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A New Target for Highly Stereoselective Katsuki–Sharpless Epoxidation – One-Pot Synthesis of C_2-Symmetric 2,2′-Bioxiranes

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The double asymmetric Katsuki–Sharpless epoxidation of a conjugated diallyl alcohol affords excellent enantioselectivity (>97 % *ee*), the product being isolated as the stable *p*-nitrobenzoate **5a** or tosylate **5b**. The optical purities of the chiral epoxides were determined by HPLC on chiral columns, while the molecular structures of compounds **5a** and **7** and the absolute configuration of mono-epoxide **12** were confirmed by X-ray crystallography. Possible π–π stacking interaction has been evaluated by ab initio calculation.

Introduction

The asymmetric Katsuki–Sharpless epoxidation of allyl alcohols plays a pivotal role in organic chemistry for the generation of chiral epoxides,[1,2] which serve as useful chiral building blocks for further transformations. The catalytic reaction does not require expensive reagents or special equipment, while the mild reaction conditions and the toleration of a range of functional groups are especially noteworthy. In general, the stereochemistry of the resultant epoxy alcohols can be unambiguously predicted by common rules. In the case of Lewis acid-sensitive epoxides a facile in situ derivatization has been suggested.[3]

In a few cases, stereoselective bis-epoxidation of prochiral diallyl alcohols has also been investigated.[4] The double epoxidation also usually proceeds with high diastereo- and enantioselectivity, but it is interesting to note that conjugated dienes have never been subjected to Katsuki–Sharpless epoxidation. Here we report the first example of this transformation, which proceeds with high stereoselectivity. The products of such transformations might serve as building blocks in syntheses of chiral multifunctional compounds, in particular as chiral ligands for enantioselective catalysts.

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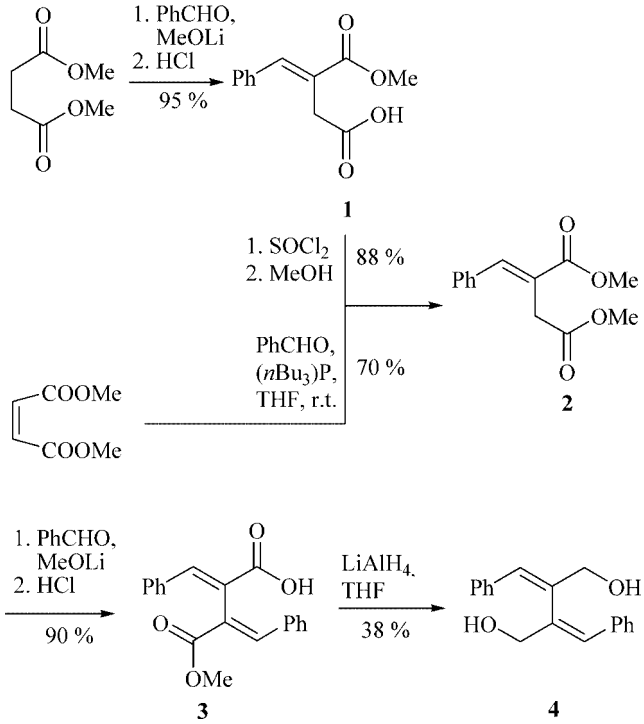
Results and Discussion

1. Synthesis of Diallyl Alcohol

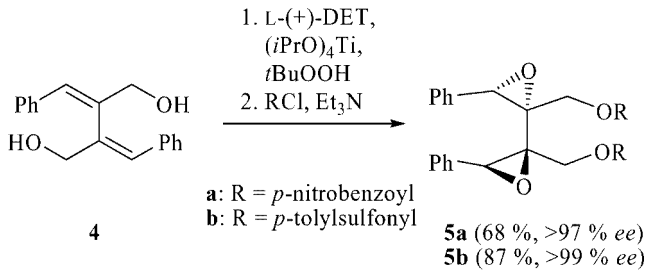
As a substrate for the epoxidation we chose the hydroxy-functionalized (*E,E*)-butadiene **4**, which is easily available by the synthetic route depicted in Scheme 1.



Scheme 1. Synthesis of diallyl alcohol **4** used as substrate in the Katsuki–Sharpless epoxidation.

The synthesis commenced with dimethyl succinate, which was subjected to Stobbe condensation to give the benzylidene derivative **1**.[5] The free carboxylic group in the half ester **1** was reesterified by treatment with $SOCl_2$ and subsequently with MeOH to give **2**. [An alternative synthesis is the coupling between benzaldehyde and dimethyl maleate in the presence of $(n\text{Bu})_3\text{P}$ by a modified literature procedure.[6]] A second Stobbe condensation of **2** afforded the dibenzylidene hemi-ester **3**, which was reduced with $LiAlH_4$ to give the diallyl alcohol **4** in 24–29% overall yield.

The asymmetric epoxidation of **4** was performed in accordance with the Sharpless procedure in order to avoid Lewis acid-catalyzed intramolecular epoxide opening.[3] The reaction was carried out at –30 °C with a catalytic amount of a Ti^{IV} complex based on L-(+)-diethyl tartrate as a chiral ligand (Scheme 2). The chiral product was trapped by in situ esterification either with *p*-nitrobenzoyl chloride or with *p*-toluenesulfonyl chloride, at low temperature.



Scheme 2. Epoxidation of **4** and subsequent trapping of the product.

The bis-epoxides **5a** and **5b** were purified by flash chromatography on silica gel. The purification of **5a** could also be performed by crystallization, but in this case the yield decreased by ca. 5%. Compounds **5a** and **5b** are stable at room temperature.

2. Determination of Optical Purities and Absolute Configurations

To determine the optical purities of the bis-epoxides **5a** and **5b** the corresponding enantiomers of opposite configuration were synthesized by use of D-(–)-diethyl tartrate as a chiral ligand for Ti^{IV}. HPLC analyses on a chiral column showed extremely high enantioselectivity in the case of **5b** (>99% *ee*), with slightly diminished enantioselectivity in that of **5a** (>97% *ee*) (Figure 1 and Figure 2).

For the determination of the absolute stereochemistry of the epoxidation an X-ray structure analysis of **5a** was performed. The molecular structure is depicted in Figure 3. The absolute configuration could not be unambiguously derived only from this analysis, but was confirmed together by HPLC and X-ray crystallography indirectly after transformation of **5b** into the corresponding diol (vide infra).

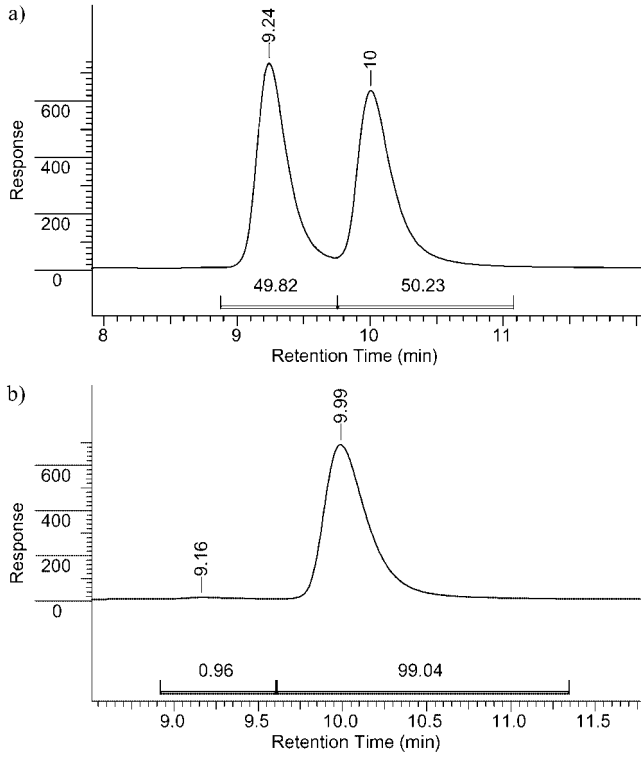


Figure 1. Chromatograms of: a) an approximately equimolar mixture of (all *R*)-**5a** and (all *S*)-**5a**, and b) the product of the asymmetric epoxidation [(all *R*)-**5a**]. Whelk(*R*,*R*) column, eluent: *n*-hexane/ethanol 8:2, 0.8 mL min^{-1}.

