An Efficient Catalytic Asymmetric Epoxidation Method

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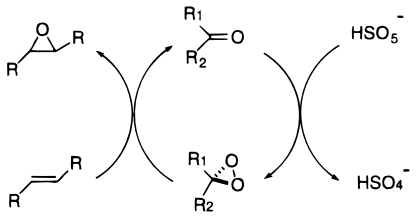
Abstract: This article describes a highly effective catalytic asymmetric epoxidation method for olefins using potassium peroxomonosulfate (Oxone, Dupont) as oxidant and a fructose-derived ketone (**1**) as catalyst. High enantioselectivies have been obtained for *trans*-disubstituted and trisubstituted olefins which can bear functional groups such as tributylsilyl ether, acetal, chloride, and ester. The enantiomeric excesses for *cis*-olefins and terminal olefins are not high yet. The current epoxidation shows that the catalyst efficiency is enhanced dramatically upon raising the pH. Mechanistic studies show that the epoxidation mainly proceeds via a spiro transition state, which provides a model for predicting the stereochemical outcome of the reaction. The planar transition state is likely to be the main competing pathway. The extent of the involvement of the planar mode is subject to the steric effect of the alkyl groups on the olefins.

Chiral epoxides are very important building blocks for the synthesis of enantiomerically pure complex molecules. Asymmetric epoxidation of olefins presents a powerful strategy for the synthesis of enantiomerically enriched epoxides. Great success has been achieved in the epoxidation of allylic alcohols,[1] unfuctionalized *cis*-olefins, and conjugated trisubstituted olefins.[2,3] However, the epoxidation of *trans*-olefins bearing no allylic alcohol group with high enantiomeric excess still remains a challenging problem.[4]

Among many other powerful epoxidation methods,[5,6] chiral dioxiranes generated *in situ* from potassium peroxomonosulfate (Oxone, DuPont) and chiral ketones have appeared to be promising reagents for asymmetric epoxidations, particularly for *trans*-olefins bearing no allylic alcohol groups (eq 1).[7−9] Since the first asymmetric epoxidation of olefins with dioxirane reported by Curci *et al*. in 1984,[9a] significant progress has been made in the area. Recently, Yang *et al*. reported an intriguing



(1)

C_2-symmetric cyclic chiral ketone derived from 1,1′-binaphthyl-2,2′-dicarboxylic acid.[9e,f] Using this ketone as catalyst, high enantioselectivity has been obtained for the epoxidation of *trans*-4,4′-disubstituted stilbenes.

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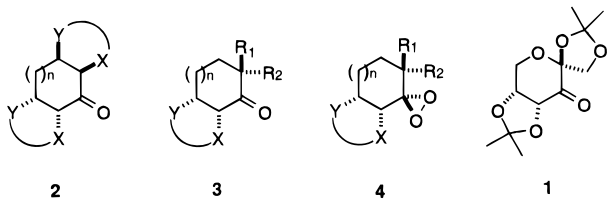
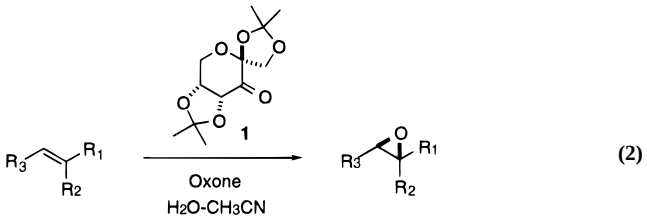


Figure 1. Ketones designed for study.

Recently, we reported a highly enantioselective epoxidation method for *trans*-olefins and trisubstituted olefins using a fructose-derived ketone (**1**) as catalyst and Oxone as oxidant (eq 2).[10] This epoxidation covered a variety of *trans*-olefins



(2)

and trisubstituted olefins. Subsequently, we found that the catalytic efficiency of ketone **1** is highly pH dependent.[11] Since our initial report, we have further optimized the reaction, including studies of solvent and temperature effects. The scope and limitation of this epoxidation have also been further examined. Our earlier studies showed that the epoxidation with ketone **1** proceeded mainly via a spiro transition state.[10] Additional studies suggest that a planar transition state is a main competing pathway. The extent of the involvement of the planar mode is dependent on the substituents on the olefins. In this paper, we report our detailed studies of this epoxidation.

Catalyst Design and Synthesis

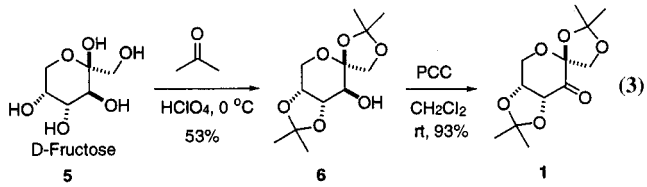
Selectivity and reactivity are two important factors that need to be considered in searching for an effective ketone catalyst. We have been focusing on ketones containing the following general features (Figure 1): (1) the stereogenic centers are close to the reacting center, resulting in efficient stereochemical communication between substrates and the catalyst; (2) the presence of fused ring(s) or a quaternary center α to the carbonyl group minimizes the epimerization of the stereogenic centers; and (3) possible competing approaches of an olefin to the reacting dioxirane can be controlled by sterically blocking one face or using a C_2- or pseudo-C_2-symmetric element.

With these structural considerations in mind, we initiated our work by investigating the feasibility of using carbohydrate-derived chiral ketones as epoxidation catalysts for the following reasons: (a) carbohydrates are chiral and readily available; (b) they are highly substituted with oxygen groups, which would be good for reactivity, as the inductive effect of oxygen activates the ketone catalyst; and (c) carbohydrate-derived ketones could have rigid conformations because of the anomeric effect, which would be desirable for selectivity. Among the ketones studied thus far, ketone **1** has been shown to be an effective epoxidation catalyst. Ketone **1** is readily prepared from very inexpensive D-fructose by ketalization and oxidation (eq 3).[12] The enantiomer of ketone catalyst **1** (ketone **ent-1**) is prepared in the same way from L-fructose (**ent-5**), which can be prepared from readily available L-sorbose by ketalization, mesylation, and one-pot acid−base treatment based on the reported procedure (eq 4).[13] The reaction sequences of this acid−base transformation are shown in eq 5.[13] Ketone **ent-1** prepared by this way shows the same enantioselectivity for the epoxidation as ketone **1**.

Table 1. Asymmetric Epoxidation of *trans*-Stilbene via Ketone **1**[a]

entry	time (h)	isolated yield (%)	ee (%)[b]
1[c]	1	31	>95
2[d]	2	39	>95
3[e]	4	40	89
4[f]	8	47	85

[a] The reactions were carried out at 0 °C (bath temperature) with substrate (1 equiv), ketone **1** (1 equiv), Oxone (5 equiv), and $NaHCO_3$ (15.5 equiv) in CH_3CN−aqueous $Na_2(EDTA)$ (4×10^{-4} M) (1.5:1 v/v) as in method A. [b] Enantioselectivity was determined by ^1H NMR shift analysis of stilbene oxide with $Eu(hfc)_3$. [c] The Oxone/$NaHCO_3$ mixture added in 45 min, and the reaction worked up after 1 h. [d] The Oxone/$NaHCO_3$ mixture added in 100 min, and the reaction worked up after 2 h. [e] The Oxone/$NaHCO_3$ mixture added in 220 min, and the reaction worked up after 4 h. [f] The Oxone/$NaHCO_3$ mixture added in 6 h, and the reaction worked up after 8 h.



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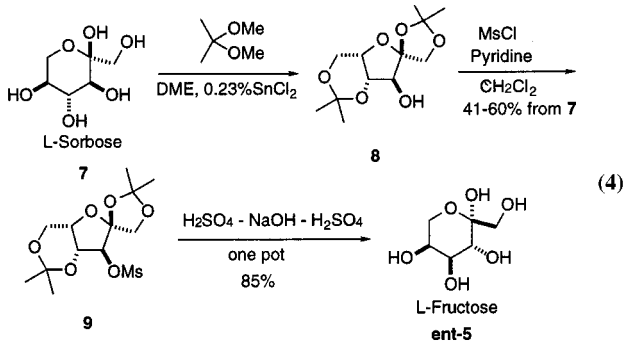

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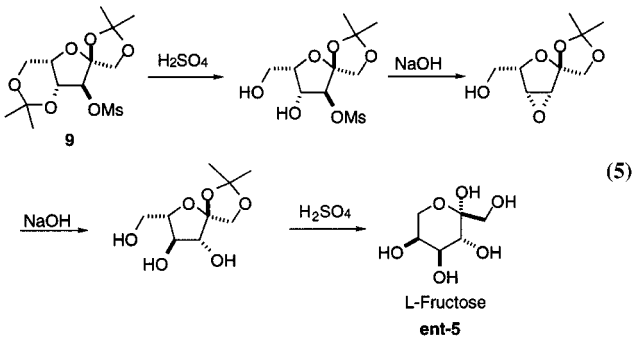

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Initial Asymmetric Epoxidation Using a Stoichiometric Amount of Ketone 1

We initiated the epoxidation using *trans*-stilbene as a test substrate. It was found that, while the yield of stilbene epoxide increased with the reaction time, the enantiomeric excess (ee) decreased (Table 1). Further examination showed that ketone

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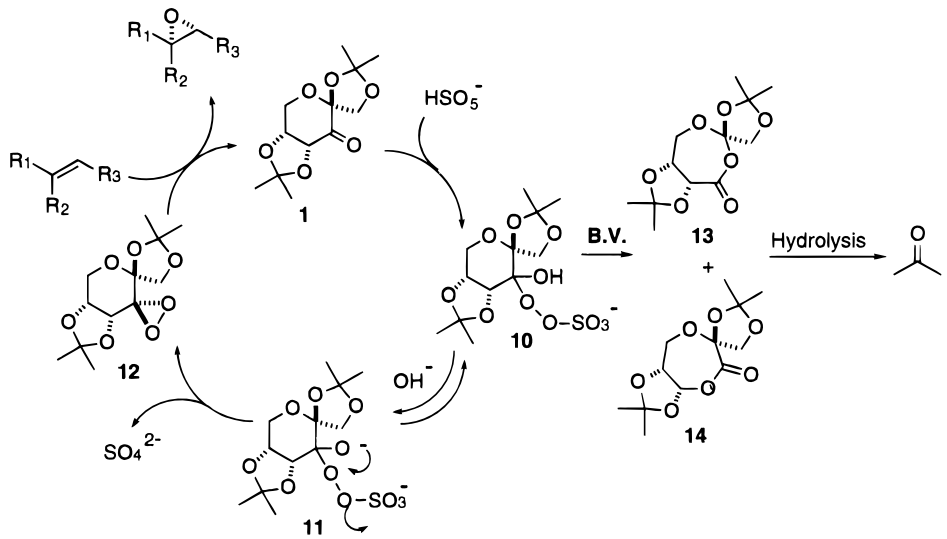

Figure 2. Possible reaction pathways of the epoxidation catalyzed by ketone **1**.

1 decomposed over time under the reaction conditions.[14] The decreased ee could be attributed to the epoxidation being catalyzed by an achiral (possibly acetone) or less enantioselective ketone resulting from the decomposition of ketone **1**. However, >95% ee could be achieved for stilbene oxide if the reaction was terminated in a short reaction time (2 h). Subsequently, we investigated the asymmetric epoxidation with a variety of olefins using an excess of ketone **1** to maximize the ee (Method A in Tables 4 and 5) and found that the epoxidation was quite general. Encouraged by the potential usefulness of this epoxidation, we decided to study the factors crucial for the reaction and to optimize reaction conditions to improve the catalyst efficiency and enantioselectivity.

A Dramatic pH Effect Leads to a Catalytic Process

The pH is a very important factor for the epoxidation with dioxiranes generated *in situ*. Generally, higher pH results in more rapid autodecomposition of Oxone, which leads to the decrease of epoxidation efficiency.[8a,g,15] For this reason, epoxidations are usually carried out at pH 7−8,[8,9] at times with the optimal pH within a narrow window of 7.8−8.0.[8g] For the asymmetric epoxidation, another issue that needs to be considered is the background reaction in the absence of chiral ketone catalyst. At high pH, the uncatalyzed background reaction could be significant.[16] Based on these considerations, our initial epoxidations were carried out at pH 7−8. However, at this pH, ketone **1** decomposed very rapidly. As a result, a large amount of ketone was required to achieve good conversion of substrates. Our results to date imply that the Baeyer−Villiger reaction could be one of the major decomposition pathways for the catalyst (Figure 2), although no direct evidence has been obtained thus far.[14] Further analysis of the reaction scheme shown in Figure 2 suggests that the competing Baeyer−Villiger reaction may be reduced at a higher pH, since higher pH favors the equilibrium toward intermediate **11**. This would consequently lead to a more efficient formation of dioxirane **12**.[17] We surmised that the autodecomposition of Oxone and uncatalyzed background reaction at high pH could possibly be overridden if ketone **1** had a sufficient reactivity. A systematic pH study was, therefore, carried out to address these questions.

