Highly Stereoselective Nucleophilic Epoxidation of Simple Vinyl Sulfoxides†

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The nucleophilic epoxidation of readily available vinyl and dienyl sulfoxides with MOO-*t*-Bu (M = Li, Na, K) takes place in good yields, with complete preservation of double bond geometry in most cases and with moderate to excellent diastereofacial selectivity to produce enantio- and diastereomerically pure α,*β*-epoxy sulfoxides, valuable synthetic intermediates. Subsequent straightforward oxidation at sulfur affords the corresponding enantiopure sulfonyl oxiranes. For (1*E*)-2-sulfinyl dienes, the facial selectivity of this novel process may be controlled by the choice of metal (Li vs Na).

Introduction

Asymmetric epoxidations of allylic alcohols and unfunctionalized alkenes are fundamental processes in contemporary organic synthesis.[1,2] In contrast to these well-established methodologies, there are few protocols available for effecting asymmetric epoxidations of electron deficient alkenes, and therefore, this field has been attracting a great deal of attention in recent years.[3] An alternative approach to enantiopure oxiranes relies on the diastereoselective epoxidation of an enantiomerically pure alkene. In this context, Jackson conclusively established that the treatment of a variety of enantiopure (*E*)-*N*-(*p*-tolylsulfonyl) vinyl sulfoximines, available in four steps from racemic methyl phenyl sulfoxide, with LiOO-*t*-Bu produces the corresponding oxiranes with perfect geometric and facial selectivity and in high yields.[4,5] These oxiranes have been subsequently transformed into a variety of enantiomerically enriched bromohydrins by reaction with $MgBr_2$ and "in situ" reduction with *n*-Bu_4NBH_4.[4c]

In connection with our interest in the development of sulfur-directed synthetic strategies,[6] we required an efficient route to enantiopure vinyl epoxy sulfoxides of general structure **B**, R^2 = vinyl (Scheme 1), with high regiocontrol, *E*-*Z* stereocontrol, and diastereofacial selectivity. Inspection of the literature revealed that while the chemistry of sulfinyl oxiranes has been thoroughly studied,[7] the existing routes to these intermediates are somewhat limited. A general approach employs the condensation between a metalated α-chloro sulfoxide, **E**, and an aldehyde to produce an almost equimolar mixture

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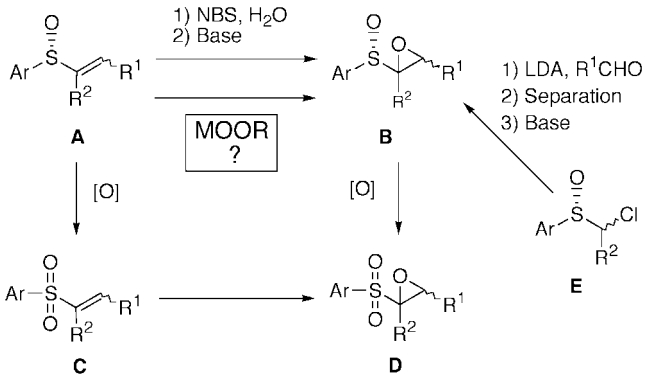
Scheme 1

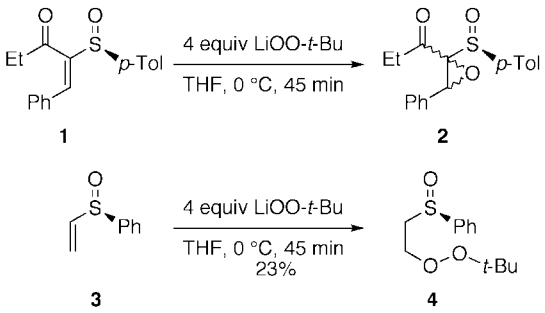


of two diastereomeric chlorohydrins due to low 1,3 asymmetric induction.[8] Chromatographic separation followed by base-induced cyclization affords the desired epoxides. Alternatively, a vinyl sulfoxide, **A**, R^1 = Ph, R^2 = H, has been treated with aqueous *N*-bromosuccinimide to produce a mixture of bromohydrins with good selectivity; after separation, the major diastereomer was transformed into the corresponding epoxide as described above.[9]

We perceived that neither existing route was well suited to our purposes; indeed, the synthesis and subsequent metalation of an enantiomerically pure α-chloro allyl sulfoxide (**E**, R^2 = vinyl) could be plagued with regio- and stereochemical problems, including a low configurational stability at sulfur.[10] Alternatively, the bromohydrin route would require a regioselective electrophilic addition to the most electron deficient double bond of a readily available 2-sulfinyl diene system.[11] An alternative approach was then considered, and it was envisioned that the desired vinyl epoxy sulfoxides **B**, R^2 = vinyl, could be obtained by regioselective nucleophilic epoxidation of the most electron deficient double bond of 2-sulfinyl dienes, in close analogy to related findings for 2-sulfonyl dienes.[12] Furthermore, the synthetic usefulness of enantiopure sulfinyl and sulfonyl oxiranes (**B** and **D**, Scheme 1)[5,7,13] prompted us to undertake the development of the unprecedented nucleophilic epoxidation of simple vinyl sulfoxides as a general reaction.

Two difficulties associated with this approach to sulfinyl oxiranes **B** (Scheme 1) were apparent at the inception

Scheme 2



of this research. Alkenyl sulfoxides **A**, $R^1 \neq$ H, display a relatively low reactivity with nucleophiles,[14] and the sulfinyl functionality is labile toward oxidation, either at the vinyl sulfoxide stage, **A**, to produce vinyl sulfones **C**, which would afford racemic epoxy sulfones **D**, or at the sulfinyl oxirane stage, **B**, leading to scalemic epoxy sulfones **D**.[15] Considering these potential problems, the viability and, at best, the facial selectivity of the proposed epoxidation became a matter of concern. In this paper we report a full account of our efforts in this field,[16] which have resulted in an efficient and practical methodology to prepare a variety of optically pure sulfinyl and sulfonyl oxiranes from readily available alkenyl sulfoxides.

Epoxidation of Vinyl and Dienyl Sulfoxides

To establish if an activated vinyl sulfoxide could undergo the proposed epoxidation without significant oxidation to the sulfone, our initial efforts were focused on keto vinyl sulfoxide **1** (Scheme 2), which afforded a complex mixture of four diastereomeric epoxides, **2**, presumably geometric and facial isomers. Lowering the reaction temperature to −78 °C gave a somewhat less complex mixture but still devoid of synthetic usefulness. The epoxidation of commercially available phenyl vinyl sulfoxide **3** was then studied, and a low yield of peroxide **4** was obtained as the only product which could be characterized from the complex reaction mixtures. In view of these disappointing results, these examples were not pursued further. Nonetheless, these experiments had demonstrated that the reaction conditions were compatible with the sulfinyl functionality, at least for short reaction times.

Table 1 gathers our results on the epoxidation of simple *E* alkenyl sulfoxides **5**. Despite extensive experimentation, phenyl-substituted substrate **5a** (Table 1, entries 1−4) was found to be totally unreactive, though forcing reaction conditions led to variable amounts of epoxy sulfone **6a**, starting material, and the corresponding vinyl sulfone. Since the lack of reactivity of **5a** with nucleophiles is well-known,[17] we sought to enhance the electron-withdrawing character of the sulfinyl moiety by means

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(13) For a synthesis of Hemibrevetoxin B based on sulfonyl oxiranes, see: (a) Mori, Y.; Yaegashi, K.; Furukawa, H. *J. Am. Chem. Soc.* **1997**, *119*, 4557−4558. For related studies, see: (b)Mori, Y.; Yaegashi, K.; Furukawa, H. *J. Am. Chem. Soc.* **1996**, *118*, 8158−8159. (c) Mori, Y.; Yaegashi, K.; Kazutaka, I.; Yamamori, Y.; Furukawa, H. *Tetrahedron Lett.* **1996**, *37*, 2605−2608. (d) Mori, Y.; Yaegashi, K.; Furukawa, H. *Tetrahedron* **1997**, *53*, 12917−12932. See also: (e) Takemoto, Y.; Kuraoka, S.; Ohra, T.; Yonetoku, Y.; Iwata, C. *Tetrahedron* **1997**, *53*, 603−616. For an early report on the α-lithiation of sulfonyl oxiranes, see: (f) Ashwell, M.; Clegg, W.; Jackson, R. F. W. *J. Chem. Soc., Perkin Trans. 1* **1991**, 897−908.

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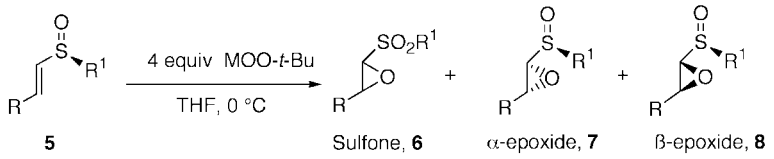
(15) For the oxidation of sulfoxides with *t*-BuOOH, see: Breton, G. W.; Fields, J. D.; Kropp, P. J. *Tetrahedron Lett.* **1995**, *36*, 3825−3828.

(16) For a preliminary communication, see: Fernández de la Pradilla, R.; Castro, S.; Manzano, P.; Priego, J.; Viso, A. *J. Org. Chem.* **1996**, *61*, 3586−3587.

(17) Styryl sulfoxides **9a** and, especially, **5a** undergo conjugate addition with benzylamine much slower than related, less conjugated, substrates. See: (a) Pyne, S. G.; Griffith, R.; Edwards, M. *Tetrahedron Lett.* **1988**, 29, 2089−2092. (b) Pyne, S. G.; Bloem, P.; Griffith, R. *Tetrahedron* **1989**, *45*, 7013−7022. (c) Pyne, S. G.; Bloem, P.; Chapman, S. L.; Dixon, C. E.; Griffith, R. *J. Org. Chem.* **1990**, *55*, 1086−1093.

Table 1. Epoxidation of *E* Vinyl Sulfoxides



5 Sulfone, **6** α-epoxide, **7** ß-epoxide, **8**

entry	substrate	R	R^1	M	time (min)	sulfone[a]	α-epoxide[a]	β-epoxide[a]	yield[b] (%)
1	**5a**	Ph	*p*-Tol	Li	3 days	**6a** (63)	–	–	–
2[c]	**5a**	Ph	*p*-Tol	Li	7 h	**6a** (17)	–	–	–
3	**5a**	Ph	*p*-Tol	Na	270	**6a** (91)	–	–	–
4	**5a**	Ph	*p*-Tol	K	300	**6a** (24)	–	–	–
5	**5b**	Ph	*o*-NO_2–Ph	Li	1 day	–	–	–	NR
6	**5c**	*n*-Bu	*p*-Tol	Li	240	**6c** (25)	**7c** (58)	**8c** (17)	70
7	**5c**	*n*-Bu	*p*-Tol	Na	90	**6c** (13)	**7c** (83)	**8c** (4)	75
8[d]	**5c**	*n*-Bu	*p*-Tol	K	9	**6c** (–)	**7c** (94)	**8c** (6)	65
9	**5d**	$(CH_2)_2$Ph	*p*-Tol	Na	220	**6d** (2)	**7d** (97)	**8d** (1)	67
10[e]	**5e**	*t*-Bu	*p*-Tol	Na	5 days	**6e** (1)	**7e** (10)	–	–
11[f]	**5e**	*t*-Bu	*p*-Tol	K	3 days	**6e** (13)	**7e** (37)	–	87
12[g]	**5f**	*n*-Bu	*t*-Bu	K	75 h	**6f** (8)	**7f** (82)	–	65

[a] Ratios of products measured by integration of the 300 MHz ^{1}H NMR spectra of crude reaction mixtures are in parentheses. [b] Unoptimized combined yields of pure products. [c] Reaction conducted in Et_2O. [d] Reaction conducted with 2 equiv of KOO-*t*-Bu. [e] Starting material detected in crude reaction mixture (89% ratio). [f] Starting material detected in crude reaction mixture (50% ratio). [g] Starting material detected in crude reaction mixture (10% ratio).

of an *o*-nitrophenyl substituent.[18] Unfortunately, substrate **5b** was found to be strikingly unreactive with LiOO-*t*-Bu (Table 1, entry 5) and led to complete decomposition with NaOO-*t*-Bu.

A simple alkyl-substituted substrate, **5c**, was studied next, and our initial efforts led to almost exclusive formation of sulfone **6c**. After screening the qualitative influence of stoichiometry, temperature, concentration, and time on the reaction, the desired epoxy sulfoxides **7c** and **8c**, were obtained albeit in low selectivity and along with substantial amounts of sulfone **6c** (Table 1, entry 6). It should be pointed out that in most cases, very careful monitoring of the reaction by TLC was crucial since vinyl and epoxy sulfoxides present very similar chromatographic mobilities; in addition, the reaction temperature was also found to be a key factor to the success of the process with 0 °C showing the best balance between the rates of epoxidation and undesired overoxidation. In an attempt to improve the yield and selectivity of this process, the effect of the metal cation was examined. The use of NaOO-*t*-Bu, generated from oil free NaH, resulted in a substantial enhancement of the reaction rate and selectivity, along with less overoxidation to the sulfone (Table 1, entry 7). Finally, the use of KOO-*t*-Bu, generated from oil free KH, produced a very fast reaction with good stereoselectivity but in slightly lower yield than with NaOO-*t*-Bu. It should be pointed out that, to the best of our knowledge, NaOO-*t*-Bu has not been used before for related processes, and it may be the reagent of choice for epoxidations of moderately reactive substrates.

The nucleophilic epoxidation of alkenyl sulfoxide **5d** (Table 1, entry 9) led to crystalline oxirane **7d** as practically a single isomer. Entries 10 and 11 (Table 1) show that the process is viable, though not synthetically useful at this stage, even when the β-carbon is highly hindered by a *tert*-butyl substituent. Finally, the epoxidation of racemic **5f**, the *tert*-butyl sulfoxide analogue of **5c**,[19] was studied, and a fair yield of oxirane **7f** was obtained in a somewhat sluggish reaction (Table 1, entry 12).

