Non-Photochemical Route to Chiral Disubstituted [7]Thiaheterohelicenes via Biaryl- and Carbonyl-Coupling Reactions

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Received February 13, 1997[⊗]

Non-photochemical syntheses of optically active dimethyl[7]thiaheterohelicenes (*P*)-(+)-**14** and (*M*)-(−)-**14** are described. The key transformations in the syntheses are the metal-mediated biaryl coupling reactions between two benzodithiophene units having oxazoline moieties and the intramolecular McMurry coupling reaction of the biaryl dialdehydes (*S*)-**13** and (*R*)-**13**. The configuration of the atropisomer **10a** obtained from the biaryl coupling reaction was shown to be *S* by X-ray analysis.

Introduction

Chiral functionalized helicenes and their heterocyclic analogs are of considerable interest in both materials[1] and molecular recognition research[2] in view of their very high specific optical rotations and nonplanar π-electron structures.[3] In the synthesis of these overcrowded aromatic helices, the oxidative photocyclization of 1,2-diarylethylenes in the presence of I_2 or under oxygen atmosphere is a crucial step, but the process has several drawbacks and limitations:[4] (1) the reaction usually requires very dilute conditions, (2) the oxidative photocyclization reaction is not compatible with the presence of acid-sensitive functional groups because of generation of HI during dehydrogenation of the dihydro intermediates by I_2, and (3) olefins having nitro and amino functional groups cannot be employed because the singlet electronic state leading to the ring closure decays by an $S_1 \rightarrow T_1$ intersystem crossing.[4] These drawbacks restrict large-scale preparation of optically active helicenes containing functional groups. Several non-photochemical routes to helicene derivatives have been reported, including Friedel−Crafts acylation,[5] intramolecular oxidative cyclization,[6] the cyclization of ammonium salt or bis(phosphonium salt),[7] and acid- or base-catalyzed condensation reactions.[8−10] Katz and co-workers have reported a non-photochemical procedure based on a Diels−Alder reaction, in which they employed benzoquinone as a dienophile and bis(1-alkoxyethenyl)arenes as dienes for the construction of [5]- and [6]helicenebis(quinones).[11] These authors have recently succeeded in the preparation of chiral helical bisquinones by optical resolution of the Diels−Alder adduct with (−)-camphanoyl chloride. However, there is still a need for complementary methods that proceed under mild conditions and extend the range of application. We now wish to report a non-photochemical method for the synthesis of chiral disubstituted [7]thiaheterohelicenes using metal-mediated coupling reactions as the key synthetic steps.

Results and Discussion

Our initial route to racemic thiaheterohelicene **1a** was based on a photochemical process that utilized the Wittig reaction for the formation of a vinylene bridge between the two R^3 groups of functionalized benzodithiophene subunits such as **4d** and **4e** and the oxidative cyclization for the construction of a new aromatic ring at the R^2 positions of the resulting diarylethylene **2**[2e] (Scheme 1). The present non-photochemical route to chiral thia-

[⊗] Abstract published in *Advance ACS Abstracts,* June 1, 1997.

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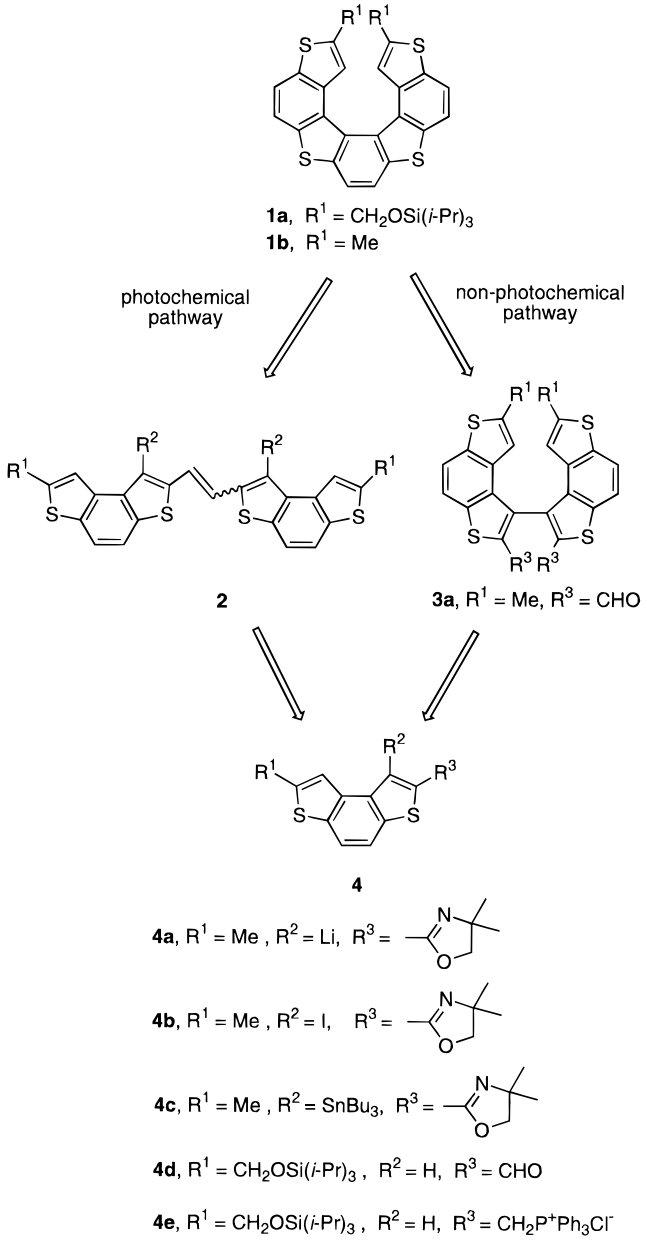
S0022-3263(97)00272-7 CCC: $14.00

