Chiral Molecular Glass: Synthesis and Characterization of Enantiomerically Pure Thiophene-Based [7]Helicene

Makoto Miyasaka,[a] Andrzej Rajca,*[a] Maren Pink,[b] and Suchada Rajca[a]

Abstract: Synthesis of thiophene-based [7]helicenes, which are functionalized for both design of organic chiral glasses with strong chiroptical properties and for further homologation to higher [*n*]helicenes, is reported. The key synthetic transformations are kinetic resolution of the intermediate diketone and the annelation step forming the center benzene ring by means of an intramolecular McMurry reaction. Based upon X-ray crystallographic determinations of the absolute configurations for (+)-enantiomers of the diketone and the [7]helicene, stereochemical correlation between the (*R*) axial chirality of the diketone and the (*M*) helical chirality of the [7]helicene is established. One such enantiopure trimethylsilyl-substituted [7]helicene possesses enchanced chiroptical properties and forms a chiral molecular glass.

Keywords: chirality · helical structures · heterocycles · kinetic resolution · molecular glass · oligothiophenes

Introduction

[*n*]Helicenes are especially suitable building blocks for organic materials with extraordinary strong chiral, especially chiroptical, properties.[1] These chiral properties are greatly enhanced with increasing number (n) of *ortho*-annelated aromatic rings.[1] Although Newman's pioneering synthesis of enantiomerically pure (enantiopure) [6]helicene is nearly 50 years old,[2] more recent work of Katz and co-workers[3] led to a resurgence of interest in synthesis of functionalized [*n*]helicenes.[4–12] Nonphotochemical syntheses of enantiopure [*n*]helicenes with $n \leq 7$ have been reported.[3,5–10] Many of these asymmetric syntheses have been based on the resolution of the racemic derivatives with a chiral auxiliary.[3,10a] The development of a new asymmetric synthesis of enantiopure [*n*]helicenes, with adequate functionalization for both efficient homologation to extended helicenes and good solubility, is a challenge.

Recently, we reported iterative synthesis of carbon–sulfur [7]helicene **1**, a novel oligothiophene, which corresponds to a fragment of an intriguing $(C_2S)_n$ carbon–sulfur helix (Figure 1).[13,14] The asymmetric synthesis of **1** was developed and the syntheses of the higher homologues of **1** are in progress.[15] Anticipating solubility problems, especially for extended [*n*]helicenes, we designed a new building block, [7]helicene **2**, in which the center thiophene ring in **1** is replaced by a benzene ring functionalized with solubilizing alkyl chains (Figure 1).

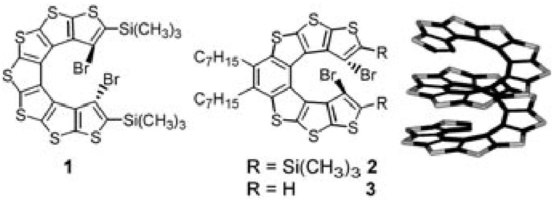


Figure 1. Carbon–sulfur helicenes **1**, **2**, **3**, and $(C_2S)_n$ helix.

We now report the synthesis of enantiopure [7]helicenes **2** and **3**, and their properties in the solid state. Notably, enantiopure **2** would not crystallize, but instead forms a rare chiral molecular glass.[16–18] This relatively unexplored phenomenon is important, because a significant part of applications for organic materials, especially involving optics and optoelectronics, requires strictly isotropic glasses.[17] One such emerging application involves chiral waveguides with novel polarization modes,[18] for which isotropic chiral glasses with enormous optical rotatory powers (optical rotations) are required.

---

[a] Dr. M. Miyasaka, Prof. A. Rajca, Dr. S. Rajca
Department of Chemistry, University of Nebraska
Lincoln, NE 68588–0304 (USA)
Fax: (+1) 402-471-9402
E-mail: arajca1@unl.edu

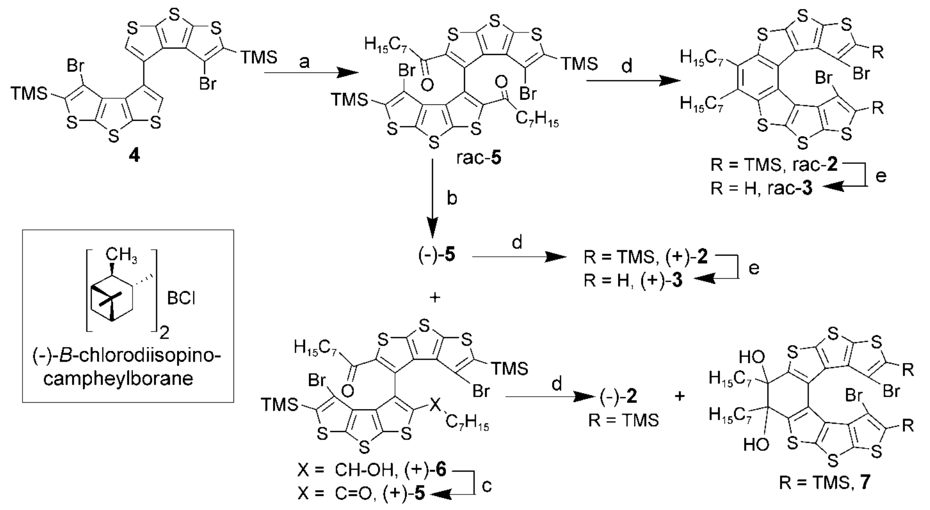
[b] Dr. M. Pink
IUMSC, Department of Chemistry, Indiana University
Bloomington, IN 47405 (USA)

Supporting information for this article is available on the WWW under http://www.chemeurj.org/ or from the author.

DOI: 10.1002/chem.200400635

Results and Discussion

The LDA-mediated dilithiation of **4**[13] at the unprotected α-positions was followed by addition of *N*-methoxy-*N*-methyloctanamide to provide racemic diketone (rac-**5**) in 54–65 % yield (Scheme 1).[19,20] By using (−)-*B*-chlorodiisopinocampheylborane,[21] kinetic resolution of rac-**5** was carried out till approximately 50 % conversion to alcohol **6** was achieved (~3 days at 45–50 °C). The unreacted diketone (−)-**5** was isolated in ~40 % yield. Oxidation of alcohol (+)-**6** with PCC gave diketone (+)-**5** in 80–92 % yield (or ~40 % yield based upon rac-**5**). Enantiomeric excess (*ee*) for both (−)-**5** and (+)-**5** was in the 70–80 % *ee* range, as determined by HPLC analysis. Treatment of enantiomerically enriched (+)-**5** ($[\alpha]_D^{RT}=+91$) with diethyl ether gave enantiopure diketone (+)-**5** ($[\alpha]_D^{RT}=+134$, 99+ % *ee*) in 21 % yield (based upon alcohol **6**), as a diethyl ether soluble fraction.



Scheme 1. Reagents and conditions: a) LDA, diethyl ether, *N*-methoxy-*N*-methyloctanamide, 54–65 %; b) (−)-*B*-chlorodiisopinocampheylborane, diethyl ether, 40 % (for (−)-**5** with 70–80 % *ee*), 40 % (for (+)-**6** with 70–80 % *ee*); c) PCC, CH_2Cl_2, 80–92 %; d) $TiCl_3$, Zn, DME, 38 % (for rac-**2** from rac-**5**), 17–63 % (for (+)-**2** with ~50–90 % *ee* from (−)-**5** with 71–91 % *ee*), ~28 % [for (−)-**2** with ~74 % *ee* (NMR) from (+)-**5** with 56 % *ee*]; e) TFA, chloroform, 94 % (for rac-**3**).

The intramolecular McMurry reaction of diketone **5**, using $TiCl_3$/Zn/DME (instant method), gave the target [7]helicene **2** in 17–63 % yield (Scheme 1).[22–24] The wide range of the isolated yields for **2** is associated with the formation of diol **7** (and its de-silylated derivatives); in particular, the *trans* isomer of **7** is expected to be unreactive toward the deoxygenation to the corresponding "olefin", that is, [7]helicene **2**.[22] The ^{1}H NMR analyses of the crude reaction mixtures suggest that the overall yield for the ring closure (**2** + **7**) is nearly constant (70–80 %); however, the relative content of **2** versus **7** has a wide distribution (Table 1s, Supporting Information).

Fractional crystallization of enantiomerically enriched **2** from isopropanol/ether gave pure enantiomers; for example, (+)-**2** with ~50 % *ee* gives (+)-**2** with 99 % *ee* ($[\alpha]_D^{RT}=+1166$) in nearly quantitative yield (or 19 % yield based upon diketone **5**). Deprotection of the TMS group gave [7]helicene **3** (Scheme 1).

