# Enantioselective Preparation of 4-Substituted Cyclohexenes by Radical Fragmentation of Sulfoxides

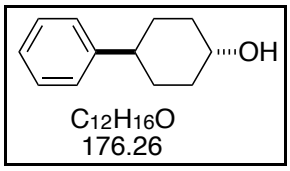
Christoph Imboden, Félix Villar and Philippe Renaud*

*Université de Fribourg, Institut de Chimie Organique, Pérolles*
*CH-1700 Fribourg, Switzerland*

# SUPPORTING INFORMATION

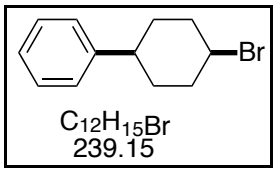
*General*. THF was freshly distilled from K under $N_2$, toluene from Na under $N_2$, $CH_2Cl_2$ and benzene from $CaH_2$, $Et_2O$ from Na/benzophenone. Irradiations were conducted using a sun lamp *Osram Ultra-Vitalux 300 W*. Flash column chromatography (FC) and filtration: silica gel *Merck* (*60,* 70-230 mesh); elution with EtOAc and hexane or petroleum ether (p.e.); TLC: *Merck* or *Macherey-Nagel silica gel 60* $F_{254}$ anal. plates; detection with UV, $I_2$, or by spraying with a soln. of phosphomolybdic acid (25g), $Ce(SO)_4$ $4H_2O$ (10 g), conc. $H_2SO_4$ (60 ml) and $H_2O$ (940 ml) with subsequent heating. All the reagents were obtained from *Fluka* and *Aldrich* and used as received unless otherwise specified. M.p.: not corrected; *Büchi-Tottoli* apparatus. FT-IR: *Mattson-Unicam 5000*. NMR: *Varian Gemini 200* ($^1$H = 200 MHz, $^{13}$C = 50.3 MHz); *Bruker AM-360* ($^1$H = 360.13 MHz); *Bruker Advance DRX-500* ($^1$H = 500.13 MHz, $^{13}$C = 125.76 MHz); unless otherwise indicated, spectra were recorded in $CDCl_3$; for $^1$H chemical shifts δ in ppm rel. to TMS (= 0 ppm); for $^{13}$C chemical shifts δ in ppm rel. to $CHCl_3$ (= 77.0 ppm); GC: *CE instruments HRGC series* with the following chiral colum: 6-TBDMS-2,3-Di-Et-β-cyclodextrine. MS: *Finnigan 1020*; *Nermag R10-10C; Vacuum Generators Micromass E70/70* and *Hewlett-Packard 5988A*; CI, chemical ionisation with $NH_3$ or $CH_4$; EI, electron ionisation at 70 eV. Elemental analysis: *Ilse Beetz, Mikroanalytisches Laboratorium,* D-8640 Kronach, Germany and *Ciba; Mikrolabor*, CH-1723 Marly, Switzerland.

trans-4-*Phenylcyclohexanol* . A soln. of 4-phenylcyclohexanone (1.0 g, 5.7 mmol) in




$Et_2O$ (35 ml) was added at 0 °C to a suspension of $LiAlH_4$ (0.44 g, 12 mmol) in $Et_2O$ (35 ml). The gray suspension was heated under reflux for 2 h. After cooling to r.t., the reaction mixture was hydrolyzed with EtOAc (20 ml) and $H_2O$ (40 ml). The organic layer was dried ($Na_2SO_4$), filtered and evaporated to afford 4-phenylcyclohexanol (0.75 g, 74%) as a mixture of isomers (*cis*/*trans* 1:7) . Recrystallization in refluxing hexane (38 ml) afforded *trans*-4-phenylcyclohexanol (0.60 g, 60%). White crystals. M.p.: 120-121 °C. $^1$H-NMR (360 MHz): 7.37-7.10 (*m*, 5 arom. H); 3.68 (*tt*, J = 10.5, 4.2, C*H*OH); 2.48 (*tt*, J = 11.6, 3.3, C*H*Ph); 2.15-2.01 (*m*, 2 $H_{eq}$, CH*H*CHOH), 2.00-1.85 (*m*, 2 $H_{eq}$, CH*H*CHPh); 1.74 (*s*, OH); 1.62-1.34 (*m*, 4 $H_{ax}$, C*H*HCHPh, C*H*HCHOH). $^{13}$C-NMR (50.3 MHz): 146.51 (*s*), 128.32 (*d*), 126.73 (*d*), 126.02 (*d*), 70.58 (*d*), 43.40 (*d*), 35.93 (*t*), 32.42 (*t*). IR (KBr): 3427, 3059, 3028, 2922, 2854, 1942, 1871, 1797, 1601, 1492, 1450. MS (EI): 176 (8, $[M]^+$), 158 (100), 143 (90), 130 (55), 117 (43), 104 (56), 91 (44), 78 (15). Anal. calc. for $C_{12}H_{16}O$ (176.26): C 81.77, H 9.15; found: C 81.67, H 9.28.

