Synthesis and Stereochemical Characterization of Some Optically Active 1,2-Dinaphthylethane-1,2-diols

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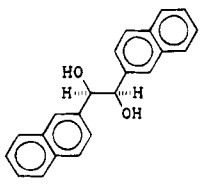
Three new diols, 1,2-di(2-naphthyl)ethane-1,2-diol, 1-(1-naphthyl)-2-(2-naphthyl)ethane-1,2-diol, and 1,2-di(1-naphthyl)ethane-1,2-diol, have been prepared in optically active form by catalytic asymmetric syn-dihydroxylation of the corresponding (*E*)-olefins. The complete stereochemical characterization was easily accomplished by transforming them into the corresponding isopropylidene ketals. These derivatives can be separated by HPLC on a Chiralcel OD column allowing the determination of the ee, and at same time, their CD spectra have been analyzed, allowing a safe assignment of absolute configuration in conjunction with molecular mechanics calculations and an exciton-coupling treatment.

Introduction

C_2-symmetric chiral auxiliaries containing the 1,2-diol fragment have enjoyed a lot of attention in recent years.[1] A reason for that can be certainly found in the availability of a large number of chiral compounds derived from (*R,R*)-tartaric acid, which is the cheapest commercially available chiral compound. By means of such chiral auxiliares, very high levels of enantioselection have been obtained (e.g., Sharpless epoxidation of allylic alcohols[2]). In addition to this type of auxiliaries, where the 1,2-diol fragment is accompanied by other functional groups (i.e., esters or amides) even simple aliphatic diols such as 2,3-butanediol[3] have been used in asymmetric synthesis. Recently, optically active 1,2-diphenylethane-1,2-diol has been employed quite successfully as chiral controller in different organic reactions[4] and as an intermediate in the preparation of chiral crown ethers.[5]

We have prepared compounds **1–3**, analogs of 1,2-diphenylethane-1,2-diol, in optically active form, being attracted by the different patterns of substitution and by the different relative disposition of the two π-systems.



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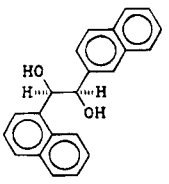

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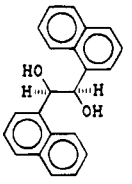

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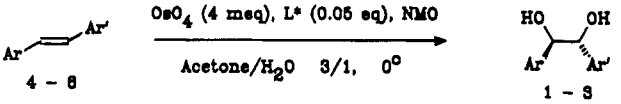
To the best of our knowledge, only compound **1** has been previously described in the literature[6,7] but neither the absolute configuration nor the optical purity of the samples were reported. This paper describes a short route to optically pure **1-3** and the complete stereochemical characterization of **1–3** by circular dichroism spectroscopy.

Results and Discussion

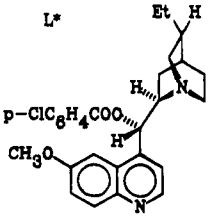
Synthesis. The route to **1–3** is based on the syn-dihydroxylation procedure as described by Sharpless[8] starting from the corresponding olefins. 1,2-Dinaphthyl-



4 Ar=Ar'=2-Naphthyl

5 Ar=2-Naphthyl, Ar'=1-Naphthyl

6 Ar=Ar'=1-Naphthyl



ethylenes **4–6** were prepared following known procedures[9] involving the Wittig reaction. The necessary phosphonium salts were obtained from the corresponding halides ($C_{10}H_7CH_2X$) and triphenylphosphine in refluxing *o*-xylene and were purified by crystallization from water. The ylides, obtained from the phosphonium salts and EtONa in EtOH, reacted rapidly with α- and β-naphthaldehyde to give the desidered olefins as cis/trans mixtures. Pure (*E*)-olefins were obtained by refluxing the crude product in *o*-xylene in the presence of traces of iodine and subsequent crystallization (**4** and **5** from benzene, **6** from EtOH). The stereochemical purity of the

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(6) Chênevert, R.; Ampleman, G. *Synthesis* **1987**, 739.

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Table 1.

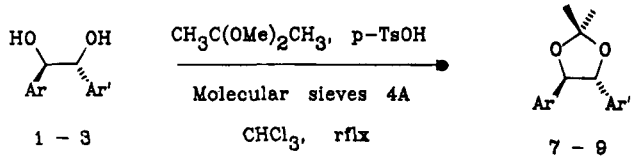
olefin	diol	time	chemical yield (%)	$[\alpha]_D$ (c = 1, THF)
4	1	7 days	90	212
5	2	27 h	85	130
6	3	23 h	62	48

crystallized products was established by HPLC (no cis-olefin was detected), and the melting points were in agreement with those reported in the literature.[9] (*E*)-1,2-Dinaphthylethylenes underwent asymmetric syn-dihydroxylation in acetone/H_2O employing catalytic amounts of OsO_4, dihydroquinidine 9-*O*-(4-chlorobenzoate), and NMO, in excess, as the reoxidant. The results obtained are summarized in Table 1.