The structures of rac-**2**, (+)-**3**, rac-**3**, (+)-**5**, and rac-**5** were confirmed by the X-ray crystallographic analyses (Table 1 and Figure 2).[25]

Excluding different conformations and crystallographic disorder of the alkyl chains, the molecules in all five crystals show approximate C_2 symmetry. Determinations of the absolute configurations for diketone (+)-**5** and [7]helicene (+)-**3** indicate the *R* axial and *P* helical chiralities, respectively. Therefore, stereochemical correlation between *R* axial and *M* helical chiralities is established, as the starting diketone and the product [7]helicene in the McMurry reaction have the opposite signs for their values of $[\alpha]_D^{RT}$.[26] Also, the positive sign of $[\alpha]_D^{RT}$ is usually found for *P* [*n*]helicenes.[1]

For both racemic and enantiopure diketone **5**, the dithienothiophene units, consisting of three annelated thiophene rings, are approximately planar.[27] The bis(dithienothiophene) moiety of rac-**5** adopts a transoid conformation with the dihedral (interplanar) angle of 96.0° between the dithienothiophene units. The analogous interplanar angles for the five unique molecules in the asymmetric unit of (+)-**5** are 100.4, 100.3, 99.3, 88.9, and 85.9°, indicating a significant degree of flexibility between *transoid* and *cisoid* conformations.[28]

The crystal of rac-**3**, which was selected for the X-ray crystallographic analysis, was found to be essentially identical to that of (+)-**3** (Table 1), except for its *M* helical chirality. This indicates that crystals of rac-**3**, which are obtained from isopropanol/benzene, correspond to a conglomerate, that is, each enantiomer crystallizes separately.[29]

[7]Helicenes **1**, **2**, and **3** possess similar but not identical helical structures.[13] The individual benzene and thiophene rings are approximately planar with mean deviations of the least-square planes between 0.01 and 0.06 Å. The angles between the least-square planes of neighboring rings are in the ranges 7.9–11.2°, 6.8–11.2°, and 9.9–12.7° for **1**, rac-**2**, and (+)-**3**, respectively; with the middle ring as a reference, the corresponding inner helix climbs are 2.92 (for **1**), 3.15 (C1–C17 for rac-**2**), and 3.52 Å (C2–C17 for (+)-**3**). Interplanar angles between the terminal thiophene rings are 54.1, 40.2, and 59.1° for **1**, rac-**2**, and (+)-**3**, respectively. Compared to the all-thiophene [7]helicene **1**, the replacement of the center thiophene ring in **1** with the benzene ring in rac-**2** and (+)-**3** increases the climb of the helix, as expected; surprisingly, the effect of the trimethylsilyl versus hydrogen substitution at the terminal α-positions of the [7]helicene rac-**2** versus (+)-**3** appears to be quite substantial, though it is not clear to what extent these structural differences may be induced by the crystal packing.

Table 1. Summary of the X-ray crystallographic data for **2**, **3**, and **5**.

	rac-**2**	(+)-**3**	rac-**3**	(+)-**5**	rac-**5**
formula	$C_{38}H_{48}Br_2S_6Si_2$	$C_{32}H_{32}Br_2S_6$	$C_{32}H_{32}Br_2S_6$	$C_{38}H_{48}Br_2O_2S_6Si_2$	$C_{38}H_{48}Br_2O_2S_6Si_2$
M_r	913.12	768.76	768.76	945.12	945.12
T [K]	130(2)	173(2)	173(2)	120(2)	133(2)
crystal size [mm^3]	$0.22\times0.17\times0.03$	$0.100\times0.012\times0.008$	$0.12\times0.01\times0.008$	$0.15\times0.13\times0.10$	$0.20\times0.10\times0.08$
crystal shape	colorless plate	colorless needle	colorless needle	colorless block	colorless plate
crystal system	monoclinic	orthorhombic	orthorhombic	monoclinic	triclinic
space group	$C2/c$	$P2_12_12_1$	$P2_12_12_1$	$P2_1$	$P\bar{1}$
a [Å]	33.599(4)	8.2267(10)	8.2472(9)	19.504(4)	13.2328(6)
b [Å]	14.7475(17)	14.142(2)	14.0368(15)	27.050(6)	14.1097(6)
c [Å]	19.925(2)	27.841(13)	27.583(3)	20.928(4)	14.4864(6)
α [°]	90	90	90	90	114.866(1)
β [°]	122.005(2)	90	90	92.364(6)	107.842(1)
γ [°]	90	90	90	90	102.969(1)
V [Å^3]	8372.5(17)	3239.0(16)	3193.2(6)	11032(4)	2131.64(16)
Z	8	4	4	10	2
ρ_{calcd} [g cm^{-3}]	1.449	1.576	1.599	1.423	1.472
$2\theta_{max}$ [°]	55	36.40	36.96	53	55
radiation	$Mo_{K\alpha}$	synchrotron	synchrotron	$Mo_{K\alpha}$	$Mo_{K\alpha}$
λ [Å]	0.71073	0.559408	0.559408	0.71073	0.71073
μ [mm^{-1}]	2.320	1.551	1.573	2.207	2.284
max/min transmission	0.9337/0.6293	0.9877/0.8603	0.9875/0.8585	0.8095/0.7331	0.8384/0.6580
collected reflns	56022	17373	39047	75017	32322
independent reflns	9637 ($R_{int}=0.0747$)	4648 ($R_{int}=0.1887$)	4809 ($R_{int}=0.1076$)	45027 ($R_{int}=0.0616$)	9778 ($R_{int}=0.0401$)
observed reflns [$I>2\sigma(I)$]	7333	4501	4478	34666	7764
data/restraints/parameters	9637/0/489	4648/9/370	4809/0/363	45027/196/2345	9778/0/459
GOF on $\lvert F^2\rvert$ (all data)	1.010	1.118	1.216	0.989	1.013
R_1/wR_2 [$I>2\sigma(I)$]	0.0323/0.0680	0.0563/0.1312	0.0324/0.0939	0.0525/0.1116	0.0330/0.0737
R_1/wR_2 (all data)	0.0544/0.0759	0.0598/0.1476	0.0388/0.1137	0.0762/0.1198	0.0479/0.0807
Flack parameter	–	0.030(17)	0.077(15)	0.009(4)	–
residual peak/hole [e Å^{-3}]	0.890/−0.421	0.684/−2.225	0.947/−0.825	1.229/−0.540	0.757/−0.322

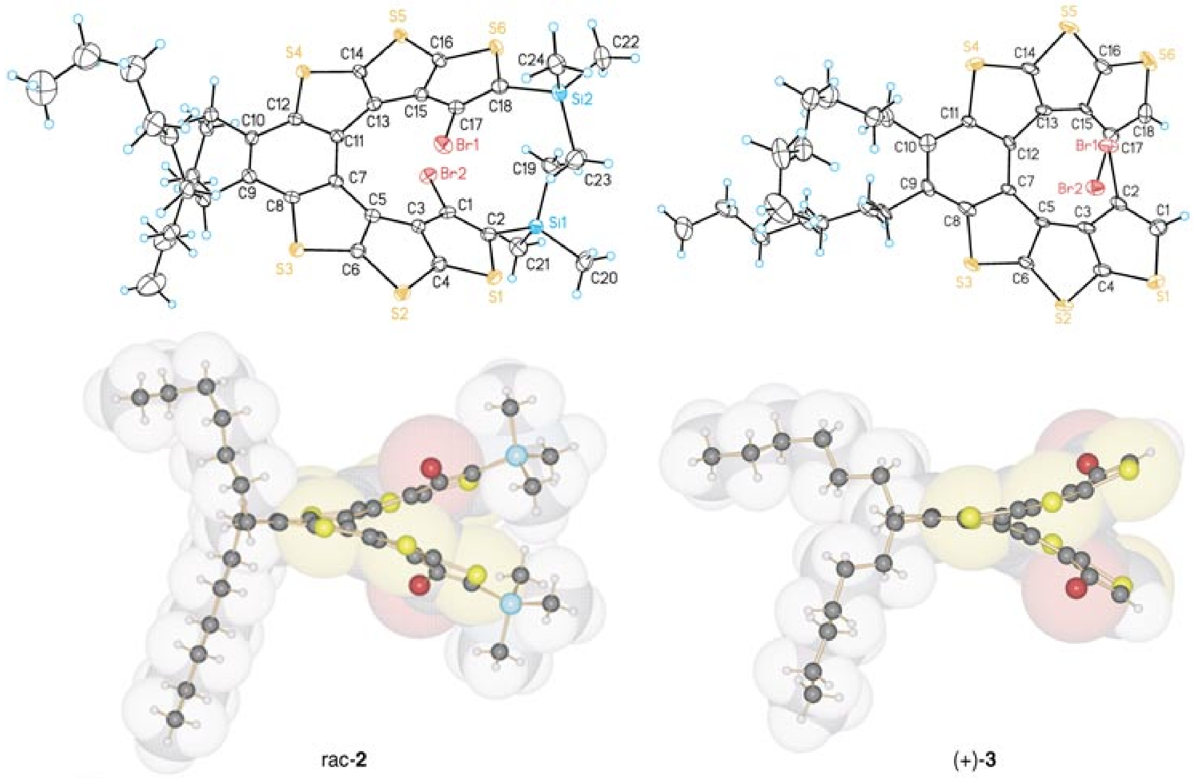


Figure 2. Molecular structure and conformation for [7]helicenes rac-**2** (left plots) and (+)-**3** (right plots).[25a] (Structure of rac-**3** is not shown.) Atom numbering and disorder for the C_7-alkyl chains are omitted for clarity. In the Ortep plots, all atoms, except for the hydrogen atoms are depicted with thermal ellipsoids set at the 50% probability level.

