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Pd-catalyzed asymmetric synthesis of allylic *tert*-butyl sulfones and sulfides: Kinetic resolution of the allylic substrate by a chiral Pd-complex

Hans-Joachim Gais,* Holger Eichelmann, Nicole Spalthoff, Frank Gerhards, Michael Frank and Gerhard Raabe

Institut für Organische Chemie der Rheinisch-Westfälischen Technischen Hochschule Aachen, Professor-Pirlet-Straße 1, 52056 Aachen, Germany

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Abstract

The acyclic and cyclic allylic *tert*-butyl sulfones **3**, *ent*-**3**, **11a**, **11b** and **15a–c** of 89–98% ee were synthesized in 40–92% yield by a Pd-catalyzed reaction of the respective allylic acetates and carbonates *rac*-**1a**, *rac*-**1b**, *rac*-**10a**, *rac*-**10b** and *rac*-**14a–c** with LiO_2St-Bu in the presence of the chiral ligands **2a**, *ent*-**2b** and **12**. Formation of the *n*-butyl sulfones **13a** and **13b** of 95% ee was observed. Reactions of *rac*-**1a** and **1b**/*ent*-**1b** with LiO_2St-Bu in the presence of **2a** and *ent*-**2b**, respectively, in THF under heterogeneous conditions were accompanied by a kinetic resolution of the allylic substrates. The faster reacting allylic substrate and the preferentially formed sulfone had the same absolute configuration. The allylic *tert*-butyl sulfide **17** of 92% ee was obtained in 63% yield by the Pd-catalyzed reaction of *rac*-**1b** with Me_3SiSt-Bu in the presence of *ent*-**2b**.

1. Introduction

The Pd-catalyzed allylic alkylation[1] of aryl sulfinates[2–5] provides for an effective route for the asymmetric synthesis of allylic aryl sulfones. In a continuation of previous studies,[3] we were interested to see whether this method could be extended to the asymmetric synthesis of allylic alkyl sulfones and of allylic sulfides. Sulfones **I** and **II**, bearing a *tert*-butyl group at the S-atom, are of special interest because of their potential utilization in the synthesis of chiral nonracemic allylic α-sulfonyl carbanions.[6] Herein we describe the Pd-catalyzed asymmetric synthesis of cyclic and acyclic allylic *tert*-butyl sulfones as well as of an allylic *tert*-butyl sulfide. In addition we report on the observation of a kinetic resolution of the allylic substrate during the Pd-catalyzed substitution and the determination of its stereochemistry.

* Corresponding author.

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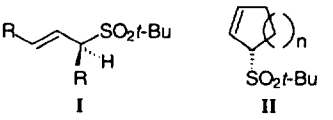
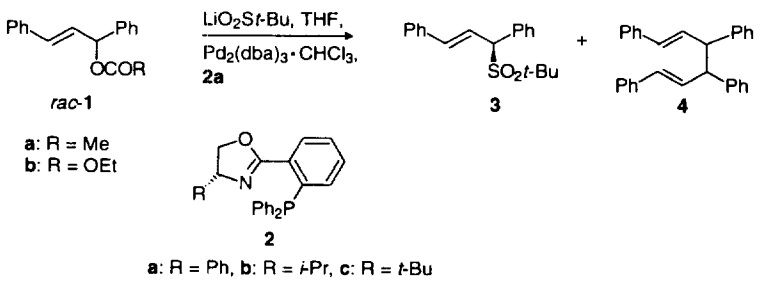


2. Results and discussion

2.1. Acyclic allylic sulfones and kinetic resolution

Lithium *tert*-butylsulfinate was prepared as a colorless solid by reaction of *tert*-butyllithium with a large excess of sulfur dioxide in *n*-hexane–*n*-pentane.[7] The LiO_2St-Bu thus obtained was contaminated with approximately 4% of lithium *tert*-butylsulfonate according to NMR and IR spectroscopy. Although in THF as a solvent the amount of LiO_3St-Bu was lower (1–2%), the formation of other unidentified side products made this solvent less suitable. LiO_2St-Bu has a low solubility in anhydrous THF (0.074 M), thus, Pd-catalyzed reactions in this solvent proceeded under heterogeneous conditions (vide infra).

Treatment of acetate *rac*-**1a** with LiO_2St-Bu in the presence of $Pd_2(dba)_3 \cdot CHCl_3$ (dba=dibenzylideneacetone) (1.5 mol%) and *P,N*-ligand **2a**[8–11] (6.6 mol%) in THF (25°C, 8 days) gave sulfone **3** with an ee value of 93% (HPLC) in 69% chemical yield (Scheme 1). Similar results were obtained with carbonate *rac*-**1b** as substrate.



Scheme 1.

Sulfone **3** was contaminated by approximately 7% of diene **4** which was formed as a mixture of diastereomers.[12] A chromatographic separation of **3** and **4** on silica gel or aluminum oxide proved not to be possible because of the instability of **3** under these conditions. However, crystallization of the mixture of **3** and **4** from ethanol gave pure **3** of ≥99% ee (HPLC) in 40% yield. The use of *ent*-**2b**[8–11] and *ent*-**2c**[8–11] instead of **2a** as ligands led to formation of *ent*-**3** of 91% ee (90% ee) in 71% (69%) chemical yield. Sulfone **3** was shown to have the (*S*) configuration by X-ray structure analysis[13] (Fig. 1).

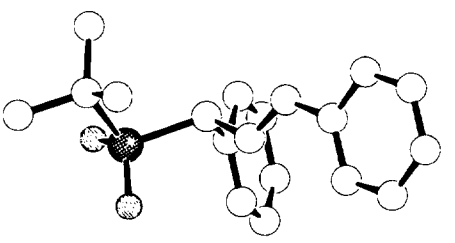
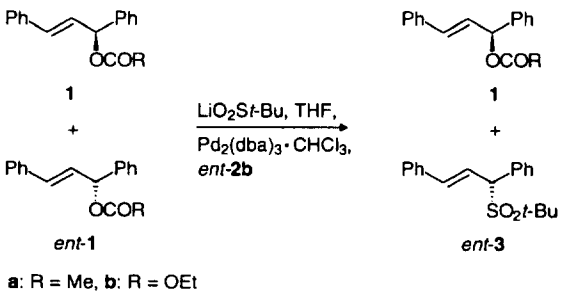


Fig. 1. Structure of **3** in the crystal. Selected bond distances (Å) and bond angles (deg): S–O 1.442(2), S–*t*-Bu 1.823(3), S–C 1.840(3), O–S–O 117.3(1), C–S–C 106.0(2)

Under the heterogeneous conditions employed the reactions of acetate *rac*-**1a** and carbonate *rac*-**1b** with LiO_2St-Bu (2 equiv.) in THF were rather slow. As a result, their course could be easily followed by HPLC analysis on a chiral column. This led to the observation that the alkylations of *tert*-butylsulfinate in the presence of **2a** and *ent*-**2b** were accompanied by a kinetic resolution of the racemic substrates *rac*-**1a** and *rac*-**1b**. HPLC analysis of the reaction mixture obtained upon treatment of *rac*-**1a** with LiO_2St-Bu in the presence of $Pd_2(dba)_3 \cdot CHCl_3$ (1.6 mol%) and *ent*-**2b** (6.6 mol%) showed, after approximately 40% conversion, formation of sulfone *ent*-**3** of 91% ee and acetate **1a** of 94% ee (Scheme 2). Upon further reaction, **1a** was converted to *ent*-**3** as well. The ee value of sulfone *ent*-**3**, however, did not practically change. By using **2a** as a ligand, opposite results were obtained in the reaction of *rac*-**1a** with LiO_2St-Bu under the above conditions. The reaction mixture contained, after approximately 60% conversion, sulfone **3** of 89% ee and *ent*-**1a** of 93% ee. Because of the instability of **3** and *ent*-**1a** on silica gel and aluminum oxide, a chromatographic separation of both compounds was not possible.



