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Nucleophilic epoxidation of γ-alkoxy dienyl sulfoxide derivatives

Roberto Fernández de la Pradilla,* María Victoria Buergo, Carlos Montero and Alma Viso*

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

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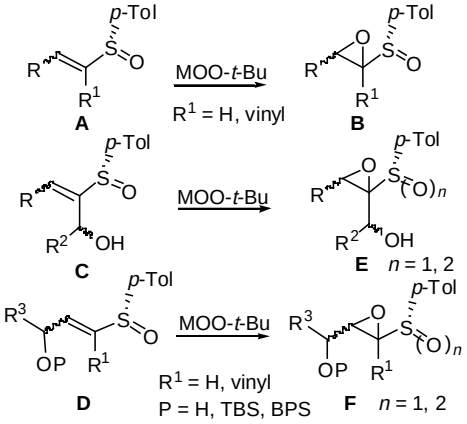
Abstract—(*E*,*E*) and (*Z*,*E*) γ-alkoxy dienyl sulfones undergo nucleophilic epoxidation with remarkable regio- and stereoselectivity to render *syn* oxiranes in a process mainly controlled by the alkoxy stereocenter. Upon epoxidation γ-hydroxy dienyl sulfoxides provide sulfinyl and sulfonyl oxiranes along with bis-epoxides formed through a Payne rearrangement that can be prevented by silylation of the OH group. Interestingly, the presence of a γ-silyloxy group can invert the stereochemical trend of the molecule affording mainly an *anti* epoxidation process.

1. Introduction

The asymmetric epoxidation of electron deficient alkenes has attracted a great deal of attention in the last decade[1] as an efficient route towards enantiopure functionalized epoxides, very attractive building blocks.[2] In this context, our group has demonstrated that simple α,β-unsaturated sulfoxides **A** (R^1=H) undergo nucleophilic epoxidation by treatment with metalated hydroperoxides with complete preservation of double bond geometry and with moderate to excellent facial selectivity to produce enantio- and diastereomerically pure α,β-epoxy sulfoxides **B** (R^1=H). Related 2-sulfinyl dienes **A** (R^1=vinyl) have also resulted suitable substrates for these epoxidations and the facial diastereoselectivity may be controlled by the choice of the counterion (LiOO-*t*-Bu vs NaOO-*t*-Bu).[3] Subsequently, we have explored the behavior of α′-(1-hydroxyalkyl)vinyl sulfoxides **C**,[4] and γ-alkoxy vinyl sulfoxides **D** (R^1=H, P=TBS, BPS),[5] bearing an additional stereocenter and with a reinforcing/non-reinforcing scenario being operative. The above work has led to the development of a new method for the synthesis of enantiopure sulfinyl and sulfonyl oxiranes **B**, **E** and **F**.[6] In connection with these efforts, we have also examined the nucleophilic epoxidation of γ-hydroxy dienyl sulfoxides **D** (R^1=vinyl). Among others, we have studied the effect of the *E*/*Z* geometry on the electrophilic double bond, of the relative configuration of the hydroxyl and sulfinyl stereocenters, of the protection at the hydroxyl group as well as the reactivity of the related γ-hydroxy dienyl sulfones in this epoxidation. Now we report in full our results (Scheme 1).



Scheme 1.

2. Discussion and results

2.1. Preparation of the starting dienes

The set of dienyl sulfoxides and sulfones chosen for this study was synthesized following a procedure previously reported by us.[7] The method entails submitting the two diastereomeric *anti* sulfinyl chlorohydrins **G** to one-pot base-induced (KO-*t*-Bu) epoxide formation/rearrangement to generate enantiopure hydroxy 2-sulfinyl dienes **D** through the diasteromeric epoxy vinyl sulfoxides **H** that, if desired, can also be isolated. This efficient reaction allows for the selective synthesis of *E*/*E* or *Z*/*E* dienyl sulfoxides **D** depending on the relative stereochemistry of the sulfinyl

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* Corresponding authors. Fax: 34 91 564 4853;
e-mail addresses: iqofp19@iqog.csic.es; iqov379@iqog.csic.es

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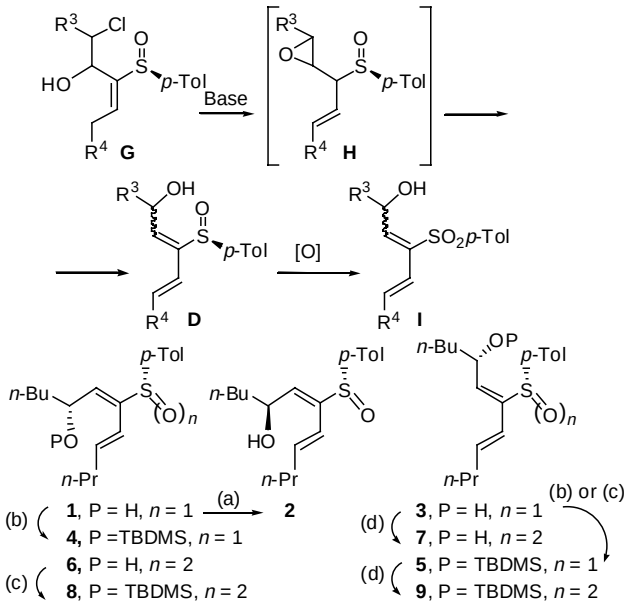


(a) i. PPh_3, DIAD, p-$NO_2C_6H_4CO_2H$, 0 °C THF, 90 min; ii. K_2CO_3, MeOH, 0 °C, 2 h, 72% overall yield. (b) TBDMSCl, imidazole, CH_2Cl_2, 0 °C to rt, 95 min, 79%. (c) TBDMSOTf, Et_3N, DMAP, 0 °C to rt, 23 min, 98%. (d) MMPP, MeOH, rt, 24 h, 60–64%.

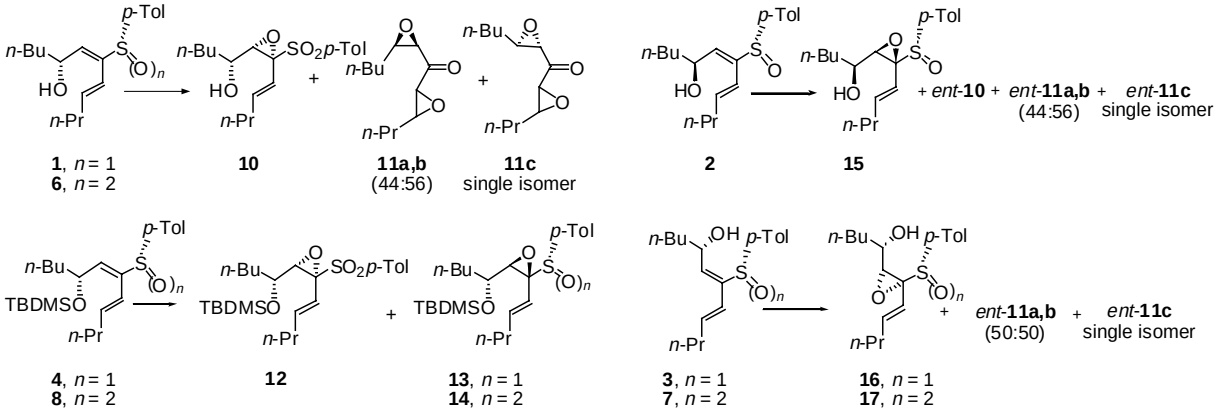
Scheme 2.

chlorohydrin precursor, **G**. Further oxidation (MMPP) allowed for the simple transformation of dienyl sulfoxides **D** into γ-hydroxy dienyl sulfones **I** without any detectable loss of stereochemical integrity. In particular, dienyl sulfoxides **1** and **3**, and dienyl sulfones **6** and **7** were prepared for the present work. In addition, (*E*,*E*)-γ-hydroxy dienyl sulfoxide **1** was submitted to Mitsunobu conditions followed by debenzoylation to give diastereomeric diene **2** in good yield and as a single isomer. Finally, to assess the influence of the hydroxyl group in the epoxidation process dienyl sulfoxide **1** as well as dienyl sulfone **6** were protected as silyl ethers in good yields to afford dienes **4** and **8**, respectively. Surprisingly, (*Z*,*E*)-dienyl sulfoxide **3** showed a low reactivity under silylation conditions and the resulting silyloxy diene **5** was unstable under standard chromatographic purification leading to *E*/*E* dienes and diastereomerization at sulfur.[8] However, with careful manipulation a small amount of **5** could be isolated and then treated with MMPP to afford γ-silyloxy dienyl sulfone **9** in good yield (Scheme 2).