The effect of the alkene geometry on the process was then addressed, and the results obtained for a variety of *Z* vinyl sulfoxides, **9**, are shown in Table 2. Phenyl-substituted sulfoxide **9a** produced α-epoxide **11a** in high yield and with excellent facial selectivity with either lithium or, even better, the sodium reagents (Table 2, entries 1 and 2). In addition, overoxidation to the sulfone was hardly a problem in these cases. It should be mentioned that the minor isomer obtained, which we originally assigned as a *cis*-β-epoxide,[16] was later found to be the elusive *trans*-α-isomer, **7a** (Table 1).

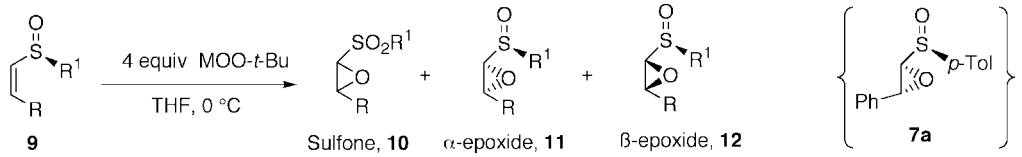
Entries 3–5 illustrate the remarkable selectivity found for substrates bearing Me and *n*-Bu substituents at the β-carbon. Furthermore, high yields and selectivities were also obtained for *i*-Pr- and even *t*-Bu-substituted alkenyl sulfoxides **9d** and **9e** (Table 2, entries 6–8). The possibility of using *tert*-butyl sulfoxides was also examined with excellent results for the *Z* geometrical isomer, **9f** (Table 2, entry 9). Finally, sulfinyl oxirane **11g**, immediate precursor of a key component of Mori's recent Hemibrevetoxin B synthesis,[13a] was prepared in a short (four steps from 1,4-butanediol) and highly stereocontrolled sequence.

To determine the scope of the methodology, the epoxidation of more highly substituted substrates was explored, and the results obtained are shown in Scheme 3. To our dismay, both **13** and **14**, representative examples of α,β-disubstituted vinyl sulfoxides, were found to be completely unreactive under a number of experimental conditions. It should be noted that a dramatic loss of reactivity has been reported for related α,β-disubstituted vinyl sulfones and sulfoximines.[5h,4a] At this stage of the project, the reactivity of phenyl-substituted substrates

(18) *o*-Nitrophenyl ethynyl sulfoxides display an enhanced reactivity with nucleophiles relative to their *p*-tolyl analogues. See: (a) Lee, A. W. M.; Chan, W. H. *Topics Curr. Chem.* **1997**, *190*, 103–129. (b) Lee, A. W. M.; Chan, W. H.; Tao, Y.; Lee, Y. K. *J. Chem. Soc., Perkin Trans. 1* **1994**, 477–481.

(19) The use of *tert*-butyl sulfoxides allows for improved stereocontrol *vs* their *p*-tolyl analogues in some cases. For the preparation of optically pure *tert*-butyl sulfoxides, see: Khiar, N.; Fernández, I.; Alcudia, F. *Tetrahedron Lett.* **1994**, 35, 5719–5722, and references therein.

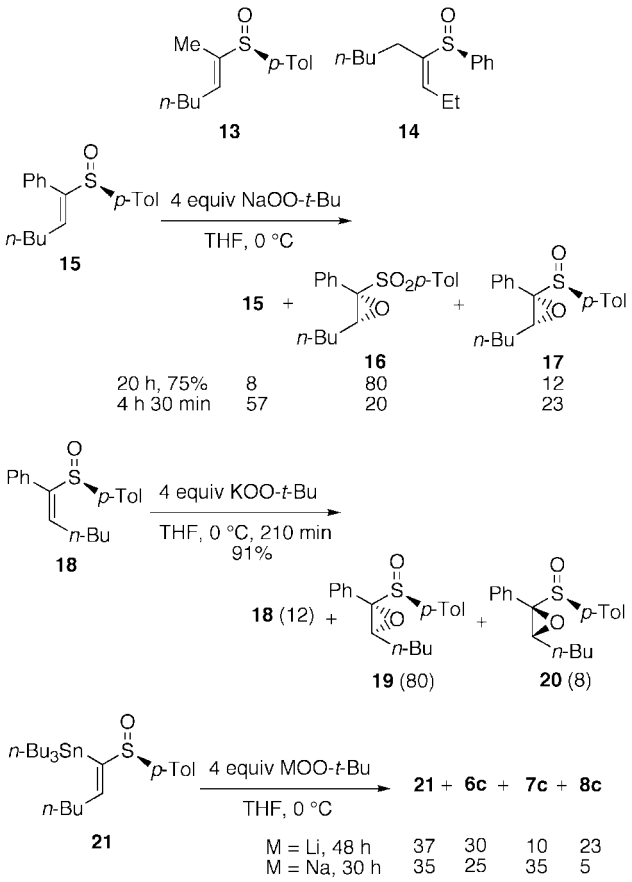
Table 2. Epoxidation of *Z* Vinyl Sulfoxides



entry	substrate	R	R^1	M	time (min)	sulfone[a]	α-epoxide[a]	β-epoxide[a]	yield[b] (%)
1[c]	**9a**	Ph	*p*-Tol	Li	240	**10a** (6)	**11a** (86)	–	84
2[d]	**9a**	Ph	*p*-Tol	Na	30	**10a** (3)	**11a** (96)	–	89
3	**9b**	Me	*p*-Tol	Li	150	**10b** (6)	**11b** (92)	**12b** (2)	63
4	**9b**	Me	*p*-Tol	Na	100	–	**11b** (98)	**12b** (2)	80
5	**9c**	*n*-Bu	*p*-Tol	Li	20	–	**11c** (98)	**12c** (2)	74
6[e]	**9d**	*i*-Pr	*p*-Tol	Na	2 days	**10d** (13)	**11d** (85)	**12d** (2)	90
7[f]	**9d**	*i*-Pr	*p*-Tol	K	1 day	**10d** (3)	**11d** (73)	**12d** (1)	87
8[g]	**9e**	*t*-Bu	*p*-Tol	Na	1 day	**10e** (3)	**11e** (85)	**12e** (2)	81
9	**9f**	*n*-Bu	*t*-Bu	Li	210	–	**11f** (98)	**12f** (2)	79
10[h]	**9g**	$(CH_2)_3OTBDPS$	*p*-Tol	Na	25	**10g** (1)	**11g** (92)	**12g** (2)	77

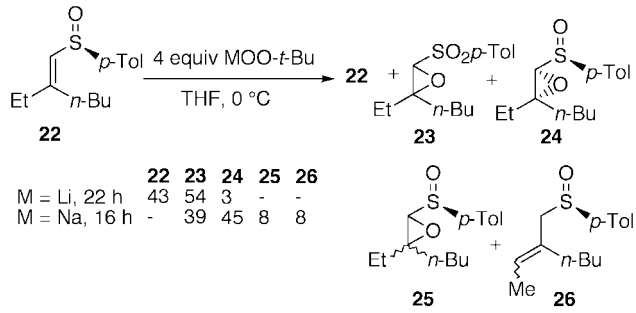
[a] Ratios of products measured by integration of the 300 MHz ^1H NMR spectra of crude reaction mixtures are in parentheses. [b] Unoptimized combined yields of pure products. [c] *Trans* oxirane **7a** detected in crude reaction mixture (8% ratio). [d] *Trans* oxirane **7a** detected in crude reaction mixture (1% ratio). [e] Reaction conducted with 6 equiv of NaOO-*t*-Bu. [f] Starting material detected in crude reaction mixture (23% ratio). [g] Starting material detected in crude reaction mixture (10% ratio). [h] Corresponding allyl sulfoxide detected in crude reaction mixture (5% ratio).

Scheme 3



15 and **18** was examined. Our selection of these substrates was dictated by concurrent results on preliminary epoxidations of 2-sulfinyl dienes. However, a clean epoxidation of *E* isomer **15** could not be achieved; instead, variable mixtures of starting material, epoxy sulfone **16**, and small amounts of epoxy sulfoxide **17** were obtained. Moreover, the use of KOO-*t*-Bu produced even more complex mixtures of the above compounds and allylic sulfoxides. In sharp contrast, the *Z* isomer **18** led to oxiranes **19** and **20** in good yields and with high selectivity. Finally, the reactivity of vinyl stannane **21**[6b] was examined, and complex mixtures of starting material and destannylated oxiranes **6c**, **7c**, and **8c**, identical to those derived from **5c** (Table 1, entries 6 and 7), were obtained. The reversal of selectivity found for the epoxidation of **21** with LiOO-*t*-Bu (**7c**:**8c**, 1:2.3), relative to **5c** (**7c**:**8c**, 3.4:1), suggests that, at least to some extent, cleavage of the tin–carbon bond took place after epoxidation had occurred. Therefore, it appears that substitution at the α-position can significantly alter the facial selectivity of the epoxidation with LiOO-*t*-Bu for this geometry.

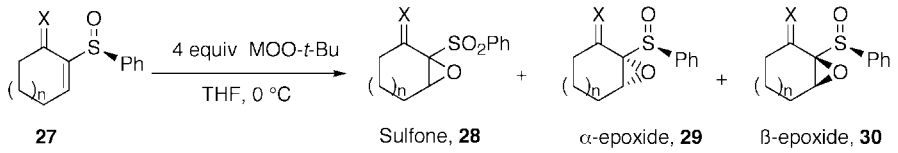
Scheme 4



The influence of an additional substituent at the β-carbon was examined next, and the results obtained for the epoxidation of **22** are shown in Scheme 4. Not too unexpectedly, **22** was found to be significantly less reactive than the disubstituted alkenes studied in Tables 1 and 2. Indeed, LiOO-*t*-Bu led to low conversions, and prolonged reaction times afforded mixtures of starting material and epoxy sulfone **23**. On the other hand, NaOO-*t*-Bu led to higher conversions, but complex mixtures of products **23**–**26**, including an allylic sulfoxide, **26**, were also obtained; therefore, this case was not studied in more detail.

Table 3 is composed of our efforts on the epoxidation of cyclic substrates **27**. The simple cyclohexenyl sulfoxide **27a** led to variable mixtures of starting material, vinyl sulfone, and epoxy sulfone (Table 3, entries 1 and 2). For this substrate, the use of KOO-*t*-Bu produced even more complex mixtures of the above compounds and the corresponding allylic sulfoxide. In contrast, the more

Table 3. Epoxidation of Cyclic Vinyl Sulfoxides

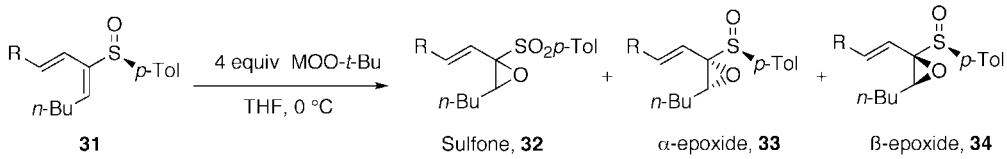


27 Sulfone, **28** α-epoxide, **29** ß-epoxide, **30**

entry	substrate	X	*n*	M	time (min)	sulfone[a]	α-epoxide[a]	*β*-epoxide[a]	yield[b] (%)
1[c]	**27a**	H, H	1	Li	26 h	**28a** (19)	–	–	–
2[d]	**27a**	H, H	1	Na	31 h	**28a** (35)	trace	–	–
3	**27a**	H, H	1	K	510		see text		
4[e]	**27b**	O	1	Na	17	–	**29b** (36)	**30b** (64)	44
5[f]	**27b**	O	1	Na	40	–	**29b** (44)	**30b** (56)	–
6[e]	**27b**	O	1	Li	10	–	**29b** (9)	**30b** (91)	48
7[g]	**27b**	O	1	Li	240	–	**29b** (15)	**30b** (85)	–
8[h]	**27c**	O	0	Li	5	–	**29c** (40)	**30c** (60)	47

[a] Ratios of products measured by integration of the 300 MHz ^{1}H NMR spectra of crude reaction mixtures are in parentheses. [b] Unoptimized combined yields of pure products. [c] Starting material (42% ratio) and vinyl sulfone (39% ratio) detected in crude reaction mixture. [d] Starting material (42% ratio) and vinyl sulfone (13% ratio) detected in crude reaction mixture. [e] Reaction conducted at −78 °C. [f] Reaction performed by adding a solution of a 1:1 mixture of **27b** and $ZnBr_2$ to a cold (−78 °C) solution of NaOO-*t*-Bu. [g] Reaction performed by adding a solution of LiOO-*t*-Bu to a cold (−78 °C) solution of a 1:1 mixture of $ZnBr_2$ and **27b** and subsequent slow warming to room temperature. [h] Two equivalents of LiOO-*t*-Bu used.

Table 4. Epoxidation of (1*E*)-2-Sulfinyl Dienes



31 Sulfone, **32** α-epoxide, **33** ß-epoxide, **34**

entry	substrate	R	M	time (min)	sulfone[a]	α-epoxide[a]	*β*-epoxide[a]	yield[b] (%)
1	**31a**	H	Li	120	–	**33a** (20)	**34a** (80)	75
2	**31a**	H	Na	90	**32a** (8)	**33a** (84)	**34a** (8)	61
3	**31b**	Ph	Li	2 h	**32b** (2)	**33b** (12)	**34b** (86)	74
4	**31b**	Ph	Na	45	**32b** (9)	**33b** (64)	**34b** (27)	76
5[c]	**31b**	Ph	Na	15	**32b** (7)	**33b** (77)	**34b** (16)	74
6	**31c**	CH_2OH	Li	26 h	–	trace	–	–
7	**31c**	CH_2OH	Na	120	**32c** (3)	**33c** (97)	–	80
8[d]	**31d**	$CH_2OTBDPS$	Li	27 h	–	**33d** (15)	**34d** (5)	–

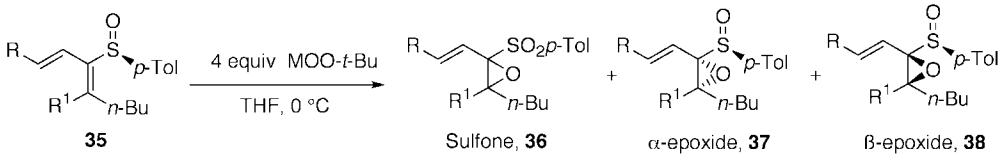
[a] Ratios of products measured by integration of the 300 MHz ^{1}H NMR spectra of crude reaction mixtures are in parentheses. [b] Unoptimized combined yields of pure products. [c] Reaction conducted at −20 °C. [d] Starting material detected in crude reaction mixture (80% ratio).

activated keto sulfoxide **27b** underwent smooth epoxidation even at −78 °C, albeit in low yields (Table 3, entries 4−7). While in this case, with NaOO-*t*-Bu, even in the presence of $ZnBr_2$, the selectivity found was poor, the use of LiOO-*t*-Bu resulted in an acceptable ratio in favor of the *β* isomer. In a final attempt to alter the stereochemical outcome of the process, an inverse addition protocol with LiOO-*t*-Bu and $ZnBr_2$ was carried out; this experiment resulted in a slight decrease in selectivity and very slow reaction rate (compare entries 6 and 7, Table 3). The five-membered ring analogue **27c** underwent a smooth reaction to produce epoxides **29c** and **30c** in low isolated yield and with marginal facial selectivity.

