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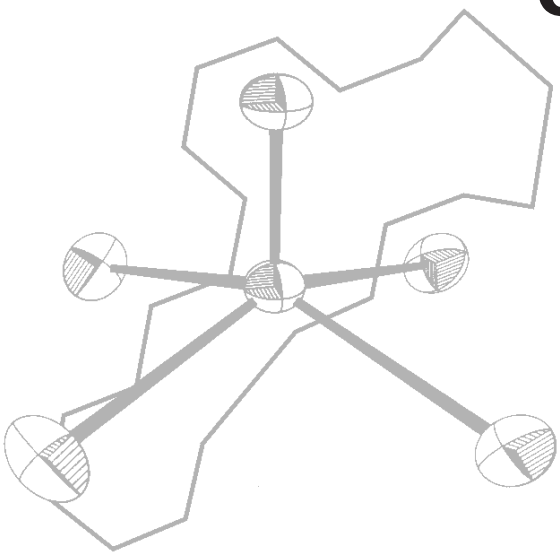

Volume 53, 2000

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Aust. J. Chem., 2000, **53**, 925–938

Atropisomerism of 2,2′-Binaphthalenes

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Dedicated to Dr John Zdysiewicz on the occasion of his retirement

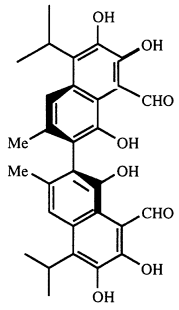
The synthesis of diastereo-enriched substituted (4*S*)-4-isopropyl-2-(2,2′-binaphthalen-1-yl)-4,5-dihydrooxazoles from substituted 2-naphthalenylmagnesium bromides and (4*S*)-4-isopropyl-2-(2-methoxynaphthalen-1-yl)-4,5-dihydrooxazole (4) and (4*S*)-4-isopropyl-2-(2,3-dimethoxynaphthalen-1-yl)-4,5-dihydrooxazole (5) is described. The product oxazolines were converted into a number of derivatives and the free energy barriers to internal rotation of several of these derivatives were determined. The determination of the X-ray crystal structures and the c.d. spectra of (*S*,1*S*)-*N*-[2-hydroxy-1-(isopropyl)ethyl]-3-methoxy-1′,*N*-dimethyl-2,2′-binaphthalene-1-carboxamide (22) and (*R*,4*S*)-4-isopropyl-3-methyl-2-(1′,2′,4′-trimethyl-2,2′-binaphthalen-1-yl)-4,5-dihydrooxazolium iodide (38) allowed the assignment of the absolute configurations of all the synthetic 2,2′-binaphthalenes by comparison of their c.d. spectra with those of compounds (22) and (38).

Keywords: Asymmetric synthesis; atropomers; 2,2′-binaphthalenes; circular dichroic spectra; rotational barriers.

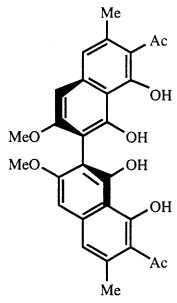
A number of enantiopure atropomers of various derivatives of 1,1′-binaphthalene have achieved wide use in asymmetric synthesis and in the separation of racemic mixtures.[1] The free energy barriers to rotation in many such compounds have also been measured.[2] The atropisomerism of 2,2′-binaphthalenes has, on the other hand, been little explored.

A number of natural products are known which are based on the 2,2′-binaphthalene system and occur as atropomers. The first to be recorded[3] was gossypol, which occurs in cotton seeds in racemic form. The structure of gossypol was elucidated by Adams and his coworkers in 1938.[4] The (+)-(*S*)-atropomer (1) occurs in *Thespesia populnea*[5] and since the (–)-atropomer has the ability to inhibit maturation of human sperm there has been renewed interest in its chemistry.[6] (+)-(*S*)-Gossypol (1) has recently been synthesized.[7] The free energy barrier to rotation[8] in gossypol has been estimated to be above 210 kJ mol^{-1} and the absolute configuration[9] has been determined by the exciton chirality method.[10] Other natural products which are also not easily thermally racemized are sporandol (2),[11] the flavomannins[12] and the cardinalins,[13] which have also had their absolute configurations determined by the exciton chirality method. The synthetic 2,2′-binaphthol (3)[14] has been resolved and the free energy barrier to rotation has been estimated to be 168 kJ mol^{-1}.

