1186, 581, 556, 476 cm$^{-1}$; MS (EI) *m/z* 212 ($M^+$), 197, 154, 126, 84, 49; HRMS (EI) calcd for $C_{14}H_{12}O_2$ 212.0837, found 212.0824.

**2,7-Bis(1,1-dimethoxyethyl)naphthalene (19).** Diketone **18** (10.64 g, 50.14 mmol), $HC(OCH_3)_3$ (13.7 mL, 125 mmol), and *p*-TsOH·$H_2O$ (954 mg, 5 mmol) in 100 mL of MeOH were stirred at 25 °C for 2 h, while three 5.5 mL portions (50.1 mmol each) of additional $HC(OCH_3)_3$ were added at 30 min intervals. $Et_3N$ (25 mL) was added, and the solution was poured into $Et_2O$ (220 mL), washed (2×) with saturated aqueous $NaHCO_3$ and $H_2O$, and dried ($K_2CO_3$). Evaporation of the solvent and heating *in vacuo* gave 15.3 g (100%) of **19**, a viscous syrup. $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 8.05 Hz (s, 2H), 7.82 (d, $J$ = 8.7 Hz, 2H), 7.58 (dd, $J$ = 8.6 and $J$ = 1.6 Hz, 2H), 3.24 (s, 12H), 1.61 (s, 6H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 140.67, 132.99, 132.41, 127.59, 126.17, 124.65, 101.88, 49.16, 26.08; IR ($CDCl_3$) 2993, 2944, 2833, 1371, 1276, 1193, 1181, 1142, 1109, 1083, 1037 cm$^{-1}$; MS (EI) *m/z* 304 ($M^+$), 273, 241, 227, 89, 43; HRMS (EI) calcd for $C_{18}H_{24}O_4$ 304.1675, found 304.1690.

**2,7-Bis(1-methoxyethenyl)naphthalene (10a).** Acetal **19** (200 mg, 0.66 mmol), pyridine (0.66 mL), $Me_3SiCl$ (0.45 mL, 3.54 mmol), and benzoic acid (8 mg, 0.07 mmol) were heated at 65 °C for 2 h. Aqueous NaOH (15%) was added, and the mixture was extracted (3×) with $Et_2O$. Washing (saturated aqueous $NaHCO_3$), drying ($K_2CO_3$), evaporation, trituration with hexanes, and drying *in vacuo* afforded 124 mg (78%) of solid **10a**. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.13 (s, 2H), 7.76 (d, $J$ = 8.7 Hz), 7.69 (dd, $J$ = 8.7 Hz and $J$ = 1.7 Hz, 2H), 4.80 (d, $J$ = 3.0 Hz, 2H), 4.32 (d, $J$ = 3.0 Hz, 2H), 3.81 (s, 6H); MS (EI) *m/z* 240 ($M^+$), 197, 183, 165, 150, 139; HRMS (EI) calcd for $C_{16}H_{16}O_2$ 240.1150, found 240.1153.

**1,4,13,16-Tetrahydro-1,4,13,16-tetraoxo-6,11-dimethoxy[6]helicene (11a).** Diene **10a** (1.165 g, 4.85 mmol) and *p*-benzoquinone (6.81 g, 63.0 mmol) in 49 mL of toluene were heated in a bath of oil at 110 °C for 66 h. The mixture, diluted with $CH_2Cl_2$ (100 mL), was filtered through Celite, which was washed with $CH_2Cl_2$ until deep red-colored material ceased to wash out. Chromatography, repeated three times (eluting with 10% $Et_2O$ in $CH_2Cl_2$), gave 1.02 g (47%) of **11a**, a red solid, mp >220 °C. $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 8.43 (d, $J$ = 8.7 Hz, 1H), 7.97 (d, $J$ = 8.7 Hz, 1H), 7.54 (s, 1H), 6.79 (d, $J$ = 10.2 Hz, 1H), 6.63 (d, $J$= 10.0 Hz, 1H), 4.22 (s, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 185.20, 185.10, 159.30, 140.20, 135.70, 133.70, 133.10, 131.20, 128.60, 127.60, 127.20, 126.40, 122.20, 101.43, 56.60; IR ($CDCl_3$) 1658, 1596, 1514, 1311, 1294, 1232, 1215, 1024 cm$^{-1}$; MS (EI) *m/z* 448 ($M^+$), 322, 244; HRMS (EI) calcd for $C_{28}H_{16}O_6$ 448.0947, found 448.0972.

**2,7-Bis(1-(dodecyloxy)ethenyl)naphthalene (10b).** The preparation of naphthalene-2,7-dicarboxylic acid was patterned on Yang's preparation of the corresponding dialdehyde.[27a] *t*-BuLi (in pentane, 1.7M, 165 mL, 280 mol) was added slowly to a solution of 2,7-dibromonaphthalene[25] (20 g, 70 mmol) in 175 mL THF at −78 °C. The mixture was poured onto an equal volume of dry ice, and after 700 mL of 1 M NaOH had been added, the solution was washed with EtOAc (3×) to which some benzene and $H_2O$ were added to clear emulsions. The mixture was acidified with 1 M HCl, filtered through Celite, and washed once with EtOH. A solution of the precipitate in THF (ca. 1 L) was filtered and stripped, and, after drying *in vacuo*, gave 11.65 g (77%) of naphthalene-2,7-dicarboxylic acid, a tan powder. $^1$H NMR (200 MHz, DMSO-$d_6$) $\delta$ 13.18 (br s, 2H), 8.73 (s, 2H), 8.06 (s, 4H).

A mixture of the diacid (10 g, 46.3 mmol), diazabicyclo[5.4.0]undec-7-ene (14.5 mL, 97.1 mmol), and 22.2 mL (92.5 mmol) of *n*-$C_{12}H_{25}Br$ in 231 mL of THF was refluxed overnight, poured into 1 M HCl, and extracted (3×) into EtOAc, which was washed with $H_2O$ (2×) and saturated aqueous $NaHCO_3$, dried ($MgSO_4$), and stripped of solvent. The crude product was recrystallized from hexanes. A second crop was obtained from EtOH. The total was 3.0 g (12%). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.72 (s, 2H), 8.18 (dd, $J$ = 8.6 and 1.5 Hz, 2H), 7.93 (d, $J$ = 8.8 Hz, 2H), 4.40 (t, $J$ = 6.8 Hz, 4H), 1.83 (quintet, $J$ = 7.9 Hz, 4H), 1.55−1.15 (m, 12H), 0.87 (t, $J$ = 7.0 Hz, 6H).

