Expeditious Procedure To Synthesize Ethers and Esters of Tri- and Tetrahydroxy[6]helicenebisquinones from the Dye-Intermediates Disodium 4-Hydroxy- and 4,5-Dihydroxynaphthalene-2,7-disulfonates†

Kamil Paruch,‡ Libor Vyklický,‡ Thomas J. Katz,*,‡ Christopher D. Incarvito,§ and Arnold L. Rheingold§

Department of Chemistry, Columbia University, New York, New York 10027, and Department of Chemistry and Biochemistry, University of Delaware, Newark, Delaware 19716

tjk1@columbia.edu

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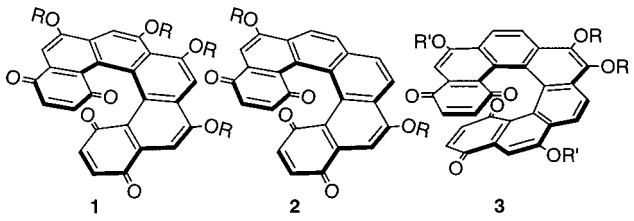
A procedure is described for synthesizing appreciable quantities of both the tetradodecyloxy[6]-helicenebisquinone **1** (R = dodecyl), which exhibits unique optical properties but previously was difficult to prepare, and a variety of analogues. The synthesis starts from disodium 4,5-dihydroxynaphthalene-2,7-disulfonate, the commercially available dye-intermediate known as chromotropic acid. It gives enantiopure **1**, with R = $(i\text{-Pr})_3$Si, whose silyl groups can be replaced by dodecyl and hexanoyl groups. The same procedure applied to disodium 4-hydroxynaphthalene-2,7-disulfonate, also an inexpensive, commercially available chemical, works equally well to produce the corresponding molecules that have one fewer side chain. Key steps are the use of tosyl groups to protect phenols and of a method described seven years ago by Satoh, Itoh, Miura, and Nomura to transform the sulfonic acid functions to iodides. The structure of tetra-(1*S*)-camphanate **20**, the ester of the reduction product of (−)-**1** [R = $(i\text{-Pr})_3$Si], was analyzed by X-ray diffraction. It shows the absolute configurations and supports the presumed basis for the rule that the (1*S*)-camphanates of (*P*)-helicen-1-ols are more polar than their (*M*)-diastereomers.

Introduction

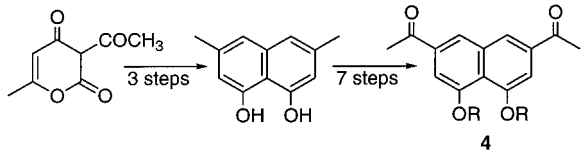
It is unfortunate that of all the helicenes, molecule **1** (R = dodecyl) was found to exhibit the previously unknown properties of self-assembly into helical columnar stacks as well as a high second-order nonlinear optical response owing to the chirality of the assembly.[1] It is unfortunate because **1** is much harder to synthesize[1a,b] than related structures such as **2** and **3** (R = dodecyl).[2,3]



1 **2** **3**

The problem is not the key step that builds the helicene skeleton, the reaction of an enol ether of an aryl bis-methyl ketone with 1,4-benzoquinone.[1b,4] That reaction works well for all three of these molecules. The problem is that, as outlined in Scheme 1, 10 steps are required from a commercially available material (dehydroacetic acid) to synthesize the precursor of **1**, structure **4**.

Scheme 1



4

There is a second difficulty. After the helicene skeleton is constructed, it has been impossible to alter the alkyl groups that were incorporated from **4**. Attempts to overcome the problem by replacing them with protecting groups were only partially successful. When the protecting groups were pivalates, the yield of the transformation that led to the helicene was very poor.[1a,b]

Only few known naphthalenes have the required substitution pattern. 2,7-Dimethyl-4,5-dihydroxynaphthalene is available in three steps from dehydroacetic acid.[5] Naphthalic anhydride derivatives **5** (X = NO_2 and

† Dedicated to Dr. Alfred P. Bader in appreciation of his support for Czech students.

‡ Columbia University.

§ University of Delaware.

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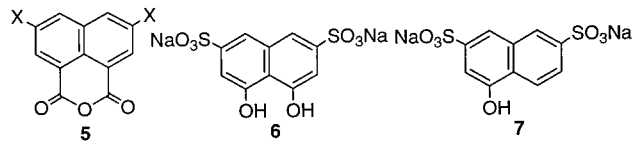
SO_3H) are obtained by nitrating[6] and sulfonating[7] 1,8-naphthalic anhydride and can be transformed into derivatives such as **5** (X = OH and Cl).[7] The structurally related **5** (X = CO_2H) has been prepared from mesitylene.[8] 1,3,6,8-Tetrahydroxynaphthalene has been made from methyl 3,5-dihydroxybenzoate as well as from chromotropic acid (see below).[9] And chromotropic acid (**6**) can be made by hydrolyzing 1-aminonaphthalene-3,6,8-trisulfonic acid ("Koch-acid" in the dye industry).[10] The first of these was used previously to prepare **4**, but the last looked like an attractive alternative because to install the required functional groups seemed easy and because chromotropic acid is commercially available and inexpensive. However, although this acid has the correct substitution pattern, with oxygens correctly positioned, the only transformations it is known to undergo are two O-diacylations,[11] two O-monoalkylations,[12] alkali fusion to give 1,3,6,8-tetrahydroxynaphthalene,[9b] and a number of electrophilic substitutions, mainly diazo-couplings ortho to the hydroxyls. None of these appear useful in advancing the structure toward the goal.

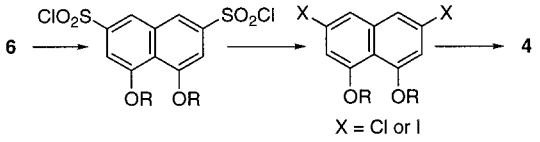


In this paper, we describe a way to convert chromotropic acid into **4**, R = TIPS, and then into enantiopure **1**, R = TIPS. The transformations are efficient, and the product has the flexibility to act as the precursor for derivatives of **1** that are substituted by a variety of alkyl and ester groups. Similar procedures convert disulfonic acid **7**, also an inexpensive, commercially available chemical, into the corresponding [6]helicenebisquinones that have three substituents in place of the four in **1**.

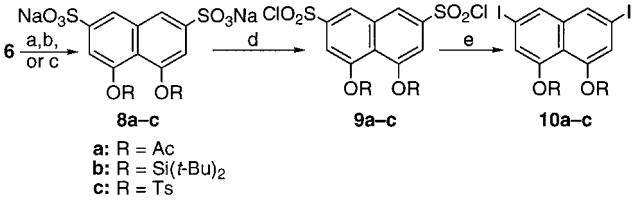
Results

The essential step to convert chromotropic acid (**6**) into **4** is to replace the sulfonic acid functions with acetyl groups. Although it is known that related transformations, in which aryl−sulfur bonds are replaced by aryl−carbon bonds, can be brought about directly by fusing the salts of arylsulfonic acids with KCN, the yields are low.[13] However, with the aid of noble metal catalysts, the chlorides of arylsulfonic acids can be desulfonated, either with incorporation of other groups—carbon monoxide,[14] vinyl groups,[15] or iodine[16]—or without, this last giving the aryl chlorides.[17] Of these transformations, those producing the aryl halides are particularly attractive because if applied to chromotropic acid (**6**), further transformation of the halogen substituents into acetyl groups would complete the synthesis (Scheme 2).

Scheme 2



Scheme 3[a]



[a] Reaction conditions and yields: (a) Ac_2O, NaOH, H_2O (40%); (b) $(t\text{-Bu})_2SiCl_2$, 1-hydroxybenzotriazole, Et_3N, DMF (53%); (c) TsCl, Na_2CO_3, H_2O (55%); (d) $SOCl_2$, DMF (small amount), reflux (89−92%); (e) ZnI_2, LiCl, Ti(O-*i*-Pr)$_4$, $PdCl_2(PhCN)_2$ (2.6 mol %), diglyme, 155 °C (yield of **10b**, 31%; of **10c**, 52%).

However, before the sulfonic acid can be converted into its acid chloride, the hydroxyl groups must be protected. But no diethers of chromotropic acid are known, and a number of attempts to prepare them failed.[12] Among the reagents we tried were the following: Me_2SO_4[18] and MeI in the presence of KOH or K_2CO_3; Ph_2CCl_2, TIPSOTf, and Ph_2SiCl_2 in the presence of triethylamine; Et_3OSbCl_6;[19] and methanolic HCl.[2,4c] Experiments that did succeed (Scheme 3) gave the following: the diacetate (**8a**, in 40% yield) when chromotropic acid was treated with Ac_2O in aqueous NaOH;[11b] the cyclic silyl ether (**8b**, in 53% yield) when the acid was treated with $(t\text{-Bu})_2SiCl_2$, triethylamine, and 1-hydroxybenzotriazole in DMF; and the ditosylate (**8c**, in 55% yield) when the acid was treated with tosyl chloride in aqueous sodium carbonate. All of these were converted into their sulfonyl chlorides, **9a**−**c**.

Accordingly (Scheme 3), **9a**−**c** were subjected to the conditions of desulfonylative iodination reported by Satoh, Itoh, Miura, and Nomura.[16] Compound **9c** was found to undergo the transformation in the highest yield (52%). Siloxane **9b** gave a 31% yield, while diacetate **9a** gave no recognizable products. Because the yield is higher and the cost less, the tosylate was used for the synthesis in preference to the silyl ether.

