Supporting Information for

Nucleophilic Epoxidation of α' -Hydroxy Vinyl Sulfoxides

Roberto Fernández de la Pradilla,^{,†} Jorge Fernández,[†] Pilar Manzano,[†] Paloma Méndez,[†] Julián Priego,[†] Mariola Tortosa,[†] Alma Viso,[†] Martín Martínez-Ripoll,[‡] and Ana Rodríguez.[§]*

[†] Instituto de Química Orgánica, CSIC, Juan de la Cierva, 3, 28006 Madrid, Spain.

Fax: 34-91-564-4853 ; 34-91-562-1829

E-mail: iqofp19@iqog.csic.es

[‡] Departamento de Cristalografía, Instituto de Química-Física Rocasolano, CSIC, Serrano 119, 28006 Madrid, Spain.

[§] Departamento de Química Inorgánica, Orgánica y Bioquímica, Facultad de Químicas, Campus Universitario, Universidad de Castilla-La Mancha, 13071 Ciudad Real, Spain.

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Materials and Methods

Reagents and solvents were handled by using standard syringe techniques. All reactions were carried out under an argon atmosphere. Hexane, toluene and CH_2Cl_2 were distilled from CaH_2 , and THF and Et_2O from sodium. $(\text{MeO})_2\text{P}(\text{O})\text{Me}$, Et_3N and $i\text{-Pr}_2\text{NH}$ were distilled from CaH_2 . Crude products were purified by flash chromatography on Merck 230-400 mesh silica gel with distilled solvents. Analytical TLC was carried out on Merck (Kieselgel 60F-254) silica gel plates with detection by UV light, iodine, acidic vanillin solution, 10% phosphomolybdic acid solution in ethanol. All reagents were commercial products purchased from Aldrich, Acros, Fluka or Merck. Organolithium reagents were titrated prior to use.¹ NaH and KH (60% in mineral oil) were washed repeatedly with dry hexane and dried prior to use. Through this section, the volume of solvents is reported in mL/mmol of starting material. Infrared spectra (IR) were obtained on a Perkin-Elmer 681 and on a Perkin-Elmer Spectrum one. ^1H and ^{13}C NMR spectra were recorded on a Bruker AM-200 (200 MHz), Varian Gemini-200 (200 MHz), Varian INOVA-300 (300 MHz) and Varian INOVA-400 (400 MHz) using CDCl_3 as solvent and with the residual solvent signal as internal reference (CDCl_3 , 7.24 and 77.0 ppm). The following abbreviations are used to describe peak patterns when appropriate: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad). Melting points were determined on a Reichert Kofler microscope and are uncorrected. Optical rotations were measured on a Perkin-Elmer 241 polarimeter at 20 °C using a sodium lamp and in CHCl_3 solution. Low resolution mass spectra were recorded by direct injection on a Hewlett Packard 5973 MSD instrument using the electronic impact technique with an ionization energy of 70 eV or on a Hewlett Packard 1100 MSD instrument using the atmospheric pressure chemical ionization (APCI) or electrospray (ES) chemical ionization techniques in its positive or negative modes. Elemental analyses were carried out on a Perkin-Elmer 240 C and on a Heraeus CHN-O-Rapid instruments at Instituto de Química Orgánica, CSIC (Madrid).

1. General Procedure for Synthesis of *E* Hydroxy Vinyl Sulfoxides

A round-bottomed flask was charged with THF (3.5 mL/mmol) and 2.6 equiv of freshly distilled $i\text{-Pr}_2\text{NH}$, and cooled to -78°C . To the above solution was added 2.5 equiv of $n\text{-BuLi}$ and the resulting LDA solution (*ca.* 0.3 M) was stirred at this temperature. After 10 min a solution of 1 equiv of a mixture of vinyl sulfoxides in THF (2 mL/mmol), previously dried over 4 Å sieves, was added dropwise slowly (*ca.* 8 min/mmol of sulfoxide) to produce a pale yellow solution. After stirring for an

additional 10 min at -78°C , 5 equiv of freshly distilled aldehyde was added dropwise and the resulting colorless solution was stirred at this temperature for 10 min. The reaction mixture was quenched with a saturated solution of NH_4Cl (2 mL/mmol) and H_2O (2 mL/mmol), diluted with EtOAc (3 mL/mmol) and the layers were separated. The aqueous layer was extracted with EtOAc (3 times, 4 mL/mmol). The combined organic extracts were washed with a saturated solution of NaCl (4 mL/mmol), dried over MgSO_4 and concentrated under reduced pressure to give a crude product which was purified by column chromatography (CH_2Cl_2 -EtOAc mixtures) to give pure hydroxy vinyl sulfoxides.

1.1. Synthesis of (+)-(*E*)-2-Methyl-4-(*SS*)-(p-tolylsulfinyl)non-4-en-3-(*S*)-ol, **3b**, and (+)-(*E*)-2-Methyl-4-(*SS*)-(p-tolylsulfinyl)non-4-en-3-(*R*)-ol, **4b**.

From *i*-Pr₂NH (0.76 mL, 587 mg, 5.80 mmol) in 20 mL of THF with *n*-BuLi (1.6 M, 3.47 mL, 5.55 mmol) and a solution of the mixture of vinyl sulfoxides **1** and **2** (493 mg, 2.22 mmol) in 1.5 mL of THF, and isobutyraldehyde (1.01 mL, 802 mg, 11.1 mmol), according to the general procedure, a 62:38 mixture of hydroxy vinyl sulfoxides **3b** and **4b** was obtained. Purification by column chromatography (0-50% EtOAc- CH_2Cl_2), gave 170 mg (26%) of **4b** as a white solid, recrystallized from 5% EtOAc-hexane, 149 mg (23%) of **3b** as a white solid, recrystallized from 5% EtOAc-hexane, and 123 mg (19%) of a mixture of these alcohols.

Data of **3b**: mp: 73-74 $^{\circ}\text{C}$. $R_f = 0.12$ (5% EtOAc- CH_2Cl_2). $[\alpha]_{\text{D}}^{20} = +23.4$ ($c = 0.245$). **¹H NMR (300 MHz)** δ 0.66 (d, 3 H, $J = 6.7$ Hz, CH_3 *i*-Pr), 0.89 (t, 3 H, $J = 7.2$ Hz, CH_3 *n*-Bu), 0.94 (d, 3 H, $J = 6.5$ Hz, CH_3 *i*-Pr), 1.26-1.48 (m, 4 H, 2 H-7, 2 H-8), 1.82-1.92 (m, 1 H, H-2), 2.20-2.39 (m, 2 H, 2 H-6), 2.37 (s, 3 H, CH_3 *p*-Tol), 2.63 (d, 1 H, $J = 5.7$ Hz, OH), 3.94 (dd, 1 H, $J = 8.7, 5.7$ Hz, H-3), 6.24 (t, 1 H, $J = 7.6$ Hz, H-5), 7.26 (d, 2 H, $J = 7.8$ Hz, *p*-Tol), 7.50 (d, 2 H, $J = 8.3$ Hz, *p*-Tol). **¹³C NMR (50 MHz)** δ 13.9 (CH_3 *n*-Bu), 19.0 (CH_3 *i*-Pr), 19.1 (CH_3 *i*-Pr), 21.4 (CH_3 *p*-Tol), 22.4 (C-8), 28.6 (C-6), 31.2 (C-7), 33.6 (C-2), 75.2 (C-3), 125.7 (2 C *p*-Tol), 129.8 (2 C *p*-Tol), 136.9 (C-5), 140.3, 141.7, 145.0. **IR (KBr)**: 3440, 2905, 2880, 2820, 1570, 1468, 1440, 1350, 1010, 780 cm^{-1} . **MS (ES)**: 317 $[\text{M}+\text{Na}]^+$ (100%). **Anal. calcd for $\text{C}_{17}\text{H}_{26}\text{O}_2\text{S}$** : C, 69.34; H, 8.90; S, 10.89. **Found**: C, 69.62; H, 9.20; S, 10.99.

Data of **4b**: mp: 65-66 °C. R_f = 0.28 (10% EtOAc-CH₂Cl₂). $[\alpha]^{20}_D$ = +59.7 (c = 0.255). **¹H NMR (300 MHz)** δ 0.65 (d, 3 H, J = 6.8 Hz, CH₃ *i*-Pr), 0.91 (t, 3 H, J = 7.2 Hz, CH₃ *n*-Bu), 0.97 (d, 3 H, J = 6.6 Hz, CH₃ *i*-Pr), 1.30-1.52 (m, 4 H, 2 H-7, 2 H-8), 1.82-1.94 (m, 1 H, H-2), 2.21-2.36 (m, 3 H, 2 H-6, OH), 2.38 (s, 3 H, CH₃ *p*-Tol), 4.16 (dd, 1 H, J = 9.3, 5.6 Hz, H-3), 6.51 (t, 1 H, J = 7.6 Hz, H-5), 7.26 (d, 2 H, J = 7.9 Hz, *p*-Tol), 7.52 (d, 2 H, J = 8.3 Hz, *p*-Tol). **¹³C NMR (50 MHz)** δ 13.8 (CH₃ *n*-Bu), 18.9 (2 CH₃ *i*-Pr), 21.3 (CH₃ *p*-Tol), 22.4 (C-8), 28.3 (C-6), 31.0 (C-7), 33.3 (C-2), 75.5 (C-3), 125.0 (2 C *p*-Tol) 129.7 (2 C *p*-Tol), 138.1 (C-5), 141.2, 144.7, 153.4. **IR** (CCl₄): 3450, 3000, 2980, 2910, 1615, 1510, 1485, 1400, 1100, 1040, 830 cm⁻¹. **MS** (APCI): 295 [M+1]⁺ (100%).

1.2. Synthesis of (+)-(E)-2,2-Dimethyl-4-(S*S*)-(p-tolylsulfinyl)non-4-en-3-(S)-ol, **3c**, and (+)-(E)-2,2-Dimethyl-4-(S*S*)-(p-tolylsulfinyl)non-4-en-3-(R)-ol, **4c**.

From *i*-Pr₂NH (0.68 mL, 525 mg, 5.16 mmol) in 18 mL of THF with *n*-BuLi (1.6 M, 3.10 mL, 4.96 mmol) and a solution of the mixture of vinyl sulfoxides **1** and **2** (440 mg, 1.98 mmol) in 1.5 mL of THF, and pivalaldehyde (1.07 mL, 849 mg, 9.86 mmol), according to the general procedure, a 72:28 mixture of hydroxy vinyl sulfoxides **3c** and **4c** was obtained. Purification by column chromatography (0-40% EtOAc-CH₂Cl₂), gave 89 mg (15%) of **4c** as a white solid, recrystallized from 5% EtOAc-hexane, 269 mg (44%) of **3c** as a white solid, recrystallized from 5% EtOAc-hexane and 120 mg (20%) of a mixture of these alcohols.

Data of **3c**: mp: 85-86 °C. R_f = 0.26 (10% EtOAc-CH₂Cl₂). $[\alpha]^{20}_D$ = +174.8 (c = 0.491). **¹H NMR (200 MHz)** δ 0.87 (t, 3 H, J = 7.1 Hz, CH₃ *n*-Bu), 0.99 (s, 9 H, 3 CH₃ *t*-Bu), 1.21-1.48 (m, 4 H, 2 H-7, 2 H-8), 2.21-2.55 (m, 3 H, 2 H-6, OH), 2.38 (s, 3 H, CH₃ *p*-Tol), 3.80 (d, 1 H, J = 4.8 Hz, H-3), 6.30 (t, 1 H, J = 7.6 Hz, H-5), 7.27 (d, 2 H, J = 8.1 Hz, *p*-Tol), 7.53 (d, 2 H, J = 8.2 Hz, *p*-Tol). **¹³C NMR (50 MHz)** δ 13.8 (CH₃ *n*-Bu), 21.4 (CH₃ *p*-Tol), 22.4 (C-8), 26.8 (3 C, 3 CH₃ *t*-Bu), 29.5 (C-6), 31.4 (C-7), 37.5 (C-2), 78.9 (C-3), 126.4 (2 C *p*-Tol), 130.0 (2 C *p*-Tol), 135.5 (C-5), 141.0, 142.1, 143.5. **IR** (CHCl₃): 3410, 2895, 2805, 1605, 1565, 1460, 1450, 1435, 1185, 1150, 1050, 775, 725 cm⁻¹. **MS** (ES): 331 [M+Na]⁺ (100%). **Anal. calcd for C₁₈H₂₈O₂S**: C, 70.08; H, 9.15; S, 10.40. **Found**: C, 70.04; H, 9.19; S, 10.14.

Data of **4c**: mp: 118-119 °C. *R_f* = 0.37 (10% EtOAc-CH₂Cl₂). [α]²⁰_D = +169.0 (*c* = 1.18).

¹H NMR (300 MHz) δ 0.89 (t, 3 H, *J* = 7.2 Hz, CH₃ *n*-Bu), 1.02 (s, 9 H, 3 CH₃ *t*-Bu), 1.16 (d, 1 H, *J* = 4.0 Hz, OH), 1.27-1.50 (m, 4 H, 2 H-7, 2 H-8), 2.19-2.27 (m, 2 H, 2 H-6), 2.36 (s, 3 H, CH₃ *p*-Tol), 4.39 (d, 1 H, *J* = 4.0 Hz, H-3), 6.71 (dd, 1 H, *J* = 8.1, 7.0 Hz, H-5), 7.22 (d, 2 H, *J* = 7.8 Hz, *p*-Tol), 7.57 (d, 2 H, *J* = 8.3 Hz, *p*-Tol). **¹³C NMR (50 MHz)** δ 13.8 (CH₃ *n*-Bu), 21.3 (CH₃ *p*-Tol), 22.4 (C-8), 26.5 (3 C, 3 CH₃ *t*-Bu), 29.0 (C-6), 31.1 (C-7), 37.3 (C-2), 76.5 (C-3), 125.6 (2 C *p*-Tol), 129.6 (2 C *p*-Tol), 134.8 (C-5), 141.1, 144.0, 145.2. **IR** (CHCl₃): 3200, 2900, 2800, 1600, 1460, 1430, 1330, 1040, 970 cm⁻¹. **MS** (ES): 331 [M+Na]⁺ (100%), 309 [M+1]⁺; 343 [M+Cl]⁻. **Anal.** calcd for C₁₈H₂₈O₂S: C, 70.08; H, 9.15; S, 10.40. **Found**: C, 70.14; H, 8.92; S, 10.37.

2. Synthesis of 1-(*p*-tolylsulfenyl)-1-hexyne, **8**.

A solution of 1-hexyne (1.7 mL, 15 mmol) in 30 mL of THF was cooled to -78 °C and *n*-BuLi (1.6 M, 9.45 mL, 15 mmol) was added. The reaction was stirred for 30 min and a premixed solution (1 h, rt) of *p*-tolyl disulfide (3.75 g, 15 mmol) and CH₃I (0.97 mL, 15 mmol) in THF (30 mL) was then added dropwise. The mixture was allowed to warm to rt, monitored by TLC until completion (1 h at rt) and then quenched with a saturated solution of NH₄Cl (30 mL) and H₂O (30 mL). The layers were separated and the aqueous phase was extracted with EtOAc (3 times). The combined organic layers were washed with a saturated solution of NaCl, dried over MgSO₄ and concentrated under reduced pressure. The crude product was purified by column chromatography (hexane) to give a 78:22 mixture of **8** and **8'** (3.39 g) as a yellow oil. A pure sample of **8** was obtained by a second careful chromatography.

Data of **8**: *R_f* = 0.28 (hexane). **¹H NMR (200 MHz)** δ 0.92 (t, 3 H, *J* = 7.0 Hz, CH₃ *n*-Bu), 1.36-1.64 (m, 4 H, H-5, H-4), 2.31 (s, 3 H, CH₃ *p*-Tol), 2.42 (t, 2 H, *J* = 6.9 Hz, H-3), 7.12 (d, 2 H, *J* = 8.6 Hz, *p*-Tol), 7.29 (d, 2 H, *J* = 8.4 Hz, *p*-Tol). **¹³C NMR (50 MHz)** δ 13.6 (CH₃ *n*-Bu), 20.0 (C-3), 20.9 (CH₃ *p*-Tol), 22.0 (C-5), 30.7 (C-4), 65.0 (C-1), 99.3 (C-2), 126.0 (2 C *p*-Tol), 129.8 (2 C *p*-Tol), 130.0 (C-1' *p*-Tol), 136.0 (C 4' *p*-Tol). **IR** (film): 2958, 2929, 2871, 1491, 1464, 1084, 1016, 802 cm⁻¹. **MS** (APCI): 409 [2M+1]⁺, 237, 205 [M+1]⁺ (100%).

3. Synthesis of (*E*)-1-tri-*n*-Butylstannyl-1-(*p*-tolylsulfenyl)-1-hexene, **9**.

To a solution of a mixture of 1-(*p*-tolylsulfenyl)-1-hexyne **8** and methyl *p*-tolyl sulfide **8'** (3.39 g) in 105 mL of dry toluene, at room temperature, tetrakis(triphenylphosphine)palladium(0) (2% mol) was added. The resulting solution was stirred for 10 min and then freshly distilled tributyltin hydride (1.1 equiv, 4.44 mL, 16.5 mmol) was added dropwise rapidly. After a few minutes complete conversion was detected by TLC. Toluene was removed under reduced pressure and the oily residue was purified by column chromatography (hexane, 7 g SiO₂/mmol stannane) affording 6.08 g (12.3 mmol, 82 % overall yield from 1-hexyne) of vinyl stannane **9**.

Data of **9**: *R_f* = 0.56 (hexane). **¹H NMR (300 MHz)** δ 0.64-0.69 (m, 6 H, *n*-Bu), 0.82 (t, 9 H, *J* = 7.2 Hz, 3 CH₃ *n*-Bu), 0.90 (t, 3 H, *J* = 7.0 Hz, CH₃ *n*-Bu), 1.14-1.44 (m, 16 H), 2.29 (s, 3 H, CH₃ *p*-Tol), 2.36-2.43 (m, 2 H, H-3), 5.97 (t, 1 H, *J* = 6.8 Hz, H-2), 7.04 (d, 2 H, *J* = 7.9 Hz, *p*-Tol), 7.17 (d, 2 H, *J* = 8.3 Hz, *p*-Tol). **¹³C NMR (75 MHz)** δ 11.1 (3 C), 13.2 (3 C), 13.6, 21.0 (CH₃ *p*-Tol), 22.3, 27.3 (3 C), 28.8 (3 C), 30.7, 31.5, 129.4 (2 C *p*-Tol), 130.4 (2 C *p*-Tol), 134.4, 135.9, 136.9, 147.6. **IR** (film): 2956, 2924, 2871, 2853, 1572, 1491, 1463, 1418, 1376, 1340, 1292, 1179, 1072, 1018, 960, 863, 805 cm⁻¹. **MS** (ES): 521, 495 [M+1]⁺, 413, 313 (100%).