2.2. Nucleophilic epoxidation of dienyl sulfoxides and sulfones

At the beginning of this study, we submitted (*E*,*E*)-dienyl sulfones **6** and **8** to epoxidation with NaOO-*t*-Bu to assess the effect of the alkoxy group as the only stereocenter in the molecule (Table 1, entries 1 and 2). The nucleophilic epoxidation of γ-hydroxy dienyl sulfone **6** was remarkably

Table 1. Nucleophilic epoxidation of γ-alkoxy dienyl sulfoxides and sulfones

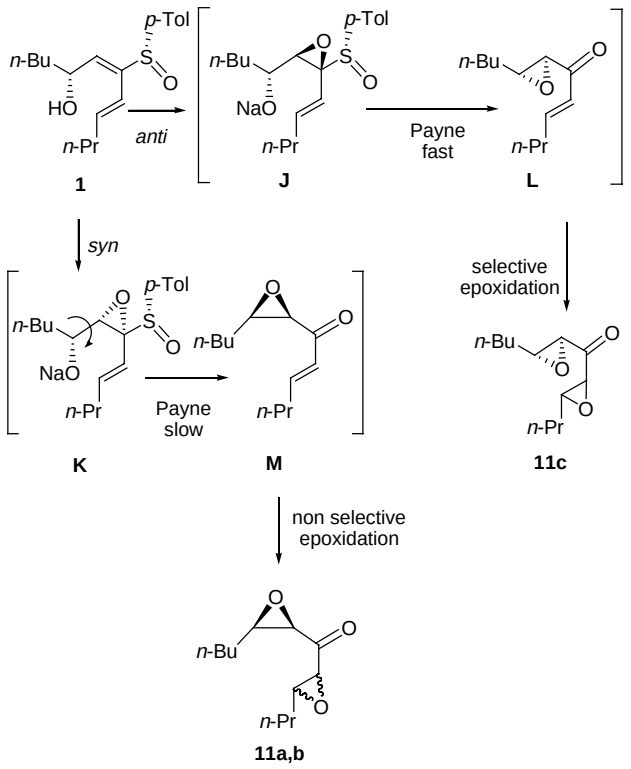


Entry	Compounds	Conditions[a]	*syn*						*anti*			Yield (%)[b]
			10/*ent*-**10**	**12**	**15**	**16**	**17**	**11a,b**/*ent*-**11a,b**[c]	**13**	**14**	**11c**/*ent*-**11c**[d]	
1	**6**	NaOO*t*-Bu, 105 m	100 (**10**)									89
2	**8**	NaOO*t*-Bu, 4 days		46						54		75[e]
3	**1**	NaOO*t*-Bu, 3 h	27 (**10**)					52 (**11a,b**)			21 (**11c**)	62
4	**4**	KOO*t*-Bu, 4 days		10					43	47		82[f]
5	**2**	NaOO*t*-Bu, 70 m	4 (*ent*-**10**)		80			11 (*ent*-**11a,b**)			5 (*ent*-**11c**)	93
6	**7**	NaOO*t*-Bu, 55 m					100					82
7	**3**	NaOO*t*-Bu, 45 m				72	4	2 (*ent*-**11a,b**)			22 (*ent*-**11c**)	61[g]

[a] All reactions were conducted in THF at 0 °C.
[b] Combined yield of isolated epoxides.
[c] As a 44:56 mixture of diastereomers except for entry 7 where an equimolecular mixture was detected.
[d] As a single isomer. The absolute configuration was not confirmed.
[e] Starting material (5%) in the crude reaction mixture (^{1}H NMR).
[f] Starting material (12%) in the crude reaction mixture (^{1}H NMR).
[g] Starting material (11%) in the crude reaction mixture (^{1}H NMR).

regio- and stereoselective affording *syn* sulfonyl oxirane **10** as a single diastereoisomer. In contrast, γ-silyloxy dienyl sulfone **8** underwent a slower epoxidation (>4 days) to give a 46:54 mixture of *syn* and *anti* sulfonyl oxiranes **12** and **14** under similar reaction conditions. To further probe the stereochemical assignment of the above sulfonyl oxiranes, **10** was silylated using TBDMSCl and imidazole rendering **12** with a moderate yield (29%) and conversion (70% recovered starting material), however, at this point we did not further optimize this reaction. The high stereodirecting capability of the free hydroxyl group was again observed for the nucleophilic epoxidation of (*Z*,*E*)-γ-hydroxy dienyl sulfone **7** (entry 6). Thus treatment of **7** with NaOO-*t*-Bu in THF afforded exclusively *syn* sulfonyl oxirane **17** in 55 min and with an excellent yield (82%).

Subsequently we examined the behavior of (*E*,*E*)-γ-hydroxy dienyl sulfoxides **1** and **2** with an additional stereocenter at sulfur (entries 3 and 5). Treatment of **1** with NaOO-*t*-Bu after 3 h provided as minor product sulfonyl oxirane **10** (27%) along with bis-epoxides **11ab** (52%, as a 44:55 mixture of diastereoisomers) and **11c** (21%, as a single diastereoisomer). Shortening the reaction time allowed for detection of variable amounts of the sulfinyl oxirane (**10′** not shown) precursor of **10**, however, starting material was always recovered. The formation of bis-epoxides **11a–c** has been rationalized in terms of a Payne rearrangement,[9] (Scheme 3) of sulfinyl oxiranes **J** (*anti*) and **K** (*syn*) to generate α,β-unsaturated epoxy ketones **L** and **M** that undergo in situ second selective or non selective nucleophilic epoxidation providing **11c** and **11ab**, respectively. In this context, minor *anti* oxirane **J** would suffer a rapid Payne process while major *syn* oxirane **K** would require rotation around Cβ–Cγ to adopt a suitable arrangement and this slows down the Payne rearrangement.



Scheme 3.

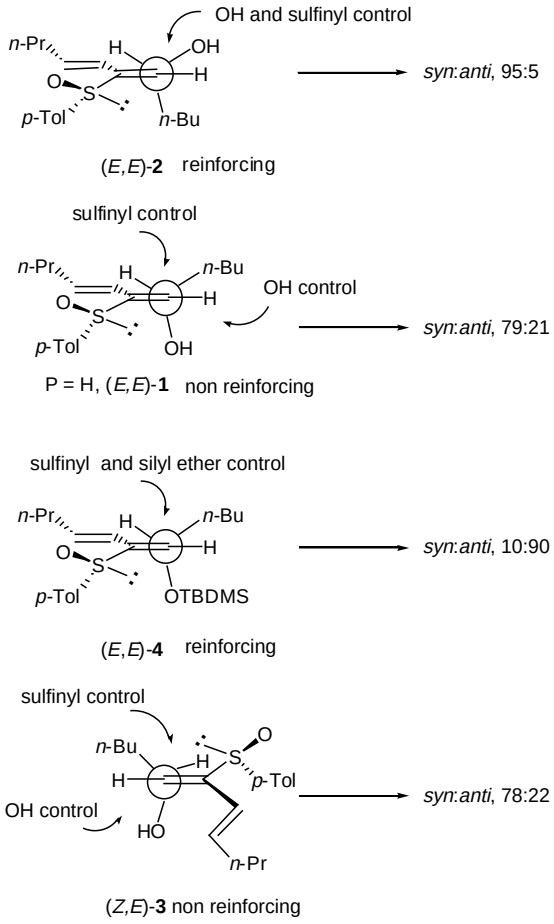
The behavior of dienyl sulfoxide **2** with opposite relative configuration at the stereocenters is parallel to **1**. Thus, nucleophilic epoxidation of **2** afforded after 70 min an 80:4:11:5 mixture of *syn* sulfinyl oxirane **15**, *syn* sulfonyl oxirane *ent*-**10** and bis-epoxides **11ab** (44:46) and **11c**. Stereochemical correlation between **15** and *ent*-**10** was easily provided by oxidation of **15** with MMPP to render *ent*-**10** in 59% yield. Taking into account the overall ratio of final epoxides, hydroxy dienyl sulfoxide **2** provides a 95:5 mixture of *syn* and *anti* epoxides[10] with a reinforcing combination of stereodirecting elements (hydroxyl and sulfinyl) while **1** provides a 79:21 *syn*:*anti* mixture with a non-reinforcing arrangement of the stereocenters.