Scheme 2.

Treatment of *rac*-**1b** and **1b**:*ent*-**1b** (93:7) (vide infra) with LiO_2St-Bu in THF in the presence of $Pd_2(dba)_3 \cdot CHCl_3$ (9 mol%) and **2a** (40 mol%) gave similar results as in the case of *rac*-**1a**. As revealed by the continuous monitoring of the reaction of **1b**:*ent*-**1b** (93:7) by HPLC analysis, the ee value of **1b** gradually dropped to 0%, and after a reaction time of 50 h *ent*-**1b** of 80% ee remained (Fig. 2). We note that in this experiment, where higher amounts of catalyst and ligand were used (vide supra), the ee value of sulfone **3** was considerably lower (76–81%).

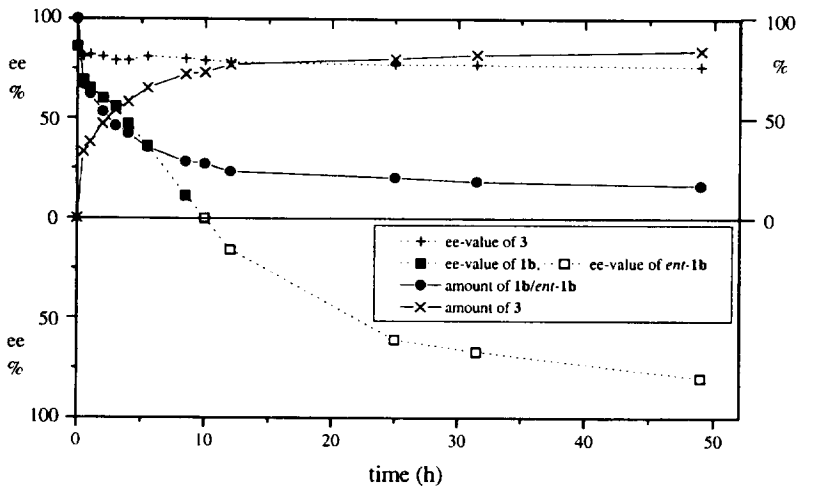
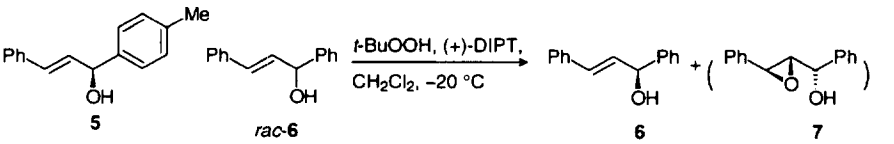


Fig. 2. Time dependence of the ratios of **1b**:*ent*-**1b** and **3**:*ent*-**3** in the Pd-catalyzed reaction of **1b**:*ent*-**1b** (93:7) with LiO_2St-Bu in the presence of **2a**

The above described kinetic resolutions are not without precedent. Hayashi et al. reported on the kinetic resolution of a racemic allylic acetate in the Pd-catalyzed allylic alkylation of a soft C-nucleophile in the presence of a chiral *P,P*-ligand.[14] However, the stereochemistry of this kinetic resolution was not fully established. Thus, we decided to determine the absolute configurations of carbonate **1b** and acetate **1a** as well. The methyl substituted alcohol **5** had been previously synthesized[15] by the kinetic resolution of *rac*-**5** using the Sharpless epoxidation method (Scheme 3).[16] Subjecting alcohol *rac*-**6** to this method by using (+)-L-diisopropyl tartrate gave **6** with an ee value of 86% (HPLC) in 29% yield. The rather low yield of **6** is due to its extensive decomposition during chromatography on silica gel. Besides **6**, epoxide **7** and its epimer were formed, but were not isolated.[17]

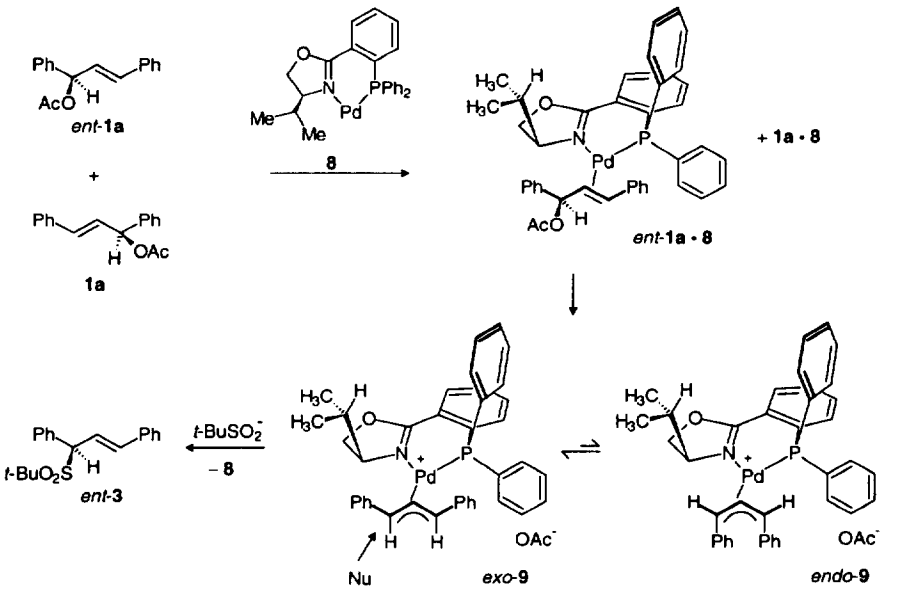


Scheme 3.

