Supporting Information for

Metal-Catalyzed Oxidation and Epoxidation of α - Hydroxy Vinyl and Dienyl Sulfoxides

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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, benzene and CH_2Cl_2 were distilled from CaH_2 , and THF and Et_2O from sodium. $(\text{MeO})_2\text{P}(\text{O})\text{Me}$, $\text{BF}_3\cdot\text{OEt}_2$, SnCl_4 , Et_3N , and *i*- Pr_2NH were distilled from CaH_2 . Crude products were purified by flash chromatography on 230-400 mesh silica gel with distilled solvents. Analytical TLC was carried out on silica gel plates with detection by UV light, iodine, acidic vanillin solution, 10% phosphomolybdic acid solution in ethanol. All reagents were commercial products. Organolithium reagents were titrated prior to use.¹ Through this section, the volume of solvents is reported in mL/mmol of starting material. ^1H and ^{13}C NMR spectra were recorded at 200, 300, 400 or 500 MHz (^1H) 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), ap (apparent). Melting points are uncorrected. Optical rotations were measured at 20 °C using a sodium lamp and in CHCl_3 solution. Low resolution mass spectra were recorded using the electronic impact technique with an ionization energy of 70 eV or using the atmospheric pressure chemical ionization (APCI) or electrospray (ES) chemical ionization techniques in its positive or negative modes.

1. Preparation of Starting Materials.

1.1. General Procedure for Synthesis of Hydroxy Vinyl and Dienyl Sulfoxides.

A round-bottomed flask was charged with THF (3.5 mL/mmol) and 2.6 equiv of freshly distilled *i*- Pr_2NH , and cooled to $-78\text{ }^\circ\text{C}$. To the above solution was added 2.5 equiv of *n*-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 *Z/E* mixture of vinyl or dienyl 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 $-78\text{ }^\circ\text{C}$, 3-5 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 that was purified by column chromatography using the appropriate mixture of eluents.

1.2. Synthesis of (±)-(E)-(3*R*,*S*_S)-4-(*tert*-Butylsulfinyl)-1-phenylnon-4-en-3-ol, **1e, and (±)-(E)-(3*S*,*S*_S)-4-(*tert*-Butylsulfinyl)-1-phenylnon-4-en-3-ol, **1e'**.**

From an *E/Z* mixture of 1-hexenyl *t*-butyl sulfoxides,² (564 mg, 3.0 mmol, 1.0 equiv) with 2.5 equiv of LDA and with hydrocinnamaldehyde (1.97 mL, 2010 mg, 15.0 mmol), following the general procedure, a 47:63 mixture of alcohols **1e** and **1e'** was obtained. Chromatographic separation (5-20% EtOAc-CH₂Cl₂), gave **1e'** (578 mg, 54%) and **1e** (330 mg, 31%) as white solids.

Data for **1e**: mp: 117-118 °C. *R*_f = 0.20 (50% EtOAc-hexane). ¹H NMR (300 MHz) δ 0.88 (t, 3 H, *J* = 6.9 Hz), 1.17-1.41 (m, 13 H), 1.93-2.31 (m, 4 H), 2.68-2.78 (m, 1 H), 2.85-2.92 (m, 1 H), 4.50 (ddd, 1 H, *J* = 9.9, 3.6 Hz), 5.78 (m, 1 H, *J* = 7.6 Hz), 7.15-7.30 (m, 5 H). ¹³C NMR (75 MHz) δ 13.7, 22.4, 24.0 (3 C), 28.4, 31.3, 32.4, 40.7, 57.2, 70.6, 125.9, 128.4, 128.5, 137.2, 141.4, 141.5. IR (KBr): 3339 (br), 2957, 2927, 2860, 1643, 1603, 1496, 1455, 1364, 1170, 1018, 749, 699 cm⁻¹. MS (ES): 323 [M+1]⁺ (100%), 345 [M+Na]⁺. Anal. calcd for C₁₉H₃₀O₂S: C, 70.76; H, 9.38; S, 9.94. Found: C, 70.32; H, 9.29; S, 10.11.

Data for **1e'**: mp: 116-117 °C. *R*_f = 0.23 (50% EtOAc-hexane) ¹H NMR (300 MHz) δ 0.89 (t, 3 H, *J* = 7.0 Hz), 1.21-1.44 (m, 13 H), 1.97-2.17 (m, 2 H), 2.30-2.40 (m, 2 H), 2.63-2.73 (m, 1 H), 2.80-2.86 (m, 1 H), 4.64 (q, 1 H), 6.09 (t, 1 H, *J* = 7.7 Hz), 7.15-7.30 (m, 5 H). ¹³C NMR (75 MHz) δ 13.8, 22.4, 23.6 (3 C), 28.6, 31.3, 32.4, 39.3, 56.4, 67.4, 126.0, 128.5, 128.6, 137.1, 140.5, 141.5. IR (KBr): 3319 (br), 2956, 2920, 2858, 1636, 1495, 1454, 1363, 1171, 1068, 1030, 1005, 748, 700 cm⁻¹. MS (ES): 323 [M+1]⁺ (100%), 345 [M+Na]⁺. Anal. calcd for C₁₉H₃₀O₂S: C, 70.76; H, 9.38; S, 9.94. Found: C, 70.45; H, 9.49; S, 10.33.

1.3. Synthesis of (±)-(E)-(3*R*,*S*_S)-2-(*tert*-Butylsulfinyl)-1-phenylpent-1-en-3-ol, **1g, and (±)-(E)-(3*S*,*S*_S)-2-(*t*-Butylsulfinyl)-1-phenylpent-1-en-3-ol, **1g'**.**

From an *E/Z* mixture of 2-phenyl-1-etenyl *t*-butyl sulfoxides,² (625 mg, 3.0 mmol, 1.0 equiv) with 2.5 equiv of LDA and with propionaldehyde (1.09 mL, 15.0 mmol), following the general procedure, a

45:65 mixture of alcohols **1g** and **1g'** was obtained. Chromatographic separation (10-50% EtOAc-hexane), gave **1g'** (416 mg, 52%) and **1g** (288 mg, 31%) as white solids.

Data for **1g**: mp: 123-124 °C. $R_f = 0.22$ (50% EtOAc-hexane). $^1\text{H NMR}$ (300 MHz) δ 0.95 (t, 3 H, $J = 7.4$ Hz), 1.37(s, 9 H), 1.72-2.00 (m, 2 H), 3.77 (br d, 1 H, $J = 7.8$ Hz), 4.63 (m, 1 H), 6.85 (s, 1 H), 7.32-7.41 (m, 3 H), 7.46-7.49 (m, 2 H). $^{13}\text{C NMR}$ (75 MHz) δ 10.6, 24.2 (3 C), 30.9, 58.5, 73.5, 128.6, 128.7 (2 C), 129.5 (2 C), 133.9, 134.5, 144.2. IR (CH₂Cl₂): 3590 (br), 3363, 3047, 2967, 1458, 1365, 1272, 1267, 1166, 1008, 750, 745, 729, 719, 712, 703 cm⁻¹. MS (APCI): 267 [M+1]⁺ (100%), 209, 193, 175, 135. Anal. calcd for C₁₅H₂₂O₂S: C, 67.63; H, 8.32; S, 12.04. Found: C, 67.86; H, 8.17; S, 11.91.

Data for **1g'**: mp: 120-122 °C. $R_f = 0.20$ (50% EtOAc-hexane). $^1\text{H NMR}$ (300 MHz) δ 0.90 (t, 3 H, $J = 7.3$ Hz), 1.33(s, 9 H), 1.75-1.82 (m, 2 H), 3.74 (br, 1 H), 4.72 (m, 1 H), 7.27 (s, 1 H), 7.28-7.39 (m, 3 H), 7.53-7.57 (m, 2 H). $^{13}\text{C NMR}$ (75 MHz) δ 10.2, 23.7 (3 C), 29.3, 57.3, 69.6, 128.4, 128.5 (2 C), 129.6 (2 C), 134.5, 136.4, 144.5. IR (CH₂Cl₂): 3595 (br), 2967, 1262, 1257, 1053, 764, 758, 753, 740, 734, 727, 720, 703 cm⁻¹. MS (APCI): 267 [M+1]⁺ (100%), 193, 175, 136. Anal. calcd for C₁₅H₂₂O₂S: C, 67.63; H, 8.32; S, 12.04. Found: C, 67.31; H, 8.23; S, 11.83.

1.4. Synthesis of (±)-(2*R*,*S*_S)-1-Cyclohexylidenyl-1-(*p*-tolylsulfinyl)butan-2-ol, **3**, and (±)-(2*S*,*S*_S)-1-Cyclohexylidenyl-1-(*p*-tolylsulfinyl)butan-2-ol, **3'**.

From racemic cyclohexylidenemethyl *p*-tolyl sulfoxide,³ (234 mg, 1 mmol, 1.0 equiv) with 2.5 equiv of LDA and with propionaldehyde (0.22 mL, 3.0 mmol, 3.0 equiv), following the general procedure, a 39:61 mixture of alcohols **3** and **3'** was obtained. Chromatographic separation (10-80% EtOAc-hexane) afforded **3** (105 mg, 36%) and **3'** (74 mg, 25%) as white solids.

Data for **3**: mp: 121-125 °C. $R_f = 0.11$ (20% EtOAc-hexane). $^1\text{H NMR}$ (200 MHz) δ 0.79 (t, 3 H, $J = 7.4$ Hz), 1.41-1.83 (m, 8 H), 2.38 (s, 3 H), 2.39-2.52 (m, 2 H), 2.64-2.83 (m, 2 H), 2.88 (br s, 1 H), 4.47-4.54 (m, 1 H), 7.28 (d, 2 H, $J = 7.9$ Hz), 7.43 (d, 2 H, $J = 8.2$ Hz). $^{13}\text{C NMR}$ (50 MHz) δ 10.7, 21.2, 26.2, 27.9, 28.3, 30.7, 32.2, 32.3, 71.7, 124.3 (2 C), 129.8 (2 C), 136.9, 140.3, 140.9, 153.4. IR (KBr): 3391, 3284, 2931, 1625, 1448, 1082, 1005 cm⁻¹. MS (ES): 607 [2M+Na]⁺ (100%), 293 [M+1]⁺. Anal. calcd for C₁₇H₂₄O₂S: C, 69.82; H, 8.27; S, 10.96. Found: C, 69.80; H, 8.03; S, 10.75.

Data for **3'**: mp: 118-122 °C. R_f = 0.13 (40% EtOAc-hexane). $^1\text{H NMR}$ (200 MHz) δ 0.77 (t, 3 H, J = 7.4 Hz), 1.06-1.18 (m, 1 H), 1.52-1.82 (m, 7 H), 2.37 (s, 3 H), 2.37-2.41 (m, 2 H), 2.50-2.56 (m, 1 H), 2.62-2.68 (m, 1 H), 3.33 (d, 1 H, J = 5.9 Hz), 4.50 (dd, 1 H, J = 5.4, 4.6 Hz), 7.26 (d, 2 H, J = 8.3 Hz), 7.45 (d, 2 H, J = 8.3 Hz). $^{13}\text{C NMR}$ (50 MHz) δ 10.9, 21.2, 26.1, 27.8, 28.0, 31.9, 32.1, 32.2, 70.3, 124.6 (2 C), 129.7 (2 C), 137.8, 140.4, 140.9, 151.0. IR (KBr): 3384, 2931, 2853, 1632, 1452, 1081, 1042, 802 cm^{-1} . MS (APCI): 293 $[\text{M}+1]^+$, 275 $[\text{M}-\text{H}_2\text{O}]^+$ (100%). Anal. calcd for $\text{C}_{17}\text{H}_{24}\text{O}_2\text{S}$: C, 69.82; H, 8.27; S, 10.96. Found: C, 69.75; H, 8.40; S, 10.77.

1.5. Synthesis of ($\pm$)-(4*E*,6*E*)-(3*R*,*S*₅)-4-(*p*-Tolylsulfinyl)octa-4,6-dien-3-ol, **6d, and ($\pm$)-(4*E*,6*E*)-(3*S*,*S*₅)-4-(*p*-Tolylsulfinyl)octa-4,6-dien-3-ol, **6d'**.**

From 1,3-pentadienyl *p*-tolyl sulfoxide,³ (247mg, 1.20 mmol) with 2.5 equiv of LDA and with propionaldehyde (0.28 mL, 3.85 mmol), following the general procedure, a 45:55 mixture of hydroxy trienyl sulfoxides **6d** and **6d'** was obtained. Chromatographic purification (0-80% EtOAc- CH_2Cl_2), gave **6d** (88 mg, 28%) as a colorless oil and **6d'** (109 mg, 34%) colorless oil.

