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# ENANTIOSELECTIVE DIHYDROXYLATION OF OLEFINS BY OSMIUM TETROXIDE IN THE PRESENCE OF AN OPTICALLY ACTIVE 1,1'-BINAPHTHYL DIAMINE DERIVATIVE

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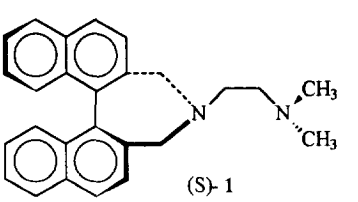
**Abstract:** The chiral diamine (S)-**1**, introduced by Cram and Mazaleyrat, has been reprepared following a different sequence which involves the resolution of diacid (RS)-**3**. The e.e. (via HPLC and NMR), the absolute configuration (via CD) and the most stable conformation (via UV and molecular mechanics calculations) of (S)-**1** have been determined. (S)-**1** has been employed as a chiral auxiliary in the stoichiometric *syn*-dihydroxylation of olefins obtaining optically active 1,2-diols with e.e.s up to 98%. Copyright © 1996 Published by Elsevier Science Ltd

## INTRODUCTION

Even if the enantioselective catalytic *syn*-dihydroxylation of unfunctionalized olefins has made tremendous progress both in homogeneous[1] and heterogeneous phase[2], the stoichiometric version of this reaction continues to be an area of very active and successful research[3]. Optically active diamines constitute the chiral controller of choice and nowadays several different structures are known to afford excellent enantioselectivities[3]. Interestingly, all of them are systems possessing stereogenic centers, only one example having been reported[3f] of a chiral inducer owing its chirality to atropoisomerism, i.e.,(S)-6-(2-dimethylaminoethyl)-1,11-dimethyl-6,7-dihydro-5H-dibenz[c,e]azepine, which affords almost complete enantioselectivity in the oxidation of (E)-stilbene to (+)-(1R,2R)-1,2-diphenyl-1,2-ethanediol.

Stimulated by this observation we decided to insert, in our research programme, devoted to the use of binaphthylic nitrogen ligands with $C_2$-symmetry as chiral auxiliaries in asymmetric synthesis[4], a study of the stoichiometric *syn*-dihydroxylation of simple olefins employing the ligand (S)-N-(2-dimethylaminoethyl)-4,5-dihydro-3H-dinaphtho[2,1-c:1',2'-e]azepine, (S)-**1**, taking into account its structural similarity with the biphenyl



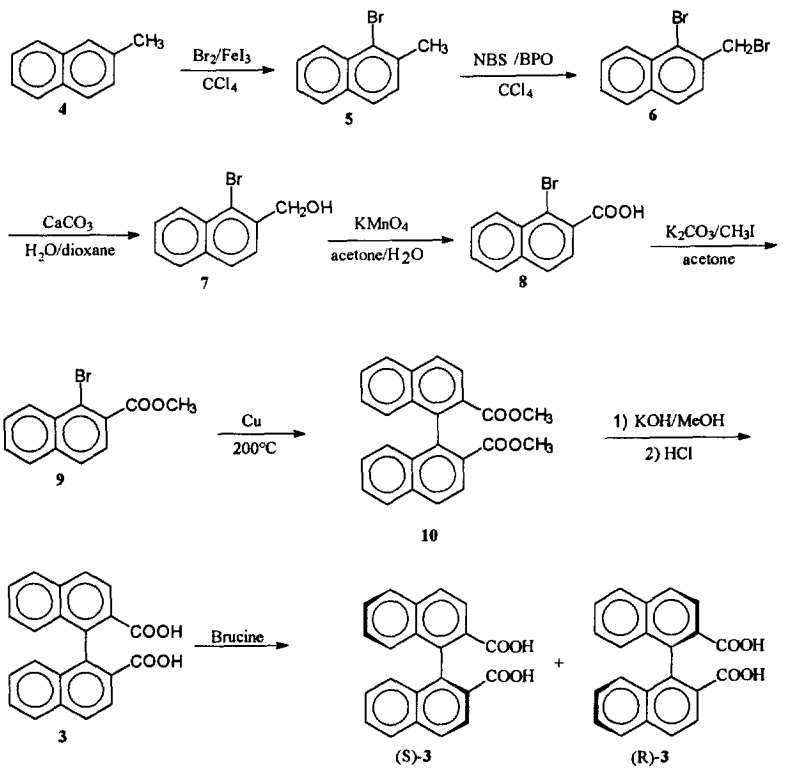

(S)-1

inducer described above[3f] and the importance of the 1,1'-binaphthyl skeleton in affording high extent of asymmetric induction[5].