As expected, protection of the hydroxyl group as silyl ether prevented the Payne rearrangement from taking place, however, a lower reactivity as well as a reversal of stereoselectivity was observed (entry 4). In fact, epoxidation of γ-silyloxy dienyl sulfoxide **4** was carried out with the more reactive KOO-*t*-Bu[3–5] affording a mixture of sulfonyl oxiranes **12** (10) and **14** (47) along with sulfinyl oxirane **13** (43). A chemical correlation between **13** and **14** was established by treatment of **13** with MMPP to give **14** in 74% yield. The inversion of the overall *syn*:*anti* ratio (10:90) compared with **1** (*syn*:*anti*, 79:29) is noteworthy.[11]

Finally, to assess the influence of the stereochemistry of the double bond, the nucleophilic epoxidation of (*Z*,*E*)-γ-hydroxy dienyl sulfoxide **3** was examined (Table 1, entry 7). The reaction mixture showed a mixture of *syn* sulfinyl and sulfonyl oxiranes **16** (72) and **17** (4) and again significant amounts of bis-epoxides *ent*-**11a**,**b** (2) and *ent*-**11c** (22) from the Payne rearrangement with an overall *syn*:*anti* ratio of 78:22. Further oxidation (MMPP) of **16** rendered **17** in 62% yield. At this point, we envisioned the protection of the free hydroxyl group to prevent the Payne process. However, the silylation of **3** was not a straightforward process due to the unstable nature of **5** and, surprisingly, γ-silyloxy dienyl sulfone **9** was unreactive under the nucleophilic epoxidation conditions examined. Therefore, we did not pursue any further the epoxidation of these (*Z*,*E*)-dienes.

The structural assignment of the epoxides was based mainly in their NMR data. The oxidation state at sulfur was determined by the slightly higher chemical shifts of *H-ortho* (*p*-TolS), *H* (epox) and *C* (arom)-S for sulfonyl oxiranes. The relative configuration of the sulfinyl and sulfonyl oxiranes was indirectly assessed through the cis/trans stereochemistry of bis epoxides (see Scheme 3): **11a**,**b** [$J^{1,3}$(*cis*-butyl oxirane)=4.8 Hz, *syn* epoxidation] and **11c** [$J^{1,3}$(*trans*-butyl oxirane)=1.9 Hz, *anti* epoxidation].

The stereochemical outcome of the nucleophilic epoxidation is primarily controlled by stereoelectronic effects and can be understood in terms of an initial nucleophilic attack of the metalated peroxide to the reactive conformers of the alkoxy dienes (Scheme 4). For (*E*,*E*)-dienyl sulfoxides **1** and **2**, an *s*-cis conformation for the unsaturated sulfoxide (Cα=Cβ/S-:),[12] along with an *s*-trans conformation for the dienyl



Scheme 4.

system would be probably adopted to minimize $A^{1,3}$ strain stronger than $A^{1,2}$ strain caused by the interaction between the sulfinyl and butenyl groups. Besides, in agreement with the observed coupling constant between allylic and vinylic protons for the dienes ($J=8$–9 Hz) the Cγ–H bond would be coplanar to the dienyl system with a dihedral angle of 180°.[13] In this context, the diastereofacial selectivity for each substrate (**1** and **2**) would be determined by the relative configuration of the two stereogenic centers, sulfoxide and hydroxyl group. A reinforcing scenario is working for **2** that produces a 95:5 mixture of epoxidation *syn* to the OH group, while a non reinforcing contribution of the sulfoxide diminishes the stronger stereodirecting ability of the hydroxyl group in **1** to provide a less selective epoxidation (*syn*:*anti*, 79:21). However, for this particular relative stereochemistry, the presence of a silyl ether (**4**) results in a reinforcing scenario and thus reverts the *syn*:*anti* outcome of the epoxidation (10:90).[11] Similarly, (*Z*,*E*)-dienyl sulfoxide **3** would adopt an *s*-cis reactive conformation for the dienyl system and the nucleophilic epoxidation would occur mainly *syn* (*syn*:*anti*, 78:22) to the hydroxyl group since a non reinforcing contribution of the stereodirecting elements is taking place.

In summary, we have demonstrated that (*E*,*E*) and (*Z*,*E*) γ-hydroxy dienyl sulfones undergo nucleophilic epoxidation with remarkable regio- and stereoselectivity to render *syn* epoxides in a process mainly controlled by the hydroxyl stereocenter. Upon epoxidation, γ-hydroxy dienyl sulfoxides provide sulfinyl and sulfonyl oxiranes, along with significant amounts of bis-epoxides probably formed through a Payne rearrangement that can be prevented by silylation of the OH group. In terms of stereochemistry, an additional stereocenter at sulfur implies a reinforcing/non-reinforcing scenario with the free hydroxyl group as the stronger *syn* stereodirecting element of the epoxidation. Interestingly, the presence of a γ-silyloxy group can invert the stereochemical outcome of the process affording mainly an *anti* epoxidation process.

3. Experimental

3.1. General procedures

Reagents and solvents were handled by using standard syringe techniques. Hexane, toluene, and CH_2Cl_2 were distilled from CaH_2, and Et_2O from sodium. DMF was dried over CaH_2 and filtered before distillation under reduced pressure. Then, it was collected over 4 Å molecular sieves and argon was bubbled through for 10 min before storing it. Et_3N was distilled from CaH_2. Crude products were purified by flash chromatography on Merck 230–400 mesh silica gel with distilled solvents. Analytical TLC was carried out on Merck (Kieselgel 60F-254) silica gel plates with detection by UV light, iodine, acidic vanillin solution, 10% phosphomolybdic acid solution in ethanol. All reagents were commercial products purchased from Aldrich, Acros, Fluka or Merck. Organolithium reagents were titrated by reaction with 3,4-dimethoxybenzaldehyde prior to use. NaH and KH (60% in mineral oil) were washed repeatedly with dry hexane and dried prior to use. Through this section, the volume of solvents is reported in mL/mmol of starting material. Infrared spectra (IR) were obtained on a Perkin-Elmer 681 and on a Perkin-Elmer Spectrum one. ^1H and ^{13}C NMR spectra were recorded on a Brüker AM-200 (200 MHz), Varian Gemini-200 (200 MHz), Varian INOVA-300 (300 MHz) and Varian INOVA-400 (400 MHz) using $CDCl_3$ as solvent and with the residual solvent signal as internal reference ($CDCl_3$, 7.24 and 77.0 ppm). The following abbreviations are used to describe peak patterns when appropriate: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad). Melting points were determined on a Reichert Kofler microscope and are uncorrected. Optical rotations were measured on a Perkin-Elmer 241 polarimeter at 20 °C using a sodium lamp and in $CHCl_3$ solution. Low resolution mass spectra were recorded by direct injection on a Hewlett Packard 5973 MSD instrument using the electronic impact technique with an ionization energy of 70 eV or on a Hewlett Packard 1100 MSD instrument using the atmospheric pressure chemical ionization (APCI) or electrospray (ES) chemical ionization techniques in its positive or negative modes. Elemental analyses were carried out on a Perkin-Elmer 240 C and on a Heraus CHN-O-Rapid instruments at Instituto de Química Orgánica, CSIC (Madrid).

