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Enantiomerically Pure Titanium Complexes Containing an [OSSO]-Type Bis(phenolate) Ligand: Synthesis, Structure, and Formation of Optically Active Oligostyrenes

Geert-Jan M. Meppelder,[a] Klaus Beckerle,[a] Ramanujachary Manivannan,[a] Bing Lian,[a] Gerhard Raabe,[b] Thomas P. Spaniol,[a] and Jun Okuda*[a]

Dedicated to Professor Ryoji Noyori on the occasion of his 70th birthday

Abstract: Chiral 1,2-*trans*-dithiocyclohexanediyl-bridged bis(phenols) of the type [2,2′-{HOC_6H_2-6-R^1-4-R^2}$_2S_2C_6H_{10}$] ([OSSO]H_2, R^1 = *t*Bu, *i*Pr, H; R^2 = *t*Bu, *i*Pr, Me) could be conveniently and selectively synthesized in three steps, starting from cyclohexene oxide and arene thiolate. The racemic bis(phenols) could be resolved using an enantiopure (*S*)-camphorsulfonic ester auxiliary or by (chiral) HPLC. Complexation of the racemic bis(phenols) to TiX_4 (X = Cl, O*i*Pr) proceeds in a diastereoselective fashion to give only the Λ,*R*,*R* and Δ,*S*,*S* enantiomers. Racemic [Ti{(OC_6H_2-6-*t*Bu-4-Me)$_2S_2C_6H_{10}$}Cl_2] reacts with benzyl magnesium bromide to afford the crystallographically characterized dibenzyl complex. The benzyl cation formed using $B(C_6F_5)_3$ in C_6D_5Br slowly decomposes at temperatures above +10 °C. When treated with methylaluminoxane, the dichloro complexes [Ti{OSSO}Cl_2] polymerize styrene with activities up to 146 kg (mol catalyst)$^{-1}$ [styrene (mol L^{-1})]$^{-1}$ h^{-1}; diisopropoxy complexes [Ti{OSSO}(O*i*Pr)$_2$] show mere trace activity. With 1-hexene as a chain-transfer agent, activated enantiopure titanium complexes give low-molecular-weight homochiral isotactic oligostyrenes, terminated by one to five 1-hexene units with M_n values as low as 750 g mol^{-1} for R = *t*Bu and 1290 g mol^{-1} for R = Me. Below $M_n \approx 5000$ these oligostyrenes show optical activity.

Keywords: catalysis · chirality · polymerization · styrene · titanium

Introduction

The term "cryptochirality" was introduced by Mislow and Bickart in 1977 to describe a chiral molecule whose chirality cannot be operationally determined.[1] This term applies to isotactic poly(α-olefins) in which a large number of chiral centers are formed from prochiral olefins. Their optical activity cannot be measured in solution, since high-molecular-weight polymers possess pseudo-C_s symmetry.[2,3] Optically active poly(α-olefins) can be obtained in cases where the pseudosymmetry is destroyed,[4] for example by (co)polymerization of a chiral monomer[5,6] or by the presence of specific stereosequences in the main chain of the polymer.[7,9b] Often, optical activity stems from the formation of helical structures with a preferred screw sense.[8] The development of well-defined,[9] chiral, and in rare cases enantiopure[10] *ansa*-metallocene complexes has allowed the observation of enantiofacial selectivity of insertion of the prochiral olefin insertion at the metal center during oligomerization.[3,6,11] At what degree of polymerization the observable optical activity of poly(α-olefins) disappears and whether "homochiral" isotactic poly(α-olefins) can be accessed are questions insufficiently addressed so far.[12]

We have recently shown that chiral, configurationally rigid bis(phenolato) titanium catalysts derived from the linear, 1,ω-dithioalkanediyl-bridged [OSSO]-type ligand efficiently polymerize styrene to give isotactic polystyrene (*i*PS).[13] Previously, *i*PS has been prepared using heterogeneous Ziegler-type catalysts and characterized as the first crystallizable polyolefin by Natta and co-workers.[14] In con-

[a] G.-J. M. Meppelder, Dr. K. Beckerle, Dr. R. Manivannan, Dr. B. Lian, Dr. T. P. Spaniol, Prof. Dr. J. Okuda
Institute of Inorganic Chemistry
RWTH Aachen University
Landoltweg 1, 52056 Aachen (Germany)
Fax: (+49) 241-80-92644
E-mail: jun.okuda@ac.rwth-aachen.de

[b] Prof. Dr. G. Raabe
Institute of Organic Chemistry
RWTH Aachen University
Landoltweg 1, 52056 Aachen (Germany)

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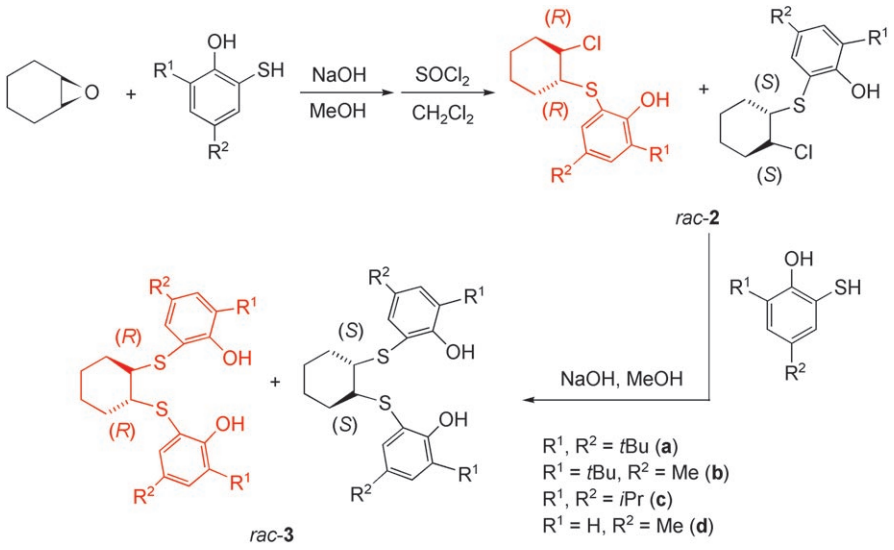
trast to homogeneous catalysts for the syndiotactic polymerization of styrene, of which many have been discovered since their introduction by Ishihara and co-workers,[15,16] very few other homogeneous catalysts for the production of highly isotactic polystyrene are known.[17,18] Although the aforementioned [OSSO]-titanium complexes are chiral, they are not easily resolved, partly because complexation of the ligand to the titanium center is not stereoselective.[19] We have recently prepared optically active catalyst precursors which feature an inherently chiral, 1,2-dithiocyclohexanediyl-bridged [OSSO] ligand. By utilizing chain-transfer methodology in the presence of 1-hexene, we demonstrate that the insertion of styrene in such post-metallocene catalysts[20] occurs stereospecifically, giving optically active *i*PS oligomers.[12,21]



Scheme 1. Synthesis of racemic ligands **3a**–**d**.

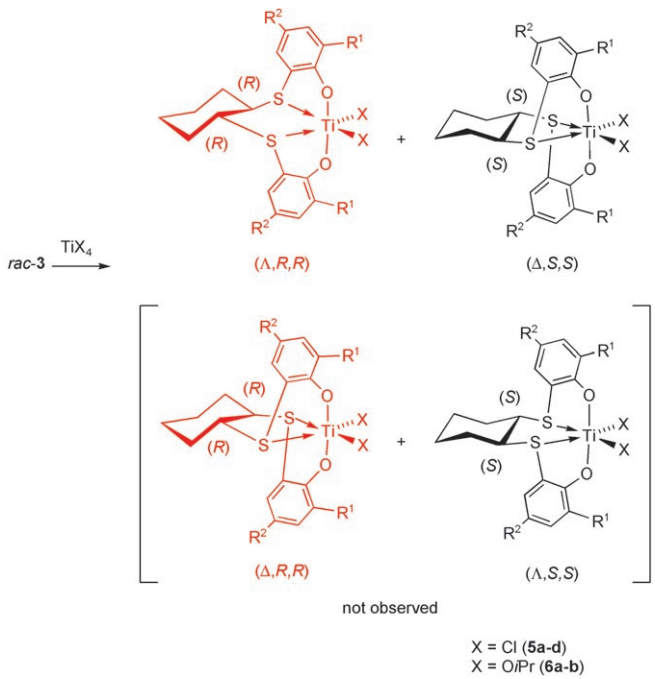
Results and Discussion

Synthesis and Characterization

The racemic bis(phenol) ligand precursors could be obtained in three steps by consecutive nucleophilic substitutions (Scheme 1). The syntheses feature ring opening of cyclohexene oxide by a hydroxyarene thiolate to give the appropriate (*trans*-2-hydroxycyclohexyl)phenol. Chlorination of the hydroxycyclohexyl moiety with thionyl chloride in CH_2Cl_2 and subsequent substitution by a second equivalent of arene thiolate afforded the racemic bis(phenols) in 61% (**3a**) and 90% (**3b**) overall yield, respectively. Exclusively *trans*-bis(phenol) was formed owing to anchimeric assistance of the thioarene moiety via a thiiranium intermediate.[22] This is in agreement with X-ray analysis of single crystals of *rac*-**2a**, which shows a *trans* product.

For chiral resolution, compounds *rac*-**3a**,**b** were modified with a suitable chiral ancillary. Lithiation of the ligand with *n*BuLi and subsequent reaction with two equivalents of (1*S*)-camphorsulfonyl chloride in diethyl ether afforded the diastereomeric bis((1*S*)-camphorsulfonates) (*S*,*S*,*S*,*S*)- and (*R*,*R*,*S*,*S*)-**4a,b** in good yield. Traces of starting material and monosubstituted product were removed by column chromatography. Fractional crystallizaton of the diastereomers was attempted from a variety of common solvents, with acetone and cyclohexane found to be most suitable for **4a** and **4b**, respectively. Hydrolytic cleavage of the sulfonate ester with aqueous NaOH in a 1:1 mixture of THF and methanol afforded the enantiopure bis(phenols) (−)-(*R*,*R*)-**3a,b** and (+)-(*S*,*S*)-**3a**. In the case of **4b** the second diastereomer could not be obtained in more than 71% *de*, even after repeated recrystallizations. Alternatively, access to all enantiopure bis(phenols) was achieved by preparative (chiral) HPLC of **4a** and *rac*-**3b**.[23] The absolute configuration of the chiral bis(phenols) **3a** and **3b** was established by single-crystal X-ray crystallography of enantiopure **3a** and diastereomers **4a** and **4b**.[24a] The chiral bis(phenolates) were further characterized by optical rotation and CD spectroscopy.[24b]

Reaction of racemic **3a**,**b** with TiX_4 in pentane proceeded smoothly to give the appropriate [Ti{OSSO}X_2] complexes (**5a**,**b**: X = Cl; **6a**,**b**: X = O*i*Pr) in good yield (Scheme 2). The ^{1}H NMR spectra of **5** and **6** all show a single set of reso-



Scheme 2. Synthesis of racemic complexes **5** and **6**.

nances for the arene substituents of the ligand, which suggests the formation of C_2-symmetrical species of *cis*-α geometry.[25] High-temperature NMR measurements show that these complexes **5** and **6** are configurationally stable at 80 °C and that no significant decomposition occurs. Dithiobutane-bridged [OSSO]-titanium complexes with *ortho* substituents smaller than *t*Bu are not configurationally stable at room temperature (R = H) or at 80 °C (R = *i*Pr).[26] To determine the stabilizing effect of the bridge on the configuration of the titanium complex, analogous dithiocyclohexane-bridged racemic bis(phenols) [2,2′-{HOC_6H_2-4,6-*i*Pr_2}$_2S_2C_6H_{10}$] (*rac*-**3c**) and [2,2′-{HOC_6H_3-4-Me}$_2S_2C_6H_{10}$] (*rac*-**3d**) and their respective dichloro titanium complexes (*rac*-**5c**,**d**) were synthesized. A stable *cis*-α configuration was inferred from X-ray single-crystal diffraction data of **5d** (see the Supporting Information) and NMR spectra of **5c** and **5d**, which feature single C_2-symmetrical species. Remarkably, variable-temperature NMR in $C_2D_2Cl_4$ showed complex **5d** to be configurationally stable up to 100 °C.

