Supporting Information for

**Sulfur-Directed Synthesis of Enantiopure Hydroxy 2-
Sulfinyl Butadienes.[†]**

Roberto Fernández de la Pradilla, María Victoria Buergo, María Victoria Martínez, Carlos
Montero, Mariola Tortosa and Alma Viso.*

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

Fax: 34-91-564-4853

E-mail: iqofp19@iqog.csic.es

[†] Taken in part from the M. S. Theses of M. V. M. and M. V. B., and Ph. D. Theses of C. M. and M. T.

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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 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 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. ^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). 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. The optical purity of starting materials **1a**,² **1b**,³ **1c**,⁴ **1d**⁴ and **1g**⁵ was established by comparing their optical rotations with those reported in the literature. The optical purity of *E* substrates obtained by lithiation with LDA of *Z* isomers and protonation was monitored similarly. Since 1-Naphth(2-OMe) containing derivatives were relatively poor substrates for this chemistry their enantiomeric purity was not studied.

1. Preparation of Starting Materials

1.1. General Procedure for the Condensation between Vinyl Sulfoxides and α -Chloroaldehydes

See printed version of the paper.

1.2. Synthesis of (+)-(2*R*,3*S*,*S*_s)-(4*E*)-2-Chloro-1-phenyl-4-(*p*-tolylsulfinyl)hept-4-en-3-ol, (**3b**), and (–)-(2*S*,3*R*,*S*_s)-(4*E*)-2-Chloro-1-phenyl-4-(*p*-tolylsulfinyl)hept-4-en-3-ol, (**4b**).

From a 70:30 *Z/E* mixture of vinyl sulfoxides **1b** (300 mg, 1.54 mmol, 1.0 equiv), 2.5 equiv of LDA and racemic 2-chlorohydrocinnamaldehyde (1168 mg, 6.93 mmol, 4.5 equiv) following the general procedure a 48:52 mixture of anti chlorohydrins **3b** and **4b** was obtained. Separation by chromatography (5-40% EtOAc-hexane) afforded 157 mg (0.43 mmol, 28%) of **3b** and 171 mg (0.47 mmol, 30%) of **4b** as colorless oils further recrystallized from Et₂O-hexane to yield white solids.

Data for **3b**: mp: 122-123 °C. $R_f = 0.36$ (30% EtOAc-hexane). $[\alpha]_D^{20} +38.1$ ($c = 0.96$). ¹H NMR (200 MHz) δ 1.13 (t, 3 H, $J = 7.5$ Hz), 2.32 (qd, 2 H, $J = 7.5, 2.4$ Hz), 2.40 (s, 3 H), 2.75 (dd, 1 H, $J = 14.5, 9.7$ Hz), 3.42 (dd, 1 H, $J = 14.4, 2.5$ Hz), 3.64 (td, 1 H, $J = 9.2, 2.6$ Hz), 4.77 (dd, 1 H, $J = 8.7, 6.3$ Hz), 4.98 (d, 1 H, $J = 6.2$ Hz), 6.62 (t, 1 H, $J = 7.5$ Hz), 7.07 (dm, 2 H, $J = 7.7$ Hz), 7.22 (m, 3 H), 7.31 (d, 2 H, $J = 8.4$ Hz), 7.57 (d, 2 H, $J = 8.3$ Hz). ¹³C NMR (50 MHz) δ 13.0, 21.3, 22.6, 39.4, 64.2, 75.7, 124.7 (2 C), 126.5, 128.1 (2 C), 129.4 (2 C), 129.9 (2 C), 137.4, 139.2, 141.6, 145.2. IR (KBr): 3280, 2970, 1630, 1600, 1490, 1450, 1310, 1200, 1105, 1080, 810, 740, 700 cm⁻¹. MS (EI): 362 [M]⁺, 354, 308, 264, 223, 187, 169, 140, 124, 92, 91 (100%), 77, 65. Anal. calcd for C₂₀H₂₃ClO₂S: C, 66.19; H, 6.39; Cl, 9.77; S, 8.84. Found: C, 66.22; H, 6.40; Cl, 9.49; S, 8.58.

Data for **4b**: mp: 107-109 °C. $R_f = 0.19$ (30% EtOAc-hexane). $[\alpha]_D^{20} -43.2$ ($c = 1.97$). ¹H NMR (200 MHz) δ 1.04 (t, 3 H, $J = 7.5$ Hz), 2.30 (oct, 2 H, $J = 7.5$ Hz), 2.41 (s, 3 H), 2.88 (dd, 1 H, $J = 14.4, 9.3$ Hz), 3.41 (dd, 1 H, $J = 14.4, 2.7$ Hz), 3.85 (br s, 1 H), 4.19 (tm, 1 H, $J = 9.2$ Hz), 4.66 (br d, 1 H, $J = 8.5$ Hz), 6.10 (t, 1 H, $J = 7.6$ Hz), 7.15-7.33 (m, 7 H), 7.56 (d, 2 H, $J = 8.3$ Hz). ¹³C NMR (50 MHz) δ 13.2, 21.4, 22.5, 39.6, 63.9, 73.1, 125.8 (2 C), 126.7, 128.1 (2 C), 129.7 (2 C), 130.1 (2 C), 137.2, 140.1, 140.7, 141.9, 142.1. IR (KBr): 3380, 3020, 2980, 2920, 1600, 1490, 1400, 1080, 1040, 1020, 1010, 930, 800, 750, 690, 640 cm⁻¹. MS (EI): 362 [M]⁺, 308, 223, 187, 154, 141, 139, 123, 105, 92, 91 (100%), 77, 65, 45. Anal. calcd for C₂₀H₂₃ClO₂S: C, 66.19; H, 6.39; Cl, 9.77; S, 8.84. Found: C, 66.36; H, 6.50; Cl, 9.58; S, 8.84.

1.3. Synthesis of (+)-(2*R*,3*S*,*S*_s)-(4*E*)-2-Chloro-7-methyl-1-phenyl-4-(*p*-tolylsulfinyl)oct-4-en-3-ol, (**3c**), and (-)-(2*S*,3*R*,*S*_s)-(4*E*)-2-Chloro-7-methyl-1-phenyl-4-(*p*-tolylsulfinyl)oct-4-en-3-ol, (**4c**).

From a 66:34 *Z/E* mixture of vinyl sulfoxides **1c** (269 mg, 1.21 mmol, 1.0 equiv), 2.5 equiv of LDA, racemic 2-chlorohydrocinnamaldehyde (918 mg, 5.44 mmol, 4.5 equiv), following the general

procedure, a 58:42 mixture of *anti* chlorohydrins **3c** and **4c** was obtained. Chromatographic separation (5-40% EtOAc-hexane) afforded 156 mg (0.399 mmol, 33%) of **3c** and 116 mg (0.299 mmol, 25%) of **4c** as colorless oils that were recrystallized from Et₂O-hexane to give white solids.

Data for **3c**: mp: 126-128 °C. $R_f = 0.25$ (30% EtOAc-hexane). $[\alpha]_D^{20} +52.3$ ($c = 1.23$). ¹H NMR (200 MHz) δ 0.97 (d, 6 H, $J = 6.6$ Hz), 1.83 (sept, 1 H, $J = 6.7$ Hz), 2.20 (t, 2 H, $J = 7.1$ Hz), 2.37 (s, 3 H), 2.73 (dd, 1 H, $J = 14.5, 9.8$ Hz), 3.42 (dd, 1 H, $J = 14.5, 2.6$ Hz), 3.68 (tm, 1 H, $J = 9.4, 2.5$ Hz), 4.78 (dd, 1 H, $J = 8.6, 6.3$ Hz), 4.91 (d, 1 H, $J = 6.3$ Hz), 6.65 (t, 1 H, $J = 7.4$ Hz), 7.05 (dm, 2 H, $J = 7.7$ Hz), 7.17-7.24 (m, 3 H), 7.29 (d, 2 H, $J = 7.9$ Hz), 7.56 (d, 2 H, $J = 8.3$ Hz). ¹³C NMR (50 MHz) δ 21.3, 22.2, 22.6, 28.3, 37.8, 39.4, 64.8, 75.8, 124.7 (2 C), 126.5, 128.1 (2 C), 129.3 (2 C), 129.9 (2 C), 137.4, 139.0, 140.1, 141.6, 142.7. IR (KBr): 3290, 2960, 1490, 1460, 1450, 1100, 1020, 1010, 800, 750, 700 cm⁻¹. MS (EI): 390 [M]⁺, 373, 336, 251, 215, 197, 172, 140, 139, 103, 92, 91 (100%), 77, 43. Anal. calcd for C₂₂H₂₇ClO₂S: C, 67.59; H, 6.96; Cl, 9.07; S, 8.20. Found: C, 67.79; H, 7.06; Cl, 8.85; S, 8.06.

Data for **4c**: mp: 127-129 °C. $R_f = 0.15$ (30% EtOAc-hexane). $[\alpha]_D^{20} -40.6$ ($c = 1.43$). ¹H NMR (200 MHz) δ 0.87 (d, 3 H, $J = 5.6$ Hz), 0.90 (d, 3 H, $J = 5.6$ Hz), 1.72 (m, 1 H), 2.17 (m, 2 H), 2.41 (s, 3 H), 2.89 (dd, 1 H, $J = 14.4, 9.3$ Hz), 3.45 (dd, 1 H, $J = 14.4, 2.7$ Hz), 3.85 (d, 1 H, $J = 7.4$ Hz), 4.25 (td, 1 H, $J = 9.0, 2.7$ Hz), 4.65 (dd, 1 H, $J = 8.3, 7.7$ Hz), 6.10 (t, 1 H, $J = 7.5$ Hz), 7.16-7.33 (m, 7 H), 7.57 (d, 2 H, $J = 8.2$ Hz). ¹³C NMR (50 MHz) δ 21.4, 22.2, 22.4, 28.5, 37.7, 39.8, 64.0, 73.4, 125.9 (2 C), 126.7, 128.2 (2 C), 129.7 (2 C), 130.0 (2 C), 137.2, 138.2, 140.2, 142.2, 142.9. IR (KBr): 3400, 3120, 2960, 1490, 1450, 1080, 1040, 1015, 930, 800, 750, 700, 650 cm⁻¹. MS (EI): 390 [M]⁺, 337, 251, 234, 215, 197, 172, 155, 140, 105, 92, 91 (100%), 77, 43, 41. Anal. calcd for C₂₂H₂₇ClO₂S: C, 67.59; H, 6.96; Cl, 9.07; S, 8.20. Found: C, 67.78; H, 6.93; Cl, 8.90; S, 8.17.

1.4. Synthesis of (+)-(5*S*,6*R*,*S*_s)-(3*E*)-6-Chloro-2-methyl-4-(*p*-tolylsulfinyl)dec-3-en-5-ol, (**3d**), and (–)-(5*R*,6*S*,*S*_s)-(3*E*)-6-Chloro-2-methyl-4-(*p*-tolylsulfinyl)dec-3-en-5-ol, (**4d**).

From a 98:2 *Z/E* mixture of vinyl sulfoxides **1d** (210 mg, 1.00 mmol, 1.0 equiv), 2.5 equiv of LDA, racemic 2-chlorohexanal (475 mg, 3.50 mmol, 3.5 equiv), following the general procedure, a 52:48 mixture of *anti* chlorohydrins **3d** and **4d** was obtained. Chromatographic separation (5-40% EtOAc-

hexane) afforded 130 mg (0.38 mmol, 38%) of **3d** and 121 mg (0.35 mmol, 35%) of **4d** as white solids that were recrystallized from EtOAc-hexane (**3d**), and CH₂Cl₂-hexane (**4d**).

Data for **3d**: mp: 164-165 °C. $R_f = 0.44$ (30% EtOAc-hexane). $[\alpha]_D^{20} +3.60$ ($c = 0.64$). ¹H NMR (300 MHz) δ 0.87 (t, 3 H, $J = 7.1$ Hz), 1.10 (d, 3 H, $J = 6.6$ Hz), 1.14 (d, 3 H, $J = 6.6$ Hz), 1.24-1.62 (m, 5 H), 2.04 (m, 1 H), 2.42 (s, 3 H), 2.84 (dsept, 1 H, $J = 10.6, 6.5$ Hz), 3.58 (ddd, 1 H, $J = 9.6, 8.4, 2.6$ Hz), 4.44 (d, 1 H, $J = 6.6$ Hz), 4.70 (dd, 1 H, $J = 8.2, 6.5$ Hz), 6.37 (d, 1 H, $J = 10.5$ Hz), 7.31 (d, 2 H, $J = 7.9$ Hz), 7.54 (d, 2 H, $J = 8.3$ Hz). ¹³C NMR (50 MHz) δ 13.9, 21.4, 22.0, 22.2, 28.1, 28.4, 33.1, 64.0, 73.9, 125.9 (2 C), 130.0 (2 C), 140.3, 140.4, 142.0, 144.8. IR (KBr): 3400, 2960, 2880, 2860, 1630, 1690, 1490, 1460, 1360, 1120, 1080, 980, 800, 670 cm⁻¹. MS (EI): 343 [M+1]⁺, 325, 289, 237, 185, 149, 140 (100%), 107, 97, 92, 91, 69, 55, 43, 41. Anal. calcd for C₁₈H₂₇ClO₂S: C, 63.04; H, 7.94; Cl, 10.34; S, 9.35. Found: C, 63.07; H, 7.96; Cl, 10.61; S, 9.59.

Data for **4d**: mp: 136-138 °C. $R_f = 0.24$ (30% EtOAc-hexane). $[\alpha]_D^{20} -22.8$ ($c = 0.66$). ¹H NMR (300 MHz) δ 0.89 (t, 3 H, $J = 7.1$ Hz), 1.01 (d, 3 H, $J = 6.6$ Hz), 1.06 (d, 3 H, $J = 6.5$ Hz), 1.21-1.66 (m, 5 H), 2.00 (m, 1 H), 2.41 (s, 3 H), 2.86 (dsept, 1 H, $J = 10.7, 6.6$ Hz), 3.56 (br s, 1 H), 3.98 (td, 1 H, $J = 8.9, 2.4$ Hz), 4.57 (m, 1 H), 5.89 (d, 1 H, $J = 10.7$ Hz), 7.31 (d, 2 H, $J = 7.9$ Hz), 7.55 (d, 2 H, $J = 8.3$ Hz). ¹³C NMR (50 MHz) δ 13.9, 21.4, 22.0, 22.2, 28.1, 28.4, 33.1, 64.0, 73.9, 125.9 (2 C), 130.0 (2 C), 140.3, 140.4, 142.0, 144.8. IR (KBr): 3400, 2960, 2920, 2860, 1490, 1080, 1030, 1010, 800, 740, 640 cm⁻¹. MS (EI): 343 [M+1]⁺, 325, 289, 237, 185, 149, 140 (100%), 107, 97, 92, 91, 69, 55, 43, 41. Anal. calcd for C₁₈H₂₇ClO₂S: C, 63.04; H, 7.94; Cl, 10.34; S, 9.35. Found: C, 63.21; H, 8.04; Cl, 10.37; S, 9.06.

1.5. Synthesis of (-)-(3*R*,4*S*,*S*_s)-(5*E*)-3-Chloro-2-methyl-5-(*p*-tolylsulfinyl)dec-5-en-4-ol, (**3e**), and (-)-(3*S*,4*R*,*S*_s)-(5*E*)-3-Chloro-2-methyl-5-(*p*-tolylsulfinyl)dec-5-en-4-ol, (**4e**).

From an 88:12 *Z/E* mixture of vinyl sulfoxides **1a** (667 mg, 3.0 mmol, 1.0 equiv), 2.5 equiv of LDA, racemic 2-chloroisovaleraldehyde (1081 mg, 9.0 mmol, 3.0 equiv), following the general procedure, a 56:44 mixture of *anti* chlorohydrins **3e** and **4e** was obtained. Chromatographic separation (5-40% EtOAc-hexane) afforded 447 mg (1.30 mmol, 43%) of **3e** and 353 mg (1.03 mmol, 32%) of **4e** as colorless oils that were recrystallized from Et₂O-hexane to give white solids.

Data for **3e**: mp: 88-90 °C. R_f = 0.37 (30% EtOAc-hexane). $[\alpha]_D^{20}$ -37.5 (c = 0.12). ^1H NMR (300 MHz) δ 0.78 (d, 3 H, J = 6.8 Hz), 0.82 (d, 3 H, J = 6.6 Hz), 0.93 (t, 3 H, J = 7.20 Hz), 1.35-1.54 (m, 4 H), 2.20-2.42 (m, 3 H), 2.41 (s, 3 H), 3.47 (dd, 1 H, J = 10.4, 2.3 Hz), 4.78 (dd, 1 H, J = 10.4, 7.5 Hz), 4.99 (d, 1 H, J = 7.6 Hz), 6.56 (t, 1 H, J = 7.4 Hz), 7.30 (d, 2 H, J = 8.3 Hz), 7.53 (d, 2 H, J = 8.5 Hz). ^{13}C NMR (50 MHz) δ 13.8, 14.1, 20.6, 21.3, 22.3, 28.1, 28.6, 30.6, 69.0, 74.0, 124.5 (2 C), 129.7 (2 C), 138.9, 139.5, 141.4, 143.6. IR (CCl₄): 3300, 2930, 2900, 2840, 1620, 1580, 1480, 1450, 1370, 1350, 1280, 1230, 1160, 1060, 1030, 1000, 700 cm⁻¹. MS (EI): 342 [M]⁺, 289, 251, 140 (100%), 92, 69, 55, 43. Anal. calcd for C₁₈H₂₇ClO₂S: C, 63.04; H, 7.94; Cl, 10.34; S, 9.35. Found: C, 62.84; H, 7.62; Cl, 10.03; S, 9.51.

Data for **4e**: mp: 122-125 °C. R_f = 0.20 (30% EtOAc-hexane). $[\alpha]_D^{20}$ -13.3 (c = 0.22). ^1H NMR (300 MHz) δ 0.87 (t, 3 H, J = 7.1 Hz), 0.89 (d, 3 H, J = 6.6 Hz), 1.02 (d, 3 H, J = 6.7 Hz), 1.22-1.46 (m, 4 H), 2.21-2.29 (m, 2 H), 2.40 (s, 3 H), 2.51 (septd, 1 H, J = 6.7, 2.2 Hz), 3.74 (d, 1 H, J = 8.4 Hz), 4.25 (dd, 1 H, J = 10.4, 2.2 Hz), 4.63 (dd, 1 H, J = 10.8, 8.2 Hz), 5.91 (t, 1 H, J = 7.5 Hz), 7.30 (d, 2 H, J = 7.3 Hz), 7.55 (d, 2 H, J = 7.5 Hz). ^{13}C NMR (50 MHz) δ 13.8, 14.3, 20.4, 21.4, 22.3, 28.6, 30.1, 69.4, 72.0, 126.0 (2 C), 130.0 (2 C), 138.8, 140.5, 142.1, 142.6. IR (CCl₄): 3260, 3020, 2980, 2920, 1570, 1470, 1040, 1350, 1220, 1190, 1060, 1030, 990 cm⁻¹. MS (EI): 342 [M]⁺, 289, 251, 140 (100%), 92, 69, 55, 43. Anal. calcd for C₁₈H₂₇ClO₂S: C, 63.04; H, 7.94; Cl, 10.34; S, 9.35. Found: C, 62.78; H, 8.21; Cl, 9.94; S, 9.13.

1.6. Synthesis of (+)-(5*R*,6*S*,*R*_s)-(7*E*)-5-Chloro-7-(2-methoxynaphthalen-1-ylsulfinyl)dodec-7-en-6-ol, (3f), and (+)-(5*S*,6*R*,*R*_s)-(7*E*)-5-Chloro-7-(2-methoxynaphthalen-1-ylsulfinyl)dodec-7-en-6-ol, (4f).

From a 50:50 *Z/E* mixture of vinyl sulfoxides **1e** (293 mg, 1.02 mmol, 1.0 equiv), 2.5 equiv of LDA and racemic 2-chlorohexanal (623 mg, 4.59 mmol, 4.5 equiv), following the general procedure, a 57:43 mixture of *anti* chlorohydrins **3f** and **4f** was obtained. Purification by chromatography (5-40% EtOAc-hexane) afforded 30 mg of **3f** (0.07 mmol, 7%) as a white solid, 200 mg (0.47 mmol, 47%) of a mixture of **3f** and **4f** and 75 mg (0.18 mmol, 18%) of **4f**. The mixture of **3f** and **4f** was recrystallized

twice from EtOAc–hexane affording 60 mg of pure **3f** as a white solid. A further recrystallization of the mother liquor from Et₂O–hexane afforded 60 mg of **4f** as a white solid.