4. General Procedure for Synthesis of *Z* Hydroxy Vinyl Sulfides

To a cold (−78 °C) solution of vinyl stannane **9** in THF (5 mL/mmol), was added 1.1 equiv of *n*-BuLi. After 30 min a solution of 2-3 equiv of aldehyde in THF (1 mL/mmol of aldehyde) was added. After 15 min the reaction was quenched with saturated NH₄Cl (3 mL/mmol) and H₂O (3 mL/mmol). The aqueous layer was extracted with EtOAc (3 times, 4 mL/mmol) and the combined organic extracts were washed with a saturated solution of NaCl, dried over anhydrous MgSO₄, filtered and concentrated under reduced pressure. The resulting crude reaction mixture was purified by column chromatography on silica gel.

4.1. Synthesis of (±)-(Z)-4-(*p*-Tolylsulfenyl)non-4-en-2-ol, **10e**.

From a 64:36 mixture of **9** and hexa-*n*-butyl diestannane (2.68 g, 5.41 mmol), *n*-BuLi (2.0 M, 3.0 mL, 6.0 mmol) and 2 equiv of propionaldehyde (0.79 mL, 630 mg, 10.8 mmol), following the general procedure, an 86:14 mixture of **10e** and (Z)-1-(*p*-tolylsulfenyl)-1-hexene **10e'** was obtained. Purification by column chromatography (0-30% EtOAc-hexane) afforded 722 mg (55%, from 1-hexyne, over 3 steps) of vinyl sulfide **10e**, as a colorless oil.

Data of **10e**: *R_f* = 0.29 (15% EtOAc-hexane). **¹H NMR (200 MHz)** δ 0.86 (t, 6 H, *J* = 7.1 Hz, CH₃ *n*-Bu, CH₃ Et), 1.23-1.43 (m, 4 H, 2 H-7, 2 H-8), 1.50-1.75 (m, 2 H, CH₂ Et), 1.82 (d, 1 H, *J* = 6.2 Hz, OH), 2.28 (s, 3 H, CH₃ *p*-Tol), 2.26-2.38 (m, 2 H, 2 H-6), 4.00 (ap q, 1 H, *J* = 6.2 Hz, H-3), 6.22 (t, 1 H, *J* = 7.1 Hz, H-5), 7.04 (d, 2 H, *J* = 8.1 Hz, *p*-Tol), 7.16 (d, 2 H, *J* = 8.2 Hz, *p*-Tol). **¹³C NMR (50 MHz)** δ 9.8 (CH₃ Et), 13.9 (CH₃ *n*-Bu), 20.9 (CH₃ *p*-Tol), 22.3 (CH₂ *n*-Bu), 29.0, 29.3, 31.1, 76.7 (C-3), 128.4 (2 C *p*-Tol), 129.7 (2 C *p*-Tol), 132.3, 135.4, 135.6, 138.7 (C-5). **IR (film)**: 3391, 2959, 1644, 1491, 1455, 1078, 1005, 805 cm⁻¹. **MS (ES)**: 287 [M+Na]⁺, 265 [M+1]⁺, 247 [M-17]⁺ (100%).

4.2. Synthesis of (±)-(Z)-1-Phenyl-2-(*p*-tolylsulfenyl)hept-2-en-1-ol, **10f**.

From stannane **9** (6.00 g, 12.10 mmol), *n*-BuLi (9.1 mL, 1.6 M, 14.52 mmol) and 2 equiv of benzaldehyde (2.45 mL, 2.56 g, 24.20 mmol), following the general procedure, a 94:6 mixture of hydroxy sulfide **10f** and vinyl sulfide **10e'** was obtained. Purification by chromatography gave 158 mg (0.76 mmol, 6%) of **10e'** and 3.53 g (11.3 mmol, 93%) of **10f**, as colorless oils.

Data of **10f**: *R_f* = 0.22 (10% EtOAc-hexane). **¹H NMR (200 MHz)** δ 0.87 (t, 3 H, *J* = 7.1 Hz, CH₃ *n*-Bu), 1.20-1.45 (m, 4 H, 2 CH₂ *n*-Bu), 2.29 (s, 3 H, CH₃ *p*-Tol), 2.32 (m, 2 H, H-4), 2.44 (d, 1 H, *J* = 5.0 Hz, OH), 5.15 (d, 1 H, *J* = 4.4 Hz, H-1), 6.27 (dd, 1 H, *J* = 7.2, 1.1 Hz, H-3), 7.04 (d, 2 H, *J* = 8.2 Hz), 7.14 (d, 2 H, *J* = 8.4 Hz), 7.26-7.32 (m, 5 H). **¹³C NMR (50 MHz)** δ 13.9 (CH₃ *n*-Bu), 20.9 (CH₃ *p*-Tol), 22.4 (C-6), 29.4 (C-4), 31.1 (C-5), 76.5 (C-1), 126.7 (2 C), 127.6, 128.2 (2

C), 129.1 (2 C), 129.7 (2 C), 131.7, 135.8, 136.0, 139.0, 141.8. **IR** (CCl₄): 3380, 3000, 2920, 2890, 2840, 2820, 1470, 1435, 1360, 1065, 1000, 785, 680 cm⁻¹. **MS** (APCI): 589 [2(M-18)+1]⁺ (100%), 295 [(M-18)+1]⁺, 171.

5. Synthesis of (±)-(Z)-5-Phenyl-4-(*p*-tolylsulfenyl)pent-4-en-3-ol, **10g**, and (±)-(E)-5-Phenyl-4-(*p*-tolylsulfenyl)pent-4-en-3-ol, **10g'**.

To a cold (-78 °C) solution of a 98:2 mixture of vinyl sulfides **11** and **11'** (281 mg, 1.26 mmol) in THF (13 mL), *n*-BuLi (2.0 M, 1.26 mL, 2.52 mmol) was added dropwise. After 30 min freshly distilled propionaldehyde (0.27 mL, 215 mg, 3.7 mmol) was added and, after stirring for 20 min, the reaction was quenched with a saturated solution of NH₄Cl (3 mL/mmol) and H₂O (3 mL/mmol). The crude mixture was extracted with EtOAc (3 times, 4 mL/mmol), the layers were separated and the organic extracts were washed with a saturated solution of NaCl (2 times, 4 mL/mmol), dried over MgSO₄, filtered and concentrated under reduced pressure to give a crude product that was purified by column chromatography (0-30% EtOAc-hexane) affording 247 mg (69%) of hydroxy vinyl sulfide **10g**, as a colorless oil, 2 mg (1%) of hydroxy vinyl sulfide **10g'**, as a colorless oil and 24 mg (7%) of starting material.

Data of **10g**: *R_f* = 0.20 (15% EtOAc-hexane). **¹H NMR (200 MHz)** δ 0.92 (t, 3 H, *J* = 7.4 Hz, CH₃ Et), 1.59-1.89 (m, 3 H, CH₂ Et, OH), 2.27 (s, 3 H, CH₃ *p*-Tol), 4.12 (dd, 1 H, *J* = 12.2, 5.1 Hz, H-3), 7.03 (d, 2 H, *J* = 8.1 Hz, *p*-Tol), 7.16-7.32 (m, 6 H, 5 Ph, H-5), 7.62 (d, 2 H, *J* = 7.3 Hz, *p*-Tol). **¹³C NMR (50 MHz)** δ 9.8 (CH₃ Et), 20.9 (CH₃ *p*-Tol), 29.4 (CH₂ Et), 76.2 (C-3), 127.7 (C-4' Ph), 127.9 (2 C Ar), 129.4 (2 C Ar), 129.5 (2 C Ar), 129.7 (2 C Ar), 130.9, 133.3 (C-5), 135.7, 136.3, 136.7. **IR** (film): 3391, 2964, 2924, 1597, 1491, 1445, 1084, 1017, 806, 754 cm⁻¹. **MS** (ES): 307 [M+Na]⁺ (100%), 591 [2M+Na]⁺.

Data of **10g'**: *R_f* = 0.26 (15% EtOAc-hexane). **¹H NMR (300 MHz)** δ 0.92 (t, 3 H, *J* = 7.4 Hz, CH₃ Et), 1.66-1.84 (m, 2 H, CH₂ Et), 1.92 (d, 1 H, *J* = 7.3 Hz, OH), 2.33 (s, 3 H, CH₃ *p*-Tol), 4.70 (dt, 1 H, *J* = 7.3, 6.5 Hz, H-3), 6.44 (s, 1 H, H-5), 7.13-7.32 (m, 7 H, ArH), 7.42 (d, 2 H, *J* = 8.3 Hz, *p*-Tol). **¹³C NMR (50 MHz)** δ 10.3 (CH₃ Et), 21.2 (CH₃ *p*-Tol), 29.6 (CH₂ Et), 71.8 (C-3), 127.1 (CH Ph), 128.3 (2 C Ar), 128.5 (2 C Ar), 129.6 (C-5), 130.2 (2 C Ar), 131.5 (2 C Ar), 133.2 (2 C

Ar), 136.4, 138.0, 143.1. **IR** (film): 3400, 3021, 2963, 2926, 1598, 1491, 1445, 1084, 1017, 970, 808, 755, 695 cm⁻¹. **MS** (ES): 307 [M+Na]⁺ (100%).

6. General Procedure for Oxidation of Hydroxy Vinyl Sulfides

To a solution of the hydroxy vinyl sulfide in acetone (5 mL/mmol), 3.0 equiv of K₂CO₃ was added, the mixture was cooled to -78 °C, and 1.1 equiv of 70% *m*-CPBA was added and the reaction mixture was allowed to warm up slowly to rt and monitored by TLC. The reaction was quenched with 1 M aqueous Na₂S₂O₄ (4 mL/mmol) and a saturated solution of NaHCO₃ (2 mL/mmol) and extracted with EtOAc (3 times, 4 mL/mmol). The organic layer was washed with a saturated solution of NaHCO₃ (4 mL/mmol) and with a saturated solution of NaCl (4 mL/mmol), dried over MgSO₄, filtered and concentrated under reduced pressure to give a crude product that was purified by column chromatography (EtOAc-CH₂Cl₂) to give the desired hydroxy vinyl sulfoxides.

6.1. Synthesis of (±)-(Z)-4-(*SS*)-(p-Tolylsulfinyl)non-4-en-3-(*S*)-ol, **3e**, and (±)-(Z)-4-(*SS*)-(p-Tolylsulfinyl)non-4-en-3-(*R*)-ol, **4e**.

From hydroxy vinyl sulfide **10e** (691 mg, 2.61 mmol) in 13 mL of acetone with K₂CO₃ (1086 mg, 7.86 mmol) and *m*-CPBA (709 mg, 2.88 mmol), according to the general procedure (50 min), a 62:38 mixture of hydroxy vinyl sulfoxides **3e** and **4e** was obtained. Purification by column chromatography (0-50% EtOAc-CH₂Cl₂), gave 139 mg (20%) of **3e** as a white solid, recrystallized from hexane, 195 mg (27%) of **4e** as a white solid, recrystallized from 5% EtOAc-hexane, and 332 mg (45%) of a mixture of **3e** and **4e**.

Data of **3e**: **mp**: 60-61 °C. *R_f* = 0.11 (10% EtOAc-CH₂Cl₂). **¹H NMR (300 MHz)** δ 0.65 (t, 3 H, *J* = 7.3 Hz, CH₃), 0.94 (t, 3 H, *J* = 7.1 Hz, CH₃), 1.31-1.68 (m, 6 H), 2.39 (s, 3 H, CH₃ *p*-Tol), 2.39-2.50 (m, 1 H), 2.63-2.76 (m, 1 H), 3.59 (d, 1 H, *J* = 2.3 Hz, OH), 4.18 (td, 1 H, *J* = 8.4, 2.3 Hz, H-3), 6.18 (dd, 1 H, *J* = 8.5, 6.8 Hz, H-5), 7.29 (d, 2 H, *J* = 8.5 Hz, *p*-Tol), 7.41 (d, 2 H, *J* = 8.2 Hz, *p*-

Tol). **¹³C NMR (50 MHz)** δ 9.7 (CH₃ Et), 13.6 (CH₃ *n*-Bu), 21.0 (CH₃ *p*-Tol), 22.0, 27.7, 28.3, 31.1, 68.3 (C-3), 123.9 (2 C *p*-Tol), 129.6 (2 C *p*-Tol), 137.8 (C-5), 138.9, 140.6, 145.2. **IR** (KBr): 3324, 2950, 2868, 1639, 1492, 1465, 1079, 1025, 810 cm⁻¹. **MS** (ES): 583 [2M+Na]⁺, 303 [M+Na]⁺, 281 [M+1]⁺ (100%).

Data of **4e**: **mp**: 72-73 °C. **R_f** = 0.18 (10% EtOAc-CH₂Cl₂). **¹H NMR (200 MHz)** δ 0.82 (t, 3 H, *J* = 7.3 Hz, CH₃), 0.91 (t, 3 H, *J* = 7.3 Hz, CH₃), 1.32-1.67 (m, 6 H), 2.36 (s, 3 H, CH₃ *p*-Tol), 2.27-2.44 (m, 2 H), 2.56-2.75 (m, 1 H), 4.25 (dt, 1 H, *J* = 11.7, 6.4 Hz, H-3), 6.24 (dd, 1 H, *J* = 8.9, 6.3 Hz, H-5), 7.27 (d, 2 H, *J* = 8.1 Hz, *p*-Tol), 7.46 (d, 2 H, *J* = 8.2 Hz, *p*-Tol). **¹³C NMR (50 MHz)** δ 9.9 (CH₃ Et), 13.7 (CH₃ *n*-Bu), 21.2 (CH₃ *p*-Tol), 22.1, 28.3, 30.4, 31.2, 70.5 (C-3), 124.3 (2 C *p*-Tol), 129.8 (2 C *p*-Tol), 138.8 (C-5), 139.9, 140.6, 145.4. **IR** (KBr): 3306, 2956, 2871, 1636, 1493, 1456, 1323, 1082, 1020, 1001, 973, 809 cm⁻¹. **MS** (ES): 583 [2M+Na]⁺ (100%), 303 [M+Na]⁺, 281 [M+1]⁺.

6.2. Synthesis of (±)-(Z)-1-Phenyl-2-(S_S)-(p-tolylsulfinyl)-2-en-1-(S)-ol, **3f**, and (±)-(Z)-1-Phenyl-2-(S_S)-(p-tolylsulfinyl)-2-en-1-(R)-ol, **4f**.

From hydroxy vinyl sulfide **10f** (1.2 g, 3.80 mmol), *m*-CPBA (936 mg, 3.80 mmol, 70%) and K₂CO₃ (1.6 g, 11.40 mmol), according to the general procedure in CH₂Cl₂ (2 h), a 90:8:1:1 mixture of **3f**, **4f**, **10f** and **12f** was obtained. Direct recrystallization from the crude (1% EtOAc-hexane) gave 1.03 g (3.18 mmol, 84%) of **3f**. Purification by chromatography of the mother liquours gave 12 mg (0.04 mmol, 1%) of **10f**, 15 mg (0.04 mmol, 1%) of sulfone **12f**, 85 mg (0.26 mmol, 7%) of **4f**, as a white solid recrystallized from Et₂O-hexane, and 8 mg (0.02 mmol) of **3f**. When the reaction was carried out in acetone, a 67:33 mixture of **3f** and **4f** was obtained (91%).

Data of **3f**: **mp**: 104-106 °C. **R_f** = 0.20 (10% EtOAc-CH₂Cl₂). **¹H NMR (300 MHz)** δ 0.89 (t, 3 H, *J* = 7.1 Hz, CH₃ *n*-Bu), 1.24-1.42 (m, 4 H, 2 CH₂ *n*-Bu), 2.35 (m, 1 H, H-4), 2.43 (s, 3 H, CH₃ *p*-Tol), 2.65 (m, 1 H, H-4), 4.33 (s, 1 H, OH), 5.46 (s, 1 H, H-1), 5.64 (dd, 1 H, *J* = 8.3, 6.8 Hz, H-3), 7.00-7.04 (m, 2 H), 7.16-7.26 (m, 3 H), 7.34 (d, 2 H, *J* = 8.3 Hz, *p*-Tol), 7.49 (d, 2 H, *J* = 8.3 Hz, *p*-Tol). **¹³C NMR (50 MHz)** δ 13.7 (CH₃ *n*-Bu), 21.3 (CH₃ *p*-Tol), 22.2 (C-6), 28.6 (C-4), 31.1 (C-5),

71.1 (C-1), 124.3 (2 C), 126.5 (2 C), 127.4, 128.1 (2 C), 130.0 (2 C), 139.0, 139.8, 141.2, 146.3. **IR** (KBr): 3240, 3000, 2980, 2890, 2810, 1615, 1525, 1450, 1425, 1055, 1045, 1030, 990, 982, 888, 780, 730, 670, 612 cm^{-1} . **MS** (APCI): 329 $[\text{M}+1]^+$, 311 $[(\text{M}-18)+1]^+$ (100%), 171. **Anal. calcd for** $\text{C}_{20}\text{H}_{24}\text{O}_2\text{S}$: C, 73.13; H, 7.36; S, 9.76. **Found**: C, 73.11; H, 7.60; S, 10.02.

Data of **4f**: **mp**: 72-73 °C. **R_f** = 0.40 (10% EtOAc- CH_2Cl_2). **^1H NMR (200 MHz)** δ 0.87 (t, 3 H, J = 7.0 Hz, CH_3 *n*-Bu), 1.20-1.44 (m, 4 H, 2 CH_2 *n*-Bu), 2.17-2.34 (m, 1 H, H-4), 2.37 (s, 3 H, CH_3 *p*-Tol), 2.44-2.63 (m, 1 H, H-4), 3.31 (d, 1 H, J = 4.8 Hz, OH), 5.70 (d, 1 H, J = 4.8 Hz, H-1), 5.89 (dd, 1 H, J = 8.8, 6.7 Hz, H-3), 7.18-7.32 (m, 7 H), 7.47 (d, 2 H, J = 8.2 Hz, *p*-Tol). **^{13}C NMR (50 MHz)** δ 13.7 (CH_3 *n*-Bu), 21.3 (CH_3 *p*-Tol), 22.2 (C-6), 28.6 (C-4), 30.9 (C-5), 71.2 (C-1), 124.8 (2 C), 126.4 (2 C), 127.2, 128.0 (2 C), 129.9 (2 C), 140.2, 140.9, 141.0, 141.3, 146.1. **IR** (KBr): 3360, 3010, 2970, 2900, 2880, 2800, 1465, 1420, 1050, 1005, 995, 985 cm^{-1} . **MS** (APCI): 329 $[\text{M}+1]^+$, 311 $[(\text{M}-18)+1]^+$ (100%), 171. **Anal. calcd for** $\text{C}_{20}\text{H}_{24}\text{O}_2\text{S}$: C, 73.13; H, 7.36; S, 9.76. **Found**: C, 73.12; H, 7.65; S, 9.81.