cis-*4-Phenyl-1-bromocyclohexane*. To a soln. of *trans*-4-phenylcyclohexanol (4.0 g, 22.7 mmol) in $CH_2Cl_2$ (120 ml) was added $CBr_4$ (10.53 g, 31.7 mmol) at r.t. under $N_2$. After strirring for 10 min, the soln. was cooled at 0 °C and $PPh_3$ (17.8 g, 68 mmol) was added. The resulting yellow suspension was stirred for 3 h at r.t. and then filtered through *Celite*. Purification by FC (hexane) afforded a colorless oil (4.3 g) containing the desired bromide and 4-phenyl-1-cyclohexene in a 3:1 ratio. Distillation under reduced presure (112 °C / 1.3 mbar) afforded *cis*-4-phenyl-1-bromocyclohexane (3.1 g, 57%). White solid. M.p.: 63 °C. B.p.: 112-115 °C / 1.0 mbar. $^1$H-NMR (360 MHz): 7.40-7.15 (*m*, 5 arom. H); 4.74 (*m*, CHBr); 2.55 (*tt*, J = 11.9, 3.4, CHPh); 2.29-1.87 (*m*, 2 $H_{ax}$, C*H*HCHBr, 4 $H_{eq}$, CH*H*CHBr, C*H*HCHPh); 1.80-1.68 (*m*, 2 $H_{ax}$, CH*H*CPh). $^{13}$C-NMR (50.3 MHz): 146.73 (*s*), 128.42 (*d*), 126.84 (*d*), 126.14 (*d*), 54.10 (*d*), 43.70 (*d*), 35.00 (*t*), 28.54 (*t*). IR (KBr): 3061, 3026, 2933, 1602, 1492, 1438, 1228, 955. MS (EI): 240 (67, $[M+1]^+$), 156 (100), 117 (5), 91 (5). Anal. calc. for $C_{12}H_{15}Br$ (239.15): C 60.27, H 6.32; found: C 60.37, H 6.31.




*(±)-2-Bromophenyl 4-phenylcyclohexyl sulfoxide*((±)-**1a**). According to Ono[1]. To a stirred mixture of DBU (636 mg, 4.2 mmol) and *o*-bromothiophenol (790 mg, 0.8 ml, 4.2 mmol) in benzene (13 ml) was added at r.t. *cis*-4-phenyl-1-bromocyclohexane (1.0 g, 4.2 mmol) in benzene (10 ml). The resulting mixture was stirred for 2 h at r.t. The precipitated DBU·HBr was removed by filtration. The filtrate was washed with $H_2O$ (10 ml), dried ($MgSO_4$), filtered and evaporated. Purification by FC (hexane) afforded 2-bromophenyl 4-phenylcyclohexyl sulfide ( 653 mg, 45%) as a colorless oil which was directly used for the oxidation step.