As summarized in Scheme 4, KOH in refluxing EtOH removes the tosyl groups from **10c**, and subsequent treatment with TIPSOTf and Et_3N in refluxing dichloro-

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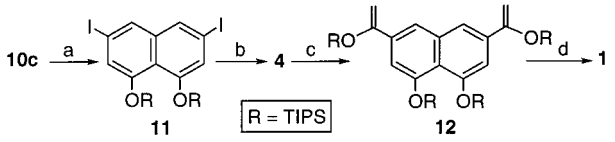
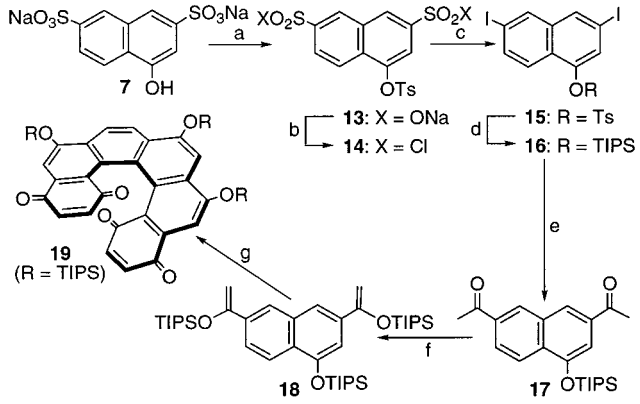
Scheme 4[a]



[a] Reaction conditions and yields: (a) (i) KOH, EtOH, reflux; (ii) TIPSOTf, Et_3N, $(CH_2Cl)_2$, reflux (80%); (b) *n*-BuLi, then *N*-methoxy-*N*-methylacetamide, Et_2O, −100 °C to +25 °C (66%); (c) TIPSOTf, Et_3N, CH_2Cl_2 (100%); (d) 1,4-benzoquinone, $PhCH_3$, 90 °C (40%).

Scheme 5[a]



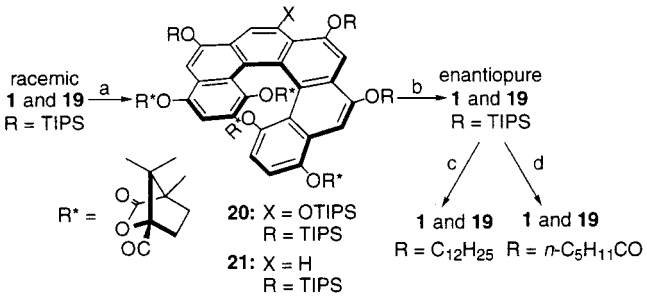
[a] Reaction conditions and yields: (a) TsCl, Na_2CO_3, H_2O (55%); (b) $SOCl_2$, DMF (72%); (c) ZnI_2, LiCl, $Ti(Oi\text{-}Pr)_4$, $PdCl_2(PhCN)_2$ (3 mol %), diglyme, 160 °C (46%); (d) (i) KOH, EtOH, reflux; (ii) TIPSOTf, Et_3N, CH_2Cl_2 (77%); (e) *n*-BuLi, then *N*-methoxy-*N*-methylacetamide, Et_2O, −100 °C to +25 °C (52%); (f) TIPSOTf, Et_3N, CH_2Cl_2 (100%); (g) 1,4-benzoquinone, $PhCH_3$, 90 °C (38%).

ethane puts TIPS groups in their place. Weinreb's procedure[20] then converts the iodides in the resulting **11** (R = TIPS) into aryl methyl ketones. The yield of **4** (R = TIPS) is 66%. Like other diacetylarenes,[1a,b,2−4] **4** when combined with TIPSOTf and Et_3N in CH_2Cl_2 and then with 1,4-benzoquinone in $PhCH_3$ produces the corresponding helicene, **1** (R = TIPS). The yield is 40%.

When the sequence of reactions was carried out starting with technical grade chromotropic acid, 200 g of **6** gave 185 g of **8c** and 120 g of **8c** gave 14.7 g of **1** (R = TIPS). Thus, appreciable amounts can be made easily at moderate cost. Similarly, disodium 4-hydroxynaphthalene-2,7-disulfonate (**7**), which is an even cheaper chemical than chromotropic acid, was transformed into [6]-helicenebisquinone **19** (Scheme 5). Starting from 100 g of technical grade **7**, 79 g of **13** was obtained, and this was converted into 5.9 g of **19**.

The method used to resolve the enantiomers of **1** and **19** (R = TIPS, Scheme 6) was that used previously to resolve the enantiomers of a [6]helicenebisquinone having only two TIPSO side chains[21] and is related to the original procedure used to resolve the enantiomers of **1** (R = dodecyl).[1b] In the case of both **1** and **19**, reduction with Zn followed by esterification with (1*S*)-camphanoyl chloride and Et_3N in CH_2Cl_2 gave diastereomeric tetracamphanates **20** and **21**. If DMAP is added to the reaction mixtures, the yields improve and the reaction times are shortened. In the case of both **20** and **21**, chromatography on silica gel separates the diastereomers. Since methyllithium removes the camphanates from the individual diastereomers and chloranil oxidizes the resulting hydroquinones, enantiopure **1** and **19** (R = TIPS) can be prepared in gram quantities.

Scheme 6[a]



[a] Reaction conditions and yields: (a) Zn, (1*S*)-camphanoyl chloride, DMAP, Et_3N, CH_2Cl_2 [79% of (*P*)-**20**, 75% of (*M*)-**20**; 67% of (*P*)-**21**, 74% of (*M*)-**21**]; (b) (i) MeLi, Et_2O, −78 °C to +25 °C, then aqueous NH_4Cl; (ii) chloranil [87% of (*P*)-**1**, 88% of (*M*)-**1**; 61% of (*P*)-**19**, 73% of (M)-**19**]; (c) $C_{12}H_{25}I$, CsF, DMF, 60 °C [58% of **1**, 61% of **19**]; (d) $C_5H_{11}COCl$, CsF, DMAP, DMF, 25 °C [68% of **1**, 71% of **19**].

As Scheme 6 also shows, replacing the TIPS groups in **1** by dodecyl groups gives the tetraether, identical with that synthesized previously,[1a,b] and replacing the TIPS groups in **19** gives a new triether analogue. The reagents are dodecyl iodide and CsF in DMF,[22] a combination used previously for related transformations.[3] The yields are 58 and 61%, respectively. Similarly, when the reagents are hexanoyl chloride, CsF, and DMAP in DMF, hexanoyl groups replace the four TIPS groups of **1** and the three of **19**. The yields are 68−71%.

A crystal suitable for X-ray diffraction analysis was grown of the less polar of the diastereomeric tetracamphanates **20**. The analysis shows, on the basis of the known absolute configurations of the camphanate moieties,[23] that this diastereomer has the (*M*)-configuration. The absolute structure parameter confirms this assignment. The X-ray analysis also shows the conformations of the camphanate groups with respect to the helicene skeletons, providing support for a hypothesis relating these conformations, the relative polarities of diastereomeric helicenol camphanates, and the absolute configurations of the diastereomers.[3a,21] There are two molecules in the crystal's unit cell. Table 1 summarizes two angles that define the conformations of both the inner and outer camphanates with respect to the ring system in the two independent molecules. In keeping with the usage in the previous study of camphanate conformations,[21] the two angles are called **c** (the dihedral angle $O_1{=}C_2{-}C_3{-}O_4$) and **a** [the dihedral angle (H)C−C−O−C(=O)]. The structures of the two molecules, with values of the angles **c**, are displayed in Figure 1.

Discussion

The method of synthesis described provides a way to prepare a helicene, **1** ($R = C_{12}H_{25}$), whose properties are

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(22) Good yields could be obtained in some of these experiments only when the CsF was ground to a fine powder by shaking it, by means of a Wig-L-Bug, with a glass bead.
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Table 1. Dihedral Angles O=C−C−O (angle c) and (H)C−C−O−C(=O) (angle a) Defining, in Part, the Conformations of the Camphanates with Respect to the Helicene Ring System in (*M*)-(−)-20[a]

inside		outside	
c	**a**	**c**	**a**
−140.5	106.0	151.0	86.2
−163.7	104.7	150.7	59.8
−129.0	94.9	−154.9	−60.0
−29.8	−23.0	172.4	88.0

[a] The angles are listed for the camphanates attached to the oxygens on the inside and outside of the helicene, and the first two lines refer to one of the two independent molecules in the unit cell, the last two to the other. Angles are in degrees.

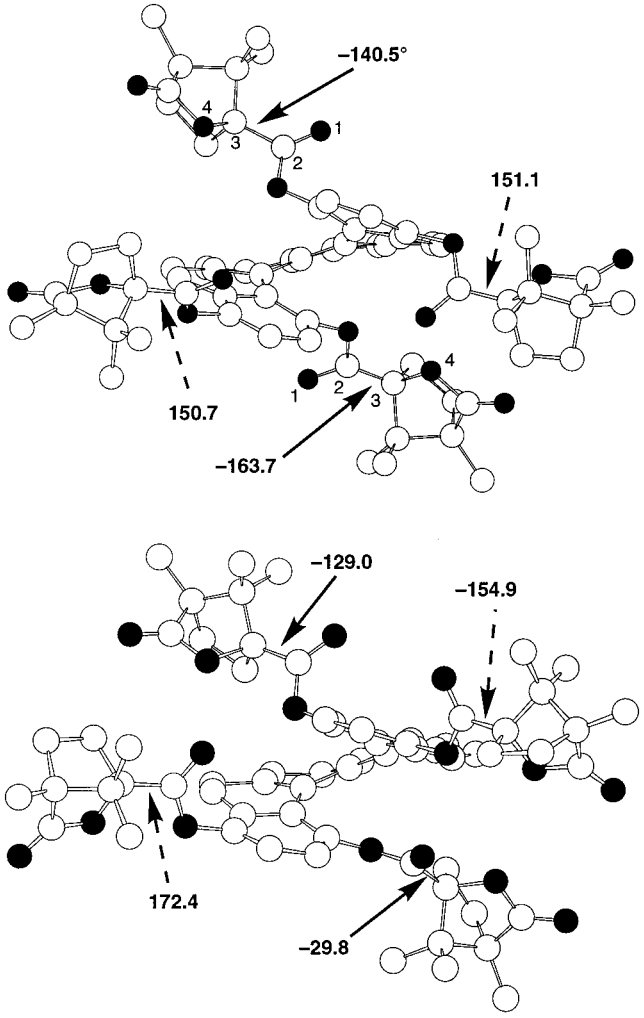

Figure 1. Structure of (*M*)-(−)-**20** according to X-ray diffraction analysis. The two independent molecules in the unit cell are both displayed. The O=C−C−O dihedral angles are shown with dark arrows for the inner camphanate groups and dotted arrows for the outer camphanate groups. Oxygen atoms are shown in black, carbons in white. Hydrogens and the TIPSO groups have been omitted for clarity.

interesting. Because it gives the structure with TIPS groups in place of dodecyls, the method also provides the flexibility required to easily prepare derivatives that have other side chains, and because it is much shorter than those reported before, the synthesis provides a way to make these materials in much larger amounts than were previously practical. In addition, the method is sufficiently general that it can be used to prepare the related helicenes **19**, which have only three side chains.