The observation of a single product in the NMR spectra of compounds **5** and **6** excludes formation of diastereomer pairs. Thus, introduction of a chiral 1,2-dithiocyclohexanediyl backbone in *rac*-**3** resulted in diasteroselective formation of only one pair of enantiomers of complexes *rac*-**5** and *rac*-**6**. This result was supported by X-ray diffraction of single crystals obtained in the synthesis of *rac*-**5a**. Only enantiomers (Λ,*R*,*R*)-**5** and (Δ,*S*,*S*)-**5** were present; (Δ,*R*,*R*)-**5** and (Λ,*S*,*S*)-**5** were not observed. The reaction of enantiopure bis(phenols) (−)-(*R*,*R*)-**3** and (+)-(*S*,*S*)-**3** with TiX_4 therefore leads to the corresponding optically active complexes (Λ,*R*,*R*)-[Ti{OSSO}X_2] and (Δ,*S*,*S*)-[Ti{OSSO}X_2] respectively, which were all fully characterized. Noteworthy is the change of the sign of rotation between chiral complexes **5** and **6**. The Cotton effect in the CD spectra of the corresponding enantiomers of **5a** and **6b** in CH_2Cl_2 shows the same sign up to about 425 nm (Figure 1). At higher wavelengths the Δε value approaches zero for **6b**.

The absolute configuration of complexes (−)-(Λ,*R*,*R*)-**5b** and (+)-(Λ,*R*,*R*)-**6b** was established by single-crystal X-ray crystallography, which corroborated the expected *cis*-α configuration of the tetradentate ligand around an octahedral titanium center. The structural features of complex (Λ,*R*,*R*)-**5b** (Figure 2, Table 1), which was crystallized from CH_2Cl_2, closely resemble those of the recently published *rac*-**5a** and 1,4-dithiobutanediyl-bridged [Ti{OSSO}Cl_2] complexes, with phenoxy groups in the apical positions and the chloride ligands in *cis* positions.[26,28] Bond lengths and angles are well

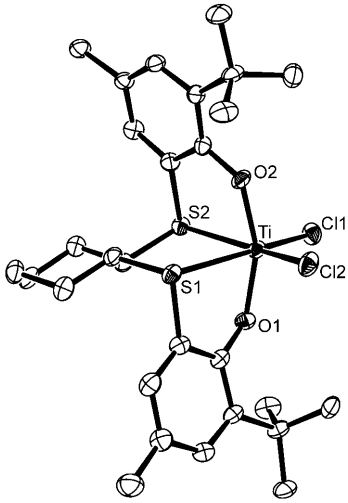


Figure 2. ORTEP diagram of (Λ,*R*,*R*)-**5b.** Hydrogen atoms are omitted for clarity; thermal ellipsoids are drawn at the 50% probability level.[27]

Table 1. Selected bond lengths (Å) and angles (°) for complexes (Λ,*R*,*R*)-**5b** and **7**.

(Λ,*R*,*R*)-**5b**		**7**	
Ti-O1	1.858(4)	Ti-O1	1.873(2)
Ti-O2	1.855(4)	Ti-O2	1.989(2)
Ti-S1	2.6353(17)	Ti-S1	2.7382(12)
Ti-S2	2.6206(16)	Ti-S2	2.6468(13)
Ti-Cl1	2.2676(17)	Ti-C29	2.138(4)
Ti-Cl2	2.2509(17)	Ti-C36	2.145(3)
O1-Ti-O2	158.50(19)	O1-Ti-O2	159.60(10)
S1-Ti-S2	78.77(5)	S1-Ti-S2	76.82(3)
Cl1-Ti-Cl2	106.96(7)	C29-Ti-C36	119.17(15)
		Ti-C29-C30	100.3(3)
		Ti-C36-C37	119.0(2)

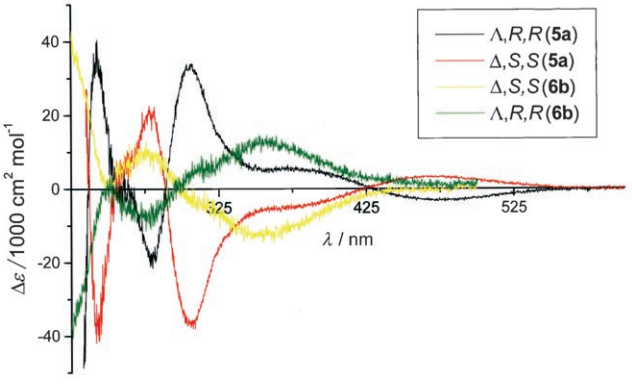
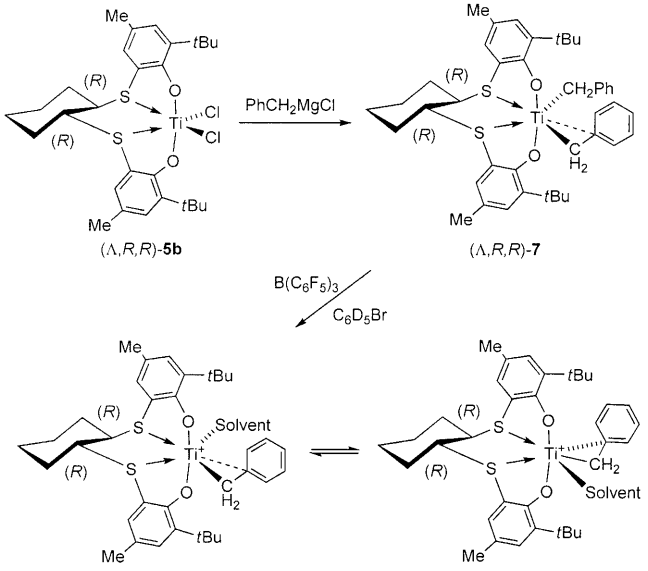


Figure 1. CD spectra (CH_2Cl_2, 25 °C) of the enantiomerically pure titanium complexes **5a** and **6b**.

within the range commonly observed for structurally related complexes (Table 1).[13,29,30] Only poorly diffracting single crystals of diisopropoxy titanium complex (Λ,*R*,*R*)-**6b** could be obtained from hexamethyldisiloxane solution (see the Supporting Information). The unit cell contains three crystallographically independent molecules with slightly varying bond lengths and bond angles. With 1.749(7)–1.790(7) Å the isopropoxy Ti–O bonds are considerably shorter than the Ti–Cl bonds of *rac*-**5b** (2.2509(17)–2.2676(17) Å), which causes a lengthening of the phenolic Ti–O bonds from 1.855(4)–1.858(4) Å to 1.920(7)–1.935(7) Å. The large Ti-O-C bond angles of the isopropoxy ligands (141.6(11)–168.1(8)°) suggest significant Ti–O π interaction.[19a,31]

Benzyl Cation

To gain some insight into the active species of isospecific styrene polymerization using the above mentioned titanium complexes, the synthesis and characterization of the benzyl cation was attempted (Scheme 3).[29a,b] Reaction of **5b** with



Scheme 3. Synthesis of dibenzyl **7** and formation of diastereomeric benzyl cation.

two equivalents of benzylmagnesium chloride proceeds smoothly in pentane at low temperature to give the appropriate dibenzyl titanium complex **7** in 56% yield. The ^{1}H NMR spectroscopic data of **7** in C_6D_6 is consistent with the expected *cis*-α geometry of the ligand around the titanium center. The benzylic protons appear as AB doublets at $\delta = 3.42$ and 3.50 ppm, with a coupling constant of $^2J_{HH} = 9.0$ Hz; in the ^{13}C NMR spectrum the benzylic carbon is found at $\delta = 88.9$ ppm. The coupling constant of $^1J_{CH} = 132$ Hz exceeds values normally found for η^1-coordinated benzyl moieties (122–126 Hz)[32] and was found to be similar to that of the closely related [Ti{$(OC_6H_2$-4,6-tBu$_2)_2$S$(CH_2)_2$S}$(CH_2Ph)_2$].[29a] No significant high-field shift was observed for the *ortho*-H resonances of the benzyl group, which suggests that partial η^2 coordination to the metal center in solution is weak.[32a,b,33,34] In the solid state **7** is stable at −30 °C for prolonged periods, and single crystals suitable for X-ray analysis could be grown from a pentane solution at −30 °C over a period of several days. The solid-state structure (Figure 3, Table 1) shows the *cis*-benzyl moieties and the [OSSO] ligand in a distorted octahedral environment (O1-Ti-O2 = 159.60(10)°). The benzyl ligands coordinate in η^1 and partial η^2 bonding modes, with Ti-C$_\alpha$-C$_{ipso}$ bond angles of 119.0(2)° and 100.3(3)°, respectively. The more acute bond angle associated with η^2 coordination results in a relatively short Ti–C$_{ipso}$ bond length of 2.797(4) Å. The increased steric requirement of the benzyl ligands over

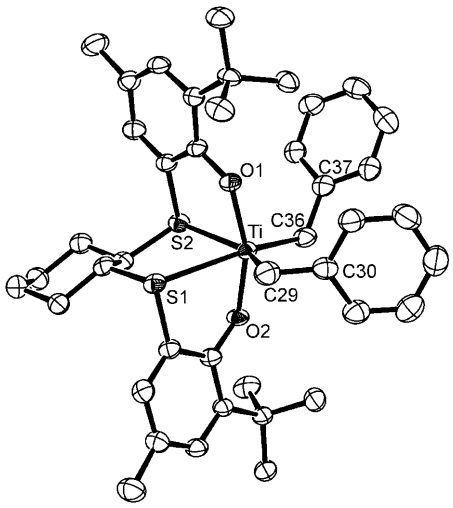


Figure 3. ORTEP diagram of (Λ,*R*,*R*)-**7.** Hydrogen atoms are omitted for clarity; thermal ellipsoids are drawn at the 50% probability level.[27]

the chloro ligands is reflected in the large increase in bond angle from 106.96(7)° (Cl1-Ti-Cl2) to 119.17(15)° (C29-Ti-C36). The widening of this angle causes a reduction of the S1-Ti-S2 bond angle from 78.77(5)° (**5b**) to 76.82(3)° (**7**) and subsequent lengthening of the Ti–S1 bond *trans* to the η^1-benzyl moiety by about 0.09 Å to accommodate the C_2S_2Ti framework. A similar bond-lengthening effect was observed for [Ti{$(OC_6H_2$-4,6-tBu$_2)_2$S$(CH_2)_2$S}$(CH_2Ph)_2$], although in that case the Ti–S bond *trans* to the η^2-coordinated benzyl group was affected. Notably, the structural features of both dibenzyl complexes are dissimilar. While the phenyl rings of the benzyl groups of [Ti{$(OC_6H_2$-4,6-tBu$_2)_2$S$(CH_2)_2$S}$(CH_2Ph)_2$] are directed outwards from each other to reduce steric interactions, the η^2-benzyl moiety of **7** is pointed *towards* the other benzyl group, leading to an increase in the C-Ti-C bond angle (90.57(8)° vs. 119.17(15)°) and a decrease in respective titanium–sulfur bond lenths of 0.10–0.15 Å (2.8836(7), 2.7472(7) Å vs. 2.7382(12), 2.6468(13) Å).