3.2. General procedure for silylation of sulfinyl alcohols

(a) With *tert*-butyldimethylsilyl chloride: under an atmosphere of argon, 1.1 equiv of *tert*-butyldimethylsilyl chloride was added to a cold (0 °C) solution of the sulfinyl

alcohol and 1.2 equiv of imidazole in CH_2Cl_2 (10 mL/mmol) and the reaction mixture was allowed to warm up to rt and monitored by TLC. Upon completion the reaction was quenched with H_2O (1 mL/mmol), diluted with CH_2Cl_2 (10 mL/mmol) and the layers were separated. The aqueous phase was extracted with CH_2Cl_2 (three times, 10 mL/mmol) and the combined organic extracts were washed with a saturated solution of NaCl (4 mL/mmol), dried over $MgSO_4$, filtered and concentrated under reduced pressure to give a crude product that was purified by column chromatography on silica gel using a gradient of the appropriate solvents. (b) With *tert*-butyldimethylsilyl triflate: under an atmosphere of argon, 2.0 equiv of freshly distilled *tert*-butyldimethylsilyl triflate was added to a cold (0 °C) solution of the sulfinyl alcohol, 2 equiv of Et_3N and 2–3 crystals of DMAP in THF (7 mL/mmol) and the reaction mixture was allowed to warm up to rt and monitored by TLC. Upon completion 3 equiv of Et_3N was added and the reaction was quenched with a saturated solution of $NaHCO_3$ (4 mL/mmol) and H_2O (4 mL/mmol), diluted with EtOAc (10 mL/mmol) and the layers were separated. The aqueous phase was extracted with EtOAc (three times, 10 mL/mmol) and the combined organic extracts were washed with a saturated solution of NaCl (4 mL/mmol), dried over $MgSO_4$, filtered and concentrated under reduced pressure to give a crude product that was purified by column chromatography on silica gel using a gradient of the appropriate solvents.

3.2.1. Synthesis of *tert*-butyldimethylsilyl ether of (+)-(5*R*,S_S)-(6*E*,8*E*)-7-(*p*-tolylsulfinyl)-6,8-dodecadien-5-ol, 4. From hydroxy dienyl sulfoxide **1** (15.8 mg, 0.049 mmol) in CH_2Cl_2 (0.50 mL), imidazole (4 mg, 0.06 mmol), *tert*-butyldimethylsilyl chloride (8.4 mg, 0.05 mmol) according to the general procedure (95 min), after chromatography (5–50% Et_2O–hexane), 16.8 mg (79%) of silylated diene **4** was obtained as a colorless oil. Data for **4**: R_f=0.37 (30% EtOAc–hexane). $[\alpha]_D^{20}$ +81.1 (*c* 0.90). ^{1}H NMR (300 MHz) δ −0.05 (s, 3H, TBDMS), −0.02 (s, 3H, TBDMS), 0.77 (t, 3H, *J*=7.4 Hz), 0.83–0.85 (m, 3H), 0.84 (s, 9H, TBDMS), 1.21–1.36 (m, 6H), 1.45–1.62 (m, 2H), 1.99 (m, 2H), 2.35 (s, 3H, CH_3–*p*-Tol), 4.46 (ddd, 1H, *J*=8.7, 7.2, 5.5 Hz, H-5), 5.83 (m, 2H, H-8, H-9), 6.32 (d, 1H, *J*=8.7 Hz, H-6), 7.21 (dd, 2H, *J*=8.5, 0.6 Hz, ArH), 7.45 (d, 2H, *J*=8.3 Hz, ArH). ^{13}C NMR (50 MHz) δ −4.8, −4.3, 13.4, 14.0, 18.1, 21.4, 22.1, 22.6, 25.8 (3C), 27.3, 35.5, 37.7, 69.2, 119.5, 125.5 (2C), 129.6 (2C), 135.5, 138.6, 140.6, 141.4. IR (CCl_4): 2920, 2900, 2820, 1620, 1570, 1480, 1440, 1240, 1060, 1030, 990, 820, 790 cm^{-1}. Anal. Calcd for $C_{25}H_{42}O_2SSi$: C, 69.07; H, 9.74; S, 7.38. Found: C, 69.13; H, 9.55; S, 7.23.

3.2.2. Synthesis of *tert*-butyldimethylsilyl ether of (−)-(5*S*,S_S)-(6*Z*,8*E*)-7-(*p*-tolylsulfinyl)-6,8-dodecadien-5-ol, 5, *tert*-butyldimethylsilyl ether of (5*S*,S_S)-(6*E*,8*E*)-7-(*p*-tolylsulfinyl)-6,8-dodecadien-5-ol, 5′, and *tert*-butyldimethylsilyl ether of (5*S*,R_S)-(6*E*,8*E*)-7-(*p*-tolylsulfinyl)-6,8-dodecadien-5-ol, *ent*-4. Three different procedures (a), (b), and (c) were employed for the synthesis of **5**. (a) From hydroxy dienyl sulfoxide **3** (25.5 mg, 0.08 mmol) in CH_2Cl_2 (1.0 mL), imidazole (6.5 mg, 0.10 mmol), *tert*-butyldimethylsilyl chloride (13.6 mg, 0.09 mmol) according to the general procedure (27 h), after chromatography (5–50% EtOAc–hexane), 11.6 mg (34%) of an inseparable mixture (20:80) of silylated dienes **5′** and *ent*-**4** was obtained as a colorless oil. (b) From hydroxy dienyl sulfoxide **3** (14.3 mg, 0.044 mmol) in DMF (1.0 mL), Et_3N (9 mg, 12 μL, 0.089 mmol), 2 crystals of DMAP, *tert*-butyldimethylsilyl triflate (18.1 mg, 16 μL, 0.067 mmol) according to the general procedure (3 h, two additions of reagents in the above amounts), after chromatography (5–30% EtOAc–hexane), 5.9 mg (32%) of diene **5** was obtained as a colorless oil, rather unstable in silica gel, and 7.4 mg (52%) of starting material was obtained. (c) From hydroxy dienyl sulfoxide **3** (24.5 mg, 0.07 mmol) in THF (0.53 mL), Et_3N (15.2 mg, 21 μL, 0.15 mmol), 2 crystals of DMAP, *tert*-butyldimethylsilyl triflate (26 μL, 29.9 mg, 0.11 mmol) according to the general procedure (6 h 20 min, four additions of reagents in the above amounts), after chromatography (5–30% EtOAc–hexane), 15 mg (49%) of a 32:68 inseparable mixture of **5′** and *ent*-**4** was obtained. Data for **5**: R_f=0.42 (20% EtOAc–hexane). $[\alpha]_D^{20}$ −82.0 (*c* 0.68). ^{1}H NMR (300 MHz) δ 0.03 (s, 3H, TBDMS), 0.07 (s, 3H, TBDMS), 0.73 (t, 3H, *J*=7.4 Hz), 0.88 (t, 3H, *J*=5.9 Hz), 0.89 (s, 9H, TBDMS), 1.19–1.70 (m, 8H), 1.94 (q, 2H, *J*=6.7 Hz), 2.37 (s, 3H, CH_3–*p*-Tol), 5.07 (q, 1H, *J*=6.7 Hz, H-5), 5.74 (d, 1H, *J*=15.7 Hz, H-8), 5.95 (dt, 1H, *J*=15.7, 6.6 Hz, H-9), 6.08 (d, 1H, *J*=8.7 Hz, H-6), 7.25 (d, 2H, *J*=8.5 Hz, ArH), 7.44 (d, 2H, *J*=8.2 Hz, ArH). ^{13}C NMR (50 MHz) δ −4.2, −4.1, 13.4, 14.0, 19.1, 21.3, 22.6, 25.8 (3C), 27.1, 29.7, 35.0, 38.4, 69.0, 121.1, 124.7 (2C), 129.6 (2C), 136.9, 139.5, 140.5, 140.6, 141.4. IR (CCl_4): 2930, 2900, 2820, 1720, 1480, 1450, 1240, 1060, 1030, 1000, 780 cm^{-1}. MS (APCI): 425 [M+Na]$^-$, 171 (100%). Data for **5′** from a 38:68 mixture of **5′** and *ent*-**4**: R_f=0.40 (20% EtOAc–hexane). ^{1}H NMR (200 MHz) δ −0.06 (s, 3H, TBDMS), −0.03 (s, 3H, TBDMS), 0.75–0.92 (m, 6H, 2 CH_3), 0.82 (s, 9H, TBDMS), 1.16–1.36 (m, 6H), 1.40–1.61 (m, 2H), 1.98 (m, 2H), 2.36 (s, 3H, CH_3–*p*-Tol), 4.48 (m, 1H, H-5), 5.84 (m, 2H, H-8 and H-9), 6.31 (d, 1H, *J*=8.4 Hz, H-6), 7.21 (d, 2H, *J*=8.1 Hz, ArH), 7.47 (d, 2H, *J*=8.2 Hz, ArH). The data of *ent*-**4** was identical to its enantiomer.

