



Synthesis of enantiomerically pure (*E*)-1,1,3,3,6,6-hexamethyl-1-sila-4-cycloheptene and its absolute configuration

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Abstract

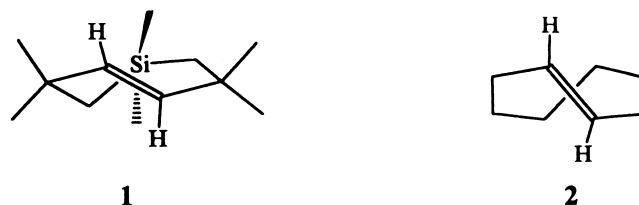
The title compound **1**, a highly strained (*E*)-cycloalkene, was prepared in enantiomerically pure form from the corresponding *trans*-1,2-diol **4** via the thionocarbonate **5**. The racemic **4** was separated by enantioselective HPLC on an amylose tris(3,5-dimethylphenylcarbamate) column. The absolute configuration of **1** was determined by circular dichroism spectroscopy in connection with theoretical calculations; the (+)-enantiomer has the (*S*)- and the (–)-enantiomer the (*R*)-configuration. © 1999 Elsevier Science Ltd. All rights reserved.

1. Introduction

(*E*)-1,1,3,3,6,6-Hexamethyl-1-sila-4-cycloheptene **1** is the smallest non-bridged (*E*)-cycloalkene that can be isolated in pure form at room temperature; it is significantly more strained than (*E*)-cyclooctene **2** (Scheme 1).¹ In the course of our investigations on structure–chiroptic relationships we have been interested in the influence of increasing strain and distorted geometries on the optical activity of organic molecules. The comparison of the structural parameters and the electronic circular dichroism (CD) spectra of **1** and **2** may thus provide a more detailed picture of the basic carbon–carbon double bond chromophore.

An X-ray structure analysis and the ¹H NMR spectrum have shown that **1** is chiral and that its barrier to racemization should be sufficiently high for resolution at room temperature. A separation of the racemate

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Scheme 1.

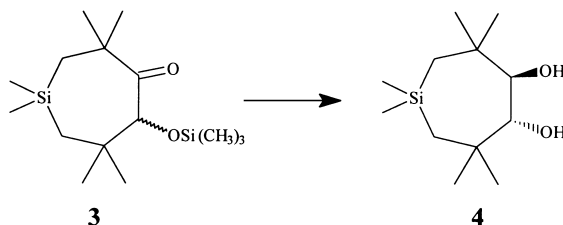
into its two enantiomers was possible by gas chromatography on an analytical cyclodextrin type column.¹ However, for several spectroscopic investigations, the determination of the absolute configuration of **1** and reactions, a larger amount of enantiomerically pure compound (EPC) was required.

2. Results and discussion

2.1. Chromatographic resolution of (\pm)-1,1,3,3,6,6-hexamethyl-1-sila-trans-4,5-cycloheptanediol **4**

Cope and co-workers had separated the enantiomers of (*E*)-cyclooctene **2** via the (+)-*trans*-dichloro(α -methylbenzylamine) platinum(II) complexes by fractional crystallization.² Compound **1** yielded the corresponding platinum(II) complex, but the separation of the diastereomers was not successful.³

Since **4** is the starting material for the synthesis of **1**, an asymmetric synthesis of **4** or a resolution of the racemate of **4** was envisaged (Scheme 2).



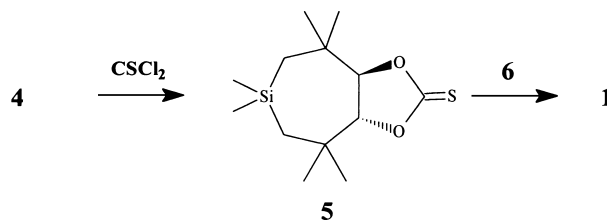
Scheme 2.

Because several attempts to reduce the silylated acyloin **3** to **4** enantioselectively failed, preparative HPLC of racemic **4** was performed on a semipreparative silica gel column which was coated with amylose tris(3,5-dimethylphenylcarbamate).⁴ In each of the 198 runs, three fractions were taken and the middle fraction was not used for further enantioseparation. The (–)-enantiomer of **4** was isolated in 72.6% (e.e. 96%) and the (+)-enantiomer in 70.8% (e.e. 91%) yield.