The diester (1.0 g, 1.81 mmol) was added to 6.75 mL of Tebbe's reagent (0.67 M, in toluene—see the preparation above of **8a**) at −40 °C, and then 18.1 mL of THF was slowly added. The mixture was allowed to warm overnight to 25 °C. After it had been cooled to −10 °C, 3.8 mL of 1 M NaOH was added, and the product was extracted with $CH_2Cl_2$ (5×). A yellow solid precipitate, formed when hexanes containing some $Et_3N$ were added, was removed by filteration through 1:1 basic $Al_2O_3$−Celite, which was washed with hexanes containing some $Et_3N$. After solvent had been removed from the filtrate, the residue was dissolved in 9 mL of $Et_2O$ (pretreated with basic $Al_2O_3$) and cooled overnight in a freezer (−20 °C). A quick suction filtration and a single wash with cold $Et_2O$, followed by drying *in vacuo*, gave 103 mg (10%) of **10b**, an amorphous white solid. $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 8.13 (s, 2H), 7.76 (d, $J$ = 8.8 Hz, 2H), 7.70 (dd, $J$ = 8.6 and 1.6 Hz, 2H), 4.78 (d, $J$ = 2.6 Hz, 2H), 4.29 (d, $J$ = 2.6 Hz, 2H), 3.91 (t, $J$ = 6.4 Hz, 4H), 1.83 (quintet, $J$ = 7.6 Hz, 4H), 1.60−1.20 (m, 12H), 0.87 (t, $J$ = 7.2 Hz, 6H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 159.93, 134.24, 133.25, 132.91, 127.24, 124.93, 123.77, 82.70, 67.96, 31.94, 29.71, 29.67, 29.64, 29.48, 29.38, 29.12, 26.34, 22.71, 14.12.

**1,4,13,16-Tetrahydro-1,4,13,16-tetraoxo-6,11-bis(dodecyloxy)[6]helicene (11b).** Diene **10b** (379 mg, 0.69 mmol), *p*-benzoquinone (970 mg, 8.98 mmol), and 35 mg of basic $Al_2O_3$ in 6.9 mL of toluene were refluxed for 49 h. The mixture was filtered through Celite, which was washed with $CH_2Cl_2$ until dark red-colored material ceased to elute. Solvent was removed, and heating *in vacuo* at 100 °C sublimed excess benzoquinone onto a cold condenser. Chromatography (1.25 in. × 6 in., eluting with 20% EtOAc−hexanes) gave 280 mg (54%) of slightly impure helicene **11b**. $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 8.45 (d, $J$ = 8.6

(62) Less pure $AlCl_3$ resulted in significant protodesilylation.

Hz, 2H), 7.95 (d, 8.6 Hz, 2H), 7.50 (s, 2H), 6.78 (d, $J = 10.0$ Hz, 2H), 6.62 (d, $J = 10.0$ Hz, 2H), 4.36 (m, 4H), 2.10 (m, 4H), 1.58 (m, 4H), 1.15−1.55 (m, 32H), 0.89 (t, $J = 6.8$ Hz, 6H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 185.18, 185.16, 158.83, 140.20, 135.61, 133.67, 133.02, 131.25, 128.45, 127.61, 126.89, 126.40, 122.10, 101.98, 69.45, 31.94, 29.70, 29.67, 29.64, 29.61, 29.42, 29.38, 29.35, 29.10, 26.21, 22.71, 22.69, 14.13; MS (EI) *m/z* 757 ($MH^+$), 741, 713, 589, 571.

**2,2′-(2,7-Naphthalenediyl)bis(2-methyl-1,3-dioxolane) (20).** Diketone **18** (23.7 g, 0.112 mol), ethylene glycol (19 mL, 0.335 mol), *p*-TsOH·$H_2O$ (2.1 g, 0.011 mol), and 223 mL of benzene were refluxed in a Dean−Stark apparatus for 10 h. Water was removed from the trap, which was then filled with 4 Å molecular sieves, and reflux was continued for another 10 h. $Et_3N$ (75 mL) was added, and the solution was poured into saturated aqueous $NaHCO_3$. Extraction with benzene (3×), washing with saturated aqueous $NaHCO_3$, and drying, ultimately *in vacuo*, gave 32.0 g (95%) of **20**, mp 70−76 °C (from PhH). A repetition of the experiment gave 33.4 g of **20** (a 100% yield). $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.98 (s, 2H), 7.82 (d, $J = 8.5$ Hz, 2H), 7.57 (d, $J = 8.7$ Hz, 2H), 4.08 (m, 4H), 3.81 (m, 4H), 1.74 (s, 6H). $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 140.99, 132.54, 127.84, 124.35, 123.90, 108.91, 64.52 (two peaks), 27.59. IR ($CDCl_3$) 2991, 2892, 1375, 1262, 1218, 1199, 1181, 1111, 1040 cm$^{-1}$; MS (EI) *m/z* 300 ($M^+$), 285, 241, 87. HRMS (EI) calcd for $C_{18}H_{20}O_4$ 300.1362, found 300.1377.

**2,7-Bis[1-(2-butoxyethoxy)ethenyl]naphthalene (10c).** $Me_3SiCl$ (77.0 mL, 65.9 g, 0.607 mol) was added to dioxolane **20** (33.4 g, 0.111 mol), $Et_3N$ (91 mL, 0.653 mol), and NaI (91.0 g, 0.607 mol, previously dried by vigorous heating until vapors ceased to evolve) in 225 mL of $CH_3CN$. After it had refluxed for 1 h, $Et_3N$ (120 mL) and $Et_2O$ (500 mL) were added, and the mixture was poured into saturated aqueous $NaHCO_3$. Extraction ($Et_2O$), washing (saturated aqueous $NaHCO_3$, and back extraction with $Et_2O$), drying ($K_2CO_3$), and removal of solvent *in vacuo* gave 45.8 g of **21**, an oil that, although contaminated with silyl impurities, was used directly in the next step. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.14 (s, 2H), 7.76 (d, $J = 8.8$ Hz, 2H), 7.70 (dd, $J = 8.7$ Hz and $J = 1.6$ Hz, 2H), 4.80 (d, $J = 2.8$ Hz, 2H), 4.32 (d, $J = 2.9$ Hz, 2H), 4.02 (s, 8H), 0.19 (s, 18H).

