A General, Multitechnique Approach to the Stereochemical Characterization of 1,2-Diarylethane-1,2-diols

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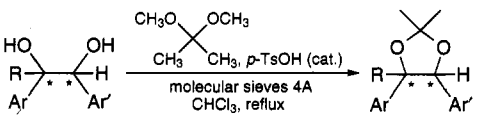
A general method which allows the nonempirical stereochemical characterization of 1,2-diarylethane-1,2-diols, obtained by the Sharpless catalytic asymmetric dihydroxylation of (*E*)-ArCR=CHAr′ olefins, has been devised. The basis of the method is the transformation into the corresponding ketals with acetone. These derivatives can be resolved on the Daicel Chiralcel OD column, allowing the determination of the ee, while the absolute configuration is assigned by the analysis of their circular dichroism (CD) spectra and by the helicity of the cholesteric phase induced in nematic liquid crystals.

Introduction

Due to their usefulness as intermediates for a variety of synthetic processes, optically active 1,2-diols are of great importance for synthetic organic chemists.[1,2] The determination of the enantiomeric purity and the absolute configuration must be carried out before the use of the diols. This work has often been approached separately, with chirooptical methods being employed for configurational purposes[3] and chromatographic methods being used for ee determinations.[4] These compounds were first derivatized as benzoates, to introduce chromophoric groups necessary in the analysis of the CD spectra, or as aromatic carbamates, in order to assist the chromatographic chiral recognition process. The most studied systems are chiral cyclic derivatives and acyclic polyols such as glycerols[3b] and related compounds. Less attention has been paid to 1,2-diols possessing aromatic groups such as 1,2-diarylethane-1,2-diols.[5] These compounds already contain aromatic groups, which can work as chromophores or take part in a chromatographic chiral recognition process; therefore, in principle, they do not need any derivatization for CD or chiral HPLC analysis.

Modern techniques[6] of stereochemical characterization rely upon the analysis of CD spectra and upon correlations based on NMR spectroscopy in chiral solvents and LC with chiral stationary phases (CSPs). The basis for the correct application of these techniques is provided by a safe knowledge of the most populated molecular conformation.

Chart 1



An accurate conformational analysis[7] of the present compounds has proved to be difficult, due to the following reasons: (1) the possibility of rotation around the C*–C* bond and (2) the existence of intermolecular hydrogen bonding, with the formation of molecular aggregates in equilibrium.

The solution to this problem is provided by a well-known procedure of synthetic organic chemistry: the protection of a carbonyl group with 1,2-ethanediol. We can use this reaction in the reverse way and protect the 1,2-diol function by a derivative of a simple carbonyl compound, acetone (Chart 1), obtaining a series of compounds which are rigid, nonassociated molecules. Therefore, the determination of the molecular conformation can be carried out by means of molecular mechanics calculations and nuclear magnetic resonance spectroscopy, in a more simple and reliable way, with respect to the starting diols. Such a transformation is easy to accomplish and occurs without racemization.[8] The choice of 2,2-dimethoxypropane (a synthetic equivalent of the symmetric, transparent ketone, acetone) prevents the formation of stereoisomers, and no other chromophoric groups are introduced. In addition, these rigid aromatic derivatives might result separable by LC upon those CSPs, such as the cellulose derivatives of the Chiralcel family, which are known[9] to separate conformationally locked aromatic compounds.

To conclude, the aim of this work was to check if an isopropylidene ketal derivative of 1,2-diarylethane-1,2-diols could be used to determine both the absolute

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(2) 1,2-Diols as chiral auxiliaries: Whitesell, J. K. *Chem. Rev.* **1989**, *89*, 1581. Sakai, K.; Suemune, H. *Tetrahedron Asymmetry* **1993**, *4*, 2109.

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(4) Pirkle, W. H.; Mahler, G. S.; Pochapsky, T. C.; Hyun, M. H. *J. Chromatogr.* **1987**, *388*, 307.

(5) (a) Imuta, M.; Ziffer, H. *J. Org. Chem.* **1978**, *43*, 3319. (b) Brienne, M. J.; Collet, A. *J. Chem. Res.* **1978**, 60.

(6) A general discussion of modern methods of configurational assignment can be found in the following: (a) Eliel, E. L.; Wilen, S. H. *Stereochemistry of carbon compounds*; J. Wiley & Sons: New York, 1994. (b) Stipanovic, R. D.; Mc Cormick, J. P.; Schlemper, E. O.; Hamper, B. C.; Shinmyonzu, T.; Pirkle, W. H. *J. Org. Chem.* **1986**, *51*, 2500.