The rotational barrier in 1,1′-biphenyl[15] is *c.* 8 kJ mol^{-1} and this rises to 90.5 kJ mol^{-1} on benzannelation to give 1,1′-binaphthalene.[16] The free energy barrier to rotation in 2,2′-binaphthalene[17] is estimated to be 29–38 kJ mol^{-1} so that this benzannelation, although remote from the biaryl linkage, has a substantial effect. The free energy barrier in 1,1′-binaphthalene is at the lower limit for the isolation of atropomers at room temperature.[15]



(1)



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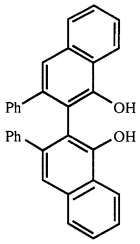
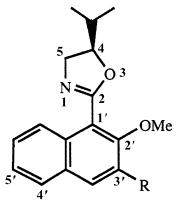


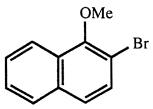
(3)

In view of the dearth of data on atropisomerism in the 2,2′-binaphthalene series, we decided to synthesize a number of these compounds and to investigate their free energy barriers to racemization. At the outset it appeared likely that at least two substituents at the positions *ortho* to the biaryl linkage would be required to obtain atropomers that would be thermally stable to racemization at room temperature. For the synthesis of the naturally occurring 1,2′-binaphthoquinones isodiospyrin and 8′-hydroxyisodiospyrin[18] in enantiopure form we adopted the Meyers oxazoline method[19] and this appeared to be suitable for adaptation to the present work.

Manuscript received 15 September 2000 10.1071/CH00122 0004-9425/00/110925



(4) R = H
(5) R = OMe



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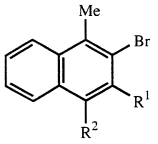


	R^1	R^2
(7)	H	H
(8)	Me	H
(9)	H	Me
(10)	Me	Me

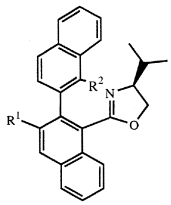
Table 1. Products of coupling reactions between Grignard reagents and oxazolines

Bromo compound	Oxazoline	Product	Yield (%)	D.e. (%)
2-Bromonaphthalene	(5)	(11)	95	0
(6)	(4)	(12)	91	0
(6)	(5)	(13)	91	56.8[A]
(7)	(5)	(17)	92	73.3[A]
(9)	(5)	(24)	96	56.6[A]
(8)	(4)	(28)	76	39.9[B]
(8)	(5)	(33)	82	37.0[A]
(10)	(4)	(37)	82	30.8[B]
(10)	(5)	(44)	23	20.8[A]

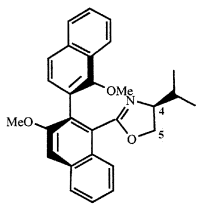
[A] In favour of axial (*S*)-diastereomer
[B] In favour of axial (*R*)-diastereomer

For this purpose we required oxazolines in enantiopure form and we chose compounds (4) and (5) for investigation. Compound (4) was easily prepared from the known 2-methoxynaphthalene-1-carboxylic acid[20] and (+)-(*S*)-valinol[21] by a standard method.[22] For the synthesis of the oxazoline (5) the starting material was 2,3-dimethoxynaphthalene which, on bromination by the method of Mitchell and his coworkers,[23] supplied 1-bromo-2,3-dimethoxynaphthalene. Carboxylation of the Grignard reagent derived from this bromo compound afforded 2,3-dimethoxynaphthalene-1-carboxylic acid,[24] which was converted into the required oxazoline (5). A number of bromo compounds were required as precursors to Grignard reagents for the synthesis of 2,2′-binaphthalenes by nucleophilic displacement of the methoxy group at the 2-positions of the oxazolines (4) and (5). 2-Bromo-1-methoxynaphthalene (6)[25] was prepared by methylation of 2-bromo-1-naphthalenol available by bromination of 1-naphthalenol.[26] 2-Bromo-1-methylnaphthalene (7) was obtained from the amine by a Sandmeyer reaction.[27] 2-Bromo-1,3-dimethylnaphthalene (8)[28] was prepared from 2,3-dimethylindene.[29] Bromination of 1,4-dimethylnaphthalene[30] and 1,2,3-trimethylnaphthalene, each of which was prepared from 1-methylnaphthalene, provided the bromo compounds (9)[31] and (10).[32]

The results of coupling between the oxazolines (4) and (5) and Grignard reagents derived from 2-bromonaphthalene and compounds (6)–(10) are summarized in Table 1. An