Crude **21** (45.8 g) was stirred under argon for 2.5 h with $K_2CO_3$ (24.4 g, 0.177 mol) and MeOH (450 mL). Precipitates were filtered, the solvent was stripped, and the residue, in ether (ca. 600 mL), was washed (saturated aqueous $NaHCO_3$, with $Et_2O$ back extraction) and dried ($K_2CO_3$). After the solvent had been stripped, the addition of benzene (ca. 300 mL) transformed the resulting oil into a white solid. Heating dissolved it, and cooling precipitated it. It was filtered, washed with benzene, and while moist, used directly in the next step. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.14 (s, 2H), 7.77 (d, $J = 8.7$ Hz, 2H), 7.69 (dd, $J = 8.7$ Hz and $J = 1.7$ Hz, 2H), 4.84 (d, $J = 3.0$ Hz, 2H), 4.36 (d, $J = 3.0$ Hz, 2H), 4.06 (s, 8H), 2.05 (broad s, 2H).

*n*-BuBr (50.0 mL, 0.467 mol) was added to this material and powdered KOH (50.6 g, 0.904 mol) in DMSO (225 mL), and the mixture was stirred for 4.5 h. $Et_3N$ (200 mL) was added, and the mixture was poured onto ice and saturated aqueous $NaHCO_3$ (800 mL). Extraction ($Et_2O$, 3×), washing (saturated aqueous $NaHCO_3$), drying ($K_2CO_3$), stripping, and heating in a vacuum at 130 °C for 30 min gave 41.9 g (92% from dioxolane **20**) of pure **10c**, an oil. A similar experiment converted 23.7 g of **20** into 48.9 g of **10c** (an 88% yield). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.14 Hz (s, 2H), 7.75 (d, $J = 8.6$ Hz, 2H), 7.70 (dd, $J = 8.7$ Hz and $J = 1.7$ Hz, 2H), 4.81 (d, $J = 2.9$ Hz, 2H), 4.32 (d, $J = 2.9$ Hz, 2H), 4.08 (t, $J = 5.0$ Hz, 4H), 3.86 (t, $J = 5.0$ Hz, 4H), 3.59 (t, $J = 6.7$ Hz, 4H), 1.63 (quintet, $J = 7.1$ Hz, 4H), 1.43 (sextet, $J = 7.5$ Hz, 4H), 0.95 (t, $J = 7.5$ Hz, 6H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 159.77, 133.90, 133.30, 132.86, 127.25, 125.11, 123.84, 83.31, 71.34, 69.04, 67.44, 31.81, 19.34, 13.98. IR ($CDCl_3$) 2960, 2935, 2874, 1644, 1598, 1457, 1339, 1286, 1235, 1117 cm$^{-1}$; MS (EI) *m/z* 413 ($MH^+$), 341, 297, 241, 225, 212, 197, 152; HRMS (EI) calcd for $C_{26}H_{37}O_4$ 413.2614, found 413.2681.

**1,4,13,16-Tetrahydro-1,4,13,16-tetraoxo-6,11-bis(2-butoxyethoxy)-[6]helicene (11c).** Diene **10c** (20.0 g, 48.5 mmol) and *p*-benzoquinone (68.3 g, 632 mmol) in 120 mL of toluene were heated in an oil bath at 100 °C for 65 h, cooled to 25 °C, and filtered. The precipitate was boiled for 5 min in $CHCl_3$ and refiltered, and this was repeated three times, when TLC analysis (6% THF in toluene, $R_f = 0.4$) failed to show additional **11c** in the filtrate. The solvent was stripped and the residue heated at 100 °C to sublime excess benzoquinone from it into a trap. Boiling for 10 min with $CCl_4$ (300 mL, repeated twice), cooling, filtering, and one more wash with $CCl_4$ (ca. 200 mL) then gave, after chromatography (3 in. × 6 in., eluting with 6% THF in toluene), 14.2 g (47%) of **11c**, a red solid, mp 163−164 °C. A similar experiment converted 48.9 g of **10c** into 32.2 g (44%) of **11c**. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.47 (d, $J = 8.6$ Hz, 2H), 7.96 (d, $J = 8.7$ Hz, 2H), 7.53 (s, 2H), 6.78 (d, $J = 10.2$ Hz, 2H), 6.63 (d, $J = 10.2$ Hz, 2H), 4.57 (m, 2H), 4.48 (m, 2H), 4.01 (m, 4H), 3.64 (t, $J = 6.60$ Hz, 4H), 1.66 (m, 4H), 1.45 (m, 4H), 0.96 (t, $J = 7.40$ Hz, 6H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 185.20, 185.10, 158.50, 140.20, 135.60, 133.50, 133.10, 131.20, 128.50, 127.60, 127.2, 126.3, 122.20, 102.10, 71.50, 68.8 (two peaks), 31.78, 19.30, 13.90. IR ($CDCl_3$) 2961, 2935, 2873, 1663, 1596, 1514, 1308, 1294, 1231, 1214, 1128, 1102 cm$^{-1}$; MS (EI) *m/z* 620 ($M^+$), 419; HRMS (EI) calcd for $C_{38}H_{36}O_8$, 620.2410, found 620.2429. Anal. Calcd for $C_{38}H_{36}O_8$: C, 73.53; H, 5.85. Found: C, 73.21; H, 5.74.

The yields are much lower when the reaction mixtures are refluxed (bp of toluene is 111 °C) rather than heated in a bath at 100 °C. Thus, when 21.8 g (52.9 mmol) of **10c** and 75 g (690 mmol) of *p*-benzoquinone were refluxed in toluene for 12 h and then heated at 100 °C for 53 h, the yield was only 28% (9.3 g).