6.3. Synthesis of ($\pm$)-(Z)-5-Phenyl-4-(S_S)-(p-tolylsulfinyl)pent-4-en-3-(S)-ol, **3g, ($\pm$)-(Z)-5-Phenyl-4-(S_S)-(p-tolylsulfinyl)pent-4-en-3-(R)-ol, **4g**, and (Z)-5-Phenyl-4-(p-tolylsulfonyl)pent-4-en-3-ol, **12g**.**

From hydroxy vinyl sulfide **10g** (202 mg, 0.71 mmol) in 3.50 mL of acetone with K_2CO_3 (294 mg, 2.13 mmol) and *m*-CPBA (192 mg, 0.78 mmol), according to the general procedure (6 h 30 min), a 50:42:8 mixture of hydroxy vinyl sulfoxides **3g**, **4g** and hydroxy vinyl sulfone **12g** was obtained. Purification by column chromatography (0-50% EtOAc- CH_2Cl_2), gave 86 mg (40%) of **3g** as a white solid, recrystallized from 5% EtOAc-hexane, 49 mg (23%) of **4g** as a white solid, recrystallized from 5% EtOAc-hexane, 34 mg (16%) of a mixture of **3g** and **4g**, and 28 mg (13%) of sulfone **12g** as a white solid, recrystallized from 5% EtOAc-hexane.

Data of **3g**: **mp**: 90-91 °C. **R_f** = 0.12 (10% EtOAc- CH_2Cl_2). **^1H NMR (200 MHz)** δ 0.73 (t, 3 H, J = 7.4 Hz, CH_3 Et), 1.33-1.72 (m, 2 H, CH_2 Et), 2.38 (s, 3 H, CH_3 *p*-Tol), 3.80 (br s, 1 H, OH), 4.41 (dd, 1 H, J = 7.5, 5.9 Hz, H-3), 7.24-7.29 (m, 3 H, 3 H ArH), 7.38-7.51 (m, 7 H, 6 H ArH, H-5).

¹³C NMR (50 MHz) δ 10.0 (CH₃ Et), 21.3 (CH₃ *p*-Tol), 28.2 (CH₂ Et), 69.1 (C-3), 124.4 (2 C Ar), 128.5 (2 C Ar), 128.9 (CH Ph), 129.7 (2 C Ar), 129.9 (2 C Ar), 133.7, 135.9 (C-5), 138.6, 141.0, 146.4. **IR** (KBr): 3373, 2923, 1624, 1491, 1447, 1079, 1035, 981, 800, 753, 698 cm⁻¹. **MS** (ES): 323 [M+Na]⁺ (100%).

Data of **4g**: **mp**: 81-82 °C. **R_f** = 0.16 (5% EtOAc-CH₂Cl₂). **¹H NMR (200 MHz)** δ 0.92 (t, 3 H, *J* = 7.3 Hz, CH₃ Et), 1.66-1.80 (m, 2 H, CH₂ Et), 2.34 (s, 3 H, CH₃ *p*-Tol), 2.48 (br s, 1 H, OH), 4.38 (dd, 1 H, *J* = 7.5, 5.1 Hz, H-3), 7.22 (d, 2 H, *J* = 7.9 Hz, *p*-Tol), 7.32-7.50 (m, 8 H, 7 H ArH, H-5). **¹³C NMR (50 MHz)** δ 10.0 (CH₃ Et), 21.2 (CH₃ *p*-Tol), 31.1 (CH₂ Et), 70.5 (C-3), 124.5 (2 C Ar), 128.5 (2 C Ar), 128.8 (CH Ph), 129.7 (2 C Ar), 129.9 (2 C Ar), 133.8, 136.6 (C-5), 139.5, 140.9, 147.0. **IR** (KBr): 3348, 2980, 1635, 1450, 1446, 1080, 1020, 1110, 808, 754, 695 cm⁻¹. **MS** (ES): 323 [M+Na]⁺ (100%).

Data of **12g**: **mp**: 99-100 °C. **R_f** = 0.34 (5% EtOAc-CH₂Cl₂). **¹H NMR (300 MHz)** δ 1.07 (t, 3 H, *J* = 7.4 Hz, CH₃ Et), 1.90-2.08 (m, 2 H, CH₂ Et), 2.29 (s, 3 H, CH₃ *p*-Tol), 3.07 (br s, 1 H, OH), 4.56 (m, 1 H, H-3), 6.98 (d, 2 H, *J* = 8.0 Hz, *p*-Tol), 7.09-7.21 (m, 6 H, 5 H Ph, H-5), 7.32 (d, 2 H, *J* = 8.3 Hz, *p*-Tol). **¹³C NMR (50 MHz)** δ 10.5 (CH₃ Et), 21.5 (CH₃ *p*-Tol), 29.6 (CH₂ Et), 74.8 (C-3), 127.5 (2 C Ar), 127.6 (2 C Ar), 128.3 (CH Ph), 128.9 (4 C Ar), 133.2, 137.6, 139.2 (C-5), 143.7, 146.1. **IR** (KBr): 3494, 2995, 1630, 1500, 1445, 1300, 1140, 1080, 960, 815 cm⁻¹. **MS** (ES): 339 [M+Na]⁺ (100%).

6.4. Synthesis of (±)-(S_S)-2-(Phenylsulfinyl)-2-cyclohexen-1-(S)-ol, **3d**, and (±)-(S_S)-2-(Phenylsulfinyl)-2-cyclohexen-1-(R)-ol, **4d**.

From hydroxy vinyl sulfide **6** (327 mg, 1.58 mmol) in CH₂Cl₂ (9.4 mL), K₂CO₃ (1095 mg, 7.932 mmol) and *m*-CPBA (397 mg, 3.09 mmol), according to the general procedure (6 h), a 27:73 mixture of **3d** and **4d** was obtained. Purification by column chromatography (15-100% EtOAc-hexane), gave 202 mg (65%) of **4d** as a colorless oil, and 71 mg (23%) of **3d** as white solid, recrystallized from Et₂O-hexane.

Data of **3d**: **mp**: 93-94 °C. **R_f** = 0.12 (50% EtOAc-hexane). **¹H NMR (300 MHz)** δ 1.49-1.58 (m, 1 H, H-5), 1.69-1.81 (m, 3 H, H-5, H-6), 2.10-2.33 (m, 2 H, H-4), 2.62 (br s, 1 H, OH), 4.13

(br s, 1 H, H-1), 6.58 (t, 1 H, $J = 3.8$ Hz, H-3), 7.42-7.49 (m, 3 H, Ph), 7.64-7.69 (m, 2 H, Ph). **^{13}C NMR (50 MHz)** δ 17.8, 25.9, 32.0, 62.7, 125.3 (2 C Ph), 129.2 (2 C Ph), 131.1, 133.0, 143.1, 145.2. **IR** (film): 3340 (br), 3060, 2980, 2940, 2860, 1440, 1230, 1180, 1140, 1080, 1040, 995, 750, 720, 690 cm^{-1} . **MS** (APCI): 223 $[\text{M}+1]^+$ (100%); 257 $[\text{M}+\text{Cl}]^-$, 119 (100%).

Data of **4d**: $R_f = 0.21$ (50% EtOAc-hexane). **^1H NMR (300 MHz)** δ 1.39-1.56 (m, 2 H, H-5), 1.74-1.91 (m, 2 H, H-6), 2.09 (dddd, 1 H, $J = 19.0, 8.7, 5.6, 2.9, 1.2$ Hz, H-4), 2.37 (dq, 1 H, $J = 18.6, 4.9$ Hz, H-4), 3.88 (br s, 1 H, OH), 4.26 (t, 1 H, $J = 4.0$ Hz, H-1), 6.76 (dd, 1 H, $J = 4.8, 2.9$ Hz, H-3), 7.43-7.54 (m, 3 H, Ph), 7.56-7.61 (m, 2 H, Ph). **^{13}C NMR (50 MHz)** δ 16.9, 26.3, 30.9, 62.9, 124.3 (2 C Ph), 129.2 (2 C Ph), 130.7, 139.0, 141.9, 143.6. **IR** (CHCl_3): 3310 (br), 2970, 2910, 2850, 2780, 1590, 1535, 1430, 1230, 1135, 1115, 1100, 1040, 950, 930, 650 cm^{-1} .

7. General Procedure for Oxidation of Sulfoxides with MMPP

To a cold (0 °C) solution of sulfoxide in MeOH (10 mL/mmol) was added 1.5-1.8 equiv of magnesium monoperoxyphthalate hexahydrate (MMPP). The mixture was stirred from 0 °C to rt, monitored by TLC until completion and then quenched with a saturated solution of NaHCO_3 (4 mL/mmol). After removal of MeOH under reduced pressure, the mixture was diluted with EtOAc (5 mL/mmol), the layers were separated and the aqueous phase was extracted with EtOAc (3 times, 4 mL/mmol). The combined organic layers were washed with a saturated solution of NaCl (1 mL/mmol), dried over MgSO_4 , filtered and concentrated under reduced pressure to give a crude product that was purified by gradient column chromatography using EtOAc-hexane mixtures.

7.1. Synthesis of (+)-(E)-4-(p-Tolylsulfonyl)non-4-en-3-ol, **12a**.

From hydroxy vinyl sulfoxide **3a** (33 mg, 0.12 mmol) in MeOH (1.2 mL) and MMPP (75 mg, 0.18 mmol), according to the general procedure (3 h), vinyl sulfone **12a** (28 mg, 75%) was obtained as a white solid after purification by chromatography.

Data of **12a**: mp: 65-66 °C. $R_f = 0.41$ (30% EtOAc-hexane). $[\alpha]_D^{20} = +5.0$ ($c = 2.33$). **^1H NMR (300 MHz)** δ 0.78 (t, 3 H, $J = 7.4$ Hz, CH_3 *n*-Bu), 0.89 (t, 3 H, $J = 7.2$ Hz, CH_3 Et), 1.23-1.56 (m, 4 H, 2 H-7, 2 H-8), 1.66-1.79 (m, 2 H, CH_2 Et), 2.32 (q, 2 H, $J = 7.4$ Hz, 2 H-6), 2.40 (s, 3 H, CH_3 *p*-Tol), 2.54 (d, 1 H, $J = 7.0$ Hz, OH), 4.42 (ddd, 1 H, $J = 8.7, 7.0, 5.7$ Hz, H-3), 6.88 (t, 1 H, $J = 7.7$

Hz, H-5), 7.28 (d, 2 H, $J = 8.0$ Hz, *p*-Tol), 7.71 (d, 2 H, $J = 8.4$ Hz, *p*-Tol). **^{13}C NMR (50 MHz)** δ 10.5 (CH₃ Et), 13.8 (CH₃ *n*-Bu), 21.6 (CH₃ *p*-Tol), 22.4, 28.2, 29.8, 30.7, 70.5 (C-3), 127.7 (2 C *p*-Tol), 129.7 (2 C *p*-Tol), 138.2, 143.0, 144.0, 145.1. **IR** (film): 3500, 2960, 2930, 1640, 1600, 1460, 1320, 1300, 1290, 1140, 1090, 820, 710, 670 cm⁻¹. **MS** (EI): 267, 211, 157, 139 (100%), 111, 91, 57, 55, 41.

7.2. Synthesis of (+)-(E)-2-Methyl-4-(p-tolylsulfonyl)non-4-en-3-(S)-ol, **12b**.

From hydroxy vinyl sulfoxide **3b** (55 mg, 0.247 mmol) in MeOH (2.50 mL) and MMPP (220 mg, 0.445 mmol), according to the general procedure (2 h), after chromatography (0-20% EtOAc-hexane), vinyl sulfone **12b** (43 mg, 73%) was obtained as a white solid, further recrystallized from 5% EtOAc-hexane, along with starting material (4 mg, 7%).

Data of **12b**: mp: 80-81 °C. R_f = 0.39 (20% EtOAc-hexane). $[\alpha]^{20}_D$ = +19.4 (c = 0.155). **¹H NMR (300 MHz)** δ 0.56 (d, 3 H, J = 6.7 Hz, CH₃ *i*-Pr), 0.89 (t, 3 H, J = 7.2 Hz, CH₃ *n*-Bu), 1.01 (d, 3 H, J = 6.5 Hz, CH₃ *i*-Pr), 1.23-1.47 (m, 4 H, 2 H-7, 2 H-8), 1.98-2.05 (m, 1 H, H-2), 2.30 (ap q, 2 H, J = 7.5 Hz, 2 H-6), 2.41 (s, 3 H, CH₃ *p*-Tol), 2.67 (d, 1 H, J = 7.9 Hz, OH), 4.10 (dd, 1 H, J = 9.7, 8.0 Hz, H-3), 6.88 (t, 1 H, J = 7.6 Hz, H-5), 7.29 (d, 2 H, J = 8.4 Hz, *p*-Tol), 7.73 (d, 2 H, J = 8.4 Hz, *p*-Tol). **¹³C NMR (50 MHz)** δ 13.8 (CH₃ *n*-Bu), 19.0 (CH₃ *i*-Pr), 19.5 (CH₃ *i*-Pr), 21.6 (CH₃ *p*-Tol), 22.4 (C-8), 28.4 (C-6), 30.6 (C-7), 33.3 (C-2), 75.0 (C-3), 127.8 (2 C *p*-Tol), 129.7 (2 C *p*-Tol), 138.3, 142.6, 144.1, 146.1 (C-5). **IR (CCl₄)**: 3443, 2910, 2870, 2820, 1600, 1570, 1465, 1440, 1255, 1055, 1010 cm⁻¹. **MS (ES)**: 333 [M+Na]⁺ (100%); 345 [M+Cl]⁻ (100%).

7.3. Synthesis of (+)-(E)-2,2-Dimethyl-4-(p-tolylsulfonyl)non-4-en-3-(S)-ol, **12c**.

From hydroxy vinyl sulfoxide **3c** (45 mg, 0.146 mmol) in MeOH (1.50 mL) and MMPP (131 mg, 0.263 mmol), according to the general procedure (4 h), after chromatography (0-60% EtOAc-hexane), vinyl sulfone **12c** (41 mg, 87%) was obtained as a colorless oil.

Data of **12c**: R_f = 0.37 (20% EtOAc-hexane). $[\alpha]^{20}_D$ = +5.2 (c = 0.218). **¹H NMR (300 MHz)** δ 0.81 (t, 3 H, J = 7.2 Hz, CH₃ *n*-Bu), 0.99 (s, 9 H, 3 CH₃ *t*-Bu), 1.14-1.25 (m, 2 H, 2 H-8), 1.26-1.38 (m, 2 H, 2 H-7), 2.18-2.30 (m, 2 H, 2 H-6), 2.39 (s, 3 H, CH₃ *p*-Tol), 3.25 (br s, 1 H, OH), 4.36 (d, 1 H, J = 8.2 Hz, H-3), 6.66 (t, 1 H, J = 7.4 Hz, H-5), 7.27 (d, 2 H, J = 8.3 Hz, *p*-Tol), 7.74 (d, 2 H, J = 8.1 Hz, *p*-Tol). **¹³C NMR (50 MHz)** δ 13.7 (CH₃ *n*-Bu), 21.5 (CH₃ *p*-Tol), 22.3 (C-8), 26.9 (3 C CH₃ *t*-Bu), 29.6 (C-6), 30.6 (C-7), 37.6 (C-2), 77.5 (C-3), 127.5 (2 C *p*-Tol), 129.6 (2 C *p*-Tol),

139.5, 143.2, 143.8 (C-5), 148.2. **IR** (CCl₄): 3480, 2900, 2880, 2800, 1690, 1600, 1570, 1435, 1273, 1110, 990, 760 cm⁻¹. **MS** (ES): 347 [M+Na]⁺ (100%); 359 [M+Cl]⁻ (100%).

7.4. Synthesis of (±)-(Z)-1-Phenyl-2-(*p*-tolylsulfonyl)hept-2-en-1-ol, **12f**.

From hydroxy vinyl sulfoxide **3f** (66 mg, 0.20 mmol) in MeOH (2 mL) and MMPP (198 mg, 0.40 mmol), according to the general procedure (22 h), after chromatography (CH₂Cl₂), vinyl sulfone **12f** (64 mg, 93%) was obtained as a white solid, further recrystallized from 5% EtOAc-hexane.

Data of **12f**: mp: 44-45 °C. *R_f* = 0.48 (5% EtOAc-CH₂Cl₂). **¹H NMR (200 MHz)** δ 0.79 (t, 3 H, *J* = 6.9 Hz, CH₃ *n*-Bu), 1.17-1.24 (m, 4 H, 2 H-5, 2 H-6), 2.38 (s, 3 H, CH₃ *p*-Tol), 2.48 (m, 2 H, 2 H-4), 3.51 (d, 1 H, *J* = 5.6 Hz, OH), 5.67 (d, 1 H, *J* = 5.5 Hz, H-1), 6.10 (dd, 1 H, *J* = 7.9, 7.3 Hz, H-3), 7.20 (d, 2 H, *J* = 8.0 Hz, *p*-Tol), 7.26 (s, 5 H, Ph), 7.56 (d, 2 H, *J* = 8.4 Hz, *p*-Tol). **¹³C NMR (50 MHz)** δ 13.7 (CH₃ *n*-Bu), 21.5 (CH₃ *p*-Tol), 22.3 (C-6), 28.3 (C-4), 30.6 (C-5), 73.6 (C-1), 126.6 (2 C Ar), 127.3 (2 C Ar), 127.8 (CH Ph), 128.3 (2 C Ar), 129.5 (2 C Ar), 138.6, 140.3, 143.7, 144.1, 146.7. **IR** (CCl₄): 3440, 2905, 2880, 2820, 1605, 1570, 1465, 1425, 1275, 1110, 785 cm⁻¹. **MS** (ES): 367 [M+Na]⁺ (100%).