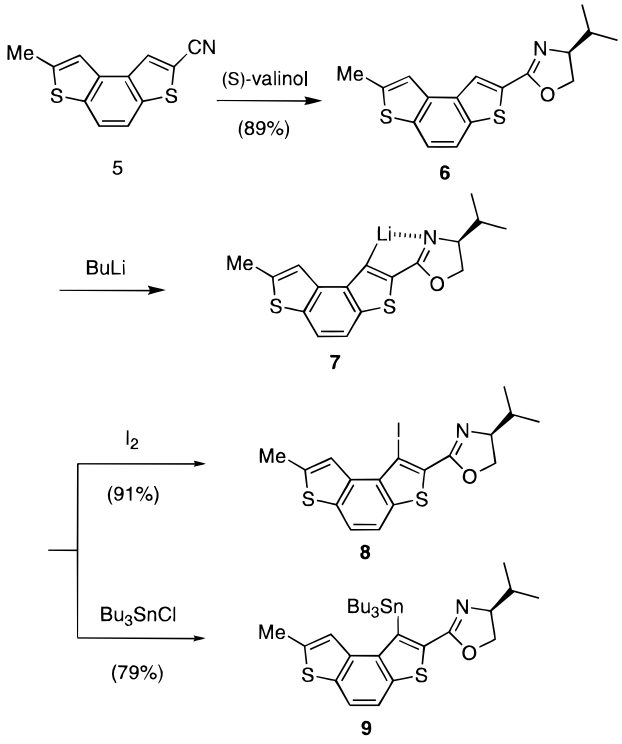
Scheme 1



heterohelicenes is based on our recent success[12] in obtaining the racemic helicene **1b** by metal-mediated biaryl coupling reactions between **4b** and **4c** and a McMurry coupling reaction of dialdehyde **3a**.

For intermolecular asymmetric biaryl coupling (Scheme 2), the chiral benzodithiophene subunit **6** was prepared in 89% yield from nitrile **5** and (*S*)-valinol, since the starting nitrile was readily obtained from 2-methyl[1,2-*b*:4,3-*b*′]dithiophene by lithiation with butyllithium, followed by reaction with I_2 and subsequent treatment with copper(I) cyanide in DMF (74% overall yield).[12] Treatment of **6** with excess butyllithium generated organolithium species[13] **7**, which upon treatment with I_2 gave **8** in 91% yield. The reaction of **7** with tributyltin chloride produced the corresponding stannane **9** in 79% yield. Since the protodestannylation occurred during the purification of **9** by chromatography on silica gel, the stannane was used without further purification. Copper(II)-mediated oxidative coupling[14] of **7** afforded the desired homocoupled biaryls **10a** and **10b** in 51% yield as an atropisomeric mixture of a 1:1.4 ratio[15] (Scheme 3 and Table 1).

Scheme 2



In contrast, intermolecular palladium-catalyzed biaryl coupling[16] of **8** and **9** afforded the atropisomers in 68% yield in a ratio of 2.9:1. When the iodide **8** was treated with activated copper powder[17,18] in DMF for 1 h, the yield of the atropisomers increased to 99% but the diastereoselectivity decreased to 2:1. Although the bis(oxazolines) **10** were not separable by silica gel column chromatography, crystallization of the atropisomeric mixture of a 2:1 ratio from hexane−EtOAc gave single crystals suitable for X-ray diffraction analysis.[19] An ORTEP drawing of the predominantly formed atropisomer **10a** with the labeling scheme is shown in Figure 1, and crystal data are listed in Table 2. The absolute configuration of the chiral axis of **10a** was determined to have an (*S*)-configuration. The dihedral angle between the two benzodithiophene subunits was 87.2°, which is very close to that of 1,1′-binaphthyl derivative (89.0°).[20]

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(15) The ratio of the diastereoisomers was determined by HPLC using a Shim-Pack CLC-SIL(M) column (hexane−2-propanol 100:1).

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(19) Recrystallization of the diastereomeric mixture of **10** from hexane−EtOAc gave the major diastereomer **10a** (>98% de) in 41% yield. The author has deposited atomic coordinates for **10a** with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 IEZ, UK.

(20) Miyano, S.; Okada, S.; Hotta, H.; Takeda, M.; Kabuto, C.; Hashimoto, H. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 1528.