The key step is the application of the procedure of Satoh, Itoh, Miura, and Nomura to replace the sulfonyl chloride groups with iodines.[16] This procedure appears not to have been applied during the 7 years since its discovery, but in the case of the two syntheses reported here, it certainly works well and on scales up to 30 times those reported in the original paper.

The method described for the preparations of **1** and **19** (R = $C_{12}H_{25}$ and $C_5H_{11}CO$) should also allow the TIPS groups on the helicene structures to be replaced by other alkyl and acyl groups.[22,24] For these preparations, structure **19** should be particularly useful because such replacements seem to take place much more easily on it than on the more sterically hindered structure **1**.

The structure displayed in Figure 1 for the two independent molecules in the crystal's unit cell proves the absolute configuration of (*M*)-(−)-**20**. The structure therefore confirms the rule that the (1*S*)-(−)-camphanates of (*P*)-helicen-1-ols are always more polar than their diastereomers.[3a,21] [In the case of both **20** and **21**, as in nineteen other cases,[3a,21] the (*M*)-helicen-1-ol's (1*S*)-camphanate has the higher R_f on silica gel.] The structures in Figure 1 also confirm the hypothesis that when a helix has the (*M*)-configuration, the lactone functions of the camphanates attached to the inside oxygens point toward the other parts of the helicene structure, whereas in (*P*)-helicene derivatives, they point outward, away from the helicene skeleton.[3a,21] The basis for the hypothesis is that the favored conformations keep the methyl groups on the camphanates' bridges away from other parts of the molecule.[21] The camphanate moieties in all previously analyzed (*M*)-helicen-1-ol (1*S*)-camphanates and for three of the four in Figure 1 on the insides of the ring structures achieve this by adopting that one of two favored conformations in which the O=C−C−O angle (angle **c**) is close to 180° and the *external carbonyl group* (C_2=O_1 in Figure 1) points away from the helicene skeleton.[25] However, in the molecule pictured on the bottom in Figure 1, one of these angles has the other favored value, close to zero (in this case −29.8°).[25] Yet the conformation still has the lactone pointing toward the inside of the molecule. The reason is that the external carbonyl group has the alternative conformation favored for aryl esters:[25] it points into the helicene skeleton. Table 1 also makes this clear. The Figure shows that this change is correlated with a change in the conformation of the opposing outside camphanate. In Table 1 this is seen as a change in the angle **a** from the usual ca. 90° to −60°.

The demonstration by the X-ray diffraction analysis that (−)-**20** has the (*M*)-configuration also shows that (−)-**1** (R = TIPS, dodecyl, and hexanoyl) have the (*M*)-configuration, for the chemical transformations that produce the latter structures from (*M*)-(−)-**20** cannot change the stereochemistry of the ring system. In addition, the similarity (displayed in the Supporting Information), between the CD spectra of (−)-**1** (R = TIPS) and of (−)-**19** (R = TIPS) implies that the latter and its derivatives, (−)-**19** with R = TIPS, dodecyl, and hexanoyl, also have this absolute stereochemistry. Above, we applied this conclusion in assigning the (*M*)-configuration to the diastereomer of **21** that has the higher R_f.

(24) Related replacements of TIPS-groups by alkyls are reported in ref 3a,b and by acyls in ref 3a.

(25) See ref 21 and references therein.

Conclusions. The dye intermediate disodium 4,5-dihydroxynaphthalene-2,7-disulfonate (chromotropic acid) can easily be converted into an enantiopure helicene whose properties are unique and significant, but whose synthesis was previously difficult. Because the synthesis gives the TIPSO-substituted helicene skeleton, it provides the flexibility to yield numerous derivatives in which the TIPS groups are replaced. When applied to the related dye intermediate disodium 4-hydroxynaphthalene-2,7-disulfonate, the procedure gives the related enantiopure helicenes that have one fewer side chain. The X-ray diffraction analysis of a helicene tetracamphanate identifies the absolute stereochemistries and supports a hypothesis relating the conformations of helicenol camphanes and the relative polarities and absolute configurations of their diastereomers.

Experimental Section

Diglyme, Et_2O, and $PhCH_3$ were distilled from Na/Ph_2CO, CH_2Cl_2, 1,2-dichloroethane, and triethylamine from CaH_2. DMF (anhydrous), ZnI_2 (98%), Zn (dust, <10 μm, 98%), 1-iodododecane (98%), and 4,5-dihydroxynaphthalene-2,7-disulfonic acid, disodium salt dihydrate (technical grade) were purchased from Aldrich. 4-Hydroxynaphthalene-2,7-disulfonic acid, disodium salt hydrate (technical grade), TsCl (99%), Ti(O-*i*-Pr)$_4$ (98%), hexanoyl chloride (87%), and CsF (99%) were purchased from Acros, TIPSOTf from GSF Chemicals, and $PdCl_2(PhCN)_2$ from Strem Chemicals. 1,4-Benzoquinone (98%, Aldrich) was purified by slurrying it in CH_2Cl_2 with two times its weight of basic alumina, filtering it through Celite, and drying it under a vacuum. *N*-Methoxy-*N*-methylacetamide[20] and (1*S*)-(−)-camphanoyl chloride[26] were synthesized. Chromatography refers to flash chromatography on silica gel.[27]

Disodium 4,5-[Di(*tert*-butyl)silyloxy]-2,7-naphthalene Disulfonate (8b). Di(*tert*-butyl)dichlorosilane (0.13 mL, 0.6 mmol) was added to a mixture of technical-grade chromotropic acid (200 mg, ca. 0.5 mmol), 1-hydroxybenzotriazole (HOBt, 13 mg, 0.10 mmol), Et_3N (0.2 mL), and DMF (1 mL) under a nitrogen atmosphere, and the solution was then stirred for 1 h at 25 °C. After water (ca. 15 mL) had been added and impurities had been extracted with CH_2Cl_2 (2 × 10 mL), EtOH (10 mL) and enough K_2CO_3 were added to form two distinct layers. The extraction with EtOH was repeated, and the solvent was evaporated from the combined alcoholic solutions. The residue, after it had been dried overnight in a vacuum, weighed 194 mg, a 60% yield of the product assuming (in accord with the NMR spectrum) that it is a complex with two molecules of DMF. Pure material could be obtained by shaking this material with EtOAc, filtering, and drying at 130 °C for 2 h: mp >250 °C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 7.66 (d, 1.3 Hz, 2H), 7.07 (d, 1.3 Hz, 2H), 1.06 ppm (s, 18H).

Disodium 4,5-Ditosyloxynaphthalene-2,7-disulfonate (8c). Na_2CO_3 (106 g, 1.00 mol) was added in portions to a stirred solution of technical-grade chromotropic acid (200 g, ca. 0.5 mol) in H_2O (1 L) in a 5 L round-bottomed flask. The mixture was stirred for 10 min, and TsCl (191 g, 1.00 mol) was added in portions. The mixture was stirred for 15 h and filtered, and the solvent was evaporated. After the residue had been suspended in MeOH (100 mL), toluene (100 mL) was added, and the solvents were evaporated. This treatment was repeated two more times. The resulting solid was dried in a vacuum at 60 °C, pulverized, shaken for 5 min with MeOH (1 L), and filtered. The solid was extracted with MeOH (2 × 1 L), and the solvent was evaporated. The resulting solid was dried in a vacuum at 100 °C, pulverized, boiled in anhydrous EtOH (2 L) for 30 min, and filtered. After two more extractions with boiling EtOH (2 and 0.5 L), the insoluble solid was dried overnight in a vacuum at 150 °C. The yield of pale rose-colored solid (mp > 250 °C) was 185 g (55%): IR (KBr) 1598, 1337, 1250, 1177, 1047 cm^{-1}; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 8.13 (d, 1.4 Hz, 2H), 7.55 (d, 8.3 Hz, 4H), 7.40 (d, 1.4 Hz, 2H), 7.36 (d, 8.3 Hz, 4H), 2.36 ppm (s, 6H); ^{13}C NMR (DMSO-d_6, 75 MHz) 146.4, 145.7, 142.2, 135.0, 131.3, 129.9, 128.4, 124.2, 119.9, 119.8, 21.2 ppm; UV−vis (MeOH, $c = 6.71 \times 10^{-5}$ M) λ_{max} (log ϵ) 239 (3.16), 287 (3.74), 329 nm (3.16); HRMS (FAB) *m*/*z* calcd for $C_{24}H_{19}Na_2O_{12}S_4$ $[M + H]^+$ 672.9555, found 672.9553.

Disodium 4-Tosyloxynaphthalene-2,7-disulfonate (13). The procedure in the preceding paragraph, when applied to disodium 4-hydroxynaphthalene-2,7-disulfonate hydrate (100 g, 0.29 mol), Na_2CO_3 (32 g, 0.3 0 mol), and TsCl (60 g, 0.32 mol) in 500 mL of H_2O, gave 79 g (55%) of slightly pink solid **13**: mp >250 °C; IR (KBr) 1628, 1596, 1192, 1038 cm^{-1}; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 8.20 (s, 1H), 8.13 (s, 1H), 7.84 (d, 8.3 Hz, 2H), 7.78 (d, 8.8 Hz, 1H), 7.74 (dd, 8.8 and 1.4 Hz, 1H), 7.57 (d, 1.4 Hz, 1H), 7.46 (d, 8.3 Hz, 2H), 2.40 ppm (s, 3H); ^{13}C NMR (DMSO-d_6, 75 MHz) 147.6, 146.9, 146.7, 145.2, 133.6, 132.5, 131.2, 129.0, 126.8, 126.5, 125.5, 124.7, 121.8, 117.6, 22.1 ppm; UV−vis (MeOH, $c = 8.2 \times 10^{-5}$ M) λ_{max} (log ϵ) 227 (4.57), 231 (4.58), 235 (4.57), 274 nm (3.59); HRMS (FAB) *m*/*z* calcd for $C_{17}H_{12}Na_3O_9S_3$ $[M + Na]^+$ 524.9336, found 524.9316.