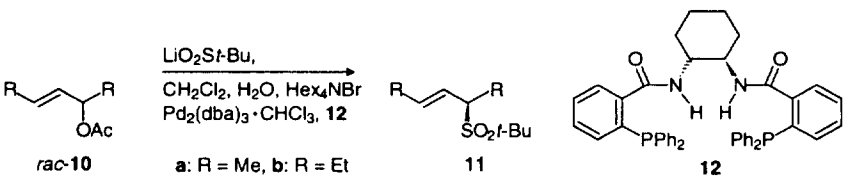
A comparison of the chiroptical data of **6** with those of **5** led to the assignment of the (*S*) configuration to **6** which was converted to acetate **1a** and carbonate **1b**, both having an ee value of 86% (HPLC). Thus, in the Pd-catalyzed substitutions of *rac*-**1b**, **1b**/*ent*-**1b** and *rac*-**1a** the faster reacting allylic substrate and the preferentially formed allylic sulfone have the same absolute configuration. This can be rationalized on the basis of a simplified version of the mechanism proposed for the Pd-catalyzed allylic alkylation of soft nucleophiles in the presence of **2a–c** and related ligands[1,18–21] as follows. The chiral Pd(0)-complex **8** reacts reversibly with *ent*-**1a** and **1a** under formation of complexes *ent*-**1a**·**8** and **1a**·**8**, respectively (Scheme 4). In *ent*-**1a**·**8** the C-atom, bearing the nucleofuge, is *trans* to the P-atom and the phenyl groups are in the *exo* position. The subsequent preferential ionization of *ent*-**1a**·**8** leads to complex *exo*-**9** which is in equilibrium with *endo*-**9** (*exo*:*endo*=9:1).[18] These steps of an enantiomer selective ionization are followed by a preferential attack of *tert*-butylsulfinate at the C-atom of *exo*-**9** which is *trans* to the P-atom, giving sulfone *ent*-**3**. A similar rationalization can be applied to the Pd-catalyzed substitutions of *rac*-**1a**, *rac*-**1b** and **1b**/*ent*-**1b** in the presence of **2a**.

Synthesis of 1,3-dialkyl substituted allyl *tert*-butyl sulfones was studied by first using *ent*-**2b** as a ligand. Treatment of *rac*-**10a** with NaO_2St-Bu[22] in THF in the presence of $Pd_2(dba)_3 \cdot CHCl_3$ and *ent*-**2b** under heterogeneous conditions for 2 days, gave a mixture of sulfone *ent*-**11a** and the corresponding sulfinate ester in a ratio of 94:6 (^{1}H NMR) in 61% yield (Scheme 5). Chromatography afforded pure sulfone *ent*-**11a** in 55% yield. However, *ent*-**11a** had an ee value of only 58% according to GC analysis. A similar low enantioselectivity had been found in the substitution of *rac*-**10a** with *p*-tolylsulfinate in the presence of *ent*-**2b**.[3] Because of the low enantioselectivity recorded in the formation of *ent*-**11a** in the presence of *ent*-**2b**, substitution of *rac*-**10a** and *rac*-**10b** was carried out in the presence of *P,P*-ligand **12**[4] which was expected to provide a higher enantioselectivity. Treatment of *rac*-**10a** with LiO_2St-Bu in the presence of $Pd_2(dba)_3 \cdot CHCl_3$ and **12** in a liquid two-phase system of water–CH_2Cl_2 (Hex_4NBr) for 4 days gave **11a** in 51% yield. Sulfone **11a** had an ee value of 98% (GC). A similar reaction of *rac*-**10b** in the presence of **12** afforded **11b** of 96% ee (GC) in 43% yield. Both reactions were rather slow and approximately 40% of the allylic substrates were recovered. The (*R*) configuration was tentatively assigned to **11a** and **11b** since a similar reaction of *rac*-**10a** and *rac*-**10b** with benzenesulfinate gave the corresponding phenyl sulfones, having the (*R*) configuration.[4]

The inadvertent treatment of *rac*-**1a** with a 1:1 mixture of LiO_2St-Bu and lithium *n*-butylsulfinate[7] in water–CH_2Cl_2 (Hex_4NBr) in the presence of $Pd_2(dba)_3 \cdot CHCl_3$ and **12** led to isolation of a 47:53 mixture of **11a** (96% ee) and the *n*-butyl sulfone **13a** in 46% yield (Scheme 6). Sulfone **13a** had an ee value of

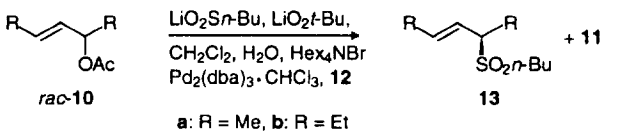


Scheme 4.



Scheme 5.

95% (GC). A similar reaction of *rac*-**10b** with LiO_2St-Bu:LiO_2Sn-Bu gave a 45:55 mixture of **11b** (96% ee) and **13b** of 95% ee in 83% yield. These results suggest that asymmetric synthesis of allylic *n*-alkyl sulfones by using lithium *n*-alkyl sulfinates[7] should be feasible as well.

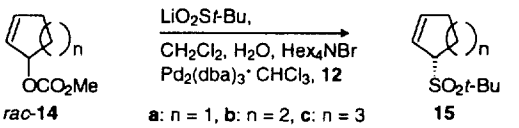


Scheme 6.

2.2. Cyclic allylic sulfones

Because of the highly enantioselective synthesis of cyclic allylic phenyl sulfones using **12**,[4] we chose this ligand for the synthesis of cyclic allylic *tert*-butyl sulfones (Scheme 7). Treatment of carbonates *rac*-**14a–c** with LiO_2St-Bu in water–CH_2Cl_2 (Hex_4NBr) in the presence of $Pd_2(dba)_3 \cdot CHCl_3$ (1.5 mol%) and **12** (4.5 mol%) for 24 h gave sulfones **15a–c** in 76%, 92% and 89% yield, respectively, with ee values of 89%, 90% and 93% (GC, ^1H NMR), respectively. Reactions of the cyclic carbonates *rac*-**14a–c** with LiO_2St-Bu in the presence of **12** were faster than those of the acylic acetates *rac*-**10a,b**. The absolute configuration of **15a–c** was tentatively assigned as (*S*) on the premise that Pd-catalyzed substitution

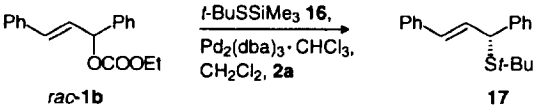
of *rac*-**14a–c** with RSO_2^- in the presence of **12** proceed with the same sense of asymmetric induction irrespective of the nature of the group R of the sulfinate.



Scheme 7.

2.3. *Acyclic allylic sulfides*

Since allylic sulfides can be selectively oxidized to the corresponding sulfones, it was of interest to see whether the asymmetric synthesis of allylic *tert*-butyl sulfides could be accomplished by a Pd-catalyzed allylic alkylation. Because of the known ability of trimethylsilyl sulfides to enter into a Pd-catalyzed allylic substitutions in the presence of achiral ligands,[23,24] we studied the reaction of *rac*-**1b** with sulfide **16**[25] in the presence of **2a** and *ent*-**2b** (Scheme 8). Treatment of *rac*-**1b** with **16** in the presence of $Pd_2(dba)_3 \cdot CHCl_3$ (5 mol%) and **2a** (13 mol%) in CH_2Cl_2 gave sulfide **17** with an ee value of 92% in 62% yield. A similar reaction of *rac*-**1b** in the presence of *ent*-**2b** led to the isolation of sulfide *ent*-**17** with an ee value of 93% (HPLC) in 63% yield. The (*R*) configuration of **17** (85% ee) was determined by its oxidation to sulfone *ent*-**3** (69% ee). The nucleophile in the substitution of *rac*-**1b** was presumably *tert*-butylthiolate formed by a desilylation of **16** by ethoxide, which in turn originated from the decomposition of the nucleofuge.[26]



Scheme 8.