Scheme 3

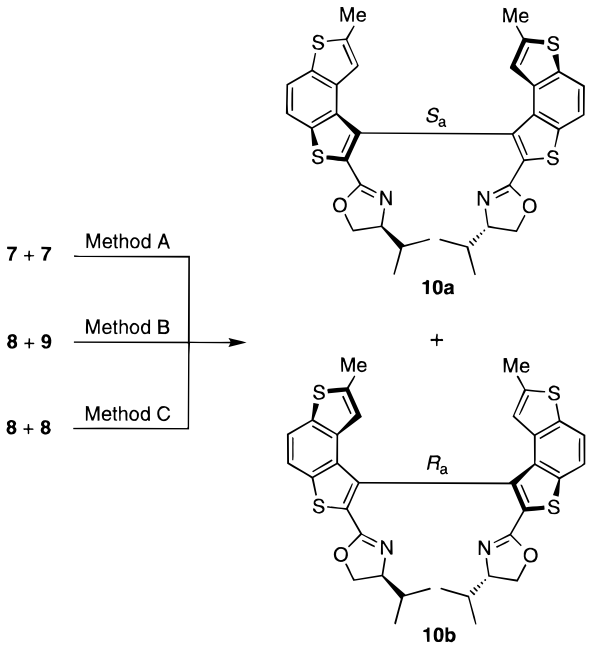

Table 1. Homocoupling and Cross-Coupling Reactions

compd		condns: method[a]	condns: metal	solvent	time (h)	T (°C)	yield (%)	product **10a**:**10b**
7	**7**	A	$CuCl_2$	ether	20	−78−0	51[b]	1:1.4
8	**9**	B	$PdCl_2(PPh_3)_2$	THF	24	65	68	2.9:1
8	**8**	C	Cu	DMF	1	100	99	2.0:1

[a] See Experimental Section. [b] 22% of **6** was isolated.

In order to examine whether the Ullman coupling of **8** proceeded in a thermodynamic or a kinetic controlled manner, the atropisomeric mixture of **10a** and **10b** in a 2:1 ratio was heated in the presence of copper powder at 100 °C for 60 h. The observed ratio (HPLC analysis)[15] was unchanged, but the yield decreased to 60%. These results rule out the atropisomerization of the biaryls **10** in the coupling and strongly support the mechanism involving asymmetric biaryl coupling. Although the mechanistic details of the atropdiastereoselectivity of the coupling are unclear at present, this provides a very useful method for the preparation of a new class of highly hindered C_2-symmetrical biaryls.

Opening of the bis(oxazolines) **10** with TFA followed by acetylation produced the amido esters **11**, which were readily separated by silica gel chromatography. Treatment of the pure atropisomer (S,S,S_a)-**11a** with $LiAlH_4$ gave the corresponding diol (*S*)-**12** in 86% yield with specific rotation $[\alpha]_D$ −48.6° (*c* 1.00, $CHCl_3$) (Scheme 4). The diol (*S*)-**12** was readily oxidized by PCC to afford dialdehyde (*S*)-**13** with specific rotation $[\alpha]_D$ −325° (*c* 1.01, $CHCl_3$). The absolute configurations of the chiral axes of (S,S,S_a)-**11a**, (*S*)-**12**, and (*S*)-**13** were ascertained by converting them to the known (*P*)-**14** helicene. The CD spectra of the *S*-enantiomer of **12** gave a negative first Cotton effect at around 330 nm and a positive second Cotton effect at around 310 nm, which are very similar to the CD spectrum of the (*S*)-enantiomer **13** (Figures 2 and 3). By a similar procedure, the enantiomeric dialdehyde (*R*)-**13** ($[\alpha]_D$ +320° (*c* 1.01, $CHCl_3$)) was obtained from (S,S,R_a)-**11b** via oxidation of the diol (*R*)-**12b** ($[\alpha]_D$ +49.3° (*c* 1.01, $CHCl_3$)). The CD spectra of the biaryl

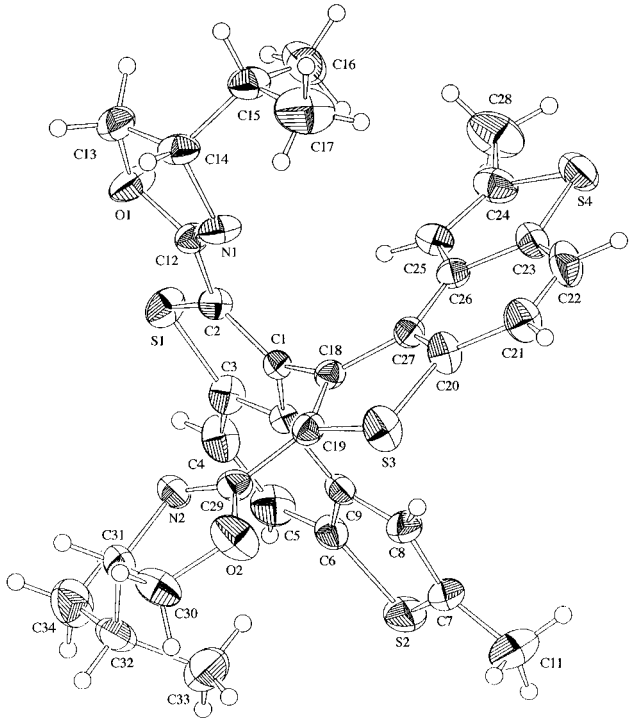

Figure 1. ORTEP drawing of **10a** showing the atom-numbering scheme and the stereoview. Thermal ellipsoids are drawn at the 30% probability level.

