Easy Synthesis of Functionalized Hetero[7]helicenes

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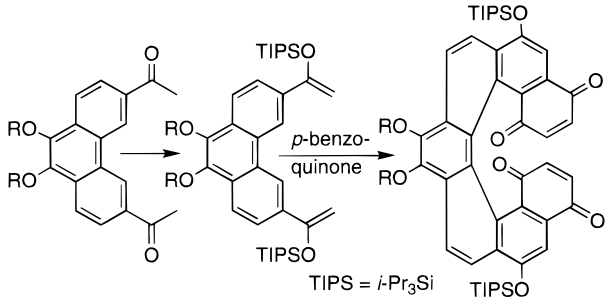
Hetero[7]helicenebisquinones can be synthesized easily on a multigram scale by combining the silyl enol ethers of 3,6-diacetyldibenzofuran, 3,6-diacetyldibenzothiophene, and 3,6-diacetylcarbazole with *p*-benzoquinone. They can be resolved into their enantiomers by a procedure that had previously been used to resolve carbohelicenebisquinones. Their absolute configurations are assigned.

Introduction

By applying steps such as those illustrated in Scheme 1 to a variety of diacetylaromatic hydrocarbons, it had been possible to synthesize [5]-,[1] [6]-,[1] and [7]-carbohelicenes[2] in much larger amounts than before and with useful functional groups. Because Friedel−Crafts acetylation, followed in the case of the nitrogen compounds by *N*-alkylation, transforms dibenzofuran, dibenzothiophene, and carbazole into their 3,6-diacetyl derivatives **2a**−**d**,[3] the possibility was considered that procedures similar to Scheme 1 would convert these heterocyclic diacetyl compounds into hetero[7]helicenes (Scheme 2). Because it is easier to prepare these diacetyls than those used for the previous syntheses based on Scheme 1,[1,2] these steps would lead easily to functionalized helicenes. They would also be significant because only three helicenes (and an OH-derivative of one of them[4]) were known in which some of the benzene rings are replaced by furans,[5] and only two (and some methyl derivatives) were known in which they are replaced by pyrroles.[6] Of these oxa- and azahelicenes, only one, an azahelicene, had been obtained optically active (but in only a minuscule amount).[6d] A number of helicenes are known in which some of the benzene rings are replaced by thiophenes, but their syntheses require more steps.[7] Moreover, helicenes synthesized according to Scheme 2 should benefit from the quinone functions, which in the case of carbocyclic analogues were useful for resolving the enantiomers,[1,2,8] for transforming the molecules into nonracemic fully conjugated polymers,[9] and for promoting the molecules' self-association into columnar aggregates and liquid crystals[8,10] that exhibit exceptional rotatory[8,10] and nonlinear optical properties.[11]

Scheme 1



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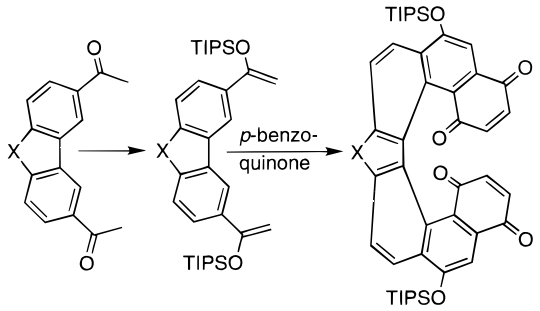
Scheme 2



2 **3** **a** X = O, **b** X = S, **c** X = NMe, **d** X = N*n*-$C_{12}H_{25}$ **4**

We show below that the heterocyclic helicenes **4a**−**d** can be prepared easily in gram quantities, that they can

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(2) Fox, J. M.; Goldberg, N. R.; Katz, T. J. *J. Org. Chem.* **1998**, *63*, 7456.

(3) For 3,6-diacetyldibenzofuran, see: (a) Bruce, M. J.; McLean, G. A.; Royles, B. L. J.; Smith, D. M.; Standring, P. N. *J. Chem. Soc., Perkin Trans. 1* **1995**, 1789 and a reference cited therein. For 3,6-diacetylcarbazole, see: (b) Buu-Hoï, N. P.; Royer, R. *Recl. Trav. Chim. Pays-Bas* **1947**, *66*, 533. (c) Plant, S. G. P.; Rogers, K. M.; Williams, S. B. C. *J. Chem. Soc.* **1935**, 741. For 3,6-diacetyldibenzothiophene, see: (a) above and (d) Albrecht, W. L.; Gustafson, D. H.; Horgan, S. W. *J. Org. Chem.* **1972**, *37*, 3355. (e) Gilman, H.; Nobis, J. F. *J. Am. Chem. Soc.* **1949**, *71*, 274. (f) Burger, A.; Wartman, W. B., Jr.; Lutz, R. E. *J. Am. Chem. Soc.* **1938**, *60*, 2628.

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(5) (a) Chatterjea, J. N.; Banerji, K. D. *J. Indian Chem. Soc.* **1970**, *47*, 576. (b) Högberg, H.-E. *Acta Chem. Scand.* **1973**, *27*, 2591. (c) Groen, M. B.; Schadenberg, H.; Wynberg, H. *J. Org. Chem.* **1971**, *36*, 2797.

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(7) (a) Lehman, P. G.; Wynberg, H. *Aust. J. Chem.* **1974**, *27*, 315 and references therein. (b) Tanaka, K.; Osuga, H.; Suzuki, H.; Shogase, Y.; Kitahara, Y. *J. Chem. Soc., Perkin Trans. 1* **1998**, 935 and references therein. (c) Osuga, H.; Suzuki, H.; Tanaka, K. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 891 and references therein. (d) Tanaka, K.; Kume, T.; Takimoto, T.; Kitahara, Y.; Suzuki, H.; Osuga, H.; Kawai, Y. *Chem. Lett.* ***1997***, 501. (e) Tanaka, K.; Suzuki, H.; Osuga, H. *J. Org. Chem.* **1997**, *62*, 4465 and references therein. (f) Tanaka, K.; Osuga, H.; Koyama, K.; Suzuki, H.; Imai, K.; Yoshida, Y. *Enantiomer* **1997**, *2*, 193. (g) Tanaka, K.; Osuga, H.; Shogase, Y.; Suzuki, H. *Tetrahedron Lett.* **1995**, *36*, 915. (h) Larsen, J.; Bechgaard, K. *Acta Chem. Scand.* **1996**, *50*, 71. (i) Dore, A.; Fabbri, D.; Gladiali, S.; Valle, G. *Tetrahedron: Asymmetry* **1995**, *6*, 779. (j) Larsen, J.; Bechgaard, K. *Acta Chem. Scand.* **1996**, *50*, 77. (k) Larsen, J.; Bechgaard, K. *J. Org. Chem.* **1996**, *61*, 1151.

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

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Table 1. Yields of 4 and 5 When 3 Was Combined with *p*-Benzoquinone in Toluene

enol ether **3**	reaction temp (°C)	reaction time (h)	yield of **4** (%)	yield of **5** (%)
a	100	48	40	22
b	105	24	33	19
c	90	11	53	23
d	85	14	50	*a*

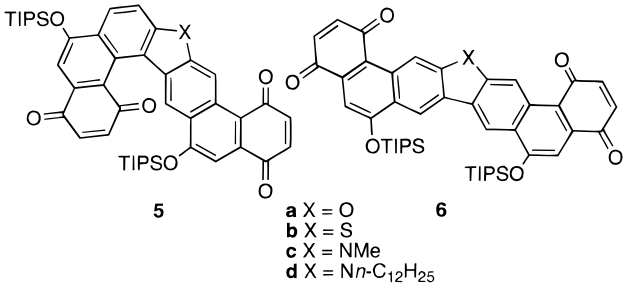
[a] Not isolated.

be resolved into their enantiomers by procedures identical to those used previously to resolve carbohelicenes, and that the enantiomers do not racemize at an appreciable rate at room temperature.

Results and Discussion

The four diacetylheteroaromatics in Scheme 2 (**2a**−**d**), with triisopropylsilyl triflate (TIPSOTf) and triethylamine in methylene chloride, gave the bis(triisopropylsilylenol ethers) **3a**−**d** in 91−99% yields, and these combined with *p*-benzoquinone in toluene as summarized in Table 1. Helicenes **4a**−**d** were obtained in acceptable yields. More significantly, because the starting enol ethers are so easy to prepare from inexpensive dibenzofuran, dibenzothiophene, and carbazole, the amounts that could be made (in our preparations, between 3.1 and 16.0 g) are large when compared to the amounts of heterohelicenes preparable by other procedures. In the reactions with *p*-benzoquinone, the helicenes **4a**−**d** form very much faster than the carbohelicenes previously prepared in similar ways, which means (for the best case) that the transformation of carbazole into *enantiomerically pure* helicene **9d** (see below) takes less than 3 days to complete.

