Acidified Alcohols as Agents to Introduce and Exchange Alkoxyls on the Periphery of Helicenes

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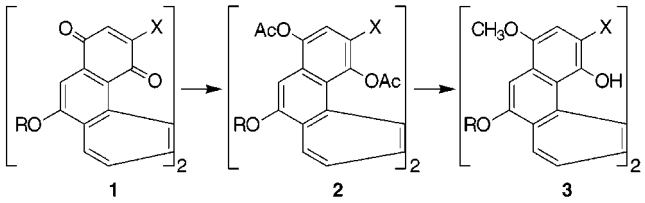
Alcohols containing HCl transform the hydroquinone reduction-products of helicenebisquinones into *p*-alkoxyphenols that have the alkoxyls specifically on the peripheries of the helices. The reactions are quick, and the yields are high. Alkoxyls at the 6-position are replaced also, but only after 2 h at 60 °C, not after the 5 min at 25 °C sufficient to replace the peripheral hydroxyls of the hydroquinones. After the remaining inside hydroxyls of a dihydroxytetramethoxy[6]helicene prepared by this procedure have been converted into camphanates, one diastereomer crystallizes from solution, allowing an enantiomer resolution to be carried out on a large scale. By then simply reapplying the procedure with alcoholic acid, a variety of resolved dihydroxytetraalkoxy[6]helicenes can be prepared in excellent yields without resolution procedures having to be developed for each. Similar procedures are effective when applied to a [7]carbohelicene.

Introduction

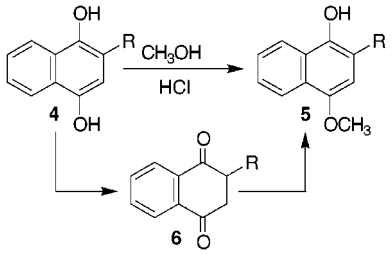
Helicenes with multiple alkoxy substituents on their periphery are the precursors of a number of new materials, including helical discotic liquid crystals,[1] self-assembling corkscrew structures with significant optical properties,[2] helical fully conjugated polymers,[3] and a helical ligand for asymmetric catalysis.[4] However, the introduction of the correct alkoxy groups at the right positions can sometimes be difficult. For example, to convert the [6]helicenebromoquinone **1** (X = Br) into methoxysalicylaldehyde **3** (X = CHO),[3] the steps used to place the methoxyls on the outside of the helix and the hydroxyls on the inside (Scheme 1) included selectively cleaving the less hindered esters of **2** (X = Br), converting the resulting phenols into methyl ethers, and then cleaving the remaining esters.

In this paper, we describe a much simpler procedure for effecting transformations such as these in a variety of helicenes. The procedure is an application of a reaction discovered by Russig[5] in 1900 (Scheme 2) that converts naphthalene-1,4-diols selectively into monoalkyl ethers and unsymmetrical naphthalene-1,4-diols specifically into one of the two possible monoethers (in Russig's case, **4** to **5**, R = CO_2H).[6,7] Russig's reaction is related to one discovered by Liebermann in 1882,[8] in which an alcohol and HCl transform α- and *β*-naphthols into naphthyl alkyl ethers.[9] It was not until 1980 that Laatsch[7b] applied this transformation to a number of naphthalene-1,4-diols and proposed a plausible mechanism, proceeding by way

Scheme 1



Scheme 2



of **6**.[10] This transformation, which we call the Russig−Laatsch reaction, puts the alkoxyl on the less hindered of the 1,4-oxygens and in the case of helicenes, as described below, does so with high specificity and yield.

†These authors contributed equally to the research.

(1) Nuckolls, C.; Katz, T. J. *J. Am. Chem. Soc.* **1998**, *120*, 9541.

(2) (a) Nuckolls, C.; Katz, T. J.; Castellanos, L. *J. Am. Chem. Soc.* **1996**, *118*, 3767. (b) Nuckolls, C.; Katz, T. J.; Katz, G.; Collings, P. J.; Castellanos, L. *J. Am. Chem. Soc.* **1999**, *121*, 79. (c) Verbiest, T.; Van Elshocht, S.; Kauranen, M.; Hellemans, L.; Snauwaert, J.; Nuckolls, C.; Katz, T. J.; Persoons, A. *Science (Washington, D.C.)* **1998**, *282*, 913. (d) Busson, B.; Kauranen, M.; Nuckolls, C.; Katz, T. J. Persoons, A. *Phys. Rev. Lett.* **2000**, *84*, 79. (e) Fox, J. M.; Katz, T. J.; Van Elshocht, S.; Verbiest, T.; Kauranen, M.; Persoons, A.; Thongpanchang, T.; Krauss, T.; Brus, L. *J. Am. Chem. Soc.* **1999**, *121*, 3453.

(3) Dai, Y.; Katz, T. J. *J. Org. Chem.* **1997**, *62*, 1274.

(4) Dreher, S. D.; Katz, T. J.; Lam, K.-C.; Rheingold, A. L. *J. Org. Chem.* **2000**, *65*, 815.

(5) Russig, F. *J. Prakt. Chem.* **1900**, *62*(2), 30.

(6) Subsequently **4**, with R = CH_3, was transformed into the ethyl ether analogous to **5** by: (a) Tishler, M.; Fieser, L. F.; Wendler, N. L. *J. Am. Chem. Soc.* **1940**, *62*, 1982. It was transformed into the methyl ether **5** by: (b) Bondinell, W. E.; DiMari, S. J.; Frydman, B.; Matsumoto, K.; Rapoport, H. *J. Org. Chem.* **1968**, *33*, 4351, and by Laatsch.[7b] Related examples, with R = OCH_3, were found by: (c) Baldwin, J. E.; Basson, H. H. *J. Org. Chem.* **1969**, *34*, 2788, and by Laatsch.[7b] Further examples with R = Br and Cl were found by Laatsch.[7b]

(7) (a) Laatsch, H. *Tetrahedron Lett.* **1976**, 3287. (b) Laatsch, H. *Liebigs Ann. Chem.* **1980**, 140. (c) Laatsch, H. *Liebigs Ann. Chem.* **1980**, 1321. (d) Laatsch, H. *Liebigs Ann. Chem.* **1985**, 251. (e) Laatsch, H. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1986**, *41B*, 377. (f) Laatsch, H. *Liebigs Ann. Chem.* **1991**, 385. (g) Laatsch, H. *Z. Naturforsch., B: Chem. Sci.* **1993**, *48*, 1291. (h) Kuroki, N.; Kitao, T.; Konishi, K. *Kôgyô Kagaku Zasshi* **1956**, *59*, 1056.

(8) (a) Liebermann, C.; Hagen, A. *Chem. Ber.* **1882**, *15*, 1427. (b) Gattermann, L. *Liebigs Ann. Chem.* **1888**, *72*, 244. (c) Bell, K. H.; McCaffery, L. F. *Aust. J. Chem.* **1993**, *46*, 731. The discovery has often been attributed to Gattermann, but Gattermann acknowledged learning the procedure from "Dr. Henriques of Berlin", presumably Robert Henriques, who at the time worked in the same laboratory as Liebermann. Henriques is said to have recommended the use of sulfuric acid for the conversion of α-naphthol into its ethyl ether, and Gattermann used this acid to prepare α-naphthyl methyl ether.

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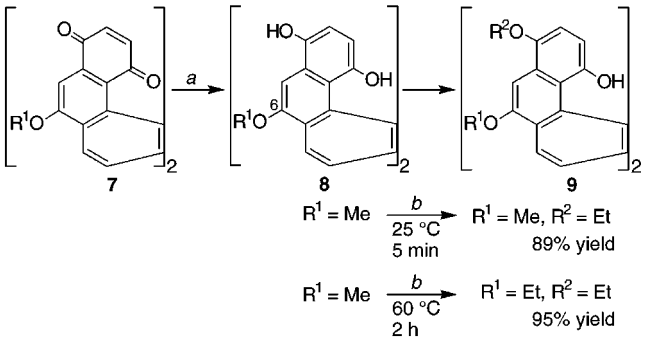
Scheme 3[a]



[a] Reaction conditions: (a) aqueous $Na_2S_2O_4$; (b) EtOH, HCl, $(ClCH_2)_2$.

This procedure is easy to carry out, and it can be used to introduce a variety of alkoxy groups in positions such as that occupied in **3** by the methoxyl, para to the hydroxyl. Remarkably, if desired, it also can be used to exchange alkoxyls at positions such as those occupied in **3** by the OR groups. In addition, because the bis-alkoxyphenols from these reactions are easier to resolve into enantiomers than the corresponding bis-1,4-diols, the alkoxyphenols can be used to prepare nonracemic bis-quinones such as **1** (X = H) more easily than was heretofore possible.

Results

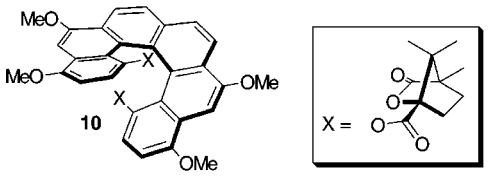
The procedure described here for the Russig−Laatsch reactions was developed in preliminary experiments. HCl gas saturated the alcohols before they were used and, unlike in Laatsch's procedure,[7a−g] was not subsequently bubbled into the reaction mixtures. Because the helicenes were often insoluble in the alcohols, 1,2-dichloroethane (bp 83 °C) was usually added as a cosolvent.