## RESULTS AND DISCUSSION

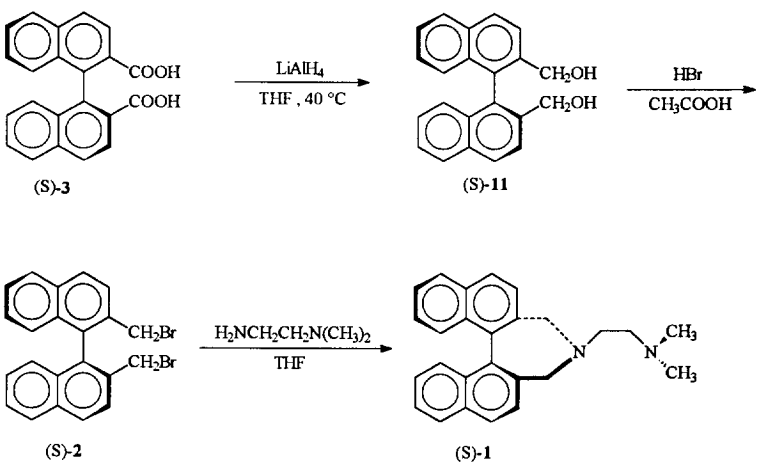
*a. Synthesis of (S)-N-(2-dimethylaminoethyl)-4,5-dihydro-3H-dinaphtho[2,1-c:1',2'-e] azepine, (S)-1*

Compound **1** was first reported by Mazaleyrat and Cram who employed it as a chiral controller in the asymmetric addition of alkyllithium reagents to aldehydes[6]. The authors prepared (R)- and (S)-**1** resolving with (-)-dibenzoyltartaric acid the racemic mixture obtained by reaction of (R,S)-2,2'-bis(bromomethyl)-1,1'-binaphthyl, **2**, with N,N-dimethylethylenediamine[6]. Since the experimental details of these reactions are not described, considering also that the resolution step represents a key point in the generation of optically active compounds in high chemical and enantiomeric excesses, we decided to prepare (S)-**1** in a different way. (S)-**1** was obtained from optically active (S)-**2** which was prepared starting from (S)-1,1'-binaphthyl-2,2'-dicarboxylic acid, (S)-**3**, synthesized by Ullmann coupling of methyl 1-bromo-2-naphthoate and successive resolution of racemic dicarboxylic acid with brucine, as described in detail in the literature[7]. The synthetic procedures, used to prepare (S)-**3** and (S)-**1** in this work, are summarized in the Schemes 1 and 2, respectively.




**SCHEME 1**

The key step of this sequence is the Ullmann coupling reaction (Scheme 1) which was described[7] to give the dimethyl 1,1'-binaphthyl-2,2'-dicarboxylate, **10**, in 80% yield from methyl 1-bromo-2-naphthoate, **9**, in the presence of activated Cu-powder in DMF under reflux. In our hands, this reaction afforded only unsatisfactory yields (~ 10%) of racemic **10**, with large amounts of methyl 2-naphthoate, (coming from **9** by loss of the bromine atom). Far better results have been obtained simply carrying out the reaction without solvent, heating a mixture of **9** and unactivated copper powder (molar ratio 1:10) for 5 hours[8]. In this way, **3** can be obtained with an overall yield of 62% starting from **9**. The transformation of (S)-**3** into (S)-**1** is straightforward[7] (Scheme 2).




**SCHEME 2**

*b. Stereochemical characterization of (S)-***1**.