8. General Procedure for Oxidation of Sulfoxides and Sulfides to Sulfones with *m*-CPBA

To a solution of the hydroxy vinyl sulfide or sulfoxide in CH₂Cl₂ or acetone (10 mL/mmol), 3.0-6.0 equiv of K₂CO₃ was added. The mixture was cooled to 0 °C, 2.5-3.0 equiv of 70% *m*-CPBA was added and the reaction mixture was allowed to warm up slowly to rt and monitored by TLC. The reaction was quenched with 1 M aqueous Na₂S₂O₄ (5 mL/mmol) and a saturated solution of NaHCO₃ (3 mL/mmol) and extracted with EtOAc (3 times, 5 mL/mmol). The organic layer was washed with a saturated solution of NaHCO₃ (2 times, 4 mL/mmol) and with a saturated solution of NaCl (4 mL/mmol), dried over MgSO₄, filtered and concentrated under reduced pressure to give a crude product that was purified by column chromatography.

8.1. Synthesis of (±)-(Z)-4-(*p*-Tolylsulfonyl)non-4-en-3-ol, **12e**.

From hydroxy vinyl sulfide **10e** (48 mg, 0.182 mmol) in CH₂Cl₂ (1 mL), K₂CO₃ (75 mg, 0.545 mmol) and *m*-CPBA (100 mg, 0.406 mmol), according to the general procedure (20 h), hydroxy vinyl sulfone **12e** (40 mg, 74%) was obtained after chromatography (0-30% EtOAc-hexane) as a colorless oil, along with starting material **10e** (3 mg, 6%).

Data of **12e**: *R_f* = 0.54 (10% EtOAc-CH₂Cl₂). **¹H NMR (300 MHz)** δ 0.81 (t, 3 H, *J* = 7.1 Hz, CH₃ Et), 0.89 (t, 3 H, *J* = 7.4 Hz, CH₃ *n*-Bu), 1.16-1.31 (m, 4 H, 2 CH₂ *n*-Bu), 1.75 (ap quint, 2 H, *J* = 7.1 Hz, CH₂ Et), 2.41 (s, 3 H, CH₃ *p*-Tol), 2.43-2.50 (m, 2 H, 2 H-6), 2.81 (br s, 1 H, OH), 4.31 (br s, 1 H, H-3), 6.23 (t, 1 H, *J* = 7.8 Hz, H-5), 7.29 (d, 2 H, *J* = 8.1 Hz, *p*-Tol), 7.79 (d, 2 H, *J* = 8.2 Hz, *p*-Tol). **¹³C NMR (50 MHz)** δ 10.4 (CH₃ Et), 13.7 (CH₃ *n*-Bu), 21.5 (CH₃ *p*-Tol), 22.3, 28.2, 29.4, 30.8, 73.7 (C-3), 127.2 (2 C *p*-Tol), 129.7 (2 C *p*-Tol), 139.1, 143.2, 144.2, 144.4 (C-5). **IR** (CHCl₃): 3480, 2920, 2880, 1610, 1570, 1470, 1435, 1260, 1110, 1060, 795 cm⁻¹. **MS** (ES): 615 [2M+Na]⁺, 319 [M+Na]⁺ (100%).

8.2. Synthesis of (±)-(Z)-5-Phenyl-4-(*p*-tolylsulfonyl)pent-4-en-3-ol, **12g**.

From hydroxy vinyl sulfoxide **4g** (28 mg, 0.093 mmol) in acetone (1 mL), K₂CO₃ (52 mg, 0.337 mmol) and *m*-CPBA (57 mg, 0.233 mmol), according to the general procedure (20 h), hydroxy vinyl sulfone **12g** (15 mg, 52%) was obtained after chromatography (0-5% EtOAc-CH₂Cl₂) as a white solid, with identical spectral data to that described before, along with starting material **4g** (8 mg, 28%).

9. General Procedure for Nucleophilic Epoxidation of Vinyl Sulfones and Sulfoxides

(a) With *t*-BuOOLi

A two-necked round-bottomed flask fitted with a tube in T for entrance and exit of argon and a polyethylene stopper, was charged with anhydrous THF (5 mL/mmol) and 4 equiv of *t*-BuOOH (80% in *t*-BuOO-*t*-Bu, Fluka), the mixture was cooled to 0 °C and then 5 equiv of *n*-BuLi was added. The mixture was stirred at 0 °C for 10 min and a solution of 1 equiv of the corresponding vinyl sulfoxide in THF (5 mL/mmol), previously dried over 4 Å sieves, was added dropwise. The reaction mixture was stirred at 0 °C until starting material disappearance, monitored by TLC. The reaction was then quenched with a 1 M solution of Na₂S₂O₄ (4 mL/mmol), diluted with EtOAc (8 mL/mmol) and the layers were separated. The aqueous layer was extracted with EtOAc (3 times, 10 mL/mmol) and the combined organic extracts were washed with a saturated solution of NaCl (4 mL/mmol), dried over anhydrous MgSO₄, filtered and concentrated under reduced pressure to give a crude product, which was purified by column chromatography on silica gel, using a gradient of mixtures of EtOAc-hexane or EtOAc-CH₂Cl₂.

(b) With *t*-BuOONa or *t*-BuOOK

A two-necked round-bottomed flask fitted with a tube in T for entrance and exit of argon and a polyethylene stopper, was charged with anhydrous THF (5 mL/mmol) and 2-4 equiv of oil free NaH or KH, the mixture was cooled to 0 °C and then 2-4 equiv of *t*-BuOOH (80% in *t*-BuOO-*t*-Bu) was added. After stirring at rt for 20-30 min, the resulting solution was cooled to 0 °C and a solution of 1 equiv of the corresponding vinyl sulfoxide in THF (2-5 mL/mmol), previously dried over 4 Å sieves, was added dropwise. The reaction mixture was stirred at 0 °C until starting material disappearance, monitored by TLC. Isolation and purification were performed as described above.

9.1. Epoxidation of Vinyl Sulfones.

9.1.1. Synthesis of (+)-(1'S,2R,3R)-3-*n*-Butyl-2-(1'-hydroxypropyl)-2-(*p*-tolylsulfonyl)oxirane, **13a**, and (–)-(1'S,2S,3S)-3-*n*-Butyl-2-(1'-hydroxypropyl)-2-(*p*-tolylsulfonyl)oxirane, **14a**.

From *t*-BuOOH (20 μ L, 18 mg, 0.2 mmol) in THF (1 mL), with *n*-BuLi (1.6 M, 0.12 mL, 0.2 mmol) and a solution of vinyl sulfone **12a** (16 mg, 0.05 mmol) in THF (0.35 mL), according to the general procedure (29 h), a 50:50 mixture of epoxy sulfones **13a** and **14a** was obtained. Purification by chromatography (5% EtOAc-hexane) gave 7 mg (39%) of **14a** and 6.5 mg (36%) of **13a** as colorless oils.

Data of **13a**: R_f = 0.26 (20% EtOAc-hexane). $[\alpha]^{20}_D$ = +38.1 (c = 0.75). **^1H NMR (300 MHz)** δ 0.90 (t, 3 H, J = 7.2 Hz, CH₃), 0.94 (t, 3 H, J = 7.4 Hz, CH₃), 1.21-1.86 (m, 8 H, 4 CH₂ *n*-Bu), 2.41 (d, 1 H, J = 6.5 Hz, OH), 2.42 (s, 3 H, CH₃ *p*-Tol), 3.69 (dd, 1 H, J = 7.6, 4.8 Hz, H-3), 3.72 (dd, 1 H, J = 6.7, 3.2 Hz, H-1'), 7.34 (d, 2 H, J = 8.2 Hz, *p*-Tol), 7.77 (d, 2 H, J = 8.3 Hz, *p*-Tol). **^{13}C NMR (50 MHz)** δ 10.9 (CH₃ Et), 13.8 (CH₃ *n*-Bu), 21.7 (CH₃ *p*-Tol), 22.3, 26.9, 27.0, 29.6, 62.7 (C-1'), 71.1 (C-3), 76.5 (C-2), 129.4 (2 C *p*-Tol), 129.7 (2 C *p*-Tol), 133.9 (C-1' *p*-Tol), 145.5 (C-4' *p*-Tol). **IR** (film): 3500, 2960, 2940, 1600, 1470, 1320, 1300, 1150, 1090, 820, 710, 660 cm⁻¹. **MS** (EI): 312 (M), 307, 279, 214, 157, 139, 97, 92, 91, 71, 69, 59 (100%), 57, 55.

Data of **14a**: R_f = 0.20 (20% EtOAc-hexane). $[\alpha]^{20}_D$ = –54.6 (c = 0.65). **^1H NMR (300 MHz)** δ 0.86 (t, 3 H, J = 7.7 Hz, CH₃), 0.89 (t, 3 H, J = 7.7 Hz, CH₃), 1.23-1.87 (m, 8 H, 4 CH₂ *n*-Bu, Et), 2.41 (d, 1 H, J = 6.3 Hz, OH), 2.42 (s, 3 H, CH₃ *p*-Tol), 3.63 (dd, 1 H, J = 7.5, 4.3 Hz, H-3), 3.90 (dt, 1 H, J = 9.4, 5.2 Hz, H-1'), 7.32 (d, 2 H, J = 8.2 Hz, *p*-Tol), 7.77 (d, 2 H, J = 8.3 Hz, *p*-Tol). **^{13}C NMR (50 MHz)** δ 10.6 (CH₃ Et), 13.8 (CH₃ *n*-Bu), 21.7 (CH₃ *p*-Tol), 22.3, 26.7, 27.4, 28.8, 62.0 (C-1'), 73.1 (C-3), 77.2 (C-2), 129.5 (4 C *p*-Tol), 133.7 (C-1' *p*-Tol), 145.3 (C-4' *p*-Tol). **IR** (film): 3510, 2960, 2930, 2880, 1600, 1410, 1320, 1300, 1150, 1080, 980, 810, 710 cm⁻¹. **MS** (EI): 214, 158, 156, 139, 92, 91, 69, 59 (100%), 57.

9.1.2. Synthesis of (+)-(1'S,2R,3R)-3-*n*-Butyl-2-(1'-hydroxy-2'-methylpropyl)-2-(*p*-tolylsulfonyl)oxirane, **13b, and (-)-(1'S,2S,3S)-3-*n*-Butyl-2-(1'-hydroxy-2'-methylpropyl)-2-(*p*-tolylsulfonyl)oxirane, **14b**.**

From *t*-BuOOH (35 μ L, 25 mg, 0.277 mmol) in THF (1.70 mL), with *n*-BuLi (1.6 M, 0.21 mL, 0.336 mmol) and a solution of vinyl sulfone **12b** (34 mg, 0.11 mmol) in THF (1.0 mL), according to the general procedure (0 °C, 45 min), a 68:32 mixture of epoxy sulfones **13b** and **14b** was obtained. Purification by chromatography (60-100% CH₂Cl₂-hexane) gave 16 mg (44%) of **13b** as a white solid recrystallized from 5% EtOAc-hexane, 4 mg (11%) of **14b** as a white solid recrystallized from 5% EtOAc-hexane and 3 mg (8%) of a mixture of epoxy sulfones.

Data of **13b**: mp: 91-92 °C. *R_f* = 0.29 (20% EtOAc-hexane). [α]²⁰_D = +60.5 (*c* = 0.527). **¹H NMR (300 MHz)** δ 0.56 (d, 3 H, *J* = 6.6 Hz, CH₃ *i*-Pr), 0.89 (t, 3 H, *J* = 7.2 Hz, CH₃ *n*-Bu), 1.00 (d, 3 H, *J* = 6.5 Hz, CH₃ *i*-Pr), 1.30-1.63 (m, 5 H), 1.76-1.87 (m, 1 H), 2.17-2.29 (m, 1 H), 2.44 (s, 3 H, CH₃ *p*-Tol), 2.88 (d, 1 H, *J* = 10.4 Hz, OH), 3.17 (ap t, 1 H, *J* = 10.1 Hz, H-1'), 3.51 (dd, 1 H, *J* = 6.9, 4.8 Hz, H-3), 7.34 (d, 2 H, *J* = 8.1 Hz, *p*-Tol), 7.78 (d, 2 H, *J* = 8.2 Hz, *p*-Tol). **¹³C NMR (50 MHz)** δ 13.9 (CH₃ *n*-Bu), 18.4 (CH₃ *i*-Pr), 19.7 (CH₃ *i*-Pr), 21.8 (CH₃ *p*-Tol), 22.4 (C-3' *n*-Bu), 27.2 (C-1' *n*-Bu), 28.6 (C-2' *n*-Bu), 32.2 (CH *i*-Pr), 62.1 (C-1'), 77.1 (C-3), 77.2 (C-2), 129.4 (2 C *p*-Tol), 129.7 (2 C *p*-Tol), 134.2 (C-1' *p*-Tol), 145.6 (C-4' *p*-Tol). **IR (KBr)**: 3495, 2956, 2870, 1598, 1467, 1302, 1149, 1056, 819, 683 cm⁻¹. **MS (ES)**: 349 [M+Na]⁺ (100%).

Data of **14b**: mp: 97-98 °C. *R_f* = 0.17 (20% EtOAc-hexane). [α]²⁰_D = -52.0 (*c* = 0.536). **¹H NMR (200 MHz)** δ 0.70 (d, 3 H, *J* = 6.6 Hz, CH₃ *i*-Pr), 0.88 (t, 3 H, *J* = 7.0 Hz, CH₃ *n*-Bu), 0.98 (d, 3 H, *J* = 6.5 Hz, CH₃ *i*-Pr), 1.13-1.58 (m, 5 H), 1.74-1.91 (m, 1 H), 2.08-2.28 (m, 1 H), 2.38 (d, 1 H, *J* = 6.4 Hz, OH), 2.43 (s, 3 H, CH₃ *p*-Tol), 3.56 (m, 2 H, H-1', H-3), 7.32 (d, 2 H, *J* = 8.3 Hz, *p*-Tol), 7.77 (d, 2 H, *J* = 8.3 Hz, *p*-Tol). **¹³C NMR (50 MHz)** δ 13.8 (CH₃ *n*-Bu), 18.8 (CH₃ *i*-Pr), 19.6 (CH₃ *i*-Pr), 21.7 (CH₃ *p*-Tol), 22.3 (C-3' *n*-Bu), 27.7 (C-1' *n*-Bu), 28.9 (C-2' *n*-Bu), 31.2 (CH *i*-Pr), 62.4 (C-1'), 76.8 (C-3), 76.9 (C-2), 129.5 (2 C *p*-Tol), 129.8 (2 C *p*-Tol), 133.0 (C-1' *p*-Tol), 145.4 (C-4' *p*-Tol). **IR (CCl₄)**: 3490, 2930, 2840, 1580, 1475, 1130, 870 cm⁻¹. **MS (APCI)**: 325 [M-1]⁻, 283 [M-43]⁻ (100%).

9.1.3. Synthesis of (+)-(1'S,2R,3R)-3-*n*-Butyl-2-(1'-hydroxy-2',2'-dimethylpropyl)-2-(*p*-tolylsulfonyl)oxirane, **13c, and (-)-(1'S,2S,3S)-3-*n*-Butyl-2-(1'-hydroxy-2',2'-dimethylpropyl)-2-(*p*-tolylsulfonyl)oxirane, **14c**.**

From *t*-BuOOH (31 μ L, 22 mg, 0.249 mmol) in THF (1.50 mL), with *n*-BuLi (1.6 M, 0.19 mL, 0.304 mmol) and a solution of vinyl sulfone **12c** (33 mg, 0.102 mmol) in THF (0.80 mL), according to the general procedure (0 $^{\circ}$ C, 3 h), a 75:25 mixture of epoxy sulfones **13c** and **14c** was obtained. Purification by chromatography (0-20% EtOAc-hexane) gave 21 mg (60%) of **13c** as a white solid recrystallized from 5% EtOAc-hexane and 8 mg (23%) of **14c** as a colorless oil.

From *t*-BuOOH (31 μ L, 22 mg, 0.249 mmol) in Et₂O (1.50 mL), with *n*-BuLi (1.16 M, 0.27 mL, 0.313 mmol) and a solution of vinyl sulfone **12c** (25 mg, 0.077 mmol) in Et₂O (0.50 mL), according to the general procedure (0 $^{\circ}$ C, 64 h), a 20:80 mixture of epoxy sulfones **13c** and **14c** was obtained. Purification by chromatography (60-100% CH₂Cl₂-hexane) gave 5 mg (19%) of **13c** and 16 mg (62%) of **14c**.

From NaH (4.2 mg, 0.175 mmol) in THF (1.10 mL), *t*-BuOOH (21 μ L, 15 mg, 0.166 mmol) and a solution of vinyl sulfone **12c** (11 mg, 0.034 mmol) in THF (0.30 mL), according to the general procedure (0 $^{\circ}$ C, 3 h), an 84:16 mixture of epoxy sulfones **13c** and **14c** was obtained. Purification by chromatography (0-20% EtOAc-hexane) gave 8 mg (67%) of a mixture of **13c** and **14c**.

Data of **13c**: mp: 98-99 $^{\circ}$ C. *R*_f = 0.35 (20% EtOAc-hexane). $[\alpha]_{\text{D}}^{20} = +16.6$ (*c* = 1.76). **¹H NMR (300 MHz, 40 $^{\circ}$ C)** δ 0.84 (t, 3 H, *J* = 7.1 Hz, CH₃ *n*-Bu), 1.12 (s, 9 H, 3 CH₃ *t*-Bu), 1.20-1.40 (m, 4 H, 2 H-2', 2 H-3' *n*-Bu), 1.44-1.70 (m, 2 H, 2 H-1' *n*-Bu), 2.44 (s, 3 H, CH₃ *p*-Tol), 2.72 (dd, 1 H, *J* = 6.5, 5.5 Hz, H-3), 3.34 (d, 1 H, *J* = 10.6 Hz, OH), 3.47 (d, 1 H, *J* = 9.5 Hz, H-1'), 7.33 (d, 2 H, *J* = 8.1 Hz, *p*-Tol), 7.76 (d, 2 H, *J* = 8.3 Hz, *p*-Tol). **¹³C NMR (50 MHz)** δ 13.8 (CH₃ *n*-Bu), 21.7 (CH₃ *p*-Tol), 22.2 (C-3' *n*-Bu), 26.9 (C-1' *n*-Bu), 27.1 (3 CH₃ *t*-Bu), 28.2 (C-2' *n*-Bu), 36.4 (C-2'), 62.3 (C-1'), 76.0 (C-2), 79.4 (C-3), 128.3 (2 C *p*-Tol), 129.7 (2 C *p*-Tol), 133.6 (C-1' *p*-Tol), 145.6 (C-4' *p*-Tol). **IR (CCl₄):** 3450, 2900, 2800, 1568, 1462, 1432, 1115, 1040, 985, 895, 782 cm⁻¹. **MS (ES):** 363

The data found for **14e** was identical to that described below.