2.2. Preparation of enantiomerically pure (*E*)-1,1,3,3,6,6-hexamethyl-1-sila-4-cycloheptene **1**

Each of the two enantiomers of **4** was converted to the corresponding thionocarbonate **5** with thiophosgene in 69% (–) and 77% (+) yield, respectively. The (–)-*trans*-diol **4** gave the (–)-*trans*-thionocarbonate **5** and (+)-**4** afforded (+)-**5** correspondingly.

Corey–Winter elimination of (+)-**5** and of (–)-**5** with 1,3-dimethyl-2-phenyl-1,3,2-diazaphospholidine **6**⁵ yielded (+)-**1** (71%; e.e. 87%) and (–)-**1** (98%; e.e. 97.4%), respectively (Scheme 3). The enantiomeric excess was determined by gas chromatography on a capillary column with heptakis(6-*O*-*tert*-butyldimethylsilyl-2,3-di-*O*-methyl)- β -cyclodextrin (50% in polysiloxane OV 1701, w/w).



Scheme 3.

The molar rotation $[\Phi]$ of (+)-**1** in *n*-hexane is $[\Phi]_{589}^{20} = 570^\circ$, while the corresponding value for (+)-**2** amounts to $[\Phi]_{589}^{20} = 455^\circ$ ¹⁵ and for (*E*)-cyclononene to $[\Phi]_{589} = 192^\circ$.¹⁶ As expected the molar rotation increases with increasing twist of the double bond.

2.3. Determination of the absolute configuration of **1**. Optical activity and CD spectra

The absolute configuration of (–)- and (+)-**1** was determined by CD spectroscopy. CD spectra were taken in *n*-hexane solution and in the gas phase (Figs. 1 and 2).

For (+)-**1** a positive CD is observed with a maximum at 215 nm in solution, and for (–)-**1** a corresponding negative CD. In the gas phase the maximum is found at 215.6 nm.

In order to assign the Cotton effects to individual electronic transitions and to determine the absolute configuration of **1**, theoretical calculations of the CD spectrum, i.e. excitation energies ΔE and rotatory strengths *R*, were performed. Recently, one of us developed a new method for this purpose, which is based on a combination of density functional theory and the single excitation configuration interaction approach (DFT/SCI).⁶ The method is clearly superior to the standard Hartree–Fock/SCI approach because dynamical electron correlation is taken implicitly into account. For recent applications of DFT/SCI to the calculation of electronic spectra of large molecules see Bulliard et al.⁷ and Pulm et al.¹⁷

In this work we employed the random-phase approximation in combination with DFT as outlined in detail by Grimme et al.^{8,12} We have used Becke's half-and-half hybrid exchange–correlation functional (BHLYP)⁹ and AO basis sets of valence double- ζ quality¹⁰ with polarization *d*-functions at the non-hydrogen atoms (VDZd). For the carbon atoms of the double bond we used a polarized valence triple- ζ AO basis¹⁰ and two sets of diffuse functions (*2s2p2d*) placed in the center of the double bond to describe the lowest Rydberg states. All calculations were performed with the TURBOMOLE suite of programs.¹¹

Throughout this work we are dealing only with vertical excited states, i.e. the ab initio Hartree–Fock/VDZd optimized geometry of the ground state is employed for the excited states also. Test calculations on **2**¹² have shown that this represents a very good approximation. A comparison of theoretical and experimental¹ bond lengths for **1** and a plot of the optimized structure is given in Fig. 3. The agreement between theory and experiment is quite good, i.e. the largest deviations occur for the Si–C bond distances which are about 0.025 Å too long. A very important structural parameter for the chirality of the compound is the torsion of the double bond as, for example, measured by the dihedral angle C3–C4–C5–C6. The agreement between theory and experiment (130.5° vs. 131°) is quite perfect. The value for this torsion angle should be compared with that found for **2** (HF/VDZ: 137.2°) showing the larger strain in the seven-membered ring (Fig. 3).