Diol **1**, when dissolved in hot $CHCl_3$, crystallizes providing the optically pure antipode. On the contrary, diol **3** is more soluble in $CHCl_3$ in its pure enantiomeric form than as a racemic mixture. As we have employed a derivative of dihydroquinidine to accomplish the enantioselective syn-dihydroxylation of olefins **4**–**6**, we could attribute, at least preliminarily, the absolute configuration (*R,R*), applying the Sharpless empirical rule,[10] to the dextrorotatory diols obtained.

Stereochemical Characterization. The complete stereochemical characterization of the three samples of diols requires the determination of the absolute configuration and of the enantiomeric excess of the compounds.

As far as the configurational aspect is concerned, CD spectroscopy offers a nice way to solve the problem. In fact, diols **1**–**3** possess chromophoric groups, i.e., the naphthalene rings, which show electronically allowed transitions ($\pi - \pi^*$), completely characterized from a spectroscopic point of view.[11] Such electronic transitions can give origin to exciton coupling[12] and, therefore, to couplet effects in the CD spectra.[12,13] If the molecular conformation is known, from the sign of such couplet effects, it is possible to establish the absolute configuration in a nonempirical and reliable way.[12,13]



To this end, the diols were converted into the corresponding isopropylidene ketals. Such derivatives are easy to obtain, no other chromophore is introduced into the molecule, and having fewer degrees of freedom with respect to the starting diols, the determination of the most stable conformation should be less problematic.

The UV spectrum of ketal **7** shows an absorption due to the allowed ^1L_a transition at 275 nm (ϵ = 10 800) (Figure 1a) which is short axis polarized and a stronger absorption (^1B, long axis polarization) that exhibits two maxima at 217 nm (ϵ = 130 200) and at 230 nm (ϵ = 121 000) (Figure 1b). In the CD spectrum (for compounds **7**-**9** the $\Delta\epsilon$ values are corrected to 100% enantiomeric purity) a positive strong couplet effect (λ = 230 nm, $\Delta\epsilon$ = 238; λ = 216 nm, $\Delta\epsilon$ = −183) is observable, due to the exciton coupling of the ^1B_b transitions of each naphthalene chromophore (Figure 1b). It is interesting to note that this is one of the few cases[14] in which the coupling effect can be observed even in the UV spectrum. Assuming the (*R,R*) configuration,[15] the lowest energy conformation of ketal **7** was determinated by means of molecular mechanics calculations[16] and the minimized structure is depicted in Figure 2. The ^1B_b transition dipoles describe a positive chirality, and therefore, for such a structure one expects a positive couplet in the CD spectrum, as experimentally observed. The assignment of (*R,R*) configuration to ketal **7** has now been confirmed. This result is independent of a detailed knowledge of the molecular conformation: in fact, even if the naphthalene fragments rotate freely around the C*−C_{Ar} bond, the ^1B transition dipoles always define a positive chirality and thus a positive couplet.

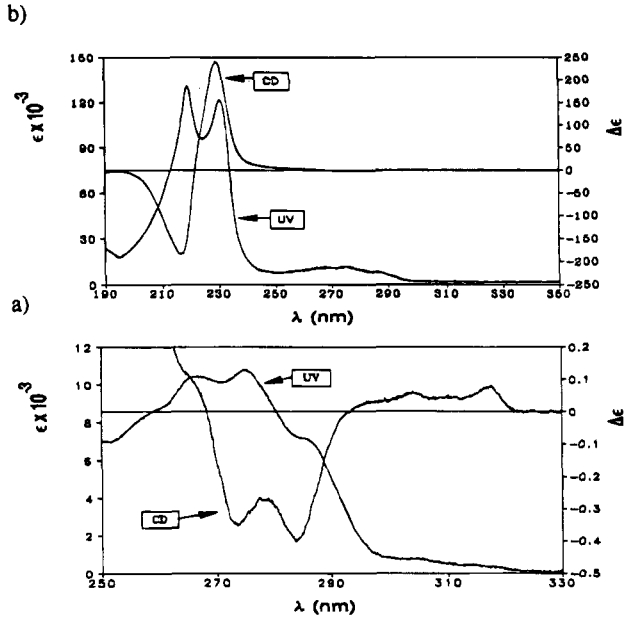


Figure 1. UV and CD spectra of **7** in the 330–250 nm spectral range (a) and in the 350–190 nm spectral range (b).

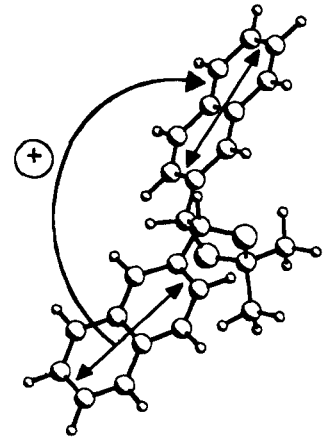


Figure 2. Most stable conformation (MMX routine) of **7**.

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(15) As suggested by Sharpless when the enantioselective syn-dihydroxylation of trans disubstituted olefins is accomplished in the presence of a chiral derivative of dihydroquinidine.
(16) MMX, Serena Software, P.O. Box 3076, Bloomington, IN 47402.