The Russig−Laatsch Reactions of [6]Helicene-tetraols 8. By means of aqueous sodium dithionite ($Na_2S_2O_4$),[11] **7** (R^1 = Me)[12] was reduced to **8** (R^1 = Me, Scheme 3), and this hydroquinone was combined with ethanolic HCl plus $(ClCH_2)_2$ for 5 min at room temperature, giving **9** (R^1 = Me, R^2 = Et) in 89% yield. If instead the reaction was carried out at 60 °C for 2 h, the methoxyls as well were completely replaced by ethoxyls. Under these conditions, **9** ($R^1 = R^2$ = Et) was obtained, and the yield was 95%.[13]

Similarly, **7** (R^1 = TIPS) was reduced to **8** (R^1 = TIPS), which with MeOH, EtOH, or BuOH, each saturated with HCl and mixed with $(ClCH_2)_2$, gave, after 2 h at 60 °C, **9** ($R^1 = R^2$ = Me, Et, and *n*-Bu) in 93%, 95%, and 90% yields, respectively. Helicene **7** with R^1 = TIPS was synthesized as described in the Experimental Section, from the TIPS-enol ether of 2,7-diacetylnaphthalene and *p*-benzoquinone. This helicene is similar to one prepared previously, **7** with R^1 = *t*-$BuMe_2Si$,[12] but the procedure used here, similar to one used previously to prepare other helicenebisquinones,[12,14] is simpler. Aryl silyl enol ethers are easy to synthesize and, when compared to their alkyl analogues, give better yields of helicenebisquinones upon reaction with *p*-benzoquinone,[12,14] Accordingly, the use described here of alcoholic acid to replace siloxyls by alkoxyls could be generally advantageous. It surmounts the need for desilylation reagents, such as CsF, and for expensive and toxic alkylating agents.[15]

The Russig−Laatsch reactions can also be carried out with long-chain alcohols, which previously had not been reported. Presumably because in previous procedures the alcohols were used in large excess, as the solvents, those that boil at high temperatures were difficult to separate from the product. However, after **8** (R^1 = TIPS) has been warmed for 2 h at 60 °C with a mixture of 10 times as many moles of dodecanol saturated with HCl and an equal volume of $(ClCH_2)_2$, the excess dodecanol can be removed by trituration with methanol, which selectively dissolves it. The yield of **9** ($R^1 = R^2 = n$-$C_{12}H_{25}$) was 80%. It probably would have been higher had not some of the helicene dissolved in the methanol.

Evidence that the alkyl groups are on the periphery and not in the positions that in **9** are occupied by the hydroxyls was shown unambiguously by the crystal structure[16] of **10**, the dextrorotatory diester of **9** ($R^1 = R^2$ = Me) with (*S*)-(−)-camphanic acid (see below). In none of these reactions was evidence found of the products in which the phenols on the inside of the helices, those labeled explicitly as OHs in structure **9**, had been alkylated. Thus, even after 7 h at 60 °C, none of the product like **9** ($R^1 = R^2$ = Me), but with OH replaced by OMe, was found when **8** (R^1 = TIPS) was combined with methanolic HCl in 1,2-dichloroethane.



The Russig−Laatsch reaction also can be used to exchange one set of alkoxyls for another. Thus, when **9** ($R^1 = R^2$ = Me) was combined for 2 h with HCl in EtOH at 75 °C or in BuOH or dodecanol at 90 °C, helicenes were obtained in which the methoxyls were replaced by ethoxyls, butoxyls, or dodecyloxyls. The yields were 93, 91, and 75%, respectively. These transformations proceeded more efficiently when methanol was removed as it formed, to prevent it from competing with the other alcohols for attachment to the aromatic nucleus. This was accomplished by carrying out the reactions above the boiling point of MeOH and capturing the distilled methanol in a cold bulb.

(9) The reaction was extended to the conversion of resorcinol to its monomethyl ether by: (a) Wallach, O.; Wüsten, M. *Chem. Ber.* **1883**, *16*, 149. It was extended to the conversion of phloroglucinol to its diethyl and dimethyl ethers by: (b) Will, W.; Albrecht, K. *Chem. Ber.* **1884**, *17*, 2098. (c) Will, W. *Chem. Ber.* **1888**, *21*, 602. The former extension was developed further by: (d) Merz, V.; Strasser, H. *J. Prakt. Chem.* **1900**, *61*, 103. The latter extension was developed further by: (e) Weidel, H.; Pollak, J. *Monatsh. Chem.* **1900**, *21*, 15, and references therein.

(10) For the tautomerism of phenols, see: (a) Forsén, S.; Nilsson, M. In *The Chemistry of the Carbonyl Group, Vol. 2*; Zabicky, J., Ed.; Interscience: New York, 1970; pp 168−183. (b) Thomson, R. H. *Quart. Rev. Chem. Soc.* **1956**, *10*, 27. (c) Pearson, M. S.; Jensky, B. J.; Greer, F. X.; Hagstrom, J. P.; Wells, N. M. *J. Org. Chem.* **1978**, *43*, 4617.

(11) Reference 2b and references in footnote 29 therein.

(12) Katz, T. J.; Liu, L.; Willmore, N. D.; Fox, J. M.; Rheingold, A. L.; Shi, S.; Nuckolls, C.; Rickman, B. H. *J. Am. Chem. Soc.* **1997**, *119*, 10054.

(13) This replacement took place even at ambient temperatures when the reaction times were greater than 5 min.

(14) (a) Fox, J. M.; Goldberg, N. R.; Katz, T. J. *J. Org. Chem.* **1998**, *63*, 7456. (b) Dreher, S. D.; Weix, D. J.; Katz, T. J. *J. Org. Chem.* **1999**, *64*, 3671.

(15) Oriyama, T.; Noda, K.; Yatabe, K. *Synlett* **1997**, 701.

(16) Thongpanchang, T.; Paruch, K.; Katz, T. J.; Rheingold, A. L.; Lam, K.-C..; Liable-Sands, L. *J. Org. Chem.*, in press.

Resolving the Enantiomers of 9. Helicenebisquinones have previously been resolved into their enantiomers by a procedure in which the quinones were reduced to hydroquinones, the latter's phenolic hydroxyls were acylated with camphanoyl chloride, and the resulting diastereomeric tetracamphanates were separated by chromatography.[2b,14] The camphanate esters, when compared to a number of esters of nonracemic acids, have proven to be particularly effective, for reasons that are now understood,[16] and the procedure using them has been applied to a large number of resolutions.[2b,14] Since the experiments described in this manuscript produce helicenediols, the possibility was tested that their diastereoisomeric *dic*amphanates would also be easy to prepare and separate even though they have only two camphanate groups per molecule, not four as in the helicenes previously resolved.

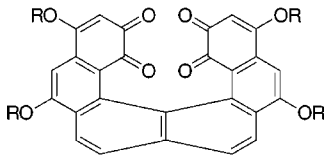
The tests were carried out with **9** ($R^1 = R^2 =$ Me). This diol was chosen because in the course of related work with a [5]helicenol (structure **16** below), the discovery was made that when the side chains are methoxyls, chromatography is not required to separated the diastereomeric camphanates as it is when the side chains are large alkoxy groups.[4] One diastereomer crystallizes.

An experimental procedure was developed that transforms diol **9** ($R^1 = R^2 =$ Me) into its dicamphanate, and because it uses only 3 mol of camphanoyl chloride per mole of the helicenediol, it is far superior to the one previously used to convert related tetraols into their tetracamphanates.[2b,14] That procedure used 12−15 mol of camphanoyl chloride per mole of helicenetetraol. In the new procedure the diol and the acid chloride are refluxed with triethylamine and 4-(dimethylamino)pyridine (DMAP) in 1,2-dichloroethane for 2 h. In the older procedure DMAP was not used.

Moreover, the dextrorotatory dicamphanate of **9** ($R^1 = R^2 =$ Me, structure **10**) crystallizes from a mixture of ethyl acetate and cyclohexane, and 5.7 g was isolated, a 66% yield. To obtain the levorotatory dicamphanate, small amounts of the (+)-isomer were removed from the remaining material by passing it in a mixture of hexane and ethyl acetate through a small plug of silica gel. A 62% yield of the (−)-isomer (5.2 g) was obtained. An additional 8−9% of each diastereomer could be isolated from residual material by means of chromatography. The camphanate groups could then be removed by combining the esters with potassium hydroxide in EtOH, and after workup, the nonracemic phenols **9** ($R^1 = R^2 =$ Me) were isolated, the (+)-enantiomer in 93% yield, and the (−)-enantiomer in 99% yield. *Noteworthy is the power of the Russig−Laatsch reaction to transform these substances into* **9** *($R^1 = R^2 =$ Et) in 93% yield, into* **9** *($R^1 = R^2 =$ n-Bu) in 91% yield, and into* **9** *($R^1 = R^2 =$ n-$C_{12}H_{25}$) in 75% yield, making it possible to obtain them in nonracemic form without a separate resolution procedure having to be developed for* each.[17] *Accordingly, the preparations of a variety of helicenes benefit from the simplicity with which* **9** *($R^1 = R^2 =$ Me) can be resolved.*

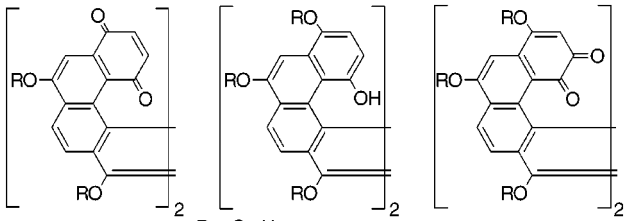
Oxidation of Russig−Laatsch Reaction Products 9. The phenol ethers **9**, like other monoalkyl ethers of hydroquinones, can be oxidized by means of ceric ammonium nitrate (CAN)[18] to *p*-quinones. Although the yields were poor when CAN and the phenols **9** were combined simultaneously in mixtures of aqueous CH_3CN and CH_2Cl_2, the yields were good when the phenol ethers in CH_2Cl_2 were added slowly to rapidly stirred solutions of CAN in aqueous CH_3CN. In this way (−)-**9** ($R^1 = R^2 =$ Me, Et, *n*-Bu, and *n*-$C_{12}H_{25}$) were transformed into (−)-**7** ($R^1 =$ Me, Et, *n*-Bu, and *n*-$C_{12}H_{25}$) in yields of 71%, 75%, 73%, and 73%, respectively, and (+)-**9** ($R^1 = R^2 =$ Me) into (+)-**7** ($R^1 =$ Me) in a yield of 74%.

If in place of CAN, the agent used for the oxidation of (−)-**9** ($R^1 = R^2 =$ *n*-$C_{12}H_{25}$) was benzeneseleninic anhydride in THF,[19] the product was a mixture of bis-*o*-, ortho-*p*-, and bis-*p*-quinones, unless 4 Å molecular sieves were added to the reaction mixture. Then the pure *o*,*o*-quinone (−)-**11** (R = *n*-$C_{12}H_{25}$) could be obtained in a yield of 68%, uncontaminated by the bis-*p*-quinone **7** ($R^1 =$ *n*-$C_{12}H_{25}$).



11

Similar Transformations of a [7]Carbohelicene. The results of experiments carried out with a [7]helicenebisquinone, **12**,[14a] were similar. Reducing **12** with zinc and AcOH,[20] and combining the resulting bishydroquinones with dodecanol, HCl, and 1,2-dichloroethane converted it cleanly into **13**. The diastereomeric dicamphanates separated easily upon chromatography, and when the camphanate esters were removed, the enantiomers of **13** were both obtained in good yields. These phenol ethers could be oxidized selectively to either bis-*p*- or bis-*o*-quinones. CAN cleanly oxidized (+)-**13** to (+)-**12** in 75% yield. Benzeneseleninic anhydride in THF containing 4 Å molecular sieves oxidized (+)-**13** to the bis-*o*-quinone, (+)-**14**, in 64% yield.