Data for **3f**: mp: 92–94 °C. R_f = 0.49 (40% EtOAc–hexane). $[\alpha]_D^{20}$ +180.5 (c = 1.20). ¹H NMR (300 MHz) δ 0.78 (t, 3 H, J = 7.1 Hz), 0.76 (t, 3 H, J = 7.2 Hz), 0.82–0.91 (m, 3 H), 1.16–1.47 (m, 6 H), 1.71 (m, 1 H), 2.24 (qd, 2 H, J = 7.4, 4.0 Hz), 2.30 (d, 1 H, J = 5.1 Hz), 3.57 (ddd, 1 H, J = 9.9, 7.3, 2.6 Hz), 3.85 (s, 3 H), 4.54 (dd, 1 H, J = 7.1, 5.1 Hz), 6.70 (t, 1 H, J = 7.7 Hz), 7.25 (d, 1 H, J = 9.0 Hz), 7.39 (ddd, 1 H, J = 8.1, 6.8, 1.2 Hz), 7.51 (ddd, 1 H, J = 8.5, 7.0, 1.6 Hz), 7.63 (dd, 1 H, J = 8.3, 1.0 Hz), 7.80 (d, 1 H, J = 9.0 Hz), 8.62 (dd, 1 H, J = 8.8, 0.7 Hz). ¹³C NMR (75 MHz) δ 13.9 (2 C), 21.7, 22.4, 28.2, 28.6, 31.2, 32.4, 56.8, 64.2, 73.6, 113.0, 120.9, 122.9, 124.6, 128.0, 128.8, 129.5, 132.2, 134.8, 138.4, 138.7, 157.2. IR (KBr): 3436, 2956, 2927, 1636, 1465, 1272, 1251, 1024 cm^{−1}. MS (ES): 423 [M+1]⁺ (100%). Anal. calcd for C₂₃H₃₁ClO₃S: C, 65.31; H, 7.39; Cl, 8.38; S, 7.58. Found: C, 65.17; H, 7.44; Cl, 8.19; S, 7.69.

Data for **4f**: mp: 92–93 °C. R_f = 0.45 (40% EtOAc–hexane). $[\alpha]_D^{20}$ +79.7 (c = 1.00). ¹H NMR (300 MHz) δ 0.78 (t, 3 H, J = 7.1 Hz), 0.90 (t, 3 H, J = 7.2 Hz), 1.20–1.49 (m, 6 H), 1.52–1.73 (m, 3 H), 2.15–2.39 (m, 3 H), 4.00 (s, 3 H), 4.20 (br s, 1 H), 4.27 (td, 1 H, J = 9.3, 2.6 Hz), 4.65 (ap d, 1 H, J = 8.5 Hz), 5.77 (t, 1 H, J = 7.7 Hz), 7.28 (d, 1 H, J = 9.0 Hz), 7.40 (ddd, 1 H, J = 8.1, 6.8, 1.2 Hz), 7.53 (ddd, 1 H, J = 8.5, 7.1, 1.5 Hz), 7.81 (dt, 1 H, J = 8.1, 0.7 Hz), 8.01 (d, 1 H, J = 9.0 Hz), 8.63 (dd, 1 H, J = 8.7, 0.8 Hz). ¹³C NMR (75 MHz) δ 13.7, 13.9, 22.1 (2 C), 28.0, 28.1, 30.9, 33.6, 56.9, 63.4, 74.7, 112.9, 120.1, 123.5, 124.6, 128.2, 128.7, 129.4, 132.0, 135.3, 135.5, 138.6, 158.1. IR (KBr): 3436, 2955, 2927, 2860, 1621, 1596, 1507, 1468, 1431, 1335, 1268, 1249, 1149, 1135, 1052, 1019, 813, 772, 751 cm^{−1}. MS (ES): 423 [M+1]⁺ (100%). Anal. calcd for C₂₃H₃₁ClO₃S: C, 65.31; H, 7.39; Cl, 8.38; S, 7.58. Found: C, 65.60; H, 7.23; Cl, 8.06; S, 7.73.

1.7. Synthesis of (–)-(2*S*,3*R*,*S*_s)-3-Chloro-1-cyclohexylidene-1-(*p*-tolylsulfinyl)heptan-2-ol, (3g**), and (–)-(2*R*,3*S*,*S*_s)-3-Chloro-1-cyclohexylidene-1-(*p*-tolylsulfinyl)heptan-2-ol, (**4g**).**

See printed version of the paper.

1.8. General Procedure for Oxidation of Sulfoxides with MMPP

See printed version of the paper.

1.9. Synthesis of (+)-(5*S*,6*R*)-(7*E*)-5-Chloro-7-(*p*-tolylsulfonyl)dodec-7-en-6-ol, (**23a**).

From chlorohydrin **4a** (80 mg, 0.22 mmol, 1.0 equiv) in MeOH (3 mL) and MMPP (246 mg, 0.45 mmol, 2.0 equiv), according to the general procedure (4 h 30 min), after chromatography (10-40% EtOAc-hexane), vinyl sulfone **23a** (63 mg, 0.17 mmol, 75%) was obtained as a white solid, further recrystallized from Et₂O-hexane.

Data for **23a**: mp: 144-149 °C. R_f = 0.46 (30% EtOAc-hexane). $[\alpha]_D^{20}$ +6.2 (c = 0.52). ¹H NMR (300 MHz) δ 0.88 (t, 3 H, J = 6.8 Hz), 0.90 (t, 3 H, J = 6.9 Hz), 1.20-1.70 (m, 9 H), 2.08 (m, 1 H), 2.37 (m, 2 H), 2.42 (s, 3 H), 3.55 (d, 1 H, J = 8.3 Hz), 3.90 (dt, 1 H, J = 9.3, 2.6 Hz), 4.55 (t, 1 H, J = 9.0 Hz), 7.01 (t, 1 H, J = 7.6 Hz), 7.30 (d, 2 H, J = 8.2 Hz), 7.73 (d, 2 H, J = 8.4 Hz). ¹³C NMR (50 MHz) δ 13.8, 13.9, 21.6, 22.1, 22.4, 27.9, 28.7, 30.4, 33.3, 63.2, 72.9, 127.8 (2 C), 129.8 (2 C), 138.0, 139.4, 144.5, 148.7. IR (CCl₄): 3460, 2960, 2920, 2860, 1630, 1600, 1470, 1400, 1280, 1260, 1130, 820 cm⁻¹. MS (EI): 373 [M+1]⁺, 267 (100%), 211, 157, 139, 111, 91, 65, 55. Anal. calcd for C₁₉H₂₉ClO₃S: C, 61.19; H, 7.84; Cl, 9.51; S, 8.60. Found: C, 61.35; H, 8.07; Cl, 9.18; S, 8.60.

In a related experiment the oxidation of **3a** gave *ent*-**23a** which had identical spectral features to those of **23a**.

Data for *ent*-**23a**: mp: 152-153 °C. $[\alpha]_D^{20}$ -8.7 (c = 0.55). NOED between H-5/H-Ar ortho: 2.5%; between H-5/H-6: 2.8%; between H-5/OH: 2.2%; between H-5/H-4: 6.1%; between H-5/H-4: 3.9%; between H-6/H-Ar ortho: 2.4%; between H-6/OH: 5.4%, between H-6/H-5: 2.8%; between H-6/H-9: 5.4%; between H-Ar ortho/H-8: 7.5%; between H-Ar ortho/OH: 2.5%; H-Ar ortho/H-5: 6.2%. MS (CI/NH₃): 392, 391, 390 [M+NH₄]⁺, 354 (100%), 338, 256, 181. HRMS calcd for C₁₉H₂₉³⁵ClSO₃NH₄ [M+NH₄]⁺: 390.1870. Found: 390.1861. Anal. calcd for C₁₉H₂₉ClO₃S: C, 61.19; H, 7.84; Cl, 9.51; S, 8.60. Found: C, 61.40; H, 8.02; S, 8.36.

1.10. Synthesis of (+)-(2*S*,3*S*)-(4*Z*)-2-[(*tert*-Butyldimethylsilyl)oxy]-4-(*p*-tolylsulfenyl)non-4-en-3-ol, (7**).**

A round-bottomed flask was charged with 20 mL of anhydrous THF (6 mL/mmol of sulfide) and [(*E*)-1-(*p*-tolylsulfenyl)hex-1-enyl]tributylstannane (1.569 g, 3.4 mmol, 1.0 equiv) and cooled to -78 °C. To the above solution was added 1.1 equiv of *n*-BuLi (2.34 mL, 3.74 mmol, 1.6 M solution), and the mixture was stirred for 15 min at this temperature. Then 1.3 equiv of (2*S*)-2-[(*tert*-butyldimethylsilyl)oxy]propanal (832 mg, 4.42 mmol) in THF (1 mL/mmol of aldehyde) was added dropwise and the resulting solution was stirred for 15 min. The reaction mixture was quenched at this temperature with a saturated solution of NH₄Cl (4 mL/mmol of sulfide) and H₂O (4 mL/mmol of sulfide) and diluted with EtOAc (3 mL/mmol of sulfide). The layers were separated and the aqueous phase was extracted twice with EtOAc (6 mL/mmol). The combined organic extracts were washed with a saturated solution of NaCl, dried over MgSO₄, filtered and concentrated under reduce pressure. Purification by chromatography (1-5% EtOAc-hexane) afforded 78 mg (0.34 mmol, 10%) of vinyl sulfide (*Z*)-1-hexenyl *p*-tolyl sulfide and 1.017 g (2.58 mmol, 76%) of an 85:15 mixture of **7** and **6**. A second chromatography of 100 mg of this mixture (70% toluene-hexane) afforded 60 mg of **7** and **6** and 40 mg of pure **7** as a colorless oil.

Data for **7**: R_f = 0.19 (70% toluene-hexane). $[\alpha]_D^{20}$ +167.5 (c = 0.82). ¹H NMR (300 MHz) δ -0.09 (s, 3 H), -0.02 (s, 3 H), 0.81 (s, 9 H), 0.85 (t, 3 H, J = 7.1 Hz), 0.98 (d, 3 H, J = 6.3 Hz), 1.24-1.44 (m, 4 H), 2.28 (s, 3 H), 2.37 (ap quint, 2 H, J = 6.9 Hz), 2.54 (br s, 1 H), 4.03 (ap s, 1 H), 4.09 (qd, 1 H, J = 6.3, 3.7 Hz), 6.36 (td, 1 H, J = 7.3, 1.5 Hz), 7.04 (d, 2 H, J = 8.3 Hz), 7.17 (d, 2 H, J = 8.3 Hz). ¹³C NMR (75 MHz) δ -5.1, -4.8, 13.9, 16.1, 18.0, 20.9, 22.4, 25.7 (3 C), 29.1, 31.3, 69.6, 76.6, 129.0 (2 C), 129.7 (2 C), 130.5, 131.7, 135.9, 138.1. IR (film): 3543, 2956, 2929, 2857, 1492, 1463, 1380, 1361, 1254, 1085, 1017, 967, 837, 806, 776 cm⁻¹. MS (ES): 417 [M+Na]⁺ (100%), 377 [(M-18)+1]⁺. Anal. calcd for C₂₂H₃₈O₂SSi: C, 66.95; H, 9.70; S, 8.12. Found: C, 67.21; H, 10.02; S, 7.92.

Partial data for **6**: R_f = 0.21 (70% toluene-hexane). ¹H NMR (300 MHz) δ 6.27 (ddd, 1H, J = 7.8, 6.6, 1.2 Hz).

1.11. Synthesis of (+)-(2*S*,3*S*,*R*_s)-(4*Z*)-2-[(*tert*-Butyldimethylsilyl)oxy]-4-(*p*-tolylsulfinyl)non-4-en-3-ol, (9**), and (–)-(2*S*,3*S*,*S*_s)-(4*Z*)-2-[(*tert*-Butyldimethylsilyl)oxy]-4-(*p*-tolylsulfinyl)non-4-en-3-ol, (**8**).**

To a solution of sulfide **7** (400 mg, 1.01 mmol, 1.0 equiv) in CH_2Cl_2 (8 mL/mmol of sulfide) was added 3.0 equiv (419 mg, 3.03 mmol) of K_2CO_3 . The mixture was cooled to -78°C and *m*-CPBA (1.01 mmol, 233 mg (75%), 1.0 equiv) was added. The resulting solution was allowed to warm up slowly, monitored by TLC until completion (4 h) and quenched with 4 mL of a 1 M solution of $\text{Na}_2\text{S}_2\text{O}_4$, 4 mL of a saturated solution of NaHCO_3 and 4 mL of water. The layers were separated and the aqueous phase was extracted twice with CH_2Cl_2 (6 mL/mmol of sulfide). The combined organic extracts were washed with a saturated solution of NaCl , dried over MgSO_4 , filtered and concentrated under reduced pressure to give a 52:48 mixture of **8** and **9**. Purification by chromatography (100% CH_2Cl_2 -5% $\text{EtOAc-CH}_2\text{Cl}_2$) afforded 134 mg (0.33 mmol, 33%) of **9** and 145 mg (0.35 mmol, 35%) of **8**, both as colorless oils. This oxidation may be carried out efficiently on the mixture of **6** and **7**.

Data for **9**: $R_f = 0.39$ (5% $\text{EtOAc-CH}_2\text{Cl}_2$). $[\alpha]_D^{20} +151.0$ ($c = 1.25$). $^1\text{H NMR}$ (300 MHz) δ -0.02 (s, 3 H), 0.04 (s, 3 H), 0.83 (s, 9 H), 0.94 (t, 3 H, $J = 7.1$ Hz), 1.03 (d, 3 H, $J = 6.1$ Hz), 1.34 - 1.56 (m, 4 H), 2.37 (s, 3 H), 2.47 (sextd, 1 H, $J = 7.0, 1.2$ Hz), 2.64 (d, 1 H, $J = 2.2$ Hz), 2.77 (dq, 1 H, $J = 9.0, 7.3$ Hz), 4.05 (m, 1 H), 4.22 (qd, 1 H, $J = 6.3, 3.4$ Hz), 6.50 (ddd, 1 H, $J = 9.0, 6.6, 1.2$ Hz), 7.26 (d, 2 H, $J = 8.2$ Hz), 7.41 (d, 2 H, $J = 8.3$ Hz). $^{13}\text{C NMR}$ (50 MHz) δ $-4.9, -4.7, 13.8, 16.1, 17.9, 21.3, 22.3, 25.8$ (3 C), $28.4, 31.5, 71.0, 71.2, 124.1$ (2 C), 129.8 (2 C), $139.6, 140.6, 140.9, 142.0$. IR (film): $3401, 2956, 2929, 2857, 1492, 1463, 1380, 1253, 1132, 1081, 1044, 1015, 970, 837, 807, 776$ cm^{-1} . MS (ES): 843 $[2\text{M}+\text{Na}]^+$, 433 $[\text{M}+\text{Na}]^+$, 411 $[\text{M}+1]^+$ (100%). Anal. calcd for $\text{C}_{22}\text{H}_{38}\text{O}_3\text{SSi}$: C, 64.34; H, 9.33; S, 7.81. Found: C, 64.02; H, 9.56; S, 7.65.

Data for **8**: $R_f = 0.18$ (5% $\text{EtOAc-CH}_2\text{Cl}_2$). $[\alpha]_D^{20} -147.9$ ($c = 0.94$). $^1\text{H NMR}$ (300 MHz) δ -0.09 (s, 3 H), -0.05 (s, 3 H), 0.77 (s, 9 H), 0.81 (d, 3 H, $J = 6.1$ Hz), 0.91 (t, 3 H, $J = 7.1$ Hz), 1.31 - 1.54 (m, 4 H), 2.37 (s, 3 H), 2.38 (ap sext, 1 H, $J = 7.2$ Hz), 2.65 (ap sext, 1 H, $J = 7.4$ Hz), 3.20 (d, 1 H, $J = 3.4$ Hz), 3.39 (qd, 1 H, $J = 6.2, 5.0$ Hz), 4.24 (dd, 1 H, $J = 4.4, 3.4$ Hz), 6.40 (ddd, 1 H, $J = 8.5, 7.0, 0.8$ Hz), 7.26 (d, 2 H, $J = 8.2$ Hz), 7.43 (d, 2 H, $J = 8.3$ Hz). $^{13}\text{C NMR}$ (50 MHz) δ $-4.9, -4.7, 13.7, 17.6, 17.8, 21.2, 22.2, 25.6$ (3 C), $28.6, 31.2, 69.7, 71.1, 124.5$ (2 C), 129.8 (2 C), $139.7, 140.2, 140.9,$

142.2. **IR** (film): 3412, 2956, 2928, 2856, 1492, 1462, 1379, 1253, 1134, 1082, 1046, 1014, 968, 835, 808, 776 cm^{-1} . **MS** (ES): 843 $[\text{2M}+\text{Na}]^+$, 411 $[\text{M}+1]^+$ (100%). **Anal. calcd for** $\text{C}_{22}\text{H}_{38}\text{O}_3\text{SSi}$: C, 64.34; H, 9.33; S, 7.81. **Found**: C, 64.62; H, 9.53; S, 7.97.

1.12. Synthesis of (+)-(2*S*,3*S*)-(4*Z*)-2-[(*tert*-Butyldimethylsilyl)oxy]-4-(*p*-tolylsulfonyl)non-4-en-3-ol, (**10**).

From sulfide **7** (52 mg, 0.13 mmol, 1.0 equiv) in 1.3 mL of MeOH and MMPP (326 mg (80%), 0.53 mmol, 4.0 equiv), according to the general procedure (5 h), sulfone **10** was obtained. Purification by chromatography (100% CH_2Cl_2) afforded 44 mg (0.1 mmol, 77%) of **10** as a colorless oil.

Data for **10**: $R_f = 0.55$ (5% EtOAc- CH_2Cl_2). $[\alpha]_D^{20} +77.9$ ($c = 1.12$). **^1H NMR (300 MHz)** δ 0.08 (s, 3 H), 0.09 (s, 3 H), 0.84 (t, 3 H, $J = 7.1$ Hz), 0.87 (s, 9 H), 1.03(d, 3 H, $J = 6.1$ Hz), 1.20-1.38 (m, 4 H), 2.40 (s, 3 H), 2.43 (m, 1 H), 2.67 (m, 1 H), 2.92 (d, 1 H, $J = 3.2$ Hz), 4.30 (qd, 1 H, $J = 6.3, 4.0$ Hz), 4.40 (ap t, 1 H, $J = 3.2$ Hz), 6.48 (dd, 1 H, $J = 7.9, 1.0$ Hz), 7.29 (d, 2 H, $J = 8.5$ Hz), 7.75 (d, 2 H, $J = 8.5$ Hz). **^{13}C NMR (50 MHz)** δ -4.8, -4.6, 13.8, 16.5, 17.9, 21.6, 22.3, 25.8 (3 C), 28.2, 30.9, 70.1, 74.0, 127.1 (2 C), 129.7 (2 C), 139.1, 144.1, 146.0. **IR** (film): 3520, 2926, 2929, 2858, 1636, 1598, 1495, 1463, 1380, 1361, 1302, 1255, 1140, 1085, 1004, 969, 837, 812, 777, 738, 706 cm^{-1} . **MS** (ES): 449 $[\text{M}+\text{Na}]^+$, 427 $[\text{M}+1]^+$ (100%), 409 $[(\text{M}-18)+1]^+$. **Anal. calcd for** $\text{C}_{22}\text{H}_{38}\text{O}_4\text{SSi}$: C, 61.93; H, 8.98; S, 7.51. **Found**: C, 62.02; H, 8.66; S, 7.42.

1.13. General Procedure for Mesylation of Hydroxy Vinyl Sulfoxides

To a cold (0 °C) solution of the alcohol in CH_2Cl_2 (10 mL/mmol) was added 5.0 equiv of freshly distilled methanesulfonyl chloride (MsCl) and 5.2 equiv of Et_3N . The reaction mixture was stirred and allowed to warm up slowly to rt and monitored by TLC. When the reaction was complete, it was quenched with saturated NH_4Cl (10 mL/mmol), diluted with EtOAc (10 mL/mmol). The layers were separated, the organic layer was washed with a saturated solution of NaCl (5 mL/mmol), dried over anhydrous MgSO_4 , filtered and concentrated under reduced pressure to give a crude product that was purified by quick chromatography on silica gel (these mesylates are slightly unstable on silica gel) using the appropriate mixture of solvents.