	R^1	R^2
(11)	OMe	H
(12)	H	OMe



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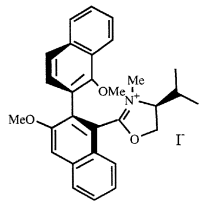

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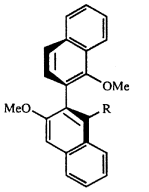
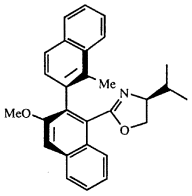
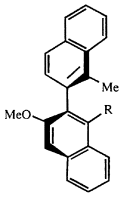
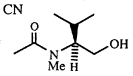


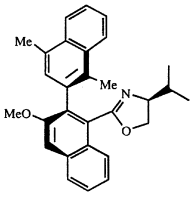
(15) R = CHO
(16) R = CH_2OH



(17)



(18) R = CHO
(19) R = CH_2OH
(20) R = Me
(21) R = CN
(22) R = 
(23) R = CONHMe



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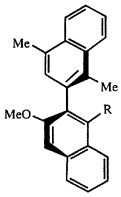
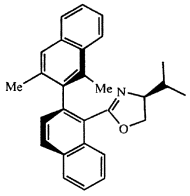


(25) R = CHO
(26) R = CH_2OH
(27) R = CN



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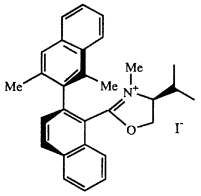

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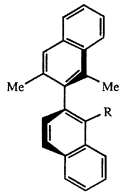
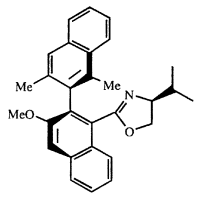


(30) R = CHO
(31) R = CH_2OH
(32) R = Me



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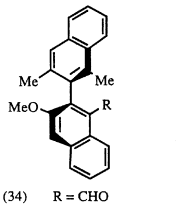
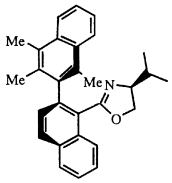


(34) R = CHO
(35) R = CH_2OH
(36) R = Me



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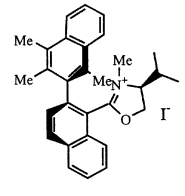

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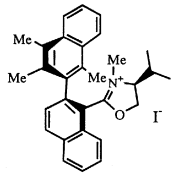

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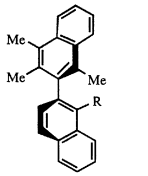
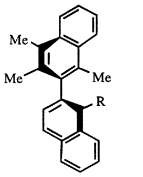
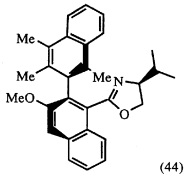


(40) R = CHO
(42) R = CH_2OH



(41) R = CHO
(43) R = CH_2OH



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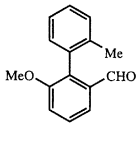