Reaction of **7** with one equivalent of B$(C_6F_5)_3$ in C_6D_5Br at −30 °C does not give clean formation of the expected [Ti{OSSO}$(CH_2Ph)]^+$[$(PhCH_2)$B$(C_6F_5)_3]^-$. In addition to the benzylic AB doublets in the ^{1}H NMR spectrum at $\delta = 3.80$ and 3.85 ppm ($^2J_{HH} = 4.8$ Hz) that we assign to TiCH$_2$ of the aforementioned species, two smaller sets of AB doublets at $\delta = 3.35/4.03$ ($^2J_{HH} = 5.9$ Hz) and 2.95/3.55 ppm ($^2J_{HH} = 7.1$ Hz) were observed. The former two signals could be correlated to ^{13}C NMR resonances at $\delta = 98.37$ and 99.87 ppm, but in contrast to [Ti{$(OC_6H_2$-4,6-tBu$_2)_2$S$(CH_2)_2$S}$(CH_2Ph)]^+$, no diastereomer formation owing to slow isomerization on the NMR time scale occurred. For the aryl substituents multiple signals, consistent with the presence of at least two C_1-symmetric species, are observed. The proton resonance for BCH$_2$ at $\delta = 3.47$ ppm integrates 1:1 in comparison with the combined TiCH$_2$ resonances. Besides the presence of residual B$(C_6F_5)_3$, ^{11}B and ^{19}F NMR spectra show no arene coordination of the anion[35] and that the ion pair is solvent separated.[36] At 10 °C the main benzyl resonances and arene

substituents coalesce to give an apparent C_2-symmetric species, featuring a broad benzyl resonance at $\delta = 3.88$ ppm in the ^{1}H NMR spectrum at 25 °C. Above 10 °C slow decomposition sets in with the third set of benzyl resonances increasing in intensity and the BCH_2 resonance collapsing.

Styrene Oligomerization

To extend our previous studies on homogeneous styrene polymerization, racemic and optically active precatalysts **5a**,**b** and **6a**,**b** were activated with MAO to give conformationally stable alkyl cations, which were tested for styrene polymerization (Table 2). In comparison to their C_2-bridged counterparts, 1,2-cyclohexanediyl-bridged bis(phenolate) titanium dichloride complexes give much less active catalysts, with **5b** producing significantly lower molecular weight *i*PS than **5a**.[26,28] Both **5a** and **5b** give polymers with narrow molecular weight distributions, consistent with the presence of a single active species. Complex **5d** polymerizes styrene with significantly lower activity, giving mainly low-molecular-weight atactic polystyrene. This demonstrates that configurational stability of the catalyst by itself is not sufficient for the production of *i*PS and that the presence of large *ortho* substituents is required for isoselective polymerization to occur. The relative stability of the titanium isopropoxy oxygen bonds in **6a** and **6b** resulted in trace activity. As expected, the chiral, high-molecular-weight isotactic polystyrene obtained from enantiopure catalysts did not show any optical activity owing to cryptochirality.

Table 2. Styrene polymerization with 1,2-dithiocyclohexanediyl-bridged bis(phenolate) titanium complexes.

Entry[a]	Complex[b]	Yield [mg]	Activity[c]	M_n[d] $\times 10^{-3}$ [g mol^{-1}]	M_w/M_n[d]
1	*rac*-**5a**	937	127	403	1.65
2	*rac*-**5b**	667	91	283	1.51
3[e]	*rac*-**5d**	14	2	7.5 1657	n.d.
4[e]	*rac*-**6a**	<5	trace	20 400	n.d.
5[e]	*rac*-**6b**	<5	trace	15 250	n.d.
6	(*R*,*R*)-**5a**	1100	146	511	1.60
7	(*S*,*S*)-**5a**	576	78	298	1.43

[a] Polymerization conditions: 1.25 μmol of complex; [Al]/[M] = 1500; 5 mL of styrene in 7.5 mL of toluene; $T = 40$ °C; $t = 2$ h. [b] Activated with MAO. [c] (kg polymer) (mol catalyst)$^{-1}$ [styrene (mol L^{-1})]$^{-1}$ h^{-1}. [d] Determined by GPC using polystyrene standard. [e] Bimodal distribution; *a*PS owing to MAO was not washed out because of low polymer yield. n.d. = not determined.

To investigate the relation between chain length and cryptochirality, a chain-tranfer agent was employed to control the molecular weight. For that purpose 1-hexene was preferred over traditional chain-transfer agents such as H_2 and $ZnEt_2$, which were found to be less suitable.[37] For the enantiomers of precatalyst **5a** it was established that by variation of the 1-hexene/styrene ratio the molecular weight of the oligostyrenes could be controlled down to about 750 g mol^{-1}. A similar set of oligomerization experiments showed that (Δ,*S*,*S*)-**5b** produces significantly higher molecular weight oligomers under similar conditions (Table 3, entries 1 and 8), with a minimum molecular weight of 1290 g mol^{-1} at high 1-hexene/styrene ratios. The molecular weight is not just dependant on the monomer ratio, but the absolute concentration is a determining factor as well.

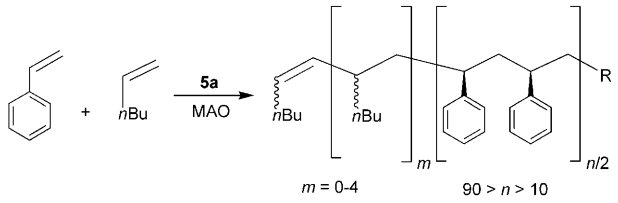
The microstructure of the co-oligomers produced by chiral **5a** and **5b** were investigated by ^{1}H and ^{13}C NMR spectroscopy. A sharp ^{13}C resonance at $\delta = 146.3$ ppm at lower 1-hexene/styrene ratios indicated the presence of isotactic oligostyrenes. The oligohexene fragments were found to be atactic. End-group analysis by NMR revealed the presence of resonances for vinylene end groups at $\delta = 5.15$ ppm (^{1}H) and 131.9 ppm (^{13}C). No vinylidene resonances were observed. We therefore conclude that β-H elimination follows exclusively after 2,1-insertion of 1-hexene. For both **5a** and **5b** at monomer ratios sufficiently large to produce oligomers with molecular weight below 2000 g mol^{-1}, an additional vinylene resonance was observed at $\delta = 5.30$ ppm in the ^{1}H NMR spectrum. Homo-oligomerization experiments of 1-hexene with precatalysts **5a** and **5b** support the formation of atactic homo-oligo(1-hexene). In accordance with our recent investigations into structurally related bis(phenolato) titanium 1-hexene oligomerization catalysts, a small amount of vinylidene-terminated oligomers was also present (90:10 vinylene/vinylidene ratio by ^{1}H NMR spectroscopy).[38] Neither stereoselectivity nor optical activity were ob-

Table 3. Oligo(1-hexene)-capped polystyrene prepared by optically active titanium dichloro complexes (+)-(Δ,*S*,*S*)-**5a** and (+)-(Δ,*S*,*S*)-**5b** activated by MAO.

Entry[a]	[Styrene] [mol L^{-1}]	[1-Hexene] [mol L^{-1}]	1-Hexene/ styrene ratio	Cat.	Yield [mg]	M_n[b] [g mol^{-1}]	M_w/M_n[b]	$[\alpha]_D^{23}$[c]
1	0.48	4.5	9.4	(+)-**5a**	568	790	1.35	+4.4(1)
2	0.64	4.5	7.0	(+)-**5a**	377	1120	1.25	+5.6(1)
3	1.6	4.5	2.8	(+)-**5a**	468	1880	1.49	+3.5(2)
4	1.6	3.4	2.1	(+)-**5a**	168	2680	1.46	+2.7(1)
5	1.6	2.3	1.4	(+)-**5a**	235	3460	1.58	+2.2(1)
6	1.6	1.4	0.9	(+)-**5a**	617	4590	1.45	+1.5(1)
7	3.2	3.2	1.0	(+)-**5a**	680	5870	1.68	–
8	0.45	4.5	10	(+)-**5b**	242	1290	1.30	+7.2(2)
9	0.45	2.4	5.3	(+)-**5b**	264	3290	1.51	+3.4(1)
10	0.90	2.4	2.7	(+)-**5b**	519	4370	1.64	+1.9(1)
11	0.90	1.8	2.0	(+)-**5b**	221	7990	1.57	–
12	0.90	0.80	0.9	(+)-**5b**	263	19130	1.28	–

[a] Reaction time for entries 1–3 and 8–10: 6 h. [b] Determined by GPC using a polystyrene standard. [c] deg cm^3 g^{-1} dm^{-1}, $c \approx 0.10$ g mL^{-1} (CH_2Cl_2).

served. MALDI-TOF mass spectroscopy of a typical oligomer sample (Table 3, entry 3) supports the GPC results, with maximum intensity peaks at $n \approx 30$ (Scheme 4). For each oligostyrene chain, peaks for one to five terminating 1-hexene



Scheme 4. Synthesis of oligohexene-terminated isotactic oligostyrenes.

units ($m = 0$–4) were observed with maximum intensity at $m = 2$. In addition, it was calculated from ^{1}H NMR spectra of oligomers produced by **5b** that on average about four 1-hexene units are present in the oligomer, which slowly increases at higher monomer ratios. In comparison, GPC results of 1-hexene homo-oligomerization experiments show a distribution from which dimers up to heptamers can be identified.

Isotactic oligostyrenes (Table 3) produced by enantiopure precatalysts (Δ,*S*,*S*)-**5a** and (Δ,*S*,*S*)-**5b** show optical activity, with specific rotation values varying from +7.2(2) to +1.5(1) deg cm^3 g^{-1} dm^{-1}. The exclusive production by (+)-(Δ,*S*,*S*)-**5a** and (+)-(Δ,*S*,*S*)-**5b** of oligomers with the same sign of rotation confirms that main-chain stereochemistry is governed by enantiomorphic site control. Previously published results show that use of the opposite enantiomer (Λ,*R*,*R*)-**5a** leads to oligomers with negative optical rotation values, which is corroborated by CD spectroscopy of a pair of enantiomeric oligomers of $M_n \approx 1100$ (see the Supporting Information). Residual catalyst or ligand contributions to the optical activity of the oligomers can be excluded, owing to their negligible concentration. Specific rotation values slowly decrease with increasing molecular weight and beyond $M_n \approx 5000$, which corresponds to an approximate degree of polymerization of 45 for styrene (factoring in an average of three 1-hexene units); no optical rotation could be measured. At this point the optical activity owing to the presence of two different end groups has been "diluted" by the increased chain length of the oligomer and the accompanying reduction in solubility beyond measuring capability. Notably, for **5a** at the low-molecular-weight end of the series the optical activity drops off. The effect occurs at high 1-hexene/styrene ratios owing to the presence of an increasing amount of homo-oligo(1-hexene), which cannot be removed during workup. This reduces the effective concentration of the chiral oligostyrene, thus lowering specific rotation values. Furthermore we cannot exclude that lower stereoselectivity of insertion occurs at the early stages of chain growth. The interaction of the styrene chain with the ligand sphere is less effective for enantiofacial discrimination.[39]

Conclusions

We have shown that the configurational stability of [OSSO]-type titanium complexes results from the diastereoselective tranfer of chirality from the *trans*-1,2-cyclohexanediyl-linked bis(phenolate) ligand to the titanium center. When activated, the helical chirality at the titanium alkyl cation is transferred from the catalyst to the incoming styrene monomer to give homochiral oligostyrene. The main-chain chirality of oligostyrene results in optical activity up to a degree of polymerization of about 45. Beyond $M_n \approx 5000$ optical activity cannot be reliably measured, rendering higher-molecular-weight polystyrenes cryptochiral.

Experimental Section

General Considerations

All operations were performed under an inert atmosphere of argon using standard Schlenk and glovebox techniques. Diethyl ether was distilled from sodium benzophenone ketyl; pentane and toluene were purified by distillation from sodium/triglyme benzophenone ketyl; dichloromethane was dried over calcium hydride; titanium tetrachloride was used as received. Deuterated solvents were dried over sodium or calcium hydride and degassed prior to use. Mercaptophenols were synthesized according to literature procedure.[40] All other chemicals were commercially available and were used after appropriate purification. NMR spectra were recorded on a Varian Unity 500 spectrometer (^{1}H 499.6 MHz, ^{13}C 125.6 MHz, ^{11}B 160.3 MHz) or on a Bruker DRX 400 spectrometer (^{1}H 400.1 MHZ, ^{13}C 125.6 MHz, ^{19}F 376.5 MHz, ^{11}B 128.4 MHz) at 25 °C, unless otherwise stated. Chemical shifts for ^{1}H and ^{13}C{^{1}H} NMR spectra were referenced internally using residual solvent resonances and reported relative to tetramethylsilane. Assignments were verified by correlated spectroscopy. Specific rotation was measured using a THG-GLOCK (ADP2003/WZZ-2S) instrument in appropriate solvents mentioned below ($\lambda = 589.3$ nm at 23 °C) in a 0.5-dm measuring cell, unless otherwise indicated. Circular dichroism spectra were recorded on an AVIV Assoc. 62DS instrument. A cell with path length of 0.1 cm and $c = 3 \times 10^{-4}$ M solution in dichloromethane was used for all measurements. Elemental analyses were performed by the departmental Microanalytical Laboratory. GPC measurements were performed on an Agilent 1100 series instrument at 35 °C, using THF as solvent against a polystyrene standard.