1.14. Synthesis of the Mesylate of (+)-(2*S*,3*S*)-(4*Z*)-2-[(*tert*-Butyldimethylsilyl)oxy]-4-(*p*-tolylsulfonyl)non-4-en-3-ol, (11**).**

From sulfone **10** (44 mg, 0.10 mmol, 1.0 equiv), MsCl (39 μ L, 0.50 mmol, 5.0 equiv) and Et₃N (73 μ L, 0.52 mmol, 5.2 equiv) in 1 mL of dry THF, according to the general procedure, mesylate **11** was obtained. Purification by chromatography afforded 38 mg (0.075 mmol, 75%) of **11** as a colorless oil.

Data for **11**: R_f = 0.42 (30% EtOAc-hexane). $[\alpha]_D^{20}$ +47.8 (c = 1.00). ¹H NMR (300 MHz) δ 0.11 (s, 3 H), 0.15 (s, 3 H), 0.82 (t, 3 H, J = 7.0 Hz), 0.89 (s, 9 H), 1.08 (d, 3 H, J = 6.4 Hz), 1.23 (m, 4 H), 2.32 (m, 1 H), 2.41 (s, 3 H), 2.63 (m, 1 H), 2.99 (s, 3 H), 4.31 (qd, 1 H, J = 6.4, 2.5 Hz), 5.47 (d, 1 H, J = 1.8 Hz), 6.58 (t, 1 H, J = 7.7 Hz), 7.31 (d, 2 H, J = 8.1 Hz), 7.80 (d, 2 H, J = 8.2 Hz). ¹³C NMR (50 MHz) δ -5.0, -4.6, 13.7, 16.3, 18.0, 21.6, 22.3, 25.8 (3 C), 28.6, 30.6, 38.6, 70.2, 82.7, 127.4 (2 C), 129.7 (2 C), 137.2, 138.6, 144.6, 149.0. IR (film): 2957, 2930, 2858, 1635, 1597, 1463, 1362, 1257, 1178, 1142, 1085, 941, 837, 778 cm⁻¹. MS (ES): 527 [M+Na]⁺, 409 [(M-MeSO₃)+1]⁺ (100%).

1.15. Synthesis of the Mesylate of (-)-(2*S*,3*S*,*S*_s)-(4*Z*)-2-[(*tert*-Butyldimethylsilyl)oxy]-4-(*p*-tolylsulfinyl)non-4-en-3-ol, (12**).**

From sulfoxide **8** (41 mg, 0.10 mmol, 1.0 equiv), MsCl (39 μ L, 0.50 mmol, 5.0 equiv) and Et₃N (73 μ L, 0.52 mmol, 5.2 equiv) in 1 mL of dry THF, according to the general procedure, an 89:11 mixture of **12** and **13** was obtained. Purification by chromatography (20-50% EtOAc-hexane) afforded 21 mg (0.042 mmol, 63%) of **12** and 3 mg (0.008 mmol, 8%) of **13**, both as colorless oils.

To a cold (0 °C) solution of **13** (39 mg, 0.10 mmol) in 1 mL of CH₂Cl₂ was added TBDMSCl (68 mg, 0.45 mmol, 4.5 equiv) and imidazole (31 mg, 0.45 mmol, 4.5 equiv). The mixture was allowed to warm up to room temperature, monitored by TLC until completion (24 h) and then quenched with 2 mL of H₂O. The layers were separated and the aqueous phase was extracted twice with CH₂Cl₂. The combined organic extracts were washed with a saturated solution of NaCl, dried over MgSO₄ and

concentrated. Purification by chromatography afforded 43 mg (0.091 mmol, 91%) of **12** as a colorless oil.

Data for **12**: $R_f = 0.34$ (30% EtOAc-hexane). $[\alpha]_D^{20} -94.1$ ($c = 0.61$). $^1\text{H NMR}$ (300 MHz) δ -0.07 (s, 3 H), 0.02 (s, 3 H), 0.33 (d, 3 H, $J = 6.3$ Hz), 0.81 (s, 9 H), 0.95 (t, 3 H, $J = 7.2$ Hz), 1.36-1.58 (m, 4 H), 2.37 (s, 3 H), 2.56 (sext, 1 H, $J = 7.1$ Hz), 2.78 (sext, 1 H, $J = 7.7$ Hz), 3.14 (s, 3 H), 3.73 (qd, 1 H, $J = 9.3, 2.9$ Hz), 5.04 (d, 1 H, $J = 2.7$ Hz), 6.88 (t, 1 H, $J = 7.8$ Hz), 7.29 (d, 2 H, $J = 8.1$ Hz), 7.39 (d, 2 H, $J = 8.3$ Hz). $^{13}\text{C NMR}$ (50 MHz) δ -5.2, -4.9, 13.8, 17.6, 17.9, 21.3, 22.3, 25.7 (3 C), 29.1, 31.2, 39.0, 70.5, 77.0, 124.1 (2 C), 130.1 (2 C), 139.1, 139.2, 141.4, 146.5. IR (film): 2958, 2928, 2856, 1635, 1463, 1354, 1259, 1175, 1082, 1045, 1015, 932, 837, 809, 780, 758 cm^{-1} . MS (ES): 489 $[\text{M}+1]^+$ (100%), 393 $[(\text{M}-\text{MeSO}_3)+1]^+$.

Data for **13**: $R_f = 0.10$ (30% EtOAc-hexane). $^1\text{H NMR}$ (300 MHz) δ 0.85 (d, 3 H, $J = 6.6$ Hz), 0.96 (t, 3 H, $J = 7.1$ Hz), 1.39-1.58 (m, 4 H), 2.59 (s, 3 H), 2.60 (sext, 1 H, $J = 7.1$ Hz), 2.82 (m, 1 H), 2.84 (s, 3 H), 3.24 (d, 1 H, $J = 5.6$ Hz), 3.79 (ap q, 1 H, $J = 6.1$ Hz), 5.06 (d, 1 H, $J = 5.6$ Hz), 6.70 (dd, 1 H, $J = 8.5, 7.1$ Hz), 7.31 (d, 2 H, $J = 8.1$ Hz), 7.44 (d, 2 H, $J = 8.3$ Hz).

1.16. Synthesis of the Mesylate of (+)-(2*S*,3*S*,*R*_s)-(4*Z*)-2-[(*tert*-Butyldimethylsilyl)oxy]-4-(*p*-tolylsulfinyl)non-4-en-3-ol, (**14**).

From sulfoxide **9** (20 mg, 0.05 mmol, 1.0 equiv), MsCl (19 μL , 0.25 mmol, 5.0 equiv) and Et_3N (38 μL , 0.27 mmol, 5.5 equiv) in 0.5 mL of dry Et_2O , according to the general procedure, mesylate **14** was obtained. Purification by chromatography afforded 21 mg (0.042 mmol, 84%) of **14** as a colorless oil.

Data for **14**: $R_f = 0.36$ (30% EtOAc-hexane). $[\alpha]_D^{20} +114.8$ ($c = 0.94$). $^1\text{H NMR}$ (300 MHz) δ -0.06 (s, 3 H), -0.08 (s, 3 H), 0.85 (s, 9 H), 0.94 (t, 3 H, $J = 7.2$ Hz), 1.10 (d, 3 H, $J = 6.3$ Hz), 1.42 (m, 2 H), 1.53 (m, 2 H), 2.39 (s, 3 H), 2.49 (ap sext, 1 H, $J = 7.1$ Hz), 2.68 (s, 3 H), 2.79 (m, 1 H), 4.32 (qd, 1 H, $J = 6.3, 2.2$ Hz), 4.96 (s, 1 H), 6.58 (dd, 1 H, $J = 8.8, 6.6$ Hz), 7.31 (d, 2 H, $J = 8.1$ Hz), 7.46 (d, 2 H, $J = 8.3$ Hz). $^{13}\text{C NMR}$ (50 MHz) δ -4.9, -4.7, 13.8, 16.1, 18.0, 21.3, 22.3, 25.8 (3 C), 28.6, 31.2, 38.0, 71.0, 81.6, 124.5 (2 C), 130.0 (2 C), 138.3, 139.0, 141.2, 143.7. IR (film): 2957, 2930, 2857, 1463, 1362, 1256, 1178, 1081, 1045, 1004, 937, 837, 809, 778, 756 cm^{-1} . MS (ES): 489 $[\text{M}+1]^+$ (100%).

2. Synthesis of Hydroxy Sulfinyl Dienes

2.1. General Procedures for the Synthesis of Hydroxy Sulfinyl Dienes

See printed version of the paper.

2.2. Synthesis of (-)-(5*S*,*S*_s)-(6*Z*,8*E*)-7-(*p*-Tolylsulfinyl)dodeca-6,8-dien-5-ol, (**17a**).

From chlorohydrin **3a** (106 mg, 0.29 mmol, 1.0 equiv) in 2 mL of THF with 2 portions of KO-*t*-Bu (36 mg, 0.32 mmol, 1.1 equiv, each) in 1.6 mL of THF according to general procedure A (1 h, 30 min) a 91:9 mixture of **17a** and **19a**, was obtained. Purification by chromatography (CH₂Cl₂-5% EtOAc-CH₂Cl₂) afforded 65 mg (0.203 mmol, 68%) of diene **17a** as a colorless oil and 13 mg (13%) of dimer **19a** as a yellow oil.

Data for **17a**: R_f = 0.28 (30% EtOAc-hexane); 0.18 (5% EtOAc-CH₂Cl₂). $[\alpha]_D^{20}$ -85.2 (c = 1.43). ¹H NMR (500 MHz) δ 0.75 (t, 3 H, J = 7.3 Hz), 0.88 (t, 3 H, J = 6.3 Hz), 1.24-1.37 (m, 6 H), 1.59-1.68 (m, 2 H), 2.00 (q, 2 H, J = 7.3 Hz), 2.37 (s, 3 H), 2.42 (d, 1 H, J = 4.1 Hz), 4.90 (m, 1 H), 5.90 (d, 1 H, J = 15.6 Hz), 6.03 (d, 1 H, J = 8.0 Hz), 6.01-6.06 (dt, 1 H, J = 15.4, 6.8 Hz), 7.26 (d, 2 H, J = 8.1 Hz), 7.52 (d, 2 H, J = 8.1 Hz). NOED between H-5/H-6: 3.0%; between H-5/OH: 4.5%; between H-5/H-4: 2.6%; between H-Ar ortho/H-8: 1.5%; H-Ar ortho/H-5: 3.0%. ¹H NMR (200 MHz, C₆D₆, T = 303 K) δ 0.66 (t, 3 H, J = 7.3 Hz), 0.83 (t, 3 H, J = 6.4 Hz), 1.12-1.51 (m, 8 H), 1.75-1.81 (m, 2 H), 1.94 (s, 3 H), 2.38 (br s, 1 H), 4.90 (m, 1 H), 5.98 (d, 1 H, J = 10.8 Hz), 6.03-6.05 (m, 2 H), 6.92 (d, 2 H, J = 8.1 Hz), 7.75 (d, 2 H, J = 8.1 Hz). At T = 313 K the only relevant change detected was δ 2.28 (br s, 1 H, OH). At T = 323 K the only relevant change was δ 2.19 (br s, 1 H, OH). ¹³C NMR (50 MHz) δ 13.5, 14.0, 21.3, 22.0, 22.5, 27.4, 35.2, 37.4, 67.2, 122.2, 124.6 (2 C), 129.8 (2 C), 137.1, 137.4, 139.6, 140.8, 145.3. IR (film): 3360, 2960, 2940, 2860, 1495, 1080, 1020, 810 cm⁻¹. MS (EI): 321 [M+1]⁺, 303 (100%), 259, 181, 140, 139, 95, 79, 67, 41. Anal. calcd for C₁₉H₂₈O₂S: C, 71.20; H, 8.81; S, 10.01. Found: C, 71.33; H, 9.02; S, 9.83.

Data for **(-)-(5*S*,10*S*,*S*₃,*S*₃)-(6*Z*,11*Z*,13*E*)-8,10-di-*n*-Butyl-7,12-(bis-*p*-tolylsulfinyl)-9-oxaheptadeca-6,11,13-trien-5-ol, 19a**: R_f = 0.28 (30% EtOAc-hexane); 0.10 (5% EtOAc-CH₂Cl₂). $[\alpha]_D^{20}$ -116.9 (c = 1.90). **¹H NMR (300 MHz)** δ 0.67 (t, 3 H, J = 7.1 Hz), 0.80 (t, 3 H, J = 7.4 Hz), 0.80-0.95 (m, 6 H), 1.20-1.86 (m, 20 H), 1.99 (m, 2 H), 2.37 (s, 3 H), 2.39 (s, 3 H), 3.50 (m, 1 H), 3.98 (dd, 1 H, J = 8.2, 2.8 Hz), 4.26 (m, 1 H), 4.98 (m, 1 H), 5.76 (d, 1 H, J = 9.2 Hz), 5.78 (dd, 1 H, J = 15.9, 1.0 Hz), 5.95 (dt, 1 H, J = 15.4, 6.5 Hz), 6.20 (d, 1 H, J = 9.3 Hz), 7.25 (d, 2 H, J = 8.7 Hz), 7.28 (d, 2 H, J = 8.0 Hz), 7.40 (d, 2 H, J = 8.3 Hz), 7.63 (d, 2 H, J = 8.3 Hz). **¹³C NMR (75 MHz)** δ 13.5, 13.9, 14.0, 14.1, 21.2, 21.3, 22.0, 22.4, 22.6, 22.8, 26.3, 27.3, 27.9, 32.7, 35.1, 37.5, 39.2, 67.3, 69.1, 70.8, 124.6, 124.7, 129.6, 129.8, 136.7, 137.3, 139.3, 139.7, 140.0, 140.5, 140.8, 141.9, 142.4, 146.2. **IR** (film): 3390, 2956, 2929, 2871, 1492, 1465, 1397, 1379, 1339, 1302, 1115, 1081, 1044, 1013, 812, 754, 734, 704 cm⁻¹. **MS** (ES): 1303 [2M+Na]⁺, 663 [M+Na]⁺, 641 [M+1]⁺ (100%).

With excess base and longer reaction times (ca 20 h), a 57:22:12:9 mixture of **17a**, **18a**, **ent-21a** and **19a** was obtained. It should be mentioned that the mixture of diastereomeric dienes **18a** and **ent-21a** had very close spectral features but with duplication of some signals in the NMR spectra. The structure of **18a** was independently secured by a different procedure.

From the 65:35 mixture of **18a:ent-21a**: R_f = 0.44 (50% EtOAc-hexane). $[\alpha]_D^{20}$ +58.1 (c = 0.69). **IR** (film): 3400, 2960, 2940, 2860, 1600, 1490, 1080, 1030, 1010, 805 cm⁻¹.

Data for **(5*S*,*S*₃)-(6*E*,8*E*)-7(*p*-Tolylsulfinyl)dodeca-6,8-dien-5-ol, 18a**: **¹H NMR (500 MHz)** δ 0.76 (t, 3 H, J = 7.3 Hz), 0.87 (t, 3 H, J = 6.6 Hz), 1.23-1.26 (m, 4 H), 1.57-1.69 (m, 4 H), 1.96-2.01 (m, 2 H), 2.34 (s, 3 H), 4.52 (m, 1 H), 5.86 (dt, 1 H, J = 16.1, 5.6 Hz), 5.92 (d, 1 H, J = 16.1 Hz), 6.33 (d, 1 H, J = 8.5 Hz), 7.21 (d, 2 H, J = 7.8 Hz), 7.47 (d, 2 H, J = 7.8 Hz). **¹³C NMR (50 MHz)** δ 13.4, 14.0, 21.4, 22.0, 22.6, 27.4, 35.4, 37.2, 68.3, 119.7, 125.7 (2 C), 129.7 (2 C), 132.8, 138.5, 140.5, 141.7, 143.4.

Data for **(5*S*,*R*₃)-(6*E*,8*E*)-7-(*p*-Tolylsulfinyl)dodeca-6,8-dien-5-ol, ent-21a**: **¹H NMR (500 MHz)** δ 0.77 (t, 3 H, J = 7.3 Hz), 0.87 (t, 3 H, J = 6.6 Hz), 1.23-1.36 (m, 4 H), 1.52-1.69 (m, 4 H), 1.96-2.01 (m, 2 H), 2.34 (s, 3 H), 4.50 (m, 1 H), 5.88 (dt, 1 H, J = 16.1, 6.0 Hz), 5.91 (d, 1 H, J = 16.1 Hz), 6.35

(d, 1 H, $J = 8.6$ Hz), 7.21 (d, 2 H, $J = 8.0$ Hz), 7.45 (d, 2 H, $J = 8.0$ Hz). ^{13}C NMR (50 MHz) δ 13.4, 14.0, 21.4, 22.0, 22.7, 27.4, 35.4, 37.1, 68.4, 119.6, 125.7 (2 C), 129.7 (2 C), 132.9, 138.8, 140.5, 141.7, 143.4.

In a separate experiment, 2 equiv of KO-*t*-Bu was added once oxirane formation was complete and a 40:40:20 mixture of **17a**, **18a** and **19a**, was obtained rapidly (5 min). The yield was not determined.

In a separate experiment, from chlorohydrin **3a** (40 mg, 0.11 mmol, 1.0 equiv) in 2.4 mL of THF with a single addition of KO-*t*-Bu (0.33 mL, 0.16 mmol, 1.5 equiv) following general procedure C, an 85:15 mixture of **17a** and **18a** was obtained. The yield was not determined.

2.3. Synthesis of (+)-(5*S*,*S*₅)-(6*E*,8*E*)-7-(*p*-Tolylsulfinyl)dodeca-6,8-dien-5-ol, (**18a**).

From chlorohydrin **3a** (28 mg, 0.078 mmol, 1.0 equiv) in 0.6 mL of THF with 2 successive additions of KO-*t*-Bu (0.17 mL, 0.086 mmol, 1.1 equiv each) according to general procedure C (25 + 5 min) a 70:30 mixture of dienes **18a** and **17a**, was obtained. Purification by chromatography (5-30% EtOAc-hexane) afforded 9 mg (0.028 mmol, 36%) of **18a** and 4 mg (0.012 mmol, 16%) of **17a** both as yellow oils.

Data for **18a**: $R_f = 0.44$ (50% EtOAc-hexane). $[\alpha]_D^{20} +94.1$ ($c = 0.76$). ^1H NMR (300 MHz) δ 0.77 (t, 3 H, $J = 7.4$ Hz), 0.87 (t, 3 H, $J = 7.0$ Hz), 1.23-1.37 (m, 4 H), 1.53-1.71 (m, 4 H), 1.99 (m, 2 H), 2.36 (s, 3 H), 4.52 (m, 1 H), 5.86 (dt, 1 H, $J = 16.1, 6.3$ Hz), 5.91 (d, 1 H, $J = 16.0$ Hz), 6.34 (d, 1 H, $J = 8.8$ Hz), 7.22 (d, 2 H, $J = 8.1$ Hz), 7.46 (d, 2 H, $J = 8.3$ Hz). ^{13}C NMR (50 MHz) δ 13.5, 14.0, 21.4, 22.0, 22.6, 27.4, 35.5, 37.0, 68.3, 119.5, 125.7 (2 C), 129.7 (2 C), 132.8, 138.7, 140.3, 141.7, 143.2. IR (CCl₄): 3320, 2980, 2900, 2820, 1660, 1630, 1580, 1470, 1430, 1350, 1010, 940, 870, 750, 680 cm⁻¹. MS (EI): 320 [M]⁺, 181, 140 (100%), 95, 79, 69, 55, 41.

2.4. Synthesis of (-)-(2*S*,*S*₅)-(3*Z*,5*E*)-1-Phenyl-4-(*p*-tolylsulfinyl)hepta-3,5-dien-2-ol, (**17b**).

From chlorohydrin **3b** (46 mg, 0.127 mmol, 1.0 equiv) in 1.5 mL of THF with 2 portions of KO-*t*-Bu (16 mg, 0.140 mmol, 1.1 equiv, each) in 0.8 mL of THF according to general procedure A (1 h, 15 min) an 88:12 mixture of **17b** and **19b** was obtained. Purification by chromatography (CH₂Cl₂-1% EtOAc/CH₂Cl₂) afforded 27 mg (0.083 mmol, 65%) of diene **17b** as a colorless oil and approx. 6 mg (14%) of dimer **19b** as a colorless oil.