12 R = $C_{12}H_{25}$ **13** **14**

Discussion

We suppose, as Laatsch proposed,[7b] that the reactions of naphthalene-1,4-diols with alcohols and acid proceed by the alcohols adding to the carbonyls of the dione tautomers. The selectivity that leads to only one of the two *p*-hydroxyls alkylating would then originate in the inability of monoethers of such structures to tautomerize

(17) The helicenes are unlikely to racemize significantly during these transformations as 1,16-dimethyl[6]helicene, an analogue of **9** that has methyls in place of hydroxyls, has to be heated to 270 °C before its half-life for racemization decreases to 7.4 h, and [6]helicene itself has to be heated to 188 °C before its half-life for racemization decreases to 3 h [(a) Borkent, J. H.; Laarhoven, W. H. *Tetrahedron* **1978**, *34*, 2565. (b) Martin, R. H.; Marchant, M. J. *Tetrahedron Lett.* **1972**, 3707]. Moreover, the near-identity of the CD spectra of **9** and **7** (see below, $R_1 = R_2 =$ Et, *n*-Bu, and *n*-$C_{12}H_{25}$), which had been heated at 60 °C for 2 h, and **9** and **7** $R_1 = R_2 =$ Me, which had not, imply that the transformations did not significantly change the enantiomeric purities.

(18) Jacob, P., III; Callery, P. S.; Shulgin, A. T.; Castagnoli, N., Jr. *J. Org. Chem.* **1976**, *41*, 3627.

(19) Barton, D. H. R.; Finet, J. P.; Thomas, M. *Tetrahedron* **1988**, *44*, 6397.

(20) Helicene bisquinones can usually be reduced with either $Na_2S_2O_4$ or Zn and AcOH. In the case of **12**, the reduction with $Na_2S_2O_4$ was sluggish and Zn and AcOH reacted faster.

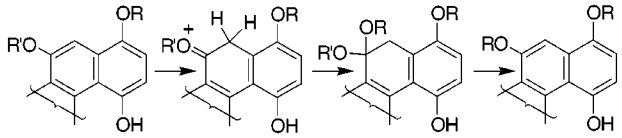
to diones. The selectivity that leads to the alkoxy groups being introduced at the periphery of the helicenes, rather than on the insides of the structures, can, however, be a consequence of either of two effects. It could be the result of the R^1O groups in the diketo-tautomer of **8** conjugating with the carbonyls. Since such conjugation would stabilize only the internal carbonyls;[21] the alcohols would add preferentially to those that are external.[22] The other possibility is that the selectivity arises from the much greater steric congestion on the inside of the helicene favoring addition to the less congested external carbonyls.

Evidence that the steric effect probably dominates was provided in an experiment reported by Laatsch.[7d] He showed that 6-ethoxynaphthalene-1,4-diol with methanol and HCl gives a 3:2 mixture of its two possible monomethyl ethers,[23] suggesting that electronic effects in the absence of steric effects do not exert much influence. Definitive evidence that in the helicenes it is not the alkoxyl at the 6-position that accounts for the selectivity (see structure **8** for the numbering), and accordingly that steric effects must account for it, was provided by an experiment in which this alkoxyl was missing. Thus, when structure **8**, but with an H in place of R^1O,[24] was combined with HCl in MeOH and 1,2-dichloroethane for 2 h at 60 °C, it gave **9** (R^1O = H, R^2 = Me) in 85% yield. If as much as 2% had been present of the products that in **9** had methoxyls in place of hydroxyls, the ^{1}H NMR analysis would have detected them. But it did not.[25] The steric effect might arise from crowding in the center of the molecule either favoring structures with fewer atoms on the inside of the helicene or restricting additions to and departures from the central carbonyls so they occur from the same direction, presumably the outside of the helicene structure.

The strength of this steric effect is indicated by the absence of detectable quantities of 1,4-dialkoxyhelicenes in any of the products of the reactions described above (even after 7 h at 60 °C). In contrast, Laatsch found that, unlike sterically hindered naphthalene-1,4-diols (in his case those that were 2-substituted[7b]), simpler and therefore less sterically hindered examples, while they usually are selectively monoalkylated after brief exposure to alcoholic solutions of HCl, do in at least three cases give appreciable amounts of dialkylated derivatives.[26]

Prior to the replacement of the R^1O and R^2O groups of **8** and **9** reported here, there seems to have been only one example of a transformation in which alcoholic acid exchanged one alkyl group for another in an alkyl aryl ether.[6c] The pathway followed when one R^2O group in **9** exchanges for another can be envisioned as the reverse of that followed when **9** is formed from **8**, but with alcohol taking the place of water. An acetal is therefore an intermediate, rather than a hemiacetal. The pathway followed when a helicene exchanges one R^1O group for another probably is similar to that followed when methanolic *p*-toluenesulfonic acid at 100 °C converts 2-naphthol into its methyl ether[27] or when a mixture of ethanol and hydrochloric acid at 180 °C converts phenol into its ethyl ether.[28] Scheme 4 summarizes the steps.

Scheme 4



However, the temperatures at which the replacements take place in the helicene structures—see Scheme 3 and the reactions of **9** (R^1 = R^2 = Me) with ethanol, butanol, and dodecanol—are considerably lower than those used by Liebermann and Gattermann to replace the hydroxyls of 1- and 2-naphthols by ethoxyls,[8a,b] and the reaction times are much shorter than those used by Bell and McCaffrey to replace the hydroxyls of dihydroxynaphthols.[8c] The difference seems to be that the protonation in Scheme 4, like other reactions of phenanthrenes and naphthalenes with electrophiles, is facilitated by **8** and **9** being derivatives of 9-phenanthrol rather than of 1- or 2-naphthols. This suggests that 9-phenanthrol itself might easily be converted into its ethyl ether by a mild treatment with ethanolic acid, and indeed it is, in 82% yield. The reagents were ethanolic HCl plus 1,2-dichloroethane at 60 °C, and the reaction time was 2 h.[29] Similarly, under the same conditions, but with methanol in place of ethanol, 9-ethoxyphenanthrene was transformed into 9-methoxyphenanthrene in almost quantitative yield. Naphthalene derivatives, however, should be, and are, less reactive. Ethanolic HCl in 1,2-dichloroethane at 60 °C for 2 h had no effect on either 1- or 2-naphthols or on 1- or 2-methoxynaphthalenes.

Conclusions

Acidified alcohols are superb reagents for introducing and replacing alkoxy groups on the periphery of helicenes. They make it possible to transform **7** (R^1 = TIPS), which is particularly easy to synthesize, into **9** (R^1 = R^2 = Me), which is particularly easy to resolve. Acidified alcohols then transform these enantiomers into nonracemic helicenes with other side chains, and CAN and benzeneselininic acids oxidize these to nonracemic *p*- and *o*-quinones that bear these side chains too. The ability to introduce and replace alkoxy groups specifically on the periphery of helicenes has also made it possible to prepare a helical ligand for asymmetric synthesis.[4] In that application (Scheme 5), the easily synthesized helical quinone **15** was converted selectively to phenol **16**, which could be resolved on a large scale and oxidized to **17**, a helical analogue of BINOL. This structure was named [5]HELOL. Simple procedures for resolving helicenes and for introducing different peripheral alkoxyl groups onto helicene skeletons also promise to make it possible to

(21) (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.

(22) See ref 12 and footnotes 22, 55, and 56 therein.

(23) Laatsch did not determine which regioisomer predominated.

(24) Yang, B.; Liu, L.; Katz, T. J.; Liberko, C. A.; Miller, L. L. *J. Am. Chem. Soc.* **1991**, *113*, 8993.

(25) ^{1}H NMR spectrum of the crude reaction mixture showed no peaks of >2% intensity at approximately 2.6 ppm, where the resonance of the inside OMe of permethoxylated **9** (R^1O = H, R^2 = Me, OH = OMe) appears (Yang, B. V. Ph.D. Dissertation, Columbia University, 1987).

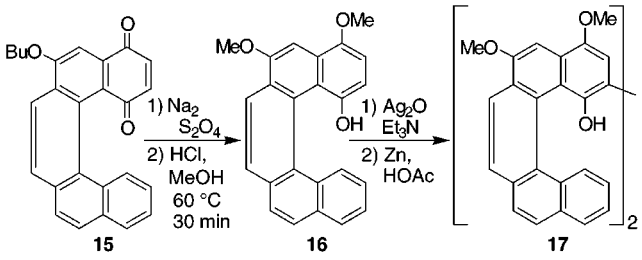
(26) After being combined with methanolic HCl at 60 °C, 6-Ethoxynaphthalene-1,4-diol gave 10% of the 1,4-dimethoxylated naphthalene. 6,7-Diethoxy- and 6,7-dimethyl-naphthalene-1,4-diols gave 28% and 32%, respectively.

(27) Wiberg, K. B.; Saegebarth, K. A. *J. Org. Chem.* **1960**, 25, 832.

(28) Oae, S.; Kiritani, R. *Bull. Chem. Soc. Jpn.* **1966**, *39*, 611.

(29) 9-Phenanthrol when combined with methanol and concd sulfuric acid had previously been found to give 9-methoxyphenanthrene, but the reaction, which was modeled on Gattermann's,[8b] was carried out at 120−130 °C. See: Japp, F. R.; Findlay, A. *J. Chem. Soc.* **1897**, *71*, 1115.

Scheme 5



synthesize a variety of structures related to those recently arduously prepared and found to self-organize into helical columnar assemblies with significant properties.[2]

Experimental Section

THF was distilled from Na/Ph_2CO; $(ClCH_2)_2$, CH_2Cl_2, and Et_3N from CaH_2. 1,4-Benzoquinone (Aldrich, 98%) was purified by slurrying it in CH_2Cl_2 with two times its weight of basic alumina, filtering through Celite, and drying under vacuum. Unless otherwise specified, "chromatography" refers to "flash chromatography".[30] $Na_2S_2O_4$ (tech, 85%), benzeneseleninic anhydride (70%), and ammonium cerium(IV) nitrate (98.5%) were purchased from Aldrich, triisopropylsilyl triflate from GFS. (1*S*)-(−)-camphanoyl chloride was synthesized.[31] The matrix for FAB mass spectra was *m*-nitrobenzyl alcohol to which KOAc was sometimes added.