Particular care has been employed in effecting a detailed stereochemical characterization of (S)-**1**, not previously reported[6]. The enantiomeric purity of (S)-**1** has been determined by HPLC (elution on the chiral stationary phase CHIRALCEL OJ, mobile phase hexane/2-propanol/triethylamine = 95/5/0.5 v/v/v at 0.5 ml/min) and by $^1$H-NMR spectroscopy (the signals of the methyl proton split in the presence of three moles of (R)-mandelic acid[9] per mole of (S)-**1** in $CDCl_3$ at room temperature). Interestingly, a sample which has been shown to be almost enantiomerically pure (> 98% by HPLC and $^1$H-NMR analysis) exhibited $[\alpha]_{546}^{22} = +293$ (c = 1.08, EtOH), a value very different from that reported by Cram and Mazaleyrat for the pure antipode[6]. The electronic spectrum of (S)-**1** shows, between 350 nm and 190 nm, the typical absorption features of the naphthalene chromophore[10]: a first band at 300 nm ($\varepsilon_{max}$ ~ 8000) and a second one in the range 220-230 nm

($\varepsilon_{227}$ ~62000 and $\varepsilon_{217}$ ~90000). In the CD spectrum several Cotton effects are observable: at 308 nm ($\Delta\varepsilon$ ~ -17), 255 nm ($\Delta\varepsilon$ ~ +40), 245 nm ($\Delta\varepsilon$ ~ -20), 228 nm ($\Delta\varepsilon$ ~ +380) and 215 nm ($\Delta\varepsilon$ ~ -280) (Fig.1).

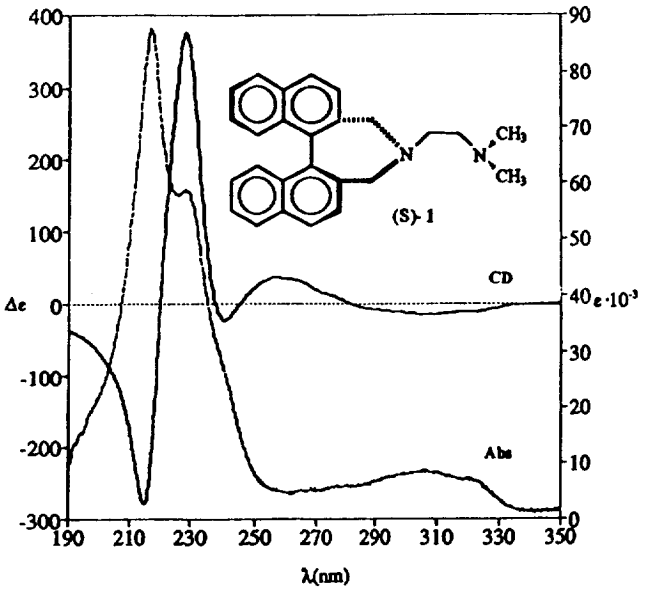



Figure 1. Absorption and CD spectra of (S)-**1** in ethanol.

The shortest wavelength Cotton effects are the two components of the couplet observable in binaphthyl systems, deriving from the coupling of the long-axis polarized transitions of the naphthalene chromophore[11]. It has been shown[11] that a positive couplet is related to the (S) absolute configuration. The observed positive couplet in the CD spectrum of (S)-**1** is a further support to its configurational assignment. It is interesting to observe that the wavelength position of the two exciton components in the CD spectrum strictly corresponds to the two absorption maxima in the absorption spectrum. The following comments can be made: (i) this is one of the few cases where the exciton components are clearly observable in the UV-spectrum[12]; (ii) it is also noteworthy that the low energy component is significantly less intense than its high energy counterpart (Fig. 1); this spectroscopic feature has been qualitatively related[13] to a small value of the dihedral angle $\theta$ between the two naphthalene rings. In order to provide a quantitative foundation to the above correlation, the UV-CD spectra of (S)-**1** have been calculated by means of the De Voe polarizability model[14,15], employing as input structure the minimum energy conformation of (S)-**1**, obtained by molecular mechanic calculations (MMX routine[16]), which is characterized by a $\theta$ value of 55°. A Lorentzian oscillator to which a polarizability value of $44D^2$ (at 225 nm) has been assigned, was employed to describe the $^1B$ (long axis polarized) transition of the naphthalene chromophore. With these parameters the following results have been obtained:

| | *Absorption* | | *Circular Dichroism* | |
|---|---|---|---|---|
| Calculated | 227*nm* | $\mathcal{E}$=41000 | 233*nm* | $\Delta\mathcal{E}$=+354 |
| | {218*nm* | $\mathcal{E}$=74000 | {218*nm* | $\Delta\mathcal{E}$=−368 |
| Experimental | 227*nm* | $\mathcal{E}$=62000 | 227*nm* | $\Delta\mathcal{E}$=+380 |
| | {217*nm* | $\mathcal{E}$=90000 | {218*nm* | $\Delta\mathcal{E}$=−280 |