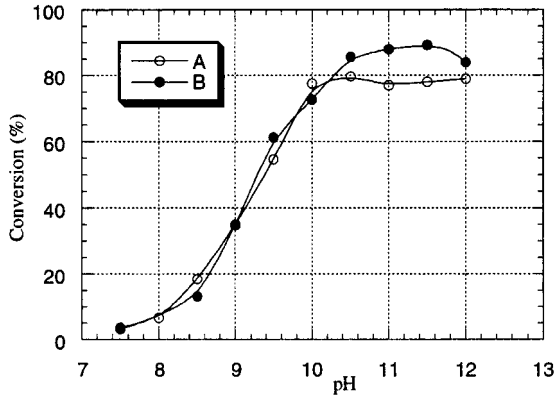

Figure 3. Plot of the conversion of *trans*-β-methylstyrene against pH using ketone **1** (0.2 equiv) as catalyst in two solvent systems, H_2O−CH_3CN (1:1.5 v/v) (A) and H_2O−CH_3CN−DMM (2:1:2 v/v) (B) (for details, see the text).

trans-β-Methylstyrene was chosen as a test substrate for the pH studies because both the conversion and ee could be easily determined by GC. The pH studies were carried out at 0 °C (ice bath) using 20 mol % of catalyst **1**. The epoxidation reactions essentially stopped after 1.5 h at all pH values studied. The results with the 1.5 h reaction time are shown in Figure 3. The pH showed a profound effect on the substrate conversion, and the higher pH was, indeed, beneficial to the catalyst efficiency, as hoped. The conversion of *trans*-β-methylstyrene to its epoxide increased more than 10-fold from a lower pH (7−8) to a higher pH (>10), and the enantioselectivity remained high at high pH (90−92% ee).[18] In addition, the amount of Oxone used in this catalytic procedure was reduced significantly, suggesting that ketone **1** was, indeed, reactive enough to

(14) Attempts to identify the decomposition products so far have been unsuccessful.

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(16) Kurihara, M.; Ito, S.; Tsutsumi, N.; Miyata, N. *Tetrahedron Lett.* **1994**, *35*, 1577−1580.

(17) (a) There is a report showing that the catalytic efficiency of cyclohexanone for the oxidation of pyridine with Oxone is maximized at a slightly higher pH (8.5). The data suggest that, at this pH, the Baeyer−Villiger process of cyclohexanone is minimized; see: Gallopo, A. R.; Edwards, J. O. *J. Org. Chem.* **1981**, *46*, 1684−1688. (b) There is also a report suggesting that the Baeyer−Villiger reaction might become significant at high pH values (pH > 11); see ref 8a.

(18) Under this condition, the epoxidation in the absence of the ketone catalyst is negligible within 2 h reaction time.

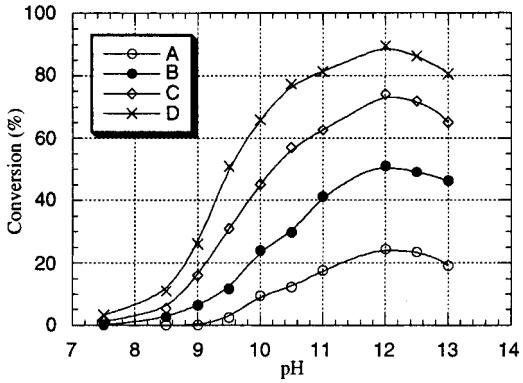


Figure 4. Plot of the conversion of *trans*-β-methylstyrene against pH using acetone (3 equiv) as catalyst in H_2O-CH_3CN (1:1.5 v/v). Samples were taken at different reaction times for the determination of conversion: 0.5 (A), 1.0 (B), 1.5 (C), and 2.0 h (D) (for details, see the text).

compete with the autodecomposition of Oxone.[19] This dramatic pH effect leads to a catalytic asymmetric epoxidation process, which significantly enhances the potential of the current epoxidation for practical use. The optimal pH range is broad, which simplifies the experimental operation. The epoxidation is typically carried out around pH 10.5, which can be conveniently achieved by adding K_2CO_3 (method B in Tables 4 and 5). Furthermore, epoxides are usually more stable under these conditions.

For comparison, the pH effect on the epoxidation of *trans*-β-methylstyrene using acetone as catalyst was also studied. The results in Figure 4 show that the efficiency of the acetone-catalyzed epoxidation is generally enhanced as well at higher pH. This could be due to the enhanced nucleophilicity of Oxone, which increase the reactivity toward acetone (it is worthy of reiteration here that the epoxidation by Oxone itself under these conditions is negligible, and the epoxidation is due solely to acetone catalysis).[18] Therefore, the enhanced epoxidation efficiency at higher pH for ketone catalyst **1** is not only due to a decrease of the Baeyer−Villiger reaction but also a result of the increase of Oxone nucleophilicity (the enhanced nucleophilicity of Oxone would suppress additional competing side reactions of the catalyst). A clearer understanding awaits further studies.

Solvent and Temperature Effects

To further optimize the enantioselectivity and conversion, a variety of solvents were tested for the epoxidation of *trans*-β-methylstyrene. The results of solvent studies are shown in Table 2. Among the solvents studied, CH_3CN[8f] was the best solvent when it was used as a single organic solvent in terms of both substrate conversion and enantioselectivity for catalyst ketone **1**. CH_3CH_3CN, Et_2O, THF, and CH_2Cl_2 were poor solvents for the current epoxidation system. Additional studies showed that the highest ee for the epoxidation of *trans*-β-methylstyrene was obtained when a mixture of CH_3CN and dimethoxymethane (DMM) (1:2 v/v) (Table 2, entry 18) was used as organic solvent. A good substrate conversion could also be achieved using this two-solvent system, although low conversion was obtained when DMM was used alone. This two-solvent system generally gave higher ee's than CH_3CN for many substrates (Tables 4 and 5), except for *cis*-olefins and terminal olefins (Table 6). The pH behavior of the $CH_3CN-DMM$ (1:2 v/v) system was similar to that of the CH_3CN system (Figure 3).

trans-β-Methylstyrene was again used as a substrate for the study of reaction temperature effect. To avoid any complication, 1 equiv of ketone catalyst **1** was used to ensure that the reaction was close to completion within a short reaction time at all temperatures tested. The results in Table 3 show that this epoxidation is slightly temperature dependent. Higher ee can be obtained at a lower temperature. A combination of solvent and temperature optimization significantly enhanced the enan-

Table 2. Solvent Effects on the Asymmetric Epoxidation of *trans*-β-Methylstyrene by Ketone **1**[a]

entry	solvent	T (°C)	time (min)	conv (%)[b]	ee(%)[c]
1	CH_3CN	20	20	100	89
2	CH_3CN	0	90	96	92
3	CH_3CH_2CN	20	60	11	80
4	DMM	20	60	36.2	91
5	DME	20	20	100	89
6	DME	0	90	92	89
7	DMF	20	20	95	86
8	dioxane	20	20	100	86
9	dioxane	0	90	96	86
10	THF	20	60	18	74
11	Et_2O	20	60	0	
12	CH_2Cl_2	20	30	<3	nd
13	CH_3CN/DMM (2:1)	20	20	100	90
14	CH_3CN/DMM (2:1)	0	90	100	92
15	CH_3CN/DMM (1:1)	20	20	98	91
16	CH_3CN/DMM (1:1)	0	90	100	93
17	CH_3CN/DMM (1:2)	20	20	94	92
18	**CH_3CN/DMM (1:2)**	**0**	**90**	**88**	**94**
19	CH_3CN/DMM (1:4)	0	90	77	94
20	DMM/DME (1:1)	20	25	66	92
21	CH_3CN/DMM/DME (1:1:2)	20	20	100	90
22	CH_3CN/DMM/DME (1:7:7)	20	20	89	90
23	CH_3CN/THF (1:1)	20	25	63	82
24	CH_3CN/Et_2O (1:1)	20	25	28	84

[a] All reactions were carried out with *trans*-β-methylstyrene (1 mmol), ketone **1** (0.3 mmol), and Oxone (1.38 mmol) in a mixture of 15 mL of organic solvent and 10 mL of 0.05 M $Na_2B_4O_7 \cdot 10H_2O$ in aqueous $Na_2(EDTA)$ (4×10^{-4} M) solution, and the pH was adjusted to 10.5 by using 1.0 M aqueous K_2CO_3 solution. [b] Conversion was determined by GC (HP-17 column). [c] Enantioselectivity was determined by chiral GC (Chiraldex γ-TA column). nd, not determined.

Table 3. Temperature Effect on the Epoxidation of *trans*-β-Methylstyrene by Ketone **1**[a]

entry	T (°C)	conv (%)[b]	ee (%)[c]
1	−11	99.4	95.7
2	−6	96.9	95.4
3	−2	97.5	95.2
4	2	99.4	94.7
5	8	99.0	93.8
6	20	99.0	93.2
7	30	96.8	91.1

[a] All reactions were carried out with *trans*-β-methylstyrene (1 mmol), ketone **1** (1 mmol), Oxone (1 mmol), K_2CO_3 (4.3 mmol), and Bu_4NHSO_4 (0.05 mmol) in 25 mL of $CH_3CN-DMM-0.05$ M $Na_2B_4O_7 \cdot 10H_2O$ in aqueous $Na_2(EDTA)$ (4×10^{-4} M) solution (1:2:2 v/v); the reactions were stopped after 20 min. [b] Conversion was determined by GC (HP-17 column). [c] Enantioselectivity was determined by chiral GC (Chiraldex γ-TA column).

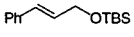
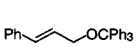
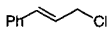
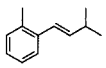
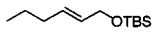
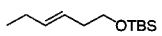
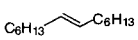
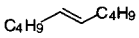
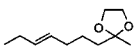
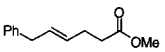
(19) In the literature, a large excess of Oxone (>5 equiv) is often used to achieve good conversions of olefins.

(20) (a) Baumstark, A. L.; McCloskey, C. J. *Tetrahedron Lett*. **1987**, *28*, 3311−3314. (b) Baumstark, A. L.; Vasquez, P. C. *J. Org. Chem*. **1988**, *53*, 3437−3439.

(21) Bach, R. D.; Andres, J. L.; Owensby, A. L.; Schlegel, H. B.; McDouall, J. J. W. *J. Am. Chem. Soc*. **1992**, *114*, 7207−7217.

(22) It is interesting to note that both experimental and theoretical studies suggested that the epoxidation of olefins with oxaziridine proceeded preferably via a planar transition state: (a) Davis, F. A.; Harakal, M. E.; Awad, S. B. *J. Am. Chem. Soc*. **1983**, *105*, 3123−3126. (b) Bach, R. D.; Wolber, G. J. *J. Am. Chem. Soc*. **1984**, *106*, 1410−1415. (c) Davis, F. A.; Chattopadhyay, S. *Tetrahedron Lett*. **1986**, *27*, 5079−5082.