9.1.5. Synthesis of (±)-(1'S,2R,3S)-3-*n*-Butyl-(1'-hydroxybenzyl)-2-(*p*-tolylsulfonyl)oxirane, **13f, and (±)-(1'S,2S,3R)-3-*n*-Butyl-(1'-hydroxybenzyl)-2-(*p*-tolylsulfonyl)oxirane, **14f**.**

From *t*-BuOOH (40 μ L, 29 mg, 0.40 mmol) in THF (1.0 mL), with *n*-BuLi (1.16 M, 0.35 mL, 0.40 mmol) and a solution of vinyl sulfone **12f** (46 mg, 0.13 mmol) in THF (1.0 mL), according to the general procedure (0 °C, 45 min), a 93:7 mixture of epoxy sulfones **13f** and **14f** was obtained. Purification by chromatography (60-100% CH₂Cl₂-hexane) gave 30 mg (63%) of epoxy sulfone **13f** as a colorless oil, 2 mg (4%) of epoxy sulfone **14f** as a colorless oil and 9 mg (19%) of a mixture of **13f** and **14f**.

From *t*-BuOOH (35 μ L, 25 mg, 0.32 mmol) in Et₂O (1.80 mL), with *n*-BuLi (1.16 M, 0.35 mL, 0.40 mmol) and a solution of vinyl sulfone **12f** (24 mg, 0.070 mmol) in Et₂O (0.50 mL), according to the general procedure (0 °C, 30 min), a 94:6 mixture of epoxy sulfones **13f** and **14f** was obtained. Purification by chromatography (60-100% CH₂Cl₂-hexane) gave 12 mg (48%) of **13f**, 3 mg (12%) of **14f**, 2 mg (8%) of a mixture of **13f** and **14f** and 2 mg (8%) of starting material.

Data of **13f**: *R_f* = 0.34 (CH₂Cl₂). **¹H NMR (300 MHz)** δ 0.86 (t, 3 H, *J* = 7.4 Hz, CH₃ *n*-Bu), 1.27-1.57 (m, 4 H, 2 CH₂ *n*-Bu), 1.99-2.07 (m, 2 H, 2 H-1' *n*-Bu), 2.41 (s, 3 H, CH₃ *p*-Tol), 2.84 (d, 1 H, *J* = 4.8 Hz, OH), 3.05 (t, 1 H, *J* = 6.4 Hz, H-3), 5.20 (d, 1 H, *J* = 4.6 Hz, H-1'), 7.25 (d, 2 H, *J* = 7.8 Hz, *p*-Tol), 7.27 (s, 5 H, Ph), 7.60 (d, 2 H, *J* = 8.3 Hz, *p*-Tol). **¹³C NMR (50 MHz)** δ 13.8 (CH₃ *n*-Bu), 21.6 (CH₃ *p*-Tol), 22.2 (C-3' *n*-Bu), 26.6 (C-1' *n*-Bu), 28.9 (C-2' *n*-Bu), 65.3 (C-1'), 71.3 (C-3), 78.7 (C-2), 127.2 (2 C Ar), 128.4 (2 C Ar), 128.5 (CH Ph), 129.0 (2 C Ar), 129.6 (2 C Ar), 135.1, 137.6, 145.2. **IR** (film): 3501, 2958, 2929, 2872, 1596, 1494, 1455, 1321, 1304, 1163, 1138, 1082, 815, 756, 700, 667 cm⁻¹. **MS** (ES): 743 [2M+Na]⁺, 383 [M+Na]⁺ (100%).

Data of **14f**: *R_f* = 0.44 (CH₂Cl₂). **¹H NMR (300 MHz)** δ 0.88 (t, 3 H, *J* = 7.0 Hz, CH₃ *n*-Bu), 1.26-1.42 (m, 4 H, 2 H-2', 2 H-3' *n*-Bu), 2.01-2.21 (m, 2 H, 2 H-1' *n*-Bu), 2.48 (s, 3 H, CH₃ *p*-Tol), 2.88 (t, 1 H, *J* = 6.5 Hz, H-3), 3.48 (d, 1 H, *J* = 3.4 Hz, OH), 5.16 (d, 1 H, *J* = 3.4 Hz, H-1'), 7.01-7.04 (m, 2 H, Ph), 7.20-7.22 (m, 3 H, Ph), 7.39 (d, 2 H, *J* = 7.9 Hz, *p*-Tol), 7.86 (d, 2 H, *J* = 8.1 Hz, *p*-Tol). **MS** (ES): 399 [M+K]⁺ (100%), 383 [M+Na]⁺.

9.1.6. Synthesis of (±)-(1'S,2R,3S)-3-Phenyl-2-(1'-hydroxypropyl)-2-(p-tolylsulfonyl)oxirane, **13g**.

From *t*-BuOOH (13 μ L, 9 mg, 0.101 mmol) in THF (1.0 mL), with *n*-BuLi (2.0 M, 0.05 mL, 0.101 mmol) and a solution of vinyl sulfone **12g** (8 mg, 0.025 mmol) in THF (0.20 mL), according to the general procedure (0 °C, 55 h), epoxy sulfone **13g** was obtained. Purification by chromatography (60-100% CH₂Cl₂-hexane) gave 6 mg (67%) of **13g** as a white solid recrystallized from 5% EtOAc-hexane.

Data of **13g**: mp: 125-126 °C. *R*_f = 0.41 (5% EtOAc-CH₂Cl₂). ¹H NMR (200 MHz) δ 1.12 (t, 3 H, *J* = 7.3 Hz, CH₃ Et), 1.70-1.92 (m, 1 H, CH₂ Et), 2.06-2.26 (m, 1 H, CH₂ Et), 2.30 (br s, 1 H, OH), 2.35 (s, 3 H, CH₃ *p*-Tol), 4.35 (dd, 1 H, *J* = 8.4, 2.9 Hz, H-1'), 4.43 (s, 1 H, H-3), 7.01-7.27 (m, 9 H, ArH). ¹³C NMR (50 MHz) δ 9.9 (CH₃ Et), 21.6 (CH₃ *p*-Tol), 26.3 (CH₂ Et), 60.6 (C-1'), 69.0 (C-3), 79.0 (C-2), 126.5 (2 C *p*-Tol), 127.9 (2 C *p*-Tol), 128.0 (CH Ph), 129.2 (4 C Ph), 131.0, 134.0, 144.8. IR (KBr): 3519, 1644, 1622, 1490, 1301, 1156, 744 cm⁻¹. MS (ES): 355 [M+Na]⁺ (100%).

9.2. Epoxidation of Vinyl Sulfoxides.

9.2.1. Synthesis of (+)-(1'S,2R,3R,S_S)-3-*n*-Butyl-2-(1'-hydroxypropyl)-2-(p-tolylsulfinyl)oxirane, **15a**, (+)-(1'S,2S,3S,S_S)-3-*n*-Butyl-2-(1'-hydroxypropyl)-2-(p-tolylsulfinyl)oxirane, **16a**, (-)-(1'S,2S,3S)-3-*n*-Butyl-2-(1'-hydroxypropyl)-2-(p-tolylsulfonyl)oxirane, **14a**, and (+)-(1'S,2R,3R)-3-*n*-Butyl-2-(1'-hydroxypropyl)-2-(p-tolylsulfonyl)oxirane, **13a**.

M = Li, 4 equiv, 24 h, Et ₂ O	-	-	95	5
M = K, 2 equiv, 40 min, THF	35	9	11	45
M = K, 2 equiv, 15 min, THF	80	20	-	-

From *t*-BuOOH (70 μ L, 63 mg, 0.7 mmol) in Et₂O (3.50 mL), with *n*-BuLi (1.6 M, 0.44 mL, 0.7 mmol) and a solution of vinyl sulfoxide **3a** (38 mg, 0.14 mmol) in Et₂O (1.0 mL), according to the

general procedure (24 h), a 5:95 mixture of epoxy sulfones **13a** and **14a** was obtained. Purification by chromatography (5-30% EtOAc-hexane) gave 32 mg (75%) of **14a**.

From KH (6 mg, 0.14 mmol) in THF (1.0 mL), *t*-BuOOH (17 μ L, 15 mg, 0.17 mmol) and a solution of vinyl sulfoxide **3a** (19 mg, 0.07 mmol) in THF (0.30 mL), according to the general procedure (15 min), an 80:20 mixture of epoxy sulfoxides **15a** and **16a** was obtained. Purification by chromatography (CH₂Cl₂-50% EtOAc/CH₂Cl₂) gave 9 mg (45%) of **15a**, as a white solid and 3 mg (15%) of **16a** as a colorless oil.

Data of **15a**: mp: 108-110 °C. *R_f* = 0.32 (20% EtOAc-CH₂Cl₂). [α]²⁰_D = +184.6 (*c* = 1.40).

¹H NMR (200 MHz) δ 0.87 (t, 3 H, *J* = 6.9 Hz, CH₃), 1.03 (t, 3 H, *J* = 7.3 Hz, CH₃), 1.23-1.46 (m, 4 H, 2 CH₂), 1.64-1.84 (m, 4 H, 2 CH₂), 2.40 (s, 3 H, CH₃ *p*-Tol), 2.64 (d, 1 H, *J* = 5.1 Hz, OH), 3.18 (dd, 1 H, *J* = 7.1, 5.3 Hz, H-3), 3.71 (dt, 1 H, *J* = 8.9, 4.8 Hz, H-1'), 7.30 (d, 2 H, *J* = 8.0 Hz, *p*-Tol), 7.52 (d, 2 H, *J* = 8.2 Hz, *p*-Tol). **¹³C NMR (50 MHz)** δ 10.5 (CH₃ Et), 13.8 (CH₃ *n*-Bu), 21.5 (CH₃ *p*-Tol), 22.3, 26.7, 27.2, 28.7, 60.9 (C-1'), 71.1 (C-3), 78.8 (C-2), 126.3 (2 C *p*-Tol), 129.7 (2 C *p*-Tol), 135.4, 142.7. **IR** (CCl₄): 3350, 2960, 2940, 1600, 1500, 1470, 1090, 1030, 1020 cm⁻¹. **MS** (EI): 267, 140 (100%), 139, 92, 91, 69, 59. **Anal. calcd for C₁₆H₂₄O₃S**: C, 64.83; H, 8.16; S, 10.82. **Found**: C, 65.12; H, 7.98; S, 10.53.

Data of **16a**: *R_f* = 0.33 (20% EtOAc-CH₂Cl₂). [α]²⁰_D = +34.0 (*c* = 0.50). **¹H NMR (300 MHz)** δ 0.74 (t, 3 H, *J* = 7.3 Hz, CH₃), 0.90 (t, 3 H, *J* = 7.3 Hz, CH₃), 1.24-1.52 (m, 6 H, 3 CH₂), 1.60-1.68 (m, 1 H), 1.79-1.85 (m, 1 H), 2.41 (s, 3 H, CH₃ *p*-Tol), 2.70 (d, 1 H, *J* = 5.4 Hz, OH), 3.37 (dd, 1 H, *J* = 7.6, 4.7 Hz, H-3), 4.02 (dt, 1 H, *J* = 8.9, 5.1 Hz, H-1'), 7.31 (d, 2 H, *J* = 8.2 Hz, *p*-Tol), 7.55 (d, 2 H, *J* = 8.2 Hz, *p*-Tol). **¹³C NMR (50 MHz)** δ 10.2 (CH₃ Et), 13.8 (CH₃ *n*-Bu), 21.5 (CH₃ *p*-Tol), 22.3, 27.1, 27.9, 29.0, 63.0 (C-1'), 71.3 (C-3), 77.4 (C-2), 125.8 (2 C *p*-Tol), 129.7 (2 C *p*-Tol), 135.9, 142.5. **IR** (film): 3390, 2980, 2950, 2880, 1600, 1500, 1460, 1080, 1040, 810 cm⁻¹. **MS** (EI): 239, 149, 140 (100%), 92, 71, 57.

9.2.2. Synthesis of (+)-(1'S,2R,3R,S_S)-3-*n*-Butyl-2-(1'-hydroxy-2'-methylpropyl)-2-(*p*-tolylsulfinyl)oxirane, **15b, (1'S,2S,3S,S_S)-3-*n*-Butyl-2-(1'-hydroxy-2'-methylpropyl)-2-(*p*-tolylsulfinyl)oxirane, **16b**, (+)-(1'S,2R,3R)-3-*n*-Butyl-2-(1'-hydroxy-2'-methylpropyl)-2-(*p*-tolylsulfonyl)oxirane, **13b**, and (-)-(1'S,2S,3S)-3-*n*-Butyl-2-(1'-hydroxy-2'-methylpropyl)-2-(*p*-tolylsulfonyl)oxirane, **14b**.**

From *t*-BuOOH (71 μ L, 51 mg, 0.566 mmol) in Et₂O (3.50 mL), with *n*-BuLi (1.6 M, 0.44 mL, 0.704 mmol) and a solution of vinyl sulfoxide **3b** (47 mg, 0.16 mmol) in Et₂O (1.20 mL), according to the general procedure (0 °C, 4 h 30 min), a 15:85 mixture of epoxy sulfones **13b** and **14b** was obtained. Purification by chromatography (0-40% EtOAc-hexane) gave 5 mg (10%) of **13b**, and 26 mg (50%) of **14b**, with identical spectral data to that described before.

From KH (13.3 mg, 0.32 mmol) in THF (2.0 mL), *t*-BuOOH (47 μ L, 34 mg, 0.38 mmol) and a solution of vinyl sulfoxide **3b** (49 mg, 0.16 mmol) in THF (1.0 mL), according to the general procedure (0 °C, 2 h), an 80:20 mixture of epoxy sulfoxides **15b** and **16b** was obtained. Purification by chromatography (0-40% EtOAc-CH₂Cl₂) gave 14 mg (28%) of **15b**, as a colorless oil 3 mg (6%) of a mixture of **15b**, **16b** and traces of starting material, and 20 mg (41%) of starting material.

Data of **15b**: *R_f* = 0.29 (10% EtOAc-CH₂Cl₂). [α]_D²⁰ = +261.6 (*c* = 0.209). **¹H NMR (300 MHz)** δ 0.85 (t, 3 H, *J* = 7.1 Hz, CH₃ *n*-Bu), 1.05 (d, 3 H, *J* = 6.8 Hz, CH₃ *i*-Pr), 1.10 (d, 3 H, *J* = 6.5 Hz, CH₃ *i*-Pr), 1.24-1.41 (m, 4 H, 2 H-2', 2 H-3' *n*-Bu), 1.56-1.78 (m, 2 H, 2 H-1' *n*-Bu), 2.28-2.39 (m, 1 H, CH *i*-Pr), 2.41 (s, 3 H, CH₃ *p*-Tol), 2.82 (d, 1 H, *J* = 7.2 Hz, OH), 2.88 (dd, 1 H, *J* = 7.4, 4.9 Hz, H-3), 3.37 (dd, 1 H, *J* = 8.7, 7.2 Hz, H-1'), 7.31 (d, 2 H, *J* = 7.9 Hz, *p*-Tol) 7.50 (d, 2 H, *J* = 8.2 Hz, *p*-Tol). **¹³C NMR (50 MHz)** δ 13.9 (CH₃ *n*-Bu), 18.9 (CH₃ *i*-Pr), 19.3 (CH₃ *i*-Pr), 21.6 (CH₃ *p*-Tol), 22.4 (C-3' *n*-Bu), 27.4 (C-1' *n*-Bu), 28.6 (C-2' *n*-Bu), 32.2 (CH *i*-Pr), 60.0 (C-1'), 76.5 (C-3), 77.2 (C-2), 126.3 (2 C *p*-Tol), 129.8 (2 C *p*-Tol), 134.4 (C-1' *p*-Tol), 142.8 (C-4' *p*-Tol). **IR (CCl₄)**: 3300, 2930, 2900, 2840, 1580, 1470, 1450, 1245, 1070, 995, 790 cm⁻¹. **MS (ES)**: 643 [2M+Na]⁺, 349 [M+K]⁺, 333 [M+Na]⁺ (100%).

Partial data of **16b**: $^1\text{H NMR}$ (300 MHz) δ 3.18 (dd, $J = 7.9, 4.3$ Hz, H-1'), 3.61 (d, $J = 9.8$ Hz, H-3).

9.2.3. Synthesis of (+)-(1'S,2R,3R)-3-*n*-Butyl-2-(1'-hydroxy-2',2'-dimethylpropyl)-2-(*p*-tolylsulfonyl)oxirane, **13c**, and (-)-(1'S,2S,3S)-3-*n*-Butyl-2-(1'-hydroxy-2',2'-dimethylpropyl)-2-(*p*-tolylsulfonyl)oxirane, **14c**.

From *t*-BuOOH (60 μL , 43 mg, 0.477 mmol) in Et_2O (2.50 mL), with *n*-BuLi (1.16 M, 0.41 mL, 0.476 mmol) and a solution of vinyl sulfoxide **3c** (37 mg, 0.17 mmol) in Et_2O (1.0 mL), according to the general procedure (0 °C, 22 h), a 21:66:13 mixture of epoxy sulfones **13c**, **14c** and vinyl sulfone **12c** was obtained. Purification by chromatography (0-30% EtOAc-hexane) gave 9 mg (22%) of **13c**, 23 mg (56%) of **14c**, 4 mg (10%) of a mixture of **13c** and **14c** and 4 mg (10%) of vinyl sulfone **12c**, with identical spectral features to those found before.

9.2.4. Synthesis of ($\pm$)-(1S,2R,3R,5S)-2,3-Epoxy-2-(phenylsulfinyl)-1-cyclohexanol, **15d**.

From KH (24 mg, 0.40 mmol) in THF (6.0 mL), *t*-BuOOH (77.4 μL , 0.42 mmol) and a solution of vinyl sulfoxide **3d** (44 mg, 0.20 mmol) in THF (4.0 mL), according to the general procedure (-30 to -10 °C, 1 h), a 60:40 mixture of epoxy sulfoxide **15d** and epoxy sulfone **13d** was obtained with 58% conversion. Purification by column chromatography (50% CH_2Cl_2 -hexane - 40% EtOAc-hexane) gave 6 mg (33%) of **15d** as a colorless oil, 7 mg (25%) of **13d** and 7 mg (29%) of starting material **3d**.