**2,7-Bis{1-[dimethyl(1,1-dimethylethyl)siloxy]ethenyl}naphthalene (10d).** Diketone **18** (5 g, 24 mmol), NaI (14.1 g, 94 mmol, previously dried in a vacuum with a flame), $Et_3N$ (15 mL, 106 mmol), *t*-$BuMe_2SiCl$ (14.2 g, 94 mmol), and $CH_3CN$ (47 mL) were refluxed for 1 h. $Et_3N$ (20 mL) and $Et_2O$ (100 mL) were added, and the solution was washed with saturated aqueous $NaHCO_3$ (which was back extracted with $Et_2O$) and then 15% aqueous NaOH (3×) and dried ($K_2CO_3$). After solvent had been removed, the residue was dried *in vacuo*. Recrystallization from a minimal amount of MeOH, containing a small amount of $Et_3N$, with final cooling at −20 °C, filtration, and two washes with cold MeOH, gave 3.49 g (88%) of **10d**, as needles. $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 8.09 (s, 2H), 7.74 (d, $J = 8.7$ Hz, 2H), 7.67 (dd, $J = 8.6$ and 1.6 Hz, 2H), 5.04 (d, $J = 1.7$ Hz, 2H), 4.53 (d, $J = 1.8$ Hz, 2H), 1.05 (s, 18H), 0.24 (s, 12H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 155.57, 135.22, 132.94, 132.88, 127.20, 125.04, 123.63, 91.75, 25.87, 18.39. IR ($CDCl_3$) 2959, 2931, 2886, 2859, 1614, 1472, 1463, 1361, 1341, 1285, 1255, 1232, 1145, 1104, 1088, 1015, 1004, 842, 831 cm$^{-1}$; MS (EI) *m/z* 441 ($MH^+$), 327, 285; HRMS (EI) calcd for $C_{26}H_{40}O_2Si_2$, 440.2567, found 440.2565.

**1,4,13,16-Tetrahydro-1,4,13,16-tetraoxo-6,11-bis[dimethyl(1,1-dimethylethyl)siloxy][6]helicene (11d).** Diene **10d (**7g, 15.9 mmol) and *p*-benzoquinone (22.3 g, 0.206 mol) in 40 mL of toluene were heated in a bath of oil at 100 °C for 72 h. The solvent was stripped from the deep red mixture, and the residue was boiled with $CCl_4$ (100 mL), stirred, cooled to 25 °C, and filtered. (The precipitates were washed with more $CCl_4$). Solvent was removed from the red solution, and heating to 100 °C in a vacuum sublimed excess benzoquinone onto a cold condenser. After being loaded onto a silica gel column with the aid of warm $CHCl_3$ and benzene, two chromatographies (3 in. × 6 in., eluting in the first with 20% EtOAc−hexanes and in the second with 80% $CH_2Cl_2$−benzene) gave, after further heating *in vacuo* at 100 °C (to collect additional benzoquinone on a condenser), 4.35 g (42%) of helicene **11d**, a red solid. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.36 (d, 8.6 Hz, 2H), 7.95 (d, $J = 8.8$ Hz, 2H), 7.51 (s, 2H), 6.77 (d, $J = 10.3$ Hz, 2H), 6.63 (d, $J = 10.0$ Hz, 2H), 1.15 (s, $J = 9$H), 0.49 (d, 6H), 0.41 (s, 6H); MS *m/z* (EI) 648 ($M^+$), 536; HRMS (EI) calcd for $C_{38}H_{41}O_6Si_2$, 649.2442, found 649.2456. Anal. Calcd for $C_{38}H_{40}O_6Si_2$: C, 70.34; H, 6.21. Found: C, 70.42; H, 6.22.

**Resolution of 11c.** Liquid dicyclohexylcarbodiimide (86.8 mL, 0.42 mol), along with THF washings, was added to a solution at 0 °C of 1-[(4-methylphenyl)sulfonyl]-(*S*)-(−)-proline (0.84 mol, prepared in 96% yield from L-proline, TsCl, and aqueous $K_2CO_3$)[63] in 421 mL of THF. The mixture was stirred at 25 °C overnight, filtered, and washed (10×) with THF. After solvent had been removed from the filtrate, the residue was dried *in vacuo* at 100 °C. The solid was taken up in boiling EtOAc (500 mL), to which hexanes (150 mL) were slowly added until a solid started to precipitate. The mixture was boiled for another 1 h and allowed to cool to 25 °C. Filtration, washing with EtOAc (3×), and drying *in vacuo* at 100 °C gave 160.5 g (73%) of *N*-tosyl-L-proline anhydride. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.76 (d,

(63) Evans, D. A.; Nelson, J. V.; Vogel, E.; Taber, T. R. *J. Am. Chem. Soc.* **1981**, *103*, 3099, and references therein.

$J$ = 8.2 Hz, 4H), 7.33 (d, $J$ = 8.1 Hz, 4H), 4.34 (dd, $J$ = 8.1 and 4.0 Hz, 2H), 3.55 (m, 2H), 3.26 (m, 2H), 2.43 (s, 6H), 2.19 (m, 2H), 2.05 (m, 4H), 1.78 (m, 2H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 167.19, 143.97, 134.83, 129.89, 127.53, 61.07, 48.63, 30.43, 24.70, 21.57.

This anhydride (1.34 g, 2.71 mmol) was dissolved in 2 mL of hot DMF, and after the solution had cooled to 0 °C, TMEDA (0.30 g, 2.59 mmol), helicenebisquinone **11c** (0.20 g, 0.32 mmol), and Zn powder (0.632 g, 9.7 mmol) were added sequentially and the mixture was stirred at 0 °C for 4.5 h. After precipitates had been filtered through Celite (washing with THF), $Et_3N$ (0.5 mL) and $H_2O$ (0.5 mL) were added to the filtrate. The solution was diluted with $CHCl_3$ (ca. 50 mL), washed with 1 M aqueous NaOH (3X, back extracting twice with $CHCl_3$), 1 M HCl, $H_2O$ (3×), and finally brine, dried ($MgSO_4$), and stripped. The residue was dissolved in 4 mL of hot acetone, loaded onto a chromatography column (1.5 in. × 14 in.), and eluted with hexane−$CH_2Cl_2$−acetone (5:4:1). The diastereomer that eluted first was (−)-**14** (0.250 g, 95%), followed by (+)-**14** (0.245 g, 93%). Both were yellow solids. A similar experiment starting with 2.00 g of **11c** gave 2.49 g of (−)-**14** (95%) and 2.50 g of (+)-**14** (95%). These were isolated by loading 1.0−1.5 g portions of the crude product dissolved in 8 mL of warm acetone onto 2.25 in. × 14 in. columns and eluting as above.

To recover excess *N*-tosyl-L-proline, the 1 M NaOH layers above were washed with $CHCl_3$, acidified with concentrated HCl, and extracted with $CHCl_3$ (3×). Washing with $H_2O$ and brine, drying ($MgSO_4$), stripping (after some benzene had been added), and drying *in vacuo*, first at 100 °C and then at ca. 130 °C, recovered 87% of practically pure *N*-tosyl-L-proline.

