A Tellurium Transposition Route to Allylic Alcohols: Overcoming Some Limitations of the Sharpless-Katsuki Asymmetric Epoxidation[1,2]

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Good yields of enantiomeric allylic alcohols can be obtained in high enantiomeric excess (ee) by combining the Sharpless-Katsuki asymmetric epoxidation process (SAE) with tellurium chemistry. The advantages of the tellurium process are as follows: (1) the 50% yield limitation on the allylic alcohol in the Sharpless kinetic resolution (SKR) can be overcome; (2) allylic tertiary alcohols which are unsatisfactory substrates in the SKR can be obtained in high optical purity; (3) optically active secondary allylic alcohols with tertiary alkyl substituents (e.g. *tert*-butyl) at C-1 can be obtained in high ee; (4) optically active sterically congested cis secondary alcohols can be obtained in high ee; and (5) the nuisance of the slow SAE of some vinyl carbinols can be avoided. The key step in the reaction sequence is either a stereospecific 1,3-transposition of double bond and alcohol functionalities or an inversion of the alcohol configuration with concomitant deoxygenation of the epoxide function in epoxy alcohols. Trans secondary allylic alcohols can be converted to cis secondary allylic alcohols by way of erythro epoxy alcohols (glycidols); threo glycidyl derivatives are converted to trans secondary allylic alcohols. These transformations are accomplished by the action of telluride ion, generated in situ from the element, on a glycidyl sulfonate ester. Reduction of elemental Te is conveniently done with rongalite ($HOCH_2SO_2Na$) in an aqueous medium. This method is satisfactory when Te^{2-} is required to attack a primary carbon site of a glycidyl sulfonate. In cases where Te^{2-} is required to attack a secondary carbon site, reduction of the tellurium must be done with $NaBH_4$ or $LiEt_3BH$. Elemental tellurium is precipitated during the course of the reactions and can be recovered and reused.

Introduction

The Sharpless-Katsuki asymmetric epoxidation (SAE)[3] and the Sharpless kinetic resolution (SKR)[4] processes allow the synthesis of a variety of optically active allylic alcohols and their epoxides in high enantiomeric excess (ee).[5] These compounds are useful in synthesis when only a single enantiomer or diastereomer is desired.[5c,6]

The SAE and SKR procedures are among the most important and widely used in asymmetric synthesis.[7] Several limitations, however, have been noted:[5] (1) as in all resolutions, yields of one enantiomeric allylic alcohol in the SKR are confined to a maximum of 50%; (2) failure is encountered in the SKR of tertiary allylic alcohols which do not bind well to the asymmetric tartrate-titanium catalyst and which also are prone to Lewis acid catalyzed decomposition via carbocations; (3) kinetic resolutions are not effective for allylic alcohols with *tert*-alkyl groups on the carbinol carbon atom; (4) kinetic resolutions for sterically congested, cis secondary allylic alcohols are slow and may give low ee; (5) monosubstituted vinyl carbinols epoxidize slowly, and days, not hours, may be required for complete reaction of the monosubstituted double bond under the catalytic conditions that are used to ensure a high ee. This last limitation is exemplified by the slow epoxidation and small k_{rel} of phenylvinylcarbinol (1-phenyl-2-propen-1-ol),[5d] although the SKR is successful.[8]

The strategy for circumventing these limitations involves tellurium-catalyzed reactions of glycidyl tosylates or mesylates analogous to conditions that we used earlier in the synthesis of 2-substituted allylic alcohols from epichlorohydrins and telluride or selenide ions.[9a,b] Some extensions of this previous work have been described briefly.[2,10] Tellurium is employed as the relatively nontoxic element[11] which is reduced in situ and treated with the appropriate organic reactants to give the desired allylic

(1) Taken in part from Discordia, R. P. Ph.D. Thesis, Syracuse University, 1990. Murphy, C. K. M.S. Thesis, Syracuse University, 1990.

(2) Preliminary reports were given at the following meetings of the American Chemical Society: (a) 198th, Miami Beach, FL, Sept 10-15, 1989, ORGN 147; (b) 199th, Boston, MA, April 22-27, 1990, ORGN 338; (c) 203rd, San Francisco, CA, April 5-10, 1992, ORGN 0291; (d) 204th, Washington, D.C., Aug 23-28, 1992, ORGN 0207, 0208.

(3) Katsuki, T.; Sharpless, K. B. *J. Am. Chem. Soc.* **1980**, *102*, 5974-5976.

(4) Martin, V. S.; Woodard, S. S.; Katsuki, T.; Yamada, Y.; Ikeda, M.; Sharpless, K. B. *J. Am. Chem. Soc.* **1981**, *103*, 6237-6240.

(5) (a) Gao, Y.; Hanson, R. M.; Klunder, J. M.; Ko, S. Y.; Masamune, H.; Sharpless, K. B. *J. Am. Chem. Soc.* **1987**, *109*, 5765-5780. (b) Johnson, R. A.; Sharpless, K. B. *Comprehensive Organic Synthesis*; Trost, B. M., Ed.; Pergamon: Oxford, 1991; Vol. 7, Chapter 3.2. We thank Professor Sharpless for providing us with a copy in advance of publication. (c) Rossiter, B. *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic Press: New York, 1985, Vol. 5, pp 193-246. (d) Finn, M. G.; Sharpless, K. B. *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic Press: New York, 1985; Vol. 5, pp 247-308.

(6) Sharpless, K. B.; Behrens, C. H.; Katsuki, T.; Lee, A. W. M.; Martin, V. S.; Takatani, M.; Viti, S. M.; Walker, F. J.; Woodard, S. S. *Pure Appl. Chem.* **1983**, *55*, 589-604.

(7) The SAE and SKR processes involved in our work utilize *tert*-butyl hydroperoxide (TBHP), titanium isopropoxide, either (+)- or (-)-diisopropyl tartrate (DIPT) or diethyl tartrate (DET), and 4A molecular sieves in dichloromethane as described in detail in ref 5a.

(8) Davis, F. A.; Thimma Reddy, R. *J. Org. Chem.* **1992**, *57*, 2599-2606.

(9) (a) Polson, G.; Dittmer, D. C. *Tetrahedron Lett.* **1986**, *27*, 5579-5582. (b) Polson, G. Ph.D. Thesis, Syracuse University, 1987.

(10) (a) Discordia, R. P.; Dittmer, D. C. *J. Org. Chem.* **1990**, *55*, 1414-1415. (b) Discordia, R. P.; Murphy, C. K.; Dittmer, D. C. *Tetrahedron Lett.* **1990**, *31*, 5603-5606. (c) Discordia, R. P.; Dittmer, D. C. U.S. Pat. 4,935,451, June 19, 1990; *Chem. Abstr.* **1990**, *113*, 190736. (d) Dittmer, D. C.; Murphy, C. K.; Discordia, R. P. U.S. Pat. 5,087,773, Feb 11, 1992; *Chem. Abstr.* **1992**, *116*, 235070.

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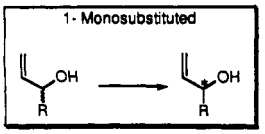
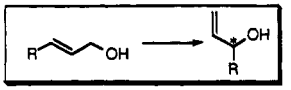
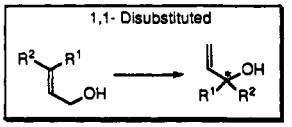
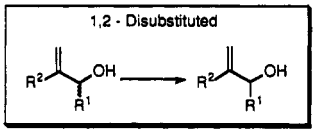
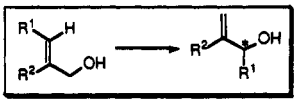
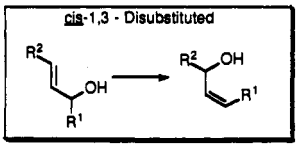
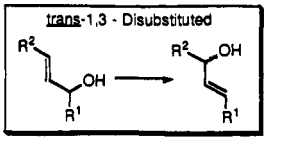
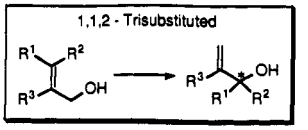
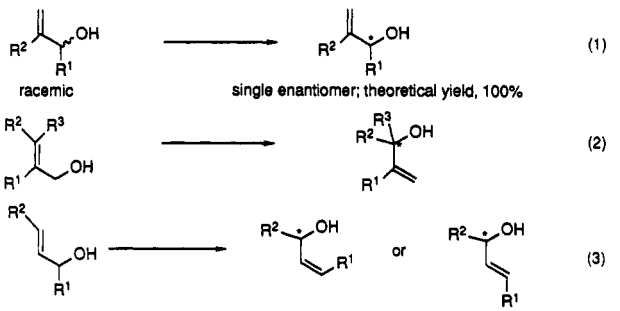
Table I. Tellurium-Mediated Syntheses of Allylic Alcohols

entry	configuration[a]	overall yield, %	% ee[b]
	1-Monosubstituted 		
1	R = $PhCH_2CH_2$	(S)	75	92
			
2	R = n-C_5H_{11} [3a]	(R)	88	>95
3	R = n-C_6H_{13} [3b]	(R)	88	>95
4	R = Ph [3c]	(R)	69	90
5	R = $PhCH_2OCH_2$ [(±)-3d]	(±)[c]	82	-
6	R = $PhCH_2OCH_2$ [(-)-3d]	(S)	60	91
7	R = $PhCH_2OCH_2$ [(+)-3d]	(R)	56	90
8	R = tert-Bu [(+)-3e]	(R)	47	>95
	1,1-Disubstituted 		
9	R^1 = Me; R^2 = $(Me)_2C{=}CHCH_2CH_2$ [(+)-8a]	(S)	56	95
10	R^1 = Me; R^2 = $(Me)_2C{=}CHCH_2CH_2$ [(-)-8b]	(R)	54	95
11	R^1 = Me; R^2 = $(Me)_2C{=}CH(CH_2)_2$-$C(CH_3){=}CH(CH_2)_2$ [8c]	(S)	86	>95
	1,2-Disubstituted 		
12	R^1 = Et; R^2 = Me [6a]	(R)	78	>95
13	R^1 = n-C_4H_9; R^2 = Me [6b]	(R)	88	94
14	R^1 = $(CH_3)_2C{=}CHCH_2$; R^2 = Me [6c]	(R)	79	92
15	R^1 = $CH_2{=}CH(CH_2)_3$; R^2 = Et [6d]	(R)	82	95
			
16	R^1 = Ph; R^2 = Me [11a]	(S)	65	>95
17	R^1 = $(Me)_2C{=}CHCH_2$; R^2 = Me [(-)-11b]	(S)	38	82[d]
18	R^1 = $(Me)_2C{=}CHCH_2$; R^2 = Me [(+)-11b]	(R)	49	82[d]
19	R^1, R^2 = $(CH_2)_4$ [11c]	(S)	40	89
	cis-1,3-Disubstituted 		
20	R^1 = c-C_6H_{11}; R^2 = Me [15a+16a]	(±)	31[e]	-
21	R^1 = R^2 = c-C_6H_{11} [15b]	(S)	30[e]	>95
22	R^1 = n-C_6H_{13}; R^2 = Et [16c]	(R)	34[e]	>95
23	R^1 = Me; R^2 = n-C_5H_{11} [15d+16d]	(±)	21[e]	-
24	R^1 = R^2 = n-Pr [15e+16e]	(±)	22[e]	-
25	R^1 = $CH_2{=}CHCH_2$; R^2 = Me [15f+16f]	(±)	23[e]	-
	trans-1,3-Disubstituted 		
26	R^1 = c-C_6H_{11}; R^2 = Me [18a]	(±)	34[e]	-
27	R^1 = Me; R^2 = n-C_6H_{11} [18b]	(±)	39[e]	-
28	R^1 = R^2 = n-Pr [18c]	(±)	22[e]	-
29	R^1 = $CH_2{=}CHCH_2$, R^2 = Me [18d]	(±)	43[e]	-
	1,1,2-Trisubstituted 		
30	R^1 = Ph; R^2 = $PhCH_2$; R^3 = Me [23]	(S)	39	93

[a] Configuration assignment is based on the rules for asymmetric epoxidation.[5] [b] Determined by ^1H NMR of MTPA ester or by use of chiral NMR shift reagent. [c] Obtained via epoxidation with m-CPBA. [d] The E starting allylic alcohol was contaminated with 6% of the Z isomer. [e] When a SKR is involved, the maximum theoretical yield is 50%. When an m-CPBA oxidation is used, the yield depends on the ratio of erythro and threo isomers of the epoxy alcohol. For a 1:1 ratio the maximum yield for a Z or an E product is also 50%.

alcohol product. Elemental tellurium is precipitated during the reaction and is recovered and reused. Table I summarizes the results of the synthesis of allylic alcohols by category. The discussion is organized according to substitution pattern. There are three distinct overall processes that install a stereogenic center, two of which are 1,3-transpositions.



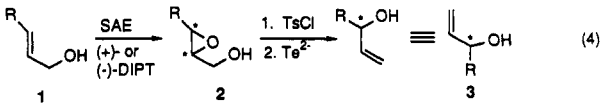
Results and Discussion

1-Monosubstituted Allylic Alcohols (Table I, Entries 1–8). Vinylcarbinols react slowly in the electrophilic SKR process, and a desired enantiomeric allylic alcohol is obtainable only in a yield of 50% or less (limitations 1 and 5 above). These alcohols can now be obtained in high optical purity from readily available 3-substituted, trans allylic alcohols, **1**, in a theoretical yield of 100%. This is accomplished by application of the relatively fast SAE process followed by conversion of the epoxy alcohol to its tosylate and treatment with telluride ion (Te^{2-}), produced in situ from tellurium and a reducing agent, to give a single enantiomer of a 1-monosubstituted allylic alcohol. The reducing agent is the inexpensive rongalite (sodium hydroxymethanesulfinate or sodium formaldehyde sulfoxylate dihydrate).[12] The ee's are high, being limited by the stereospecificity of the epoxidation step. Thus,

(11) (a) Sax, N. I.; Lewis, R. J. *Dangerous Properties of Industrial Materials*; Van Nostrand Reinhold: New York, 1989, Vol. III; p 3131. (b) Sittig, M. *Handbook of Toxic and Hazardous Chemicals and Carcinogens*, 2nd ed.; Noyes: Park Ridge, NJ, 1985; pp 828–829.

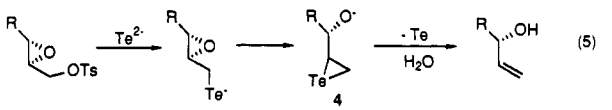
(12) (a) Obtainable from The Eastman Kodak Co., or the Aldrich Chemical Co. (b) Reduction of Te by rongalite: Tschugaeff, L.; Chlopin, W. *Ber.* 1914, *47*, 1269–1275.

1-nonen-3-ol (2, R = n-C_6H_{13}), previously obtained in unspecified yield and >96% ee after a 12-day SKR,[4] is obtained by the SAE–Te process in 88% overall yield and >95% ee after only a 30-h SAE at −30 °C [with (+)-diisopropyl tartrate (DIPT)] and a 9-h tellurium reaction. It should be noted that use of dicyclododecyl tartrate esters and 1.5 equiv of TBHP in the SKR is reported to give a faster epoxidation (2.5 days for 1-nonen-3-ol).[5a]



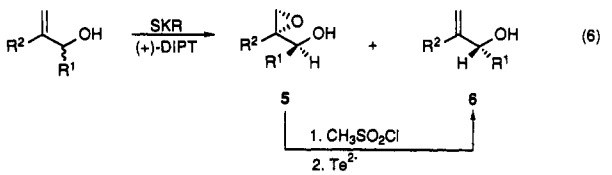
(4)

The overall reaction involves a stereospecific 1,3-allylic transposition of the OH group and the double bond. This rearrangement may be rationalized as proceeding by an attack of telluride ion at the tosylate carbon atom. The formation of an epitelluride 4 is conjectural, but such intermediates have been suggested in solution chemistry;[13a-e] their formation is indicated in the gas phase from tellurium atoms and ethylene.[13f] A telluradistannirane recently has been obtained that is stable below its melting point (175 °C).[13g] The process involving telluride ion may be called *nucleophilic reduction*[14a-g] and is analogous to the Payne rearrangement.[14h] Instead of oxygen, the tellurium atom functions as the nucleophile to effect intramolecular ring opening of the epoxide. The tellurium reaction is unique because the purported epitelluride is unstable with respect to loss of elemental Te whereas in the Payne rearrangement the newly created epoxide ring is stable.