Data for **17b**: R_f = 0.13 (30% EtOAc-hexane). $[\alpha]_D^{20}$ -74.7 (c = 1.14). ¹H NMR (200 MHz) δ 1.71 (dd, 3 H, J = 6.4, 1.4 Hz), 2.39 (s, 3 H), 2.59 (d, 1 H, J = 4.2 Hz), 2.89 (dd, 1 H, J = 13.7, 7.3 Hz), 2.99 (dd, 1 H, J = 14.0, 5.8 Hz), 5.19 (m, 1 H), 5.88 (dm, 1 H, J = 15.7 Hz), 6.08 (dq, 1 H, J = 15.6, 6.3 Hz), 6.09 (d, 1 H, J = 8.1 Hz), 7.16-7.31 (m, 7 H), 7.51 (d, 2 H, J = 8.3 Hz). ¹³C NMR (50 MHz) δ 18.6, 21.3, 43.9, 67.9, 123.2, 124.7 (2 C), 126.9, 128.7 (2 C), 129.5 (2 C), 129.8 (2 C), 132.2, 136.1, 136.8, 138.4, 140.8, 145.6. IR (CCl₄): 3360, 3040, 2960, 2920, 1640, 1600, 1490, 1450, 1260, 1080, 1020, 780, 700 cm⁻¹. MS (EI): 327, 326 [M]⁺, 235, 217, 169, 140, 123, 92, 91 (100%), 77, 65, 51, 41. Anal. calcd for C₂₀H₂₂O₂S: C, 73.58; H, 6.79; S, 9.82. Found: C, 73.35; H, 6.84; S, 9.95.

Data for (-)-(2*S*,7*S*,*S*₉,*S*₉)-(3*Z*,8*Z*,10*E*)-7-Benzyl-5-ethyl-1-phenyl-4,9-(bis-*p*-tolylsulfinyl)-6-oxadodeca-3,8,10-trien-2-ol, **19b**: R_f = 0.13 (30% EtOAc-hexane). $[\alpha]_D^{20}$ -96.1 (c = 0.67). ¹H NMR (300 MHz) δ 0.79 (t, 3 H, J = 7.1 Hz), 1.49-1.75 (m, 2 H), 1.69 (d, 3 H, J = 6.2 Hz), 2.20 (dm, 2 H, J = 5.5 Hz), 2.38 (s, 3 H), 2.39 (s, 3 H), 2.96 (dd, 2 H, J = 6.4, 3.7 Hz), 4.02 (dd, 1 H, J = 6.8, 3.7 Hz), 4.68 (dt, 1 H, J = 9.2, 5.7 Hz), 5.27 (dt, 1 H, J = 9.3, 6.5 Hz), 5.64 (d, 1 H, J = 15.7), 5.66 (m, 1 H), 5.82 (dd, 1 H, J = 15.7, 6.3 Hz), 6.28 (d, 1 H, J = 9.2 Hz), 6.75 (m, 2 H), 7.13-7.31 (m, 14 H), 7.63 (d, 2 H, J = 8.2 Hz). IR (film): 3368, 3028, 2966, 2922, 1642, 1601, 1493, 1454, 1378, 1261, 1216, 1103, 1080, 1031, 959, 811, 752, 700 cm⁻¹. MS (ES): 691 [M+K]⁺ (100%), 675 [M+Na]⁺, 653 [M+1]⁺.

2.5. Synthesis of (-)-(2*S*,*S*₅)-(3*Z*,5*E*)-7-Methyl-1-phenyl-4-(*p*-tolylsulfinyl)octa-3,5-dien-2-ol, (17c**).**

From chlorohydrin **3c** (32 mg, 0.081 mmol, 1.0 equiv) in 1.0 mL of THF with 2 portions of KO-*t*-Bu (10 mg, 0.140 mmol, 1.1 equiv, each) in 0.5 mL of THF according to general procedure A (1 h, 15 min) an 87:13 mixture of **17c** and **19c** was obtained. Purification by chromatography (30-50% Et₂O-hexane) afforded 16 mg (0.045 mmol, 55%) of diene **17c** as a colorless oil and approx. 5 mg (17%) of dimer **19c** as a colorless oil.

Data for **17c**: R_f = 0.15 (50% Et₂O-hexane). $[\alpha]_D^{20}$ -55.9 (c = 0.45). ¹H NMR (300 MHz) δ 0.93 (ap t, 6 H, J = 7.0 Hz), 2.29 (oct, 1 H, J = 6.8 Hz), 2.39 (s, 3 H), 2.65 (br s, 1 H), 2.89 (dd, 1 H, J = 13.7, 8.0 Hz), 3.00 (dd, 1 H, J = 13.6, 5.1 Hz), 5.19 (m, 1 H), 5.86 (d, 1 H, J = 15.8 Hz), 6.02 (dd, 1 H, J = 15.9, 6.7 Hz), 6.12 (d, 1 H, J = 8.5 Hz), 7.18-7.35 (m, 7 H), 7.50 (d, 2 H, J = 7.5 Hz). ¹³C NMR (50 MHz) δ 21.3, 21.9, 31.6, 43.9, 67.8, 119.5, 124.7 (2 C), 126.8, 128.7 (2 C), 129.5 (2 C), 129.7 (2 C), 136.2, 136.9, 139.5, 140.8, 144.0, 145.8. IR (CCl₄): 3360, 3020, 2960, 2860, 1640, 1600, 1490, 1450, 1260, 1080, 1020, 960, 770, 700 cm⁻¹. MS (EI): 354 [M]⁺, 263, 197, 181, 155, 141, 140, 123, 103, 92, 91 (100%), 77, 65. Anal. calcd for C₂₂H₂₆O₂S: C, 74.54; H, 7.39; S, 9.04. Found: C, 74.73; H, 7.18; S, 9.32.

Data for (2*S*,7*S*,*S*_s,*S*_s)-(3*Z*,8*Z*,10*E*)-7-Benzyl-5-(*iso*-butyl)-12-methyl-1-phenyl-4,9-(bis-*p*-tolylsulfinyl)-6-oxatri-deca-3,8,10-trien-2-ol, **19c**: R_f = 0.09 (50% Et₂O-hexane). ¹H NMR (300 MHz) δ 0.86 (m, 12 H), 1.44-1.58 (m, 4 H), 1.65 (br s, 1 H), 2.16 (m, 2 H), 2.36 (s, 3 H), 2.38 (s, 3 H), 2.91 (dd, 1 H, J = 14.0, 6.1 Hz), 3.02 (dd, 1 H, J = 14.0, 6.9 Hz), 4.18 (d, 2 H, J = 8.8 Hz), 4.78 (m, 1 H), 5.28 (m, 1 H), 5.60 (ap q, 2 H, J = 15.9 Hz), 5.65 (m, 1 H), 6.31 (d, 1 H, J = 9.3 Hz), 6.64 (m, 2 H), 7.07-7.33 (m, 14 H), 7.66 (d, 2 H, J = 7.9 Hz). Partial ¹³C NMR (50 MHz) data: δ 9.4, 18.6, 21.4, 31.3, 39.8, 44.2, 51.7, 68.1, 70.0, 72.8, 124.9, 125.0, 125.1, 126.7, 128.0, 128.6, 129.6, 129.8, 129.9, 131.7, 136.4, 136.9, 139.1, 139.2, 140.6, 141.0, 141.7, 146.0.

2.6. Synthesis of (5*S*,6*R*,*S*_s)-(7*E*)-5,6-Epoxy-9-methyl-7-(*p*-tolylsulfinyl)dec-7-ene, (15d).

From chlorohydrin **3d** (24 mg, 0.069 mmol, 1.0 equiv) in 0.7 mL of THF with 2 portions of KO-*t*-Bu (9 mg, 0.076 mmol, 1.1 equiv, each) in 0.5 mL of THF according to general procedure A (3 h) oxirane **15d** was obtained (TLC). 1.1 equiv of base was added similarly and the reaction was quenched 3 h later. Purification by chromatography (15% EtOAc-hexane) afforded 16 mg (0.052 mmol, 76%) of oxirane **15d** as a colorless oil. In a related experiment, to a cold (0 °C) solution of oxirane **15d** (16 mg, 0.052 mmol, 1.0 equiv) in 0.5 mL of THF was added NaH (4 mg, 0.156 mmol, 3.0 equiv) and the reaction mixture was stirred at rt for 14 h. Usual extractive work-up gave just recovered starting material.

Data for **15d**: R_f = 0.44 (30% EtOAc-hexane). ^1H NMR (300 MHz) δ 1.06 (d, 6 H, J = 6.6 Hz), 1.30-1.39 (m, 4 H), 1.45-1.58 (m, 2 H), 2.41 (s, 3 H), 2.89 (m, 1 H), 3.07 (td, J = 5.5, 2.3 Hz), 3.15 (br s, 1 H), 6.41 (d, 2 H, J = 10.2 Hz), 7.30 (d, 2 H, J = 7.6 Hz), 7.56 (d, 2 H, J = 8.1 Hz).

2.7. Synthesis of (+)-(5*S*,*S*₅)-(6*Z*)-9-Methyl-7-(*p*-tolylsulfinyl)deca-6,8-dien-5-ol, (17d**), (–)-(5*S*,*S*₅)-(6*Z*)-9-Methyl-8-(*iso*-propoxy)-7-(*p*-tolylsulfinyl)dec-6-en-5-ol, (**25d**), and (5*S*,6*R*,*S*₅)-(7*E*)-5,6-Epoxy-9-methyl-7-(*p*-tolylsulfinyl)dec-7-ene, (**15d**).**

To a cold (0 °C) solution of chlorohydrin **3d** (30 mg, 0.087 mmol, 1.0 equiv) in 0.4 mL of *i*-PrOH:THF (1:1) was added KOH (0.09 mL, 1 M in *i*-PrOH, 0.096 mmol, 1.1 equiv). After 1 h, 1.1 equiv of KOH was added similarly and the mixture was allowed to warm up to rt. After 3 h, 1.0 equiv of KOH was added similarly and the mixture was stirred at rt for 12 additional h. The reaction was then quenched with 1 mL of a saturated NH_4Cl solution, diluted with 5 mL of EtOAc and the layers were separated. The aqueous layer was extracted twice with 2 mL of EtOAc and the combined organic extracts were washed with a saturated solution of NaCl, dried over MgSO_4 and concentrated to give a 55:35:10 mixture of diene **17d** allylic ether **25d** and epoxide **15d**. Purification by chromatography (5-

30% EtOAc-hexane) gave 9 mg (0.029 mmol, 34%) of **17d** and 7 mg (0.019 mmol, 22%) of **25d** as a single isomer.

Data for **17d**: $R_f = 0.20$ (30% EtOAc-hexane). $[\alpha]_D^{20} +2.1$ ($c = 0.70$). $^1\text{H NMR}$ (300 MHz) δ 0.91 (t, 3 H, $J = 7.1$ Hz), 1.30-1.47 (m, 5 H), 1.55 (s, 3 H), 1.58-1.70 (m, 2 H), 1.72 (s, 3 H), 2.37 (s, 3 H), 5.04 (m, 1 H), 5.55 (s, 1 H), 5.81 (dd, 1 H, $J = 8.7, 1.4$ Hz), 7.24 (d, 2 H, $J = 8.1$ Hz), 7.51 (d, 2 H, $J = 8.3$ Hz). $^{13}\text{C NMR}$ (75 MHz) δ 13.7, 19.2, 21.1, 22.3, 26.0, 27.2, 37.5, 67.5, 114.9, 124.5 (2 C), 129.4 (2 C), 139.3, 139.5, 140.6, 143.1, 144.8. IR (film): 3367, 2958, 2928, 2858, 1651, 1493, 1448, 1378, 1216, 1081, 1029, 1013, 810, 754 cm^{-1} . MS (ES): 635 $[\text{2M}+\text{Na}]^+$, 329 $[\text{M}+\text{Na}]^+$, 289 $[(\text{M}-18)+1]^+$ (100%).

Data for **25d**: $R_f = 0.32$ (30% EtOAc-hexane). $[\alpha]_D^{20} -76.7$ ($c = 0.30$). $^1\text{H NMR}$ (300 MHz) δ 0.60 (d, 3 H, $J = 6.0$ Hz), 0.83 (d, 3 H, $J = 6.1$ Hz), 0.84 (t, 3 H, $J = 6.8$ Hz), 0.85 (d, 3 H, $J = 6.8$ Hz), 0.93 (d, 3 H, $J = 6.8$ Hz), 1.30-1.50 (m, 4 H), 1.60-1.75 (m, 2 H), 2.00 (m, 1 H), 2.40 (s, 3 H), 2.67 (sept, 1 H, $J = 6.0$ Hz), 3.65 (d, 1 H, $J = 3.7$ Hz), 3.65 (d, 1 H, $J = 3.7$ Hz), 5.05 (m, 1 H), 5.32 (d, 1 H, $J = 8.0$ Hz), 6.12 (d, 1 H, $J = 8.3$ Hz), 7.31 (d, 2 H, $J = 8.0$ Hz), 7.61 (d, 2 H, $J = 8.2$ Hz). $^{13}\text{C NMR}$ (75 MHz) δ 14.0, 15.6, 20.0, 20.4, 21.3, 22.5, 23.1, 27.4, 33.9, 37.8, 67.8, 68.5, 77.2, 124.8 (2 C), 129.7 (2 C), 139.5, 139.8, 140.9, 146.6. IR (film): 3369, 2965, 2930, 2873, 1493, 1463, 1380, 1368, 1260, 1175, 1120, 1102, 1079, 1039, 1012, 812, 756 cm^{-1} . MS (ES): 755 $[\text{2M}+\text{Na}]^+$, 389 $[\text{M}+\text{Na}]^+$, 367 $[\text{M}+1]^+$ (100%).

2.8. Synthesis of (–)-(3*S*,*S*_s)-(4*Z*,6*E*)-2-Methyl-5-(*p*-tolylsulfinyl)deca-4,6-dien-3-ol, (**17e**), and (+)-(3*S*,*S*_s)-(4*E*,6*E*)-2-Methyl-5-(*p*-tolylsulfinyl)deca-4,6-dien-3-ol, (**18e**).

From chlorohydrin **3e** (30 mg, 0.087 mmol, 1.0 equiv) in 1.7 mL of THF with KO-*t*-Bu (0.12 mL, 0.061 mmol, 0.7 equiv) according to general procedure C (25 min) a 91:9 mixture of dienes **17e** and **18e** was obtained. Purification by chromatography (5-30% EtOAc-hexane) afforded 15 mg (0.049 mmol, 56%) of diene **17e** and 2 mg (0.0065 mmol, 7%) of diene **18e**, both as colorless oils.

In a separate experiment, from chlorohydrin **3e** (33 mg, 0.096 mmol, 1.0 equiv) in 1.9 mL of THF with two sequential additions of KO-*t*-Bu (0.19 mL, 0.096 mmol, 1.0 equiv, and after 25 min 0.34 mL,

0.17 mmol, 1.8 equiv) according to general procedure C (25 + 5 min) a 50:50 mixture of dienes **17e** and **18e** was obtained. Purification by chromatography (5-30% EtOAc-hexane) afforded 8 mg (0.026 mmol, 27%) of diene **17e** and 8 mg (0.026 mmol, 27%) of **18e**, both as colorless oils.

Data for **17e**: $R_f = 0.18$ (50% EtOAc-hexane). $[\alpha]_D^{20} -67.1$ ($c = 1.42$). $^1\text{H NMR}$ (300 MHz) δ 0.76 (t, 3 H, $J = 7.4$ Hz), 0.91 (d, 3 H, $J = 6.8$ Hz), 1.00 (d, 3 H, $J = 6.7$ Hz), 1.21-1.34 (m, 2 H), 1.62 (br s, 1 H), 1.79 (sept, 1 H, $J = 6.7$ Hz), 1.95-2.02 (m, 2 H), 2.37 (s, 3 H), 4.64 (dd, 1 H, $J = 8.8, 7.0$ Hz), 5.89 (dd, 1 H, $J = 15.7, 0.9$ Hz), 6.03 (dt, 1 H, $J = 15.6, 6.6$ Hz), 6.07 (d, 1 H, $J = 8.5$ Hz), 7.25 (d, 2 H, $J = 7.6$ Hz), 7.52 (d, 2 H, $J = 8.3$ Hz). $^{13}\text{C NMR}$ (50 MHz) δ 13.5 (2 C), 18.0, 18.2, 21.3, 22.0, 34.5, 35.1, 72.2, 121.9, 124.6 (2 C), 129.7 (2 C), 135.6, 137.1, 139.5, 140.7, 146.1. IR (CCl₄): 3340, 2920, 2880, 2840, 1570, 1480, 1450, 1060, 1000, 770 cm⁻¹. MS (EI): 289 [(M-18)+1]⁺, 245, 167, 140 (100%), 123, 92, 67, 55, 43. Anal. calcd for C₁₈H₂₆O₂S: C, 70.54; H, 8.55; S, 10.46. Found: C, 70.71; H, 8.37; S, 10.65.

Data for **18e**: $R_f = 0.09$ (30% EtOAc-hexane). $[\alpha]_D^{20} +93.3$ ($c = 0.49$). $^1\text{H NMR}$ (300 MHz) δ 0.76 (t, 3 H, $J = 7.3$ Hz), 0.90 (d, 3 H, $J = 6.8$ Hz), 0.97 (d, 3 H, $J = 6.7$ Hz), 1.21-1.36 (m, 3 H), 1.83 (sept, 1 H, $J = 6.7$ Hz), 2.01 (q, 2 H, $J = 6.8$ Hz), 2.35 (s, 3 H), 4.23 (dd, 1 H, $J = 8.5, 6.5$ Hz), 5.83-5.99 (m, 2 H, H-6), 6.36 (d, 1 H, $J = 8.9$ Hz), 7.21 (d, 2 H, $J = 7.9$ Hz), 7.48 (d, 2 H, $J = 8.2$ Hz). $^{13}\text{C NMR}$ (50 MHz) δ 13.4, 18.0, 18.3, 21.4, 22.0, 34.6, 35.4, 73.0, 119.9, 125.7 (2 C), 129.7 (2 C), 131.2, 138.3, 140.4, 141.7, 143.9. IR (CCl₄): 3340, 2920, 2840, 1630, 1580, 1480, 1450, 1360, 1240, 1160, 1070, 1020, 950 cm⁻¹. MS (APCI): 307 [M+1]⁺, 289, 167.

2.9. Synthesis of (+)-(5*S*,6*R*,*R*_s)-(7*E*)-5,6-Epoxy-7-(2-methoxynaphthalen-1-ylsulfinyl)dodeca-7-ene, (**15f**).

From chlorohydrin **3f** (31 mg, 0.07 mmol, 1.0 equiv) in 1.5 mL of THF with 2 successive additions of KO-*t*-Bu (0.15 mL, 0.07 mmol, 1.0 equiv, and an equal amount after 30 min) according to general procedure C (1 h, 30 min), epoxy sulfoxide **15f** was obtained. Purification by chromatography (15-30% EtOAc-hexane) afforded 20 mg (0.05 mmol, 71%) of **15f** as a colorless oil.

Data for **15f**: $R_f = 0.17$ (30% EtOAc-hexane). $[\alpha]_D^{20} +252.8$ ($c = 1.98$). $^1\text{H NMR}$ (300 MHz) δ 0.77 (t, 3 H, $J = 6.7$ Hz), 0.90 (t, 3 H, $J = 7.2$ Hz), 1.06-1.28 (m, 6 H), 1.36 (m, 2 H), 1.47 (m, 2 H),

2.39 (q, 2 H, $J = 7.4$ Hz), 2.69 (td, 1 H, $J = 5.3, 2.3$ Hz), 2.97 (ap s, 1 H), 3.99 (s, 3 H), 6.61 (t, 1 H, $J = 7.8$ Hz), 7.25 (d, 1 H, $J = 9.0$ Hz), 7.36 (ddd, 1 H, $J = 8.1, 6.8, 1.2$ Hz), 7.47 (ddd, 1 H, $J = 8.5, 7.0, 1.6$ Hz), 7.77 (d, 1 H, $J = 8.3$ Hz), 7.93 (d, 1 H, $J = 9.0$ Hz), 8.64 (d, 1 H, $J = 8.5$ Hz). **^{13}C NMR (75 MHz)** δ 13.7, 13.9, 22.3 (2 C), 27.5, 27.8, 31.3 (2 C), 53.8, 57.0, 59.6, 113.2, 120.6, 123.0, 124.4, 127.7, 128.6, 129.3, 132.4, 134.6, 135.2, 137.8, 158.0. **IR** (film): 2956, 2929, 2858, 1621, 1591, 1506, 1467, 1335, 1272, 1251, 1150, 1135, 1053, 1025, 812, 773, 749 cm^{-1} . **MS** (ES): 795 $[\text{2M}+\text{Na}]^+$, 409 $[\text{M}+\text{Na}]^+$, 387 $[\text{M}+1]^+$ (100%). **Anal. calcd for $\text{C}_{23}\text{H}_{30}\text{O}_3\text{S}$:** C, 71.46; H, 7.82; S, 8.30. **Found:** C, 71.67; H, 7.64; S, 8.45.