3.2.3. Synthesis of *tert*-butyldimethylsilyl ether of (+)-(5*R*)-(6*E*,8*E*)-7-(*p*-tolylsulfonyl)-6,8-dodecadien-5-ol, 8. From hydroxy dienyl sulfone **6** (29.3 mg, 0.087 mmol) in THF (0.61 mL), Et_3N (26.3 mg, 36 μL), 2 crystals of DMAP, *tert*-butyldimethylsilyl triflate (34.5 mg, 30 μL, 0.130 mmol) according to the general procedure (23 min), after chromatography (5–50% EtOAc–hexane), 35.6 mg (98%) of **8** was obtained as a pale yellow oil. Data for **8**: R_f=0.43 (20% EtOAc–hexane). $[\alpha]_D^{20}$ +24.1 (*c* 0.85). ^{1}H NMR (300 MHz) δ −0.07 (s, 3H, TBDMS), −0.04 (s, 3H, TBDMS), 0.80 (t, 3H, *J*=7.3 Hz), 0.84 (s, 9H, TBDMS), 0.86 (t, 3H, *J*=7.0 Hz), 1.22–1.44 (m, 6H), 1.54–1.61 (m, 2H), 2.02 (q, 2H, *J*=6.9 Hz), 2.40 (s, 3H, CH_3–*p*-Tol), 4.38 (m, 1H, H-5), 5.81 (d, 1H, *J*=16.1 Hz, H-8), 5.87 (dt, *J*=15.9, 6.1 Hz, H-9), 6.74 (d, 1H, *J*=8.6 Hz, H-6), 7.26 (d, 2H, *J*=7.9 Hz, ArH), 7.66 (d, 2H, *J*=8.2 Hz, ArH). ^{13}C NMR (75 MHz) δ −4.9, −4.3, 13.5, 14.0, 18.1, 21.6, 22.0, 22.5, 25.7 (3C), 27.2, 35.4, 37.1, 69.0, 118.2, 128.2 (2C), 129.5 (2C), 136.8, 138.5, 141.2, 143.0, 144.0. IR (CCl_4): 2910, 2820, 1630, 1580, 1470, 1440, 1390, 1300, 1240, 1150, 1070, 920, 650 cm^{-1}. Anal. Calcd for $C_{25}H_{42}O_3SSi$: C, 66.62; H, 9.39; S, 7.11. Found: C, 66.74; H, 9.59; S, 7.03.

3.3. General procedure for oxidation of sulfoxides with MMPP

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

3.3.1. Synthesis of *tert*-butyldimethylsilyl ether of (+)-(5*S*)-(6*Z*,8*E*)-7-(*p*-tolylsulfonyl)-6,8-dodecadien-5-ol, 9. From sulfinyl diene **5** (10.5 mg, 0.026 mmol) in MeOH (0.30 mL) and MMPP (64.3 mg, 0.104 mmol), according to the general procedure (24 h), after chromatography (2–15% EtOAc–hexane), dienyl sulfone **9** (7 mg, 64%) was obtained as a colorless oil. Data for **9**: R_f=0.30 (2×15% EtOAc–exane). ^{1}H NMR (300 MHz) δ −0.06 (s, 3H, TBDMS), 0.04 (s, 3H, TBDMS), 0.81 (t, 3H, J=7.3 Hz), 0.85 (s, 9H, TBDMS), 0.88 (t, 3H, J=5.9 Hz), 1.24–1.38 (m, 8H, 4CH_2), 2.01 (qd, 2H, J=7.3, 1.5 Hz, H-4), 2.40 (s, 3H, CH3–*p*-Tol), 5.31 (dt, 1H, J=7.9, 3.8 Hz, H-5), 5.77 (dt, 1H, J=15.5, 7.0 Hz, H-9), 6.06 (d, 1H, J=8.1 Hz, H-6), 6.05 (d, 1H, J=15.0 Hz, H-8), 7.28 (d, 2H, J=8.5 Hz, ArH), 7.70 (d, 2H, J=8.3 Hz, ArH). ^{13}C NMR (50 MHz) δ −4.8, −4.4, 13.5, 14.0, 18.1, 21.6, 22.0, 22.6, 25.8 (3C), 27.4, 34.8, 37.7, 68.3, 124.3, 127.7 (2C), 129.5 (2C), 134.0, 137.0, 137.6, 144.2, 144.7.

3.4. General procedure for nucleophilic epoxidation of dienyl sulfoxides and sulfones

A two-necked round-bottomed flask fitted with a tube in T for entrance and exit of argon and a polyethylene stopper, was charged with anhydrous THF (5 mL/mmol) and 2–4 equiv of oil free NaH or KH (washed with hexane and dried), the mixture was cooled to 0 °C and then 2–4 equiv of *t*-BuOOH (80% in *t*-BuOO-*t*-Bu) was added. After stirring at rt for 20–30 min, the resulting solution was cooled to 0 °C and a solution of 1 equiv of the corresponding dienyl sulfoxide or sulfone in THF (7 mL/mmol), previously dried over 4 Å sieves, was added dropwise. The reaction mixture was stirred at 0 °C until starting material disappearance, monitored by TLC. Subsequently, a 10% solution of $Na_2S_2O_4$ (4 mL/mmol) and EtOAc (8 mL/mmol) was added. After separation, the aqueous layer was extracted with EtOAc (3×10 mL/mmol). The combined organic extracts were washed with brine and dried with anhydrous $MgSO_4$. Filtration and evaporation of the solvent under reduced pressure provided a crude product that was purified by column chromatography on silica gel.

3.4.1. Synthesis of (−)-(2*S*,3*S*,1′*R*)-(*E*)-3-(1′-hydroxypentyl)-2-(1-pentenyl)-2-(*p*-tolylsulfonyl)oxirane, 10. From NaH (7 mg, 0.31 mmol) in THF (1.50 mL), *t*-BuOOH (40 μL, 35.1 mg, 0.31 mmol) and a solution of dienyl sulfone **6** (26.2 mg, 0.078 mmol) in THF (0.50 mL), according to the general procedure (0 °C, 105 min), hydroxy sulfonyl oxirane **10** was obtained. Purification by chromatography (5–30% EtOAc–hexane) gave 24.5 mg (89%) of **10** as a colorless oil. Data for **10**: R_f=0.34 (30% EtOAc–hexane). $[\alpha]_D^{20}$ −43.5 (*c* 1.01). ^{1}H NMR (300 MHz) δ 0.75 (t, 3H, J=7.3 Hz), 0.88 (t, 3H, J=7.3 Hz), 1.20–1.32 (m, 6H), 1.46–1.70 (m, 2H), 1.92 (br s, 1H, OH), 1.96 (ap q, 2H, J=6.6 Hz), 2.42 (s, 3H, CH_3–*p*-Tol), 3.28 (dt, 1H, J=8.0, 5.6 Hz, H-1′), 3.81 (d, 1H, J=8.2 Hz, H-3), 5.65 (dt, 1H, J=15.6, 6.7 Hz, H-2″), 5.79 (dt, 1H, J=15.5, 1.2 Hz, H-1″), 7.30 (dd, 2H, J=8.5, 0.6 Hz, ArH), 7.68 (dd, 2H, J=8.4, 1.9 Hz, ArH). ^{13}C NMR (75 MHz) δ 13.4, 13.8, 21.7 (2C), 22.5, 26.8, 33.0, 34.2, 65.1, 69.6, 76.0, 116.3, 129.4 (2C), 129.6 (2C), 132.4, 141.3, 145.3. IR (CCl_4): 3460, 2920, 2900, 2840, 1640, 1580, 1450, 1240, 1170, 640 cm^{-1}. MS (APCI): 353 $[M+1]^+$, 197 (100%). Anal. Calcd for $C_{19}H_{28}O_4S$: C, 64.74; H, 8.01; S, 9.10. Found: C, 64.55; H, 8.22; S, 9.09.