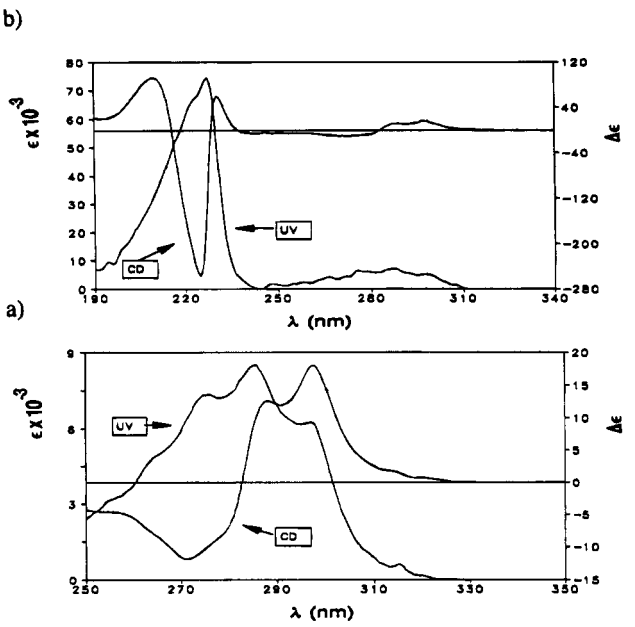


Figure 3. UV and CD spectra of **9** in the 350–250 nm spectral range (a) and in the 340–190 nm spectral range (b).

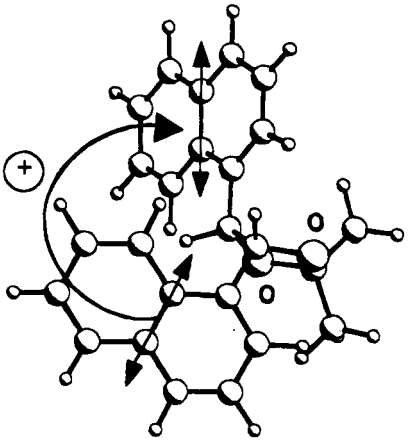


Figure 4. Most stable conformation (MMX routine) of **9**.

The UV spectrum of ketal **9** shows the ^1L_a absorption at 286 nm (ϵ = 8500) (Figure 3a) followed by the strong ^1B absorption at 227 nm (ϵ = 74 300) (Figure 3b). The CD spectrum is more complex and shows a positive couplet around 280 nm (λ = 298 nm, $\Delta\epsilon$ = 18; λ = 271, $\Delta\epsilon$ = −12) (Figure 3a). In the 250–200 nm zone, one can observe three optically active absorptions (λ = 230, $\Delta\epsilon$ = 60; λ = 225, $\Delta\epsilon$ = −257; λ = 209, $\Delta\epsilon$ = 92) (Figure 3b). The assignment of the absolute configuration was based on the couplet at 280 nm. The most stable conformation of ketal **9**, assuming the (*R,R*) configuration, as obtained by MMX calculations, is shown in Figure 4. The transition dipoles along the short axis describe a positive chirality, and therefore, for this structure a positive couplet is expected in the CD spectrum as experimentally observed. The assignment of (*R,R*) configuration to ketal **9** is therefore confirmed.

The UV spectrum of ketal **8** shows an absorption around 283 nm (ϵ = 10 500) (Figure 5a) followed by a stronger one around 223 nm (ϵ = 106 200) (Figure 5b). In the CD spectrum one can observe a weak Cotton effect at 283 nm ($\Delta\epsilon$ = 8) (Figure 5a) followed by a strong negative couplet (λ = 228, $\Delta\epsilon$ = −164; λ = 218, $\Delta\epsilon$ = 130) (Figure 5b).

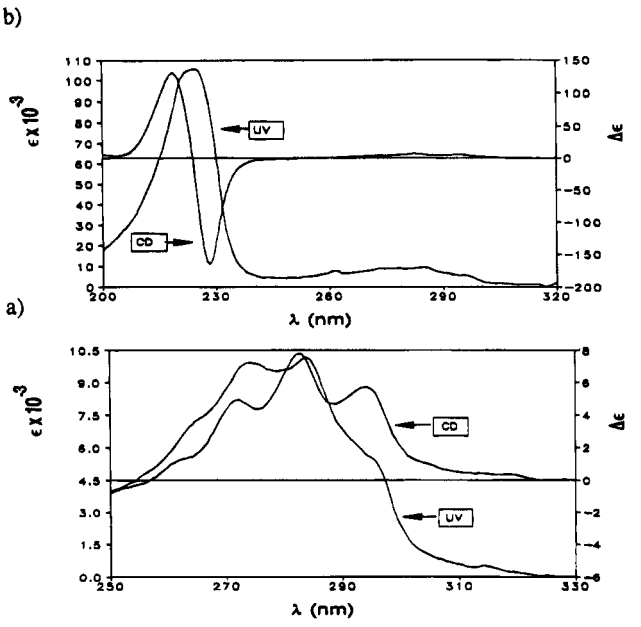


Figure 5. UV and CD spectra of **8** in the 330–250 nm spectral range (a) and in the 320–200 nm spectral range (b).