General Polymerization Procedure

Toluene, styrene, and 1-hexene were dried over sodium or calcium hydride and degassed three times prior to use. A 50-mL Schlenk tube was charged with toluene (calculated for a total volume of 15 mL), MAO solution in toluene (1.2 mL, 10 wt %; Aldrich; used as received), styrene, and 1-hexene (oligomerizations only). The mixture was allowed to warm up to 40 °C for 10 min, followed by addition of 0.5 mL of a 2.5 μM stock solution of ((Δ,*S*,*S*)-enantiopure) precatalyst in toluene. The reaction mixture was stirred at 40 °C for 2 h or 6 h and quenched by addition of 0.5 mL isopropanol. The product was precipitated from 100 mL of acidified methanol, filtered, and redissolved in a minimum of chloroform. This procedure was repeated twice with filtration of the chloroform solution through a layer of silica before the last precipitation. Oligomers were dried in vacuo to constant weight; polymers were washed with butanone prior to drying.

Crystallographic Data

Diffraction data were obtained with a Bruker AXS SMART CCD diffractometer with graphite-monochromated $Mo_{K\alpha}$ radiation using ϕ and ω scans. The data reductions as well as absorption corrections were carried out using the SMART program.[41a] The structures were solved by direct methods and Fourier methods using the programs SHELXS-86[41b] and

Table 4. Crystallographic and data collection parameters for [Ti{(OC_6H_2-4-Me-6-*t*Bu)$_2$$S_2C_6H_{10}$}$Cl_2$] ((Λ,*R*,*R*)-**5b**) and [Ti{(OC_6H_2-4-Me-6-*t*Bu)$_2$$S_2C_6H_{10}$}($CH_2C_6H_5$)$_2$] (*rac*-**7**).

	(Λ,*R*,*R*)-**5b**	*rac*-**7**
Empirical formula	$C_{28}H_{38}O_2S_2Cl_2Ti\cdot CH_2Cl_2$	$C_{42}H_{52}O_2S_2Ti\cdot 0.5\ C_5H_{12}$
M_r	674.43	1473.86
Crystal size [mm]	0.40×0.20×0.20	0.33×0.15×0.14
Crystal color	red	dark red
Crystal system	orthorhombic	triclinic
Space group	$P2_12_12_1$	$P\bar{1}$
a [Å]	12.1954(16)	12.179(4)
b [Å]	16.963(2)	12.883(4)
c [Å]	17.562(2)	13.578(4)
α [°]	90	86.936(10)
β [°]	90	89.313(9)
γ [°]	90	76.326(10)
V [Å^3]	3633.1(8)	2067.1(11)
Z	4	2
ρ_{calcd} [g cm^{-3}]	1.233	1.184
T [K]	130(2)	133(2)
$\mu(Mo_{K\alpha})$ [mm^{-1}]	0.667	0.342
$F(000)$	1408	790
θ range [°]	2.32–29.97	2.07–26.05
Reflections collected	32494	19436
Reflections obsd [$I>2\sigma(I)$]	9022	5913
Independent reflections (R_{int})	10075 (0.0519)	8118 (0.0443)
Data/restraints/parameters	10075/0/378	8118/0/454
GoF on F^2	1.157	1.044
R_1, wR_2 [$I>2\sigma(I)$]	0.0869, 0.2451	0.0628, 0.1634
R_1, wR_2 (all data)	0.0946, 0.2501	0.0892, 0.1789
Flack parameter	0.07(6)	–
Largest diff. peak/hole [e Å^{-3}]	0.871, −0.819	1.070, −0.287
CCDC number	679157	679158

SHELXL-96.[41c] Hydrogen atoms were included into calculated positions. Crystallographic data are summarized in Table 4.

Synthesis

1a: 2,4-Di-*tert*-butyl-6-(2-hydoxycyclohexylthio)phenol: Solid NaOH (1.67 g, 42.0 mmol) was added to a solution of 4,6-di-*tert*-butyl-2-mercaptophenol (10.0 g, 42.0 mmol) in methanol (100 mL). The mixture was refluxed until all NaOH dissolved, then cooled to room temperature; cyclohexene oxide (4.2 g, 42.0 mmol) was added dropwise and the mixture was refluxed for 2 h. Methanol was evaporated, water (100 mL) was added, and the aqueous phase was extracted with diethyl ether (3×100 mL). The organic layer was separated, dried over anhydrous Na_2SO_4, and evaporated to give an oil (13.1 g, 38.9 mmol, 93%). ^{1}H NMR ($CDCl_3$): δ=1.09–1.18 (m, 2H, CH C_6H_{10}), 1.22 (s, 9H, $C(CH_3)_3$), 1.23–1.34 (m, 2H, CH C_6H_{10}, partial overlap with *t*Bu signal), 1.34 (s, 9H, $C(CH_3)_3$), 1.54–1.64 (m, 2H, CH C_6H_{10}), 1.94–2.08 (m, 2H, CH C_6H_{10}), 2.51 (m, 1H, CHS), 2.77 (br s, 1H, CHO*H*), 3.28 (m, 1H, C*H*OH), 7.26 (s, 2H, arom. CH), 7.45 ppm (s, 1H, OH); ^{13}C{^{1}H} NMR ($CDCl_3$): δ=24.21 (CH_2 C_6H_{10}), 25.95 (CH_2 C_6H_{10}), 29.43 ($C(CH_3)_3$), 31.49 ($C(CH_3)_3$), 32.63 (CH_2 C_6H_{10}), 34.15 ($C(CH_3)_3$), 34.79 (CH_2 C_6H_{10}), 35.13 ($C(CH_3)_3$), 56.67 (CHS), 72.36 (CHO), 115.86 (arom.), 125.97 (arom. CH), 131.6 (arom. CH), 135.17 (arom.), 141.64 (arom.), 154.00 ppm (arom.); elemental analysis (%) calcd for $C_{20}H_{32}O_2S$ (336.54): C 71.38, H 9.58; found: C 71.12, H 9.57.

1b: 2-*tert*-Butyl-6-(2-hydroxycyclohexylthio)-4-methylphenol: Compound **1b** was prepared following the same procedure as reported for **1a** using 2-*tert*-butyl-6-mercapto-4-methylphenol (21.80 g, 111 mmol) and cyclohexene oxide (11.97 g, 122 mmol) to give a viscous oil, which slowly solidified (32.3 g, 110 mmol, 99%). ^{1}H NMR ($CDCl_3$): δ=1.19–1.35 (m, 4H, CH C_6H_{10}), 1.37 (s, 9H, $C(CH_3)_3$), 1.62–1.69 (m, 2H, CH C_6H_{10}), 2.01–2.11 (m, 2H, CH C_6H_{10}), 2.24 (s, 3H, CH_3), 2.56 (m, 1H, CHS), 2.65 (br s, 1H, CHO*H*), 3.33 (m, 1H, C*H*OH), 7.08 (d, 1H, $^4J_{HH}$=2.0 Hz, arom. CH), 7.13 (m, 1H, $^4J_{HH}$=2.0 Hz, arom. CH), 7.43 ppm (s, 1H, OH); ^{13}C{^{1}H} NMR ($CDCl_3$): δ=20.63 (CH_3), 24.23 (CH_2 C_6H_{10}), 26.03 (CH_2 C_6H_{10}), 29.38 ($C(CH_3)_3$), 32.56 (CH_2 C_6H_{10}), 34.72 (CH_2 C_6H_{10}), 34.88 ($C(CH_3)_3$), 56.98 (CHS), 72.20 (CHO), 116.06 (arom.), 128.41 (arom.), 129.80 (arom. CH), 134.99 (arom. CH), 135.86 (arom.), 154.23 ppm (arom.). M.p. 84–85 °C; elemental analysis (%) calcd for $C_{20}H_{26}O_2S$ (294.45): C 69.34, H 8.90; found: C 69.03, H 9.65.

2a: Thionyl chloride (4.6 g, 38.7 mmol) was added dropwise to a stirred solution of **1a** (13.0 g, 38.6 mmol) in CH_2Cl_2 (120 mL) and the mixture was refluxed for 2 h. After cooling the solution, water was added and the organic phase was washed with $NaHCO_3$ solution and water. After drying over anhydrous Na_2SO_4, the product was isolated as an oil (11.8 g, 33.2 mmol, 90%). ^{1}H NMR ($CDCl_3$): δ=1.29–1.34 (m, 2H, CH C_6H_{10}, overlap with *t*Bu signals), 1.31 (s, 9H, $C(CH_3)_3$), 1.36–1.49 (m, 1H, CH C_6H_{10}, overlap with *t*Bu signals), 1.34 (s, 9H, $C(CH_3)_3$), 1.71 (m, 3H, CH C_6H_{10}), 2.16 (m, 1H, CH C_6H_{10}), 2.33 (m, 1H, CH C_6H_{10}), 2.87 (m, 1H, CHS,), 3.83 (m, 1H, CHCl), 7.26 (s, 1H, OH), 7.35 (s, 1H, arom. CH), 7.38 ppm (s, 1H, arom. CH); ^{13}C{^{1}H} NMR ($CDCl_3$): δ=24.20 (CH_2 C_6H_{10}), 24.47 (CH_2 C_6H_{10}), 29.40 ($C(CH_3)_3$), 31.48 ($C(CH_3)_3$), 32.08 ($C(CH_3)_3$), 34.11 (CH_2 C_6H_{10}), 35.09 (CH_2 C_6H_{10}), 35.52 ($C(CH_3)_3$), 55.25 (CHS), 62.47 (CHCl), 116.08 (arom.), 126.05 (arom. CH), 131.31 (arom. CH), 135.04 (arom.), 141.63 (arom.), 153.64 ppm (arom.); elemental analysis (%) calcd for $C_{20}H_{31}ClOS$ (354.98): C 67.67, H 8.80; found: C 67.57, H 8.78.