The epoxidation of 2-sulfinyl dienes was examined next, and the results obtained for the 1*E* isomers **31** are shown in Table 4. Entries 1 and 2 indicate that the metal cation plays a crucial role in determining the facial selectivity of this process. A similar reversal of selectivity was found for substrate **31b** (Table 4, entries 3−5). The epoxidation of diene **31c**, bearing a free hydroxyl functionality, with LiOO-*t*-Bu was not effective, and protection as a TBDPS ether gave very low conversions of epoxides **33d** and **34d**. In contrast, NaOO-*t*-Bu produced the desired transformation in high yield and with almost perfect selectivity (Table 4, entries 6−8).

Table 5 is composed of our efforts on the epoxidation of (1*Z*)-2-sulfinyl dienes **35**. Entry 1 shows the results obtained for the simple diene **35a**, under standard conditions using LiOO-*t*-Bu. A pronounced solvent effect was found (Table 5, entries 2−4) for this epoxidation; thus, while the use of the more polar solvent DME led to a very slow reaction with comparable selectivity to THF, the use of diethyl ether produced exclusively epoxy sulfone **36a** in high yield and with ca. 84% ee. The optical purity of this sulfone was determined by comparison of the optical rotation of **36a** (entry 3, [α] = +82.8), with that of an enantiomerically pure sample ([α] = +99.5) obtained by oxidation (Oxone, MeOH) of sulfinyl epoxide **37a**. This observation suggests that in ether the reaction occurs with better selectivity (ca. 90:10) than in THF, and that sulfoxides **37a** and **38a** are oxidized very readily in ether. Entry 4 shows the best product distribution obtained after an extensive study directed to control this undesired oxidation in ether. Fortunately, the use of NaOO-*t*-Bu in THF allowed for a substantial enhancement of selectivity and in a straightforward

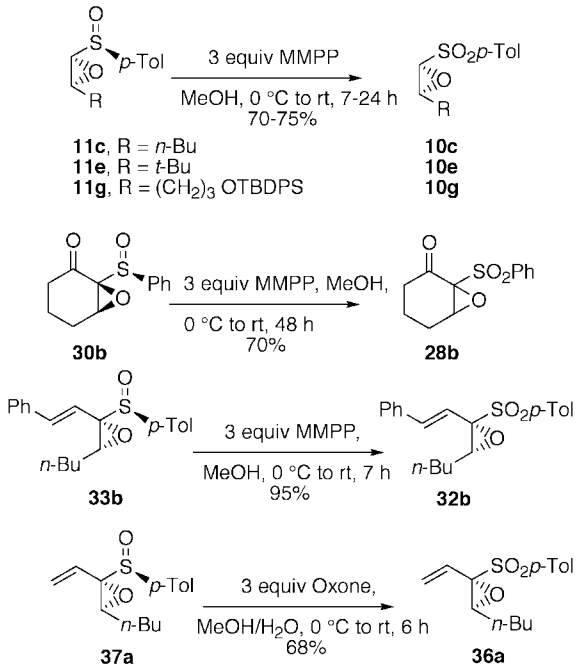
Table 5. Epoxidation of (1Z)-2-Sulfinyl Dienes



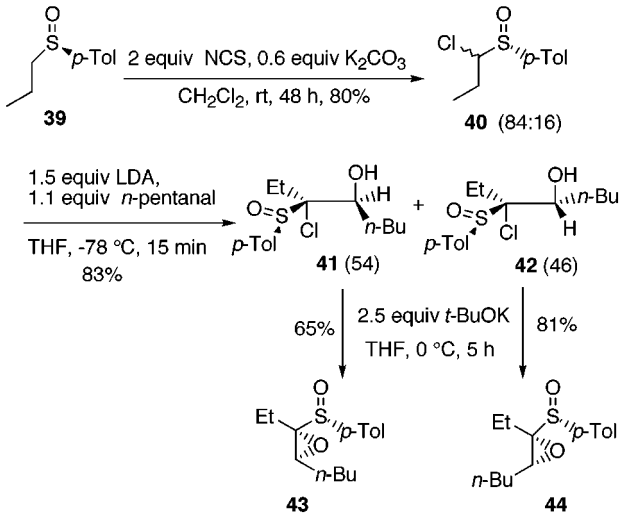
entry	substrate	R	R^1	M	time (min)	sulfone[a]	α-epoxide[a]	β-epoxide[a]	yield[b] (%)
1	**35a**	H	H	Li	120	–	**37a** (77)	**38a** (23)	83
2[c]	**35a**	H	H	Li	21 h	–	**37a** (43)	**38a** (14)	–
3[d]	**35a**	H	H	Li	120	**36a** (100)	–	–	92
4[e]	**35a**	H	H	Li	72 h	**36a** (18)	**37a** (76)	**38a** (6)	–
5	**35a**	H	H	Na	25	–	**37a** (95)	**38a** (5)	81
6	**35b**	CH_2OH	H	Na	90	**36b** (2)	**37b** (98)	–	94
7	**35c**	H	Me	Li	24 h	**36c** (12)	**37c** (58)	**38c** (28)	–
8	**35c**	H	Me	Na	160	**36c** (3)	**37c** (92)	**38c** (5)	60

[a] Ratios of products measured by integration of the 300 MHz ^{1}H NMR spectra of crude reaction mixtures are in parentheses. [b] Unoptimized combined yields of pure products. [c] Reaction conducted in DME, starting material (43% ratio) detected in crude reaction mixture. [d] Reaction conducted in Et_2O, sulfone **36a** had 84% ee. [e] Reaction conducted in Et_2O at −28 °C.

Scheme 5



Scheme 6



manner (Table 5, entry 5). These conditions were also optimal for diene **35b** with a free hydroxyl substituent, as well as, remarkably, for diene **35c**, with a fully substituted β-carbon (Table 5, entries 6 and 8).

Structural Assignments

The structure of these sulfinyl oxiranes was derived from their spectral features. To conclusively prove the oxidation state at sulfur and our ability to prepare sulfonyl oxiranes, several oxidations for representative substrates under standard conditions were carried out, and the results obtained are shown in Scheme 5. These oxidations proceeded smoothly and in good yields to produce a variety of epoxy sulfones; the chemoselectivity found for **33b** and **37a** is noteworthy and allows for a straightforward preparation of enantiomerically pure acyclic vinyl epoxy sulfones, regioisomeric to the cyclic epoxy vinyl sulfones described by Fuchs.[12c]

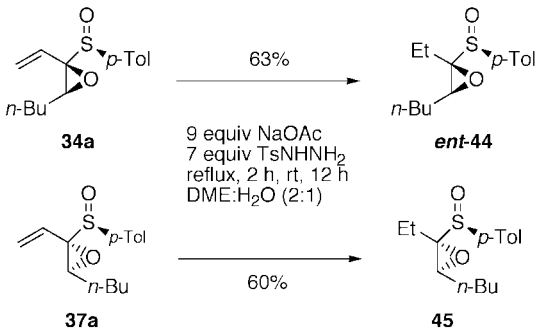
With a secure assignment of the oxidation state at sulfur, the clarification of the relative configuration of our vinyl sulfinyl oxiranes (**33a** and **34a**, Table 4; **37a** and **38a**, Table 5) was pursued. It was envisioned that the application of Yamakawa's methodology,[7,8] of known stereochemical outcome, to *n*-propyl *p*-tolyl sulfoxide **39** and *n*-pentanal should lead to two diastereomeric oxiranes which would be either enantiomeric or diastereomeric to those obtained by hydrogenation of our vinyl sulfinyl oxiranes. Thus, **39** was smoothly chlorinated to yield an inseparable mixture of chloro sulfoxides **40** (Scheme 6) which were lithiated and treated with *n*-pentanal to afford an almost equimolar mixture of chlorohydrins **41** and **42**; these were separated by chromatography and cyclized by treatment with KO-*t*-Bu to produce sulfinyl epoxides **43** and **44**.

The hydrogenation of our vinyl oxiranes **34a** and **37a** (Scheme 7) was then addressed. After several fruitless attempts to carry out catalytic hydrogenations (H_2, Pd/C, EtOH) which gave rise to complex mixtures, including products of allylic rearrangement,[20] the use of diimide produced the desired saturated sulfinyl oxiranes *ent*-**44** and **45**.[21] It should be pointed out that **43** and **45** had

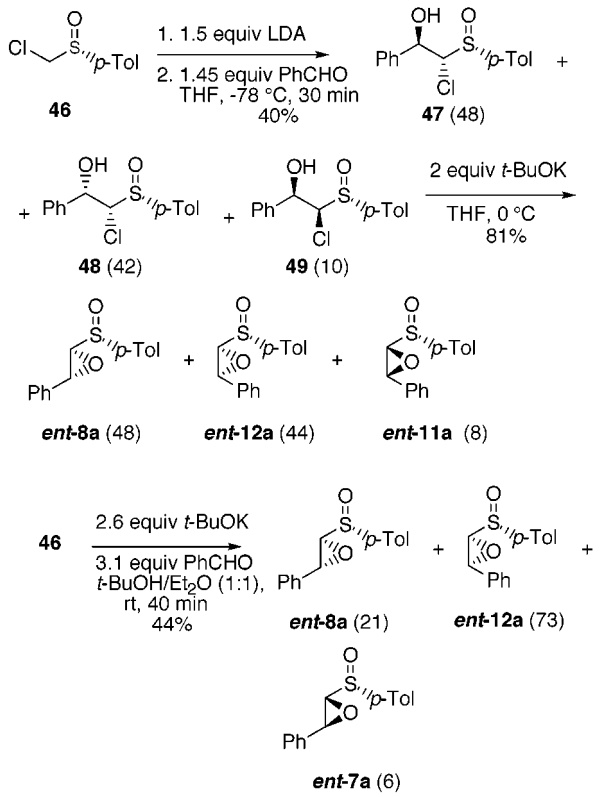
(20) This observation suggests that these vinyl oxiranes could be adequate substrates for π-allyl palladium chemistry. This possibility is being pursued in our laboratory.

(21) For a review, see: Pasto, D. J.; Taylor, R. J. K. *Org. React.* **1991**, *40*, 91−155.

Scheme 7



Scheme 8



spectral data that clearly indicated a *cis* geometry and a diastereomeric nature. In contrast, **44** and *ent*-**44** had identical spectral features and optical rotations of opposite sign (−53.6 and +52.1, respectively), thus indicating an enantiomeric relationship.

To carry out a comparable correlation for our simple oxiranes (Tables 1 and 2) the condensation between lithiated chloromethyl sulfoxide **46**[8] and benzaldehyde was explored. To our dismay, a low yield of an inseparable mixture of three diastereomeric chlorohydrins **47**−**49** was obtained (Scheme 8). The subsequent cyclization proceeded smoothly and *trans* epoxide *ent*-**8a** ($J_{2,3}$ = 1.7 Hz) was separated from the mixture of cis epoxides *ent*-**12a** ($J_{2,3}$ = 3.4 Hz) and *ent*-**11a** ($J_{2,3}$ = 3.7 Hz). Since reliable spectral data for three of the four possible diastereomeric oxiranes bearing a phenyl substituent was now available, by exclusion, the correct structure for **7a** (4.70 ppm, s, 2 H, H-2, H-3) (Table 2, entry 1) had to be the one shown, an α-*trans* oxirane, which may be formed by *β*-attack of LiOO-*t*-Bu to *Z* vinyl sulfoxide **9a**, followed by rotation around the C-2/C-3 bond and oxirane ring closure. However, it was considered that the low yield and selectivity found rendered this route unreliable to assign the structure of our major *cis* oxirane **11a**. Therefore, a more definitive structural proof was sought and an X-ray diffraction analysis of **11a** was carried out (Supporting Information); this analysis confirmed our initial tentative assignment.[16]

At this stage of the project the results of Tavares et al.,[9c] on the condensation between chloro sulfoxide **46** and benzaldehyde, were examined, in an attempt to clarify the selectivity of that process. It should be pointed out that the original report mentioned a *cis* oxirane as the main product, along with some trans oxirane, but the ratio of products and the relative stereochemistries were not discussed. In our hands, this reaction afforded a low yield (44% unoptimized) of a 21:73:6 mixture of sulfinyl epoxides *ent*-**8a**, *ent*-**12a**, and *ent*-**7a** (Scheme 8).[22]

With regard to the epoxidation of simple *E* vinyl sulfoxides (Table 1), the major products had been tentatively assigned as *β*-epoxides,[16] in analogy with our own preliminary results for (1*E*)-dienes with LiOO-*t*-Bu (Table 4, entry 1) and with some literature precedents on nucleophilic additions to alkenyl sulfoxides.[23] However, some results obtained at a later stage of this project[24] made us question the accuracy of our previous assignment. To clarify this issue, an X-ray diffraction analysis of *trans* sulfinyl oxirane **7d** was carried out (Supporting Information); this analysis unequivocally showed an α-epoxide structure for **7d**.