Data of **15d**: $R_f = 0.20$ (10% EtOAc- CH_2Cl_2). $^1\text{H NMR}$ (300 MHz) δ 1.23-1.47 (m, 3 H, H-4, H-5), 1.54-1.62 (m, 1 H, H-4), 1.66 (br d, 1 H, $J = 6.1$ Hz, OH), 1.78-1.84 (m, 1 H, H-6), 2.10 (tdd, 1 H, $J = 10.8, 5.3, 1.5$ Hz, H-6), 3.95 (dd, 1 H, $J = 2.8, 1.6$ Hz, H-3), 4.40 (br d, 1 H, $J = 4.0$ Hz, H-1), 7.51-7.56 (m, 3 H, Ph), 7.71-7.75 (m, 2 H, Ph). $^{13}\text{C NMR}$ (75 MHz) δ 14.8, 23.9, 30.6, 59.6 (C-1), 61.0 (C-3), 75.0 (C-2), 125.2 (2 C Ph), 129.3 (2 C Ph), 131.9, 139.8. IR (CHCl_3): 3300 (br), 2980, 2930, 1430, 1400, 1170, 1040, 950, 880, 840, 640 cm^{-1} .

9.2.5. Synthesis of (+)-(1'*R*,2*S*,3*S*)-3-*n*-Butyl-2-(1'-hydroxypropyl)-2-(*p*-tolylsulfonyl)oxirane, *ent*-13a, (-)-(1'*R*,2*R*,3*R*)-3-*n*-Butyl-2-(1'-hydroxypropyl)-2-(*p*-tolylsulfonyl)oxirane, *ent*-14a, and (+)-(1'*R*,2*R*,3*R*,*SS*)-3-*n*-Butyl-2-(1'-hydroxypropyl)-2-(*p*-tolylsulfinyl)oxirane, 18a.**

From *t*-BuOOH (18 μ L, 16 mg, 0.20 mmol) in Et₂O (1.0 mL), with *n*-BuLi (1.6 M, 0.12 mL, 0.2 mmol) and a solution of vinyl sulfoxide **4a** (15 mg, 0.05 mmol) in Et₂O (0.35 mL), according to the general procedure (24 h), a 98:2 mixture of epoxy sulfones *ent*-14a and *ent*-13a was obtained. Purification by chromatography (0-30% EtOAc-hexane) gave 11.9 mg (70%) of *ent*-14a, and 0.5 mg (3%) of *ent*-13a, as colorless oils with identical spectral data to that described before. Similarly, when the reaction was carried out in THF (5 h), a 72:28 mixture of *ent*-14a and *ent*-13a was obtained (70%).

From NaH (18 mg, 0.45 mmol) in THF (2.5 mL), *t*-BuOOH (56 μ L, 50 mg, 0.45 mmol) and a solution of vinyl sulfoxide **4a** (42 mg, 0.15 mmol) in THF (1.0 mL), according to the general procedure (45 min), a 10:21:8:61 mixture of starting material, epoxy sulfones *ent*-14a, *ent*-13a and epoxy sulfoxide **18a** was obtained. Purification by chromatography (5-50% EtOAc-hexane) gave 7 mg (13%) of *ent*-14a, 3 mg (6%) of *ent*-13a and 22 mg (41%) of **18a** as colorless oils.

From KH (7 mg, 0.18 mmol) in THF (1.5 mL), *t*-BuOOH (22 μ L, 20 mg, 0.18 mmol) and a solution of vinyl sulfoxide **4a** (24 mg, 0.09 mmol) in THF (0.6 mL), according to the general procedure (45 min), a 20:5:75 mixture of epoxy sulfones *ent*-14a, *ent*-13a and epoxy sulfoxide **18a** was obtained. Purification by chromatography (5-30% EtOAc-hexane) gave 4 mg (15%) of *ent*-14a, and 11 mg (44%) of **18a** as colorless oils.

Data of **18a**: *R*_f = 0.31 (10% EtOAc-CH₂Cl₂). [α]_D²⁰ = +153.9 (*c* = 0.80). ¹H NMR (300 MHz) δ 0.89 (t, 3 H, *J* = 7.2 Hz, CH₃), 1.01 (t, 3 H, *J* = 7.4 Hz, CH₃), 1.32-1.50 (m, 4 H, 2 CH₂), 1.63-1.97 (m, 4 H, 2 CH₂), 2.38 (s, 4 H, OH, CH₃ *p*-Tol), 3.58 (dd, 1 H, *J* = 7.5, 4.0 Hz, H-3), 3.73 (dt, 1 H, *J* = 8.8, 4.4 Hz, H-1'), 7.26 (d, 2 H, *J* = 8.2 Hz, *p*-Tol), 7.56 (d, 2 H, *J* = 8.3 Hz, *p*-Tol). ¹³C NMR (50 MHz) δ 10.3 (CH₃ Et), 13.8 (CH₃ *n*-Bu), 21.5 (CH₃ *p*-Tol), 22.3, 26.9, 27.9, 28.8, 61.4

(C-1'), 74.0 (C-3), 81.1 (C-2), 126.4 (2 C *p*-Tol), 129.4 (2 C *p*-Tol), 137.1 (C-1' *p*-Tol), 142.0 (C-4' *p*-Tol). **IR** (film): 3390, 2960, 2930, 2870, 1600, 1490, 1460, 1080, 1035, 1010, 805 cm⁻¹. **MS** (EI): 296, 278, 140 (100%), 139, 123, 92, 91, 79, 69, 59, 41.

9.2.6. Synthesis of (1'*R*,2*R*,3*R*,*S**S*)-3-*n*-Butyl-2-(1'-hydroxy-2'-methylpropyl)-2-(*p*-tolylsulfinyl)oxirane, **18b**.

From NaH (14.2 mg, 0.59 mmol) in THF (3.80 mL), *t*-BuOOH (74 µL, 53 mg, 0.59 mmol) and a solution of vinyl sulfoxide **4b** (46 mg, 0.16 mmol) in THF (1.70 mL), according to the general procedure (0 °C, 4 h), a >20:<80 mixture of epoxy sulfoxides **17b** and **18b** was obtained. Purification by chromatography (0-40% EtOAc-hexane) gave 18 mg of an inseparable 35:65 mixture of **18b** and starting material. Isomer **17b** was not isolated.

Partial data of **18b**: **¹H NMR (300 MHz)** δ 3.39 (d, 1 H, *J* = 9.9 Hz, H-1'), 3.68 (dd, 1 H, *J* = 8.5, 3.3 Hz, H-3).

9.2.7. Synthesis of (±)-(1*R*,2*S*,3*S*,*S**S*)-2,3-Epoxy-2-(phenylsulfinyl)-1-cyclohexanol, **17d**.

From KH (12 mg, 0.20 mmol) in THF (3.0 mL), *t*-BuOOH (38.7 µL, 0.21 mmol) and a solution of vinyl sulfoxide **4d** (22 mg, 0.10 mmol) in THF (1.0 mL), according to the general procedure (-20 to -10 °C, 35 min), a 96:4 mixture of epoxy sulfoxide **17d** and epoxy sulfone **13d** was obtained with 81% conversion. Purification by column chromatography (15-60% EtOAc-hexane) gave 14 mg (73%) of **17d** as a colorless oil and 3 mg of a mixture of **13d** and starting material **4d**.

Data of **17d**: *R_f* = 0.23 (40% EtOAc-CH₂Cl₂). **¹H NMR (200 MHz)** δ 1.18-2.02 (m, 6 H, H-4, H-5, H-6), 2.63 (br, 1 H, OH), 3.64 (dd, 1 H, *J* = 3.3, 1.3 Hz, H-3), 4.44 (br t, 1 H, *J* = 4.8 Hz, H-1), 7.52-7.57 (m, 3 H, Ph), 7.63-7.70 (m, 2 H, Ph). **¹³C RMN (50 MHz)** δ 16.0, 23.4, 29.7, 58.3 (C-1), 64.5 (C-3), 76.5 (C-2), 125.3 (2 C Ph), 129.3 (2 C Ph), 131.8, 139.5. **IR** (CHCl₃): 3300 (br), 2970, 2915, 2860, 2780, 1690, 1430, 1400, 1170, 1040, 950, 900, 840, 640 cm⁻¹.

9.2.8. Synthesis of (±)-(1'S,2R,3S,S_S)-3-*n*-Butyl-2-(1'-hydroxypropyl)-2-(*p*-tolylsulfinyl)oxirane, **15e.**

From *t*-BuOOH (25 μ L, 18 mg, 0.20 mmol) in Et₂O (1.25 mL), with *n*-BuLi (1.82 M, 0.14 mL, 0.25 mmol) and a solution of vinyl sulfoxide **3e** (19 mg, 0.063 mmol) in Et₂O (0.50 mL), according to the general procedure (0 °C, 4 h 30 min), a 65:35 mixture of epoxy sulfoxide **15e** and epoxy sulfone **13e** was obtained. Purification by chromatography (0-15% EtOAc-CH₂Cl₂) gave 14 mg (70%) of **15e**, as a white solid, recrystallized from 5% EtOAc-hexane, and 4 mg (10%) of epoxy sulfone **13e**.

From NaH (6.1 mg, 0.25 mmol) in THF (1.0 mL), *t*-BuOOH (36 μ L, 26 mg, 0.28 mmol) and a solution of vinyl sulfoxide **3e** (19 mg, 0.063 mmol) in THF (0.50 mL), according to the general procedure (-35 to 0 °C, 1 h 45 min), epoxy sulfoxide **15e** was obtained. Purification by chromatography (0-20% Et₂O-CH₂Cl₂) gave 18 mg (90%) of **15e**, as a white solid, recrystallized from 5% EtOAc-hexane.

Data of **15e**: mp: 53-54 °C. *R_f* = 0.37 (10% EtOAc-CH₂Cl₂). **¹H NMR (300 MHz)** δ 0.77 (t, 3 H, *J* = 7.3 Hz, CH₃), 0.95 (t, 3 H, *J* = 7.2 Hz, CH₃), 1.03-1.09 (m, 1 H), 1.10-1.29 (m, 1 H), 1.40-1.67 (m, 4 H), 1.93-2.01 (m, 2 H), 2.43 (s, 3 H, CH₃ *p*-Tol), 3.17 (m, 1 H, OH), 3.27 (m, 1 H, H-3), 4.03 (ddd, 1 H, *J* = 8.5, 3.9, 1.9 Hz, H-1'), 7.36 (d, 2 H, *J* = 7.9 Hz, *p*-Tol), 7.56 (d, 2 H, *J* = 8.2 Hz, *p*-Tol). **¹³C NMR (50 MHz)** δ 9.5 (CH₃ Et), 13.8 (CH₃ *n*-Bu), 21.4 (CH₃ *p*-Tol), 22.2, 25.4, 28.2, 29.2, 62.1 (C-1'), 68.0 (C-3), 79.5 (C-2), 124.8 (2 C *p*-Tol), 130.2 (2 C *p*-Tol), 136.7 (C-1' *p*-Tol), 142.4 (C-4' *p*-Tol). **IR** (KBr): 3400, 2931, 1628, 1588, 1455, 1022, 806 cm⁻¹. **MS** (ES): 615 [2M+Na]⁺ (100%), 319 [M+Na]⁺, 297 [M+1]⁺.

9.2.9. Synthesis of (±)-(1'S,2R,3S,S_S)-3-*n*-Butyl-2-(1'-hydroxybenzyl)-2-(*p*-tolylsulfinyl)oxirane, **15f.**

From *t*-BuOOH (60 μ L, 43 mg, 0.118 mmol) in Et₂O (1.80 mL), with *n*-BuLi (1.16 M, 0.52 mL, 0.60 mmol) and a solution of vinyl sulfoxide **3f** (49 mg, 0.15 mmol) in Et₂O (0.50 mL), according to the general procedure (0 °C, 2 h), a 93:7 mixture of epoxy sulfoxide **15f** and epoxy sulfone **13f** was obtained. Purification by chromatography (0-10% EtOAc-CH₂Cl₂) gave 31 mg (60%) of **15f**, as a colorless oil, and 4 mg (7%) of **13f**.

From NaH (9 mg, 0.38 mmol) in THF (2.50 mL), *t*-BuOOH (56 μ L, 40 mg, 0.45 mmol) and a solution of vinyl sulfoxide **3f** (49 mg, 0.15 mmol) in THF (1.10 mL), according to the general procedure (-20 °C, 20 min), a 98:2 mixture of epoxy sulfoxide **15f** and epoxy sulfone **13f** was obtained. Purification by chromatography (0-30% Et₂O-CH₂Cl₂) gave 44 mg (85%) **15f**.

Data of **15f**: *R_f* = 0.41 (5% EtOAc-CH₂Cl₂). **¹H NMR (300 MHz)** δ 0.87 (t, 3 H, *J* = 7.1 Hz, CH₃ *n*-Bu), 1.24-1.50 (m, 4 H, 2 H-2', 2 H-3' *n*-Bu), 1.79-1.86 (m, 2 H, 2 H-1' *n*-Bu), 2.43 (ap t, 1 H, *J* = 6.3 Hz, H-3), 2.47 (s, 3 H, CH₃ *p*-Tol), 4.54 (d, 1 H, *J* = 1.2 Hz, OH), 5.37 (d, 1 H, *J* = 1.0 Hz, H-1'), 7.02-7.06 (m, 2 H, Ph), 7.19-7.23 (m, 3 H, Ph), 7.41 (d, 2 H, *J* = 7.9 Hz, *p*-Tol), 7.61 (d, 2 H, *J* = 8.3 Hz, *p*-Tol). **¹³C NMR (50 MHz)** δ 13.8 (CH₃ *n*-Bu), 21.5 (CH₃ *p*-Tol), 22.2 (C-3' *n*-Bu), 28.7 (C-1' *n*-Bu), 29.0 (C-2' *n*-Bu), 63.2 (C-1'), 71.6 (C-3), 79.7 (C-2), 124.6 (2 C Ar), 127.2 (2 C Ar), 128.1 (2 C Ar), 128.3 (CH Ph), 130.5 (2 C Ar), 136.6, 136.7, 142.6. **IR** (film): 3377, 2957, 2928, 1596, 1493, 1453, 1337, 1199, 1083, 1053, 1025, 917, 810, 731 cm⁻¹. **MS** (ES): 367 [M+Na]⁺ (100%).

9.2.10. Synthesis of (±)-(1'S,2R,3S,5S)-3-Phenyl-2-(1'-hydroxypropyl)-2-(p-tolylsulfinyl)oxirane, **15g.**

From *t*-BuOOH (25 μ L, 18 mg, 0.20 mmol) in Et₂O (1.25 mL), with *n*-BuLi (1.82 M, 0.14 mL, 0.25 mmol) and a solution of vinyl sulfoxide **3g** (19 mg, 0.063 mmol) in Et₂O (0.50 mL), according to the general procedure (0 °C, 5 h 45 min), a 92:8 mixture of epoxy sulfoxide **15g** and epoxy sulfone **13g** was obtained. Purification by chromatography (0-15% EtOAc-CH₂Cl₂) gave 14 mg (70%) of **15g**, as a white solid, recrystallized from 5% EtOAc-hexane, and 4 mg (10%) of **13g**.

From NaH (6.1 mg, 0.25 mmol) in THF (1.0 mL), *t*-BuOOH (36 μ L, 26 mg, 0.28 mmol) and a solution of vinyl sulfoxide **3g** (19 mg, 0.063 mmol) in THF (0.50 mL), according to the general procedure (-30 °C, 4 h 30 min), epoxy sulfoxide **15g** was obtained. Purification by chromatography (0-20% Et₂O-CH₂Cl₂) gave 18 mg (90%) of **15g**, as a white solid, recrystallized from 5% EtOAc-hexane.

Data of **15g**: mp: 120-121 °C. *R_f* = 0.33 (10% EtOAc-CH₂Cl₂). **¹H NMR (300 MHz)** δ 0.81 (t, 3 H, *J* = 7.3 Hz, CH₃ Et), 1.06-1.14 (m, 1 H, CH₂ Et), 1.24-1.42 (m, 1 H, CH₂), 2.34 (s, 3 H, CH₃ *p*-Tol), 3.82 (m, 1 H, OH), 4.28 (s, 1 H, H-3), 4.46 (ddd, 1 H, *J* = 8.4, 4.4, 1.7 Hz, H-1'), 6.88 (d, 2 H, *J* = 8.3 Hz, *p*-Tol), 7.15 (d, 2 H, *J* = 8.5 Hz, *p*-Tol), 7.39-7.46 (m, 5 H, Ph). **¹³C NMR (50 MHz)** δ 9.6 (CH₃ Et), 21.4 (CH₃ *p*-Tol), 25.1 (CH₂ Et), 61.5 (C-1'), 67.8 (C-3), 81.7 (C-2), 124.4 (2 C Ar), 127.2 (2 C Ar), 128.6 (2 C Ar), 129.2 (CH Ph), 129.9 (2 C Ar), 132.0, 135.8, 142.3. **IR** (KBr): 3449, 1622, 1495, 1455, 1082, 1045, 804, 748 cm⁻¹. **MS** (ES): 339 [M+Na]⁺ (100%).

9.2.11. Synthesis of (±)-(1'*R*,2*S*,3*R*,*SS*)-3-*n*-Butyl-2-(1'-hydroxypropyl)-2-(*p*-tolylsulfinyl)oxirane, **17e**, and (±)-(1'*R*,2*R*,3*S*,*S**S*)-3-*n*-Butyl-2-(1'-hydroxypropyl)-2-(*p*-tolylsulfinyl)oxirane, **18e**.**

From KH (7 mg, 0.17 mmol) in THF (1.0 mL), *t*-BuOOH (27 µL, 16 mg, 0.18 mmol) and a solution of vinyl sulfoxide **4e** (13 mg, 0.043 mmol) in THF (0.30 mL), according to the general procedure (-10 to 0 °C, 3 h), a 52:48 mixture of epoxy sulfoxides **17e** and **18e** was obtained. Purification by chromatography (0-60% EtOAc-CH₂Cl₂) gave 6 mg (29%) of **17e**, as a white solid, recrystallized from 5% EtOAc-hexane, 4 mg (19%) of **18e**, as a colorless oil and 9 mg (45%) of starting material.