Table 4. Asymmetric Epoxidation of Representative *trans*-Disubstituted Olefins by Ketone **1 ent-1**

Entry	Substrate	Method[a]	T (°C)	Yield[c] (%)	ee (%)	Config.[j]
1		A	0	73	95.2[e]	(+)-(R,R)[23a]
		B	0	75	97[e]	
		C	0	78	**98.9**[e]	
		C	20	85	97.9[e]	
		C (**ent-1**)	0	81	**98.3**[e]	(-)-(S,S)
2		A	0	81	88[g]	(+)-(R,R)[23b]
		B	0	93	91.7[f]	
		C	-10	94	**95.5**[f]	
		C (**ent-1**)	-10	94	**95.7**[f]	(-)-(S,S)
3		A	0	74	93[g]	(+)-(R,R)[23c]
		B	0	87	94[g]	
		C	0	71	**95.2**[e]	
4		C	0	55	94.0[e]	(+)-(R,R)[k]
5		A	0	61	93[g]	(+)-(2S,3R)[23c]
		C	0	49	**96.2**[f]	
6		A	0	41	93[g]	(+)-(2S,3R)[k]
7		C	-10	91[d]	93.3[f]	(+)-(R,R)[k]
8		C	-10	78[d]	95.7[f]	(-)-(R,R)[k]
9		A	0	80	93[h]	(+)-(R,R)[23c]
		C	-10	83	**94.5**[h]	
10		A	0	84	87[h]	(+)-(R,R)[23c]
		C	-10	85	**93**[h]	
11		A	0	81	90[i]	(+)-(R,R)[23d]
		B[b]	0	88	93[i]	
		C	-10	89	**95**[i]	
12		B[b]	0	70	91[i]	(+)-(R,R)[23e]
13		C	-10	92	92[g]	(+)-(R,R)[23f]
14		B	0	76	91[g]	(+)-(R,R)[23d]
		C	0	68	**92**[g]	

[a] Method A: all reactions were carried out at 0 °C (bath temperature) with substrate (1 equiv), ketone (3 equiv), Oxone (5 equiv), and $NaHCO_3$ (15.5 equiv) in CH_3CN−aqueous Na_2(EDTA) (4×10^{-4} M) solution (1.5:1, v/v). The reactions were stopped after 2 h (ref 10). Method B: all reactions were carried out with substrate (1 equiv), ketone (0.3 equiv), Oxone (1.38 equiv), and K_2CO_3 (5.8 equiv) in CH_3CN−0.05 M $Na_2B_4O_7 \cdot 10H_2O$ of aqueous Na_2(EDTA) (4×10^{-4} M) solution (1.5:1 v/v). The reactions were stopped after 1.5 h (ref 11). Method C: all reactions were carried out with substrate (1 equiv), ketone (0.3 equiv), Oxone (1.38 equiv), and K_2CO_3 (5.8 equiv) in CH_3CN−DMM−0.05 M $Na_2B_4O_7 \cdot 10H_2O$ of aqueous Na_2(EDTA) (4×10^{-4} M) solution (1:2:2, v/v). The reactions were stopped after 30 min for 20 °C, 1.5 h for 0 °C, and 2 h for −10 °C. [b] 0.2 equiv of ketone was used. [c] The epoxides were purified by flash chromatography and gave satisfactory spectroscopic characterization. [d] The yield is for the mixture of *trans*- and *cis*-epoxides. In entry 7, 29.3% ee (GC) was obtained for the *cis*-epoxide; in entry 8, 25.7% ee (GC) was obtained for the *cis*-epoxide. [e] Enantioselectivity was determined by chiral HPLC (Chiralcel OD). [f] Enantioselectivity was determined by chiral GC (Chiraldex γ-TA column). [g] Enantioselectivity was determined by ^{1}H NMR shift analysis of the epoxide products directly with Eu(hfc)$_3$. [h] Enantioselectivity was determined by ^{1}H NMR shift analysis of the derived acetate with Eu(hfc)$_3$. [i] The epoxide was opened (NaOMe−MeOH), and the resulting alcohol was converted to its acetate; enantioselectivity was determined by ^{1}H NMR shift analysis of the resulting acetate with Eu(hfc)$_3$. [j] The absolute configurations were determined by comparing the measured optical rotations with the reported ones. [k] The absolute configuration was tentatively assumed by analogy based on the spiro reaction mode.

tioselectivity for many substrates (method C *vs* methods A and B) (Tables 4 and 5).

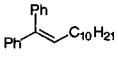
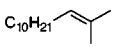
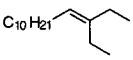
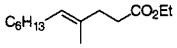
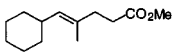
Substrate Scope

The results in Tables 4 show that the epoxidation-catalyzed by ketone **1** is quite effective toward a variety of *trans*-olefins. High ee can be obtained with *trans*-7-tetradecene (Table 4, entry 11), suggesting that this epoxidation may be general for simple unfunctionalized *trans*-olefins. The olefin substrates can bear a wide range of groups, such as tributylsilyl ether, trityl group, acetal, chloride, and ester. Trisubstituted olefins also show high

(23) (a) Chang, H.-T.; Sharpless, K. B. *J. Org. Chem.* **1996,** *61*, 6456−6457. (b) Witkop, B.; Foltz, C. M. *J. Am. Chem. Soc.* **1957**, *79*, 197−201. (c) See ref 10. (d) See ref 11. (e) Tanner, D.; Birgersson, C.; Gogoll, A.; Luthman, K. *Tetrahedron* **1994**, *50*, 9797−9824. (f) Compared with its dioxane analogues: Oehlschlager, A. C.; Johnston, B. D. *J. Org. Chem.* **1987**, *52*, 940−943.

(24) (a) Reference 2d. (b) Berti, G, Macchia, B.; Macchia, F; Monti, L. *J. Org. Chem.* **1968**, *33*, 4045−4049. (c) Satoh, T.; Oohara, T.; Ueda, Y.; Yamakawa, K. *J. Org. Chem.* **1989**, *54*, 3130−3136. (d) Tani, K.; Hanafusa, M.; Otsuka, S. *Tetrahedron Letters* **1979**, *32*, 3017−3020. (e) Zhang, W.; Loebach, J. L.; Wilson, S. R.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1990**, *112*, 2801−2803.

Table 5. Asymmetric Epoxidation of Representative Trisubstituted Olefins by Ketone **1 ent-1**

Entry	Substrate	Method[a]	T (°C)	Yield[b] (%)	ee (%)	Config.[h]
1		A	0	73	92[e]	(+)-(R,R)[24a]
		C	0	89	**95.5**[e]	
2		A	0	65	92.2[e]	(-)-(R)[24a]
		C	0	54	**96.7**[e]	
3		A	0	69	91[f]	(-)-(R,R)[24b]
		C	-10	94	**98**[f]	
4		A	0	74	94[e]	(-)-(1S,2R)[i]
		C	-10	98	**95.2**[e]	
5		B	0	66	93.5[e]	(+)-(R)[24c]
		C	0	92	**97.0**[e]	
6		C	-10	89[c]	96.8[f]	(R,R)[i]
7		C	-10	93	76.4[f]	(+)-(R)[i]
8		C	-10	97	86.5[g]	(+)-(R)[24c]
9		C	-10	35 (100[d])	91[f]	(-)-(R)[i]
10		C	-10	94	88.5[g]	(+)-(R)[i]
11		C	-10	91	83.5[g]	(+)-(R,R)[i]
12		C	-10	89	94[g]	(+)-(R,R)[i]
13		C	-10	77 (100[d])	81[f]	(+)-(1S,2R)[24d,e]
14		C (**ent-1**)	-10	41	97.2[f]	(-)-(R,R)[i]

[a] Methods are the same as in Table 4. [b] The epoxides were purified by flash chromatography and gave satisfactory spectroscopic characterization. [c] The yield is for the mixture of *trans*- and *cis*-epoxides. 83% ee (GC) was obtained for the *cis*-epoxide. [d] The conversion was determined by GC (HP-17 column). [e] Enantioselectivity was determined by chiral HPLC (Chiralcel OD). [f] Enantioselectivity was determined by chiral GC (Chiraldex γ-TA column). [g] Enantioselectivity was determined by ^{1}H NMR shift analysis of the epoxide products directly with Eu(hfc)$_3$. [h] The absolute configurations were determined by comparing the measured optical rotations with the reported ones. [i] The absolute configuration was tentatively assumed by analogy based on the spiro reaction mode.

selectivity (Table 5). However, the current ketone catalyst is not effective toward *cis*-olefins and terminal olefins. For these types of olefins, new catalysts need to be developed upon gaining more mechanistic information.

Discussion

Understanding the reaction mode of the dioxirane-mediated epoxidation is critical for developing a reliable model to predict the stereochemical outcome of the reaction and for designing a more effective ketone catalyst. Two mechanistic extremes (planar and spiro) are presented in Figure 5.[7c,d,9f,10,] A spiro transition state was proposed by Baumstark *et al*., based on the observation that *cis*-hexenes were 7−9-fold more reactive than the corresponding *trans*-hexenes for epoxidation using dimethyldioxirane.[20] This proposal came from the analysis of steric effects in both transition states. The lower reactivity of *trans*-hexenes can be attributed to the fact that there is a unfavorable steric interaction between the alkyl group of the *trans*-olefin and methyl group of dioxirane in the spiro-*trans* transition state, while such interaction does not exist in the spiro-*cis* transition state (Figure 6). On the other hand, the above steric interaction exists in both planar-*trans* and planar-*cis* transition states. Therefore, the different reactivity of *trans*- and *cis*-hexenes is consistent with a spiro rather than a planar transition state (Figure 6). The difference of the reactivity between *trans*- and *cis*-olefins was found to be dependent on the size of the alkyl groups of the olefins. The *trans* isomers of both β-methylstyrenes and stilbenes were found to be slightly more reactive than the *cis* isomers, suggesting that the steric interaction between the phenyl group and methyl group of dioxirane is minimal due

(25) (a) Corey, E. J.; Shibata, S.; Bakshi, R. K. *J. Org. Chem.* **1988**, *53*, 2861−2863. (b) Chattopadhyay, S.; Mamdapur, V. R.; Chadha, M. S. *Tetrahedron* **1990**, *46*, 3667−3672. (c) Fujisawa, T.; Takemura, I.; Ukaji, Y. *Tetrahedron Lett.* **1990**, *31*, 5479−5482. (d) Akhtar, M. N.; Boyd, D. R.; Hamilton, J. G. *J. Chem. Soc., Perkin Trans. 1*, **1979**, 2437−2440. (e) Jacobsen, E. N.; Zhang, W. PCT Int. Appl. W091 14,694, 1992; U.S. Appl. 496,992, 1992; *Chem. Abstr.* **1992**, *117*, 106067f.

Table 6. Asymmetric Epoxidation of Representative *cis*-Disubstituted & Terminal Olefins by Ketone **1**

Entry	Substrate	Method[a]	T (°C)	Yield[b] (%)	ee (%)	Config.[f]
1	Ph	B	-10	64	13.6[c]	(+)-(R)[25a]
		C	-10	90	24.3[c]	
2	C_8H_{17}	B	-10	80	27[e]	(+)-(R)[25b]
		C	-10	92	17[e]	
3	iPr_3Si	B	-10	92.2	35[e]	(-)[g]
		C	-10	99	31[e]	
4	Ph	B	-10	81.3	27.6[d]	(-)-(S)[25c]
		C	-10	95	19.6[d]	
5		B	-10	85.2	32[e]	(-)-(1S,2R)[24e,25d]
		C	-10	92	12[e]	
6		B	-10	50	56.2[c]	(+)-(R,R)[24e,25e]
		C	-10	43	61.4[c]	

[a] Methods are the same as in Table 4. All reactions were stopped after 2 h. [b] The epoxides were purified by flash chromatography and gave satisfactory spectroscopic characterization. [c] Enantioselectivity was determined by chiral GC (Chiraldex γ-TA column). [d] Enantioselectivity was determined by chiral HPLC (Chiralcel OD). [e] Enantioselectivity was determined by ^{1}H NMR shift analysis of the epoxide products directly with Eu(hfc)$_3$. [f] The absolute configurations were determined by comparing the measured optical rotations with the reported ones. [g] The absolute configuration is not ascertained.

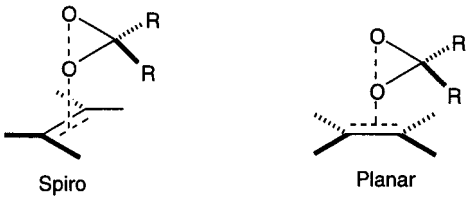


Figure 5. Spiro and planar transition states for the dioxirane epoxidation of olefins.