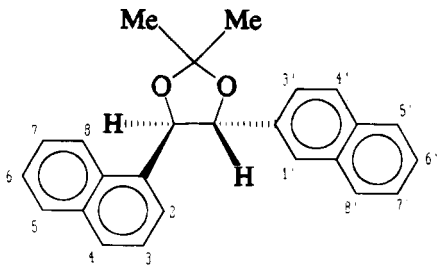
Table 2. ^{1}H-NMR Chemical Shifts (300 MHz, $CDCl_3$, 25 °C, δ in ppm Referred to TMS as External Standard) and Coupling Constants (J_{i-j}, Hz) of the Ketal 8 (0.2 M)

	δ	J_{i-j}
Me	1.810	
CH-α	5.640	α-β, 8.4
CH-β	5.230	β-α, 8.4
H-2	7.814	2–3, 7.0
H-3	7.526	3–2, 7.0; 3–4, 8.0
H-4	7.830	4–3, 8.0
H-5	7.806	5–6, 8.4; 5–7, 1.7
H-6	7.323	6–5, 8.4; 6–7, 7.0; 6–8, 2.0
H-7	7.030	7–6, 7.0; 7–5, 1.7; 7–8, 9.0
H-8	7.451	8–7, 9.0; 8–6, 2.0
H-1′	7.664	1′–3′, 2.0
H-3′	7.323	3′–4′, 8.4; 3′–1′, 2.0
H-4′	7.751	4′–3′, 8.4
H-5′	7.676	5′–6′, 8.9; 5′–7′, 2.0
H-6′	7.428	6′–5′, 8.9; 6′–7′, 7.0; 6′–8′, 1.7
H-7′	7.455	7′–6′, 7.0; 7′–5′, 2.0; 7′–8′, 8.2
H-8′	7.805	8′–7′, 8.2; 8′–6′, 1.7

In order to correlate the sign of the couplet to the absolute configuration, the determination of the molecular conformation was necessary: this was done by means of NMR spectroscopy. The ^{1}H NMR spectrum of the compound **8**, in chloroform-*d* solution, is mainly divided into three spectral regions. In the high field region, the two methyl groups give rise to a single resonance at 1.81 ppm. The spectral region between 5.0 and 6.0 ppm contains two well-resolved doublets centered at 5.23 and 5.64 ppm, which are due to the two methine protons bound to the β- and α-naphthalene ring, respectively. The aromatic protons give rise to a complex set of absorptions between 6.8 and 8.0 ppm, the complete assignment of which (Table 2) was accomplished by analysis of the 2D DQF-COSY spectrum (see Chart 1 for numbering scheme).

The conformation of **8** was established by analysis of the 2D NOESY spectrum, in the same solvent. In particular, the most significant data were obtained by analyzing the traces (Figure 6) of this 2D spectrum corresponding to the aromatic protons adjacent to the alkyl substituent (i.e., H-1′ and H-3′ for the β-substituted ring and H-2 and H-8 for the α-substituted one). As shown in Figure 6a, the aromatic proton H-2 gives rise

Chart 1



to comparable intramolecular NOEs at the CH-α and CH-β protons, whereas the proton H-8 (Figure 6c) gives a large NOE on the CH-α proton and a less intense effect on the CH-β proton. As far as the other two aromatic protons H-1′ and H-3′ are concerned, the H-1′ generates a stronger NOE at CH-β than it does at CH-α (Figure 6b) and the H-3′ gives rise to significant NOEs on both CH-α and CH-β protons (Figure 6d).

These results clearly indicate that the two aromatic protons H-2 and H-3′ are in proximity of both CH-α and CH-β protons; the H-8 proton is closer to CH-α than to CH-β and the reverse is true for H-1′. Accordingly, the traces corresponding to the CH-α (Figure 7b) and CH-β (Figure 7a) protons show prevalent NOEs at the aromatic protons H-8 and H-1′, respectively. Furthermore, the value of the vicinal coupling constant between the two methine protons CH-α and CH-β (8.4 Hz) was used to calculate the dihedral angle Hβ−C−C−Hα by means of a Karplus type equation:[17] the value obtained was 145°, which is perfectly compatible with the stereochemical restraints imposed by the rigidity of the ketal moiety.

The structure of **8** depicted in Figure 8 is consistent with the above results. For such a structure, where the absolute configuration of the two stereogenic centers has been assumed to be R, the ^1B transition dipoles define a negative chirality and a negative couplet has to be expected, as experimentally found. Thus, for ketal **8**, the assignment of absolute configuration (*R,R*) has also been confirmed.