4,5-Diacetoxy-2,7-naphthalenedisulfonyl Chloride (9a). Disodium 4,5-diacetoxy-2,7-naphthalenedisulfonate[11b] (155 mg, 0.35 mmol), $SOCl_2$ (1 mL), and DMF (0.1 mL) were refluxed for 2 h. Cold water (15 mL) was added, the mixture was extracted with CH_2Cl_2 (4 × 15 mL), and the combined organic extracts were dried over Na_2SO_4. A quick filtration through a pad of silica gel, evaporation, and vacuum-drying gave 75 mg (49%) of yellow solid. Attempts to purify it failed: ^{1}H NMR ($CDCl_3$, 300 MHz) 8.69 (d, 1.8 Hz, 2H), 7.90 (d, 1.8 Hz, 2H), 2.49 ppm (s, 6H); IR (KBr) 1780, 1377, 1174 cm^{-1}.

4,5-[Di(*tert*-butyl)siloxy]-2,7-naphthalenedisulfonyl Chloride (9b). A mixture of **8b** (60 mg, 0.12 mmol), $SOCl_2$ (1 mL), and DMF (1 drop) was refluxed for 1 h. After water (10 mL) had been added and the product extracted into CH_2Cl_2 (2 × 10 mL), the combined organic solutions were washed with water and dried over $MgSO_4$, and the solvent was evaporated. After it had been dried in a vacuum, the resulting acid chloride (36 mg, 61% yield) was only slightly impure and was used directly in the next step: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.28 (d, 1.7 Hz, 2H), 7.62 (d, 1.7 Hz, 2H), 1.14 ppm (s, 18H); IR (KBr) 1591, 1383, 1172, 1106 cm^{-1}.

4,5-[Di(*tert*-butyl)siloxy]-2,7-diiodonaphthalene (10b). Anhydrous diglyme (1.5 mL) was added to a mixture of **9b** (33 mg, 0.044 mmol), ZnI_2 (100 mg, 0.31 mmol), LiCl (3 mg, 0.05 mmol), Ti(O-*i*-Pr)$_4$ (15 μL, 0.05 mmol), and $PdCl_2(PPh_3)_2$ (3 mg, 4 μmol) under nitrogen. The mixture was refluxed for 24 h, poured into water, and extracted twice with petroleum ether. The combined organic solutions were washed with water and dried (Na_2SO_4), and the solvent was stripped. Preparative TLC on silica gel (eluent: petroleum ether) gave 11 mg (31%) of a solid, **10b**: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.64 (d, 1.4 Hz, 2H), 7.22 (d, 1.4 Hz, 2H) 1.11 ppm (s, 18H).

4,5-Ditosyloxynaphthalene-2,7-disulfonyl Chloride (9c). DMF (3.0 mL) was added to **8c** (120 g, 0.18 mol) and $SOCl_2$ (400 mL, 5.48 mol), and in a fume hood the mixture was stirred and refluxed for 2 h under a drying tube. The mixture was poured carefully onto crushed ice (3 L) and filtered. The solid was washed with cold H_2O (1 L), and mixed with CH_2Cl_2 (2 L). The aqueous layer was extracted further with CH_2Cl_2 (500 mL and 300 mL), and the combined CH_2Cl_2 extracts were dried over $MgSO_4$ and filtered. The solvent was evaporated. Drying in a vacuum at 100 °C afforded 106 g (89%) of a pale yellow solid that was used directly in the next step.

For characterization and analysis, a sample was recrystallized from 1:2 EtOAc/$(CH_2Cl)_2$. This gave a white solid: mp 219−221 °C; IR (KBr) 3074, 1590, 1382, 1344, 1193, 1179, 1053, 1038, 911 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.66 (d, 1.8 Hz, 2H), 7.73 (d, 8.4 Hz, 4H), 7.70 (d, 1.8 Hz, 2H), 7.36 (d, 8.4 Hz, 4H), 2.48 ppm (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) 146.8, 145.5, 143.1, 133.8, 130.9, 130.1, 129.1, 128.5, 128.0, 121.0, 21.0 ppm; UV−vis (CH_3CN, $c = 3.84 \times 10^{-5}$ M) λ_{max} (log ϵ)

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228 (4.69), 246 (4.68), 292 (3.73), 327 (3.53), 342 nm (3.58). Anal. Calcd for $C_{24}H_{18}Cl_2O_{10}S_4$: C, 43.31; H, 2.73. Found: C, 43.22; H, 2.81.

4-Tosyloxynaphthalene-2,7-disulfonyl Chloride (14). Following the procedure described for **9c**, **13** (78.5 g, 156 mmol), 340 mL of $SOCl_2$ (4.7 mol), and 5 mL of DMF gave 55.5 g (72%) of a pale yellow solid. A quick chromatographic purification on neutral alumina (eluent: CH_2Cl_2) gave an analytically pure sample (a white solid, mp 156−158 °C): IR (KBr) 3078, 1588, 1376, 1175 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.76 (d, 1.9 Hz, 1H), 8.66 (d, 1.5 Hz, 1H), 8.39 (d, 9.1 Hz, 1H), 8.23 (dd, 9.1 and 1.9 Hz, 1H), 7.81 (d, 8.4 Hz, 2H), 7.69 (d, 1.8 Hz, 1H), 7.39 (d, 8.5 Hz, 2H), 2.48 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) 147.6, 147.4, 144.6, 143.2, 133.3, 132.2, 131.4, 130.9, 130.4, 129.1, 128.9, 126.7, 126.2, 118.6, 22.3; UV−vis (CH_3CN, $c = 4.80 \times 10^{-5}$ M) λ_{max} (log ϵ) 222 (4.52), 225 (4.53), 228 (4.55), 232 (4.56), 237 (4.57), 240 (4.59), 244 (4.61), 251 nm (4.59); HRMS (FAB) *m/z* calcd for $C_{17}H_{12}Cl_2O_7S_3$ 493.9122, found 493.9149.

4,5-Ditosyloxy-2,7-diiodonaphthalene (10c). A dry 2 L round-bottomed flask fitted with a reflux condenser and containing **9c** (100.0 g, 0.150 mol), ZnI_2 (120.0 g, 0.376 mol), LiCl (6.0 g, 0.140 mol), and $PdCl_2(PhCN)_2$ (1.5 g, 3.9 mmol) was evacuated three times and flushed with N_2. Diglyme (1 L) and Ti(O*i*-Pr)$_4$ (20.0 mL, 0.068 mol) were added through a septum, and the mixture was stirred and heated in an oil bath at 155 °C for 14 h. The reaction mixture was poured into 0.05 M HCl (10 L) and filtered through a wad of Celite. The filter cake was mixed with CH_2Cl_2 (0.75 L, then 3 × 0.3 L), and each time the mixture was filtered. The filtrate was dried over $MgSO_4$, filtered, and concentrated to ca. 500 mL. The solution was poured onto silica gel (4 in d × 2 in h), and the product was eluted with CH_2Cl_2 (3 × 300 mL). The brown solid left when the solvent was evaporated was loaded onto silica gel (4 in d × 2 in h) that had been topped with sand, and the product was eluted with CH_2Cl_2. Evaporation of the solvent and drying in a vacuum gave an orange-yellow solid that was boiled for 10 min in EtOAc (250 mL). Anhydrous EtOH (250 mL) was added, and after the mixture had been allowed to stand overnight at 4 °C, the precipitated solid was filtered and washed in the filter funnel with EtOH (200 mL). Drying in a vacuum yielded 56 g (52%) of a pale yellow solid that was used for the next step. Analytically pure **10c** (a white solid mp 220−222 °C) was obtained by column chromatography (silica gel, 5:1 CH_2Cl_2/hexane): IR (KBr) 3096, 1604, 1570, 1379, 1357, 1329, 1239, 1190, 1174, 1032 cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz) δ 8.38 (d, 1.5 Hz, 2H), 7.57 (d, 8.3 Hz, 4H), 7.40 (d, 8.1 Hz, 4H), 7.17 (d, 1.5 Hz, 2H), 2.39 ppm (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) 145.8, 143.1, 137.9, 134.8, 131.6, 130.6, 129.5, 129.0, 119.9, 90.8, 21.7 ppm; UV−vis (CH_3CN, $c = 3.81 \times 10^{-5}$ M) λ_{max} (log ϵ) 230 (4.67), 258 (4.70), 290 (sh, 3.87), 300 (sh, 3.80), 315 nm (sh, 3.59). Anal. Calcd for $C_{24}H_{18}I_2O_6S_2$: C, 40.02; H, 2.52. Found: C, 40.07; H, 2.46.

4-Tosyloxy-2,7-diiodonaphthalene (15). Following the procedure in the previous paragraph, **14** (50 g, 100 mmol), ZnI_2 (80 g, 250 mmol), LiCl (2.1 g, 50 mmol), Ti(O-*i*-Pr)$_4$ (14.8 mL, 50 mmol), and $PdCl_2(PhCN)_2$ (1.1 g, 3 mmol) in diglyme (1.6 L) gave 25 g (46%) of a white solid after chromatography on a small amount of silica gel (eluent: 2:1 hexane/CH_2Cl_2): mp 153−155 °C; IR (KBr) 1604, 1565, 1379, 1355, 1174 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.09 (d, 1.5 Hz, 1H), 8.0 (s, 1H), 7.77 (d, 8.3 Hz, 2H), 7.67 (dd, 8.9 and 1.6 Hz, 1H), 7.56 (d, 8.9 Hz, 1H), 7.43 (d, 1.5 Hz, 1H), 7.33 (d, 8.2 Hz, 2H), 2.46 ppm (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) 146.1, 145.7, 137.0, 135.9, 135.2, 134.7, 132.2, 130.1, 128.6, 127.8, 125.4, 123.7, 94.0, 89.8, 21.9 ppm; UV−vis (CH_3CN, $c = 5.24 \times 10^{-5}$ M) λ_{max} (log ϵ) 227 (4.55), 230 (4.56), 234 (4.56), 245 (4.61), 253 nm (4.64). Anal. Calcd for $C_{17}H_{12}I_2O_3S$: C, 37.11; H, 2.20. Found: C, 37.21; H, 2.17.