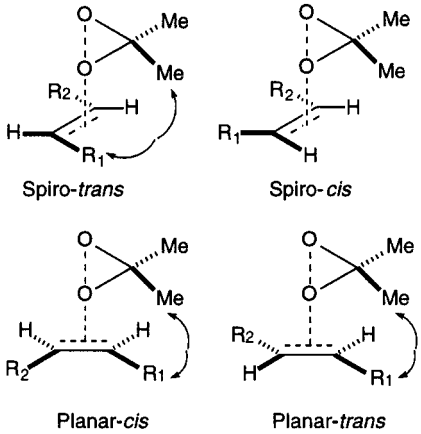


Figure 6. Spiro and planar transition states for the epoxidation of *trans*- and *cis*-olefins with dimethyldioxirane.

to the flat nature of the phenyl group.[20] Calculations by Bach *et al*. show that the optimized transition state for oxygen atom transfer from dimethyldioxirane to ethylene is the spiro transition state.[21,22] The spiro orientation of the transition state could benefit from a stabilizing interaction of an oxygen lone pair with the π^* orbital of the alkene.[21]

Stereochemical analysis provides another valuable way to address this issue. Figure 7 lists a few of the possible reaction transition states for the epoxidation between the olefin and the dioxirane of ketone **1**. Due to the steric repulsion, transition states **B**−**G** are disfavored (for *trans*-disubstituted olefins where R_2 = H, **B** is similar to **A** and **G** is similar to **H**). The favored transition states spiro **A** and planar **H** result in the opposite

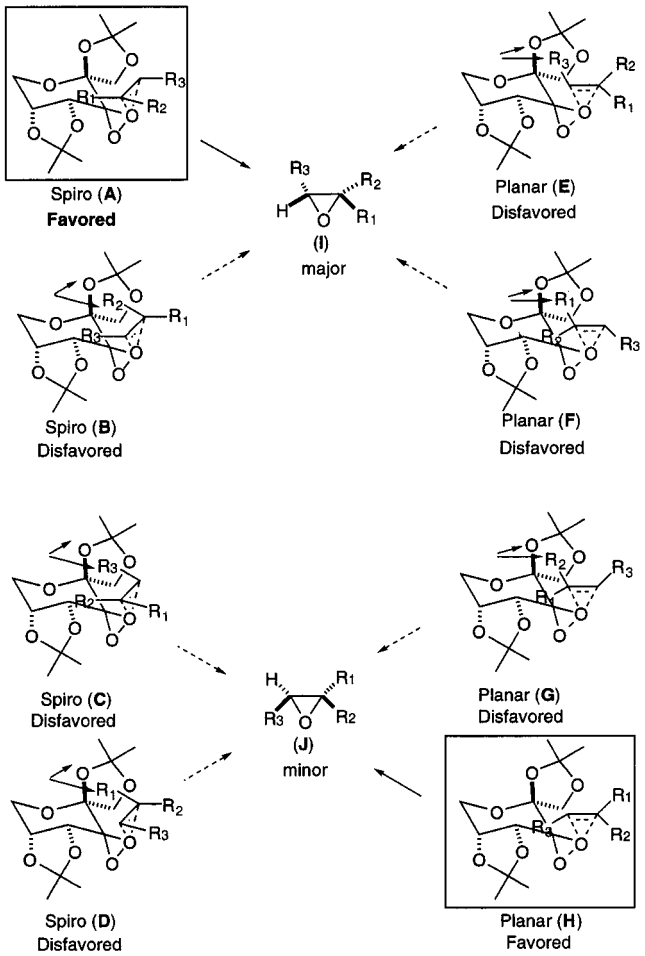
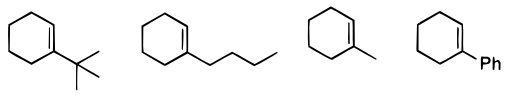


Figure 7. Spiro and planar transition states for the epoxidation catalyzed by ketone **1**.

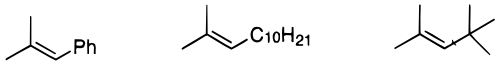
stereochemistry for the epoxide product. Therefore, analyzing the stereochemistry of resulting epoxides will allow us to determine which of these two transition states is favored.

For *trans*-disubstituted and trisubstitued olefins, all the examples with known epoxide configurations in Tables 4 and



26% ee 79% ee 81% ee 98% ee

Figure 8. Effect of the size of R_1 on enantioselectivities (decreasing the size of R_1 results in a higher ee).



76.4% ee 86.5% ee 91% ee

Figure 9. Effect of the size of R_3 on enantioselectivities (increasing the size of R_3 results in a higher ee).

76.4% ee 96.8% ee

Figure 10. Effect of the size of R_1 and R_3 on enantioselectivities (decreasing the size of R_1 and increasing the size of R_3 enhance the ee).

5 show that epoxide **I** is formed predominately, which supports a spiro transition state. This analysis provides us with a model to predict the stereochemistry of the formed epoxide given an olefin substrate. Furthermore, the ee obtained would permit us to estimate the energy difference between the spiro transition state (**A**) and the planar transition state (**H**). For example, the ee of the formed *trans*-stilbene oxide is about 98% at 0 °C, which can be translated into an approximately 2.5 kcal mol^{-1} energy difference between the two transition states. Given that the steric interaction between the phenyl group and the six-membered moiety of the catalyst is minimal due to the flatness of the phenyl group, this number (~2.5 kcal mol^{-1}) could reflect the intrinsic energy difference (stereoelectronic origin) between the spiro and planar transition states for the epoxidation of stilbene by the current dioxirane under the reaction conditions. As mentioned above, the energy difference could be due to the stabilizing interaction of an oxygen lone pair with the π^* orbital of the alkene in the spiro transition state. It should be expected that the energy difference will vary with substituents on the olefins since the energy level of π^* is affected by the substituents.

Analyzing transition states spiro **A** and planar **H** indicates that the energy difference should also be subject to the steric effect of substituents on the olefin. Higher ee can be obtained by decreasing the size of R_1 (favoring spiro **A)** and increasing the size of R_3 (disfavoring planar **H**). This is, indeed, the case, particularly for trisubstituted olefins (for *trans*-disubstituted olefins where $R_2 = H$, transition state **B** is also feasible, which provides an additional option to minimize the steric interaction). The representative cases presented in Figures 8−10 clearly show the above trend, indicating that transition state planar **H** is the major competing reaction mode. This information is valuable for designing a more enantioselective ketone catalyst in the future.

The current ketone catalyst (**1**) is very effective for *trans*-olefins and trisubstituted olefins but not for *cis*-olefins and terminal olefins yet. For *cis*-olefins ($R_1 = H$), both electronic and steric effects should favor the spiro transition states over the planar transition states. Spiro **A** and **D** are likely to be the two main competing pathways. Molecular model analysis indicates that the main secondary interaction between the olefin and catalyst is the interaction between the olefin substituents and the spiro cyclic ketal ring of the catalyst (interactions **a** and **b**) (Figure 11). The enantioselectivity depends on the

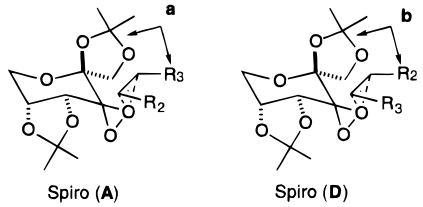


Figure 11. Two spiro transition states for the epoxidation of *cis*-olefin.

energy difference between **a** and **b**. The greater the difference of the size of R_2 and R_3 is, the higher the ee is. The examples in Table 6 (entries 5 and 6) verify the trend. The further enhancement of the ee will rely on widening the energy difference between **a** and **b** either by varying R_2 and R_3 and/or by modifying the catalyst. For terminal olefins (assuming $R_1 = R_2 = H$), spiro **A**, spiro **D**, planar **F**, and planar **G** are among the likely reaction pathways. The lower ee obtained for terminal olefins with catalyst **1** (Table 6) suggests that the energy difference among these the transition states is small. At this moment, it is difficult to explicitly identify which of the reaction modes predominates. New catalysts need to be developed for the epoxidation of terminal olefins in order to gain more insights and achieve good selectivity.

In summary, we have found that a ketone derived from fructose is a promising catalyst for asymmetric epoxidation. A few favorable features of this epoxidation are worth noting: (1) The reaction is highly selective for a variety of *trans*-disubstituted and trisubstituted olefins. The epoxidation proceeds mainly via a spiro transition state, allowing us to predict the resulting stereochemistry of the epoxide product with a reasonable level of confidence. (2) The reaction conditions are mild, and the reaction is rapid. (3) The workup is very easy. Simple extraction of the reaction mixture with hexane allows a clean separation between the epoxide and the ketone catalyst. The epoxide stays in the organic phase, and the catalyst remains in aqueous layer. (4) The reaction is environmentally friendly. Water is used as cosolvent, and no toxic metals are involved.

Future efforts will be devoted to the optimization of the ketone structure to enhance both enantioselectivity and stability of the ketone to make this process even more efficient and general.

Experimental Section

General Methods. Oxone was purchased from Aldrich (it has been found that the oxidation activity of the purchased Oxone occasionally varies with different batches). All glassware used for the epoxidation was carefully washed to be free of any trace metals which catalyze the decomposition of Oxone. Melting points were obtained using chromatographically purified material unless otherwise stated. The 300 MHz ^1H NMR and 75.5 MHz ^{13}C NMR spectra were measured on a Bruker ACE-300 spectrometer in $CDCl_3$. Proton chemical shifts (δ) are given relative to internal TMS (0.00 ppm), and carbon chemical shifts are given relative to $CDCl_3$ (77.23 ppm). Infrared spectra were recorded on a Perkin-Elmer 1600 Series FT-IR spectrometer. High-resolution mass spectra were performed at the mass spectrometry facility of Colorado State University. Elemental analyses were performed by M-H-W Laboratories (Phoenix, AZ). Optical rotations were measured on an Autopol III automatic polarimeter in a 10 cm cell. Silica gel 60 of E. Merck Co. was employed for all flash chromatography.

1,2:4,5-Di-*O*-isopropylidene-D-erythro-2,3-hexodiuro-2,6-pyranose (1). Perchloric acid (70%, 8.6 mL) was added to a suspension of D-fructose (36.84 g, 204.7 mmol) in acetone (740 mL) and 2,2-dimethoxypropane (14.8 mL, 120 mmol) at 0 °C (ice bath). After the reaction mixture was stirred under nitrogen at 0 °C for 6 h, concentrated ammonium hydroxide was added to pH 7−8. After the resulting mixture was stirred for another 5 min, the solvent was removed under reduced pressure, and the solid residue was recrystallized from hexane−

CH_2Cl_2 (4:1 v/v) to afford white needles (alcohol **6**) (28.34 g, 53.2%): mp 117−118.5 °C, $[\alpha]^{25}_D = -144.2°$ (c 1.0, $CHCl_3$) [lit.[26] mp 118−119 °C, $[\alpha]^{23}_D = -145°$ (*c* 1.4, $CHCl_3$)]; IR (KBr) 3547 cm^{-1}; ^1H NMR δ 4.22 (ddd, $J = 5.7, 2.7, 0.9$ Hz, 1H), 4.19 (d, $J = 9.0$ Hz, 1H), 4.13 (dd, $J = 6.8, 5.7$ Hz, 1H), 4.12 (dd, $J = 13.2, 2.7$ Hz, 1H), 4.01 (dd, $J = 13.2, 0.9$ Hz, 1H), 3.98 (d, $J = 9.0$ Hz, 1H), 3.67 (dd, $J = 8.1, 6.8$ Hz, 1H), 1.99 (d, $J = 8.1$ Hz, 1H), 1.54 (s, 3H), 1.52 (s, 3H), 1.44 (s, 3H), 1.37 (s, 3H); ^{13}C NMR δ 112.0, 109.6, 104.7, 77.48, 73.53, 73.52, 70.60, 60.96, 28.13, 26.62, 26.46, 26.14.

PCC (11.64 g, 54 mmol) was added portionwise over 15 min to a mixture of alcohol **6** (5.2 g, 20 mmol) and powdered 3 Å molecular sieves (22 g, activated at 180−200 °C under vacuum) in dichloromethane (100 mL). After the reaction mixture was stirred for 3 h under nitrogen, it was filtered through Celite and washed carefully with ether. The filtrate was concentrated, and the residue was purified by passing it through a short silica gel column (hexane−ether, 1:1 v/v) to afford a white solid (4.80 g, 93.0%), which was recrystallized from hexane−CH_2Cl_2 to give white crystals (ketone **1**): mp 101.5−103 °C, $[\alpha]^{25}_D = -125.4°$ (*c* 1.0, $CHCl_3$) (lit.[27] mp 101.5−102.5 °C, $[\alpha]_D = -126.4°$ (*c* 1.0, $CHCl_3$); IR (KBr) 1749 cm^{-1}; ^1H NMR δ 4.73 (d, $J = 5.7$ Hz, 1H), 4.61 (d, $J = 9.5$ Hz, 1H), 4.55 (ddd, $J = 5.7, 2.2, 1.0$ Hz, 1H), 4.39 (dd, $J = 13.4, 2.2$ Hz, 1H), 4.12 (d, $J = 13.4$ Hz, 1H), 4.00 (d, $J = 9.5$ Hz, 1H), 1.55 (s, 3H), 1.46 (s, 3H), 1.40 (s, 6H); ^{13}C NMR δ 197.1, 114.0, 110.8, 104.3, 78.11, 76.07, 70.20, 60.28, 27.33, 26.70, 26.24, 26.20. Anal. Calcd for $C_{13}H_{20}O_5$: C, 55.81; H, 7.02. Found: C, 55.47; H, 7.10.