**(+)-14**: $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.68 (d, $J$ = 8.4 Hz, 2H), 8.31 (d, $J$ = 8.4 Hz, 2H), 7.86 (d, $J$ = 8.0 Hz, 4H), 7.46 (s, 2H), 7.38 (d, $J$ = 8.0 Hz, 4H), 7.19 (d, $J$ = 8.0 Hz, 4H), 7.0 (d, $J$ = 8.4 Hz, 4H), 6.69 (d, 8.0 Hz, 2H), 6.27 (d, 8.4 Hz, 2H), 4.65 (m, 4H), 4.56 (m, 2H), 3.99 (m, 4H), 3.65 (t, $J$ = 6.4 Hz, 6H), 3.25 (m, 2H), 3.10 (m, 4H), 2.96 (m, 2H), 2.47 (s, 6H), 2.28 (s, 6H), 2.25 (m, 2H), 2.16 (m, 2H), 1.87−1.51 (m, 14 H), 1.40 (sextet, $J$ = 7.6 Hz, 4H), 0.92 (t, $J$ = 7.2 Hz, 6H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 171.41, 169.27, 154.11, 143.96, 143.84, 142.94, 142.61, 135.89, 134.99, 131.86, 129.95 (two peaks), 129.13 (two peaks), 127.75, 127.68, 127.55 (two peaks), 127.20 (two peaks), 126.86, 125.95, 124.88, 120.58, 120.43, 118.02, 115.94, 97.66, 71.40, 69.25, 68.65, 60.45, 59.48, 48.67, 47.76, 32.00, 31.21, 30.62, 25.02, 24.08, 21.57, 21.39, 19.38, 13.98; IR ($CDCl_3$) 2961, 2933, 2874, 1770, 1619, 1608, 1528, 1511, 1495, 1460, 1446, 1342, 1292, 1262, 1198, 1164, 1132, 1095, 1024, 842, 816, 589 cm$^{-1}$; MS (EI) *m/z* 1630 ($MH^+$), 1476, 1378, 1127, 876, 625; HRMS Calcd for $C_{86}H_{93}N_4O_{20}S_4$ 1629.5270, found 1629.5256.

**(−)-14**: $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.51 (d, $J$ = 8.4 Hz, 2H), 8.00 (d, $J$ = 8.4 Hz, 2H), 7.88 (d, $J$ = 8.0 Hz, 4H), 7.71 (d, 8.4 Hz, 4H), 7.60 (s, 2H), 7.45 (d, $J$ = 8.0 Hz, 4H), 7.32 (d, $J$ = 8.4 Hz, 4H), 6.94 (d, $J$ = 8.4 Hz, 2H), 6.27 (d, $J$ = 8.4 Hz, 2H), 4.80 (dd, $J$ = 8.4 and 4.8 Hz, 2H), 4.52 (t, $J$ = 4.4 Hz, 4H), 3.88 (m, 4H), 3.53 (m, 2H), 3.48 (t, $J$ = 6.4 Hz, 4H), 3.36 (m, 4H), 3.17 (m, 2H), 3.00 (q, 8.8 Hz, 2H), 2.44 (s, 6H), 2.42 (s, 6H), 2.37 (s, 4H), 2.18 (m, 2H), 1.87 (septet, $J$ = 6.8 Hz, 2H), 1.52 (pentet, $J$ = 6.8 Hz, 4H), 1.35 (m, 8H), 1.16 (m, 2H), 0.89 (t, $J$ = 7.6 Hz, 6H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 171.01, 169.37, 154.00, 143.84, 143.62, 143.54, 143.21, 135.58, 135.08, 131.16, 129.85 (two peaks), 129.80 (two peaks), 129.97 , 127.72 (two peaks), 127.49 (two peaks), 127.08, 126.43, 126.12, 124.66, 121.06, 120.37, 118.78, 116.36, 98.00, 70.88, 69.17, 68.64, 60.71, 58.66, 48.64, 47.85, 31.92, 31.42, 29.70, 25.08, 23.91, 21.48 (two peaks), 19.32, 13.95; IR ($CDCl_3$) 2961, 2933, 2874, 1769, 1619, 1609, 1527, 1511, 1461, 1446, 1351, 1341, 1293, 1199, 1163, 1133, 1095, 1013, 842, 816, 589 cm$^{-1}$; MS (EI) *m/z* 1630 ($MH^+$), 1476, 1378, 1127, 876, 625; HRMS Calcd for $C_{86}H_{93}N_4O_{20}S_4$ 1629.5270, found 1629.5230.

**Recovery of Nonracemic Helicenes 11c from Tetraesters 14.** The diastereomerically pure helicenebisquinone (+)-**14** (3.04 g, 1.87 mmol) as a solid (washed in with THF) was added in portions to a stirred mixture of $LiAlH_4$ (849 mg, 22.4 mmol) in 18.7 mL of THF at 0 °C. The mixture was refluxed for 3 h, cooled to 0 °C, and while still under a $N_2$ atmosphere, slowly quenched, while being stirred, with saturated aqueous $NH_4Cl$ (ca. 1 mL), 1 M HCl (ca. 10 mL, added slowly), and finally more 1 M HCl (100 mL). The bright yellow solution obtained by extraction with ethyl acetate (3×), washing with water (1×), and drying ($MgSO_4$), when treated with chloranil (1.15 g, 4.47 mmol) immediately turned red. The solution was filtered, washed twice with saturated aqueous $NaHCO_3$, dried ($MgSO_4$), and filtered again. After the solvent had been stripped, chromatography (eluting with 5% THF in toluene), followed by drying *in vacuo* at 25 °C, gave 1.09 g (94%) of pure helicene (+)-**11c**, a noncrystalline solid. The $^1$H NMR and $^{13}$C NMR spectra were identical to those of the racemic material. $[\alpha]_D$ = +2249 (*c* 0.0105, $CH_3CN$). UV-vis ($CH_3CN$, $c = 1.66 \times 10^{-5}$ M) $\lambda_{max\ (nm)}$ (log $\epsilon$) 300 (4.5), 282 (4.3), 248 (4.7). CD ($c = 1.66 \times 10^{-5}$ M, $CH_3CN$) nm ([$\theta$]) 352 ($-4.9 \times 10^6$), 297 ($3.8 \times 10^6$), 260 ($-2.6 \times 10^6$), 226 ($5.1 \times 10^6$), 214 ($-1.7 \times 10^6$). The same reaction conditions applied to the other diastereomer, (−)-**14**, gave pure (−)-**1**. $[\alpha]_D$ = −2247 (*c* = 0.110 g/L, $CH_3CN$). UV-vis ($CH_3CN$, $c = 1.66 \times 10^{-5}$ M) $\lambda_{max\ (nm)}$ (log $\epsilon$) 300 (4.5), 282 (4.3), 249 (4.7). CD ($c = 1.66 \times 10^{-5}$ M, $CH_3CN$), nm ([$\theta$]), 351 ($4.7 \times 10^6$), 296 ($-3.8 \times 10^6$), 259 ($2.4 \times 10^6$), 226 ($-5.8 \times 10^6$), 213 ($1.5 \times 10^6$).