Table 2. X-ray Crystallgraphic Data for Atropisomer 10a

formula	$C_{34}H_{32}N_2O_2S_4$	Z	6
molecular wt	628.88	radiation	Cu Kα
space grp	$P6_5$ (#170)	2θ max, deg	120.2°
cell constant		no. of reflns measd	2987
a, Å	9.456(6)	no. of unique collcd	2506
c, Å	62.850(7)	no. of $I > 3.00\sigma(I)$	2111
V, Å^3	4866(6)	no. of variables	379
D_c, g cm^{-3}	1.287	*R*	0.045
μ, cm^{-1}	29.47	R_W	0.076

enantiomers **12** and **13** showed almost perfect mirror-image shapes.

The intramolecular McMurry coupling reaction[21] of (*S*)-**13** smoothly proceeded using $TiCl_3$·$DME_{1.5}$/Zn−Cu to give the desired helicene (*P*)-**14** in 52% yield. The optical purity of the helicene (*P*)-**14** was determined to be >99% ee by HPLC analysis using Chiralcel OD.[22] The high optical purity indicates that the configurational stability of **11**−**13** is very high; atropisomerization of these compounds was not observed during the course of the reaction. In a similar fashion, (*M*)-**14** with >99% ee was obtained in 53% yield by the carbonyl coupling reaction of (*R*)-**13**. These results demonstrated a complete transfer of the (*S*)-axial chirality of biaryls **10**−**13** into the (*P*)-helicity of the thiaheterohelicene **14** and the (*R*)-chirality of **10**−**13** into the (*M*)-helicity of **14** (Figure 4). The observed stereochemical correlation is closely parallel to the previous finding by Bestmann,[7] in which case the (*S*)-enantiomer of 2,2′-bis(bromomethyl)-1,1′-binaphthol is transformed into (*P*)-pentahelicene with >99% ee. It is interesting to note that the transformation of the axial chirality of (*S*)- and (*R*)-**13** into the helicity of (*P*)- and

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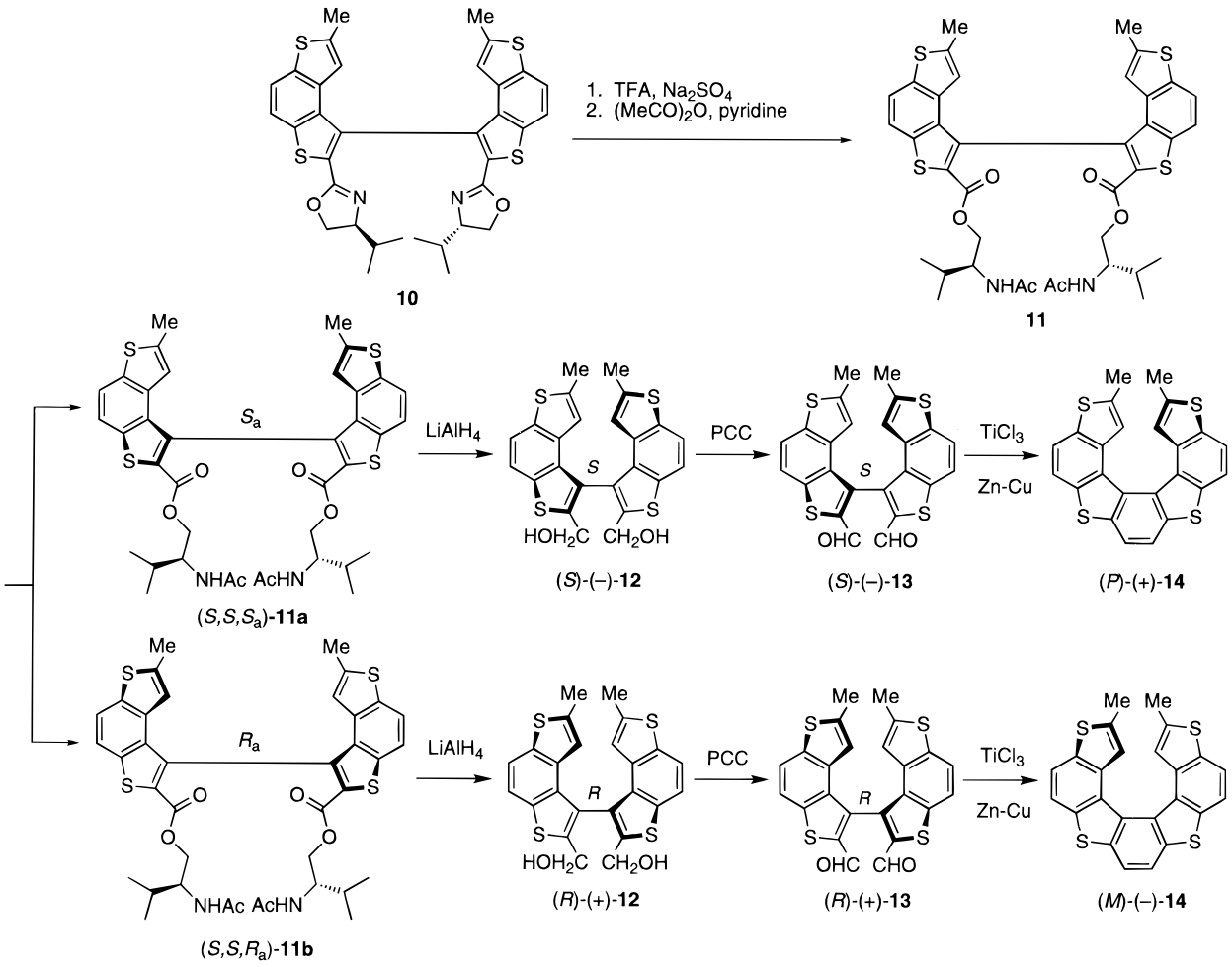
(22) The optical purities of the enantiomers were determined by HPLC using a Chiralcel OD column (hexane−EtOH 100:0.2).