Data for **6d**: R_f = 0.34 (30% EtOAc- CH_2Cl_2). $^1\text{H NMR}$ (200 MHz) δ 0.82 (t, 3 H, J = 7.4 Hz), 1.44-1.54 (m, 1 H), 1.61-1.73 (m, 1 H), 1.85 (dd, 3 H, J = 6.8, 1.6 Hz), 2.30 (d, 1 H, J = 2.0 Hz), 2.36 (s, 3 H), 4.41-4.47 (m, 1 H), 6.10 (dq, 1 H, J = 13.7, 6.8 Hz), 6.47 (ddq, 1 H, J = 14.5, 11.3, 1.7 Hz), 6.87 (d, 1 H, J = 11.2 Hz), 7.24 (d, 2 H, J = 7.9 Hz), 7.50 (d, 2 H, J = 8.3 Hz). $^{13}\text{C NMR}$ (50 MHz) δ 10.3, 18.7, 21.4, 30.3, 70.9, 125.2 (2 C), 125.6, 129.8 (2 C), 134.2, 138.9, 141.0, 141.3, 143.0. IR (film): 3367, 2964, 1644, 1492, 1451, 1080, 1025, 809 cm^{-1} . MS (ES): 265 $[\text{M}+1]^+$ (100%). Anal. calcd for $\text{C}_{15}\text{H}_{20}\text{O}_2\text{S}$: C, 68.14; H, 7.62; S, 12.13. Found: C, 68.43; H, 7.30; S, 11.81.

Data for **6d'**: R_f = 0.22 (30% EtOAc- CH_2Cl_2). $^1\text{H NMR}$ (200 MHz) δ 0.75 (t, 3 H, J = 7.4 Hz), 1.11-1.22 (m, 1 H), 1.44-1.54 (m, 1 H), 1.83 (dd, 3 H, J = 6.8, 1.7 Hz), 2.35 (s, 3 H), 3.03 (br s, 1 H), 4.34 (dd, 1 H, J = 9.5, 8.6 Hz), 6.03 (dq, 1 H, J = 14.9, 6.8, 0.6 Hz), 6.51 (ddq, 1 H, J = 14.9, 11.2, 1.7 Hz), 6.76 (d, 1 H, J = 11.2 Hz), 7.23 (d, 2 H, J = 7.8 Hz), 7.47 (d, 2 H, J = 8.2 Hz). $^{13}\text{C NMR}$ (50 MHz) δ 10.5, 18.7, 21.4, 30.5, 69.8, 125.4 (2 C), 126.0, 129.8 (2 C), 133.3, 138.2, 140.1, 141.4, 144.0. IR (film): 3359, 2964, 2930, 1644, 1492, 1450, 1080, 1027, 810 cm^{-1} . MS (ES): 551 $[2\text{M}+1]^+$, 265 $[\text{M}+1]^+$ (100%). Anal. calcd for $\text{C}_{15}\text{H}_{20}\text{O}_2\text{S}$: C, 68.14; H, 7.62; S, 12.13. Found: C, 68.01; H, 7.84; S, 12.33.

1.6. Synthesis of (±)-(4E)-(3R,S_S)-2-Methyl-4-(p-tolylsulfinyl)hepta-1,4,6-trien-3-ol, **7c, and (±)-(4E)-(3S,S_S)-2-Methyl-4-(p-tolylsulfinyl)hepta-1,4,6-trien-3-ol, **7c'**.**

From 1-butadienyl *p*-tolyl sulfoxide,³ (135 mg, 0.70 mmol) with 2.5 equiv of LDA and with methacrolein (0.29 mL, 3.50 mmol), following the general procedure, a 40:60 mixture of hydroxy trienyl sulfoxides **7c** and **7c'** was obtained. Chromatographic purification (5-30% EtOAc-hexane and 1-100% EtOAc-CH₂Cl₂), gave **7c** (47 mg, 26%) as a colorless oil and **7c'** (67 mg, 37%) as a pale yellow oil and 14 mg (7%) of mixture.

Data for **7c**: R_f = 0.32 (15% EtOAc-hexane); 0.38 (15% EtOAc-CH₂Cl₂). ¹H NMR (300 MHz) δ 1.55 (dd, 3 H, J = 2.0, 0.8 Hz), 2.27 (d, 1 H, J = 4.6 Hz), 2.36 (s, 3 H), 4.91-4.93 (m, 2 H), 5.08 (m, 1 H), 5.46 (ddd, 1 H, J = 10.4, 1.6, 0.5 Hz), 5.58 (ddd, 1 H, J = 16.7, 1.6, 0.5 Hz), 6.77 (ddd, 1 H, J = 16.7, 11.2, 10.0 Hz), 7.00 (d, 1 H, J = 11.2 Hz), 7.24 (d, 2 H, J = 8.3 Hz), 7.52 (d, 2 H, J = 8.4 Hz). ¹³C NMR (75 MHz) δ 19.4, 21.8, 71.2, 112.6, 125.9 (2 C), 126.0 (2 C), 130.3, 130.6, 134.9, 140.9, 142.1, 144.4, 144.7. IR (film): 3351 (br), 2922, 1653, 1595, 1492, 1449, 1303, 1144, 1081, 1031, 810, 754 cm⁻¹. MS (ES): 263 [M+1]⁺ (100%), 285 [M+Na]⁺, 245 [M-18]⁺. Anal. calcd for C₁₅H₁₈O₂S: C, 68.67; H, 6.92; S, 12.22. Found: C, 69.01; H, 7.03; S, 12.02.

Data for **7c'**: R_f = 0.27 (15% EtOAc-hexane); 0.24 (15% EtOAc-CH₂Cl₂). ¹H NMR (300 MHz) δ 1.37 (s, 3 H), 2.36 (s, 3 H), 3.21 (br s, 1 H), 4.75 (br s, 1 H), 4.80 (quint, 1 H, J = 1.5 Hz), 5.00 (m, 1 H), 5.40-5.44 (m, 1 H), 5.46-5.56 (m, 1 H), 6.80-6.90 (m, 2 H), 7.23 (d, 2 H, J = 8.4 Hz), 7.48 (d, 2 H, J = 8.2 Hz). ¹³C NMR (75 MHz) δ 19.3, 21.9, 71.1, 112.8, 125.7 (2 C), 126.1 (2 C), 130.4, 131.2, 135.2, 139.9, 142.4, 144.0, 145.1. IR (film): 3367 (br), 2922, 1652, 1595, 1492, 1449, 1303, 1144, 1081, 1034, 1013, 907, 809, 754 cm⁻¹. MS (ES): 263 [M+1]⁺ (100%), 245 [M-18]⁺. Anal. calcd for C₁₅H₁₈O₂S: C, 68.67; H, 6.92; S, 12.22. Found: C, 68.35; H, 7.14; S, 11.90.

2. Metal-Catalyzed Epoxidations.

2.1. General Procedure for Oxidation/Epoxidation of Unsaturated Sulfoxides with VO(acac)₂/*t*-BuOOH.

To a solution of the vinyl or dienyl sulfoxide in anhydrous benzene (4 mL/mmol) was added the catalyst, generally VO(acac)₂ (0.01 M in benzene, 0.05 equiv). After stirring for 5 min at rt, *t*-BuOOH was added (0.5 M in benzene, typically 80% in *t*-BuOO*t*-Bu) and the mixture changed from blue to red. A rapid oxidation to the alkenyl or dienyl sulfone followed and if necessary additional amounts of VO(acac)₂ and *t*-BuOOH were added at 1-3 h intervals or upon discoloration of the mixture, until disappearance of the alkenyl sulfone. Upon completion (TLC), the reaction was quenched with 1 M Na₂S₂O₄, diluted with EtOAc (8 mL/mmol) and the layers were separated. The aqueous layer was extracted with EtOAc and the combined organic layers 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 that was purified by chromatography on silica gel using the appropriate mixture of eluents. In most cases, especially those involving the obtention of vinyl oxiranes, higher yields were obtained with 5 equiv of *t*-BuOOH and purifying the crude products as soon as possible. The precise rate of the epoxidation is highly dependent on the type of commercial *t*-BuOOH used with the aqueous reagent being slowest and the commercially available anhydrous reagents being fastest.

2.2. Synthesis of (–)-(1'*R*,2*S*,3*S*)-3-*n*-Butyl-2-(1'-hydroxypropyl)-2-(*p*-tolylsulfonyl)oxirane, **8a**.

From a solution of vinyl sulfoxide **1a**,⁴ (24 mg, 0.09 mmol) in C₆H₆ (0.8 mL) with VO(acac)₂ (0.1 equiv) and *t*-BuOOH (2.5 equiv) according to the general procedure (3 days) epoxy sulfone **8a** (19 mg, 75%) was obtained as a colorless oil after chromatography. The data was identical data to that found before.⁵

2.3. Synthesis of (–)-(1'*R*,2*S*,3*S*)-3-*n*-Butyl-2-(1'-hydroxy-2'-methylpropyl)-2-(*p*-tolylsulfonyl)oxirane, **8b**.

From a solution of vinyl sulfoxide **1b**,⁵ (37 mg, 0.126 mmol) in C₆H₆ (1.5 mL) with VO(acac)₂ (0.15 equiv) and *t*-BuOOH (3.0 equiv) according to the general procedure (28 h) epoxy sulfone **8b** (31 mg, 76%) was obtained as a white solid after chromatography (50-100% CH₂Cl₂-hexane). The data was identical data to that found before.⁵

2.4. Synthesis of (–)-(1′*R*,2*S*,3*S*)-3-*n*-Butyl-2-(1′-hydroxy-2′,2′-dimethylpropyl)-2-(*p*-tolylsulfonyl)oxirane, **8c**.

From a solution of vinyl sulfoxide **1c**,⁵ (34 mg, 0.11 mmol) in C₆H₆ (1.7 mL) with VO(acac)₂ (0.25 equiv) and *t*-BuOOH (4.0 equiv) according to the general procedure (132 h) epoxy sulfone **8c** (31 mg, 84%) was obtained as a white solid after chromatography (50-100% CH₂Cl₂-hexane). The data was identical data to that found before.⁵

2.5. Synthesis of (±)-(1′*S*,2′*R*,2*S*,3*S*)-2-(1′-Hydroxy-2′-chloropentyl)-3-*i*-propyl-2-(*p*-tolylsulfinyl)oxirane, **8d**.

From a solution of sulfenyl chlorohydrin **1d**⁶ (20 mg, 0.06 mmol) in C₆H₆ (3.6 mL) with VO(acac)₂ (0.65 equiv) and *t*-BuOOH (9.0 equiv) according to the general procedure (56 h) a 33:67 mixture of vinyl sulfone **1d''** and epoxy sulfone **8d** was obtained. Chromatography (0-50% EtOAc-hexane) gave **1d''** (3.8 mg, 18%) and **8d** (10.3 mg, 47%) as colorless oils.

Data for **1d''**: *R*_f = 0.38 (20% EtOAc-hexane). ¹H NMR (200 MHz) δ 0.88 (t, 3 H, *J* = 7.1 Hz), 1.12 (d, 6 H, *J* = 6.6 Hz), 1.20-1.70 (m, 4 H), 2.42 (s, 3 H), 2.81-2.93 (m, 1 H), 3.61 (d, 1 H, *J* = 8.8 Hz), 3.87 (dt, 1 H, *J* = 9.2, 2.6 Hz), 4.55 (dd, 1 H, *J* = 9.2, 8.8 Hz), 6.82 (d, 1 H, *J* = 10.6 Hz), 7.31 (d, 2 H, *J* = 8.4 Hz), 7.72 (d, 2 H, *J* = 8.1 Hz).