3.4.2. Synthesis of (2*S*,3*S*,1′*R*)-(*E*)-3-[1′-(*tert*-butyldimethylsilyloxy)-*n*-pentyl]-2-(1-pentenyl)-2-(*p*-tolylsulfonyl)oxirane, 12, and (2*R*,3*R*,1′*R*)-(*E*)-3-[1′-(*tert*-butyldimethylsilyloxy)-*n*-pentyl]-2-(1-pentenyl)-2-(*p*-tolylsulfonyl)oxirane, 14. From NaH (6.4 mg, 0.26 mmol) in THF (1.30 mL), *t*-BuOOH (33 μL, 30 mg, 0.26 mmol) and a solution of dienyl sulfone **8** (27.8 mg, 0.066 mmol) in THF (0.46 mL), according to the general procedure (4 days, 6 h), a 44:51:5 mixture of sulfonyl oxiranes **12** and **14** and starting material was obtained. Purification by chromatography (5–30% EtOAc–hexane) gave 22.3 mg (75%) of an inseparable mixture of **12** and **14** as a colorless oil, and 2 mg (5%) of starting material. Spectral data measured for **12** and **14** was identical to those described below.

3.4.3. Synthesis of (−)-(2*S*,3*S*,1′*R*,S_S)-(*E*)-3-(1′-hydroxypentyl)-2-(pentenyl)-2-(*p*-tolylsulfinyl)oxirane, 10′, (−)-(2*S*,3*S*,1′*R*)-(*E*)-3-(1′-hydroxypentyl)-2-(1-pentenyl)-2-(*p*-tolylsulfonyl)oxirane, 10, (7*R*,8*R*)-6-oxadodecanyl-4,7-bis-oxirane, 11c, (7*S*,8*R*)-6-oxadodecanyl-4,7-bis-oxirane, 11a,b. From NaH (7.8 mg, 0.32 mmol) in THF (1.60 mL), *t*-BuOOH (41 μL, 37 mg, 0.32 mmol) and a solution of dienyl sulfoxide **1** (26 mg, 0.081 mmol) in THF (0.56 mL), according to the general procedure (1 h), a 46:9:18:9:18 mixture of **10′**, **11c**, **11a**,**b**, **10** and **1** was obtained (^{1}H NMR of an aliquot). After 2 h (total reaction time), a 26:10:38:16:10 mixture of **10′**, **11c**, **11a**,**b**, **10** and **1** was obtained. Purification by chromatography (5–50% EtOAc–hexane) gave 4.25 mg (25%) of bis oxiranes **11c** and **11a**,**b**, 3.25 mg (11%) of sulfonyl oxirane **10**, 4.15 mg (21%) of sulfinyl oxirane **10′** and 3.7 mg (7%) of starting material as colorless oils. Alternatively, from NaH (13.5 mg, 0.40 mmol) in THF (2.15 mL), *t*-BuOOH (55 μL, 50 mg, 0.40 mmol) and a solution of dienyl sulfoxide **1** (35.2 mg, 0.11 mmol) in THF (0.76 mL), according to the general procedure (3 h) a 21:52:27 mixture of bis oxiranes **11c** and **11a**,**b** and sulfonyl oxirane **10** was obtained. Purification by chromatography (5–50% Et_2O–hexane) gave 4 mg (18%) of **11c** and 10 mg (44%) of **11a**,**b**. Data for **10′**: R_f=0.21 (2×30% EtOAc–hexane). $[\alpha]_D^{20}$ −17.9 (*c* 0.41). ^{1}H NMR (300 MHz) δ 0.78 (t, 3H, J=7.4 Hz), 0.83 (t, 3H, J=7.1 Hz), 1.16–1.59 (m, 9H), 1.96 (qd, 2H, J=7.1, 1.5 Hz),

2.40 (s, 3H, CH_3–*p*-Tol), 3.33 (dt, 1H, J=7.9, 5.4 Hz, H-1′), 3.67 (d, 1H, J=8.0 Hz, H-3), 5.43 (dt, 1H, J=15.6, 1.5 Hz, H-1″), 5.72 (dt, 1H, J=15.6, 6.8 Hz, H-2″), 7.28 (d, 2H, J=7.8 Hz, ArH), 7.46 (d, 2H, J=8.3 Hz, ArH). ^{13}C NMR (75 MHz) δ 13.5, 13.8, 21.5, 21.8, 22.5, 26.8, 33.0, 34.5, 64.6, 69.8, 76.5, 115.1, 125.4 (2C), 129.5 (2C), 136.7, 141.4, 142.2. IR (CCl_4): 3360, 2920, 2900, 2820, 1630, 1470, 1440, 1240, 1070, 1000, 770 cm^{-1}. Data for **11a**,**b** (as an inseparable 44:56 mixture of diastereomers): R_f=0.46 (50% Et_2O–hexane). ^{1}H NMR (400 MHz) δ 0.88 (t, 3H, J=7.3 Hz, CH_3), 0.92–1.0 (m, 9H, CH_3), 1.23–1.70 (m, 20H), 3.08 (td, 1H, J=5.9, 1.9 Hz), 3.20–3.26 (m, 3H), 3.39 (d, 1H, J=1.9 Hz, CH–CO), 3.47 (d, 1H, J=1.9 Hz, CH–CO), 3.58 (d, 1H, J=4.8 Hz, CH–CO), 3.77 (d, 1H, J=4.8 Hz, CH–CO). ^{13}C NMR (125 MHz) δ 13.7, 13.9, 19.1, 19.7, 22.3, 22.4, 26.7, 27.2, 27.8, 28.3, 28.4, 31.4, 31.5, 33.6, 33.7, 56.0, 56.4, 58.6, 58.7, 59.1, 59.3, 59.4, 211.7. IR (CCl_4): 2960, 2930, 2875, 1720, 1460, 1430, 1380, 1230, 1190, 1090, 1050, 1020, 880 cm^{-1}. MS (EI): 212 [M]$^+$, 169, 127, 97, 71, 55 (100%), 43, 41. Data for **11c**: R_f=0.52 (50% Et_2O–hexane). ^{1}H NMR (400 MHz) δ 0.90 (t, 3H, J=7.2 Hz), 0.96 (t, 3H, J=7.2 Hz), 1.34–1.66 (m, 10H), 3.07 (tt, 1H, J=5.6, 1.7 Hz), 3.16 (td, 1H, J=5.6, 1.7 Hz), 3.30 (d, 1H, J=1.9 Hz, CH–CO), 3.42 (d, 1H, J=2.1 Hz, CH–CO). ^{13}C NMR (50 MHz) δ 13.7, 13.9, 19.1, 22.3, 27.8, 31.5, 33.8, 56.8, 57.2, 57.3, 59.2, 211.7. IR (CCl_4): 2960, 2930, 2875, 1720, 1460, 1430, 1380, 1230, 1190, 1090, 1050, 1020, 880 cm^{-1}. MS (EI): 127, 97, 71, 55 (100%), 43, 41, 39. The data of **10** was identical to that found before.