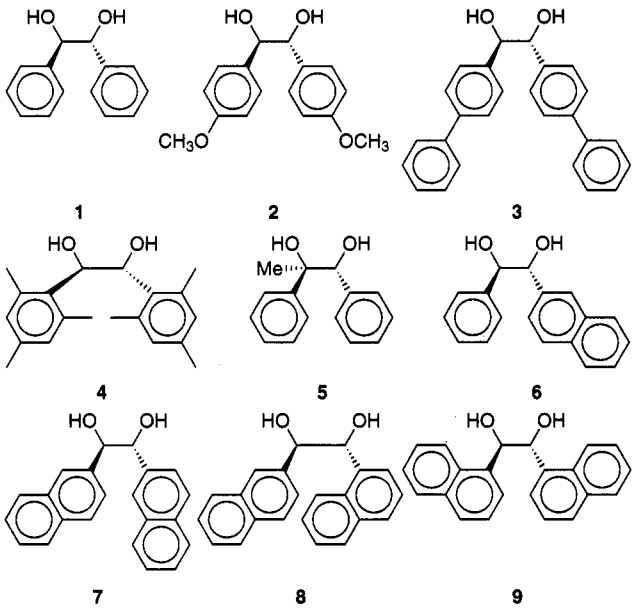
(7) Taking into account the comment of a reviewer, we point out here that the conformational analysis around the aryl–C* bond of the diols is relevant to assign spectroscopically the absolute configuration only in the case of compound **8b** (see later). Therefore this particular stereochemical point will be considered here only for **8b**.

(8) When a sample of **1** (ee = 95%) is transformed into the corresponding isopropylidene ketal in the standard conditions described in this paper, no racemization occurs (i.e., the ee of the ketal is 95%).

(9) Taylor, D. R.; Maher, K. *J. Chromatogr. Sci.* **1992**, *30*, 67.

0022-3263/95/1960-8289$09.00/0

Chart 2



configuration and the enantiomeric excess of a 1,2-diarylethane-1,2-diol.

Results and Discussion

Synthesis. The 1,2-diarylethane-1,2-diols (compounds **1**–**9**) treated in the present paper are reported in Chart 2.[10] The route to **1**–**9**, is based on the asymmetric *syn*-dihydroxylation procedure[11] of the corresponding (*E*)-olefins (**1a**–**9a**), which, when not commercially available as **1a**–**3a** and **5a**, have been prepared by standard Wittig reactions of the suitable carbonyl and $ArCH_2X$ counterparts. Pure (*E*)-olefins were obtained by refluxing the crude product in *o*-xylene in the presence of traces of iodine and subsequent crystallization. Compounds **1a**–**9a** were then submitted to catalytic asymmetric *syn*-dihydroxylation reaction employing standard conditions (catalytic OsO_4, dihydroquinidine 9-*O*-(4-chlorobenzoate), *N*-methylmorpholine *N*-oxide as secondary oxidant, acetone/water, 3/1, 0 °C). In these conditions, optically active diols (**1**, **2**, **6**–**9**) were obtained in chemical yields ranging from 70 to 95% while **5a** afforded a sample of **5**, showing a low rotatory power, and the olefins **3a** and **4a** did not provide the diols **3** and **4** in satisfactory yields. Samples of **5** having higher rotatory power were obtained employing $K_3Fe(CN)_6$ as secondary oxidant in *t*-BuOH/H_2O. Satisfactory yields of optically active diols **3** and **4** were achieved only when the *syn*-dihydroxylation was carried out in stoichiometric conditions, employing dihydroquinidine 9-*O*-acetate as the chiral auxiliary in toluene. However in all cases these reactions provided dextrorotatory samples of diols **1**–**9**. Application of the Sharpless empirical rule[11a] leads to the prediction of (*R*,*R*) absolute configuration for the two stereogenic centers. Finally, the optically active diols **1**–**9** were converted into the corresponding isopropylidene ketals, by treating the diols with 2,2-dimethoxypropane in $CHCl_3$ in the presence of molecular sieves and catalytic amounts of *p*-toluensulfonic acid.