Data for **8d**: *R*_f = 0.29 (20% EtOAc-hexane). ¹H NMR (200 MHz) δ 0.86 (t, 3 H, *J* = 7.2 Hz), 1.08 (d, 6 H, *J* = 6.6 Hz), 1.20-1.70 (m, 4 H), 2.02 (s, 1 H), 2.45 (s, 3 H), 3.42 (d, 1 H, *J* = 9.6 Hz), 3.54 (s, 1 H), 3.57 (d, 1 H, *J* = 9.6 Hz), 4.12 (t, 1 H, *J* = 8.1 Hz), 7.34 (d, 2 H, *J* = 8.6 Hz), 7.80 (d, 2 H, *J* = 8.2 Hz). ¹³C NMR (75 MHz) δ 13.3, 18.5, 18.7, 20.1, 26.9, 27.2, 36.1, 60.4, 66.7, 75.2, 76.3, 129.2 (2 C), 129.8 (2 C), 134.3, 145.8. IR (film): 3501, 2963, 2927, 2869, 1595, 1465, 1400, 1315, 1259, 1140, 1082, 1046, 976, 810, 720 cm⁻¹. MS (ES): 399 [M+K]⁺ (100%), 383 [M+Na]⁺. Anal. calcd for C₁₇H₂₅ClO₄S: C, 56.58; H, 6.98; S, 8.88. Found: C, 56.71; H, 7.23; S, 9.19.

2.6. Synthesis of (±)-(1'*R*,2*S*,3*S*)-3-*n*-Butyl-2-(*tert*-butylsulfonyl)-2-(3'-phenyl-1'-hydroxypropyl)oxirane, **8e**.

From a solution of vinyl sulfoxide **1e** (32 mg, 0.1 mmol) in C_6H_6 (2.9 mL) with $\text{VO}(\text{acac})_2$ (0.25 equiv) and *t*-BuOOH (8.5 equiv) according to the general procedure (4 days) epoxy sulfone **8e** (19 mg, 54%) was obtained as a colorless oil after chromatography (5-30% EtOAc-hexane).

Data for **8e**: $R_f = 0.39$ (30% EtOAc-hexane). $^1\text{H NMR}$ (300 MHz) δ 0.90 (t, 3 H, $J = 7.2$ Hz), 1.17-1.54 (m, 4 H), 1.39 (s, 9 H), 1.61-1.82 (m, 2 H), 2.01 (dddd, 1 H, $J = 14.0, 10.4, 9.4, 4.9$ Hz), 2.29 (dddd, 1 H, $J = 13.7, 9.8, 7.3, 2.3$ Hz), 2.51 (br d, 1 H, $J = 5.5$ Hz), 2.73 (ddd, 1 H, $J = 13.8, 9.3, 7.3$ Hz), 2.95 (ddd, 1 H, $J = 14.2, 9.9, 4.8$ Hz), 3.66 (dd, 1 H, $J = 7.7, 4.5$ Hz), 4.09 (br dd, 1 H, $J = 10.5, 2.3$ Hz), 7.14-7.30 (m, 5 H). $^{13}\text{C NMR}$ (50 MHz) δ 13.8, 22.3, 24.1 (3 C), 27.1, 28.8, 32.4, 35.1, 62.9, 63.9, 68.9, 79.5, 126.0, 128.4 (2 C), 128.6 (2 C), 141.1. IR (CHCl_3): 3420 (br), 2940, 2880, 2850, 2780, 1560, 1450, 1440, 1410, 1350, 1320, 1250, 1170, 1070, 880, 650, 620 cm^{-1} . MS (APCI): 391 $[\text{M}+\text{Cl}]^+$, 389 $[\text{M}+\text{Cl}]^+$ (100%), 373 $[\text{M}+\text{NH}_4]^+$, 356 $[\text{M}+1]^+$ (100%). Anal. calcd for $\text{C}_{19}\text{H}_{30}\text{O}_4\text{S}$: C, 64.37; H, 8.53; S, 9.05. Found: C, 64.14; H, 8.72; S, 9.33.

2.7. Synthesis of (+)-(1'*R*,2*R*,3*R*)-2-(1'-Hydroxypropyl)-3-phenyl-2-(*p*-tolylsulfonyl)oxirane, **9f**.

From a solution of vinyl sulfoxide **1f**,⁴ (30 mg, 0.1 mmol) in C_6H_6 (1.9 mL) with $\text{VO}(\text{acac})_2$ (0.15 equiv) and *t*-BuOOH (7.0 equiv) according to the general procedure (72 h) epoxy sulfone **9f** (22 mg, 60%) was obtained as a white solid (recrystallized from Et_2O -hexane) after chromatography (0-5% EtOAc- CH_2Cl_2).

Data for **9f**: mp: 94-96 °C. $R_f = 0.37$ (1% EtOAc- CH_2Cl_2). $[\alpha]_D^{20} = +20.1$ ($c = 0.60$). $^1\text{H NMR}$ (200 MHz) δ 0.74 (t, 3 H, $J = 7.4$ Hz), 1.59 (quint, 2 H, $J = 7.4$ Hz), 2.48 (s, 3 H), 2.65 (br s, 1 H), 3.23 (br s, 1 H), 4.80 (s, 1 H), 7.32-7.40 (m, 7 H), 7.75 (d, 2 H, $J = 8.4$ Hz). $^{13}\text{C NMR}$ (50 MHz) δ 10.4, 21.8, 27.1, 62.5, 71.6, 78.7, 126.5 (2 C), 128.5 (2 C), 128.9, 129.5 (2 C), 129.8 (2 C), 131.4, 134.5, 145.7. IR (KBr): 3540, 2990, 2980, 2960, 1600, 1450, 1400, 1310, 1300, 1290, 1140, 1080, 1060, 1030, 920, 820, 760, 710, 690 cm^{-1} . MS (APCI): 331 $[\text{M}-1]^-$ (100%); 333 $[\text{M}+1]^+$ (100%). Anal. calcd for $\text{C}_{18}\text{H}_{20}\text{O}_4\text{S}$: C, 65.04; H, 6.06; S, 9.65. Found: C, 65.29; H, 6.39; S, 9.30.

2.8. Synthesis of (±)-(1'*R*,2*R*,3*R*)-2-(1'-Hydroxypropyl)-3-phenyl-2-(*tert*-buylsulfonyl)oxirane, **9g.**

From a solution of vinyl sulfoxide **1g** (40 mg, 0.152 mmol) in C₆H₆ (1.3 mL) with VO(acac)₂ (0.30 equiv) and *t*-BuOOH (7.0 equiv) according to the general procedure (86 h) epoxy sulfone **9g** (20 mg, 44%) was obtained as a white solid after chromatography (5-20% EtOAc-hexane).

Data for **9g**: mp: 88-90 °C. *R_f* = 0.13 (15% EtOAc-hexane). ¹H NMR (300 MHz) δ 0.92 (t, 3 H, *J* = 7.3 Hz), 1.51 (s, 9 H), 1.75-1.81 (m, 2 H), 2.52 (d, 1 H, *J* = 10.4 Hz), 3.34 (dt, 1 H, *J* = 9.8, 4.7 Hz), 4.75 (s, 1 H), 7.35 (s, 5 H). ¹³C NMR (75 MHz) δ 10.6, 23.9 (3 C), 26.9, 63.2, 64.0, 72.0, 81.5, 126.4 (2 C), 128.6 (2 C), 128.9, 131.6. IR (KBr): 3488, 2970, 2933, 2875, 1626, 1499, 1457, 1391, 1371, 1317, 1285, 1266, 1232, 1195, 1129, 1111, 1095, 1075, 1061, 1021, 981, 916, 798, 762, 714, 700, 605, 583, 535, 473 cm⁻¹. MS (ES): 316 [M+18]⁺ (100%), 299 [M+1]⁺, 321 [M+Na]⁺. Anal. calcd for C₁₅H₂₂O₄S: C, 60.38; H, 7.43; S, 10.75. Found: C, 60.68; H, 7.24; S, 10.97.

2.9. Synthesis of (±)-(1'*S*,2*R*,3*S*)-3-*n*-Butyl-(1'-hydroxybenzyl)-2-(*p*-tolylsulfonyl)oxirane, **10a, and (±)-(2*S*,3*S*)-2-Benzoyl-3-*n*-butyl-2-(*p*-tolylsulfonyl)oxirane, **10a'**.**

From a solution of vinyl sulfoxide **2a**,⁵ (60 mg, 0.192 mmol) in C₆H₆ (1.7 mL) with VO(acac)₂ (0.25 equiv) and *t*-BuOOH (5.5 equiv) according to the general procedure (85 h) a 50:50 mixture of epoxy sulfone **10a** and epoxy ketone **10a'** was obtained. Chromatography (50-100% CH₂Cl₂-hexane) gave **10a** (28 mg, 41%) with identical data to that found before,⁵ and **10a'** (27 mg, 39%) as a white solid (recrystallized from 5% EtOAc-hexane).

Data of **10a'**: mp: 77-78 °C. *R_f* = 0.14 (5% Et₂O-hexane). ¹H NMR (200 MHz) δ 0.93 (t, 3 H, *J* = 7.1 Hz), 1.39-1.62 (m, 4 H), 2.16-2.25 (m, 2 H), 2.40 (s, 3 H), 3.27 (dd, 1 H, *J* = 7.2, 5.2 Hz), 7.26 (d, 2 H, *J* = 8.2 Hz), 7.37-7.48 (m, 2 H), 7.54-7.69 (m, 3 H), 7.93 (d, 2 H, *J* = 8.2 Hz). ¹³C NMR (50 MHz) δ 13.8, 21.7, 22.3, 26.7, 28.9, 65.0, 78.5, 128.5 (2 C), 129.4, 129.7 (2 C), 130.0 (2 C), 130.8 (2 C), 134.0, 134.4, 145.8, 190.7. IR (Nujol): 2926, 2855, 1671, 1596, 1452, 1325, 1297, 1163, 1177,

1082, 972, 822, 697 cm^{-1} . **MS** (ES): 381 $[\text{M}+\text{Na}]^+$ (100%). **Anal. calcd for** $\text{C}_{20}\text{H}_{22}\text{O}_4\text{S}$: C, 67.01; H, 6.19; S, 8.95. **Found**: C, 66.84; H, 6.48; S, 9.04 .

2.10. Synthesis of ($\pm$)-(1'*S*,2*R*,3*S*)-2-(1'-Hydroxypropyl)-3-phenyl-2-(*p*-tolylsulfonyl)oxirane, **10b.**

From a solution of vinyl sulfoxide **2b**,⁵ (32 mg, 0.113 mmol) in C_6H_6 (2.0 mL) with $\text{VO}(\text{acac})_2$ (0.15 equiv) and *t*-BuOOH (5.0 equiv) according to the general procedure (6 h) epoxy sulfone **10b** (33 mg, 87%) was obtained after chromatography (0-10% $\text{EtOAc}-\text{CH}_2\text{Cl}_2$). The data was identical to that found before.⁵

2.11. Synthesis of ($\pm$)-(1'*S*,2*R*,3*S*)-3-*n*-Butyl-2-(1'-hydroxypropyl)-2-(*p*-tolylsulfonyl)oxirane, **10c.**

From a solution of vinyl sulfide **2c**,⁵ (30 mg, 0.113 mmol) in C_6H_6 (1.2 mL) with $\text{VO}(\text{acac})_2$ (0.20 equiv) and *t*-BuOOH (6.0 equiv) according to the general procedure (20 h) epoxy sulfone **10c** (27 mg, 72%) was obtained after chromatography (50-100% CH_2Cl_2 -hexane). The data was identical data to that found before.⁵

2.12. Epoxidation of ($\pm$)-(2*R*,*S*₅)-1-Cyclohexylidenyl-1-(*p*-tolylsulfinyl)butan-2-ol, **3.**

From a solution of vinyl sulfoxide **3** (66 mg, 0.24 mmol) in C_6H_6 (0.4 mL) with $\text{VO}(\text{acac})_2$ (0.15 equiv) and *t*-BuOOH (3.0 equiv) according to the general procedure (4 h) epoxy sulfone **12** (66 mg, 91%) was obtained after chromatography (0-50% EtOAc -hexane) as a white solid that was recrystallized from CH_2Cl_2 -hexane.