3.4.4. Synthesis of (+)-(2*R*,3*R*,1′*S*,S_S)-(*E*)-3-(1′-hydroxypentyl)-2-(1-pentenyl)-2-(*p*-tolylsulfinyl)oxirane, 15, (+)-(2*R*,3*R*,1′*S*)-(*E*)-3-(1′-hydroxypentyl)-2-(1-pentenyl)-2-(*p*-tolylsulfonyl)oxirane *ent*-10, (7*R*,8*S*)-6-oxadodecanyl-4,7-bis-oxirane, *ent*-11a,b, (7*S*,8*S*)-6-oxado- decanyl-4,7-bis-oxirane, *ent*-11c. From NaH (2.2 mg, 0.094 mmol) in THF (0.47), *t*-BuOOH (12 μL, 11 mg, 0.094 mmol) and a solution of dienyl sulfoxide **2** (7.5 mg, 0.023 mmol) in THF (0.16 mL), according to the general procedure (70 min), an 80:4:11:5 of sulfinyl oxirane **15**, sulfonyl oxirane *ent*-**10**, and bis oxiranes *ent*-**11a**,**b** and *ent*-**11c**, was obtained. Purification by chromatography (5–50% EtOAc–hexane) gave 5.4 mg (76%) of **15**, 0.3 mg (4%) of *ent*-**10** and 0.5 mg (13%) of *ent*-**11c** and *ent*-**11a**,**b** as colorless oils. Data for **15**: R_f=0.25 (50% EtOAc–hexane). $[\alpha]_D^{20}$ +48.9 (*c* 0.60). ^{1}H NMR (300 MHz) δ 0.80 (t, 3H, J=7.4 Hz), 0.87 (t, 3H, J=7.2 Hz), 1.20–1.39 (m, 6H), 1.36–1.62 (m, 2H), 1.81 (d, 1H, J=2.4 Hz, OH), 1.99 (qd, 2H, J=7.0, 1.5 Hz), 2.39 (s, 3H, CH_3–*p*-Tol), 3.35 (m, 1H, H-1′), 3.61 (d, 1H, J=8.1 Hz, H-3), 5.40 (dt, 1H, J=15.7, 1.5 Hz, H-1″), 5.67 (dt, 1H, J=15.7, 6.8 Hz, H-2″), 7.26 (d, 2H, J=7.9 Hz, ArH), 7.46 (d, 2H, J=8.2 Hz, ArH). ^{13}C NMR (50 MHz) δ 13.5, 13.8, 21.5, 21.8, 22.5, 26.9, 33.0, 34.5, 64.5, 69.8, 78.8, 117.4, 126.1 (2C), 129.3 (2C), 135.6, 141.1, 142.3. IR (CCl_4): 3350, 2920, 2890, 2820, 2840, 1730, 1540, 1470, 1450, 1380, 1240, 1070, 1000, 770, 640 cm^{-1}. Anal. Calcd for $C_{19}H_{28}O_3S$: C, 67.82; H, 8.39; S, 9.53. Found: C, 67.65; H, 8.42; S, 9.44. The data for *ent*-**10**, *ent*-**11c** and *ent*-**11a**,**b** was identical to that of their enantiomers.

3.4.5. Synthesis of (+)-(2*R*,3*R*,1′*R*,S_S)-(*E*)-3-[1′-(*tert*-butyldimethylsilyloxy)-*n*-pentyl]-2-(1-pentenyl)-2-(*p*-tolylsulfinyl)oxirane, 13, (2*S*,3*S*,1′*R*)-(*E*)-3-[1′-(*tert*-butyldimethylsilyloxy)-*n*-pentyl]-2-(1-pentenyl)-2-(*p*-tolylsulfonyl)oxirane, 12, (+)-(2*R*,3*R*,1′*R*)-(*E*)-3-[1′-(*tert*-butyldimethylsilyloxy)-*n*-pentyl]-2-(1-pentenyl)-2-(*p*-tolylsulfonyl)oxirane, 14. From KH (10.7 mg, 0.26 mmol) in THF (1.30 mL), *t*-BuOOH (33 μL, 30 mg, 0.26 mmol) and a solution of dienyl sulfoxide **4** (29 mg, 0.06 mmol) in THF (0.46 mL), according to the general procedure (94 h), a 9:41:37:12 of sulfonyl oxiranes **12** and **14**, sulfinyl oxirane **13** and starting material was obtained. Purification by chromatography (5–15% EtOAc–CH_2Cl_2) gave 11.3 mg (38%) of **13**, 14 mg (44%) of an 82:18 inseparable mixture of **14** and **12** and 3.1 mg (11%) of starting material, as colorless oils. Data for **13**: R_f=0.45 (2×15% EtOAc–hexane). $[\alpha]_D^{20}$ +80.1 (*c* 1.11). ^{1}H NMR (300 MHz) δ −0.06 (s, 3H, TBDMS), −0.02 (s, 3H, TBDMS), 0.79 (t, 3H, J=7.4 Hz), 0.85 (s, 9H, TBDMS), 0.87 (t, 3H, J=7.2 Hz), 1.24–1.51 (m, 8H), 2.00 (q, 2H, J=6.8 Hz), 2.37 (s, 3H, CH_3–*p*-Tol), 3.36 (dt, 1H, J=8.0, 5.6 Hz, H-1′), 3.60 (d, 1H, J=7.9 Hz, H-3), 5.48 (d, 1H, J=15.5 Hz, H-1″), 5.60 (dt, 1H, J=15.5, 6.3 Hz, H-2″), 7.24 (d, 2H, J=7.9 Hz, ArH), 7.47 (d, 2H, J=8.2 Hz, ArH). ^{13}C NMR (75 MHz) δ −4.4, −4.2, 13.6, 14.0, 18.0, 21.5, 21.9, 22.7, 25.7 (3C), 26.3, 34.5, 35.1, 63.8, 68.2, 78.5, 117.1, 125.9 (2C), 129.3 (2C), 136.1, 140.7, 142.0. IR (CCl_4): 2920, 2900, 2820, 1530, 1440, 1240, 1060, 990, 770 cm^{-1}. Data for **12**: R_f=0.48 (15% EtOAc–hexane). ^{1}H NMR (300 MHz) δ −0.04 (s, 3H, TBDMS), 0.05 (s, 3H, TBDMS), 0.76 (t, 3H, J=7.3 Hz), 0.80–0.90 (m, 3H), 0.86 (s, 9H, TBDMS), 1.23–1.60 (m, 8H), 1.96 (q, 2H, J=6.3 Hz), 2.42 (s, 3H, CH_3–*p*-Tol), 3.22 (dt, 1H, J=8.1, 4.9 Hz, H-1′), 3.77 (d, 1H, J=8.2 Hz, H-3), 5.65 (dt, 1H, J=15.5, 7.0 Hz, H-2″), 5.82 (d, 1H, J=15.5 Hz, H-1″), 7.29 (d, 2H, J=8.4 Hz, ArH), 7.68 (d, 2H, J=8.4 Hz, ArH). Data for **14**: R_f=0.37 (15% EtOAc–hexane). $[\alpha]_D^{20}$ +6.6 (*c* 0.83). ^{1}H NMR (300 MHz) δ −0.02 (s, 3H, TBDMS), 0.03 (s, 3H, TBDMS), 0.76 (t, 3H, J=7.3 Hz), 0.80–0.90 (m, 3H), 0.86 (s, 9H, TBDMS), 1.22–1.39 (m, 6H), 1.52–1.56 (m, 2H), 1.99 (m, 2H), 2.41 (s, 3H, CH_3–*p*-Tol), 3.30 (ddd, 1H, J=7.9, 6.1, 5.3 Hz, H-1′), 3.82 (d, 1H, J=7.9 Hz, H-3), 5.55 (dt, 1H, J=15.5, 7.0 Hz, H-2″), 5.93 (dt, 1H, J=15.5, 1.5 Hz, H-1″), 7.29 (d, 2H, J=8.7 Hz, ArH), 7.69 (d, 2H, J=8.3 Hz, ArH). ^{13}C NMR (75 MHz) δ −4.5, −4.1, 13.5, 14.0, 21.7, 21.8, 22.6, 25.7 (3C), 26.4, 29.7, 34.2, 35.1, 65.1, 67.6, 76.6, 116.5, 129.4 (2C), 129.5 (2C), 132.9, 140.8, 145.5. IR (CCl_4): 2920, 2890, 2820, 1440, 1310, 1240, 1130, 1070, 1000, 640 cm^{-1}. MS (APCI): 489 [M+Na]$^-$, 244 (100%).