Analysis of CD Data. All of the compounds prepared present aromatic chromophores which are reasonably well characterized from a spectroscopic point of view.[12] Taking into account that the ketals **1b**–**9b** are compounds whose conformations can be reliably defined, the interpretation of their CD spectra in terms of Harada–Nakanishi exciton chirality rules could afford the absolute configuration quite easily.[13] Table 1 shows that all the ketals studied (with the seeming exception of compounds **8b** and **9b**, whose behavior will be dealt with later) exhibit a positive couplet in correlation with the electrically allowed $\pi \rightarrow \pi^*$ transition, polarized along the C*–Ar bond. Such behavior can be easily explained when taking into account the fact that the most stable conformation of such compounds (obtained by MMX[14] calculations and NMR spectroscopy[10]) can be represented by the general structure of Figure 1a when the (*R*,*R*) configuration of the stereogenic centers has been assumed. Here the electric transition moments of the aforementioned transitions show a positive chirality, with a positive couplet being expected. This can be seen in the cases of **1b**–**7b**. Compounds **8b** and **9b** constitute the only apparent exception. Owing to the different geometrical situation,[10] in the (*R*,*R*) configuration, the ^1B transition dipole of the naphthalene chromophore shows a negative chirality system, which leads to a negative couplet (see Figure 1b,c). In these cases, the (*R*,*R*) configuration of the two stereogenic centers is confirmed.

Although **7b**–**9b** have the same absolute configuration, the spectra do not show any common features. This is a consequence of the different relative dispositions of the transition dipoles in the two compounds. This fact shows again that great care has to be taken in configurational determinations by means of circular dichroism spectra, if a reliable assignment of molecular structure has not been previously carried out. In cases like the present one, a simple comparison between CD data can not be used to accomplish configurational correlations.

Analysis of Induced Cholesterics. When a small amount of an optically active compound is dissolved in a nematic liquid crystal (e.g. MBBA, (*p*-methoxybenzylidene)butylamine), a cholesteric mesophase is formed. It has been shown that from the knowledge of the screw sense it is possible to assign the molecular chirality of the solute.[15] The helicity of the cholesteric phase can be determined by measuring the CD induced in the lowest energy $\pi \rightarrow \pi^*$ transition of the MBBA solvent, with a positive CD being related to a right-handed cholesteric.[16] The helicities of the cholesterics induced by our samples are reported in Table 1. First of all, it can be noticed that there is a good configurational correlation. All the samples *induce the same helicity*, independent of the substitution pattern, indicating that all have the same configuration. Taking into account that **1b** has a known

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(13) Harada, N.; Nakanishi, K. *Circular dichroism spectroscopy - exciton coupling in organic chemistry*; University Science Books: Mill Valley, 1983.

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(16) Gottarelli, G.; Spada, G. P. Application of CD to the study of some cholesteric mesophases. In *Circular Dichroism. Principles and applications*; Nakanishi, K., Berova, N., Woody, R. W., Eds.; VCH Publishers Inc.: New York, 1994; pp 105–119.

Table 1

compd	Ar_1	Ar_2	R	absolute configuration[a]	CD couplet[b]	cholesteric helicity
1b	Ph	Ph	H	(R,R)	(+)	LH
2b	*p*-CH_3OPh	*p*-CH_3OPh	H	(R,R)	(+)	LH
3b	*p*-PhC_6H_4	*p*-PhC_6H_4	H	(R,R)	(+)	LH
4b	2,4,6-$Me_3C_6H_2$	2,4,6-$Me_3C_6H_2$	H	(R,R)	(+)	LH
5b	Ph	Ph	Me	(*R*,*R*)	(+)	LH
6b	Ph	2-naphth	H	(*R*,*R*)	(+)	LH
7b	2-naphth	2-naphth	H	(*R*,*R*)	(+)	LH
8b	2-naphth	1-naphth	H	(*R*,*R*)	(−)	LH
9b	1-naphth	1-naphth	H	(*R*,*R*)	(−)	LH

[a] Absolute configuration assigned on the basis of the Sharpless rule: quinidine derivatives lead to the formation of (*R*,*R*) diols starting from (*E*)-olefins having the general formula $Ar_1R{=}CHAr_2$, where Ar_1 and Ar_2 are aromatic groups and R is an alkyl substituent. [b] Sign of the CD couplet relative to the long-axis polarized $\pi-\pi^*$ transition of the aromatic chromophores Ar_1 and Ar_2.