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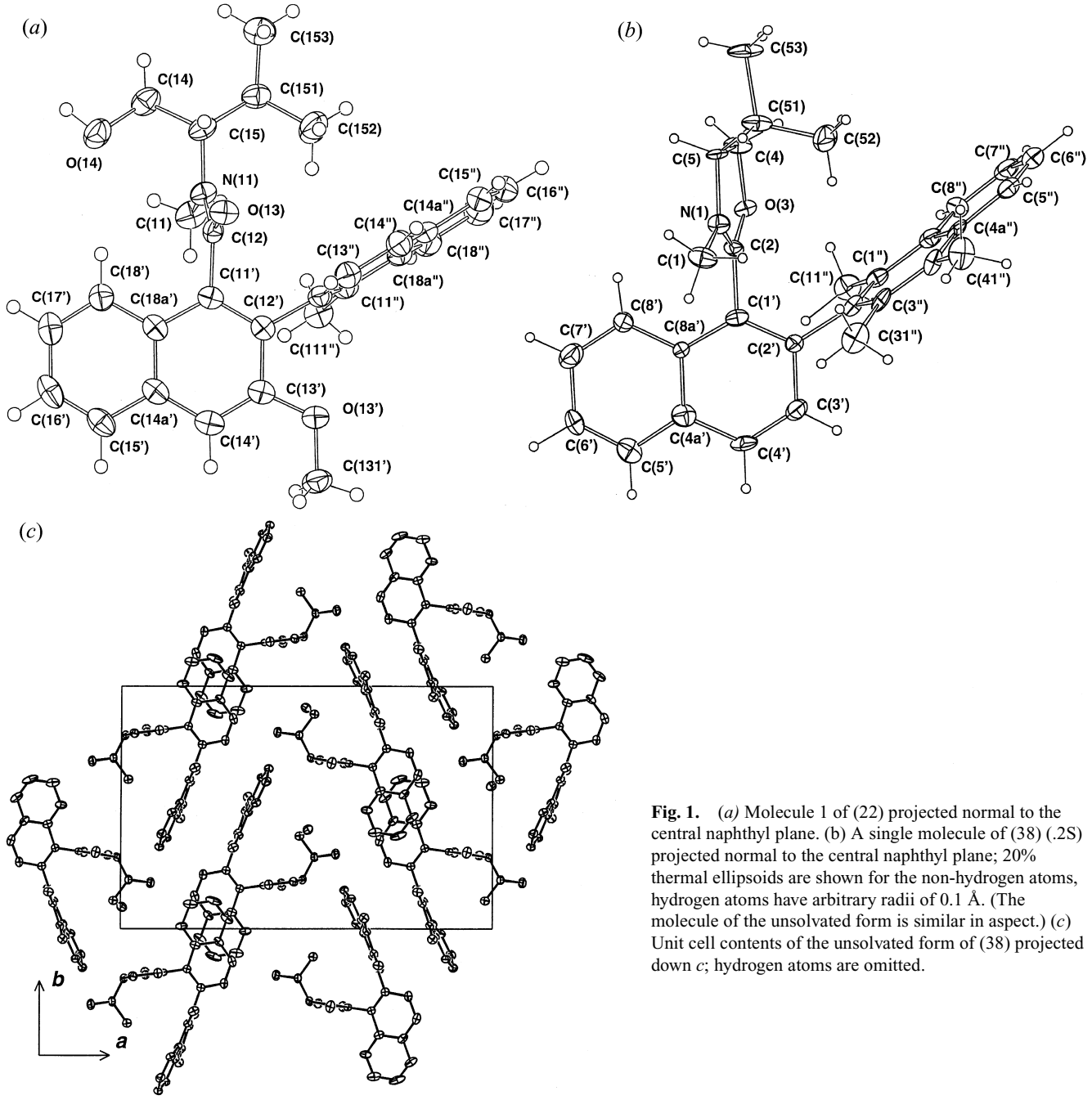


Fig. 1. (*a)* Molecule 1 of (22) projected normal to the central naphthyl plane. (b) A single molecule of (38) (.2S) projected normal to the central naphthyl plane; 20% thermal ellipsoids are shown for the non-hydrogen atoms, hydrogen atoms have arbitrary radii of 0.1 Å. (The molecule of the unsolvated form is similar in aspect.) (*c*) Unit cell contents of the unsolvated form of (38) projected down *c*; hydrogen atoms are omitted.

excess of the Grignard reagent generated in tetrahydrofuran (thf) was allowed to react with the oxazoline in thf at room temperature. This generally resulted in a high yield of the coupled product except for the cases of the binaphthalenes (28), (33), (37) and (44) when it was necessary to boil the reaction mixtures in order to achieve efficient coupling. In the case of the highly hindered compound (44) the yield was poor even under these conditions. In all cases except compounds (11) and (12) a moderate to good diastereomeric excess (d.e.) resulted and the magnitude of this excess was easily determined by integration of the ^{1}H n.m.r. spectra of the products.

In order to determine the absolute configuration of the major products of these coupling reactions one pure diastereomer secured from each series of reactions based on the oxazolines (4) and (5) was chosen for X-ray crystal structure determination. Thus, the diasteriomeric mixture of oxazolines resulting from the coupling of the Grignard reagent derived from the bromo compound (7) and the oxazoline (5) was converted by treatment with an excess of iodomethane in nitromethane at 50° into the derived methiodides. Hydrolysis of these compounds was achieved by treatment with aqueous potassium hydroxide with methanol and thf as cosolvents at 60°. Radial chromatography of the resultant mixture of amides allowed the major diastereomer to be isolated in a pure state. An X-ray crystal structure determination on this compound revealed that its axial configuration was *S* as shown in Fig. 1*a* and structure (22). The c.d. spectrum of this compound (Fig. 2) reveals the presence of a bisignate couplet