The above analysis of the CD spectra of compounds **7-9** deserves some more comment:

1. Interestingly, the configurational assignment of ketal **9** has been made exploiting the exciton couplet of the 280 nm absorption band, allied to the ^1L_a transition of the naphthalene chromophore. This coupling is not expected to be present in the other two analogs, **7** and **8**, because there is free rotation of the 2-naphthyl residue around the C*−C_{Ar} bond. On the contrary, in compound **9** a conformation, where the ^1L_a dipoles are fixed in a mutual disposition suitable for exciton coupling, is strongly prevailing.

2. Compounds **7** and **8**, although they have the same (*R,R*) absolute configuration, show in the 240−220 nm region couplet effects of opposite sign. This is a consequence of the different conformation that the two compounds assume. This fact shows again that great care has to be exerted in configurational determinations by means of circular dichroism spectra, if a reliable assignment of molecular conformation has not previously been carried out. In cases like the present one, a simple comparison between CD data can not be used to accomplish configurational correlations: although **7-9** have the same absolute configuration, the spectra do not show any common feature (Table 3).

The three ketals can also be easily separated into their enantiomers by HPLC on a chiral stationary phase (Daicel, Chiralcel OD), and therefore, it was possible to determine the enantiomeric excess of the starting diols.

Interestingly, in all three cases the first eluted enantiomer was the one of (*R,R*) configuration.

By measuring the enantiomeric excess of samples of known $[\alpha]_D$, it was also possible to extrapolate the values of $[\alpha]_D^{max}$ for the three diols (Table 4) and for the corresponding ketals (Table 5).

Experimental Section

General. 1- and 2-naphthaldehyde were commercially available (Aldrich); 1-naphthaldehyde was distilled under N_2 atmosphere. [(1-Naphthyl)methyl]triphenylphosphonium chloride and [(2-naphthyl)methyl]triphenylphosphonium bromide were obtained from the corresponding halides using standard procedures.[7] Ethyl alcohol was distilled over $Mg(OEt)_2$ 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 $CDCl_3$ or DMSO-d_6 on a 200 MHz spectrometer with TMS as reference. DQF-COSY and NOESY spectra were recorded using a Varian VXR-300 spectrometer, and the temperature was controlled to ±0.1 °C. The NOESY spectra were recorded in phase-sensitive mode. A mixing time of 0.6 s was used. A spectral width of about 3000 Hz was used in both f_1 and f_2 dimensions. The pulse delay was mantained at 5 s; 1024 hypercomplex increments of eight scans were collected. The double-quantum-filtered (DQF) COSY experiment was performed in the phase-sensitive mode using time-proportional phase incrementation (TPPI) with a spectral width of 3000 Hz; 1024 increments of eight scans and 2K data points were acquired. The relaxation delay was 5 s. HPLC analyses were carried out with a JASCO Twinkle instrument, using a Merck column, LiChrosorb Si 60 (10 μm), and a Daicel column, Chiralcel OD. The chromatographic analyses were monitored at 254 nm. Specific rotations, $[\alpha]_D$, are reported in deg/dm at the specified temperature, and the concentration (*c*) is given in grams per 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.

(*E*)-1,2-Di(2-naphthyl)ethylene, 4. To 50 mL of dry EtOH, in a 250 mL round-bottomed flask, was added 0.5 g (23 mmol) of sodium in small portions. To the resulting solution was added 5.35 g (11 mmol) of [(2-naphthyl)methyl]-triphenylphosphonium bromide, and the solution became yellow. After the mixture was stirred for 1 h at rt, 1.72 g (8.38 mmol) of 2-naphthaldehyde was added, and the mixture was stirred at rt for 24 h. After addition of 10 mL of distilled water, the product was filtered and dried. The solid obtained was refluxed in boiling *o*-xylene containing a trace of iodine for 24 h. After filtration, the product was obtained as a white solid (1.59 g, 5.68 mmol, 52% yield): mp = 258−259 °C (lit.[9b] mp 259 °C); ^{1}H-NMR (200 MHz, $CDCl_3$, δ) 8.09−7.46 (m, 8H); ^{13}C-NMR (200 MHz, $CDCl_3$, δ) 134.86, 133.74, 133.07, 129.11, 128.34, 128, 127.69, 126.67, 126.35, 125.94, 123.51. Anal. Calcd for $C_{22}H_{16}$: C, 94.25; H, 5.75. Found: C, 93.29; H, 5.82.

(*E*)-1-(1-Naphthyl)-2-(2-naphthyl)ethylene, 5. Olefin **5** was prepared from 2-naphthaldehyde and [(1-naphthyl)methyl]triphenylphosphonium chloride following the same procedure described above. The product obtained after isomerization was crystallized from benzene (yield 44%): mp = 185 °C (lit.[18] mp 191−192 °C); ^{1}H-NMR (200 MHz, $CDCl_3$, δ) 8.29 (d, J = 8 Hz, 1H), 8.02 (d, J = 16 Hz, 1H), 7.94−7.79 (m, 8H), 7.6−7.4 (m, 5H), 7.32 (d, J = 16 Hz, 1H). Anal. Calcd for $C_{22}H_{16}$: C, 94.25; H, 5.75. Found: C, 95.19; H, 5.90.