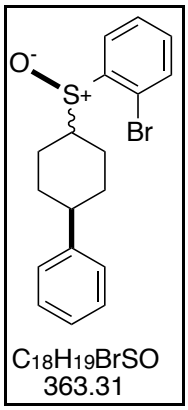
2-Bromophenyl 4-phenylcyclohexyl sulfide (2 g, 5.7 mmol) was dissolved in $CH_2Cl_2$ (50 ml) and treated at –20 °C with a dried ($MgSO_4$) soln. of *m*-CPBA (1.42 g, 5.7 mmol) in $CH_2Cl_2$ (40 ml) over a period of 30 min. The soln. was stirred for 1 h at –10 °C before being allowed to warm to r.t. KF (1.4 g, 25 mmol) was added and the resulting suspension was stirred overnight and then filtered through *Celite*. The solvent was evaporated. Purification by FC (EtOAc/hexane 1:5) afforded (±)-**1a** (1.95 g, 93 %) in a 1:2 *cis*/*trans* ratio. *Trans*- and *cis*-(±)-**1a** were separated by FC.

*trans*-(±)-**1a**: White solid. $^1$H-NMR (500 MHz): 7.83-7.81 (*m*, 1 arom. H); 7.59-7.53 (*m*, 2 arom. H); 7.38-7.34 (*m*, 1 arom. H); 7.31-7.23 (*m*, 3 arom. H); 7.20-7.14 (*m*, 2 arom. H); 3.01 (*tt*, J = 12.5, 3.8, CHSO); 2.53 (*tt*, J = 12.2, 3.4, CHPh); 2.31-2.23 (*m*, 1 $H_{eq}$, C*H*HCHSO); 2.13-2.06 (*m*, 1 $H_{eq}$, C*H*HCHPh); 2.03-1.86 (*m*, 2 $H_{eq}$, C*H*HCHSO, C*H*HCHPh); 1.83-1.72 (*m*, 1 $H_{ax}$, CH*H*CHSO); 1.65-1.50 (*m*, 2 $H_{ax}$, CH*H*CHPh, CH*H*CHSO); 1.49-1.38 (*m*, 1 $H_{ax}$, CH*H*CHPh). $^{13}$C-NMR (125 MHz): 146.05 (*s*), 141.67 (*s*), 132.96 (*d*), 132.05 (*d*), 128.39 (*d*), 127.93 (*d*), 127.70 (*d*), 126.66 (*d*), 126.21 (*d*), 119.36 (*s*), 58.91 (*d*), 43.13 (*d*), 33.47 (*t*), 32.76 (*t*), 27.70 (*t*), 21.58 (*t*).

*cis*-(±)-**1a**: $^1$H-NMR (500 MHz): 7.93-7.90 (*m*, 1 arom. H); 7.59-7.54 (*m*, 2 arom. H); 7.39-7.16 (*m*, 6 arom. H); 3.04-3.00 (*m*, CHSO); 2.71 (*tt*, J = 10.5, 3.6 CHPh); 2.54-2.45 (*m*, 1 $H_{eq}$, C*H*HCHSO); 2.19-2.06 (*m*, 2 $H_{eq}$, C*H*HCHPh); 2.00-1.81 (*m*, 1 $H_{eq}$ C*H*HCHSO, 2 $H_{ax}$ CH*H*CHPh, 1 $H_{ax}$ CH*H*CHSO); 1.78-1.68 (*m*, 1 $H_{ax}$ CH*H*CHSO). $^{13}$C-NMR (125 MHz): 146.00 (*s*), 144.65 (*s*), 132.79 (*d*), 132.39 (*d*), 128.60 (*d*), 128.43 (*d*), 127.28 (*d*), 126.90 (*d*), 126.11 (*d*), 121.18 (*s*), 62.71 (*d*), 42.27 (*d*), 30.84 (*t*), 29.06 (*t*), 26.30 (*t*), 23.94(*t*).

IR (KBr): 3300, 3051, 2930, 2359, 2094, 1961, 1809, 1599, 1564, 1492, 1444. MS (EI): 364 (18, $[M+1]^+$), 205 (26), 203 (25), 159 (37), 129 (2), 104 (22), 91 (100), 55 (10). Anal. calc. for $C_{18}H_{19}BrOS$ (363.31): C 59.51, H 5.27; found: C 59.68, H 5.26.