Scheme 4



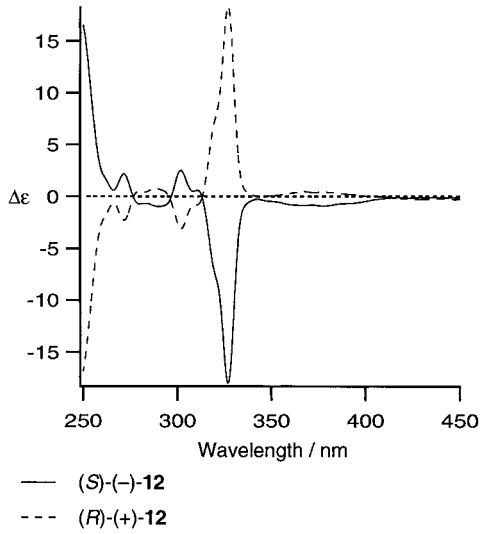


Figure 2. CD spectra of diol **12** in $CHCl_3$.

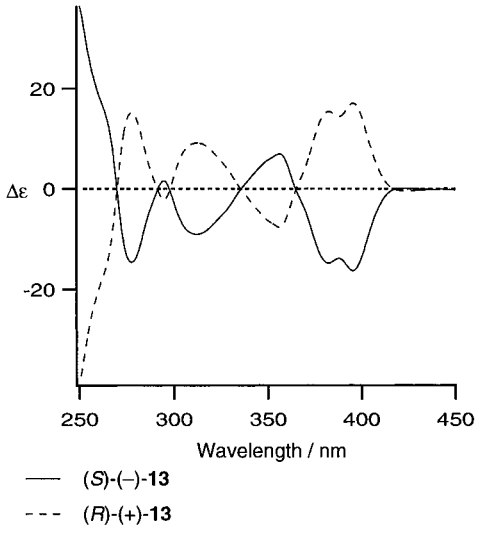


Figure 3. CD spectra of dialdehyde **13** in $CHCl_3$.

(*M*)-**14** increased their specific rotations to +2720° (*c* 0.0557, $CHCl_3$) and −2690° (*c* 0.0569, $CHCl_3$), respectively.

In summary, we have developed a practical synthesis of optically active dimethylthiaheterohelicenes **14** using asymmetric biaryl coupling reactions and the intramolecular McMurry coupling reaction as the key steps. The methyl groups of **14** can be easily converted to other functionalities such as the bromomethyl moiety,[23] and thus, **14** is useful for further synthetic studies. This method also provides a convenient approach to a new class of atropisomeric biaryl derivatives with C_2-symmetry such as **12** and **13**, which are expected to have broad applications in asymmetric reactions. Further work on the asymmetric synthesis of chiral heterohelicenes via enantio- and diastereoselective biaryl coupling reactions is in progress.

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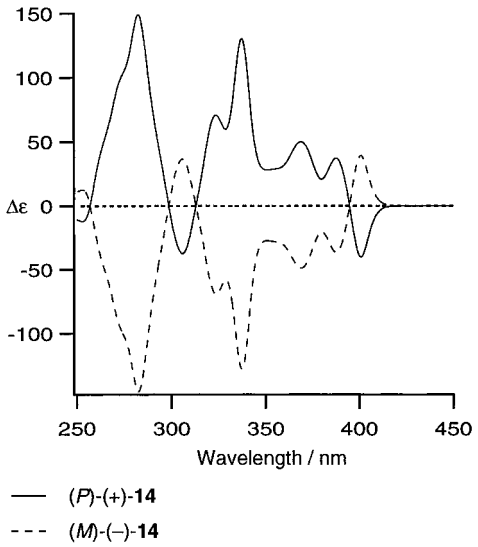

Figure 4. CD spectra of helicene **14** in $CHCl_3$.

Experimental Section

General Methods. All reactions were carried out under argon atmosphere. THF and ether were distilled under argon atmosphere from sodium benzophenone ketyl immediately before use. Benzene and CH_2Cl_2 were distilled from CaH_2 and stored over 4 Å molecular sieves. The hexane solution of BuLi (Kanto Chemicals) was titrated using diphenylacetic acid.[24] Optical rotation was measured in 1 dm lengths cells; $[\alpha]_D$ values are given in 10^{-1} deg·cm^2·g^{-1}. Silica gel (Wakogel) of the size 100−200 mesh was used for column chromatography.