2b: Thionyl chloride (16.4 g, 10.0 mL, 138 mmol) was slowly added to a stirred solution of **1b** (32.3 g, 110 mmol) in CH_2Cl_2 (270 mL) at −30 °C. The reaction micture was allowed to warm up to room temperature and then refluxed for 10 h. After removal of the volatiles the resulting oil was taken up in diethyl ether (300 mL) and water (120 mL) and stirred for 10 min. The organic layer was separated and sequentially washed with $NaHCO_3$ (2×150 mL) and water (150 mL), dried over anhydrous Na_2SO_4, and evaporated to give **2b** as a red oil (33.6 g, 107 mmol, 98%). ^{1}H NMR ($CDCl_3$): δ=1.32 (m, 2H, CH C_6H_{10}), 1.40 (s, 9H, $C(CH_3)_3$), 1.43–1.53 (m, 1H, CH C_6H_{10}), 1.72 (m, 3H, CH C_6H_{10}), 2.15 (m, 1H, CH C_6H_{10}), 2.26 (s, 3H, CH_3), 2.35 (m, 1H, CH C_6H_{10}), 2.89 (m, 1H, CHS), 3.84 (m, 1H, CHCl), 7.08 (d, 1H, $^4J_{HH}$=1.8 Hz, arom. CH), 7.15 (d, 1H, $^4J_{HH}$=1.8 Hz, arom. CH), 7.20 ppm (s, 1H, OH); ^{13}C{^{1}H} NMR ($CDCl_3$): δ=20.64 (CH_3), 24.30 (CH_2 C_6H_{10}), 24.55 (CH_2 C_6H_{10}), 29.36 ($C(CH_3)_3$), 32.12 (CH_2 C_6H_{10}), 34.90 ($C(CH_3)_3$), 35.62 (CH_2 C_6H_{10}), 55.50 (CHS), 62.68 (CHCl), 116.55 (arom.), 128.42 (arom.), 129.94 (arom. CH), 134.72 (arom. CH), 135.77 (arom.), 153.91 ppm (arom.); MS (EI) *m/z* (%): 312 (53) [M^+], 297 (23) [M^+-CH_3], 276 (13) [M^+−Cl], 196 (61) [(1-*t*Bu-4-Me-6-S-$C_6H_2OH)^+$], 181 (100) [(1-*t*Bu-4-Me-6-S-$C_6H_2OH)^+$-CH_3], 81 (42) [$C_6H_9^+$].

rac-**3a**: Solid NaOH (1.69 g, 42.3 mmol) was added to a solution of 4,6-di-*tert*-butyl-2-mercaptophenol (10.0 g, 42.3 mmol) in methanol (100 mL), refluxed until all NaOH dissolved, and cooled to room temperature. A solution of **2a** (15.0 g, 42.3 mmol) in methanol (100 mL) was added dropwise and the mixture was refluxed for 2 h. Methanol was evaporated, water was added, and the mixture was extracted with diethyl ether (3× 100 mL). The organic layer was separated, dried over anhydrous Na_2SO_4, and evaporated to give a white powder (17.7 g, 31.7 mmol, 75%). ^{1}H NMR ($CDCl_3$): δ=1.23 (m, 2H, CH C_6H_{10}), 1.32 (s, 18H, $C(CH_3)_3$), 1.38–1.49 (m, 2H, CH C_6H_{10}, overlap with *t*Bu signal), 1.45 (s, 18H, $C(CH_3)_3$), 1.68 (m, 2H, CH C_6H_{10}), 2.06 (m, 2H, CH C_6H_{10}), 2.81 (m, 2H CHS), 7.36 (d, 2H, $^4J_{HH}$=2.3 Hz, arom. CH), 7.40 (d, 2H, $^4J_{HH}$=2.3 Hz, arom. CH), 7.45 ppm (s, 1H, OH); ^{13}C{^{1}H} NMR ($CDCl_3$): δ=25.47 (CH_2 C_6H_{10}), 29.66 ($C(CH_3)_3$), 31.72 ($C(CH_3)_3$), 33.49 ($C(CH_3)_3$), 34.07 ($C(CH_3)_3$), 35.37 (CH_2 C_6H_{10}), 52.73 (CHS), 116.10 (arom.), 126.14 (arom. CH), 131.64 (arom. CH), 135.15 (arom.), 141.74 (arom.), 153.93 ppm (arom.); elemental analysis (%) calcd for $C_{34}H_{52}O_2S_2$ (556.91): C 73.33, H 9.41, S 11.52; found: C 72.69, H 9.19, S 11.44.

rac-**3b**: In an analogous procedure as reported for compound *rac*-**3a**, 2-*tert*-butyl-6-mercapto-4-methylphenol (21.1 g, 107 mmol) and solid NaOH (4.32 g, 108 mmol) were treated with **2b** (33.6 g, 107 mmol) in methanol (360 mL) for 4 h to give *rac*-**3b** as a white powder (47.1 g, 99.6 mmol, 93%). ^{1}H NMR ($CDCl_3$): δ=1.23 (m, 2H, CH C_6H_{10}), 1.40–1.52 (m, 2H, CH C_6H_{10}, overlap with *t*Bu signal), 1.46 (s, 18H, $C(CH_3)_3$), 1.68 (m, 2H, CH C_6H_{10}), 2.08 (m, 2H, CH C_6H_{10}), 2.29 (s, 6H, CH_3), 2.79

(m, 2H, CHS), 7.14 (d, 2H, $^4J_{HH}$=2.1 Hz, arom. CH), 7.22 (m, 2H, $^4J_{HH}$=2.1 Hz, arom. CH), 7.46 ppm (s, 2H, OH); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ=20.63 (CH_3), 25.32 (CH_2 C_6H_{10}), 29.42 (C(CH_3)$_3$), 33.35 (CH_2 C_6H_{10}), 34.88 (C(CH_3)$_3$), 52.79 (CHS), 116.43 (arom.), 128.32 (arom.), 129.73 (arom. CH), 134.73 (arom. CH), 135.68 (arom.), 154.11 ppm (arom.). M.p. 118.5–120.5 °C; elemental analysis (%) calcd for $C_{28}H_{40}O_2S_2$ (472.74): C 71.14, H 8.53, S 13.57; found: C 71.12, H 8.42, S 13.56.

rac-**3c**: This compound was prepared in the same manner as *rac*-**3** and isolated as a viscous oil in 73% yield (three steps, based on the mercaptophenol). ^1H NMR ($CDCl_3$): δ=1.08–1.28 (m, 2H, CH C_6H_{10}, overlap with *i*Pr signals), 1.16–1.30 (m, 24H, CH(CH_3)$_2$), 1.32–1.53 (m, 2H, CH C_6H_{10}), 1.65 (m, 2H, CH C_6H_{10}), 2.03 (m, 2H, CH C_6H_{10}), 2.75 (m, 2H, CHS, partial overlap with *i*Pr signal), 2.81 (septet, 2H, C*H*(CH_3)$_2$), 3.31 (septet, 2H, C*H*(CH_3)$_2$), 7.07 (d, 2H, $^4J_{HH}$=2.2 Hz, arom. CH), 7.18 (d, 2H, $^4J_{HH}$=2.2 Hz, arom. CH), 7.23 ppm (s, 2H, OH); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ=22.57 (CH(CH_3)$_2$), 24.25 (CH(CH_3)$_2$), 25.53 (CH_2 C_6H_{10}), 27.96 (*C*H(CH_3)$_2$), 33.41 (*C*H(CH_3)$_2$), 33.86 (CH_2 C_6H_{10}), 52.56 (CHS), 115.07 (arom.), 126.57 (arom. CH), 131.94 (arom. CH), 134.38 (arom.), 140.15 (arom.), 153.15 ppm (arom.); elemental analysis (%) calcd for $C_{30}H_{44}O_2S_2$ (500.81): C 71.95, H 8.86; found: C 72.69, H 9.19.

rac-**3d**: This compound was prepared in the same manner as *rac*-**3** and isolated as a white solid in 58% yield (three steps, based on the mercaptophenol). ^1H NMR ($CDCl_3$): δ=1.16 (m, 2H, CH C_6H_{10}), 1.39 (m, 2H, CH C_6H_{10}), 1.63 (m, 2H, CH C_6H_{10}), 2.00 (m, 2H, CH C_6H_{10}), 2.25 (s, 6H, CH_3), 2.73 (m, 2H CHS), 6.90 (d, 2H, $^3J_{HH}$=8.3 Hz, arom. CH), 7.05 (s, 2H, OH), 7.09 (dd, 2H, $^3J_{HH}$=8.3 Hz, $^4J_{HH}$=2.3 Hz, arom. CH), 7.24 ppm (m, 2H, $^4J_{HH}$=2.3 Hz, arom. CH); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ=20.34 (CH_3), 25.46 (CH_2 C_6H_{10}), 33.76 (CH_2 C_6H_{10}) 52.31 (CHS), 114.89 (arom. CH), 115.39 (arom.), 129.78 (arom.), 132.39 (arom. CH), 137.56 (arom. CH), 155.74 ppm (arom.). M.p. 103–104 °C; elemental analysis (%) calcd for $C_{20}H_{24}O_2S_2$ (360.54): C 66.63, H 6.71; found: C 66.80, H 7.01.

4a: {*trans*-1,2-Dithiocyclohexanediyl-2,2′-bis(4,6-di-*tert*-butylphenoxy)}-bis((1*S*)-camphor-10-sulfonate): 2.5 M *n*BuLi in hexane (15 mL, 2.40 g, 37.5 mmol) was added to a solution of *rac*-**3a** (9.5 g, 17 mmol) in diethyl ether (100 mL) at −20 °C. The mixture was allowed to warm up to room temperature, (1*S*)-camphor-10-sulfonylchloride (9.83 g, 40 mmol) in diethyl ether (150 mL) was added, and the reaction mixture was heated at reflux for 12 h. Subsequently, an NH_4Cl solution (100 mL) was added and the organic layer was extracted, washed with water, and dried over anhydrous Na_2SO_4 to obtain 16.0 g of crude product, which was purified by column chromatography using 5% ethyl acetate/hexane mixture as eluent (R_f=0.2 in 10% ethyl acetate/hexane) to afford **4a** (12.8 g, 13.0 mmol, 76%).

{(1*R*,2*R*)-Dithiocyclohexanediyl-2,2′-bis(4,6-di-*tert*-butylphenoxy)}-bis((1*S*)-camphor-10-sulfonate) ((*R*,*R*,*S*,*S*)-**4a**): Crystallization of **4a** from 75 mL of acetone afforded diastereomer (*R*,*R*,*S*,*S*)-**4a** in 70% yield (4.5 g, 4.6 mmol). X-ray quality crystals were grown by recrystallization from acetone. Alternatively, (*R*,*R*,*S*,*S*)-**4a** was obtained by preparative HPLC of **4a** on a Kromasil Si 100 column, using cyclohexane/ethyl acetate 98:2. $[\alpha]_D^{23}$=−42.3 (c=30 mg mL^{-1}, $CHCl_3$); ^1H NMR ($CDCl_3$): δ=0.98 (s, 6H, CH_3), 1.20 (s, 6H, CH_3), 1.24 (s, 18H, C(CH_3)$_3$), 1.39–1.46 (m, 6H, CH_2), 1.46 (s, 18H, C(CH_3)$_3$), 1.67–1.79 (m, 4H, CH_2), 1.92–2.13 (m, 8H, CH and CH_2), 2.38–2.47 (m, 2H, CH_2), 2.53–2.64 (m, 2H, CH_2), 3.23 (br s, 2H, CHS), 4.14 (d, 2H, $^2J_{HH}$=14.8 Hz, SO_2CH), 4.51 (d, 2H, $^2J_{HH}$=14.8 Hz, SO_2CH), 7.36 (d, 2H, $^4J_{HH}$=2.2 Hz, arom. CH), 7.37 ppm (d, 2H, $^4J_{HH}$=2.2 Hz, arom. CH); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ=19.86 (CH_3), 20.22 (CH_3), 23.40 (CH_2 C_6H_{10}), 25.29 (CH_2), 26.96 (CH_2), 29.98 (CH_2 C_6H_{10}), 31.27 (C(CH_3)$_3$), 31.40 (C(CH_3)$_3$), 34.66 (*C*(CH_3)$_3$), 35.89 (*C*(CH_3)$_3$), 42.48 (CH_2), 42.95 (CH), 47.90 (C_q(CH_3)$_2$), 50.32 (CH_2S), 51.50 (CHS), 58.67 (C_q(C=O)), 125.88 (arom. CH), 128.85 (arom.), 131.09 (arom. CH), 144.02 (arom.), 146.86 (arom.), 149.09 (arom.), 214.11 ppm (C=O). M.p. 142 °C; elemental analysis (%) calcd for $C_{54}H_{80}O_8S_4$ (985.46): C 65.82, H 8.18; found: C 65.53, H 8.19.