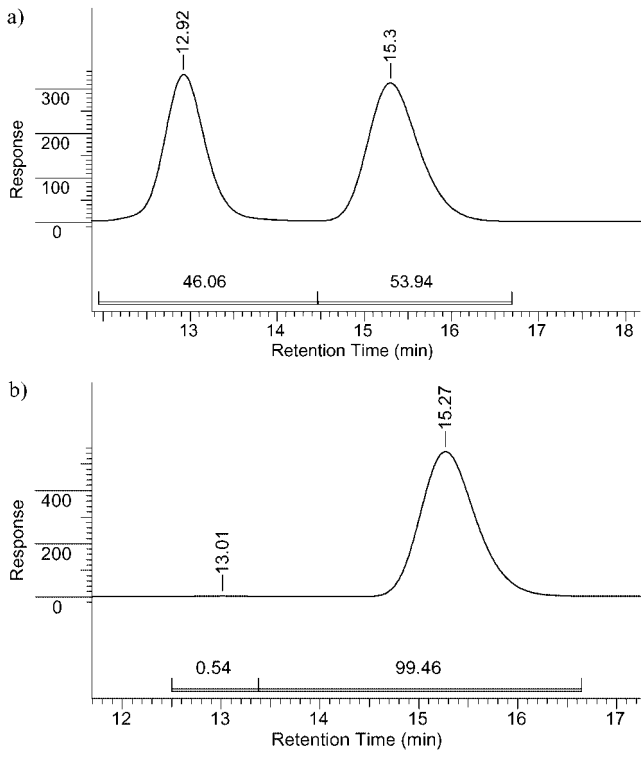


Figure 2. Chromatograms of: a) an approximately equimolar mixture of (all *R*)-**5b** and (all *S*)-**5b**, and b) the product of the asymmetric epoxidation [(all *S*)-**5b**]. Whelk(*R*,*R*) column, eluent: *n*-hexane/ethanol 8:2, 0.8 mL min^{-1}].

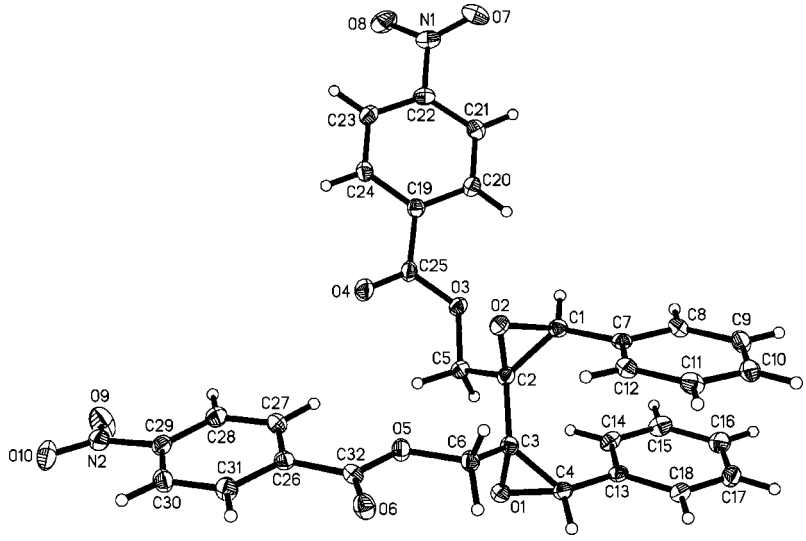
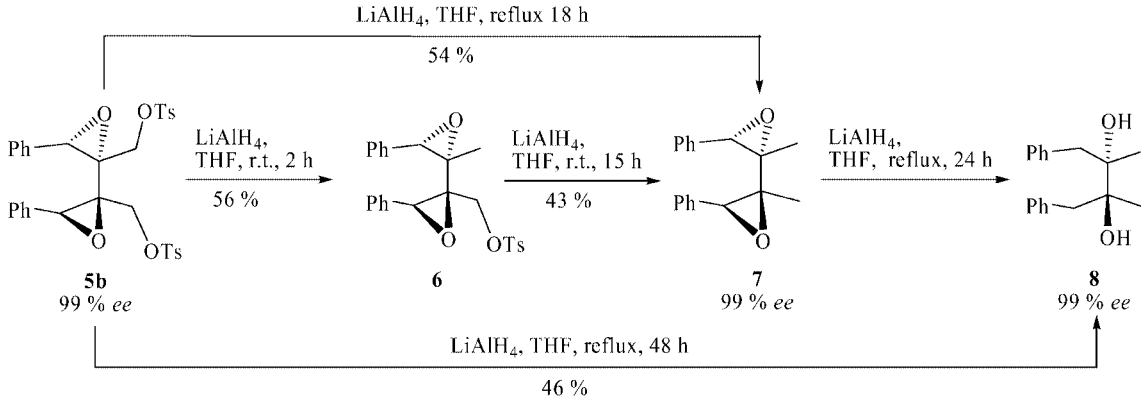


Figure 3. Molecular structure of **5a**. The thermal ellipsoids correspond to 30% probability.



Scheme 3. Reduction of **5b**.

The bis-*O*-tosylate **5b** was reduced with $LiAlH_4$ (Scheme 3) in a step in which the course of the reaction was dependent on the conditions. At room temperature and after 2 h it yielded the monotosylate **6** in 56% yield, and this could be converted into the bis-epoxide **7** by further treatment with $LiAlH_4$. Compound **7** could also be obtained in one step and in 54% yield by heating **5b** with $LiAlH_4$ at reflux for 18 h. Further extended heating of the reaction mixture opened the epoxide rings and furnished the vicinal diol **8**.

The structure of **7** was confirmed by X-ray crystallography. It is displayed in Figure 4 and shows C_2 symmetry.

The (*R*,*R*)-diol **8** had previously been described by Sharpless et al., who obtained this compound in 29% *ee* by another method.[7] The optical rotation of the product was measured as $[\alpha]_D^{20} = 7.2$ ($c = 0.98$, EtOH). The value of our product **8** was $[\alpha]_D^{20} = -56.5$ ($c = 10$, EtOH), which provides additional evidence that the *all-S* isomer is formed under the conditions of the Katsuki–Sharpless epoxidation with L-(+)-diethyl tartrate.

In order to study whether the double epoxidation of butadiene **4** is a consecutive process or proceeds in parallel we studied the reaction with application of only one equivalent of *t*BuOOH instead of an excess as described above (Scheme 4). Under these conditions and even with prolonged reaction times the corresponding mono-epoxide was formed exclusively. After derivatization with *p*-nitrobenzoyl chloride the epoxide **9** and the diester **10** derived from unconverted diene **4** were isolated.