(*S*)-2-(4-Isopropyloxazolin-2-yl)-7-methylbenzo[1,2-*b*:4,3-*b*′]dithiophene (6). In a 50 mL two-necked flask was heated $ZnCl_2$ (0.15 g, 11 mmol, 11 mol %) at 300 °C under high vacuum for 1 h and cooled. After the mixture was cooled to room temperature, **5** (2.29 g, 10 mmol), (*S*)-valinol (1.65 g, 16 mmol), and chlorobenzene (30 mL) were added. The mixture was heated under reflux for 12 h, and the solvent was removed under reduced pressure. The residue was dissolved in $CHCl_3$, and the solution was washed with dilute HCl, aqueous $NaHCO_3$, and brine and dried over Na_2SO_4. The solvent was evaporated, and the residue was recrystallized from hexane−EtOAc to give **6** as white needles (2.80 g, 89%): mp 138−139 °C; ^{1}H NMR ($CDCl_3$) δ 0.96 (d, J = 6.7 Hz, 3H), 1.06 (d, J = 6.7 Hz, 3H), 1.84−2.01 (m, 1H), 2.67 (d, J = 1.1 Hz, 3H), 4.10−4.26 (m, 2H), 4.40−4.55 (m, 1H), 7.34 (d, J = 1.1 Hz, 1H), 7.68 (d, J = 8.5 Hz, 1H), 7.75 (d, J = 8.5 Hz, 1H), 8.12 (s, 1H); IR (KBr) 1646, 1509, 1354 cm^{-1}. Anal. Calcd for $C_{17}H_{17}NOS_2$: C, 64.73; H, 5.43; N, 4.44. Found: C, 64.75; H, 5.50; N, 4.32.

(*S*)-1-Iodo-2-(4-isopropyloxazolin-2-yl)-7-methylbenzo[1,2-*b*:4,3-*b*′]dithiophene (8). To a stirred solution of **6** (1.58 g, 5.0 mmol) in dry ether (180 mL) was added BuLi (8.0 mmol, 5.0 mL of 1.60 M solution in hexane) at −78 °C, and the mixture was stirred for 1 h at −78 °C. To the resulting yellow suspension was added I_2 (2.03 g, 8.0 mmol) in ether (15 mL). The reaction mixture was allowed to warm to room temperature and stirred for 2 h. The reaction was quenched by saturated aqueous NH_4Cl. The organic phase was separated, washed with brine and aqueous Na_2SO_3, and dried over Na_2SO_4. The solvent was evaporated, and the residue was recrystallized from hexane−EtOAc to give **8** as white needles (2.01 g, 91%): mp 135−137 °C; ^{1}H NMR ($CDCl_3$) δ 1.00 (d, J = 6.7 Hz, 3H), 1.09 (d, J = 6.7 Hz, 3H), 1.85−2.04 (m, 1H), 2.71 (d, J = 1.1 Hz, 3H), 4.12−4.26 (m, 2H), 4.42−4.56 (m, 1H), 7.69 (d, J = 8.6 Hz, 1H), 7.81 (d, J = 8.6 Hz, 1H), 8.91 (d, J = 1.1 Hz, 1H); IR (KBr) 1636, 1493, 1061, 980 cm^{-1}. Anal. Calcd for $C_{17}H_{16}INOS_2$: C, 46.26; H, 3.65; N, 3.17. Found: C, 46.32; H, 3.66; N, 3.12.

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(*S*)-2-(4-Isopropyloxazolin-2-yl)-1-(tributylstannyl)-7-methylbenzo[1,2-*b*:4,3-*b*′]dithiophene (9). To a stirred solution of **6** (0.12 g, 0.37 mmol) in dry ether (30 mL) was added BuLi (0.56 mmol, 0.35 mL of 1.62 M solution in hexane) at −78 °C under argon, and the mixture was stirred for 1 h at −78 °C. To the resulting yellow suspension was added Bu_3SnCl (0.17 mL, 0.60 mmol) in ether (5 mL). The reaction mixture was allowed to warm to room temperature and stirred overnight. The reaction was quenched by saturated aqueous NH_4Cl. The organic phase was separated, washed with brine, and dried over Na_2SO_4. The solvent was evaporated, and the residue was purified by GPC using $CHCl_3$ as the eluent to give **9** as a pale yellow oil (0.18 g, 79%). NMR analysis of the crude product indicated that virtually pure product was formed, but the compound decomposed to starting material when it was purified by column chromatography (silica gel, hexane−EtOAc 10:1); therefore, an elemental analysis was not possible: ^{1}H NMR ($CDCl_3$) δ 0.79−1.95 (m, 34H), 2.65 (d, J = 1.1 Hz, 3H), 4.00−4.22 (m, 2H), 4.40−4.55 (m, 1H), 7.42 (d, J = 1.1 Hz, 1H), 7.70 (d, J = 8.7 Hz, 1H), 7.75 (d, J = 8.7 Hz, 1H).

2,2′-Bis(4-(*S*)-isopropyloxazol-2-yl)-7,7′-dimethyl-1,1′-bi[benzo[1,2-*b*:4,3-*b*′]dithiophene] (10). Method A (Coupling Reaction Catalyzed by $CuCl_2$). To a stirred solution of **6** (158 mg, 0.50 mmol) in dry ether (20 mL) was added BuLi (0.80 mmol, 0.50 mL of 1.60 M solution in hexane) at −78 °C, and the mixture was stirred for 2 h at −78 °C. To the resulting yellow suspension was added anhydrous $CuCl_2$ (0.20 g, 1.5 mmol). After being stirred for 2 h at −78 °C, the reaction mixture was allowed to warm to room temperature and stirred overnight. The reaction was quenched by saturated aqueous NH_4Cl. The organic phase was separated, washed with dilute HCl, aqueous Na_2CO_3, and brine, and dried over Na_2SO_4. The solvent was evaporated, and the residue was chromatographed on silica gel using hexane−EtOAc (5:1) to give **10** (79 mg, 51%) as a mixture of diasetereoisomers (1:1.4).