**1,4,13,16-Tetrahydro-1,4,13,16-tetraoxo-6,11-bis[1-(2-butoxyethoxy)ethenyl]-3,14-bis[1-[2-hydroxymethyl)pyrrolidinyl]][6]helicene (15).** Helicenebisquinone **11c** (4 g, 6.5 mmol) was added to a solution of (*S*)-2-(hydroxymethyl)pyrrolidine[20] (3.26 g, 32.2 mmol) and $Cu(OAc)_2 \cdot H_2O$ (6.69 g, 33.5 mmol) in 32 mL of $CHCl_3$ plus 32 mL of MeOH, and the solution was refluxed under $O_2$ for 20 h. Dilution with $CHCl_3$ (150 mL), washing with 1 M HCl, 30% aqueous $NH_3$ (3×), and $H_2O$, drying ($MgSO_4$), and stripping gave 5.78 g of crude **15** as a solid. Chromatography (2.25 in. × 6.5 in., eluting with 15% EtOH in $CHCl_3$) gave 2.10 g of (+)-**15** ($R_f$ 0.33) and 2.21 g of (−)-**15** ($R_f$ 0.42), an 82% yield. (+)-**15**: $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.16 (d, $J$ = 8.4, 2H), 7.90 (d, $J$ = 8.8 Hz, 2H), 6.59 (br s, 2H), 5.31 (s, 2H), 4.14 (m, 1H), 3.96 (m, 2H), 3.84 (m, 1H), 3.35 − 3.77 (m, $J$ = 14H), 3.26 (m, 2H), 2.61 (m, 2H), 1.85 (m, 4H), 1.65 (pentet, $J$ = 7.4 Hz, 4H), 1.45 (sextet, 8.0 Hz, 4H), 1.76−1.40 (m, 10H), 0.99 (t, $J$ = 7.2 Hz, 6H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 183.40, 181.79, 180.74, 158.76, 151.05, 135.60, 131.81, 130.90, 127.66, 127.49, 126.92, 126.33, 121.95, 102.17, 100.89, 71.48, 68.76, 65.33, 62.45, 50.43, 31.69, 28.30, 21.10, 29.29, 13.93. IR ($CDCl_3$) 3628, 3450, 2962, 2936, 2874, 1667, 1611, 1592, 1554, 1511, 1480, 1456, 1409, 1381, 1349, 1287, 1232, 1211, 1440, 1086, 1040, 1016 cm$^{-1}$; MS (EI) *m/z* 819 (MH+), 787, 590.; HRMS calcd for $C_{48}H_{55}N_2O_{10}$ 819.3857, found 819.3825. $[\alpha]_D$ = +4071 (*c* 0.0206, $CHCl_3$). UV-vis ($CH_3CN$, $c = 1.25 \times 10^{-5}$ M) $\lambda_{max\ (nm)}$ (log $\epsilon$) 407 (4.0), 330 (4.5), 297 (4.6). CD ($CH_3CN$, $c = 1.25 \times 10^{-5}$ M), nm ([$\theta$]), 268 ($8.3 \times 10^6$), 306 ($-5.3 \times 10^6$), 330 ($-7.8 \times 10^6$), 409 ($5.7 \times 10^6$), 452 ($4.0 \times 10^6$). (−)-**15**: $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.36 (d, $J$ = 8.7 Hz, 2H), 7.89 (d, $J$ = 8.7 Hz, 2H), 7.46 (br s, 2H), 5.33 (br s, 2H), 4.53 (m, 2H), 4.41 (m, 2H), 3.97 (t, $J$ = 4.6 Hz, 4H), 3.63 (t, $J$ = 6.6 Hz, 4H), 3.50 (m, 2H), 3.31 (m, 8H), 1.96 (m, 8H), 1.66 (quintet, 6.6 Hz, 4H), 1.44 (sextet, 7.2 Hz, 4H), 0.96 (t, $J$ = 7.4 Hz, 6H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 181.57, 180.18, 157.46, 151.28, 135.54, 131.46, 130.16, 126.54 (two peaks), 126.22, 126.04, 122.07, 101.20, 100.08, 71.25, 68.87, 67.59, 61.96, 60.10, 52.20, 31.65, 26.46, 23.86, 19.30, 13.94. IR ($CDCl_3$) 3307, 2961, 2935, 2875, 1669, 1593, 1558, 1512, 1482, 1466, 1430, 1410, 1364, 1342, 1240, 1233, 1211, 1088, 1048, 1008 cm$^{-1}$; MS (EI) *m/z* 819 (MH+), 789, 590. HRMS calcd for $C_{48}H_{55}N_2O_{10}$ 819.3857, found 819.3854. $[\alpha]_D$ = −3738 (*c* 0.0215, $CHCl_3$); UV-vis ($CH_3CN$, $c = 6.26 \times 10^{-5}$ M) $\lambda_{max\ (nm)}$ (log $\epsilon$) 409 (4.0), 324 (4.5), 299 (4.6). CD ($CH_3CN$, $c = 1.21 \times 10^{-5}$ M), nm ([$\theta$]), 270 ($-8.8 \times 10^6$), 302 ($4.9 \times 10^6$), 333 ($9.1 \times 10^6$), 415 ($-6.5 \times 10^6$), 443 ($-5.0 \times 10^6$).

**Addition of L-Prolinol to (−)-11c.** A mixture of (−)-**11c** (4 mg, 7 $\mu$mol), L-prolinol (9 mg, 90 $\mu$mol) and $Cu(OAc)_2$ (7 mg, 40 $\mu$mol) in 1 mL of 1:1 MeOH−$CHCl_3$ open to the air was refluxed for 12 h. Dilution with $CH_2Cl_2$, aqueous workup, solvent removal, and trituration with hexane left a red solid. Chromatography (eluting with 15% EtOH in $CHCl_3$) gave (−)-**15c** (5 mg, 94%), whose $^1$H NMR spectrum was identical to that recorded above.