(5)

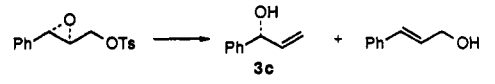
Entry 1 (eq 6, R^1 = $PhCH_2CH_2$, R^2 = H) in Table I (also entries 12–15) exemplifies our earlier method for obtaining 1- (or 1,2-) substituted allylic alcohols in high optical purity with a theoretical yield of 100%.[10a,c] Attack by Te^{2-} at the less hindered terminal epoxide carbon atom apparently is involved.



(6)

Compound 3 where R = n-C_5H_{11} (Table I, entry 2) is called "matsutake alcohol" because it is the chief constituent of the fragrance of the prized mushroom, *Tricholoma matsutake*.[15] The (*R*)-(−)-enantiomer has an intense mushroom-like odor whereas the (*S*)-(+)-isomer is said to have an herbaceous odor and less intense mushroom character.[16] The only previous synthesis of (*R*)-(−)-"matsutake alcohol" utilized (*R*)-pantolactone;[17] an overall yield of 41% was obtained as compared with our yield of 88%. Entries 5 and 7 in Table I contrast racemic and asymmetric syntheses from a trans precursor. Opposite stereochemistry should result from cis allylic alcohols, but these are epoxidized more slowly and the enantiofacial selectivity is more variable.[5]

Table II. Conditions for Transposition of Epoxycinnamyl Tosylate



conditions	yields (% ee) 3c	3-phenyl-2-propen-1-ol
Te, $HOCH_2SO_2Na$, NaOH, H_2O, rt	48 (>90)	32
Te, $HOCH_2SO_2Na$, NaOH, H_2O, β-cyclodextrin, rt	73 (>90)	7
Te, $NaBH_4$, DMF, rt, N_2	60 (>90)	5
Te, $LiEt_3BH$, THF, n-$Bu_4N^+F^-$, rt	78 (>90)	1.6

The transposition of the epoxy tosylate from cinnamyl alcohol is a special challenge. Contributions from the relatively stable benzyl carbocation to a transition state[18] involving telluride attack at C-3 may be sufficient to alter the regiochemistry and stereochemistry. Table II shows the effect of various reaction conditions on the regiochemistry. Entry 4 in Table I corresponds to the best result in Table II for selective attack by telluride ion at C-1 achieved by use of a Te–$LiEt_3BH$–n-$Bu_4N^+F^-$ system in THF to perform the transposition. The tellurium–rongalite reagent alone gives low regioselectivity probably because the aqueous medium enhances the contribution of a carbocation intermediate; but the ee (>90%) of the transposition product, 1-phenyl-2-propen-1-ol, is satisfactory. The addition of β-cyclodextrin to the Te–rongalite system improves the regioselectivity, possibly by complexing with the phenyl ring to hinder attack at C-3[19a] or by complexing with the *p*-tolyl ring to increase the leaving group ability of the tosyl group. The latter seems more important since substitution of a mesylate for a tosylate gave a reaction mixture showing at least four components by TLC. When Te is reduced by boron hydrides, boranes may be produced as byproducts. Addition of F^- to the $LiEt_3BH$–Te reduction mixture may be expected to remove Et_3B and, thus, suppress side reactions catalyzed by the borane. Omission of fluoride ion resulted in a complex mixture including carbonyl-containing products. The borane or diborane produced with $NaBH_4$–Te in DMF

(13) (a) Clive, D. L. J.; Menchen, S. M. *J. Org. Chem.* **1980**, *45*, 2347–2354. (b) Bäckvall, J.-E.; Engman, L. *Tetrahedron Lett.* **1981**, *22*, 1919–1922. (c) Clive, D. L. J.; Beaulieu, P. L. *J. Org. Chem.* **1982**, *47*, 1124–1126. (d) Barton, D. H. R.; Fekih, A.; Lusinchi, X. *Tetrahedron Lett.* **1985**, *26*, 6197–6200. (e) Zingaro, R. A.; Herrera, C. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 1382–1384. (f) Connor, J.; Greig, G.; Strausz, O. P. *J. Am. Chem. Soc.* **1969**, *91*, 5695–5696. (g) Schäfer, A.; Weidenbruch, M.; Saak, W.; Pohl, S.; Marsmann, H. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 834–836.

(14) (a) We are indebted to Dr. Douglas A. Livingstone for suggesting this terminology. Some other examples of nucleophilic reductions involving Te: (b) Yamashita, M.; Kato, Y.; Suemitsu, R. *Chem. Lett.* **1980**, 847–848. (c) Kambe, N.; Kondo, K.; Morita, S.; Murai, S.; Sonoda, N. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 1009. (d) Osuka, A.; Suzuki, H. *Chem. Lett.* **1983**, 119–120. (e) Osuka, A.; Taka-oka, K.; Suzuki, H. *Chem. Lett.* **1984**, 271–272. (f) Barton, D. H. R.; Fekih, A.; Lusinchi, X. *Tetrahedron Lett.* **1985**, *26*, 3693–3696. (g) Huang, X.; Pi, J.-H. *Synth. Commun.* **1990**, *20*, 2297–2300. (h) Payne, G. B. *J. Org. Chem.* **1962**, *27*, 3819–3822.

(15) Wood, W. F.; Fesler, M. *J. Chem. Ed.* **1986**, *63*, 92.

(16) Mosandl, A.; Heusinger, G.; Gessner, M. *J. Agric. Food Chem.* **1986**, *34*, 122–126.

(17) Helmchen, G.; Ihrig, K.; Schindler, H. *Tetrahedron Lett.* **1987**, *28*, 183–186.

(18) (a) Pross, A. *Adv. Phys. Org. Chem.* **1985**, *21*, 99–196. (b) Pross, A. *Acc. Chem. Res.* **1985**, *18*, 212–219. (c) Pross, A.; Shaik, S. S. *Acc. Chem. Res.* **1983**, *16*, 363–370. (d) Shaik, S. S. *J. Am. Chem. Soc.* **1983**, *105*, 4359–4367.

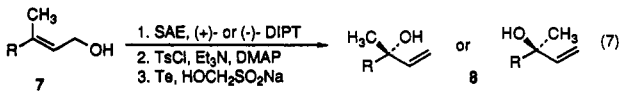
(19) (a) Cyclodextrins have been used to improve regioselectivity of nucleophilic ring opening of styrene oxide: Hu, Y.; Uno, M.; Haroda, A.; Takahashi, S. *Chem. Lett.* **1990**, 797–798. (b) Brown, H. C.; Heim, P. *J. Org. Chem.* **1973**, *38*, 912–916. (c) Burgess, K.; Jennings, L. D. *J. Am. Chem. Soc.* **1991**, *113*, 6129–6139. (d) Burgess, K.; Jennings, L. D. *J. Am. Chem. Soc.* **1990**, *112*, 7434–7436.

may be rendered inactive by reaction with the solvent since amides are readily reduced.[19b] The nitrogen stream also may have helped in removal of the borane. The obtention of enantiomerically enriched 1-phenyl-2-propen-1-ol by a biological resolution via the acetate has been successful.[19c,d] Interestingly, the methyl-substituted cinnamyl system (Table I, entry 16) posed no particular problem in the SAE–Te–rongalite process.

The kinetic resolution of allylic alcohol **3e** (R = *t*-Bu) yielded product of only 10% ee, prompting Schweiter and Sharpless to observe that "...resolution is evidently not effective for allylic alcohols with *tert*-alkyl groups on the carbinol carbon".[20a] The SAE–Te process gives **3e** in high ee (Table I, entry 8).

An alternative synthesis of 1-substituted allylic alcohols involves the addition of divinylzinc to aldehydes catalyzed by chiral ligands derived from camphor-10-sulfonic acid.[20b] (*S*)-1-Phenyl-2-propen-1-ol was obtained in 96% yield and 87% ee by this method, and good yields and high ee were reported for (*R*)-1-nonen-3-ol, (*R*)-1-octen-3-ol, and (*S*)-1-cyclohexyl-2-propen-1-ol.[20b] Asymmetric alkylations of acrolein and methacrolein with dimethyl- and diethylzinc also yield optically active allylic alcohols.[20k]

1,1-Disubstituted Allylic Alcohols (Table I, Entries 9–11). Tertiary allylic alcohols are generally unsatisfactory substrates for the SKR (limitation 2 above)[5b] although two examples of the SAE process applied to tertiary allylic alcohols have been reported.[20c–e] These alcohols are ideal targets for the SAE–Te transposition process starting with 3,3-disubstituted primary allylic alcohols. The only limitation on this method would appear to be the size of the substituent cis to the CH_2OH function. The SAE does not work well with bulky cis groups,[5c] but a *cis*-benzyl group gave good results when (–)-DET was used.[20f] Both (+)-[10b] and (–)-linalool and (+)-nerolidol have been obtained in good yield and ee from geraniol and *trans,trans*-farnesol, respectively. Previously, enantiomerically pure (3*R*)-(–)-linalool had been prepared in nine steps from a resolved precursor[20g] and a route to pure (3*S*)-(+)-linalool had been reported that involves six steps from a chiral template.[20h] (+)-Linalool in combination with *m*- and *p*-cresols is the male sex pheromone of the cabbage looper moth.[20i] (3*R*)-(–)-Linalool is an intermediate in the synthesis of (3*R*)-(–)-frontalin, an aggregation pheromone of the southern pine beetle.[20j]



7 8 (7)

1,2-Disubstituted Allylic Alcohols (Table I, Entries 12–19). Our earlier work on the reactions of epichlorohydrins did not demonstrate conclusively the regiochemistry of telluride attack; i.e. did Te^{2-} react at the chloromethyl group or at one of the carbon atoms of the oxirane ring?[9a] Results with deuterium-labeled epoxy tosylate **9** are best explained by attack at the terminal oxirane carbon (Scheme I).

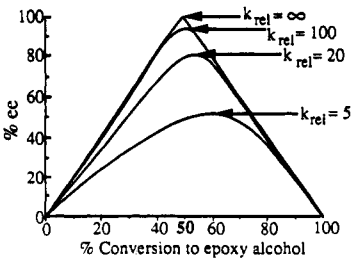
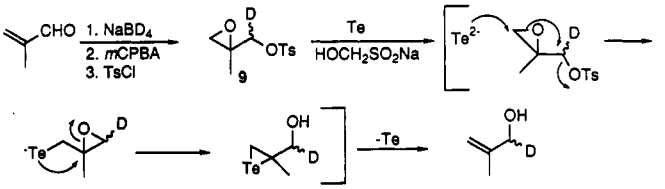


Figure 1. Maximum achievable enantiomeric excess of allylic alcohol as a function of the extent of epoxidation in the SKR–Te transposition process applied to secondary allylic alcohols with a terminal double bond (eq 6).

Scheme I



The mechanism of Scheme I implies an inversion at the tosylate carbon atom. This was confirmed by applying the tellurium nucleophilic reduction to optically active 1,2-disubstituted glycidyl alcohol derivatives obtained via the SKR process. As we reported earlier,[10a] the Sharpless method coupled with the Te-catalyzed conversion of glycidyl mesylates or tosylates enables one to obtain a single enantiomer in good yield and high ee (eq 6; Table I, entries 12–15), thus circumventing the limitation of 50% imposed on the yield by a resolution process alone (limitation 1 above).

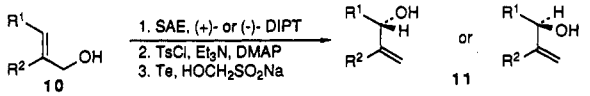
The ee of the allylic alcohol is determined by the SKR process, no loss in ee being observed in the Te reaction. In the SKR, highest ee's of less reactive allylic alcohols are obtained by allowing the epoxidation to go well beyond 50% at the expense of the yield of the allylic alcohol. However, permitting the reaction of eq 6 to go beyond 50% epoxidation in order to maximize the ee of the allylic alcohol **6** results in a lower ee of the epoxy alcohol, **5**. Since **5** is converted to **6** by the Te–rongalite reagent, little latitude can be permitted in the percent conversion of racemic allylic alcohol to optically active epoxide if a high ee for **6** is desired. The SKR–Te process is sensitive to k_{rel}, the ratio of rate constants for asymmetric epoxidation of the fast-reacting to the slow-reacting enantiomeric allylic alcohol.[5] Figure 1 shows the dependence of the ee on the percent conversion to epoxide. It differs from an earlier graph by Sharpless and coworkers[4,5c,21] in that the ee applies to the *total* allylic alcohol, which consists of the alcohol that is unreacted after the SKR combined with the alcohol resulting from treatment of the glycidyl mesylate with Te^{2-}. The overall ee's and yields are given in Table I (entries 12–15). An ee of 90% or greater for **6** is obtainable from racemic allylic alcohol when $k_{rel} \geq 100$.

The SAE–Te transposition procedure described for the synthesis of 1-mono- and 1,1-disubstituted allylic alcohols, in contrast to the SKR–Te process of eq 6, is attractive because no kinetic resolution is required. The problem of when to stop the epoxidation–resolution in order to maximize ee (see Figure 1) and the tedious monitoring of

(20) (a) Schweiter, M. J.; Sharpless, K. B. *Tetrahedron Lett.* **1985**, *26*, 2543–2546. (b) Oppolzer, W.; Radinov, R. N. *Tetrahedron Lett.* **1988**, *29*, 5645–5648. (c) Wang, Z.; Zhou, W. *Tetrahedron* **1987**, *43*, 2935–2944. (d) Wang, Z.; Zhou, W. *Synth. Commun.* **1989**, *19*, 2627–2632. (e) Takano, S.; Iwabuchi, Y.; Ogasawara, K. *Tetrahedron Lett.* **1991**, *32*, 3527–3528. (f) Erickson, T. J. *J. Org. Chem.* **1986**, *51*, 934–935. (g) Barner, R.; Hübscher, J. *Helv. Chim. Acta* **1983**, *66*, 880–890. (h) Ohwa, M.; Kogure, T.; Eliel, E. L. *J. Org. Chem.* **1986**, *51*, 2599–2601. (i) Landolt, P. J.; Heath, R. R. *Science* **1990**, *249*, 1026–1028. (j) Cooke, F.; Roy, G.; Magnus, P. *Organometallics* **1982**, *1*, 893–897. (k) Hayashi, M.; Kaneko, T.; Oguni, N. *J. Chem. Soc., Perkin Trans. 1* **1991**, 25–28.

(21) Gonnella, N. C.; Nakanishi, K.; Martin, V. S.; Sharpless, K. B. *J. Am. Chem. Soc.* **1982**, *104*, 3775–3776.