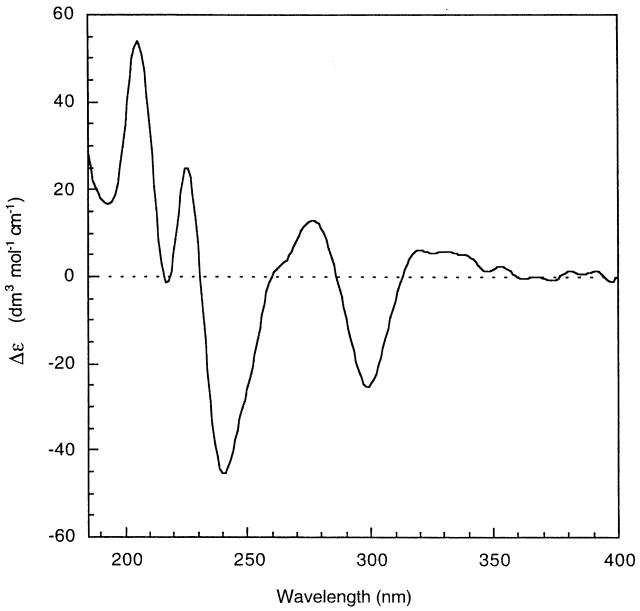


Fig. 2. C.d. spectrum of compound (22).

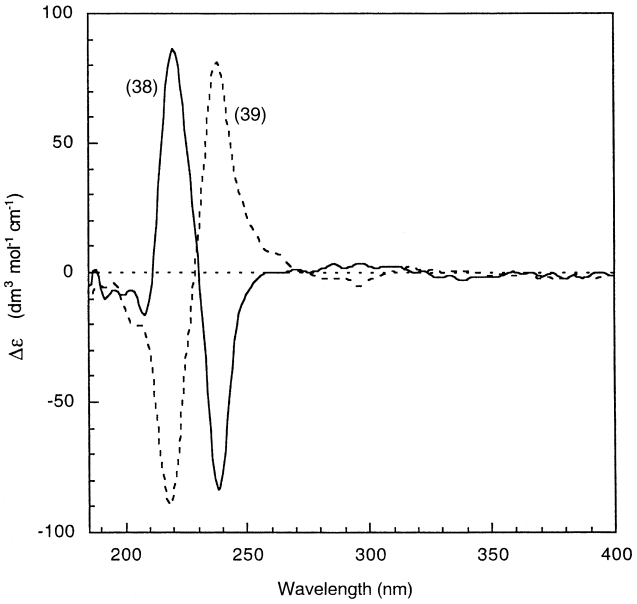


Fig. 3. C.d. spectra of the diastereomeric methiodides (38) and (39).

centred at 230 nm with ΣΔε 68. The X-ray crystal structure of the amide shows that the dihedral angles between the naphthalene planes of the two independent molecules of the asymmetric unit are 85.06(8) and 77.39(8)° (torsion angles C(1′)–C(2′)–C(2′′)–C(3′′) 81.8(4) and 78.0(4)°) so that even in solution there is likely to be little electron delocalization between the two naphthalene chromophores. The centre of the bisignate couplet is near the wavelength of the naphthalene ^1B_b transition band for which the direction of the electron transition dipole moment is along the long axis of the naphthalene ring[10] and, given the magnitude of ΣΔε, the requirements for exciton chirality are met. The longer wavelength extremum of the couplet for compound (22) is negative and that at shorter wavelength is positive, so that the electron transition dipole moments exhibit left-handed screwness (negative exciton chirality),[10] in keeping with the *S*-axial configuration. Hence, the major diastereomer (17) resulting from the coupling reaction also has the *S*-axial configuration and the c.d. spectrum of the mixture of oxazolines (73.3% d.e.) resulting from the coupling reaction also shows negative exciton chirality.

The diastereomeric mixture of oxazolines resulting from the coupling of the Grignard reagent derived from the bromo compound (6) and the oxazoline (4) was similarly converted into the methiodides (38) and (39). Fractional crystallization of this mixture allowed each diastereomer to be isolated in a pure state. X-Ray crystal structure determinations on the major diasteromeric salt (unsolvated and acetone-solvated forms, independently determined and internally consistent in their indications of absolute configuration), demonstrated that its axial configuration was *R* as shown in Fig. 1*b* and structure (38). The c.d. spectra of the *R* (38) and *S* (39) methiodides are shown in Fig. 3. The spectra are mirror images of each other and each shows a bisignate couplet near 230 nm with ΣΔε *c.* 160. The X-ray crystal structures of the methiodide shows that the dihedral angles between the naphthalene planes are 68.5(2) (unsolvated form) and 88.5(5)° (solvated form) (torsion angles C(1′)–C(2′)–C(2′′)–C(3′′) 108.2(6) and 88(2)°, respectively), so that the conditions for exciton chirality are again met. The longer wavelength extremum of the couplet for compound (38) is negative and that at shorter wavelength is positive, constituting negative exciton chirality in keeping with the *R*-axial configuration, the Cahn–Ingold–Prelog priorities of the fiducial atoms having changed from compound (22) to compound (38) on account of the 3-methoxy group in compound (22).