{(1*S*,2*S*)-Dithiocyclohexanediyl-2,2′-bis(4,6-di-*tert*-butylphenoxy)}bis((1*S*)-camphor-10-sulfonate) ((*S*,*S*,*S*,*S*)-**4a**): The mother liquor gave 6.0 g of compound (*S*,*S*,*S*,*S*)-**4a** (95% *de*) upon standing for 24 h, which was recrystallized from acetone to give the pure product in 75% yield (4.8 g, 4.9 mmol). Alternatively, (*S*,*S*,*S*,*S*)-**4a** was obtained by preparative HPLC of **4a**. $[\alpha]_D^{23}$=+24.2 (c=30 mg mL^{-1}, $CHCl_3$); ^1H NMR ($CDCl_3$): δ=0.98 (s, 6H, CH_3), 1.21 (s, 6H, CH_3), 1.25 (s, 18H, C(CH_3)$_3$), 1.37–1.47 (m, 6H, CH_2), 1.46 (s, 18H, C(CH_3)$_3$), 1.60–1.76 (m, 4H, CH_2), 1.93–2.10 (m, 9H, CH and CH_2), 2.38–2.64 (m, 3H, CH_2), 3.28 (br s, 2H, CHS), 4.12 (d, $^2J_{HH}$=14.8 Hz, SO_2CH), 4.52 (d, $^2J_{HH}$=14.8 Hz, SO_2CH), 7.33 (d, 2H, $^4J_{HH}$=2.2 Hz, arom. CH), 7.38 ppm (d, 2H, $^4J_{HH}$=2.2 Hz, arom. CH); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ=19.92 (CH_3), 20.24 (CH_3), 23.42 (CH_2 C_6H_{10}), 25.34 (CH_2), 26.99 (CH_2), 29.98 (CH_2 C_6H_{10}), 31.29 (C(CH_3)$_3$), 31.39 (C-(CH_3)$_3$), 34.70 (*C*(CH_3)$_3$), 35.89 (C_q(CH_3)$_3$), 42.54 (CH_2), 42.89 (CH), 47.98 (*C*(CH_3)$_2$), 50.18 (CH_2S), 51.52 (CHS), 58.68 (C_q(C=O)), 125.69 (arom. CH), 129.21 (arom.), 130.55 (arom. CH), 144.07 (arom.), 146.94 (arom.), 149.14 (arom.), 214.28 ppm (C=O). M.p. 208 °C; elemental analysis (%) calcd for $C_{54}H_{80}O_8S_4$ (985.46): C 65.82, H 8.18; found: C 66.24, H 8.29.

4b: {*trans*-1,2-Dithiocyclohexanediyl-2,2′-bis(6-*tert*-butyl-4-methylphenoxy)}bis((1*S*)-camphor-10-sulfonate): Compound **4b** was prepared following the same procedure as reported for compound **4a**, treating 2.5 M *n*BuLi in hexane (37 mL, 5.93 g, 92.5 mmol) and **4** (20.0 g, 42,3 mmol) with (1*S*)-camphor-10-sulfonyl chloride (24.3 g, 96.9 mmol) in THF (350 mL) to obtain 38.4 g of crude product. Column chromatography using 5% ethyl acetate/hexane (R_f=0.25 in 10% ethyl acetate/hexane) to obtain **4b** (31.8 g, 35.3 mmol, 83%) as a white powder.

{(1*R*,2*R*)-Dithiocyclohexanediyl-2,2′-bis(6-*tert*-butyl-4-methylphenoxy)}-bis((1*S*)-camphor-10-sulfonate) ((*R*,*R*,*S*,*S*)-**4b**): Fractional crystallization of **4b** from 300 mL of cyclohexane afforded (*R*,*R*,*S*,*S*)-**4b** in 74% yield (11.8 g, 13.1 mmol). $[\alpha]_D^{23}$=−48.6 (c=10 mg mL^{-1}, CH_2Cl_2); ^1H NMR ($CDCl_3$): δ=0.97 (s, 6H, CH_3), 1.19 (s, 6H, CH_3), 1.44 (s, 18H, C(CH_3)$_3$), 1.43–1.46 (m, 4H, CH, overlap with *t*Bu signal), 1.63 (m, 4H, CH), 1.71 (ddd, J_{HH}=14.1 Hz, J_{HH}=9.4 Hz, J_{HH}=4.6 Hz, 2H, CH), 1.95 (d, 2H, J_{HH}=18.3 Hz, CH), 2.07 (m, 2H, CH, overlapping), 2.11 (t, 2H, J_{HH}=4.6 Hz, CH, overlapping), 2.14 (m, 2H, CH, overlapping), 2.21 (s, 6H, CH_3), 2.42 (dt, 2H, J_{HH}=18.3 Hz, J_{HH}=4.0 Hz, 2H, CH), 2.57 (m, 2H, CH), 3.18 (br s, 2H, CHS), 4.16 (d, 2H, $^2J_{HH}$=15.0 Hz, SO_2CH), 4.45 (d, 2H, $^2J_{HH}$=15.0 Hz, SO_2CH), 7.04 (d, 2H, $^4J_{HH}$=2.0 Hz, arom. CH), 7.14 ppm (d, 2H, $^4J_{HH}$=2.0 Hz, arom. CH); $^{13}C\{H\}$ NMR ($CDCl_3$): δ=19.83 (C(CH_3)$_2$), 20.24 (C(CH_3)$_2$) 20.94 (CH_3), 23.02 (CH_2 C_6H_{10}), 25.23 (CH_2), 26.91 (CH_2), 26.95 (CH_2), 29.27 (CH_2 C_6H_{10}), 31.39 (C(CH_3)$_3$), 35.60 (*C*(CH_3)$_3$), 42.49 (*C*H_2(C=O)), 42.94 (CH), 47.87 (*C*(CH_3)$_2$), 50.22 (CH_2S), 51.51 (CHS), 58.66 (CH_2C_q), 129.47 (arom. CH), 129.91 (arom.), 133.65 (arom. CH), 136.26 (arom.), 144.60 (arom.), 146.64 (arom.), 214.17 ppm (C=O). M.p. 187–188.5 °C; elemental analysis (%) calcd for $C_{48}H_{68}O_8S_4{\cdot}C_6H_{12}$ (901.30): C 65.82; H 8.18; found: C 65.99; H 8.42.

{(1*S*,2*S*)-Dithiocyclohexanediyl-2,2′-bis(6-*tert*-butyl-4-methylphenoxy)}-bis((1*S*)-camphor-10-sulfonate) ((*S*,*S*,*S*,*S*)-**4b**): From the mother liquor after four recrystallizations from cyclohexane (*S*,*S*,*S*,*S*)-**4b** could be isolated in 30% yield (4.8 g, 5.3 mmol) in 71% *de*. Suitable single crystals were measured by X-ray analysis. ^1H NMR ($CDCl_3$): δ=0.98 (s, 6H, CH_3), 1.20 (s, 6H, CH_3), 1.44 (s, 18H, C(CH_3)$_3$), 1.41–1.46 (m, 4H, CH, overlap with *t*Bu signals), 1.54–1.67 (m, 4H, CH), 1.70 (ddd, J_{HH}=18.9 Hz, J_{HH}=9.6 Hz, J_{HH}=5.3 Hz 2H, CH), 1.96 (d, 2H, J_{HH}=18.3 Hz, CH), 2.03–2.14 (m, 6H, CH), 2.24 (s, 6H, CH_3), 2.42 (dt, 2H, J_{HH}=18.5 Hz, J_{HH}=3.9 Hz, 2H, CH), 2.58 (m, 2H, CH), 3.22 (br s, 2H, CHS), 4.14 (d, 2H, $^2J_{HH}$=14.8 Hz, SO_2CH), 4.52 (d, 2H, $^2J_{HH}$=14.9 Hz, SO_2CH), 7.05 (d, $^4J_{HH}$=1.8 Hz, arom. CH), 7.16 ppm (d, $^4J_{HH}$=1.8 Hz, arom. CH); $^{13}C\{H\}$ NMR ($CDCl_3$): δ=19.88 (C(CH_3)$_2$), 20.28 (C(CH_3)$_2$), 20.97 (CH_3), 23.21 (CH_2 C_6H_{10}), 25.32 (CH_2), 26.92 (CH_2), 26.97 (CH_2), 29.73 (CH_2 C_6H_{10}), 31.38 (C(CH_3)$_3$), 31.39 (C(CH_3)$_3$), 34.70 (*C*(CH_3)$_3$), 35.60 (*C*(CH_3)$_3$), 42.53 (*C*H_2(C=O)), 42.93 (CH), 47.94 (*C*(CH_3)$_2$), 50.24 (CH_2S)), 51.67 (CHS), 58.69 (CH_2C_q), 125.69 (arom. CH), 129.21 (arom.), 130.55 (arom. CH), 144.07 (arom.), 146.94 (arom.), 149.14 (arom.), 214.28 ppm (C=O); elemental analysis (%) calcd for $C_{48}H_{68}O_8S_4$ (901.30): C 63.97, H 7.60; found: C 63.99, H 8.07.

(*R*,*R*)-**3a**: Refluxing (*R*,*R*,*S*,*S*)-**4a** (2.50 g, 2.54 mmol) in THF/MeOH 1:1 (30 mL) with 1.5 M aqueous NaOH solution (30 mL) for 8 h, followed by extraction with diethyl ether and drying over Na_2SO_4, afforded (*R*,*R*)-**3a** in 90% yield (1.27 g, 2.29 mmol). M.p. 113–115 °C; $[\alpha]_D^{23}$=−72.4 (c=

30 mg mL^{-1}, $CHCl_3$); elemental analysis (%) calcd for $C_{34}H_{52}O_2S_2$ (556.91): C 73.33, H 9.41; found: C 73.99, H 9.19.

(*S*,*S*)-**3a**: Following the same procedure as reported for the preparation of (*R*,*R*)-**3a**, compound (*S*,*S*)-**3a** was obtained in 93% yield (1.68 g, 3.02 mmol). M.p. 113–115 °C; $[\alpha]_D^{23} = +71.0$ ($c = 30$ mg mL^{-1}, $CHCl_3$); elemental analysis (%) calcd for $C_{34}H_{52}O_2S_2$ (556.91): C 73.33, H 9.41; found: C 72.96, H 9.79.

(*R*,*R*)-**3b**: Following the same procedure reported as for the preparation of (*R*,*R*)-**3a** afforded compound (*R*,*R*)-**3b** in 79% yield (5.3 g, 11.2 mmol). Alternatively, (*R*,*R*)-**3b** was obtained by preparative chiral HPLC of *rac*-**3b**, using *n*-hexane/isopropanol (2 L/1 mL) on a ChiralPak AD 50 mm column, in two passes. M.p. 114–115 °C; $[\alpha]_D^{23} = -105$ ($c = 3.1$ mg mL^{-1}, CH_2Cl_2); elemental analysis (%) calcd for $C_{28}H_{40}O_2S_2$ (472.74): C 71.14, H 8.53, S 13.57; found: C 71.24, H 8.57, S 13.46.

(*S*,*S*)-**3b**: Enantiopure (*S*,*S*)-**3b** was obtained by chiral HPLC. M.p. 114.5–115.5 °C; $[\alpha]_D^{23} = +103$ ($c = 4.1$ mg mL^{-1}, CH_2Cl_2).

rac-**5a**: Neat titanium tetrachloride (47 μL, 0.08 g, 0.43 mmol) was added dropwise to a solution of *rac*-**3a** (0.24 g, 0.43 mmol) in pentane (30 mL) at −10 °C. The mixture was allowed to warm up to room temperature and stirred for 2 h. A red powder precipitated and was washed with pentane (2×15 mL) and dried in vacuo to give *rac*-**5a** (0.25 g, 0.37 mmol, 86%). Crystals suitable for X-ray analysis were obtained as toluene solvate by slow evaporation of a toluene solution at room temperature. ^{1}H NMR (C_6D_6): $\delta = 0.36$ (m, 2H, CH C_6H_{10}), 1.13 (m, 2H, CH C_6H_{10}, overlapping with *t*Bu signal), 1.18 (s, 18H, $C(CH_3)_3$), 1.32 (m, 2H, CH C_6H_{10}), 1.59 (s, 18H, $C(CH_3)_3$), 1.78 (m, 2H, CH C_6H_{10}), 2.49 (m, 2H, CHS), 7.10 (d, 2H, $^4J_{HH} = 2.2$ Hz, arom. CH), 7.47 ppm (d, 2H, $^4J_{HH} = 2.2$ Hz, arom. CH); ^{13}C{^{1}H} NMR (C_6D_6): $\delta = 25.10$ (CH_2 C_6H_{10}), 29.82 ($C(CH_3)_3$), 31.59 ($C(CH_3)_3$), 32.41 (CH_2 C_6H_{10}), 34.61 ($C(CH_3)_3$), 35.87 ($C(CH_3)_3$), 55.59 (CHS), 117.42 (arom.), 127.33 (arom. CH), 129.70 (arom. CH), 137.18 (arom.), 144.03 (arom.), 167.64 ppm (arom.); UV/Vis (CH_2Cl_2): $\lambda_{max} = 400$ nm; elemental analysis (%) calcd for $C_{34}H_{50}Cl_2O_2S_2Ti$ (673.66): C 60.62, H 7.48; found: C 60.63, H 7.86.

