

Keywords: cluster compounds • indium • nanoparticles • phosphorus

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- [7] 1·2.5 toluene: crystal dimensions $0.04 \times 0.03 \times 0.01 \text{ mm}^3$, $a = 1509.7(5)$, $b = 1518.5(4)$, $c = 2623.0(5) \text{ pm}$, $\alpha = 92.98(3)$, $\beta = 94.21(3)$, $\gamma = 91.37(3)^\circ$, $V = 5986(3) \times 10^6 \text{ pm}^3$; triclinic $P\bar{1}$, $Z = 2$, $\rho_{\text{calc}} = 1.596 \text{ g cm}^{-3}$, $\mu(\text{MoK}\alpha) = 2.067 \text{ mm}^{-1}$, STOE IPDS, Siemens rotating anode, graphite monochromator, $\text{MoK}\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$, $T = 190 \text{ K}$, $2\theta_{\text{max}} = 45^\circ$; a total of 19264 reflections measured, 13093 independent reflections ($R_{\text{int}} = 0.0605$), 9568 independent reflections with $F_o > 4\sigma(F_o)$. The structure was solved by direct methods and refined by full-matrix least-squares techniques against F^2 , 749 parameters (In, P, Cl, refined anisotropically, C atoms of the phenyl groups refined anisotropically, C atoms of ethyl groups and solvent molecules were refined isotropically with split positions; H atoms were calculated for the phenyl groups only), $R1 = 0.0832$; $wR2 = 0.2153$, residual electron density 3.004 e \AA^{-3} . Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-118782. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).
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Asymmetric Synthesis of Overcrowded Alkenes by Transfer of Axial Single Bond Chirality to Axial Double Bond Chirality**

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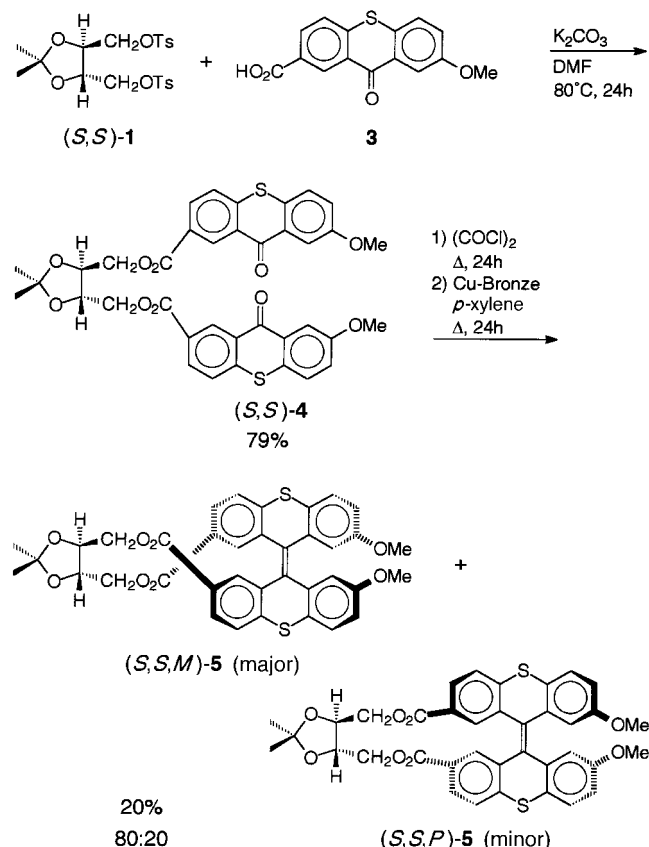
Sterically overcrowded alkenes have attracted considerable interest in view of their unique photochromic and thermochromic properties. In addition the beautiful architecture of these structures is as fascinating as their potential applications.^[1] Although they lack a stereogenic center they can exist as stable, optically active stereoisomers as a consequence of the presence of substituents that cause sufficient hindrance between the upper and lower half of the alkene and enforce a helical distortion to the entire molecule. Unsymmetrical *cis* and *trans* isomers of overcrowded alkenes were shown to act as chiroptical molecular switches suitable for reversible data storage,^[2] while other applications include photomodulation of liquid-crystalline materials^[3] and thin polymer films.^[4] A practical synthetic route towards enantiomerically pure over-