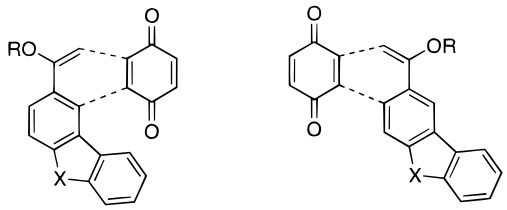
Helicenes **4a**−**d** are accompanied by significant amounts of the isomeric products with structures **5a**−**d** (see Table 1). Structures **5a**−**d** were assigned on the basis of the



5 **a** X = O **6**
b X = S
c X = NMe
d X = N*n*-$C_{12}H_{25}$

^{1}H NMR spectra, each of which displays aromatic proton resonances comprised of six doublets and four singlets. Moreover, in each case, one of the singlets is at δ ca. 10 ppm, indicative of the lone proton in the bay region of the ring system.[12] None of the third possible isomeric

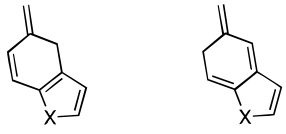
Scheme 3



α β

structures, **6a**−**d**, which would be expected to have two doublet and three singlet aromatic resonances, were detected. Helicenes **4a**−**d** are all easily separable from their isomers, **5a**−**d**, and in the case of **4d**, the separation could be accomplished simply by triturating the mixture with pentanes. The isomer is soluble; the helicene is not! Accordingly, this helicene is easily and cheaply preparable on a large scale. To separate the other helicenes (**4a**−**c**) from their isomers required silica gel chromatography, which, although not difficult, is more expensive.

Side-products analogous to **5** are not observed in Scheme 1, the corresponding preparation of the carbocyclic product **1**. The regioselectivity of this reaction is presumed to reflect the greater reactivity of α-positions compared to β-positions in naphthalenes, which, as indicated in Scheme 3 (here X = CH=CH), can be attributed to the loss of the second ring's aromatic structure when additions are to β- rather than to α-positions. Accordingly, we speculate that the lower regioselectivity in Scheme 2 is a consequence of an energy difference between the two modes of reaction in Scheme 3 that is smaller when X = O, N, and S than when X = CH=CH.[13] Because there are no analogous Diels−Alder reactions of appropriate vinylbenzofurans, -thiophenes, or -pyrroles as precedents, we used the Spartan AM1 computer program[14] to model simplified transition-state structures **7** and **8**. We then compared the energies of



7 **a** X = O **8**
b X = S
c X = NH
d X = CH=CH

the two structures in the heterocyclic and carbocyclic systems. In accord with the hypothesis, the calculated differences between **7a** and **8a** (4.6 kcal/mol), **7b** and **8b** (8.6 kcal/mol), and **7c** and **8c** (8.6 kcal/mol) are significantly lower than between **7d** and **8d** (17.4 kcal/mol). Analogy between these Diels−Alder reactions and stilbene photocyclizations also provides support: electronic effects similar to those considered for the two modes of reaction in Scheme 3 have been invoked to explain the regioselectivities of the photoprocesses.[15] Moreover, in the absence of significant steric hindrance, the regioselec-

(10) (a) Nuckolls, C.; Katz, T. J. *J. Am. Chem. Soc.* **1998**, *120*, 9541. (b) Nuckolls, C.; Katz, T. J.; Verbiest, T.; Van Elshocht, S.; Kuball, H.-G.; Kiesewalter, S.; Lovinger, A. J.; Persoons, A. *J. Am. Chem. Soc.* **1998**, *120*, 8656.

(11) (a) 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. (b) 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.

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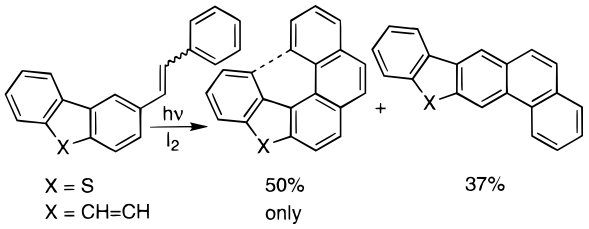
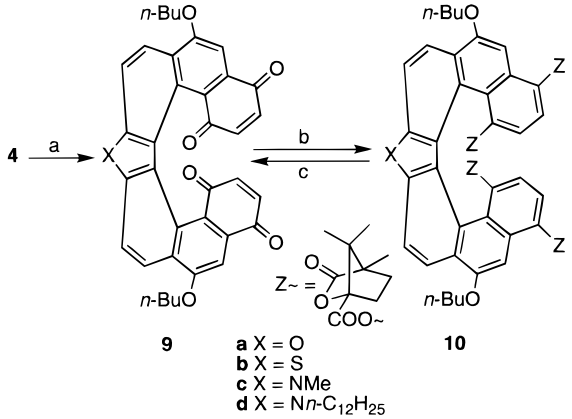
(13) The aromatic stabilization of benzene is greater than that of furan, thiophene, and pyrrole (Bird, C. W.; Cheeseman, G. W. H. In *Comprehensive Heterocylic Chemistry*; Katritzky, A. R., Rees, C. W., Eds.; Pergamon: Oxford, 1984; Vol. 4, pp 28−32). Accordingly, derivatives of the latter three should lose less upon reaction by pathway β.

(14) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.

Scheme 4



Scheme 5



[a] Reagents and conditions: (a) CsF, *n*-BuI, DMF, 60 °C (86−99% yields); (b) (*S*)-(−)-camphanoyl chloride, Zn, $(Me_2NCH_2)_2$, PhMe, reflux (75−92% yields); (c) MeLi or BuLi, then chloranil (63−88% yields).

tivity of photocyclization, like that of the Diels−Alder reactions considered above, seems to be lower when X = S than when X = CH=CH, at least for the example illustrated in Scheme 4.[16,17]

Presumably steric effects can divert the bonds from forming at the electronically favored α-position. Thus, that Scheme 2 gives **4** and **5** but not **6** suggests that the electronic effects that direct the cycloadditions to α in Scheme 3 cause the first of the Diels−Alders to convert the ring system into a derivative of [5]helicene, but when X = O, N, and S, these effects are partially overcome in the second Diels−Alder reaction by steric repulsions. However, when X = CH=CH, the electronic effect is more powerful; it is not overcome by similar or greater steric hindrance. Accordingly, Scheme 1 gives **1** uncontaminated by significant amounts of the analogue of **5**.

Resolution of the Enantiomers of the Heterohelicenebisquinones. As shown in Scheme 5, cesium fluoride removed the triisopropylsilyl groups, and alkyl iodide replaced them with alkyls. Reduction by zinc and esterification with (*S*)-(−)-camphanoyl chloride gave camphanate esters **10a**−**d**, each of which was separated into its diastereomers by silica gel chromatography. In each case, the diastereomeric excess was greater than 97%.

The absolute configurations of the camphanate esters are implied by their CD spectra. Figure 1 shows these

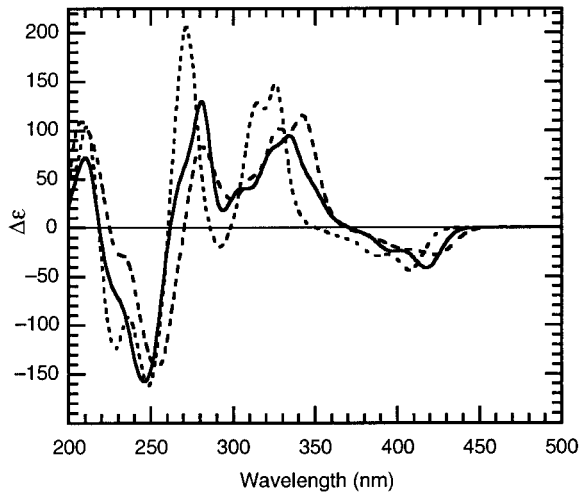
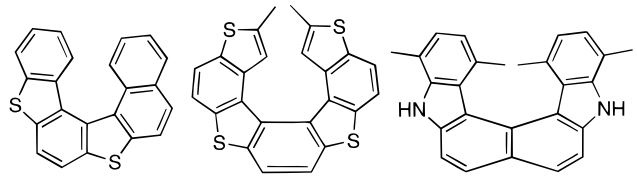


Figure 1. CD spectra of 2.4×10^{-5} M solutions of (*P*)-(+)-**10a** (···), (*P*)-(+)-**10b** (- - -), and (*P*)-(+)-**10c** (—) in CH_3CN.

spectra for the isomers of **10a**−**c** that are dextrorotatory at 589 nm (the wavelength of the sodium D line), and the Supporting Information includes the spectra of their diastereomers. The latter are essentially mirror images of the former. The CD spectrum of (+)-**10b** between 250 and 350 nm and near 400 nm is similar to the CD spectra of the dextrorotatory enantiomers of three thiohelicenes known to have (*P*)-, or right-handed, helicity: the parent of **10b**, in which the BuO and Z groups are replaced by Hs;[18] **11**;[19] and **12**.[7e] Accordingly, it is likely that (+)-**10b** also has (*P*)-helicity. Moreover, the similarity of the three CD spectra in Figure 1 implies that all three molecules have the same helicity. Because the CD spectra of (+)- and (−)-**10d** are almost identical to those of (+)- and (−)-**10c**, their dextrorotatory isomers, too, undoubtedly have the same helicity. Accordingly, (+)-**10a**, (+)-**10c**, and (+)-**10d** are all assigned (*P*)-configurations. For (+)-**10c** and (+)-**10d**, this assignment agrees with the similarity between their CD spectra and that of (+)-**13**, which is believed to have (*P*)-helicity because its CD spectrum matches one calculated.[6d,20]



11 **12** **13**

That the helicities are unchanged when camphanates **10** are stored and transformed at room temperature into helicenebisquinones **9** is shown by experiments in which samples of **9a**−**c** in DMF were heated at 78 °C for 24 h. The circular dichroisms of **9b** and **9c** decreased by 5−13%, and that of **9a** decreased by 45%. Moreover, the specific rotations of the (+)- and (−)-**9b** (prepared,

(15) Mallory, F. B.; Mallory C. W. *Organic Reactions*; Wiley: New York, 1984; Vol. 30, p 48ff.