3. Conclusion

The Pd-catalyzed asymmetric allylic alkylation of *tert*-butylsulfinate in the presence of *P*,*P*-ligand **12** proceeds with high enantioselectivity and provides for an easy access to cyclic and acyclic allylic *tert*-butyl sulfones. An enantiomer differentiating ionization of the allylic substrate by the chiral Pd–*P*,*N*-ligand complexes has been experimentally verified in the reactions of *rac*-**1a** and **1b**/*ent*-**1b** in the presence of ligands **2a** and *ent*-**2b**. In accordance with the currently proposed mechanism of the Pd-catalyzed allylic alkylation, the faster reacting substrate and the preferentially formed product have the same configuration. The Pd-catalyzed allylic alkylation of S-nucleophiles in the presence of **2a**, *ent*-**2b** and **12** proceeds with the same sense and with a similar degree of asymmetric induction as with C- and N-nucleophiles. Allylic sulfides can perhaps be obtained as well with high enantioselectivity by this method. We note, however, that reaction of *rac*-**1b** with sulfide **16** required considerably larger amounts of catalyst and ligand as compared to those with sulfinates.

4. Experimental section

All reactions were carried out in an atmosphere of argon with Schlenk and syringe techniques. Suspensions of LiO_2St-Bu and NaO_2St-Bu in THF were prepared by ultrasonication. THF was distilled under argon from potassium benzophenone ketyl. *n*-Pentane was distilled under argon from sodium benzophenone ketyl in the presence of diglyme (10% v/v). Water was deoxygenated under argon by the freeze–thaw technique. CH_2Cl_2 was distilled under argon. TLC was performed on E. Merck plates coated with silica gel 60 F254 (0.2 mm). Chromatography was performed with E. Merck silica gel 60 (230–400 mesh) and silica gel 60 (70–230 mesh). Melting points are uncorrected. ^{1}H NMR chemical shifts are reported in ppm relative to Me_4Si: δ 0.00 as the internal standard. Coupling constants (*J*) are given in Hz. ^{13}C NMR chemical shifts are reported in ppm relative to Me_4Si: δ 0.00 as the internal standard. Peaks in the ^{13}C NMR spectra are denoted as 'u' for carbons with zero or two attached protons or as 'd' for carbons with one or three attached protons, as determined from the APT pulse sequence. Determination of enantiomer composition by capillary GC analysis was performed with a 2,3-dipentyl-6-*O*-methyl-γ-cyclodextrin column (25 m×0.25 mm, 0.25 μm) (Lipodex-γ) and a permethyl-β-cyclodextrin column (25 m×0.25 mm, 0.25 μm) (Lipodex-E). HPLC was done with a Baker Chiracel OD-H column. Retention times (t_R) are given in min.

4.1. *Lithium* tert-*butylsulfinate*

To a solution of SO_2 (150 mL, 3.45 mol) in *n*-hexane (300 mL) was added, within 3 h at −70°C with a double-ended needle, a solution of *tert*-BuLi in *n*-pentane (300 mL, 1.6 M, 0.48 mol). After stirring the yellow–brown suspension at this temperature for 1 h, it was allowed to warm to room temperature over 24 h. A stream of dry argon was passed through the flask to remove last traces of SO_2. The solvents were removed in vacuum under argon and stirring. Drying of the remaining solid for 3 days under high vacuum gave LiO_2St-Bu (5.48 g, 90%) as a colorless solid which contained 4% of LiO_3St-Bu: ^{1}H NMR (300 MHz, D_2O) δ 0.83 (s, 9H); ^{13}C NMR (75.5 MHz, D_2O) δ 23.33 (d), 57.02 (u); IR (KBr) (in part) ν 1005 (s). LiO_3St-Bu: ^{1}H NMR (300 MHz, D_2O) δ 1.16 (s, 9H); ^{13}C NMR (75.5 MHz, D_2O) δ 27.02 (d), 57.99 (u); IR (KBr) (in part) ν 1180 (s) cm^{-1}.

4.2. (−)-(S,E)-*1,3-Diphenyl-3-(*tert-*butylsulfonyl)prop-1-ene* **3**

To a solution of $Pd_2(dba)_3 \cdot CHCl_3$ (155 mg, 0.15 mmol) in THF (5 mL) was added **2a** (268 mg, 0.66 mmol) at room temperature. After stirring the mixture for 15 min, a solution of *rac*-**1a** (2.524 g, 10 mmol) in THF (2 mL) was added. Stirring was continued for 15 min and a suspension of LiO_2St-Bu (1.282 g, 20 mmol) in THF (3 mL) was added. After stirring the mixture for 8 days at room temperature, brine (10 mL) was added and the mixture was extracted with THF. The organic phase was dried ($MgSO_4$) and concentrated under vacuum. The residue contained 2.374 g of a mixture of **3** and **4** in a ratio of 12:1 (HPLC), corresponding to a 69% chemical yield of **3**; 93% ee (HPLC). Recrystallization of the crude material from EtOH gave **3** (1.006 g, 40%): ≥99% ee (HPLC); mp 160°C; $[\alpha]_D^{22}$ −25.2 (*c* 0.17, EtOH); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.36 (s, 9H), 5.07 (dd, *J*=6.4, *J*=2.0, 1H), 6.64 (dd, *J*=16.1, *J*=2.0, 1H), 6.70 (dd, *J*=16.1, *J*=6.4, 1H), 7.23–7.43 (m, 8H), 7.52–7.57 (m, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 24.60 (d), 62.65 (u), 68.88 (d), 122.53 (d), 126.76 (d), 128.43 (d), 128.66 (d), 128.89 (d), 128.92 (d), 129.68 (d), 133.57 (u), 135.87 (u), 136.32 (d); MS (EI, 70 eV) *m/z* (rel. intensity) 314 (M^+, 0.5), 209 (5), 194 (21), 193 (100), 178 (17), 165 (7), 115 (73), 91 (22), 65 (6), 57 (34); IR (KBr) ν 3084 (w), 3062 (w), 3043 (w), 3028 (w), 2992 (m), 2976 (m), 1494 (m), 1476 (m), 1457 (m), 1448 (m), 1279 (s), 1210 (m),

1188 (m), 1108 (s), 1067 (m), 1029 (m), 979 (m), 749 (s), 718 (m), 698 (s), 676 (s) cm^{-1}. Anal. Calcd for $C_{19}H_{22}O_2S$: C, 72.58; H, 7.06. Found C, 72.57; H, 7.05. From the mother liquor impure **4** was isolated by chromatography as a mixture of diastereomers. Data for **4**: ^1H NMR (300 MHz, $CDCl_3$) δ 3.89 (m, 2H), 6.19 (d, *J*=15.8, 1H), 6.31 (ddd, *J*=15.8, *J*=5.4, *J*=2.4, 1H), 6.39 (d, *J*=15.8, 1H), 6.54 (ddd, *J*=15.8, *J*=5.4, *J*=2.4, 1H), 7.05–7.35 (m, 20H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 55.20 (d), 55.31 (d), 126.12 (d), 126.16 (d), 126.24 (d), 126.50 (d), 127.01 (d), 127.14 (d), 128.18 (d), 128.33 (d), 128.37 (d), 128.38 (d), 128.43 (d), 128.62 (d), 131.12 (d), 131.36 (d), 131.90 (d), 132.15 (d), 137.49 (u), 137.53 (u), 142.39 (u), 142.63 (u); GC–MS (CI, MeOH, in part) *m/z* (rel. intensity) 385 (M^++1, 2), 309 (13), 283 (5), 231 (9), 205 (18), 194 (16), 193 (100), 167 (24).