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crowded alkenes is still a challenging goal.^[5] Methodology has been developed for the synthesis of optically active biaryls in which control of the chirality of an axial single bond is achieved by the coupling of two aryl moieties to a chiral bridge.^[6] Based on a related principle we present the synthesis of stable enantiomers of an overcrowded alkene, which features axial double bond chirality, by using (–)-2,3-*O*-isopropylidene-*L*-threitol-1,4-ditosylate ((*S,S*)-**1**), (+)-(*R*)-1,1'-binaphthol ((*R*)-**2**), and (–)-(*S*)-1,1'-binaphthol ((*S*)-**2**) as chiral auxiliaries. In our most successful approach two halves of the envisioned alkene were first coupled to the binaphthol chiral bridge. A diastereoselective intramolecular coupling reaction then afforded the corresponding overcrowded alkenes. As no racemization was observed after removal of the chiral bridge this sequence implies the realization of the intriguing concept of conveying axial single bond chirality to stable axial double bond chirality. Moreover, we report for the first time the determination of the absolute configuration of enantiomerically pure bis-thioxanthylidenes as accomplished by X-ray analysis.

Initially we focussed on chiral template **1**, which is derived from tartaric acid (Scheme 1). An earlier attempt by Yip et al. to prepare optically active bifluorenylidenes^[7] along these lines resulted in the complete loss of optical activity as a result of the product having a low barrier to racemization.



Scheme 1. Synthetic route towards optically active overcrowded alkenes **5** with (*S,S*)-**1** used as a chiral template. *S,S* denotes the configuration of the threitol moiety whereas *M* (left-handed helix) and *P* (right-handed helix) define the helicity at the diester side of the overcrowded alkene part of the molecule.

The preorganized system (*S,S*)-**4** was prepared from 7-methoxy-9-oxo-9*H*-thioxanthene-2-carboxylic acid (**3**)^[8] and (*S,S*)-**1**. An intramolecular copper-promoted *gem*-dichloride coupling reaction^[9] afforded the sterically overcrowded alkenes (*S,S,M*)-**5** (major product) and (*S,S,P*)-**5** (minor product) in 20% yield.^[10] This rather low yield is a result of the extensive formation of oligomers during the coupling reaction, which unfortunately could not be suppressed by working at high dilution. The newly formed alkene moiety is chiral as a consequence of its folded structure, which explains the formation of two diastereoisomers. A diastereomeric excess of 60% was determined by 1H NMR spectroscopy. Recrystallization from acetone gave crystals of pure (*S,S,P*)-**5** that were suitable for X-ray analysis (Figure 1). The unique

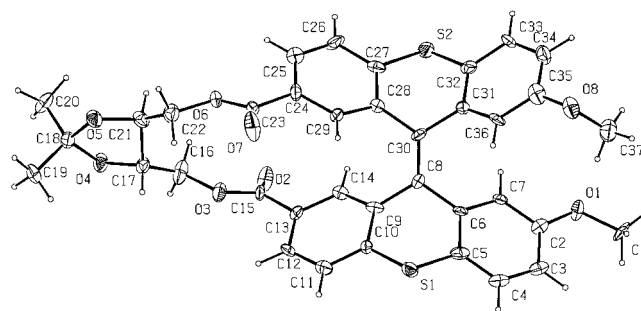
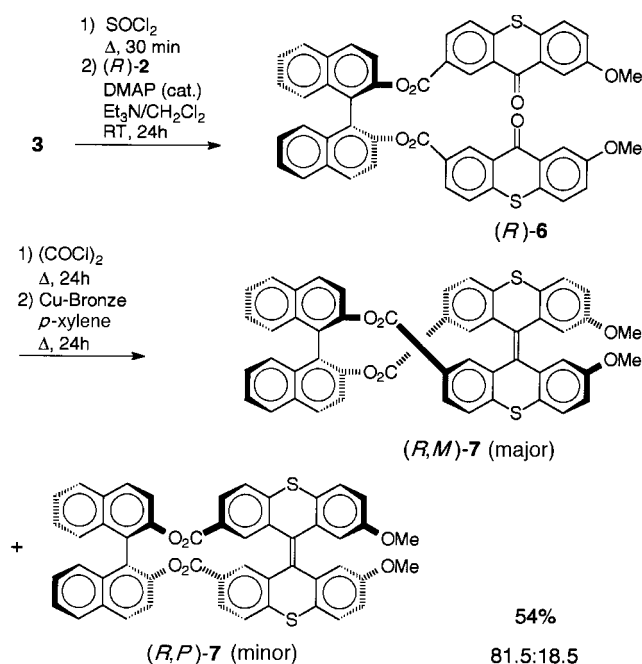


Figure 1. ORTEP plot of (*S,S,P*)-**5** (minor product).

folded structure of the overcrowded alkene part of (*S,S,P*)-**5** is clearly visible and based on the 2*S*,3*S* configuration of the *L*-threitol moiety a (*P*)-configuration for the diester moiety is established. The helical structure of (*S,S,P*)-**5** is quantified by torsion angles of 50.6° (C8–C30–C28–C29) and –3.9° (C9–C8–C30–C28). The major isomer (*S,S,M*)-**5** could not be obtained diastereomerically pure, despite several attempts.