Data for **12**: mp: 110-112 °C. R_f = 0.30 (20% EtOAc-hexane). $^1\text{H NMR}$ (200 MHz) δ 0.98 (t, 3 H, J = 7.4 Hz), 1.44-1.92 (m, 10 H), 1.92-2.02 (m, 2 H), 2.14 (m, 1 H), 2.43 (s, 3 H), 3.81-3.85 (m, 1 H), 7.34 (d, 2 H, J = 7.9 Hz), 7.78 (d, 2 H, J = 8.4 Hz). $^{13}\text{C NMR}$ (50 MHz) δ 11.3, 21.7, 24.9 (2 C), 25.3, 26.2, 30.7, 31.1, 71.3, 72.3, 83.9, 128.5 (2 C), 129.8 (2 C), 136.2, 145.0. IR (KBr): 3511, 3434, 2939, 1289, 1145, 659 cm^{-1} . MS (ES): 671 $[\text{2M}+\text{Na}]^+$, 347 $[\text{M}+\text{Na}]^+$ (100%). Anal. calcd for $\text{C}_{17}\text{H}_{24}\text{O}_4\text{S}$: C, 62.93; H, 7.46; S, 9.88. Found: C, 62.75; H, 7.35; S, 10.12.

2.13. Synthesis of (±)-2-(Phenylsulfonyl)-2-cyclopenten-1-ol, **4a''**.

From a solution of vinyl sulfide **4a**,⁷ (17 mg, 0.088 mmol) in C_6H_6 (3.3 mL) with $\text{VO}(\text{acac})_2$ (0.30 equiv) and $t\text{-BuOOH}$ (7.0 equiv) according to the general procedure (5 days) vinyl sulfone **4a''** (9 mg, 46%) was obtained after chromatography (5-50% EtOAc-hexane). Formation of **4a''** was observed after 5 min.

Data for **4a''**: R_f = 0.35 (50% EtOAc-hexane). $^1\text{H NMR}$ (200 MHz) δ 1.98-2.02 (m, 1 H), 2.21-2.52 (m, 2 H), 2.66-2.73 (m, 1 H), 4.94 (dt, 1 H, J = 7.5, 2.4 Hz), 6.92 (t, 1 H, J = 2.1 Hz), 7.51-7.65 (m, 3 H), 7.95 (dd, 2 H, J = 6.6, 1.4 Hz).

2.14. Synthesis of (±)-2-(Phenylsulfonyl)-2-cyclohexen-1-ol, **4b''**.

From a solution of vinyl sulfide **4b**,⁷ (19 mg, 0.092 mmol) in C_6H_6 (1.9 mL) with $\text{VO}(\text{acac})_2$ (0.20 equiv) and $t\text{-BuOOH}$ (7.5 equiv) according to the general procedure (24 h) vinyl sulfone **4b''** (14 mg, 64%) was obtained after chromatography (50% CH_2Cl_2 -hexane to 40% EtOAc- CH_2Cl_2). The data was identical data to that found in the literature.⁸ In a related experiment, treatment of vinyl sulfone **4b''** with $\text{Ti}(\text{O-}i\text{-Pr})_4$ (0.2 equiv) and $t\text{-BuOOH}$ (2.0 equiv) in C_6H_6 (1.0 mL) gave just recovered starting material.

3. Metal-Catalyzed Epoxidation of Dienyl Sulfoxides.

3.1. Synthesis of (±)-(1'*R*,2*S*,3*S*)-2-(1'-Hydroxypropyl)-2-(*p*-tolylsulfonyl)-3-vinyloxirane, **13a**.

From a solution of dienyl sulfoxide **6a**,⁹ (27.3 mg, 0.11 mmol) in C₆H₆ (4.0 mL) with VO(acac)₂ (0.20 equiv) and *t*-BuOOH (3.0 equiv, 5.0-6.0 M in decane) according to the general procedure (7 h) epoxy sulfone **13a** was obtained. Chromatography (80% CH₂Cl₂-hexane-50% EtOAc-hexane) gave oxirane **13a** (22.8 mg, 73%) as a colorless oil.

Data for **13a**: *R*_f = 0.23 (30% Et₂O-hexane). ¹H NMR (200 MHz) δ 0.94 (t, 3 H, *J* = 7.4 Hz), 1.58-1.68 (m, 1 H), 1.88-1.99 (m, 1 H), 2.21 (br s, 1 H), 2.45 (s, 3 H), 3.84 (dd, 1 H, *J* = 9.9, 3.2 Hz), 4.19 (d, 1 H, *J* = 7.8 Hz), 5.50 (ddd, 1 H, *J* = 10.4, 1.1, 0.7 Hz), 5.62 (ddd, 1 H, *J* = 17.3, 1.1, 0.7 Hz), 5.95 (ddd, 1 H, *J* = 17.2, 10.4, 7.8 Hz), 7.36 (d, 2 H, *J* = 8.6 Hz), 7.78 (d, 2 H, *J* = 8.4 Hz). ¹³C NMR (75 MHz)-DEPT δ 10.7, 21.7, 26.9, 61.9, 69.9, 77.5, 124.5, 129.4, 129.5 (2 C), 129.8 (2 C), 133.1, 145.7. IR (film): 3514 (br), 2933, 1597, 1455, 1324, 1149, 1088, 814, 706, 660 cm⁻¹. MS (ES): 587 [2M+Na]⁺, 305 [M+Na]⁺ (100%), 300 [M+NH₄]⁺. Anal. calcd for C₁₄H₁₈O₄S: C, 59.55; H, 6.43; S, 11.36. Found: C, 59.80; H, 6.14; S, 11.18.

3.2. Synthesis of (+)-(1'*R*,2*S*,3*S*)-2-(1'-hydroxybenzyl)-2-(*p*-tolylsulfonyl)-3-vinyloxirane, **13b**.

From a solution of dienyl sulfoxide **6b**,⁹ (300 mg, 1.01 mmol) in C₆H₆ (5.0 mL) with VO(acac)₂ (0.15 equiv) and *t*-BuOOH (5.0 equiv, 5.0-6.0 M in decane) according to the general procedure (1 day) a 72:28 mixture of **13b** and **14b** was obtained. Chromatography (5-30% EtOAc-hexane, then 0-5% EtOAc-CH₂Cl₂) gave sulfonyl oxirane **13b** (221 mg, 67%) as a white solid recrystallized from Et₂O-hexane. Long reaction times (2-6 days) and the use of more than 3.5 equiv of *t*-BuOOH led to increased amounts of ketone **14b**; alternatively short reaction times (6-7 h) and lesser amounts of *t*-BuOOH substantially diminish the rate of the reaction and significant amounts of dienyl sulfone are produced. Under optimized conditions (30% VO(acac)₂, 3.5 equiv *t*-BuOOH, in toluene, 2 days), hydroxy oxirane **13b** was obtained along with small amounts of dienyl sulfone.

Data for **13b**: mp: 132-134 °C. *R*_f = 0.35 (30% EtOAc-hexane); 0.24 (1% EtOAc-CH₂Cl₂). [α]_D²⁰ = +10.8 (*c* = 0.60). ¹H NMR (300 MHz) δ 2.32 (s, 3 H), 3.80 (d, 1 H, *J* = 10.6 Hz), 4.56 (d, 1 H, *J* =

6.2 Hz), 4.94 (d, 1 H, $J = 10.6$ Hz), 5.58 (d, 1 H, $J = 10.6$ Hz), 5.71 (d, 1 H, $J = 17.1$ Hz), 5.97 (ddd, 1 H, $J = 17.1, 10.7, 6.2$ Hz), 6.97 (d, 2 H, $J = 8.1$ Hz), 7.03-7.15 (m, 5 H), 7.22 (d, 2 H, $J = 7.5$ Hz). ^{13}C NMR (50 MHz) δ 21.6, 62.1, 70.6, 78.0, 124.1, 125.8 (2 C), 127.7, 128.0 (2 C), 128.8, 128.9 (2 C), 129.1 (2 C), 133.9, 137.9, 144.6. IR (KBr): 3530, 3480, 2930, 1600, 1500, 1490, 1460, 1315, 1300, 1180, 1160, 1150, 1090, 1060, 1000, 940, 810, 780, 750, 710, 670 cm^{-1} . MS (EI): 174, 157, 146, 139, 129, 118, 107, 91 (100%), 77, 65, 57, 39. MS (APCI): 329 $[\text{M}-1]^-$, 155 (100%). Anal. calcd for $\text{C}_{18}\text{H}_{18}\text{O}_4\text{S}$: C, 65.43; H, 5.49; S, 9.70. Found: C, 65.48; H, 5.45; S, 9.65.

3.3. Synthesis of (+)-(2*R*,3*S*)-2-Benzoyl-2-(*p*-tolylsulfonyl)-3-vinyloxirane, **14b**.

To a solution of hydroxy oxirane **13b** (70 mg, 0.21 mmol) in 2 mL of CH_2Cl_2 was added NaOAc (86 mg, 1.05 mmol) and PCC (185 mg, 0.84 mmol) with stirring. After 7 h at rt, the mixture was filtered through SiO_2 (100 mg) to produce a crude product with 89% conversion (^1H NMR), that was purified by chromatography (5-60% EtOAc-hexane), to afford keto vinyl oxirane **14b** (50 mg, 79%) as a white solid that was recrystallized from EtOAc-hexane (1:3) and starting material (1 mg).

Data for **14b**: mp: 121-124 $^\circ\text{C}$. $R_f = 0.35$ (30% EtOAc-hexane); 0.45 (1% EtOAc- CH_2Cl_2). $[\alpha]_{\text{D}}^{20} = +16.4$ ($c = 1.12$). ^1H NMR (300 MHz) δ 2.42 (s, 3 H), 4.49 (d, 1 H, $J = 7.7$ Hz), 5.21-5.32 (ddd, 1 H, $J = 16.1, 10.5, 7.5$ Hz), 5.36 (dd, 1 H, $J = 10.5, 1.5$ Hz), 5.63 (ddd, 1 H, $J = 16.7, 1.4, 0.7$ Hz), 7.30 (dd br, 2 H, $J = 8.5, 0.6$ Hz), 7.42 (tt br, 2 H, $J = 8.0, 1.6$ Hz), 7.59 (tt, 1 H, $J = 7.5, 1.3$ Hz), 7.65 (d, 2 H, $J = 8.4$ Hz), 7.90 (dd, 2 H, $J = 8.0, 0.7$ Hz). ^{13}C NMR (50 MHz) δ 21.8, 62.5, 77.2, 124.7, 128.5 (2 C), 129.0, 129.5 (2 C), 129.9 (2 C), 130.2 (2 C), 132.7, 134.6, 134.7, 146.2, 187.9. IR (KBr): 2920, 1680, 1590, 1450, 1330, 1310, 1290, 1230, 1170, 1150, 1090, 980, 950, 820, 760, 690, 670, 650 cm^{-1} . MS (APCI): 327 $(\text{M}-1)^-$ (100%); 329 $(\text{M}+1)^+$ (100%). Anal. calcd for $\text{C}_{18}\text{H}_{16}\text{O}_4\text{S}$: C, 65.84; H, 4.91; S, 9.76. Found: C, 65.52; H, 5.24; S, 9.53.

3.4. Synthesis of ($\pm$)-(2*R*,3*S*)-2-[(1'-Hydroxy-1'-methyl)ethyl]-2-(*p*-tolylsulfonyl)-3-vinyloxirane, **13c**.

From a solution of dienyl sulfoxide **6c**,⁹ (501 mg, 2.0 mmol) in C₆H₆ (10.0 mL) with VO(acac)₂ (0.15 equiv) and *t*-BuOOH (3.0 equiv, 5.0-6.0 M in decane) according to the general procedure (6 h 15 min) epoxy sulfone **13c** was obtained. Chromatography (20-100% Et₂O-hexane) gave sulfonyl oxirane **13c** (485 mg, 86%) as a white solid. In some experiments small amounts of a by-product tentatively characterized as **13c'** (inseparable 70:30 mixture of isomers) were isolated.