This study provided access to the mixed diester **12**, as illustrated in Scheme 5. In the first step, the monoester **11** was formed by a selective esterification of one hydroxy group with *p*-nitrobenzoyl chloride, while subsequent asymmetric Katsuki–Sharpless epoxidation of the remaining allyl alcohol moiety and treatment with *p*-bromobenzoyl chloride yielded the α,β-unsaturated epoxide **12**.

The molecular structure of the *p*-bromobenzoyl compound **12** is depicted in Figure 5. It gives clear evidence for its absolute configuration – (*S*) – at C-2 [Flack parameter in this case is equal to –0.006(15)].

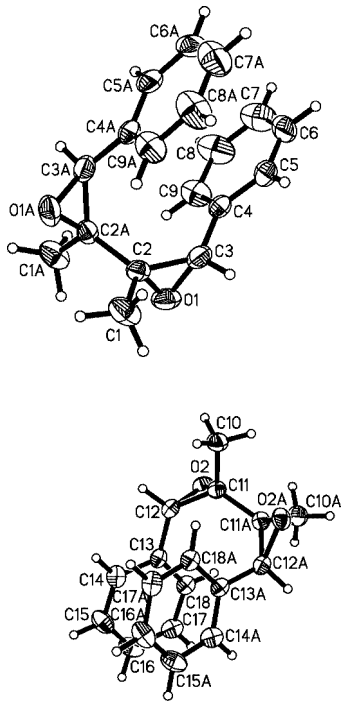
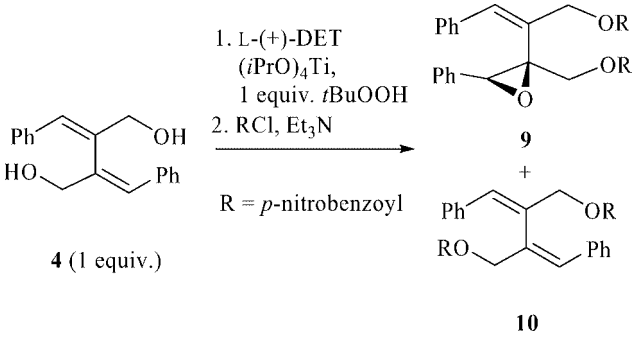
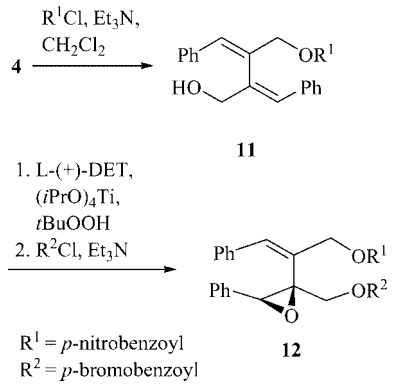


Figure 4. Molecular structure of **7** (two different molecules). The thermal ellipsoids correspond to 30% probability.



Scheme 4. Monoepoxidation of diallyl alcohol **4**.



Scheme 5. Synthesis of a mixed diester monoepoxide.

4. Structure and Reactivity

The epoxides **5** and **7** were found to be less reactive than expected: for the full conversion of **5b** into **8** the reaction mixture had to be heated with a large excess of $LiAlH_4$ for 48 h, while heating of **5a** at reflux in acetonitrile solution with $BnNH_2$ for 24 h in the presence of a stoichiometric amount of $LiClO_4$ gave only the starting material. Employment of $PhP(SiMe_3)_2$ as a nucleophile for **7** was also unsuccessful: NMR analysis showed only starting compound, without any trace of the targeted phospholane, even after 6 h heating at 110 °C in the absence of solvent.

A careful inspection of the X-ray structural analyses of **5a**, **7** and **12** reveals nearly parallel alignments of the two phenyl rings. The angle between the two phenyl planes in **5a**, defined by C7–C12 and C13–C18, is 4.39(9) °. Moreover, the positions of the two phenyl rings are staggered (Figure 6, a), which gives a hint of possible π–π stacking interactions.[8,9] The smallest distance between two carbon atoms in different rings (C7 and C13) is 3.158(2) Å (Figure 6, b), due to which arrangement the O2–C2 and C3–O1 bonds are oriented in an *anti* conformation.

Indications of possible parallel displaced π–π interactions in solution were provided by some unusual spectro-

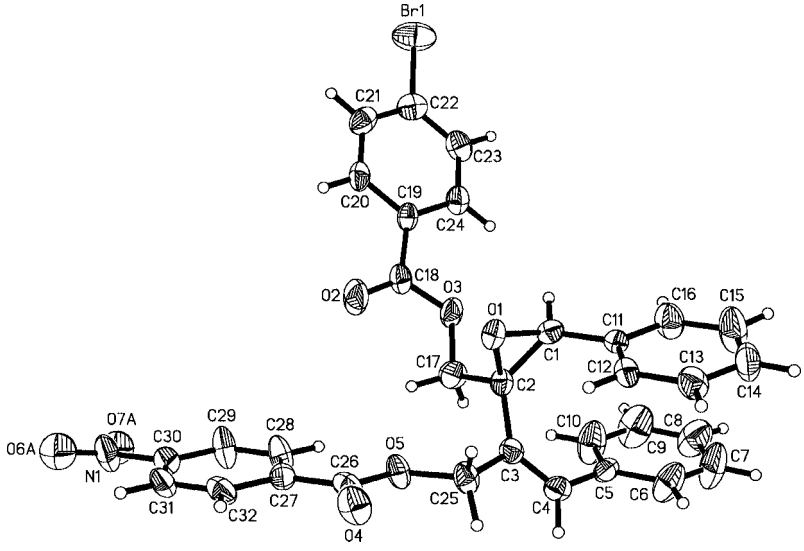


Figure 5. Molecular structure of **12**. The thermal ellipsoids correspond to 30% probability.