Helicenebisquinone 7 (R^1 = TIPS). Triisopropylsilyl triflate (64.4 g, 0.21 mol, 56.5 mL) was added under N_2 to a solution, cooled in an ice bath, of 2,7-diacetylnaphthalene (21.2 g, 0.1 mol) and Et_3N (84 mL) in CH_2Cl_2 (300 mL). After 10 min the ice bath was removed, and the mixture was stirred for 1 h. The mixture was washed with saturated aqueous $NaHCO_3$ and dried (K_2CO_3), and the solvents were evaporated. The residue, dissolved in 1:1 hexane−benzene + 3% triethylamine, was quickly chromatographed on a plug of neutral alumina (1.5 in d × 4 in h), eluting with this same solvent. The product in vacuo (0.1 mm) was heated at 130 °C for 4 h, affording 52.1 g (99%) of 2,7-bis[1-(triisopropylsiloxy)ethenyl]-naphthalene, a pale orange oil. ^{1}H NMR (acetone-d_6, 400 MHz): δ 8.24 (d, 2 H, 0.6 Hz), 7.82 (m, 4 H), 5.16 (d, 2 H, 2.0 Hz), 4.59 (d, 2 H, 2.0 Hz), 1.39 (m, 6 H), 1.18 ppm (d, 36 H, 7.1 Hz). ^{13}C NMR (acetone-d_6, 75 MHz): δ 156.5, 136.1, 134.0, 133.8, 128.2, 125.5, 124.5, 91.5, 18.5, 13.5 ppm.

This oil (52.1 g, 99.4 mmol) under N_2, in a flask fitted with a bulb to trap small amounts of benzoquinone that sublimed and then a reflux condenser, was heated at 120 °C for 3 days with 1,4-benzoquinone (161.2 g, 1.42 mol) in heptane (900 mL). The mixture was cooled to room temperature and filtered through Celite, which was washed with hexane (ca. 1 L) until the filtrate was no longer red. The solvents were evaporated, and the residue was dissolved in CH_2Cl_2 (100 mL), loaded onto a plug of silica gel (4 in d × 2.5 in h), and eluted with 1:1 CH_2Cl_2−hexane. The solvents were evaporated, the crude product was divided into halves, and each was chromatographed on silica gel (5 in d × 8 in h), eluting with CH_2Cl_2. The solvent was evaporated, and the residue was shaken with 5:1 MeOH−H_2O (240 mL). The solid was filtered and washed with 5:1 MeOH−H_2O (300 mL) and MeOH (40 mL). Drying in vacuo (0.1 mm) at 90 °C for 12 h afforded 22.19 g (31%) of **7**, a bright orange powder. Mp: >250 °C. IR (CCl_4): 2948, 2864, 1664, 1511 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.42 (d, 2 H, 8.6 Hz), 7.95 (d, 2 H, 8.6 Hz), 7.54 (s, 2 H), 6.76 (d, 2 H, 10.1 Hz), 6.63 (d, 2 H, 10.1 Hz), 1.53 (m, 6 H), 1.23 ppm (m, 36 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 185.1, 156.7, 140.3, 135.5, 133.4, 133.0, 131.9, 129.8, 128.5, 127.2, 126.6, 122.6, 109.3, 18.1, 13.0 ppm. UV−vis (CH_3CN, $c = 4.2 \times 10^{-5}$ M): λ_{max} (log ϵ) 244 (4.59), 278 (4.35), 299 (4.51), 340 (3.91), 366 (4.02), 423 (sh, 3.66), 490 nm (3.52). Anal. Calcd for $C_{44}H_{52}O_6Si_2$: C, 72.09; H, 7.15. Found: C, 71.86; H, 7.18.

Reduction of Bisquinones. Procedure A. Water (twice the volume of the organics), followed by $Na_2S_2O_4$ (25 mol/mol helicene), was added to the helicenebisquinone dissolved in 3:1 EtOAc−CH_2Cl_2 (0.07 M). The solution was shaken by means of a mechanical shaker until it was yellow (approximately 1 h), then poured into a separatory funnel, and the aqueous layer was removed. The organics were washed once with brine and dried (Na_2SO_4). The solvent was evaporated. The Russig−Laatsch procedure (procedure C) was applied immediately to the resulting moderately air-sensitive bishydroquinones.

Procedure B. Acetone (0.02 M) and AcOH (10 mol/mol helicene) were added to the helicenebisquinone and Zn dust (25 mol/mol helicene), and the mixture was stirred under N_2 until it was yellow (10−15 min). The Zn was removed by filtration through Celite, and the Celite was washed with CH_2Cl_2. The organics were washed with H_2O (3×) and dried (Na_2SO_4), and the solvent was evaporated. The Russig−Laatsch procedure (procedure C) was applied immediately to the resulting moderately air-sensitive bishydroquinones.

Russig−Laatsch Procedure. Procedure C. Saturated HCl solutions were prepared by bubbling HCl gas into ice-cooled alcohols. The solutions were stored at 4 °C until they were used. The substrate was dissolved in 1,2-dichloroethane, the HCl solution of the desired alcohol was added, and the solution under N_2 and at 60 °C was stirred for 2 h (unless otherwise noted). The reaction mixtures were worked up by pouring them into EtOAc, washing them with H_2O, drying them (Na_2SO_4), and evaporating the solvent.

9 ($R^1 = R^2$ = Et). **7** (R^1 = Me, 0.20 g, 0.47 mmol), when reduced according to procedure A, gave **8** (R^1 = Me), a yellow solid, which was subjected to procedure C (2.0 mL of 1,2-dichloroethane, 8.0 mL of EtOH). Elution from a short column of silica gel, first with 10% EtOAc−hexanes and then with 50% EtOAc−hexanes, gave 0.24 g (95% yield) of bright yellow **9** ($R^1 = R^2$ = Et). Mp: 218−220 °C. IR (CCl_4): 3563, 2981, 1617, 1602 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.57 (d, 2 H, 8.4 Hz), 8.07 (d, 2 H, 8.4 Hz), 7.66 (s, 2 H), 6.56 (d, 2 H, 8.4 Hz), 5.93 (d, 2 H, 8.4 Hz), 4.46 (m, 2 H), 4.35 (m, 2 H), 4.20 (m, 2 H), 4.08 (m, 2 H), 3.47 (s, 2 H), 1.64 (t, 6 H, 6.9 Hz), 1.52 ppm (t, 2 H, 6.9 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 152.2, 147.7, 145.8, 131.6, 126.3, 125.8, 125.4, 124.9, 121.7, 120.9, 116.0, 109.1, 108.5, 98.7, 65.1, 64.0, 15.1, 14.9 ppm. HRMS (FAB): *m*/*z* calcd for $C_{34}H_{32}O_8$ 536.2199, found 536.2211.

9 (R^1 = Me, R^2 = Et). **7** (R^1 = Me, 0.16 g, 0.36 mmol), when reduced according to procedure A, gave **8** (R^1 = Me), a yellow solid, which was subjected to procedure C (1.2 mL of 1,2-dichloroethane, 6.0 mL of EtOH). However, the reaction temperature was 25 °C and the reaction time 5 min. Elution from a short column of silica gel, first with 10% EtOAc−hexanes and then with 50% EtOAc−hexanes, gave 0.16 g (89% yield) of bright yellow **9** (R^1 = Me, R^2 = Et). Mp: >250 ° C. IR (CCl_4): 3564, 2973, 2936 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.57 (d, 2 H, 8.4 Hz), 8.15(d, 2 H, 8.4 Hz), 7.71 (s, 2 H), 6.60 (d, 2 H, 8.5 Hz), 5.97 (d, 2 H, 8.5 Hz), 4.25 (m, 2 H), 4.21 (s, 6 H), 4.13 (m, 2 H), 1.54 ppm (s, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 152.9, 147.7, 145.7, 131.6, 126.5, 125.7, 125.3, 125.0, 121.7, 120.9, 116.1, 109.0, 108.5, 98.0, 65.0, 55.8, 15.1 ppm. HRMS (FAB): *m*/*z* calcd for $C_{32}H_{28}O_6$ 508.1886, found 508.1879.

9 ($R^1 = R^2$ = Me). When reduced according to procedure A, **7** (R^1 = TIPS, 15.0 g, 20.5 mmol) gave **8** (R^1 = TIPS), a yellow solid, which was subjected to procedure C (83 mL of 1,2-dichloroethane, 330 mL of MeOH). This afforded a yellow sludge, which was mixed with EtOAc (50 mL) and hexane (250 mL), chromatographed on a plug of silica gel (3 in d × 1.5 in h), eluting first with 5:1 hexanes−EtOAc (300 mL) and then with EtOAc (1 L). The solvent was evaporated. Drying in vacuo (0.1 mm) afforded 10.2 g (104%) of **9** ($R^1 = R^2$ = Me), a yellow solid, which, although it contained a small amount of impurity, was used in the resolution step. A similar experiment, using 0.70 g of **7** (R^1 = TIPS) under the same conditions, gave 0.42 g (92%) of essentially pure material. This was further purified by means of silica gel chromatography. Mp: >240 ° C. IR

(30) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.
(31) Gerlach, H.; Kappes, D.; Boeckman, R. K.; Maw, G. N. *Organic Syntheses* **1993**, *71*, 48.

(CCl_4): 3568, 2938 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 8.53 (d, 2 H, 8.4 Hz), 8.08 (d, 2 H, 8.4 Hz), 7.66 (s, 2 H), 6.56 (d, 2 H, 8.5 Hz), 5.95 (d, 2 H, 8.5 Hz), 4.17 (s, 6 H), 3.95 (s, 6 H), 3.44 ppm (br s, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 153.0, 148.5, 145.6, 131.6, 126.5, 125.7, 125.0, 124.8, 121.8, 120.8, 116.1, 108.4, 107.1, 97.9, 56.3, 55.9 ppm. HRMS (FAB): *m/z* calcd for $C_{30}H_{24}O_6$ 480.1573, found 480.1560.

9 ($R^1 = R^2$ = Et). Procedure A applied to **7** (R^1 = TIPS, 0.25 g, 0.34 mmol) gave **8** (R^1 = TIPS), which was subjected to procedure C (1.4 mL of 1,2-dichloroethane, 5.4 mL of EtOH). Elution from a short column of silica gel, first with 10% EtOAc−hexanes and then with 50% EtOAc−hexanes, gave 0.17 g (93% yield) of bright yellow **9** ($R^1 = R^2$ = Et), mp 218−220 °C. Its ^1H and ^{13}C NMR spectra were identical to those of the sample prepared above **7** (R^1 = Me).