Data for **13c**: *R_f* = 0.37 (30% EtOAc-CH₂Cl₂); 0.15 (40% EtOAc-hexane). ¹H NMR (300 MHz) δ 1.41 (s, 3 H), 1.45 (s, 3 H), 2.37 (s, 1 H), 2.43 (s, 3 H), 4.15 (d, 1 H, *J* = 8.2 Hz), 5.48 (dd, 1 H, *J* = 10.5, 0.8 Hz), 5.61 (dd, 1 H, *J* = 17.2, 0.7 Hz), 6.13 (ddd, 1 H, *J* = 17.2, 10.5, 8.2 Hz), 7.32 (d, 2 H, *J* = 8.6 Hz), 7.78 (d, 2 H, *J* = 8.2 Hz). ¹³C NMR (50 MHz) δ 21.7, 26.5, 28.9, 62.8, 70.8, 82.0, 124.9, 129.4 (2 C), 129.5 (2 C), 130.3, 134.9, 145.2. IR (KBr): 3436, 2924, 1147, 659 cm⁻¹. MS (APCI): 281 [M-1]⁻ (100%). Anal. calcd for C₁₄H₁₈O₄S: C, 59.55; H, 6.43; S, 11.36. Found: C, 59.81; H, 6.18; S, 11.02.

Data for **13c'** (major, from the mixture): *R_f* = 0.22 (40% EtOAc-hexane). ¹H NMR (300 MHz) δ 1.21 (s, 9 H), 1.23 (s, 9 H), 1.42 (s, 3 H), 1.44 (s, 3 H), 2.40 (s, 3 H), 3.27 (s, 1 H), 3.99 (dd, 1 H, *J* = 12.6, 5.1 Hz), 4.18 (dd, 1 H, *J* = 12.6, 6.2 Hz), 5.54 (ddd, 1 H, *J* = 9.5, 6.2, 5.1 Hz), 6.94 (d, 1 H, *J* = 9.4 Hz), 7.26 (d, 2 H, *J* = 8.1 Hz), 7.71 (d, 2 H, *J* = 8.4 Hz). ¹³C NMR (75 MHz) δ 26.2 (3 C), 26.3 (3 C), 30.7, 31.5, 45.3 (2 C), 72.9 (CH), 74.5, 81.2, 127.4 (2 C), 129.5 (2 C), 138.7, 139.7, 143.7, 150.2. MS (ES): 467 [M+Na]⁺, 462 (100%).

Data for **13c'** (minor, from the mixture): *R_f* = 0.22 (40% EtOAc-hexane). ¹H RMN (200 MHz) δ 1.20 (s, 9 H), 1.22 (s, 9 H), 1.43 (s, 3 H), 1.44 (s, 3 H), 2.38 (s, 3 H), 3.82 (s, 1 H), 4.03 (dd, 1 H, *J* = 12.6, 6.0 Hz), 4.18 (m, 1 H), 5.44 (ddd, 1 H, *J* = 8.8, 6.2, 2.7 Hz), 6.47 (d, 1 H, *J* = 9.0 Hz), 7.26 (d, 2 H, *J* = 8.1 Hz), 7.88 (d, 2 H, *J* = 8.4 Hz).

3.5. Attempted epoxidation of (±)-(4*E*,6*E*)-(3*R*,*S*_s)-4-(*p*-Tolylsulfinyl)octa-4,6-dien-3-ol, **6d**.

From a solution of dienyl sulfoxide **6d** (19.15 mg, 0.07 mmol) in C₆H₆ (2.3 mL) with VO(acac)₂ (0.10 equiv) and *t*-BuOOH (3.0 equiv, 5.0-6.0 M in decane) according to the general procedure (1 h 30 min) dienyl sulfone **6d''** was obtained within a complex mixture of products. Chromatography (0-50% EtOAc-CH₂Cl₂) gave **6d''** (7.0 mg, 35%) as a colorless oil.

Data for **6d''**: *R_f* = 0.15 (20% EtOAc-hexane). ¹H NMR (300 MHz) δ 0.81 (t, 3 H, *J* = 7.2 Hz), 1.50-1.62 (m, 1 H), 1.64-1.81 (m, 1 H), 1.89 (dd, 3 H, *J* = 6.8, 1.5 Hz), 2.40 (s, 3 H), 2.44 (s, 1 H), 4.47 (dd, 1 H, *J* = 8.7, 5.4 Hz), 6.24 (dq, 1 H, *J* = 15.0, 6.8, 0.7 Hz), 6.55 (ddq, 1 H, *J* = 15.0, 11.4, 1.6 Hz), 7.24-7.34 (m, 3 H), 7.73 (d, 2 H, *J* = 8.3 Hz). ¹³C NMR (50 MHz) δ 10.5, 19.1, 21.6, 30.2, 70.7, 125.5, 127.8 (2 C), 129.8 (2 C), 138.1, 139.2, 140.2, 141.0, 144.1. IR (film): 3499 (br), 2927, 1640, 1597, 1493, 1454, 1288, 1141, 1084, 1018, 876, 706 cm⁻¹. MS (ES): 583 [2M+Na]⁺, 303 [M+Na]⁺ (100%). Anal. calcd for C₁₅H₂₀O₃S: C, 64.26; H, 7.19; S, 11.44. Found: C, 64.43; H, 7.39; S, 11.21.

3.6. Synthesis of (+)-(4*E*)-(3*R*)-4-(*p*-Tolylsulfonyl)hepta-1,4,6-trien-3-ol, **7a''**.

From a solution of trienyl sulfoxide **7a**,⁹ (20 mg, 0.08 mmol) in C₆H₆ (0.5 mL) with VO(acac)₂ (0.05 equiv) and *t*-BuOOH (1.3 equiv, 70% in H₂O) according to the general procedure (30 min) trienyl sulfone **7a''** (15 mg, 70%) was obtained as a pale yellow oil after chromatography (0-20% EtOAc-CH₂Cl₂). The data was identical data to that found before for its enantiomer except from the sign of the optical rotation.⁹

3.7. Synthesis of (+)-(3*R*,4*S*,5*S*)-4,5-Epoxy-4-(*p*-tolylsulfonyl)hepta-1,6-dien-3-ol, **15a**, and (+)-(2*R*,3*R*,4*S*,5*S*)-1,2-4,5-Diepoxy-4-(*p*-tolylsulfonyl)hept-6-en-3-ol, **16a**.

Conditions

5% VO(acac) ₂ , 2 equiv aq. <i>t</i> -BuOOH, 7 days, 79%	64:36
10% VO(acac) ₂ , 5 equiv <i>t</i> -BuOOH, 4 h, 65%	100:0
15% VO(acac) ₂ , 9 equiv <i>t</i> -BuOOH, 22 h, 62%	28:72

From a solution of trienyl sulfoxide **7a**,⁹ (21 mg, 0.08 mmol) in C₆H₆ (0.9 mL) with VO(acac)₂ (0.05 equiv) and *t*-BuOOH (2.0 equiv, 70% in H₂O) according to the general procedure (7 days) a 64:36 mixture of monoepoxide **15a** and bisepoxide **16a** was obtained. Chromatography (0-20% EtOAc-CH₂Cl₂) gave **15a** (10 mg, 43%) and **16a** (6 mg, 25%) as pale yellow oils. It should be mentioned that this experiment was difficult to reproduce.

From a solution of trienyl sulfoxide **7a**,⁹ (100 mg, 0.4 mmol) in C₆H₆ (1.6 mL) with VO(acac)₂ (0.1 equiv) and *t*-BuOOH (5.0 equiv, 5.0-6.0 M in decane) according to the general procedure (4 h) monoepoxide **15a** (73 mg, 65%) was obtained as a colorless oil after chromatography (0-5% EtOAc-CH₂Cl₂).

From a solution of trienyl sulfoxide **7a**,⁹ (47 mg, 0.19 mmol) in C₆H₆ (3.1 mL) with VO(acac)₂ (0.15 equiv) and *t*-BuOOH (9.0 equiv, 3 M in isooctane) according to the general procedure (22 h) a 28:72 mixture of monoepoxide **15a** and bisepoxide **16a** was obtained. Chromatography (0-20% EtOAc-CH₂Cl₂) gave **15a** (9 mg, 17%) and **16a** (24 mg, 45%) as pale yellow oils.

Data for **15a**: *R_f* = 0.47 (10% EtOAc-CH₂Cl₂). [α]_D²⁰ = +10.2 (*c* = 0.60). ¹H NMR (200 MHz) δ 2.46 (s, 3 H), 2.83 (d, 1 H, *J* = 7.3 Hz), 4.36 (d, 1 H, *J* = 7.0 Hz), 4.42 (m, 1 H), 5.17 (dd, 1 H, *J* = 10.5, 1.8 Hz), 5.43 (dd, 1 H, *J* = 17.2, 1.7 Hz), 5.54 (dd, 1 H, *J* = 11.0, 0.7 Hz), 5.63 (dd, 1 H, *J* = 16.5, 0.7 Hz), 5.70-6.01 (m, 2 H, H-2), 7.35 (d, 2 H, *J* = 8.1 Hz), 7.76 (d, 2 H, *J* = 8.3 Hz). ¹³C NMR (50 MHz) δ 21.7, 62.2, 69.0, 117.3, 124.4, 128.7, 129.7 (2 C), 129.9 (2 C), 133.4, 134.3, 145.8. IR (CHCl₃): 3480, 2990, 1600, 1320, 1150, 1090, 815, 670 cm⁻¹. MS (ED): 280 [M]⁺, 278, 246, 172, 155, 139, 123, 107, 91 (100%), 65, 45, 39. Anal. calcd for C₁₄H₁₆O₄S: C, 59.98; H, 5.75; S, 11.44. Found: C, 60.23; H, 6.01; S, 11.16.

Data for **16a**: *R_f* = 0.34 (10% EtOAc-CH₂Cl₂). [α]_D²⁰ = +11.7 (*c* = 1.90). ¹H NMR (200 MHz) δ 2.45 (s, 3 H), 2.46 (d, 1 H, *J* = 5.5 Hz), 2.67 (dd, 1 H, *J* = 5.0, 3.9 Hz), 2.87 (dd, 1 H, *J* = 5.0, 2.7 Hz), 3.29 (m, 1 H), 4.18 (m, 1 H), 4.24 (d, 1 H, *J* = 7.0 Hz), 5.52 (dd, 1 H, *J* = 10.9, 0.7 Hz), 5.63 (dd, 1 H, *J* = 17.0, 0.7 Hz), 5.87 (ddd, 1 H, *J* = 17.2, 10.3, 7.0 Hz), 7.37 (d, 2 H, *J* = 8.2 Hz), 7.81 (d, 2 H, *J* = 8.3 Hz). ¹³C NMR (50 MHz) δ 21.7, 44.6, 51.8, 61.6, 66.6, 124.5, 128.7, 129.6 (2 C), 129.9 (2 C), 132.9, 146.1. IR (CHCl₃): 3500, 2960, 1600, 1320, 1305, 1150, 1090, 970, 815, 660 cm⁻¹. MS (ED): 278, 246, 173, 155, 139, 123, 91 (100%), 77, 65, 39. Anal. calcd for C₁₄H₁₆O₅S: C, 56.74; H, 5.44; S, 10.82. Found: C, 56.37; H, 5.72; S, 10.97.

3.8. Synthesis of (+)-(2*E*,5*E*)-(4*R*)-5-(*p*-Tolylsulfonyl)octa-2,5,7-trien-4-ol, **7b'', (2*S*,3*S*,4*R*,5*S*,6*S*)-2,3-5,6-Diepoxy-5-(*p*-tolylsulfonyl)oct-7-en-4-ol, **16b**, and (2*R*,3*R*,4*R*,5*S*,6*S*)-2,3-5,6-Diepoxy-5-(*p*-tolylsulfonyl)oct-7-en-4-ol, **17b**.**

From a solution of trienyl sulfoxide **7b**,⁹ (30 mg, 0.12 mmol) in C₆H₆ (1.0 mL) with VO(acac)₂ (0.15 equiv) and *t*-BuOOH (5.0 equiv, 5.0-6.0 M in decane) according to the general procedure (9 h) an inseparable 77:23 mixture of bisepoxides **16b** and **17b** (23 mg, 65%) was obtained as a colorless oil after chromatography (0-10% EtOAc-CH₂Cl₂).

From a solution of trienyl sulfoxide **7b**,⁹ (13 mg, 0.05 mmol) in CH₂Cl₂ (0.5 mL) with Ti(O-*i*-Pr)₄ (0.25 equiv) and *t*-BuOOH (4.0 equiv, 3.0 M in isooctane) according to the general procedure (20 h) an inseparable 36:64 mixture of bisepoxides **16b** and **17b** (5 mg, 40%) was obtained as a colorless oil after chromatography (0-10% EtOAc-CH₂Cl₂).