**Adduct of 11c and Pyrrolidine.** A mixture prepared by adding pyrrolidine (0.24 mL, 0.20 g, 2.8 mmol) to a solution of **11c** (50 mg, 81 mmol) and $Cu(OAc)_2$ (0.20 g, 1.22 mmol) in 6 mL of 1:1 MeOH−$CH_2Cl_2$ was refluxed for 1 h while open to the air. After the solvent had been stripped, the residue triturated with hexane, and a solution in $CH_2Cl_2$ filtered, chromatography (0.5 in. × 3 in., eluting with 25% acetone in $CH_2Cl_2$) gave an adduct, seemingly **15** without the hydroxymethyl groups (56 mg, 92%), a red-orange solid, mp 208−212 °C. The $^1$H NMR integrals in the region of quinone proton resonance imply this to be >95% one isomer. $^1$H NMR $\delta$ 8.38 (d, $J$

= 8.7 Hz, 2H), 7.87 (d, $J$ = 8.7 Hz, 2H), 7.49 (s, 2H), 5.43 (s, 2H), 4.55 (m, 2H), 4.42 (m, 2H), 3.98 (t, $J$ = 4.8 Hz, 4H), 3.64 (t, $J$ = 6.6 Hz, 4H), 3.46 (m, 2H), 3.22 (m, 4H), 2.97 (m, 2H), 2.04 (m, 2H), 1.84 (m, 6H), 1.66 (m, 4H), 1.45 (m, 4H), 0.97 (t, $J$ = 7.4 Hz, 6H); $^{13}$C NMR $\delta$ 183.46, 180.94, 158.82, 151.04, 136.26, 132.48, 130.88, 127.71, 127.39, 127.05, 126.31, 122.05, 101.07, 100.79, 71.53, 68.90, 68.83, 50.92, 50.26, 31.79, 26.13, 23.81, 19.33, 13.94; MS (EI) *m/z* 759 ($MH^+$), 657, 622, 590, 570, 542; HRMS calcd for $C_{46}H_{50}N_2O_8$ 758.3568, found 758.3558.

**Adducts of 3 and Pyrrolidine.** A mixture formed by adding pyrrolidine (51 mg, 60 $\mu$l, 0.72 mmol) to a solution of **3** (8 mg, 21 $\mu$mol) and $Cu(OAc)_2$ (51 mg, 0.309 mmol) in 1.5 mL of 1:1 MeOH−$CH_2Cl_2$, while open to the air, was refluxed for 1.5 h. After solvent had been stripped, the residue triturated with hexane, and a solution in $CH_2Cl_2$ filtered through a short plug of silica (washed through with 1:1 $CH_2Cl_2$−acetone), preparative TLC (60 Å, 1000 $\mu$ silica gel, from Whatman, developed with 30% acetone in $CH_2Cl_2$) separated a symmetrical and an unsymmetrical adduct. The $^1$H NMR spectra of the former exhibits a single quinone hydrogen resonance, at $\delta$ 5.47, and that of the latter exhibits two, at $\delta$ 5.57 and 5.43. The intensities of these peaks in the spectrum of the crude product (4.5:1.0:1.0) showed the ratio of the symmetrical and unsymmetrical adducts to be 2.3:1.

**Reductive Acetylation of Helicene Diol (−)-15.** A mixture of 100 mg of (−)-**15**, 253 mg of Zn powder, 1.24 mL of $Ac_2O$, and a catalytic amount of $Me_4N^+Br^-$ [64] were heated to ca. 130 °C for about 2 min. $Et_3N$ (0.5 mL) was added, and heating was continued for another few minutes. The mixture was filtered, and the precipitate, after it had been washed with EtOAc, was dried *in vacuo* at 100 °C. Chromatography (0.75 in. × 5 in., eluting with 40% EtOAc in hexanes) gave 104 mg (80%) of helicene hexaacetate (−)-**16**, mp 142−144 °C. $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 8.44 (d, $J$ = 8.4 Hz, 2H), 7.95 (d, $J$ = 8.4 Hz, 2H), 7.10 (s, 2H), 6.91 (s, 2H), 4.51 (pentet, 5.2 Hz, 3H), 4.38 (pentet, 5.2 Hz, 2H), 4.00 (t, $J$ = 5.1 Hz, 4H), 3.93 (dd, 3.2 and 10.9 Hz, 2H), 3.66 (t, $J$ = 6.4 Hz, 4H), 3.54 (m, 2H), 3.08 (m, 2H), 2.80 (m, 2H), 2.46 (s, 6H), 2.05 (s, 6H), 1.59−1.90 (m, 12H), 1.44 (sextet, $J$ = 7.2 Hz, 4H), 0.96 (t, $J$ = 7.4 Hz, 6H), 0.83 (s, 6H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 170.78, 168.81, 167.87, 151.46, 143.64, 136.10, 131.76, 131.13, 126.44, 126.36, 124.00, 122.76, 120.37, 119.59, 110.61, 97.73, 71.47, 69.28, 68.58, 64.30, 59.25, 50.26, 31.87, 28.14, 23.47, 21.26, 20.94, 19.53, 19.33, 13.95; IR ($CDCl_3$) 2963, 2935, 2875, 1756, 1613, 1515, 1474, 1410, 1386, 1354, 1304, 1257, 1229, 1206, 1190, 1162, 1129, 1036, 980, 806; MS (EI) *m/z* 1075 (MH+), 1033, 1002, 990, 974, 960, 930. HRMS calcd for $C_{60}H_{70}N_2O_{16}$ 1074.4730, found 1074.4727; $[\alpha]_D$ = −2308 (*c* 0.0217, $CHCl_3$). A crystal suitable for X-ray diffraction analysis was obtained from EtOAc−hexane.

**Crystallographic Structure Determination for 16.** Preliminary photographic evidence showed 2/*m* Laue symmetry. The assignment of the noncentrosymmetric space group $P2_1$ was based on systematic absences in the diffraction data and the chirality requirement. No corrections for absorption were applied to the data.

To solve the structure, which contains 148 light atoms, we used direct methods and controlled the composition of the subset used for the initial stage of tangent refinement. A single unique and correct solution was found among 50,000 solutions generated using a subset based on the highest estimated α-values. Negative quartets were used to assist in the selection of the best subset phase permutations. Data limitations allowed anisotropic refinement of only the nitrogen and oxygen atoms. Hydrogen atoms were treated as idealized fixed contributions. The enantiomer reported was chosen on the basis of the known stereochemistry of the residues derived from proline. Computations used the SHELXTL (ver. 4.2) library of programs (G. Sheldrick, Siemens XRD, Madison, WI). The results and details are in the Supplementary Information.