1,2:4,5-Di-*O*-isopropylidene-L-erythro-2,3-hexodiuro-2,6-pyranose (ent-1). A solution of 1,2-dimethoxyethane (0.5 mL) containing $SnCl_2$ (0.0125 g, 0.066 mmol) was added to a suspension of L-sorbose (5 g, 27.75 mmol) in 2,2-dimethoxypropane (15 mL). The mixture was refluxed gently with stirring until it was clear and then evaporated to a syrup (alcohol **8**).

The syrup was dissolved in CH_2Cl_2 (15 mL), followed by the addition of pyridine (3.5 mL, 43.3 mmol) and DMAP (catalytic amount). The solution was then cooled in an ice bath, and methanesulfonyl chloride (3.3 mL, 42.6 mmol) was added dropwise. After the reaction mixture was stirred for 2 h at 0 °C, water was added. The mixture was extracted with CH_2Cl_2. The combined organic layers were washed with brine, dried (Na_2SO_4), filtered, and concentrated to give crude mesylate **9**. Recrystallization from ethanol gave colorless needles (3.63 g, 41% yield for two steps) [in a separate run, the crude mesylate was flash chromatographed (hexane−EtOAc, 3:1 v/v) to give **9** as a pale yellow solid (5.3 g, 60%)]. mp 120−121 °C (lit.[13] mp 123−124 °C); IR (KBr) 1376, 1348, 1181, 1071 cm^{-1}; ^1H NMR δ 4.87 (d, $J = 1.8$ Hz, 1H), 4.47 (dd, $J = 3.0, 1.8$ Hz, 1H), 4.25 (d, $J = 9.7$ Hz, 1H), 4.22 (m, 1H), 4.20 (d, $J = 9.7$ Hz, 1H), 4.01 (dd, $J = 13.2, 3.2$ Hz, 1H), 3.92 (dd, $J = 13.2, 3.2$ Hz, 1H), 1.56 (s, 3H), 1.48 (s, 3H), 1.43 (s, 3H), 1.39 (s, 3H); ^{13}C NMR δ 111.8, 110.0, 98.47, 84.4, 73.53, 73.42, 72.31, 60.54, 39.07, 28.30, 26.13, 26.14, 20.14.

To a solution of mesylate **9** (29.5 g, 87.3 mmol) in acetone (236 mL) was added an aqueous solution of 0.25% H_2SO_4 (177 mL). After being stirred at 25 °C for 20 h, the solution was made alkaline with 9 M NaOH (23.6 mL). The resulting mixture was heated at 70−80 °C for 48 h, acidified to pH ∼1 with 9 M H_2SO_4, and heated at 70−80 °C for 20 min. After being neutralized with 2 M NaOH, the mixture was taken to dryness, and the residue was extracted with ethanol (500 mL). The ethanol solution was concentrated to a syrup (L-fructose) (14 g, 85%).

The resulting crude L-fructose was directly converted to ketone **ent-1** as D-fructose. The resulted ketone **ent-1** [mp 102−103 °C (recrystallized from hexane−CH_2Cl_2 (4:1 v/v)), $[\alpha]^{25}_D = +123°$ (*c* 0.58, $CHCl_3$)] showed the same enantioselectivity as ketone **1**.

Procedure for pH study. To a 100 mL three-neck round-bottom flask were added buffer (10 mL) [4×10^{-4} M aqueous Na_2(EDTA), adjusting with 1.0 M KOH for pH 7.5−8.0; 0.05 M $Na_2B_4O_7 \cdot 10H_2O$ in 4×10^{-4} M aqueous Na_2(EDTA), adjusting with 1.0 M aqueous KH_2PO_4 for pH 8.5−10.5; 0.05 M aq K_2HPO_4 plus 0.1 M aqueous NaOH (2:1 v/v), adjusting with 1.0 M KH_2PO_4 for pH 11.0−12.0; 0.05 M aq K_2HPO_4 plus 0.1 M aqueous NaOH (2:1 v/v), adjusting with 1.0 M KOH for pH 12.5−13.0], acetonitrile (15 mL), *trans*-β-methylstyrene (0.118 g, 1 mmol), tetrabutylammonium hydrogen sulfate (0.015 g, 0.04 mmol), and ketone **1** (0.0516 g, 0.2 mmol). The reaction mixture was cooled with an ice bath. A solution of Oxone (1.54 g, 2.5 mmol) in aqueous Na_2(EDTA) (4×10^{-4} M, 10 mL) was added through a syringe pump at a speed of 4.1 mL/h. The reaction pH was monitored with a Corning 320 pH meter with a Corning "3-in-1" pH combination electrode and was maintained within ±0.1 by adding 0.5 N aqueous KOH. The conversion and ee values were checked by GC every 30 min.

General Epoxidation Procedures. Method A. Aqueous Na_2(EDTA) (1×10^{-4} M, 10 mL) and a catalytic amount of tetrabutylammonium hydrogen sulfate were added to a solution of *trans*-stilbene (0.18 g, 1 mmol) in acetonitrile (15 mL) with vigorous stirring at 0 °C. A mixture of Oxone (3.07 g, 5 mmol) and sodium bicarbonate (1.3 g, 15.5 mmol) was pulverized, and a small portion of this mixture was added to the reaction mixture to bring the pH to >7. After 5 min, ketone **1** (0.77 g, 3 mmol) was added portionwise over a period of 1 h. Simultaneously, the rest of the Oxone and sodium bicarbonate was added portionwise over 50 min. After completion of the addition of ketone **1**, the reaction mixture was stirred for another 1 h at 0 °C, diluted with water (30 mL), and extracted with hexanes (4×40 mL). The combined extracts were washed with brine, dried (Na_2SO_4), filtered, concentrated, and purified by flash chromatography [the silica gel was buffered with 1% triethylamine solution in hexane; hexane−ether (1:0 to 50:1 v/v) was used as the eluent] to afford *trans*-stilbene oxide as white crystals (0.149 g, 73% yield, 95.2% ee).

Method B. To a 100 mL three-neck round-bottom flask were added buffer (0.05 M $Na_2B_4O_7 \cdot 10H_2O$ in 4×10^{-4} M aqueous Na_2(EDTA), 10 mL), acetonitrile (15 mL), *trans*-β-methylstyrene (0.118 g, 1 mmol), tetrabutylammonium hydrogen sulfate (0.015 g, 0.04 mmol), and ketone **1** (0.0774 g, 0.3 mmol). The reaction mixture was cooled with an ice bath. A solution of Oxone (0.85 g, 1.38 mmol) in aqueous Na_2(EDTA) (4×10^{-4} M, 6.5 mL) and a solution of K_2CO_3 (0.8 g, 5.8 mmol) in water (6.5 mL) were added dropwise through two separate addition funnels over a period of 1.5 h (under this condition, the reaction pH is around 10.5; it is recommended that both Oxone and K_2CO_3 be added uniformly over 1.5 h). At this point, the reaction was immediately quenched by addition of pentane and water. The mixture was extracted with pentane (3×30 mL), washed with brine, dried over Na_2SO_4, purified by flash chromatography [the silica gel was buffered with 1% Et_3N in pentane; pentane−ether (1:0 to 50:1 v/v) was used as eluent] to afford *trans*-β-methylstyrene oxide as colorless liquid (0.124 g, 93% yield, 92% ee).

Method C. (a) Reaction at 20 °C. *trans*-Stilbene (0.181 g, 1 mmol) was dissolved in acetonitrile−DMM (15 mL, 1:2, v/v). Subsequently were added buffer (10 mL, 0.05 M solution of $Na_2B_4O_7 \cdot 10H_2O$ in 4×10^{-4} M aqueous Na_2(EDTA)), tetrabutylammonium hydrogen sulfate (0.015 g, 0.04 mmol), and ketone **1** (0.0774 g, 0.3 mmol). A solution of Oxone (1.0 g, 1.6 mmol) in aqueous Na_2(EDTA) (4×10^{-4} M, 6.5 mL) and a solution of K_2CO_3 (0.93 g, 6.74 mmol) in water (6.5 mL) were added dropwise separately over a period of 30 min (via addition funnels). The reaction was then worked up by the same procedure as in method A to afford *trans*-stilbene oxide (0.166 g, 85% yield, 97.9% ee).

(b) Reaction at 0 °C. *trans*-Stilbene (0.181 g, 1 mmol) was dissolved in acetonitrile−DMM (15 mL, 1:2, v/v). Subsequently were added buffer (10 mL, 0.05 M solution of $Na_2B_4O_7 \cdot 10H_2O$ in 4×10^{-4} M aqueous Na_2(EDTA)), tetrabutylammonium hydrogen sulfate (0.015 g, 0.04 mmol), and ketone **1** (0.0774 g, 0.3 mmol). The mixture was cooled with an ice bath. A solution of Oxone (0.85 g, 1.38 mmol) in aqueous Na_2(EDTA) (4×10^{-4} M, 6.5 mL) and a solution of K_2CO_3 (0.8 g, 5.8 mmol) in water (6.5 mL) were added dropwise separately over a period of 1.5 h (via syringe pumps or addition funnels). The reaction was then worked up by the same procedure as in method A to afford *trans*-stilbene oxide (0.153 g, 78% yield, 98.9% ee).

(c) Reaction at −10 °C. *trans*-β-Methylstyrene (0.118 g, 1 mmol) was dissolved in acetonitrile−DMM (15 mL, 1:2 v/v). Buffer (10 mL, 0.05 M solution of $Na_2B_4O_7 \cdot 10H_2O$ in 4×10^{-4} M aqueous Na_2(EDTA)), tetrabutylammonium hydrogen sulfate (15 mg, 0.04 mmol), and ketone **1** (0.0774 g, 0.3 mmol) were added with stirring. The

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mixture was cooled to about −10 °C (inside) (outside temperature was about −12 to −15 °C) via a NaCl−ice bath. A solution of Oxone (0.85 g, 1.38 mmol) in aqueous Na_2(EDTA) (4×10^{-4} M, 6.5 mL) and a solution of K_2CO_3 (0.8 g, 5.8 mmol) in water (6.5 mL) were added dropwise separately over a period of 2 h (via syringe pumps or addition funnels). The reaction was then worked up by the same procedure as in method B to afford *trans*-*β*-methylstyrene oxide (0.126 g, 94% yield, 95.5% ee).

***trans*-Stilbene Oxide (Table 4, Entry 1).** White crystals: mp 68−70 °C (recrystallized from hexane), $[\alpha]^{25}_D = +356.1°$ (*c* 0.95, benzene) (Table 4, entry 1, method C at 0 °C); −358.1° (*c* 0.82, benzene) [Table 4, entry 1, method C (**ent-1**)] [lit.[23a] mp 68−69 °C, $[\alpha]_D = +361°$ (*c* 2.05, benzene) for (*R, R*)-form].

***trans*-*β*-Methylstyrene oxide (Table 4, Entry 2).** Colorless oil: $[\alpha]^{25}_D = +47.8°$ (*c* 1.04, $CHCl_3$) (Table 4, entry 2, method C); −46.9° (*c* 0.88, $CHCl_3$) [Table 4, entry 2, method C (**ent-1**)] [lit.[23b] +47.2° (*c* 1.10, $CHCl_3$) for (*R*)-form].

(*R,R*)-2-[(*tert*-Butyldimethylsiloxy)methyl]-3-phenyloxirane (Table 4, Entry 3). The olefin substrate was prepared from cinnamyl alcohol and *tert*-butyldimethylsilyl chloride[28] to give a colorless oil: IR (KBr) 3060, 3027, 2954, 2931, 2856, 1656, 1599, 1495, 1467, 1379, 1254, 1125, 1073, 964, 834, 777, 729, 690 cm^{-1}; ^1H NMR δ 7.36−7.1 (m, 5H), 6.54 (dt, $J = 15.9$, 1.8 Hz, 1H), 6.23 (dt, $J = 15.9$, 5.1 Hz, 1H), 4.3 (dd, $J = 5.1$, 1,8 Hz, 2H), 0.89 (s, 9H), 0.062 (s, 6H); ^{13}C NMR δ 137.3, 129.7, 129.3, 128.7, 127.5, 126.6, 64.06, 26.18, 18.65, −4.947.

Epoxide. Colorless oil: $[\alpha]^{25}_D = +39.7°$ (*c* 1.0, CH_2Cl_2) (Table 4, entry 3, method C); IR (KBr) 3062, 3030, 2954, 2931, 2857, 2890, 1605, 1498, 1464, 1385, 1254, 1138, 1106, 1050, 887, 836, 778, 697 cm^{-1}; ^1H NMR δ 7.4−7.2 (m, 5H), 3.97 (dd, $J = 12$, 3.3 Hz, 1H), 3.82 (dd, $J = 12.0$, 4.2 Hz, 1H), 3.8 (d, $J = 2.4$ Hz, 1H), 3.14 (ddd, $J = 4.2$, 3.3, 2.4 Hz, 1H), 0.92 (s, 9H), 0.13 (s, 3H), 0.12 (s, 3H); ^{13}C NMR δ 137.5, 128.7, 128.3, 125.9, 63.24, 62.94, 56.11, 26.1, 18.61, −5.06; HRMS calcd for $C_{15}H_{22}O_2Si$ ($M^+ - 1$) 263.1465, found 263.1467.