To a cold (0 °C) solution of Ti(O-*i*-Pr)₄ (35 µL, 34 mg, 0.12 mmol) in CH₂Cl₂ (1 mL) was added D-(-)-DET (1.6 equiv, 27 µL, 33 mg, 0.16 mmol). After stirring for 5 min, a solution of sulfoxide **7b**,⁹ (25 mg, 0.10 mmol) in CH₂Cl₂ (1 mL) was added followed by *t*-BuOOH (6 equiv, 3 M in isooctane, 0.10 mL, 0.60 mmol) and the reaction mixture was kept in a refrigerator (4 °C) for 17 h. Standard work-up and chromatography (5-60% EtOAc-hexane) gave trienyl sulfone **7b''** (24 mg, 91%) as a colorless oil.

Data for **7b''**: *R*_f = 0.26 (30% EtOAc-hexane). [α]_D²⁰ = +16.3 (*c* = 0.80). **¹H NMR (300 MHz)** δ 1.53 (d, 3 H, *J* = 6.2 Hz), 2.40 (s, 3 H), 2.54 (br s, 1 H), 5.07 (br d, 1 H, *J* = 5.3 Hz), 5.39 (ddd, 1 H, *J* = 15.3, 5.7, 1.5 Hz), 5.54 (dq, 1 H, *J* = 15.3, 6.5, 1.2 Hz), 5.63 (d, 1 H, *J* = 10.4 Hz), 5.70 (d, 1 H, *J* = 16.5 Hz), 6.86 (ddd, 1 H, *J* = 16.9, 11.4, 10.0 Hz), 7.29 (d, 2 H, *J* = 7.9 Hz), 7.30 (d, 1 H, *J* = 11.7 Hz), 7.71 (d, 2 H, *J* = 8.3 Hz). **¹³C NMR (50 MHz)** δ 17.4, 21.6, 69.1, 128.1 (2 C), 128.6, 129.7 (2 C), 130.1, 130.5, 139.8, 144.2. **IR** (film): 3450 (br), 2940, 2890, 2820, 1610, 1570, 1430, 1280, 1270, 1120, 1060, 1010, 940, 790, 680, 650 cm⁻¹. **Anal. calcd for C₁₅H₁₈O₃S**: C, 64.72; H, 6.52; S, 11.52. **Found**: C, 64.95; H, 6.18; S, 11.16.

Data for **16b** (from the mixture): *R*_f = 0.21 (2 x 30% EtOAc-hexane); 0.36 (10% EtOAc-CH₂Cl₂). **¹H NMR (300 MHz)** δ 1.26 (d, 3 H, *J* = 5.0 Hz), 2.34 (d, 1 H, *J* = 4.5 Hz), 2.45 (s, 3 H), 3.11-3.17 (m, 2 H), 4.16 (d, 1 H, *J* = 7.4 Hz), 4.22 (br dd, 1 H, *J* = 4.2, 2.1 Hz), 5.51 (dt, 1 H, *J* = 10.5, 1.0 Hz), 5.63 (dt, 1 H, *J* = 17.2, 1.0 Hz), 5.85 (ddd, 1 H, *J* = 17.5, 10.5, 7.5 Hz), 7.37 (dd, 2 H, *J* = 8.6, 0.6 Hz), 7.80 (d, 2 H, *J* = 8.6 Hz). **¹³C NMR (50 MHz)** δ 16.7, 21.8, 52.1, 58.7, 61.5, 65.9, 75.9, 124.4,

128.9, 129.6 (2 C), 130.0 (2 C), 132.4, 146.1. **IR** (CCl₄): 3425 (br), 2920, 2890, 1570, 1420, 1360, 1130, 1060, 950, 910, 680 cm⁻¹. **MS** (ES): 309 [M-1]⁻, 171 (100%); 333 [M+Na]⁺, 319 (100%). **Anal. calcd for** C₁₅H₁₈O₅S: C, 58.05; H, 5.85; S, 10.33. **Found:** C, 58.40; H, 6.04; S, 10.17.

Partial data for **17b** (from the mixture): *R_f* = 0.23 (2 x 30% EtOAc-hexane); 0.36 (10% EtOAc-CH₂Cl₂). **¹H NMR (300 MHz)** δ 1.18 (d, 3 H, *J* = 5.1 Hz), 2.45 (s, 3 H), 2.58 (d, 1 H, *J* = 7.2 Hz), 2.90 (dd, 1 H, *J* = 4.8, 2.3 Hz), 3.00 (qd, 1 H, *J* = 5.2, 2.2 Hz), 3.81 (dd, 1 H, *J* = 7.2, 4.8 Hz), 4.26 (d, 1 H, *J* = 7.2 Hz), 5.54 (dt, 1 H, *J* = 10.5, 1.1 Hz), 5.62 (dt, 1 H, *J* = 17.1, 1.1 Hz), 5.93 (ddd, 1 H, *J* = 17.5, 10.4, 7.0 Hz), 7.36 (dd, 2 H, *J* = 8.7, 0.7 Hz), 7.82 (d, 2 H, *J* = 8.3 Hz). **¹³C NMR (50 MHz)** δ 16.8, 52.5, 58.3, 62.0, 68.4, 77.2, 124.6, 128.7, 129.8 (2 C), 129.9 (2 C).

4. Synthetic Applications.

4.1. General Procedure for Ozonolysis of Vinyl Sulfonyl Oxiranes.

Through a cold (-78 °C) solution of 1 equiv of the vinyl oxirane in CH₂Cl₂ (19 mL/mmol) was bubbled O₂ for 10 min, followed by O₃ (6% in O₂) for 7 min and then O₂ (5 min). An excess of SMe₂ (5 equiv) was then added dropwise and the mixture was stirred at rt for 1-2 h. The solvent was removed under reduced pressure and the crude product was purified by chromatography on silica gel using the appropriate mixture of eluents.

4.2. Synthesis of (-)-(3*S*,4*S*,5*R*)-3,4-Epoxy-5-phenyl-4-(*p*-tolylsulfonyl)tetrahydrofuran-2-ol, **18b**.

From vinyl oxirane **13b** (330 mg, 1.0 mmol) in 19 mL of CH₂Cl₂ bubbling O₃ (7 min) and with SMe₂ (5.0 equiv, 0.37 mL, 4.99 mmol), according to the general procedure, lactol **18b** (90:10 mixture of anomers, 292 mg, 88%) was obtained as a white solid after chromatography (10-40% EtOAc-hexane).

Data for **18b**: **mp**: 169-175 °C. *R_f* = 0.12 (2% EtOAc-CH₂Cl₂). [α]_D²⁰ = -14.6 (*c* = 0.25). **¹H NMR (400 MHz)** δ 2.41 (s, 3 H, major), 2.43 (s, 3 H, minor), 3.30 (br s, 1 H, major), 4.33 (s, 1 H, major), 4.34 (s, 1 H, minor), 5.05 (s, 1 H, major), 5.20 (s, 1 H, minor), 5.58 (s, 1 H, major), 5.78 (s, 1 H, minor), 7.14 (dd, 2 H, *J* = 8.0, 2.0 Hz, minor), 7.20-7.38 (m, 10 H), 7.40-7.43 (m, 4 H), 7.47 (d, 2 H, *J* = 8.0 Hz, minor). **¹³C NMR (50 MHz)** δ 21.7, 65.0, 77.0, 82.0, 95.1, 128.2 (2 C major), 128.5, 129.1

(2 C major), 129.1, 129.2, 129.6 (2 C major), 129.7 (2 C major), 129.8, 134.1, 135.0, 145.6. **IR** (CHCl_3): 3420 (br), 3020, 2990, 2880, 1580, 1480, 1310, 1140, 1120, 1070, 680 cm^{-1} . **MS** (EI): 332 $[\text{M}]^+$, 303, 211, 176, 157, 147, 139, 131, 107 (100%), 91, 79, 71, 63, 51, 43. **MS** (APCI): 355 $[\text{M}+\text{Na}]^+$, 139 (100%); 369 $[\text{M}+\text{Cl}]^-$, 367 (100%). **MS** (ES): 355 $[\text{M}+\text{Na}]^+$, 337 (100%); 369 $[\text{M}+\text{Cl}]^-$, 367 $[\text{M}+\text{Cl}]^-$ (100%). **Anal. calcd for** $\text{C}_{17}\text{H}_{16}\text{O}_5\text{S}$: C, 61.43; H, 4.85; S, 9.65. **Found**: C, 61.70; H, 5.07; S, 9.92.

4.3. Synthesis of (±)-(3*S*,4*S*,5*R*)-3,4-Epoxy-5-ethyl-4-(*p*-tolylsulfonyl)tetrahydrofuran-2-ol, **18a**.

From vinyl oxirane **13a** (320 mg, 1.13 mmol) in 22 mL of CH_2Cl_2 bubbling O_3 (10 min) and with SMe_2 (5.0 equiv, 0.42 mL, 5.67 mmol), according to the general procedure, lactol **18a** (81:19 mixture of anomers, 287 mg, 89%) was obtained as a white solid recrystallized from CH_2Cl_2 -hexane after chromatography (5-40% EtOAc-hexane).

Data for **18a**: mp: 110-115 °C. $R_f = 0.12$ (30% EtOAc-hexane). **^1H NMR (400 MHz)** δ 1.01 (t, 3 H, $J = 7.3$ Hz), 1.81-1.93 (m, 1 H), 2.03-2.13 (m, 1 H), 2.45 (s, 3 H), 2.85 (d, 1 H, $J = 11.9$ Hz, minor), 3.13 (br s, 1 H, major), 3.95 (dd, 1 H, $J = 11.5, 2.9$ Hz, major), 4.02 (s, 1 H, major), 4.07 (s, 1 H, minor), 4.15 (dd, 1 H, $J = 9.3, 3.3$ Hz, minor), 5.35 (s, 1 H, major), 5.38 (d, 1 H, $J = 11.9$ Hz, minor), 7.38 (d, 2 H, $J = 8.4$ Hz), 7.79 (d, 2 H, $J = 8.2$ Hz). **^{13}C NMR (50 MHz)** δ 10.5, 21.7, 26.4, 62.5, 75.8, 79.3, 94.5, 128.8, 130.0, 133.5, 146.1. **IR** (KBr): 3510 (br), 2984, 1594, 1318, 1159, 1144, 1034, 1050, 813, 660 cm^{-1} . **Anal. calcd for** $\text{C}_{13}\text{H}_{16}\text{O}_5\text{S}$: C, 54.92; H, 5.67; S, 11.28. **Found**: C, 54.94; H, 5.84; S, 11.31.

4.4. Synthesis of (–)-(1'*R*,2*S*,3*S*)-2-(1'-Hydroxybenzyl)-3-(hydroxymethyl)-2-(*p*-tolylsulfonyl)oxirane, **20**.

To a cold (0 °C) solution of lactol **18b** (10 mg, 0.03 mmol) in 2 mL of EtOH was added NaBH_4 (6 equiv, 7 mg, 0.18 mmol). The mixture was stirred until the reaction was complete (TLC, 1 h), the solvent was removed under reduced pressure and EtOAc (4 mL) and H_2O (2 mL) was added. Standard

isolation gave a crude product that was purified by chromatography (20-80% EtOAc-hexane) to give diol **20** (7 mg, 70%) as a colorless oil.

Data for **20**: R_f = 0.21 (50% EtOAc-hexane). $[\alpha]_D^{20} = -7.5$ (c = 0.51). $^1\text{H NMR}$ (400 MHz) δ 1.55 (br, 2 H), 2.33 (s, 3 H), 3.91 (dd, 1 H, J = 12.7, 5.9 Hz), 3.96 (dd, 1 H, J = 12.8, 5.6 Hz), 4.26 (dd, 1 H, J = 5.9, 5.6 Hz), 5.05 (s, 1 H), 7.00 (d, 2 H, J = 8.5 Hz), 7.07-7.24 (m, 7 H). $^{13}\text{C NMR}$ (100 MHz) δ 21.6, 59.9, 60.8, 71.1, 77.2, 125.4 (2 C), 127.9, 128.1 (2 C), 128.8 (2 C), 129.3 (2 C), 133.6, 137.2, 144.8. **IR** (CCl_4): 3450 (br), 2930, 2900, 2820, 1530, 1440, 1400, 1300, 1250, 1130, 850 cm^{-1} . **MS** (ES): 357 $[\text{M}+\text{Na}]^+$ (100%); 371 $[\text{M}+\text{Cl}]^-$, 369 $[\text{M}+\text{Cl}]^-$, 171 (100%). **Anal. calcd for $\text{C}_{17}\text{H}_{18}\text{O}_5\text{S}$** : C, 61.06; H, 5.43; S, 9.59. **Found**: C, 61.40; H, 5.71; S, 9.26.