2.10. Synthesis of (+)-(5*S*,*R*_s)-(6*Z*,8*E*)-7-(2-Methoxynaphthalen-1-ylsulfinyl)dodeca-6,8-dien-5-ol, (17f**), and (5*S*,*R*_s)-(6*E*,8*E*)-7-(2-Methoxynaphthalen-1-ylsulfinyl)dodeca-6,8-dien-5-ol, (**18f**).**

From epoxy sulfoxide **15f** (20 mg, 0.05 mmol, 1.0 equiv) in 1 mL of THF with 6 additions of KO-*t*-Bu (0.1 mL, 0.05 mmol, 1.0 equiv and 5 additions of 50 μ L each after 3 h, 12 h, 13 h, 14 h and 15 h) according to the general procedure C (16 h) a 50:40:10 mixture of starting material, **17f** and **18f** was obtained. Purification by chromatography (20-50% EtOAc-hexane) afforded 10 mg (0.025 mmol, 50%) of epoxy sulfoxide **15f**, 8 mg (0.021 mmol, 40%) of **17f** and 2 mg (0.006 mmol, 10%) of **18f** both as yellow oils.

Data for **17f**: $R_f = 0.39$ (50% EtOAc-hexane). $[\alpha]_D^{20} +98.3$ ($c = 0.26$). $^1\text{H NMR}$ (300 MHz) δ 0.62 (t, 3 H, $J = 7.1$ Hz), 0.93 (t, 3 H, $J = 7.0$ Hz), 1.14 (sextd, 2 H, $J = 7.3, 2.2$ Hz), 1.32-1.76 (m, 6 H), 1.86 (m, 2 H), 2.51 (br s, 1 H), 4.01 (s, 3 H), 4.99 (qd, 1 H, $J = 7.1, 6.1$ Hz), 5.82 (dt, 1 H, $J = 15.4, 6.8$ Hz), 5.98 (dd, 1 H, $J = 8.8, 1.0$ Hz), 6.13 (ddd, 1 H, $J = 15.6, 2.7, 1.5$ Hz), 7.23 (d, 1 H, $J = 9.0$ Hz), 7.41 (ddd, 1 H, $J = 8.1, 6.8, 1.2$ Hz), 7.54 (ddd, 1 H, $J = 8.7, 7.0, 1.6$ Hz), 7.60 (dt, 1 H, $J = 8.1, 0.7$ Hz), 7.93 (d, 1 H, $J = 8.8$ Hz), 9.18 (d, 1 H, $J = 8.8$ Hz). $^{13}\text{C NMR}$ (75 MHz) δ 13.3, 14.1, 21.7, 22.7, 27.6, 34.8, 36.5, 57.6, 67.2, 113.5, 122.0, 122.8, 123.5, 124.7, 127.7, 128.5, 129.9, 133.0, 134.3, 135.9, 136.6, 144.7, 155.6. IR (film): 3390, 2957, 2929, 2859, 1620, 1593, 1507, 1465, 1430, 1272, 1251, 1150, 1023, 810, 751 cm^{-1} . MS (ES): 795 $[\text{2M}+\text{Na}]^+$, 409 $[\text{M}+\text{Na}]^+$, 369 $[(\text{M}-18)+1]^+$ (100%).

Data for **18f**: $R_f = 0.19$ (50% EtOAc-hexane). $^1\text{H NMR}$ (300 MHz) δ 0.56 (t, 3 H, $J = 7.3$ Hz), 0.86 (m, 2 H), 0.88 (t, 3 H, $J = 7.0$ Hz), 1.20-1.40 (m, 4 H), 1.42-1.65 (m, 2 H), 1.68-1.91 (m, 2 H), 3.98 (s, 3 H), 4.55 (m, 1 H), 5.76 (dt, 1 H, $J = 16.1, 6.0$ Hz), 5.84 (d, 1 H, $J = 16.1$ Hz), 6.50 (d, 1 H, $J = 8.8$ Hz), 7.20 (d, 1 H, $J = 9.3$ Hz), 7.36 (ddd, 1 H, $J = 8.1, 6.8, 1.2$ Hz), 7.49 (ddd, 1 H, $J = 8.3, 6.8, 1.5$ Hz), 7.76 (d, 1 H, $J = 8.3$ Hz), 7.91 (d, 1 H, $J = 9.0$ Hz), 8.62 (dd, 1 H, $J = 7.6, 1.0$ Hz). IR (film): 3369, 2957, 2928, 2858, 1621, 1594, 1507, 1466, 1430, 1335, 1272, 1250, 1150, 1135, 1024, 811, 749 cm^{-1} . MS (ES): 387 $[\text{M}+1]^+$ (100%).

2.11. Synthesis of (+)-(3*S*,*S*₅)-(1*Z*)-1-Cyclohexenyl-1-(*p*-tolylsulfinyl)hept-1-en-3-ol, (**17g**).

See printed version of the paper.

2.12. Synthesis of (+)-(5*R*,*S*₅)-(6*E*,8*E*)-7-(*p*-Tolylsulfinyl)dodeca-6,8-dien-5-ol, (**21a**).

From chlorohydrin **4a** (60 mg, 0.168 mmol, 1.0 equiv) in 1.0 mL of THF with 2 portions of KO-*t*-Bu (21 mg, 0.185 mmol, 1.1 equiv, each) in 0.5 mL of THF according to general procedure A (1 h, 15 min) an 88:12 mixture of **21a** and **22a** was obtained. Purification by chromatography (5-30% EtOAc-hexane) afforded 28 mg (0.087 mmol, 52%) of diene **21a** as a colorless oil and 9 mg (17%) of **22a** as a colorless oil.

From chlorohydrin **4a** (42 mg, 0.084 mmol, 1.0 equiv) in 1.0 mL of THF with 3 portions of KO-*t*-Bu (10 mg, 0.092 mmol, 1.1 equiv, each) in 0.5 mL of THF according to general procedure A (1 h, 30 min) an 80:20 mixture of **21a** and **22a** was obtained. Purification by chromatography (5-30% EtOAc-hexane) afforded 18 mg (0.056 mmol, 67%) of diene **21a** as a colorless oil.

From chlorohydrin **4a** (80 mg, 0.224 mmol, 1.0 equiv) in 2.2 mL of THF with 2 portions of KO-*t*-Bu (27 mg, 0.25 mmol, 1.1 equiv and after 1 h 50 mg, 0.45 mmol, 2.0 equiv) in THF according to general procedure B (1 h + 5 min) a 96:4 mixture of **21a** and **22a** was obtained. Purification by chromatography (5-30% EtOAc-hexane) afforded 42 mg (0.13 mmol, 59%) of diene **21a** as a colorless oil and approximately 3 mg (4%) of **22a** as a colorless oil.

When this experiment was carried out according to procedure C with a single addition of 1.0 equiv of KO-*t*-Bu (0.5 M in THF), an 81:19 mixture of **21a** and **22a** was obtained. The yield was not determined.

Data for **21a**: $R_f = 0.44$ (50% EtOAc-hexane). $[\alpha]_D^{20} +79.1$ ($c = 0.87$). $^1\text{H NMR}$ (500 MHz) δ 0.78 (t, 3 H, $J = 7.3$ Hz), 0.87 (t, 3 H, $J = 6.8$ Hz), 1.23-1.37 (m, 4 H), 1.53-1.71 (m, 4 H), 1.99 (m, 2 H), 2.36 (s, 3 H), 4.52 (m, 1 H), 5.86 (dt, 1 H, $J = 16.1, 6.3$ Hz), 5.91 (d, 1 H, $J = 16.1$ Hz), 6.35 (d, 1 H, $J = 8.8$ Hz), 7.22 (d, 2 H, $J = 8.1$ Hz), 7.46 (d, 2 H, $J = 8.1$ Hz). DNOE between H-5/H-6: 1.6%; between H-5/H-8: 3.6%; between H-5/H-9: 3.6%; between H-6/H-Ar ortho: 1.3%; H-6/H-5: 3.0%. $^{13}\text{C NMR}$ (50 MHz) δ 13.9, 14.4, 21.8, 22.4, 23.0, 27.8, 35.9, 37.5, 68.8, 120.0, 126.1 (2 C), 130.2 (2 C), 133.3, 139.2, 140.9, 142.1, 143.9. IR (film): 3400, 2960, 2935, 2840, 1600, 1490, 1460, 1080, 1040, 1015, 960, 810 cm^{-1} . MS (CI/ CH_4): 321 $[\text{M}+1]^+$, 303, 287, 181 (100%), 165, 153, 140, 125, 109, 95, 85. HRMS calcd for $\text{C}_{19}\text{H}_{28}\text{O}_2\text{SH}$ $[\text{M}+1]^+$: 321.1888. Found: 321.1877. Anal. calcd for $\text{C}_{19}\text{H}_{28}\text{O}_2\text{S}$: C, 71.20; H, 8.81; S, 10.01. Found: C, 71.36; H, 8.64; S, 9.92.

Data for (+)-(5*R*,10*R*,*S*_s,*S*_s)-(6*Z*,11*E*,13*E*)-8,10-di-*n*-Butyl-7,12-(bis-*p*-tolylsulfinyl)-9-oxaheptadeca-6,11,13-trien-5-ol, **22a**: $R_f = 0.21$ (30 % EtOAc-hexane). $[\alpha]_D^{20} +132.5$ ($c = 0.48$). $^1\text{H NMR}$ (200 MHz) δ 0.61-1.73 (m, 28 H), 1.90-2.15 (m, 4 H), 2.37 (s, 3 H), 2.39 (s, 3 H), 2.58 (d, 1 H, $J = 4.5$ Hz), 2.92 (d, 1 H, $J = 7.0$ Hz), 3.60 (dd, 1 H, $J = 9.0, 6.7$ Hz), 4.01 (dt, 1 H, $J = 9.0, 7.0$ Hz), 4.63 (m, 1 H), 5.51 (m, 1 H), 5.86 (m, 2 H), 6.14 (d, 1 H, $J = 9.9$ Hz), 6.52 (d, 1 H, $J = 7.2$ Hz), 7.21-7.30 (m, 4 H), 7.38-7.49 (m, 4 H). IR (film): 3390, 2958, 2929, 2860, 1596, 1492, 1456, 1399, 1378, 1261, 1082, 1047, 808, 755, 704 cm^{-1} . MS (ES): 663 $[\text{M}+\text{Na}]^+$, 641 $[\text{M}+1]^+$ (100%).

2.13. Synthesis of (+)-(5*R*)-(6*E*,8*E*)-7-(*p*-Tolylsulfonyl)dodeca-6,8-dien-5-ol, (**24a**).

From chlorohydrin **23a** (30 mg, 0.080 mmol, 1.0 equiv) in 1 mL of THF and KO-*t*-Bu (20 mg, 0.176 mmol, 2.2 equiv) in 1 mL of THF, from -78°C to rt, according to general procedure A (5 h), **24a** was obtained. Purification by chromatography (5-20% EtOAc-hexane) afforded 14 mg (0.042 mmol, 53%) of diene **24a** as a colorless oil.

Data for **24a**: $R_f = 0.20$ (30% EtOAc-hexane). $[\alpha]_D^{20} +4.0$ ($c = 0.85$). $^1\text{H NMR}$ (300 MHz) δ 0.77 (t, 3 H, $J = 7.3$ Hz), 0.87 (t, 3 H, $J = 6.9$ Hz), 1.21-1.70 (m, 8 H), 1.75 (br s, 1 H), 2.02 (m, 2 H), 2.40 (s, 3 H), 4.40 (m, 1 H), 5.93 (m, 2 H), 6.76 (d, 1 H, $J = 8.8$ Hz), 7.26 (d, 2 H, $J = 7.9$ Hz), 7.67 (d, 2 H, $J = 8.3$ Hz). $^{13}\text{C NMR}$ (50 MHz) δ 13.4, 13.9, 21.6, 21.9, 22.5, 27.2, 35.4, 36.7, 68.3, 118.1, 128.2

(2 C), 129.5 (2 C), 136.5, 140.9 (2 C), 141.8, 144.1. **IR** (CCl₄): 3520, 2960, 2880, 1600, 1520, 1310, 1150, 1090, 1020, 980, 780, 670 cm⁻¹. **MS** (EI): 336 [M]⁺, 181, 157, 139, 137, 95, 91, 85 (100%), 79, 69, 67, 55, 53, 41.

2.14. Synthesis of (+)-(2*R*,*S*₅)-(3*E*,5*E*)-1-Phenyl-4-(*p*-tolylsulfinyl)hepta-3,5-dien-2-ol, (**21b**).

From chlorohydrin **4b** (50 mg, 0.137 mmol, 1.0 equiv) in 1.6 mL of THF with 2 portions of KO-*t*-Bu (17 mg, 0.151 mmol, 1.1 equiv, each) in 0.8 mL of THF according to general procedure A (1 h, 15 min) an 86:14 mixture of **21b** and **22b** was obtained with other by-products which could not be isolated. Purification by chromatography (5-30% EtOAc-hexane) afforded 21 mg, (0.064 mmol, 47%) of **21b** as a white solid which was recrystallized from 20% EtOAc-hexane, and 6 mg (0.009 mmol, 13%) of **22b** as a colorless oil.

Data for **21b**: mp: 149-150 °C. R_f = 0.13 (2x30% EtOAc-hexane). $[\alpha]_D^{20}$ +50.6 (c = 1.53). **¹H NMR (300 MHz)** δ 1.65 (m, 3 H), 2.12 (br s, 1 H), 2.40 (s, 3 H), 2.90 (dd, 1 H, J = 13.3, 6.9 Hz), 3.06 (dd, 1 H, J = 13.3, 6.6 Hz), 4.76 (m, 1 H), 5.72 (m, 2 H), 6.40 (d, 1 H, J = 8.8 Hz), 7.17-7.27 (m, 7 H), 7.36 (d, 2 H, J = 8.0 Hz). **¹³C NMR (50 MHz)** δ 18.7, 21.2, 43.5, 69.2, 120.5, 125.6 (2 C), 126.5, 128.3 (2 C), 129.4 (2 C), 129.5 (2 C), 131.2, 133.7, 136.7, 140.0, 141.5, 145.6. **IR** (CCl₄): 3380, 3030, 2930, 2860, 1590, 1490, 1450, 1260, 1080, 1030, 960, 780, 700 cm⁻¹. **MS** (EI): 327 [M+1]⁺, 309, 235, 169, 141, 140, 103, 92, 91 (100%), 65, 63, 39. **Anal. calcd for C₂₀H₂₂O₂S**: C, 73.58; H, 6.79; S, 9.82. **Found**: C, 73.45; H, 6.88; S, 9.70.

Partial data for (2*R*,7*R*,*S*₅,*S*₅)-(3*Z*,8*E*,10*E*)-7-Benzyl-5-ethyl-4,9-(bis-*p*-tolylsulfinyl)-6-oxadodeca-3,8,10-trien-2-ol, **22b**: R_f = 0.07 (2x30% EtOAc-hexane). **¹H NMR (200 MHz)** δ 1.65 (d, 3 H, J = 7.1 Hz), 2.38 (s, 6 H), 2.60 (dd, 1 H, J = 9.6, 5.5 Hz), 2.74-2.30 (m, 3 H), 3.55 (dm, 1 H, J = 5.2 Hz), 4.25 (m, 1 H), 4.80 (m, 1 H), 5.59-5.72 (m, 2 H), 6.13 (d, 1 H, J = 8.5 Hz), 6.38 (d, 1 H, J = 8.6 Hz), 6.51 (d, 2 H, J = 7.4 Hz), 6.90-7.50 (m, 12 H).

2.15. Synthesis of (+)-(2*R*,*S*_s)-(3*E*,5*E*)-7-Methyl-1-phenyl-4-(*p*-tolylsulfinyl)octa-3,5-dien-2-ol, (21c).

From chlorohydrin **4c** (30 mg, 0.077 mmol, 1.0 equiv) in 1 mL of THF with 2 portions of KO-*t*-Bu (10 mg, 0.085 mmol, 1.1 equiv, each) in 0.5 mL of THF according to general procedure A (4 h) an 80:20 mixture of **21c** and **22c** was obtained. Purification by chromatography (10-40% EtOAc-hexane) afforded 13 mg, (0.037 mmol, 48%) of diene **21c** as a colorless oil and approximately 6 mg (18%) of **22c** as a colorless oil.

Data for **21c**: R_f = 0.24 (50% EtOAc-hexane); 0.09 (5% EtOAc-CH₂Cl₂). $[\alpha]_D^{20}$ +51.1 (c = 1.01). **¹H NMR (300 MHz)** δ 0.83 (d, 3 H, J = 6.8 Hz), 0.85 (d, 3 H, J = 6.9 Hz), 1.63 (br s, 1 H), 2.15 (m, 1 H), 2.39 (s, 3 H), 2.87 (dd, 1 H, J = 13.3, 7.2 Hz), 3.06 (dd, 1 H, J = 13.3, 6.4 Hz), 4.73 (ap q, 1 H, J = 6.8 Hz), 5.53 (m, 2 H), 6.38 (d, 1 H, J = 8.8 Hz), 7.12-7.23 (m, 7 H), 7.35 (d, 2 H, J = 8.3 Hz). **¹³C NMR (50 MHz)** δ 21.4, 21.8, 29.7, 31.9, 43.7, 69.6, 116.5, 125.7 (2 C), 126.6, 128.5 (2 C), 129.5 (2 C), 129.7 (2 C), 131.0, 136.9, 140.2, 141.6, 144.2, 145.9. **IR** (CCl₄): 3380, 3020, 2960, 2860, 1640, 1590, 1490, 1450, 1180, 1080, 1035, 970, 780, 700 cm⁻¹. **MS** (EI): 355 [M+1]⁺, 293, 197, 155, 141, 140, 103, 92, 91 (100%), 77, 65, 41. **Anal. calcd for C₂₂H₂₆O₂S**: C, 74.54; H, 7.39; S, 9.04. **Found**: C, 74.71; H, 7.18; S, 9.33.

Data for **(2*R*,7*R*,*S*_s,*S*_s)-(3*Z*,8*E*,10*E*)-7-Benzyl-5-(*iso*-butyl)-12-methyl-1-phenyl-4,9-(bis-*p*-tolylsulfinyl)-6-oxatri-deca-3,8,10-trien-2-ol, **22c****: R_f = 0.38 (50% EtOAc-hexane). **¹H NMR (300 MHz)** δ 0.34 (d, 3 H, J = 6.6 Hz), 0.60 (d, 3 H, J = 6.7 Hz), 0.83 (d, 3 H, J = 6.7 Hz), 0.88 (d, 3 H, J = 6.7 Hz), 1.80 (d, 1 H, J = 5.1 Hz), 2.20 (sext, 2 H, J = 6.3 Hz), 2.29-2.43 (m, 2 H), 2.37 (s, 3 H), 2.38 (s, 3 H), 2.64 (dd, 1 H, J = 13.2, 7.6 Hz), 2.79 (dd, 1 H, J = 13.3, 6.6 Hz), 2.92 (dd, 1 H, J = 13.0, 6.2 Hz), 2.93 (dd, 1 H, J = 13.2, 6.9 Hz), 3.52 (d, 1 H, J = 10.1 Hz), 4.38 (dd, 1 H, J = 9.0, 7.0 Hz), 4.82 (dt, 1 H, J = 8.5, 5.2 Hz), 5.46 (m, 2 H), 6.14 (d, 1 H, J = 9.5 Hz), 6.49 (d, 1 H, J = 8.7 Hz), 7.00-7.35 (m, 18 H).

2.16. Synthesis of (5*R*,6*S*,*S_s*)-(7*E*)-5,6-Epoxy-9-methyl-7-(*p*-tolylsulfinyl)dec-7-ene, (**16d**).

From chlorohydrin **4d** (21 mg, 0.061 mmol, 1.0 equiv) in 0.5 mL of THF with 2 portions of KO-*t*-Bu (8 mg, 0.067 mmol, 1.1 equiv, each) in 0.5 mL of THF according to general procedure A (3 h 30 min) oxirane **16d** was obtained (TLC). 1.1 equiv of base was added similarly and the reaction was quenched 3 h later. Purification by chromatography (15% EtOAc-hexane) afforded 14 mg (0.046 mmol, 75%) of oxirane **16d** as a colorless oil. In a related experiment, to a cold (0 °C) solution of chlorohydrin **4d** (22 mg, 0.064 mmol, 1.0 equiv) in 0.5 mL of THF was added KH (5 mg, 0.192 mmol, 3.2 equiv) and the reaction mixture was stirred at rt for 22 h. Usual extractive work-up gave oxirane **16d**. The yield was not determined.