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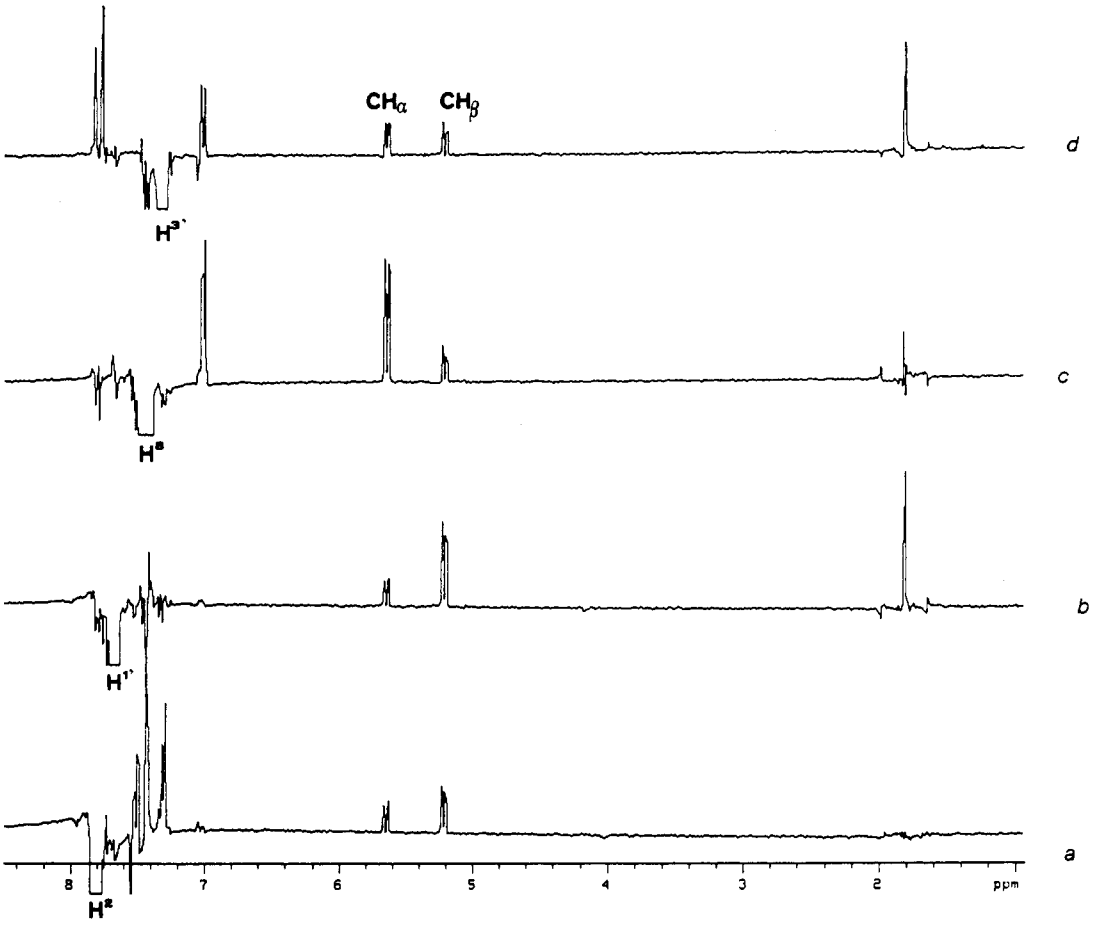

Figure 6. Traces of the 300 MHz NOESY ($CDCl_3$; 25 °C) spectrum of **8**.