(*R,R*)-2-Phenyl-3-[(triphenylmethoxy)methyl]oxirane (Table 4, Entry 4). The olefin substrate was prepared from cinnamyl alcohol and triphenylmethyl chloride[29] to give white crystals: mp 122−124 °C (recrystallized from hexane); IR (KBr) 3057, 3027, 2925, 2853, 1661, 1597, 1490, 1446, 1219, 1103, 1056, 965, 743, 700 cm^{-1}. ^1H NMR δ 7.55−7.2 (m, 20H), 6.7 (dt, $J = 15.9$, 1.8 Hz, 1H), 6.3 (dt, $J = 15.9$, 5.4 Hz, 1H), 3.78 (dd, $J = 5.4$, 1.8 Hz, 2H); ^{13}C NMR δ 144.3, 137.3, 130.8, 128.8, 128.7, 128.1, 128.0, 127.6, 127.2, 126.8, 126.6, 87.12, 65.07.

Epoxide. White crystals: mp 116−118 °C (recrystallized from hexane); $[\alpha]^{25}_D = +34.1°$ (*c* 0.74, $CHCl_3$); IR (KBr) 3056, 3025, 2925, 2863, 1598, 1491, 1448, 1220, 1083, 748 cm^{-1}; ^1H NMR δ 7.5−7.2 (m, 20H), 3.78 (d, $J = 1.8$ Hz, 1H), 3.45 (m, 1H), 3.26 (m, 2H); ^{13}C NMR δ 144.0, 137.3, 128.9, 128.7, 128.4, 128.1, 127.3, 125.9, 87.05, 64.38, 61.53, 56.36. Anal. Calcd for $C_{28}H_{24}O_2$: C, 85.68; H, 6.16. Found: C, 85.47; H, 6.40.

(2*S*,3*R*)-2-(Chloromethyl)-3-phenyloxirane (Table 4, Entry 5). Colorless oil: $[\alpha]^{25}_D = +26.2°$ (*c* 0.9, $CHCl_3$) (Table 4, entry 5, method C); IR (KBr) 3055, 3033, 2990, 1604, 1497, 1460, 1265, 930, 878, 748, 697 cm^{-1}; ^1H NMR δ 7.35−7.15 (m, 5H), 3.77 (d, $J = 2.1$ Hz, 1H), 3.66 (dd, $J = 12$, 5.1 Hz, 1H), 3.60 (dd, $J = 12.0$, 5.7 Hz, 1H), 3.22 (ddd, $J = 5.7$, 5.1, 2.1 Hz, 1H); ^{13}C NMR δ 136.1, 128.8, 128.8, 125.9, 61.18, 58.76, 44.56; HRMS calcd for C_9H_9ClO (M^+) 168.0342, 170.0312 (^{37}Cl), found 168.0349, 170.0312 (^{37}Cl).

(2*S*,3*R*)-2-(Ethylenedioxymethyl)-3-phenyloxirane (Table 4, Entry 6). The olefin substrate was prepared by ketalization of cinnamyl aldehyde with ethylene glycol[30] to give a colorless oil: IR (KBr) 3058, 3028, 2956, 2885, 1677, 1600, 1493, 1451, 1394, 1148, 1063, 961, 749, 693 cm^{-1}; ^1H NMR δ 7.45−7.2 (m, 5H), 6.78 (d, $J = 15.9$ Hz, 1H), 6.17 (dd, $J = 15.9$, 6.0 Hz, 1H), 6.43 (d, $J = 6.0$ Hz, 1H), 4.1−3.9 (m, 4H); ^{13}C NMR δ 135.9, 135.0, 128.7, 128.5, 127.0, 125.2, 103.9, 65.13.

Epoxide. Colorless oil: $[\alpha]^{25}_D = +40.5°$ (*c* 1.2, $CHCl_3$); IR (KBr) 3058, 3028, 2983, 2889, 1606, 1495, 1468, 1380, 1148, 1115, 944, 756, 699 cm^{-1}; ^1H NMR δ 7.4−7.2 (m, 5H), 5.02 (d, $J = 3.6$ Hz, 1H), 4.12−3.91 (m, 4H), 3.90 (d, $J = 2.1$ Hz, 1H), 3.15 (dd, $J = 3.6$, 2.1 Hz, 1H); ^{13}C NMR δ 136.5, 128.7, 128.6, 126.0, 102.6, 65.77, 65.59, 61.58, 55.47; HRMS calcd for $C_{11}H_{12}O_3$ (M^+) 192.0786, found 192.0783.

(*R,R*)-2-Methyl-3-(2-methylphenyl)oxirane (Table 4, Entry 7). The olefin substrate was prepared from *o*-methylbenzyltriphenylphosphonium bromide and acetaldehyde by Wittig reaction with a ratio of *trans/cis* = 2.3 (determined by ^1H NMR). *trans*-Olefin: ^1H NMR δ 7.41−7.09 (m, 4H), 6.59 (dq, $J = 15.6$, 1.8 Hz), 6.10 (dq, $J = 15.6$, 6.6 Hz, 1H), 2.33 (s, 3H), 1.90 (dd, $J = 6.6$, 1.8 Hz). *cis*-Olefin: ^1H NMR δ 7.41−7.09 (m, 4H), 6.45 (dq, $J = 11.4$, 1.8 Hz, 1H), 5.82 (dq, $J = 11.4$, 6.9 Hz), 2.25 (s, 3H), 1.74 (dd, $J = 6.9$, 1.8 Hz, 3H).

Epoxides. *trans/cis* = 2.33 (determined by GC). *trans*-Epoxide (purified from *cis*-epoxide): colorless oil, $[\alpha]^{25}_D = +29.4°$ (*c* 0.32, benzene); IR (KBr) 3062, 3024, 2967, 2927, 1606, 1490, 1458, 1378, 1020, 956, 862, 747 cm^{-1}; ^1H NMR δ 7.3−7.2 (m, 4H), 3.71 (d, $J = 2.1$ Hz, 1H), 2.92 (dq, $J = 5.1$, 2.1 Hz, 1H), 2.4 (s, 3H), 1.48 (d, $J = 5.1$ Hz, 3H); ^{13}C NMR δ 136.2, 135.9, 129.9, 127.6, 126.3, 124.3, 58.22, 57.77, 19.02, 18.17. *cis*-Epoxide: ^1H NMR δ 7.3−7.2 (m, 4H), 4.04 (d, $J = 4.5$ Hz, 1H), 3.41 (dq, $J = 5.4$, 4.5 Hz, 1H), 2.33 (s, 3H), 1.01 (d, $J = 5.4$ Hz, 3H); ^{13}C NMR δ 135.8, 134.0, 129.7, 127.4, 126.7, 125.7, 56.68, 54.69, 18.86, 13.06. Anal. Calcd for $C_{10}H_{12}O$ (*trans* and *cis*): C, 81.04; H, 8.16. Found: C, 81.21; H 8.16.

(*R,R*)-2-Isopropyl-3-(2-methylphenyl)oxirane (Table 4, Entry 8). The olefin substrate was prepared from *o*-methylbenzyltriphenylphosphonium bromide and isobutyraldehyde via Wittig reaction with a ratio of *trans/cis* = 4.1 (determined by ^1H NMR). *trans*-Olefin: ^1H NMR δ 7.44−7.1 (m, 4H), 6.53 (d, $J = 15.7$ Hz, 1H), 6.05 (dd, $J = 15.7$, 6.6 Hz, 1H), 2.48 (m, $J = 6.6$ Hz, 1H), 2.33 (s, 3H), 1.10 (d, $J = 6.6$ Hz, 6H). *cis*-Olefin: ^1H NMR δ 7.44−7.10 (m, 4H), 6.29 (d, $J = 11.4$ Hz, 1H), 5.51 (dd, $J = 11.4$, 10.2 Hz, 1H), 2.62 (m, 1H), 2.25 (s, 3H), 0.98 (d, $J = 6.6$ Hz, 3H).

Epoxides. *trans/cis* = 3.8 (determined by GC). *trans*-Epoxide (purified from *cis*-epoxide): colorless oil. $[\alpha]^{25}_D = -21.2°$ (*c* 0.6, benzene); IR (KBr) 3062, 3025, 2962, 2872, 1606, 1491, 1463, 1382, 1366, 1043, 945, 895, 750 cm^{-1}; ^1H NMR δ 7.3−7.1 (m, 4H), 3.79 (d, $J = 2.1$ Hz, 1H), 2.62 (dd, $J = 6.9$, 2.1 Hz, 1H), 2.39 (s, 3H), 1.69 (m, 1H), 1.11 (d, $J = 6.6$ Hz, 3H), 1.06 (d, $J = 6.6$ Hz, 3H); ^{13}C NMR δ 136.4, 135.7, 129.9, 127.6, 126.3, 67.86, 56.05, 31.19, 19.43, 19.06, 18.69. *cis*-Epoxide: ^1H NMR δ 7.3−7.2 (m, 4H), 4.07 (d, $J = 4.2$ Hz, 1H), 2.94 (dd, $J = 8.4$, 4.2 Hz, 1H), 2.36 (s, 3H), 1.61 (m, 1H), 1.1 (d, $J = 6.6$ Hz, 3H), 0.71 (d, $J = 6.6$ Hz, 3H); ^{13}C NMR δ 135.6, 134.2, 129.7, 127.3, 126.2, 125.6, 65.1, 56.94, 26.37, 20.24, 18.96, 18.46. Anal. Calcd for $C_{12}H_{16}O$ (*trans* and *cis*): C, 81.77; H, 9.15. Found: C, 81.80; H, 9.36.

(*R,R*)-2-[(*tert*-Butyldimethylsiloxy)methyl]-3-propyloxirane (Table 4, Entry 9). The olefin substrate was prepared from *trans*-2-hexen-1-ol and *tert*-butyldimethylsilyl chloride[28] to give a colorless oil: IR (KBr) 2957, 2931, 2858, 1671, 1465, 1381, 1255, 1104, 1062, 969. 838, 776 cm^{-1}; ^1H NMR δ 5.65 (dt, $J = 15.3$, 6.3 Hz, 1H), 5.53 (dt, $J = 15.3$, 5.1 Hz, 1H), 4.13 (d, $J = 5.1$ Hz, 2H), 2.01 (dt, $J = 6.6$, 6.3 Hz, 2H), 1.4 (m, $J = 7.5$, 6.6 Hz, 2H), 0.91 (t, $J = 7.5$ Hz, 3H), 0.914 (s, 9H), 0.075 (s, 6H); ^{13}C NMR δ 131.5, 129.5, 64.31, 34.54, 26.2, 22.59, 18.65, 13.91, −4.89.

Epoxide. Colorless oil: $[\alpha]^{25}_D = +17.7°$ (*c* 0.74, $CHCl_3$) (Table 4, entry 9, method C); IR (KBr) 2957, 2932, 2859, 1467, 1254, 1129, 1095, 838, 778, 665 cm^{-1}. ^1H NMR δ 3.78 (dd, $J = 11.7$, 3.4 Hz, 1H), 3.67 (dd, $J = 11.7$, 4.5 Hz, 1H), 2.87−2.79 (m, 2H), 1.6−1.4 (m, 4H), 0.96 (t, $J = 7.2$ Hz, 3H), 0.90 (s, 9H), 0.078 (s, 3H), 0.069 (s, 3H); ^{13}C NMR δ 63.9, 58.85, 56.43, 33.94, 26.08, 19.51, 18.56, 14.11, −5.076, −5.133; HRMS calcd for $C_{12}H_{25}O_2Si$ ($M^+ - 1$) 229.1623, found 229.1618.

(*R,R*)-2-[1-(*tert*-Butyldimethylsiloxy)ethyl]-3-ethyloxirane (Table 4, Entry 10). The olefin substrate was prepared from *trans*-3-hexen-1-ol and *tert*-butyldimethylsilyl chloride[28] to give a colorless oil: IR (KBr) 2957, 2931, 2858, 1468, 1384, 1254, 1103, 966, 836, 776 cm^{-1}; ^1H NMR δ 5.53 (dt, $J = 15.3$, 6.0 Hz, 1H), 5.39 (dt, $J = 15.3$, 6.6 Hz, 1H), 3.62 (t, $J = 6.9$ Hz, 1H), 2.21 (dt, $J = 6.9$, 6.6 Hz, 1H), 2.01 (m,

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J = 7.5, 6.0 Hz, 2H), 0.97 (t, J = 7.5 Hz, 3H), 0.90 (s, 9H), 0.059 (s, 6H); ^{13}C NMR δ 134.3, 125.6, 63.6, 36.52, 26.17, 25.91, 18.6, 14.02, −5.028.