[*(*R*)*-cis *and (*R*)*-trans]-*2-Bromophenyl 4-phenylcyclohexyl sulfoxide* (*cis*-**1a** and *trans*-**1a**). A soln. of the Grignard reagent prepared from Mg (608 mg, 25 mmol), 4-phenyl-1-bromocyclohexane (6 g, 25 mmol) in THF (50 ml) at 30-35 °C, was added at 4-6 °C to a soln. of **3** (9.0 g, 25 mmol) in benzene (50 ml). The soln. was stirred at r.t. for 2-3 h. The gray reaction mixture was hydrolysed with sat. $NH_4Cl$ (25 ml) and the aqueous layer was extracted with $Et_2O$ (65 ml). The collected organic layers were washed with brine (30 ml), dried ($Na_2SO_4$), filtered and evaporated. Purification by FC (EtOAc/hexane 1:4) gave **1a** (6.0 g, 67%) in a 1:4 *cis*/*trans* ratio. *Trans*- and *cis*-**1a** were separated by further FC.




Epimerization of *trans*-**1a**. A soln. of 2.5M *n*-BuLi in hexane (0.12 ml., 0.3 mmol) was added to a soln. of (*i*-Pr)$_2$NH (0.043 ml, 0.3 mmol) in THF (3 ml) at –40°C. The soln. was kept at this temperature for 20 min then cooled at –78°C and a soln. of *trans*-**1a** (91mg, 0.25 mmol) in THF (1 ml) was added dropwise. After 35 min. at –78°C the reaction was treated with a soln. of 2,6-di-*tert*-butyl-4-methylphenol (165 mg, 0.75 mmol) in THF (1 ml). The clear solution was allowed to warm to rt, $Et_2O$ was added and the organic phase was washed successively with 10% HCl, sat. $NaHCO_3$ and sat. NaCl. The organic phase was dried ($MgSO_4$) and the solvent was evaporated to afford a colorless oil containing *cis*-**1a** and *trans*-**1a** in a 2:1 ratio. FC (hexane/$Et_2O$, 1:1) furnished the well separated *cis*-**1a** (48 mg, 52%) and *trans*-**1a** (23 mg, 25%).

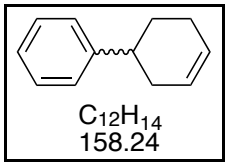
*trans*-**1a**: White solid. $[\alpha]_D$ = +229.45° (c = 1, acetone). M.p.: 104-106 °C. $^1$H-NMR (500 MHz): 7.83-7.81 (*m*, 1 arom. H); 7.59-7.53 (*m*, 2 arom. H); 7.38-7.34 (*m*, 1 arom. H); 7.31-7.23 (*m*, 3 arom. H); 7.20-7.14 (*m*, 2 arom. H); 3.01 (*tt*, J = 12.5, 3.8, CHSO); 2.53 (*tt*, J = 12.2, 3.4, CHPh); 2.31-2.23 (*m*, 1 $H_{eq}$, C*H*HCHSO); 2.13-2.06 (*m*, 1 $H_{eq}$, C*H*HCHPh); 2.03-1.86 (*m*, 2 $H_{eq}$, C*H*HCHSO, C*H*HCHPh); 1.83-1.72 (*m*, 1 $H_{ax}$, CH*H*CHSO); 1.65-1.50 (*m*, 2 $H_{ax}$, CH*H*CHPh, CH*H*CHSO); 1.49-1.38 (*m*, 1 $H_{ax}$, CH*H*CHPh). $^{13}$C-NMR

(125 MHz): 146.05 (*s*), 141.67 (*s*), 132.96 (*d*), 132.05 (*d*), 128.39 (*d*), 127.93 (*d*), 127.70 (*d*), 126.66 (*d*), 126.21 (*d*), 119.36 (*s*), 58.91 (*d*), 43.13 (*d*), 33.47 (*t*), 32.76 (*t*), 27.70 (*t*), 21.58 (*t*).