4,5-Bis(triisopropylsiloxy)-2,7-diiodonaphthalene (11). A solution of KOH (38.9 g, 695 mmol) in anhydrous EtOH (750 mL) was added under N_2 to **10c** (50.0 g, 69.5 mmol). The mixture was stirred and refluxed for 150 min, cooled to ambient temperature, and while still under N_2, quenched with 5 M HCl (200 mL). It was poured into H_2O (2 L), extracted with EtOAc (1 L, 2 × 200 mL), washed with 2:1 H_2O/brine (2 × 1 L) and brine (100 mL), dried over Na_2SO_4, and filtered. Evaporation of the solvent and drying in a vacuum at 25 °C gave 28.6 g (100%) of crude 4,5-dihydroxy-2,7-diiodonaphthalene, which was used directly in the next step. A pure sample was prepared similarly in quantitative yield from analytically pure **10c**: mp 184−186 °C; IR (CCl_4) 3584, 3477, 1615, 1594, 1358, 1261 cm^{-1}; ^1H NMR (acetone-d_6, 400 MHz) δ 10.34 (s, 2H), 7.68 (d, 1.4 Hz, 2H), 7.09 ppm (d, 1.4 Hz, 2H); ^{13}C NMR (acetone-d_6, 75 MHz) 155.5, 139.5, 127.9, 118.7, 113.8, 93.2 ppm.

The solid from the previous step was mixed under N_2 with 1,2-dichloroethane (200 mL) and Et_3N (50 mL), and TIPSOTf (44.8 mL, 0.167 mol) was added to the stirring mixture. After the mixture had stirred and refluxed for 24 h, it was poured onto saturated aqueous $NaHCO_3$ (1 L) and extracted with hexane (1 L, 2 × 150 mL). The combined extracts were dried over Na_2SO_4, filtered, and concentrated to ca. 100 mL. The oily material was loaded onto silica gel (5 in d × 4 in h), and the product was eluted with hexane. Evaporation of the solvent and drying in a vacuum gave 38.1 g (80%) of pure **11** (a white solid, mp 106−107 °C): IR (CCl_4) 2948, 2869, 1589, 1553, 1466, 1360, 1260, 1092, 885, 840 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.58 (d, 1.5 Hz, 2H), 7.09 (d, 1.5 Hz, 2H), 1.32 (m, 6H), 1.04 ppm (d, 7.5 Hz, 36H); ^{13}C NMR ($CDCl_3$, 75 MHz) 153.9, 139.1, 128.5, 124.0, 120.4, 91.3, 17.9, 13.1 ppm; UV−vis (CH_3CN, $c = 5.23 \times 10^{-5}$ M) λ_{max} (log ϵ) 230 (sh, 4.39), 253 (4.66), 302 (3.72), 316 (3.76), 330 (3.76), 343 nm (3.75). Anal. Calcd for $C_{28}H_{46}I_2O_2Si_2$: C, 46.41; H, 6.40. Found: C, 46.39; H, 6.40.

4-Triisopropylsiloxy-2,7-diiodonaphthalene (16). When the procedure described above for the preparation of **11** was applied to 25 g (45.4 mmol) of **15**, 12.7 g (227 mmol) of KOH, and 230 mL of EtOH, it gave 16.8 g (a 93% yield) of crude 4-hydroxy-2,7-diiodonaphthalene, which was used directly in the next step. An analytically pure sample (a white solid, mp 156−159 °C) was obtained by chromatography on silica gel (eluent: 85:15 hexane/EtOAc): IR (KBr) 3297, 1570, 829 cm^{-1}; ^1H NMR (acetone-d_6, 400 MHz) δ 9.60 (broad s, 1H), 8.23 (d, 1.7 Hz, 1H), 7.96 (d, 8.8 Hz, 1H), 7.79 (s, 1H), 7.76 (dd, 8.8 and 1.7 Hz, 1H), 7.25 ppm (d, 1.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) 154.8, 138.2, 135.8, 134.7, 127.7, 125.1, 123.7, 118.2, 93.8, 92.8 ppm; UV−vis (CH_3CN, $c = 4.20 \times 10^{-5}$ M) λ_{max} (log ϵ) 218 (4.36), 252 nm (4.73); HRMS (FAB) *m/z* calcd for $C_{10}H_6I_2O_1$ 395.8508, found 395.8497.

TIPSOTf (12.5 mL, 46 mmol) was added at 0 °C to a stirred mixture under N_2 of crude 4-hydroxy-2,7-diiodonaphthalene (16.6 g, 42 mmol), CH_2Cl_2 (170 mL), and Et_3N (30 mL, 210 mmol). The mixture was stirred at 25 °C for 2 h, poured into saturated aqueous $NaHCO_3$, and extracted with CH_2Cl_2. The extract was dried over Na_2SO_4 and filtered, and the solvent was evaporated. The residue, dissolved in hexane, was poured onto a short column of silica gel, and the product was eluted with hexane. Evaporation of the solvent and drying in a vacuum gave 17.9 g (77%) of a slightly yellow oil: IR (NaCl window) 2945, 2867, 1604, 1563 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.04 (d, 1.5 Hz, 1H), 7.90 (d, 8.9 Hz, 1H), 7.70 (m, 2H), 7.13 (d, 1.3 Hz, 1H), 1.40 (m, 7.5 Hz, 3H), 1.15 ppm (d, 7.5 Hz, 18H); ^{13}C NMR ($CDCl_3$, 75 MHz) 152.7, 137.3, 135.0, 134.3, 128.3, 125.6, 124.7, 121.4, 93.4, 91.8, 18.1, 13.0 ppm; UV−vis (CH_3CN, $c = 4.64 \times 10^{-5}$ M) λ_{max} (log ϵ) 221 (4.37), 243 (4.55), 247 (4.61), 251 (4.60), 254 nm (4.58); HRMS (FAB) *m/z* calcd for $C_{19}H_{26}I_2O_1Si$ 551.9842, found 551.9819.

4,5-Bis-(triisopropylsiloxy)-2,7-diacetylnaphthalene (4, R = TIPS). *n*-BuLi (2.5 M in hexanes, 91.6 mL, 230 mmol) was added slowly under N_2 at −100 °C to a stirred solution of **11** (37.5 g, 54.5 mmol) in dry Et_2O (260 mL). The mixture was stirred for 5 min at −100 °C, and then *N*-methoxy-*N*-methylacetamide (17.5 mL, 164 mmol) was added during 5 min. The solution was stirred at −100 °C for 15 min and then at 25 °C for 1 h. Hexane (0.5 L) was added, and the solution was washed with saturated aqueous NH_4Cl (300 mL) and H_2O (2 × 1 L), dried over Na_2SO_4, and filtered. The solvent was evaporated, and the residue was chromatographed on silica gel (5 in d × 4 in h). Impurities were eluted with 1:1 hexane/CH_2Cl_2, the product with CH_2Cl_2. Evaporation of the solvent and drying

in a vacuum gave 19.9 g (66%) of a white solid: mp 116−117 °C (recrystallized from MeOH); IR (CCl_4) 2948, 2869, 1686, 1574, 1379, 1354, 1216, 1108, 884 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.09 (d, 1.5 Hz, 2H), 7.51 (d, 1.5 Hz, 2H), 2.69 (s, 6H), 1.37 (m, 6H), 1.05 ppm (d, 7.5 Hz, 36H); ^{13}C NMR ($CDCl_3$, 75 MHz) 197.2, 154.0, 136.1, 135.2, 126.4, 124.6, 114.5, 26.5, 17.9, 13.1 ppm; UV−vis (CH_3CN, $c = 6.65 \times 10^{-5}$ M) λ_{max} (log ϵ) 233 (sh, 4.36), 264 (4.56), 366 (3.85), 385 nm (3.96); HRMS (FAB) *m/z* calcd for $C_{32}H_{53}O_4Si_2$ $[M + H]^+$ 557.3482, found 557.3471.

4-Triisopropylsiloxy-2,7-diacetylnaphthalene (17). When the procedure in the previous paragraph was applied to **16** (17.9 g, 32.4 mmol), *n*-BuLi (2.5 M in hexanes, 61 mL, 152 mmol), and *N*-methoxy-*N*-methylacetamide (15 g, 146 mmol) in 200 mL of Et_2O, it afforded, after chromatography on silica gel (eluent 90:10 hexane/ethyl acetate), 6.5 g (52%) of white solid **17**: mp 94−95 °C; IR (KBr) 2946, 2868, 1683 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.53 (d, 1.6 Hz, 1H), 8.33 (d, 8.8 Hz, 1H), 8.17 (s, 1H), 8.12 (dd, 8.8 and 1.7 Hz, 1H) 7.54 (d, 1.4 Hz, 1H) 2.73 (s, 3H), 2.70 (s, 3H), 1.44 (m, 3H), 1.15 ppm (d, 7.5 Hz, 18H); ^{13}C NMR ($CDCl_3$, 75 MHz) 197.8, 197.4, 152.6, 135.9, 135.6, 133.4, 132.2, 131.3, 125.9, 124.6, 123.6, 111.6, 26.9, 26.7, 18.2, 13.1 ppm; UV−vis (CH_3CN, $c = 4.00 \times 10^{-5}$ M) λ_{max} (log ϵ) 264 nm (4.68). Anal. Calcd for $C_{23}H_{32}O_3Si_1$: C, 71.83; H, 8.39. Found: C, 71.85; H, 8.28.

4,5-Bis(triisopropylsiloxy)-2,7-bis-[1-(triisopropylsiloxy)ethenyl]naphthalene (12, R = TIPS). TIPSOTf (19.25 mL, 71.6 mmol) was added at 0 °C under N_2 to a stirred solution of **4** (19.0 g, 34.1 mmol) and Et_3N (38 mL) in CH_2Cl_2 (150 mL). The solution was stirred for 15 min at 0 °C and then for 2 h at 25 °C. Hexane (600 mL) was added. The solution was washed with 10% aqueous Na_2CO_3 (3 × 300 mL), dried over K_2CO_3, and filtered. Evaporation of the solvent and drying in a vacuum at 90 °C gave 29.7 g (100%) of **12**, a slightly orange oil: IR (CCl_4) 2946, 2868, 1562, 1464, 1384, 1285, 1017, 884 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.68 (d, 1.5 Hz, 2H), 7.04 (d, 1.5 Hz, 2H), 4.87 (d, 1.7 Hz, 2H), 4.47 (d, 1.7 Hz, 2H), 1.36−1.30 (m, 12H), 1.15 (d, 7.3 Hz, 36 H), 1.04 ppm (d, 7.5 Hz, 36H); ^{13}C NMR ($CDCl_3$, 75 MHz) 155.9, 152.7, 137.0, 135.1, 121.8, 118.8, 112.5, 90.6, 18.1, 18.0, 13.3, 12.9 ppm.