9 ($R^1 = R^2$ = *n*-Bu). Procedure A applied to **7** (R^1 = TIPS, 0.25 g, 0.34 mmol) gave **8** (R^1 = TIPS), which was subjected to procedure C (1.4 mL of 1,2-dichloroethane, 5.4 mL of BuOH). Elution from a short column of silica gel, first with 10% EtOAc−hexanes and then with 50% EtOAc−hexanes, gave 0.20 g (90% yield) of **9** ($R^1 = R^2$ = *n*-Bu), a bright yellow oily wax. IR (CCl_4): 3565, 2962, 2931, 1661, 1600 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 8.58 (d, 2 H, 8.4 Hz), 8.10 (d, 2 H, 8.5 Hz), 7.68 (s, 2 H), 6.59 (d, 2 H, 8.5 Hz), 5.95 (d, 2 H, 8.5 Hz), 4.40 (m, 2 H), 4.31 (m, 2 H), 4.20 (m, 2 H), 3.47 (s, 2 H), 2.02 (m, 4 H), 1.91 (m, 4 H), 1.68 (m, 8 H), 1.07 ppm (m, 12 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 152.2, 147.7, 145.7, 131.5, 126.2, 125.8, 125.4, 124.9, 121.7, 120.8, 116.0, 109.0, 108.4, 98.6, 69.3, 68.0, 31.5, 31.3, 19.6, 19.5, 14.0 ppm. HRMS (FAB): *m/z* calcd for $C_{42}H_{48}O_6$ 648.3451, found 648.3452.

9 ($R^1 = R^2$ = Dodecyl). Procedure A applied to **7** (R^1 = TIPS, 0.20 g, 0.47 mmol) gave **8** (R^1 = TIPS), which was subjected to procedure C (0.40 mL of 1,2-dichloroethane, 0.23 mL of EtOH). To remove excess dodecanol, the product was shaken with 15 mL of MeOH, and the resulting yellow solid was filtered on Celite, washed with MeOH, and removed from the Celite by means of CH_2Cl_2, which was then evaporated. The MeOH wash was repeated. The solids were evacuated (0.1 mm) overnight, giving 0.060 g (80% yield) of bright yellow **9** ($R^1 = R^2$ = dodecyl). Mp: 98−100 °C. IR (CCl_4): 3562, 2928, 2856 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 8.59 (d, 2 H, 8.4 Hz), 8.12 (d, 2 H, 8.5 Hz), 7.69 (s, 2 H), 6.58 (d, 2 H, 8.5 Hz), 5.95 (d, 2 H, 8.5 Hz), 4.40 (m, 2 H), 4.30 (m, 2 H), 4.17 (m, 2 H), 4.00 (m, 2 H), 3.43 (s, 2H), 2.03 (m, 4 H), 1.91 (m, 4 H), 1.65 (m, 8 H), 1.28 (m, 66 H), 0.88, ppm (m, 13 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 152.3, 147.9, 145.7, 131.6, 126.4, 125.9, 125.5, 124.9, 121.7, 121.0, 116.0, 109.1, 108.5, 98.7, 69.7, 68.4, 31.9, 29.7, 29.6, 29.4, 26.4, 22.7, 14.1 ppm. HRMS (FAB): *m/z* calcd for $C_{74}H_{112}O_6$ 1096.8459, found 1096.8463.

Preparation of [7]Helicene 13. Procedure B was applied to **12** (1.0 g, 0.85 mmol), and the resulting yellow solid was subjected to procedure C (1.9 mL of 1,2-dichloroethane, 1.9 mL of dodecanol). The yield of yellow-brown oily solid **13**, which after trituration with MeOH (30 mL), as described above for **9** ($R^1 = R^2$ = dodecyl), was very pure, was 1.20 g (97% yield). IR (CCl_4): 3561, 2902, 2852 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 8.51 (d, 2 H, 8.7 Hz), 8.42 (d, 2 H, 8.7 Hz), 7.14 (s, 2 H), 6.31 (d, 2 H, 8.5 Hz), 5.88 (d, 2 H, 8.5 Hz), 4.47 (m, 2 H), 4.30 (m, 4 H), 4.16 (m, 2 H), 3.92 (m, 4 H), 3.48 (s, 3 H), 2.00 (m, 9 H), 1.88 (m, 2 H), 1.63 (m, 8 H), 1.29 (m, 111 H), 0.89 ppm (m, 21 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 152.0, 147.5, 143.9, 143.4, 128.0, 126.3, 124.4, 124.0, 122.1, 121.4, 120.1, 117.7, 109.3, 106.9, 98.4, 74.1, 69.0, 68.4, 32.0, 30.6, 29.7, 29.4, 26.6, 26.4, 26.3, 22.7, 14.1 ppm. HRMS (FAB): *m/z* calcd for $C_{102}H_{162}O_8$ 1515.2270, found 1515.2286.

9 (R^1O = H, R^2 = Me). When reduced according to procedure A, **7** (R^1 = H, 25 mg, 0.064 mmol) gave **8** (R^1O = H, R^2 = H), a yellow solid, which was subjected to procedure C (0.26 mL of 1,2-dichloroethane, 1.1 mL of MeOH). The ^1H NMR spectrum of the crude material showed <2% of any compounds to be present in which **9** is methylated at the inside position (OMe in place of **9**'s OH). Elution with CH_2Cl_2 from a short column of silica gel gave 0.023 g (85% yield) of bright yellow solid **9** (R^1O = H, R^2 = Me). Mp: 213-215 °C. IR (CCl_4): 3564, 2933 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 8.43 (d, 2 H, 8.7 Hz), 8.12 (d, 2 H, 8.1 Hz), 8.06 (d, 2 H, 8.1 Hz), 7.92 (d, 2 H, 8.7 Hz), 6.62 (d, 2 H, 8.5 Hz), 6.11 (d, 2 H, 8.5 Hz), 3.98 ppm (s, 6 H), 3.41 ppm (s, 2 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 149.6, 145.4, 131.4, 126.9 (two peaks), 125.4, 124.6, 123.1, 122.3, 119.8, 111.0, 106.9, 56.4 ppm. HRMS (FAB): *m/z* calcd for $C_{28}H_{20}O_4$ 420.1362, found 420.1373.

9-Ethoxyphenanthrene from 9-Phenanthrol. Tech grade 9-phenanthrol (0.20 g, 1.0 mmol), dissolved in 1,2-dichloroethane (4.2 mL), was heated with EtOH−HCl (16.8 mL) for 2 h at 60 °C and worked up, according to procedure C. The crude product, a white solid, was chromatographed, giving 0.16 g of 9-ethoxyphenanthrene (82% yield, assuming 9-phenanthrol to be 85% pure). Mp: 103−104 °C. ^1H NMR ($CDCl_3$, 300 MHz): δ 8.63 (d, 1 H, 7.8 Hz), 8.56 (d, 1 H, 7.5 Hz), 8.40 (d, 1 H, 7.7 Hz), 7.74 (m, 1 H), 7.63 (m, 2 H), 7.49 (m, 2 H), 6.95 (s, 1 H), 4.28 (q, 7.0 Hz, 2 H), 1.58 ppm (t, 7.0 Hz, 3 H).[32] ^{13}C NMR ($CDCl_3$, 75 MHz): δ 152.8, 133.0, 131.2, 127.2, 127.0, 126.8, 126.3, 124.1, 122.6, 122.4, 102.5, 63.5, 14.8 ppm.

9-Methoxyphenanthrene from 9-Ethoxyphenanthrene. 9-Ethoxy-phenanthrene (0.10 g, 0.45 mmol), dissolved in 1,2-dichloroethane (1.8 mL), was heated with MeOH−HCl (7.2 mL) for 2 h at 60 °C and worked up according to procedure C. Obtained was a while solid, which was highly pure 9-methoxyphenanthrene (0.94 g, 100% yield). Mp: 94−95 °C. ^1H NMR ($CDCl_3$, 300 MHz): δ 8.63 (d, 1 H, 7.8 Hz), 8.56 (d, 1 H, 7.5 Hz), 8.40 (d, 1 H, 7.7 Hz), 7.73 (d, 1 H, 9.0 Hz), 7.63 (m, 2 H), 7.49 (m, 2 H), 6.95 (s, 1 H), 4.05 pm (s, 3 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 153.5, 132.9, 131.2, 127.2, 127.0, 126.8, 126.5, 126.4, 126.3, 124.1, 122.4, 101.8, 55.3 ppm.[33]

Attempted Reactions of 1- and 2-Naphthols and of 1- and 2-Methoxynaphthalenes with EtOH. These experiments were conducted according to procedure C on a 1 mmol scale, using 16 mL of an HCl-saturated solution of EtOH and 4 mL of 1,2-dichloroethane. After 2 h at 60 °C, no changes in the starting materials could be detected.

(*P*)-(+)- and (*M*)-(−)-10. Slightly impure **9** ($R^1 = R^2$ = Me, 10.20 g, 20.5 mmol) was refluxed for 1 h with (1*S*)-(−)-camphanoyl chloride (13.3 g, 61.5 mmol), DMAP (2.5 g, 20.5 mmol), and Et_3N (45 mL) in 1,2-dichloroethane (300 mL). The solution was poured into 5:1 H_2O−AcOH (1 L), and 100 mL of brine was added. Extraction with EtOAc, washing with 10:1 H_2O−AcOH, H_2O, and saturated $NaHCO_3$, drying (Na_2SO_4), evaporation, and drying in vacuo (0.1 mm) at 90 °C for 2 h, gave a yellow-orange material, which was shaken for 15 min with 100 mL of hexane. The liquid was decanted, and the residue was shaken vigorously for 30 min with 400 mL of 8:1 hexanes−Et_2O and 50 g of sand. Filtration through Celite, washing with hexane (100 mL), removal of the product from the Celite with CH_2Cl_2, addition of cyclohexane (100 mL), evaporation of the solvents, and drying in vacuo at 90 °C for 2 h gave a solid, which was dissolved in boiling EtOAc (1 L). Cyclohexane (900 mL) was added, and the mixture was allowed to stand at room temperature for 3 days. The precipitate was filtered, washed with 2:1 cyclohexanes−EtOAc (150 mL), and dried overnight in vacuo (0.1 mm) at 100 °C. This afforded 5.67 g (66%) of (*P*)-(+)-**10**.