*cis*-**1a**: White solid. $[\alpha]_D$ = +130.2° (c = 1, acetone). M.p.: 104.5-105.7 °C. $^1$H-NMR (500 MHz): 7.93-7.90 (*m*, 1 arom. H); 7.59-7.54 (*m*, 2 arom. H); 7.39-7.16 (*m*, 6 arom. H); 3.04-3.00 (*m*, CHSO); 2.71 (*tt*, J = 10.5, 3.6 CHPh); 2.54-2.45 (*m*, 1 $H_{eq}$, C*H*HCHSO); 2.19-2.06 (*m*, 2 $H_{eq}$, C*H*HCHPh); 2.00-1.81 (*m*, 1 $H_{eq}$ C*H*HCHSO, 2 $H_{ax}$ CH*H*CHPh, 1 $H_{ax}$ CH*H*CHSO); 1.78-1.68 (*m*, 1 $H_{ax}$ CH*H*CHSO). $^{13}$C-NMR (125 MHz): 146.00 (*s*), 144.65 (*s*), 132.79 (*d*), 132.39 (*d*), 128.60 (*d*), 128.43 (*d*), 127.28 (*d*), 126.90 (*d*), 126.11 (*d*), 121.18 (*s*), 62.71 (*d*), 42.27 (*d*), 30.84 (*t*), 29.06 (*t*), 26.30 (*t*), 23.94(*t*).

IR (KBr): 3300, 3051, 2930, 2359, 2094, 1961, 1809, 1599, 1564, 1492, 1444. MS (EI): 364 (18, $[M+1]^+$), 205 (26), 203 (25), 159 (37), 129 (2), 104 (22), 91 (100), 55 (10). Anal. calc. for $C_{18}H_{19}BrOS$ (363.31): C 59.51, H 5.27; found: C 59.68, H 5.26.

*(±)-4-Phenylcyclohexene* ((±)-**2a**). Radical elimination in benzene.




A soln. of $Bu_3SnH$ (437 mg, 1.5 mmol, 0.39 ml) and AIBN (242 mg, 1.5 mmol) in benzene (10 ml) was added during 12 h (seringue pump) at 80 °C to a soln. of (±)-**1a** (363 mg, 1 mmol) in benzene (20 ml). After the addition was finished, the soln. was heated under reflux for 1 h. The solvent was evaporated to 15 ml and conc. HCl (3 drops) was added to destroy the excess of $Bu_3SnH$. The heterogenous mixture was stirred for 1 h at r.t. The organic phase was treated with 1 M NaOH (15 ml) and vigorously stirred for 4 h at r.t. to eliminate tin halides[2]. The organic layer was washed with brine (15 ml), dried ($Na_2SO_4$), filtered and evaporated. Purification by FC (hexane) afforded (±)-**2a** (148 mg, 93%). Colorless oil. GC (120 °C): retention times : $t_r(S)$ = 11.9 min; $t_r(R)$ = 12.6 min. B.p.: 85 °C / 5 mbar. $^1$H-NMR (360 MHz): 7.37-7.10 (*m*, 5 arom. H); 5.81-5.69 (*m*, 2 H, C=CH); 2.84-2.73 (*m*, CHPh); 2.35-2.05 (*m*, 4 H, $H_2$-C(3), $H_{eq}$-C(6), $H_{eq}$-C(5)); 1.97-1.86 (*m*, $H_{ax}$-C(6)); 1.80-1.67 (*m*, $H_{ax}$-C(5)). $^{13}$C-NMR (50 MHz): 147.27 (*s*), 128.31 (*d*), 126.85 (*d*), 126.84 (*d*), 126.73 (*d*), 125.91 (*d*), 40.12 (*d*), 33.39 (*t*), 29.68 (*t*), 25.87 (*t*). IR (film): 3061, 3024, 2917, 2837, 1942, 1876, 1799, 1492, 1452. MS (EI): 158 (22, $[M]^+$), 128 (9), 104 (100), 91 (12), 78 (14), 65 (6), 51 (9).

*(*R *and* S*)-4-Phenylcyclohexene* (**2a**).

Without Lewis acids.