4-Triisopropylsiloxy-2,7-bis-(1-(triisopropylsiloxy)ethenyl)naphthalene (18). When the procedure in the previous paragraph was applied to 6.5 g (17 mmol) of **17**, 12 mL (85 mmol) of Et_3N, and 10 mL (37 mmol) of TIPSOTf in CH_2Cl_2, it afforded 12 g (101%) of **18**, a colorless oil, which was used directly in the next step. An analytical sample was obtained by quickly chromatographing a sample on a short column of neutral alumina (eluent: hexane): IR (CCl_4) 2946, 2868, 1609, 1464, 1286, 1016, 883 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.12 (d, 8.8 Hz, 1H), 8.10 (s, 1H),7.75 (s, 1H), 7.68 (dd, 8.8 and 1.7 Hz, 1H), 7.11 (d, 1.3 Hz, 1H), 5.00 (d, 1.7 Hz, 1H), 4.89 (d, 1.6 Hz, 1H), 4.51 (d, 1.7 Hz, 1H), 4.48 (d, 1.6 Hz, 1H), 1.43−1.30 (m, 9H), 1.16 ppm (d, 7.5 Hz, 54 H); ^{13}C NMR ($CDCl_3$, 75 MHz) 156.3, 156.0, 151.6, 135.8, 135.5, 134.4, 127.3, 124.8, 122.9, 122.3, 118.2, 109.9, 90.6, 90.7, 18.1, 13.1, 12.9, 12.5 ppm.

Tetrakis(triisopropylsiloxy)[6]helicenebisquinone 1, R = TIPS. A solution under N_2 of **12** (29.7 g, 34.1 mmol) and 1,4-benzoquinone (55.3 g, 512 mmol) in $PhCH_3$ (136 mL) was stirred at 90 °C for 6.5 d. After it had cooled to 25 °C and hexane (1 L) had been added, the mixture was filtered through a wad of Celite. The Celite was then washed with hexane (ca. 200 mL) until the filtrate was no longer red. The solvent was evaporated, and residual 1,4-benzoquinone was sublimed at 100 °C into a vacuum. The residue, dissolved in a minimal amount of CH_2Cl_2, was loaded onto a short column of silica gel (4 in d × 3 in h), and the red product was eluted with CH_2Cl_2. Chromatography on silica gel (4.5 in d × 8 in h) with 10:1 hexane/EtOAc yielded 14.7 g (40%) of a dark red solid: mp 123−125 °C; IR (CCl_4) 2948, 2870, 1664, 1597, 1580, 1494, 1346, 1248, 1226, 1083, 1003 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.65 (s, 2H), 7.43 (s, 2H), 6.68 (d, 10.2 Hz, 2H), 6.52 (d, 10.2 Hz, 2H), 1.53−1.43 (m, 12H), 1.23 (d, 7.5 Hz, 18H), 1.20 (d, 7.5 Hz, 18H), 1.11 (d, 7.5 Hz, 18H), 1.05 ppm (d, 7.5 Hz, 18H); ^{13}C NMR ($CDCl_3$, 75 MHz) 185.1, 184.8, 154.7, 154.3, 140.0, 135.7, 133.5, 131.8, 130.2, 128.0, 127.4, 124.5, 109.1, 108.7, 18.0, 17.7, 13.4, 13.2 ppm. Anal. Calcd for $C_{62}H_{92}O_8Si_4$: C, 69.10; H, 8.60. Found: C, 69.22; H, 8.84.

Tris(triisopropylsiloxy)[6]helicenebisquinone 19, R = TIPS. The same procedure was applied to **18** (11.9 g, 17 mmol) and 1,4-benzoquinone (27.5 g, 255 mmol) in 70 mL of $PhCH_3$. Workup and chromatography (eluent 9:1 hexane/ethyl acetate) gave crude product, which was purified by chromatography on neutral alumina (2 in d × 1.5 in h, eluent: CH_2Cl_2). The yield of red solid **19** was 5.9 g (38%): mp 119−125 °C; IR (KBr) 2946, 2868, 1664, 1506, 1226 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.43 (s, 2H), 7.73 (s, 1H), 7.52 (s, 1H), 7.48 (s, 1H), 6.75 (d, 10.1 Hz, 1H), 6.73 (d, 10.1 Hz, 1H), 6.63 (d, 10.1 Hz, 1H), 6.60 (d, 10.1 Hz, 1H) 1.58−1.50 (m, 9H), 1.23 ppm (m, 54H); ^{13}C NMR ($CDCl_3$, 75 MHz) 185.5, 185.2, 156.6, 155.4, 152.6, 140.6, 140.2, 135.8, 135.6, 133.5, 131.9, 131.6, 131.0, 130.0, 129.3, 128.8, 128.0, 127.8, 127.5, 123.2, 122.3, 109.2, 106.1, 18.3, 18.2, 13.5, 13.4, 13.2 ppm. Anal. Calcd for $C_{53}H_{72}O_7Si_3$: C, 70.31; H, 8.02. Found: C, 70.02; H, 7.92.

***(M)*-(−)- and *(P)*-(+)-20.** CH_2Cl_2 (200 mL) and Et_3N (20 mL) were added under N_2 to a mixture of **1** (R = OTIPS, 5.00 g, 4.63 mmol), Zn (15.2 g, 233 mmol), (1*S*)-camphanoyl chloride (10.0 g, 46 mmol), and DMAP (255 mg, 2.09 mmol), and the mixture was stirred vigorously for 24 h. Hexane (800 mL) was added, and the mixture was filtered through a wad of Celite. The filtrate was washed with saturated aqueous $NaHCO_3$ (3 × 200 mL), dried over Na_2SO_4, and filtered. After the solvent had been evaporated, the residual solid was dissolved in a minimal amount of 1:3 CH_2Cl_2/hexane and loaded onto a column of silica gel that had been soaked with 3:1 hexane/EtOAc. Impurities were eluted with 3:1 hexane/EtOAc, crude (*M*)-(−)-**20** with 2:1 hexane/EtOAc, and pure (*P*)-(+)-**20** with 3:2 hexane/EtOAc. (*M*)-(−)-**20** was rechromatographed with 5:1 $PhCH_3$/EtOAc. The yield of (*P*)-(+)-**20** was 3.28 g (79%), and the yield of (*M*)-(−)-**20** was 3.15 g (75%).

(*M*)-(−)-**20**: mp >240 °C; $[\alpha]_D$ −281 ($c = 0.033$, CH_3CN); IR (CCl_4) 2946, 2868, 1797, 1754, 1588, 1464, 1375, 1312, 1262, 1166, 1095, 1047 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.80 (s, 2H), 7.39 (s, 2H), 6.95 (d, 8.5 Hz, 2H), 6.44 (d, 8.5 Hz, 2H), 2.76 (m, 2H), 2.39 (m, 2H), 2.07 (m, 2H), 1.84 (m, 2H), 1.59−1.05 (m, 92H), 0.89 (s, 6H), 0.84 (d, 7.5 Hz, 18H), 0.52 (s, 6H), 0.34 ppm (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) 178.0, 177.7, 165.9, 163.9, 152.0, 149.9, 143.5, 142.5, 129.6, 127.7, 125.9, 121.4, 121.2, 121.1, 117.3, 114.4, 109.9, 105.2, 91.1, 89.6, 55.0, 54.5, 53.9, 30.9, 29.1, 28.9, 28.6, 18.2, 18.0, 17.7, 17.0, 16.9, 16.1, 13.4, 13.3, 9.8, 9.5 ppm; UV−vis (CH_3CN, $c = 3.31 \times 10^{-5}$ M) λ_{max} (log ϵ) 208 (4.71), 268 (sh, 4.73), 279 (4.76), 302 (sh, 4.42), 341 (4.39), 358 nm (sh, 4.31); CD ($c = 3.31 \times 10^{-5}$ M, CH_3CN), nm ($\Delta\epsilon$) 216 (−93), 267 (146), 302 (−39), 328 (10), 341 (sh, −8), 360 (−78). Anal. Calcd for $C_{102}H_{144}O_{20}Si_4$: C, 67.96; H, 8.05. Found: C, 67.88; H, 8.08.

(*P*)-(+)-**20**: mp >240 °C; $[\alpha]_D$ +188 ($c = 0.036$, CH_3CN); IR (CCl_4) 2947, 2869, 1801, 1777, 1760, 1585, 1464, 1375, 1258, 1204, 1167, 1094, 1042 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.73 (s, 2H), 7.17 (s, 2H), 6.83 (d, 8.3 Hz, 2H), 6.24 (d, 8.3 Hz, 2H), 2.70 (m, 2H), 2.31 (m, 2H), 2.10 (m, 2H), 1.89 (m, 2H), 1.70 (m, 2H), 1.53−0.79 (m, 120H), 0.56 ppm (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) 177.6, 177.4, 166.1, 164.5, 153.1, 150.8, 143.6, 142.6, 130.6, 128.0, 125.0, 123.0, 122.4, 120.6, 118.1, 116.2, 110.1, 104.6, 90.8, 90.3, 54.8, 54.3, 54.2, 31.0, 29.0, 27.8, 18.1, 17.9, 17.8, 17.6, 17.1, 16.9 (2 peaks), 16.6, 13.5, 13.2, 9.7, 9.6 ppm; UV−vis (CH_3CN, $c = 4.05 \times 10^{-5}$ M) λ_{max} (log ϵ) 206 (4.66), 269 (sh, 4.73), 278 (4.74), 301 (sh, 4.43), 314 (sh, 4.37), 363 nm (sh, 4.15); CD ($c = 4.05 \times 10^{-5}$ M, CH_3CN), nm ($\Delta\epsilon$) 207 (sh, 90), 217 (141), 269 (−147), 302 (30), 327 (−9), 362 (58); HRMS (FAB) *m/z* calcd for $C_{102}H_{144}O_{20}Si_4$ 1801.9357, found 1801.9325.