It is interesting to note that the experimental features of the CD spectrum (sign of the couplet, wavelength position of the two extrema, intensities of the effect) are quite well reproduced, providing a spectroscopic support to the configurational assignment of this binaphthyl derivative. Also the shape of the absorption spectrum is very well reproduced: in fact, the calculated spectrum shows two maxima, with the low energy one being less intense than the high energy one, as found experimentally. This is a quantitative support for the qualitative correlation between the shape of absorption and the dihedral angle $\theta$[13].

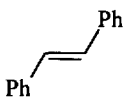
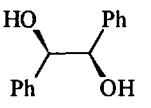
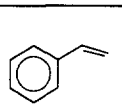
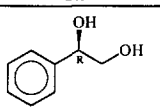
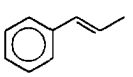
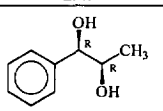
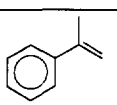
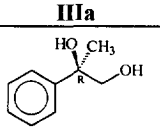
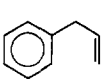
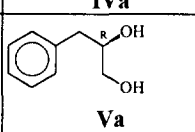
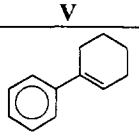
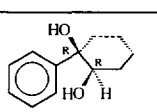
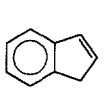
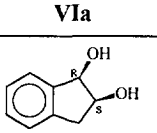
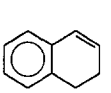
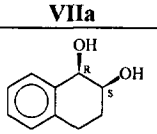
*c. Asymmetric dihydroxylation reactions*

The reaction of the olefins **I-VIII** with $OsO_4$ in the presence of (S)-**1** in THF at -78°C for 12 hrs, afforded, after quenching with $Na_2S_2O_5$ and acidic work-up, the corresponding diols, **Ia-VIIIa** (Table 1).

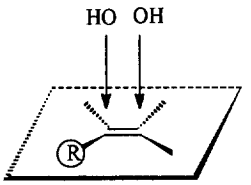
(S)-**1** can be quantitatively recovered without any loss of enantiomeric purity. It is noteworthy that all the reactions have been carried out with the same sample of (S)-**1**. The absolute configuration of products **Ia-VIIIa** was established by comparison of the rotatory powers with the literature values[3i], whilst the enantiomeric excesses have been determined by HPLC on the chiral stationary phases Chiralcel OB, OJ and Chiralpack AD, eluting the underivatized diols with mobile phases of hexane/2-propanol[17]. Runs 1-2 indicate some interesting aspects of this reaction: i) there is a strong temperature effect on the e.e., in fact, **I** is transformed in the corresponding diol with 96% e.e. at -78°C (run 1), but at room temperature the e.e. is reduced to half (run 2); ii) by using (S)-**1** with 30% e.e., a product having 30% e.e is obtained (run 3). This shows that non linear effects are absent in this reaction[18]. Olefins (E)-**I**, and (E)-**III** and terminal conjugated olefins, **II** and **IV**, are transformed in corresponding diols **Ia**, **IIa**, **IIIa**, **IVa** in very high e.e.'s (runs 1,4-6). Moderate e.e.'s are obtained for the non conjugated olefin **V** (run 7), and for the *cis*-olefins **VI**, **VII** and **VIII** (runs 8-10).

As far as the *cis*-cyclic olefins **VI-VIII** are concerned, (S)-**1** affords in the case of **VII** one of the highest e.e. reported[3h] for the diol **VIIa**, whilst the values of enantiomeric purity of the diols **VIa** and **VIIIa** are lower. In particular, olefin **VIII** continues to be a very poor substrate for this reaction, independently of the kind of the chiral inducer employed[19]. The stereochemical outcome of this reaction can be formally rationalized by the following simplified model in which the $OsO_4$/(S)-**1** complex attacks the same face of the olefins, as reported in Chart 1.