The results of the calculations for the CD spectrum are given in Table 1 and a simulation for the (*S*)-enantiomer in comparison with experimental gas phase data is displayed in Fig. 4. First of all we noticed that the positions and relative intensities for all bands in the experimental spectrum, i.e. the intense positive band A at 215 nm, the shoulder around 190 nm (B) and the two negative features at 180 and 160 nm (C and D) are nicely reproduced by the calculation. Thus, we can assign the absolute configuration

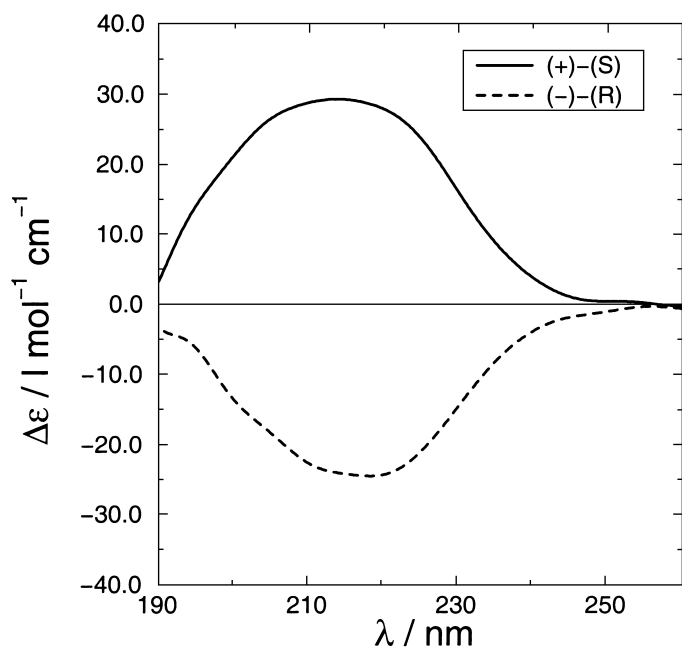
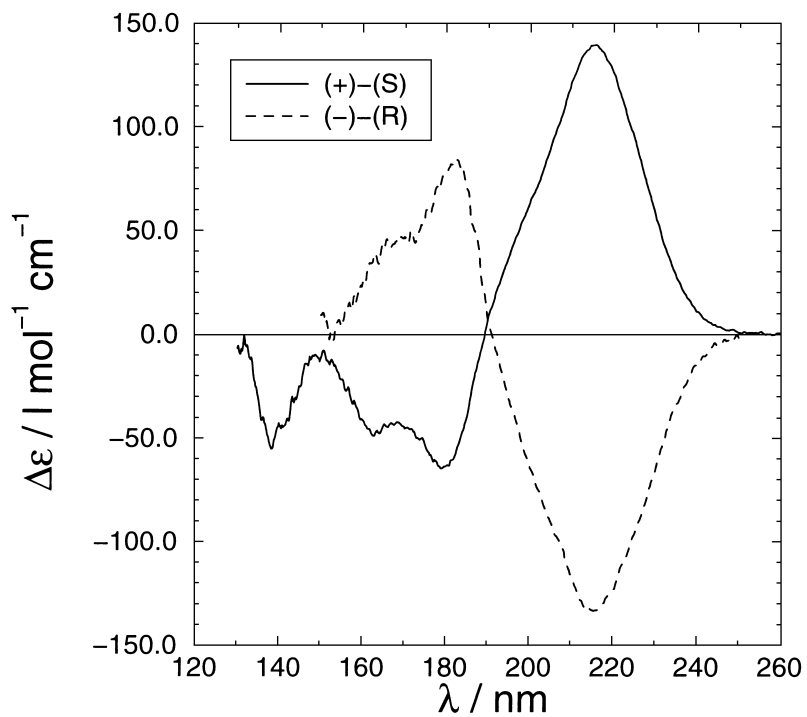
Figure 1. CD spectra of (+)- and (-)-1 in *n*-hexane