Our stereochemical assignment for cyclic keto sulfinyl oxiranes **29** and **30** (Table 3) is tentative and relies on comparison of the ^{1}H NMR chemical shifts of the oxirane protons of **29b** and **30b** with those of related acyclic substrates **7c**/**8c** (Table 1) and **33a**/**34a** (Table 4), for which the *β*-epoxides had slightly more deshielded oxirane protons ($\Delta\delta$ = 0.12 and 0.05 ppm, respectively). In addition, the *β*-epoxides **8c** and **34a** showed a slightly higher chromatographic mobility (ΔR_f = 0.05 and 0.03, respectively), comparable to the behavior found for **30b** relative to **29b** (ΔR_f = 0.07). Finally, in the presence of $ZnBr_2$, a small but significant enhancement of α selectivity was found; this observation is consistent with Posner's results on additions of carbon-centered nucleophiles to these systems.[25]

Results and Discussion

The stereochemical outcome of the nucleophilic epoxidation of simple vinyl and dienyl sulfoxides with NaOO-*t*-Bu or KOO-*t*-Bu may be rationalized in terms of an initial nucleophilic addition to the α-face of reactive conformation **A** (Scheme 9), with an *s-trans* coplanar arrangement of S=O and C=C bonds, followed by epoxide

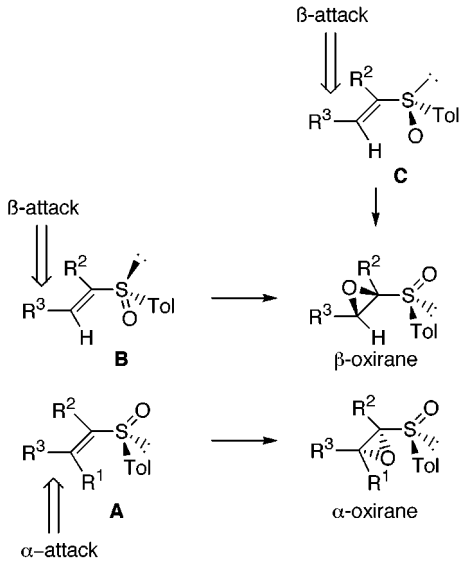
(22) We have also reproduced the results of Tsuchihashi (ref 9a) on the treatment of *E* sulfoxide **5a** with aqueous NBS and subsequent base-induced cyclization of the major bromohydrin to produce oxirane **8a**; however, an attempt to apply this protocol to *Z* sulfoxide **9a** led to a low conversion (ca. 25% after 4 h) of an equimolar mixture of bromohydrins.

(23) For additions of malonate anions to **5a** and **9a**, see: (a) Tsuchihashi, G.; Mitamura, S.; Ogura, K. *Tetrahedron Lett.* **1976**, 855−858. (b) See ref 17c.

(24) These include the reversal of diastereoselectivity found for 1*E* sulfinyl dienes **31a** and **31b** and stannane **21** upon a change in the metal from Li to Na, as well as the stereochemical outcome of the epoxidation of related α-(1-hydroxyalkyl) and *γ*-oxygenated vinyl sulfoxides, see: Fernández de la Pradilla, R.; Manzano, P.; Priego, J.; Viso, A.; Martínez-Ripoll, M.; Rodríguez, A. *Tetrahedron Lett.* **1996**, *37*, 6793−6796.

(25) Posner, G. H. *Acc. Chem. Res.* **1987**, *20*, 72−78, and references therein.

Scheme 9



ring closure. In these cases, we believe that steric hindrance by the bulky tolyl group is the main factor behind the high stereoselectivity found. With regard to epoxidations with LiOO-*t*-Bu, most cases studied show a diminished α selectivity relative to Na or KOO-*t*-Bu. This trend is particularly important for *E* vinyl sulfoxides, and it suggests a larger degree of *β*-attack to reactive conformation **B**, in which the S=O and C=C bonds are syn coplanar. Alternatively, conformation **C**, which places the sulfinyl oxygen above the plain of the alkene, could be operative by promoting coordination of the sulfinyl oxygen with lithium and thus placing the nucleophilic peroxide moiety at the *β*-face and in close proximity to the reactive site. This larger participation of conformation **B** or **C** for *E* alkenyl sulfoxides may be attributed to a diminished allylic 1,3-strain between the sulfinyl moiety and the *cis* hydrogen relative to the cases were $R^1 \neq H$.[26]

Further pieces of evidence in favor of a reaction pathway involving sulfinyl oxygen coordination with lithium are the lack of reactivity found for dienes **31c** and **31d** with LiOO-*t*-Bu (Table 4, entries 6 and 8) and the observed reversal of facial selectivity found for 1*E* diene **31a** (R^2 = vinyl, R^3 = *n*-Bu) and stannane **21** (R^2 = *n*-Bu_3Sn, R^3 = *n*-Bu) upon a change of the metal. In these cases, NaOO-*t*-Bu yields predominantly the α-oxirane, perhaps via reactive conformer **A** (R^1 = H), and LiOO-*t*-Bu gives a moderately *β*-selective process, presumably via coordination of lithium to the sulfinyl oxygen and counterclockwise rotation about the C−S bond to yield reactive conformer **C**. The related clockwise rotation is likely to suffer a severe steric interaction between the *p*-tolyl moiety and the R^2 substituent due to allylic 1,2-strain. For the 1*Z* diene isomer **35a** (R^1 = *n*-Bu, R^2 = vinyl, R^3 = H), allylic 1,3-strain between the sulfinyl moiety and R^1 precludes the counterclockwise rotation mode from being dominant, and the experimental result with LiOO-*t*-Bu is just a decrease of α-selectivity.

With regard to cyclic keto sulfoxide **27b**, the results obtained with NaOO-*t*-Bu may reflect an enhanced participation of conformer **B** due to C=O/S=O dipole repulsion,[25] and the use of LiOO-*t*-Bu further increases the relative participation of conformer **C**, as discussed above.

Conclusions

A novel methodology to effect the nucleophilic epoxidation of vinyl and dienyl sulfoxides has been developed. The scope of this protocol has been defined, and in this fashion, a variety of enantiopure epoxy sulfoxides and epoxy sulfones are now readily available by short and highly stereocontrolled sequences. Of the different substitution patterns studied, the simple *Z* vinyl sulfoxides **9**, and (1*E*)- or (1*Z*)-2-sulfinyl dienes **31** and **35**, are particularly good substrates for this process. In most cases, the geometry of the starting materials is fully transferred to the resulting oxiranes, and the reaction occurs in good yields and with good to excellent facial selectivity. The possibility of controlling the diastereoselectivity of the epoxidation of (1*E*)-2-sulfinyl dienes by a simple change in the metal cation (Li to Na) is remarkable. Additional extensions of this unique methodology as well as applications to the synthesis of natural products are being pursued in our laboratory.

Experimental Section

Materials and Methods. All reactions were carried out under a positive pressure of dry argon, using freshly distilled solvents under anhydrous conditions. Reagents and solvents were handled by using standard syringe techniques. Et_2O and THF were distilled from sodium and benzophenone. 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, and 15% $KMnO_4$ in water containing 5% NaOH and 10% K_2CO_3. All reagents were commercial products purchased from Aldrich, Fluka, or Merck. Commercially available organometallic reagents were used: *n*-BuLi (solution in hexane) was titrated before use.[27] Infrared spectra (IR) were obtained on a Perkin-Elmer 681. ^1H and ^{13}C NMR spectra were recorded at 200 or 300 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), quint (quintuplet), sext (sextet), m (multiplet), ap (apparent), br (broad). Melting points are uncorrected. Optical rotations were measured at 20 °C using a sodium lamp and in $CHCl_3$ solution. The vinyl sulfoxides used in this study were prepared by literature methods: **1**;[6d] **5a**, **9a**, **5b**, **9b**;[28] **5c**;[29] **9c**, **9d**, **9e**, **9g**;[30] **5d**;[30,31] **5e**;[31] **9f**, **5f**;[31,32] **13**;[31] **14**;[33] **15**, **18**,

(26) For a review, see: (a) Hoffman, R. W. *Chem. Rev.* **1989**, *89*, 1841−1860. See also: (b) Koizumi, T.; Arai, Y.; Takayama, H.; Kuriyama, K.; Shiro, M. *Tetrahedron Lett.* **1987**, *28*, 3689−3692.

(27) Watson, S. C.; Eastham, J. E. *J. Organomet. Chem.* **1967**, *9*, 165−168.

(28) Andersen, K. K. *Tetrahedron Lett.* **1962**, 93−96.

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

(30) (a) Craig, D.; Daniels, K.; McKenzie, A. R. *Tetrahedron* **1993**, 49, 11263−11304. Vinyl sulfoxide **9g** was prepared from 4-[(*tert*-butyldiphenylsilyl)oxy]-1-butanal, available in two steps from 1,4-butanediol (1. NaH, THF, *t*-$BuPh_2SiCl$, 87%. 2. PCC, NaOAc, CH_2Cl_2, 84%). See: (b) McDougal, P. G.; Rico, J. G.; Oh, Y.-I.; Condon, B. D. *J. Org. Chem.* **1986**, *51*, 3388−3390.

(31) (a) Posner, G. H.; Tang, P. W.; Mallamo, J. P. *Tetrahedron Lett.* **1978**, 3995−3998. (b) Okamura, H.; Mitsuhira, Y.; Miura, M.; Takei, H. *Chem. Lett.* **1978**, 517−520. (c) Fawcett, J.; House, S.; Jenkins, P. R.; Lawrence, N. J.; Russell, D. R. *J. Chem. Soc., Perkin Trans.1* **1993**, 67−73.

(32) Free radical addition of 2-methyl-2-propanethiol to 1-hexyne and oxidation with *m*-CPBA. See: Jacobs, T. L.; Illingworth, G. E. *J. Org. Chem.* **1963**, *28*, 2692.

21;[6b] **22**;[34] **27a**;[35] **27b**, **27c**;[36] **31a**, **31b**, **31c**, **35a**, **35b**, **35c**;[6b] **39**;[28] **46**.[8]

General Procedure for the Synthesis of 2-(*p*-Tolylsulfinyl)-1,3-butadienes and 1-Phenyl-1-hexenyl *p*-Tolyl Sulfoxides.[6b] To a solution of 1 equiv of an α-iodovinyl sulfoxide in anhydrous THF (10 mL/mmol), at room temperature and under an atmosphere of argon, was added 20% Ph_3As followed by 1 equiv of 2,6-di-*tert*-butyl-4-methylphenol (BHT) and 1.1 equiv of the corresponding vinyl stannane. Argon was bubbled through the reaction mixture for 10 min, and 5% $Pd_2(dba)_3{\cdot}CHCl_3$ was then added. The resulting mixture was refluxed (silicone bath at 70 °C) for **31c** or stirred at room temperature for **35b**, until disappearance of starting material by TLC, approximately 2 h. In the case of **18**, the above conditions were not appropriate; adequate results were obtained by using DMF and $PdCl_2(CH_3CN)_2$ in a very slow coupling. The reaction mixture was quenched with a saturated solution of KF (3 mL/mmol) and diluted with EtOAc (10 mL/mmol), and the layers were separated. The aqueous layer was extracted with EtOAc (three times, 10 mL/mmol), and the combined organic layers were washed with a saturated solution of NaCl (3 mL/mmol) and dried over anhydrous $MgSO_4$. Removal of the drying agent by filtration and concentration under reduced pressure gave a crude product which was purified by column chromatography on silica gel using gradient elution with EtOAc−hexane mixtures. Complete removal of traces of *n*-Bu_3SnI frequently required a second chromatography.

Synthesis of (−)-(*S*)-(*Z*)-1-Phenyl-1-hexenyl *p*-Tolyl Sulfoxide, 18. From (−)-(*S*)-(1*E*)-1-iodo-1-(*p*-tolylsulfinyl)-1-hexene (95 mg, 0.27 mmol) in 2.7 mL of DMF, Ph_3As (15.3 mg, 0.05 mmol), BHT (60.1 mg, 0.27 mmol), Bu_3SnPh (0.16 mL, 180 mg, 0.49 mmol), and $PdCl_2(CH_3CN)_2$ (5.60 mg, 0.022 mmol), according to the general procedure (216 h), an 80:20 mixture of vinyl sulfoxides **18** and **9c** was obtained. Purification by chromatography (50% CH_2Cl_2−hexane−2% EtOAc−CH_2Cl_2) afforded 39 mg of **18** (40%) as a colorless oil. Data of **18**: $R_f = 0.26$ (15% EtOAc−hexane). $[\alpha]^{20}_D = -47.5$ ($c = 0.55$). ^{1}H NMR (300 MHz) δ 0.97 (t, 3 H $J = 7.0$ Hz), 1.52 (m, 4 H), 2.31 (s, 3 H), 2.67 (m, 1 H), 2.84 (m, 1 H), 6.16 (dd, 1 H, $J =$ 8.4, 7.2 Hz), 7.01−7.27 (m, 9 H). ^{13}C NMR (50 MHz) δ 13.9, 21.3, 22.4, 28.5, 31.7, 124.4 (2 C), 127.6 (2 C), 128.0 (2 C), 129.4 (2 C), 134.2, 139.0, 140.4, 141.6, 145.3.

Synthesis of (−)-(*R*)-(1*Z*,3*E*)-1-*n*-Butyl-4-(hydroxymethyl)-2-(*p*-tolylsulfinyl)-1,3-butadiene, 35b. From (−)-(*S*)-(1*E*)-1-iodo-1-(*p*-tolylsulfinyl)-1-hexene (372 mg, 1.07 mmol) in 7 mL of THF, with BHT (236 mg, 1.07 mmol), Ph_3As (66 mg, 0.21 mmol), (2*E*)-3-(tributylstannyl)propen-1-ol (446 mg, 1.23 mmol) in 3 mL of THF, and $Pd_2(dba)_3{\cdot}CHCl_3$ (55 mg, 0.05 mmol), according to the general procedure and after purification by chromatography (10−100% EtOAc−hexane), diene **35b** (238 mg, 80%) was obtained as a colorless oil. Data of **35b**: $R_f = 0.16$ (75% EtOAc−hexane). $[\alpha]^{20}_D = -162.1$ ($c = 1.55$). ^{1}H NMR (300 MHz) δ 0.94 (t, 3 H, $J = 7.1$ Hz), 1.37−1.55 (m, 4 H), 1.61 (br s, 1 H), 2.37 (s, 3 H), 2.51 (m, 1 H), 2.70 (m, 1 H), 4.07 (t, 2 H, $J = 5.2$ Hz), 6.06 (d, 1 H, $J = 16.0$ Hz), 6.15 (dt, 1 H, $J = 15.7$, 4.8 Hz), 6.24 (t, 1 H, $J = 7.9$ Hz), 7.26 (d, 2 H, $J = 8.2$ Hz), 7.40 (d, 2 H, $J = 8.2$ Hz). ^{13}C NMR (50 MHz) δ 13.9, 21.3, 22.3, 28.6, 31.6, 63.1, 121.6, 124.3 (2 C), 129.8 (2 C), 133.7, 138.6, 139.7, 140.7, 142.2.