A soln. of $Bu_3SnH$ (437 mg, 1.5 mmol, 0.39 ml) and AIBN (242 mg, 1.5 mmol) in benzene (10 ml) was added during 12 h (syringe pump) at 10 ºC under irradiation (300 W sun lamp) to a soln. of *trans*- or *cis*-**1a** (363 mg, 1 mmol) in benzene (20 ml). The soln. was stirred for 1 h under irradiation at 10 ºC and the solvent was concentrated to 15 ml. Conc. HCl (3 drops) was added and the heterogenous mixture was stirred for 1 h at r.t. The organic phase was treated with 1 M NaOH (15 ml) and vigorously stirred for 4 h at r.t. to eliminate tin halides[2]. The organic layer was washed with brine (15 ml), dried ($Na_2SO_4$), filtered and evaporated. Purification by FC (hexane) afforded **2a**. Starting from *trans*-**1a**: **2a (**118 mg, 75%), *R*/*S* 1:1. Starting from *cis*-**1a**: **2a** (102 mg, 65%), *R*/*S* 85:15.

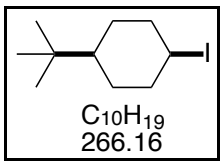
In the presence of Lewis acids.

To a soln. of the phenol (4 mmol) in benzene (10 ml) was added at r.t. a 1 M soln. of $Me_3Al$ in toluene (2 mmol, 2 ml). The colorless soln. was stirred for 30 min at r.t., cooled to 0 ºC and a soln. of *cis*-**1a** (1 mmol, 363 mg) in benzene (10 ml) was added. The soln. was stirred for 1 h at r.t. and a soln. of $Bu_3SnH$ (1.5 mmol) and AIBN (1.5 mmol) in benzene (10 ml) was added under irradiation over 12 h at 6-10 ºC. The reaction mixture was stirred for 1 h at 6-10 ºC under irradiation. Work up as mentioned above. 2,6-Di-*tert*-butyl-*p*-cresol: **2a** (95 mg, 60%, *R*/*S* 88:12); 2,6-diphenylphenol: **2a** (102 mg, 65%, *R*/*S* 92:8); phenol: **2a** (90 mg, 57%, *R*/*S* 93:7).

Thermal elimination.

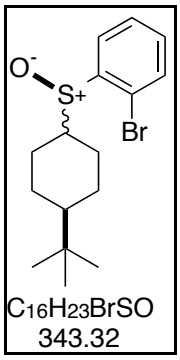
*Trans*- or *cis*-**1a** (363 mg, 1 mmol) was heated in steps of 50 ºC in a bulb to bulb distillation apparatus under reduced presure (5 mbar). Elimination process started at 200 ºC (*cis*-**1a**) and 230 ºC (*trans*-**1a**). Compound **2a** was collected in a trap cooled with liquid nitrogen. Starting from *cis*-**1a**: **2a** ( 99 mg, 64%), *S*/*R* 77:23. Starting from *trans*-**1a**: **2a** (90 mg, 57%), *R*/*S* 72:28. GC (120 ºC): retention times: $t_r(S)$ = 11.9 min; $t_r(R)$ = 12.6 min. Colorless oil.

cis-*4-tert-Butylcyclohexyl iodide*. A suspension of 4-*tert*-butylcyclohexanol (8.0 g, 51.2 mmol), $I_2$ (40.1 g, 158 mmol), imidazol (13.9 g, 205 mmol) and $PPh_3$ (53.7 g, 205 mmol) in toluene (1.3 l) was stirred at 60 ºC for 4 h. After cooling to r.t., the brown suspension was washed with sat. $NaHCO_3$ (800 ml), sat. $Na_2S_2O_4$ (300 ml), dried ($Na_2SO_4$), filtered and evaporated. The residue was dissolved in pentane and the resulting white precipitate of $Ph_3PO$ was eliminated by filtration through *Celite*. The crude product was purified by FC (pentane). Distillation under reduced presure (50 ºC / 0.1 mbar) afforded *cis*-4-*tert*-butylcyclohexyl iodide (4.0 g, 29%). White solid. M.p.: 35-36ºC. B.p.: 74-76 ºC / 0.73 mbar. $^1$H-NMR (360 MHz): 4.91-4.85 (*m*, CHI); 2.20-2.08 (*m*, 2 H, $H_{eq}$-C(2,6)); 1.73-1.40