Data for **16d**: R_f = 0.22 (20% EtOAc-hexane). $^1\text{H NMR}$ (200 MHz) δ 0.82 (t, 3 H, J = 6.6 Hz), 1.09 (d, 3 H, J = 6.6 Hz), 1.10 (d, 3 H, J = 6.7 Hz), 1.00-1.35 (m, 6 H), 2.40 (s, 3 H), 2.45 (dd, 1 H, J = 7.5, 2.4 Hz), 3.01 (m, 1 H), 3.23 (dd, 1 H, J = 2.3, 0.8 Hz), 6.45 (dd, 2 H, J = 10.2, 0.9 Hz), 7.29 (d, 2 H, J = 8.1 Hz), 7.49 (d, 2 H, J = 8.1 Hz).

2.17. Synthesis of (+)-(5*R*,*S_s*)-(6*E*)-9-Methyl-8-(*iso*-propoxy)-7-(*p*-tolylsulfinyl)deca-6-en-5-ol, (**26d**).

From chlorohydrin **4d** (30 mg, 0.087 mmol, 1.0 equiv) in 0.4 mL of *i*-PrOH:THF (1:1) with 3 additions of KOH (0.10 mL, 0.010 mmol, 1.1 equiv, each) as described before (3 days) allylic ether **26d** was obtained as a single isomer. Purification by chromatography (10-30% EtOAc-hexane) afforded 10 mg (0.028 mmol, 32%) of **26d** as a colorless oil.

Data for **26d**: R_f = 0.25 (30% EtOAc-hexane). $[\alpha]_D^{20}$ +59.9 (c = 0.51). $^1\text{H NMR}$ (200 MHz) δ 0.63 (d, 3 H, J = 6.2 Hz), 0.78 (d, 3 H, J = 6.9 Hz), 0.82 (d, 3 H, J = 6.1 Hz), 0.93 (t, 3 H, J = 7.0 Hz), 0.97 (d, 3 H, J = 6.4 Hz), 1.21-1.72 (m, 6 H), 2.03 (sept, 1 H, J = 7.4 Hz), 2.39 (s, 3 H), 2.78 (quint, 1

H, $J = 6.1$ Hz), 3.10 (br s, 1 H), 3.73 (d, 1 H, $J = 8.1$ Hz), 4.60 (m, 1 H), 6.57 (d, 1 H, $J = 7.3$ Hz), 7.29 (d, 2 H, $J = 8.2$ Hz), 7.53 (d, 2 H, $J = 8.1$ Hz). ^{13}C NMR (75 MHz) δ 14.0, 19.2, 19.4, 20.9, 21.4, 22.4, 22.6, 27.5, 33.4, 37.0, 67.7, 69.9, 77.2, 125.4 (2 C), 129.7 (2 C), 139.1, 140.4, 141.6, 148.0. IR (film): 3369, 2962, 2930, 2872, 1493, 1466, 1380, 1261, 1156, 1116, 1081, 1039, 808, 756 cm^{-1} . MS (ES): 755 $[2\text{M}+\text{Na}]^+$, 389 $[\text{M}+\text{Na}]^+$, 367 $[\text{M}+1]^+$ (100%).

2.18. Synthesis of (+)-(3*R*,5*S*)-(4*E*,6*E*)-2-methyl-5-(*p*-tolylsulfinyl)deca-4,6-dien-3-ol, (**21e**).

From chlorohydrin **4e** (15 mg, 0.044 mmol, 1.0 equiv) in 0.8 mL of THF with KO-*t*-Bu (0.06 mL, 0.031 mmol, 0.7 equiv) according to general procedure C (5 min) a 50:50 mixture of diene and an unidentified product was obtained. Purification by chromatography (10-30% EtOAc-hexane) afforded 5 mg (0.016 mmol, 37%) of diene **21e** as a colorless oil.

Data for **21e**: $R_f = 0.38$ (5% EtOAc- CH_2Cl_2). $[\alpha]_D^{20} +118.1$ ($c = 0.74$). ^1H NMR (300 MHz) δ 0.77 (t, 3 H, $J = 7.4$ Hz), 0.90 (d, 3 H, $J = 6.8$ Hz), 0.97 (d, 3 H, $J = 6.8$ Hz), 1.20-1.38 (m, 2 H), 1.84 (sept, 1 H, $J = 6.7$ Hz), 1.96-2.15 (m, 2 H), 2.36 (s, 3 H), 2.40 (br s, 1 H), 4.25 (dd, 1 H, $J = 8.9, 6.4$ Hz), 5.82-5.99 (m, 2 H, H-6), 6.38 (d, 1 H, $J = 9.0$ Hz), 7.22 (d, 2 H, $J = 7.8$ Hz), 7.47 (d, 2 H, $J = 8.2$ Hz). ^{13}C NMR (75 MHz) δ 13.4, 18.0, 18.3, 21.4, 22.0, 34.6, 35.4, 73.0, 119.9, 125.7 (2 C), 129.7 (2 C), 131.1, 138.3, 140.4, 141.7, 144.0. IR (film): 3378, 2959, 2928, 2872, 1596, 1493, 1464, 1380, 1366, 1260, 1216, 1179, 1082, 1035, 1014, 963, 809, 703 cm^{-1} . MS (ES): 635 $[2\text{M}+\text{Na}]^+$, 613 $[2\text{M}+1]^+$, 329 $[\text{M}+\text{Na}]^+$, 307 $[\text{M}+1]^+$ (100%).

2.19. Synthesis of (+)-(5*R*,6*S*,*R*_s)-(7*E*)-5,6-Epoxy-7-(2-methoxynaphthalen-1-ylsulfinyl)dodeca-7-ene, (**16f**).

From chlorohydrin **4f** (42 mg, 0.10 mmol, 1.0 equiv) in 2.0 mL of THF with 2 successive additions of KO-*t*-Bu (0.20 mL, 0.10 mmol, 1.0 equiv, and an equal amount after 30 min) according to general procedure C (1 h, 30 min), epoxy sulfoxide **16f** was obtained. We did not observe any diene formation after the second KO-*t*-Bu addition so we quenched the reaction mixture and isolated the epoxide. Purification by chromatography (15-30% EtOAc-hexane) afforded 30 mg (0.078 mmol, 78%) of **16f** as a colorless oil.

Data for **16f**: R_f = 0.17 (30% EtOAc-hexane). $[\alpha]_D^{20}$ +248.1 (c = 1.95). $^1\text{H NMR}$ (300 MHz) δ 0.72 (t, 3 H, J = 7.2 Hz), 0.90 (t, 3 H, J = 7.2 Hz), 0.96-1.18 (m, 4 H), 1.39 (m, 4 H), 1.50 (m, 2 H), 2.46 (q, 2 H, J = 7.5 Hz), 2.76 (td, 1 H, J = 4.9, 2.4 Hz), 2.86 (dd, 1 H, J = 2.4, 1.2 Hz), 3.99 (s, 3 H), 6.74 (td, 1 H, J = 7.8, 1.2 Hz), 7.24 (d, 1 H, J = 9.0 Hz), 7.38 (ddd, 1 H, J = 8.2, 7.0, 1.2 Hz), 7.49 (ddd, 1 H, J = 8.5, 7.0, 1.5 Hz), 7.78 (dt, 1 H, J = 8.1, 0.7 Hz), 7.95 (d, 1 H, J = 9.0 Hz), 8.66 (dd, 1 H, J = 8.7, 1.0 Hz). $^{13}\text{C NMR}$ (50 MHz) δ 13.8, 13.9, 22.2, 22.4, 27.5, 28.2, 31.2, 31.3, 52.6, 56.8, 57.3, 112.8, 120.0, 123.0, 124.6, 128.0, 128.7, 129.4, 132.4, 134.9, 137.3, 138.4, 157.8. IR (film): 2956, 2930, 2858, 1621, 1593, 1506, 1466, 1272, 1250, 1150, 1053, 1025, 812, 749 cm^{-1} . MS (ES): 795 $[\text{2M}+\text{Na}]^+$, 409 $[\text{M}+\text{Na}]^+$, 387 $[\text{M}+1]^+$ (100%).

2.20. Synthesis of (+)-(5*R*,*R*_s)-(6*E*,8*E*)-7-(2-Methoxynaphthalen-1-ylsulfinyl)dodeca-6,8-dien-5-ol, (21f**), and (5*R*,*R*_s)-(6*Z*,8*E*)-7-(2-Methoxynaphthalen-1-ylsulfinyl)dodeca-6,8-dien-5-ol, (**20f**).**

From epoxy sulfoxide **16f** (20 mg, 0.05 mmol, 1.0 equiv) in 1 mL of THF with 2 additions of KO-*t*-Bu (0.1 mL, 0.05 mmol, 1.0 equiv and after 3 h, 50 μL , 0.025 mmol, 0.5 equiv) according to general procedure C (3 h 30 min) a 78:11:11 mixture of **21f**, **20f** and **22f** was obtained. Purification by chromatography (20-80% EtOAc-hexane) afforded 12 mg (0.03 mmol, 60%) of **21f**, 2 mg (0.005 mmol, 10%) of **20f**, and 1 mg (0.002 mmol, 8%) of **22f**, all of them as colorless oils.

Data for **21f**: R_f = 0.21 (50% EtOAc-hexane). $[\alpha]_D^{20}$ +192.1 (c = 0.30). $^1\text{H NMR}$ (300 MHz) δ 0.59 (t, 3 H, J = 7.3 Hz), 0.85 (m, 3 H), 0.98-1.18 (m, 2 H), 1.24-1.38 (m, 3 H), 1.54 (m, 2 H), 1.70-1.93 (m, 3 H), 3.98 (s, 3 H), 4.56 (dt, 1 H, J = 8.9, 6.5 Hz), 5.70 (dt, 1 H, J = 16.1, 6.0 Hz), 5.78 (d, 1

H, $J = 16.1$ Hz), 6.53 (d, 1 H, $J = 9.0$ Hz), 7.20 (d, 1 H, $J = 9.0$ Hz), 7.35 (ddd, 1 H, $J = 8.1, 6.6, 1.2$ Hz), 7.45 (ddd, 1 H, $J = 8.6, 6.9, 1.6$ Hz), 7.75 (d, 1 H, $J = 8.1$ Hz), 7.91 (d, 1 H, $J = 9.0$ Hz), 8.64 (d, 1 H, $J = 8.8$ Hz). ^{13}C NMR (50 MHz) δ 13.3, 14.0, 21.8, 22.7, 27.3, 35.3, 37.2, 56.7, 68.6, 112.8, 119.7, 119.9, 123.2, 124.4, 127.7, 128.7, 129.4, 132.9, 134.7, 137.9, 142.0, 153.8, 157.7. IR (film): 3337, 2928, 1622, 1594, 1508, 1466, 1251, 1215, 1150, 1023, 810, 752 cm^{-1} . MS (ES): 773 $[\text{2M}+1]^+$, 387 $[\text{M}+1]^+$ (100%).

Data for **20f**: $R_f = 0.31$ (50% EtOAc-hexane). ^1H NMR (300 MHz) δ 0.57 (t, 3 H, $J = 7.1$ Hz), 0.84 (t, 3 H, $J = 7.0$ Hz), 1.04-1.86 (m, 11 H), 3.99 (s, 3 H), 4.85 (m, 1 H), 5.76 (m, 2 H), 6.12 (d, 1 H, $J = 8.1$ Hz), 7.23 (d, 1 H, $J = 9.0$ Hz), 7.40 (ddd, 1 H, $J = 8.1, 6.8, 1.2$ Hz), 7.56 (ddd, 1 H, $J = 8.7, 7.0, 1.6$ Hz), 7.78 (d, 1 H, $J = 8.1$ Hz), 7.96 (d, 1 H, $J = 9.2$ Hz), 8.74 (d, 1 H, $J = 8.3$ Hz). MS (ES): 773 $[\text{2M}+1]^+$, 387 $[\text{M}+1]^+$ (100%).

Data for **22f**: $R_f = 0.18$ (80% EtOAc-hexane). ^1H NMR (300 MHz) δ 0.20-1.80 (m, 32 H), 2.21 (m, 2 H), 3.76 (m, 1 H), 4.00 (s, 3 H), 4.10 (s, 3 H), 4.11 (m, 1 H), 4.72 (m, 1 H), 5.65 (d, 1 H, $J = 10.0$ Hz), 6.06 (m, 1 H), 6.74 (d, 1 H, $J = 8.1$ Hz), 6.86 (m, 2 H), 7.24 (m, 2 H), 7.40 (m, 3 H), 7.67 (t, 1 H, $J = 8.3$ Hz), 7.78 (ap t, 2 H, $J = 8.3$ Hz), 7.95 (ap t, 2 H, $J = 6.8$ Hz), 8.67 (d, 1 H, $J = 8.5$ Hz), 8.84 (d, 1 H, $J = 8.8$ Hz). MS (ES): 773 $[\text{M}+1]^+$ (100%).

2.21. Synthesis of (+)-(3*R*,*S*₅)-(1*E*)-1-Cyclohexenyl-1-(*p*-tolylsulfinyl)hept-1-en-3-ol, (**21g**), and (3*R*,*S*₅)-(1*Z*)-1-Cyclohexenyl-1-(*p*-tolylsulfinyl)hept-1-en-3-ol, (**20g**).

See printed version of the paper.

2.22. General Procedure for the Synthesis of Epoxy *Z* Vinyl Sulfoxides

To a solution of the mesylate derivative in THF (10 mL/mmol), at room temperature, was added 1.5 equiv of $n\text{-Bu}_4\text{NF}$ (1.0 M solution in THF) and the reaction immediately turned brown. After 30 min the reaction mixture was quenched with a saturated solution of NH_4Cl (4 mL/mmol of mesylate) and H_2O (4 mL/mmol of mesylate) and diluted with EtOAc. The layers were separated and the aqueous phase was extracted twice with EtOAc. The combined organic extracts were washed with a saturated

Data for **30**: $R_f = 0.54$ (50% EtOAc-hexane). $[\alpha]_D^{20} +249.1$ ($c = 1.54$). **^1H NMR (300 MHz) δ** 0.88 (d, 3 H, $J = 5.4$ Hz), 0.94 (t, 3 H, $J = 7.2$ Hz), 1.33-1.52 (m, 4 H), 2.10 (qd, 1 H, $J = 5.2, 2.0$ Hz), 2.40 (s, 3 H), 2.47 (m, 1 H), 2.66 (m, 1 H), 3.40 (d, 1 H, $J = 1.0$ Hz), 6.07 (ddd, 1 H, $J = 8.4, 7.4, 1.1$ Hz), 7.30 (d, 2 H, $J = 8.1$ Hz), 7.43 (d, 2 H, $J = 8.3$ Hz). **^{13}C NMR (50 MHz) δ** 13.8, 17.2, 21.3, 22.2, 27.9, 31.4, 53.5, 59.2, 124.0 (2 C), 129.7 (2 C), 136.5, 139.4, 140.8, 141.1. **IR** (film): 2961, 2927, 2858, 1647, 1596, 1492, 1457, 1376, 1260, 1176, 1081, 1044, 1016, 847, 810, 756 cm^{-1} . **MS** (ES): 279 $[\text{M}+1]^+$ (100%).

Data for **29**: $R_f = 0.21$ (30% EtOAc-hexane). $[\alpha]_D^{20} -124.9$ ($c = 0.67$). **^1H NMR (300 MHz) δ** 0.92 (t, 3 H, $J = 7.2$ Hz), 1.29 (d, 3 H, $J = 7.6$ Hz), 1.32-1.49 (m, 4 H), 2.39 (s, 3 H), 2.47 (sextd, 1 H, $J = 7.1, 1.1$ Hz), 2.63 (ap quint, 1 H, $J = 7.3$ Hz), 2.86 (qd, 1 H, $J = 5.1, 2.2$ Hz), 2.96 (s, 1 H), 6.09 (ddd, 1 H, $J = 8.1, 7.1, 1.0$ Hz), 7.23 (d, 2 H, $J = 8.1$ Hz), 7.46 (d, 2 H, $J = 8.3$ Hz). **^{13}C NMR (50 MHz) δ** 13.8, 17.4, 21.3, 22.3, 28.1, 31.3, 53.8, 58.3, 124.2 (2 C), 130.0 (2 C), 137.3, 139.4, 141.0.

141.7. **IR** (film): 2957, 2928, 2858, 1492, 1458, 1356, 1176, 1081, 1047, 933, 843, 809 cm^{-1} . **MS** (ES): 279 $[\text{M}+1]^+$ (100%).

2.25. Synthesis of (–)-(2*S*,*R*_s)-(4*E*,6*E*)-4-(*p*-Tolylsulfinyl)non-4,6-dien-2-ol, (*ent*-21h).

From epoxide **30** (13 mg, 0.047 mmol, 1.0 equiv) in 1 mL of THF with 2 successive additions of KO-*t*-Bu (66 μL , 0.033 mmol, 0.7 equiv and an equal amount after 1 h) according to general procedure C (3 h) diene *ent*-**21h** was obtained. Purification by chromatography (10-50% EtOAc-hexane) afforded 9 mg (0.032 mmol, 69%) of *ent*-**21h** as a colorless oil.

Data for *ent*-**21h**: R_f = 0.17 (50% EtOAc-hexane). $[\alpha]_D^{20}$ –62.3 (c = 0.57). **¹H NMR (300 MHz)** δ 0.77 (t, 3 H, J = 7.3 Hz), 1.30 (m, 2 H), 1.36 (d, 3 H, J = 6.3 Hz), 1.74 (br s, 1 H), 2.00 (m, 2 H), 2.36 (s, 3 H), 4.73 (m, 1 H), 5.82 (dt, 1 H, J = 16.1, 5.9 Hz), 5.91 (d, 1 H, J = 16.3 Hz), 6.38 (d, 1 H, J = 8.5 Hz), 7.23 (d, 2 H, J = 8.1 Hz), 7.46 (d, 2 H, J = 8.3 Hz). **¹³C NMR (75 MHz)** δ 13.4, 21.4, 22.0, 23.3, 35.4, 64.7, 119.3, 125.6 (2 C), 129.7 (2 C), 133.8, 139.0, 140.3, 141.7, 142.8. **IR** (film): 3369, 2963, 2927, 2872, 1492, 1454, 1262, 1216, 1082, 1038, 1014, 809, 759 cm^{-1} . **MS** (ES): 557 $[2\text{M}+1]^+$, 279 $[\text{M}+1]^+$ (100%).

2.26. Synthesis of (+)-(2*S*,*S*_s)-(4*E*,6*E*)-4-(*p*-Tolylsulfinyl)non-4,6-dien-2-ol, (**18h**), and (–)-(2*S*,*S*_s)-(4*Z*,6*E*)-4-(*p*-Tolylsulfinyl)non-4,6-dien-2-ol, (**17h**).

To a solution of mesylate **12** (57 mg, 0.12 mmol, 1.0 equiv) in 1.2 mL of THF, TBAF (0.24 mL 1M, 0.24 mmol, 2.0 equiv) was added according to the general procedure for the synthesis of epoxy sulfoxides. After 30 min formation of epoxide **29** was observed by TLC and 1.2 mL of THF was added. The mixture was cooled to 0 °C and 3 additions of KO-*t*-Bu in THF (0.16 mL, 0.08 mmol, 0.7 equiv, an equal amount after 1 h and 72 μ L, 0.036 mmol, 0.3 equiv 1 h later) were added. The reaction was monitored by TLC until completion and then quenched according to the general procedure C to give a 90:10 mixture of dienes **18h** and **17h**. Purification by chromatography (10-50% EtOAc-hexane) afforded 2 mg (0.008 mmol, 7%) of **17h** and 21 mg (0.075 mmol, 62%) of **18h**, both as colorless oils.

In a related experiment, from epoxide **29** (22 mg, 0.079 mmol, 1.0 equiv) in 1.6 mL of THF with KO-*t*-Bu (0.11 mL, 0.055 mmol, 0.7 equiv) according to the general procedure C a complex mixture of products was obtained. Purification by chromatography (10-80% EtOAc-hexane) afforded 7 mg (0.025 mmol, 32%) of pure **17h** as a colorless oil along with a mixture of by-products which structure was not determined.