Figure 2. CD spectra of (+)- and (-)-1 in the gas phase

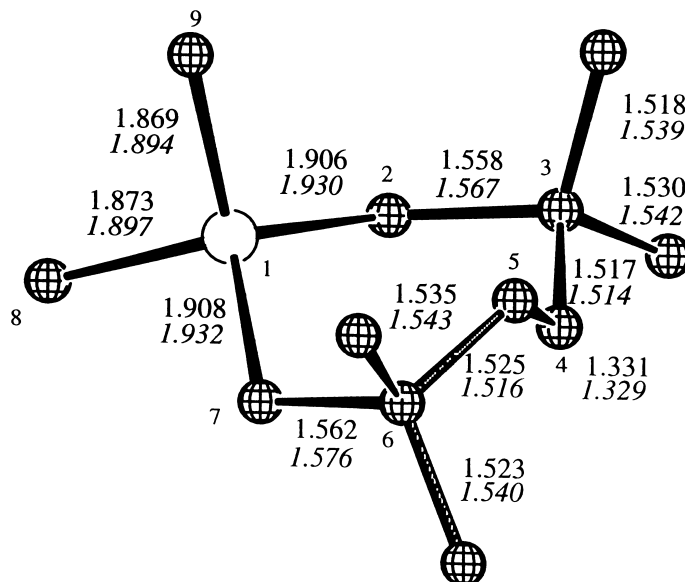


Figure 3. Comparison of experimental and theoretical (HF/SVD, written in italics) bond lengths (in Å) for **1**. The hydrogens have been omitted. The dihedral angle C3–C4–C5–C6 describing the torsion about the double bond is calculated to be 130.5° (exp.: 131°)¹

by comparison of theory and experiment as (+)-(S). This is the same correlation between optical activity and absolute configuration which has been found in **2**.¹⁴

According to the data given in Table 1, the lowest excited singlet state of **1** is of $\pi \rightarrow \pi^*$ character, however mixed with $\pi \rightarrow 3s$ and $\pi \rightarrow 3p$ Rydberg components. Compared to the corresponding state in **2**¹² the R value is nearly doubled and the excitation energy is red-shifted by 0.6 eV. As in **2** the $\pi \rightarrow 3s$ and $\pi \rightarrow 3p$ states, the latter forming the shoulder B, have positive rotatory strengths. Next follows the negative band C, which is made from $\pi \rightarrow 3d$ Rydberg states and the valence shell $\sigma(\text{C-H}, \text{C-C}) \rightarrow \pi^*$ excitation. The latter state contributes predominantly in **2** to the second strong negative band in the CD spectrum¹³ while the former have positive R values in **2** (and negative for **1**). The negative band D, which is not found for **2**, is indicative of the silicon atom in the molecule. The relatively high-lying $\sigma(\text{Si-C})$ orbitals generate several valence and Rydberg states.

In summary, we conclude that the higher strain in **1** compared to **2** induces a larger torsion angle of the double bond which increases the Cotton effect of the valence $\pi \rightarrow \pi^*$ state and decreases the intensity of the valence $\sigma \rightarrow \pi^*(\text{C-H}, \text{C-C})$ excitation (by a factor of about four). Both valence states are lowered in energy so that the $\pi \rightarrow \pi^*$ state becomes the lowest excited state and the $\pi \rightarrow \sigma^*$ state is only slightly above the $\pi \rightarrow 3d$ manifold.

Finally, we want to comment on the absolute CD intensities. In the calculations, we obtain a consistent picture, i.e. the positive maximum at 210 nm in the spectrum of **1** has a $\Delta\epsilon$ of 63 $\text{M}^{-1} \text{cm}^{-1}$. The corresponding value for **2** is about 35 (both, theory and experiment).^{12,13} However, the experimental spectra in solution and in the gas phase (see Figs. 1 and 2) differ by a factor of about four (30 vs. 135 $\text{M}^{-1} \text{cm}^{-1}$). Presently, we have no explanation for this difference but we notice, however, that the theoretical result is relatively near to the average of the two experimental values.

Table 1
Vertical singlet-singlet excitation energies ΔE , oscillator strengths f , rotatory strengths R and differences of ground and excited state $\langle r^2 \rangle$ expectation values for (+)-(S)-**1** at the DFT/RPA level of theory