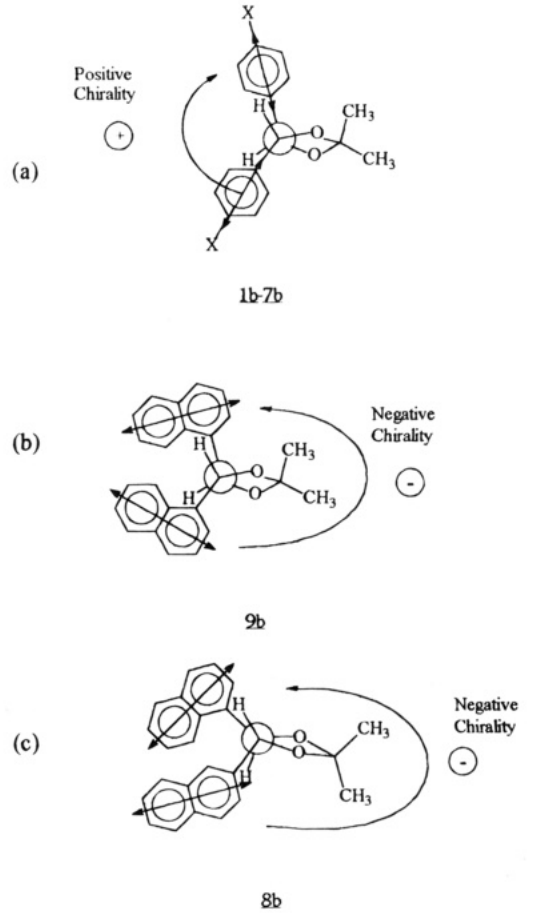

Figure 1. The most stable conformation for ketals **1b**−**7b** (a), **9b** (b), and **8b** (c). The transition dipoles of the long-axis polarized $\pi \rightarrow \pi^*$ excitation of the aromatic chromophores, as well as the exciton chirality defined by such transition moments, are indicated.

(*R*,*R*) configuration (1,2-diphenylethane-1,2-diol is a known compound[17]), it is possible from this correlation to assign, empirically, the (*R*,*R*) absolute configuration to all the present compounds. The same data can be interpreted at a nonempirical level, formulating a mechanism of interaction between the chiral solute and the nematic solvent. The absolute stereochemistry of the compounds can be determined by making use of the model of induction, proposed by G. Gottarelli et al.,[18] in the case of 1,2-diaryl epoxides, a class of compounds which is clearly structurally related to the present ones. The

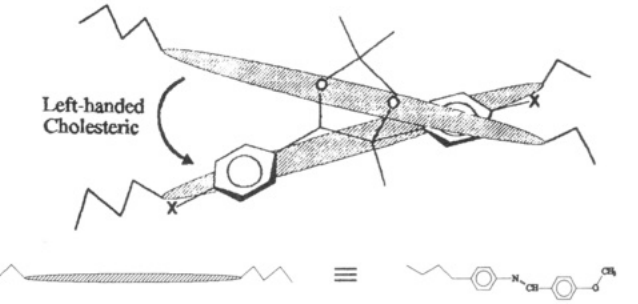

Figure 2. Model for induction of a left-handed cholesteric mesophase in MBBA, by an (*R*,*R*)-isopropylidene ketal derived from diols **1**−**9**.

induction of a cholesteric mesophase in MBBA by the isopropylidene ketals **1b**−**9b** is schematically represented in Figure 2. It can therefore be stated that, owing to the (*R*,*R*) absolute configuration assumed and the particular conformation of the sample, the dopant molecule is aligned with its long axis parallel to the rodlike molecules of the solvent, with the five-membered ring disturbing the parallel alignment of the other solvent molecules and imposing the correct sense of twist.

LC chromatography upon CSPs. As discussed in the introductory section of this work, the aim of the investigation was 2-fold: (1) to find a suitable CSP capable of resolving the present isopropylidene ketals, in order to measure their ee and (2) to find a correlation between the absolute configuration of the enantiomers of the substrates and their retention on a CSP.