Evaporating the solvent from the filtrate gave a solid, which was dissolved in EtOAc (100 mL), and hexane (150 mL) was added. The suspension was chromatographed on a plug of silica gel (3.5 in d × 1.8 in h), eluting with 12 portions of 3:2 hexanes−EtOAc (100 mL each). The resulting solid was boiled in 20:1 cyclohexanes−EtOAc (200 mL), and after the mixture had cooled to room temperature, was filtered and dried in vacuo (0.1 mm), affording 5.31 g (62%) of (*M*)−(−)-**10**. The silica gel plug was washed with 1:1 CH_2Cl_2−EtOAc, and after the solvent had been evaporated, the residue was chromatographed, eluting with 1:1 hexanes−EtOAc. This afforded an additional 0.66 g (8%) of (*M*)-(−)-**10**. The later fractions, containing (*P*)-(+)-**10**, were dissolved in 20 mL of boiling EtOAc, and after 10 mL of cyclohexane had been added, cooling

(32) The melting point and ^1H NMRs match those published. Muller, P.; Pautex, N. *Helv. Chim. Acta* **1988**, 71, 1630.

(33) The melting point and ^1H and ^{13}C NMRs match those published. Stuhr-Hansen, N.; Henriksen, L. *Synth. Commun.* **1997**, *27*, 89.

to room temperature gave a precipitate that was dried in vacuo at 90 °C. An additional 0.74 g (9%) of (*P*)-(+)-**10** was obtained.

(*M*)-(−)-10. Mp: >250 °C. $[\alpha]_D$: −1410 (*c* 0.020, CH_3CN). IR (CCl_4): 2973, 1790, 1747 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 8.45 (d, 2 H, 8.4 Hz), 7.96 (d, 2 H, 8.5 Hz), 7.70 (s, 2 H), 6.54 (d, 2 H, 8.4 Hz), 6.05 (d, 2 H, 8.4 Hz), 4.23 (s, 6 H), 4.02 (s, 6 H), 1.52 (m, 2 H), 1.42 (m, 2 H), 1.15 (m, 2 H), 0.92 (s, 6 H), 0.80 (m, 2 H), 0.57 (s, 6 H), 0.43 ppm (s, 6 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 178.2, 165.5, 154.0, 152.9, 140.3, 130.7, 126.2, 126.0 (2 peaks), 120.7, 120.1, 113.9, 105.0, 98.2, 89.5, 56.1, 55.8, 54.5, 54.2, 29.3, 28.8, 16.2, 16.1, 9.5 ppm. UV−vis (CH_3CN, $c = 3.6 \times 10^{-5}$ M): λ_{max} (log ϵ) 225 (4.28), 254 (4.51), 263 (sh, 4.50), 283 (sh, 4.39), 309 (4.20), 314 (sh, 4.33), 327 (4.44), 351 (sh, 4.03), 407 (3.46), 432 nm (3.46). CD ($c = 3.6 \times 10^{-5}$ M, CH_3CN), nm ($\Delta\epsilon$): 229 (−27), 251 (122), 261 (sh, 85), 280 (sh, 9), 299 (−40), 314 (−3), 323 (−0.3), 344 (−97), 364 (sh, −81), 431 (11). Anal. Calcd for $C_{50}H_{48}O_{12}$: C, 71.42; H, 5.75. Found C, 71.41; H, 5.73.

(*P*)-(+)-10. Mp: >250 °C. $[\alpha]_D$: +1120 (*c* 0.020, CH_3CN). IR (CCl_4): 2965, 2940, 1797, 1764 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 8.43 (d, 2 H, 8.4 Hz), 7.98 (d, 2 H, 8.5 Hz), 7.57 (s, 2 H), 6.53 (d, 2 H, 8.4 Hz), 5.94 (d, 2 H, 8.4 Hz), 4.19 (s, 6 H), 4.01 (s, 6 H), 1.63 (m, 2 H), 1.46 (m, 4 H), 1.15 (m, 2 H), 0.94 (s, 6 H), 0.67 (s, 6 H), 0.25 ppm (s, 6 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 177.5, 165.8, 154.1, 153.0, 140.6, 131.4, 127.0, 126.6, 125.5, 125.4, 124.7, 121.0, 120.7, 114.6, 105.0, 97.5, 90.2, 56.1, 55.9, 54.3, 53.9, 29.1, 28.9, 16.6, 16.1, 9.5 ppm. UV−vis (hexane, $c = 3.0 \times 10^{-5}$ M): λ_{max} (log ϵ) 225 (4.18), 253 (4.46), 263 (sh, 4.44), 283 (sh, 4.32), 326 (4.35), 344 (sh, 3.94), 431 nm (3.31). CD ($c = 3.0 \times 10^{-5}$ M, CH_3CN), nm ($\Delta\epsilon$): 231 (44), 252 (−121), 263 (sh, −92), 281 (sh, −20), 299 (19), 323 (−20), 344 (91), 360 (sh, 78), 431 (−8). HRMS (FAB): *m*/*z* calcd for $C_{50}H_{48}O_{12}$ 840.3146, found 840.3162.

(*M*)-(−)- and (*P*)-(+)-9 ($R^1 = R^2 =$ Me). A flask containing (*M*)-(−)-**10** (2.1 g, 2.5 mmol) and KOH (5.6 g, 0.1 mol) was evacuated and filled with N_2 three times. EtOH (30 mL), previously degassed by boiling under N_2, was added by syringe. After the mixture had stirred for 1 h at 25 °C (during which time it turned deep red), aqueous HCl was added, whereupon the color turned to yellow. Addition of H_2O, extraction with EtOAc, washing with brine, drying (Na_2SO_4), evaporation, and chromatography (eluents: CH_2Cl_2 to 30:1 CH_2Cl_2−EtOAc) gave 1.1 g (93% yield) of (*M*)-(−)-**9** ($R^1 = R^2 =$ Me). The same procedure applied to (*P*)-(+)-**10** gave 1.2 g (99% yield) of (*P*)-(+)-**9** ($R^1 = R^2 =$ Me). Mp: 158−160 °C. $[\alpha]_D$: +2030 (*c* 0.010, CH_3CN). The ^1H NMR and ^{13}C NMR spectra of (*M*)-(−)-**9** and (*P*)-(+)-**9** ($R^1 = R^2 =$ Me) were identical to that of the racemic material. UV−vis of (*M*)-(−)-**9** ($R^1 = R^2 =$ Me, in CH_3CN, $c = 3.2 \times 10^{-5}$ M): λ_{max} (log ϵ) 239 (4.67), 258 (sh, 4.51), 271 (4.34), 291 (4.39), 303 (4.33), 321 (4.40), 369 (3.94), 430 nm (3.32). CD of (*M*)−(−)-**9** ($R^1 = R^2 =$ Me, in CH_3CN, $c = 3.2 \times 10^{-5}$ M), nm ($\Delta\epsilon$): 238 (−44), 257 (sh, −13), 263 (−7), 272 (sh, −10), 291 (−41), 307 (−67), 317 (−13), 350 (128), 396 (sh, 11), 439 (−4).

The (*P*)-(+)- and (*M*)-(−)-Dicamphanates of 13. A solution of **13** (1.2 g, 0.79 mmol), (1*S*)-(−)-camphanoyl chloride (0.51 g, 2.37 mmol), DMAP (0.096 g, 0.79 mmol), and Et_3N (2.7 mL) in 1,2-dichloroethane (30 mL) was refluxed for 2 h. The cooled reaction mixture was poured into 1 M HCl, and after the organic layer had been washed with H_2O, saturated aqueous $NaHCO_3$, and H_2O, dried (Na_2SO_4), and freed of solvent, the diastereomers were separated by silica gel chromatography (eluents from hexanes to CH_2Cl_2). Obtained were 0.65 g (88% yield) of oily (*P*)-(+)-**13**-dicamphanate and 0.54 g (73% yield) of (*M*)-(−)-**13**-dicamphanate.

(*P*)-(+)-13-dicamphanate. $[\alpha]_D$: +550 (*c* 0.016, hexane). IR (CCl_4): 2967, 2902, 2852, 1796, 1778 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 8.32 (d, 2 H, 8.7 Hz), 8.28 (d, 2 H, 8.7 Hz), 7.07 (s, 2 H), 6.31 (d, 2 H, 8.5 Hz), 5.83 (d, 2 H, 8.5 Hz), 4.31 (m, 4 H), 4.15 (m, 4 H), 4.03 (m, 2 H), 3.90 (m, 2 H), 8.32 (d, 2 H, 8.7 Hz), 1.97 (m, 13 H), 1.74 (m, 2 H), 1.60 (m, 17 H), 1.29 (m, 112 H), 1.18 (m, 2 H), 0.99 (s, 6 H), 0.90 (m, 21 H), 0.72 (s, 6 H), 0.58 ppm (s, 6 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 177.4, 165.6, 153.0, 151.7, 143.6, 138.2, 128.2, 126.9, 124.9, 124.7, 123.2, 121.9, 121.0, 120.8, 115.7, 104.3, 97.7, 90.5, 74.0, 68.3, 54.4, 54.2, 31.9, 30.7, 29.7, 29.5, 29.4, 28.7, 28.4, 26.5, 26.4, 26.3, 22.7, 16.8, 16.6, 14.1, 9.5 ppm. UV−vis (hexane, $c = 3.0 \times 10^{-5}$ M): λ_{max} (log ϵ) 234 (4.40), 254 (4.46), 268 (4.41), 284 (4.46), 320 (sh, 4.34), 388 nm (sh, 3.78). CD ($c = 3.0 \times 10^{-5}$ M, hexane), nm ($\Delta\epsilon$): 223 (sh, 44), 240 (162), 261, (−31), 268 (−23), 290 (−110), 317 (sh, −67), 373 (92), 399 (sh, 54). HRMS (FAB): *m*/*z* + K calcd for $C_{122}H_{186}O_{14}$ 1914.3480, found 1914.3400.