The electronic absorption (UV-visible) and circular dichroism (CD) spectra for (+)-**2** and (+)-**3** in cyclohexane show similar spectral patterns characteristic of helicenes (Figure 3).[1,30,31] However, the spectra for (+)-**2** are significantly more intense and somewhat red-shifted relative to those of (+)-**3**. Consequently, the specific rotation ($[\alpha]_D^{RT}$) and especially molar rotation ($[\Phi]_D^{RT}$) are significantly greater for (+)-**2** than those for (+)-**3**.[31]

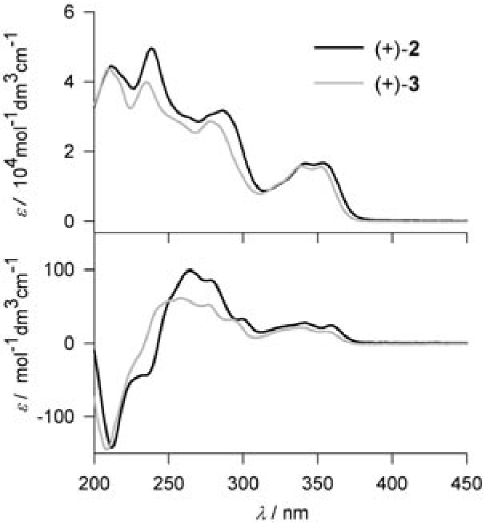


Figure 3. Electronic absorption (top plot) and circular dichroism (bottom plot) spectra of (+)-**2** and (+)-**3** in cyclohexane at room temperature.

Differential scanning calorimetric (DSC) analyses of racemic and enantiopure helicenes **2** and **3** are plotted in Figure 4. Notably, (+)-**2** helicene shows only a broad shoulder that may correspond to a glass-like endothermic transition ($\Delta H = 3$–$4\,\mathrm{kJ\,mol^{-1}}$) with an onset at 61 ± 1 °C. This is in contrast to its racemic counterpart, in which a melting-like endothermic transition is observed; in fact both the enthalpy of fusion ($\Delta H = 34 \pm 1\,\mathrm{kJ\,mol^{-1}}$) and the temperature of fusion (onset at 161 ± 2 °C and peak at 165 ± 1 °C) are much higher relative to those for (+)-**2**. Also, melting-like endothermic transitions are observed for both enantiomer and racemate of [7]helicene **3**; the corresponding onset temperatures are 138 ± 2 °C ($\Delta H = 30 \pm 1\,\mathrm{kJ\,mol^{-1}}$) and 136 ± 1 °C ($\Delta H = 37 \pm 1\,\mathrm{kJ\,mol^{-1}}$).[32,33]

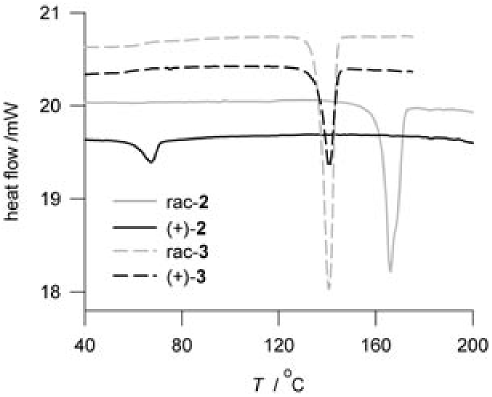


Figure 4. Plots of differential scanning calorimetry (DSC) data for [7]helicenes **2** and **3**.

The glassy behavior may in principle be associated with inefficient packing of molecules. It is well known that among the 230 crystallographic space groups, only 65 space groups are compatible with enantiopure molecules. In particular, the absence of the inversion centers and/or glide planes, which are precluded for crystals of enantiopure molecules, may lead to unfavorable interactions from juxtaposed polar groups.[34] For small, achiral organic molecules, the difficulty in crystallization may typically be associated with rigid, "tetrahedral-like" shapes.[16] Both compounds **2** and **3** adopt four-armed chiral shapes (including "flexible" alkyl groups) in the crystals (Figure 2); possibly, with the trimethylsilyl groups, the shape of **2** approaches closer to a tetrahedral-like structure. These minute molecular-shape differences lead to different crystal packings of rac-**2** and **3**, and might contribute to glass-like behavior of enantiopure **2**.

In the crystal of rac-**2**, homochiral [7]helicene molecules form π-stacked columns along the *b* axis; the unit cell contains four such stacks (Figure 5). Consecutive molecules within the stack are rotated around their helical axes, leading to strong π overlap between the two terminal thiophene rings for the nearest neighbor molecules; for example, each [7]helicene molecule possesses six short S···S contacts (S2···S6 = 3.58, S1···S5 = 3.60, S2···S5 = 3.60 Å, and their symmetry related counterparts) with its two homochiral neighbors within the stack. Along the *a* axis, inefficient packing of the alkyl groups from the homochiral columns leads to voids (282 Å^3 or about 3 % of the cell volume) with no significant electron density. The columns of opposite handedness are closely packed along the *c* axis; each [7]helicene possesses two contacts (S3···S6 = S6···S3 = 3.63 Å) with its two heterochiral neighbors.

In the crystal of (+)-**3** (or conglomerate), homochiral [7]helicene molecules form herringbone-like chains along the *b* axis; each molecule has six short S···S (3.585 Å), S···C (3.396 Å), and Br···Br (3.623 Å) contacts with its two nearest neighbors. Along the *c* axis, multiple short contacts (S···alkyl group) between the herringbone-like chains are found. The molecules that are related by the translation along the *a* axis may be viewed as loosely π-stacked (with shortest S···S contacts of 3.96 Å).

Conclusion

A synthesis of enantiopure, highly functionalized thiophene-based [7]helicenes has been developed. The functionalization with both solubilizing heptyl groups at the center benzene ring and bromine atoms at the β-positions of the terminal thiophene rings should facilitate the synthesis of the extended, enantiopure [*n*]helicenes. Enantiopure **3**, a possible starting material for such a synthesis, should be relatively accessible because of the conglomerate behavior for rac-**3**. The trimethylsilyl groups in enantiopure **2** both enhance the chiroptical properties and induce glass-like behavior.[35]

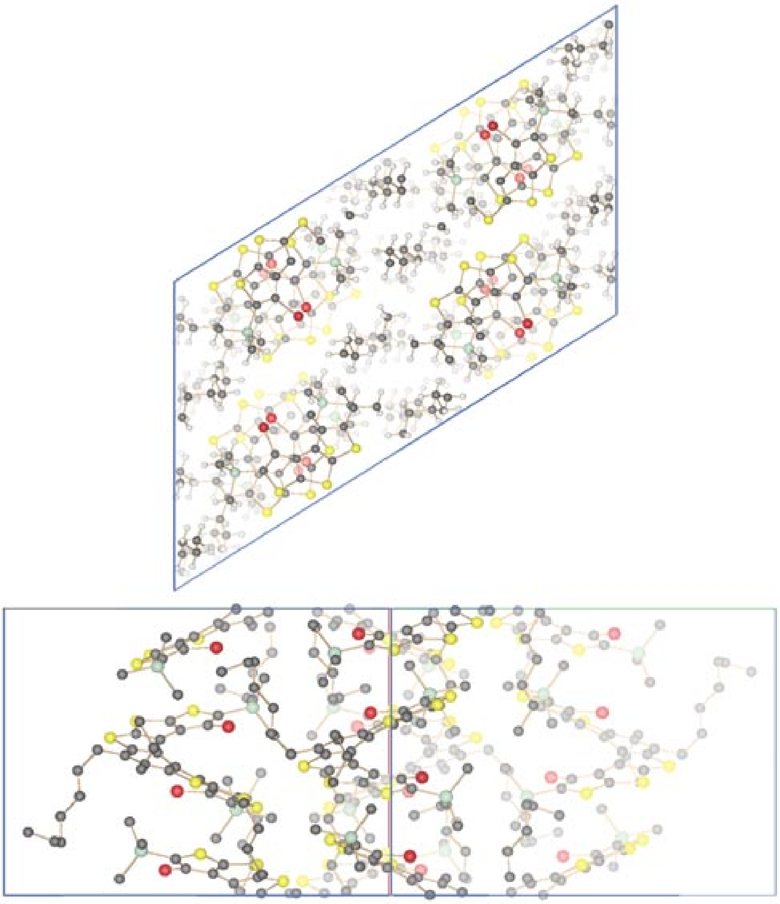


Figure 5. Unit cells showing molecular packing of [7]helicene rac-**2**: view along (top plot) and normal (bottom plot with hydrogen atoms omitted for clarity) to the crystallographic *b* axis. The fading correlates with the depth of the three-dimensional structures.

Experimental Section

UV-visible electronic absorption and CD spectroscopy: Concurrent electronic absorption (UV-visible) and circular dichroism (CD) spectra were recorded at ambient temperature on a Shimadzu (UV-2401PC) spectrometer and a Jasco (J-810) spectropolarimeter, respectively. Typically, 1 mm path length quartz cells were used. UV-visible Lambert–Beer plots for [7]helicenes (+)-**2** and (+)-**3** in cyclohexane were obtained by using five concentrations ($c = \sim 2\times10^{-5}$–2×10^{-4} M, $R = 0.999$). The four out of five most concentrated solutions were used to obtain CD spectra; the values of $\Delta\varepsilon_{max}$ were calculated by using corrected concentrations based upon Lambert–Beer plots ($R = 0.999$). For each [7]helicene, two samples were examined.