General Procedure for Nucleophilic Epoxidation of Vinyl Sulfoxides. (a) With LiOO-*t*-Bu. A two-necked round-bottomed flask fitted with a T-tube for entrance and exit of argon and a polyethylene stopper was charged with anhydrous THF (10 mL/mmol) and 4 equiv of *t*-BuOOH (80% in *t*-BuOO-*t*-Bu, Fluka), the mixture was cooled to 0 °C, and then 5 equiv of *n*-BuLi was added. The mixture was stirred at 0 °C for 10 min, and a solution of 1 equiv of the corresponding vinyl sulfoxide in THF (10 mL/mmol), previously dried over 4 Å sieves, was added dropwise. The reaction mixture was stirred at 0 °C until starting material disappearance, monitored by TLC. The reaction was then quenched with a saturated solution of $Na_2S_2O_4$ (4 mL/mmol) and diluted with EtOAc (8 mL/mmol), and the layers were separated. The aqueous layer was extracted with EtOAc (three times), and the combined organic extracts were washed with a saturated solution of NaCl (4 mL/mmol), dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure to give a crude product, which was purified by column chromatography on silica gel, using the appropriate mixture of EtOAc−hexane.

(b) With NaOO-*t*-Bu or KOO-*t*-Bu. A two-necked round-bottomed flask fitted with a T-tube for entrance and exit of argon and a polyethylene stopper was charged with anhydrous THF (10 mL/mmol) and 4 equiv of oil free NaH or KH (washed with hexane and dried), the mixture was cooled to 0 °C, and then 4 equiv of *t*-BuOOH (80% in *t*-BuOO-*t*-Bu) was added. After stirring at 25 °C for 20−30 min, the resulting solution was cooled to 0 °C, and a solution of 1 equiv of the corresponding vinyl sulfoxide in THF (10 mL/mmol), previously dried over 4 Å sieves, was added dropwise. The reaction mixture was stirred at 0 °C until starting material disappearance, monitored by TLC. Isolation and purification were performed as described above. In some cases 2 equiv of KH/*t*-BuOOH was used.

Synthesis of (+)-(*E*)-3-*n*-Butyl-2-(*p*-tolylsulfonyl)oxirane, 6c, (+)-(2*R*,3*R*,S_S)-3-*n*-Butyl-2-(*p*-tolylsulfinyl)oxirane, 7c, and (+)-(2*S*,3*S*,S_S)-3-*n*-Butyl-2-(*p*-tolylsulfinyl)oxirane, 8c. From *t*-BuOOH (85 μL, 61 mg, 0.68 mmol) in 4 mL of THF with *n*-BuLi (1.48 M, 0.57 mL, 0.85 mmol) and a solution of (+)-(*R*)-(*E*)-1-hexenyl *p*-tolyl sulfoxide, **5c**, (37 mg, 0.17 mmol) in 1 mL of THF, according to the general procedure (4 h), a 25:58:17 mixture of epoxy sulfone **6c** and epoxy sulfoxides **7c** and **8c** was obtained. Purification by chromatography (5−20% EtOAc−hexane) afforded 7 mg (18%) of **6c**, 5 mg (12%) of **8c**, and 16 mg (40%) of **7c** as colorless oils.

From NaH (11.5 mg, 0.48 mmol) in 3 mL of THF, with *t*-BuOOH (60 μL, 43 mg, 0.48 mmol) and a solution of (+)-(*R*)-(*E*)-1-hexenyl *p*-tolyl sulfoxide, **5c**, (27 mg, 0.12 mmol) in 1 mL of THF, according to the general procedure (1 h 30 min), a 13:83:4 mixture of epoxy sulfone **6c** and epoxy sulfoxides **7c** and **8c** was obtained. Purification by chromatography (5−20% EtOAc−hexane) afforded 3 mg (10%) of **6c**, 18 mg (62%) of **7c**, and 1 mg (3%) of **8c** as colorless oils.

From KH (8 mg, 0.20 mmol) in 1.25 mL of THF, with *t*-BuOOH (25 μL, 18 mg, 0.25 mmol) and a solution of (+)-(*R*)-(*E*)-1-hexenyl *p*-tolyl sulfoxide, **5c**, (22 mg, 0.10 mmol) in 0.70 mL of THF, according to the general procedure (9 min), a 94:6 mixture of epoxy sulfoxides **7c** and **8c** was obtained. Purification by chromatography (5−20% EtOAc−hexane) afforded 1 mg (4%) of **8c** and 14.5 mg (61%) of **7c** as colorless oils. Data of **6c**: $R_f = 0.30$ (20% EtOAc−hexane). $[\alpha]^{20}_D = +49.3$ ($c =$ 1.00). ^{1}H NMR (300 MHz) δ 0.88 (t, 3 H, $J = 7.1$ Hz), 1.33−1.44 (m, 4 H), 1.59−1.70 (m, 2 H), 2.44 (s, 3 H), 3.59 (ddd, 1 H, $J = 6.5$, 4.9, 1.7 Hz), 3.85 (d, 1 H, $J = 1.7$ Hz), 7.36 (d, 2 H, $J = 8.0$ Hz), 7.78 (d, 2 H, $J = 8.3$ Hz). ^{13}C NMR (50 MHz) δ 13.8, 21.7, 22.1, 27.5, 30.0, 58.0, 68.4, 128.7 (2 C), 130.0 (2 C), 134.0, 145.5. Data of **8c**: $R_f = 0.33$ (30% EtOAc−hexane). $[\alpha]^{20}_D = +113.3$ ($c = 0.70$). ^{1}H NMR (300 MHz) δ 0.84 (t, 3 H, $J = 7.1$ Hz), 1.23−1.39 (m, 4 H), 1.56−1.63 (m, 2 H), 2.41 (s, 3 H), 3.58 (td, 1 H, $J = 5.7$, 1.8 Hz), 3.66 (d, 1 H, $J = 1.9$ Hz), 7.34 (d, 2 H, $J = 8.0$ Hz), 7.54 (d, 2 H, $J = 8.3$ Hz). ^{13}C NMR (50 MHz) δ 13.8, 21.5, 22.2, 27.7, 30.3, 56.2, 72.8, 124.4 (2 C), 130.1 (2 C), 137.7, 142.3. Data of **7c**: $R_f = 0.28$ (30% EtOAc−hexane). $[\alpha]^{20}_D = +195.6$ ($c = 1.10$). ^{1}H NMR (300 MHz) δ 0.85 (t, 3 H, $J = 7.1$ Hz), 1.23−1.40 (m, 4 H), 1.57−1.64 (m, 2 H), 2.40 (s, 3 H), 3.36 (td, 1 H, $J = 5.7$, 1.9 Hz), 3.76 (d, 1 H,

(33) Prepared from commercially available phenyl vinyl sulfoxide by the following sequence: 1. LDA, THF, −78 °C. 2. EtCHO. 3. MsCl, Et_3N, THF. 4. *n*-BuCuCNLi, THF. Unpublished results from our laboratories. For related transformations, see ref 6d.

(34) Truce, W. E.; Lusch, M. J. *J. Org. Chem.* **1978**, *43*, 2252−2258. See also ref 29.

(35) Prepared from cyclohexanone and thiophenol and subsequent oxidation with *m*-CPBA. See: Labiad, B.; Villemin, D. *Synthesis* **1989**, 143−144.

(36) Yechezkel, T.; Ghera, E.; Ostercamp, D.; Hassner, A. *J. Org. Chem.* **1995**, *60*, 5135−5142. For the preparation of related enantiopure keto vinyl sulfoxides, see: Hulce, M.; Mallamo, J. P.; Frye, L. L.; Kogan, T. P.; Posner, G. H. *Organic Syntheses*; Wiley: New York, 1990; Coll. Vol. VII, pp 495−500.

J = 1.9 Hz), 7.33 (d, 2 H, J = 8.0 Hz), 7.53 (d, 2 H, J = 8.3 Hz). ^{13}C NMR (50 MHz) δ 13.8, 21.5, 22.2, 27.7, 30.3, 56.7, 72.7, 124.7 (2 C), 130.1 (2 C), 137.1, 142.3.

Synthesis of (*E*)-3-(2-Phenylethyl)-2-(*p*-tolylsulfonyl)oxirane, 6d, (+)-(2*R*,3*R*,*S*$_S$)-3-(2-Phenylethyl)-2-(*p*-tolylsulfinyl)oxirane, 7d, and (2*S*,3*S*,*S*$_S$)-3-(2-Phenylethyl)-2-(*p*-tolylsulfinyl)oxirane, 8d. From NaH (29 mg, 1.20 mmol) in 7 mL of THF, with *t*-BuOOH (0.15 mL, 108 mg, 1.50 mmol) and a solution of (*R*)-(*E*)-4-phenyl-1-butenyl *p*-tolyl sulfoxide **5d** (83 mg, 0.30 mmol) in 2 mL of THF, according to the general procedure (220 min), a 2:97:1 mixture of epoxy sulfone **6d** epoxy sulfoxide **7d** and vinyl sulfoxide **5d** was obtained. Purification by chromatography (50% CH_2Cl_2−hexane−60% EtOAc−CH_2Cl_2) afforded 57 mg of **7d** (67%) as a white solid. Partial data of **6d**: R_f = 0.38 (5% CH_2Cl_2−EtOAc). ^{1}H NMR (200 MHz) δ 3.63 (td, 1 H), 3.86 (d, 1 H, J = 2.1 Hz), 7.80 (d, 2 H, J = 8.0 Hz). Data of **7d**: mp: 93−96 °C (5% EtOAc−hexane). R_f = 0.22 (5% CH_2Cl_2−EtOAc). $[\alpha]^{20}_D$ = +189.7 (c = 1.17). ^{1}H NMR (300 MHz) δ 1.92−1.99 (m, 2 H), 2.42 (s, 3 H), 2.74 (m, 2 H), 3.45 (td, 1 H, J = 5.7, 1.8 Hz), 3.73 (d, 1 H, J = 2.0 Hz), 7.14−7.36 (m, 7 H), 7.53 (d, 2 H, J = 8.2 Hz). ^{13}C NMR (50 MHz) δ 21.4, 31.7, 32.4, 56.1, 72.7, 124.8, 126.3, 128.3, 128.6, 130.1, 137.0, 140.3, 142.3.

Synthesis of (*Z*)-3-Phenyl-2-(*p*-tolylsulfonyl)oxirane, 10a, (−)-(2*R*,3*S*,*S*$_S$)-3-Phenyl-2-(*p*-tolylsulfinyl)oxirane, 11a, and (−)-(2*R*,3*R*,*S*$_S$)-3-Phenyl-2-(*p*-tolylsulfinyl)oxirane, 7a. From *t*-BuOOH (0.20 mL, 144 mg, 1.6 mmol) in 4 mL of THF, with *n*-BuLi (1.27 M, 1.57 mL, 2.0 mmol) and a solution of (−)-(*R*)-(*Z*)-2-phenyl-1-*p*-tolylsulfinyl ethylene, **9a**, (97 mg, 0.40 mmol) in 4 mL of THF, according to the general procedure (4 h), a 6:86:8 mixture of epoxy sulfone **10a** and epoxy sulfoxides **11a** and **7a** was obtained. Purification by chromatography (5−40% EtOAc−hexane) and recrystallization (20% EtOAc−hexane) afforded 4 mg (4%) of **10a**, 73 mg (71%) of **11a**, and 9 mg (9%) of **7a** as white solids.

From NaH (94 mg, 3.9 mmol) in 20 mL of THF, with *t*-BuOOH (0.49 mL, 353 mg, 3.92 mmol) and a solution of (−)-(*R*)-(*Z*)-2-phenyl-1-*p*-tolylsulfinyl ethylene, **9a**, (237 mg, 0.98 mmol) in 7 mL of THF, according to the general procedure (30 min), a 3:96:1 mixture of epoxy sulfone **10a** and epoxy sulfoxides **11a** and **7a** was obtained. Recrystallization (20% EtOAc−hexane) afforded 200 mg of **11a** (79%), and purification by chromatography of the mother liquors (10−30% EtOAc−hexane) afforded 25 mg of **11a** (10%) as a white solid. Data of **10a**: R_f = 0.42 (30% EtOAc−hexane). ^{1}H NMR (300 MHz) δ 2.40 (s, 3 H), 4.28 (d, 1 H, J = 3.9 Hz), 4.34 (d, 1 H, J = 3.8 Hz), 7.20 (d, 2 H, J = 8.2 Hz), 7.29−7.32 (m, 5 H), 7.47 (d, 2 H, J = 8.3 Hz). Data of **11a**: mp: 130−132 °C (20% EtOAc−hexane). R_f = 0.24 (30% EtOAc−hexane). $[\alpha]^{20}_D$ = −259.4 (c = 1.24). ^{1}H NMR (300 MHz) δ 2.36 (s, 3 H), 4.17 (d, 1 H, J = 3.7 Hz), 4.20 (d, 1 H, J = 3.8 Hz), 7.01 (d, 2 H, J = 8.2 Hz), 7.19 (d, 2 H, J = 7.9 Hz), 7.37−7.40 (m, 5 H). ^{13}C NMR (50 MHz) δ 21.4, 57.5, 78.4, 124.1 (2 C), 126.6 (2 C), 128.5 (2 C), 129.0, 130.0 (2 C), 132.3, 137.0, 142.3. Data of **7a**: mp: 109−110 °C (20% EtOAc−hexane). R_f = 0.32 (30% EtOAc−hexane). $[\alpha]^{20}_D$ = −4.8 (c = 0.31). ^{1}H NMR (300 MHz) δ 2.42 (s, 3 H), 4.70 (s, 2 H), 7.32 (d, 2 H, J = 7.9 Hz), 7.46 (t, 2 H, J = 7.6 Hz), 7.60 (t, 1 H, J = 7.4 Hz), 7.74 (d, 2 H, J = 8.4 Hz), 7.93 (d, 2 H, J = 7.2 Hz). ^{13}C NMR (50 MHz) δ 21.7, 63.6, 80.6, 128.6 (2 C), 128.8 (2 C), 129.3 (2 C), 129.8 (2 C), 134.3, 135.8, 145.4, 151.9.