(*M*)-(−)-13-Dicamphanate. $[\alpha]_D$: −920 (*c* 0.016, hexane). IR (CCl_4): 2967, 2909, 2852, 1793, 1743 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 8.42 (d, 2 H, 8.7 Hz), 8.35 (d, 2 H, 8.7 Hz), 7.05 (s, 2 H), 6.27 (d, 2 H, 8.5 Hz), 5.94 (d, 2 H, 8.5 Hz), 4.32 (m, 4 H), 4.15 (m, 2 H), 4.06 (m, 4 H), 3.90 (m, 2 H), 2.00 (m, 12 H), 1.58 (m, 12 H), 1.29 (m, 103 H), 0.97 (m, 2 H), 0.92 (s, 2 H), 0.90 (m, 26 H), 0.57 (s, 6 H), 0.41 ppm (s, 6 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 177.7, 165.8, 153.3, 151.6, 143.5, 138.2, 127.7, 127.0, 125.1, 124.2, 122.4, 122.0, 121.4, 120.8, 114.8, 103.9, 97.5, 89.5, 73.9, 68.4, 68.2, 54.1 (2 peaks), 53.3, 31.9, 30.7, 29.7, 29.5, 29.3, 28.5, 26.5, 26.4, 26.3, 22.6, 16.1, 16.0, 14.1, 9.4 ppm. UV−vis (hexane, $c = 2.9 \times 10^{-5}$ M): λ_{max} (log ϵ) 232 (4.42), 254 (4.47), 265 (4.44), 283 (4.50), 320 (sh, 4.37), 388 nm (sh, 3.80). CD ($c = 2.9 \times 10^{-5}$ M, hexane), nm ($\Delta\epsilon$): 219 (sh, −62), 237 (−218), 261 (sh, 15), 286 (169), 315 (92), 373 (−115), 396 (sh, −82). HRMS (FAB): *m*/*z* + K calcd for $C_{122}H_{186}O_{14}$ 1914.3480, found 1914.3514.

(*P*)-(+)-13. A flask containing (*P*)-(+)-**13-dicamphanate** (0.56 g, 0.30 mmol) was evacuated and filled with N_2 three times, and MeLi in Et_2O (2.2 mL, 1.6 M, 3.5 mmol) was added. After the mixture had stirred for 1 h at 25 °C (turning deep red in the process), the reaction was quenched by the addition of saturated aqueous NH_4Cl, whereupon the color turned yellow. Addition of H_2O, extraction with EtOAc, washing with brine, drying (Na_2SO_4), evaporation, and chromatography (eluent: CH_2Cl_2) gave 0.44 g (97% yield) of (*P*)-(+)-**13**, an oil. $[\alpha]_D$: +690 (*c* 0.016, hexane). The ^1H NMR and ^{13}C NMR spectra of (*P*)-(+)-**13** were identical to that of the racemic material. UV−vis (hexane, $c = 3.5 \times 10^{-5}$ M): λ_{max} (log ϵ) 215 (4.41), 233 (4.33), 255 (4.43), 288 (4.31), 309 (4.38), 375 nm (sh, 3.95). CD ($c = 3.5 \times 10^{-5}$ M, hexane), nm ($\Delta\epsilon$): 233 (98), 250 (sh, 31), 273 (−116), 305 (−76), 343 (sh, 49), 370 (67), 424 (sh, 27).

Preparation of Optically Active Russig-Laatsch Products. Procedure D. After an HCl-saturated solution of the alcohol had been added to a resolved Russig−Laatsch product, the solution was heated at the specified temperature for 2 h. A Hickman distillation head that was attached to the flask trapped the methanol that formed. The reaction mixture was poured into EtOAc, which was then washed with water, dried (Na_2SO_4), and evaporated.

(*M*)-(−)-9 ($R^1 = R^2 =$ Et). (*M*)-(−)-**9** ($R^1 = R^2 =$ Me, 0.10 g, 0.21 mmol) was heated at 75 °C with EtOH−HCl (1.0 mL) and worked up according to procedure D. Elution by CH_2Cl_2 from a short column of silica gel gave 0.10 g (93% yield) of (*M*)-(−)-**9** ($R^1 = R^2 =$ Et), a bright yellow solid. Mp: 114−116 °C. $[\alpha]_D$: −1700 (c 0.011, CH_3CN). The ^1H NMR and ^{13}C NMR spectra were identical to those of the racemic material, prepared above from **7** ($R^1 =$ Me) and from **7** ($R^1 =$ TIPS). UV−vis (CH_3CN, $c = 4.2 \times 10^{-5}$ M): λ_{max} (log ϵ) 240 (4.40), 259 (4.35), 273 (4.24), 291 (4.28), 305 (4.22), 323 (4.28) 344 (sh, 4.03), 430 nm (sh, 3.29). CD ($c = 4.2 \times 10^{-5}$ M, CH_3CN), nm ($\Delta\epsilon$): 239 (38), 254 (15), 263 (7), 270 (sh, 11), 292 (40), 308 (10), 315 (16), 350 (−117), 439 (4).

(*M*)-(−)-9 ($R^1 = R^2 =$ *n*-Bu). (*M*)-(−)-**9** ($R^1 = R^2 =$ Me, 0.10 g, 0.21 mmol) was heated with HCl in BuOH (0.95 mL) at 90 °C and worked up according to procedure D. Elution by hexanes, then CH_2Cl_2, from a short plug of silica gel gave 0.12 g (91% yield) of (*M*)-(−)-**9** ($R^1 = R^2 =$ *n*-Bu), a bright yellow oily wax. $[\alpha]_D$: −1510 (*c* 0.013, CH_3CN). The ^1H NMR and ^{13}C NMR spectra were identical to those of the racemic material, prepared above from **7** ($R^1 =$ TIPS). UV−vis (CH_3CN, $c = 4.0 \times 10^{-5}$ M): λ_{max} (log ϵ) 221 (4.34), 240 (4.42), 259 (sh, 4.38), 277 (4.29), 292 (4.31), 306 (4.28), 321 (4.31), 350 (sh, 4.06), 430 nm (sh, 340). CD ($c = 4.0 \times 10^{-5}$ M, CH_3CN), nm ($\Delta\epsilon$): 242 (29), 254 (sh, 20), 263 (13), 271 (16), 293 (43), 307 (19), 314 (22), 351 (−114), 42 (3).

(*M*)-(−)-9 (R¹ = R² = Dodecyl). (*M*)-(−)-**9** ($R^1 = R^2$ = Me, 0.11 g, 0.23 mmol) was heated with HCl in dodecanol (1.0 mL) at 90 °C and worked up according to procedure D. The product was triturated with MeOH (15 mL) as described above for **9** ($R^1 = R^2$ = dodecyl). Obtained was 0.21 g (84% yield) of (*M*)-(−)-**9** ($R^1 = R^2$ = dodecyl), a bright yellow solid. Mp: 72−74 °C. $[\alpha]_D$: −770 (*c* 0.022, hexane). The ^{1}H NMR and ^{13}C NMR spectra were identical to those of the racemic material, prepared above from **7** (R^1 = TIPS). UV−vis (CH_3CN, $c = 1.9 \times 10^{-5}$ M): λ_{max} (log ϵ) 221(4.55), 243 (4.78), 260 (sh, 4.57), 278 (4.38), 293 (4.42), 306 (4.33), 328 (4.45), 355 (sh, 4.08), 389 nm (sh, 3.90). CD ($c = 1.9 \times 10^{-5}$ M, CH_3CN), nm ($\Delta\epsilon$): 228 (31), 238 (19), 249 (25), 264 (16), 271 (20), 278 (15), 291 (37), 316 (−13), 326 (19), 356 (−116), 446 (8).

Preparation of Bis-*p*-quinones. Procedure E. The Russig−Laatsch products, dissolved in *x* mL of CH_2Cl_2, were added in drops during 1 h to a rapidly stirring solution at room temperature of cerric ammonium nitrate (CAN, 10 molar equivalents) in *x* mL of H_2O and *x* mL of acetonitrile. After this had stirred for 30 min, the mixture was poured into a separatory funnel containing EtOAc and H_2O, which was gently swirled. (Vigorous shaking produced an emulsion.) The organics were dried (Na_2SO_4), and the solvent was evaporated.

(*M*)-(−)-7 (R¹ = Me). Procedure E was followed, using 1.0 g (2.1 mmol) of (*M*)- (−)-**9** ($R^1 = R^2$ = Me), $x = 170$. Chromatography (eluent: 20:1 CH_2Cl_2−EtOAc) provided 0.66 g (71% yield) of (*M*)-(−)-**7** (R^1 = Me), a red solid. Mp: >250 °C. $[\alpha]_D$: −3210 (*c* 0.006, CH_3CN). CD ($c = 2.6 \times 10^{-5}$ M, CH_3CN), nm ($\Delta\epsilon$): 226 (11), 233 (2), 236 (3), 260 (−47), 297 (66), 307 (sh, 47), 351 (−87), 395 (−11), 435 (−18).

(*P*)-(+)-7 (R¹ = Me). Procedure E was followed, using 1.2 g (2.4 mmol) of (*P*)-(+)-**9** ($R^1 = R^2$ = Me), $x = 180$. Chromatography (eluent: 20:1 CH_2Cl_2−EtOAc) provided 0.81 g (74% yield) of (*P*)-(+)-**7** (R^1 = Me). $[\alpha]_D$: 3210 (*c* 0.007, CH_3CN). UV−vis (CH_3CN, $c = 3.2 \times 10^{-5}$ M): λ_{max} (log ϵ) 233 (4.66), 244 (sh, 4.64), 279 (4.33), 297 (4.49), 339 (3.86), 366 nm (3.92). CD ($c = 3.2 \times 10^{-5}$ M, CH_3CN), nm ($\Delta\epsilon$): 226 (−11), 234 (−2), 238 (−3), 259 (47), 297 (−64), 308 (sh, −45), 351 (85), 395 (11), 435 (17). The ^{1}H and ^{13}C NMR spectra of (+)- and (−)-**7** were identical to those of the racemic material.[12]

(*M*)-(−)-7 (R¹ = Et). Procedure E was followed, using 80 mg (0.15 mmol) of (*M*-(−)-**9** ($R^1 = R^2$ = Et), $x = 12$. Chromatography (eluent: 20:1 CH_2Cl_2−EtOAc) provided 53 mg (75% yield) of (*M*)-(−)-**7** (R^1 = Et), a red solid. Mp: >250 °C. $[\alpha]_D$: −3180 (*c* 0.010, CH_3CN). IR (CCl_4) 2978, 1661, 1596, 1515 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.45 (d, 2 H, 8.7 Hz), 7.94 (d, 2 H, 8.7 Hz), 7.50 (s, 2 H), 6.77 (d, 2 H, 10.1 Hz), 6.62 (d, 2 H, 10.1 Hz), 4.49 (m, 2 H), 4.39 (m, 2 H), 1.64 ppm (m, 6 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 185.1, 158.6, 140.1, 135.5, 133.6, 132.9, 131.1, 128.4, 127.5, 126.8, 126.3, 122.0, 101.9, 65.0, 14.6 ppm. UV−vis (CH_3CN, $c = 2.5 \times 10^{-5}$ M): λ_{max} (log ϵ) 236 (4.65), 243 (sh, 4.64), 281 (4.32), 298 (4.48), 340 (3.84), 363 (3.92), 426 nm (3.62). CD ($c = 2.5 \times 10^{-5}$ M, CH_3CN), nm ($\Delta\epsilon$): 227 (11), 236 (sh, 1.0), 258 (−45), 297 (63), 352 (−86), 400 (−10), 435 (−18). HRMS (FAB): *m*/*z* calcd for $C_{30}H_{20}O_6$ 476.1260, found 476.1257.