Determination of enantiomeric excess (*ee*): The *ee*'s were determined by HPLC. In addition, for selected samples of [7]helicene **3**, ^{1}H NMR spectroscopy with chiral shift agents was utilized.[36] HPLC was carried out on Waters 600 and Waters 486 (Tunable Absorbance Detector, $\lambda = 254$ nm) instruments equipped with a CHIRALPAK® AD-H [250×4.6 mm (*l*× inner diameter)] column. For the diketone and the [7]helicenes, hexane/isopropanol (95:5, v/v) and hexane were used, respectively. The flow rate was 1.0 mL min^{-1}.

Differential scanning calorimetry (DSC): Perkin–Elmer DSC7 along with TAC 7/DX as a thermal analysis control was used. Before measurement, the sample chamber was cleaned, by means of a baking procedure (heat at 100 °C min^{-1} up to 600 °C, stay at 600 °C for 7 min, and return to ambient temperature). Indium (0.248 mg) was measured as a standard calibration (onset: 156.60 °C, $\Delta H = 28.45$ J g^{-1}), by using the same parameters as for the sample measurement under nitrogen (e.g., heating rate: 20 °C min^{-1}, monitoring range: 30–200 °C). The [7]helicenes (0.480–1.296 mg) were compressed in standard aluminum pans (Perkin–Elmer). Following the DSC measurements, melting points (in melting point apparatus) were re-checked; the remainder of the sample was examined by ^{1}H NMR ([D]chloroform) spectroscopy. For enantiopure samples, the *ee* was re-checked by HPLC, as described in the preceding section; no racemization was detected.

X-ray crystallography: Crystals were obtained by slow evaporation of solvent at ambient temperature. Th following solvents were used (compound, sample label): benzene/isopropanol 1:1 (diketone rac-**5**, MM-2-75-cryst1), methanol (diketone (+)-**5**, MM-7-51-cryst2), isopropanol, (rac-**2**, MM-6-43+45-cryst1), benzene/isopropanol, 1:1 (rac-**3**, MM-6-90-wash-cryst1), heptane/diethyl ether, 9/1 ((+)-**3**, MM-6-94-TP-cryst2).

The data were collected on a Bruker SMART6000 system at the Indiana University and at beamline 15ID, ChemMatCARS, at the Advanced Photon Source, Argonne National Laboratory in Chicago. For the data collection, single crystals were placed onto the tip of a 0.1 mm diameter glass capillary.

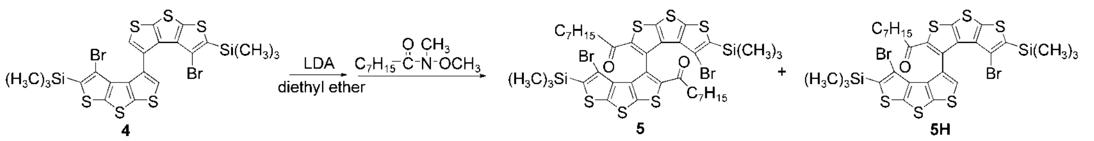
Structures of rac-2, (+)-5, and rac-5: The data collections with $Mo_{K\alpha}$ radiation (graphite monochromator) were carried out with a frame time of 20 s and a detector distance of 5.0 or 5.1 cm. A randomly oriented region of a sphere in reciprocal space was surveyed. Four major sections of frames were collected with 0.30° steps in ω at different φ settings and a detector position of −43° in 2θ. An additional set of 50 frames was collected in order to model decay (for rac-**2** and rac-**5**). Data to a resolution of 0.77 Å (for rac-**2** and rac-**5**) 0.84 Å (for (+)-**5**) were considered in the reduction. Final cell constants were calculated from the *xyz* centroids of strong reflections from the actual data collection after integration (SAINT 6.1[37a]). The intensity data were corrected for absorption (SADABS[37b]).

Structures of (+)-3 and rac-3: Analogous procedures were used for the data collection using synchrotron radiation (wavelength of 0.55000 Å, energy of 22.0 keV, diamond 111 monochromator, two mirrors to exclude higher harmonics) with a frame time of 2 s and a detector distance of 5.5 cm. A hemisphere in reciprocal space was surveyed. Frames were collected with 0.50° steps in ω and φ at 0° and 90°, and with 0.50° steps in φ and ω at 0°; for all three sets 2θ remained at 0°. For accurate atom form factors, the wavelength of 0.559408 Å, corresponding to $Ag_{K\alpha}$ radiation, was used in refinements.

The space groups were determined based on intensity statistics and systematic absences. The structures were solved using SHELXS-97 (or SIR92[38a]) and refined with SHELXL-97 (SHELXTL-Plus V5.10,[38b]). Direct-methods solutions were calculated, which provided most non-hydrogen atoms from the E-maps. Full-matrix least-squares/difference Fourier cycles were performed, which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. Additional crystal and refinement information is summarized in Table 1.

General: In the MS data, 3-NBA = 3-nitrobenzyl alcohol and % RA is % relative amplitude.

Diketone rac-5: *n*BuLi (2.23 M, 1.6 mL, 3.57 mmol) was added drop-wise to diisopropylamine (0.52 mL, 3.71 mmol) in diethyl ether (6.4 mL) at



0°C ($[c]_{\mathrm{LDA}}=0.419$ M). The solution of LDA (2.8 equiv, 6.76 mL, 2.831 mmol) was added to a suspension of compound **4** (700.4 mg, 1.011 mmol) in diethyl ether (210 mL). The nearly homogenous reaction mixture was stirred for 3.5 h at 0°C (pale yellow-orange), and then *N*-methoxy-*N*-methyloctanamide (0.71 mL, 3.033 mmol, 3 equiv) was added dropwise (neat or as solution in diethyl ether) at −78°C. After 3 h at −78°C, the reaction mixture was warmed up to room temperature for overnight, resulting in a pale yellow, clear solution. The usual aqueous workup with diethyl ether gave the crude product as an orange viscous liquid/oil. Column chromatography (silica, hexane/benzene, 1:1, v/v) gave the three fractions: F1, starting material **4** ($R_f=0.91$); F2, monoketone side product **5H** ($R_f=0.66$, Supporting Information); F3, diketone rac-**5** ($R_f=0.41$).

From three reactions on 700, 300, and 300 mg scales (labels: MM-5-21, -26, and -46), 1.129 g (64%) of diketone rac-**5**, 0.2978 g (19%) of monoketone **5H**, and 75.8 mg (6%) of **4** were obtained from 1.301 g of starting material **4**. The other three reactions on 50 mg scales with the solution of *N*-methoxy-*N*-methyloctanamide in diethyl ether, 125.6 mg (54–65%) of diketone, 45.8 mg (21–28%) of monoketone **5H**, and 9.9 mg (5–8%) of **4** were obtained from 150.6 mg of starting material **4**.

Data for rac-5: M.p. = 146–147°C; ^{1}H NMR (500 MHz, [D]chloroform): $\delta=2.33$–2.18 (m, 4H), 1.48–1.34 (m, 4H), 1.156 (quintet $J=6.8$ Hz, 4H), 1.052 (quintet $J=7.2$ Hz, 4H), 1.03–0.85 (m, 8H), 0.814 (t, $J=7.2$ Hz, 6H), 0.322 ppm (s, 18H); ^{13}C{^{1}H} NMR (100 MHz, [D]chloroform): $\delta=$ 193.6 (C=O), 146.3, 145.7, 144.8, 140.3, 139.1, 138.8, 132.1, 108.5, 40.1, 31.5, 29.0, 28.7, 24.3, 22.6, 14.1, −0.89 ppm ($J(^{29}\mathrm{Si},^{13}\mathrm{C})=54$ Hz); IR: $\tilde{\nu}=$ 2953, 2925, 2854 (C−H), 1649 cm^{-1} (C=O); LR/HR FABMS (3-NBA matrix): *m/z* (% RA for *m/z* = 700–2000, deviation for the formula): 945.9899 $[M+4]^+$ (67, −5.9 ppm for $^{12}C_{38}{}^{1}H_{48}O_{2}{}^{28}Si_{2}{}^{32}S_{6}{}^{81}Br_{2}$), 943.9883 $[M+2]^+$ (48, −2.1 ppm for $^{12}C_{38}{}^{1}H_{48}O_{2}{}^{28}Si_{2}{}^{32}S_{6}{}^{79}Br{}^{81}Br$), 941.9846 $[M]^+$ (14, 4.0 ppm for $^{12}C_{38}{}^{1}H_{48}O_{2}{}^{28}Si_{2}{}^{32}S_{6}{}^{79}Br_{2}$). Crystallized from benzene/isopropanol (1:1) for the single-crystal X-ray analysis. HPLC (CHIRALPAK® AD-H, hexane/isopropanol, 95:5, 1 mL min^{-1}).