With reference to point one, we found that Chiralcel OD gave an efficient separation of all the compounds available. In Table 2 are stated the α values obtained, while in Figure 3 is reported a typical resolution of both the racemic (below) and the optically active (above) substrate. Table 2 shows that all the substrates have been produced by the *syn*-dihydroxylation reaction, in high ee (≥81%). The elution upon Chiralcel OD constitutes a very efficient method for the ee determination of these compounds. The availability of optically active derivatives, having now known absolute configurations (CD, liquid crystals, Sharpless rule), allows the elution order to be established. As it can be seen in Table 2 the (*R*,*R*) antipode is eluted first for 1,2-diphenylethanediol isopropylidene ketal, **1b**, but this is not a general rule; for **2b**, **3b**, and **4b**, the reverse is true. Looking again at Table 2 it can be seen that, for six derivatives, the (*R*,*R*) antipode is eluted first, and for the remaining three the elution order is reversed. This fact is a clear indication that the LC technique for assigning absolute configurations must be used with great care, as different chiral

(17) Berti, G.; Bottari, F. *J. Org. Chem.* **1960**, *25*, 1286.
(18) Gottarelli, G.; Mariani, P.; Spada, G. P.; Samorì, B.; Forni, A.; Solladiè, G.; Hibert, M. *Tetrahedron* **1983**, *39*, 1337.

Table 2

compd	Ar_1	Ar_2	R	absolute configuration	α^a	k_1	ee, %	elution order
1b	Ph	Ph	H	(*R*,*R*)	1.54[b]	0.43	95	1st
2b	*p*-CH_3OPh	*p*-CH_3OPh	H	(*R*,*R*)	1.34[c]	1.77	92	2nd
3b	*p*-PhC_6H_4	*p*-PhC_6H_4	H	(*R*,*R*)	1.49[d]	0.80	99	2nd
4b	2,4,6-$Me_3C_6H_2$	2,4,6-$Me_3C_6H_2$	H	(*R*,*R*)	1.23[b]	0.55	83	2nd
5b	Ph	Ph	Me	(*R*,*R*)	1.21[c]	0.82	81.5	1st
6b	Ph	2-naphth	H	(*R*,*R*)	1.13[b]	1.42	85.5	1st
7b	2-naphth	2-naphth	H	(*R*,*R*)	1.61[d]	0.64	98	1st
8b	2-naphth	1-naphth	H	(*R*,*R*)	1.75[f]	0.81	90	1st
9b	1-naphth	1-naphth	H	(*R*,*R*)	2.48[f]	0.60	98	1st

[a] $\alpha = k_2/k_1$ and $k_1 = (t_1 - t_0)/t_0$ where t_1 and t_0 denote the retention time and the void time, respectively. The elution rate was 0.5 mL/min in all cases, with the elution solvent being hexane/2-propanol in the following proportions: (*b*) 99/1, (*c*) 98/2, (*d*) 90/10, (*e*) 99.5/0.5, (*f*) 95/5.

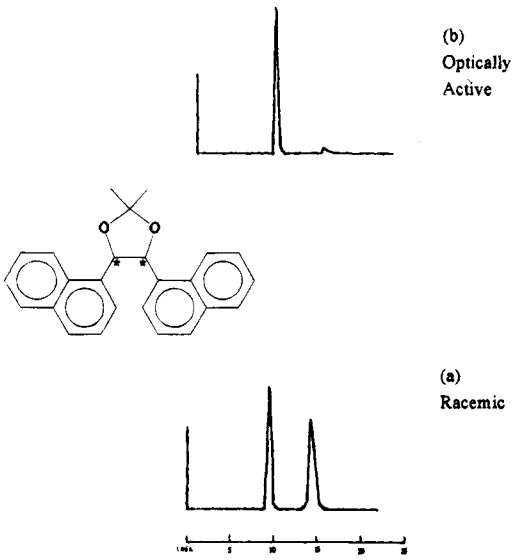

Figure 3. Resolution of racemic (a) and optically active (b) ketal **9b**, upon Chiralcel OD CSP, using hexane/2-propanol (95/5) at 0.5 mL/min $\lambda = 254$ nm.

discrimination mechanisms can work even in the case of similar compounds.

Conclusions

The most important result of this work is that by simply blocking the rotation around the C_1-C_2 bond in 1,2-diarylethane-1,2-diols, with the introduction of a dioxolane ring with acetone, it is possible to achieve a nonempirical and safe stereochemical characterization of these compounds. This derivatization allows a reliable conformational determination, which, in turn, constitutes the basis for the nonempirical analysis of the CD spectra of these derivatives and also of the cholesteric mesophases induction in MBBA. In addition, this simple transformation makes available a group of compounds which are separable in enantiomers by means of the CSP Chiralcel OD, allowing for an accurate determination of the ee. In conclusion, with only one derivative it is possible to carry out the assignment of the absolute configuration and of the ee, while up to now, two different derivatives were used, as discussed in the Introduction, for the stereochemical characterization of 1,2-diols. Interestingly, in all cases, the absolute configuration assigned by the present nonempiral method is in agreement with the empirical rule proposed by Sharpless.