(*M*)-(−)-7 (R¹ = *n*-Bu). Procedure E was followed, using 0.11 g (0.16 mmol) of (*M*)-(−)-**9** ($R^1 = R^2$ = *n*-Bu), $x = 13$. Chromatography (eluents from CH_2Cl_2 to 20:1 CH_2Cl_2−EtOAc) provided 0.63 g (73% yield) of (*M*)-(−)-**7** (R^1 = *n*-Bu), a red solid. Mp: 206−207 °C. $[\alpha]_D$: −2930 (*c* 0.011, CH_3CN). IR (CCl_4): 2965, 1665, 1595, 1515 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.45 (d, 2 H, 8.6 Hz), 7.96 (d, 2 H, 8.7 Hz), 7.51 (s, 2 H), 6.78 (d, 2 H, 10.2 Hz), 6.63 (d, 2 H, 10.2 Hz), 4.43 (m, 2 H), 4.34 (m, 2 H), 2.01 (m, 4 H), 1.66 (m, 4 H), 1.08 ppm (t, 6 H, 7.3 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 185.2, 158.8, 140.2, 135.6, 133.6, 133.0, 131.2, 128.4, 127.6, 126.9, 126.3, 122.1, 101.9, 69.1, 31.1, 19.4, 13.9 ppm. UV−vis (CH_3CN, $c = 3.1 \times 10^{-5}$ M): λ_{max} (log ϵ) 235 (4.64), 246 (4.64), 280 (4.35), 298 (4.49), 341 (3.86), 367 nm (3.94). CD ($c = 3.1 \times 10^{-5}$ M, CH_3CN), nm ($\Delta\epsilon$): 226 (13), 237 (sh, 1), 260 (−47), 297 (70), 351 (−89), 399 (−11), 437 (−17). HRMS (FAB): *m*/*z* calcd for $C_{34}H_{26}O_6$ 530.1729, found 530.1723.

(*M*)-(−)-7 (R¹ = dodecyl). Procedure E was followed, using 0.20 g (0.18 mmol) of (*M*)-(−)-**9** ($R^1 = R^2$ = dodecyl), $x = 15$. Chromatography (eluent: CH_2Cl_2) provided 0.10 g (73% yield) of (*M*)-(−)-**7** (R^1 = dodecyl), a red wax. Mp: 208−209 °C. $[\alpha]_D$: −2410 (*c* 0.011, CH_2Cl_2). IR (CCl_4): 2925, 2851, 1666, 1513 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.44 (d, 2 H, 8.7 Hz), 7.95 (d, 2 H, 8.7 Hz), 7.50 (s, 2 H), 6.78 (d, 2 H, 10.1 Hz), 6.63 (d, 2 H, 10.1 Hz), 4.44 (m, 2 H), 4.33 (m, 2 H), 2.01 (m, 4 H), 1.61 (m, 4 H), 1.29 (m, 32 H), 0.89 ppm (m, 6 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 185.2, 158.8, 140.2, 135.6, 133.6, 133.0, 131.2, 128.5, 127.6, 126.9, 126.4, 122.1, 102.0, 69.4, 31.9, 29.6, 29.4, 29.1, 26.2, 22.7, 14.1 ppm. UV−vis (hexane, $c = 3.5 \times 10^{-5}$ M): λ_{max} (log ϵ) 236 (4.64), 245 (sh, 4.63), 277 (4.30), 297 (4.52), 338 (3.84), 363 (3.98), 430 nm (sh, 3.69). CD ($c = 3.5 \times 10^{-5}$ M, hexane), nm ($\Delta\epsilon$): 241 (−5), 262 (−36), 297 (72), 352 (−93), 394 (−15), 433 (−21), 522 (2). HRMS (FAB): *m*/*z* calcd for $C_{50}H_{60}O_6$ 756.4390, found 756.4421.

(*P*)-(+)-12. Procedure E was followed, using 0.10 g (0.067 mmol) of **13**, $x = 5$. Chromatography (eluent: 4:1 CH_2Cl_2−hexanes) provided 0.058 g (75% yield) of (*P*)−(+)-**12**, a red-brown wax. $[\alpha]_D$: +1570 (*c* 0.016, CH_2Cl_2) (lit.[13b] $[\alpha]_D$ +1480 (*c* 0.050, CH_2Cl_2)). The ^{1}H NMR and ^{13}C NMR spectra of (*P*)-(+)-**12** were identical to those of the racemic material.[14a]

Preparation of Bis-*o*-quinones. Procedure F. A solution of the Russig−Laatsch products in dry THF was stirred for 15 min with activated 4 Å molecular sieves in a flame-dried flask before it was added by cannula to a solution of benzeneselenininc anhydride (3 mol/mol helicene) in the same amount of dry THF that had been stirred in another flame-dried flask for 15 min with 4 Å molecular sieves. A minimal amount of THF was used to complete the transfer. The mixture, after it had stirred under N_2 for 2 h at room temperature, was poured into aqueous $NaHCO_3$. The organics were washed with H_2O and dried (Na_2SO_4), and the solvent was evaporated.

(*M*)-(−)-11 (R¹ = R² = dodecyl). Following procedure F, the amount of (*M*)-(−)-**9** ($R^1 = R^2$ = dodecyl) was 0.10 g (0.091 mmol) and of THF 2 × 5 mL. Silica gel chromatography (eluent: CH_2Cl_2) gave the red-brown product (0.070 g, 68% yield). Mp: 62−64 °C. $[\alpha]_D$: −2950 (*c* 0.020, hexane). IR (CCl_4): 2928, 2856, 1662, 1595 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.29 (d, 2 H, 8.6 Hz), 7.79 (d. 2 H, 8.7 Hz), 7.32 (s, 2 H), 5.71 (s, 2 H), 4.35 (m, 2 H), 4.26 (m, 2 H), 4.17 (m, 2 H), 4.07 (m, 2H), 1.99 (m, 8 H), 1.56 (m, 73 H), 1.29 (m, 73 H), 0.88 ppm (m, 12 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 182.3, 182.2, 168.2, 159.7, 135.1, 133.5, 133.1, 127.5, 125.9 (2 peaks), 125.3, 122.0, 102.3, 101.9, 70.1, 69.0, 31.9, 29.6, 29.4 (2 peaks), 29.3, 29.1, 28.4, 26.2, 26.0, 22.7, 14.1 ppm. UV−vis (CH_3CN, $c = 2.7 \times 10^{-5}$ M): λ_{max} (log ϵ) 242 (4.74), 269 (4.53), 293 (4.62), 321 nm (sh, 4.33). CD ($c = 2.7 \times 10^{-5}$ M, CH_3CN), nm ($\Delta\epsilon$): 234 (−117), 250 (−8), 253 (−10), 300 (179), 380 (−125), 431 (sh, −35). HRMS (FAB): *m*/*z* + K calcd for $C_{74}H_{108}O_8$ 1163.7632, found 1163.7681.

(*P*)-(+)-14. Following procedure F, the amount of (*P*)-(+)-**13** was 0.25 g (0.16 mmol) and of THF 2 × 5 20 mL. Silica gel chromatography (eluents: 1:1 hexane−CH_2Cl_2 to CH_2Cl_2) gave the orange-brown waxy product, 0.16 g (64% yield). Mp: 52−53 °C. $[\alpha]_D$: +2180 (*c* 0.14, dodecane). IR (CCl_4): 2928, 2856, 1661, 1599 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.24 (s, 4 H), 7.05 (s, 2 H), 5.59 (s, 2 H), 4.37 (m, 4 H), 4.18 (m, 4 H), 4.00 (m, 4 H), 1.92 (m, 12 H), 1.56 (m, 9 H), 1.29 (m, 104 H), 0.89 ppm (m, 18 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 181.1, 176.9, 168.5, 160.8, 144.8, 131.3, 130.3, 128.3, 126.2, 125.0, 124.1, 122.8, 120.7, 102.2, 100.7, 74.0, 69.9, 69.1, 31.9, 30.4, 29.6, 29.5, 29.4, 29.3, 29.1, 28.4, 26.2, 22.7, 17.7, 14.1 ppm. UV−vis (dodecane, $c = 2.0 \times 10^{-5}$ M): λ_{max} (log ϵ) 217 (sh, 4.42), 260 (3.67), 282 (4.45), 304 (4.50), 352 (sh, 4.55), 431 nm (3.65). CD ($c = 2.0 \times 10^{-5}$ M, dodecane), nm ($\Delta\epsilon$): 240 (35), 243 (−17), 262 (18), 300 (−139), 358 (138), 410 (12), 459 (22). HRMS (FAB): *m*/*z* + K calcd for $C_{102}H_{158}O_{10}$ 1582.1492, found 1582.1489.

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Supporting Information Available: Graphs showing the ^{1}H and ^{13}C NMR and IR spectra of **7** (R^1 = TIPS), (*M*)-(−)-**7** (R^1 = Et, *n*-Bu, dodecyl), **9** ($R^1 = R^2$ = Me, Et, *n*-Bu, dodecyl; R^1O = H, R^2 = Me; R^1 = Me, R^2 = Et), (*P*)-(+)- and (*M*)-(−)-**10**, (*M*)-(−)-**11**, **13**, (*P*)-(+)- and (*M*)-(−)-**13**-dicamphanates, (*M*)-(−)-**14**; the UV and CD spectra of (*P*)-(+)- and (*M*)-(−)-**7** (R^1 = Me), (*M*)-(−)-**7** (R^1 = Et, *n*-Bu, dodecyl), (*P*)-(+)-**9** ($R^1 = R^2$ = Me), (*M*)-(−)-**9** ($R^1 = R^2$ = Et, *n*-Bu, dodecyl), (*P*)-(+)- and (*M*)-(−)-**10**, (*M*)-(−)-**11**, (*P*)-(+)-, and (*M*)-(−)-**13**, (*P*)-(+)- and (*M*)-(−)-**13**-dicamphanates, (*M*)-(−)-**14**; and ^{1}H and ^{13}C NMR spectra of 2,7-bis-[1-(triisopropylsiloxy)ethenyl]naphthalene. This material is available free of charge via the Internet at http://pubs.acs.org.

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