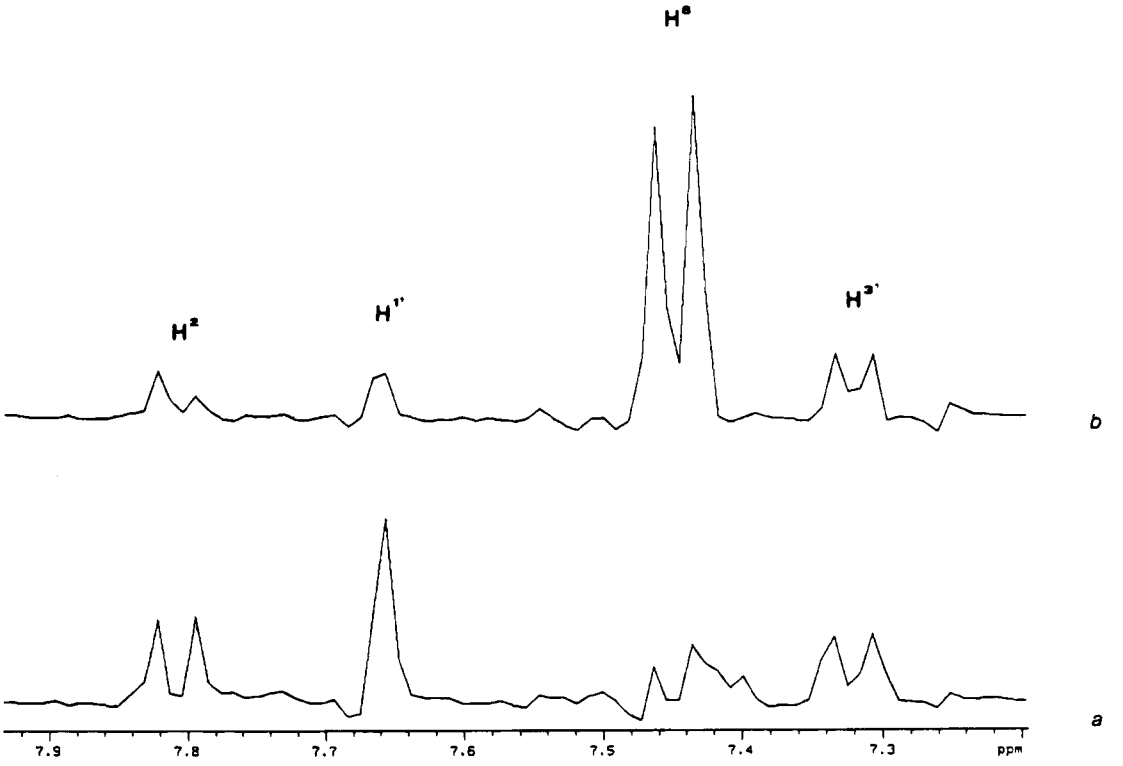

Figure 7. Traces of the 300 MHz NOESY ($CDCl_3$; 25 °C) spectrum of **8**.

***(E)*-1,2-Di(1-naphthyl)ethylene, 6.** Olefin **6** was prepared from 1-naphthaldehyde and [(1-naphthyl)methyl]triphenylphosphonium chloride following the same procedure described above for (*E*)-di(2-naphthyl)ethene. As 1-naphthaldehyde was contamined with 2-naphthaldehyde, the isomerization product was crystallized five times from ethyl alcohol in order to eliminate the 1-(1-naphthyl)-2-(2-naphthyl)ethene present as a byproduct (yield 31%): mp = 163 °C (lit.[9b] mp 162 °C); ^{1}H-

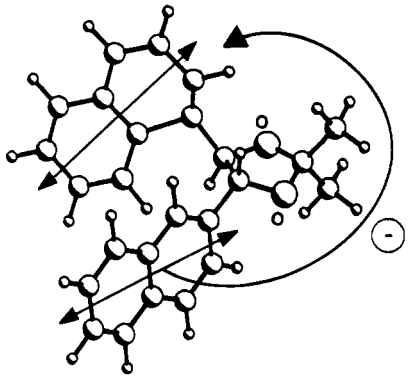

Figure 8. Most stable conformation of **8**.

Table 3.

ketal	EXA/IPA	ϕ (mL/min)	K_1	α
7	90/10	0.5	0.64	1.6
8	95/5	0.5	0.8	1.75
9	95/5	0.5	0.6	2.5

Table 4.

diol	$[\alpha]_D$	c in THF	T (°C)	ee (%)	$[\alpha]_D^{max}$
1	220	1	17	98	224
2	137	1.1	18	90	152
3	66.5	1.05	20	98	68

Table 5.

ketal	$[\alpha]_D$	c in $CHCl_3$	T (°C)	ee (%)	$[\alpha]_D^{max}$
7	183	1	18	97.5	188
8	51.7	1.08	24	99	52
9	−50	0.98	17	98	−51

NMR (200 MHz, $CDCl_3$, δ) 8.3–8.22 (m, 1H), 7.91 (s, 1H), 7.9–7.8 (m, 3H), 7.59–7.46 (m, 3H). Anal. Calcd for $C_{22}H_{16}$: C, 94.25; H, 5.75. Found: C, 94.07; H, 5.79.

(*R,R*)-(+)-1,2-Di(2-naphthyl)ethane-1,2-diol, 1. To a solution of 800 mg (5.92 mmol) of *N*-methylmorpholine *N*-oxide in 5 mL of distilled water, in a 100 mL round-bottomed flask, were added 1 g (3.57 mmol) of (*E*)-1,2-di(2-naphthyl)ethene, **4**, 15 mL of acetone, and 85 mg (0.18 mmol) of dihydroquinidine 9-*O*-(4-chlorobenzoate). The reaction mixture was cooled to 0 °C, and after addition of 2.2 mL of OsO_4 (0.0066 M in CH_3CN), it was stirred for 7 days at 0 °C. Two g (10.5 mmol) of $Na_2S_2O_5$ was then added to the mixture which was diluted with 20 mL of THF and stirred at rt for 1 h. Anhydrous sodium sulfate was added, and the mixture was stirred for an additional 5 h. The suspension was filtered through a Buchner funnel, the solid was rinsed thoroughly with THF, and the filtrate was concentrated to a solid which was transferred to a filter and washed with Et_2O. The remaining solid was mainly the desired diol which was obtained chemically pure by column chromatography (silica gel: eluting with $CHCl_3$ to eliminate olefin impurities, THF to recover the diol) (yield 90%): mp = 242–244 °C; $[\alpha]_D$ = 212 (c = 1, THF); ^{1}H-NMR (200 MHz, DMSO-d_6, δ) 7.85–7.2 (m, 7H), 5.6 (s, 1H), 4.9 (s, 1H). Anal. Calcd for $C_{22}H_{18}O_2$: C, 84.05; H, 5.77. Found: C, 85.17; H, 5.68.