(16) The dashed line in Scheme 4 indicates that photoirradiation cyclizes the carbocyclic [5]helicene further, to benzo[*g*,*h*,*i*]perylene.[17b]

(17) For X = S, see: (a) Tedjamulia, M. L.; Tominaga, Y.; Castle, R. N.; Lee, M. L. *J. Heterocycl. Chem.* **1983**, *20*, 861. For X = CH=CH, see: (b) Dietz, F.; Scholz, M. *Tetrahedron* **1968**, *24*, 6845. (c) Le Guen, M. M. J.; Shafig, Y. E.-D.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1979**, 803.

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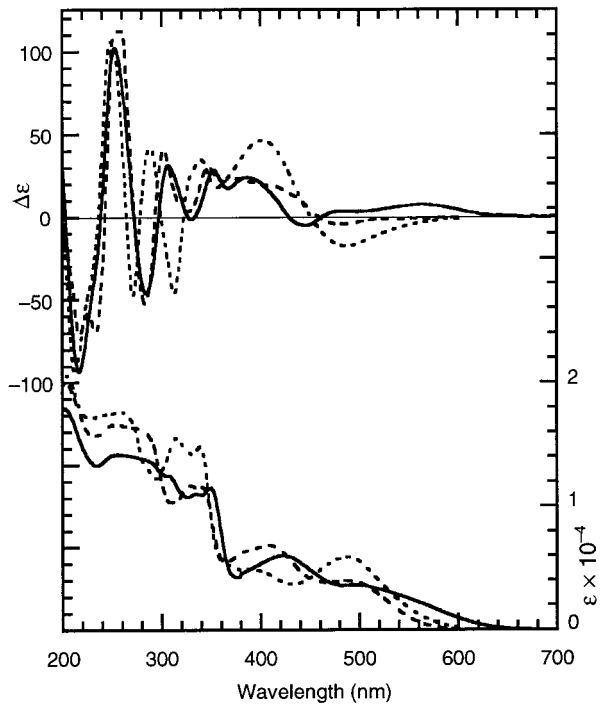

Figure 2. CD spectra (top, ordinate on the left) and UV−vis absorption spectra (bottom, ordinate on the right) of 5.4×10^{-5} M solutions of (*P*)-**9a** (···), (*P*)-(+)-**9b** (- - -), and (*P*)-**9c** (—) in CH_3CN.

respectively, from the (+)- and (−)-diastereomers of **10b**) are identical except for their signs: +1350 and −1300. Thus, the CD spectra of **9a**−**d** derived from dextrorotatory **10a**−**d** (Figure 2 and Supporting Information) are those of the (*P*)-enantiomers. In accord with the assignment, the CD peaks between ca. 350 and 400 nm and at ca. 253 nm are positive, and the one at ca. 279 nm negative, as in the spectra of (+)-(*P*)-**1** (TIPS replaced by $C_{12}H_{25}$, and R = $C_{12}H_{25}$ or R,R = Ph_2C).[2] We note incidentally that the specific rotations of **9a**, **9c**, and **9d** at the D wavelength could not be measured because the compounds absorb too strongly at 589 nm (Figure 2).

Conclusions

Grams of hetero[7]helicenes **4a**−**d** can be synthesized in only three or four steps from cheap materials. Furthermore, helicene **4d** can be obtained pure without the need for chromatography. The enantiomers can be resolved by the same procedure previously used to resolve those of carbohelicenes, and their absolute configurations could be assigned. **9a** and **10a** are the first nonracemic oxahelicenes to have been made.

Experimental Section

THF was distilled from Na/benzophenone; toluene was distilled from Na; and CH_2Cl_2, $ClCH_2CH_2Cl$, and Et_3N were distilled from CaH_2. Dibenzofuran (97%, Aldrich), $AlCl_3$ (99%, Aldrich), acetyl chloride (98%, Aldrich), dibenzothiophene (98%, Aldrich), carbazole (96%, Acros), CS_2 (anhydrous, 99+%, Aldrich), dimethyl sulfate (99+%, Aldrich), triisopropylsilyl triflate (GFS, 98%), 1-iodobutane (99%, Aldrich), 1-iodododecane (99%, Acros), CsF (99%, Aldrich), *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA, Aldrich, anhydrous, 99.5%), MeLi (1.6 M in Et_2O, Acros), *n*-BuLi (2.6M in hexanes, Acros), and chloranil (99%, Aldrich) were used without purification. DMF (Aldrich, anhydrous, 99.8%) was boiled and cooled under N_2 prior to use. Zn dust (Aldrich, <10 μm, 98%) was activated prior to use.[21] (*S*)-(−)-Camphanic acid was prepared on a 100 g scale.[22] 1,4-Benzoquinone (Aldrich, 98%) was purified by slurrying it in CH_2Cl_2 with 4 times its weight of basic alumina, filtering through Celite, and drying under vacuum. Glassware was flame-dried under vacuum and cooled under N_2. Reactions were run under N_2. Additions by syringe were through rubber septa. Chromatography refers to flash chromatography. Whatman 60 Å silica plates were used for TLC analyses.

Preparation of Diacetyl Compounds. Dibenzofuran with acetyl chloride and $AlCl_3$ in 1,2-dichloroethane gave **2a**[3a] (mp 161−162; lit.[23] 161−162 °C). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.64 (d, 2H, 1.8 Hz), 8.16 (dd, 2H, 1.8 and 6.8 Hz), 7.64 (d, 2H, 8.7 Hz), 2.74 ppm (s, 6H).[24] ^{13}C NMR ($CDCl_3$, 75 MHz): δ 196.9, 159.5, 133.1, 128.7, 124.1, 121.9, 112.0, 26.8 ppm.

Dibenzothiophene similarly gave **2b**[3a] (mp 204−205 °C; lit.[3d] 204−205.5 °C). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.81 (d, 2H, 1.6 Hz), 8.09 (dd, 2H, 1.6 and 6.8 Hz), 7.93 (d, 2H, 8.4 Hz), 2.76 ppm (s, 6H).[3d] ^{13}C NMR ($CDCl_3$, 75 MHz): δ 197.4, 144.7, 135.3, 134.2, 126.9, 122.9, 122.0, 26.8 ppm, similar to that reported.[25]

Carbazole with acetyl chloride and $AlCl_3$ in CS_2 gave 3,6-diacetylcarbazole[3b] (mp 232−233 °C; lit.[3b] 232 °C). ^{1}H NMR (DMSO-d_6, referenced to the DMSO peak, 400 MHz): δ 12.06 (s, 1H), 9.00 (d, 2H, 1.6 Hz), 8.05 (dd, 2H, 1.6 and 6.9 Hz), 7.59 (d, 2H, 8.6 Hz), 2.68 ppm (s, 6H). ^{13}C NMR (DMSO-d_6, referenced to the DMSO peak, 75 MHz): δ 197.1, 143.3, 129.2, 126.4, 122.7, 122.5, 111.3, 26.7 ppm. With dimethyl sulfate and KOH in acetone[3c] the latter gave **2c** (mp 195−196 °C, lit.[3c] 195 °C). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.73 (d, 2H, 1.3 Hz), 8.16 (dd, 2H, 1.7 and 5.9 Hz), 7.41 (d, 2H, 8.6 Hz), 3.88 (s, 3H), 2.73 ppm (s, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 197.4, 144.3, 129.8, 127.0, 122.8, 121.8, 108.7, 29.5, 26.6 ppm.

3,6-Diacetylcarbazole (10.0 g, 40 mmol) was refluxed for 1 h with 1-iodododecane (35.4 g, 119 mmol, 30.0 mL), KOH-saturated H_2O (50 mL), and acetone (200 mL). After it had cooled to room temperature, the reaction mixture was diluted with Et_2O, washed twice with H_2O, and dried (Na_2SO_4). The solvent was removed. The addition of hexanes (ca. 250 mL) precipitated a white solid, which when filtered, washed with cold hexanes, and dried, amounted to 15.8 g (95%) of pure **2d**, mp 97−99 °C. IR (CCl_4) 1680 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.80 (d, 2H, 1.6 Hz), 8.18 (dd, 2H, 1.7 and 7.0 Hz), 7.46 (d, 2H, 8.7 Hz), 4.35 (t, 2H, 7.2 Hz), 2.75 (s, 6H), 1.89 (m, 2H), 1.34 (m, 2H), 1.22 (m, 18H), 0.87 ppm (t, 3H, 6.7 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 197.4, 143.9, 129.7, 127.0, 122.8, 122.0, 109.0, 43.6, 31.9, 29.5, 29.3 (m), 28.9, 27.2, 26.7, 22.6, 14.1 ppm. Anal. Calcd for $C_{28}H_{37}NO_2$: C, 80.13; H, 8.90; N, 3.34. Found: C, 79.94; H, 9.06; N, 3.22.

General Procedure A. Preparation of Silyl Enol Ethers. 3,6-Bis[1-(triisopropylsiloxy)-ethenyl]-*N*-methylcarbazole (3c). Triisopropylsilyl triflate (12.1 g, 39.6 mmol, 10.6 mL) was added to a solution, cooled in an ice bath, of **2c** (5.0 g, 18.9 mmol) and Et_3N (15.7 mL) in CH_2Cl_2 (95 mL), and the mixture was warmed to room temperature and then stirred for 2 h. The reaction mixture was diluted with CH_2Cl_2, washed three times with saturated $NaHCO_3$, and dried (Na_2SO_4). The solvent was evaporated. The pink solid was dissolved in a minimal amount of CH_2Cl_2, and MeOH was added until a precipitate formed. The CH_2Cl_2 was evaporated, and the solid in the remaining MeOH was filtered, washed with MeOH, and heated at 100 °C for 2 h in a vacuum, giving 10.2 g (94%) of a white solid (**3c**, mp 166−170 °C). ^{1}H NMR (acetone-d_6, referenced to the acetone peak, 300 MHz): δ 8.46 (d, 2H, 1.4 Hz), 7.83 (m, 2H), 7.49 (m, 2H), 4.98 (d, 2H, 1.7 Hz), 4.45 (d,

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(24) Our ^{1}H NMR spectra of **2a** and **2b** do not match those in ref 3a. However, the spectrum of **2b** does match that in ref 3d.