State	ΔE (eV)	ΔE (nm)	f^a	R^a (10^{-40} cgs)	$\langle r^2 \rangle - \langle r^2 \rangle (GZ)^b$ a_0^2	Assignment
Band A ^c						
2a	5.90	210	.0734	70.7	37.8	$\pi \rightarrow \pi^*$
3a	6.00	207	.0662	38.9	59.8	$\pi \rightarrow 3s$
Band B						
4a	6.33	196	.0174	19.1	76.1	
5a	6.52	190	.0033	0.5	118.3	$\pi \rightarrow 3p$
6a	6.54	190	.0065	4.9	113.1	
Band C						
7a	6.89	180	.0099	-2.6	127.5	
8a	6.95	178	.0121	-6.2	144.3	
9a	6.98	178	.0004	0.3	156.5	$\pi \rightarrow 3d$
10a	7.00	177	.0069	-8.1	154.6	
11a	7.04	176	.0024	-10.4	132.1	
12a	7.13	174	.0198	-23.5	39.0	σ (C-H, C-C) $\rightarrow \pi^*$
Band D						
13a	7.41	167	.0087	-7.6	10.0	σ (Si-C) $\rightarrow \pi^*$
14a	7.42	167	.0110	-19.3	100.5	$\pi \rightarrow$ higher Rydberg
15a	7.44	167	.0571	17.0	71.1	σ (Si-C) $\rightarrow 3s$
16a	7.46	166	.0469	7.4	65.7	σ (Si-C) $\rightarrow 3s$
17a	7.65	162	.0153	-16.8	6.4	σ (Si-C) $\rightarrow \pi^*$

^a Calculated in the velocity formalism which is origin independent for R .

^b The $\langle r^2 \rangle$ value of the ground state is $209.9 a_0^2$. Large positive $\langle r^2 \rangle - \langle r^2 \rangle (GZ)$ values indicate that the excited state has a larger electronic spatial extent than the ground state.

^c The $\pi \rightarrow \pi^*$ and $\pi \rightarrow 3s$ states of this band are mixed with each other and there are also some contributions from $\pi \rightarrow 3p$.

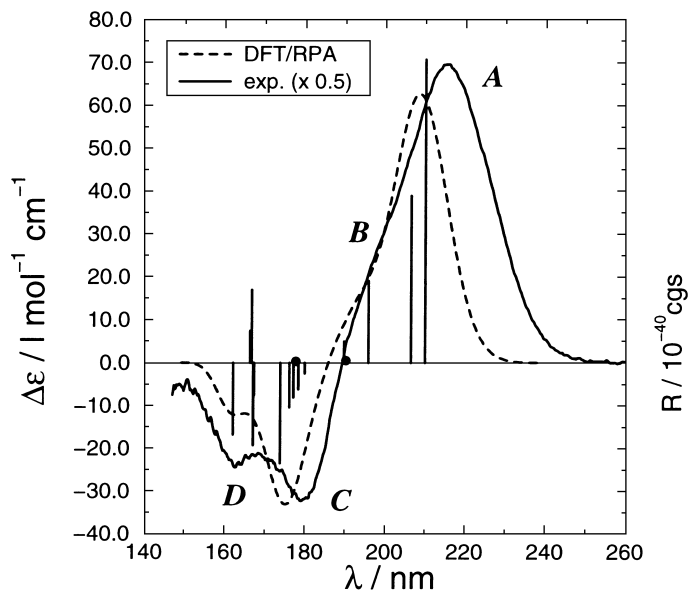


Figure 4. Comparison of experimental gas phase and theoretical (DFT/RPA) CD spectra of (+)-(-)-**1**. The lines and filled dots indicate the position of the calculated states. The simulation of the spectrum has been performed by summing rotatory strengths weighted Gaussian curves with a mean half width of 0.4 eV for each transition

3. Experimental

3.1. General

Melting points: Electrothermal melting point apparatus, uncorrected. ^1H NMR: WP 80 Bruker (80 MHz); AC 250P Bruker (250 MHz); WM 400 Bruker (400 MHz). ^{13}C NMR: AC 250P Bruker (62.90 MHz). MS: 311A Varian MAT, 70 eV; Spectro System MAT 188 Finigan MAT.

3.2. CD spectra

CD spectra in solution were measured on a JASCO spectropolarimeter J 720; 1 mm cell; (+)-enantiomer 4.8×10^{-4} mol/L, (-)-enantiomer 5.6×10^{-4} mol/L in *n*-hexane.

CD measurements in the gas phase were carried out using synchrotron radiation from the 3.5 GeV storage ring ELSA of the Institute of Physics in Bonn. For the experiments reported here, ELSA was operated with an electron energy of 2.3 GeV and currents between 80 mA and 20 mA. The final CD spectra were normalized for this decay. The experimental set-up used for the measurements reported has been described in all details in previous publications.^{17,18} Thus, only a short description will be given in the following. Experiments were carried out at the beamline BN2 in the SR-laboratory at ELSA.