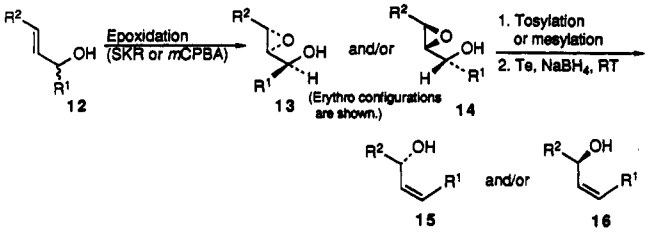
the progress of the reaction are avoided. Entries 16–19 in Table I show that the transposition may be a preferred alternative to the earlier SKR–Te scheme. Entries 14, 17, and 18 in Table I are for the two optically active forms of 2,6-dimethyl-1,5-heptadien-3-ol (11, $R^1 = Me_2C{=}CHCH_2$, R^2 = Me), the acetate of the (*R*)-(+)-isomer being the pheromone of the Comstock mealybug, *Pseudococcus comstocki*, an insect that is very harmful to a number of agricultural crops including apples and pears.[22] The (*R*)-(+)-allylic alcohol has been prepared in low ee from L-phenylalanine,[23a] in high ee by two SKR's of the racemic alcohol,[23a] and by action of zinc dust in acetic acid on (2*R*,3*R*)-2,3-epoxy-2,6-dimethyl-5-heptenyl iodide.[23b] The (*S*)-(−)-enantiomer also was prepared by the last method from the (2*S*,3*S*)-epoxy iodide.[23b] The slightly lower ee given for entries 17 and 18 are caused by a 6% cis allylic alcohol impurity. When allowance is made for this impurity (which leads to the opposite enantiomer from the trans starting material), the ee is in excess of 90%. Entry 19 illustrates the transposition in a cyclic system starting with cyclohexenemethanol. The (*S*)-2-methylenecyclohexanol product was obtained in 40% overall yield and 89% ee. The SKR applied to racemic 2-methylenecyclohexanol gave a yield of 46% and 80% ee.[24a] It may be noted that the terminal double bonds in the products from transposition may be subjected to ozonolysis to yield optically active α-hydroxycarbonyl compounds[24b] and that they also provide a convenient site for chain extension, for example by a hydroboration–oxidation–Wittig reaction sequence.[25a,b]



10 11

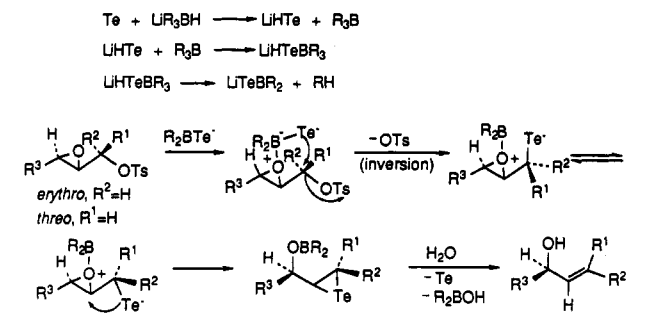
1,3-Disubstituted Allylic Alcohols (Table I, Entries 20–29). The Sharpless kinetic resolution (SKR) applied to cis secondary, 1,3-disubstituted allylic alcohols may give low enantioselectivity if the cis substituent is bulky. Only about a 10% ee was observed in the kinetic resolution of *cis*-1,3-dicyclohexyl-2-propen-1-ol [(*Z*)-α-(2-cyclohexylethenyl)cyclohexanemethanol].[4] Kinetic resolutions of other cis-1,3-disubstituted allylic alcohols may be slow, whereas SKR's of trans allylic alcohols usually are satisfactory and many examples of these important enantiomerically enriched intermediates have been prepared.[5] Recently, Oppolzer and Radinov have obtained (*E*)- and (*Z*)-allylic alcohols in 73 → 98% ee by reaction of (*E*)- or (*Z*)-1-alkenylzinc intermediates with aldehydes in the presence of enantiomerically pure amino alcohol ligands.[26] *n*-Hexyl and methyl were the only (*Z*)-substituents.[26b] Both

Scheme II



12 13 14 15 16

Scheme III



cis- and trans-1,3-disubstituted allylic alcohols are available via appropriate Wittig reactions or by partial reduction of the triple bond of acetylenic alcohols.[5b] Isomerizations of *trans*-alkenes to *cis*-alkenes are known, but isomerizations of *cis*- to the more thermodynamically stable *trans*-alkenes are more common.[27] Conversions of epoxides to alkenes can invert the configuration of the alkene from which the epoxide was originally derived.[28] A conversion of trans allylic alcohols to the cis isomers has been demonstrated by Julia and co-workers who reduced (*E*)-3-hydroxy-1-propenyl sulfones to (*Z*)-allylic alcohols.[29]

The limitation of the SKR when applied to sterically congested 1,3-cis-disubstituted (secondary) allylic alcohols can be overcome by a tellurium-induced transposition of a tosylate or mesylate of a glycidol derived from a 1,3-trans-disubstituted allylic alcohol. Preliminary reports on the conversion of trans to cis allylic alcohols by this method have appeared.[10b,d] The overall process is illustrated in Scheme II. The trans erythro epoxy alcohol (glycidol) is required, and the SKR process gives mainly that isomer.[4] Where $R^1 = R^2$ = c-C_6H_{11}, a 27% yield of the (−)-cis allylic alcohol (15, $R^1 = R^2$ = c-C_6H_{11}) was obtained in 95% ee from the *trans*-alcohol via the SKR–Te process. According to the empirical rules for SKR[5] and the presumed mechanism for the Te transposition (Scheme III), the configuration of this cis allylic alcohol should be (*S*). In a similar manner, (−)-(*Z*)-4-undecen-3-ol (16, R^1 = Et, R^2 = *n*-C_6H_{13}) was obtained in 34% yield and 95% ee (SKR takes 21 h) from (±)-(*E*)-3-undecen-5-ol (12, R^1 = *n*-C_6H_{13}, R^2 = Et). Previously, the kinetic resolution of (±)-(*Z*)-4-undecen-3-ol with (+)-DIPT took 2 days and gave the (*R*)-allylic alcohol in 82% ee.[4,5c] The Te transposition reaction also has been applied to racemic mixtures of sulfonates of 13 and 14. If m-CPBA is used for the epoxidation, a mixture of racemic erythro and threo isomers is obtained. The separation of these isomers is accomplished by conversion to tosylate derivatives fol-

(22) (a) Bierl-Leonhardt, B. A.; Moreno, D. S.; Schwarz, M.; Forster, H. S.; Plimmer, J. R.; DeVilbiss, E. D. *Life Sci.* **1980**, *27*, 399–402. (b) Bierl-Leonhardt, B. A.; Moreno, D. S.; Schwarz, M.; Forster, H. S.; Plimmer, J. R.; DeVilbiss, E. D. *J. Chem. Ecol.* **1982**, *8*, 689–699. (c) Negishi, T.; Uchida, M.; Tamaki, Y.; Mori, K.; Ishiwatari, T.; Asano, S.; Nakagawa, K. *Appl. Entomol. Zoolog.* **1980**, *15*, 328–333. (d) Uchida, M.; Nakagawa, K.; Negishi, T.; Asano, S.; Mori, K. *Agric. Biol. Chem.* **1981**, *45*, 369–372.

(23) (a) Nakagawa, N.; Mori, K. *Agric. Biol. Chem.* **1984**, *48*, 2799–2803. (b) Mori, K.; Ueda, H. *Tetrahedron* **1981**, *37*, 2581–2583.

(24) (a) Ronald, R. C.; Ruder, S. M.; Lillie, T. S. *Tetrahedron Lett.* **1987**, *28*, 131–134. (b) Overman, L. E.; Lin, H.-H. *J. Org. Chem.* **1985**, *50*, 3670–3672.

(25) (a) Finan, J. M.; Kishi, Y. *Tetrahedron Lett.* **1982**, *23*, 2719–2722. (b) Nicolaou, K. C.; Uenishi, J. *J. Chem. Soc., Chem. Commun.* **1982**, 1292–1293.

(26) (a) Oppolzer, W.; Radinov, R. N. *Helv. Chim. Acta* **1992**, *75*, 170–173. (b) Oppolzer, W.; Radinov, R. N. *Tetrahedron Lett.* **1991**, *32*, 5777–5780.

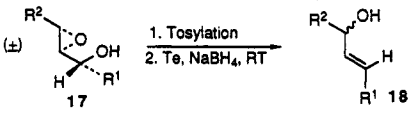
(27) For a list of both types of isomerization, see: Larock, R. C. *Comprehensive Organic Transformations*; VCH: New York, 1989; p 109.

(28) March, J. *Advanced Organic Chemistry*, 3rd ed.; Wiley: New York, 1985; p 920.

(29) Cuvigny, T.; du Penhoat, C. H.; Julia, M. *Recl. Trav. Chim. Pays-Bas* **1986**, *105*, 409–421.

lowed by flash chromatography. Mesylate derivatives appear to be somewhat less stable on silica gel.[30]

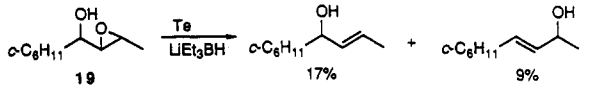
Subjection of *threo*-glycidyl tosylates **17a–d** to the Te transposition yields trans allylic alcohols **18a–d** (see Table I for structures). Because optically active secondary trans allylic alcohols are readily available by the SKR process (unlike sterically congested cis allylic alcohols)[4,5] there is no need to apply the Te transposition to optically active starting materials. Use of racemic *threo*-epoxy tosylates demonstrates the stereochemistry of the process with specific formation of trans allylic alcohols.



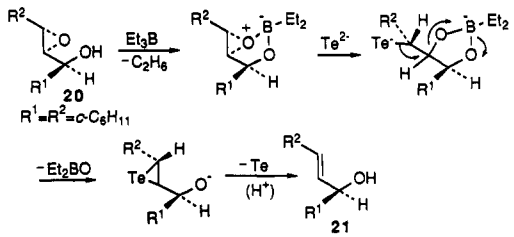
For the success of the transposition of trans, secondary epoxy tosylates it is necessary to use a boron hydride (e.g. $LiEt_3BH$) to reduce Te. The boron hydride is likely to produce boranes,[31] and these apparently are necessary for the success of allylic transpositions involving sulfonate esters of **13**, **14**, or **17** in which steric hindrance at C-1 and C-3 of the epoxy tosylate retards attack by Te^{2-}. Treatment of *threo*-epoxy tosylate **17c** ($R^1 = R^2 = n$-Pr) with $Te–LiEt_3BH$ in THF gave a 90% yield of trans allylic alcohol, **18c**. The transposition of the tosylate of **17c** by Te^{2-} in the absence of boranes was very slow, but addition of Et_3B approximately doubled the rate of appearance of **18c**. No reaction at room temperature of glycidyl tosylates of secondary alcohols was observed when $Li(MeOH)_3BH$ was used to reduce Te (The reduction of Te occurred readily). Since the trimethoxyborane byproduct from the reduction is expected to be a poorer Lewis acid than triethylborane,[32] this result supports a boron-catalyzed process such as that shown in Scheme III. The boron telluride intermediate has an analog in $PhSeB(OEt)_3^-$ produced in the reduction of diphenyldiselenide by $NaBH_4$ in ethanol.[33]

The behavior of the postulated boron telluride species shown in Scheme III is analogous to the intramolecular behavior of boron and aluminum hydrides in reductions of α,β-unsaturated epoxides in which the boron or aluminum atom complexes with the epoxide oxygen atom, thus directing hydride attack on the carbon–carbon double bond.[34a–c] Somewhat related is the pronounced regioselectivity of the reduction of epoxy alcohols (glycidols) to 1,3-diols by Red-Al (Aldrich).[34d–g] Intramolecular delivery of nucleophiles to epoxy alcohols also may be facilitated by titanium(IV) reagents.[34g,h]

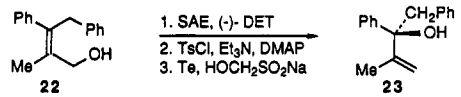
When a mixture of *erythro*- and *threo*-epoxy alcohols **19** is treated with $Te–LiEt_3BH$, deoxygenation of the epoxide function was the main result along with a low yield of transposed allylic alcohol. The recovered epoxy alcohol was enriched in the erythro isomer. The triethylborane byproduct may complex with the hydroxy group to enhance its leaving group activity in the transposition reaction. *threo*-Epoxy alcohols undergo titanium(IV)-mediated nucleophilic substitution reactions more readily than erythro isomers.[34g]



When *erythro*-epoxy allylic alcohol **20** (55% ee)[4] was treated in the same way, only (*E*)-allylic alcohol **21** was obtained in 94% yield (55% ee). The configuration of the hydroxyl group is retained and unlike the epoxy tosylate no rearrangement to the (*Z*)-allylic alcohol is observed. In this instance, the triethylborane produced in the reduction of Te may prefer to complex with the "harder" alcohol oxygen atom rather than the "softer" telluride ion. The favored site of attack by nucleophiles in many intermolecular substitution reactions involving epoxy alcohols is predominately at C-3,[34g–i] the major exceptions being observed in reductions with Red-Al.[34d–g]



1,1,2-Trisubstituted Allylic Alcohols (Table I, Entry 30). Only one example has been studied since 2,3,3-trisubstituted allylic alcohols are difficulty accessible. The starting allylic alcohol **22** has been obtained previously in low overall yield (13%) from deoxybenzoin, and it has been satisfactorily converted to the optically active epoxy alcohol by SAE with (–)-DET.[20f] The telluride-catalyzed transposition via $Te–HOCH_2SO_2Na$ gave a 41% yield of tertiary allylic alcohol **23**.



Comparisons with Other Allylic Transposition Methods. The transposition reactions described above are unique in that Te is used to effect the 1,3-allylic shift of double bond and hydroxyl group. Tellurium is recovered and reused so that the reaction is stoichiometric only in the reducing agent. The displacement reactions involving Te^{2-} are stereospecific as required by the S_N2 mechanism.

(30) The methine proton of the carbinol carbon atom in the threo glycidols appears in the ^1H NMR spectrum at consistently higher field than that of the erythro isomers. This may be the result of the formation of a more stable intramolecular hydrogen bond between the hydroxyl group and the epoxide oxygen in the threo isomer because of less steric congestion as indicated by models. Conversion of the threo and erythro glycidols to their tosylates reverses the shielding of the methine proton; this proton in the erythro isomer now resonates at higher field than that in the threo isomer. This may be due to a smaller dipole moment of the erythro tosylate expected from consideration of the lowest energy rotamer. [For a discussion of the rotamer energies of glycidols, see: Roush, W. R.; Brown, R. J.; DiMare, M. *J. Org. Chem.* **1983**, *48*, 5083–5093.]

(31) Care should be taken not to ignore the possible contribution of boranes to reactions effected by $Te–NaBH_4$ or $Te–LiEt_3BH$.

(32) Larson, J. W.; McMahon, T. B. *J. Am. Chem. Soc.* **1985**, *107*, 766–773.

(33) (a) Miyashita, M.; Hoshino, M.; Yoshikoshi, A. *Tetrahedron Lett.* **1988**, *29*, 347–350. (b) Miyashita, M.; Hoshino, M.; Suzuki, T.; Yoshikoshi, A. *Chem. Lett.* **1988**, 507–508.