Separate reduction of the methiodides (38) and (39) with sodium borohydride followed by acidic cleavage of the intermediate oxazolidines[33] yielded the enantiomeric aldehydes (40) and (41). On reduction of these aldehydes with sodium borohydride the enantiomeric alcohols (42) and (43) were obtained. The aldehyde (40) did not undergo racemization during 54 h in boiling tetrachloroethene (394 K), so that compounds (40)–(43) are presumably enantiomerically pure. This was shown to be the case since the ^1H n.m.r. spectrum of the Mosher ester prepared from the alcohol (42) showed that its enantiomeric excess (e.e.) was 98.7%. Their c.d. spectra also exhibit exciton chirality and the spectra of the aldehydes (40) and (41) are shown in Fig. 4.

Determination of the c.d. spectra of the other diastereomeric mixtures of the 2,2′-binaphthalenes resulting from the coupling reactions showed that the major diastereomers produced, (13), (24), (33) and (44), all had the *S*-axial configuration except compound (38), which had the *R*-axial configuration. The absolute configurations of the derivatives prepared from these compounds were congruent with those of their parents. In general, the diastereomeric mixtures of oxazolines resulting from coupling were converted into the methiodides and these were reduced to the

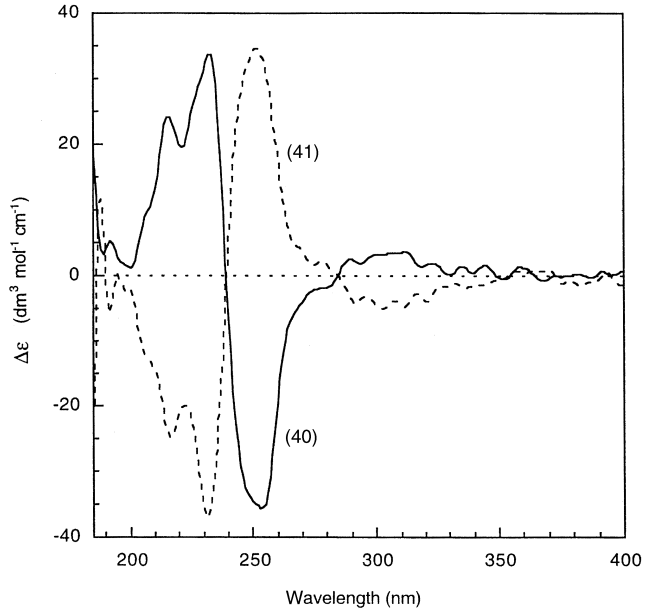
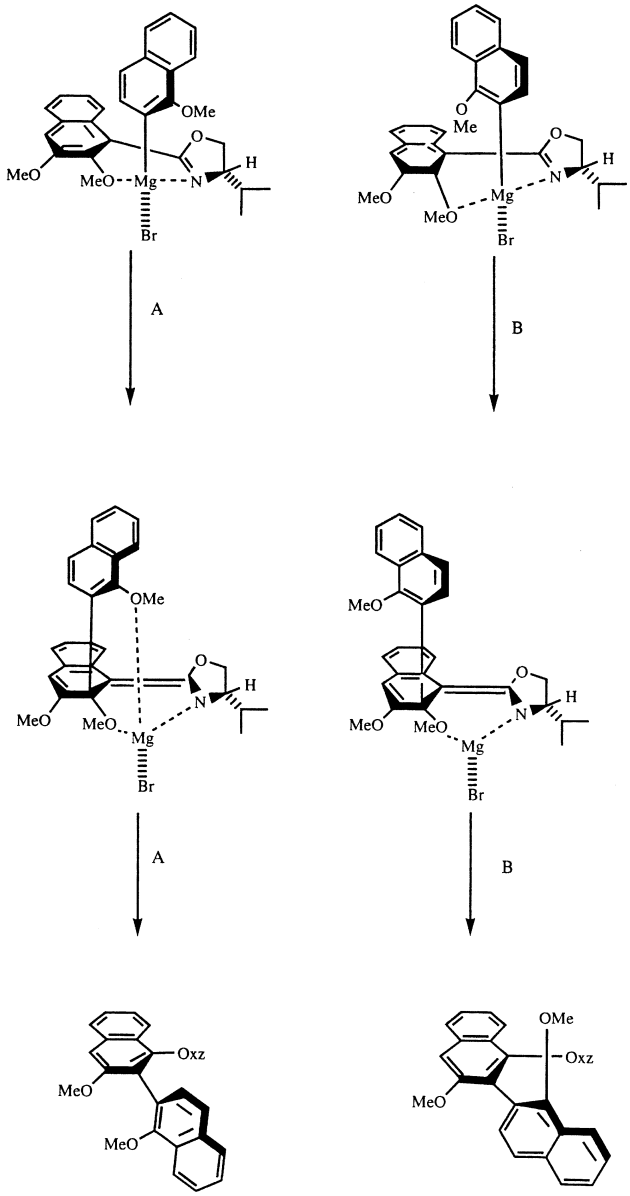