(25) Filimonov, V. D.; Filippova, T. A.; Lopatinskii, V. P.; Sukhoroslova, M. M. *Chem. Heterocycl. Compd.* **1984**, *20*, 165.

2H, 1.7 Hz), 3.91 (s, 3H), 1.36 (m, 6H), 1.19 ppm (m, 38H). ^{13}C NMR (acetone-d_6, referenced to the acetone peak, 75 MHz): δ 157.3, 142.0, 129.6, 124.1, 122.9, 117.2, 109.0, 88.5, 18.1, 13.2 ppm.

3,6-Bis-[1-(triisopropylsiloxy)ethenyl]dibenzofuran (3a). Procedure A. Triisopropylsilyl triflate (10.1 g, 33 mmol, 8.9 mL), CH_2Cl_2 (80 mL), Et_3N (13.0 mL), and **2a** (4.0 g, 15.7 mmol) were used. The oily product was purified by dissolving it in 1:1 hexanes/benzene (+3% Et_3N) and quickly flushing it with the same solvents down a short column of neutral alumina. This gave 8.5 g (96%) of a yellow oil (**3a**). ^{1}H NMR (acetone-d_6, referenced to the acetone peak, 300 MHz): δ 8.40 (d, 2H, 1.6 Hz), 7.87 (dd, 2H, 8.7 Hz), 7.60 (dd, 2H, 8.6 Hz), 5.05 (d, 2H, 2.0 Hz), 4.51 (d, 2H, 1.9 Hz), 1.36 (m, 6H), 1.18 ppm (d, 38H, 7.1 Hz). ^{13}C NMR (acetone-d_6, referenced to the acetone peak, 75 MHz): δ 157.5, 156.7, 134.1, 126.0, 124.8, 118.2, 112.0, 90.3, 18.5, 13.5 ppm.

3,6-Bis[1-(triisopropylsiloxy)ethenyl]dibenzothiophene (3b). Procedure A. Triisopropylsilyl triflate (8.8 g, 28.5 mmol, 7.7 mL), CH_2Cl_2 (70 mL), Et_3N (11.3 mL), and **2b** (3.6 g, 13.4 mmol) were used. The oily product was purified in the same way as **3a**. This gave 7.2 g (91%) of a light yellow oil (**3b**). ^{1}H NMR (acetone-d_6, referenced to the acetone peak, 300 MHz): δ 8.58 (d, 2H, 1.5 Hz), 7.96 (dd, 2H, 8.5 Hz), 7.85 (dd, 2H, 8.5 Hz), 5.12 (d, 2H, 2.0 Hz), 4.57 (d, 2H, 2 Hz), 1.40 (m, 6H), 1.19 ppm (d, 36H, 7.2 Hz). ^{13}C NMR (acetone-d_6, referenced to the acetone peak, 75 MHz): δ 156.4, 140.1, 135.8, 135.3, 124.9, 123.0, 118.5, 90.5, 18.1, 13.1 ppm.

3,6-Bis[1-(triisopropylsiloxy)-ethenyl]-*N*-dodecylcarbazole (3d). Procedure A. Triisopropylsilyl triflate (21.8 g, 71 mmol, 19.1 mL), CH_2Cl_2 (160 mL), Et_3N (28 mL), and **2d** (14.2 g, 34 mmol) were used. The oily product was purified in the same way as **3a**. This gave 24.5 g (99%) of a light yellow oil (**3d**). ^{1}H NMR (acetone-d_6, referenced to the acetone peak, 300 MHz): δ 8.46 (d, 2H, 1.4 Hz), 7.81 (dd, 2H, 1.7 and 6.9 Hz), 7.52 (d, 2H, 8.8 Hz), 4.97 (d, 2H, 1.6 Hz), 4.44 (d, 2H, 1.6 Hz), 4.40 (t, 2H, 7 Hz), 1.87 (m, 2H), 1.42 (m, 6H), 1.21 (m, 52H), 0.85 ppm (t, 3H, 7 Hz). ^{13}C NMR (acetone-d_6, referenced to the acetone peak, 75 MHz): δ 157.7, 141.8, 129.9, 124.4, 123.5, 117.7, 109.5, 88.8, 43.6, 32.6, 29.6 (m), 27.8, 23.3, 18.6, 14.4, 13.6 ppm.

General Procedure B. Preparation of Hetero[7]-helicenebisquinones. Azahelicenebisquinone 4c. A flask containing **3c** (9.1 g, 15.8 mmol) and *p*-benzoquinone (51.3 g, 474 mmol) was fitted with a reflux condenser and then evacuated and filled with N_2 three times. Toluene (60 mL) was syringed in, and the mixture was heated in an oil bath at 90 °C for 11 h. The reaction mixture was then cooled to room temperature, and CH_2Cl_2 was added. The mixture was filtered through Celite, and the solvent was evaporated. Sublimation at 120 °C under a vacuum of ca. 1 mmHg transferred excess benzoquinone into a cold trap. The crude material was divided into two equal portions, and each was chromatographed (eluents from 1:1 hexanes/CH_2Cl_2 to 20:1 CH_2Cl_2/ethyl acetate) on a 600 mL coarse fritted funnel packed with silica gel. The silica gel was washed with acetone until it was colorless, and it was then reused. The mixed fractions were rechromatographed similarly on the recycled silica gel. The resulting red/purple solid (R_f 0.64, CH_2Cl_2), after it had been heated overnight in a vacuum at 120 °C, amounted to 6.5 g (53%) of **4c** (mp > 225 °C). IR (CCl_4) 1663, 1570 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.32 (d, 2H, 9.0 Hz), 7.74 (d, 2H, 9.0 Hz), 7.29 (s, 2H), 6.66 (d, 2H, 10.1 Hz), 6.39 (d, 2H, 10.1 Hz), 4.07 (s, 3H), 1.51 (m, 6H), and a pair of doublets (10.4 Hz) at 1.21 and 1.20 ppm (37H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 186.2, 182.0, 159.4, 141.0, 140.3, 135.1, 133.7, 127.4, 126.4, 123.3, 121.3, 119.5, 112.9, 106.6, 29.6, 18.1, 13.1 ppm. UV−vis (CH_3CN, $c = 3.7 \times 10^{-5}$ M), λ_{max} (log ϵ): 500 (3.56), 420 (3.77), 350 (4.13), 335 (4.13), 310 (4.19), 285 (sh, 4.25), 260 nm (4.29). Anal. Calcd for $C_{47}H_{55}NO_6Si_2$: C, 71.80; H, 7.07; N, 1.78. Found: C, 71.67; H, 6.93; N, 1.73.

Also isolated in this chromatographic procedure was 2.9 g (23%) of a green/black solid (**5c**, R_f 0.44, CH_2Cl_2; mp > 225 °C). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 9.77(s, 1H), 8.50 (d, 1H, 9.1 Hz), 8.33 (s, 1H), 7.74 (d, 1H, 9.1 Hz), 7.43 (s, 1H), 7.38 (s, 1H), 7.02 (d, 1H, 10.1 Hz), 6.88 (d, 2H, 10.1 Hz), 6.84 (d, 1H, 10.1 Hz), 6.78 (d, 1H, 10.1 Hz), 4.05 (s, 3H), 1.46 (m, 7H), 1.15 ppm (m, 39H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 187.8, 187.1, 187.0, 183.8, 159.5, 159.3, 146.5, 143.6, 141.7, 141.6, 135.8, 135.6, 135.3, 134.3, 130.3, 128.0, 126.6 (two peaks), 125.1, 124.6, 123.1, 120.2, 116.6, 113.1, 107.2, 106.0, 105.4, 30.2, 18.7, 18.5, 13.6, 13.5 ppm. UV−vis (CH_2Cl_2, $c = 3.7 \times 10^{-5}$ M), λ_{max} (log ϵ): 580 (3.58), 450 (3.94), 365 (sh, 4.10), 345 (4.20), 290 (4.30), 240 nm (4.30).

Oxahelicenebisquinone 4a. Procedure B. Compound **3a** (8.4 g, 14.8 mmol) in toluene (55 mL) was combined with *p*-benzoquinone (48.0 g, 440 mmol) and heated at 100 °C for 48 h. The crude product was divided into two portions, and each was chromatographed (eluents from 4:1 CH_2Cl_2/hexanes to CH_2Cl_2). The silica gel was washed, and mixed fractions were rechromatographed on it. This gave 4.5 g (39%) of a brilliant orange solid (**4a**, R_f 0.80, CH_2Cl_2; mp > 225 °C). IR (CCl_4) 1663, 1570 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.45 (d, 2H, 9.1 Hz), 7.92 (d, 2H, 9.0 Hz), 7.40 (s, 2H), 6.74 (d, 2H, 10.2 Hz), 6.50 (d, 2H, 10.2 Hz), 1.53 (m, 8H), and two doublets (10.8 Hz) at 1.23 and 1.20 ppm (39H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 185.9, 182.7, 159.1, 156.8, 140.1, 135.6, 133.5, 127.8, 127.6, 124.8, 123.1, 122.1, 114.6, 107.1, 18.0, 13.0 ppm. UV−vis (CH_2Cl_2, $c = 3.2 \times 10^{-5}$ M), λ_{max} (log ϵ): 490 (3.82), 390 (3.72), 340 (4.22), 319 (4.25), 260 (4.37), 240 nm (4.37). Anal. Calcd for $C_{46}H_{52}O_7Si_2$: C, 71.46; H, 6.79. Found: C, 71.57; H, 6.78.