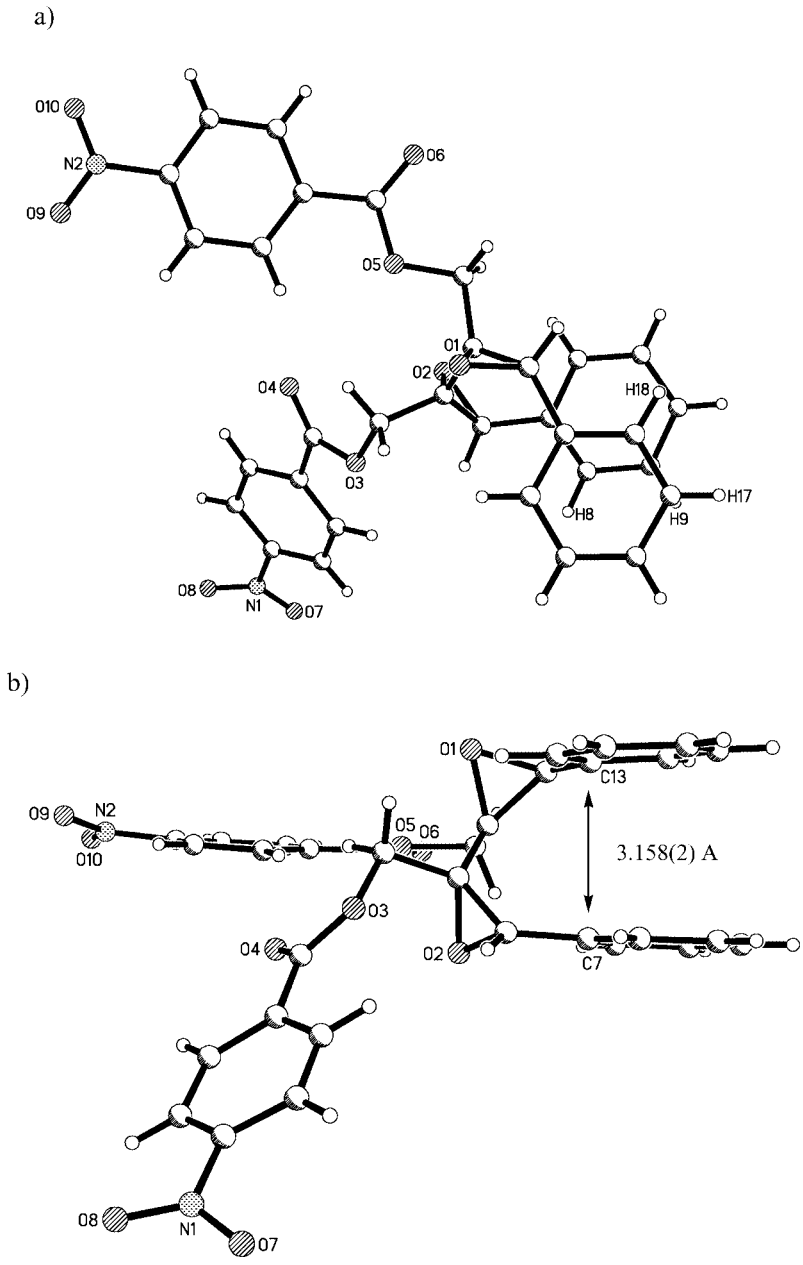


Figure 6. Different views of the structure of **5a**.

scopic data. The ^{1}H NMR spectra of **7**, **5a** and **5b** each contained a broad four-proton signal, which was shifted to higher field in relation to the resonances of other aromatic protons. For comparison, the ^{1}H NMR spectra of *cis*- or *trans*-β-methylstyrene oxide did not show this feature. This broad signal could be assigned to H^8, H^9, H^{17} and H^{18} (Figure 6, a), which should be influenced by the aromatic ring current effect. UV spectroscopy showed a bathochromic shift of the absorption maximum of **7** by 22 nm in relation to that of *cis*-β-methylstyrene oxide.[10] We speculated that this geometrical arrangement in **5** and **7** could hinder the attack of nucleophiles, causing the low reactivity.

In order to evaluate the strength of such assumed π–π stacking interactions we carried out ab initio calculations at the electron-correlated MP2/6-31G* level of theory. Different views of the optimized structures for **7** and **7′** (H instead of Me groups) are shown in Figure 7.

The MP2/6-31G*-optimized structural parameters given in Table 1 agree reasonably well with the X-ray structural analyses of **5a** and **7**. This agreement between theory, X-ray analysis and spectroscopic data in solution indicates that the relative positions of the two phenyl rings are not caused by crystallization, and therefore that there is no structural difference between gas phase and solid state.

To quantify the interaction we employed the homodesmotic equation,[11] in which we used the mono-epoxide and ethane as reference molecules. Homodesmotic equations have been successfully used to estimate long-distance interactions.[12] For **7** the calculated homodesmotic reaction energy is only –1.80 kcal mol^{-1} at the MP2/6-31G* level

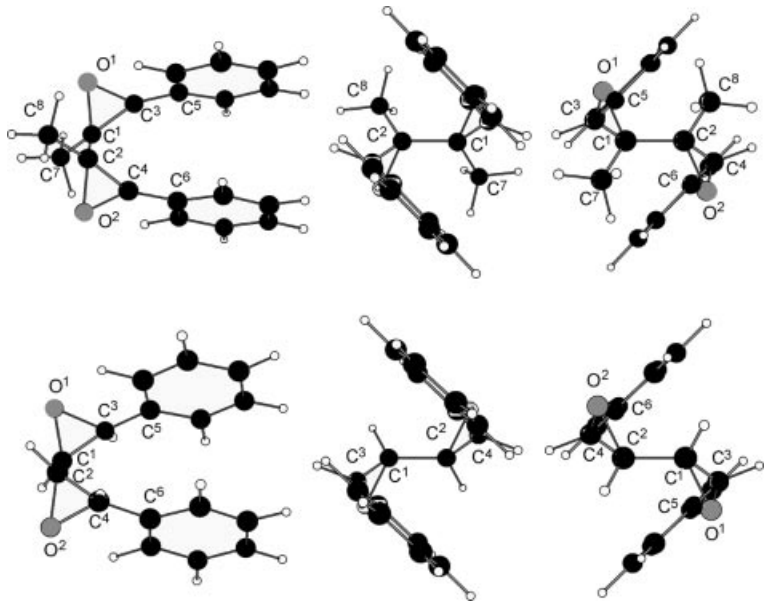
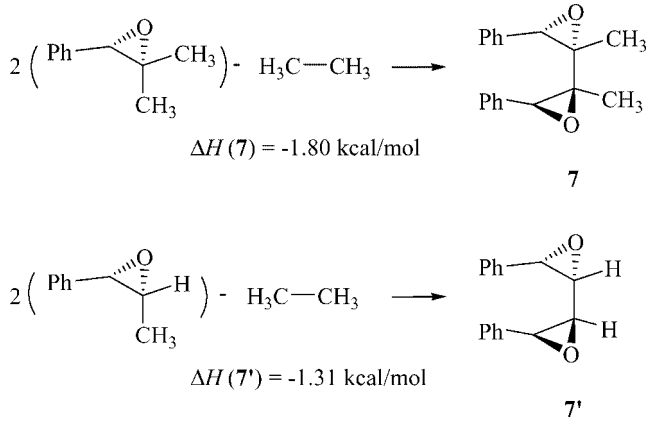


Figure 7. MP2/6-31G*-optimized structures of **7** (top) and **7′** (bottom) in different views.

Table 1. MP2/6-31G*-optimized bond parameters and comparison with the available X-ray data.[a]

	7[a]	**7′**	**5a**[a]
C1–C2	1.510 [1.522(5)], [1.518(5)]	1.496	[1.521(2)]
C1–C3	1.485 [1.470(4)], [1.484(4)]	1.480	[1.472(2)], [1.480(2)]
C1–O1	1.449 [1.435(4)], [1.445(3)]	1.441	[1.433(2)], [1.447(2)]
O1–C3	1.4478 [1.444(4)], [1.447(3)]	1.446	[1.446(2)], [1.4411(2)]
C1–C7	1.509 [1.483(4)], [1.497(4)]		[1.518(2)], [1.504(2)]
C3–C5	1.482 [1.485(5)], [1.487(4)]	1.482	[1.487(2), [1.488(2)]
C5–C6[b]	3.702 [3.156(6)], [3.188(3)]	3.158	[3.158(2)]
O1–C1–C2–O2	170.95 [168.8(2)], [169.9(2)]	163.2	[166.0(1)]
C7–C1–C2–C8	–93.48 [–96.6(3)], [–94.9(3)]		[–99.9(2)]
C3–C1–C2–C4	–54.50 [–56.3(5)], [–56.3(4)]	–59.8	[–57.8(2)]

[a] The X-ray data are given in parentheses. [b] Distance (no bond).



Scheme 6. Theoretical investigation of π–π stacking phenomena.