(34) (a) Parish, E. J.; Schroepfer, G. J., Jr. *Tetrahedron Lett.* **1976**, 3775–3778. (b) Zaidlewicz, M.; Uzarewicz, A.; Sarnowski, R. *Synthesis* **1979**, 62–64. (c) Lenox, R. S.; Katzenellenbogen, J. A. *J. Am. Chem. Soc.* **1973**, *95*, 957–959. (d) Ma, P.; Martin, V. S.; Masamune, S.; Sharpless, K. B.; Viti, S. M. *J. Org. Chem.* **1982**, *47*, 1378–1380. (e) Finan, J. M.; Kishi, Y. *Tetrahedron Lett.* **1982**, *23*, 2719–2722. (f) Viti, S. M. *Tetrahedron Lett.* **1982**, *23*, 4541–4544. (g) Kirshenbaum, K. S.; Sharpless, K. B. *Chem. Lett.* **1987**, 11–14. (h) Caron, M.; Sharpless, K. B. *J. Org. Chem.* **1985**, *50*, 1560–1563. (i) Onaka, M.; Sugita, K.; Takeuchi, H.; Izumi, Y. *J. Chem. Soc., Chem. Commun.* **1988**, 1173.

There is a reasonable possibility that the reaction can be made truly catalytic in Te by continuously reducing the element as it is formed during the reaction.

There are a number of other transposition reactions that, in principle, can accomplish the same result as tellurium.[35] Only a few of them have been applied to optically active allylic alcohol derivatives. The rearrangements of epiiodo- and epibromohydrins induced by zinc[23a,b,36a-g] or by *n*-butyllithium[36d,i] show good stereospecificity, and the zinc method has been used in the synthesis of (−)-nerolidol in a process that compares favorably with our synthesis via tellurium.[36c,f] An extra step is involved in the conversion of a tosylate to an iodide which is avoided in the Te-catalyzed rearrangement. Trialkylstannates can replace zinc, and both reagents have given good stereochemical results in transpositions although cis–trans isomerization and S_N2' reactions may occur.[36g] Iodide ion has replaced zinc in the conversion of epiiodohydrins to allylic alcohols.[36h]

The well-known base-catalyzed (e.g. LDA, *n*-BuLi) rearrangement of epoxides[37a,b] has been applied to optically active epichlorohydrins to give optically active 3-hydroxyalkynes via a 1,3-transposition.[37c-e] Treatment of epoxides with optically active bases gives optically active allylic alcohols (3–31% ee),[37f,g] and kinetic resolutions via optically active lithium amides have been reported.[37h] A related reaction is the reductive ring opening of deoxy halo sugars.[37i-k] Allylsilanes have been converted to allylic alcohols in a transposition involving the epoxide;[37l,m] the carbon atom bearing the silicon mimics the carbanion-like carbon of the transition state in the aforesaid epoxide ring opening. Dissolving metals (Li, Na, Ca) in liquid ammonia effect transposition of allylic epoxy sulfonate esters, sulfones, or nitriles, but stereochemistry about the double bond may be lost in the electron-transfer process.[38] 1,3-Rearrangements of epoxy alcohols with Ti(III)[39a] (patterned after work by Nugent and Rajan Babu on epoxide ring openings[39b]) and reactions of an epibromohydrin[39c] and of thionoesters[40] with tributyltin radicals involve radical intermediates; side reactions have been observed. Treatment of epichlorohydrins with Zn–Cu(I) iodide couple under ultrasonication gives good yields of transposed allylic alcohols via radical intermediates. Good stereoselectivity was observed in the transposition of (−)-*cis*-carveol.[41]

Allylic esters and related compounds undergo catalyzed (usually by Hg^{2+} or Pd^{2+}) S_Ni'-type[42] rearrangements.[43] Although cationic intermediates may be involved, retention of optical purity has been observed in several cases.[43d,g,i,j,l,m] The action of peroxy acids on allylic tin derivatives gives modest yields of transposed allylic alcohols.[44] Allylic peroxides also undergo rearrangement either thermally (the Schenck–Brill reaction[45a-d]) or via trifluoroacetic anhydride.[45e]

Other transpositions that can lead to allylic alcohols or their derivatives may be classed formally as [2, 3] or [3, 3] rearrangements although there is overlap with the S_Ni' category. These rearrangements involve allylic sulfoxides,[46] selenoxides,[8,47] telluroxides,[48] iodates,[49] cyanates,[50] vanadates, tungstates, and molybdates,[51] xanthates,[52] chromate esters[53] (oxidation of the transposed alcohol occurs), and amine oxides (the Meisenheimer rearrangement).[54] Chirality transfer has been observed in the rearrangement of aryl cinnamyl selenoxides of high enantiomeric purity to 1-phenyl-2-propen-1-ol, obtained in 41–62% ee.[8] (*S*)-Linalool in 67% ee also was obtained by a selenoxide rearrangement.[47j] Chirality transfer in

(35) Some of these rearrangements are summarized in a useful compendium: Larock, R. C. *Comprehensive Organic Transformations*; VCH: New York, 1989; pp 114–119, 191, 480, 581.

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[2,3] rearrangements also occurs with optically active allylic sulfoxides.[46a,h-j] A final class of transposition includes the Wharton rearrangement which yields allylic alcohols by rearrangement of enones.[55a-d] It was not always successful.[38a,55e-g] The reverse process, the transposition of allylic alcohol derivatives to rearranged α,β-unsaturated carbonyl compounds, also is known.[53,56] The Büchi-Vederas reaction transposes only carbonyl functionalities.[55e,57]

The tellurium transposition process has the following advantages: (1) The tellurium is recovered and can be reused; only the reducing agent is consumed. If the latter is the inexpensive rongalite, the procedure is economical. However, rongalite has not proved useful in all cases, and the more costly boron hydrides may be required, particularly where Te^{2-} attack is required at a secondary carbon atom of a sulfonate ester. (See Table I, entries 20–29 and Table II.) (2) The process avoids the complications that can occur with the use of dissolving metals, peroxides, and with transpositions that involve carbocation or radical intermediates, all of which may yield byproducts and possible loss of stereochemistry. For example, compounds with functional groups that are easily reduced are not suitable for transpositions by means of dissolving metals. (3) High temperatures are avoided, thus minimizing side reactions. (4) Very strong bases or acids are avoided. (The rongalite reaction does involve dilute, aqueous sodium hydroxide to ensure formation of Te^{2-} over HTe^-.) (5) In the rongalite process water is the major reaction solvent. Thus, large quantities of organic solvents are not required in this step. Not all of the various transposition methods described above are applicable to the products of the Sharpless asymmetric epoxidation. The addition of vinylzinc compounds to carbonyl groups directed by chiral ligands so far has been restricted to aldehydes.[20b] This last method thus does not provide access to optically active tertiary allylic alcohols that are available by the SAE–Te transposition process.

Reaction Conditions and Scope. The scope of the reaction as known at the present time with respect to substitution pattern is summarized in Table I. Selenide ion can accomplish the same result as Te^{2-}, but more strenuous conditions are required.[58] Halogen atoms and nitro groups should not be present since they are likely to react with Te^{2-}.[59] Ester groups are tolerated.[2d] Tosylation of epoxy alcohols works well with tosyl chloride, but the anhydride may be used if there is danger of attack by chloride ions on the epoxides.

Elemental Te is used as a powder (200 mesh). As with many finely divided materials there may be a tendency for oxidation by oxygen, and we ordinarily carry out operations under an inert gas (Ar, N_2). Storage of the Te powder without special precautions to exclude air seems to cause no complications, although it may be prudent to keep the opened bottle in an inert atmosphere. Care should be taken to avoid inhalation of the Te dust or contact of the skin with telluride solutions. Although elemental Te is of low toxicity (divalent Te is readily oxidized to the element), contact with the element may cause the socially unacceptable garlic-like "tellurium breath".[11b]

Rongalite is a nontoxic, inexpensive, and convenient solid reducing agent, but it is also a source of sulfoxylate ions, good nucleophiles[60] that could compete with telluride ions. We have not observed any difficulties that could be attributed to reactions of SO_2^{2-} or HSO_2^-. Rongalite does not have an infinite shelf life, and if the age of the reagent is in doubt, fresh material should be used. Its reducing ability may be determined by an iodometric titration.[61] The ratios of the concentrations of Te, rongalite, sodium hydroxide, and organic substrate should be approximately 2:6:10:1, but the exact ratio is not very critical. Increase in the concentration of Te^{2-} (Te and reducing agent) will increase the rate, but the workup will entail oxidation of a larger excess of Te^{2-}. If it is possible to make the reaction truly catalytic in Te, problems of workup due to Te^0 will be minimized. If borohydrides are used to reduce Te, the chemist should be aware of the presence of boranes that could cause byproduct formation, although their presence seems essential in transpositions involving secondary tosylates. Incomplete reduction of Te results in permanganate-colored solutions presumably of $(Te)_n^{2-}$.[12b,62] We have observed that stirring (magnetic) of Te powder with

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$NaBH_4$ in the absence of solvent results in a purple cast to the gray solid and that addition of methanol gives an immediate purple solution with gas evolution. This observation suggests that Te can be reduced in the solid state, but further work is needed to determine if this method will be useful. Rongalite reductions invariably give purple solutions whereas the borohydrides may give solutions that are nearly colorless (especially if methanol is present) containing mainly monomeric telluride (n = 1). This behavior has been used to explain the predominance of tellurophene formation from acetylenic epoxy alcohol derivatives on switching from rongalite to methanolic borohydride in the reduction of Te.[63]

In the usual procedure, tellurium is reduced by rongalite around 50 °C, and the deep purple reduction mixture is cooled to room temperature or lower before the sulfonate ester in THF or other convenient solvent is added. A low yield in the tellurium step may signify lack of solubility of the organic compound which can be avoided by increasing the proportion of organic solvent in the aqueous mixture. Progress of the reaction should be followed by TLC. Workup entails passage of air through the reaction mixture to precipitate finely divided elemental Te. Occasionally a Te mirror may form. Prolonged passage of air should be avoided to prevent loss of product by vaporization. A time of 30–60 min is sufficient. Use of a cold trap or dry ice condenser may be helpful. Long contact with air also may oxidize Te further to tellurites or tellurates.[62b] The last traces of Te^{2-} may be destroyed by very careful dropwise addition of aqueous H_2O_2. The reduction potential of Te ($Te + 2e^- \rightarrow Te^{2-}$) is −1.14 V and indicates that Te^{2-} has a strong tendency to be oxidized to the element. Therefore, removal of remaining small quantities of Te^{2-} by conversion to Te is straightforward. The elemental tellurium may be recovered in one of three ways: (1) Careful filtration through a pad of Celite. The top Te layer is distinct and is removed by scraping. There will be some contamination by Celite. It is not harmful. (2) Separation by flotation of Celite. After filtration as in 1, the Te layer plus accompanying Celite is added to bromoform (d = 2.9). Te (d = 6.25) sinks and Celite (silica, d = 2.0–2.6) floats. Ultrasonication may help to "clean" the Celite. (3) Centrifugation of a Te–Celite slurry obtained from the top layer of the Celite pad in the first method. The more dense Te will form a layer below the Celite. If there is only a small quantity of Celite relative to Te, the top Celite layer may be removed along with a small amount of Te to leave the remainder of the Te uncontaminated. All glassware in which tellurium reactions are performed should be cleaned in a Chlorox bath (oxidation to tellurites and tellurates) to avoid any possibility of the accidental formation of malodorous H_2Te.

Experimental Section

^{13}C and ^1H NMR spectra were taken at 75 and 300 MHz, respectively, in $CDCl_3$ unless otherwise specified. Optical rotations were obtained by means of a Perkin-Elmer 241 polarimeter. Reactions were monitored by TLC on silica gel (250 μm) and visualized by ultraviolet light, phosphomolybdic acid, I_2, or anisaldehyde. Elemental analyses were performed by either Galbraith Laboratories, Knoxville, TN, or E & R Microanalytical Laboratory, Inc., Corona, NY. Melting points were obtained either on a hot-stage apparatus or in a Pyrex capillary (uncorrected). Ee's of secondary alcohols were determined by ^1H NMR spectroscopy of esters of (*R*)-(+)-α-methoxy-α-(trifluoromethyl)phenylacetic acid (MTPA or Mosher reagent);[64] ee's of tertiary alcohols were determined by the use of the chiral shift reagent, Eu(hfc)$_3$.[65] An ee > 95% signifies that no absorption caused by the presence of the other enantiomer could be observed. MTPA esters of racemic alcohols were used on occasion to identify the chemical shifts of diastereotopic protons. Benzene-d_6 solvent often gives better resolution of these protons than does $CDCl_3$.

Unless otherwise noted, materials were obtained from commercial sources and used without further purification. Rongalite (sodium hydroxymethanesulfinate dihydrate) was stored in a freezer. THF was distilled from sodium/benzophenone, and hexanes were fractionally distilled. Methylene chloride was distilled if it had been stabilized with methanol and should not be stored over sieves.[5a] Ether was distilled from lithium aluminum hydride. DMF was purified by drying with calcium hydride and distillation from barium oxide. Methanesulfonic anhydride is hygroscopic and was recrystallized from CH_2Cl_2/hexanes prior to use and is stored in a desiccator. *p*-Toluenesulfonyl chloride was recrystallized from CH_2Cl_2/hexanes. Pyridine and triethylamine were distilled before use. All reagents used in the Sharpless asymmetric epoxidations were purified as previously described.[5a] (*R*)-(+)-α-Methoxy-α-(trifluoromethyl)phenylacetyl chloride (MTPACl) was prepared from the acid by treatment with oxalyl chloride in hexanes with a few drops of DMF, and MTPA esters were prepared as described previously.[5a] Experimental details for entries 1 and 12–15 in Table I have been given previously in a supplementary section[10a] and will not be repeated here, and details for entries 20–29 are included in the supplementary material to this paper.

SAE Procedures. Asymmetric epoxidations were performed with minor variations according to the methods published by Sharpless and co-workers.[5a,b] Catalytic amounts of titanium–tartrate complex were used except where otherwise stated. Activated, powdered 4A molecular sieves were added to CH_2Cl_2 at room temperature and the mixture was cooled to −20 °C. (The amount of CH_2Cl_2 was chosen to give a 0.2–0.5 M solution of allylic alcohol when it is added later.) DIPT (6–12 mol %) and $Ti(OiPr)_4$ (5–10 mol %) were added sequentially by syringe. The mixture was stirred for 5 min, and anhydrous TBHP (1.2–2.0 molar equiv) was added slowly (5–10 min). This catalyst preparation was stirred for 45 min at −20 °C, and the allylic alcohol (1 molar equiv) in a minimum amount of CH_2Cl_2 was added during 20 min while the temperature was maintained between −20 and −15 °C. The reaction mixture was stored in a freezer at −34 ± 5 °C, and the progress of the reaction was followed by TLC. Workup for hydrophobic epoxy alcohols via $FeSO_4$–tartaric acid was as described previously.[5a] For hydrophilic epoxy alcohols, workup involved triethanolamine[66] (1.5 molar equiv of 1.0 M amine in CH_2Cl_2) which was added to the epoxidation mixture at 0 °C. The mixture was stirred for 1 h and filtered quickly through silica gel on a sintered-glass funnel. The silica gel was washed with ether (200 mL), and the combined organic solutions were concentrated to the original volume on a rotary evaporator. The solution was treated with a precooled (0 °C) solution of NaOH (30%) in saturated, aqueous NaCl (10 mL) and stirred for 1 h at 0 °C. Addition of water (50 mL), extraction with ether (2 × 50 mL), drying over Na_2SO_4, and concentration yielded the crude product. This procedure does not remove excess TBHP. It can be removed either by azeotropic distillation with toluene, crystallization of the product, or by flash chromatography on silica gel.