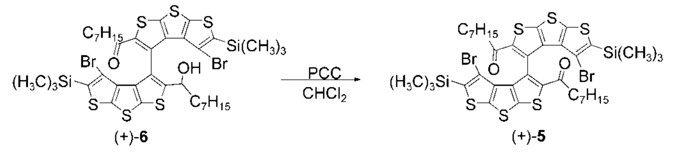
Kinetic resolution of diketone rac-5: Diketone rac-**5** (369 mg, 0.390 mmol) in diethyl ether (40 mL) was added to (−)-*B*-chlorodiisopinocampheylborane (351 mg, 1.093 mmol, 2.8 equiv) in diethyl ether (46 mL) at −25°C in a Schlenk vessel. Subsequently, the reaction mixture was allowed to attain room temperature for 0.5 h, and then 50°C. Small aliquots were withdrawn from the reaction mixture; after the aqueous workup of the aliquot, TLC (pentane/ethyl acetate, 10:1, v/v) and ^{1}H NMR analyses were carried to evaluate reaction progress. When the analysis of the aliquot indicated that the ratio of diketone **5** and alcohol **6** reached nearly 50:50 (after ~72 h at 50°C), based upon the relative peak integrations in the TMS region of the ^{1}H NMR spectrum [$\delta=0.323$ (s, 18H, **5**), 0.319 (s, 9H, **6**), 0.312 ppm (s, 9H, **6**)], diethanolamine was added to the reaction mixture. The yellow suspension was filtered to remove the boron complex, and then the usual aqueous workup with diethyl ether was carried out. Purification of the crude product (yellow viscous liquid/oil) by column chromatography (silica, hexane/benzene, 1:3, v/v) gave the two fractions: F1: diketone (−)-**5** ($R_f=0.70$), 153.7 mg (42%), $[\alpha]_{\mathrm{D}}^{\mathrm{RT}}=-90$ ($c=4.365\times10^{-3}$ in chloroform), 71% *ee* (HPLC); F2: alcohol (+)-**6** ($R_f=0.28$), 115.3 mg (31%), $[\alpha]_{\mathrm{D}}^{\mathrm{RT}}=+34$ ($c=2.205\times10^{-3}$ in chloroform) (label: MM-5-67). (After the PCC-based oxidation of this sample of (+)-**6**, the corresponding diketone (+)-**5** had 56% *ee* by HPLC.)

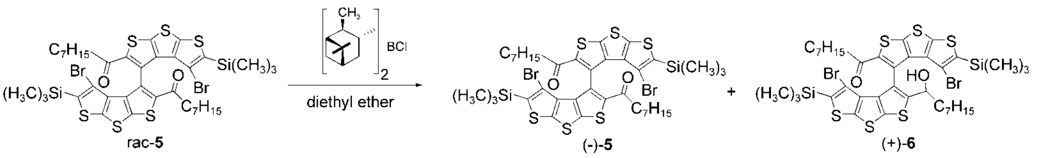
In another resolution experiment (label: MM-6-69), diketone (−)-**5** {122.2 mg, 41%, $[\alpha]_{\mathrm{D}}^{\mathrm{RT}}=-99$ ($c=2.20\times10^{-3}$ in chloroform), 85% *ee* (HPLC)} and alcohol (+)-**6** {120 mg, 40%, $[\alpha]_{\mathrm{D}}^{\mathrm{RT}}=32.3$ ($c=2.19\times10^{-3}$ in chloroform)} were obtained from 297 mg of rac-**5** (45°C for 80 h). Further treatment of diketone (−)-**5** with diethyl ether gave two fractions: solid, 6%, $[\alpha]_{\mathrm{D}}^{\mathrm{RT}}=-45$ ($c=4.15\times10^{-3}$ in CDCl$_3$), 31% *ee* (HPLC) and filtrate, 35%, $[\alpha]_{\mathrm{D}}^{\mathrm{RT}}=-114$ ($c=2.84\times10^{-3}$ in CDCl$_3$), 89% *ee* (HPLC).

Data for diketone (−)-5: $R_f=0.76$ (pentane/ethyl acetate). 71% *ee* (HPLC); m.p. 72–74°C (changed to a somewhat transparent solid), ~90°C (cloudy solid), 95–100°C (jelly-like, white, viscous) 140°C (completely clear liquid). ^{1}H NMR (500 MHz, [D]chloroform): $\delta=2.35$–2.14 (m, 4H), 1.48–1.36 (m, 4H), 1.159 (quintet $J=7.0$ Hz, 4H), 1.055 (quintet $J=7.5$ Hz, 4H), 1.02–0.85 (m, 8H), 0.816 (t, $J=7.0$ Hz, 6H), 0.323 (s, 18H); IR: $\tilde{\nu}=2953$, 2926, 2855 (C−H), 1648 cm^{-1} (C=O); LR/HR FABMS (3-NBA matrix): *m/z* (% RA for *m/z* = 700–2000, deviation for the formula): 946.9966 $[M+4+\mathrm{H}]^+$ (79, −4.7 ppm for $^{12}C_{38}{}^{1}H_{48}O_{2}{}^{28}Si_{2}{}^{32}S_{6}{}^{81}Br_{2}$), 943.9953 $[M+2+\mathrm{H}]^+$ (100, −4.1 ppm for $^{12}C_{38}{}^{1}H_{48}O_{2}{}^{28}Si_{2}{}^{32}S_{6}{}^{79}Br{}^{81}Br$), 941.9910 $[M]^+$ (14, −2.8 ppm for $^{12}C_{38}{}^{1}H_{48}O_{2}{}^{28}Si_{2}{}^{32}S_{6}{}^{79}Br_{2}$).

Data for alcohol (+)-6: $R_f=0.45$ (pentane/ethyl acetate); 56% *ee* (HPLC) for the diketone obtained from oxidation of this alcohol; m.p. 47–50°C (clear viscous), 57–58°C (clear oil); ^{1}H NMR (500 MHz, [D]chloroform): $\delta=4.574$ (dt, $J=2.8$, 7.2 Hz, 1H), 2.627 (d, $J=2.8$ Hz, 1H; exch D$_2$O), 2.57–2.40 (m, 2H), 1.775 (q, $J=7.6$ Hz, 2H), 1.481 (quintet $J=7.6$ Hz, 2H), 1.38–0.87 (m, 4H), 1.1–0.85 (m, 18H), 0.810 (t, $J=$ 6.8 Hz, 3H), 0.805 (t, $J=6.8$ Hz, 3H), 0.318 (s, 9H), 0.311 ppm (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, [D]chloroform): $\delta=195.4$ (C=O), 149.5, 145.4, 144.6, 144.1, 143.5, 140.38, 140.29, 139.8, 138.8, 138.6, 137.47, 137.35, 132.79, 125.6, 108.8, 108.3, 69.0, 41.0, 37.8, 31.8, 31.6, 29.08, 29.04, 28.80, 28.75, 25.5, 24.4, 22.55, 22.51, 14.10, 14.08, −0.85, −0.91 ppm; IR: $\tilde{\nu}=$ 3447 (O−H), 2957, 2924, 2854 (C−H), 1636 cm^{-1} (C=O); LR/HR FABMS (3-NBA matrix): *m/z* (% RA for *m/z* = 700–1500, deviation for the formula): 948.0009 $[M+4]^+$ (12, −1.1 ppm for $^{12}C_{38}{}^{1}H_{50}O_{2}{}^{28}Si_{2}{}^{32}S_{6}{}^{81}Br_{2}$), 946.0031 $[M+2]^+$ (15, −1.1 ppm for $^{12}C_{38}{}^{1}H_{50}O_{2}{}^{28}Si_{2}{}^{32}S_{6}{}^{79}Br{}^{81}Br$), 944.0021 $[M]^+$ (7.6, 2.1 ppm for $^{12}C_{38}{}^{1}H_{50}O_{2}{}^{28}Si_{2}{}^{32}S_{6}{}^{79}Br_{2}$), 930.9987 $[M+4-\mathrm{OH}]^+$ (77, −1.6 ppm for $^{12}C_{38}{}^{1}H_{49}O_{1}{}^{28}Si_{2}{}^{32}S_{6}{}^{81}Br_{2}$), 929.0004 $[M+2-\mathrm{OH}]^+$ (100, −1.3 ppm for $^{12}C_{38}{}^{1}H_{49}O_{1}{}^{28}Si_{2}{}^{32}S_{6}{}^{79}Br{}^{81}Br$), 927.0000 $[\mathrm{M}-\mathrm{OH}]^+$ (46, 1.5 ppm for $^{12}C_{38}{}^{1}H_{49}O_{1}{}^{28}Si_{2}{}^{32}S_{6}{}^{79}Br_{2}$).

Oxidation of alcohol (+)-6 to diketone (+)-5: PCC (72 mg, 0.190 mmol) was added to a stirred solution of alcohol (+)-**6** (120 mg, 0.1267 mmol, $[\alpha]_{\mathrm{D}}^{\mathrm{RT}}=+32.3$ ($c=2.185\times10^{-3}$ in chloroform)) in dry CH$_2$Cl$_2$ (1 mL). After TLC showed absence of the starting material (~12 h), the reaction mixture was filtered through Celite. Column chromatography (pentane/ethyl acetate, 10:1) gave the product as a pale yellow solid {96.0 mg, 80%, $[\alpha]_{\mathrm{D}}^{\mathrm{RT}}=+90.8$ ($c=5.61\times10^{-3}$ in CDCl$_3$)}. Two treatments with di-



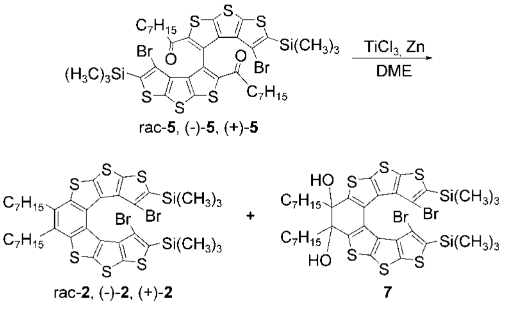


ethyl ether (1–2 mL) gave 44.7 mg of enantiopure (+)-**5** ($[\alpha]_{\mathrm{D}}^{\mathrm{RT}}=+134$, 99% *ee*), as diethyl ether soluble fraction; two diethyl ether insoluble fractions were also isolated: 24.7 mg ($[\alpha]_{\mathrm{D}}^{\mathrm{RT}}=+17$, 10% *ee*) and 18.4 mg ($[\alpha]_{\mathrm{D}}^{\mathrm{RT}}=+104$, 73% *ee*) (label: MM-6-88).