Fig. 4. C.d. spectra of the enantiomeric aldehydes (40) and (41).

oxazolidines with sodium borohydride prior to hydrolysis to the aldehydes. Thus, for example, the mixture of oxazolines rich in the diastereomer (17) gave the aldehyde (18) which was reduced to the alcohol (19). The e.e. of the alcohol was determined to be 57.7% from its ^{1}H n.m.r. spectrum determined in the presence of europium(III) tris[3-(heptafluoropropylhydroxymethylene)-(+)-camphorate] (see Experimental section). Some racemization had thus occurred during the reduction process since the d.e. of the starting oxazoline was 73.3%. The alcohol (19) was converted into its mesylate and this on reduction with lithium aluminium hydride afforded the methyl compound (20). The aldehyde (18) was also converted via the derived oxime into the nitrile (21). Hydrolysis of the mixture of methiodides provided the amide (22) (see above) which was isolated in enantiopure form by chromatography. Further hydrolysis of this compound supplied the amide (23).

The methiodides derived from the mixture of oxazolines enriched in the diastereomer (13) on heating in nitromethane at 50° underwent an asymmetric transformation of the first kind (see later) and the predominant diastereomer (14) present at equilibrium proved to have the *R*-axial configuration. Fractional crystallization allowed the separation of this diastereomer in a pure state and thus the preparation of the aldehyde (15). Reduction of the aldehyde (15) provided the alcohol (16) and integration of the ^{1}H n.m.r. spectrum of this compound determined in the presence of (+)-(*S*)-1-(anthracen-9-yl)-2,2,2-trifluoroethanol showed the e.e. to be 91.7%, so that little racemization had occurred during these transformations.

Fractional crystallization of the mixture of oxazolines enriched in the diastereomer (28) allowed this isomer to be obtained in a pure state. It was converted sequentially into the methiodide (29), the aldehyde (30), the alcohol (31) and finally the methyl compound (32). All these compounds are



Scheme 1. Stereochemistry of the coupling reaction.

assumed to be enantiomerically pure since, in the presence of the anthracenyl shift reagent, the ^{1}H n.m.r. spectrum of the (*R*)-alcohol (31) showed no signals for the enantiomeric alcohol which were present in a sample prepared from the diastereomeric mixture of methiodides.

Little racemization also occurred during the conversion of the oxazoline (33) into the alcohol (35). The d.e. of the starting oxazoline was 37.0% and the e.e. of the alcohol obtained was 35.5% as shown by the ^{1}H n.m.r. spectra of the derived Mosher esters (see Experimental section).

It is pertinent to comment here on the stereochemical outcome of the coupling reactions. In Scheme 1 is depicted the course of the reaction between the Grignard reagent derived from the bromonaphthalene (6) and the oxazoline (5). It is known that the isopropyl substituents on oxazolines such as (5) control the direction of attack of the Grignard reagent[18] so that it would attack from the face of the

Table 2. Free energy barriers and rates of inversion for compounds (13) and (14)