Also isolated in the chromatographic procedure was 2.5 g (22%) of orange/red solid **5a** (R_f 0.64, CH_2Cl_2; mp > 225 °C). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 9.97 (s, 1H), 8.62 (d, 1H, 9.2 Hz), 8.28 (s, 1H), 7.96 (d, 1H, 9.1 Hz), 7.57 (s, 1H), 7.50 (s, 1H), 7.12 (d, 1H, 10.2 Hz), 6.99 (d, 1H, 10.1 Hz), 6.96 (d, 1H, 10.1 Hz), 6.90 (d, 1H, 10.1 Hz), 1.53 (m, 9H), and a pair of doublets (10.2 and 10.3 Hz, respectively) at 1.22 and 1.19 ppm (42H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 187.0, 186.2, 183.6, 160.5, 159.1, 158.8, 157.9, 141.2, 140.8, 135.6, 135.3, 135.2, 134.2, 131.0, 127.9, 127.2, 126.5, 125.6, 123.3, 120.3, 119.0, 115.2, 108.5, 107.6, 106.0, 18.3, 18.1, 13.3, 13.1 ppm. UV−vis (CH_3CN, $c = 3.4 \times 10^{-5}$ M), λ_{max} (log ϵ): 490 (3.75), 410 (3.96), 343 (sh, 4.10), 320 (4.20), 260 (4.34), 210 nm (4.35).

Thiahelicenebisquinone 4b. Procedure B. Compound **3b** (7.1 g, 12 mmol) in toluene (45 mL) was combined with *p*-benzoquinone (39 g, 360 mmol) and heated at 110 °C for 24 h. This gave, after chromatography as for **4c**, 3.1 g (33%) of orange solid **4b** (R_f 0.84, CH_2Cl_2; mp > 225 °C). IR (CCl_4) 1663, 1570 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.32 (d, 2H, 8.7 Hz), 8.01 (d, 2H, 8.7 Hz), 7.37 (s, 2H), 6.61 (d, 2H, 10.1 Hz), 6.11 (d, 2H, 10.1 Hz), 1.53 (m, 7H), 1.22 ppm (m, 38H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 185.5, 180.8, 159.7, 141.3, 140.3, 134.3, 132.9, 128.9, 127.5, 123.4, 122.1, 121.4, 107.1, 18.1, 13.0 ppm. UV−vis (CH_3CN, $c = 3.8 \times 10^{-5}$ M), λ_{max} (log ϵ): 500 (3.69), 400 (3.92), 330 (4.20), 250 nm (4.31). Anal. Calcd for $C_{46}H_{52}O_6SSi_2$: C, 69.99; H, 6.65. Found: C, 69.83; H, 6.49.

Also isolated was 1.8 g (19%) of orange/red solid **5b** (R_f 0.63, CH_2Cl_2; mp > 225 °C). ^{1}H NMR δ ($CDCl_3$, 300 MHz): δ 10.24 (s, 1H), 8.63 (s, 1H), 8.47 (d, 1H, 8.8 Hz), 8.06 (d, 1H, 8.8 Hz), 7.58 (s, 1H), 7.48 (s, 1H), 6.97 (m, 2H), 6.91 (m, 2H), 1.53 (m, 13H), 1.20 (m, 67H!); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 186.9, 186.1, 186.0, 183.7, 158.7, 158.5, 145.2, 141.9, 141.0, 140.5, 136.7, 135.5, 135.3, 135.0, 134.1, 130.6, 129.3, 127.0, 123.7, 123.0, 121.5, 121.2, 119.7, 108.0, 106.1, 18.2, 18.0, 13.0 ppm (two peaks). UV−vis (CH_3CN, $c = 3.9 \times 10^{-5}$ M), λ_{max} (log ϵ): 490 (3.60), 420 (3.81), 330 (sh, 4.10), 290 (4.26), 260 (4.27), 230 nm (4.26).

Azahelicenebisquinone 4d. Procedure B. Compound **3d** (24.5 g, 33.5 mmol) in toluene (125 mL) was combined with *p*-benzoquinone (108 g, 1 mol) and heated at 85 °C for 14 h. The reaction mixture was then diluted with CH_2Cl_2 and filtered through Celite, and the solvent was evaporated. The residue was triturated with 200 mL of pentanes and filtered on Celite. The solids were washed with pentanes until the filtrate came through clear. The collected solid, containing **4d** and benzoquinone, was washed from the Celite with CH_2Cl_2, and the solvent was evaporated. Benzoquinone was removed by sublimation under vacuum at 100 °C for several hours.

Obtained was 16.0 g (50%) of a red/purple solid (mp 210−211 °C). IR (CCl_4) 1663, 1569 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz) δ 8.30 (d, 2H, 9.0 Hz), 7.73 (d, 2H, 9.0 Hz), 7.27 (s, 2H), 6.65 (d, 2H, 10.1 Hz), 6.40 (d, 2H, 10.1 Hz), 4.47 (t, 2H, 7.6 Hz), 2.02 (m, 2H), 1.51 (m, 5H), 1.40 (m, 1H), 1.20 (m, 48H), 0.87 ppm (t, 3H, 7.0 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 186.3, 181.9, 159.3, 140.5, 140.3, 135.1, 133.6, 127.5, 123.2, 121.2, 119.6, 113.0, 106.4, 43.7, 31.2, 30.1, 29.5, 29.3 (m), 27.4, 22.7, 18.1, 14.1, 13.0 ppm. Anal. Calcd for $C_{58}H_{77}O_6NSi_2$: C, 74.06; H, 8.27; N, 1.49. Found: C, 73.84; H, 8.28; N, 1.37.

General Procedure C. Replacement of Siloxy with Alkyl Side Chains. Azahelicenebisquinone 9c. A flask containing **4c** (1.5 g, 1.9 mmol) and CsF (1.16 g, 7.6 mmol) was evacuated and filled with N_2 three times. *n*-Butyl iodide (8.7 g, 47.5 mmol, 5.4 mL) was added by syringe, and DMF (90 mL) was added through a cannula. The reaction mixture was heated to 70 °C for 3 h, cooled to room temperature, and poured into H_2O (0.5 L). The resulting mixture was filtered through Celite and washed with H_2O (200 mL). The purple/red solid was rinsed from the Celite with CH_2Cl_2, washed with H_2O (3 × 300 mL), dried (Na_2SO_4), and to remove trace impurities, poured onto ca. 50 g of silica gel in a fritted funnel and washed from it with CH_2Cl_2. The solvent was evaporated, giving 1.0 g (94%) of a red/purple solid (**9c**, mp > 225 °C). IR (CCl_4) 1662, 1573 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 8.34 (d, 2H, 9.0 Hz), 7.72 (d, 2H, 9.0 Hz), 7.28 (s, 2H), 6.69 (d, 2H, 10.1 Hz), 6.43 (d, 2H, 10.1 Hz), 4.35 (m, 4H), 4.07 (s, 3H), 1.98 (m, 4H), 1.65 (m, 4H), 1.08 ppm (t, 6H, 7.4 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 186.4, 182.0, 161.2, 140.9, 140.0, 135.1, 133.9, 126.7, 124.0, 123.1, 120.7, 119.2, 112.8, 99.3, 68.9, 31.1, 29.6, 19.4, 13.9 ppm. Anal. Calcd for $C_{37}H_{31}NO_6$: C, 75.87; H, 5.35; N, 2.38. Found: C, 75.80; H, 5.36; N, 2.57.

Oxahelicenebisquinone 9a. Procedure C. Compound **4a** (0.70 g, 0.91 mmol), CsF (0.55 g, 3.6 mmol), *n*-butyl iodide (4.3 g, 22.9 mmol, 2.6 mL), and DMF (30 mL) were used. Obtained was 0.51 g (99%) of a red solid (**9a**, mp > 225 °C). IR (CCl_4) 1664, 1571 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz) δ 8.48 (d, 2H, 9.1 Hz), 7.92 (d, 2H, 9.1 Hz), 7.38 (s, 2H), 6.76 (d, 2H, 10.1 Hz), 6.50 (d, 2H, 10.1 Hz), 4.38 (m, 4H), 2.00 (m, 4H), 1.66 (m, 4H), 1.08 ppm (t, 7H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 186.1, 182.8, 161.0, 156.7, 139.9, 135.7, 133.8, 127.0, 125.5, 124.5, 122.6, 122.0, 114.6, 100.0, 69.2, 31.1, 19.4, 13.9 ppm. HRMS (FAB): *m*/*z* calcd for $C_{36}H_{28}O_7$: 573.2249, found 573.1910.

Thiahelicenebisquinone 9b. Procedure C. Compound **4b** (0.50 g, 0.64 mmol), CsF (0.39 g, 2.56 mmol), *n*-butyl iodide (2.9 g, 16.0 mmol, 1.8 mL), and DMF (30 mL) were used. Obtained was 0.34 g (91%) of an orange solid (**9b**, mp > 225 °C). IR (CCl_4) 1664, 1570 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 8.34 (d, 2H, 8.8 Hz), 8.03 (d, 2H, 8.7 Hz), 7.37 (s, 2H), 6.65 (d, 2H, 10.1 Hz), 6.21 (d, 2H, 10.1 Hz), 4.37 (m, 4H), 2.02 (m, 4H), 1.68 (m, 5H), 1.10 ppm (t, 7H, 7.4 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 185.7, 180.8, 161.5, 141.4, 140.1, 134.6, 134.2, 132.8, 127.0, 126.8, 123.4, 122.0, 120.9, 99.9, 69.2, 31.1, 19.4, 13.9 ppm. Anal. Calcd for $C_{36}H_{28}O_6S$: C, 73.44; H, 4.80. Found: C, 73.13; H, 4.95.