(Scheme 6), which indicates a very weak stabilizing interaction between the two phenyl rings. In order to check the substitution effect of the methyl group we also replaced the methyl groups by hydrogen atoms (**7′**). However, the calculated homodesmotic reaction energy, of –1.31 kcal mol^{-1}, is also very small, and no significant effects of methyl substitution can be found. In addition, the structural parameters of **7** and **7′**, especially the length of the shortest C–C bond and the distance between the phenyl ring centres, are very similar, and since these distances in **5a** are also very similar to those in **7** and **7′**, we can conclude that the interaction of the phenyl rings in **5a** should be in the same range as those of **7** and **7′** and hence very weak. The observed low reactivity of the bis-epoxide towards nucleophiles can hardly therefore be interpreted solely in terms of arguments based on π–π stacking interactions. In addition, we also carried out QCISD(T)/6-31G*//MP2/6-31G* single-point energy calculations on **7′** and the homodesmotic reaction energy was found to be +0.97 kcal mol^{-1}, again indicating negligible interaction between the two phenyl rings. Since highly correlated calculations with larger basis sets including polarization and diffuse functions are not possible with present systems, it is to be expected that the energetic interaction between the two phenyl rings found on the basis of our calculations is probably not significant.

Conclusions

As a first example, the double asymmetric Katsuki–Sharpless epoxidation of a conjugated diallyl alcohol was investigated, and was found to afford the desired bis-epoxide with excellent enantioselectivity (>97% *ee*). The reaction proceeds in a stepwise manner and the product was trapped by acylation or tosylation. HPLC on chiral columns was used to determine the optical purities of the products, and X-ray structural analyses were employed to confirm the relative and absolute configurations. By reduction of the bis-*O*-tosylate **5b** with $LiAlH_4$ the corresponding enantiopure vicinal alcohol was obtained. The synthesized bis-epoxides possess low reactivity towards nucleophiles. One reason for such low reactivity might be π–π stacking interactions between the phenyl rings, but it might instead be more convincingly attributed to the sterically crowded environment of the epoxide units.

Experimental Section

General: All reagents were purchased from commercial sources and were used without additional purification unless otherwise mentioned. Solvents were dried and freshly distilled under argon before use. Thin-layer chromatography was performed on precoated TLC plates (silica gel). Melting points are corrected. The optical rotations were measured on a "Gyromat-HP" instrument. NMR spectra were recorded at the following frequencies: 250.13 MHz (^{1}H), 75.48 MHz (^{13}C), 121.49 MHz (^{31}P). Chemical shifts of ^{1}H and ^{13}C NMR spectra are reported in ppm downfield from TMS as an internal standard, while chemical shifts of ^{31}P NMR spectra are referenced to H_3PO_4 as an external standard. Elemental analyses were performed with a LEGO CHNS-932, mass spectra were recorded on an AMD 402 spectrometer, and UV/Vis spectra were recorded with a Perkin–Elmer Lambda 2 spectrometer. The enantiomeric excesses of compounds **5**, **7** and **8** were measured on a Agilent 1100 Series HPLC instrument. The syntheses of only one enantiomer from each enantiomeric pair are given below.

X-ray Crystallographic Study of Complexes 5a: Data were collected with a Bruker-AXS SMART 6 K diffractometer with use of graphite-monochromated Cu-K_α radiation and ω-scans.

Compound 5a: Space group $P2_12_12_1$, orthorhombic, a = 10.5922, b = 11.9304, c = 21.6245 Å, V = 2732.67 Å^3, Z = 4, $\rho_{calcd.}$ = 1.450 g cm^{-3},16357 reflections measured, 5077 were independent of symmetry, of which 4672 were observed [$I > 2\sigma(I)$], R_1 = 0.0321, wR_2 (all data) = 0.0809, 397 parameters.

X-ray Crystallographic Study of Complexes 7 and 12: Data were collected with a STOE-IPDS diffractometer with use of graphite-monochromated Mo-K_α radiation.

Compound 7: Space group $C2$, monoclinic, a = 15.243(3), b = 8.861(2), c = 12.800(3) Å, β = 122.77(3)°, V = 1453.6(5) Å^3, Z = 4, $\rho_{calcd.}$ = 1.217 g cm^{-3}, 11744 reflections measured, 3345 were independent of symmetry, of which 2017 were observed [$I > 2\sigma(I)$], R_1 = 0.051, wR_2 (all data) = 0.139, 181 parameters.

Complex 12: Space group $P2_12_12_1$, orthorhombic, a = 6.8896(4), b = 19.085(2), c = 21.344(2) Å, V = 2806.5(3) Å^3, Z = 4, $\rho_{calcd.}$ = 1.454 g cm^{-3}, 39350 reflections measured, 5522 were independent of symmetry, of which 2698 were observed [$I > 2\sigma(I)$], R_1 = 0.051, wR_2 (all data) = 0.116, 369 parameters. The structures were solved by direct methods [SHELXS-97: G. M. Sheldrick, University of Göttingen, Germany, **1997**.] and refined by full-matrix, least-squares techniques against F^2 [SHELXL-97: G. M. Sheldrick, University of Göttingen, Germany, **1997**.] XP (Bruker AXS) was used for structural representations.

CCDC-617872 (for **5a**), -617873 (for **7**) and -617874 (for **12**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Compounds **1** and **4** are known and could be synthesized by the methods reported in the literature.[5,6,13] For the synthesis of bis-epoxides **5a** and **5b** we used the method described by Sharpless for the formation of monoepoxides followed by in situ derivatization.[3]

Dimethyl (*E*)-2-Benzylidenesuccinate (2). Method A: $SOCl_2$ (26 mL, 0.354 mol) was added dropwise with stirring at room temperature to a solution of **1** (52 g, 0.236 mol) in CH_2Cl_2 (150 mL). The mixture was heated at reflux until the end of gas evolution (approximately 6 h), the solvent and $SOCl_2$ were evaporated, and MeOH (100 mL) and Et_3N (36 mL) were added consecutively with stirring. The stirring was continued overnight, the solvent was evaporated, and the residue was dissolved in EtOAc, washed with water, aq. $NaHCO_3$ solution, a diluted solution of HCl and brine and dried with Na_2SO_4. The solvent was evaporated and the product was distilled under vacuum (0.8 mbar, 125–130 °C) to give **2** (45 g, 82% yield). ^{1}H NMR ($CDCl_3$): δ = 3.92 (s, 2 H), 4.10 (s, 3 H), 4.20 (s, 3 H), 7.68–7.79 (m, 5 H), 8.28 (s, 1 H).

Method B: Tri-*n*-butylphosphane (95%, 64 mL, 1.4 equiv.) was added slowly by syringe, under Ar at 20–25 °C, to a stirred solution of dimethyl maleate (28.8 g, 0.2 mol) and benzaldehyde (21.2 g, 0.2 mol) in dry THF (300 mL), and stirring was continued for 20 h. The mixture was diluted with CH_2Cl_2 (1 L) and stirred for 0.5 h. Water (400 mL) containing H_2O_2 (30%, 34 mL) was added to oxidise the remaining nBu$_3$P. The organic phase was washed with $NaHCO_3$ (1 M) and dried (Na_2SO_4), and the solvents were evaporated. TLC indicated that the residue contained the desired product, tri-*n*-butylphosphane oxide and some starting aldehyde. Flash chromatography (Merck 60 silica gel; *n*-heptane/ethyl acetate 2:1) gave the pure diester as a an oil (33 g, 70% yield).