Data for **18h**: R_f = 0.23 (50% EtOAc-hexane). $[\alpha]_D^{20}$ +108.7 (c = 0.79). $^1\text{H NMR}$ (300 MHz) δ 0.76 (t, 3 H, J = 7.3 Hz), 1.30 (m, 2 H), 1.35 (d, 3 H, J = 6.3 Hz), 1.82 (br s, 1 H), 2.00 (m, 2 H), 2.36 (s, 3 H), 4.71 (ap quint, 1 H, J = 6.8 Hz), 5.85 (dt, 1 H, J = 16.1, 5.8 Hz), 5.93 (d, 1 H, J = 16.1 Hz), 6.37 (d, 1 H, J = 8.3 Hz), 7.23 (d, 2 H, J = 8.1 Hz), 7.48 (d, 2 H, J = 8.1 Hz). $^{13}\text{C NMR}$ (75 MHz) δ 13.4, 21.4, 22.0, 23.4, 35.4, 64.5, 119.4, 125.7 (2 C), 129.7 (2 C), 133.6, 138.6, 140.2, 141.7, 142.6. IR (film): 3392, 2963, 2927, 2871, 1647, 1595, 1492, 1455, 1261, 1082, 1052, 1014, 964, 809, 753 cm^{-1} . MS (ES): 557 $[2\text{M}+1]^+$, 279 $[\text{M}+1]^+$ (100%).

Data for **17h**: R_f = 0.30 (10% EtOAc- CH_2Cl_2). $[\alpha]_D^{20}$ -59.2 (c = 0.26). $^1\text{H NMR}$ (300 MHz) δ 0.78 (t, 3 H, J = 7.4 Hz), 1.17-1.37 (m, 2 H), 1.36 (d, 3 H, J = 6.1 Hz), 2.01 (q, 2 H, J = 7.1 Hz), 2.38 (s, 3 H), 2.47 (br s, 1 H), 5.13 (dq, 1 H, J = 8.1, 6.3 Hz), 5.88 (d, 1 H, J = 15.9 Hz), 6.04 (dt, 1 H, J = 15.9, 6.6 Hz), 6.05 (d, 1 H, J = 8.5 Hz), 7.27 (d, 2 H, J = 8.3 Hz), 7.53 (d, 2 H, J = 8.1 Hz). $^{13}\text{C NMR}$ (75 MHz) δ 13.5, 21.3, 22.0, 23.8, 35.1, 63.3, 122.3, 124.6 (2 C), 129.8 (2 C), 137.2, 138.2, 139.5, 140.9, 144.6. IR (film): 3366, 2961, 2927, 2871, 1640, 1595, 1493, 1455, 1377, 1258, 1125, 1080, 1029, 1013, 811, 756 cm^{-1} . MS (ES): 557 $[2\text{M}+1]^+$, 279 $[\text{M}+1]^+$ (100%).

2.27. Synthesis of (-)-(2S)-(4E,6E)-4-(p-Tolylsulfonyl)non-4,6-dien-2-ol, (*ent*-24h).

From mesylate **11** (34 mg, 0.07 mmol) and TBAF (0.14 mL, 0.14 mmol, 2.0 equiv) in 0.7 mL of THF according to the general procedure (4 h) a 67:4:29 mixture of *ent*-24h, **31** and **28** was obtained along with traces of the diol **11'**. Both mesylate and epoxide have identical R_f so formation of epoxide could not be detected by TLC. Purification by chromatography (10-50% EtOAc-hexane) afforded 5 mg (0.017 mmol, 24%) of **28**, 14 mg (0.047 mmol, 67%) of a 95:5 mixture of *ent*-24h and **31** and 2 mg of diol **11'**, all of them as colorless oils. A second column chromatography of the mixture (2% EtOAc-CH₂Cl₂) afforded 1 mg of **31** and 13 mg of *ent*-24h.

Data for *ent*-24h: R_f = 0.16 (5% EtOAc-CH₂Cl₂). $[\alpha]_D^{20}$ -9.4 (c = 1.13). ¹H NMR (300 MHz) δ 0.78 (t, 3 H, J = 7.3 Hz), 1.33 (m, 2 H), 1.34 (d, 3 H, J = 6.3 Hz), 1.71 (br s, 1 H), 2.03 (m, 2 H), 2.40 (s, 3 H), 4.61 (dq, 1 H, J = 8.4, 6.5 Hz), 5.88 (m, 2 H), 6.78 (d, 1 H, J = 8.5 Hz), 7.27 (d, 2 H, J = 8.5 Hz), 7.68 (d, 2 H, J = 8.3 Hz). ¹³C NMR (50 MHz) δ 13.4, 21.6, 21.8, 22.9, 35.3, 64.6, 118.1, 128.2 (2 C), 129.6 (2 C), 136.4, 140.4, 141.6, 142.0, 144.2. IR (film): 3497, 2960, 2929, 2872, 1597, 1454, 1368, 1287, 1138, 1085, 957, 813 cm⁻¹. MS (ES): 611 [2M+Na]⁺, 317 [M+Na]⁺, 277 [(M-18)+1]⁺ (100%).

Data for (2S)-(4Z,6E)-4-(p-Tolylsulfonyl)non-4,6-dien-2-ol, **31**: R_f = 0.21 (5% EtOAc-CH₂Cl₂). ¹H NMR (300 MHz) δ 0.81 (t, 3 H, J = 7.3 Hz), 1.18-1.42 (m, 2 H), 1.33 (d, 3 H, J = 6.3 Hz), 2.02 (qd, 2 H, J = 7.2, 1.3 Hz), 2.42 (s, 3 H), 2.45 (d, 1 H, J = 3.9 Hz), 5.32 (m, 1 H), 5.86 (dt, 1 H, J = 15.4, 6.8 Hz), 6.06 (d, 1 H, J = 15.4 Hz), 6.13 (d, 1 H, J = 8.3 Hz), 7.30 (d, 2 H, J = 8.1 Hz), 7.72 (d, 2 H, J = 8.3 Hz).

Data for (2S,3R)-(4Z)-2,3-Epoxy-4-(p-tolylsulfonyl)non-4-ene, **28**: R_f = 0.53 (50% EtOAc-hexane). ¹H NMR (300 MHz) δ 0.86 (t, 3 H, J = 7.2 Hz), 1.26 (d, 3 H, J = 5.1 Hz), 1.22-1.39 (m, 4 H), 2.43 (s, 3 H), 2.51 (qd, 1 H, J = 5.1, 2.1 Hz), 2.56-2.65 (m, 2 H), 3.42 (m, 1 H), 6.16 (td, 1 H, J = 7.9, 1.1 Hz), 7.33 (d, 2 H, J = 8.1 Hz), 7.76 (d, 2 H, J = 8.5 Hz).

Data for **(2*S*,3*S*)-(4*Z*)-4-(*p*-Tolylsulfonyl)non-4-ene-2,3-diol, 11'**: R_f = 0.11 (80% EtOAc-hexane).
¹H NMR (300MHz) δ 0.82 (t, 3 H, J = 7.1 Hz), 1.19 (d, 3 H, J = 6.3 Hz), 1.26 (m, 4 H), 2.10 (br s, 1 H), 2.42 (s, 3 H), 2.49 (m, 2 H), 2.93 (d, 1 H, J = 5.9 Hz), 4.16 (m, 1 H), 4.34 (t, 1 H, J = 5.7 Hz), 6.44 (t, 1 H, J = 7.8 Hz), 7.31 (d, 2 H, J = 8.5 Hz), 7.80 (d, 2 H, J = 8.3 Hz).

2.28. General Procedure for Mitsunobu Inversions

To a solution of 1.0 equiv of alcohol in the appropriate solvent (THF, benzene) was added at rt Ph_3P , followed by the carboxylic acid ($p\text{-NO}_2\text{C}_6\text{H}_4\text{CO}_2\text{H}$ or $\text{C}_6\text{H}_5\text{CO}_2\text{H}$) and diisopropyl azodicarboxylate (DIAD) or diethyl azodicarboxylate (DEAD). The reaction was stirred at rt until disappearance of starting material (TLC) and then quenched with a saturated solution of NaHCO_3 (15 mL/mmol) and diluted with EtOAc (30 mL/mmol). The layers were separated, the organic layer was washed with a saturated solution of NaCl (15 mL/mmol), dried over anhydrous MgSO_4 , filtered and concentrated under reduced pressure to give a crude product that was purified by chromatography on silica gel using the appropriate mixture of solvents.

2.29. Mitsunobu Inversion / Deprotection Protocol to Transform (21a) in (18a).

From hydroxy diene **21a** (10 mg, 0.031 mmol, 1.0 equiv), p -nitrobenzoic acid (20.3 mg, 0.12 mmol, 4.0 equiv), PPh_3 (31.9 mg, 0.12 mmol, 4.0 equiv) and DIAD (25.9 mg, 0.025 mL, 4.0 equiv) in 0.6 mL of THF, following the general procedure, the corresponding p -nitrobenzoate was obtained. After partial purification by chromatography (10-20% EtOAc-hexane), the residue was dissolved in 1 mL of MeOH and K_2CO_3 (9 mg, 0.062 mmol, 2.0 equiv) was added. After 2 h 15 min at rt, the reaction was quenched with 1 mL of H_2O and diluted with 5 mL of EtOAc. The layers were separated, the aqueous layer was extracted with 2 mL of EtOAc and the combined organic layers were washed with 2 mL of saturated NaCl, dried over MgSO_4 and concentrated under reduced pressure to yield a crude product that was purified by column chromatography to afford pure diene **18a** (7 mg, 0.022 mmol, 71%, two steps) with identical spectral features to those found before.

2.30. Synthesis of (–)-(5*R*,*S*₅)-(6*Z*,8*E*)-7-(*p*-Tolylsulfinyl)dodeca-6,8-dien-5-ol, (**20a**).

From hydroxy diene **17a** (20 mg, 0.062 mmol, 1.0 equiv), benzoic acid (23 mg, 0.19 mmol, 3.0 equiv), PPh_3 (50 mg, 0.19 mmol, 3.0 equiv) and DEAD (87 μL (40% Tol), 0.19 mmol, 3.0 equiv) in 0.7 mL of benzene, following the general procedure (30 min), a (50:25:25) mixture of benzoates **17a'**, **18a'** and **21a'** was obtained. Purification by chromatography afforded 10 mg (0.023 mmol, 37%) of **18a'** and **21a'** and 9 mg (0.021 mmol, 34%) of **17a'**.

To a solution of **17a'** (9 mg, 0.021 mmol) in 0.5 mL of anhydrous MeOH was added .01 equiv of MeONa (1 mg, 0.021 mmol). After 2 h the reaction mixture was quenched with 1 mL of H_2O , MeOH was removed under reduced pressure and the residue was diluted with 3 mL of EtOAc and 3 mL of H_2O . The layers were separated and the aqueous phase was extracted twice with EtOAc. The combined organic extracts were washed with a saturated solution of NaCl, dried over MgSO_4 and concentrated under pressure. The crude product was purified by chromatography (20% EtOAc-hexane) to give 4 mg (0.013 mmol, 62%) of **20a** as a colorless oil.

Data for **20a**: R_f = 0.23 (50% EtOAc-hexane). $[\alpha]_D^{20}$ -44.4 (c = 0.30). $^1\text{H NMR}$ (300 MHz) δ 0.74 (t, 3 H, J = 7.4 Hz), 0.91 (t, 3 H, J = 7.1 Hz), 1.20-1.76 (m, 8 H), 1.96 (q, 2 H, J = 7.1 Hz), 2.38 (s, 3 H), 2.60 (br s, 1 H), 5.02 (m, 1 H), 5.83 (dd, 1 H, J = 15.9, 1.0 Hz), 5.94 (dt, J = 15.9, 6.4 Hz), 6.13 (d, 1 H, J = 8.3 Hz), 7.26 (d, 2 H, J = 8.5 Hz), 7.46 (d, 2 H, J = 8.3 Hz). $^{13}\text{C NMR}$ (75 MHz) δ 13.4, 14.0, 21.4, 22.0, 22.6, 27.6, 35.0, 36.8, 67.0, 121.2, 125.1 (2 C), 129.9 (2 C), 137.1, 138.4, 139.3, 141.2, 143.2. IR (film): 3377, 2959, 2927, 2859, 1640, 1492, 1463, 1378, 1260, 1216, 1082, 1039, 1014, 963, 807, 756 cm^{-1} . MS (ES): 663 $[2\text{M}+\text{Na}]^+$, 343 $[\text{M}+\text{Na}]^+$, 303 $[(\text{M}-18)+1]^+$ (100%).

2.31. Synthesis of (–)-(S_s)-(6Z,8E)-7-(p-Tolylsulfinyl)dodeca-6,8-dien-5-one, (**27a**).

To a solution of **17a** (12 mg, 0.037 mmol, 1.0 equiv) in CH₂Cl₂, at room temperature, was added MnO₂ (32 mg, 0.37 mmol, 10.0 equiv). The reaction mixture was monitored by TLC until completion and filtered through celite. Purification of the crude product by chromatography (100% CH₂Cl₂) afforded 10 mg (0.031 mmol, 84%) of **27a** as a yellow solid that was recrystallized from hexane.

Data for **27a**: mp: 61-63 °C. R_f = 0.29 (30% EtOAc-hexane). $[\alpha]_D^{20}$ –440.8 (c = 0.89). ¹H NMR (300 MHz) δ 0.86 (t, 3 H, J = 7.3 Hz), 0.91 (t, 3 H, J = 7.2 Hz), 1.27-1.48 (m, 4 H), 1.60 (m, 2 H), 2.15 (q, 2 H, J = 7.2 Hz), 2.35 (s, 3 H), 2.51 (dt, 1 H, J = 16.4, 7.4 Hz), 2.62 (dt, 1 H, J = 16.4, 7.4 Hz), 6.35 (dt, 1 H, J = 15.7, 6.9 Hz), 6.57 (dm, 1 H, J = 15.6 Hz), 6.69 (s, 1 H), 7.22 (d, 2 H, J = 8.3 Hz), 7.72 (d, 2 H, J = 8.3 Hz). ¹³C NMR (50 MHz) δ 13.6, 13.8, 21.3, 21.9, 22.3, 26.2, 35.5, 43.0, 118.5, 123.1, 125.4 (2 C), 129.6 (2 C), 140.9 (2 C), 141.3, 160.6, 199.0. IR (KBr): 2956, 2928, 2871, 1682, 1589, 1489, 1465, 1406, 1378, 1260, 1143, 1074, 1039, 1017, 965, 814, 754 cm^{–1}. MS (ES): 659 [2M+Na]⁺, 341 [M+Na]⁺, 319 [M+1]⁺ (100%).

2.32. Reduction of dienone (**27a**) with DIBALH.

To a cold (–78 °C) solution of dienone **27a** (8 mg, 0.025 mmol, 1.0 equiv) in 0.3 mL of anhydrous hexane, was added dropwise a 1.0 M solution of DIBALH in hexane (50 μ L, 0.050 mmol, 2.0 equiv). After 15 min starting material disappearance was observed by TLC and the mixture was quenched with 1 mL of H₂O and diluted with EtOAc. The layers were separated and the aqueous phase was extracted twice with EtOAc. The combined organic extracts were washed with a saturated solution of NaCl, dried over MgSO₄ and concentrated under pressure. The crude product was purified by chromatography (5-30% EtOAc-hexane) to give 2 mg (0.010 mmol, 40%) of keto vinyl sulfide as a

colorless oil, 2 mg (0.007 mmol, 28%) of (6*E*,8*E*)-dodeca-6,8-dien-5-ol as a colorless oil and 2 mg (0.006 mmol, 24%) of starting material.

Data for (6*Z*,8*E*)-7-(*p*-Tolysulfenyl)dodeca-6,8-dien-5-one: $R_f = 0.57$ (30% EtOAc-hexane). ^1H NMR (300 MHz) δ 0.86 (t, 3 H, $J = 6.6$ Hz), 0.93 (t, 3 H, $J = 7.3$ Hz), 1.22-1.46 (m, 4 H), 1.89 (t, 2 H, $J = 7.3$ Hz), 2.36 (s, 3 H), 2.53 (t, 2 H, $J = 7.3$ Hz), 5.56 (d, 1 H, $J = 14.9$ Hz), 6.05 (dt, 1 H, $J = 15.0, 6.8$ Hz), 6.45 (s, 1 H), 7.13 (d, 2 H, $J = 7.6$ Hz), 7.33 (d, 2 H, $J = 7.8$ Hz).

Data for (6*E*,8*E*)-Dodeca-6,8-dien-5-ol: $R_f = 0.46$ (30% EtOAc-hexane). ^1H NMR (300 MHz) δ 0.88 (m, 6 H), 1.20-1.60 (m, 9 H), 2.07 (q, 2 H, $J = 7.6$ Hz), 4.13 (m, 1 H), 5.58 (dd, 1 H, $J = 15.0, 7.0$ Hz), 5.70 (dt, 1 H, $J = 15.0, 7.1$ Hz), 6.03 (dd, 1 H, $J = 14.6, 10.7$ Hz), 6.18 (dd, 1 H, $J = 15.1, 10.5$ Hz).

2.33. Reduction of dienone (27a) with LiAlH_4 .

To a cold (-78°C) solution of dienone **27a** (8 mg, 0.025 mmol, 1.0 equiv) in 0.3 mL of anhydrous THF, was added LiAlH_4 (1.30 mg, 0.037 mmol, 1.5 equiv). The mixture was allowed to warm up, quenched after 1 h (-50°C) with 5 drops of MeOH and 1 mL of H_2O and diluted with EtOAc. The layers were separated and the aqueous phase was extracted twice with EtOAc. The combined organic extracts were washed with a saturated solution of NaCl, dried over MgSO_4 and concentrated under reduced pressure. The complex crude product was purified by chromatography (5-50% EtOAc-hexane) to give 2 mg (0.006 mmol, 24%) of **20a** as a colorless oil along with some by-products of unknown structure.

2.34. Reduction of dienone (27a) with $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}/\text{NaBH}_4$.

To a cold (0°C) solution of dienone **27a** (8 mg, 0.025 mmol, 1.0 equiv) in 0.3 mL MeOH, was added $\text{CeCl}_3 \cdot \text{H}_2\text{O}$ and NaBH_4 . After 15 min starting material disappearance was observed by TLC and

the mixture was quenched with 1 mL of a saturated solution of NH_4Cl and 1 mL of H_2O and diluted with EtOAc. The layers were separated and the aqueous phase was extracted twice with EtOAc. The combined organic extracts were washed with a saturated solution of NaCl, dried over MgSO_4 and concentrated under pressure. The crude product was purified by chromatography (5-50% EtOAc-hexane) to give 6 mg (0.019 mmol, 76%) of **17a** as a colorless oil.

3. Oxidation to Hydroxy Sulfonyl Dienes

3.1. Synthesis of (+)-(5*R*)-(6*E*,8*E*)-7-(*p*-Tolylsulfonyl)dodeca-6,8-dien-5-ol, (**24a**).

From sulfenyl diene **21a** (114 mg, 0.355 mmol, 1.0 equiv) in MeOH (1.5 mL) and MMPP (330 mg, 0.53 mmol, 1.5 equiv), according to the general procedure (1 h 40 min), after chromatography (1-5% EtOAc- CH_2Cl_2), sulfonyl diene **24a** (89 mg, 0.264 mmol, 74%) was obtained as a colorless oil with identical spectral features to those found before.

3.2. Synthesis of (+)-(5*S*)-(6*Z*,8*E*)-7-(*p*-Tolylsulfonyl)dodeca-6,8-dien-5-ol, (**32a**).

See printed version of the paper.

3.3. Synthesis of (+)-(2*S*)-(3*Z*,5*E*)-1-Phenyl-4-(*p*-tolylsulfonyl)hepta-3,5-dien-2-ol, (**32b**).

From sulfinyl diene **17b** (53 mg, 0.162 mmol, 1.0 equiv) in MeOH (3 mL) and MMPP (267 mg, 0.486 mmol, 3 equiv), according to the general procedure (21 h), after chromatography (10-30% EtOAc-hexane), sulfonyl diene **32b** (32 mg, 0.093 mmol, 67%) was obtained as a colorless oil.

Data for **32b**: $R_f = 0.25$ (30% EtOAc-hexane). $[\alpha]_D^{20} +12.5$ ($c = 0.20$). $^1\text{H NMR}$ (200 MHz) δ 1.50 (br s, 1 H), 1.71 (dd, 3 H, $J = 6.4, 1.5$ Hz), 2.41 (s, 3 H), 2.85 (dd, 1 H, $J = 13.5, 7.8$ Hz), 3.00 (dd, 1 H, $J = 13.5, 5.1$ Hz), 5.42 (td, 1 H, $J = 8.2, 5.1$ Hz), 5.85 (dq, 1 H, $J = 15.3, 6.4$ Hz), 6.06 (dd, 1 H, $J = 15.3, 1.3$ Hz), 6.17 (d, 1 H, $J = 8.5$ Hz), 7.20-7.35 (m, 7 H), 7.64 (d, 2 H, $J = 8.4$ Hz). $^{13}\text{C NMR}$ (50 MHz) δ 18.5, 21.6, 43.5, 68.1, 124.8, 126.8, 127.4 (2 C), 128.6 (2 C), 129.6 (2 C), 129.8 (2 C), 132.7, 137.1, 137.8, 140.9, 141.4, 144.4. IR (CCl₄): 3420, 3040, 2960, 2920, 2860, 1600, 1490, 1450, 1320, 1290, 1150, 1080, 1030, 960, 790, 760, 700, 680 cm⁻¹. Anal. calcd for C₂₀H₂₂O₃S: C, 70.15; H, 6.48; S, 9.36. Found: C, 70.33; H, 6.73; S, 9.55.