From other three reactions on 13, 12, and 110 mg scales, 119.8 mg (80–94%) of nonracemic diketone (+)-**5** was obtained.

Diketone (+)-5: 99+ % *ee* (HPLC). M.p. (powder sample) 41–43 °C (bulk solid, not powder, does not move well), 44–45 °C (cloudy solid), 50–60 °C (clear solid, solid shape was remaining), 62–63 °C (completely clear liquid, no solid shape). M.p. (single crystals from methanol, including the X-ray crystallographic sample) 85 °C (crystals become sticky), 85–87 °C (crystals and jelly-like solid), ~90 °C (clear viscous liquid/oil); ^{1}H NMR (400 MHz, [D]chloroform): $\delta=2.250$ (dt, $J=4.0$, 7.3 Hz, 4H), 1.48–1.36 (m, 4H), 1.156 (quintet $J=7.2$ Hz, 4H), 1.052 (quintet $J=6.8$ Hz, 4H), 1.0–0.85 (m, 8H), 0.815 (d, $J=7.2$ Hz, 6H), 0.322 ppm (s, 18H). IR: $\tilde{\nu}=2954$, 2926, 2855 (C–H), 1649 cm^{-1} (C=O); UV/Vis (cyclohexane): $\lambda_{\max}$ ($\varepsilon_{\max}$) = 241 (6.36×10^4), 247 (6.16×10^4), 269 (2.31×10^4), 290 (1.57×10^4), 324 nm (2.21×10^4 mol^{-1}dm^{3}cm^{-1}); CD (cyclohexane): $\lambda_{\max}$ ($\Delta\varepsilon_{\max}$) = 206 (−22), 228 (5.7), 237 (−21), 251 (23), 288 (−2.3), 317 (34), 345 nm (−14 mol^{-1}dm^{3}cm^{-1}); LR/HR FABMS (3-NBA matrix): *m/z* (% RA for $m/z=600$–1500, deviation for the formula): 946.9898 $[M+4+\mathrm{H}]^+$ (78, 2.5 ppm for $^{12}\mathrm{C}_{38}{}^{1}\mathrm{H}_{49}\mathrm{O}_2{}^{28}\mathrm{Si}_2{}^{32}\mathrm{S}_6{}^{81}\mathrm{Br}_2$), 944.9911 $[M+2+\mathrm{H}]^+$ (100, 3.2 ppm for $^{12}\mathrm{C}_{38}{}^{1}\mathrm{H}_{49}\mathrm{O}_2{}^{28}\mathrm{Si}_2{}^{32}\mathrm{S}_6{}^{79}\mathrm{Br}{}^{81}\mathrm{Br}$), 942.9927 $[M+\mathrm{H}]^+$ (44, 3.7 ppm for $^{12}\mathrm{C}_{38}{}^{1}\mathrm{H}_{49}\mathrm{O}_2{}^{28}\mathrm{Si}_2{}^{32}\mathrm{S}_6{}^{79}\mathrm{Br}_2$).

[7]Helicene 2: Nonracemic diketone (−)-**5** (30 mg, 31.7 μmol, 1 equiv) in DME (3 mL) was added to a Schlenk vessel containing TiCl$_3$ (26.0 mg, 0.169 mmol, 5.3 equiv) and Zn (31.5 mg, 0.482 mmol, 15 equiv). The reaction mixture was stirred at ambient temperature for 1 h, and then at 85–90 °C for 24 h. After cooling to ambient temperature, the reaction mixture (DME solution) was filtered through the silica plug (~1 cm) on air and the filtrate was concentrated under vacuo. The residue was filtered again through the silica plug to give two fractions: the less polar fraction (hexane a eluent) contained [7]helicene (+)-**2** and the more polar fraction (hexane/benzene) contained diol **7**.



The less polar fraction was subjected to column chromatography and/or PTLC, followed by treatment with methanol or methanol/diethyl ether, to give [7]helicene **2**. From five reactions on 28, 30, 30, 30, and 19 mg scales, 47.0 mg {36%, $[\alpha]_{\mathrm{D}}^{\mathrm{RT}}=+680$, ~50% *ee* (HPLC)} of [7]helicene (+)-**2** was obtained from 136.3 mg of diketone (−)-**5** ($[\alpha]_{\mathrm{D}}^{\mathrm{RT}}=-90$, 71% *ee*). Also, 16.6 mg of [7]helicene (+)-**2** {12%, ~50% *ee* (HPLC)}, containing about 10% of unknown impurity, was isolated. After fractional crystallization of nonracemic [7]helicene (+)-**2** (41.8 mg, $[\alpha]_{\mathrm{D}}^{\mathrm{RT}}=+680$) from isopropanol/diethyl ether, enantiopure (+)-**2** {25.9 mg, 19%, $[\alpha]_{\mathrm{D}}^{\mathrm{RT}}=+1166$, 99+ % *ee* (HPLC)} was obtained.

The more polar fraction (50 mg, $R_{\mathrm{f}}=0$ in hexane) was isolated as a yellow solid and was not purified further.

Analogous procedures were to obtain rac-**2**; synthesis and isolation of (−)-**2** and diol **7** (the more polar fraction) are described in the Supporting Information.

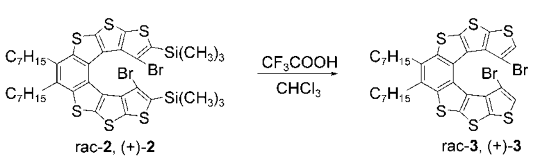
[7]Helicene (+)-2: $R_{\mathrm{f}}=0.70$ (hexane); 99+ % *ee* (HPLC) (label: MM-7-61-run1); M.p. (air) ~55 °C (powder becomes a bulk solid), 60–65 °C (slowly changed to clear solid), 73–75 °C (almost clear jellylike, particle shape is still preserved), ~83 °C (completely clear waxlike); DSC: glass-like transition was observed with peak at 67.4 °C ($\Delta H=3.1$–3.8 kJ mol^{-1}). $[\alpha]_{\mathrm{D}}^{\mathrm{RT}}=+1166$ ($c=0.000715$ in cyclohexane); $[\Phi]_{\mathrm{D}}^{\mathrm{RT}}=+10648$; ^{1}H NMR (400 MHz, [D]chloroform): $\delta=3.02$–2.89 (m, 4H), 1.84–1.70 (m, 4H), 1.525 (quintet, $J=7.2$ Hz, 4H, overlapped with H$_2$O peak), 1.46–1.23 (m, 12H), 0.907 (t, $J=6.8$ Hz, 6H), 0.258 ppm (s, 18H, $J(^{13}\mathrm{C},{}^{1}\mathrm{H})=120$ Hz); IR: $\tilde{\nu}=2954$, 2926, 2854 cm^{-1} (C–H); UV/Vis (cyclohexane, 1 mm pathlength): $\lambda_{\max}$ ($\varepsilon_{\max}$) = 212 (4.41×10^4), 239 (4.91×10^4), 286 (3.15×10^4), 342 (1.64×10^4), 353 nm (1.66×10^4 mol^{-1}dm^{3}cm^{-1}); CD (cyclohexane, 1 mm pathlength): $\lambda_{\max}$ ($\Delta\varepsilon_{\max}$) = 212 (−142), 265 (+99), 278 (+86), 300 (+33), 342 (+28), 359 nm (+24 mol^{-1}dm^{3}cm^{-1}).

From 10 mg scale reaction, 5.7 mg (63%, $[\alpha]_{\mathrm{D}}^{\mathrm{RT}}=+945$, ~90% *ee*) of (+)-**2** was obtained from 9.3 mg of (−)-**5** ($[\alpha]_{\mathrm{D}}^{\mathrm{RT}}=-111$, 91% *ee*) (label: MM-6-51).

From other two reactions on 70 and 30 mg scales, 16.3 mg (17%, ~70% *ee*) of (+)-**2** was obtained from 100 mg of (−)-**5** ($[\alpha]_{\mathrm{D}}^{\mathrm{RT}}=-114$, 89% *ee*). In these two reactions, the polar fraction was the major component.