*4.3. (+)-(R,E)-1,3-Diphenyl-3-(*tert*-butylsulfonyl)prop-1-ene* ent-**3**

Following the procedure described for the synthesis of **3**, $Pd_2(dba)_3 \cdot CHCl_3$ (7.8 mg, 8 μmol), *ent*-**2b** (12.3 mg, 33 μmol) or *ent*-**2c** (12.8 mg, 33 μmol), *rac*-**1a** (126 mg, 0.5 mmol) and LiO_2St-Bu (128 mg, 1 mmol) in THF (1 mL) gave an oil which contained 127 mg (110 mg) of a mixture of *ent*-**3** and **4** in a ratio of 9:1 (11:1) (HPLC), corresponding to a 71% (63%) chemical yield of *ent*-**3**; 91% ee (90% ee) (HPLC).

4.4. Kinetic resolution of rac-***1a*** *and* ***1b***:ent-***1b*** *(93:7)*

Determination of conversion, product formation and enantiomer ratios: HPLC; chiral column; Baker Chiracel OD-H; flow rate: 0.5 mL/min; solvent: *n*-hexane:*i*-PrOH, 9:1; detection: UV 254 nm; t_R(**3**)=23.75, t_R(*ent*-**3**)=25.24, t_R(*ent*-**1b**)=23.75, t_R(**1b**)=25.24, t_R(*ent*-**1a**)=12.02, t_R(**1a**)=12.90, t_R(**4**)=8.72 and 9.28. Peak assignment was made by coinjection with authentic samples.

rac-**1a** and *ent*-**2b**: Following the procedure described for the synthesis of **3**, $Pd_2(dba)_3 \cdot CHCl_3$ (7.8 mg, 8 μmol), *ent*-**2b** (13.4 mg, 33 μmol), *rac*-**1a** (126 mg, 0.5 mmol) and LiO_2St-Bu (128 mg, 1 mmol) in THF (1 mL) gave, after 2 days at room temperature, a mixture which contained *ent*-**3** of 91% ee and **1a** of 94% ee in a ratio of 60:40. The ratio of **3** to **4** was 2:1.

rac-**1a** and **2a**: Following the procedure described for the synthesis of **3**, $Pd_2(dba)_3 \cdot CHCl_3$ (7.8 mg, 8 μmol), **2a** (12.3 mg, 33 μmol), *rac*-**1a** (126 mg, 0.5 mmol) and LiO_2St-Bu (128 mg, 1 mmol) in THF (1 mL) gave, after 2 days at room temperature, a mixture which contained **3** of 89% ee and *ent*-**1a** of 93% ee in a ratio of 40:60. The ratio of *ent*-**3** to **4** was 26:1.

1b:*ent*-**1b** (93:7) and **2a**: Following the procedure described for the synthesis of **3**, $Pd_2(dba)_3 \cdot CHCl_3$ (16.8 mg, 0.016 mmol), **2a** (28.6 mg, 0.070 mmol), **1b** (56.7 mg, 0.172 mmol) (86% ee) and LiO_2St-Bu (73 mg, 0.561 mmol) were combined in THF (10 mL), and the mixture was stirred at room temperature. During the course of the reaction aliquots (0.05 mL) were withdrawn and analyzed by HPLC.

4.5. (−)-(S,E)-1,3-Diphenyl-prop-2-en-1-ol ***6***

To a solution of *rac*-**6** (3.862 g, 18.4 mmol) in CH_2Cl_2 (60 mL) were added (+)-L-diisopropyltartrate (0.58 mL, 2.76 mmol) and activated molecular sieve (20 g, 3 Å). The suspension was cooled to −20°C and $Ti(O\text{-}iPr)_4$ (523 mg, 1.84 mmol) was added. After stirring the mixture for 30 min, it was treated at −20°C with a solution of *t*-BuOOH (4.2 mL, 3 M, 12.87 mmol) in isooctane. Stirring of the mixture was continued for 39 h at −20°C, and an aqueous solution (60 mL) of $FeSO_4$ (5.76 g) and citric acid (2.04 g) was added. After stirring the mixture for 30 min at room temperature, it was extracted with CH_2Cl_2. The organic phase was stirred vigorously with an aqueous solution of NaOH (18.5 g) and NaCl (3.1 g),

washed with brine, dried (Na_2SO_4), and concentrated under vacuum. Chromatography (*n*-hexane:EtOAc, 4:1) of the residue gave 2.33 g of a mixture of **6**, **7** and *epi*-**7** in a ratio of 42:48:9 (^{1}H NMR). The mixture was dissolved in ether:water (1:1, 50 mL) and NaOH was added until a pH value of 10 was reached. After stirring the mixture for 7 days at room temperature, the ratio of the three compounds had changed to 70:29:1 (GC). The mixture was extracted with ether. The organic phase was dried ($MgSO_4$) and concentrated under vacuum. Purification of the residue by chromatography (*n*-hexane:EtOAc, 10:1) gave **6** (560 mg, 29%) as a colorless oil: 86% ee [HPLC: *n*-hexane:*i*-PrOH, 9:1, t_R(**6**)=34.98, t_R(*ent*-**6**)=45.57]; $[\alpha]_D^{20}$ −23.7 (*c* 0.67, MeOH). The NMR spectroscopic data of compound **6**, as obtained above, were identical with those of *rac*-**6**.

4.6. *Ethyl (−)-(S,E)-1,3-diphenyl-prop-2-enyl carbonate* **1b**

To a solution of **6** (442 mg, 2.10 mmol) in THF (10 mL) were added pyridine (0.75 mL) and 4-dimethylaminopyridine (5 mg). The solution was cooled to 0°C and ClCOOEt (0.70 mL, 7.4 mmol) was added dropwise with stirring. After stirring the mixture for 12 h, brine was added and the mixture was extracted with ether. The organic phase was successively washed with 2 N HCl and brine and dried ($MgSO_4$). Concentration of the organic phase and drying of the residue under vacuum gave **1b** (530 mg, 90%) as a colorless oil: 86% ee (HPLC); $[\alpha]_D^{22}$ −1.8 (*c* 0.27, MeOH). Anal. Calcd for $C_{18}H_{18}O_3$: C, 76.57; H, 6.43. Found: C, 76.62; H, 6.40. The NMR spectroscopic data of the thus obtained **1b** were identical with those of *rac*-**1b**.