Azahelicenebisquinone 9d. Procedure C. Compound **4d** (0.50 g, 0.53 mmol), CsF (0.32 g, 2.1 mmol), 1-iodododecane (4.0 g, 13.5 mmol, 3.3 mL), and DMF (26 mL) were used. The reaction mixture was poured into 100 mL of Et_2O and washed three times with 100 mL of H_2O. After it had been dried (Na_2SO_4), the solvent was evaporated. Chromatography, eluting first with pure hexanes to remove excess 1-iodododecane and then with CH_2Cl_2, gave 0.44 g (86%) of a red/purple solid (**9d**, mp 208−209 °C). IR (CCl_4) 1662 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 8.32 (d, 2H, 9.0 Hz), 7.72 (d, 2H, 9.0 Hz), 7.26 (s, 2H), 6.68 (d, 2H, 10.1 Hz), 6.42 (s, 2H, 10.1 Hz), 4.49 (m, 2H), 4.33 (m, 4H), 2.01 (m, 6H), 1.61 (m, 6H), 1.28 (m, 54H), 0.87 ppm (m, 10H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 186.5, 182.0, 161.3, 14.5, 140.1, 135.2, 134.0, 126.9, 124.0, 123.2, 120.7, 119.5, 112.9, 99.3, 43.8, 31.9, 30.1, 29.6 (m), 29.4, 27.4, 26.2, 22.7, 14.1 ppm. Anal. Calcd for $C_{64}H_{85}NO_6$: C, 79.69; H, 8.90; N, 1.45. Found: C, 79.81; H, 9.19; N, 1.40.

General Procedure D. Preparation of Tetracamphanate Esters. Tetracamphanate 10c. Toluene (35 mL) and TMEDA (8.9 g, 88 mmol, 11.6 mL) were syringed sequentially into a N_2-purged flask with condenser containing **9c** (0.45 g, 0.77 mmol), Zn (0.78 g, 11.9 mmol), and (*S*)-(−)-camphanoyl chloride (2.5 g, 11.5 mmol). The reaction mixture was heated at reflux for 1 h, whereupon it turned yellow. It was cooled to room temperature and filtered through Celite. After the filtrate had been diluted with CH_2Cl_2, washed twice with 1 N HCl and twice with saturated aqueous $NaHCO_3$, and dried (Na_2SO_4), the solvent was removed, giving a yellow/orange foam. Chromatography on silica gel (eluents from toluene to 5:1 toluene/THF) gave the levorotatory diastereomer, (*M*)-(−)-**10c** (0.45 g, 91%), mp > 225 °C, and the dextrorotatory diastereomer, (*P*)-(+)-**10c** (0.46 g, 92%), mp > 225 °C. The latter was purified further by chromatography. The same solvents were used.

The ^1H NMR spectra of the diastereomers would have detected 3% of (*P*)-(+)-**10c** in the sample of (*M*)-(−)-**10c** and 1% of (*M*)-(−)-**10c** in the sample of (*P*)-(+)-**10c**. Accordingly, the enantiomeric purities of (+)- and (*M*)-(−)-**10c** were ≥99% and ≥97%, respectively. Similar analyses (see below) showed the enantiomeric purities of (+)- and (*M*)-(−)-**10a** to be ≥99% and ≥98%, respectively, of both (+)- and (*M*)-(−)-**10b** to be ≥99%, and of both (*P*)-(+)-**10d** and (*M*)-(−)-**10d** to be ≥99%.

(*M*)-(−)-**10c**: $[\alpha]_D$ −280 (*c* 0.060, CH_2Cl_2). IR (CCl_4) 1799, 1752 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 8.76 (d, 2H, 8.8 Hz), 7.93 (d, 2H, 8.8 Hz), 7.17 (d, 2H, 8.4 Hz), 7.11 (s, 2H), 6.00 (d, 2H, 8.4 Hz), 4.33 (m, 4H), 4.26 (s, 3H), 2.76 (m, 2H), 2.43 (m, 2H), 2.12 (m, 2H), 2.04 (m, 4H), 1.89 (m, 2H), 1.70 (m, 4H), 1.35 (s, 6H), 1.31 (s, 6H), 1.26 (s, 7H), 1.15 (m, 2H), 1.09 (t, 3H, 7.3 Hz), 0.79 (s, 6H), 0.41 (m, 2H), 0.27 (s, 6H), 0.19 ppm (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 178.0, 177.3, 166.5, 164.5, 155.1, 144.3, 141.3, 139.2, 127.0, 124.7, 122.7, 121.2, 120.8, 120.0, 119.6, 114.9, 108.6, 93.3, 91.5, 89.3, 68.2, 55.1, 54.6, 53.9, 53.6, 31.5, 31.2, 29.8, 29.1, 28.3, 28.0, 19.7, 17.3, 17.1, 16.0, 15.1, 14.0, 9.9, 9.5 ppm. UV−vis (CH_3CN, $c = 2.4 \times 10^{-5}$ M): λ_{max} (log ϵ) 417 (3.81), 396 (3.72), 330 (4.23), 300 (4.29), 273 (4.36), 230 nm (4.34). CD ($c = 2.4 \times 10^{-5}$, CH_3CN), nm ($\Delta\epsilon$): 210 (−137), 245 (306), 281 (−253), 294 (−36), 335 (−204), 418 (75). Anal. Calcd for $C_{77}H_{83}O_{18}N$: C, 70.56; H, 6.40; N, 1.07. Found: C, 70.26; H, 6.48; N, 0.96.

(*P*)-(+)-**10c**: $[\alpha]_D$ +220 (*c* 0.045, CH_2Cl_2). IR (CCl_4) 1799 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 8.69 (d, 2H, 8.8 Hz), 7.99 (d, 2H, 8.9 Hz), 7.13 (d, 2H, 8.4 Hz), 6.99 (s, 2H), 6.02 (d, 2H, 8.3 Hz), 4.33 (m, 2H), 4.32 (m, 3H), 4.24 (m, 2H), 2.82 (m, 2H), 2.46 (m, 2H), 2.15 (m, 2H), 2.04 (m, 4H), 1.92 (m, 2H), 1.71 (m, 3H), three singlets (20H total) at 1.30, 1.27, and 1.26, 1.14 (m, 2H), 1.11 (t, 6H, 7.4 Hz), 0.82 (s, 6H), 0.33 (s, 12H), 0.05 (m, 2H), −0.27 ppm (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 177.7, 177.2, 166.6, 164.2, 155.0, 144.7, 141.5, 140.0, 126.8, 124.6, 121.8, 120.3, 120.2, 119.5, 115.4, 110.0, 93.1, 91.2, 90.0, 68.1, 55.0, 54.5, 54.1, 53.6, 31.3, 31.2, 30.0, 29.2, 28.7, 26.7, 19.8, 17.2, 17.1, 16.1, 13.9, 9.8, 9.4 ppm. UV−vis (CH_3CN, $c = 2.4 \times 10^{-5}$ M), λ_{max} (log ϵ): 417 (3.81), 396 (3.70), 330 (4.18), 300 (4.25), 273 (4.34), 230 nm (4.31). CD ($c = 2.4 \times 10^{-5}$, CH_3CN), nm ($\Delta\epsilon$): 210 (72), 245 (−160), 281 (135), 294 (19), 335 (94), 418 (−40). Anal. Calcd for $C_{77}H_{83}O_{18}N$: C, 70.56; H, 6.40; N, 1.07. Found: C, 70.41; H, 6.49; N, 0.97.

Tetracamphanate 10a. Procedure D. Compound **9a** (0.35 g, 0.61 mmol), toluene (25 mL), TMEDA (7.2 g, 61 mmol, 9.4 mL), Zn (0.62 g, 9.7 mmol), and (*S*)-(−)-camphanoyl chloride (2.0 g, 9.2 mmol) were used. Column chromatograpy on silica gel (eluents from 10:1 hexanes/ethyl acetate to 1.5:1 hexanes/ethyl acetate) gave the levorotatory diastereomer, (*M*)-(−)-**10a** (0.34 g, 85%), mp > 225 °C, and the dextrorotatory diastereomer, (*P*)-(+)-**10a** (0.30 g, 76%), mp > 225 °C. The latter was purified further by chromatography. The same solvents were used.