[7]Helicene rac-2: From two reactions on 20 and 18 mg scales, 13.7 mg (38%) of rac-**2** was obtained from 37.3 mg of diketone rac-**5**. M.p. 164–165 °C; DSC: melting-like transition was observed with peak at 165.3–166.1 °C ($\Delta H=33.3$–33.8 kJ mol^{-1}); ^{1}H NMR (400 MHz, [D]chloroform): $\delta=3.03$–2.89 (m, 4H), 1.86–1.69 (m 4H), 1.525 (quintet, $J=7.2$ Hz, 4H, overlapped with H$_2$O peak), 1.46–1.23 (m, 12H), 0.910 (t, $J=6.8$ Hz, 6H), 0.261 ppm (s, 18H); ^{13}C{^{1}H} NMR (100 MHz, [D]chloroform): $\delta=144.2$, 141.83, 141.68, 138.3, 137.0, 135.2, 130.2, 124.7, 110.0, 31.94, 31.82, 30.2, 29.9, 29.1, 22.7, 14.1, −0.93 ppm ($J(^{29}\mathrm{Si},{}^{13}\mathrm{C})=54$ Hz); IR: $\tilde{\nu}=2954$, 2926, 2855 cm^{-1} (C–H); LR/HR FABMS (3-NBA matrix): *m/z* (% RA for $m/z=700$–1200, deviation for the formula): 913.9940 $[M+4]^+$ (83, 0.5 ppm for $^{12}\mathrm{C}_{38}{}^{1}\mathrm{H}_{48}{}^{28}\mathrm{Si}_2{}^{32}\mathrm{S}_6{}^{81}\mathrm{Br}_2$), 911.9952 $[M+2]^+$ (100, 1.5 ppm for $^{12}\mathrm{C}_{38}{}^{1}\mathrm{H}_{48}{}^{28}\mathrm{Si}_2{}^{32}\mathrm{S}_6{}^{79}\mathrm{Br}{}^{81}\mathrm{Br}$), 909.9966 $[M]^+$ (43, 2.1 ppm for $^{12}\mathrm{C}_{38}{}^{1}\mathrm{H}_{48}{}^{28}\mathrm{Si}_2{}^{32}\mathrm{S}_6{}^{79}\mathrm{Br}_2$).

[7]Helicene 3: Trifluoroacetic acid (0.25 mL) was added to a solution of [7]helicene rac-**2** (9.6 mg, 10.5 μmol) in chloroform (1.5 mL). The reaction was monitored by TLC (hexane) or ^{1}H NMR spectroscopy (in CDCl$_3$). Typically, reaction was completed after 10–15 min at room temperature. The usual aqueous workup with diethyl ether gave the crude product as a pale yellow solid. Filtration through a short silica plug using pentane gave [7]helicene rac-**3** (7.6 mg, 94%). Using a similar procedure, (+)-**3** (2.0 mg, 85%) was obtained from 2.8 mg of (+)-**2**.



[7]Helicene rac-3: $R_{\mathrm{f}}=0.30$ (hexane); crystals obtained by evaporation of methanol/diethyl ether: m.p. 142–143 °C; DSC: melting-like transition was observed with peak at 140.7–141.0 °C ($\Delta H=36.5$–37.1 kJ mol^{-1}). Crystals obtained by slow evaporation from benzene/isopropanol (1:1), including the X-ray crystallographic sample, possess non-uniform melting behavior as observed in a melting point apparatus; however, a small, selected sample of such crystals showed m.p. 113–115 °C. For a 0.677 mg sample, DSC shows a relatively broad peak (onset at ~93 °C, peak at ~115 °C, $\Delta H\approx25$ kJ mol^{-1}); ^{1}H NMR (400 MHz, [D]chloroform): $\delta=7.107$ (s, 2H), 3.05–2.90 (m, 4H), 1.85–1.70 (m, 4H), 1.527 (quintet $J=7.6$ Hz, 4H, overlapped with H$_2$O), 1.46–1.29 (m, 12H), 0.908 (t, $J=6.8$ Hz, 6H); IR: $\tilde{\nu}=3103$, 2954, 2924, 2853 cm^{-1} (C–H); LR/HR FABMS (3-NBA matrix): *m/z* (% RA for $m/z=500$–1100, deviation for the formula): 769.9182 $[M+4]^+$ (76, −3.6 ppm for $^{12}\mathrm{C}_{32}{}^{1}\mathrm{H}_{32}{}^{32}\mathrm{S}_6{}^{81}\mathrm{Br}_2$), 767.9186 $[M+2]^+$ (100, −1.4 ppm for $^{12}\mathrm{C}_{32}{}^{1}\mathrm{H}_{32}{}^{32}\mathrm{S}_6{}^{79}\mathrm{Br}{}^{81}\mathrm{Br}$), 765.9198 $[M]^+$ (42, −0.4 ppm for $^{12}\mathrm{C}_{32}{}^{1}\mathrm{H}_{32}{}^{32}\mathrm{S}_6{}^{79}\mathrm{Br}_2$).

[7]Helicene (+)-3: 95+ % *ee* (^{1}H NMR chiral shift agents), 99+ % *ee* (HPLC); m.p. 139–140 °C (95–100 °C bulky solid, 138 °C somewhat clear); DSC: melting-like transition was observed with peak at 141–143 °C ($\Delta H=28.5$–30.6 kJ mol^{-1}); $[\alpha]_{\mathrm{D}}^{\mathrm{RT}}=+1006$ ($c=0.0000316$ in cyclohexane); $[\Phi]_{\mathrm{D}}^{\mathrm{RT}}=+7734$; ^{1}H NMR (400 MHz, [D]chloroform): $\delta=7.108$ (s, 2H), 3.04–2.90 (m, 4H), 1.85–1.70 (m, 4H), 1.526 (quintet $J=7.2$ Hz, 4H, overlapped with H_2O), 1.46–1.29 (m, 12H), 0.908 (t, $J=6.8$ Hz, 6H); UV/Vis (cyclohexane, 1 mm pathlength): λ_{max} (ε_{max})=210 (4.40×10^4), 235 (4.01×10^4), 277 (2.88×10^4), 339 (1.60×10^4), 353 nm (1.56×10^4 $mol^{-1}dm^3cm^{-1}$); CD (cyclohexane, 1 mm pathlength): λ_{max} ($\Delta\varepsilon_{max}$)=209 (−145), 258 (+62), 276 (+53), 292 (+32), 337 (+22), 356 nm (+16 $mol^{-1}dm^3cm^{-1}$).

Acknowledgement

This research was supported by the National Science Foundation (CHE-0107241) and the Office of Naval research (N00014–03–1–0550). ChemMatCARS Sector 15 is principally supported by the National Science Foundation/Department of Energy under grant number CHE-0087817 and by the Illinois Board of Higher Education. The advanced Photon Source is supported by the US Department of Energy, Basic Energy Sciences, Office of Science, under Contract No. W-31-109-Eng-38. MS analyses were carried out at the Nebraska Center for Mass Spectrometry. We thank Rick Albro and Professor Craig Eckhardt for the help with the DSC measurements. We thank Y. Kim and Dr. W. N. Herman for the preliminary optical studies of films of (+)-**2** [7]helicene.

[1] a) P. P. Meurer, F. Vögtle, *Top. Curr. Chem.* **1985**, *127*, 1–76; b) W. H. Laarhoven, W. J. C. Prinsen, *Top. Curr. Chem.* **1984**, *125*, 63–130.

[2] a) M. S. Newman, W. B. Lutz, D. Lednicer, *J. Am. Chem. Soc.* **1955**, *77*, 3420–3421; b) M. S. Newman, D. Lednicer, *J. Am. Chem. Soc.* **1956**, *78*, 4765–4770.

[3] a) T. J. Katz, *Angew. Chem.* **2000**, *112*, 1997–1999; *Angew. Chem. Int. Ed.* **2000**, *39*, 1921–1923; b) C. Nuckolls, T. J. Katz, G. Katz, P. J. Collings, L. Catellanos, *J. Am. Chem. Soc.* **1999**, *121*, 79–88; c) K. E. S. Phillips, T. J. Katz, S. Jockusch, A. J. Lovinger, N. J. Turro, *J. Am. Chem. Soc.* **2001**, *123*, 11899–11907; d) L. Vyklinckỳ, S. H. Eichhorn, T. J. Katz, *Chem. Mater.* **2003**, *15*, 3594–3601.

[4] a) A. Urbano, *Angew. Chem.* **2003**, *115*, 4116–4119; *Angew. Chem. Int. Ed.* **2003**, *42*, 3986–3989; b) C. Schmuck, *Angew. Chem.* **2003**, *115*, 2552–2556; *Angew. Chem. Int. Ed.* **2003**, *42*, 2448–2452.

[5] a) F. Teplý, I. G. Stará, I. Starý, A. Kollárovič, D. Šaman, S. Vyskočil, P. Fiedler, *J. Org. Chem.* **2003**, *68*, 5193–5197; b) F. Teplý, I. G. Stará, I. Starý, A. Kollárovič, D. Šaman, L. Rulíšek, P. Fiedler, *J. Am. Chem. Soc.* **2002**, *124*, 9175–9180.

[6] Y. Ogawa, M. Toyama, M. Karikomi, K. Seki, K. Haga, T. Uyehara, *Tetrahedron Lett.* **2003**, *44*, 2167–2170;

[7] M. C. Carreño, S, García-Cerrada, A. Urbano, *J. Am. Chem. Soc.* **2001**, *123*, 7929–7930.

[8] K. Tanaka, H. Suzuki, H. Osuga, *J. Org. Chem.* **1997**, *62*, 4465–4470.

[9] a) F. Dubois, M. Gingras, *Tetrahedron Lett.* **1998**, *39*, 5039–5040; b) M. Gingras, F. Dubois, *Tetrahedron Lett.* **1999**, *40*, 1309–1312.

[10] a) J. E. Field, G. Muller, J. P. Riehl, D. Venkataraman, *J. Am. Chem. Soc.* **2003**, *125*, 11808–11809; b) J. E. Field, T. J. Hill, D. Venkataraman, *J. Org. Chem.* **2003**, *68*, 6071–6078.