4.7. *(+)-(S,E)-4-(*tert*-Butylsulfonyl)-pent-2-ene* ent-**11a**

To a solution of $Pd_2(dba)_3 \cdot CHCl_3$ (403 mg, 0.39 mmol) and *ent*-**2b** (640 mg, 1.72 mmol) in THF (50 mL) was added a solution of *rac*-**10a** (2.00 g, 15.6 mmol) in THF (2 mL). After stirring the mixture for 15 min, a suspension of NaO_2S*t*-Bu (4.50 g, 31.2 mmol) in THF (60 mL) was added at room temperature. After stirring the suspension for 2 days at room temperature, brine was added and stirring was continued for 1 h. The organic phase was washed with brine and the aqueous phase was extracted with $CHCl_3$. The combined organic phases were dried ($MgSO_4$) and concentrated under vacuum to give 1.72 g of a mixture of *ent*-**11a** and the corresponding sulfinate ester in a ratio of 94:6 (GC) as a viscous, yellow oil. Chromatography (EtOAc:*n*-hexane, 1:4) of the oil afforded *ent*-**11a** (1.62 g, 55%) as a colorless oil: 58% ee [GC, Lipodex-E, t_R (**11a**)=33.3, t_R (*ent*-**11a**)=34.0]; $[\alpha]_D^{22}$ +4.3 (*c* 1.30, EtOH); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.43 (s, 9H), 1.48 (d, *J*=7.1, 3H), 1.75 (dd, *J*=6.4, *J*=1.3, 3H), 3.90 (dq, *J*=9.1, *J*=7.1, 1H), 5.58 (ddq, *J*=15.4, *J*=9.1, *J*=1.7, 1H), 5.75 (dq, *J*=15.8, *J*=6.4, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.8 (d), 17.9 (d), 24.49 (d), 58.13 (d), 61.35 (u), 127.49 (d), 130.66 (d); MS (EI, 70 eV) *m/z* (rel. intensity) 190 (M^+, 2), 162 (5), 150 (1), 135 (2), 125 (7), 124 (7), 123 (100), 69 (6), 57 (5); IR (neat) ν 2980 (m), 2940 (m), 1450 (m), 1285 (s), 1115 (s), 1015 (m), 975 (m), 720 (m), 650 (m) cm^{-1}. Anal. Calcd for $C_9H_{18}O_2S$: C, 56.80; H, 9.53. Found: C, 56.76; H, 9.79.

4.8. *(−)-(R,E)-4-(*tert*-Butylsulfonyl)-pent-2-ene* **11a**

To a solution of $Pd_2(dba)_3 \cdot CHCl_3$ (15.5 mg, 0.015 mmol) and **12** (31.4 mg, 0.045 mmol) in CH_2Cl_2 (5 mL) was added a solution of *rac*-**10a** (128 mg, 1.0 mmol) in CH_2Cl_2 (1 mL) at room temperature. The mixture was stirred for 15 min, cooled to 0°C and a suspension of LiO_2S*t*-Bu (256 mg, 2.0 mmol) and Hex_4NBr (21 mg) in CH_2Cl_2 (10 mL) as well as water (3 mL) were added rapidly. After stirring the suspension for 4 days at room temperature, brine was added and stirring was continued for 1 h.

The organic phase was washed with brine, and the aqueous phase was extracted with CH_2Cl_2. The combined organic phases were dried ($MgSO_4$) and concentrated in vacuum. Purification of the residue by chromatography (EtOAc:NEt_3:*n*-hexane, 12.5:1:77.5) gave **11a** (98 mg, 51%) as a colorless oil: 98% ee (GC, Lipodex-E); $[\alpha]_D^{22}$ −11.2 (*c* 1.00, EtOH).

4.9. (−)-(R,E)-5-(tert-*Butylsulfonyl*)-hept-3-ene *11b*

Following the procedure described for the synthesis of **11a**, $Pd_2(dba)_3 \cdot CHCl_3$ (15.5 mg, 0.015 mmol), **12** (31.4 mg, 0.045 mmol) in CH_2Cl_2 (5 mL), *rac*-**10b** (156 mg, 1.0 mmol) in CH_2Cl_2 (1 mL), LiO_2St-Bu (256 mg, 2.0 mmol) and Hex_4NBr (21 mg) in CH_2Cl_2 (10 mL) as well as water (3 mL) gave **11b** (95 mg, 43%) as a colourless oil: 96% ee [GC, Lipodex-E, t_R (**11b**)=30.8, t_R (*ent*-**11b**)=31.1]; $[\alpha]_D^{22}$ −31.4 (*c* 1.00, EtOH); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.94 (t, *J*=7.4, 3H), 1.03 (t, *J*=7.4, 3H), 1.42 (s, 9H), 1.68 (m, 1H), 2.18 (m, 3H), 3.55 (dt, *J*=10.1, *J*=3.3, 1H), 5.45 (ddt, *J*=15.6, *J*=9.9, *J*=1.6, 1H), 5.75 (dt, *J*=15.6, *J*=6.3, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 11.35 (d), 13.58 (d), 20.97 (u), 25.10 (d), 26.13 (u), 62.20 (u), 65.34 (d), 124.46 (d), 139.48 (d); MS (EI, 70 eV) *m/z* (rel. intensity) 219 (M^+, 1), 162 (5), 125 (5), 124 (5), 123 (100), 69 (6), 57 (5); IR (neat) ν 2980 (s), 2940 (s), 1460 (m), 1280 (s), 1115 (s), 1015 (m), 975 (m), 800 (w), 720 (m), 660 (m) cm^{-1}. Anal. Calcd for $C_{11}H_{22}O_2S$: C, 60.51; H, 10.16. Found: C, 60.62; H, 10.48.

4.10. (R,E)-4-(n-*Butylsulfonyl*)-pent-2-ene *13a and 11a*

To a solution of $Pd_2(dba)_3 \cdot CHCl_3$ (15.5 mg, 0.015 mmol) and **12** (31.4 mg, 0.045 mmol) in CH_2Cl_2 (5 mL) was added a solution of *rac*-**10a** (128 mg, 1.0 mmol) in CH_2Cl_2 (1 mL) at room temperature. The mixture was stirred for 15 min, cooled to 0°C, and a suspension of LiO_2St-Bu (128 mg, 1.0 mmol), LiO_2Sn-Bu (128 mg, 1.0 mmol) and Hex_4NBr (21 mg) in CH_2Cl_2 (10 mL) as well as water (3 mL) were added rapidly. After stirring the suspension for 48 h at room temperature, brine was added and stirring was continued for 1 h. The organic phase was washed with brine and the aqueous phase was extracted with CH_2Cl_2. The combined organic phases were dried ($MgSO_4$) and concentrated in vacuum. Purification of the residue by chromatography (EtOAc:NEt_3:*n*-hexane, 12.5:1:76.5) gave 87 mg (46%) of a mixture of **11a** (96% ee) (GC, Lipodex-E) and **13a** (95% ee) (GC, Lipodex-E, t_R(**13a**)=37.4, t_R(*ent*-**13a**)=37.7) in a ratio of 47:53 (GC, ^{1}H NMR) as a colorless oil. **13a**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.95 (t, *J*=7.1, 3H), 1.47 (d, *J*=7.1, 3H), 1.78 (dd, *J*=6.3, *J*=1.6, 3H), 1.82 (m, 4H), 2.92 (t, *J*=8.2, 2H), 3.59 (dq, *J*=7.7, *J*=7.7, 1H), 5.53 (ddq, *J*=15.4, *J*=8.5, *J*=1.3, 1H), 5.83 (dq, *J*=15.4, *J*=6.3, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 12.57 (d), 13.58 (d), 18.17 (d), 23.37 (u), 21.86 (u), 49.06 (u), 61.12 (d), 130.64 (d), 132.98 (d); GC–MS (EI, 70 eV) *m/z* (rel. intensity) 163 (6), 125 (11), 124 (11), 123 (66), 105 (17), 89 (40), 69 (91), 61 (10), 53 (17), 43 (100), 42 (13), 41 (73), 39 (31), 32 (13).