(*m*, 4 H, H-C(3,5), $H_{ax}$-C(2,6)); 1.14-1.00 (*m*, H-C(4)); 0.89 (*s*, *t*-Bu). $^{13}$C-NMR (50.3 MHz): 47.84 (*d*), 37.77 (*d*), 36.91 (*t*), 27.46 (*q*), 23.39 (*t*). IR (film): 2943, 2864, 1477, 1365, 1244, 1180, 1014. MS (EI): 265 (2, $[M-1]^+$), 139 (81), 83 (80), 69 (10), 57 (100). Anal. calc. for $C_{10}H_{19}I$ (266.16): C45.13, H 7.20; found: C45.26, H 7.31.

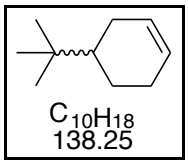
[*(*R*)*-cis *and (*R*)*-trans]-*2-Bromophenyl 4-(tert-butyl)cyclohexyl sulfoxide* (*cis*-**1b** and *trans*-**1b**). A soln. of the Grignard reagent, prepared from Mg (420 mg, 17 mmol), *tert*-butylcyclohexyl iodide (4.6 g, 17.28 mmol) in $Et_2O$ (35 ml) at a temperature < 35 ºC, was added at 0 ºC to a soln. **3** (4.1 g, 11.5 mmol) in benzene (25 ml). The gray soln. was stirred at r.t. for 2-3 h. The reaction mixture was hydrolyzed with sat. $NH_4Cl$ (25 ml) and the aqueous layer was extracted with $Et_2O$ (50 ml). The collected organic layers were washed with brine (100 ml), dried ($Na_2SO_4$), filtered and evaporated. Purification by FC (EtOAc:hexane 1:4) afforded **1b** (2.56 g, 65%) in a 1:10 *cis*/*trans* ratio. *Trans*-**1b** (1.0 g, 2.9 mmol) can be epimerized by treatment in THF (10 ml) with 1 M LDA (3.5 ml) at –30 ºC followed by protonation with $H_2O$ (0.1 ml).




*trans*-**1b**: Colorless oil. $[\alpha]_D$ = +200.6º (c = 1, acetone). $^1$H-NMR (360 MHz): 7.80-7.77 (*m*, 1 arom. H); 7.57-7.51 (*m*, 2 arom. H); 7.36-7.33 (*m*, 1 arom.H); 2.85 (*tt*, J = 12.6, 3.9, CHSO); 2.19-2.12 (*m*, 1 $H_{eq}$, C*H*HCHSO); 1.99-1.93 (*m*, 1 $H_{eq}$, C*H*HCHSO); 1.89-1.84 (*m*, 1 $H_{eq}$, C*H*HCHC$(CH_3)_3$); 1.77-1.67 (*m*, 1 $H_{ax}$, CH*H*CHSO); 1.61-1.51 (*m*, 1 $H_{ax}$, CH*H*CHC$(CH_3)_3$); 1.51-1.44 (*m*, 1 $H_{eq}$, C*H*HCHC$(CH_3)_3$); 1.16-0.91 (*m*, 1 $H_{ax}$, CH*H*CHSO, 1 $H_{ax}$, CH*H*CHC$(CH_3)_3$, C*H*C$(CH_3)_3$), 0.82 (*s*, *t*-Bu). $^{13}$C-NMR (125 MHz): 141.92 (*s*), 132.89 (*d*), 131.95 (*d*), 127.86 (*d*), 127.67 (*d*), 119.43 (*s*), 59.84 (*d*), 46.93 (*d*), 32.31 (*s*), 27.76 (*t*), 27.42 (*q*), 26.98 (*t*), 26.22 (*t*), 22.13 (*t*).