Experimental Section

General. (*E*)-α-Methylstilbene, 2-naphthaldehyde, (*E*)-4,4′-dimethoxystilbene, and (*E*)-4,4′-diphenylstilbene were commercially available (Aldrich). 1-Phenyl-2-naphthylethene was prepared as previously described.[19] Samples of racemic diols were prepared from the corresponding olefins in acetone/H_2O with catalytic amounts of OsO_4 and quinuclidine in the same conditions reported for asymmetric preparations. Ethyl alcohol was distilled over $Mg(OEt)_2$ under N_2 atmosphere. Toluene was distilled over Na under N_2 atmosphere. Precoated TLC (plastic) sheets from Merck (silica gel 60 F_{254}) were used, and for column chromatography, Merck silica gel 60/230−400 mesh was used. Melting points were taken on a Kofler apparatus and are uncorrected. NMR spectra were recorded in $CDCl_3$ on a 200 MHz spectrometer with TMS as reference. HPLC analyses were carried out with a JASCO Twinkle instrument, using a Daicel column, Chiralcel OD. The chromatographic analyses were monitored at 254, 230, and 220 nm. Specific rotations, $[\alpha]_D$, are reported in deg/dm at the specified temperature, and the concentration (*c*) is given in g/100 mL in the specified solvent. CD spectra were recorded on a JASCO J-600 spectrometer and absorbance spectra on a JASCO UVIDEC 710 spectrophotometer.

(*R*,*R*)-(+)-1,2-Bis(4-methoxyphenyl)ethane-1,2-diol (2). To a solution of 430 mg (3.18 mmol) of *N*-methylmorpholine *N*-oxide in 5 mL of distilled water, in a 100 mL round-bottomed flask, were added 518 mg (2.16 mmol) of (*E*)-4,4′-dimethoxystilbene, **2a**, 15 mL of acetone, and 49 mg (0.11 mmol) of dihydroquinine 9-*O*-(4-chlorobenzoate). The reaction mixture was cooled to 0 °C, and after the addition of 1.1 mL of OsO_4 (7.1×10^{-3} M in CH_3CN), it was stirred for 17 h at 0 °C. Next, 1.6 g of $Na_2S_2O_5$ was added, and the mixture was diluted with 20 mL of CH_2Cl_2 and stirred for 1 h at rt. Anhydrous Na_2SO_4 was added, and the mixture was stirred for an additional 5 h. The suspension was filtered, and the filtrate was concentrated to a solid. The solid was dissolved in 20 mL of AcOEt, transferred to a separatory funnel, and washed subsequentially with H_2O (2 × 10 mL), 1 M H_2SO_4 (3 × 10 mL), and brine (2 × 10 mL). The organic layer was dried (Na_2SO_4) and the solvent removed. Diol **2** was obtained as chemically pure by column chromatography (silica gel: $CHCl_3$ to eliminate olefin impurities, Et_2O to recover the diol) (yield 70%): mp 119−120 °C [lit.[20] mp 119−120 °C]; $[\alpha]^{22}_D = 130.2$ ($c = 0.725$, EtOH); ^{1}H-NMR (200 MHz, $CDCl_3$, δ) 7.03 (d, 4H), 6.75 (d, 4H), 4.62 (s, 2H), 3.75 (s, 6H), 2.85 (s, 2H). Anal. Calcd for $C_{16}H_{18}O_4$: C, 70.06; H, 6.61. Found: C, 71.32; H, 6.63.

(*R*,*R*)-(+)-1,2-Di(4-biphenylyl)ethane-1,2-diol (3). To 25 mL of dry toluene in a 100 mL round-bottomed flask was added 164 mg (0.49 mmol) of olefin **3a** together with 181 mg (0.49 mmol) of dihydroquinidine 9-*O*-acetate and 130 mg (0.51 mmol) of OsO_4, and the reaction mixture was stirred at rt. After 19 h the solvent was removed, and 80 mL of a 1:1 mixture of THF and $Na_2S_2O_5$ saturated solution was added. After 3 h of stirring at rt, the mixture was filtered and the filtrate transferred to a separatory funnel. After separation, the aqueous layer was extracted again with THF, and the organic extracts were dried (Na_2SO_4) overnight. The solvent was removed under reduced pressure and the diol purified by

(19) Geerts, J. P.; Martin, R. H. *Bull. Soc. Chim. Belg.* **1960**, *69*, 563.