4.11. (R,E)-5-(n-*Butylsulfonyl*)-hept-3-ene *13b and 11b*

Following the procedure described for the synthesis of **13a**, $Pd_2(dba)_3 \cdot CHCl_3$ (77.5 mg, 0.075 mmol), **15** (157 mg, 0.274 mmol) in CH_2Cl_2 (20 mL), *rac*-**10b** (750 mg, 5.0 mmol) in CH_2Cl_2 (1 mL), LiO_2St-Bu (1.28 g, 5 mmol), LiO_2Sn-Bu (1.28 g, 5 mmol), and Hex_4NBr (21 mg) in CH_2Cl_2 (20 mL) and water (10 mL) gave 910 mg (83%) of a mixture **11b** (96% ee) (GC, Lipodex-E) and **13b** (95% ee) (GC, Lipodex-E, t_R(**13b**)=35.5, t_R(*ent*-**13b**)=35.8) in a ratio of 45:55 (^{1}H NMR) as a colorless oil. **13b**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.94 (t, *J*=7.4, 3H) 0.98 (t, *J*=7.4, 3H), 1.03 (t, *J*=7.4, 3H), 1.45 (m, 2H), 1.80 (m, 3H), 2.15 (m, 3H), 2.94 (m, 2H), 3.32 (dt, *J*=15.4, *J*=10.0, *J*=3.3, 1H), 5.36 (ddt, *J*=15.4, *J*=9.7, *J*=1.7, 1H),

5.86 (dq, J=15.5, J=6.2, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 11.13 (d), 13.06 (d), 13.57 (d), 19.95 (u), 21.86 (u), 23.48 (u), 25.74 (u), 49.06 (u), 67.76 (d), 121.98 (d), 141.51 (d); GC–MS (EI, 70 eV) *m/z* (rel. intensity) 217 (M^+, 1), 123 (100), 97 (20), 81 (5), 65 (1), 55 (9), 53 (4), 41 (5), 39 (15).

4.12. (−)-(S)-3-(tert-*Butylsulfonyl)cyclopent-1-ene* **15a**

A mixture of *rac*-**14a** (0.13 g, 0.93 mmol), $Pd_2(dba)_3 \cdot CHCl_3$ (15 mg, 14 μmol) and **12** (31 mg, 45 μmol) in CH_2Cl_2 (3 mL) was stirred for 30 min at room temperature. The yellow solution was cooled to 0°C and a cold (0°C) suspension of LiO_2S*t*-Bu (256 mg, 2 mmol) and Hex_4NBr (24 mg, 55.2 μmol) in CH_2Cl_2 (3 mL) was added. Subsequently, water (3 mL) was added quickly to the mixture. After stirring the reaction mixture for 1 day at room temperature, brine (10 mL) was added and the mixture was stirred for 1 h. The aqueous phase was extracted with CH_2Cl_2, and the combined organic phases were concentrated in vacuum. Purification of the residue by chromatography (*n*-hexane:EtOAc:NEt_3, 13:76:1) gave **15a** (133 mg, 76%) as a colorless solid: 89% ee [GC, Lipodex-E: t_R (**15a**)=33.62, t_R (*ent*-**15a**)=33.75; ^{1}H NMR (300 MHz, $CDCl_3$, 30 mol% Eu(hfc)$_3$): δ (*t*-Bu) (**15a**) 2.47, δ (*t*-Bu) (*ent*-**15a**) 2.50]; mp 58°C; $[\alpha]_D^{22}$ −192.6 (*c* 1.02, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.44 (s, 9H), 2.16–2.75 (m, 4H), 4.40 (m, 1H), 5.78–5.83 (ddt, J=5.7, J=2.3, J=2.0, 1H), 6.19–6.23 (ddt, J=5.7, J=2.0, J=1.3, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 24.16 (d), 25.99 (u), 32.69 (u), 60.15 (u), 64.73 (d), 123.85 (d), 139.18 (d); MS (EI, 70 eV) *m/z* (rel. intensity) 67 (M^+-SO_2t-Bu, 100), 66 (20), 57 (78); IR (KBr) ν 3327 (w), 3085 (w), 3057 (m), 2973 (s), 2933 (s), 2854 (m), 1627 (m), 1577 (w), 1479 (s), 1465 (s), 1398 (m), 1372 (m), 1352 (m), 1278 (s), 1196 (m), 1107 (s), 1014 (s), 988 (m), 942 (w), 917 (s), 805 (m), 742 (s), 671 (s), 616 (s) cm^{-1}. Anal. Calcd for $C_9H_{16}O_2S$: C, 57.41; H, 8.57. Found: C, 57.36; H, 8.76.

4.13. (−)-(S)-3-(tert-*Butylsulfonyl)-cyclohex-1-ene* **15b**

Following the procedure described for the synthesis of **15a**, *rac*-**14b** (0.80 g, 5.1 mmol), $Pd_2(dba)_3 \cdot CHCl_3$ (75 mg, 72.4 μmol), **12** (155 mg, 0.22 mmol), LiO_2S*t*-Bu (1.3 g, 10 mmol) and Hex_4NBr (125 mg, 0.3 mmol) in CH_2Cl_2 (60 mL) and water (30 mL) gave, after 1 h at 0°C and 2 h at room temperature, **15b** (0.97 g, 92%) as a colorless solid: 90% ee [^{1}H NMR (300 MHz, $CDCl_3$, 30 mol% Eu(hfc)$_3$): δ (*t*-Bu) (**15b**) 2.08, δ (*t*-Bu) (*ent*-**15b**) 2.12]; mp 55°C; $[\alpha]_D^{22}$ −170 (*c* 0.99, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.45 (s, 9H), 1.58–1.70 (m, 1H), 1.94–2.28 (m, 5H), 3.93 (m, 1H), 5.84 (ddt, J=10.4, J=4.0, J=2.0, 1H), 6.12 (ddt, J=10.4, J=4.0, J=2.3, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.14 (u), 23.90 (u), 24.28 (d), 24.37 (u), 55.23 (d), 61.27 (u), 119.75 (d), 134.64 (d); MS (EI, 70 eV) *m/z* (rel. intensity) 81 (M^+-SO_2t-Bu, 34), 80 (29), 79 (23), 77 (10), 57 (100), 53 (11); IR (KBr) ν 3392 (m), 3042 (m), 2981 (st), 2943 (st), 2921 (st), 2870 (m), 2839 (m), 1676 (w), 1647 (w), 1589 (w), 1471 (s), 1449 (m), 1433 (m), 1397 (m), 1385 (m), 1370 (m), 1364 (m), 1331 (m), 1283 (s), 1249 (s), 1242 (s), 1210 (s), 1188 (s), 1112 (s), 1044 (m), 1022 (m), 991 (m), 946 (w), 935 (m), 896 (s), 871 (m), 835 (m), 801 (m), 762 (m), 746 (m), 736 (m), 717 (m), 675 (s), 628 (s) cm^{-1}. Anal. Calcd for $C_{10}H_{18}O_2S$: C, 59.37; H, 8.97. Found: C, 59.10; H, 9.01.