[11] a) J. Larsen, K. Bechgaard, *J. Org. Chem.* **1996**, *61*, 1151–1152; b) J. Larsen, K. Bechgaard, *Acta Chem. Scand.* **1996**, *50*, 71–76; c) *Acta Chem. Scand.* **1996**, *50*, 77–82.

[12] a) S. Han, A. D. Bond, R. L. Disch, D. Holmes, J. M. Schulman, S. J. Teat, K. P. C. Vollhardt, G. D. Whitener, *Angew. Chem.* **2002**, *114*, 3357–3361; *Angew. Chem. Int. Ed.* **2002**, *41*, 3223–3227; b) S. Han, D. R. Anderson, A. D. Bond, H. V. Chu, R. L. Disch, D. Holmes, J. M. Schulman, S. J. Teat, K. P. C. Vollhardt, G. D. Whitener, *Angew. Chem.* **2002**, *114*, 3361–3364; *Angew. Chem. Int. Ed.* **2002**, *41*, 3227–3230.

[13] A. Rajca, H. Wang, M. Pink, S. Rajca, *Angew. Chem.* **2000**, *112*, 4655–4657; *Angew. Chem. Int. Ed.* **2000**, *39*, 4481–4483.

[14] Thiophene–phenylene-based helicenes: a) H. Wynberg, *Acc. Chem. Res.* **1971**, *4*, 65–73; b) K. Yamada, S. Ogashiwa, H. Tanaka, H. Nakagawa, H. Kawazura, *Chem. Lett.* **1981**, 343–346; c) K. Yamada, Y. Kobori, H. Nakagawa, *Chem. Commun.* **2000**, 97–98; d) T. Caronna, R. Sinisi, M. Catellani, L. Malpezzi, S. V. Meille, A. Mele, *Chem. Commun.* **2000**, 1139–1140; e) Y. Kitahara, K. Tanaka, *Chem. Commun.* **2002**, 932–933; f) see references [3c,8,11].

[15] a) T. B. Friedman, X. Cao, A. Rajca, H. Wang, L. A. Nafie, *J. Phys. Chem. A* **2003**, *107*, 7692–7696; b) M. Miyasaka, A. Rajca, *Synlett* **2004**, 177–182; c) A. Rajca, M. Miyasaka, M. Pink, H. Wang, S. Rajca, *J. Am. Chem. Soc.*, in press.

[16] I. Aujard, J.-P. Baltaze, J.-B. Baudin, E. Cogne, F. Ferrage, L. Jullien, E. Perez, V. Prevost, L. M. Qian, O. Ruel, *J. Am. Chem. Soc.* **2001**, *123*, 8177–8188.

[17] a) J. Salbeck, J. Bauer, F. Weissortel, *Polym. Prepr.* **1997**, *38*, 349–350; b) S. Wang, W. J. Oldham, Jr., R. A. Hudack, Jr., G. C. Bazan, *J. Am. Chem. Soc.* **2000**, *122*, 5695–5709; c) M. He, R. J. Twieg, U. Gubler, D. Wright, W. E. Moerner, *Chem. Mater.* **2003**, *15*, 1156–1164; d) C. Wu, T.-L. Liu, W.-Y. Hung, Y.-T. Lin, K.-T. Wong, R.-T. Chen, Y.-M. Chen, Y.-Y. Chien, *J. Am. Chem. Soc.* **2003**, *125*, 3710–3711.

[18] a) Y. Kim, W. L. Cao, J. Goldhar, C. H. Lee, W. N. Herman, *Polym. Prepr.* **2002**, *43*, 594–595; b) W. N. Herman, *J. Opt. Soc. Am. A* **2001**, *18*, 2806–2818.

[19] S. Nahm, S. M. Weinreb, *Tetrahedron Lett.* **1981**, *22*, 3815–3818.

[20] By using (−)-sparteine, negligible enantiomeric excess (*ee*) is found in isolated diketone **5** (see Supporting Information).

[21] Reduction using *B*-chlorodiisopinocampheylborane: a) P. V. Ramachandran, G.-M. Chen, H. C. Brown, *J. Org. Chem.* **1996**, *61*, 88–94; b) P. V. Ramachandran, G.-M. Chen, Z.-H. Lu, H. C. Brown, *Tetrahedron Lett.* **1996**, *37*, 3795–3798.

[22] J. E. McMurry, *Chem. Rev.* **1989**, *89*, 1513–1524.

[23] A. Fürstner, A. Hupperts, A. Ptock, E. Janssen, *J. Org. Chem.* **1994**, *59*, 5215–5229.

[24] Syntheses of [7]helicenes (ref. [8]) and [5]helicenes (ref. [9a]) using the McMurry reaction of dialdehydes were reported.

[25] Schakal99, a computer program for the graphic representation of molecular and crystallographic models, E. Keller, Universitaet Freiburg, Germany; CCDC-233519 (rac-**2**), CCDC-233520 ((+)-**3**), CCDC-233521 (rac-**3**), CCDC-242232 ((+)-**5**), and CCDC-242233 (rac-**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk).

[26] Stereochemical correlations between 1,1′-binapthyls and [5]helicenes were reported, though lacking direct determinations of absolute configurations by X-ray crystallography for the axially chiral starting material and the helicene product: a) H. J. Bestmann, W. Both, *Angew. Chem.* **1972**, *84*, 293; *Angew. Chem. Int. Ed. Engl. Angew. Chem. Int. Ed.* **1972**, *11*, 296; b) I. G. Stará, I. Starý, M. Tichý, J. Závada, V. Hanuš, *J. Am. Chem. Soc.* **1984**, *116*, 5084–5088.

[27] In rac-**5** and (+)-**5**, the mean deviations from calculated least-square planes including three thiophene rings of each dithienothiophene subunit are in the 0.02–0.06 Å range.

[28] Analogous dihedral angles are 68.6° and 103.1° for the racemic and the enantiomeric forms of 1,1′-binapthyl: R. B. Kress, E. N. Duesler, M. C. Etter, I. C. Paul, D. Y. Curtin, *J. Am. Chem. Soc.* **1980**, *102*, 7709–7714.

[29] E. L. Eliel, S. H. Wilen, *Stereochemistry of Organic Compounds*, Wiley, New York, **1994**.

[30] In cyclohexane, the UV/Vis and CD spectra of (+)-**2** and (+)-**3** show significant bathochromic shift relative to those of (−)-**1**.

[31] Substituent effects on chiroptical properties of the all-phenylene [6]helicene: C. Wachsmann, E. Weber, M. Czugler, W. Seichter, *Eur. J. Org. Chem.* **2003**, 2863–2876.

[32] All samples of rac-**3** for the DSC measurements in Figure 4 were treated with MeOH/diethyl ether; those samples most likely correspond to a different polymorph (racemic compound), compared to the single crystals of the racemic conglomerate obtained from isopropanol/benzene and studied by crystallography. Melting behavior for the crystals remaining after the X-ray crystallographic analysis is non-uniform as observed in a melting point apparatus; for a 0.677 mg sample, DSC shows a relatively broad peak (onset at ~93 °C, peak at ~115 °C, $\Delta H \approx 25$ kJ mol^{-1}). The melting point of the conglomerate, which is close to the eutectic temperature T_e^A of the enantiomers, may be estimated using the simplified Schröder–van Laar equation, $T_e^A=[(1/T_{fus}^A)+(R\ln2)/(\Delta H_{fus}^A)]^{-1}$, for example: J. Jacques, A. Collet, S. H. Wilen, *Enantiomers, Racemates and Resolu-*

tions, Wiley, New York, **1981** (and Krieger, Malabar, Florida, **1994**). By using the DSC data for crystals of (+)-**3** (T^{A}_{fus} ≈ 136 °C ≈ 409 K (onset) and ΔH^{A}_{fus} ≈ 28.5 kJ mol^{-1}), T^{A}_{e} ≈ 105 °C is estimated for conglomerate rac-**3**.

[33] Melting points for [6]helicene: (+)-[6]helicene, m.p. 270 °C; racemic conglomerate [6]helicene, m.p. 238–240 °C; M. S. Newman, R. S. Darlak, L. Tsai, *J. Am. Chem. Soc.* **1967**, *89*, 6191 – 6193.

[34] C. P. Brock, W. B. Schweizer, J. D. Dunitz, *J. Am. Chem. Soc.* **1991**, *113*, 9811 – 9820.

[35] Transparent films of [7]helicene (+)-**2** on glass slides were obtained by casting from cyclohexanone. Preliminary studies suggest that such films are isotropic within experimental uncertainty (Δn ≈ 0.0003) in the λ = 630–1550 nm range; rotatory powers are 11 and 6.0 ° mm^{-1} at λ = 670 and 850 nm, respectively: Y. Kim and W. N. Herman, unpublished data.

[36] A. Rajca, H. Wang, P. Bolshov, S. Rajca, *Tetrahedron* **2001**, *57*, 3725 – 3735.

[37] a) SAINT 6.1, Bruker Analytical X-Ray Systems, Madison, WI, **1999**; b) SADABS: R. Blessing, *Acta Crystallogr. Sect. A* **1995**, *51*, 33 – 38.

[38] SIR92: a) A. Altomare, G, Cascarno, C. Giacovazzo, A. Gualardi *J. Appl. Crystallogr.* **1993**, *26*, 343 – 350; b) SHELXTL-Plus V5.10: Bruker Analytical X-Ray Systems, Madison, WI.

Received: June 24, 2004