3.4. Synthesis of (+)-(3S)-(4Z,6E)-2-Methyl-5-(*p*-tolylsulfonyl)deca-4,6-dien-3-ol, (**32e**).

From sulfinyl diene **17e** (20 mg, 0.065 mmol, 1.0 equiv) in MeOH (1 mL) and MMPP (48 mg, 0.078 mmol, 1.2 equiv), according to the general procedure (13 h), after chromatography (5-20% EtOAc-hexane), sulfonyl diene **32e** (15 mg, 0.046 mmol, 71%) was obtained as a colorless oil.

Data for **32e**: $R_f = 0.35$ (30% EtOAc-hexane). $[\alpha]_D^{20} +60.6$ ($c = 0.66$). $^1\text{H NMR}$ (300 MHz) δ 0.80 (t, 3 H, $J = 7.4$ Hz), 0.83 (d, 3 H, $J = 7.8$ Hz), 0.97 (d, 3 H, $J = 6.7$ Hz), 1.32 (sext, 2 H, $J = 7.3$ Hz), 1.77 (sext, 1 H, $J = 6.6$ Hz), 2.02 (q, 2 H, $J = 7.1$ Hz), 2.41 (s, 3 H), 2.43 (br s, 1 H), 4.84 (m, 1 H), 5.85 (dt, 1 H, $J = 15.6, 7.1$ Hz), 6.08 (d, 1 H, $J = 15.6$ Hz), 6.15 (d, 1 H, $J = 9.0$ Hz), 7.29 (d, 2 H, $J = 7.9$ Hz), 7.72 (d, 2 H, $J = 7.9$ Hz). $^{13}\text{C NMR}$ (50 MHz) δ 13.5, 17.8, 18.4, 21.6, 21.9, 34.1, 34.8, 71.1, 124.0, 127.5 (2 C), 129.7 (2 C), 137.7, 137.8, 141.0, 142.1, 144.5. IR (CCl₄): 3440, 2930, 2840, 1580, 1470, 1450, 1250, 1140, 1070, 1000, 770, 660 cm⁻¹. MS (APCI): 305 [M-17]⁻, 149, 139. Anal. calcd for C₁₈H₂₆O₃S: C, 67.04; H, 8.13; S, 9.94. Found: C, 66.80; H, 7.93; S, 10.06.

4. Synthesis of Chlorodienes

4.1. Synthesis of the Mesylate of (+)-(5*R*,6*S*,*S*₅)-(7*E*)-5-Chloro-7-(*p*-tolylsulfinyl)dodec-7-en-6-ol, (**33a**).

From chlorohydrin **3a** (32 mg, 0.089 mmol, 1.0 equiv), MsCl (35 μL , 0.45 mmol, 5.0 equiv) and Et₃N (64 μL , 0.46 mmol, 5.2 equiv) in 1 mL of CH₂Cl₂, according to the general procedure, mesylate **33a** was obtained. Chromatographic purification (5-30% EtOAc-hexane) gave **33a** (20 mg, 0.046 mmol, 51%) as a colorless oil.

Data for **33a**: R_f = 0.27 (30% EtOAc-hexane). $[\alpha]_D^{20}$ +88.8 (c = 1.75). ¹H NMR (300 MHz) δ 0.90 (t, 3 H, J = 7.0 Hz), 0.92 (t, 3 H, J = 7.0 Hz), 1.24-1.67 (m, 10 H), 1.96 (m, 1 H), 2.39 (s, 3 H, Me-*p*-Tol), 2.43 (s, 3 H), 2.46 (m, 1 H), 4.17 (ddd, 1 H, J = 9.8, 7.1, 2.8 Hz), 5.40 (d, 1 H, J = 7.1 Hz), 6.80 (t, 1 H, J = 7.6 Hz), 7.30 (d, 2 H, J = 8.1 Hz), 7.55 (d, 2 H, J = 8.2 Hz). ¹³C NMR (50 MHz) δ 13.6 (2 C), 21.2, 21.8, 22.2, 27.9, 28.6, 30.6, 32.2, 37.8, 61.5, 79.1, 125.4 (2 C), 129.7 (2 C), 139.0, 140.0, 141.9, 142.6. IR (CCl₄): 2960, 2930, 2880, 1740, 1640, 1600, 1490, 1460, 1370, 1180, 1090, 1050, 1020, 910, 840, 780 cm⁻¹.

4.2. Synthesis of the Mesylate of (-)-(5*S*,6*R*,*S*₅)-(7*E*)-5-Chloro-7-(*p*-tolylsulfinyl)dodec-7-en-6-ol, (**34a**).

From chlorohydrin **4a** (41 mg, 0.114 mmol, 1.0 equiv), MsCl (44 μL , 0.57 mmol, 5.0 equiv) and Et₃N (82 μL , 0.59 mmol, 5.2 equiv) in 1 mL of CH₂Cl₂, according to the general procedure, mesylate **34a** was obtained. Chromatographic purification (5-30% EtOAc-hexane) gave **34a** (31 mg, 0.071 mmol, 62%) as a colorless oil.

Data for **34a**: R_f = 0.25 (30% EtOAc-hexane). $[\alpha]_D^{20}$ +8.6 (c = 0.50). ¹H NMR (300 MHz) δ 0.84 (t, 3 H, J = 7.0 Hz), 0.91 (t, 3 H, J = 7.2 Hz), 1.16-1.58 (m, 10 H), 1.85 (m, 1 H), 2.38 (m, 1 H), 2.39

(s, 3 H), 2.81 (s, 3 H), 3.67 (td, 1 H, $J = 9.5, 2.6$ Hz), 5.40 (d, 1 H, $J = 8.7$ Hz), 6.70 (t, 1 H, $J = 7.7$ Hz), 7.30 (d, 2 H, $J = 8.2$ Hz), 7.53 (d, 2 H, $J = 8.2$ Hz). ^{13}C NMR (50 MHz) δ 13.6 (2 C), 21.2, 21.5, 22.2, 27.6, 28.8, 30.5, 32.8, 38.5, 60.5, 78.5, 125.4 (2 C), 129.8 (2 C), 139.3, 139.5, 142.1, 143.0. IR (film): 2961, 2929, 2861, 1636, 1595, 1492, 1465, 1364, 1260, 1176, 1082, 1047, 1015, 927, 840, 759 cm^{-1} . MS (ES): 891 $[\text{2M}+\text{Na}]^+$, 457 $[\text{M}+\text{Na}]^+$, 435 $[\text{M}+1]^+$ (100%).

4.3. Synthesis of (5*R*,*S*_s)-(6*E*,8*E*)-5-Chloro-7-(*p*-tolylsulfinyl)dodeca-6,8-diene, (35), (5*R*,*S*_s)-(6*Z*,8*E*)-5-Chloro-7-(*p*-tolylsulfinyl)dodeca-6,8-diene, (36), and (*S*_s)-(5*E*,7*E*)-6-Mesyloxy-7-(*p*-tolylsulfinyl)dodeca-5,7-diene, (37).

From mesylate **33a** (25 mg, 0.057 mmol, 1.0 equiv) in 1 mL THF with a suspension of (7 mg, 0.063 mmol, 1.1 equiv) in 0.4 mL of THF according to procedure A (25 h), with a second addition of 1.1 equiv of base after 4 h, a 37:15:48 mixture of chlorodienes **35** and **36** and mesylate **37** (assignment tentative) was obtained with 95% conversion. Purification by column chromatography (5-50% EtOAc-hexane) gave pure products. The yield was not determined. In a related experiment but at shorter reaction time (4 h) with 1.1 equiv de KO-*t*-Bu a similar product distribution was obtained with 23% conversion.

Data for **35**: $R_f = 0.30$ (20% EtOAc-hexane). ^1H NMR (200 MHz) δ 0.79 (t, 3 H, $J = 7.3$ Hz), 0.91 (t, 3 H, $J = 6.8$ Hz), 1.25-1.44 (m, 6 H), 1.85-2.07 (m, 4 H), 2.39 (s, 3 H), 4.72 (t, 1 H, $J = 7.1$ Hz), 5.80 (d, 1 H, $J = 15.5$ Hz), 5.95 (dt, 1 H, $J = 15.5, 6.3$ Hz), 6.42 (d, 1 H, $J = 10.3$ Hz), 7.26 (d, 2 H, $J = 8.1$ Hz), 7.48 (d, 2 H, $J = 8.2$ Hz).

Data for **36**: $R_f = 0.40$ (20% EtOAc-hexane). ^1H NMR (200 MHz) δ 0.80 (t, 3 H, $J = 7.4$ Hz), 0.92 (t, 3 H, $J = 6.5$ Hz), 1.25-1.54 (m, 6 H), 1.82 (m, 2 H), 2.02 (q, 2 H, $J = 7.0$ Hz), 2.40 (s, 3 H), 5.52 (m, 1 H), 5.90 (d, 1 H, $J = 15.8$ Hz), 6.01-6.12 (m, 2 H), 7.29 (d, 2 H, $J = 8.1$ Hz), 7.46 (d, 2 H, $J = 8.3$ Hz). ^{13}C NMR (50 MHz) δ 13.9, 14.4, 21.9, 22.4, 22.6, 29.1, 35.9, 38.9, 56.9, 118.9, 125.7, 126.0 (2 C), 130.1, 130.2 (2 C), 131.2, 140.9, 148.4.

Partial data for **37** (from a 50:50 mixture of **35** and **37**): $R_f = 0.28$ (20% EtOAc-hexane). ^1H NMR (200 MHz) δ 2.38 (s, 3 H), 2.99 (s, 3 H), 5.71 (dd, 1 H, $J = 8.8, 6.4$ Hz), 6.76 (dd, 1 H, $J = 8.2, 6.7$ Hz).

4.4. Synthesis of (+)-(5*S*,*S*₅)-(6*E*,8*E*)-5-Chloro-7-(*p*-tolylsulfinyl)dodeca-6,8-diene, (38), and (5*S*,*S*₅)-(6*Z*,8*E*)-5-Chloro-7-(*p*-tolylsulfinyl)dodeca-6,8-diene, (39).

From mesylate **34a** (17 mg, 0.039 mmol, 1.0 equiv) in 0.5 mL THF with a suspension of KO-*t*-Bu (5 mg, 0.047 mmol, 1.1 equiv) in 0.4 mL of THF according to procedure A (16 h) a 64:36 mixture of chlorodienes **38** and **39** was obtained with 61% conversion. Purification by column chromatography (5-50% EtOAc-hexane) gave pure products. The yield was not determined. In a related experiment but at shorter reaction time (2 h) a similar product distribution was obtained with 36% conversion.

Data for **38**: R_f = 0.30 (30% EtOAc-hexane). $[\alpha]_D^{20}$ +63.42 (c = 0.63). $^1\text{H NMR}$ (200 MHz) δ 0.77 (t, 3 H, J = 7.4 Hz), 0.89 (t, 3 H, J = 7.1 Hz), 1.24-1.53 (m, 8 H), 1.80-2.02 (m, 2 H), 2.36 (s, 3 H), 4.70 (dt, 1 H, J = 10.2, 7.0 Hz), 5.83-5.96 (m, 2 H), 6.43 (d, 1 H, J = 10.3 Hz), 7.23 (d, 2 H, J = 8.3 Hz), 7.49 (d, 2 H, J = 8.2 Hz). $^{13}\text{C NMR}$ (75 MHz) δ 13.4, 13.9, 21.4, 21.9, 22.1, 28.6, 35.4, 38.4, 56.4, 119.2, 126.1 (2 C), 129.2 (2 C), 129.9, 139.7, 140.3, 142.1, 144.8. IR (film): 2960, 2871, 2928, 1645, 1596, 1492, 1456, 1379, 1303, 1260, 1083, 1054, 1016, 808, 756 cm^{-1} . MS (ES): 699 $[2\text{M}+\text{Na}]^+$, 361 $[\text{M}+\text{Na}]^+$, 339 $[\text{M}+1]^+$ (100%).

Data for **39**: R_f = 0.40 (20% EtOAc-hexane). $^1\text{H NMR}$ (200 MHz) δ 0.76 (t, 3 H, J = 7.3 Hz), 0.95 (t, 3 H, J = 6.9 Hz), 1.20-1.71 (m, 8 H), 1.86-2.06 (m, 2 H), 2.41 (s, 3 H), 5.40 (dt, 1 H, J = 10.6, 7.0 Hz), 5.85 (d, 1 H, J = 15.9 Hz), 6.03-6.14 (m, 2 H), 7.31 (d, 2 H, J = 8.2 Hz), 7.54 (d, 2 H, J = 8.2 Hz).

4.5. Synthesis of (+)-(5*R*,6*R*,*S*₅)-(7*E*)-5,6-Epoxy-7-(*p*-tolylsulfinyl)dodec-7-ene, (40).

From chlorohydrin **4a** (55 mg, 0.15 mmol, 1.0 equiv), benzoic acid (55 mg, 0.45 mmol, 3.0 equiv), PPh₃ (118 mg, 0.45 mmol, 3.0 equiv) and DEAD (78 mg, 0.2 mL (40% in toluene), 0.45 mmol, 3.0 equiv) in 1.5 mL of benzene, following the general procedure, the corresponding benzoate was

obtained along with 60% of starting material. Purification by chromatography (80-100% CH₂Cl₂-hexane), afforded 14 mg of impure benzoate and 32 mg (0.09 mmol, 60%) of **4a**.

The impure benzoate was dissolved in 0.5 mL of MeOH and NaOMe (1.6 mg, 0.03 mmol, 1.0 equiv) was added. After 12 h the mixture was quenched with 0.5 mL of a saturated solution of NH₄Cl and 0.5 mL of H₂O and diluted with EtOAc. The layers were separated and the aqueous phase was extracted twice with EtOAc. The combined organic extracts were washed with a saturated solution of NaCl, dried over MgSO₄ and concentrated under pressure. Purification by chromatography afforded 6 mg (0.019 mmol, 68%) of epoxide **40** as a colorless oil. Along with the epoxide, 2 mg (0.006 mmol, 21%) of the chlorodiene **38** was obtained. It is conceivable that **38** derives from basic treatment of S_N2 or S_N2' products formed in the Mitsunobu reaction.

Data for **40**: R_f = 0.14 (100% CH₂Cl₂). $[\alpha]_D^{20}$ +191.2 (c = 0.40). **¹H NMR (300 MHz)** δ 0.89 (t, 3 H, J = 7.1 Hz), 0.90 (t, 3 H, J = 7.2 Hz), 1.30-1.56 (m, 10 H), 2.27 (q, 2 H, J = 7.2 Hz), 2.37 (s, 3 H), 3.02 (m, 1 H), 3.30 (m, 1 H), 6.54 (td, 1 H, J = 7.7, 1.5 Hz), 7.26 (d, 2 H, J = 8.3 Hz), 7.60 (d, 2 H, J = 8.3 Hz). **¹³C NMR (50 MHz)** δ 13.8, 13.9, 21.4, 22.4, 22.5, 28.0, 28.1, 28.4, 31.0, 53.0, 58.5, 125.7 (2 C), 129.8 (2 C), 134.5, 138.9, 140.4, 141.7. **IR** (film): 2957, 2928, 2859, 1493, 1465, 1378, 1278, 1082, 1053, 1016, 809 cm⁻¹. **MS** (ES): 663 [2M+Na]⁺, 343 [M+Na]⁺, 321 [M+1]⁺ (100%).

5. Optical purity of Hydroxy 2-Sulfinyl Butadienes

The optical purity of our hydroxy 2-sulfinyl butadienes was established by synthesis of the (*S*)-2-methoxy-2-phenyl acetates of dienes (**±**)-**21g** and (+)-**21g** and a detailed ¹H NMR study of the crude products (96% ee). This is in agreement with the optical purity of commercial (–)-(1*R*)-Menthyl-(*S*)-*p*-toluenesulfinate and (*S*)-2-Methoxy-2-phenyl acetic acid (98% for both reactants), therefore no significant racemization took place either during *Z-E* vinyl sulfoxide isomerization or subsequent chlorohydrin treatment with base.

5.1. Synthesis of (+)-(3*R*,*S*_s)-(1*E*)-1-Cyclohexenyl-1-(*p*-tolylsulfinyl)hept-1-en-3-yl (*S*)-2-methoxy-2-phenyl acetate, (41), and (3*S*,*R*_s)-(1*E*)-1-Cyclohexenyl-1-(*p*-tolylsulfinyl)hept-1-en-3-yl (*S*)-2-methoxy-2-phenyl acetate, (42).

To a solution of diene **(±)-21g** (10 mg, 0.03 mmol, 1.0 equiv) in 0.3 mL of CH_2Cl_2 , at 0 °C, 2-methoxy-2-phenyl acetic acid (5 mg, 0.03 mmol, 1.0 equiv), dicyclohexylcarbodiimide (7 mg, 0.033 mmol, 1.1 equiv) and dimethylaminopyridine (1.5 mg, 0.012 mmol, 0.4 equiv) were added. The mixture was allowed to warm to room temperature and monitored by TLC until starting material disappearance (2 h). The reaction mixture was filtered to remove dicyclohexylurea and the crude product was purified by chromatography (30% EtOAc-hexane) to give 13 mg (0.027 mmol, 90%) of a 50:50 mixture of **41** and **42**.

In an identical experiment with **(+)-21g**, 13 mg (0.027 mmol, 90%) of a 98:2 mixture of esters **41** and **42** was obtained (96% ee).

Data for **41**: $R_f = 0.34$ (30% EtOAc-hexane). $[\alpha]_D^{20} +209.72$ ($c = 1.08$). $^1\text{H NMR}$ (300MHz) δ 0.67 (t, 3 H, $J = 7.2$ Hz), 0.80-0.97 (m, 2 H), 1.00-1.12 (m, 2 H), 1.32-1.71 (m, 7 H), 1.74-1.96 (m, 3 H), 2.36 (s, 3 H), 3.37 (s, 3 H), 4.70 (s, 1 H), 5.19 (ap sept, 1 H, $J = 1.9$ Hz), 5.43 (ddd, 1 H, $J = 9.3, 8.1, 5.4$ Hz), 6.19 (d, 1 H, $J = 9.3$ Hz), 7.19 (dm, 2 H, $J = 8.5$ Hz), 7.29-7.42 (m, 7 H). $^{13}\text{C NMR}$ (50 MHz) δ 13.7, 21.4, 21.5, 22.1, 22.3, 25.3, 26.7, 29.2, 34.1, 57.2, 71.3, 82.3, 125.5 (2 C), 126.5, 127.2 (2 C), 128.5(2 C), 128.6, 129.0, 129.4 (2 C), 132.4, 136.4, 139.7, 141.7, 151.8, 169.8. IR (film): 2930, 2860, 1748, 1596, 1492, 1455, 1333, 1302, 1260, 1174, 1113, 1083, 1055, 1016, 965, 922, 890, 809, 754 cm^{-1} .

Partial data for **42**: $R_f = 0.34$ (30% EtOAc-hexane). $^1\text{H NMR}$ (300MHz) δ 0.83 (t, 3 H, $J = 7.1$ Hz), 2.36 (s, 3 H), 3.39 (s, 3 H), 4.72 (s, 1 H), 5.06 (m, 1 H), 5.44 (m, 1 H), 6.05 (d, 1 H, $J = 9.5$ Hz), 7.18 (d, 2 H, $J = 8.1$ Hz), 7.28-7.43 (m, 7 H).

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 $^1\text{H NMR}$ of the crude reaction mixture.

2. Kosugi, H.; Kitaoka, M.; Tagami, K.; Takahashi, A.; Uda, H. *J. Org. Chem.* **1987**, 52, 1078-1082.

3. Marsan, M. P.; Warnock, W.; Muller, I.; Nakatani, Y.; Ourisson, G.; Milon, A. *J. Org. Chem.* **1996**, *61*, 4252-4257.
4. Cinquini, M.; Cozzi, F.; Raimondi, L. *Gazz. Chim. Ital.* **1986**, *116*, 185-187.
5. Hoffman, R. W.; Maak, N. *Tetrahedron Lett.* **1976**, *26*, 2237-2240.