(*M*)-(−)-**10a**: $[\alpha]_D$ −310 (*c* 0.027, CH_2Cl_2). IR (CCl_4) 1800, 1753 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 8.75 (d, 2H, 8.8 Hz), 8.01 (d, 2H, 8.8 Hz), 7.17 (d, 2H, 8.4 Hz), 7.10 (s, 2H), 6.03 (d, 2H, 8.4 Hz), 4.34 (m, 2H), 4.27 (m, 2H), 2.75 (m, 2H), 2.41 (m, 2H), 2.11 (m, 2H), 2.04 (m, 4H), 1.89 (m, 2H), 1.68 (d, 4H, 7.0 Hz), three singlets (20H total) at 1.34, 1.29, and 1.25, 1.17 (m, 2H), 1.08 (t, 6H, 7.3 Hz), 0.82 (m, 2H), 0.82 (s, 6H), 0.35 (s, 6H), 0.27 (m, 2H), 0.25 ppm (s, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 177.8, 176.9, 166.4, 164.9, 155.1, 154.9, 144.5, 141.3,

127.4, 124.8, 123.0, 121.4, 121.1, 120.3, 114.6, 110.8, 94.2, 91.4, 89.0, 68.3, 55.1, 54.5, 54.0, 53.8, 31.4, 31.2, 29.0, 28.7, 28.3, 19.6, 17.2, 17.1, 16.0, 15.6, 14.0, 9.8, 9.4 ppm. UV−vis (CH_3CN, $c = 2.4 \times 10^{-5}$ M), λ_{max} (log ϵ): 405 (3.96), 386 (3.83), 322 (4.31), 300 (4.39), 260 (sh, 4.51), 210 nm (4.57). CD ($c = 2.4 \times 10^{-5}$, CH_3CN), nm ($\Delta\epsilon$): 210 (−90), 228 (133), 236 (110), 248 (156), 272 (−197), 292 (15), 314 (−138), 319 (−132), 325 (−160), 408 (40). Anal. Calcd for $C_{76}H_{80}O_{19}$: C, 70.34; H, 6.23. Found: C, 70.28; H, 6.28.

(*P*)-(+)-**10a**: $[\alpha]_D$ +260 (*c* 0.027, CH_2Cl_2). IR (CCl_4) 1801, 1759 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 8.70 (d, 2H, 8.8 Hz), 8.08 (d, 2H, 8.8 Hz), 7.16 (d, 2H, 8.4 Hz), 7.02 (s, 2H), 6.07 (d, 2H, 8.4 Hz), 4.34 (m, 2H), 4.24 (m, 2H), 2.79 (m, 2H), 2.45 (m, 2H), 2.14 (m, 2H), 2.03 (m, 4H), 1.92 (m, 2H), 1.70 (m, 4H), three singlets (22H total) at 1.30, 1.27, and 1.26, 1.10 (t, 6H, 7.4 Hz), 0.84 (s, 6H), 0.52 (m, 2H), 0.34 (s, 6H), 0.31 (s, 6H), −0.11 ppm (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz) 177.6, 176.8, 166.6, 164.6, 155.5, 154.7, 144.8, 141.3, 127.1, 124.3, 124.0, 122.1, 121.8, 121.4, 120.7, 115.4, 112.2, 94.3, 90.9, 89.9, 68.2, 54.9, 54.4, 54.0, 53.7, 31.2, 29.6, 29.0, 28.5, 27.1, 19.6, 17.1, 16.1, 16.0, 13.8, 9.7, 9.3 ppm. UV−vis (CH_3CN, $c = 2.4 \times 10^{-5}$ M), λ_{max} (log ϵ): 405 (3.96), 386 (3.83), 322 (4.31), 300 (4.39), 260 (sh, 4.51), 225 (sh, 4.49), 210 nm (4.57). CD ($c = 2.4 \times 10^{-5}$, CH_3CN), nm ($\Delta\epsilon$): 210 (102), 228 (−121), 236 (−93), 249 (−160), 272 (203), 292 (−19), 314 (127), 319 (121), 325 (145), 408 (−45). HRMS (FAB): *m*/*z* calcd for $C_{76}H_{80}O_{19}$: 1296.6206, found 1296.5303.

Tetracamphanate 10b. Procedure D. Compound **9b** (0.31 g, 0.52 mmol), toluene (25 mL), TMEDA (6.1 g, 52 mmol, 7.9 mL), Zn (0.52 g, 8.1 mmol), and (S)-(−)-camphanoyl chloride (1.7 g, 8.1 mmol) were used. Chromatography on silica gel (eluents from CH_2Cl_2 to 3:1 CH_2Cl_2/ethyl acetate) gave the levorotatory diastereomer, (*M*)-(−)-**10b** (0.31 g, 91%), mp > 225 °C, and the dextrorotatory diastereomer, (*P*)-(+)-**10b** (0.24 g, 71%), mp > 225 °C. The latter was purified further by chromatography. The same solvents were used.

(*M*)-(−)-**10b**: $[\alpha]_D$ −470 (*c* 0.031, CH_2Cl_2). IR (CCl_4) 1799, 1754 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 8.71 (d, 2H, 8.5 Hz), 8.12 (d, 2H, 8.5 Hz), 7.07 (d, 2H, 9.4 Hz), 7.04 (s, 1H), 6.09 (d, 2H, 8.4 Hz), 4.36 (m, 2H), 4.22 (m, 2H), 2.72 (m, 2H), 2.41 (m, 2H), 2.10 (m, 2H), 2.04 (m, 4H), 1.87 (m, 2H), 1.67 (m, 4H), three singlets (22H total) at 1.30, 1.28, and 1.24, 1.08 (t, 6H, 7.4 Hz), 1.00 (m, 2H), 0.43 (s, 6H), 0.32 (s, 6H), −0.10 ppm (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 177.8, 177.2, 166.1, 164.9, 154.8, 144.4, 141.8, 138.2, 133.1, 127.3, 126.3, 125.4, 122.2, 121.0, 120.9, 120.0, 116.1, 94.7, 91.2, 89.1, 68.3, 55.0, 54.5, 54.1, 53.9, 31.3, 31.2, 29.0, 28.8, 28.3, 19.5, 17.2, 17.0, 16.1, 15.7, 13.9, 9.7, 9.4 ppm. UV−vis (CH_3CN, $c = 2.4 \times 10^{-5}$ M), λ_{max} (log ϵ): 420 (3.68), 335 (4.28), 320 (4.31), 306 (4.32), 276 (4.50), 260 nm (sh, 4.45). CD ($c = 2.4 \times 10^{-5}$, CH_3CN), nm ($\Delta\epsilon$): 210 (−161), 230 (101), 250 (268), 281 (−198), 338 (−213), 418 (67). Anal. Calcd for $C_{76}H_{80}O_{18}S$: C, 69.48; H, 6.15. Found: C, 69.21; H, 6.08.

(*P*)-(+)-**10b**: $[\alpha]_D$ +460 (*c* 0.031, CH_2Cl_2). IR (CCl_4) 1800, 1754 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 8.61 (d, 2H, 8.5 Hz), 8.17 (d, 2H, 8.5 Hz), 7.06 (d. 2H, 8.4 Hz), 6.99 (s, 2H), 6.06 (d, 2H, 8.4 Hz), 4.25 (m, 4H), 2.80 (m, 2H), 2.43 (m, 2H), 2.14 (m, 2H), 2.03 (m, 4H), 1.93 (m, 2H), 1.60 (m, 4H), 1.50 (m, 2H), three singlets (16H total) at 1.27, 1.25, and 1.22, 1.11 (t, 6H, 7.4 Hz), 0.91 (s, 6H), 0.63 (m, 2H), 0.48 (s, 6H), 0.43 (s, 6H), 0.10 ppm (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 177.7, 177.0, 166.2, 164.8, 154.6, 144.8, 142.1, 139.7, 133.2, 127.5, 125.9, 125.4, 122.1, 121.9, 121.0, 120.9, 117.4, 94.7, 91.2, 90.0, 68.2, 55.0, 54.7, 54.3, 53.9, 31.3, 30.8, 29.2, 28.8, 27.4, 19.8, 17.2, 16.9, 16.2 (two peaks), 14.0, 9.8, 9.5 ppm. UV−vis (CH_3CN, $c = 2.4 \times 10^{-5}$ M): λ_{max} (log ϵ) 420 (3.68), 335 (4.28), 320 (4.31), 306 (4.30), 276 (4.45), 260 nm (sh, 4.42). CD ($c = 2.4 \times 10^{-5}$, CH_3CN), nm ($\Delta\epsilon$): 208 (110), 230 (−26), 253 (−141), 280 (81), 300 (29), 342 (116), 423 (−28). Anal. Calcd for $C_{76}H_{80}O_{18}S$: C, 69.48; H, 6.15. Found: C, 69.15; H, 6.12.

Tetracamphanate 10d. Procedure D. Compound **9d** (0.40 g, 0.42 mmol), toluene (20 mL), TMEDA (4.9 g, 42 mmol, 6.3 mL), Zn (0.42 g, 6.5 mmol) and (S)-(−)-camphanoyl chloride (1.4 g, 6.3 mmol) were used. Chromatography on silica gel (eluents from hexanes to 3:1 hexanes/ethyl acetate) gave the levorotatory diastereomer, (*M*)-(−)-**10d** (0.25 g, 75%), mp 159−160 °C, and the dextrorotatory diastereomer, (*P*)-(+)-**10d** (0.27 g, 77%), mp 163−165 °C. The latter was purified further by chromatography. The same solvents were used.

(*M*)-(−)-**10d**: $[\alpha]_D$ −300 (*c* 0.057, CH_2Cl_2). IR (CCl_4) 1799, 1750 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 8.74 (d, 2H, 8.8 Hz), 7.91 (d, 8.8 Hz), 7.16 (d, 2H, 8.5 Hz), 7.10 (s, 2H), 6.0 (d, 8.5 Hz), 4.69 (m, 2H), 4.30 (m, 4H), 2.77 (m, 2H), 2.43 (m, 2H), 2.10 (m, 2H), 2.05 (m, 6H), 1.89 (m, 2H), 1.31 (m, 72H), 1.11 (m, 2H), 0.89 (m, 9H), 0.78 (s, 6H), 0.45 (m, 2H), 0.29 (s, 6H), 0.13 (m, 2H), 0.03 ppm (s, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 177.9, 177.1, 166.4, 164.5, 155.1, 144.3, 141.3, 138.5, 127.0, 124.8, 122.6, 121.1, 120.8, 119.9, 119.5, 114.7, 108.7, 93.2, 91.4, 89.2, 68.5, 55.1, 54.5, 53.9, 53.5, 43.5, 31.9, 31.2, 29.9, 29.6 (m), 22.7, 17.3, 17.1, 16.0, 15.3, 14.1, 9.8, 9.5 ppm. UV−vis (CH_3CN, $c = 2.6 \times 10^{-5}$ M), λ_{max} (log ϵ): 417 (3.93), 397 (3.84), 334 (4.37), 300 (4.45), 280 (sh, 4.52), 273 (4.53), 230 (sh, 4.51), 210 nm (4.58). CD ($c = 2.6 \times 10^{-5}$, CH_3CN), nm ($\Delta\epsilon$): 210 (−70), 245 (153), 281 (−137), 294 (−15), 335 (−105), 418 (38). Anal. Calcd for $C_{104}H_{137}NO_{18}$: C, 73.93; H, 8.19; N, 0.83. Found: C, 73.98; H, 8.29; N, 0.70.