Method B (Stille Coupling). To a stirred solution of $PdCl_2(PPh_3)_2$ (20.5 mg, 29.2 μmol, 10 mol %) in dry THF (5 mL) were added **8** (129 mg, 0.292 mmol) and **9** (177 mg, 0.292 mmol), and the mixture was heated under reflux for 24 h. The reaction mixture was diluted with EtOAc, washed with brine, and dried over Na_2SO_4. The solvent was evaporated, and the residue was chromatographed on silica gel using hexane−EtOAc (5:1) to give **10** (124 mg, 68%) as a mixture of diastereoisomers (2.9:1).

Method C (Ullmann Coupling). To a stirred solution of **8** (1.33 g, 3 mmol) in dry DMF (15 mL) was added freshly activated copper powder (0.96 g, 15 mmol). The mixture was heated at 100 °C for 1 h. After cooling, the reaction mixture was diluted with ethyl acetate, washed with aqueous ammonia and brine, and dried over Na_2SO_4. The ratio of the diastereomer was determined as 2.0:1 by HPLC analysis. The solvent was evaporated, and the residue was recrystallized from hexane−EtOAc to give diastereomerically pure (>98% de) bisoxazoline **10a** as pale yellow crystals (0.39 g, 41%). The filtrate was concentrated *in vacuo*, and the residue was chromatographed on silica gel using hexane−EtOAc (5:1) to give **10** (0.55 g, 58%) as a mixture of diastereoisomers (1:1.4). **(*S*)-10**: mp 244−247 °C; ^{1}H NMR ($CDCl_3$) δ 0.69 (d, J = 6.7 Hz, 6H), 0.71 (d, J = 6.7 Hz, 6H), 1.48−1.69 (m, 2H), 2.26 (d, J = 1.1 Hz, 6H), 3.73−4.00 (m, 6H), 5.94 (br s, 2H), 7.77 (s, 4H); IR (KBr) 1640, 1350, 1229 cm^{-1}. Anal. Calcd for $C_{34}H_{32}N_2O_2S_4$: C, 64.94; H, 5.13; N, 4.45. Found: C, 64.99; H, 5.20; N, 4.42.

Bis(2-(*S*)-acetamido-3-methyl-1-butyl)-7,7′-dimethyl-1,1′-bi[benzo[1,2-*b*:4,3-*b*′]dithiophene]-2,2′-dicarboxylate (11). To a stirred solution of a diastereomeric mixture (1:1.4) of **10** (0.55 g, 0.88 mmol) in THF (20 mL) was added 1 mL of H_2O, Na_2SO_4 (11 g), and then TFA (2.2 mL, 28 mmol), and the suspension was stirred overnight at room temperature. After filtration, the solvent was removed under reduced pressure and dried *in vacuo*, and the resulting residue was dissolved in dry CH_2Cl_2 (20 mL). To the stirred solution were added pyridine (4 mL) and acetic anhydride (4 mL), and the mixture was stirred overnight at room temperature. The reaction mixture was washed with diluted HCl and brine and dried over Na_2SO_4. The solvent was evaporated to give **11**

(0.65 g, 99%). The diastereoisomer was chromatographed on silica gel using $CHCl_3$−EtOH (100:0.2) to give (*R*)-**11** (0.33 g 50%) and (*S*)-**11** (0.25 g, 38%) together with a small amount of unseparated mixture (0.05 g, 8%). (*S*)-**11**: mp 115−118 °C; ^{1}H NMR ($CDCl_3$) δ 0.23 (d, J = 6.6 Hz, 6H), 0.47 (d, J = 6.6 Hz, 6H), 0.82−0.92 (m, 2H), 1.26 (d, J = 2.4 Hz, 4H), 1.96 (d, J = 1.0 Hz, 6H), 2.33 (s, 6H), 3.41−3.53 (m, 2H), 3.95 (dd, J = 11.6, 2.6 Hz, 2H), 4.17 (dd, J = 11.6, 2.6 Hz, 2H), 4.67 (d, J = 9.5 Hz, 2H), 5.84 (d, J = 1.0 Hz, 2H), 7.86 (d, J = 8.7 Hz, 2H), 7.93 (d, J = 8.6 Hz, 2H); IR (KBr) 1699, 1653, 1289, 1229 cm^{-1}. Anal. Calcd for $C_{38}H_{40}N_2O_6S_4$: C, 60.94; H, 5.38; N, 3.74. Found: C, 60.76; H, 5.73; N, 3.52. (*R*)-**11**: mp 132−135 °C; ^{1}H NMR ($CDCl_3$) δ 0.59−0.75 (m, 12H), 0.83−0.92 (m, 2H), 1.26 (d, J = 2.4 Hz, 4H), 1.49 (d, J = 1.0 Hz, 6H), 2.32 (s, 6H), 3.51−3.63 (m, 2H), 4.00 (dd, J = 11.5, 3.0 Hz, 2H), 4.17 (dd, J = 11.5, 3.0 Hz, 2H), 4.22 (d, J = 9.5 Hz, 2H), 5.78 (d, J = 1.0 Hz, 2H), 7.86 (d, J = 8.6 Hz, 2H), 7.92 (d, J = 8.6 Hz, 2H); IR (KBr) 1701, 1655, 1291, 1229 cm^{-1}. Anal. Calcd for $C_{38}H_{40}N_2O_6S_4$: C, 60.94; H, 5.38; N, 3.74. Found: C, 61.48; H, 5.97; N, 3.46.