The first optical element in this beamline is a plane float glass mirror reflecting the VUV into the CD beamline. A toroidal mirror focuses this VUV light onto the entrance slit of a 1 m, 15° normal incidence monochromator (Acton Research Company). This monochromator was equipped with a 600 lines per mm Al/MgF₂ coated grating allowing wavelengths between 110 nm and 600 nm. For the molecules investigated here, CD spectra were scanned at 0.2 nm increments and the spectral resolution $\Delta\lambda$ was about 2 nm. This gave the best compromise between high resolution and a good signal-to-noise ratio.

The monochromized beam exiting from the monochromator was focused by a spherical mirror through a CaF₂ photoelastic modulator (Hinds PEM-80), used at a modulation frequency of 50 kHz. There is no

need for linear polarization as in commercial instruments because the mirror and the monochromator retain the linear polarization of the incoming synchrotron radiation beam. The circularly polarized light passes through a 43 cm gas cell sealed by two LiF windows and CD spectra are recorded by a solar blind photomultiplier (EMI 9426) using the standard lock-in technique.¹⁹ External heating coils heat the cell and a MKS baratron 622A determines the pressure on an absolute scale. We recorded the CD spectra at pressures between 0.2 and 0.8 Torr at 45°C in wavelength sections and optimized the pressure in these sections to obtain the best signal possible.

3.3. Chromatographic resolution of (\pm)-1,1,3,3,6,6-hexamethyl-1-sila-trans-4,5-cycloheptanediol **4**

A solution of 1570 mg (6.81 mmol) of racemic **4**¹ in 19.8 mL *n*-hexane was continuously applied in portions of 100 μ L to a semipreparative chiral HPLC column (column: amylose tris(3,5-dimethylphenylcarbamate) on silica gel, 25 \times 1 cm; eluent: *n*-hexane:2-propanol 95:5; flow rate: 2.26 mL/min; pressure: ca. 12 bar; detection: polarimeter (KNAUER, Chiral Detector A1000)). The (–)-enantiomer was eluted after 14 min 10 s and the (+)-enantiomer after 16 min 25 s (time from injection to detection in the polarimeter). Three fractions were taken from each run:

fraction 1: (–)-enantiomer;

intermediate fraction;

fraction 2: (+)-enantiomer.

After distillation of the solvent, 570.2 mg (2.48 mmol, 72.6%) (–)-enantiomer, e.e. 95.9% (fraction 1), and 555.6 mg (2.41 mmol, 70.8%) (+)-enantiomer, e.e. 91.4% (fraction 2), were obtained. The enantiomeric excess of the fractions obtained by preparative enantiomeric resolution was analyzed by enantioselective gas chromatography using a 25 m (0.25 mm i.d.) fused silica capillary column with heptakis(6-*O*-*tert*-butyldimethylsilyl)-2,3-di-*O*-methyl)- β -cyclodextrin (50% in polysiloxane OV 1701, w/w isothermal at 150°C).²⁰ The (+)-enantiomer was eluted after 11.4 min and the (–)-enantiomer after 12.9 min. The specific rotations were extrapolated to 100% enantiomeric purity:

(–)-**4**: $[\alpha]_{589}^{20} = -25.4$ (ethanol, *c*=1.2);

(+)-**4**: $[\alpha]_{589}^{20} = +23.9$ (ethanol, *c*=1.4).

¹H NMR (250 MHz, CDCl₃): δ 0.03 (s, 6H, SiCH₃), 0.65 (s, 4H, SiCH₂), 0.92/1.08 (2s, each 6H, CCH₃), 2.75 (s, 2H, OH), 3.41 (s, 2H, CHO) ppm. ¹³C NMR (62.90 MHz, CDCl₃): δ 0.57 (SiCH₃), 22.45/31.45 (CCH₃), 30.08 (SiCH₂), 37.58 (C_q), 75.70 (CHO) ppm. MS (70 eV): *m/z* (%) 215 (0.1, M⁺–CH₃), 141 (82, C₈H₁₇Si), 75 (100). Anal. calcd for C₁₂H₂₆O₂Si: C 62.55, H 11.37; found C 62.71, H 11.27.