(Λ,*R*,*R*)-**5a**: Following the same procedure as reported for the preparation of *rac*-**5a**, starting from (*R*,*R*)-**3a** (0.25 g, 0.45 mmol) and titanium tetrachloride (50 μL, 0.085 g, 0.45 mmol), (Λ,*R*,*R*)-**5a** was obtained in 87% yield (0.27 g, 0.39 mmol). Crystals suitable for X-ray analysis were obtained by slow evaporation of a toluene solution at room temperature. $[\alpha]_D^{23} = -252$ ($c = 2$ mg mL^{-1}, CH_2Cl_2); elemental analysis (%) calcd for $C_{34}H_{50}Cl_2O_2S_2Ti$ (673.66): C 60.62, H 7.48; found: C 61.56, H 7.89.

(Δ,*S*,*S*)-**5a**: Following the same procedure as reported for the preparation of *rac*-**5a**, starting from (*S*,*S*)-**3a** (0.25 g, 0.45 mmol) and titanium tetrachloride (50 μL, 0.085 g, 0.45 mmol), **(**Δ,*S*,*S*)-**5a** was obtained in 82% yield (0.25 g, 0.37 mmol). Crystals suitable for X-ray analysis were obtained from dichloromethane solution at room temperature. $[\alpha]_D^{23} = +251$ ($c = 2$ mg mL^{-1}, CH_2Cl_2); elemental analysis (%) calcd for $C_{34}H_{50}Cl_2O_2S_2Ti \cdot 0.5\,C_7H_8$ (719.73): C 62.58, H 7.56 found: C 62.04, H 7.22.

rac-**5b**: Neat titanium tetrachloride (200 μL, 0.34 g, 1.81 mmol) was added dropwise to a solution of *rac*-**3b** (0.86 g, 1.81 mmol) in pentane (80 mL) at room temperature and stirred for 2 h. A red powder, which precipitated immediately, was washed with pentane (2×20 mL) and dried in vacuo to give *rac*-**5b** (1.00 g, 1.70 mmol, 94%). ^{1}H NMR ($CDCl_3$): $\delta =$ 1.06 (m, 2H, CH C_6H_{10}), 1.49 (s, 18H, $C(CH_3)_3$), 1.59 (m, 2H, CH C_6H_{10}), 1.70 (m, 2H, CH C_6H_{10}), 2.22 (m, 2H, CH C_6H_{10}), 2.30 (s, 6H, CH_3), 2.61 (m, 2H, CHS), 6.98 (d, 2H, $^4J_{HH} = 2.0$ Hz, arom. CH), 7.19 ppm (d, 2H, $^4J_{HH} = 2.0$ Hz, arom. CH); ^{13}C{^{1}H} NMR ($CDCl_3$): $\delta =$ 20.99 (CH_3), 25.01 (CH_2 C_6H_{10}), 29.45 ($C(CH_3)_3$), 32.13 (CH_2 C_6H_{10}), 35.18 ($C(CH_3)_3$), 55.43 (CHS), 116.98 (arom.), 130.65 (arom.), 130.96 (arom. CH), 132.60 (arom. CH), 137.31 (arom.), 167.29 ppm (arom.); elemental analysis (%) calcd for $C_{28}H_{38}Cl_2O_2S_2Ti$ (589.53): C 57.05, H 6.50; found: C 56.72, H 6.65.

(Λ,*R*,*R*)-**5b**: Following the same procedure as reported for the preparation of *rac*-**5b**, (Λ,*R*,*R*)-**5b** was obtained in 92% yield. Crystals suitable for X-ray analysis were obtained by slow evaporation of a CH_2Cl_2 solution at room temperature. $[\alpha]_D^{23} = -210$ ($l = 1.0$ dm, $c = 0.75$ mg mL^{-1}, CH_2Cl_2); elemental analysis (%) calcd for $C_{28}H_{38}Cl_2O_2S_2Ti$ (589.53): C 57.05, H 6.50, S 10.88; found: C 57.21, H 6.49, S 10.79.

(Δ,*S*,*S*)-**5b**: Following the same procedure as reported for the preparation of *rac*-**5a**, starting from (*S*,*S*)**-3b** (54 mg, 0.11 mmol) and titanium tetrachloride (13 μL, 22 mg, 0.12 mmol), **(**Δ,*S*,*S*)-**5b** was obtained in 99% yield (66 mg, 0.11 mmol); $[\alpha]_D^{23} = +213$ ($l = 1.0$ dm, $c = 0.73$ mg mL^{-1}, CH_2Cl_2); elemental analysis (%) calcd for $C_{28}H_{38}Cl_2O_2S_2Ti \cdot 0.5\,C_5H_{12}$ (625.61): C 58.56, H 7.09; found: C 58.34, H 7.05.

rac-**5c**: Neat titanium tetrachloride (145 μL, 0.25 g, 1.32 mmol) was added dropwise to a solution of *rac*-**3c** (0.66 g, 1.32 mmol) in toluene (10 mL) at −30 °C. The mixture was allowed to warm up to room temperature and stirred for 2 h. The solvent was removed under reduced pressure and the residue was recrystallized from toluene to give *rac*-**5c** (0.65 g, 1.05 mmol, 80%) as a red powder. ^{1}H NMR ($CDCl_3$): $\delta = 1.03$ (m, 2H, CH C_6H_{10}), 1.22 (dd, $^3J_{HH} = 6.9$ Hz, $^4J_{HH} = 1.7$ Hz, 12H, CH-(CH_3)$_2$), 1.32 (dd, $^3J_{HH} = 6.9$ Hz, $^4J_{HH} = 1.3$ Hz, 12H, CH(CH_3)$_2$), 1.59 (m, 2H, CH C_6H_{10}), 1.72 (m, 2H, CH C_6H_{10}), 2.25 (m, 2H, CH C_6H_{10}), 2.65 (m, 2H, CHS), 2.85 (septet, $^3J_{HH} = 6.9$ Hz, 2H, C*H*(CH_3)$_2$), 3.31 (septet, $^3J_{HH} = 6.9$ Hz, 2H, C*H*(CH_3)$_2$), 6.98 (d, 2H, $^4J_{HH} = 2.0$ Hz, arom. CH), 7.15 ppm (d, 2H, $^4J_{HH} = 2.0$ Hz, arom. CH); ^{13}C{^{1}H} NMR ($CDCl_3$): $\delta =$ 22.07 (CH(CH_3)$_2$), 22.55 (CH(CH_3)$_2$), 24.11 (CH(CH_3)$_2$), 24.15 (CH-(CH_3)$_2$), 25.15 (CH_2 C_6H_{10}), 29.25 (*C*H(CH_3)$_2$), 32.21 (CH_2 C_6H_{10}), 33.55 (*C*H(CH_3)$_2$), 55.47 (CHS), 115.78 (arom.), 128.32 (arom. CH), 129.57 (arom. CH), 135.39 (arom.), 142.25 (arom.), 166.73 ppm (arom.); elemental analysis (%) calcd for $C_{30}H_{42}O_2S_2Cl_2Ti$ (617.59): C 58.34, H 6.85; found: C 58.16, H 6.79.

rac-**5d**: Neat titanium tetrachloride (110 μL, 0.19 g, 1.0 mmol) was added dropwise to a solution of *rac*-**3d** (0.36 g, 1.0 mmol) in toluene (10 mL) at −30 °C. The mixture was allowed to warm up to room temperature and stirred overnight. The solvent was removed under reduced pressure, the residue was washed with pentane (2×10 mL) and subsequently dried in vacuo to give *rac*-**5d** (0.25 g, 0.37 mmol, 86%) as a red powder. Crystals suitable for X-ray analysis could be obtained from toluene solution. ^{1}H NMR ($CDCl_3$): $\delta = 1.05$ (m, 2H, CH C_6H_{10}), 1.61 (m, 2H, CH C_6H_{10}), 2.25 (m, 2H, CH C_6H_{10}, partial overlap with Me signal), 2.31 (s, 3H, CH_3), 2.71 (m, 2H, CHS), 6.78 (d, 2H, $^3J_{HH} = 8.4$ Hz, arom. CH), 7.12 (m, 2H, arom. CH), 7.22 ppm (dd, $^3J_{HH} = 8.4$ Hz, $^4J_{HH} = 2.2$ Hz, arom. CH); ^{13}C{^{1}H} NMR ($CDCl_3$): $\delta = 20.64$ (CH_3), 24.29 (CH_2 C_6H_{10}), 32.00 (CH_2 C_6H_{10}), 55.63 (CHS), 115.15 (arom. CH), 115.57 (arom.), 131.68 (arom.), 134.01 (arom. CH), 135.09 (arom. CH), 168.52 ppm (arom.); elemental analysis (%) calcd for $C_{20}H_{22}O_2S_2Cl_2Ti$ (477.33): C 60.62, H 7.48; found: C 60.63, H 7.86.

rac-**6a**: Neat titanium tetra(isopropoxide) (126 μL, 0.12 g, 0.41 mmol) was added to a stirred solution of *rac*-**3a** (0.23 g, 0.41 mmol) in pentane (25 mL). The resulting yellow solution was stirred for 2 h. All volatiles were removed under reduced pressure and the resulting pale yellow solid was dissolved in pentane and stored at −78 °C for several days to give *rac*-**6a** in 71% yield (0.21 g, 0.29 mmol). ^{1}H NMR (C_6D_6): $\delta = 0.40$ (m, 2H, CH C_6H_{10}), 1.05–1.16 (m, 2H, CH C_6H_{10}), 1.25 (d, 6H, $^3J_{HH} = 6.1$ Hz, CH(CH_3)$_2$), 1.29 (s, 18H, $C(CH_3)_3$), 1.30 (d, 6H, $^3J_{HH} = 6.1$ Hz, CH-(CH_3)$_2$), 1.46–1.66 (m, 2H, CH C_6H_{10}), 1.74 (s, 18H, $C(CH_3)_3$), 1.91 (m, 2H, CH C_6H_{10}), 2.53 (m, 2H, CHS), 4.89 (septet, 2H, $^3J_{HH} = 6.1$ Hz, C*H*-(CH_3)$_2$), 7.35 (d, 2H, $^4J_{HH} = 2.5$ Hz, arom. CH), 7.58 ppm (d, 2H, $^4J_{HH} =$ 2.5 Hz, arom. CH). ^{13}C{^{1}H} NMR (C_6D_6): $\delta = 25.54$ (CH_2 C_6H_{10}), 26.15 (CH(CH_3)$_2$), 26.79 (CH(CH_3)$_2$), 29.84 ($C(CH_3)_3$), 31.79 ($C(CH_3)_3$), 33.08 (CH_2 C_6H_{10}), 34.25 ($C(CH_3)_3$), 35.84 ($C(CH_3)_3$), 53.17 (CHS), 79.80 (*C*H-(CH_3)$_2$), 114.94 (arom.), 126.52 (arom. CH), 130.28 (arom. CH), 136.98 (arom.), 139.60 (arom.), 168.01 ppm (arom.); elemental analysis (%) calcd for $C_{40}H_{64}O_4S_2Ti$ (720.96): C 66.64, H 8.95; found: C 66.34, H 8.75.