In order to develop a synthetically useful asymmetric route we employed (*R*)-**2** and (*S*)-**2** as chiral templates (Scheme 2 for (*R*)-**2**, the same procedure was applied for (*S*)-**2**). The diester (*R*)-**6** was prepared from thioxanthone **3** and (*R*)-**2** in two steps in nearly quantitative yield. More importantly the yield of the subsequent intramolecular *gem*-dichloride coupling reaction with Cu-bronze increased considerably and diastereoisomers (*R,M*)-**7** (major product) and (*R,P*)-**7** (minor product) were obtained in 54% yield in a 81.5:18.5 ratio (1H NMR). Apparently the more rigid binaphthol-based chiral diester bridge of the tetrachloride derived from (*R*)-**6** enforces a more favorable geometry to the two thioxanthene moieties and suppresses oligomer formation through intermolecular coupling. The diastereoisomers (*R,M*)-**7** and (*R,P*)-**7** were readily separated by column chromatography.

It should be emphasized that both a folded and twisted helical shaped structural moiety is present in the same molecule. The two diastereoisomers differ significantly in structure as is visualized in Scheme 2. Although the binaphthyl part is twisted and the thioxanthylidene is folded in both isomers, the formation of the “cross-coupled” product (*R,M*)-**7** is strongly favored over the “linearly coupled” product (*R,P*)-**7**. Figure 2 shows an optimized space filling model^[11] of (*R,M*)-**7** revealing a double-helix-type structure that is



Scheme 2. Synthetic route towards optically active overcrowded alkenes **7** with (*R*)-**2** used as a chiral template. *R* and *S* denote the configuration of the binaphthol moiety whereas *M* (left-handed helix) and *P* (right-handed helix) define the helicity at the diester side of the overcrowded alkene part of the molecule.

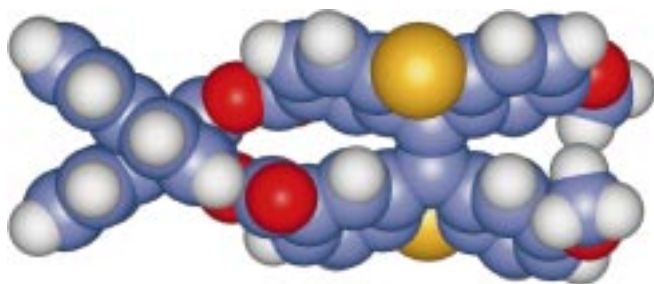
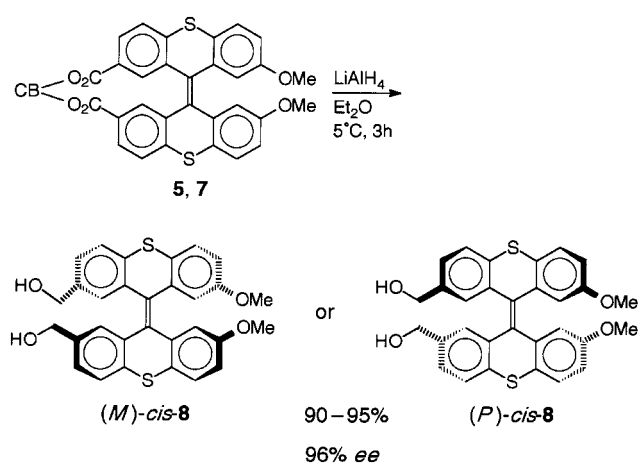


Figure 2. A model of (*R,M*)-**7** (major product) optimized with a CHARMM 23 force field as implemented in Quanta97/CHARMM. The structure is viewed along the binaphthol single bond and the alkene double bond.