General *m*-CPBA Epoxidations. A solution (0.2–0.5 M) of 3-chloroperoxybenzoic acid (*m*-CPBA) (1.1 molar equiv) in CH_2Cl_2 was added slowly (15 min) to a solution of the allylic alcohol (0.2–0.5 M) with Na_2CO_3 (1.2–1.5 molar equiv) in CH_2Cl_2. The reaction was stirred and followed by TLC. At completion,

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aqueous $Na_2S_2O_3$ (1.0 M) was added, and the mixture was stirred until the *m*-CPBA was consumed as indicated by TLC. The layers were separated, and the aqueous phase is extracted with CH_2Cl_2 (2 × 20 mL), dried ($MgSO_4$), and filtered, and the solvents were removed. Further purification may be accomplished by flash chromatography or by distillation (Kugelrohr).

General Procedures for Te Reactions. 1. Te–Rongalite. A modified procedure of Tschugaeff and Chlopin was adopted.[12b] A mixture of Te powder (200 mesh), rongalite ($HOCH_2SO_2$-$Na{\cdot}2H_2O$), and aqueous NaOH (1.0 M) in approximate molar ratios of 1:3–4:3–10 was heated at 50 °C for 2 h under N_2. The original black suspension of Te is transformed into a deep purple solution of reduced Te. The solution is cooled to room temperature or lower prior to addition of the mesylate or tosylate of the epoxy alcohol in THF or dioxane (the ratio of substrate to Te is approximately 1:2). The progress of the reaction is followed by TLC (silica gel). During the reaction, gray, elemental Te precipitates; when the reaction is complete, a stream of air or O_2 is introduced to oxidize unreacted telluride ions. If the reaction appears to be proceeding too slowly, addition of more organic solvent (e.g. THF) to assist solubilization of the organic substrate and/or an increase in the amount of Te to accelerate the rate may be helpful. The reaction mixture is filtered through Celite, the filter aid is washed with ether, and the combined ether–water mixture is extracted with ether (typically 4 × 20 mL). If the ether solution is yellow, careful dropwise addition of hydrogen peroxide (3%) effects decolorization. The ether extracts are washed with a saturated, aqueous solution of sodium thiosulfate to remove excess peroxide if it was added and with saturated, aqueous NaCl solution. The ether solution is dried ($MgSO_4$), and the solvent is removed by careful evaporation. The product may be purified by distillation or by chromatography on silica gel with elution by ether–pentane (3:7 or 5:5) or ether–hexanes (1:4).

2. Te–$NaBH_4$–DMF. A modification of the procedure of Zhou and Chen was used.[67] The molar ratio of Te–$NaBH_4$–epoxy tosylate is approximately 1:2–2.5:1 in DMF (12 mL/6 mmol of Te). *tert*-Butyl alcohol is omitted from the original procedure.[67] The mixture is heated at 70–80 °C until the disappearance of Te and the formation of a purple solution. The epoxy tosylate is added in a small amount of DMF (3 mL for 3 mmol) at room temperature. Workup is as described for rongalite.

3. Te–$LiEt_3BH$–THF. The procedure of Gladysz, Hornby, and Garbe[68] for the reduction of Se as adapted by Clive and co-workers was used.[69] The mole ratios of Te:$LiEt_3BH$:epoxy tosylate were 1.2:2.4:1.0. For 7.2 mmol of Te, 50 mL of THF was used and the epoxy tosylate (6 mmol) was added in THF (15 mL) at room temperature. Workup is as described for rongalite.

Preparation of Sulfonate Esters of Epoxy Alcohols. 1. Mesylates. Freshly recrystallized methanesulfonic anhydride (1.1 equiv) in CH_2Cl_2 (to make a 1–2 M solution) was added to a solution of the epoxy alcohol (0.25 M), pyridine (1.25 molar equiv) and DMAP (2 mol %) in CH_2Cl_2 at room temperature during 15 min. When the epoxy alcohol is consumed as indicated by ^1H NMR, water sufficient to dissolve the precipitated pyridinium salts was added. Extraction with CH_2Cl_2 (3 × 20 mL), drying ($MgSO_4$), and removal of solvent yielded the mesylate. The mesylates decompose on silica gel and were used without further purification.

2. Tosylates. Freshly recrystallized TsCl (1.05 molar equiv) in CH_2Cl_2 was added to a solution of the epoxy alcohol (1 molar equiv), freshly distilled triethylamine (1.5 molar equiv), and DMAP (2 mol %) in CH_2Cl_2 at 0 °C. The reaction was kept at −10 °C for 10–20 h. When the reaction was complete (TLC), water (half the volume of the reaction mixture) was added, and the mixture was extracted with CH_2Cl_2 (3 × 20 mL). The organic phase was washed with water (2 × 20 mL) and dried ($MgSO_4$). Removal of the solvent gave the tosylate which was purified by flash chromatography (silica gel) or by crystallization.

Regioselectivity of Telluride Attack on a Deuterated Epoxy Tosylate. 2-Methyl-2-propen-1-ol-*1-d* was prepared by reduction of methacrolein (2.5 g, 36 mmol) in a well-stirred methanol solution of $CeCl_3{\cdot}7H_2O$ (90 mL, 0.4 M)[70] with $NaBD_4$ (1.5 g, 36 mmol). After 5 min, water (75 mL) was added (vigorous gas evolution), and the mixture was extracted with ether (4 × 20 mL). The aqueous layer was saturated with NaCl followed by further extraction with ether. The residual water was removed by distillation in the presence of benzene. Methanol was removed by fractional distillation, and the residue was distilled (Kugelrohr, 113–115 °C) to give the deuterated allylic alcohol (2.20 g, 30.2 mmol, 84%): ^1H NMR δ 1.72 (s, 3), 2.20 (br s, 1, exchanges in D_2O), 4.00 (br s, 1), 4.80 (s, 1), 4.91 (s, 1); ^{13}C NMR δ 19.0, 66.4 (t, J = 38), 109.7, 145.0. The spectroscopic data were comparable with those of an authentic sample of undeuterated compound and to published spectra.[71] **2,3-Epoxy-2-methyl-1-propanol-*1-d*.** 2-Methyl-2-propen-1-ol-*1-d* in CH_2Cl_2 (100 mL)–Na_2CO_3 (4.25 g) was epoxidized by *m*-CPBA (6.3 g, 35 mmol) in CH_2Cl_2 (50 mL) to give the deuterated epoxy alcohol [^1H NMR ($CDCl_3$) δ 1.33 (s, 3), 2.60 (d, 1, J = 4.8), 2.83 (d, 1, J = 4.8), 3.22 (s, 1, exchanges in D_2O), 3.55–3.64 (br d, 1, J = 12)] that was converted to the tosylate by treating the crude product (0.020 g, 0.22 mmol) in triethylamine (0.032 g, 0.33 mmol)–CH_2Cl_2 (1.5 mL) at −25 °C with *p*-toluenesulfonyl chloride (0.0418 g, 0.22 mmol) in CH_2Cl_2 (5 mL) for 9 h. The tosylate was a white, viscous oil (0.045 g, 0.19 mmol, 86%): ^1H NMR δ 1.36 (s, 3), 2.46 (s, 3), 2.64 (d, 1, J = 4.6), 2.70 (d, 1, J = 4.6), 3.93 (br s, 0.5), 4.05 (br s, 0.5), 7.60 (d, 2, J = 8), 7.80 (d, 2, J = 8); ^{13}C NMR δ 21.45, 23.85, 49.90, 57.23, 71.17 (t, J = 22.8), 127.73, 129.75, 132.42, 144.94. The tosylate (0.010 g, 0.041 mmol) in THF (2 mL) was added to a purple solution obtained by reduction of Te (0.0105 g, 0.041 mmol) and rongalite (0.019 g, 0.12 mmol)–NaOH (12 mL, 0.01 N) under N_2. The workup was modified by addition of $CDCl_3$ to the crude product followed by distillation to remove residual water as the azeotrope. The ^1H NMR and ^{13}C NMR spectra were identical with those of 2-methyl-2-propen-1-ol-*1-d*.

(*R*)-(−)-1-Octen-3-ol ["Matsutake Alcohol" (3a)] (Table I, Entry 2). *trans*-2-Octen-1-ol[72] (2.00 g, 15.6 mmol), obtained by reduction of *trans*-2-octenal by $NaBH_4$–$CeCl_3$,[70] was epoxidized asymmetrically according to the general procedure with (−)-DIPT as the chiral ligand to give the (2*R*,3*R*)-(+)-epoxy alcohol, **2a**. It was recrystallized from ether–hexanes as white needles (2.09 g, 14.5 mmol, 93%, >95% ee by NMR of MTPA ester): mp 31–32 °C, 35–36 °C [lit.[73] mp 37–38 °C; (−)-isomer, mp 35–37 °C,[73] 38–39.5 °C,[5a] 29.5–30 °C[74]]; $[\alpha]^{25}_D$ +30.3° (*c* 4.7, $CHCl_3$), +36.3° (*c* 3.55, $CHCl_3$) (from a second preparation) [lit.[73] $[\alpha]_D$ +43.0° (*c* 1.0, $CHCl_3$); (−)-isomer $[\alpha]^{25}_D$ −42.7° (*c* 4.7, $CHCl_3$), >98% ee;[5a] $[\alpha]^{25}_D$ −36.8° (*c* 0.61, $CHCl_3$);[74] $[\alpha]^{25}_D$ −38.1° (*c* 1.48, $CHCl_3$);[74] $[\alpha]_D$ −39.4° (*c* 1.0, $CHCl_3$);[73] $[\alpha]^{22}_D$ −44.6° (*c* 2, $CHCl_3$), 92 ● 2% ee;[75] $[\alpha]^{22}_D$ −29.4° (*c* 3.0, $CHCl_3$), >99% ee;[76] $[\alpha]^{20}_D$ −35.1°;[77] $[\alpha]_D$ −44° (*c* 1.0, $CHCl_3$);[78] $[\alpha]^{25}_D$ −34.6° (*c* 5.7, $CHCl_3$), 95% ee[79]]; ^{13}C NMR δ 13.97, 22.54, 25.60, 31.50, 31.55, 55.98, 58.39, 61.68. The ^1H NMR spectrum was reported previously.[5a,73] The liquid tosylate of **2a** (3.51 g, 11.8 mmol, 100%) was prepared from (+)-epoxy alcohol **2a** (1.70 g, 11.8 mmol) according to the general procedure: $[\alpha]^{25}_D$ +26.6° (*c* 11.8, $CHCl_3$); ^1H NMR δ 0.87 (t, 3, J = 6.6), 1.20–1.60 (br m, 8), 2.44 (s, 3), 2.77 (dt, 1, J = 1.8, 4.5), 2.93 (m, 1), 3.95 (dd, 1, J = 5.7), 4.18 (dd, 1, J = 3.9), 7.34 (d, 2), 7.78 (d, 2); ^{13}C NMR δ 13.84, 21.56, 22.39, 25.29, 31.14, 31.34, 54.43, 56.65, 70.19, 127.84, 129.83, 132.60, 145.00.

Treatment of tosylate (2.00 g, 6.71 mmol) with Te (2 molar equiv)–rongalite at room temperature for 6 h as described in the

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general procedure gave, after workup, "matsutake alcohol" **3a** as a golden oil (0.815 g, 6.37 mmol, 95%, >95% ee by NMR of MTPA ester): $[\alpha]^{25}_D$ −18.8° (*c* 4.6, EtOH) [lit. $[\alpha]^{20}_D$ −18.4° (neat, uncorrected for density), 98% ee,[16] $[\alpha]^{25}_D$ −20.2° (*c* 7.3, EtOH)[17]]; ^{1}H NMR δ 0.89 (t, 3, *J* = 6.9), 1.10–1.65 (br m, 8), 1.96 (br s, 1), 4.08 (dd, 1, *J* = 6.3), 5.09 (d, 1, *J* = 10.2), 5.21 (d, 1, *J* = 17.4), 5.88 (m, 1); ^{13}C NMR δ 13.96, 22.54, 24.95, 31.70, 36.93, 73.19, 114.41, 141.29.

(*R*)-(−)-1-Nonen-3-ol (3b) (Table I, Entry 3). *trans*-2-Nonen-1-ol,[73] **1b**, was prepared by reduction of *trans*-2-nonenal by $NaBH_4$–$CeCl_3$.[70] Asymmetric epoxidation of **1b** (1.42 g, 10.0 mmol) according to the general procedure [(−)-DIPT] gave the (2*R*,3*R*)-(+)-epoxy alcohol, **2b**, as white needles (1.44 g, 9.11 mmol, 91%, >95% ee from NMR of MTPA ester): mp 35.0–35.5 °C [lit.[73] mp 40–41 °C]; $[\alpha]^{25}_D$ +33.1° [*c* 3.1, $CHCl_3$], $[\alpha]^{23}_D$ +31.9° (88% ee from ^{1}H NMR of MTPA ester) (*c* 2.8, $CDCl_3$) [lit.[73] $[\alpha]_D$ +39.7° (*c* 1.0, $CHCl_3$)]; ^{1}H NMR δ 0.88 (t, 3, *J* = 5.7), 1.20–1.70 (br m, 10), 1.70 (br s, 1) 2.93 (m, 2), 3.62 (dd, 1, *J* = 4.2), 3.91 (dd, 1, *J* = 2.1); ^{13}C NMR δ 14.05, 22.55, 25.89, 29.05, 31.55, 31.70, 55.97, 58.37, 61.68. The pale yellow liquid tosylate (1.44 g, 4.62 mmol, 100%) was obtained from the (+)-epoxy alcohol **2b** (0.730 g, 4.62 mmol) according to the general procedure: $[\alpha]^{25}_D$ +26.8° (*c* 6.7, $CHCl_3$); ^{1}H NMR δ 0.87 (t, 3, *J* = 7.1), 1.15–1.60 (br m, 10), 2.44 (s, 3), 2.77 (dt, 1, *J* = 2.1, 5.5), 2.93 (m, 1), 3.97 (dd, 1, *J* = 5.9), 4.16 (dd, 1, *J* = 3.7), 7.34 (d, 2), 7.78 (d, 2); ^{13}C NMR δ 13.99, 21.61, 22.47, 25.65, 28.89, 31.24, 31.60, 54.47, 56.74, 70.17, 127.90, 129.85, 132.70, 145.00.

The epoxy tosylate (0.936 g, 3.00 mmol) was treated with Te (2 molar equiv)-rongalite for 4 h at room temperature according to the general procedure. (*R*)-(−)-1-Nonen-3-ol, **3b**, was obtained as a golden oil (0.415 g, 2.92 mmol, 97%, >95% ee from NMR of MTPA ester): $[\alpha]^{25}_D$ −17.5° (*c* 1.4, EtOH) [lit. $[\alpha]^{25}_D$ −14.9° (*c* 1.13, EtOH);[5a] $[\alpha]^{25}_D$ −17.0° (*c* 0.96, EtOH);[5a] $[\alpha]^{24}_D$ −19.1° (*c* 6.7, EtOH)[4]]; ^{1}H NMR δ 0.90 (t, 3, *J* = 6.8), 1.10–1.65 (br m 10), 4.11 (m, 1), 5.11 (d, 1, *J* = 10.2), 5.23 (d, 1, *J* = 17.1), 5.88 (m, 1); ^{13}C NMR δ 14.07, 25.58, 25.29, 29.20, 31.79, 37.04, 73.29, 114.51, 141.32. Use of Te–$NaBH(OMe)_3$–MeOH instead of rongalite gave an 84% yield of **3b**, but the reaction took 10 h to go to completion.