(*R,R*)-(+)-1-(1-Naphthyl)-2-(2-naphthyl)ethane-1,2-diol, 2. Diol **2** was prepared from olefin **5** by the same procedure described above. The reaction was stopped after 27 h by subsequential addition of $Na_2S_2O_5$, CH_2Cl_2, and Na_2SO_4. The mixture was then filtered, and the filtrate was concentrated to a solid. The solid was dissolved in 80 mL of CH_2Cl_2, transferred to a separatory funnel, and washed subsequently with H_2O (2 × 30 mL), 1 M H_2SO_4 (3 × 30 mL), and brine (2 × 30 mL). The organic layer was dried (Na_2SO_4) and the solvent removed. Diol **2** was obtained chemically pure by column chromatography (silica gel: $CHCl_3$ to eliminate olefin impurities, THF to recover the diol) (yield 85%): mp = 230 °C; $[\alpha]^{23}_D$ = 130 (c = 1.03, THF); ^{1}H-NMR (200 MHz, $CDCl_3$, δ) 7.95–7.1 (m, 14 H), 5.45 (d, J = 6 Hz, 1H), 5.1 (d, J = 6 Hz, 1H), 3.1 (s, 2H). Anal. Calcd for $C_{22}H_{18}O_2$: C, 84.05; H, 5.77. Found: C, 84.70; H, 5.81.

(*R,R*)-(+)-1,2-Di(1-naphthyl)ethane-1,2-diol, 3. Diol **3** was prepared from olefin **6** by the same procedure as described for diol **1**. The reaction was stopped after 23 h and worked up in the same way as for diol **2** (yield, after chromatography, 94%): $[\alpha]^{24}_D$ = 48 (c = 0.86, THF); ^{1}H-NMR (200 MHz, $CDCl_3$, δ) 8–7.75 (m, 4H), 7.5–7.2 (m, 3H), 5.8 (s, 1H), 2.65 (s, 1H). Anal. Calcd for $C_{22}H_{18}O_2$: C, 84.05; H, 5.77. Found: C, 83.28; H, 5.79.

(*R,R*)-(+)-2,2′-Dimethyl-4,5-di(2-naphthyl)-1,3-dioxolane, 7. To 100 mL of $CHCl_3$, in the 250 mL round-bottomed flask fitted with a Kumagawa extractor, were added 59 mg (0.188 mmol) of diol **1**, 0.2 mL of 2,2′-dimethoxypropane, and traces of 4-toluenesulfonic acid. In the syphon tank, 4 g of molecular sieves was introduced inside a filter pad. After 3 h reflux, the heat was removed and the reaction mixture was transferred to separatory funnel and washed subsequentially with 10% aqueous $NaHCO_3$ (2 × 30 mL) and H_2O (2 × 30 mL). The organic layer was dried (Na_2SO_4) overnight and then concentrated to a solid. Ketal **7** was obtained chemically pure after TLC (silica gel, $CHCl_3$) (yield 94%): mp = 182 °C; $[\alpha]^{18}_D$ = 190 (c = 1, $CHCl_3$); ^{1}H-NMR (200 MHz, $CDCl_3$, δ) 7.9–7.3 (m, 7H), 5.02 (s, 1H), 1.8 (s, 3H). Anal. Calcd for $C_{25}H_{22}O_2$: C, 84.72; H, 6.26. Found: C, 83.80; H, 6.15.

(*R,R*)-(+)-2,2′-Dimethyl-4-(1-naphthyl)-5-(2-naphthyl)-1,3-dioxolane, 8. Ketal **8** was prepared following the same procedure described above (yield, after chromatography, 92%): mp = 123 °C; $[\alpha]^{23}_D$ = 52 (c = 1.05, $CHCl_3$); ^{1}H-NMR (200 MHz, $CDCl_3$, δ) 7.9–7 (m, 14H), 5.65 (d, J = 9 Hz, 1H), 5.2 (d, J = 9 Hz, 1H), 1.8 (s, 6H). Anal. Calcd for $C_{25}H_{22}O_2$: C, 84.72; H, 6.26. Found: C, 84.69; H, 6.29.

(*R,R*)-(−)-2,2′-Dimethyl-4,5-(1-naphthyl)-1,3-dioxolane, 9. Ketal **9** was prepared following the same procedure described above for ketal **7** (yield, after chromatography, 96%): mp = 138 °C; $[\alpha]^{17}_D$ = −50; ^{1}H-NMR (200 MHz, $CDCl_3$, δ) 7.9–6.8 (m, 7H), 5.75 (s, 1H), 1.85 (s, 3H). Anal. Calcd for $C_{25}H_{22}O_2$: C, 84.72; H, 6.26. Found: C, 86.77; H, 6.23.