(20) Yamamoto, K., Ando, H., Shuetake, T., Chikamatsu, H., *J. Chem. Soc., Chem. Comm.* **1989**, 754.

column chromatography (silica gel: $CHCl_3$ to eliminate olefin impurities, Et_2O to recover the diol) (yield 95%): mp 237–240 °C; $[\alpha]^{22}_D$ = 187 (*c* = 0.99, THF); ^{1}H-NMR (200 MHz, DMSO-d_6, δ) 7.70–7.25 (m, 18H), 5.48 (s, 2H), 4.74 (s, 2H). Anal. Calcd for $C_{26}H_{22}O_2$: C, 85.22; H, 6.05. Found: C, 87.05; H, 6.17.

(*R*,*R*)-(+)-1,2-Bis(2,4,6-trimethylphenyl)ethane-1,2-diol (4). Diol **4** was prepared from olefin **4a** by the same procedure as described for diol **3** (yield, after chromatography, 56%): mp 129–132 °C; $[\alpha]^{24}_D$ = 141 (*c* = 1, $CHCl_3$); ^{1}H-NMR (200 MHz, $CDCl_3$, δ) 6.68 (s, 4H), 5.4 (s, 2H), 2.92 (s, 2H), 2.18 (s, 18H). Anal. Calcd for $C_{20}H_{26}O_2$: C, 80.50; H, 8.78. Found: C, 81.23; H, 8.62.

(*R*,*R*)-(+)-1-Methyl-1,2-diphenylethane-1,2-diol (5). To a mixture of 7 mL of H_2O and 7 mL of *t*-BuOH, in a 50 mL round-bottomed flask were added 149 mg (0.4 mmol) of dihydroquinidine 9-*O*-acetate, 797 mg (2.42 mmol) of $K_3Fe(CN)_6$, 335 mg (2.42 mmol) of K_2CO_3, and 1 mL of OsO_4 (0.0118 M in CH_3CN). After the mixture was stirred for 10 min at rt, 155.5 mg (0.8 mmol) of (*E*)-α-methylstilbene was added, and the mixture was stirred for 24 h at rt. After addition of 0.8 g (6.3 mmol) of Na_2SO_3, the resulting mixture was stirred for a further hour and then the solvents were removed under reduced pressure. Water (5 mL) was added, and the mixture was extracted with ether (3 × 20 mL). The organic extracts were dried (Na_2SO_4), the solvent was removed, and the resulting oil was purified by column chromatography (silica gel: CH_2Cl_2/Et_2O, 3/1) (yield 47%): mp 89–92 °C; $[\alpha]^{26}_D$ = 34 (*c* = 1.01, THF); ^{1}H-NMR (200 MHz, $CDCl_3$, δ) 7.40–7.05 (m, 10H); 4.8 (d, 1H), 2.60 (s, 1H), 2.5 (d, 1H), 1.35 (s, 3H). Anal. Calcd for $C_{15}H_{16}O_2$: C, 78.92; H, 7.06. Found: C, 79.51; H, 7.12.

(*R*,*R*)-(+)-1-Phenyl-2-(2-naphthyl)ethane-1,2-diol (6). Diol **6** was prepared from olefin **6a** by the same procedure as described for diol **2** (yield, after chromatography, 70%): mp 130–134 °C; $[\alpha]^{18.5}$ = 128.5 (*c* = 0.975, THF); ^{1}H-NMR (200 MHz, $CDCl_3$, δ) 7.85–7.65 (m, 4H), 7.5–7.4 (m, 2H), 7.3–7.1 (m, 6H), 4.95–4.8 (dd, 2H), 2.7 (s, 2H) Anal. Calcd for $C_{18}H_{16}O_2$: C, 81.79; H, 6.1. Found: C, 82.75; H, 5.97.