(1*R*)-(+)-1-Phenyl-2-propen-1-ol (3c) (Table I, Entry 4). Asymmetric epoxidation of (*E*)-3-phenyl-2-propen-1-ol (cinnamyl alcohol) (5.0 g, 37 mmol) was performed as described by Sharpless and co-workers[5a] with (+)-DIPT as the chiral ligand to give (2*S*,3*S*)-3-phenyloxiranemethanol (**2c**) as a white solid (5.2 g, 35 mmol, 93%, 95% ee via NMR of MTPA ester): mp 48–50 °C (lit.[5a] mp 51.5–53 °C); $[\alpha]^{25}_D$ −44.9° (*c* 2.04, $CHCl_3$) [lit. $[\alpha]^{20}_D$ −49.6° (*c* 2.4, $CHCl_3$);[5a] $[\alpha]^{15}_D$ −51.9° (*c* 1.5, EtOH, >98% ee);[80] $[\alpha]^{26}_D$ −50.4° (*c* 2.4, $CHCl_3$, ca. 100% ee);[81] $[\alpha]^{25}_D$ −10.7° (*c* 2.45, $CHCl_3$);[82] $[\alpha]^{13}_D$ −51.7° (*c* 1.2, $CHCl_3$);[83] (*R*,*R*)-enantiomer: $[\alpha]^{13}_D$ +51.2° (*c* 2.6, $CHCl_3$);[83] $[\alpha]^{20}_D$ +45.9° (*c* 1.5, EtOH)[84]]; ^{13}C NMR δ 55.55, 61.21, 62.39, 125.69, 128.31, 128.50, 129.91. MTPA ester of (±)-**2c** (via *m*-CPBA oxidation): ^{1}H NMR (C_6D_6) δ 2.69–2.70 (m, 0.5), 2.74–2.75 (m, 0.5), 3.21–3.22 (d, 0.5), 3.31–3.32 (d, 0.5) 3.41 (s, 3), 3.69–3.75 (dd, 0.5), 3.79–3.85 (dd, 0.5), 4.06–4.11 (dd, 0.5), 4.21–4.26 (dd, 0.5), 6.91–7.28 (m, 8), 7.68–7.70 (d, 2). MTPA ester of (−)-**2c**: ^{1}H NMR (C_6D_6) δ 2.69–2.71 (m, 1), 3.32–3.33 (d, 1), 3.42 (s, 3), 3.80–3.86 (dd, 1), 4.07–4.12 (dd, 1), 7.01–7.10 (m, 8), 7.68–7.71 (d, 2).

The (−)-epoxy alcohol **2c** (2.0 g, 13 mmol) was converted to the tosylate (3.6 g, 12 mmol, 90%) according to the general procedure: mp 66–68 °C [lit.[85] mp 68–69 °C] $[\alpha]^{25}_D$ −44.3° (*c* 2.3, $CHCl_3$) [lit.[85] $[\alpha]_D$ −45° (*c* 2.5, $CHCl_3$)]; ^{1}H NMR δ 2.45 (s, 3), 3.23–3.26 (m, 1), 3.74–3.76 (d, 1, *J* = 1.9), 4.12–4.16 (dd, 1, *J* = 11.5, 5.6), 4.31–4.36 (dd, 1, *J* = 11.5, 3.6), 7.28–7.40 (m, 7), 7.77–7.86 (d, 2); ^{13}C NMR δ 21.61, 56.35, 58.47, 69.39, 125.64, 127.93, 128.51, 129.91, 132.61, 135.46, 145.12.

(a) Te–Rongalite Transposition. The tosylate of **2c** (0.91 g, 3.0 mmol) was treated with Te–rongalite according to the general procedure. After flash chromatography, 1-phenyl-2-propen-1-ol [0.155 g, 1.12 mmol, 39%, 90% ee via NMR of MTPA ester): $[\alpha]^{25}_D$ −0.66° (*c* 3.44, $CHCl_3$)] and cinnamyl alcohol (0.13 g, 0.92 mmol, 31%) were obtained.

(b) Te–Rongalite–β-Cyclodextrin Transposition. The reaction described in a was repeated with the addition of β-cyclodextrin (0.34 g, 10 mol %) prior to the tellurium treatment. The yield of transposed product (0.295 g, 1.97 mmol, 73%, >90% ee via NMR of MTPA ester) was increased and that of cinnamyl alcohol (0.03 g, 0.22 mmol, 7%) was decreased.

(c) Te–$NaBH_4$ Transposition. Treatment of the epoxy tosylate (1.10 g, 3.60 mmol) with Te (0.77 g, 6.0 mmol)–$NaBH_4$ (0.57 g, 15 mmol) in DMF (12 mL) for 2 h at room temperature according to the general procedure gave an oil that was purified by column chromatography on silica gel (5:1, hexanes–ethyl acetate). The reaction was purged with N_2 throughout the reaction. If the N_2 purging was omitted, the yield was lower (60%). No cinnamyl alcohol could be detected. The transposed allylic alcohol was obtained as a colorless oil (0.438 g, 2.90 mmol, 82%, 90% ee via NMR of MTPA ester): $[\alpha]^{23}_D$ +8.35° (*c* 3.58, C_6H_6) [lit. $[\alpha]^{rt}_D$ +8.2° (*c* 5.14, C_6H_6, 2-dm cell);[86] $[\alpha]^{17}_D$ +5.10° (neat, 0.5-dm cell);[87] (*S*)-enantiomer: $[\alpha]^{20}_D$ −8.4° (*c* 5.0, C_6H_6);[8] $[\alpha]^{25}_D$ −1.3° (>95% ee) (*c* 1.74, $CHCl_3$).[19c] (The specific rotations of (+)- and (−)-**3c** are unusually solvent and concentration dependent.)[47i,86]]. MTPA ester of (±)-**3c**: ^{1}H NMR (C_6D_6) δ 3.32 (s, 1.5), 3.38 (s, 1.5), 4.90–4.91 (m, 1), 5.11–5.21 (m, 1), 5.67–5.77 (m, 1), 6.40–6.43 (d, 0.5, *J* = 6.3), 6.48–6.50 (d, 0.5, *J* = 5.4), 7.00–7.30 (m, 8), 7.58–7.61 (t, 2). MTPA ester of (*R*)-(+)-**3c**: ^{1}H NMR (C_6D_6) δ 3.38 (s, 3), 4.92–4.93 (dt, 1), 5.15–5.22 (dt, 1), 5.74–5.81 (m, 1), 6.40–6.43 (d, 1, *J* = 6.3), 7.00–7.20 (m, 8), 7.56–7.59 (m, 2).

(d) Te–$LiEt_3BH$–*n*-$Bu_4N^+F^-$ Transposition. Te (0.92 g, 7.2 mmol) was reduced by $LiEt_3BH$ (14.4 mL, 1.0 M, THF, 14.4 mmol) at room temperature under N_2. After 45 min, *n*-$Bu_4N^+F^-$ (14.4 mL, 1.0 M, THF) was added. The mixture was stirred for 15 min, and the epoxy tosylate (1.8 g, 6.0 mmol) in THF (15 mL) was added via syringe. After 18 h, the reaction was worked up according to the general procedure. Chromatography (silica gel) gave the (*R*)-allylic alcohol **3c** as a colorless oil [0.63 g, 4.6 mmol, 78%, 90% ee via NMR of MTPA ester) [$[\alpha]^{24}_D$ +2.3° (*c* 1.03, C_6H_6)] along with a trace of cinnamyl alcohol (0.013 g, 0.0087 mmol, 1.4%).

(±)-, (*R*)-(+)-, and (*S*)-(−)-1-(Phenylmethoxy)-3-buten-2-ol (3d) (Table I, Entries 5–7). (*E*)-4-(Phenylmethoxy)-2-buten-1-ol[88] (0.930 g, 5.22 mmol) was epoxidized by *m*-CPBA (0.991 g, 5.74 mmol)–Na_2CO_3 in CH_2Cl_2 to racemic *trans*-3-[(phenylmethoxy)methyl]oxiranemethanol (0.962 g, 4.96 mmol, 95%). MTPA (Mosher) ester of (±)-epoxy alcohol **2d**: ^{1}H NMR (C_6D_6) δ 2.67–2.69 (m, 1), 2.70–2.76 (m, 1), 3.08–3.09 (m, 1), 3.10–3.28 (m, 1), 3.41 (s, 3), 3.66 (dd, 0.5), 3.74–3.80 (dd, 0.5), 4.08–4.21 (dd, 0.5), 4.24–4.26 (dd, 0.5), 4.27–4.31 (q, 2), 7.07–7.28 (m, 8), 7.62–7.64 (dd, 2). The epoxy alcohol (0.490 g, 2.53 mmol) was converted to its tosylate (0.876 g, 2.52 mmol, 99%), obtained as a colorless oil: ^{1}H NMR δ 2.40 (s, 3), 3.02 (br s, 1) 3.12 (br s, 1), 3.45 (AB q, 1) 3.67 (AB q, 1), 3.92 (AB q, 1), 4.21 (AB q, 1), 4.49 (AB dd, 2), 7.29 (m, 7), 7.76 (d, 2); ^{13}C NMR ($CDCl_3$) δ 21.64, 52.09, 54.87, 68.93, 69.77, 73.29, 127.80, 127.71, 127.92, 128.43, 130.00, 132.55, 145.22.

The tosylate (0.800 g, 2.30 mmol of (±)-**2d**) was treated with the Te–rongalite reagent to give (±)-**3d**[89] as a yellow oil (0.355 g, 1.99 mmol, 87%): ^{1}H NMR δ 3.02 (br s, 1) 3.40 (AB q, 1, *J* = 9.6), 3.57 (AB q, 1, *J* = 9.6), 4.39 (br m, 1), 4.60 (s, 2), 5.20 (d, 1, *J* = 10.5), 5.40 (d, 1, *J* = 16.8), 5.86 (m, 1), 7.37 (m, 5); ^{13}C NMR δ 71.47, 73.33, 73.95, 116.43, 127.73, 127.78, 128.43, 136.51, 137.77. MTPA ester of (±)-**3d**: ^{1}H NMR (C_6D_6) δ 3.16–3.33 (m, 2), 3.42 (s, 1.5), 3.52 (s, 1.5), 4.11–4.21 (m, 2), 4.89–5.09 (m, 1), 5.14–5.24 (m, 1), 5.43–5.56 (m, 1), 5.75–5.77 (m, 1), 7.03–7.21 (m, 8), 7.70–7.78 (m, 2).

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Epoxidation of the allylic alcohol (1.78 g, 10.0 mmol) under Sharpless conditions[5a] with (−)-DIPT as described previously[90] gave the (*R,R*)-epoxy alcohol (1.73 g 8.91 mmol, 89%, 90% ee via ^{1}H NMR of the MTPA ester): $[\alpha]^{24}_D$ +21.8° (*c* 2.9, $CHCl_3$) [lit. $[\alpha]^{25}_D$ +21.8° (*c* 6.5, $CHCl_3$),[90] $[\alpha]^{21}_D$ +21.4° (*c* 1.40, $CHCl_3$, >95% ee)[91]. MTPA ester of (*R,R*)-(−)-epoxy alcohol **3d**: ^{1}H NMR (C_6D_6) δ 2.69–2.74 (m, 2), 3.02–3.09 (m, 1), 3.20–3.26 (dd, 1), 3.41 (s, 3), 3.59–3.67 (dd, 1), 4.19–4.23 (dd, 1), 4.24–4.31 (m, 2), 7.02–7.26 (m, 8), 7.66–7.72 (d, 2). The epoxy alcohol (0.80 g, 4.2 mmol) was converted to the tosylate (1.3 g, 3.7 mmol, 88%) obtained as an oil.

Treatment of the crude tosylate (1.30 g, 3.74 mmol) with the Te (2 molar equiv)–rongalite reagent gave (*S*)-(−)-**3d** as a colorless oil (0.50 g, 2.8 mmol, 76%): $[\alpha]^{24}_D$ −4.3° (*c* 2.8, $CHCl_3$), 91% ee, via ^{1}H NMR of MTPA ester [lit. $[\alpha]_D$ −5.9° (*c* 0.5, $CHCl_3$),[89b] −5° (*c* 0.8, CH_2Cl_2)[92]]. MTPA ester of (*S*)-(−)-**3d**: ^{1}H NMR (C_6D_6) δ 3.15–3.32 (m, 2), 3.42 (s, 3), 4.10–4.21 (m, 2), 4.93–5.05 (m, 1), 5.12–5.24 (m, 1), 5.49–5.56 (m, 1), 5.72–5.80 (m, 1), 7.03–7.20 (m, 8), 7.69–7.78 (m, 2).

Epoxidation of the allylic alcohol via (+)-DIPT gave the (*S,S*)-epoxy alcohol (84%): $[\alpha]^{24}_D$ −20.6° (*c* 0.96, $CHCl_3$), >95% ee via ^{1}H NMR of MTPA ester. [lit. $[\alpha]^{25}_D$ −19.9° (*c* 2.66, $CHCl_3$, >95% ee),[82] $[\alpha]^{14}_D$ −20.3 (*c* 6.40, $CHCl_3$),[93] $[\alpha]^{24}_D$ −22.0° (*c* 0.50, $CHCl_3$),[94] $[\alpha]^{25}_D$ −21° (*c* 0.97 $CHCl_3$)[95]. Conversion of epoxy alcohol (2.18 g, 11.3 mmol) to the tosylate (2.8 g, 8.1 mmol, 71%), and treatment of the derivative (3.8 g, 11.3 mmol) with Te–rongalite gave (*R*)-(+)-**3d** as a colorless oil (1.89 g, 10.6 mmol, 94%): $[\alpha]^{24}_D$ +5.1° (*c* 0.45, $CHCl_3$), >90% ee [lit. $[\alpha]^{24}_D$ +4.72° (*c* 1.10, $CHCl_3$, 100% ee),[96] $[\alpha]_D$ +6.2° (*c* 1.6, $CHCl_3$),[97] $[\alpha]_D$ +5.9° (*c* 1.77, $CHCl_3$)[89b]].

(3*R*)-(+)-4,4-Dimethyl-1-penten-3-ol (3e) (Table I, Entry 8). Ethyl (*E*)-4,4-dimethyl-2-pentenoate was prepared as described previously.[98] The ester was reduced to alcohol **1e**[20a,75,98] (R = *t*-Bu) by treatment with DIBALH.[75] Asymmetric epoxidation of **1e** (3.00 g, 26.3 mmol) was performed according to the standard procedure with (+)-DET as the chiral ligand to give (2*R*,3*S*)-(−)-3-(1,1-dimethylethyl)oxiranemethanol[20a,75] (**2e**, R = *t*-Bu) (2.74 g, 21.0 mmol, 80% >95% ee via ^{1}H NMR of MTPA ester) (R_f 0.47, 1:1 hexanes–ethyl acetate) that was purified by flash chromatography (2:1 → 1:1 hexanes–ether): $[\alpha]^{23}_D$ −21.3° (*c* 5.04, $CHCl_3$); ^{1}H NMR δ 0.93 (s, 9), 1.89 (br s, 1), 2.75 (d, 1, *J* = 2.4), 3.03 (dt, 1, *J* = 2.3, 4.61), 3.60 (dd, 1, *J* = 4.6, 12.5), 3.90 (dd, 1, *J* = 2.4, 12.5); ^{13}C NMR δ 25.7, 30.4, 55.5, 62.1, 63.6; IR (film) 3424 (br, s), 1392 (m), 1365 (w), 1209 (m), 1041 (m), 964 (m), 939 (m), 898 (m), 868 (m), 783 (m) cm^{-1}. (*R*)-MTPA ester of (−)-**2e**: ^{1}H NMR (C_6D_6) δ 0.68 (s, 9), 2.22 (d, 1, *J* = 2.0), 2.67 (m, 1), 3.43 (s, 3), 3.86 (dd, 1, *J* = 6.4, 12.0), 4.00 (dd, 1, *J* = 3.4, 12.0). (*R*)-MTPA ester of (±)-**2e**: ^{1}H NMR (C_6D_6) 0.68 (s, 4.5), 0.69 (s, 4.5), 2.23 (d, 0.5), 2.31 (d, 0.5), 2.67 (m, 0.5), 2.72 (m, 0.5), 3.41 (d, 1.5), 3.43 (d, 1.5), 3.85 (2 dd, 1), 4.02 (dd, 0.5), 4.14 (dd, 0.5).