(2*E*,3*E*)-2-Benzylidene-3-(methoxycarbonyl)-4-phenylbut-3-enoic Acid (3): A solution of benzaldehyde (21.2 g, 0.2 mol) and diester **2** (45 g, 0.192 mol) in anhyd. MeOH (30 mL) was added dropwise to a solution of LiOMe in MeOH [freshly prepared by slow addition of finely divided lithium (1.4 g, 0.2 mol) to anhyd. MeOH (150 mL) with stirring and heating until total dissolution]. The mixture was heated at reflux for 36 h under argon and then cooled in an ice bath, and most of the solvent was removed in vacuo. The residue was acidified to pH 1 with aq. HCl (6 N) and extracted with EtOAc, the organic phase was washed with sat. aq. $NaHCO_3$ solution, and the aq. phase was collected. After acidification with aq. HCl (2 N), the aqueous solution was extracted with EtOAc, and removal of the solvent gave the corresponding monoester **3** as a powder (53.2 g, 90% yield). m.p. 151 °C. 150–151 °C.[14] ^{1}H NMR ($CDCl_3$): δ = 4.13 (s, 3 H), 7.55–7.90 (m, 10 H), 8.31 (s, 1 H), 8.35 (s, 1 H), 10.60–11.70 (br s, 1 H) ppm.

(2*E*,3*E*)-2,3-Dibenzylidenebutane-1,4-diol (4): A solution of **3** (5.7 g, 18.5 mmol) in THF (40 mL) was added dropwise at 0 °C over 10 min to a suspension of $LiAlH_4$ (1.1 g, 28 mmol) in THF (70 mL). After addition, the mixture was stirred for 2.5 h at room temperature and the excess $LiAlH_4$ was then quenched by addition of H_2O (no excess) and EtOH (50 mL). The inorganic compounds

were filtered off through a pad of SiO_2 and intensively washed with EtOH. The product was purified by chromatography on silica gel (CH_2Cl_2/EtOAc 1:1) to give compound **4** as a solid (1.87 g, 38% yield). m.p. 108–110 °C. 111–112 °C.[15] ^1H NMR ($CDCl_3$): δ = 4.14 (d, J = 4.27 Hz, 2 H), 4.49 (t, J = 5.65 Hz, 1 H), 6.82 (s, 1 H), 7.15–7.31 (m, 3 H), 7.51–7.59 (m, 2 H) ppm. ^{13}C NMR ([D$_6$]acetone): δ = 65.6, 126.5, 128.0, 128.9, 129.4, 138.0, 141.8 ppm.

(2*S*,3*S*)-2-(4-Nitrophenylcarbonyloxymethyl)-2-[(2*S*,3*S*)-2-(4-nitrophenylcarbonyloxymethyl)-3-phenyloxiran-2-yl]-3-phenyloxirane (5a): Ti(O*i*Pr)$_4$ (86 mg, 0.3 mmol) and molecular sieves (3 Å, 0.5 g) were added to a cooled solution (–30 °C) of L-(+)-diethyl tartrate (87 mg, 0.42 mmol) in dry CH_2Cl_2 (20 mL), the mixture was stirred at this temperature for 20 min, and a solution of *tert*-butyl hydroperoxide in decane (5.5 M, 1.1 mL, 6 mmol) was added. The mixture was stirred for a further 40 min and **4** (0.4 g, 1.5 mmol) in CH_2Cl_2 (30 mL) was added. The reaction flask was kept in a freezer at –27 °C for 2 d, P(OMe)$_3$ (0.55 mL) was then added dropwise by syringe at –30 °C over a 30 min period, and the mixture was stirred for 40 min. Subsequently, Et_3N (0.72 g, 7.1 mmol) and *p*-nitrobenzoyl chloride (1.12 g, 6 mmol) were added and the reaction mixture was stored in a freezer for another 2 d. The mixture was then allowed to warm to room temp., and stirred at this temperature for 6 h, the molecular sieves were filtered off, and the solution was washed with an aqueous solution of tartaric acid, satd. aq. $NaHCO_3$ solution and brine and dried (Na_2SO_4), and the solvents were evaporated. The product was purified by chromatography on silica gel (Merck 60, CH_2Cl_2 as eluent) to give compound **5a** [610 mg, 68% yield;, >97% *ee*, determined by HPLC, Whelk(*R*,*R*), *n*-hexane/ethanol 8:2, 0.8 mL min^{-1}]. Alternative purification: after the workup procedure the crude mixture was filtered through silica gel (a short column) and crystallized from CH_3CN (63% yield). M.p. 187 °C. $[\alpha]_D^{25}$ = –11.4 (c = 5, $CHCl_3$). ^1H NMR ($CDCl_3$): δ = 3.87 (m, 2 H), 4.62 (s, 1 H), 4.67 (s, 1 H), 4.90–5.35 (br m, 2 H), 6.60–7.00 (br m, 4 H), 7.07–7.27 (m, 6 H), 8.29 (s, 8 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 61.6, 62.3, 66.6, 124.1, 126.3, 128.5, 128.8, 131.4, 133.3, 135.3, 151.2, 164.7 ppm. DEPT ^{13}C NMR ($CDCl_3$): δ = 61.6 (CH), 66.6 (CH_2) and 124.1, 126.3, 128.5, 128.8, 131.4 (arom. CH) ppm. MS(EI): m/z = 596 [M]$^+$ ($C_{32}H_{24}N_2O_{10}$), 490, 429, 384, 340, 323, 310, 256, 218, 180, 150, 105, 104, 92, 77, 76.

(2*S*,3*S*)-2-(4-Methylphenylsulfonyloxymethyl)-2-[(2*S*,3*S*)-2-(4-methylphenylsulfonyloxymethyl)-3-phenyloxiran-2-yl]-3-phenyloxirane (5b): Ti(O*i*Pr)$_4$ (54 mg, 0.19 mmol) and molecular sieves (3 Å, 0.25 g) were added to a cooled solution (–30 °C) of L-(+)-diethyl tartrate (55 mg, 0.27 mmol) in dry CH_2Cl_2 (15 mL). The mixture was stirred at this temperature for 20 min and a solution of *tert*-butyl hydroperoxide in decane (5.5 M, 0.7 mL, 3.8 mmol) was added. The mixture was stirred for a further 40 min, **4** (0.25 g, 0.94 mmol) in CH_2Cl_2 (15 mL) was added, and the reaction flask was kept in a freezer at –27 °C for 2 d. P(OMe)$_3$ (0.35 mL) was then added dropwise by syringe at –30 °C over a period of 30 min and the mixture was stirred for 40 min. Subsequently, Et_3N (0.65 mL, 4.7 mmol) and *p*-toluenesulfonyl chloride (0.71 g, 3.73 mmol) were added and the reaction mixture was stored in a freezer for another 2 d. The mixture was then allowed to warm to room temp. and stirred at this temperature for 6 h, the molecular sieves were filtered off, and the solution was washed with an aq. solution of tartaric acid, sat. aq. $NaHCO_3$ solution and brine and dried (Na_2SO_4), and the solvents were evaporated. The product was purified by chromatography on silica gel (*n*-hexane/ethyl acetate 3:2) to give compound **5b** as an oil (650 mg, 88% yield, >99% *ee*, determined by HPLC, Chiralcel OD-H, Daicel, *n*-hexane/ethanol 9:1, 1.0 mL min^{-1}). $[\alpha]_D^{25}$ = 7.54 (c = 14, $CHCl_3$). ^1H NMR ($CDCl_3$): δ = 2.62 (s, 3 H), 3.96 (s, 1 H), 4.28–4.34 (m, 2 H), 6.87–7.05 (br s, 2 H), 7.22–7.34 (m, 3 H), 7.51 (d, J = 8 Hz, 2 H), 7.91 (d, J = 8 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 22.1 (s, CH_3), 60.8 (s, CH), 61.5 (s, C), 70.2 (s, CH_2), 126,5, 128.4, 128.5, 128.7, 130.4 (arom. CH), 132.7, 130.1, 145.6 (arom. C) ppm. MS(EI): m/z = 605.8 [M]$^+$ ($C_{32}H_{30}O_8S_2$), 514.8, 438.8, 344.9, 314.9, 260.9, 181, 180, 179, 172, 165, 154.9, 143, 105, 91, 77.