Epoxide. Colorless oil: $[\alpha]^{25}_D = +23.9°$ (*c* 1.1, $CHCl_3$) (Table 4, entry 10, method C); IR (KBr) 2956, 2932, 2859, 1469, 1386, 1254, 1100, 940, 891, 837, 777, 728, 663 cm^{-1}; ^{1}H NMR δ 3.75 (dd, J = 6.3, 6.0 Hz, 2H), 2.8 (dt, J = 6.0, 2.4 Hz, 1H), 2.69 (dt, J = 5.4, 2.4 Hz, 1H), 1.82−1.63 (m, 2H), 1.57 (m, 2H), 0.99 (t, J = 7.5 Hz, 3H), 0.90 (s, 9H), 0.06 (s, 6H); ^{13}C NMR δ 60.27, 60.17, 56.27, 35.79, 26.12, 25.36, 18.49, 10.05, −5.182; HRMS calcd for $C_{12}H_{25}O_2Si$ ($M^+ - 1$) 229.1623, found 229.1622.

(*R,R*)-2, 3-Dihexyloxirane (Table 4, Entry 11). Colorless oil: $[\alpha]^{25}_D = +26.2°$ (c 0.71, $CHCl_3$) (Table 4, entry 11, method C); IR (KBr) 2958, 2928, 2857, 1463, 1378, 1250, 1086, 901, 840, 721 cm^{-1}; ^{1}H NMR δ 2.66 (m, 2H), 1.6−1.2 (m, 20H), 0.89 (t, J = 6.9 Hz, 6H); ^{13}C NMR δ 59.1, 32.33, 31.95, 29.3, 26.2, 22.74, 14.24; HRMS calcd for $C_{14}H_{28}O$ (M^+) 212.2140, found 212.2138.

(*R,R*)-2, 3-Dibutyloxirane (Table 4, Entry 12). Colorless oil: $[\alpha]^{25}_D = +26.7°$ (*c* 0.97, CH_2Cl_2) [lit.[23e] $[\alpha]^{25}_D = +29.1°$ (*c* 1.005, CH_2Cl_2)].

(*R,R*)-2-Ethyl-3-(4,4-Ethylenedioxypentyl)oxirane (Table 4, Entry 13). The olefin substrate was prepared according to Look's method.[31]

Epoxide.[32] Colorless oil: $[\alpha]^{25}_D = +27.9°$ (*c* 2.06, ether).

(*R,R*)-2-Benzyl-3-[2-(methoxycarbonyl)ethyl]oxirane (Table 4, Entry 14). The olefin substrate was prepared by Johnson−Claisen rearrangement from an allylic alcohol resulting from an addition of vinylmagnesium bromide to phenylacetaldehyde[33] to give a colorless oil: IR (KBr) 3060, 3026, 2950, 2915, 2844, 1739, 1603, 1494, 1438, 1169, 971, 744, 699 cm^{-1}; ^{1}H NMR δ 7.35−7.13 (m, 5H), 5.67 (dt, J = 15.3, 6.6 Hz, 1H), 5.54 (dt, J = 15.3, 6.0 Hz, 1H), 3.68 (s, 3H), 3.36 (d, J = 6.6 Hz, 2H), 2.47−2.34 (m, 4H); ^{13}C NMR δ 173.7, 140.8, 130.4, 129.7, 128.6, 128.5, 126.1, 51.65, 39.09, 34.12, 27.97.

Epoxide. Colorless oil: $[\alpha]^{25}_D = +26.6°$ (*c* 1.17, $CHCl_3$) (Table 4, entry 14, method C); IR (KBr) 1737, 1603, 1495 cm^{-1}; ^{1}H NMR δ 7.4−7.15 (m, 5H), 3.65 (s, 3H), 3.0−2.75 (m, 4H), 2.43 (dd, J = 7.8, 7.2 Hz, 2H), 1.97 (dqd, J = 14.4, 7.5, 4.8 Hz, 1H), 1.77 (dq, J = 14.4, 6.9 Hz, 1H); ^{13}C NMR δ 173.43, 137.41, 129.12, 128.75, 126.83, 59.03, 57.65, 51.87, 38.56, 30.40, 27.30; HRMS calcd for $C_{13}H_{16}O_3$ (M^+) 220.1099, found 220.1097.

(*R,R*)-2-Methyl-2,3-diphenyloxirane[24a] (Table 5, Entry 1). Colorless oil: $[\alpha]^{25}_D = +113.9°$ (*c* 0.9, EtOH) (Table 5, entry 1, method C).

(*R*)-2,2,3-Triphenyloxirane[24a] (Table 5, Entry 2). White crystals: mp 91−92 °C (hexane), $[\alpha]^{25}_D = -43.2°$ (*c* 0.82, EtOH) (Table 5, entry 2, method C).

(*R,R*)-1-Phenylcyclohexene Oxide (Table 5, Entry 3). Colorless oil: $[\alpha]^{25}_D = +116.7°$ (*c* 1.21, benzene) (Table 5, entry 3, method C) [lit.[24b] $[\alpha]^{25}_D = +119.9°$ (*c* 0.60, benzene)].

(*1S,2R*)-1-Phenyl-3,4-dihydronaphthalene Oxide (Table 5, Entry 4). White crystals: mp 124−126 °C (hexane); $[\alpha]^{25}_D = -42.75°$ (*c* 0.95, $CHCl_3$) (Table 5, entry 4, method C); IR (KBr) 3066, 3028, 2999, 2938, 2846, 1603, 1490, 1450, 1307, 1156, 1042, 954, 906, 872, 757, 705 cm^{-1}; ^{1}H NMR δ 7.5−6.95 (m, 9H), 3.6 (dd, J = 2.1, 0.9 Hz, 1H), 2.93 (ddd, J = 14.4, 13.2, 6.3 Hz, 1H), 2.68 (dd, J = 14.4, 5.7 Hz, 1H), 2.45 (dddd, J = 14.4, 6.3, 3.0, 2.1 Hz, 1H), 2.02 (dddd, J = 14.4, 13.2, 5.7, 0.9 Hz, 1H); ^{13}C NMR δ 138.9, 137.4, 135.0, 130.0, 128.7, 128.3, 128.2, 128.0, 127.8, 126.1, 63.18, 60.72, 25.59, 22.33; HRMS calcd for $C_{16}H_{14}O$ (M^+) 222.1045, found 222.1038.

(*R*)-3-Decyl-2,2-diphenyloxirane (Table 5, Entry 5). The olefin substrate was prepared from undecyltriphenylphosphonium bromide and benzophenone via Wittig reaction: IR (KBr) 3056, 3024, 2924, 2854, 1598, 1493, 1461, 1444, 1366, 1073, 1029, 762, 698 cm^{-1}; ^{1}H NMR δ 7.35−7.05 (m, 10H), 6.0 (t, J = 7.4 Hz, 1H), 2.02 (dt, J = 7.4, 7.4 Hz, 2H), 1.45−1.30 (m, 2H), 1.26−1.1 (m, 14H), 0.8 (t, J = 6.5 Hz, 3H); ^{13}C NMR δ 143.2, 141.6, 140.6, 130.6, 130.2, 128.33, 128.3, 127.4, 127.0, 126.9, 32.14, 30.19, 29.98, 29.84, 29.72, 29.56, 29.51, 22.92, 14.34.

Epoxide (Table 5, Entry 5, Method C). White solid: mp 31−33 °C (hexane); $[\alpha]^{25}_D = +30.2°$ (*c* 1.24, CCl_4) [lit.[24c] $[\alpha]^{25}_D = -28.6°$ (*c* 2.3, CCl_4) for (*S*)-form].

(*R,R*)-2,3-Dimethyl-2-phenyloxirane (Table 5, Entry 6). The starting α,β-dimethylstyrene was prepared from ethyltriphenylphosphonium iodide and acetophenone via Wittig reaction,[34] with a ratio of E/Z = 5 (determined by ^{1}H NMR). *E*-Olefin: ^{1}H NMR δ 7.4−7.15 (m, 5H), 5.85 (q, J = 6.9 Hz, 1H), 2.03 (s, 3H), 1.79 (d, J = 6.9 Hz, 3H). *Z*-Olefin: ^{1}H NMR δ 7.4−7.15 (m, 5H), 5.56 (q, J = 6.9 Hz, 1H), 2.03 (s, 3H), 1.59 (d, J = 6.9 Hz, 3H).

Epoxide (*trans*/*cis* = 5.8) (determined by GC). Colorless oil. *trans*-Epoxide: ^{1}H NMR δ 7.4−7.2 (m, 5H), 2.97 (q, J = 5.4 Hz, 1H), 1.68 (s, 3H), 1.45 (d, J = 5.4 Hz, 3H); ^{13}C NMR δ 143.2, 128.5, 127.4, 125.2, 62.72, 60.53, 17.56, 14.62. *cis*-Epoxide: ^{1}H NMR δ 7.4−7.2 (m, 5H), 3.20 (q, J = 5.4 Hz, 1H), 1.67 (s, 3H), 1.01 (d, J = 5.4 Hz, 3H). Anal. Calcd for $C_{10}H_{12}O$ (*trans* and *cis*): C, 81.04; H, 8.16. Found: C, 80.89; H, 8.23.

(*R*)-2,2-Dimethyl-3-phenyloxirane (Table 5, Entry 7). The olefin substrate was prepared from benzyltriphenylphosphonium bromide and acetone via Wittig reaction[34] to give a colorless oil: IR (KBr) 3056, 3023, 2970, 2914, 2856, 1655, 1598, 1491, 1442, 1378, 981, 915, 834, 740, 698 cm^{-1}; ^{1}H NMR δ 7.35−7.12 (m, 5H), 6.27 (s, 1H), 1.90 (s, 3H), 1.86 (s, 3H); ^{13}C NMR δ 138.9, 135.7, 128.9, 128.2, 126.0, 125.4, 27.07, 19.58.

Epoxide. Colorless oil: $[\alpha]^{25}_D = +36.8°$ (*c* 0.63, benzene) [lit.[35] $[\alpha]_D = +13.1°$ (benzene) for 35% ee].

(*R*)-3-Decyl-2,2-dimethyloxirane (Table 5, Entry 8). The olefin substrate was prepared from undecyltriphenylphosphonium iodide and acetone via Wittig reaction: IR (KBr) 2958, 2924, 2854, 1676, 1461, 1377, 984, 832, 721 cm^{-1}; ^{1}H NMR δ 5.12 (t, J = 7.2 Hz, 1H), 1.95 (dt, J =7.2, 7.2 Hz, 2H), 1.68 (s, 3H), 1.60 (s, 3H), 1.85−1.2 (m, 16H), 0.88 (t, J = 6.7 Hz, 3H); ^{13}C NMR δ 131.3, 125.2, 32.17, 30.17, 29.93, 29.90, 29.86, 29.62, 28.31, 25.93, 22.94, 17.86, 14.33.

Epoxide. Colorless syrup: $[\alpha]^{25}_D = +13.2°$ (*c* 0.92, CCl_4) [lit.[24c] $[\alpha]^{25}_D = -13.7°$ (*c* 1.4, CCl_4) for (*S*)-form].

(*R*)-3-*tert*-Butyl-2,2-dimethyloxirane[36] (Table 5, Entry 9). Colorless oil: $[\alpha]^{25}_D = -21.6°$ (*c* 0.37, $CHCl_3$).

(*R*)-3-Decyl-2,2-diethyloxirane (Table 5, Entry 10). The olefin substrate was prepared from undecyltriphenylphosphonium iodide and 3-pentanone via Wittig reaction: IR (KBr) 2962, 2925, 2854, 1663, 1462, 1374, 924, 855, 721 cm^{-1}; ^{1}H NMR δ 5.07 (t, J = 7.0 Hz, 1H), 2.03 (q, J = 7.6 Hz, 2H), 2.0 (q, J = 7.6 Hz, 2H), 2.05−1.94 (m, 2H), 1.4−1.2 (m, 16H), 0.98 (t, J = 7.6 Hz, 3H), 0.95 (t, J = 7.6 Hz, 3H), 0.88 (t, J = 6.7 Hz, 3H); ^{13}C NMR δ 142.8, 123.2, 32.17, 30.47, 29.91, 29.91, 29.87, 29.67, 29.60, 29.42, 27.8, 23.40, 22.93, 14.33, 13.48, 13.16.