Epoxy alcohol **2e** (1.88 g, 14.5 mmol) was converted to its tosylate (3.88 g, 13.7 mmol, 94%) (R_f 0.2, 5:1 hexane–ethyl acetate): mp 34–35 °C; $[\alpha]^{25}_D$ −24.9° (*c* 4.13, $CHCl_3$); ^{1}H NMR δ 0.88 (s, 9), 2.44 (s, 3), 2.58 (d, 1, *J* = 2.1), 3.06 (m, 1), 3.90–3.96 (dd, 1, *J* = 6.0, 11.3), 4.17–4.22 (dd, 1, *J* = 3.6, 11.3), 7.34 (d, 2), 7.79 (d, 2); ^{13}C NMR δ 21.6, 25.6, 30.5, 51.7, 64.3, 70.5, 127.9, 129.9, 132.7, 145.0. Treatment of the tosylate (3.74 g, 13.2 mmol) with Te (2 equiv)–rongalite for 12 h gave crude product which was distilled (bulb-to-bulb) to yield **3e**[99] as a clear, colorless, pungent, volatile oil (0.95 g, 8.3 mmol, 63%, >95% ee via MTPA ester) (R_f 0.48, 2:1 hexanes–ethyl acetate): $[\alpha]^{23}_D$ +38.6° (*c* 4.83, $CHCl_3$); ^{1}H NMR[100] δ 0.91 (s, 9), 1.51 (br s, 1), 3.74 (d, 1, *J* = 6.6), 5.15–5.25 (m, 2), 5.86–5.98 (ddd, 1, *J* = 6.7, 10.4, 17.2); ^{13}C NMR δ 25.6, 34.6, 81.2, 116.3, 138.1. (*R*)-MTPA ester of (+)-**3e**: ^{1}H NMR (C_6D_6) δ 0.77 (s, 9), 3.39 (s, 3), 4.98 (d, 1, *J* = 9.7), 5.11–5.17 (m, 2), 5.46–5.58 (m, 1). (*R*)-MTPA ester of (±)-**3e**: ^{1}H NMR (C_6D_6) δ 0.73, (s, 4.5), 0.77 (s, 4.5), 3.39 (s, 1.5), 3.43 (s, 1.5), 4.98–5.05 (m, 1), 5.11–5.24 (m, 2), 5.46–5.66 (m, 1); IR (film) 3405 (br, s), 3079 (w), 1644 (w), 1395 (s), 1366 (m), 1123 (s), 1051 (s), 993 (s), 924 (m), 870 (m) cm^{-1}.

(3*S*)-(+)- and (3*R*)-(−)-Linalool (8a, 8b) (Table I, Entries 9 and 10). Geraniol [(*E*)-3,7-dimethyl-2,6-octadien-1-ol] (10.0 g, 65.0 mmol), freshly distilled, was subjected to asymmetric epoxidation [(+)-DIPT] to give (2*S*,3*S*)-2,3-epoxygeraniol (10.0 g, 58.8 mmol, 91%, >95% ee by NMR of MTPA ester): $[\alpha]^{25}_D$ −5.41° (*c* 4.1, $CHCl_3$) [lit. $[\alpha]^{24}_D$ −6.36° (94% ee) (*c* 1.5, $CHCl_3$),[3] $[\alpha]_D$ −5.89° ($CHCl_3$),[101] $[\alpha]_D$ −4.72° (95% ee) (*c* 1.5, $CHCl_3$),[102] $[\alpha]^{22}_D$ −5.34° (*c* 3.24, $CHCl_3$),[103] $[\alpha]^{25}_D$ −5.3° (91% ee) (*c* 3.0, $CHCl_3$),[5a] $[\alpha]^{20}_D$ −5.3° (*c* 3.08, $CHCl_3$),[104] $[\alpha]^{18}_D$ −4.60° (*c* 3.00, $CHCl_3$)[105]]. Asymmetric epoxidation of geraniol (5.0 g, 33 mmol) via (−)-DIPT gave (2*R*,3*R*)-2,3-epoxygeraniol (9.7 g, 28 mmol, 85%, >95% ee by NMR of MTPA ester): $[\alpha]^{24}_D$ +3.81° (*c* 3.10, $CHCl_3$) [lit. $[\alpha]^{20}_D$ +5.5° (*c* 1.50, $CHCl_3$),[104] $[\alpha]^{24}_D$ +5.6° (*c* 2.0, $CHCl_3$),[105] $[\alpha]^{20}_D$ +4° (*c* 4.9, $CHCl_3$)[106]]. (2*S*,3*S*)-2,3-Epoxygeraniol (3.0 g, 18 mmol) was converted to the tosylate, obtained as a pale brown oil (5.5 g, 17 mmol, 94%): $[\alpha]^{25}_D$ −17.1° (*c* 3.4, $CHCl_3$); ^{1}H NMR δ 1.21 (s, 3), 1.30–1.50 (m, 2), 1.59 (s, 3), 1.67 (s, 3), 2.03 (dd, 2, *J* = 7.5), 2.45 (s, 3, 2.97 (t, 1, *J* = 5.7), 4.12 (m, 2), 5.03 (m, 1, *J* = 6.9), 7.36 (d, 2, *J* = 8.1), 7.80 (d, 2, *J* = 8.1); ^{13}C NMR δ 16.57, 17.56, 21.56, 23.40, 25.54, 37.89, 58.63, 60.78, 68.56, 122.94, 127.87, 129.85, 132.25, 132.63, 145.02. (2*R*,3*R*)-2,3-Epoxygeraniol (1.0 g, 5.9 mmol) likewise was converted to the tosylate which was purified by flash chromatography on silica gel (1:2 ether–hexanes) to give a colorless oil (1.7 g, 5.1 mmol, 86%): $[\alpha]_D$ +17.4° (*c* 3.58, $CHCl_3$). Its ^{1}H NMR spectrum was identical with that of the tosylate of the (2*S*,3*S*) isomer. Treatment of the (2*R*,3*R*) tosylate (1.0 g, 3.1 mmol) in THF (12 mL) with Te (4 molar equiv) and aqueous rongalite for 5 h at room temperature according to the general procedure yielded (3*R*)-(−)-linalool (**8b**) (0.35 g, 2.3 mmol, 74%): $[\alpha]^{25}_D$ −12.33° (*c* 13.6, $CHCl_3$), 95% ee by NMR with Eu(hfc)$_3$[107] [lit. $[\alpha]_D$ −19.1° (*c* 1.3, hexane),[108] $[\alpha]^{20}_D$ −21.7° (neat), −20.7° (*c* 0.18, $CHCl_3$),[20g] $[\alpha]^{23}_D$ −17.04° (neat),[107] $[\alpha]^{20}_D$ −20.61° (neat)[109]]; ^{1}H NMR [$CDCl_3$ (0.485 g), (−)-linalool (8.25 mg, 0.0535 mmol), (+)-Eu (hfc)$_3$ (10.35 mg, 0.00867 mmol), Eu(hfc)$_3$/(−)-linalool) = 16%] δ 1.60 (s, 3 H), 1.64 (s, 3 H), 2.42 (s, 3 H), 2.75 (m, 4 H), 5.38 (m, 1 H), 5.48 (d, 1 H), 6.08 (d, 1 H), 6.87 (dd, 1 H). [(+)-Linalool (6.28 mg, 0.041 mmol), (−)-linalool (5.71 mg, 0.037 mmol) (+)-Eu(hfc)$_3$ (26.91 mg, 0.0225 mmol), Eu(hfc)$_3$/(±)-linalool = 29%]: ^{1}H NMR [$CDCl_3$ (0.75 mL)] δ 1.74 (s, 6 H), 3.15 (m, 2 H), 3.29 (s, 3 H), 3.34 (m, 2 H), 5.51 (m, 1 H), 5.68 (d, 0.46 H), 5.70 (d, 0.54 H), 6.46 (d, 0.45 H), 6.48 (d, 0.55 H), 7.30 (dd, 1 H). The % ee is assessed to be greater than 90%. The somewhat low specific rotation may indicate the presence of traces of solvent. The (2*S*,3*S*) tosylate (2.00 g, 6.20 mmol) in THF (7 mL) was treated with Te (2 molar equiv) and aqueous rongalite for 2 h according to the general procedure. The crude (*S*)-(+)-linalool (**8a**) was

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purified by flash chromatography (1:2 ether–hexanes) to give a golden oil (0.628 g, 4.08 mmol, 66%, 95% ee via NMR of MTPA ester): $[\alpha]^{25}_D$ +14.6° (c 13.6, $CHCl_3$), $[\alpha]^{24}_D$ +17.51° (neat) [lit. $[\alpha]^{22}_D$ +25° (c 0.3, MeOH),[110] $[\alpha]^{20}_D$ +21.62° (neat)[109]]; the ^1H NMR spectrum was identical with that reported previously;[20h] ^{13}C NMR δ 17.63, 22.74, 25.64, 27.79, 42.01, 73.40, 111.61, 124.28, 131.82, 144.99.

(S)-(+)-Nerolidol [(S)-(+)-3,7,11-Trimethyl-1,6,10-dodecatrien-3-ol (8c)] (Table I, Entry 11). *trans,trans*-Farnesol (3.00 g, 13.5 mmol) was subjected to SAE at −40 °C with (+)-DIPT as the chiral ligand to give 2(S),3(S)-epoxyfarnesol [3.13 g, 13.1 mmol, 97%, 95% ee via NMR with chiral shift reagent, (+)-Eu (hfc)$_3$]: $[\alpha]^{25}_D$ −6.3° (c 2.3, $CHCl_3$) [lit.[36c] (R,R)-isomer $[\alpha]^{26}_D$ +6.53° (c 4.21, $CHCl_3$)]; ^{13}C NMR δ 15.94, 16.73, 17.64, 23.54, 25.64, 26.59, 38.49, 39.61, 61.24, 61.36, 63.17, 123.15, 124.16, 131.34, 135.72. The H^1 NMR spectrum was as reported previously.[36e] The 2(S),3(S)-epoxyfarnesol (2.0 g, 8.4 mmol) was converted to the tosylate according to the general procedure. It was obtained as a yellow oil [3.2 g, 8.1 mmol, 96%, $[\alpha]^{25}_D$ −17.4° (c 3.0, $CHCl_3$)] that was used without further purification. The crude epoxy tosylate (1.0 g, 2.5 mmol) was treated with Te (2 molar equiv)–rongalite (6 molar equiv) according to the general procedure to give, after purification by chromatography (silica gel, 6:1 hexanes–ethyl acetate), (S)-(+)-nerolidol 8c as a colorless oil [0.52 g, 2.3 mmol, 92%, >95% ee via NMR with chiral shift reagent, Eu (hfc)$_3$, analogous to the procedure used with geraniol[107]]: $[\alpha]^{25}_D$ +11.5 (c 3.0, $CHCl_3$) [lit $[\alpha]_D$ +18° (EtOH),[111] $[\alpha]^{22}_D$ +15°;[112] (R)-(−)-nerolidol, lit. $[\alpha]^{23}_D$ −12.5° (c 0.022, CHCl),[113] $[\alpha]^{20}_D$ −17.9° (c 1.15, EtOH)[36c,e]; ^{13}C NMR δ 15.86, 17.53, 22.57, 25.54, 26.50, 27.69, 39.55, 41.91, 73.34, 111.51, 124.08 (C-6, C-10), 131.24, 135.36, 144.91. The ^1H NMR spectrum was as previously reported.[36e]

(S)-(+)-2-Methyl-1-phenyl-2-propen-1-ol (11a) (Table I, Entry 16). (E)-2-Methyl-3-phenyl-2-propen-1-ol (**10a**)[5a,114,115] (10 g, 68 mmol) was subjected to asymmetric epoxidation with (+)-DIPT as the chiral ligand as described previously[5a] to give (2S,3S)-2-methyl-3-phenyloxiranemethanol (9.3 g, 50.7 mmol, 84%, >95% ee via NMR of MTPA ester): mp 54–55 °C [lit.[5a] mp 57.5–58.5 °C]; $[\alpha]^{24}_D$ −14.4° (c 2.2, $CHCl_3$) [lit.[5a] $[\alpha]^{25}_D$ −16.9° (c 2.0, $CHCl_3$)]; ^{13}C NMR δ 13.41, 60.45, 63.71, 64.91, 126.35, 127.51, 128.05, 135.53. ^1H NMR and IR spectra were comparable with those reported previously.[5a,114,116] The (−)-epoxy alcohol (6.35 g, 38.7 mmol) was converted to the tosylate according to the general procedure. After chromatography, it was obtained as a colorless oil (11.6 g, 36.4 mmol, 94%): $[\alpha]^{26}_D$ −21.2° (c 2.45, $CHCl_3$); ^1H NMR δ 1.1 (s, 3), 2.45 (s, 3), 3.97 (s, 1), 4.08–4.17 (d, 2), 7.2–7.4 (m, 7), 7.80–7.88 (d, 2); ^{13}C NMR 13.31, 21.63, 60.45, 61.69, 73.59, 126.42, 127.89, 127.95, 128.13, 129.92, 132.65, 134.36, 145.09.

Treatment of the (−)-epoxy tosylate (1.6 g, 5.0 mmol) in THF (15 mL) with Te–rongalite at 0 °C for 11 h according to the general procedure gave after flash chromatography (silica gel, 1:6 ether–hexanes) the (S)-(+)-allylic alcohol 11a as a colorless oil (0.61 g, 4.1 mmol, 82%, >95% ee via NMR of MTPA ester): $[\alpha]^{26}_D$ +28° (c 2.2, $CHCl_3$); ^1H NMR δ 1.62 (s, 3), 4.97 (s, 1), 5.13 (s, 1), 5.21 (s, 1), 7.31–7.37 (m, 5); ^{13}C NMR δ 18.18, 76.57, 111.08, 126.39, 127.56, 128.30, 141.91, 147.75. Racemic 11a has been prepared previously.[117,118]

(S)-(−)-2,6-Dimethyl-1,5-heptadien-3-ol [(−)-11b] (Table I, Entry 17). (E)-2,6-Dimethyl-2,5-heptadien-1-ol (**10b**) was prepared by modification of the method of Mori and Ueda.[23b] 3-(2,6-Dimethyl-1,5-heptadienyl) 2-pyridyl sulfoxide was obtained as previously described.[23b] Trimethylphosphite (5.10 mL, 43.2 mmol), freshly distilled from elemental sodium, was added to the crude sulfoxide (ca 5.00 g, 20.0 mmol) in dry MeOH (20.0 mL) under a nitrogen atmosphere. The reaction mixture was stirred for 3 days and was quenched by addition of saturated, aqueous $NaHCO_3$ (15.0 mL). The bulk of the MeOH was removed in vacuo, water (18.0 mL) was added, and the mixture was extracted with CH_2Cl_2 (4 × 18 mL). The organic layers were combined, dried ($MgSO_4$), filtered, and concentrated in vacuo. The crude product (5.83 g) was purified by column chromatography (Merck Kieselgel 60, 1:2 ether–hexanes) to yield **10b**, a 94:6 mixture of E and Z isomers, as a clear, pale yellow oil (1.36 g, 9.69 mmol, 58.0% from the sulfide): IR (neat) 3318 (m), 2973 (m), 2917 (m), 2859 (m), 1670 (w), 1449 (m), 1378 (m), 1011 (m), 860 (w), 828 (w) cm^{-1}. ^1H NMR δ 1.49 (s, 1), 1.65 (s, 3), 1.71 (s, 6), 2.70–2.75 (t, 2 J = 7.1), 4.00 (s, 1.88, E isomer), 4.15 (s, 0.12, Z isomer), 5.10–5.13 (t, 1, J = 7.3), 5.36–5.41 (t, 1, J = 7.2); ^{13}C NMR δ 13.63, 17.69, 25.66, 26.70, 68.93, 122.4, 125.0, 134.5 (C-2, C-6).