Synthesis of (*Z*)-3-*tert*-Butyl-2-(*p*-tolylsulfonyl)oxirane, 10e, (+)-(2*R*,3*S*,*S*$_S$)-3-*tert*-Butyl-2-(*p*-tolylsulfinyl)oxirane, 11e, and (2*S*,3*R*,*S*$_S$)-3-*tert*-Butyl-2-(*p*-tolylsulfinyl)oxirane, 12e. From NaH (50 mg, 2.10 mmol) in 9 mL of THF, with *t*-BuOOH (0.26 mL, 189 mg, 2.10 mmol) and a solution of (*R*)-(*Z*)-3,3-dimethyl-1-butenyl *p*-tolyl sulfoxide (78 mg, 0.35 mmol) in 2 mL of THF, according to the general procedure (1 day), a 3:85:2:10 mixture of epoxy sulfone **10e,** epoxy sulfoxides **11e** and **12e**, and vinyl sulfoxide **9e** was obtained. Purification by chromatography (50% CH_2Cl_2−hexane-5% EtOAc−CH_2Cl_2) afforded 4 mg of **10e** (3%), 50 mg of **11e** (70%), and 6 mg of **9e** (8%) as colorless oils. Data of **11e**: R_f = 0.36 (5% CH_2Cl_2−EtOAc). $[\alpha]^{20}_D$ = +130.5 (c = 1.55). ^{1}H NMR (300 MHz) δ 1.06 (s, 9 H), 2.41 (s, 3 H), 3.00 (dd, 1 H, J = 3.8, 0.5 Hz), 3.98 (dd, 1 H, J = 3.8, 0.6 Hz), 7.35 (d, 2 H, J = 8.5 Hz), 7.63 (d, 2 H, J = 8.2 Hz). ^{13}C NMR (50 MHz) δ 21.5, 27.7, 32.1, 68.1, 78.6, 125.1 (2 C), 130.3 (2 C), 139.1, 142.8. Partial data of **12e**: R_f = 0.34 (5% CH_2Cl_2−EtOAc). ^{1}H NMR (300 MHz) δ 2.38 (s, 3 H), 2.85 (dd, 1 H, J = 3.7, 0.5 Hz), 3.70 (dd, 1H, J = 3.8, 0.5 Hz).

Synthesis of (±)-(2*R*,3*S*,*S*$_S$)-3-*n*-Butyl-2-(*tert*-butylsulfinyl)oxirane, 11f, and (±)-(2*S*,3*R*,*S*$_S$)-3-*n*-Butyl-2-(*tert*-butylsulfinyl)oxirane, 12f. From *t*-BuOOH (75 μL, 54 mg, 0.60 mmol) in 1.5 mL of THF, with *n*-BuLi (1.61 M, 0.47 mL, 0.75 mmol) and a solution of (±)-(*Z*)-1-hexenyl *tert*-butyl sulfoxide (29 mg, 0.15 mmol) in 1.5 mL of THF, according to the general procedure (3 h 30 min), a 98:2 mixture of epoxy sulfoxides **11f** and **12f** was obtained. Purification by chromatography (50% CH_2Cl_2−hexane: 10% EtOAc−CH_2Cl_2) afforded 24 mg (79%) of **11f** as a colorless oil. Data of **11f**: R_f = 0.39 (20% EtOAc−CH_2Cl_2). ^{1}H NMR (300 MHz) δ 0.89 (t, 3 H, J = 7.2 Hz), 1.31 (s, 9 H), 1.32−1.60 (m, 4 H), 1.70−1.82 (m, 2 H), 3.22 (td, 1 H, J = 8.0, 4.0 Hz), 3.84 (d, 1 H, J = 3.8 Hz). ^{13}C NMR (50 MHz) δ 13.8, 22.3, 23.2 (3 C), 28.2, 28.9, 54.8, 58.3, 66.3. Partial data of **12f**: R_f = 0.40 (20% EtOAc−CH_2Cl_2). ^{1}H NMR (300 MHz) δ 0.92 (t, 3 H, J = 7.0 Hz), 1.46 (s, 9 H), 3.23 (ddd, 1 H, J = 10.3, 6.1, 4.2 Hz), 4.07 (d, 1 H, J = 4.1 Hz).

Synthesis of (*Z*)-3′-[[(*tert*-Butyldiphenylsilyl)oxy]propyl]-1-(*p*-tolylsulfonyl)oxirane, 10g, (−)-(2*R*,3*S*,*S*$_S$)-3′-[[(*tert*-Butyldiphenylsilyl)oxy]propyl]-1-(*p*-tolylsulfinyl)-oxirane, 11g, and (2*S*,3*R*,*S*$_S$)-3′-[[(*tert*-Butyldiphenylsilyl)-oxy]propyl]-1-(*p*-tolylsulfinyl)oxirane, 12g. From NaH (22.3 mg, 0.93 mmol) in 5 mL of THF, with *t*-BuOOH (0.11 mL, 83 mg, 0.92 mmol) and a solution of (−)-(*Z*)-(*S*)-5-[(*tert*-butyldiphenylsilyl)oxy]-1-pentenyl *p*-tolyl sulfoxide (100 mg, 0.23 mmol) in 2 mL of THF, according to the general procedure (25 min), a 1:92:2:5 mixture of epoxy sulfone **10g**, epoxy sulfoxides **11g** and **12g**, and the corresponding allyl sulfoxide was obtained. Purification by chromatography (5−30% EtOAc−hexane) afforded 77 mg of **11g** (77%) as a colorless oil. Data of **11g**: R_f = 0.33 (5% EtOAc−hexane). $[\alpha]^{20}_D$ = −3.2 (c = 1.79). ^{1}H NMR (300 MHz) δ 1.05 (s, 9 H), 1.72−2.08 (m, 4 H), 2.42 (s, 3 H), 3.14 (ddd, 1 H, J = 7.9, 4.3, 3.7 Hz), 3.74 (m, 2 H), 3.90 (dd, 1 H, J = 3.8, 0.8 Hz), 7.31−7.54 (m, 8 H), 7.56 (d, 2 H, J = 8.2 Hz), 7.66 (m, 4 H). ^{13}C NMR (75 MHz) δ 19.2, 21.9, 25.9, 26.9, 29.6, 58.3, 62.9, 75.7, 124.5, 127.7, 129.7, 130.3, 133.6, 133.7, 135.5 (2 C), 138.1, 142.1. Partial data of **12g**: R_f = 0.23 (30% EtOAc−hexane). ^{1}H NMR (300 MHz) δ 2.37 (s, 3 H), 3.46 (m, 1 H), 3.89 (d, 1 H, J = 3.8 Hz).

Synthesis of (+)-(2*S*,3*S*,*S*$_S$)-3-*n*-Butyl-2-phenyl-2-(*p*-tolylsulfinyl)oxirane, 19, and (2*R*,3*R*,*S*$_S$)-3-*n*-Butyl-2-(*p*-tolylsulfinyl)oxirane, 20. From NaH (3 mg, 0.12 mmol) in 0.6 mL of THF, with *t*-BuOOH (15 μL, 11 mg, 0.12 mmol) and a solution of (−)-(*Z*)-(*S*)-1-phenyl-1-hexenyl *p*-tolyl sulfoxide (9 mg, 0.03 mmol) in 0.2 mL of THF, according to the general procedure (1 h 30 min), a 78:22 mixture of epoxy sulfoxides **19** and **20** was obtained.

From KH (5.3 mg, 0.13 mmol) in 1 mL of THF, with *t*-BuOOH (16 μL, 12 mg, 0.13 mmol) and a solution of (−)-(*Z*)-(*S*)-1-phenyl-1-hexenyl *p*-tolyl sulfoxide (10 mg, 0.033 mmol) in 0.5 mL of THF, according to the general procedure (3 h, 30 min), a 80:8:12 mixture of epoxy sulfoxides **19** and **20** and vinyl sulfoxide **18** was obtained. Purification by chromatography (25% CH_2Cl_2−hexane: 10% EtOAc−CH_2Cl_2) afforded 8.5 mg (81%) of **19** as a white solid, traces of **20**, and 1 mg (10%) of **18** as colorless oils. Data of **19**: mp: 99−101 °C (20% EtOAc−hexane). R_f = 0.15 (10% EtOAc−hexane). $[\alpha]^{20}_D$ = +70.6 (c = 0.69). ^{1}H NMR (300 MHz) δ 1.00 (t, 3 H J = 7 Hz), 1.48−1.61 (m, 4 H), 2.18−2.40 (m, 2 H), 2.34 (s, 3 H), 3.23 (t, 1 H, J = 6.3 Hz), 6.98 (dd, 2 H, J = 7.9, 1.4 Hz), 7.11−7.27 (m, 7 H). ^{13}C NMR (50 MHz) δ 14.0, 21.4, 22.4, 27.4, 29.2, 66.8, 80.5, 125.3 (2 C), 127.6 (2 C), 128.4 (2 C), 127.6, 128.4, 128.9, 129.3 (2 C), 131.7, 137.6, 141.9. Partial data of **20**: R_f = 0.18 (10% EtOAc−hexane). ^{1}H NMR (300 MHz) δ 0.94 (t, 3 H, J = 7.2 Hz), 1.43−1.65 (m, 4 H), 2.11−2.20 (m, 2 H), 2.29 (s, 3 H), 3.26 (dd, 1 H, J = 5.9, 6.9 Hz), 6.92 (dd, 2 H, J = 8.4, 1.2 Hz), 7.07−7.23 (m, 7 H).

Synthesis of (±)-(1*R*,6*S*,*S*$_S$)-1-(Phenylsulfinyl)-7-oxabicyclo[4.1.0^{1,6}]heptan-2-one, 29b, and (±)-(1*S*,6*R*,*S*$_S$)-1-

(Phenylsulfinyl)-7-oxabicyclo[4.1.0^{1,6}]heptan-2-one, 30b. From *t*-BuOOH (85 μL, 61.3 mg, 0.68 mmol) in 5 mL of THF with *n*-BuLi (1.4 M, 0.6 mL, 0.85 mmol) and a solution of (±)-2-(phenylsulfinyl)-2-cyclohexenone, **27b**, (39 mg, 0.17 mmol) in 2 mL of THF, according to the general procedure (−78 °C, 10 min), a 9:91 mixture of epoxy sulfoxides **29b** and **30b** was obtained. Purification by chromatography (5−30% EtOAc−hexane) afforded 20 mg (48%) of **30b**, as a white solid.

From NaH (9 mg, 0.40 mmol) in 2 mL of THF, with *t*-BuOOH (50 μL, 36 mg, 0.40 mmol) and a solution of (±)-2-(phenylsulfinyl)-2-cyclohexenone, **27b**, (24 mg, 0.10 mmol) in 1 mL of THF, according to the general procedure (−78 °C, 17 min), a 36:64 mixture of epoxy sulfoxides **29b** and **30b** was obtained. Purification by chromatography (1−10% EtOAc−CH_2Cl_2) afforded 7 mg (28%) of **30b**, and 4 mg (16%) of **29b** as white solids. Data of **30b**: mp: 96−99 °C. R_f = 0.38 (10% EtOAc−CH_2Cl_2). ^{1}H NMR (300 MHz) δ 1.54−1.84 (m, 4 H), 2.34−2.52 (m, 2 H), 4.21 (m, 1 H), 7.43−7.51 (m, 3 H), 7.64−7.70 (m, 2 H). ^{13}C NMR (50 MHz) δ 16.1, 22.8, 38.3, 53.1, 73.6, 126.0 (2 C), 129.3 (2 C), 131.8, 140.4, 201.5. Partial data of **29b**: R_f = 0.31 (10% EtOAc−CH_2Cl_2). ^{1}H NMR (300 MHz) δ 4.10 (m, 1 H) 7.76−7.80 (m, 5 H). ^{13}C NMR (50 MHz) δ 17.1, 23.0, 37.2, 126.3, 128.7, 131.7.

Synthesis of (−)-(*E*)-3-*n*-Butyl-2-(*p*-tolylsulfonyl)-2-vinyl oxirane, 32a, (+)-(2*S*,3*S*,*S*$_S$)-3-*n*-Butyl-2-(*p*-tolylsulfinyl)-2-vinyl oxirane, 33a, and (−)-(2*R*,3*R*,*S*$_S$)-3-*n*-Butyl-2-(*p*-tolylsulfinyl)-2-vinyl oxirane, 34a. From *t*-BuOOH (0.37 mL, 267 mg, 2.96 mmol) in 37 mL of THF, with *n*-BuLi (1.58 M, 2.37 mL, 3.75 mmol) and a solution of sulfinyl diene **31a** (184 mg, 0.74 mmol) in 8 mL of THF, according to the general procedure (2 h), a 20:80 mixture of epoxy sulfoxides **33a** and **34a** and traces of sulfone **32a** was obtained. Purification by chromatography (5−20% EtOAc−hexane) afforded 105 mg (59%) of **34a** and 28 mg (16%) of **33a** as colorless oils.