Epoxide. Colorless oil: $[\alpha]^{25}_D = +13.0°$ (*c* 1.12, CCl_4); IR (KBr) 2963, 2926, 2855, 1463, 1377, 1111, 899, 672 cm^{-1}; ^{1}H NMR δ 2.72 (dd, J = 6.3, 5.7 Hz, 1H), 1.7−1.4 (m, 6H) 1.4−1.2 (m, 16H), 0.98 (t, J = 7.5 Hz, 3H), 0.92 (t, J = 7.5 Hz, 3H), 0.88 (t, J = 7.0 Hz, 3H); ^{13}C NMR δ 64.98, 63.92, 32.11, 29.81, 29.79, 29.77, 29.77, 29.54, 28.5, 27.65, 26.98, 22.89, 22.82, 14.31, 9.542, 9.108; HRMS calcd for $C_{16}H_{33}O$ (M^+ + 1): 241.2531, found: 241.2534.

(*R,R*)-2-[2-(Ethoxycarbonyl)ethyl]-3-hexyl-2-methyloxirane (Table 5, Entry 11). The olefin substrate was prepared by Johnson−Claisen rearrangement from an allylic alcohol resulting from an addition of hexylmagnesium bromide to methacrolein[33] to give a colorless oil: IR (KBr) 2957, 2926, 2855, 1738, 1650, 1457, 1372, 1157, 1038 cm^{-1}; ^{1}H NMR δ 5.16 (t, J = 7.1 Hz, 1H), 4.11 (q, J = 7.2 Hz, 2H), 2.38 (dd, J = 7.5, 6.6 Hz, 2H), 2.29 (dd, J = 7.5, 6.6 Hz, 2H), 1.96 (dt, J = 7.1, 6.6 Hz, 2H), 1.6 (s, 3H), 1.24 (t, J = 7.2 Hz, 3H), 1.35−1.2 (m, 8H), 0.87 (t, J = 6.7 Hz, 3H); ^{13}C NMR δ 173.7, 133.3, 125.9, 60.38, 34.94, 33.51, 32.0, 29.9, 29.16, 28.09, 22.86, 16.06, 14.45, 14.28.

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Epoxide. Colorless oil: $[\alpha]^{25}_D = +9.4°$ (*c* 1.1, $CHCl_3$); IR (KBr) 1736.8 cm^{-1}; ^1H NMR δ 4.13 (q, $J = 7.2$ Hz, 2H), 2.73 (dd, $J = 6.3$, 5.7 Hz, 1H), 2.38 (dd, $J = 8.1$, 7.5 Hz, 2H), 1.89 (dd, $J = 7.5$, 4.8 Hz, 1H), 1.86 (dd, $J = 8.1$, 4.8 Hz, 1H), 1.6−1.2 (m, 10H), 1.26 (t, $J = 7.2$ Hz, 3H), 1.25 (s, 3H), 0.89 (t, $J = 6.7$ Hz, 3H); ^{13}C NMR δ 173.3, 63.6, 60.66, 59.91, 33.62, 31.95, 30.12, 29.34, 28.78, 26.61, 22.75, 16.76, 14.39, 14.25; HRMS calcd for $C_{14}H_{27}O_3$ ($M^+ + 1$) 243.1960, found 243.1959.

(*R*,*R*)-3-Cyclohexyl-2-[2-(methoxycarbonyl)ethyl]-2-methyloxirane (Table 5, Entry 12). The olefin substrate was prepared by Johnson−Claisen rearrangement from an allylic alcohol resulting from addition of cyclohexylmagnesium bromide to methacrolein[33] to give a colorless oil: IR (KBr) 2924, 2850, 1740, 1670, 1445, 1348, 1257, 1194, 1159, 1047, 893, 848 cm^{-1}; ^1H NMR δ 4.98 (d, $J = 8.7$ Hz, 1H), 3.65 (s, 3H), 2.4 (dd, $J = 8.1$, 7.2 Hz, 2H), 2.27 (dd, $J = 8.1$, 7.2 Hz, 2H), 2.1 (m, 1H), 1.7−1.5 (m, 4H), 1.61 (s, 3H), 1.35−1.1 (m, 4H), 1.0 (m, 2H); ^{13}C NMR δ 174.1, 132.1, 131.5, 51.59, 37.05, 34.94, 33.41, 33.35, 26.29, 26.22, 16.12.

Epoxide. Colorless syrup: $[\alpha]^{25}_D = +11.6°$ (*c* 0.5, $CHCl_3$); IR (KBr) 2928, 2852, 1740, 1447, 1198, 1167 cm^{-1}; ^1H NMR δ 3.68 (s, 3H), 2.5−2.3 (m, 3H), 2.0−1.5 (m, 7H), 1.27 (s, 3H), 1.3−1.05 (m, 6H); ^{13}C NMR δ 173.7, 68.03, 59.93, 51.87, 37.52, 33.82, 30.66, 29.99, 29.08, 26.39, 25.73, 25.60, 16.79; HRMS calcd for $C_{13}H_{23}O_3$ ($M^+ + 1$): 227.1647, found 227.1641.

(1*S*,2*R*)-1-Methylcyclohexene Oxide (Table 5, Entry 13). Colorless oil: $[\alpha]^{25}_D = +27.7°$ (*c* 0.68, $CHCl_3$) [lit.[24d] $[\alpha]^{25}_D = +0.61°$ (neat) for 4.5% ee].

(*R*,*R*)-1-Methyl-3,3-ethylenedioxycyclohexene Oxide (Table 5, Entry 14). The olefin substrate was prepared by ketalization of 3-methyl-2-cyclohexenone with 1,2-bis(trimethylsiloxy)ethane[37] to give a colorless oil: IR (KBr) 2937, 2874, 1675, 1438, 1354, 1189, 1102, 1082, 931 cm^{-1}; ^1H NMR δ 5.46 (s, 1H), 3.97 (m, 4H), 1.96 (t, $J = 5.1$ Hz, 2H), 1.83−1.70 (m, 4H), 1.72 (s, 3H); ^{13}C NMR δ 141.8, 122.5, 106.8, 64.57, 33.31, 30.14, 23.59, 21.12.

Epoxide. Colorless oil: $[\alpha]^{25}_D = -11.3°$ (*c* 0.72, $CHCl_3$); IR (KBr) 2953, 2883, 1666, 1442, 1423, 1185, 1139, 1072, 1058, 938, 856 cm^{-1}; ^1H NMR δ 4.1−3.95 (m, 4H), 2.82 (s, 1H), 1.90 (m, 1H), 1.70 (m, 2H), 1.52 (m, 2H), 1.42 (m, 1H), 1.36 (s, 3H); ^{13}H NMR δ 107.0, 65.17, 64.95, 61.31, 60.12, 30.99, 28.56, 23.59, 18.14. Anal. Calcd for $C_9H_{14}O_3$: C, 63.51; H, 8.29. Found: C, 63.27; H, 8.56.

(*R*)-Styrene Oxide (Table 6, Entry 1). Colorless oil: $[\alpha]^{25}_D = +10.7°$ (*c* 0.86, benzene) (Table 6, entry 1, method C) [lit.[25a] $[\alpha]^{23}_D = -44.9°$ (*c* 1.02, benzene) for (*S*)-form].

(*R*)-1-Decene Oxide (Table 6, Entry 2). Colorless oil: $[\alpha]^{25}_D = +5.2°$ (*c* 0.9, ether) (Table 6, entry 2, method B) [lit.[25b] $[\alpha]^{23}_D = -14.7°$ (*c* 1.44, ether) for (*S*)-form].

3-(Triisopropylsilyl)propene Oxide (Table 6, Entry 3). Colorless oil: $[\alpha]^{25}_D = -9.0°$ (*c* 1.45, $CHCl_3$) (Table 6, entry 3, method B); IR (KBr) 3037, 2942, 2867, 1465, 1387, 1189, 883, 831, 740, 656 cm^{-1}; ^1H NMR δ 2.81 (dddd, $J = 9.0$, 4.5, 4.2, 3.0 Hz, 1H), 2.81 (ddd, $J = 4.9$, 4.2, 1.2 Hz, 1H), 2.48 (dd, $J = 4.9$, 3.0 Hz, 1H), 1.30 (dd, $J = 14.3$, 4.5 Hz, 1H), 1.07 (m, 3H), 1.06 (d, $J = 2.7$ Hz, 18H), 0.62 (dd, $J = 14.3$, 9.0 Hz, 1H); ^{13}C NMR δ 50.86, 49.86, 18.83, 14.37, 11.20; HRMS calcd for $C_{12}H_{27}OSi$ ($M^+ + 1$): 215.1831, found 215.1832.

(*S*)-α-Methylstyrene Oxide (Table 6, Entry 4). Colorless oil: $[\alpha]^{25}_D = -0.5°$ (*c* 2.0, acetone) (Table 6, entry 4, method B) [lit.[25c] $[\alpha]^{23}_D = -2.7°$ (*c* 0.7, acetone)].

(1*S*,2*R*)-3,4-Dihydronaphthalene Oxide (Table 6, Entry 5). Colorless oil: $[\alpha]^{25}_D = -38.8°$ (*c* 0.91, $CHCl_3$) (Table 6, entry 5, method B) [lit.[25d] $[\alpha]_D = +135°$ ($CHCl_3$) for (1*R*,2*S*)-form].

(*R*,*R*)-3,3-Ethylenedioxycyclohexene Oxide[24e,25e] (Table 6, Entry 6). The olefin substrate was prepared by ketalization of 2-cyclohexenone with 1,2-bis(trimethylsiloxy)ethane.[37]

Epoxide (Table 6, Entry 6, Method C). Colorless oil: $[\alpha]^{25}_D = +3.6°$ (*c* 0.8, CH_2Cl_2).

1-Butylcyclohexene Oxide (Figure 8). The olefin substrate was prepared by reductive alkylation of cyclohexene oxide with *n*-BuLi[38] to give a colorless oil: IR (KBr) 2924, 2857, 1667, 1457, 918, 798 cm^{-1}; ^1H NMR δ 5.38 (m, 1H), 2.02−1.85 (m, 6H), 1.68−1.5 (m, 4H), 1.4−1.2 (m, 4H), 0.89 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR δ 138.3, 120.7, 38.01, 30.18, 28.53, 25.48, 23.3, 22.87, 22.69, 14.25.

Epoxide. Colorless oil: $[\alpha]^{25}_D = +14.8°$ (*c* 1.22, $CHCl_3$) (method C at 0 °C); IR (KBr) 2933, 2861, 1458, 1374, 1172, 982, 870, 842, 765, 679 cm^{-1}; ^1H NMR δ 2.94 (ddd, $J = 3.3$, 1.2, 0.9 Hz, 1H), 2.0−1.65 (m, 4H), 1.58−1.1 (m, 10H), 0.9 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR δ 60.41, 58.82, 37.76, 27.89, 27.18, 25.1, 23.01, 20.44, 19.9, 14.24; HRMS calcd for $C_{10}H_{18}O$ (M^+) 154.1358, found 154.1350.

1-*tert*-Butylcyclohexene Oxide (Figure 8). The olefin substrate was prepared by reductive alkylation of cyclohexene oxide with *t*-BuLi[38] to give a colorless oil: IR (KBr) 2928, 2854, 1656, 1463, 1362, 797 cm^{-1}; ^1H NMR δ 5.45 (m, 1H), 2.05−1.93 (m, 4H), 1.65−1.49 (m, 4H), 1.01 (s, 9H); ^{13}C NMR δ 145.8, 117.5, 35.53, 29.25, 25.75, 24.71, 23.76, 22.82.

Epoxide. Colorless oil: $[\alpha]^{25}_D = +4.7°$ (*c* 0.19, $CHCl_3$) (method C at 0 °C); IR (KBr) 2939, 2869, 1481, 1460, 1364, 1036, 918, 875, 767 cm^{-1}; ^1H NMR δ 3.12 (ddd, $J = 3.3$, 1.2, 1.2 Hz, 1H), 2.0−1.85 (m, 2H), 1.8−1.65 (m, 2H), 1.55−1.3 (m, 2H), 1.3−1.1 (m, 2H), 0.9 (s, 9H); ^{13}C NMR δ 65.0, 55.45, 34.22, 25.68, 25.40, 24.95, 21.21, 19.79; HRMS calcd for $C_{10}H_{18}O$ (M^+) 154.1358, found 154.1352.

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Supporting Information Available: NMR spectral, GC, and HPLC data for the determination of the enantiomeric excess of the formed epoxides along with the NMR data for known epoxides (24 pages). See any current masthead page for ordering and Internet access instructions.

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