2,2′-Bis(hydroxymethyl)-7,7′-dimethyl-1,1′-bi[benzo[1,2-*b*:4,3-*b*′]-dithiophene] (12). To a stirred solution of **11** (0.19 g, 0.25 mmol) in THF (10 mL) was added $LiAlH_4$ (19 mg, 0.50 mmol) and the resulting mixture stirred for 1 h at room temperature. The reaction was quenched with diluted HCl at 0 °C and diluted with $CHCl_3$. The organic phase was separated, washed with brine, and dried over Na_2SO_4. The solvent was evaporated, and the residue was passed through a short column of silica gel using $CHCl_3$−MeOH (100:3) as the eluent. The solvent was evaporated, and the residue was recrystallized from hexane−EtOAc to give **12** as a white solid (0.10 g, 86%): mp 265−268 °C dec; ^{1}H NMR ($CDCl_3$) δ 2.27 (d, J = 1.1 Hz, 6H), 4.52 (d, J = 12.7 Hz, 2H), 4.61 (d, J = 12.7 Hz, 2H), 5.95 (br s, 2H), 7.75 (d, J = 8.5 Hz, 2H), 7.82 (d, J = 8.5 Hz, 2H); IR (KBr) 3260, 1398, 1125 cm^{-1}. Anal. Calcd for $C_{24}H_{18}O_2S_4$: C, 61.77; H, 3.89. Found: C, 61.64; H, 3.87. (*S*)-(−)-**12**: $[\alpha]_D$ −48.6° (*c* 1.00, $CHCl_3$). (*R*)-(+)-**12**: $[\alpha]_D$ +49.3° (*c* 1.01, $CHCl_3$).

2,2′-Diformyl-7,7′-dimethyl-1,1′-bi[benzo[1,2-*b*:4,3-*b*′]dithiophene] (13). To a stirred suspension of **12** (97 mg, 0.21 mmol) in dry CH_2Cl_2 (10 mL) was added PCC (134 mg, 0.62 mmol), and the mixture was stirred for 2 h at room temperature. After filtration, the reaction mixture was washed with aqueous Na_2CO_3 solution and brine and dried over Na_2SO_4. The solvent was evaporated, and the residue was recrystallized from $CHCl_3$ to give **13** as a yellow solid (81 mg, 85%): mp 280−281 °C; ^{1}H NMR ($CDCl_3$) δ 2.32 (d, J = 1.1 Hz, 6H), 5.96 (br s, 2H), 7.89 (d, J = 8.8 Hz, 2H), 7.96 (d, J = 8.5 Hz, 2H), 9.68 (s, 2H); IR (KBr) 1660, 1483, 1246 cm^{-1}. Anal. Calcd for $C_{24}H_{14}O_2S_4$: C, 62.31; H, 3.05. Found: C, 62.52; H, 3.00. (*S*)-(−)-**13**: $[\alpha]_D$ −325° (*c* 1.01, $CHCl_3$). (*R*)-(+)-**13**: $[\alpha]_D$ +320° (*c* 1.01, $CHCl_3$).

2,13-Dimethyldithieno[3,2-*c*:3′,2′-*c*′]benzo[1,2-*b*:4,3-*b*′]bis[1]benzothiophene (14). To a stirred suspension of $TiCl_3$·$DME_{1.5}$ (0.25 g, 0.86 mmol) in dry DME (15 mL) was added zinc−copper couple (0.17 g, 2.09 mmol), and the mixture was heated under reflux for 1 h. Dialdehyde **13** (50 mg, 0.108 mmol) in DME (5 mL) was added dropwise over a period of 2 h. The reaction mixture was heated under reflux for an additional 36 h. After cooling, the reaction mixture was diluted with $CHCl_3$ and filtered through a Celite pad. The filtrate was washed with H_2O and brine and dried over Na_2SO_4. The solvent was evaporated, and the residue was chromatographed on silica gel using hexane to give **14** (24.6 mg, 53%) as a yellow solid: mp 228−230 °C; ^{1}H NMR ($CDCl_3$) δ 2.14 (d, J = 1.1 Hz, 6H), 6.43 (br s, 2H), 7.85 (d, J = 8.4 Hz, 2H), 7.95 (d, J = 8.4 Hz, 2H), 7.98 (s, 2H); IR (KBr) 1125, 776, 519 cm^{-1}. Anal. Calcd for $C_{24}H_{14}S_4$: C, 66.94; H, 3.28. Found: C, 67.19; H, 3.27. (*P*)-(+)-**14**: $[\alpha]_D$ +2720° (*c* 0.0557, $CHCl_3$). (*M*)-(−)-**14**: $[\alpha]_D$ −2690° (*c* 0.0569, $CHCl_3$).

Acknowledgment. This work was supported by a Grant-in Aid for Scientific Research (No. 075580899) and by Grants-in-Aid for Scientific Research on Priority Areas (Nos. 07246225 and 08236222) from the Ministry of Education, Science, Sports and Culture and a Grant-in Aid for JSPS Fellows (Nos. 6-3089 and 9-2575).

JO970272T