X-ray Diffraction Analysis of *(M)*-(−)- 20.[28] Crystals of (*M*)-(−)-**20** for X-ray diffraction analysis were obtained by allowing the solvent to evaporate from an ethanol solution. *Crystal data*: triclinic, *P*1, $a = 14.3608(5)$ Å, $b = 18.0032(5)$ Å, $c = 21.0751(7)$ Å, $\alpha = 95.441(2)°$, $\beta = 94.484(2)°$, $\gamma =$

(28) The data will be submitted to the Cambridge Crystallographic Data Base (CCDC).

107.384(2)°, V = 5143.8(3) Å^3, Z = 2, T = 173 K. Of 34 359 reflections collected, 25 383 were independent. The unit cell contains two crystallographically different, but chemically similar molecules. The Flack parameter, which refined to a value of 0.02(14), is in accord with the absolute configuration displayed. $R(F)$ = 9.19%, w$R(F^2)$ = 22.62%.

(*M*)-(−)- and (*P*)-(+)-21. CH_2Cl_2 (120 mL) and Et_3N (12.5 mL) were added under N_2 to a mixture of **19** (R = TIPS, 2.7 g, 3 mmol), Zn (9.8 g, 150 mmol), (1*S*)-camphanoyl chloride (6.3 g, 29 mmol), and DMAP (146 mg, 1.20 mmol). The mixture was stirred and refluxed for 2 h and then worked up as in the experiment above. The yield of the higher R_f isomer, (*P*)-(+)-**21**, was 1.60 g (67%). The yield of the lower R_f isomer, (*M*)-(−)-**21**, after it had been obtained pure by rechromatography (eluting with 10:1 toluene/EtOAc), was 1.77 g (74%).

(*M*)-(−)-**21**: mp >200 °C; $[\alpha]_D$ −390 (c = 0.011, CH_3CN); IR (KBr) 2947, 2869, 1799, 1752, 1261, 1093, 1044 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.54 (d, 8.7 Hz, 1H), 8.46 (d, 8.7 Hz, 1H), 7.80 (s, 1H), 7.42 (s, H), 7.40 (s, 1H), 7.00 (d, 8.4 Hz, 1H), 6.95 (d, 8.4 Hz, 1H). 6.45 (d, 8.4 Hz, 1H), 6.42 (d, 8.4 Hz, 1H) 2.75 (m, 2H), 2.39 (m, 2H), 2.06 (m, 2H), 1.85 (m, 2H), 1.59−1.03 (m, 89H), 0.88 (s, 6H), 0.49 (s, 3H), 0.48 (s, 3H) 0.24 (s, 3H), 0.18 ppm (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) 178.2, 177.7, 166.2, 164.5, 151.3, 150.8, 142.8, 142.7, 127.4, 121.5, 120.9, 118.5, 117.5, 155.0, 106.1, 105.6, 105.5, 91.3, 89.9, 55.1, 54.6, 54.4, 54.2, 31.1, 29.2, 29.0, 28.8, 18.3, 18.2, 17.2, 17.1, 16.3, 16.0, 15.9, 13.6, 13.2, 10.0, 9.7 ppm; UV−vis (CH_3CN, c = 6.74 × 10^{-5} M) λ_{max} (log ϵ) 206 (4.51), 275 (4.57), 339 nm (4.38); CD (c = 6.74 × 10^{-5} M, CH_3CN), nm ($\Delta\epsilon$) 210 (−67), 230 (−41), 250 (117), 260 (sh, 108), 281 (−13), 302 (−49), 322 (10), 355 (−70); HRMS (FAB) m/z calcd for $C_{93}H_{124}NaO_{19}Si_3$ [M + Na]$^+$ 1651.7942, found 1651.8013.

(*P*)-(+)-**21**: mp >220 °C; $[\alpha]_D$ +400 (c = 0.0099, CH_3CN); IR (KBr) 2947, 2869, 1799, 1041 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.55 (d, 8.7 Hz, 1H), 8.40 (d, 8.7 Hz, 1H), 7.74 (s, 1H), 7.21 (s, 1H), 7.18 (s, 1H), 6.89 (d, 8.3 Hz, 1H), 6.84 (d, 8.3 Hz, 1H), 6.27 (2d, 8.3 Hz, 2H), 2.71 (m, 2H), 2.32 (m, 2H), 2.10 (m, 2H), 1.89 (m, 2H), 1.70 (m, 2H), 1.60−1.38 (m, 15H), 1.27−1.17 (m, 72H), 0.95 (s, 3H), 0.94 (s, 3H), 0.81 (s, 3H), 0.78 (s, 3H), 0.55 (s, 3H), 0.49 ppm (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) 177.7, 177.3, 177.2, 166.2, 164.9, 164.8, 152.1, 151.5, 144.7, 144.1, 142.8, 142.7, 129.8, 129.4, 127.4, 126.7, 126.4, 125.5, 125.4, 122.6, 122.5, 121.2, 120.4, 119.1, 118.0, 116.2, 116.0, 105.9, 104.3, 91.0, 90.6 (2 peaks), 55.0, 54.6, 54.4, 31.2, 29.2, 18.4, 18.2, 17.2, 17.1, 17.0, 16.9, 16.7, 16.6, 13.7, 13.5, 13.3, 9.9, 9.7 ppm; UV−vis (CH_3CN, c = 6.07 × 10^{-5} M) λ_{max} (log ϵ) 206 (4.55), 272 (4.61), 339 nm (4.33); CD (c = 6.07 × 10^{-5} M, CH_3CN), nm ($\Delta\epsilon$) 210 (91), 230 (70), 252 (sh, −121), 262 (−125), 280 (8), 306 (43), 315 (−14), 357 (63); HRMS (FAB) m/z calcd for $C_{93}H_{124}O_{19}Si_3$ 1628.8045, found 1628.8115.

Nonracemic 1 (R = TIPS). MeLi (1.4 M in Et_2O, 35.5 mL, 50 mmol) was added under N_2 at −78 °C to a stirred solution of (*M*)-(−)-**20** (3.00 g, 1.67 mmol) in Et_2O (90 mL). The mixture was stirred at −78 °C for 15 min and then at 25 °C for 1 h, and it was then carefully quenched with saturated aqueous NH_4Cl (50 mL). The mixture was poured into H_2O (300 mL) and extracted with EtOAc (100 mL). The organic layer was dried over Na_2SO_4 and filtered. Chloranil (2.00 g, 8.1 mmol) was added. The mixture was stirred for 5 min and filtered. The solvent was evaporated, and the residue was mixed with hexane (50 mL) and filtered. The solvent was evaporated, and the residue was chromatographed, eluting with 80:1 $PhCH_3$/EtOAc. The yield of (*M*)-(−)-**1** (R = TIPS) was 1.58 g (88%): mp 115−117 °C; $[\alpha]_D$ −1321 (c = 0.0094, CH_3CN); CD (c = 2.42 × 10^{-5} M, CH_3CN), nm ($\Delta\epsilon$) 220 (−49), 232 (23), 258 (−144), 314 (146), 386 (−103). ^{1}H and ^{13}C NMR spectra were identical to those of the racemic compound.

Similarly, 3.00 g of (*P*)−(+)-**20** gave 1.56 g (87%) of (*P*)-(+)-**1** (R = TIPS): $[\alpha]_D$ +1334 (c = 0.0086, CH_3CN); UV−vis (CH_3CN, c = 1.84 × 10^{-5} M) λ_{max} (log ϵ) 245 (4.77), 316 (4.55), 487 nm (3.76); CD (c = 1.84 × 10^{-5} M, CH_3CN), nm ($\Delta\epsilon$) 220 (54), 231 (−21), 257 (155), 315 (−154), 387 (108).

Nonracemic 19 (R = TIPS). The same procedure, using 320 mg (0.196 mmol) of (*M*)-(−)-**21**, 4 mL (6.3 mmol) of 1.6 M MeLi in Et_2O, and 15 mL of THF, gave 130 mg (73%) of (*M*)-(−)-**19** (R = TIPS): mp 126−130 °C; $[\alpha]_D$ −1591 (c = 0.0093, CH_3CN); UV−vis (CH_3CN, c = 1.026 × 10^{-4} M) λ_{max} (log ϵ) 252 (4.38), 308 (4.37), 449 nm (3.62); CD (c = 1.026 × 10^{-4} M, CH_3CN), nm ($\Delta\epsilon$) 215 (−24), 228 (13), 237 (−5), 245 (−8), 259 (−20), 305 (51), 363 (−53), 440 (−15). Its IR and ^{1}H and ^{13}C NMR spectra were identical to those of the racemic compound.

Similarly, 84 mg (61%) of (*P*)−(+)-**19** (R = TIPS) was obtained from 250 mg (0.153 mmol) of (*P*)-(+)-**21**, 2.8 mL (4.5 mmol) of 1.6 M MeLi in Et_2O, and 12 mL of THF: $[\alpha]_D$ +1607 (c = 0.7586, CH_3CN); CD (c = 8.30 × 10^{-5} M, CH_3CN), nm ($\Delta\epsilon$) 215 (24), 229 (−15), 238 (5), 245 (sh, 12), 259 (24), 305 (−53), 364 (55), 440 (15).

(±)-1 (R = Dodecyl). 1-Iodododecane (1.95 mL, 7.90 mmol) and DMF (2 mL) were added under N_2 to a mixture of (±)-**1** (R = TIPS, 170 mg, 0.158 mmol) and CsF (192 mg, 1.26 mmol). The mixture was stirred at 60 °C for 24 h and poured into H_2O (50 mL). Brine (15 mL) was added, and the mixture was extracted with $PhCH_3$ (25 mL). The extract was dried over Na_2SO_4 and poured onto silica gel (1 in d × 1 in h). Residual 1-iodododecane was eluted with $PhCH_3$ (ca. 30 mL) and the crude product with 3:1 EtOAc/CH_2Cl_2. The solvent was evaporated, and the residue was rechromatographed, eluting with 50:1 $PhCH_3$/EtOAc. The yield of pure (±)-**1** (R = dodecyl), whose ^{1}H and ^{13}C NMR spectra were identical to those published,[1a] was 121 mg (68%).