(*P*)-(+)-**10d**: $[\alpha]_D$ +220 (*c* 0.065, CH_2Cl_2). IR (CCl_4) 1799 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 8.71 (d, 2H, 8.8 Hz), 7.99 (d, 2H, 8.8 Hz), 7.16 (d, 2H, 8.3 Hz), 7.01 (s, 2H), 6.02 (d, 2H, 8.3 Hz), 4.76 (t, 2H, 7.3 Hz), 4.35 (m, 2H), 4.24 (m, 2H), 2.84 (m, 2H), 2.49 (m, 2H), three multiplets (11H total) at 2.17, 2.07, and 1.95, 1.50 (m, 6H), 1.30 (m, 77H), 1.15 (m, 2H), 0.92 (m, 9H), 0.86 (s, 6H), 0.39 (s, 6H), 0.32 (s, 6H), 0.10 (m, 2H), −0.39 ppm (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 177.6, 177.1, 166.5, 164.3, 154.9, 144.7, 141.4, 139.1, 126.8, 124.6, 121.8, 120.3, 120.1, 119.3, 115.5, 110.0, 93.1, 91.1, 90.0, 68.4, 54.9, 54.5, 54.1, 53.6, 43.7, 31.9, 31.1, 29.6 (m), 29.5, 29.4, 29.1, 28.6, 27.4, 26.8, 22.7, 17.2, 17.1, 16.1, 14.1, 9.8, 9.4 ppm. UV−vis (CH_3CN, $c = 2.5 \times 10^{-5}$ M): λ_{max} (log ϵ) 417 (3.93), 397 (3.84), 3340 (4.37), 300 (4.45), 280 (4.52), 273 (4.53), 230 (4.51), 210 nm (4.58). CD ($c = 2.5 \times 10^{-5}$, CH_3CN), nm ($\Delta\epsilon$): 210 (72), 245 (−145), 281 (132), 294 (15), 335 (83), 418 (−39). Anal. Calcd for $C_{104}H_{137}NO_{18}$: C, 73.93; H, 8.19; N, 0.83. Found: C, 73.82; H, 8.23; N, 0.91.

General Procedure E. Preparation of Nonracemic Heterohelicenes 9 from Tetraesters 10. (*M*)-Azahelicenebisquinone 9c. MeLi in Et_2O (9.9 mL, 1.6 M, 7.1 mmol) was added to a solution of (*M*)-(−)-**10c** (0.43 g, 0.32 mmol) in THF (40.0 mL) that had been cooled to −78 °C in a dry ice/acetone bath. After several minutes, the bath was removed, and after the reaction mixture had warmed to room temperature, it was stirred for 1 h. Saturated aqueous NH_4Cl was added to quench the reaction. The mixture was then washed once with aqueous HCl (1 N) and twice with H_2O and dried (Na_2SO_4). Chloranil (0.260 g, 1.06 mmol) was added, and the reaction mixture was stirred for 15 min at room temperature, whereupon it turned from bright yellow to red/brown. After this mixture had been filtered, it was washed twice with $NaHCO_3$ and dried (Na_2SO_4). The solvent was stripped, and the dark solid was chromatographed (eluents from 1:1 hexanes/CH_2Cl_2 to CH_2Cl_2), giving (*M*)-**9c** (0.12 g, 63%), a red/purple solid (mp > 225 °C). UV−vis (CH_3CN, $c = 5.4 \times 10^{-5}$ M): λ_{max} (log ϵ) 500 (3.55), 420 (3.78), 350 (4.06), 340 (sh, 4.00), 305 (sh, 4.09), 260 nm (4.16). CD ($c = 5.4 \times 10^{-5}$, CH_3CN), nm ($\Delta\epsilon$): 217 (95), 253 (−105), 284 (47), 308 (−32), 330 (2), 352 (−29), 366 (−19), 389 (−26), 445 (5), 569 (−8). The same reaction conditions converted (*P*)-(+)-**10c** into (*P*)-**9c** (0.21 g, 85%). The ^1H and ^{13}C NMR spectra of (*M*)-**9c**, (*P*)-**9c**, and racemic **9c** were identical.

(*M*)-**9a**. Procedure E. MeLi in Et_2O (10.0 mL, 1.6 M, 6.3 mmol) was added to (*M*)-(−)-**10a** (0.33 g, 0.25 mmol) in THF (16 mL) at −78 °C. The mixture was warmed to room temperature for 1 h, and saturated aqueous NH_4Cl was added. Chloranil oxidation and chromatography gave (*M*)-**9a** (0.12 g, 80%), mp 225 °C. UV−vis (CH_3CN, $c = 5.4 \times 10^{-5}$ M), λ_{max} (log ϵ): 490 (3.77), 390 (3.68), 340 (4.17), 314 (4.19), 255 nm (4.26). CD ($c = 5.4 \times 10^{-5}$, CH_3CN), nm ($\Delta\epsilon$): 212 (98), 249 (−108), 271 (48), 288 (−44), 313 (48), 341 (−35), 358 (−18), 402 (−48), 487 (18). (*P*)-(+)-**10a** similarly gave (*P*)-**9a** (0.11 g,

87%), mp > 225 °C. The ^{1}H and ^{13}C NMR of (*M*)-**9a**, (*P*)-**9a**, and racemic **9a** were identical.

(*M*)-(−)-**9b**. Procedure E. *n*-BuLi in hexanes (2.0 mL, 2.6 M, 5.2 mmol) was added to (*M*)-(−)-**10b** (0.26 g, 0.19 mmol) in THF (15 mL) at −78 °C. After the reaction mixture had remained at −78 °C for 20 min, saturated aqueous NH_4Cl was added. Chloranil oxidation followed by silica gel chromatography gave (*M*)-(−)-**9b** (0.074 g, 65%), mp > 225 °C. $[\alpha]_D$ = −1300 (*c* 0.030, CH_2Cl_2); UV−vis (CH_3CN, $c = 5.4 \times 10^{-5}$ M), λ_{max} (log ϵ): 490 (3.61), 405 (3.85), 335 (4.08), 320 (4.07), 280 (sh, 4.21), 250 nm (4.23). CD ($c = 5.4 \times 10^{-5}$, CH_3CN), nm ($\Delta\epsilon$): 218 (71), 234 (71), 256 (−111), 283 (53), 303 (−41), 328 (−4), 347 (−41), 363 (−21). (*P*)-(+)-**10b** similarly gave (*P*)-(+)-**9b** (0.095 g, 75%), mp > 225 °C. $[\alpha]_D$ = +1350 (*c* 0.030, CH_2Cl_2). The ^{1}H and ^{13}C NMR spectra of (*M*)-(−)-**9b**, (*P*)-(+)-**9b**, and racemic **9b** were identical.

(*M*)-**9d**. Procedure E. MeLi in Et_2O (2.0 mL, 1.6M, 3.0 mmol) was added to (*M*)-(−)-**10d** (0.21 g, 0.12 mmol) in THF (14 mL) at −78 °C. The mixture was warmed to room temperature for 1 h, and saturated aqueous NH_4Cl was added. Chloranil oxidation and chromatography gave (*M*)-**9d** (0.11 g, 88%). UV−vis (CH_3CN, $c = 5.8 \times 10^{-5}$), λ_{max} (log ϵ): 500 (3.53), 420 (3.76), 350 (3.98), 335 (3.97), 305 (sh, 4.00), 260 nm (4.05). CD ($c = 5.8 \times 10^{-5}$, CH_3CN), nm ($\Delta\epsilon$): 216 (95), 253 (−109), 284 (46), 308 (−28), 330 (3), 352 (−28), 366 (−19), 389 (−25), 445 (7), 569 (−7). (*P*)-(+)-**10d** similarly gave (*P*)-**9d** (0.11 g, 84%). The ^{1}H and ^{13}C NMR of (*M*)-**9d**, (*P*)-**9d**, and racemic **9d** were identical.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra of **2a**−**d**, **3a**−**d**, **4a**−**d**, **5a**−**c**, **9a**−**d**, (*P*)-(+)-**10a**−**d**, and (*M*)-(−)-**10a**−**d**; IR spectra of **3c**, **4a**−**d**, **9a**−**d**, (*P*)-(+)-**10a**−**d**, and (*M*)-(−)-**10a**−**d**; UV spectra of **4a**−**c**, **5a**−**c**, (*P*)-**9a**−**d**, (*M*)-**9a**−**d**, (*P*)-(+)-**10a**−**d**, and (*M*)-(−)-**10a**−**d**; and CD spectra of (*P*)-**9a**−**d**, (*M*)-**9a**−**d**, (*P*)-(+)-**10a**−**d**, and (*M*)-(−)-**10a**−**d**. This material is available free of charge via the Internet at http://pubs.acs.org.

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