From NaH (7.7 mg, 0.32 mmol) in 4.2 mL of THF, with *t*-BuOOH (40 μL, 29 mg, 0.32 mmol) and a solution of sulfinyl diene **31a** (20 mg, 0.08 mmol) in 1.4 mL of THF, according to the general procedure (90 min), a 8:84:8 mixture of epoxy sulfone **32a** and epoxy sulfoxides **33a** and **34a** was obtained. Purification by chromatography (5−20% EtOAc−hexane) afforded 1 mg (4%) of **32a**, 11 mg (52%) of **33a**, and 1 mg (5%) of **34a**. Data of **32a**: From other experiments that produced substantial amounts of sulfone **32a**. The optical purity has not been determined. R_f = 0.35 (20% EtOAc−hexane). $[\alpha]^{20}_D$ = −44.0 (c = 0.59). ^{1}H NMR (200 MHz) δ 0.88 (t, 3 H, J = 7.3 Hz), 1.24−1.52 (m, 6 H), 2.42 (s, 3 H), 3.94 (t, 1 H, J = 5.8 Hz), 5.21 (dd, 1 H, J = 17.1, 1.5 Hz), 5.43 (dd, 1 H, J = 10.9, 1.5 Hz), 6.25 (dd, 1 H, J = 17.1, 10.9 Hz), 7.30 (d, 2 H, J = 8.6 Hz), 7.70 (d, 2 H, J = 8.4 Hz). ^{13}C NMR (50 MHz) δ 13.8, 21.7, 22.2, 26.6, 27.9, 63.3, 77.2, 123.9, 125.1, 129.5 (5 C), 145.1. Data of **33a**: White solid. mp: 44−46 °C (Hexane). R_f = 0.18 (20% EtOAc−hexane). $[\alpha]^{20}_D$ = +165.9 (c = 0.78). ^{1}H NMR (200 MHz) δ 0.87 (t, 3 H, J = 7.3 Hz), 1.33−1.55 (m, 6 H), 2.38 (s, 3 H), 3.68 (t, 1 H, J = 6.0 Hz), 5.26 (dd, 1 H, J = 17.2, 1.4 Hz), 5.44 (dd, 1 H, J = 10.9, 1.4 Hz), 5.81 (dd, 1 H, J = 17.2, 10.9 Hz), 7.26 (d, 2 H, J = 8.0 Hz), 7.46 (d, 2 H, J = 8.2 Hz). ^{13}C NMR (50 MHz) δ 13.9, 21.5, 22.4, 27.2, 28.0, 62.4, 79.0, 123.7, 125.9 (2 C), 126.1, 129.4 (2 C), 135.8, 142.2. Data of **34a**: R_f = 0.21 (20% EtOAc−hexane). $[\alpha]^{20}_D$ = −57.6 (c = 1.24). ^{1}H NMR (200 MHz) δ 0.87 (t, 3 H, J = 7.3 Hz), 1.29−1.55 (m, 6 H), 2.39 (s, 3 H), 3.73 (t, 1 H, J = 5.9 Hz), 5.20 (dd, 1 H, J = 17.2, 1.7 Hz), 5.39 (dd, 1 H, J = 11.1, 1.7 Hz), 5.91 (dd, 1 H, J = 17.2, 11.1 Hz), 7.27 (d, 2 H, J = 8.0 Hz), 7.48 (d, 2 H, J = 8.3 Hz). ^{13}C NMR (50 MHz) δ 13.8, 21.5, 22.2, 27.2, 28.0, 63.7, 77.2, 123.4, 123.5, 125.3 (2 C), 129.5 (2 C), 137.1, 142.0.

Synthesis of (+)-(*E*)-(2*R*,3*R*,*S*$_S$)-3-*n*-Butyl-2-(*p*-tolylsulfinyl)-2-[2′-(hydroxymethyl)vinyl]oxirane, 33c. From NaH (6.9 mg, 0.29 mmol) in 1.8 mL of THF, with *t*-BuOOH (36 μL, 26 mg, 0.28 mmol) and a solution of sulfinyl diene **31c** (20 mg, 0.072 mmol) in 0.5 mL of THF, according to the general procedure (120 min), a 3:97 mixture of epoxy sulfone **32c** and epoxy sulfoxide **33c** and trace amounts of epoxy sulfoxide **34c** was obtained. Purification by chromatography (0−40% EtOAc−CH_2Cl_2) gave 17 mg (80%) of **33c** as a colorless oil. Data of **33c**: R_f = 0.23 (20% EtOAc−CH_2Cl_2). $[\alpha]^{20}_D$ = +173.5 (c = 0.22). ^{1}H NMR (300 MHz) δ 0.94 (t, 3 H, J = 7.1 Hz), 1.23−1.49 (m, 6 H), 2.37 (s, 3 H), 2.90 (s, 1 H), 3.63 (t, 1 H, J = 5.9 Hz), 4.09 (m, 2 H), 5.78 (m, 2 H), 7.25 (d, 2 H, J = 8.4 Hz), 7.46 (d, 2 H, J = 8.3 Hz). ^{13}C NMR (50 MHz) δ 13.8, 21.4, 22.2, 27.2, 28.0, 61.9, 62.2, 78.9, 116.8, 125.7 (2 C), 129.4 (2 C), 135.7, 139.6, 142.1. Partial data of **34c**: R_f = 0.16 (20% EtOAc−CH_2Cl_2). ^{1}H NMR (200 MHz) δ 2.39 (s, 3 H), 3.75 (t, 1 H, J = 5.9 Hz).

Synthesis of (+)-(2*R*,3*S*,*S*$_S$)-3-*n*-Butyl-2-(*p*-tolylsulfinyl)-2-vinyloxirane, 37a, and (−)-(2*S*,3*R*,*S*$_S$)-3-*n*-Butyl-2-(*p*-tolylsulfinyl)-2-vinyloxirane, 38a. From *t*-BuOOH (0.25 mL, 180 mg, 2.00 mmol) in 25 mL of THF, with *n*-BuLi (1.88 mL, 1.60 M, 2.51 mmol) and a solution of sulfinyl diene **35a** (125 mg, 0.50 mmol) in 5 mL of THF, according to the general procedure (2 h), a 77:23 mixture of epoxy sulfoxides **37a** and **38a** was obtained. Purification by chromatography (5−20% EtOAc−hexane) afforded 25 mg (19%) of **38a** and 85 mg (64%) of **37a** as colorless oils.

From NaH (19.2 mg, 0.84 mmol) in 4.2 mL of THF, with *t*-BuOOH (100 μL, 72 mg, 0.8 mmol) and a solution of sulfinyl diene **35a** (50 mg, 0.20 mmol) in 1.4 mL of THF, according to the general procedure (25 min), a 95:5 mixture of epoxy sulfoxides **37a** and **38a** was obtained. Purification by chromatography (5−30% EtOAc−hexane) afforded 41 mg (77%) of **37a** and 2 mg (4%) of **38a** as colorless oils. Data of **37a**: R_f = 0.18 (20% EtOAc−hexane). $[\alpha]^{20}_D$ = +17.1 (c = 1.67). ^{1}H NMR (200 MHz) δ 0.94 (t, 3 H, J = 7.2 Hz), 1.38−1.69 (m, 4 H), 1.95−2.06 (m, 2 H), 2.39 (s, 3 H), 3.06 (dd, 1 H, J = 7.0, 6.2 Hz), 5.31 (dd, 1 H, J = 10.5, 1.5 Hz), 5.35 (dd, 1 H, J = 17.1, 1.5 Hz), 5.78 (dd, 1 H, J = 17.1, 10.5 Hz), 7.31 (d, 2 H, J = 8.6 Hz), 7.49 (d, 2 H, J = 8.3 Hz). ^{13}C NMR (50 MHz) δ 13.9, 21.4, 22.3, 28.4, 29.1, 67.2, 79.3, 122.0, 124.9, (2 C), 126.8, 129.9 (2 C), 137.7, 141.9. Data of **38a**: R_f = 0.28 (20% EtOAc−hexane). $[\alpha]^{20}_D$ = −68.0 (c = 1.20). ^{1}H NMR (200 MHz) δ 0.96 (t, 3 H, J = 7.2 Hz), 1.44−1.68 (m, 4 H), 1.94−2.24 (m, 2 H), 2.38 (s, 3 H), 3.13 (dd, 1 H, J = 6.9, 5.6 Hz), 5.10 (dd, 1 H, J = 17.1, 1.6 Hz), 5.20 (dd, 1 H, J = 10.9, 1.6 Hz), 6.24 (dd, 1 H, J = 17.2, 10.9 Hz), 7.27 (d, 2 H, J = 8.5 Hz), 7.47 (d, 2 H, J = 8.3 Hz). ^{13}C NMR (50 MHz) δ 13.9, 21.4, 22.4, 28.1, 28.4, 69.2, 75.9, 119.9, 125.0 (2 C), 126.1, 129.4 (2 C), 136.5, 141.5.

Synthesis of (+)-(2*R*,3*S*)-3-*n*-Butyl-2-(*p*-tolylsulfonyl)-2-vinyloxirane, 36a. From *t*-BuOOH (65 μL, 47 mg, 0.52 mmol) in 6.5 mL of Et_2O, with *n*-BuLi (1.6 M, 0.40 mL, 0.65 mmol) and a solution of sulfinyl diene **35a** (32.3 mg, 0.13 mmol) in 1.3 mL of Et_2O, according to the general procedure (2 h) after chromatography (5−20% EtOAc−hexane), 33.3 mg (92%) of epoxy sulfone **36a** was obtained as a colorless oil. The optical purity of this sample of **36a** is estimated at 84% ee. Data of **36a**: R_f = 0.43 (30% EtOAc−hexane). **[**$\alpha]^{20}_D$ = +82.8 (c = 3.30). ^{1}H NMR (200 MHz) δ 0.95 (t, 3 H, J = 7.0 Hz), 1.35−1.65 (m, 4 H), 2.25−2.45 (m, 2 H), 2.42 (s, 3 H), 3.02 (t, 1 H, J = 6.3 Hz), 5.14 (dd, 2 H, J = 17.0, 10.6 Hz), 5.20 (dd, 1 H, J = 16.9, 1.3 Hz), 6.19 (dd, 1 H, J = 17.0, 10.6 Hz), 7.32 (d, 2 H, J = 8.3 Hz,), 7.73 (d, 2 H, J = 8.3 Hz). ^{13}C NMR (50 MHz) δ 13.8, 21.6, 22.5, 27.0, 29.1, 71.2, 76.4, 119.7, 129.2 (2 C), 129.5 (2 C), 129.8, 145.8.

Synthesis of (+)-(*E*)-(2*R*,3*S*,*S*$_S$)-3-*n*-Butyl-2-(*p*-tolylsulfinyl-2-[2′-(hydroxymethyl)vinyl]oxirane, 37b. From NaH (67 mg, 2.8 mmol) in 17.5 mL of THF, with *t*-BuOOH (0.35 mL, 252 mg, 2.8 mmol) and a solution of sulfinyl diene **35b** (195 mg, 0.7 mmol), in 5 mL of THF, according to the general procedure (90 min), a 98:2 mixture of epoxy sulfoxide **37b** and epoxy sulfone **36b** was obtained. Purification by chromatography (10−100% EtOAc−hexane) afforded 194 mg (94%) of **37b** as a colorless oil which solidified upon standing. Data of **37b**: mp: 66−68 °C (5% EtOAc−hexane). R_f = 0.23 (75% EtOAc−hexane). $[\alpha]^{20}_D$ = +122.0 (c = 1.09). ^{1}H NMR (300 MHz) δ 0.94 (t, 3 H, J = 7.1 Hz), 1.40−1.61 (m, 4 H), 1.98 (m, 2 H), 2.30−2.50 (br m, 1 H), 2.39 (s, 3 H), 3.06 (dd, 1 H, J = 7.2, 5.4 Hz), 4.04 (m, 2 H), 5.70 (dt, 1 H, J = 15.5, 1.7 Hz), 5.93 (dt, 1 H, J = 15.4, 4.6 Hz), 7.31 (d, 2 H, J = 8.1 Hz), 7.47 (d, 2 H, J = 8.2 Hz). ^{13}C NMR (50 MHz) δ 13.9, 21.5, 22.3, 28.6, 29.1, 62.3, 67.3, 79.3, 118.5, 124.8 (2 C), 130.0 (2 C), 137.5, 137.7, 142.1. Partial data of **36b**: R_f = 0.26 (75% EtOAc−

hexane). ^{1}H NMR (300 MHz) δ 2.38 (s, 3 H), 3.17 (dd, 1 H, J = 6.9, 5.7 Hz), 4.05 (m, 2 H), 7.76 (d, 2 H, J = 8.2 Hz).

Synthesis of (*Z*)-2-Vinyl-3-*n*-butyl-3-methyl-2-(*p*-tolylsulfonyl)oxirane, 36c, (+)-(2*S*,3*S*,S_S)-2-Vinyl-3-*n*-butyl-3-methyl-2-(*p*-tolylsulfinyl)oxirane, 37c, and (2*R*,3*R*,S_S)-2-Vinyl-3-*n*-butyl-3-methyl-2-(*p*-tolylsulfinyl)oxirane, 38c. From *t*-BuOOH (23 μL, 17 mg, 0.18 mmol) in 2 mL of THF with *n*-BuLi (1.58 M, 0.14 mL, 0.23 mmol) and a solution of (*Z*)-1-*n*-butyl-1-methyl-2-(*p*-tolylsulfinyl)-1,3-butadiene (12 mg, 0.046 mmol) in 0.5 mL of THF, according to the general procedure (24 h), a 12:58:28 mixture of sulfone **36c** and sulfoxides **37c** and **38c**, along with other uncharacterized byproducts.

From NaH (9.6 mg, 0.40 mmol) in 2 mL of THF, with *t*-BuOOH (50 μL, 36 mg, 0.40 mmol) and a solution of (*Z*)-1-*n*-butyl-1-methyl-2-(*p*-tolylsulfinyl)-1,3-butadiene (26 mg, 0.10 mmol) in 0.7 mL of THF, according to the general procedure (2 h 40 min), a 3:92:5 mixture of epoxy sulfone **36c** and epoxy sulfoxides **37c** and **38c** was obtained. Purification by chromatography (5−20% EtOAc−hexane) afforded 17 mg (60%) of **37c** as a colorless oil. Data of **36c**: R_f = 0.48 (20% EtOAc−hexane). ^{1}H NMR (300 MHz) δ 0.95 (t, 3 H, J = 7.2 Hz), 1.26 (s, 3 H), 1.37−1.65 (m, 4 H), 2.24−2.43 (m, 2 H), 2.41 (s, 3 H), 5.10 (dd, 1 H, J = 17.0, 1.5 Hz), 5.24 (dd, 1 H, J = 11.0, 1.4 Hz), 6.04 (dd, 1 H, J = 17.0, 11.0 Hz), 7.28 (d, 2 H, J = 8.5 Hz), 7.69 (d, 2 H, J = 8.4 Hz). ^{13}C NMR (50 MHz) δ 13.9, 20.2, 21.6, 22.8, 28.2, 32.5, 72.5, 81.6, 122.8, 128.9, 129.2 (2 C), 129.3 (2 C), 136.5, 144.7. Data of **37c**: R_f = 0.21 (20% EtOAc−hexane). $[\alpha]^{20}_D$ = +129.9 (c = 0.27). ^{1}H NMR (300 MHz) δ 0.96 (t, 3 H, J = 7.2 Hz), 1.22 (s, 3 H), 1.39−1.64 (m, 4 H), 1.94−2.17 (m, 2 H), 2.40 (s, 3 H), 5.36−5.54 (m, 3 H), 7.31 (d, 2 H, J = 8.0 Hz), 7.48 (d, 2 H, J = 8.3 Hz). ^{13}C NMR (50 MHz) δ 14.0, 18.3, 21.4, 22.8, 27.5, 33.7, 69.6, 85.2, 124.3, 124.8 (2 C), 128.9, 129.8 (2 C), 135.4, 141.6. Partial data of **38c**: ^{1}H NMR (200 MHz) δ 0.96 (t, 3 H, J = 7.1 Hz), 1.27 (s, 3 H), 1.35−1.80 (m, 4 H), 2.05−2.20 (m, 2 H), 2.37 (s, 3 H), 4.93 (dd, 1 H, J = 17.0, 1.8 Hz), 5.35 (dd, 1 H, J = 11.0, 1.8 Hz), 6.13 (dd, 1 H, J = 17.0, 11.0 Hz), 7.24 (d, 2 H, J = 8.1 Hz), 7.43 (d, 2 H, J = 8.2 Hz).