(*M*)-(−)-1 (R = Dodecyl). 1-Iodododecane (500 μL, 2.27 mmol) and DMF (3 mL) were added under N_2 to a mixture of (−)-**1** (R = TIPS, 100 mg, 0.09 mmol) and CsF (previously ground finely by shaking with a glass bead in a Wig-L-Bug, 140 mg, 0.9 mmol). The mixture was stirred at 80 °C for 25 h. The reaction mixture was diluted with EtOAc (20 mL) and washed twice with H_2O. The extract was dried over Na_2SO_4 and chromatographed on silica gel. Residual 1-iodododecane eluted with hexane and the crude product with 90:10 hexane/EtOAc. The solvent was evaporated and the residue was chromatographed on basic alumina with 98:2 $PhCH_3$/THF. After the solvent had been evaporated, the product was dissolved in less than 1 mL of CH_2Cl_2, precipitated with ca. 40 mL of MeOH, filtered with Celite, and washed from the filter with CH_2Cl_2. The yield of pure product was 60 mg (58%). Its ^{1}H and ^{13}C NMR spectra were identical to those published,[1a] and its CD spectrum in CH_2Cl_2 (see the Supporting Information) was the mirror image of that of a sample of (+)-**1** (R = dodecyl) prepared by Nuckolls et al.[1a]

(*P*)-(+)-19 (R = Dodecyl). 1-Iodododecane (250 μL, 1 mmol) and DMF (0.75 mL) were added under N_2 to a mixture of (*P*)-(+)-**19** (R = TIPS, 30 mg, 33 μmol) and CsF (40 mg, 0.265 mmol). The mixture was stirred at 50 °C for 2 h, poured into H_2O (10 mL), and extracted with a mixture of EtOAc (15 mL) and a small amount of CH_2Cl_2. The extract was dried over Na_2SO_4 and filtered. The solvent was evaporated, and the residue was chromatographed. Residual 1-iodododecane was eluted with hexane, colored impurities with 95:5 hexane/EtOAc, and the red product with 90:10 hexane/EtOAc. After it had been dried in a vacuum, the red solid product weighed 19 mg (a 61% yield): mp 218−219 °C; $[\alpha]_D$ +1435 (c = 0.0027, dodecane); IR (KBr) 2923, 2852, 1658, 1223 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.44 (s, 2H), 7.62 (s, 1H), 7.48 (s, 1H), 7.46 (s, 1H), 6.75 (m, 2H), 6.60 (2d, 10.1 Hz, 2H), 4.33 (m, 6H), 2.01 (m, 6H), 1.61 (m, 6H), 1.46−1.28 (m, 48H), 0.88 ppm (m, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz) 185.7, 185.4, 185.3, 158.8, 157.7, 155.3, 140.4, 140.0, 135.9, 135.7, 133.8, 131.8, 131.1, 129.1, 128.2, 128.0, 127.7, 127.3, 126.8, 122.7, 121.8, 102.4, 102.0, 98.7, 69.5 (2 peaks), 68.9, 32.1, 29.8, 29.6, 29.5, 29.2, 26.5, 26.4, 22.9, 14.3 ppm; UV−vis (dodecane, c = 2.1 × 10^{-5} M) λ_{max} (log ϵ) 240 (4.71), 306 (4.52), 375 (sh, 3.77), 452 nm (3.71); CD (c = 2.1 × 10^{-5} M, dodecane), nm ($\Delta\epsilon$) 216 (24), 228 (−33), 25 (26), 266 (24), 302 (−59), 359 (62), 433 (19), 449 (18); HRMS (FAB) m/z calcd for $C_{62}H_{85}O_7$ [M + H]$^+$ 940.6217, found 940.6233.

(*P*)-(+)-1 [R = CO(CH$_2$)$_4$CH$_3$]. Hexanoyl chloride (0.56 mL, 4.0 mmol) and DMF (3 mL) were added under N_2 to a mixture of (*P*)-**1** (R = TIPS, 108 mg, 0.10 mmol), CsF (123 mg, 0.80 mmol), and DMAP (49 mg, 0.40 mmol). The mixture was stirred for 48 h, poured into 1 M HCl (50 mL), and extracted with EtOAc (30 mL). The organic layer was washed with

saturated aqueous $NaHCO_3$ (4 × 40 mL) and 1 M HCl (40 mL), dried over Na_2SO_4, and filtered. The solvent was evaporated, and the residue was chromatographed, eluting with 10:1 $PhCH_3$/EtOAc. The yield of orange waxy solid (*P*)-(+)-**1**, R = $CO(CH_2)_4CH_3$, was 58 mg (68%): mp 77−79 °C; $[\alpha]_D$ +1275 (*c* = 0.017, CH_3CN); IR (CCl_4) 2959, 2931, 1776, 1669, 1612, 1504, 1349, 1288, 1196, 1135, 1090 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.06 (s, 2H), 7.76 (s, 2H), 6.85 (d, 10.2 Hz, 2H), 6.70 (d, 10.2 Hz, 2H), 2.73 (m, 8H), 1.86 (m, 8H), 1.45 (m, 16H), 0.96 ppm (m, 12H); ^{13}C NMR ($CDCl_3$, 75 MHz) 184.7, 183.6, 171.7, 170.8, 149.4, 146.3, 139.6, 136.3, 132.7, 131.0, 129.5, 128.8, 122.8, 116.4, 115.0, 34.3 (2 peaks), 31.3, 31.2, 24.5 (2 peaks), 22.3 (2 peaks), 13.9 ppm (2 peaks); UV−vis (CH_3CN, $c = 1.50 \times 10^{-5}$ M) λ_{max} (log ϵ) 234 (4.76), 262 (sh, 4.55), 293 (4.59), 354 nm (sh, 4.04); CD ($c = 1.50 \times 10^{-5}$ M, CH_3CN), nm ($\Delta\epsilon$) 234 (sh, 62), 217 (167), 261 (85), 292 (−264), 353 (250), 421 (46). Anal. Calcd for $C_{50}H_{52}O_{12}$: C, 71.07; H, 6.20. Found: C, 70.93; H, 6.21.

(*M*)-(−)-19 [R = $CO(CH_2)_4CH_3$]. Hexanoyl chloride (100 μL, 0.72 mmol) and DMF (0.5 mL) were added under N_2 to a mixture of (*M*)-**19** (R = TIPS, 20 mg, 0.022 mmol), CsF (28 mg, 0.18 mmol), and DMAP (8 mg, 0.7 mmol). The mixture was stirred and heated at 50 °C for 2 h. Aqueous HCl (1 M, 10 mL) was added, and the mixture was extracted twice with EtOAc (10 mL). The combined extracts were washed with H_2O, dried over Na_2SO_4, and filtered. After the solvent had been evaporated, the residue was chromatographed, eluting with 20:1 toluene/EtOAc. Drying in a vacuum gave 11.3 mg (71%) of orange solid (*M*)−(−)-**19**, R = $CO(CH_2)_4CH_3$: mp 81−82 °C; $[\alpha]_D$ −1450 (*c* = 0.0057, CH_3CN); IR (KBr) 2930, 1769, 1665, 1090 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.14 (2s, 2H), 8.06 (s, 1H), 8.05 (s, 1H), 8.01 (s, 1H), 6.86 (2d, 10.1 Hz, 2H), 6.69 (2d, 10.1 Hz, 2H), 2.81 (m, 6H), 21.91 (m, 6H), 1.48 (m, 12H), 0.99 ppm (m, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz) 185.3, 184.0, 171.5, 171.4, 171.2, 150.4, 150.1, 147.4, 140.0, 139.9, 136.4 (2 peaks), 131.4 (3 peaks), 129.4, 129.2, 128.2, 127.8, 123.0, 122.3, 116.3, 113.0, 34.7, 34.6, 31.5, 24.8, 22.5, 14.1 ppm; UV−vis (CH_3CN, $c = 7.8 \times 10^{-5}$ M) λ_{max} (log ϵ) 246 (4.49), 292 (4.48), 351 (4.03), 408 (3.67); CD ($c = 7.8 \times 10^{-5}$ M, CH_3CN), nm ($\Delta\epsilon$) 216 (−44), 245 (1), 259 (−23), 291 (84), 352 (−85), 437 (−7). Anal. Calcd for $C_{50}H_{52}O_{12}$: C, 72.31; H, 5.79. Found: C, 71.97; H, 5.82.

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Supporting Information Available: ^1H, ^{13}C NMR, IR, and UV spectra of **1** (R = TIPS), (*P*)-(+)-**1** (R = $CO(CH_2)_4CH_3$), **4** (R = TIPS), **8c**, **9c**, **10**, **11**, **12** (R = TIPS), **13**, **14**, **15**, **16**, **17** (R = TIPS), **18**, **19** (R = TIPS), (*P*)-(+)-**19** (R = dodecyl), (*M*)-(−)-**19** [R = $CO(CH_2)_4CH_3$], (*P*)-(+)-**20**, (*M*)-(−)-**20**, (*P*)-(+)-**21**, (*M*)-(−)-**21**, and 4-hydroxy-2,7-diiodonaphthalene. ^1H, ^{13}C NMR, and IR spectra of 4,5-dihydroxy-2,7-diiodonaphthalene. CD spectra of (*P*)-(+)-**1** and (*M*)-(−)-**1** (R = TIPS), **1** (R = dodecyl) in CH_2Cl_2 [the (*M*)-(−)-enantiomer synthesized here and the (*P*)-(+)-enantiomer synthesized according to ref 1b], (*P*)-(+)-**1** [R = $CO(CH_2)_4CH_3$], (*P*)-(+)-**19** and (*M*)-(−)-**19** (R = TIPS), (*P*)-(+)-**19** (R = dodecyl), (*M*)-(−)-**19** [R = $CO(CH_2)_4CH_3$], (*P*)-(+)-**20**, (*M*)-(−)-**20**, (*P*)-(+)-**21**, and (*M*)-(−)-**21**. X-ray diffraction data for (*M*)-(−)-**20**. This material is available free of charge via the Internet at http://pubs.acs.org.

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