(Λ,*R*,*R*)-**6a**: Following the same procedure as reported for the preparation of *rac*-**6a**, starting from (*R*,*R*)-**3a** (0.30 g, 0.54 mmol) and titanium tetra(isopropoxide) (157 μL, 0.15 g, 0.54 mmol), (Λ,*R*,*R*)-**6a** was isolated in 79% yield (0.31 g, 0.43 mmol). $[\alpha]_D^{23} = +200$ ($c = 2.0$ mg mL^{-1}, CH_2Cl_2); elemental analysis (%) calcd for $C_{40}H_{64}O_4S_2Ti$ (720.96): C 66.64, H 8.95; found: C 66.36, H 8.95.

(Δ,*S*,*S*)-**6a**: Following the same procedure as reported for the preparation of *rac*-**6a**, starting from (*S*,*S*)-**3a** (0.30 g, 0.54 mmol) and titanium tetra(isopropoxide) (157 μL, 0.15 g, 0.54 mmol), (Δ,*S*,*S*)-**6a** was obtained in 75% yield (0.29 g, 0.40 mmol). $[\alpha]_D^{23} = -184$ ($c = 1.8$ mg mL^{-1}, CH_2Cl_2); el-

emental analysis (%) calcd for $C_{40}H_{64}O_4S_2Ti$ (720.96): C 66.64, H 8.95; found: C 66.97, H 9.15.

rac-**6b**: Neat titanium tetra(isopropoxide) (800 μL, 0.76 g, 2.69 mmol) was added to a stirred solution of *rac*-**3b** (1.28 g, 2.64 mmol) in pentane (20 mL). The resulting yellow solution was stirred for 2 h. All volatiles were removed under reduced pressure and the residue was recrystallized from hexamethyldisiloxane to afford microcrystalline pale yellow *rac*-**6b** in 68% yield (1.14 g, 1.80 mmol). ^{1}H NMR ($CDCl_3$): $\delta = 1.05$ (m, 2H, CH C_6H_{10}), 1.13 (d, $^2J_{HH} = 6.0$ Hz, $CH(CH_3)_2$, overlapping), 1.14 (d, $^2J_{HH} = 6.0$ Hz, $CH(CH_3)_2$, overlapping), 1.44 (s, 18H, $C(CH_3)_3$), 1.60 (m, 4H, CH C_6H_{10}), 2.14 (m, 2H, CH C_6H_{10}), 2.24 (s, 6H, CH_3), 2.35 (m, 2H, CHS), 4.69 (septet, $^3J_{HH} = 6.0$ Hz, $CH(CH_3)_2$), 6.93 (d, 2H, $^4J_{HH} = 2.3$ Hz, arom. CH), 7.07 ppm (d, 2H, $^4J_{HH} = 2.3$ Hz, arom. CH); ^{13}C{^{1}H} NMR ($CDCl_3$): $\delta = 20.74$ (CH_3), 25.47 (CH_2 C_6H_{10}), 25.84 ($CH(CH_3)_2$), 29.29 ($C(CH_3)_3$), 32.63 (CH_2 C_6H_{10}), 35.05 ($C(CH_3)_3$), 52.74 (CHS), 79.24 ($CH(CH_3)_2$), 114.36 (arom.), 125.45 (arom.), 129.81 (arom. CH), 133.18 (arom. CH), 137.04 (arom.), 167.45 ppm (arom.); elemental analysis (%) calcd for $C_{34}H_{52}O_4S_2Ti$ (636.80): C 64.13, H 8.23; found: C 63.70, H 8.03.

(Λ,*R*,*R*)-**6b**: Following a similar procedure as reported for the preparation of *rac*-**6b**, starting from *rac*-**3b** (0.40 g, 0.85 mmol) and titanium tetra(isopropoxide) (255 μL, 0.24 g, 0.86 mmol), (Λ,*R*,*R*)-**6b** was obtained in 72% yield. Crystals suitable for X-ray analysis could be obtained from hexamethyldisiloxane solution. $[\alpha]_D^{23} = +311$ ($c = 1.8$ mg mL^{-1}, CH_2Cl_2); elemental analysis (%) calcd for $C_{48}H_{64}O_2S_2Ti$ (636.80): C 64.13, H 8.23; found: C 63.84, H 8.04.

(Δ,*S*,*S*)-**6b**: Following a similar procedure as reported for the preparation of *rac*-**6b**, starting from *rac*-**3b** (40 mg, 0.09 mmol) and titanium tetra(isopropoxide) (27 μL, 26 mg, 0.09 mmol), (Δ,*S*,*S*)-**6b** was obtained in 81% yield. $[\alpha]_D^{23} = -317$ ($c = 2.8$ mg mL^{-1}, CH_2Cl_2); elemental analysis (%) calcd for $C_{48}H_{64}O_2S_2Ti$ (636.80): C 64.13, H 8.23; found: C 63.36, H 8.10.

7: 1.0 M Benzyl magnesium chloride in diethyl ether (2.7 mL, 0.41 g, 2.70 mmol) was added to a stirred suspension of *rac*-**5b** (0.75 g, 1.27 mmol) in pentane (40 mL) at −78 °C. The resulting dark red solution was allowed to slowly warm to 0 °C and then stirred for 1 h. The solution was filtered, concentrated, and stored at −70 °C overnight to give **7** as a dark red powder in 56% yield (0.50 g, 0.71 mmol). Crystals suitable for X-ray analysis were obtained from pentane solution at −30 °C. ^{1}H NMR (C_6D_6): $\delta = 0.17$ (m, 2H, CH C_6H_{10}), 0.93 (m, 2H, CH C_6H_{10}), 1.31 (m, 2H, CH C_6H_{10}), 1.63 (m, 2H, CH C_6H_{10}), 1.76 (s, 18H, $C(CH_3)_3$), 2.08 (m, 2H, CHS, overlapping with CH_3 signal), 2.13 (s, 6H, CH_3), 3.42 (d, 2H, $^2J_{HH} = 9.0$ Hz, TiCH), 3.50 (d, 2H, $^2J_{HH} = 9.0$ Hz, TiCH), 6.89 (t, 2H, C_6H_5 *p*-CH, overlapping with C_6H_2 signal), 6.91 (m, 2H, C_6H_2 CH), 7.06 (m, 4H, C_6H_5 *m*-CH), 7.20 (d, 4H, C_6H_5 *o*-CH), 7.26 ppm (d, 2H, $^4J_{HH} = 1.8$ Hz, C_6H_2 CH); ^{13}C{^{1}H} NMR (C_6D_6): $\delta = 20.87$ (CH_3), 25.17 (CH_2 C_6H_{10}), 30.01 ($C(CH_3)_3$), 33.13 (CH_2 C_6H_{10}), 35.50 ($C(CH_3)_3$), 53.23 (CHS), 88.94 (TiCH$_2$, $^1J_{CH} = 132$ Hz), 118.28 (arom.), 123.57 (*p*-C_6H_5), 128,29 (arom., overlapping with solvent), 128.57 (*m*-C_6H_5), 130.07 (*o*-C_6H_5), 130.58 (arom. CH), 134.01 (arom CH), 137.63 (arom.), 144.16 (*ipso*-C_6H_5), 166.84 ppm (arom.); elemental analysis (%) calcd for $C_{42}H_{52}O_2S_2Ti$ (700.89): C 71.97, H 7.48; found: C 72.03, H 7.57.

Reaction of **7** with $B(C_6F_5)_3$: Compound **7** (35 mg, 50 μmol) and $B(C_6F_5)_3$ (27 mg, 53 μmol) were weighed into a vial and dissolved in precooled C_6D_5Br. The solution was transferred immediately into an NMR (Young) tube and kept frozen until immediately before NMR spectroscopic measurement. Variable-temperature measurements were made between −30 °C and 25 °C. ^{1}H NMR (C_6D_5Br, 25 °C, selected resonances): $\delta = 0.43$ (m, CH C_6H_{10}), 0.75–1.60 (multiple resonances CH C_6H_{10}), 1.40 (s, $C(CH_3)_3$), 1.43 (s, $C(CH_3)_3$), 1.52 (s, $C(CH_3)_3$), 1.74 (m, CH C_6H_{10}), 2.14 (s, CH_3), 2.17 (s, CH_3), 2.22 (s, CH_3), 2.40 (m, CHS), 2.56 (m, CHS), 3.05 (d, $^1J_{HH} = 7.0$ Hz, TiCH$_2$), 3.36 (br s, BCH_2), 3.52 (d, $^1J_{HH} = 7.0$ Hz, TiCH$_2$), 3.76 (br), 3.88 (br s, TiCH$_2$), 6.65–7.45 ppm (arom.); ^{13}C{^{1}H} NMR (C_6D_5Br, 25 °C): $\delta = 20.86$ (CH_3), 20.98 (CH_3), 23.39 (CH_2 C_6H_{10}), 24.79 (CH_2 C_6H_{10}), 25.12 (CH_2 C_6H_{10}), 29.51 ($C(CH_3)_3$), 29.64 ($C(CH_3)_3$), 29.74 ($C(CH_3)_3$), 31.53 (CH_2 C_6H_{10}), 32.45 (br, BCH_2), 34.95 ($C(CH_3)_3$), 35.23 ($C(CH_3)_3$) , 35.44 ($C(CH_3)_3$), 59.45 (CHS), 98.37 (br, TiCH$_2$), 99.70 (TiCH$_2$) 118–164 ppm (arom.); ^{19}F NMR (C_6D_5Br, 25 °C): $\delta = -127.03$ (d, *o*-F), −141.54 (m, *p*-F), −159.03 (m, *m*-F), −134.28 (d, $^3J_{FF} = 24.0$ Hz, *o*-F), −158.78 (t, $^3J_{FF} = 21.0$ Hz , *p*-F), −163.75 ppm (t, $^3J_{FF} = 21.0$ Hz, *m*-F). ^{1}H NMR (C_6D_5Br, −30 °C, selected resonances): $\delta = 0.33$ (m, CH C_6H_{10}), 0.90 (m, CH C_6H_{10}), 1.16 (m, CH C_6H_{10}), 1.38 (s, $C(CH_3)_3$), 1.50 (s, $C(CH_3)_3$), 1.63 (m, CH C_6H_{10}), 1.89 (m, CH C_6H_{10}), 2.11 (s, CH_3), 2.16 (s, CH_3), 2.21 (s, CH_3), 2.24 (s, CH_3), 2.37 (m, CHS), 3.35 (d, $^1J_{HH} = 5.5$ Hz, TiCH$_2$), 3.48 (br s, BCH_2), 3.82 (d, $^1J_{HH} = 15.2$ Hz, TiCH$_2$), 4.02 (d, $^1J_{HH} = 5.8$ Hz, TiCH$_2$), 6.35–7.55 ppm (arom.); ^{13}C{^{1}H} NMR (C_6D_5Br, −30 °C): $\delta = 20.86$ (CH_3), 20.98 (CH_3), 23.39 (CH_2 C_6H_{10}), 24.79 (CH_2 C_6H_{10}), 25.12 (CH_2 C_6H_{10}), 29.51 ($C(CH_3)_3$), 29.64 ($C(CH_3)_3$), 29.74 ($C(CH_3)_3$), 31.53 (CH_2 C_6H_{10}), 32.45 (br, BCH_2), 34.95 ($C(CH_3)_3$), 35.23 ($C(CH_3)_3$) , 35.44 ($C(CH_3)_3$), 59.45 (CHS), 98.37 (br, TiCH$_2$), 99.70 (TiCH$_2$) 118–164 ppm (arom.); ^{19}F NMR (C_6D_5Br, −30 °C): $\delta = -127.03$ (d, *o*-F), −141.54 (m, *p*-F), −159.03 (m, *m*-F), −134.28 (d, $^3J_{FF} = 24.0$ Hz, *o*-F), −158.78 (t, $^3J_{FF} = 21.0$ Hz , *p*-F), −163.75 ppm (t, $^3J_{FF} = 21.0$ Hz, *m*-F); ^{11}B NMR (C_6D_5Br, −30 °C): $\delta = -12.53$ ppm.

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