reminiscent of the helical structure Nozaki et al. found for their double-helical oligo esters.^[12] The configurations of diastereoisomers (*R,M*)-**7** and (*R,P*)-**7** (and of diastereoisomers (*S,P*)-**7** (major product) and (*S,M*)-**7** (minor product) obtained from (*S*)-**2**) were unequivocally established after removal of the chiral bridges of all obtained diastereoisomers ((*S,S,P*)-**5** (minor product), (*R,M*)-**7**, (*R,P*)-**7**, (*S,P*)-**7**, and (*S,M*)-**7**). The overcrowded alkenes were liberated from their chiral bridge by reduction with LiAlH_4 to provide enantiomers of thioxanthylidenes (*P*)-*cis*-**8** and (*M*)-*cis*-**8** with *ee* values of $96 \pm 1\%$ as determined by chiral HPLC (Scheme 3). Based on the X-ray analysis of (*S,S,P*)-**5** the overcrowded alkene part has a *P* configuration, which leads to (*P*)-*cis*-**8** after removal of the L-threitol moiety. The analytical data of (*P*)-*cis*-**8** (optical rotation, CD data, and retention times on chiral HPLC) obtained from (*S,S,P*)-**5** were correlated with those of the enantiomers of *cis*-**8** obtained by reductive cleavage of the four diastereoisomers (*R,M*)-**7**, (*R,P*)-**7**, (*S,P*)-**7**, and (*S,M*)-**7**. The results are outlined in Table 1.



Scheme 3. Cleavage of the chiral bridge (CB) from overcrowded alkenes **5** and **7**. *M* (left-handed helix) and *P* (right-handed helix) define the helicity at the hydroxymethyl-side of **8**.

Table 1. Stereochemical correlation and optical rotation data of **5**, **7**, and **8**.

| Substrate | $[\alpha]_{\text{D}}^{20[\text{a}]}$ | Product | $[\alpha]_{\text{D}}^{20[\text{a}]}$ |
|------------------------------------|--------------------------------------|-------------------------------------|--------------------------------------|
| (<i>S,S,P</i>)- 5 (minor) | +203 ^[b] | (<i>P</i>)- <i>cis</i> - 8 | −92 |
| (<i>R,M</i>)- 7 (major) | −101 | (<i>M</i>)- <i>cis</i> - 8 | +91 |
| (<i>R,P</i>)- 7 (minor) | +120 | (<i>P</i>)- <i>cis</i> - 8 | −93 |
| (<i>S,P</i>)- 7 (major) | +100 | (<i>P</i>)- <i>cis</i> - 8 | −92 |
| (<i>S,M</i>)- 7 (minor) | −120 | (<i>M</i>)- <i>cis</i> - 8 | +91 |

[a] *c* = 1.00, CHCl_3 . [b] *c* = 0.50, CHCl_3 .

A racemization barrier ($\Delta^\ddagger G^\ominus$) of $26.7 \pm 0.5 \text{ kcal mol}^{-1}$ (polarimetry) was determined for *cis*-**8**, which is in accordance with the observation that the enantiomers of *cis*-**8** are stable at room temperature. A pair of identical CD spectra (except for the sign) were obtained for enantiomers (*P*)-*cis*-**8** and (*M*)-*cis*-**8**. Seven maxima were observed for (*M*)-*cis*-**8** (*n*-hexane/2-propanol 80/20) at wavelengths greater than 220 nm: λ_{max} ($\Delta\epsilon$) 230 nm (−3.5), 238 (+17.3), 252 (−6.2), 269 (+25.3), 291 (−38.6), 313 (+18.4), 342 (+10.7). The CD absorptions as well as the $\Delta\epsilon$ values are in good agreement with those obtained for related optically pure overcrowded alkenes that were obtained previously by preparative chiral HPLC.^[5]

In conclusion, an asymmetric synthesis method, which includes the transfer of axial single bond chirality to axial double bond chirality, for stable optically active overcrowded alkenes has been developed. The determination of the absolute configuration of the major stereoisomer revealed an appealing double-helical structure.

Experimental Section

(*R,M*)-**7** and (*R,P*)-**7** (the same procedure was used for (*S,P*)-**7** and (*S,M*)-**7**): Diester (*R*)-**6** (0.73 mmol) was refluxed overnight in oxalyl chloride (20 mL) under a nitrogen atmosphere. The excess of oxalyl chloride was evaporated under reduced pressure. The residue was dissolved in freshly distilled *p*-xylene (100 mL) and then activated Cu-bronze (15.90 mmol) was added. This mixture was refluxed overnight. After cooling, the mixture was filtered and the filtrate was concentrated in vacuo. Purification of the residue by silica gel column chromatography (CH_2Cl_2 /*n*-hexane 3/1) gave (*R,M*)-**7** (44% yield) and (*R,P*)-**7** (10% yield) as yellow solids. (*R,M*)-**7**: ^1H NMR (300 MHz, CDCl_3 , 25°C): δ = 8.02 (d, $^3J(\text{H,H})$ = 9.15 Hz, 2H; CH), 7.96 (d, $^3J(\text{H,H})$ = 8.42 Hz, 2H; CH), 7.49–7.29 (m, 12H; CH), 7.18 (d, $^3J(\text{H,H})$ = 8.42 Hz, 2H; CH), 7.07 (m, 2H; CH), 6.77 (m, 2H; CH), 6.42 (d,