General Procedure for Oxidation of Epoxy Sulfoxides to Epoxy Sulfones. A round-bottomed flask was charged with methanol (ca. 5 mL/mmol), 1 equiv of epoxy sulfoxide, and 3 equiv of MMPP (80%). The mixture was stirred at room temperature until starting material disappearance, monitoring by TLC (7−48 h). The reaction was concentrated under reduced pressure to remove methanol, quenched with 5% aqueous $NaHCO_3$ (4 mL/mmol), and diluted with EtOAc (8 mL/mmol), the layers were separated, and the aqueous layer was extracted with EtOAc (three times). The combined organic extracts were washed with a saturated solution of NaCl (4 mL/mmol), dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure to give a crude product, which was purified by column chromatography on silica gel using the appropriate mixture of EtOAc−hexane.

Synthesis of (+)-(2*R*,3*S*)-3′-[(*tert*-Butyldiphenylsilyl)oxy]-1-(*p*-tolylsulfonyl)oxirane, 10g. From epoxy sulfoxide **11g** (13 mg, 0.025 mmol) in 1 mL of methanol and MMPP (46 mg, 0.075 mmol), according to the general procedure (24 h), an 80:20 mixture of epoxy sulfone **10g** and epoxy sulfoxide **11g** was obtained. Purification by chromatography (5−40% EtOAc−hexane) afforded 2 mg of epoxy sulfoxide **11g** and 8 mg of **10g** (70%) as a colorless oil. Data of **10g**: R_f = 0.70 (5% CH_2Cl_2-EtOAc). $[\alpha]^{20}_D$ = +37.8 (c = 0.87). ^{1}H NMR (300 MHz) δ 1.04 (s, 9 H), 1.82 (quint, 2 H, J = 6.3 Hz), 2.20−2.31 (m, 2 H), 2.44 (s, 3 H), 3.28 (ddd, 1 H, J = 7.3, 5.5, 3.9 Hz), 3.74 (t, 2 H, J = 6.2 Hz), 3.90 (dd, 1 H, J = 3.9, 0.5 Hz), 7.33−7.41 (m, 8 H), 7.63−7.80 (m, 4 H), 7.82 (d, 2 H, J = 8.1 Hz). ^{13}C NMR (50 MHz) δ 19.2, 21.6, 23.6, 26.9, 29.7, 61.1, 63.2, 68.9, 127.6 (2 C), 128.3 (2 C), 129.6 (2 C), 130.0 (2 C), 133.8, 135.6 (2 C), 145.4 (2 C).

Synthesis of (−)-(2*R*,3*R*)-3-*n*-Butyl-2-(*p*-tolylsulfonyl)-2-(2′-phenylvinyl)oxirane, 32b. From epoxy sulfoxide **33b** (10 mg, 0.03 mmol) in 0.3 mL of MeOH with MMPP (56 mg, 0.09 mmol), according to the general procedure and after purification by chromatography (5−20% EtOAc−hexane), **32b** was obtained (10 mg, 95%) as a white solid. Data of **32b**: mp: 81−83 °C (10% ether−hexane). R_f = 0.41 (20% EtOAc−hexane). $[\alpha]^{20}_D$ = −104.5 (c = 0.95). ^{1}H NMR (300 MHz) δ 0.86 (t, 3 H, J = 7.1 Hz), 1.31−1.53 (m, 6 H), 2.39 (s, 3 H,), 4.02 (t, 1 H, J = 5.9 Hz), 6.41 (d, 1 H, J = 16.0 Hz), 6.57 (d, 1 H, J = 16.0 Hz), 7.25−7.32 (m, 7 H), 7.70 (d, 2 H, J = 8.3 Hz). ^{13}C NMR (50 MHz) δ 13.9, 21.7, 22.2, 26.9, 28.0, 64.0, 76.6, 115.4, 126.9 (2 C), 128.7 (2 C), 128.9, 129.4 (2 C), 129.5 (2 C), 133.0, 135.1, 137.9, 145.1.

Synthesis of (+)-(2*R*,3*S*)-3-*n*-Butyl-2-(*p*-tolylsulfonyl)-2-vinyloxirane, 36a. A 25 mL round-bottomed flask was charged with epoxy sulfoxide **37a** (10 mg, 0.038 mmol) in 0.4 mL of MeOH, and the reaction mixture was cooled at 0 °C. Oxone (70 mg, 0.11 mmol) in 0.4 mL of H_2O was then added, and the resulting mixture was stirred at room temperature for 6 h. The reaction was then quenched with a saturated solution of NH_4Cl (0.5 mL) and diluted with EtOAc (4 mL), the layers were separated, and the organic layer was washed with a saturated solution of NaCl (1 mL). The combined aqueous layer was extracted with EtOAc (three times, 3 mL). The combined organic extracts were dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure to give a crude product which was purified by chromatography on silica gel (15−30% EtOAc−hexane) to give enantiomerically pure epoxy sulfone **36a** (5.9 mg, 68%). ($[\alpha]^{20}_D$ = +99.5 (c = 0.59).

Synthesis of (−)-(3*R*,4*R*,R_S)-3-Chloro-4-hydroxy-3-(*p*-tolylsulfinyl)octane, 41, and (−)-(3*R*,4*S*,R_S)-3-Chloro-4-hydroxy-3-(*p*-tolylsulfinyl)octane, 42. A 100 mL round-bottomed flask was charged with 24 mL of THF and *i*-Pr_2NH (0.40 mL, 291 mg, 2.88 mmol) and cooled to 0 °C. To the above solution was added *n*-BuLi (1.85 mL, 1.42 M, 2.63 mmol), and the resulting LDA solution (ca. 0.1 M) was stirred at 0 °C for 15 min and then cooled to −78 °C. After 10 min, a solution of 1 equiv of chloro sulfoxide **40** (500 mg, 2.40 mmol) in 12 mL of THF, previously dried over 4 Å sieves, was added dropwise to produce a pale orange solution. After stirring for 10 min at −78 °C, 1.1 equiv of *n*-pentanal (0.30 mL, 226 mg, 2.63 mmol) was added dropwise, and the resulting colorless solution was stirred at −78 °C for 10 min. The reaction mixture was quenched with a saturated solution of NH_4Cl (10 mL) and diluted with EtOAc (24 mL), the layers were separated, and the organic layer was washed with a saturated solution of NaCl (12 mL). The aqueous layer was extracted with EtOAc (three times, 20 mL), and the combined organic extracts were dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure to give a 54:46 mixture of chlorohydrins **41** and **42** which was purified by column chromatography on silica gel (15−30% EtOAc−hexane) affording 266 mg (38%) of **41** as a white solid, 313 mg (45%) of **42** as a colorless oil and 22.8 mg of **40**. Data of **41**: mp: 71−72 °C (Hexane). R_f = 0.40 (30% EtOAc−hexane). $[\alpha]^{20}_D$ = −113.6 (c = 5.15). ^{1}H NMR (200 MHz) δ 0.82 (t, 3 H, J = 7.3 Hz), 1.33 (t, 3 H, J = 7.0 Hz), 1.18−1.60 (m, 6 H), 2.39 (dq, 1 H, J = 15.4, 7.7 Hz), 2.44 (s, 3 H), 2.76 (dq, 1 H, J = 15.4, 7.2 Hz), 3.82 (d, 1 H, J = 6.9 Hz), 4.85 (br s, 1 H), 7.35 (d, 2 H, J = 8.3 Hz), 7.68 (d, 2 H, J = 8.0 Hz). ^{13}C NMR (50 MHz) δ 8.3, 13.9, 21.5, 22.4, 24.1, 28.1, 31.7, 76.0, 85.1, 12.7 (2 C), 129.4 (2 C), 133.0, 143.1. Data of **42**: R_f = 0.32 (30% EtOAc−hexane). $[\alpha]^{20}_D$ = −84.4 (c = 4.10). ^{1}H NMR (200 MHz) δ 0.88 (t, 3 H, J = 6.8 Hz), 1.15 (t, 3 H, J = 7.4 Hz), 1.22−1.58 (m, 6 H), 2.02−2.12 (m, 2 H), 2.41 (s, 3 H), 2.59 (m, 1 H), 3.77 (ddd, 1 H, J = 10.0, 4.5, 1.9 Hz), 7.30 (d, 2 H, J = 8.3 Hz), 7.63 (d, 2 H, J = 8.0 Hz). ^{13}C NMR (50 MHz) δ 9.0, 13.9, 21.3, 22.4, 25.4, 28.4, 31.7, 74.5, 93.8, 126.9 (2 C), 129.2 (2 C), 134.8, 142.5.

General Procedure for the Synthesis of Sulfinyl Oxiranes from Sulfinyl Chlorohydrins. A 25 mL round-bottomed flask was charged with a solution of the chlorohydrin in THF (ca. 0.1 M), and the solution was cooled to 0 °C. A suspension of 2.5 equiv of *t*-BuOK in THF was then added, and the resulting yellow solution was stirred for 2 h, after which time it was quenched with a saturated solution of NH_4Cl (4 mL/mmol) and diluted with EtOAc (8 mL/mmol), the layers were separated, and the organic layer was washed with a saturated solution of NaCl (4 mL/mmol). The combined

aqueous layers were extracted with EtOAc (three times, 10 mL/mmol), and the combined organic extracts were dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure to give a crude product which was purified by column chromatography on silica gel (10−30% EtOAc−hexane).

Synthesis of (−)-(2*R*,3*R*,R_S)-3-*n*-Butyl-2-ethyl-2-(*p*-tolylsulfinyl)oxirane, 44. From chlorohydrin **42** (220 mg, 0.66 mmol) in 6.6 mL of THF, with *t*-BuOK (185 mg, 1.65 mmol), according to the general procedure, epoxide **44** (143 mg, 81%) was obtained as a colorless oil. Data of **44**: R_f = 0.35 (30% EtOAc−hexane). $[\alpha]^{20}_D$ = −53.6 (*c* = 2.02). ^{1}H NMR (300 MHz) δ 0.83 (t, 3 H, *J* = 7.7 Hz), 0.88 (t, 3 H, *J* = 7.1 Hz), 1.25−1.65 (m, 7 H), 1.81 (m, 1 H), 2.40 (s, 3 H), 3.62 (t, 1 H, *J* = 6.2 Hz), 7.27 (d, 2 H, *J* = 8.0 Hz), 7.42 (d, 2 H, *J* = 8.2 Hz,). ^{13}C NMR (50 MHz) δ 9.2, 13.7, 17.3, 21.2, 22.1, 27.5, 28.2, 60.1, 77.5, 125.2 (2 C), 129.6 (2 C), 137.3, 141.9.

General Procedure for Reduction of 2-Vinyl-2-sulfinyloxiranes. A 25 mL round-bottomed flask was charged with a solution of 1 equiv of the vinyl sulfinyl oxirane in DME (ca. 0.1 M), and 7.2 equiv of $TsNHNH_2$ was added, followed by a solution of 9.5 equiv of NaOAc in H_2O (0.2 mL/mmol). The resulting mixture was refluxed for 2 h and stirred at room temperature for 12 h, after which time it was diluted with CH_2Cl_2 (5 mL/mmol), and the layers were separated. The organic layer was washed with a saturated solution of NaCl, dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure to give a crude product which was purified by column chromatography on silica gel (5−30% EtOAc−hexane).

Synthesis of (+)-(2*S*,3*S*,S_S)-3-*n*-Butyl-2-ethyl-2-(*p*-tolylsulfinyl)oxirane, *ent*-44. From vinyl sulfinyl epoxide **34a** (30 mg, 0.11 mmol) in 1 mL of DME, with $TsNHNH_2$ (151.9 mg, 0.81 mmol) and NaOAc (86.5 mg, 1.08 mmol) in 0.5 mL of H_2O, according to the general procedure, epoxide *ent*-**44** (19.6 mg, 63%) was obtained as a colorless oil. Data of *ent*-**44**: R_f = 0.35 (30% EtOAc−hexane). $[\alpha]^{20}_D$ = +52.1 (*c* = 1.26). ^{1}H NMR (200 MHz) δ 0.83 (t, 3 H, *J* = 7.6 Hz), 0.87 (t, 3 H, *J* = 7.0 Hz), 1.25−1.65 (m, 7 H), 1.81 (m, 1 H), 2.40 (s, 3 H), 3.62 (t, 1 H, *J* = 6.2 Hz), 7.27 (d, 2 H, *J* = 8.0 Hz), 7.42 (d, 2 H, *J* = 8.3 Hz). ^{13}C NMR (50 MHz) δ 9.3, 13.8, 17.4, 21.4, 22.3, 27.7, 28.4, 60.5, 77.6, 125.4 (2 C), 129.8 (2 C), 137.5, 142.1.

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Supporting Information Available: Experimental procedures and spectroscopic data for all new compounds and X-ray diffraction analyses data for **7d** and **11a** (51 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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