*cis*-**1b**: Colorless oil. $[\alpha]_D$ = +151.2º (c = 1, acetone). $^1$H-NMR (360 MHz): 7.92-7.88 (*m*, 1 arom. H); 7.59-7.52 (*m*, 2 arom. H); 7.38-7.33 (*m*, 1 arom.H); 2.96-2.90 (*m*, CHSO); 2.63-2.54 (*m*, 1 $H_{eq}$, C*H*HCHSO); 1.88-1.46 (*m*, 1 $H_{eq}$, C*H*HCHSO, 2 $H_{ax}$, CH*H*CHSO, 2× C$H_2$CHC$(CH_3)_3$); 1.17-0.98 (*m*, C*H*C$(CH_3)_3$); 0.88 (*s*, *t*-Bu). $^{13}$C-NMR (125 MHz): 145.43 (*s*), 132.70 (*d*), 132.34 (*d*), 128.67 (*d*), 127.22 (*d*), 121.59 (*s*), 64.16 (*d*), 47.56 (*d*), 32.63 (*s*), 27.77 (*t*), 27.43 (*q*), 26.99 (*t*), 26.23 (*t*), 21.13 (*t*). IR (film): 3057, 2863, 1478, 1428, 1366, 1058, 1015, 735. MS (EI): 343 (31, $[M]^+$), 206 (41), 177 (2), 156 (7), 139 (58), 123 (18), 97 (24), 83 (92), 69 (88), 57 (100). Anal. calc. for $C_{16}H_{23}BrOS$ (343.32): C 55.98, H 6.75; found: C 55.68, H 6.82.

(R- *and* S-)-*4-(tert-Butyl)cyclohexene* (**2b**). A soln. of $Bu_3SnH$ (437 mg, 1.5 mmol, 0.39




ml) and AIBN (242 mg, 1.5 mmol) in benzene (10 ml) was added over 12 h (syringe pump) at 10 °C under irradiation (300 W sun lamp) to a soln. of *trans*- or *cis*-**1b** (343 mg, 1 mmol) in benzene (20 ml). The soln. was stirred for 1 h under irradiation at 10 °C and the solvent was concentrated to 15 ml. Conc. HCl (3 drops) was added and the heterogenous mixture was stirred for 1 h at r.t. The organic phase was treated with 1 M NaOH (15 ml) and vigorously stirred for 4 h at r.t. to eliminate tin halides[2]. The organic layer was washed with brine (10 ml), dried ($Na_2SO_4$), filtered and evaporated. Purification by FC (hexane) afforded **2b**. Starting from *trans*-**1b**: **2b** (83 mg, 60%), *R*/*S* 1:1. Starting from *cis*-**1b**: **2b** (97 mg, 70%), *R*/*S* 90:10. GC (60 °C): retention times: $t_r(S)$ = 14.15 min; $t_r(R)$ = 14.51 min. Colorless oil. $[\alpha]_D^{20}$ = +33.3° (c = 1, $CHCl_3$); ref. 3 (*S*-enantiomer) $[\alpha]_D^{20}$ = -75.9° (c = 1.1, $CHCl_3$): . B.p.: 161-163 °C. $^1$H-NMR (500 MHz): 5.73-5.62 (*m*, 2 H, C=CH); 2.15-1.93 (*m*, 3 H, $H_2$-C(3), H-C(6)); 1.85-1.71 (*m*, H-C(6), H-C(5)); 1.29 (*tdd*, J = 11.3, 6.7, 2.1, H-C(4)); 1.16 (*tdd*, J = 11.4, 10.8, 5.8, H-C(5)), 0.86 (*s*, *t*-Bu). $^{13}$C-NMR (125 MHz): 127.40 (*d*), 126.88 (*d*), 44.13 (*d*), 32.29 (*s*), 27.16 (*q*), 26.81 (*t*), 26.73 (*t*), 23.94 (*t*). IR (film): 3022, 2955, 2359, 1726, 1656, 1477, 1437, 1365, 1228. MS (EI): 138 (12, $[M]^+$), 95 (5), 80 (30), 67 (40), 57 (100).

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