3.4.6. Synthesis of (−)-(2*S*,3*R*,1′*S*)-(*E*)-3-(1′-hydroxypentyl)-2-(1-pentenyl)-2-(*p*-tolylsulfonyl)oxirane, 17. From NaH (3.7 mg, 0.15 mmol) in THF (0.80 mL), *t*-BuOOH (19 μL, 17 mg, 0.15 mmol) and a solution of dienyl sulfone **7** (13 mg, 0.038 mmol) in THF (0.26 mL), according to the general procedure (55 min), sulfonyl oxirane **17** was obtained. Purification by chromatography (5–50% Et_2O–hexane) gave 11 mg (82%) of **17**, as a colorless oil. Data for **17**: R_f=0.28 (50% Et_2O–hexane). $[\alpha]_D^{20}$ −39.2 (*c* 0.76). ^{1}H NMR (300 MHz) δ 0.68 (t, 3H, J=7.4 Hz), 0.92 (t, 3H, J=7.3 Hz), 1.18 (sext, 2H, J=7.3 Hz), 1.34–1.54 (m, 4H), 1.65–1.69 (m, 2H), 1.81–1.90 (m, 2H),

2.32 (d, 1H, J=3.6 Hz, OH), 2.42 (s, 3H, CH_3–p-Tol), 3.04 (d, 1H, J=7.8 Hz, H-3), 4.62 (m, 1H, H-1′), 5.59 (dt, 1H, J=15.5, 6.6 Hz, H-2″), 5.73 (dt, 1H, J=15.5, 1.2 Hz, H-1″), 7.31 (d, 2H, J=7.9 Hz, ArH), 7.71 (d, 2H, J=8.3 Hz, ArH). ^{13}C NMR (75 MHz) δ 13.3, 14.0, 21.5, 21.7, 22.5, 27.0, 33.6, 33.8, 67.7, 73.1, 76.8, 120.5, 129.1 (2C), 129.5 (2C), 134.4, 138.1, 145.2. IR (CCl_4): 3500, 2920, 2900, 2830, 1640, 1580, 1450, 1310, 1240, 1150, 1060, 990, 780, 660 cm^{-1}. Anal. Calcd for $C_{19}H_{28}O_4S$: C, 64.74; H, 8.01; S, 9.10. Found: C, 64.66; H, 8.25; S, 9.01.

3.4.7. Synthesis of (+)-(2*S*,3*R*,1′*S*,S_S)-(*E*)-3-(1′-hydroxypentyl)-2-(1-pentenyl)-2-(*p*-tolylsulfinyl)oxirane, 16, (−)-(2*S*,3*R*,1′*S*)-(*E*)-3-(1′-hydroxypentyl)-2-(1-pentenyl)-2-(*p*-tolylsulfonyl)oxirane, 17, (7*S*,8*S*)-6-oxadodecanyl-4,7-bis-oxirane, *ent*-11c, (7*R*,8*S*)-6-oxadodecanyl-4,7-bis-oxirane, *ent*-11a,b. From NaH (9.9 mg, 0.41 mmol) in THF (2.0 mL), *t*-BuOOH (51 μL, 46 mg, 0.41 mmol) and a solution of dienyl sulfoxide **3** (33 mg, 0.102 mmol) in THF (0.71 mL), according to the general procedure (45 min) a 65:4:18:2:11 mixture of **16**, **17**, *ent*-**11c**, *ent*-**11a**,**b** and **3** was obtained. Purification by chromatography (5–50% Et_2O–hexane, then 5–20% EtOAc–toluene) gave 14.8 mg (44%) of sulfinyl oxirane **16**, 1 mg (3%) of sulfonyl oxirane **17**, 3 mg (14%) of bis oxiranes *ent*-**11c** and *ent*-**11a**,**b** and 3 mg (10%) of starting material, as colorless oils. Data for **16**: R_f=0.30 (2×30% EtOAc–hexane). $[\alpha]_D^{20}$ +7.3 (*c* 1.17). ^{1}H NMR (300 MHz) δ 0.71 (t, 3H, J=7.4 Hz), 0.94 (t, 3H, J=7.3 Hz), 1.21 (sext, 2H, J=7.4 Hz), 1.40–1.84 (m, 6H), 1.90 (q, 2H, J=7.0 Hz), 2.10 (br s, 1H, OH), 2.38 (s, 3H, CH_3–p-Tol), 3.13 (d, 1H, J=8.2 Hz, H-3), 4.16 (dt, 1H, J=8.0, 5.5 Hz, H-1′), 5.51 (dt, 1H, J=15.5, 6.8 Hz, H-2″), 5.74 (dt, 1H, J=15.6, 1.5 Hz, H-1″), 7.27 (d, 2H, J=7.9 Hz, ArH), 7.46 (d, 2H, J=8.3 Hz, ArH). ^{13}C NMR (75 MHz) δ 13.4, 13.9, 21.4, 21.7, 22.6, 27.0, 33.3, 34.1, 69.9, 71.2, 76.4, 116.6, 125.1 (2C), 129.4 (2C), 136.1, 138.6, 141.8. IR (CCl_4): 3360, 2930, 2900, 2840, 1720, 1640, 1580, 1470, 1450, 1360, 1240, 1060, 1020, 990, 770 cm^{-1}. Anal. Calcd for $C_{19}H_{28}O_3S$: C, 67.82; H, 8.39; S, 9.53. Found: C, 67.98; H, 8.56; S, 9.71. The data for **17**, *ent*-**11c**, and *ent*-**11a**,**b** was identical to those found before.

3.4.8. Synthesis of (2*S*,3*S*,1′*R*)-(*E*)-3-[(1′-*t*-butyldimethylsilyloxy)-*n*-pentyl]-2-(1-pentenyl)-2-(*p*-tolylsulfonyl)-oxirane, 12. From hydroxy sulfonyl oxirane **10** (12.4 mg, 0.03 mmol) in CH_2Cl_2 (0.30 mL), imidazole (2.9 mg, 0.042 mmol), *t*-butyldimethylsilyl chloride (6 mg, 0.038 mmol) according to the general procedure (25 h), after chromatography (5–30% EtOAc–hexane), 4.5 mg (29%) of silylated oxirane **12** and 8.75 mg (70%) of starting material, was obtained as colorless oils. The data for **12** was identical to those found before.

3.4.9. Synthesis of (+)-(2*R*,3*R*,1′*R*)-(*E*)-3-[(1′-*tert*-butyldimethylsilyloxy)-*n*-pentyl]-2-(1-pentenyl)-2-(*p*-tolylsulfonyl)oxirane, 14. From sulfinyl oxirane **13** (11 mg, 0.02 mmol) in MeOH (0.24 mL) and MMPP (22.7 mg, 0.036 mmol), according to the general procedure (2 h), after chromatography (5–30% EtOAc–hexane), sulfonyl oxirane **14** (8.3 mg, 74%) was obtained as a colorless oil. The data for **14** was identical to those found before.

3.4.10. Synthesis of (+)-(2*R*,3*S*,1′*S*)-(*E*)-3-(1′-hydroxypentyl)-2-(1-pentenyl)-2-(*p*-tolylsulfonyl)oxirane, *ent*-10. From sulfinyl oxirane **15** (6 mg, 0.017 mmol) in MeOH (0.17 mL) and MMPP (16.5 mg, 0.026 mmol), according to the general procedure (90 min), after chromatography (5–30% EtOAc–hexane), sulfonyl oxirane *ent*-**10** (3.5 mg, 59%) was obtained as a colorless oil with data identical to that of its enantiomer except for the sign of the optical rotation ($[\alpha]_D^{20}$ +32.6 (*c* 0.35)).

3.4.11. Synthesis of (−)-(2*S*,3*R*,1′*S*)-(*E*)-3-(1′-hydroxypentyl)-2-(1-pentenyl)-2-(*p*-tolylsulfonyl)oxirane, 17. From sulfinyl oxirane **16** (10.8 mg, 0.032 mmol) in MeOH (0.32 mL) and MMPP (29.8 mg, 0.048 mmol), according to the general procedure (23 h), after chromatography (5–20% EtOAc–hexane), sulfonyl oxirane **17** (7.0 mg, 62%) was obtained as a colorless oil with data identical to that found before.

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