**1,4,10,13-Tetrahydro-1,4,10,13-tetraoxo-6,9-bis(2-butoxyethoxy)-[5]helicene (24).** 1, 4-Diacetylbenzene (16.2 g, 100 mmol), ethylene glycol (17 mL, 300 mmol), and $TsOH·H_2O$ (1.9 g, 10 mmol) in benzene (200 mL) were refluxed in a Dean−Stark apparatus for 10 h. Water was removed from the trap, 4 Å molecular sieves were added to it, and reflux was continued for another 10 h. $Et_3N$ (75 mL) and then saturated aqueous $NaHCO_3$ were added. Extraction with benzene, washing with aqueous $NaHCO_3$, and drying gave 24.4 g (98%) of 2,2′-(1,4-benzenediyl)bis[2-methyl-1,3-dioxolane], mp 177−179 °C. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.46 (s, 4H), 4.05 (t, $J$ = 6.5 Hz, 4H), 3.79 (t, $J$ = 6.5 Hz, 4H), 1.67 (s, 6H); $^{13}$C NMR $\delta$ 142.90, 125.09, 108.77, 64.48, 27.53.

The dioxolane (19.8 g, 79 mmol), $Me_3SiCl$ (40.4 mL, 428 mmol), $Et_3N$ (65 mL, 460 mmol), and NaI (63.2 g, 428 mmol, previously dried by vigorous heating until vapors ceased to evolve) were refluxed for 1 h in 110 mL of $CH_3CN$. $Et_3N$ (70 mL) and $Et_2O$ (500 mL) were added, and the mixture was poured into saturated aqueous $NaHCO_3$ (500 mL). Extraction with $CH_2Cl_2$ (2×), washing with saturated aqueous $NaHCO_3$, drying ($K_2CO_3$), and removal of solvent *in vacuo* gave an oil that, although contaminated with silyl impurities, was used directly in the next step. $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.60 (s, 4H), 4.70 (d, $J$ = 1 Hz, 2H), 4.20 (d, $J$ = 1 Hz, 2H), 3.95 (m, 8H), 0.15 (s, 18H).

This was stirred for 4 h with $K_2CO_3$ (18 g, 0.13 mol) and MeOH (325 mL). The solvent was removed, and EtOAc and saturated aqueous $NaHCO_3$ were added. Some white solid diol crystallized and was filtered (3.2 g). Another 17.2 g was obtained from the organic solution and from a further EtOAc extract of the aqueous portion. Mp 106−108 °C; $^1$H NMR (300 MHz, DMSO-$d_6$) $\delta$ 7.62 (s, 4H), 4.88 (s, 2H), 4.78 (d, $J$ = 1 Hz, 2H), 4.30 (d, $J$ = 1 Hz, 2H), 3.85 (t, $J$ = 5.3 Hz, 4H), 3.75 (t, $J$ = 5.3 Hz, 4H); $^{13}$C NMR (75 MHz, DMSO-$d_6$) $\delta$ 158.46, 135.95, 124.84, 83.24, 69.55, 59.48.

To this was added powdered KOH (36 g, 0.65 mol) in DMSO (180 mL), followed by *n*-BuBr (35 mL, 0.323 mol), and the mixture was stirred for 3.5 h. $Et_3N$ (150 mL) was added, and the mixture was poured onto ice and saturated aqueous $NaHCO_3$ (600 mL). Extraction with $Et_2O$ (3×), washing with saturated aqueous $NaHCO_3$, drying ($K_2CO_3$), and stripping gave 30.8 g (>100%) of crude 1,4-bis[1-(butoxyethoxy)-ethenyl]benzene.

This material, *p*-benzoquinone (111 g, 1.03 mol), and 4-*tert*-butylcatechol (200 mg) were refluxed for 72 h in 500 mL of benzene. A precipitate was filtered and washed with $CH_2Cl_2$ until no further red matrial eluted. After the solvent had been removed, the product, in four portions, was chromatographed (3 in. × 6 in., eluting with 5:1 $CH_2Cl_2$−petroleum ether), giving 14 g (31% yield from 1,4-diacetylbenzene) of **24**, a deep-red solid, mp 123−125 °C. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.40 (s, 2H), 7.58 (s, 2H), 6.88 (d, $J$ = 10.1 Hz, 2H), 6.77 (d, $J$ = 10.1 Hz, 2H), 4.50 (m, 4H), 3.98 (t, $J$ = 4.8 Hz, 4H), 3.61 (t, $J$ = 6.6 Hz, 4H), 1.63 (m, 4H), 1.43 (m, 4H), 0.94 (t, $J$ = 7.4 Hz, 6H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 186.1, 185.0, 158.0, 139.9, 136.0, 131.8, 129.6, 127.5, 122.2, 102,7, 71.5, 68.7, 68.6, 31.8, 19.3, 13.7; MS (EI) *m/z* 570 ($M^+$, 100%), 469 (20%), 369 (56%), 357 (18%), 314 (44%), 291 (26%), 268 (62%); HRMS (EI) calcd for $C_{34}H_{34}O_8$ 570.2254, found 570.2266. Anal. Calcd for $C_{34}H_{34}O_8$: C, 71.56; H, 6.01. Found: C, 71.92; H, 5.95.

**Acknowledgment.** We are grateful for the support provided by The National Science Foundation (NSF CHE92-24634 and CHE95-12349) and The Kanagawa Academy of Science and Technology. C.N. thanks the Organic Chemistry Division of the American Chemical Society and Pfizer, Inc., for fellowship support. B.H.R. was supported during one summer by an NSF REU grant. We thank Prof. Gerard Parkin for help in obtaining the X-ray diffraction analysis.

**Supporting Information Available:** Methods used to prepare **4a**−**c**, **6a,b**, and **12**; experimental procedures used to prepare **2**, **4a**−**c**, **5a**−**c**, **6a,b**, **7a,b**, **12**, **13**, and **24**−**26**; a listing of the X-ray diffraction analysis of **16** (25 pages). See any current masthead page for ordering and Internet access instructions.

JA9721327

(64) Fieser, L. F.; Fieser, M. *Reagents for Organic Synthesis*; Wiley: New York, 1967; Vol. 1, p 1143.