Asymmetric epoxidation of **10b** (1.36 g, 9.69 mmol) with (+)-DIPT as the chiral ligand gave the epoxy alcohol as a clear, colorless oil (0.94 g, 6.05 mmol, 66%, 84% ee by ^1H NMR of MTPA ester): $[\alpha]^{23}_D$ −10.8° (c 1.56, $CHCl_3$) [lit.[23b] $[\alpha]^{22.5}_D$ −12.2° (c 1.56, $CHCl_3$)]; ^1H NMR δ 1.31 (s, 3), 1.64 (s, 3), 1.72 (s, 3), 1.89 (br s, 1), 2.12–2.43 (m, 2), 3.02 (t, 1, J = 6.5), 3.54–3.70 (m, 2), 5.15 (m, 1); ^{13}C NMR δ 14.17, 17.91, 25.72, 27.38, 59.67, 60.98, 65.35, 118.5, 134.6. MTPA ester: ^1H NMR δ 1.02 (s, 3), 1.42 (s, 3), 1.59 (s, 3), 1.90–2.12 (m, 2), 2.61–2.65 (t, 1, J = 6.4), 3.41 (s, 0.24), 3.43 (s, 2.76), 3.82–3.86 (d, 0.08, J = 11.6), 3.83–3.87 (d, 0.92, J = 11.6), 4.07–4.11 (d, 1, J = 11.6), 5.02–5.08 (m, 1), 7.02–7.14 (m, 3), 7.68–7.71 (d, 2).

The (−)-epoxy alcohol (0.094 g, 6.05 mmol) was converted to the tosylate (1.64 g, 5.28 mmol, 87%) according to the general procedure: $[\alpha]^{23}_D$ −28.3° (c 1.44, $CHCl_3$); ^1H NMR δ 1.31 (s, 3), 1.61 (s, 3), 1.71 (s, 3), 2.08–2.37 (m, 2), 2.45 (s, 3), 2.78 (t, 1, J = 6.4), 3.91 (dd, 2, J = 20.3, 10.5), 5.09 (m, 1), 7.33–7.36 (d, 2, J = 8.1), 7.77–7.80 (d, 2, J = 8.2); ^{13}C NMR δ 14.01, 17.94, 21.66, 25.73, 27.25, 57.84, 61.05, 74.37, 118.0, 128.0, 129.9, 135.0, 145.0, 148.5.

The epoxy tosylate (1.51 g, 4.84 mmol) in THF (15 mL) was treated with Te (4.0 molar equiv)–rongalite (6.0 molar equiv)–NaOH (6.2 molar equiv) according to the general procedure to give allylic alcohol [(−)-**11b**] which was distilled (Kugelrohr) to give a colorless oil (0.45 g, 3.20 mmol, 66%, 82% ee via MTPA ester): bp 33–35 °C (0.6 mm); $[\alpha]^{23}_D$ −31.1° (c 1.81, $CHCl_3$) [lit. $[\alpha]^{23}_D$ −26.5° (c 6.11, hexane);[23b] (+)-isomer $[\alpha]^{23}_D$ +31.8° (c 5.23, n-hexane)[23a]]; ^1H NMR δ 1.64 (s, 3), 1.72 (s, 3), 1.73 (s, 3), 2.26 (t, 2), 4.05 (t, 1 H), 4.84 (s, 1), 4.96 (s, 1), 5.12 (t, 1); ^{13}C NMR δ 17.97, 25.92, 34.13, 75.20, 110.8, 119.7, 135.1, 147.0. MTPA ester: ^1H NMR (C_6D_6) δ 1.42 (s, 3), 1.47 (s, 3), 1.56 (s, 3), 2.15–2.45 (m, 2), 3.41 (s, 0.27), 3.46 (s, 2.73), 4.76 (s, 1), 4.94 (s, 1), 5.02–5.08 (t, 1), 5.41–5.46 (t, 1), 7.03–7.11 (m, 3), 7.68–7.70 (d, 2).

(R)-(+)-2,6-Dimethyl-1,5-heptadien-3-ol [(+)-11b] (Table I, Entry 18). (E)-2,6-Dimethyl-2,5-heptadien-1-ol (**10b**)[23b] was subjected to asymmetric epoxidation with (−)-DIPT as the chiral ligand to give the epoxy alcohol as a clear, colorless oil (1.92 g, 12.3 mmol, 70%, 81% ee by ^1H NMR of MTPA ester): $[\alpha]^{24}_D$ +12.6° (c 2.41, $CHCl_3$) [lit. $[\alpha]^{22.5}_D$ +12.6 (c 2.13, $CHCl_3$)[23b]]; ^1H NMR δ 1.31 (s, 3), 1.64 (s, 3), 1.73 (s, 3), 2.10–2.45 (m, 2), 3.02–3.06 (t, 1, J = 6.5), 3.55–3.70 (m, 2), 5.15 (m, 1); ^{13}C NMR was identical with that above. MTPA ester: ^1H NMR δ 1.01 (s, 3), 1.40 (s, 3), 1.57 (s, 3), 1.88–2.25 (m, 2), 2.69–2.74 (t, 1, J = 6.6), 3.41 (s, 2.72), 3.45 (s, 0.28), 3.83–3.87 (d, 1, J = 12.0), 4.07–4.11 (d, 1, J = 11.5), 5.02–5.08 (m, 1), 7.02–7.14 (m, 3), 7.68–7.71 (d, 2).

The (+)-epoxy alcohol (1.68 g, 10.8 mmol) was converted to the tosylate (3.11 g, 10.0 mmol, 93%) according to the general procedure: $[\alpha]^{24}_D$ + 23.5° (c 0.76, $CHCl_3$); ^1H NMR δ 1.31 (s, 3), 1.61 (s, 3), 1.71 (s, 3), 2.10–2.33 (m, 2), 2.45 (s, 3), 2.75–2.79 (t, 1, J = 6.4), 3.88–3.98 (dd, 2, J = 20.1, 10.5), 5.06–5.11 (m, 1), 7.33–7.36 (d, 2, J = 8.1), 7.77–7.80 (d, 2, J = 8.2).

The epoxy tosylate (3.08 g, 9.90 mmol) in THF (20 mL) was treated with Te (4.0 molar equiv)–rongalite (6.0 molar equiv)–NaOH (6.0 molar equiv) according to the general procedure to give allylic alcohol (+)-**11b** which was distilled (Kugelrohr) to

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give a clear, colorless oil (1.06 g, 7.57 mmol, 76%, 82%, ee via MTPA ester): bp 50–55 °C (1.4 mm); $[\alpha]^{24}_D$ +31.0° (c 1.98, $CHCl_3$) [lit. $[\alpha]^{22.5}_D$ +26.4° (c 5.11, n-hexane),[23b] $[\alpha]^{23}_D$ +31.8° (c 5.23, n-hexane)[23a]]; ^1H NMR δ 1.64 (s, 3), 1.72 (s, 3), 1.74 (s, 3), 2.24–2.29 (t, 2, J = 6.7), 4.04–4.08 (t, 1, J = 6.4), 4.84 (s, 1), 4.95 (s, 1), 5.09–5.15 (m, 1); ^{13}C NMR δ 17.98, 25.86, 34.12, 75.21, 110.8, 119.7, 135.1, 147.0. MTPA ester: ^1H NMR (C_6D_6) δ 1.38 (s, 3), 1.52 (s, 3), 1.57 (s, 3), 2.16–2.43 (m, 2), 3.42 (s, 2.73), 3.47 (s, 0.27), 4.80 (s, 1), 4.95–5.00 (m, 1), 5.03 (s, 1), 5.50–5.55 (t, 1, J = 6.8), 7.05–7.12 (m, 3), 7.68–7.70 (d, 2, J = 7.5).

(1S)-2-Methylenecyclohexanol (11d) (Table I, Entry 19). 1-Cyclohexene-1-methanol (1.03 g, 9.20 mmol),[119] prepared by reduction of methyl 1-cyclohexene-1-carboxylate with $LiAlH_4$, was epoxidized asymmetrically as previously described[5a] with L-(+)-diethyl tartrate (DET) as the catalyst component to give (1S)-(−)-7-oxabicyclo[4.1.0]heptane-1-methanol (0.81 g, 6.3 mmol, 68%, >92–94% ee via MTPA ester): $[\alpha]^{24}_D$ −20°, −19.7° (c 16.3, $CHCl_3$) [lit.[5a] $[\alpha]^{25}_D$ −22.8° (c 2.6, $CHCl_3$)]; ^{13}C NMR δ 19.4, 19.7, 24.2, 25.0, 55.8, 60.3, 64.7. This epoxy alcohol (0.69 g, 5.39 mmol) was converted to its tosylate isolated as an oil (1.15 g, 4.08 mmol, 76%): $[\alpha]^{24}_D$ −19.7° (c 3.02, $CHCl_3$); ^1H NMR δ 1.3–2.0 (m, 8), 2.46 (s, 3), 3.03 (d, 1, J = 3), 3.96 (br s, 2), 7.34–7.8 (dd, 4). The tosylate (1.1 g, 3.9 mmol) in THF (10 mL) was treated with aqueous Te–rongalite to give (1S)-2-methylenecyclohexanol as a colorless oil [0.33 g, 3.0 mmol, 77%, 89% ee by NMR of MTPA ester]: $[\alpha]^{24}_D$ +11.6° (c 4.4, $CHCl_3$) [lit. $[\alpha]^{25}_D$ +6.7° (80% ee, $CHCl_3$),[24a] $[\alpha]^{24}_D$ −18.0° (1R isomer) (c 0.08, ether, ee not determined)[37g]]; ^1H NMR ($CDCl_3$) δ 1.3–2.1 (m, 8), 2.4 (m, 1), 4.05–4.12 (m, 1), 4.75 (s, 1), 4.9 (s, 1); ^{13}C NMR δ 23.7, 27.7, 33.5, 36.5, 72.6, 105.0, 151.6.

15a–f, 16a–f, 18a–d (Table I, Entries 20–29). Experimental data are given in the supplementary material.

Reaction of Te–$LiEt_3BH$ with an Erythro–Threo Mixture of α-Cyclohexyl-3-methyloxiranemethanol (19). An approximately 1:1 mixture of erythro and threo isomers of 19 (0.84 g, 5 mmol) prepared by epoxidation of (E)-α-1-propenylcyclohexanemethanol was treated in THF (20 mL) with Te (0.338 g, 2.65 mmol)–$LiEt_3BH$ as described previously.[10b] After 12 h, the reaction was worked up as usual to give a yellow oil that was separated by chromatography (silica gel, 6:1 hexanes–ether) into three fractions: (E)-α-1-propenylcyclohexanemethanol (0.13 g, 0.86 mmol, 17%), (E)-4-cyclohexyl-3-buten-2-ol (0.07 g, 0.43 mmol, 8.6%), and *erythro*-α-cyclohexyl-3-methyloxiranemethanol (0.15 g, 0.88 mmol, 18%). Spectra of these compounds were identical with those obtained previously in the reactions involving the tosylate (see the supplementary material).

Reaction of Te–$LiEt_3BH$ with *erythro*-α,3-Dicyclohexyloxiranemethanol (20). *erythro*-α,3-Dicyclohexyloxiranemethanol (0.060 g, 0.270 mmol, 55% ee) obtained by SKR as described previously[4,5a] was added in THF (5 mL) to Te (0.338 g, 2.65 mmol)–$LiEt_3BH$. The reaction mixture was stirred for 12 h and worked up as usual. After chromatography as above, allylic alcohol **21** was obtained as a yellow oil (0.057 g, 0.257 mmol, 94%, 55% ee via NMR of MTPA ester): $[\alpha]^{24}_D$ −10.5° (c 1.3, EtOH) [lit.[4] $[\alpha]^{24}_D$ −19.8° (c 1.46, EtOH)]. ^1H, ^{13}C NMR and IR spectra were identical with those given in the supplementary material for the transposition of the tosylate.[10b]

(S)-(+)-1,2-Diphenyl-3-methyl-3-buten-2-ol (23) (Table I, Entry 30). The starting allylic alcohol, (E)-3,4-diphenyl-2-methyl-2-buten-1-ol, **22**, was obtained previously via a Wittig–Horner reaction of deoxybenzoin and ethyl 2-(diethoxyphosphinyl) propionate followed by reduction of the ester with $LiAlH_4$.[20f] The yield of the ester was improved from 16 to 34% by formation of the Wittig–Horner reagent in THF at −50 °C, warming to room temperature, addition of deoxybenzoin, and refluxing for 3 d: ^{13}C NMR δ 14.24, 17.57, 41.79, 60.58, 125.90, 126.38, 126.91, 127.97, 128.19, 128.29, 129.10, 138.62, 141.04, 146.56, 170.02. Reduction of the ester as described previously[20f] gave the allylic alcohol **22** in 79% yield: ^{13}C NMR δ 17.97, 39.89, 63.64, 125.85, 126.28, 127.87, 128.22, 128.44, 128.57, 132.29, 137.07, 139.68, 142.75. Asymmetric epoxidation of **22** (0.80 g, 3.4 mmol) was performed under stoichiometric conditions as described by Erickson[20f] and gave the epoxy alcohol as a colorless oil (0.60 g, 2.4 mmol, 71%, >90% ee via NMR of MTPA ester): $[\alpha]^{24}_D$ +13.02° (c 1.29, $CHCl_3$). The epoxy alcohol (0.54 g, 2.1 mmol) was converted to the tosylate (0.71 g, 1.73 mmol, 83%): mp 97.5–100 °C; $[\alpha]^{24}_D$ +32.2° (c 0.258, $CHCl_3$); ^1H NMR δ 1.00 (s, 1), 2.46 (s, 3), 3.22–3.27 (dd, 4), 4.34–4.36 (dd, 2), 6.84–7.89 (m, 14). Treatment of the tosylate (0.60 g, 1.5 mmol) in THF (2 mL) with Te (2 molar equiv)–rongalite (6 molar equiv)–NaOH (6 molar equiv) according to the general procedure gave a pale yellow oil which was purified by flash chromatography to give the (+)-tertiary allylic alcohol **23** [0.23 g, 0.97 mmol, 66%, 93% ee via NMR with chiral shift reagent, Eu (hfc)$_3$]: bp 85 °C (0.38 mmHg); $[\alpha]^{24}_D$ +121.2° (c 1.19, $CHCl_3$); ^1H NMR δ 1.85 (s, 3), 1.91–1.98 (br s, 1), 3.35–3.44 (dd, 2), 4.9 (t, 1), 5.16–5.20 (s, 1), 6.85–7.38 (m, 10); ^{13}C NMR δ 19.47, 45.39, 78.45, 111.09, 125.78, 126.64, 126.79, 127.83, 127.95, 130.69, 136.02, 144.28, 149.14; HRMS for $C_{17}H_{18}O$ calcd 238.1357, found 238.1351.

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Supplementary Material Available: Experimental details and data (12 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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