(2*S*,3*S*)-2-[(2*S*,3*S*)-2-Methyl-3-phenyloxiran-2-yl]-2-(4-methylphenylsulfonyloxymethyl)-3-phenyloxirane (6): $LiAlH_4$ (0.18 g, 4.7 mmol) was added in three portions (at intervals of 30 min) to a solution of **5b** (2.25 g, 3.7 mmol) in dry THF (10 mL). After the last addition, the mixture was stirred for another 30 min and diethyl ether (15 mL) was added. The excess of $LiAlH_4$ was quenched by the addition of H_2O, the inorganic residue was filtered off, and chromatography on silica gel (Merck 60, *n*-hexane/ethyl acetate 2:1) afforded **6** (900 mg, 56% yield) as an oil, together with **7** (100 mg, 10% yield) as a solid. $[\alpha]_D^{25}$ = 4.4 (c = 5, $CHCl_3$). ^1H NMR ($CDCl_3$): δ = 1.46 (s, 3 H), 2.45 (s, 3 H), 3.56 (s, 1 H), 3.76 (s, 1 H), 4.05–4.22 (m, 2 H), 6.8–7.23 (m, 10 H), 7.35 (d, J = 8 Hz, 2 H), 7.77 (d, J = 8 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 22.1 (s, CH_3), 22.2 (s, CH_3), 61.2 (s, CH), 61.8 (s, C), 63.2 (s, C), 64.3 (s, CH), 70.9 (s, CH_2), 126.5, 126.9, 127.9, 128.2, 128.4, 128.5, 128.5, 130.3 (all s, arom. CH), 132.9, 133.9, 134.8, 145.5 (all s, arom. C) ppm. MS (CI, isobutane): m/z = 437 [M + H]$^+$ ($C_{25}H_{24}O_5S$ + H), 419, 331, 265, 247, 219, 205, 180,133, 105. MS (EI): m/z = 436 [M]$^+$ ($C_{25}H_{24}O_5S$), 400, 330, 264, 235, 206, 181, 180, 175, 165, 158, 154, 145, 139, 115, 105, 91, 77.

(2*S*,3*S*)-2-Methyl-2-[(2*S*,3*S*)-2-methyl-3-phenyloxiran-2-yl]-3-phenyloxirane (7). Method A: $LiAlH_4$ (0.078 g, 2.06 mmol) was added at r.t. to a solution of **6** (0.9 g, 2.06 mmol) in dry THF (5 mL) and the mixture was stirred for 14 h. Another portion of $LiAlH_4$ (0.030 g, 0.79 mmol) was added and stirring was continued for the next 30 min. Excess $LiAlH_4$ was quenched by the addition of H_2O and EtOAc (15 mL), the inorganic residue was filtered off, and chromatography on silica (*n*-hexane/ethyl acetate 3:1) gave **7** (235 mg, 43% yield).

Method B: $LiAlH_4$ (0.054 g, 1.4 mmol) was added to a solution of **5b** (0.42 g, 0.7 mmol) in dry THF (10 mL) and the mixture was stirred near its boiling point for approximately 18 h (TLC monitoring). Excess $LiAlH_4$ was decomposed by the addition of H_2O and EtOAc (10 mL), the inorganic residue was filtered off, and chromatography on silica (*n*-hexane/ethyl acetate 3:1) gave **7** (100 mg, 54% yield, >99% *ee*, determined by HPLC, Chiralcel OD-H, Daicel, *n*-hexane/ethanol 99.5/0.5, 1.0 mL min^{-1}) and **8** (16 mg, 8% yield). An analytical sample of **7** could be obtained by sublimation (90 °C, 0.3 mbar) or by crystallization from *n*-hexane. m.p. 103–104 °C. $[\alpha]_D^{25}$ = 38.2 (c = 3, $CHCl_3$). ^1H NMR ($CDCl_3$): δ = 1.43 (s, 3 H), 3.57 (s, 1 H), 7.03–7.15 (br m, 2 H), 7.16–7.25 (m, 3 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 21.6 (CH_3), 63.8 (s, C), 64.4 (CH), 126.8, 127.7, 128.4 (all s, arom. CH), 135.7 (s, arom. C) ppm. MS (EI): m/z = 266 [M]$^+$ ($C_{18}H_{18}O_2$), 248, 181, 180, 179, 178, 165, 160, 159, 145, 117, 197, 106, 105, 91, 89, 79, 77, 51.

(2*R*,3*R*)-2,3-Dimethyl-1,4-diphenylbutane-2,3-diol (8): $LiAlH_4$ (0.134 g, 3.53 mmol) was added at room temp. to a solution of **5b** (2.14 g, 3.53 mmol) in dry THF (15 mL) and the mixture was stirred near its boiling point for 24 h. Another portion of $LiAlH_4$ (0.11 g, 2.9 mmol) was added and the mixture was stirred near its boiling point for another 24 h (TLC monitoring). Excess $LiAlH_4$ was decomposed by the addition of H_2O and ether (15 mL) and the inorganic residue was filtered off. Chromatography on silica (*n*-hexane/ethyl acetate 4:1) gave **8** (438 mg, 46% yield, >99% *ee*, determined by HPLC, Chiralcel OD-H, Daicel, *n*-hexane/ethanol 9:1, 1.0 mL min^{-1}). M.p. 75 °C. $[\alpha]_D^{25}$ = –56.5 (c = 10, ethanol). ^1H

NMR ($CDCl_3$): δ = 1.17 (s, 3 H), 2.00 (brs, 1 H), 2.72 (d, J = 13 Hz, 1 H), 3.14 (d, J = 13 Hz, 1 H), 7.25–7.34 (m, 5 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 21.8 (s, CH_3), 42.5 (s, CH_2), 77.1 (s, C), 126.8, 128.6, 131.4 (all s, arom. CH), 138.1 (s, arom. C). MS (CI, isobutane): m/z = 291 ([M – 2 H_2O + isobutyl]$^+$ ($C_{22}H_{27}$), 277, 253, 235, 179, 161, 135, 105, 91, 79. MS (EI): m/z = 179 [M – Bn]$^+$, 161 [M – Bn – H_2O]$^+$, 143, 135, 117,105, 91, 77, 65, 57. Elemental analysis (%) calcd for $C_{18}H_{22}O_2$: C 79.96, H 8.20; found: C 79.85, H 7.94.

(2*S*,3*S*)-2-[(*Z*)-1-(4-Nitrophenylcarbonyloxymethyl)-2-phenyl-1-ethenyl]-2-[1-(4-nitrophenyl)vinyloxymethyl]-3-phenyloxirane (9): Ti(O*i*Pr)$_4$ (54 mg, 0.19 mmol) and molecular sieves (3 Å, 0.25 g) were added to a cooled (–30 °C) solution of L-(+)-diethyl tartrate (55 mg, 0.26 mmol) in dry CH_2Cl_2 (10 mL). The mixture was stirred at this temperature for 20 min, a solution of *tert*-butyl hydroperoxide in decane (5.5 M 0.35 mL, 1.88 mmol) was added, the mixture was stirred for a further 40 min, and **4** (0.5 g, 1.88 mmol) in CH_2Cl_2 (10 mL) was added. The reaction flask was kept in a freezer for 5 d at –27 °C, $P(OMe)_3$ (0.18 mL) was then added dropwise by syringe at –30 °C over a period of 30 min, and the mixture was stirred for 40 min. Subsequently, Et_3N (0.9 g, 8.9 mmol) and *p*-nitrobenzoyl chloride (1.4 g, 7.5 mmol) were added, and the reaction mixture was stored in a freezer for another 2 d and was then allowed to warm to room temp. and stirred at this temperature for 6 h. The molecular sieves were filtered off, the solution was washed with an aq. solution of tartaric acid, sat. aq. $NaHCO_3$ solution and brine and dried (Na_2SO_4), and the solvents were evaporated. The mixture was chromatographed on silica gel (Merck 60, CH_2Cl_2 as eluent) to give **9** and **10** in a ratio of 2:1.