4.5. General Procedure for Acetylation.

To a solution of the substrate in anhydrous CH_2Cl_2 (10 mL/mmol) was added Ac_2O (3-6 equiv) followed by Et_3N (3-6 equiv) and a few crystals of DMAP. The reaction mixture was stirred and monitored by TLC until completion. Removal of the solvent under reduced pressure gave a crude product that was purified by chromatography on silica gel with the appropriate mixture of eluents.

4.6. Synthesis of the acetate of (–)-(3*S*,4*S*,5*R*)-3,4-epoxy-5-phenyl-4-(*p*-tolylsulfonyl)tetrahydrofuran-2-ol, **19b**.

From lactol **18b** (42 mg, 0.13 mmol) in 4.0 mL of CH_2Cl_2 with Ac_2O (70 μL , 0.76 mmol), Et_3N (110 μL , 0.76 mmol) and 2 crystals of DMAP according to the general procedure (3 h), acetylated lactol **19b** (inseparable 90:10 mixture of isomers, 39 mg, 80%) was obtained after chromatography (5-50% EtOAc-hexane) as a white solid that was recrystallized from CH_2Cl_2 -hexane.

Data for **19b** (major, from the mixture): **mp**: 114-118 $^\circ\text{C}$. R_f = 0.18 (30% EtOAc-hexane); 0.12 (2% EtOAc- CH_2Cl_2). $^1\text{H NMR}$ (300 MHz) δ 2.16 (s, 3 H), 2.44 (s, 3 H), 4.44 (s, 1 H), 4.99 (s, 1 H), 6.34 (s, 1 H), 7.27 (d, 2 H, J = 8.4 Hz), 7.33-7.39 (m, 5 H), 7.47 (d, 2 H, J = 8.4 Hz). $^{13}\text{C NMR}$ (50 MHz) δ 21.0, 21.7, 64.2, 76.5, 82.6, 93.4, 128.1 (2 C), 129.1 (2 C), 129.4 (2 C), 129.6, 129.8 (2 C), 134.2, 146.0, 168.9. **IR** (CHCl_3): 3060, 2990, 2900, 2820, 1730 (br), 1480, 1440, 1320, 1200, 1150, 1130, 1070, 960, 680, 650 cm^{-1} . **Anal. calcd for $\text{C}_{19}\text{H}_{18}\text{O}_6\text{S}$** : C, 60.95; H, 4.85; S, 8.56. **Found**: C, 60.64; H, 4.97; S, 8.36.

Partial data for **19b** (minor, from the mixture): $R_f = 0.18$ (30% EtOAc-hexane). $^1\text{H NMR}$ (300 MHz) δ 2.12 (s, 3 H), 2.43 (s, 3 H), 4.47 (s, 1 H), 6.57 (s, 1 H), 7.17 (dd, 2 H, $J = 7.6, 1.4$ Hz). $^{13}\text{C NMR}$ (50 MHz) δ 20.7, 63.2, 78.0, 82.1, 93.9, 128.4, 129.2.

4.7. Synthesis of the acetate of (±)-(3*S*,4*S*,5*R*)-3,4-Epoxy-5-ethyl-4-(*p*-tolylsulfonyl)tetrahydrofuran-2-ol, **19a**.

From lactol **18a** (142 mg, 0.50 mmol) in 15 mL of CH_2Cl_2 with Ac_2O (0.28 mL, 3.0 mmol), Et_3N (0.4 mL, 3.0 mmol) and 2 crystals of DMAP according to the general procedure (2 h), acetylated lactol **19a** (inseparable 89:11 mixture of isomers, 163 mg, 100%) was obtained after chromatography (0-5% EtOAc- CH_2Cl_2) as a white solid.

Data for **19a**: mp: 114-118 °C. $R_f = 0.27$ (30% EtOAc-hexane). $^1\text{H NMR}$ (200 MHz) δ 0.98 (t, 3 H, $J = 7.3$ Hz), 1.78-1.87 (m, 1 H), 2.01-2.12 (m, 1 H), 2.09 (s, 3 H), 2.45 (s, 3 H), 3.98 (dd, 1 H, $J = 11.5, 3.1$ Hz), 4.12 (s, 1 H), 4.20 (s, 1 H, minor), 4.26 (dd, 1 H, $J = 8.6, 3.1$ Hz, minor), 6.15 (s, 1 H, major), 6.20 (s, 1 H, minor), 7.38 (d, 2 H, $J = 8.6$ Hz), 7.80 (d, 2 H, $J = 8.4$ Hz). $^{13}\text{C NMR}$ (50 MHz) δ 10.3, 21.0, 21.8, 26.0, 61.7, 75.5, 80.3, 93.3, 128.9 (2 C), 130.1 (2 C), 133.5, 146.3, 169.3. IR (KBr): 1748, 1597, 1370, 1242, 1015, 967, 880, 705 cm^{-1} . Anal. calcd for $\text{C}_{15}\text{H}_{18}\text{O}_6\text{S}$: C, 55.20; H, 5.56; S, 9.82. Found: C, 55.41; H, 5.28; S, 9.65.

4.8. Attempted allylation of the acetate of (–)-(3*S*,4*S*,5*R*)-3,4-epoxy-5-phenyl-4-(*p*-tolylsulfonyl)tetrahydrofuran-2-ol, **19b**.

To a cold (0 °C) solution of acetylated lactol **19b** (10 mg, 0.03 mmol) in anhydrous CH_3CN (1 mL) was added allyltrimethylsilane (2.0 equiv, 8 μL , 0.05 mmol) followed by freshly distilled $\text{BF}_3\cdot\text{OEt}_2$ (2.0 equiv, 7 μL , 0.05 mmol). The reaction mixture was stirred and allowed to warm up to rt over 1 h and additional allyltrimethylsilane (3.0 equiv, 13 μL , 0.08 mmol) and $\text{BF}_3\cdot\text{OEt}_2$ (3 equiv, 10 μL , 0.08 mmol) was added. After 36 h at rt the starting material had disappeared and the reaction was quenched

with saturated NaHCO_3 solution. Standard extractive work-up with EtOAc gave a 34:64:2 mixture of lactol **18b**, ethyl glycoside **21b** and tetrahydrofuran **22b**. Chromatographic purification (5-60% EtOAc-hexane) gave **18b** (2 mg, 22%) and an inseparable mixture of **21b** (82:19 mixture) and **22b** (60:40 mixture) (4 mg, 41%).

Data for **21b** (major): $R_f = 0.33$ (30% EtOAc-hexane). $^1\text{H NMR}$ (300 MHz) δ 1.22 (t, 3 H, $J = 7.1$ Hz), 2.42 (s, 3 H), 3.52 (dq, 1 H, $J = 9.6, 7.1$ Hz), 3.76 (dq, 1 H, $J = 9.5, 7.2$ Hz), 4.30 (d, 1 H, $J = 0.5$ Hz), 4.98 (s, 1 H), 5.16 (d, 1 H, $J = 0.7$ Hz), 7.21-7.45 (m, 9 H). **DNOE**: between H-2/H-3: 4.6%; between H-2/H- α : 4.6%; between H-2/H- α : 1.1%; between H-3/H-2: 3.1%; between H-3/H-ortho *p*-Tol: 0.8%; between H-5/H-3: 1.6%; between H-5/H-ortho Ph: 0.42%. $^{13}\text{C NMR}$ (125 MHz) δ 14.8, 21.7, 64.3, 64.4, 81.7, 100.2, 128.0 (2 C), 129.1 (2 C), 129.1, 129.7 (4 C), 134.2, 135.4, 145.5. **IR** (CCl_4): 3040, 3000, 2940-2820 (br), 1480, 1440, 1320, 1150, 1090, 1020, 970, 680, 650 cm^{-1} . **MS** (APCI): 361 $[\text{M}+1]^+$, 181(100%); 359 $[\text{M}-1]^-$, 155 (100%).

Partial data for **21b** (minor): $R_f = 0.33$ (30% EtOAc-hexane). $^1\text{H NMR}$ (300 MHz) δ 4.33 (d, 1 H, $J = 0.5$ Hz), 5.01 (s, 1 H), 5.21 (d, 1 H, $J = 0.7$ Hz).

Partial data for **22b**: $R_f = 0.33$ (30% EtOAc-hexane). $^1\text{H NMR}$ (300 MHz) δ 3.98 (dt, 1 H, $J = 6.1, 1.0$ Hz, minor), 4.01 (dt, 1 H, $J = 6.1, 1.0$ Hz, major), 4.21 (s, 1 H, minor), 4.24 (s, 1 H, major), 4.18-4.28 (m, 2 H), 5.22 (dd, 1 H, $J = 10.2, 1.7$ Hz), 5.29 (dq, 1 H, $J = 17.0, 1.7$ Hz), 5.88 (ddd, 1 H, $J = 17.0, 10.2, 5.1$ Hz, major), 5.88 (ddd, 1 H, $J = 17.0, 10.2, 5.1$ Hz, minor), 7.17-7.19 (m, 5 H), 7.48-7.52 (m, 4 H).

4.9. Allylation with SnCl_4 of the acetate of (-)-(3*S*,4*S*,5*R*)-3,4-epoxy-5-phenyl-4-(*p*-tolylsulfonyl)tetrahydrofuran-2-ol, **19b**.

To a cold ($-78\text{ }^\circ\text{C}$) solution of acetylated lactol **19b** (10 mg, 0.03 mmol) in anhydrous CH_2Cl_2 (1 mL) was added allyltrimethylsilane (5.0 equiv, 22 μL , 0.14 mmol) followed by freshly distilled SnCl_4 (2.0 equiv, 6 μL , 0.05 mmol). The reaction mixture was stirred and allowed to warm up to rt over 4 h. The reaction was quenched with saturated NaHCO_3 solution and standard extractive work-up with CH_2Cl_2 gave tetrahydrofuran **23b** along with other products of undetermined structure. Chromatographic purification (5-80% EtOAc-hexane) gave **23b** (4 mg, 48%) as a colorless oil.

Data for **23b**: $R_f = 0.19$ (1% EtOAc-CH₂Cl₂). ¹H NMR (300 MHz) δ 2.09 (s, 3 H), 2.27 (dd, 1 H, $J = 14.2, 8.1$ Hz), 2.32 (ddt, 1 H, $J = 14.2, 6.8, 1.2$ Hz), 2.39-2.44 (m, 1 H), 2.46-2.51 (m, 1 H), 4.31 (ddd, 1 H, $J = 7.8, 6.1, 5.4$ Hz), 4.90 (s, 1 H), 5.10-5.20 (m, 4 H), 5.27 (d, 1 H, $J = 8.1$ Hz), 5.79-5.86 (m, 2 H), 7.38 (s, 5 H). **DNOE**: between H-5/Ph: 4.9%; between H-5/H- α' : 3.3%; between H-5/H-3: 2.6%; between H-2/H- α : 3.5%. ¹³C NMR (125 MHz) δ 21.0, 37.5, 40.5, 78.2, 78.9, 84.7, 118.1, 119.8, 127.8 (2 C), 128.2 (2 C), 128.4, 131.7, 133.3, 136.2, 169.8. **MS** (ED): 302 [M]⁺, 261, 224, 201, 155, 131, 105, 95 (100%), 77, 67, 55, 43. **Anal. calcd for C₁₈H₂₂O₄**: C, 71.50; H, 7.33. **Found**: C, 71.77; H, 7.02.

4.10. Synthesis of (–)-(1'*R*,2*R*,3*S*)-2-(1'-*O*-Acetylhydroxybenzyl)-2-(*p*-tolylsulfonyl)-3-vinyloxirane, **24b**.

From vinyl oxirane **13b** (100 mg, 0.30 mmol) in 3 mL of CH₂Cl₂ with Ac₂O (85 μ L, 0.90 mmol), Et₃N (0.13 mL, 0.90 mmol) and 2 crystals of DMAP according to the general procedure (17 h), acetate **24b** (93 mg, 91%) was obtained after chromatography (5-40% EtOAc-hexane) as a colorless oil.