**Table 1**. Enantioselective syn-dihydroxylation of olefins by means of $OsO_4$ and (S)-**1**[a].

| run | Olefin | Product | Absolute configuration | Chemical yield[b] % | e.e[c] % |
|---|---|---|---|---|---|
| 1<br>2[d]<br>3[e] |  <br>**I** |  <br>**Ia** | R,R<br>R,R<br>R,R | 47<br>90<br>90 | 98<br>66<br>30 |
| 4 |  <br>**II** |  <br>**IIa** | R | 83 | 96 |
| 5 |  <br>**III** |  <br>**IIIa** | 1R,2R | 59 | 84 |
| 6 |  <br>**IV** |  <br>**IVa** | R | 64 | 81 |
| 7 |  <br>**V** |  <br>**Va** | R | 68 | 47 |
| 8 |  <br>**VI** |  <br>**VIa** | R,R | 90 | 35 |
| 9 |  <br>**VII** |  <br>**VIIa** | 1R,2S | 75 | 53 |
| 10 |  <br>**VIII** |  <br>**VIIIa** | 1R,2S | 25 | 13 |

a) All the reactions have been carried out in THF at -78°C with a molar ratio olefin/$OsO_4$/ (S)-**1** = 1/1/1; b) Chemical yields refer to isolated product; c) E.e.'s have been determined by HPLC on the chiral stationary phases CHIRALCEL OB, OJ and CHIRALPACK AD, on the underivatived diols; d) THF at room temp.; e) (S)-**1** having 30% e.e.




R = Ph, Bn Chart 1

A possible origin of the observed enantioselectivity can be found in the following mechanism. Assuming that only a complex $OsO_4$/(S)-**1** is formed in solution, its structure can be obtained from the examination of molecular models (Fig. 2). The relevant characteristics of such a structure are as follows:

1. The coordination of the two nitrogen atoms to the metal gives rise to a 5-membered chelate ring that can assume the two conformations below


δ λ

Owing to the chirality of the binaphthyl moiety, they are in a diastereoisomeric relationship

(S)-λ ⟹ (S)-δ

The examination of molecular models does not point out any difference in stability, and taking into account that the λ ⟹ δ interconversion barrier is generally small[20], to simplify the discussion we shall talk about planar chelate rings.

2. Looking at Figure 2, it can be observed that the small dihedral angle between the naphthalene rings is cause of a steric screen for $O_1$ (eq) and $O_3$ (ax): in fact a larger aperture of this binaphthyl "minor groove"[21] would have caused a major distance between the two oxygen atoms and the -$CH_2$- groups and then less steric hindrance. As a consequence there is only one reactive site in this complex, constituted by the $O_4$-Os-$O_2$ region, which can be used, following the [3+2] mechanism, to rationalize our experimental results[3c, 22]. With this in mind, taking the case of styrene as illustrative, the examination of the molecular models reveals that the substrate will approach the reactive site of the complex mainly exposing the *Si* face, as represented in Figure 2. This preferred approach is a consequence of two facts: i) in this way, the stacking of the naphthalene ring of the ligand and the phenyl ring of the substrate takes place, giving rise to a favourable π-π interaction[23] ; ii) the other approach (attack of the oxygen atoms on the *Re* face of the double bond) would locate the phenyl ring in a crowded region [i.e. near to the -$N(CH_3)_2$ moiety of the complex] and then to a significant steric repulsion. The preferred attack of $O_2$,$O_4$ on the *Si* face of the double bond leads the (R,R) diol as major product. With this model the stereochemical result obtained with (E)-β-methylstyrene, **III**, and α-methylstyrene, **IV**, can be explained as well. In the case of 3-phenylpropene, **V**, the aromatic ring and the double bond are not conjugated,

and they form a dihedral angle of 80° (MMX calculations[16]). This fact does not allow the existence of π-π stabilizing interaction neither approaching the *Re* face nor the *Si* one, making the possible reaction pathways nearer in energy than the cases above and hence lowering the e.e.. The e.e. obtained in the case of indene, **VII**, can be rationalized on the basis of the above observations: owing to its planar structure (MMX calculations[16]) **VII** behaves as styrene, **II**, does; here, however, the $-CH_2-$ group causes some steric hindrance. Molecular models examination, in fact, reveals that even in the low-energy approach (exposure of the *Si* face towards the $O_2$-$O_4$ atoms) one of the two hydrogens of the $-CH_2-$ group will interact with the naphthyl ring of the ligand, hindering a full π-π stacking of the two aromatic moieties. As a consequence, the $\Delta(\Delta G^{\ddagger})$ between the two possible reaction pathways (*Si-Si* vs. *Re-Re* attach) is not marked as for **II**. Analogous effects are certainly even more important in the case of **VI** and **VIII** where the cyclohexyl group or the two $-CH_2-$ moieties, respectively, can create a significant steric hindrance in both the competing pathways leading to a poor enantioselectivity.