$^3J(\text{H,H}) = 2.56 \text{ Hz}$, 2H; CH), 3.43 (s, 6H; CH_3); ^{13}C NMR (300 MHz, CDCl_3 , 25°C): $\delta = 164.11$, 158.00, 146.93, 142.18, 135.60, 134.91, 133.25, 131.30, 131.05, 129.12, 128.22, 127.97, 126.93, 126.88, 126.84, 126.62, 125.92, 125.74, 125.51, 123.41, 122.17, 115.09, 113.55, 54.99; HR-MS calcd for $\text{C}_{30}\text{H}_{30}\text{O}_6\text{S}_2$: 790.1484; found: 790.1494. (*R,P*)-**7**: ^1H NMR (300 MHz, CDCl_3 , 25°C): $\delta = 8.01$ (m, 4H; CH), 7.59–7.42 (m, 12H; CH), 7.30 (m, 2H; CH), 7.13 (d, $^3J(\text{H,H}) = 8.42 \text{ Hz}$, 2H; CH), 6.83 (dd, $^3J(\text{H,H}) = 2.56$, 8.42 Hz, 2H; CH), 6.42 (d, $^3J(\text{H,H}) = 2.56 \text{ Hz}$, 2H; CH), 3.43 (s, 6H; CH_3); ^{13}C NMR (300 MHz, CDCl_3 , 25°C): $\delta = 165.10$, 158.24, 146.76, 141.50, 136.38, 134.00, 133.34, 132.82, 131.54, 131.04, 129.51, 127.87, 127.65, 127.45, 127.33, 127.01, 126.83, 126.43, 125.51, 125.23, 123.09, 122.31, 115.55, 114.36, 55.02; HR-MS calcd for $\text{C}_{30}\text{H}_{30}\text{O}_6\text{S}_2$: 790.1484; found: 790.1494.

Compounds (*S,S,M*)-**5** and (*S,S,P*)-**5** were prepared analogously. A standard LiAlH_4 reduction afforded (*M*)-*cis*-**8** or (*P*)-*cis*-**8**. All new compounds were fully characterized.

The *ee* value of *cis*-**8** was determined by chiral HPLC (Daicel, Chiralcel OD column, flow rate 1.0 mL min^{-1} , *n*-hexane/*i*PrOH, 99/1): t_{ret} 98.1 min for (*M*)-*cis*-**8** and t_{ret} 125.1 min for (*P*)-*cis*-**8**.

The racemization barrier ($\Delta^\ddagger G^\circ$) of *cis*-**8** was determined by polarimetry (1,2-dibromoethane, $k = 7.22 \times 10^{-5}$ at 70.0°C).

X-ray crystal structure analysis of (*R,M*)-**7**: Crystal dimensions $0.15 \times 0.25 \times 0.52 \text{ mm}$, monoclinic, space group $P2_1$, $a = 9.598(1)$, $b = 14.288(6)$, $c = 12.383(3) \text{ \AA}$, $\beta = 110.77(1)^\circ$, $V = 1587.8(8) \text{ \AA}^3$, $Z = 2$, $\rho_{\text{calcd}} = 1.395 \text{ g cm}^{-3}$, $T = 130 \text{ K}$, $F(000) = 696$. Enraf-Nonius CAD-4 F^2 diffractometer, $\lambda(\text{MoK}\alpha) = 0.71073 \text{ \AA}$, $\mu = 2.2 \text{ cm}^{-1}$. The final refinement on F^2 carried out by full-matrix least-squares techniques converged at $wR(F^2) = 0.2108$ for 2909 reflections with $F_o^2 \geq 0$ and $R(F) = 0.0701$ for 2460 reflections obeying $F_o > 4.0\sigma(F_o)$ and 438 parameters. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-115682. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Influence of Perfluoroarene – Arene Interactions on the Phase Behavior of Liquid Crystalline and Polymeric Materials**

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Supramolecular chemistry, the chemistry of noncovalent intermolecular interactions such as hydrogen bonds, ionic interactions, metal–ion interactions, or the hydrophobic effect, is essential for processes in biological and synthetic systems, such as molecular recognition, catalysis, transport,

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