From NaH (19 mg, 0.81 mmol) in THF (4.0 mL), *t*-BuOOH (100 µL, 0.81 mmol) and a solution of vinyl sulfoxide **4e** (57 mg, 0.203 mmol) in THF (1.50 mL), according to the general procedure (-20 to 0 °C, 3 h), a 33:16:51 mixture of epoxy sulfoxides **17e** and **18e** and starting material was obtained. Purification by chromatography (0-10% EtOAc-CH₂Cl₂) gave 17 mg (27%) of **17e**, 8 mg (13%) of **18e**, and 24 mg (42%) of starting material.

Data of **17e**: mp: 72-73 °C. *R_f* = 0.46 (10% EtOAc-hexane). **¹H NMR (300 MHz)** δ 0.91 (t, 3 H, *J* = 7.3 Hz, CH₃), 0.97 (t, 3 H, *J* = 7.2 Hz, CH₃), 1.41-1.65 (m, 5 H), 1.73 (d, 1 H, *J* = 3.5 Hz, OH), 1.88 (ddt, 1 H, *J* = 14.0, 7.6, 3.2 Hz), 2.02-2.09 (m, 2 H), 2.41 (s, 3 H, CH₃ *p*-Tol), 3.44 (t, 1 H, *J* = 6.4 Hz, H-3), 3.78 (td, 1 H, *J* = 8.8, 3.3 Hz, H-1'), 7.32 (d, 2 H, *J* = 8.5 Hz, *p*-Tol), 7.56 (d, 2 H, *J* = 8.4 Hz, *p*-Tol). **¹³C NMR (75 MHz)** δ 9.8 (CH₃ Et), 13.9 (CH₃ *n*-Bu), 21.4 (CH₃ *p*-Tol), 22.4, 27.2, 27.5, 28.5, 62.2 (C-1'), 68.0 (C-3), 75.2 (C-2), 125.0 (2 C *p*-Tol), 129.8 (2 C *p*-Tol), 136.2 (C-1' *p*-Tol), 141.7 (C-4' *p*-Tol). **IR** (CHCl₃): 3340, 2900, 2810, 1570, 1465, 1435, 1360, 1270, 1113, 1065, 780 cm⁻¹. **MS** (ES): 615 [2M+Na]⁺, 319 [M+Na]⁺ (100%). **Anal. calcd for C₁₆H₂₄O₃S**: C, 64.83; H, 8.16; S, 10.82. **Found**: C, 64.80; H, 7.68; S, 10.70.

Data of **18e**: *R_f* = 0.22 (10% EtOAc-CH₂Cl₂). **¹H NMR (300 MHz)** δ 0.88 (t, 3 H, *J* = 7.3 Hz, CH₃), 0.94 (t, 3 H, *J* = 7.2 Hz, CH₃), 1.27-1.68 (m, 6 H, 2 H-2', 2 H-3' *n*-Bu, CH₂ Et), 1.88-1.97 (m, 2 H, 2 H-1', *n*-Bu), 2.41 (s, 3 H, CH₃ *p*-Tol), 3.34 (dd, 1 H, *J* = 8.1, 4.4 Hz, H-3), 4.04 (dd, 1 H, *J*

= 9.0, 4.3 Hz, H-1'), 7.35 (d, 2 H, J = 7.9 Hz, *p*-Tol), 7.57 (d, 2 H, J = 8.3 Hz, *p*-Tol). **¹³C NMR (75 MHz)** δ 9.9 (CH₃ Et), 13.9 (CH₃ *n*-Bu), 21.5 (CH₃ *p*-Tol), 22.3, 25.9, 28.6, 29.3, 61.2 (C-1'), 68.9 (C-3), 80.5 (C-2), 124.6 (2 C *p*-Tol), 130.3 (2 C *p*-Tol), 137.1 (C-1' *p*-Tol), 142.0 (C-4' *p*-Tol). **IR** (CHCl₃): 3340, 2910, 2880, 1570, 1465, 1430, 1055, 1005, 780 cm⁻¹. **MS** (ES): 615 [2M+Na]⁺, 319 [M+Na]⁺ (100%).

9.2.12. Synthesis of (±)-(1'*R*,2*S*,3*R*,*SS*)-3-*n*-Butyl-2-(1'-hydroxybenzyl)-2-(*p*-tolylsulfinyl)oxirane, **13f**, (±)-(1'*R*,2*R*,3*S*)-3-*n*-Butyl-(1'-hydroxybenzyl)-2-(*p*-tolylsulfonyl)oxirane, **14f**, and (±)-(2*R*,3*S*)-3-*n*-Butyl-2-(*p*-tolylsulfonyl)oxirane, **14f'**.**

From *t*-BuOOH (24 μ L, 17 mg, 0.21 mmol) in Et₂O (1.0 mL), with *n*-BuLi (1.16 M, 0.21 mL, 0.24 mmol) and a solution of vinyl sulfoxide **4f** (19 mg, 0.063 mmol) in Et₂O (0.50 mL), according to the general procedure (0 °C, 5 h), a 63:13:24 mixture of epoxy sulfones **13f**, **14f** and **14f'** was obtained with 60% conversion. Purification by chromatography (0-10% EtOAc-CH₂Cl₂) gave 6 mg (27%) of **13f**, 3 mg (14%) of **14f**, 5 mg (36%) of **14f'** and 4 mg (20%) of starting material, as colorless oils.

9.2.13. Synthesis of (±)-(1'*R*,2*S*,3*R*,*SS*)-3-*n*-Butyl-2-(1'-hydroxybenzyl)-2-(*p*-tolylsulfinyl)oxirane, **17f**, and (±)-(1'*R*,2*R*,3*S*,*S**S*)-3-*n*-Butyl-2-(1'-hydroxybenzyl)-2-(*p*-tolylsulfinyl)oxirane, **18f**.**

From NaH (6.6 mg, 0.28 mmol) in THF (1.70 mL), *t*-BuOOH (36 μ L, 26 mg, 0.28 mmol) and a solution of vinyl sulfoxide **4f** (36 mg, 0.11 mmol) in THF (0.80 mL), according to the general procedure (-35 to 0 °C, 2 h), a 78:4:18 mixture of epoxy sulfoxides **17f** and **18f** and epoxy sulfone **13f** was obtained. Purification by chromatography (0-10% Et₂O-CH₂Cl₂) gave 20 mg (53%) of **17f**, as a white solid, recrystallized from 5% EtOAc-hexane, 2 mg (5%) of **18f** and 4 mg (10%) of **13f**.

Data of **17f**: **mp**: 99-100 °C. **R_f** = 0.36 (5% Et₂O-CH₂Cl₂). **¹H NMR (400 MHz)** δ 0.91 (t, 3 H, J = 7.1 Hz, CH₃ *n*-Bu), 1.25-1.51 (m, 4 H, 2 H-2', 2 H-3' *n*-Bu) 1.89-1.96 (m, 2 H, 2 H-1' *n*-Bu), 2.41 (s, 3 H, CH₃ *p*-Tol), 2.53 (d, 1 H, J = 6.3 Hz, OH), 2.88 (t, 1 H, J = 6.3 Hz, H-3), 5.43 (d, 1 H,

$J = 6.2$ Hz, H-1'), 7.25-7.30 (m, 7 H, ArH), 7.55 (d, 2 H, $J = 8.2$ Hz, *p*-Tol). **^{13}C NMR (50 MHz)** δ 13.8 (CH₃ *n*-Bu), 21.4 (CH₃ *p*-Tol), 22.3 (C-3' *n*-Bu), 27.8 (C-1' *n*-Bu), 28.1 (C-2' *n*-Bu), 65.8 (C-1'), 68.5 (C-3), 77.3 (C-2), 125.1 (2 C Ar), 126.3 (2 C Ar), 127.7 (CH Ph), 128.2 (2 C Ar), 129.8 (2 C Ar), 136.0, 139.2, 141.7. **IR** (KBr): 3338, 2926, 1644, 1592, 1453, 1268, 1088, 1035, 813, 698 cm⁻¹. **MS** (ES): 367 [M+Na]⁺ (100%). **Anal. calcd for C₂₀H₂₄O₃S**: C, 69.73; H, 7.02; S, 9.31. **Found**: C, 69.36; H, 7.33; S, 9.65.

Partial data of **18f**: **^1H NMR (200 MHz)** δ 2.42 (s, 3 H, CH₃ *p*-Tol), 2.98 (dd, 1 H, $J = 7.8$, 4.7 Hz, H-3), 5.36 (s, 1 H, H-1').

9.2.14. Synthesis of (±)-(1'*R*,2*S*,3*R*,*S**S*)-3-Phenyl-2-(1'-hydroxypropyl)-2-(*p*-tolylsulfinyl)oxirane, **17g**, and (±)-(1'*R*,2*R*,3*S*,*S**S*)-3-Phenyl-2-(1'-hydroxypropyl)-2-(*p*-tolylsulfinyl)oxirane, **18g**.

From **KH** (7 mg, 0.17 mmol) in THF (1.0 mL), *t*-BuOOH (22 μL , 16 mg, 0.18 mmol) and a solution of vinyl sulfoxide **4g** (13 mg, 0.043 mmol) in THF (0.30 mL), according to the general procedure (-20 to 4 °C, 92 h), a 15:85 mixture of epoxy sulfoxides **17g** and **18g** was obtained. Purification by chromatography (0-60% EtOAc-CH₂Cl₂) gave 7 mg (50%) of **18g**, as a white solid, recrystallized from 5% EtOAc-hexane, 3 mg (21%) of a mixture of **17g** and **18g** and 1 mg (8%) of starting material.

Data of **17g**: *R_f* = 0.32 (5% EtOAc-CH₂Cl₂). **^1H NMR (200 MHz)** δ 1.01 (t, 3 H, $J = 7.3$ Hz, CH₃ Et), 1.62-1.77 (m, 1 H, CH₂ Et), 1.87 (d, 1 H, $J = 3.5$ Hz, OH), 1.94-2.06 (m, 1 H, CH₂ Et), 2.42 (s, 3 H, CH₃ *p*-Tol), 3.92 (td, 1 H, $J = 8.4$, 3.5 Hz, H-1'), 4.62 (s, 1 H, H-3), 7.34 (d, 2 H, $J = 8.1$ Hz, *p*-Tol), 7.40-7.47 (m, 5 H, Ph), 7.59 (d, 2 H, $J = 8.2$ Hz, *p*-Tol). **MS** (APCI): 317 [M+1]⁺, 177 [M-139]⁺ (100%).

Data of **18g**: **mp**: 156-157 °C. *R_f* = 0.15 (5% EtOAc-CH₂Cl₂). **^1H NMR (400 MHz)** δ 0.97 (t, 3 H, $J = 7.4$ Hz, CH₃ Et), 1.40-1.51 (m, 1 H, CH₂ Et), 1.80 (ddt, 1 H, $J = 14.3$, 6.8, 4.2 Hz, CH₂ Et), 2.33 (s, 3 H, CH₃ *p*-Tol), 4.31 (ap quint, $J = 4.2$, 1 H, H-1'), 4.43 (s, 1 H, H-3), 7.00 (d, 2 H, $J = 7.6$ Hz, *p*-Tol), 7.17 (d, 2 H, $J = 7.9$ Hz, *p*-Tol), 7.32-7.48 (m, 5 H, Ph). **^{13}C NMR (50 MHz)** δ 10.0 (CH₃ Et), 21.4 (CH₃ *p*-Tol), 26.1 (CH₂ Et), 60.0 (C-1'), 67.8 (C-3), 82.8 (C-2), 124.1 (2 C Ar), 127.2

(2 C Ar), 128.5 (2 C Ar), 128.9 (CH Ph), 130.1 (2 C Ar), 132.5, 136.6, 142.0. **IR** (KBr): 3409, 2973, 1633, 1494, 1450, 1112, 1082, 1037, 1013, 913, 804 cm⁻¹. **MS** (ES): 655 [2M+Na]⁺ (100%), 355 [M+K]⁺, 339 [M+Na]⁺, 317 [M+1]⁺.

10. Chemical Correlations

10.1. Oxidation of (+)-(1'S,2S,3S,S_S)-3-*n*-Butyl-2-(1'-hydroxypropyl)-2-(*p*-tolylsulfinyl)oxirane, **16a**.

From hydroxy epoxy sulfoxide **16a** (4 mg, 0.02 mmol) in MeOH (0.2 mL) and MMPP (16 mg, 0.04 mmol), according to the general procedure (24 h), after chromatography (5-30% EtOAc-hexane), epoxy sulfone **14a** (3 mg, 75%) was obtained as a colorless oil.

10.2. Oxidation of (+)-(1'S,2R,3R,S_S)-3-*n*-Butyl-2-(1'-hydroxy-2'-methylpropyl)-2-(*p*-tolylsulfinyl)oxirane, **15b**.

From hydroxy epoxy sulfoxide **15b** (4 mg, 0.013 mmol) in MeOH (0.50 mL) and MMPP (16 mg, 0.032 mmol), according to the general procedure (0 °C, 16 h), after chromatography (0-20% EtOAc-CH₂Cl₂), epoxy sulfone **13b** (2 mg, 48%) was obtained as a colorless oil with identical spectral data to that described above.

10.3. Oxidation of (1'*R*,2*R*,3*R*,*S**S*)-3-*n*-Butyl-2-(1'-hydroxy-2'-methylpropyl)-2-(*p*-tolylsulfinyl)oxirane, **18b**.

From a 40:60 mixture of epoxy sulfoxide **18b** and vinyl sulfoxide **4b** (16 mg, 0.013 mmol) in MeOH (0.50 mL) and MMPP (62 mg, 0.125 mmol), according to the general procedure (0 °C, 7 h 35 min), a 40:60 mixture of epoxy sulfone **ent-14b** and vinyl sulfone **ent-12b** was obtained as a colorless oil with identical spectral data to that described above.

10.4. Oxidation of (±)-(1*S*,2*R*,3*R*,*S**S*)-2,3-Epoxy-2-(phenylsulfinyl)-1-cyclohexanol, **15d**.

From hydroxy epoxy sulfoxide **15d** (4 mg, 0.02 mmol) in MeOH (1 mL) and MMPP (25 mg, 0.05 mmol), according to the general procedure (3 h 30 min), after chromatography (20-60% EtOAc-hexane), epoxy sulfone **13d** (2 mg, 47%) was obtained as a white solid.

10.5. Oxidation of (±)-(1*R*,2*S*,3*S*,*S**S*)-2,3-Epoxy-2-(phenylsulfinyl)-1-cyclohexanol, **17d**.

From hydroxy epoxy sulfoxide **17d** (6 mg, 0.034 mmol) in MeOH (1 mL) and MMPP (50 mg, 0.1 mmol), according to the general procedure (1 h), after chromatography (20-60% EtOAc-hexane), epoxy sulfone **13d** (3 mg, 48%) was obtained as a white solid that was recrystallized from EtOAc-hexane.

Data of **13d**: mp: 95-98 °C. *R*_f = 0.31 (50% EtOAc-hexane). ¹H NMR (300 MHz) δ 1.29-1.60 (m, 3 H, H-5, OH), 1.78-1.89 (m, 2 H, H-4), 2.00-2.09 (m, 2 H, H-6), 4.04 (dd, 1 H, *J* = 2.8, 1.6 Hz, H-3), 4.77 (t, 1 H, *J* = 4.8 Hz, H-1), 7.49-7.58 (m, 2 H, Ph), 7.64-7.70 (m, 1 H, Ph), 7.91-7.95 (m, 2 H, Ph). ¹³C NMR (75 MHz) δ 14.7, 23.5, 30.1, 59.9 (C-1), 63.5 (C-2), 74.0 (C-3), 129.0 (2 C Ph), 129.5 (2 C Ph), 134.3, 136.6. IR (film): 3350 (br), 2930, 2860, 1440, 1080, 1040, 750 cm⁻¹. MS (APCI): 253 [M-1]⁻, 141 (100%).

10.6. Oxidation of (±)-(1'S,2R,3S,S_S)-3-*n*-Butyl-2-(1'-hydroxypropyl)-2-(*p*-tolylsulfinyl)oxirane, **15e**.

From epoxy sulfoxide **15e** (14 mg, 0.047 mmol) in CH₂Cl₂ (0.50 mL), K₂CO₃ (33 mg, 0.24 mmol) and *m*-CPBA (32 mg, 0.13 mmol), according to the general procedure (rt, 96 h), epoxy sulfone **13e** (10 mg, 67%) was obtained after chromatography (0-30% EtOAc-hexane) with identical spectral data to that described above.

10.7. General Procedure for Oxidation with *t*-BuOOH/VO(acac)₂.

To a solution of the sulfoxide in benzene (4 mL/mmol) at room temperature was added VO(acac)₂ (0.10 M solution in benzene, or solid). After 5 min a solution of *t*-BuOOH (5.5 M in decane), if necessary, further diluted in benzene to measure accurately (0.5 mL/mmol) was added and the mixture turned reddish. Often, sequential additions of reagents were needed to assure completion of the reaction (TLC). The reaction was then quenched with 1 M Na₂S₂O₄ solution (4 mL/mmol), diluted with EtOAc (4 mL/mmol) and the aqueous layer was extracted with EtOAc (2 times, 4 mL/mmol). The combined organic extracts were washed with saturated NaCl (4 mL/mmol), dried over MgSO₄, filtered and concentrated under reduced pressure to give a crude product that was filtered through a plug of silica gel to remove the catalyst. After monitoring by ¹H NMR, the crude product was purified by column chromatography on silica gel using the appropriate mixture of solvents.

10.7.1. Oxidation of (±)-(1'R,2S,3R,S_S)-3-*n*-Butyl-2-(1'-hydroxypropyl)-2-(*p*-tolylsulfinyl)oxirane, **17e**.

From epoxy sulfoxide **17e** (4 mg, 0.013 mmol) in benzene (0.70 mL), with VO(acac)₂ (2 mg, 0.008 mmol, 2 additions), *t*-BuOOH (12 μL, 0.066 mmol), following the general procedure (20 h), epoxy sulfone **13e** (4 mg, 95%) was obtained after column chromatography (0-5% EtOAc-CH₂Cl₂).

10.7.2. Oxidation of (±)-(1'*R*,2*R*,3*S*,*SS*)-3-Phenyl-(1'-hydroxypropyl)-2-(*p*-tolylsulfinyl)oxirane, **18e**.**

From epoxy sulfoxide **18e** (4 mg, 0.013 mmol) in benzene (0.50 mL), with VO(acac)₂ (1 mg, 0.004 mmol, 1 additions), *t*-BuOOH (10 μ L, 0.055 mmol), following the general procedure (24 h), epoxy sulfone **14e** (4 mg, 95%) was obtained after column chromatography (0-10% Et₂O-CH₂Cl₂).