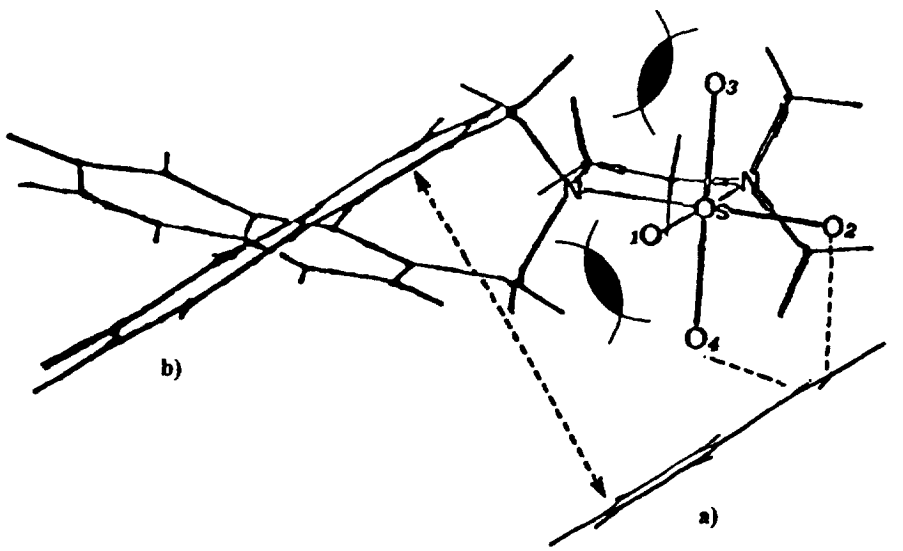



Figure 2. A possible mode of approach of styrene (a) to the (S)-1/$OsO_4$ complex (b). The steric bulk exerted by the $-CH_2-$ groups of (S)-1 toward $O_1$ and $O_3$ is pointed out.

## CONCLUDING REMARKS

With this investigation, two important goals have been achieved:

1. Compound **1** has been obtained in a straightforward manner starting from a very cheap compound, 2-methylnaphthalene, and using standard laboratory procedures. It has been fully characterized from a

stereochemical point of view; in fact the enantiomeric purity and most stable conformation have been determined for the first time, whilst the absolute configuration has been further supported.

2. Compound **1** has been employed as a chiral controller in some asymmetric dihydroxylation reactions of (E)-olefins affording the corresponding diols in e.e. up to 98%. A possible mechanism of the observed enantioselectivity has been formulated which is dependent on the conformation of the ligand (the small dihedral angle between the naphthalene rings plays an important role) and on the intervention of stabilizing $\pi$-$\pi$ interaction. It is interesting to note, in this respect, that in the (S)-**1**/$OsO_4$ complex a small "reactive site" is created; for this reason the "active complex" is very sensitive to the structure of the substrate.

However, the most important result of this work is that the diamine (S)-**1**, designed by Cram and originally used in the asymmetric addition of alkyllithiums to aldehydes, can also act as chiral auxiliary in a reaction where a transition metal is involved. Therefore, its use as chiral ligand to form complexes like $MX_n$(diamine), (M= transition metal, X= anionic group i.e. Cl, acac), to be employed as catalytic precursors in stereoselective processes, is a natural and promising development of the present investigation.