Compound 9: M.p. 165 °C. ^1H NMR ($CDCl_3$): δ = 4.49 (s, 2 H), 7.31 (s, 1 H), 7.59–7.72 (m, 3 H), 7.93– 8.01 (m, 2 H), 8.26 (d, J = 9.16 Hz, 2 H), 8.51 (d, J = 9.16 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 69.7 (s, CH_2), 123.8 (s, CH), 124.2 (s, CH), 128.8 (s, CH), 129.1 (s, CH), 131.1 (s, CH), 132.1 (s, C), 134.3 (s, CH), 135.5 (s, C), 135.9 (s, C), 150.8 (s, C–NO_2), 164.7 [s, C(O)O–] ppm.

Compound 10: ^1H NMR ($CDCl_3$): δ = 4.31 (s, 1 H), 4.64–5.32 (m, 4 H), 6.78 (s, 1 H), 6.98–7.49 (m, 10 H), 8.07–8.33 (m, 8 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 63.5, 65.0, 67.0, 69.0, 124.0, 124.1, 126.3, 126.7, 126.9, 128.2, 128.4, 128.6, 128.8, 129.3, 131.2, 131.3, 131.4, 133.4, 133.7, 135.1, 151.9 (s, C–NO_2), 151.1 (s, C–NO_2), 164.6 [s, C(O)O–], 164.7 [s, C(O)O–] ppm.

(*E*)-3-Hydroxymethyl-4-phenyl-2-[(*E*)-1-phenylmethylidene]-3-butenyl 4-Nitrobenzoate (11): A solution of *p*-nitrobenzoyl chloride (0.35 g, 1.88 mmol) in CH_2Cl_2 (5 mL) was added dropwise with stirring over 30 min at room temp. to a solution of **4** (0.5 g, 1.88 mmol) and Et_3N (0.2 g, 2 mmol) in CH_2Cl_2 (5 mL). The mixture was stirred for 3 h at room temp., washed with water, sat. aq. $NaHCO_3$ solution and brine and dried (Na_2SO_4), and the solvents were evaporated. Chromatography on silica gel (Merck 60, chloroform/ethyl acetate 2:1) provided the monoester **11** (468 mg, 60% yield) and the corresponding diester (300 mg, 28% yield). ^1H NMR ($CDCl_3$): δ = 1.97 (s, 1 H), 4.28 (s, 2 H), 5.05 (s, 2 H), 6.84 (s, 1 H), 6.87 (s, 1 H), 7.21–7.38 (m, 6 H), 7.51–7.62 (m, 4 H), 7.96 (d, J = 9 Hz, 2 H), 8.20 (d, J = 9 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 66.7 (CH_2), 70.0 (CH_2), 123.8, 128.1, 128.7, 128.8, 129.0, 129.1, 129.2, 131.1, 132.8, 133.6, 135.6, 136.0, 136.7, 138.2, 150.8 (C–NO_2), 164.9 [-C(O)O-] ppm. MS (EI): m/z = 415 [M]$^+$ ($C_{25}H_{21}NO_5$), 397, 266, 248, 230, 229, 219, 218, 217, 215, 205, 202, 167, 142, 141, 129, 128, 115, 105, 91, 77, 65.

(2*S*,3*S*)-2-(4-Bromophenylcarbonyloxymethyl)-2-[(*Z*)-1-(4-nitrophenylcarbonyloxymethyl)-2-phenyleth-1-enyl]-3-phenyloxirane (12): Ti(O*i*Pr)$_4$ (30 mg, 0.106 mmol) and molecular sieves (3 Å, 0.25 g) were added to a cooled solution (–30 °C) of L-(+)-diethyl tartrate (30 mg, 0.146 mmol) in dry CH_2Cl_2 (10 mL). The mixture was stirred at this temperature for 20 min, a solution of *tert*-butyl hydroperoxide in decane (5.5 M, 0.35 mL, 1.93 mmol) was added, the mixture was stirred for a further 40 min, and **11** (0.41 g, 0.988 mmol) in CH_2Cl_2 (10 mL) was added. The reaction flask was kept in a freezer at –27 °C for 3 d, $P(OMe)_3$ (0.18 mL) was then added dropwise by syringe at –30 °C over a period of 30 min, and the mixture was stirred for 40 min. Subsequently, Et_3N (0.24 g, 2.4 mmol) and *p*-bromobenzoyl chloride (0.44 g, 2 mmol) were added and the reaction mixture was stored in a freezer for another 2 d, then allowed to warm to room temp. and stirred at this temperature for 6 h. The molecular sieves were filtered off, the solution was washed with an aqueous solution of tartaric acid, sat. aq. $NaHCO_3$ solution and brine and dried (Na_2SO_4), and the solvents were evaporated. The product was purified by chromatography on silica gel (Merck 60, CH_2Cl_2/*n*-hexane 3:1) to give compound **12** (285 mg, 63% yield). Analytical samples were obtained by crystallization from CH_3CN or EtOH or a mixture of CCl_4/EtOAc. M.p. 159–160 °C. $[\alpha]_D^{25}$ = –55.9 (c = 5, $CHCl_3$). ^1H NMR ($CDCl_3$): δ = 4.69 (s, 1 H), 5.06 (d, J = 12.51, 1 H), 5.19–5.65 (m, 3 H), 7.16 (s, 1 H), 7.37–7.48 (m, 3 H), 7.48–7.59 (m, 3 H), 7.60–7.77 (m, 4 H), 7.00 (d, J = 8.55 Hz, 2 H), 8.22 (d, J = 8.55 Hz, 2 H), 8.51–8.68 (m, 4 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 63.2 (s, CH), 64.8 (s, C), 66.1 (s, CH_2), 68.6 (s, CH_2), 123.5 (s, CH), 126.5 (s, CH), 126.6 (s, C), 127.6 (s, CH), 128.0 (s, CH), 128.3 (s, CH), 128.5 (s, C), 128.9 (s, CH), 130.7 (s, CH), 131.2 (s, CH), 131.8 (s, CH), 133.5 (s, C), 134.5 (s, C), 135.2 (s, C), 150.5 (s, C–NO_2), 164.2 [s, C(O)O–], 165.2 [s, C(O)O–] ppm.

Computational Part: All structures (**7** and **7′**) and the reference molecules were optimized at the MP2/6-31G* level of theory. They are characterized as energy minimum structures at MP2/6-31G*. Both **7** and **7′** have C_2 symmetry. All calculations were performed with the Gaussian 03 program.[16] The MP2/6-31G* total electronic energies (au) are –844.43455 (**7**), –766.08322 (**7′**), –461.96321 (2,2-dimethyl-3-phenyloxirane), –422.78794 (2-methyl-3-phenyloxirane) and –79.49474 (ethane). The QCISD(T)/6-31G*//MP2/6-31G* single-point energies are –766.27423 (**7′**), –422.90518 (2-methyl-3-phenyloxirane) and –79.53459 (ethane).

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