(*R*,*R*)-(+)-2,2′-Dimethyl-4,5-diphenyl-1,3-dioxolane (1b). To 100 mL of $CHCl_3$, in a 250 mL round-bottomed flask fitted with a Kumagawa extractor, was added 62 mg (0.29 mmol) of diol **1**, 0.1 mL of 2,2′-dimethoxypropane, and traces of 4-toluenesulfonic acid. In the syphon tank, 4 g of molecular sieves (4A) were introduced inside a filter pad. After 3 h of reflux, the heat was removed and the reaction mixture was transferred to a separatory funnel and washed subsequentially with 10% aqueous $NaHCO_3$ (2 × 30mL) and H_2O (2 × 30 mL). The organic layer was dried (Na_2SO_4) overnight and then concentrated to a solid. Ketal **1b** was obtained chemically pure after TLC (silica gel: $CHCl_3$) (yield 60%): mp 44–46 °C; $[\alpha]^{20}_D$ = 71 (*c* = 1.01, $CHCl_3$); ee = 98%; ^{1}H-NMR (200 MHz, $CDCl_3$, δ) 7.4–7.2 (m, 10H), 4.78 (s, 2H), 1.7 (s, 6H). Anal. Calcd for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 79.15; H, 6.98.

(*R*,*R*)-(+)-2,2′-Dimethyl-4,5-bis(4-methoxyphenyl)-1,3-dioxolane (2b). Ketal **2b** was prepared following the same procedure as described for **1b** (yield, after chromatography, 64%): $[\alpha]^{20}_D$ = 117 (*c* = 0.985, EtOH); ee = 92%; ^{1}H-NMR (200 MHz, $CDCl_3$, δ) 7.15 (d, 4H), 6.84 (d, 4H), 4.67 (s, 2H), 3.78 (s, 6H), 1.65 (s, 6H). Anal. Calcd for $C_{19}H_{22}O_4$: C, 72.59; H, 7.05. Found: C, 71.87; H, 6.58.

(*R*,*R*)-(+)-2,2′-Dimethyl-4,5-di(4-biphenylyl)-1,3-dioxolane (3b). Ketal **3b** was prepared following the same procedure as described for **1b** (yield, after chromatography, 53%): mp 161–163 °C; $[\alpha]^{23}_D$ = 299 (*c* = 1.01, $CHCl_3$); ee = 99%; ^{1}H-NMR (200 MHz, $CDCl_3$, δ) 7.6 (m, 8H), 7.3–7.5 (m, 10H), 4.85 (s, 2H), 1.7 (s, 6H). Anal. Calcd for $C_{29}H_{26}O_2$: C, 85.68; H, 6.45. Found: C, 83.29; H, 6.42.

(*R*,*R*)-(+)-2,2′-Dimethyl-4,5-bis(2,4,6-trimethylphenyl)-1,3-dioxolane (4b). Ketal **4b** was prepared following the same procedure as described for **1b** (yield, after chromatography, 86%): mp 182–184 °C; $[\alpha]^{24}_D$ = 156 (*c* = 1, $CHCl_3$); ee = 83%; ^{1}H-NMR (200 MHz, $CDCl_3$, δ) 6.68 (s, 4H), 5.55 (s, 2H), 2.18 (s, 18H), 1.69 (s, 6H). Anal. Calcd for $C_{23}H_{30}O_2$: C, 81.11; H, 9.18. Found: C, 80.27; H, 9.16.

(*R*,*R*)-(−)-2,2′,4-Trimethyl-4,5-diphenyl-1,3-dioxolane (5b). Ketal **5b** was prepared following the same procedure as described for **1b** (yield, after chromatography, 95%): mp 101–104 °C; $[\alpha]^{26}_D$ = −8.5 (*c* = 0.807, $CHCl_3$); ee = 81.5%; ^{1}H-NMR (200 MHz, $CDCl_3$, δ) 7.4–7.2 (m, 10H), 4.96 (s, 1H), 1.72 (s, 3H), 1.62 (s, 3H), 1.25 (s, 3H). Anal. Calcd for $C_{18}H_{20}O_2$: C, 80.56; H, 7.51. Found: C, 82.41; H, 7.68.

(*R*,*R*)-(+)-2,2′-Dimethyl-4-phenyl-5-(2-naphthyl)-1,3-dioxolane (6b). Ketal **6b** was prepared following the same procedure as described for **1b** (yield, after chromatography, 69%): mp 104–107 °C; $[\alpha]^{20}_D$ = 61 (*c* = 1.165, $CHCl_3$); ee = 85.5%; ^{1}H-NMR (200 MHz, $CDCl_3$, δ) 7.85–7.7 (m, 3H), 7.68 (s, 1H), 7.5–7.45 (m, 2H), 7.35–7.2 (m, 6H), 4.95–4.8 (dd, 2H), 1.73 (d, 6H) Anal. Calcd for $C_{21}H_{20}O_2$: C, 82.86; H, 6.62. Found: C, 81.75; H, 6.57.

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