Data of **14e**: *R_f* = 0.63 (10% EtOAc-CH₂Cl₂). **¹H NMR (200 MHz)** δ 0.76 (t, 3 H, *J* = 7.3 Hz, CH₃), 0.92 (t, 3 H, *J* = 7.3 Hz, CH₃), 1.21-1.54 (m, 6 H, 2 H-2', 2 H-3' *n*-Bu, CH₂ Et), 2.15 (dt, 2 H, *J* = 14.7, 6.4 Hz, 2 H-1' *n*-Bu), 2.45 (s, 3 H, CH₃ *p*-Tol), 2.83 (d, 1 H, *J* = 4.2 Hz, OH), 3.26 (t, 1 H, *J* = 6.3 Hz, H-3), 3.86 (ap dt, 1 H, *J* = 6.8, 4.4 Hz, H-1'), 7.36 (d, 2 H, *J* = 7.9 Hz, *p*-Tol), 7.81 (d, 2 H, *J* = 8.2 Hz, *p*-Tol). **¹³C NMR (50 MHz)** δ 10.2 (CH₃ Et), 13.9 (CH₃ *n*-Bu), 21.7 (CH₃ *p*-Tol), 22.3, 23.9, 26.7, 29.2, 63.7 (C-1'), 72.8 (C-3), 77.2 (C-2), 129.0 (2 C *p*-Tol), 129.8 (2 C *p*-Tol), 134.7 (C-1' *p*-Tol), 145.4 (C-4' *p*-Tol). **IR** (film): 3500, 2975, 2860, 1590, 1450, 1310, 1160, 1125, 1075, 935, 805 cm⁻¹. **MS** (ES): 647 [2M+Na]⁺, 335 [M+Na]⁺ (100%).

10.8. Oxidation of (±)-(1'*S*,2*R*,3*S*,*SS*)-3-*n*-Butyl-2-(1'-hydroxybenzyl)-2-(*p*-tolylsulfinyl)oxirane, **15f**.**

From hydroxy epoxy sulfoxide **15f** (13 mg, 0.038 mmol) in MeOH (0.40 mL) and MMPP (47 mg, 0.076 mmol), according to the general procedure (0 °C, 1 h 35 min), after chromatography (0-10% EtOAc-CH₂Cl₂), epoxy sulfone **13f** (8 mg, 57%) was obtained as a colorless oil with identical spectral data to that described above.

10.9. Oxidation of (±)-(1'*R*,2*S*,3*R*,*SS*)-3-*n*-Butyl-2-(1'-hydroxybenzyl)-2-(*p*-tolylsulfinyl)oxirane, **17f**.**

From hydroxy epoxy sulfoxide **17f** (9 mg, 0.026 mmol) in MeOH (0.50 mL) and MMPP (32 mg, 0.065 mmol), according to the general procedure (4 °C, 28 h), after chromatography (0-10% EtOAc-CH₂Cl₂), epoxy sulfone **13f** (6 mg, 60%) was obtained as a colorless oil with identical spectral data to that described above.

10.10. Oxidation of (±)-(1'*S*,2*R*,3*S*,*SS*)-3-Phenyl-2-(1'-hydroxypropyl)-2-(*p*-tolylsulfinyl)oxirane, **15g**.**

From hydroxy epoxy sulfoxide **15g** (5 mg, 0.016 mmol) in MeOH (0.50 mL) and MMPP (30 mg, 0.06 mmol), according to the general procedure (0 °C to rt, 10 h), after chromatography (0-10% EtOAc-CH₂Cl₂), epoxy sulfone **13g** (4 mg, 80%) was obtained as a colorless oil with identical spectral data to that described above.

10.11. Oxidation of (±)-(1'*R*,2*S*,3*R*,*SS*)-3-Phenyl-(1'-hydroxypropyl)-2-(*p*-tolylsulfinyl)oxirane, **17g**.**

From epoxy sulfoxide **17g** (2 mg, 0.006 mmol) in CH₂Cl₂ (0.50 mL), K₂CO₃ (5 mg, 0.032 mmol) and *m*-CPBA (5 mg, 0.019 mmol), according to the general procedure (4 °C, 18 h 30 min), epoxy sulfone **13g** (1 mg, 50%) was obtained after chromatography (0-10% EtOAc-CH₂Cl₂) with identical spectral data to that described above.

10.12. Oxidation of (±)-(1'*R*,2*R*,3*S*,5*S*)-3-Phenyl-(1'-hydroxypropyl)-2-(*p*-tolylsulfinyl)oxirane, **18g.**

From epoxy sulfoxide **18g** (6 mg, 0.013 mmol) in benzene (0.70 mL), with VO(acac)₂ (1 mg, 0.004 mmol, 1 addition), *t*-BuOOH (12 μL, 0.066 mmol), following the general procedure (14 h), epoxy sulfone **14g** (4 mg, 95%) was obtained after column chromatography (0-10% Et₂O-CH₂Cl₂).

Data of **14g**: *R*_f = 0.19 (5% EtOAc-CH₂Cl₂). **¹H NMR (200 MHz)** δ 1.02 (t, 3 H, *J* = 7.4 Hz, CH₃ Et), 1.59-1.80 (m, 2 H, CH₂ Et), 2.37 (s, 3 H, CH₃ *p*-Tol), 2.99 (d, 1 H, *J* = 5.9 Hz, OH), 4.23 (dt, 1 H, *J* = 9.0, 5.4 Hz, H-1'), 4.36 (s, 1 H, H-3), 7.06-7.21 (m, 7 H, ArH), 7.32 (d, 2 H, *J* = 8.6 Hz, *p*-Tol). **¹³C NMR (75 MHz)** δ 10.4 (CH₃ Et), 21.6 (CH₃ *p*-Tol), 25.0 (CH₂ Et), 61.6 (C-1'), 73.1 (C-3), 79.6 (C-2), 126.6 (2 C Ar), 127.9 (2 C Ar), 128.0 (CH Ph), 129.1 (2 C Ar), 129.3 (2 C Ar), 131.1, 134.0, 144.9. **IR** (CHCl₃): 3512, 3020, 2926, 2801, 1597, 1495, 1453, 1319, 1216, 1156, 1081, 813, 756 cm⁻¹. **MS** (ES): 355 [M+Na]⁺ (100%), 687 [2M+Na]⁺.

10.13. Synthesis of (±)-(Z)-2,2-Dimethyl-4-nonen-3-ol, **19.**

To a cold (−78 °C) solution of racemic vinyl sulfoxide **3c** (41 mg, 0.13 mmol) in Et₂O (1.5 mL), MeLi (0.88 M, 0.44 mL, 0.39 mmol) followed by *t*-BuLi (1.5 M, 0.34 mL, 0.51 mmol) was added dropwise. After 10 min, the reaction was quenched with MeOH (4 mL/mmol) and H₂O (4 mL/mmol), extracted with EtOAc (3 times, 5 mL/mmol) and the organic layer was washed with a saturated solution of NaCl (4 mL/mmol), dried over MgSO₄, filtered and concentrated under reduced pressure to give a crude mixture that was purified by chromatography (0-10% Et₂O-CH₂Cl₂) to give 10 mg (45%) of allylic alcohol **19**, and 13 mg of *t*-butyl *p*-tolyl sulfoxide.

Data of **19**: *R*_f = 0.65 (10% EtOAc-CH₂Cl₂). **¹H NMR (300 MHz)** δ 0.88 (s, 9 H, 3 CH₃ *t*-Bu), 0.86-0.93 (m, 3 H, CH₃ *n*-Bu), 1.23-1.36 (m, 4 H, 2 H-7, 2 H-8), 1.50 (br s, 1 H, OH), 1.98-2.17 (m, 2 H, 2 H-6), 4.06 (d, 1 H, *J* = 9.2 Hz, H-3), 5.40 (ddt, 1 H, *J* = 11.0, 9.4, 1.6 Hz, H-4), 5.49-5.58

(m, 1 H, H-5). **¹³C NMR (50 MHz)** δ 14.1 (CH₃ *n*-Bu), 22.5 (C-8), 25.6 (3 CH₃ *t*-Bu), 27.7 (C-6), 29.0 (C-7), 45.5 (C-2), 75.0 (C-3), 129.1 (C-4), 133.8 (C-5). **IR** (CHCl₃): 3435, 2960, 2921, 2851, 1464, 1095, 803 cm⁻¹.

10.14. General Procedure for Epoxidation with *m*-CPBA.

To a solution of the corresponding allylic alcohol in CH₂Cl₂ (10 mL/mmol) was added K₂CO₃ (4.0 equiv), the resulting suspension was cooled to 0 °C and 70% *m*-CPBA (2.5 equiv) was added. The mixture was stirred and allowed to warm up to 4 °C (refrigerator) and monitored by TLC until completion. The reaction was quenched with 1 M Na₂S₂O₄ (5 mL/mmol) and saturated NaHCO₃ (3 mL/mmol) and extracted with EtOAc (3 times, 5 mL/mmol). The organic layer was washed with saturated NaCl (4 mL/mmol), dried over MgSO₄ filtered and concentrated under reduced pressure to give a crude product that was purified by column chromatography.

10.15. Synthesis of (±)-(1'*S*,2*R*,3*S*)-3-*n*-Butyl-2-(1'-hydroxy-2',2'-dimethylpropyl)oxirane, *syn*-20.

From allylic alcohol **19** (10 mg, 0.059 mmol) in CH₂Cl₂ (0.60 mL), with K₂CO₃ (32 mg, 0.235 mmol), and *m*-CPBA (36 mg, 0.15 mmol), following the general procedure 4 °C (20 h), epoxy alcohol *syn*-**20** (7 mg, 64%) was obtained after column chromatography (0-20% Et₂O-CH₂Cl₂) as a single isomer.

Data of *syn*-**20**: *R_f* = 0.25 (CH₂Cl₂). **¹H NMR (300 MHz)** δ 0.87 (t, 3 H, *J* = 7.3 Hz, CH₃ *n*-Bu), 0.96 (s, 9 H, 3 CH₃ *t*-Bu), 1.27-1.54 (m, 6 H), 3.02-3.10 (m, 2 H, H-2, H-3), 3.06 (d, 1 H, *J* = 7.2 Hz, H-1'). **¹³C NMR (50 MHz)** δ 14.0 (CH₃ *n*-Bu), 22.5 (C-3' *n*-Bu), 25.5 (3 CH₃ *t*-Bu), 28.1, 29.0, 34.3 (C-2' *t*-Bu), 57.7, 59.5, 75.1 (C-1').

10.16. Synthesis of (±)-(1'S,2R,3R)-3-*n*-Butyl-2-(1'-hydroxy-2',2'-dimethylpropyl)oxirane, **21**.

A round-bottomed flask was charged with anhydrous MeOH (1.0 mL), epoxy sulfone **13c** (35 mg, 0.103 mmol), Na₂HPO₄ (5.9 mg, 0.412 mmol) and this mixture was cooled to 0 °C. Then, Na(Hg) (6%, 1300 mg) was added, in small pieces and the mixture was quenched with a saturated solution of NH₄Cl (4 mL/mmol) and H₂O (4 mL/mmol). The crude mixture was extracted with EtOAc (3 times, 4 mL/mmol), the organic extract was washed with saturated solution of NaCl, dried over MgSO₄, filtered and concentrated under reduced pressure to give the crude product, that was purified by column chromatography (0-15% EtOAc-hexane), affording 8 mg (42%) of **21** and 12 mg (34%) of starting material.

Data of **21**: *R_f* = 0.10 (CH₂Cl₂). ¹H NMR (400 MHz) δ 0.89 (t, 3 H, *J* = 7.9 Hz, CH₃ *n*-Bu), 0.96 (s, 9 H, 3 CH₃ *t*-Bu), 1.34-1.44 (m, 4 H, 2 H-2', 2 H-3' *n*-Bu), 1.48-1.55 (m, 2 H, 2 H-1' *n*-Bu), 1.93 (d, *J* = 6.0 Hz, OH), 2.82-2.85 (m, 1 H), 2.85-2.88 (m, 1 H), 3.06 (dd, 1 H, *J* = 5.9, 5.0 Hz, H-1'). ¹³C NMR (50 MHz) δ 13.9 (CH₃ *n*-Bu), 22.5 (C-3' *n*-Bu), 25.8 (3 CH₃ *t*-Bu), 28.1, 29.0, 34.7 (C-2), 57.1, 58.5, 78.2 (C-1'). IR (CHCl₃): 3469, 2928, 2871, 1466, 1364, 1142, 1016 cm⁻¹. MS (ES): 209 [M+Na]⁺, 169 [M-17]⁺ (100%).

10.17. Synthesis of the *p*-nitrobenzoate of (+)-(1'R,2R,3R,5S)-3-*n*-Butyl-2-(1'-hydroxypropyl)-2-(*p*-tolylsulfinyl)oxirane, **18a**, **22**.

A round-bottomed flask was charged with THF (0.6 mL), epoxy sulfoxide **18a** (18 mg, 0.060 mmol), freshly distilled Et₃N (20 μL, 14.5 mg, 0.12 mmol) and 2-3 crystals of DMAP and the resulting mixture was cooled to 0 °C. After 10 min *p*-nitrobenzoyl chloride (17 mg, 0.090 mmol) was added and, after stirring for 4 h, the reaction was quenched with a saturated solution of NaHCO₃ (4 mL/mmol). The mixture was extracted with EtOAc (3 times, 8 mL/mmol), washed with a saturated solution of NaCl (4 mL/mmol), dried over MgSO₄, filtered and concentrated under reduced pressure to give a crude product, that was purified by column chromatography (5-30% EtOAc-hexane), affording

18 mg (67%) of **22** as a white solid.

Data of **22**: mp: 107-109 °C. $R_f = 0.20$ (30% EtOAc-hexane). $[\alpha]^{20}_D = +62.4$ ($c = 0.60$).

¹H NMR (200 MHz) δ 0.91 (t, 3 H, $J = 7.1$ Hz, CH₃), 0.93 (t, 3 H, $J = 7.4$ Hz, CH₃), 1.32-2.15 (m, 8 H, 4 CH₂), 2.33 (s, 3 H, CH₃ *p*-Tol), 3.67 (dd, 1 H, $J = 7.8, 4.1$ Hz, H-3), 5.34 (dd, 1 H, $J = 8.6, 6.2$ Hz, H-1'), 7.22 (d, 2 H, $J = 8.4$ Hz, *p*-Tol), 7.65 (d, 2 H, $J = 8.2$ Hz, *p*-Tol), 7.72 (d, 2 H, $J = 8.9$ Hz, *p*-NO₂Bz), 8.16 (d, 2 H, $J = 8.9$ Hz, *p*-NO₂Bz). **¹³C NMR (50 MHz)** δ 10.6 (CH₃ Et), 14.6 (CH₃ *n*-Bu), 22.2, 23.1, 25.2, 25.9, 28.8, 62.1 (C-1'), 75.4 (C-3), 77.5 (C-2), 123.9 (2 C Ar), 127.7 (2 C Ar), 130.5 (2 C Ar), 131.4 (2 C Ar), 135.2, 138.0, 143.5, 148.6, 174.0. **IR** (CHCl₃): 3020, 2960, 2930, 1730, 1610, 1530, 1350, 1270, 1230, 1100, 1040, 1020 cm⁻¹. **MS** (EI): 445 [M]⁺, 306, 274, 236, 208, 155, 150 (100%), 139, 120, 97, 69, 55.

10.18. Synthesis of (±)-(1'S,2S,3S)-3-Phenyl-2-(1'-hydroxypropyl)oxirane, **23**.

To a cold (-78°C) solution of epoxy sulfoxide **15g** (8 mg, 0.025 mmol) in THF (0.40 mL), *n*-BuLi (1.8 M, 0.13 mL, 0.23 mmol) was added dropwise and, after stirring during 55 min, the mixture was quenched with a saturated solution of NH₄Cl. The crude mixture was extracted with EtOAc (3 times, 4 mL/mmol), the organic extract was washed with saturated solution of NaCl, dried over MgSO₄, filtered and concentrated under reduced pressure to give a crude product, that was purified by column chromatography (0-30% EtOAc-hexane), affording 3 mg (68%) of **23** and 5 mg of *n*-butyl *p*-tolyl sulfoxide.

Data of **23**: $R_f = 0.32$ (30% EtOAc-hexane). **¹H NMR (200 MHz)** δ 1.02 (t, 3 H, $J = 7.5$ Hz, CH₃ Et), 1.48-1.78 (m, 2 H, CH₂ Et), 1.93 (d, 1 H, $J = 2.2$ Hz, OH), 3.07 (t, 1 H, $J = 2.6$ Hz, H-2), 3.86-3.94 (m, 1 H, H-1'), 3.95 (d, 1 H, $J = 2.0$ Hz, H-3), 7.26-7.37 (m, 5 H, Ph).

10.19. Synthesis of (±)-(1'S,2S,3S)-3-Phenyl-2-(1'-hydroxypropyl)oxirane, **23, and (±)-(1'S,2R,3R)-3-Phenyl-2-(1'-hydroxypropyl)oxirane, **24**.**

From 5-phenyl-(*E*)-pent-4-en-3-ol (39 mg, 0.24 mmol) in CH₂Cl₂ (1.80 mL), with K₂CO₃ (135 mg, 0.977 mmol), and *m*-CPBA (132 mg, 0.54 mmol), following the general procedure 0 °C (6 h 30 min), a 25:75 mixture of epoxy alcohols **23** and **25** (43 mg, 90%) was obtained after column chromatography (0-20% Et₂O-CH₂Cl₂) as a colorless oil.

Data of **25**: *R_f* = 0.32 (30% EtOAc-hexane). **¹H NMR (200 MHz)** δ 1.03 (t, 3 H, *J* = 7.4 Hz, CH₃ Et), 1.52-1.78 (m, 2 H, CH₂ Et), 2.68 (br s, 1 H, OH), 3.04 (dd, 1 H, *J* = 4.8, 2.2 Hz, H-2), 3.57 (td, 1 H, *J* = 6.7, 4.9 Hz, H-1'), 3.87 (d, 1 H, *J* = 2.0 Hz, H-3), 7.24-7.35 (m, 5 H, Ph).

1. Watson, S. C.; Eastham, J. E. *J. Organomet. Chem.* **1967**, 9, 165-168.