## EXPERIMENTAL SECTION

Melting points were measured using a Kofler apparatus and are not corrected. Optical rotation were taken with a JASCO Dip-360 digital polarimeter. $^1H$ NMR spectra were taken in $CDCl_3$ with Varian Gemini 200 at 200 Hz or Varian VXR at 300 Hz. $^{13}C$ NMR spectra were taken in $CDCl_3$ with Varian VXR at 75 MHz. Chemical shift values are expressed in ppm relative to internal tetramethylsilane. Abbreviations are as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet, br, broad. Mass spectra (Ionspray) were taken with Perkin Elmer Sciex API III mass spectrometer. Mass spectra (EI) were carried out on a VG 7070 E spectrometer. The products of the asymmetric reactions were identified by $^1H$ NMR and mass spectrometry. Their optical purity was determined by HPLC on a chiral stationary phase using a JASCO PU-980 chromatograph equipped with a UV-975 JASCO detector, working at $\lambda$=220 nm with a flow of 0.5 ml $min^{-1}$. CD spectra were recorded on JASCO J-600 spectrometer and absorbance spectra on a JASCO UVIDEC 710 spectrophotometer.

**Preparation of (R)- and (S)-1,1'-binaphthyl-2,2'-dicarboxylic acid, 3.**

The synthesis and the resolution of (R)- and (S)-**3** (scheme 1) were carried out as reported in the literature[7a]. Only the steps performed in a different way are described in detail.

*Methyl 1-bromo-2-naphthoate*, **9**[24]. 1-Bromo naphthoic acid, **8** (25 g, 99.5 mmol), anhydrous $K_2CO_3$ (43 g, 311 mmol), acetone (250 ml) and methyl iodide (30 ml, 480 mmol) were introduced into a three-necked round bottomed flask equipped with a mechanical stirrer and a reflux condenser, under a nitrogen atmosphere. The mixture was refluxed for 6 h and filtered. The filtrate was evaporated to dryness under vacuum. The crude solid was purified by flash chromatography ($SiO_2$, $CCl_4$), yielding the white crystalline ester **9** (25.2 g, 95 mmol, yield 95%), mp 57-59°C (lit[7a] mp 58°C). The ester obtained was spectroscopically and physically identical with that in the literature[7a].

*Dimethyl 1,1'-binaphthyl-2,2'-dicarboxylate, **10** (without solvent).* A mixture of methyl 1-bromo-2-naphthoate, **9** (7 g, 26.4 mmol) and copper bronze (14 g) in a round-bottomed flask under nitrogen atmosphere was heated in an oil-bath at 190°C under magnetic stirring for 5h. The product was extracted with hot toluene and the filtrate was evaporated to dryness. The crude product was recrystallized from methanol, giving **10** (3 g, 8.1 mmol, yield 62%) as yellow plates, mp 156-158°C (lit.[7a,8] mp 158°C); NMR (200Mz, $CDCl_3$, δ ): 8,2-7,1 (m,12 H); 3,5 (s,6H).

*Dimethyl 1,1'-binaphthyl-2,2'-dicarboxylate, **10** (in DMF ).* Distilled DMF ( 90 ml), methyl 1-bromo-2-naphthoate, **9** (6 g, 22.6 mmol), and freshly activated and dry copper bronze[25] (12 g) were placed into a three-necked round bottomed flask equipped with a mechanical stirrer and a reflux condenser, under a nitrogen atmosphere. The stirred mixture was gently refluxed for 8h, cooled and filtered through a glass frit. The residue was washed throughly with hot toluene. The combined filtrates were extracted with 2N HCl, then with chilled water and dried over anhydrous $Na_2SO_4$. Evaporation of the solvent under reduced pressure gave a crude pruduct that was purified by flash cromatografy ($SiO_2$, hexane:acetone = 9:1) affording methyl 2-naphthoate (3.2 g, 17.3 mmol, yield 76%), and **10** (0.9 g, 2.4 mmol, 21%).

*Methyl 2-naphthoate:* MS, *m/z* (% rel. int.):186, $M^+$ (90); 155, $M^+$– OMe (100); 127, $M^+$–COOMe (90). $^1$H-NMR (200 MHz, $CDCl_3$) δ 8.6-7.5 (m, 7 H, aromatics), 4.0 (s, 3H, -$COOCH_3$),

**Preparation of (S)-N-(2-dimethylaminoethyl)-4,5-dihydro-3H-dinaphtho[2,1-c:1',2'-e]-azepine, (S)-1.**

The synthesis of (S)-**1** was performed as reported in scheme 2 starting from (S)-1,1'-binaphthyl-2,2'-dicarboxylic acid, **3**. (S)-(-)-2,2'-Bis(hydroxymethyl)-1,1'-binaphthyl, **11**, and (S)-2,2'-bis(bromomethyl)-1,1'-binaphthyl, **2**, were prepared as reported in the literature[3f, 7a, 24b].