4.14. (−)-(S)-3-(tert-*Butylsulfonyl)-cyclohept-1-ene* **15c**

Following the procedure described for the synthesis of **15a**, *rac*-**14c** (172 mg, 1 mmol), $Pd_2(dba)_3 \cdot CHCl_3$ (15.5 mg, 15 μmol), **12** (31.3 mg, 45 μmol), LiO_2S*t*-Bu (256 mg, 2 mmol) and Hex_4NBr (25 mg, 57.5 μmol) in CH_2Cl_2 (6 mL) and water (3 mL) gave, after 2 h, **15c** (192 mg, 89%) as a colorless solid: 93% ee [GC, Lipodex-E: t_R (**15c**)=33.84, t_R (*ent*-**15c**)=34.20; ^{1}H NMR (300

MHz, $CDCl_3$, 30 mol% Eu(hfc)$_3$): δ (*t*-Bu) (**15c**) 1.98, δ (*t*-Bu) (*ent*-**15c**) 2.11]; mp 48°C; $[\alpha]_D^{22}$ −94 (*c* 1.01, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.43 (s, 9H), 1.45–1.91 (m, 4H), 2.08–2.39 (m, 4H), 3.98 (m, 1H), 5.63–6.10 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 24.39 (d), 25.78 (u), 26.52 (u), 27.93 (u), 29.34 (u), 59.06 (d), 61.36 (u), 126.90 (d), 135.31 (d); MS (EI, 70 eV) *m/z* (rel. intensity) 95 ($M^+ - SO_2t$-Bu, 52), 94 (11), 67 (24), 57 (100); IR (KBr) ν 3033 (m), 2972 (m), 2931 (s), 2859 (m), 1650 (w), 1473 (s), 1448 (m), 1398 (w), 1367 (m), 1282 (s), 1232 (m), 1191 (m), 1106 (s), 1067 (m), 1023 (w), 958 (w), 835 (m), 792 (m), 747 (m), 698 (m), 670 (s), 638 (m) cm^{-1}. Anal. Calcd for $C_{11}H_{20}O_2S$: C, 61.07; H, 9.32. Found: C, 60.94; H, 9.30.

*4.15. (−)-(R,E)-1,3-Diphenyl-3-(*tert*-butylsulfenyl)-prop-2-ene* **17**

To a solution of *rac*-**1b** (2.82 g, 10 mmol) in CH_2Cl_2 (50 mL) was added a solution of $Pd_2(dba)_3 \cdot CHCl_3$ (518 mg, 0.5 mmol) and *ent*-**2b** (748 mg, 2 mmol) in CH_2Cl_2 (20 mL) at room temperature. After stirring the mixture for 30 min, a solution of **16** (2 mL, 10 mmol) in CH_2Cl_2 (30 mL) was added gradually (1 mL/h). Stirring of the mixture was continued for 4 days at room temperature. Water was added and the aqueous phase was extracted with CH_2Cl_2. The combined organic phases were washed with brine, dried ($MgSO_4$), and concentrated under vacuum. Purification of the residue by chromatography (*n*-hexane:EtOAc, 60:1) gave **17** (1.78 g, 63%) as a colorless oil which crystallized readily: mp 46–47°C, 92% ee [HPLC: *n*-hexane:*i*-PrOH=100:0.3, t_R (**17**)=16.49, t_R (*ent*-**17**)=17.95]; $[\alpha]_D^{22}$ −20.9 (*c* 0.99, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.31 (s, 9H), 4.75 (d, *J*=6.7, 1H), 6.42 (d, *J*=15.8, 1H), 6.48 (dd, *J*=15.8, *J*=6.7, 1H), 7.42–7.09 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 31.77 (d), 44.84 (u), 50.58 (d), 127.29 (d), 127.71 (d), 126.62 (d), 128.24 (d), 128.85 (d), 130.50 (d), 132.36 (d), 137.12 (u), 142.55 (u); IR (kap) ν 3081 (m), 3059 (m), 3026 (s), 2960 (s), 2939 (s), 2922 (s), 2896 (m), 2861 (m), 1599 (m), 1493 (s), 1471 (m), 1451 (s), 1390 (m), 1364 (s), 1307 (w), 1209 (m), 1159 (s), 1073 (m), 1029 (m), 965 (s), 912 (w), 871 (w), 841 (w), 801 (m) cm^{-1}; MS (EI) *m/z* (rel. intensity) 282 (M^+, 5), 194 (14), 193 (100), 178 (10), 115 (78), 91 (16). Anal. Calcd for $C_{19}H_{22}S$: C, 80.80; H, 7.85. Found: C, 80.67; H, 7.92.

4.16. Oxidation of **17** *to* ent-**3**

To a solution of **17** (282 mg, 1 mmol, 85% ee) in dioxane (4 mL) was added at 0°C a solution of oxone (938 mg, 1.53 mmol) in water (4 mL). Stirring of the mixture was continued for 4 h at room temperature. Water (10 mL) was added to the white slurry, and the mixture was extracted with $CHCl_3$. The combined organic phases were washed with brine, dried ($MgSO_4$), and concentrated under vacuum. Recrystallization of the residue from EtOH gave *ent*-**3** (202 mg, 64%) of 69% ee (HPLC).

4.17. Structure determination of the sulfone **3**

Single crystals of **3** were obtained by recrystallization from EtOA–*n*-hexane at room temperature. Compound **3** crystallizes in the orthorhombic space group $P2_12_12_1$ (No. 19). 25 Reflections in the range of 11.04°<θ<21.91° were used to determine the cell constants *a*=8.8678(5), *b*=20.7233(9), and *c*=9.5767(3) Å. At a cell volume of 1759.9 Å^3 and *Z*=4, the calculated density amounts to 1.187 g cm^{-3}. 8646 Reflections (*Friedel* pairs; *h*: 0→±11; *k*: 0→±25; *l*: 0→±11) were collected at room temperature on a ENRAF NONIUS CAD4 four circle diffractometer employing graphite-monochromated Cu-*K*α radiation (λ=1.54179 Å), and merged (R_{int}=0.03(4)) to give 3569 'independent' and 2718 observed (I>2σ(I)) reflections. The data were corrected for Lorentz and polarization but not for absorption effects.

The structure was solved by direct methods as implemented in the XTAL3.2 crystallographic program package,[27] employing GENSIN[28] to generate structure invariant relationships and GENTAN[29] for the general tangent phasing procedure. All hydrogen atoms were calculated in idealized positions and their positional parameters were kept constant in the refinement process. Their U_{is} were fixed at 1.5 times the isotropic displacement parameter of the relevant heavy atoms prior to the final full-matrix least-squares refinement on F of 200 variables which converged at R=0.048 (R_w=0.041, $w=\sigma^{-2}$), an error of fit of 1.612, and a residual electron density of $-0.6/+0.4$ e·Å^{-3}, r^*=1235.[30] The absolute configuration of **3** as given in Fig. 1 was determined by calculating Flack's absolute structure parameter.[31]

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Note added in proof: Sulfones **11a** (98% ee) and **11b** (96% ee) were obtained in 96% yield (2 h) and 97% yield (6 h) by using instead of *rac*-**10a** and *rac*-**10b** the corresponding racemic carbonates.