3.4. (+)- and (–)-1,1,3,3,6,6-Hexamethyl-1-sila-trans-4,5-cycloheptanethionocarbonate **5**

To a stirred solution of 541.5 mg (2.35 mmol) (+)-**4** (e.e. 91.4%) in 50 mL dry CH₂Cl₂ were added at 0°C 0.4 mL pyridine, 10 mg 4-(dimethylamino)pyridine and 0.184 mL (2.4 mmol) thiophosgene; after 1 h, 0.2 g silica gel was added to absorb excess thiophosgene and the solution stirred for another hour at room temperature. After filtration and removal of CH₂Cl₂ the remaining crude product was purified by flash chromatography on silica gel with CH₂Cl₂ as eluent. Concentration afforded 495.4 mg (1.82 mmol, 77%) (+)-**5**; m.p. 201–202°C. Using the same protocol, 558.2 mg (2.43 mmol) (–)-**4** (e.e. 95.9%) was converted to 456.2 mg (1.68 mmol, 69%) (–)-**5**; m.p. 201–202°C.

Assuming complete retention of configuration during the preparation of **5** the following specific rotations were extrapolated:

(–)-**5**: $[\alpha]_{589}^{20} = -7.3$ (dichloromethane, *c*=0.82);

(+)-**5**: $[\alpha]_{589}^{20} = +5.0$ (dichloromethane, $c=0.97$).

$^1\text{H NMR}$ (80 MHz, C_6D_6): δ -0.29 (s, 6H, SiCH₃), 0.09 (s, 4H, SiCH₂), 0.68, 0.93 (each 1s, each 6H, CCH₃), 3.98 (s, 2H, CHO) ppm. $^{13}\text{C NMR}$ (62.90 MHz, CDCl_3): δ 0.08 (SiCH₃), 22.73, 30.87 (CCH₃), 28.54 (SiCH₂), 35.73 (C_q), 89.26 (CHO), 222.48 (C=S). MS (70 eV): m/z (%) 272 (12, M⁺), 196 (5, C₁₂H₂₄Si⁺), 195 (31), 141 (47), 127 (67), 85 (44), 75 (100), 73 (62), 59 (100). Anal. calcd for C₁₃H₂₄O₂SSi (272.49): C 57.31, H 8.88; found: C 58.14, H 8.88.

3.5. (+)- and (-)-(E)-1,1,3,3,6,6-Hexamethyl-1-sila-4-cycloheptene **1**

A mixture of 320 mg (1.176 mmol) (+)-**5** and 233 mg (1.2 mmol) **6** (Aldrich) was kept under N₂ in a closed flask for 2 d at 40°C. Alkene **1** was obtained by distillation from the reaction mixture at 80°C and 0.1 torr. Yield: 165 mg (0.84 mmol, 71%) (+)-**1** of 96% purity (determined by gas chromatography). The e.e. (87%) was determined on the same column as used for the diol **4** (isothermal at 80°C, retention time 5.12 min).

Using the same protocol, 337 mg (1.24 mmol) (-)-**5** and 313 mg (1.6 mmol) **6** yielded 239 mg (1.22 mol, 98%) (-)-**1** of 95% purity. The e.e. was 97% (retention time 5.68 min).

(-)-**1**: $[\alpha]_{589}^{20} = -263.1$ (D₈-toluene, $c=1.34$);

(+)-**1**: $[\alpha]_{589}^{20} = +289.8$ (D₈-toluene, $c=1.47$).

$^1\text{H NMR}$ (400 MHz, C_6D_6): δ -0.04 (s, 6H, SiCH₃), 0.63 (AB, $J_{AB}=15.0$ Hz, 4H, CH₂), 1.18/1.26 (2s, each 6H, CCH₃), 5.59 (s, 2H, =CH) ppm. $^{13}\text{C NMR}$ (62.90 MHz, C_6D_6): δ 0.33 (SiCH₃), 26.11/31.99 (CCH₃), 38.00 (C_q), 39.00 (SiCH₂), 138.22 (C=C) ppm. MS (70 eV): m/z (%) 196 (3, M⁺), 181 (8, M⁺-CH₃), 140 (70, C₈H₁₆Si), 125 (100, C₇H₁₃Si). Anal. calcd for C₁₂H₂₄Si: C 73.38, H 12.32; found: C 73.58, H 12.40.

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