*(S)-N-(2-dimethylaminoethyl)-4,5-dihydro-3H-dinaphtho[2,1-c:1',2'-e]azepine, (S)-1.* (S)-2,2'-bis(bromomethyl)-1,1'-binaphthyl, **2** (0.35 g 0.8 mmol), 2-dimethylaminoethylamine (0.51 ml, 4.7 mmol) and dry THF (10 ml) were introduced into a three-necked round bottomed flask, equipped with a mechanical stirrer and a reflux condenser, under a nitrogen atmosphere. The solution was refluxed for 48 h. After completion of the reaction, the solvent was removed by evaporation under reduced pressure and the crude product was partitioned between aqueous 3 N NaOH and chloroform. The organic extracts were concentrated and dried over anhydrous $Na_2SO_4$. The solvent was removed under vacuum and the residue was washed throughly with pentane and dried yielding (S)-**1** (0.272, 0.74 mmol) as a white solid: mp 52-53°C; $[\alpha]_{546}^{22}$ = + 293 (c 1.08, EtOH) {lit.[6] $[\alpha]_{546}^{25}$ = + 413}. $^1$H NMR (300 Mz, $CDCl_3$), (aromatic protons) δ 7.9-7.2 (m, 12H,). 4.75 (d, 2H, Ar-C(H)H). 3.25 (Ar-C(H)H-). 2.8-2.4 (m, 4H, -$CH_2$-$CH_2$-). 2.3 (s, 6H, -$CH_3$). $^{13}$C-NMR (75 MHz, $CDCl_3$), (aromatic carbons), δ 125.2, 125.6, 127.4, 127.8, 128.2, 131.2, 133.0, 133.4; (aliphatic carbons), δ 46.0, 53.2, 54.6, 58.0. MS (Ionspray) *m/z* (% rel. int.): 367, $M^+$ (20); 322, $M^+$– $HNMe_2$ (100); 72, $^+CH_2$-$CH_2$-$NMe_2$ (60). UV (EtOH, 0.52 mg $ml^{-1}$) $\lambda_{max}$ (nm) ($\varepsilon_{max}$): 217 (89000), 227 (60000), 300 (8000). CD (EtOH, 0.52 mg $ml^{-1}$) λ max (nm) ($\Delta\varepsilon_{max}$): 215 (-280), 212 (0), 228 (+380), 240 (0), 245 (-20), 250(0), 255 (+40), 280 (0), 308 (-17),

330 (0). The enantiomeric excess of underivatized (S)-1 was determined by HPLC on CHIRALCEL OJ using the following conditions: eluent, hexane/2-propanol/triethylamine 95/5/0.5 (v,v,v); detector UV, λ=220 nm; flow 0.5 ml $min^{-1}$.

**Asymmetric dihydroxylation of the olefins I-VIII by osmium tetroxide with the chiral diamine (S)-1.**

*General procedure.* A solution of osmium tetroxide (0.128 g, 0.5 mmol) in THF (2 ml) was added, under nitrogen, to a Schlenk tube containing a cooled (-78°C) solution of the chiral diamine (S)-1 ( 0.2 g, 0.55 mmol ) in THF (10 ml). The olefin (0.5 mmol) in THF (2 ml) was successively added to the bright orange solution and the whole was stirred for 12h at -78°C. A saturated solution of sodium metabisulfite in water/THF was added and the reaction mixture refluxed for 2 h. The resulting brown precipitate was filtered off. The filtrate was concentrated and partitioned between acqueus (10%) $NaHCO_3$ and ethyl acetate. The organic extracts were dried over anhydrous $Na_2SO_4$. Evaporation of the solvent under reduced pressure gave a crude product that was purified by flash chromatography ($SiO_2$, diethyl ether) affording the diol that was characterized by MS spectrometry and by $^1H$ NMR analysis. The absolute configuration was established by comparison with literature reports[3i] and the e.e. was determined by HPLC on chiral stationary phase (see Table 1). The diamine (S)-1 was recovered (~95%) by washing the silica with methanol.

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