Data for **24b**: $R_f = 0.17$ (20% EtOAc-hexane). $[\alpha]_D^{20} = -6.2$ ($c = 0.78$). ¹H NMR (200 MHz) δ 2.04 (s, 3 H), 2.39 (s, 3 H), 4.42 (dd, 1 H, $J = 6.7, 3.8$ Hz), 5.45-5.51 (m, 1 H), 5.62-5.66 (m, 2 H), 6.24 (s, 1 H), 7.18 (d, 2 H, $J = 8.5$ Hz), 7.22-7.24 (m, 5 H), 7.49 (d, 2 H, $J = 8.3$ Hz). ¹³C NMR (50 MHz) δ 20.6, 21.6, 61.8, 70.2, 124.5, 127.5 (2 C), 128.2 (2 C), 128.5, 129.1, 129.2 (2 C), 129.4 (2 C), 133.9, 134.3, 145.0, 168.8. **IR** (CCl₄): 3020, 2980, 2900, 2880, 1730, 1570, 1470, 1430, 1340, 1300, 1280, 1120, 1060, 950, 910, 660, 630 cm⁻¹. **MS** (APCI): 371 [M-1]⁻, 155 (100%). **Anal. calcd for C₂₀H₂₀O₅S**: C, 64.50; H, 5.41; S, 8.61. **Found**: C, 64.83; H, 5.74; S, 8.32.

4.11. Synthesis of (+)-(1'*R*,2*S*,3*S*)-2-(1'-*O*-Acetylhydroxybenzyl)-2-(*p*-tolylsulfonyl)-3-formyloxirane, **25b**.

From vinyl oxirane **24b** (57 mg, 0.15 mmol) in 3 mL of CH₂Cl₂ bubbling O₃ (7 min) and with SMe₂ (5.0 equiv, 0.06 mL, 0.82 mmol), according to the general procedure, aldehyde **25b** (30 mg, 53%) was obtained as a colorless oil after chromatography (50% CH₂Cl₂-hexane - 1-100% EtOAc-CH₂Cl₂ - 1-50% MeOH-EtOAc), along with a more polar product sparingly soluble in CHCl₃ tentatively characterized as acid **26b** (33 mg, 47%).

Data for **25b**: R_f = 0.14 (30% EtOAc-hexane). $[\alpha]_D^{20}$ = +22.8 (c = 1.32). ¹H NMR (200 MHz) δ 1.95 (s, 3 H), 2.41 (s, 3 H), 4.18 (d, 1 H, J = 3.6 Hz), 6.37 (s, 1 H), 7.21-7.28 (m, 7 H), 7.60 (d, 2 H, J = 8.4 Hz), 8.95 (d, 1 H, J = 3.6 Hz). ¹³C NMR (50 MHz) δ 20.6, 21.7, 60.1, 69.5, 127.9 (2 C), 128.7 (2 C), 129.4, 129.5 (2 C), 129.8 (2 C), 133.3, 133.6, 145.9, 168.7, 192.4. IR (CCl₄): 3020, 2990, 2920, 2880, 2810, 1715, 1590, 1470, 1430, 1350, 1310, 1200, 1130, 1060, 670, 640 cm⁻¹. Anal. calcd for C₁₉H₁₈O₆S: C, 60.95; H, 4.85; S, 8.56. Found: C, 61.24; H, 5.02; S, 8.21.

Data for **26b**: R_f = 0.06 (20% EtOAc-CH₂Cl₂). ¹H NMR (DMSO-d₆, 200 MHz) δ 2.15 (s, 3 H), 2.37 (s, 3 H), 5.84 (s, 1 H), 6.57 (br s, 1 H), 7.17-7.23 (m, 4 H), 7.44-7.58 (m, 5 H), 9.67 (br s, 1 H).

4.12. Synthesis of (–)-(α*R*,1′*S*,2*S*,3*S*)-2-(α-*O*-Acetylhydroxybenzyl)-3-(1′-hydroxybut-3′-enyl)-2-(*p*-tolylsulfonyl)oxirane, **27b, and (α*R*,α′*R*,2*S*,3*S*)-2-(α-*O*-Acetylhydroxybenzyl)-3-(1′-hydroxybut-3′-enyl)-2-(*p*-tolylsulfonyl)oxirane, **28b**.**

To a cold (–78 °C) solution of aldehyde **25b** (21 mg, 0.06 mmol) in anhydrous CH₂Cl₂ (1 mL) was added allyltributylstannane (3.0 equiv, 52 μ L, 0.17 mmol) followed by freshly distilled BF₃·OEt₂ (4.0 equiv, 28 μ L, 0.22 mmol). The reaction mixture was stirred and allowed to warm up to rt over 5 h and 30 min. The reaction was quenched with saturated NaHCO₃ solution and standard extractive work-up with EtOAc gave an 80:20 mixture of allylated carbinols **27b** and **28b**. Chromatographic purification (5-40% EtOAc-hexane) gave **27b** (12 mg, 54%) and **28b** (4 mg, 18%) as colorless oils.

Data for **27b**: R_f = 0.20 (30% EtOAc-hexane). $[\alpha]_D^{20}$ = –6.8 (c = 0.80). ¹H NMR (300 MHz) δ 2.18 (s, 3 H), 2.38 (s, 3 H), 2.42-2.49 (m, 2 H), 3.01 (br s, 1 H), 3.71 (m, 1 H), 3.73 (d, 1 H, J = 8.6 Hz), 5.15 (dq, 1 H, J = 10.2, 1.0 Hz), 5.17 (dq, 1 H, J = 17.1, 1.6 Hz), 5.88 (dddd, 1 H, J = 17.0, 10.3, 7.3, 6.8 Hz), 6.11 (s, 1 H), 7.13-7.27 (m, 7 H), 7.52 (d, 2 H, J = 8.4 Hz). ¹H NMR (C₆D₆, 500 MHz)

δ 1.75 (s, 3 H), 1.78 (s, 3 H), 2.27 (ddt, 1 H, $J = 14.4, 7.3, 1.2$ Hz), 2.28-2.35 (m, 1 H), 3.38 (br d, 1 H, $J = 2.9$ Hz), 3.69 (m), 3.87 (d, 1 H, $J = 8.8$ Hz), 4.98 (d, 1 H, $J = 11.0$ Hz), 4.99 (d, 1 H, $J = 16.4$ Hz), 5.88 (dddd, 1 H, $J = 16.4, 14.2, 11.0, 7.1$ Hz), 6.16 (s, 1 H), 6.54 (d, 2 H, $J = 8.5$ Hz), 6.97-7.02 (m, 3 H), 7.42 (dt, 2 H, $J = 8.3, 0.7$ Hz), 7.60 (d, 2 H, $J = 8.3$ Hz). ^{13}C NMR (50 MHz) δ 21.0, 21.6, 39.1, 62.7, 67.3, 69.7, 74.7, 118.7, 126.9 (2 C), 128.1 (2 C), 128.3, 129.4 (2 C), 129.5 (2 C), 132.9, 133.8, 134.0, 145.2, 170.6. IR (CCl₄): 3400 (br), 2900, 1720, 1620, 1480, 1430, 1350, 1310, 1210, 1130, 900, 680 cm⁻¹. MS (ES): 453 [M+Cl]⁻, 451 [M+Cl]⁻ (100%), 415 [M-1]⁻; 439 [M+Na]⁺ (100%). **Anal. calcd for C₂₂H₂₄O₆S**: C, 63.44; H, 5.81; S, 7.70. **Found**: C, 63.06; H, 5.97; S, 8.02.

Data for **28b**: $R_f = 0.15$ (30% EtOAc-hexane). ^1H NMR (300 MHz) δ 2.09 (s, 3 H), 2.15-2.30 (m, 2 H), 2.38 (s, 3 H), 3.56 (ddd, 1 H, $J = 7.6, 4.3, 3.3$ Hz), 3.86 (d, 1 H, $J = 7.3$ Hz), 5.11 (dq, 1 H, $J = 17.0, 1.6$ Hz), 5.14 (dq, 1 H, $J = 10.4, 1.0$ Hz), 5.67 (dddd, 1 H, $J = 17.1, 10.4, 7.5, 6.7$ Hz), 6.43 (s, 1 H), 7.14-7.31 (m, 7 H), 7.49 (d, 2 H, $J = 8.3$ Hz). ^{13}C NMR (75 MHz) δ 20.7, 21.7, 38.6, 63.9, 67.1, 70.4, 76.8, 119.4, 126.8 (2 C), 128.3 (2 C), 128.5, 129.3 (2 C), 129.4 (2 C), 132.3, 134.1, 134.3, 145.0, 169.0. IR (CCl₄): 3480, 3040, 3000, 2890, 2820, 1730, 1625, 1580, 1480, 1430, 1350, 1300, 1200, 1130, 900, 670 cm⁻¹.

From an 80:20 mixture of **27b** and **28b** (6 mg, 0.03 mmol) in 1 mL of CH₂Cl₂ with Ac₂O (8 μ L, 0.08 mmol), Et₃N (11 μ L, 0.08 mmol) and 2 crystals of DMAP according to the general procedure (20 h), an inseparable 80:20 mixture of diacetates **29b** and **30b** (5 mg, 80%) was obtained after chromatography (5-50% EtOAc-hexane) as a colorless oil.

Data for **29b** (from the mixture): $R_f = 0.13$ (20% EtOAc-hexane). ^1H NMR (300 MHz) δ 1.95 (s, 3 H), 2.13 (s, 3 H), 2.40 (s, 3 H), 2.39-2.44 (m, 2 H), 4.08 (d, 1 H, $J = 8.2$ Hz), 4.64-4.74 (m, 1 H), 4.99-5.15 (m, 2 H), 5.60-5.90 (m, 1 H), 6.30 (s, 1 H), 7.17-7.59 (m, 7 H), 8.07 (dd, 2 H, $J = 8.4, 1.3$ Hz).

Partial data for **30b** (from the mixture): $R_f = 0.13$ (20% EtOAc-hexane). ^1H NMR (300 MHz) δ 1.89 (s, 3 H), 2.13 (s, 3 H), 3.94 (d, 1 H, $J = 8.9$ Hz), 4.90 (dt, 1 H, $J = 7.9, 3.8$ Hz), 5.46-5.60 (m, 1 H), 6.29 (s, 1 H), 7.17-7.59 (m, 9 H).

5. References and Notes.

1. Watson, S. C.; Eastham, J. E. *J. Organomet. Chem.* **1967**, 9, 165-168. In some cases this procedure was not completely accurate particularly for "old" bottles of reagent. Then, the reagent was titrated by reaction with a slight excess of 3,4-dimethoxybenzaldehyde in THF, standard work-up and measuring accurate integrals in the ^1H NMR of the crude reaction mixture.

2. Racemic *t*-butyl sulfoxides were prepared by free radical addition of 2-methyl-2-propanethiol to terminal alkynes (see: Jacobs, T. L.; Illingworth, G. E. *J. Org. Chem.* **1963**, 28, 2692) and oxidation with *m*CPBA in CH₂Cl₂.
3. Prepared in one step by the procedure of Craig: Craig, D.; Daniels, K.; McKenzie, A. R. *Tetrahedron* **1993**, 49, 11263-11304.
4. Marino, J. P.; Viso, A.; Lee, J.-D.; Fernández de la Pradilla, R.; Fernández, P.; Rubio, M. B. *J. Org. Chem.* **1997**, 62, 645-653.
5. Fernández de la Pradilla, R.; Fernández, J.; Manzano, P.; Méndez, P.; Priego, J.; Tortosa, M.; Viso, A.; Martínez-Ripoll, M.; Rodríguez, A. *J. Org. Chem.* **2002**, 67, 8166-8177.
6. This chlorohydrin was prepared as described in: Fernández de la Pradilla, R.; Buergo, M. V.; Martínez, M. V.; Montero, C.; Tortosa, M.; Viso, A. *J. Org. Chem.* **2004**, 69, 1978-1986.
7. The cyclic sulfides were prepared by DIBAL reduction following direct sulfenylation of the cyclic ketones as described in: Monteiro, H. J. *J. Org. Chem.* **1977**, 43, 2324-2326.
8. Meyers, D. J.; Fuchs, P. L. *J. Org. Chem.* **2002**, 67, 202-204.
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