Cpd	$k_{S\rightarrow R}$ (s^{-1})	$k_{R\rightarrow S}$ (s^{-1})	$\Delta G^{\ddagger}$ (kJ mol^{-1})	T (K)	Solvent
(13)	$(4.03 \pm 0.25)10^{-6}$	$(2.46 \pm 0.15)10^{-6}$	115.3 ± 0.2	334	$CHCl_3$
(14)	$(1.33 \pm 0.05)10^{-5}$	$(1.02 \pm 0.04)10^{-5}$	108.0 ± 0.1	323	$MeNO_2$

oxazoline remote from the isopropyl group as depicted in Scheme 1 in both paths A and B. The rotamer that leads to the σ-complex in which the methoxy group of the Grignard reagent is chelated to the magnesium would be expected to be preferred, path A rather than path B, and it is seen that this leads to the product with *S*-axial configuration as observed (56.8% d.e.). When the Grignard reagent derived from the bromo compound (7) is used in which the chelating methoxy group of compound (6) is replaced by a non-chelating methyl group, the d.e. is higher (73.3%) but the stereochemical outcome is still a preference for the *S*-axial configuration, so that path A is preferred. The pathway involves less steric interaction between the methyl group and the naphthalene ring of the oxazoline so that steric effects are more important than chelation. The d.e. falls again with increased methyl substitution so that with the Grignard reagent derived from 2-bromo-1,3-dimethylnaphthalene (8) it is 37.0% but still with a preference for the *S*-axial configuration. This implies that the steric demand of a methyl group at the α-position of a naphthalene is greater than that of a methyl group at the β-position, probably on account of the steric interaction between the α-methyl group and the hydrogen at the *peri*-position. A similar analysis accounts for the stereoselectivity in the formation of the oxazoline (28).

The free energy barriers to internal rotation in the oxazolines (11) and (12) were estimated from their variable-temperature ^{1}H n.m.r. spectra by measuring the coalescence temperature[34] of an aromatic signal in the case of compound (11) and of a methyl signal in that of compound (12). For compound (11) in ($^2H_8$)toluene at 276 ± 2 K, the rate constant was 57 s^{-1}, which gave $\Delta G^{\ddagger}$ = 58.1 ± 0.6 kJ mol^{-1}. For compound (12) in ($^2H_4$)methanol at 276 ± 2 K the rate constant was 172 s^{-1}, which gave $\Delta G^{\ddagger}$ = 55.6 ± 0.6 kJ mol^{-1}. The free energy barriers are similar, as expected since the internal rotation leading to the lower energy transition state for compound (12) would be that where a methoxy passes a hydrogen on one side and the oxazoline entity passes a hydrogen on the other side, which of necessity is the pathway for that for compound (11).

It was observed that the mixture of oxazolines enriched in the diastereomer (13) underwent an asymmetric transformation of the first kind on boiling in chloroform. By starting with material of d.e. 51.2%, in favour of the (*S*)-diastereomer (13), the d.e. at equilibrium was found to be 24.2% in favour of the (*R*)-diastereomer. The rates of inversion and the free energy barrier for this reversible first-order reaction are shown in Table 2 and were determined by integration of the methyl doublets at δ_H 0.69 and 0.72 for the (*S*)-diastereomer and at δ_H 0.61 and 0.64 for the (*R*)-diastereomer in their ^{1}H n.m.r. spectra at 200 MHz. When this mixture of oxazolines of d.e. 51.2% was converted into the methiodides by treatment with an excess of iodomethane at 323 K it was found that the reaction was complete after *c.* 3 h and the d.e. of the product had fallen to 40.5% in favour of the (*S*)-diastereomer. When methiodides of d.e. 45.6% in favour of the (*R*)-diastereomer (14) were heated in nitromethane at 323 K the d.e. at equilibrium was found to be 13.5% in favour of (14). The rates of inversion and the free energy barriers are shown in Table 2 and they were determined in a similar manner to those for the oxazolines by integration of the methyl doublets at δ_H –0.08 ((*S*)-diastereomer) and 0.08 ((*R*)-diastereomer).

The rates of racemization and the free energy barriers to internal rotation for compounds (15), (16), (18), (21), (23), (25) and (30) are shown in Table 3. These were determined by polarimetry[35] at 394 K in tetrachloroethene except for compound (15) where chloroform at 298 K was the solvent. It is known[36,37] that the ability of a group at a position *ortho* to the biaryl linkage to inhibit racemization depends on its size, and a good measure of this is the effective van der Waal's radius of the group.[37] The data in Table 3 are in keeping with previous results and clearly show that a methyl group (radius 1.80 ± 0.03 Å) is more effective than a methoxy group (radius 1.52 ± 0.03 Å) at inhibiting rotation. Comparison of the free energy for compound (18) with its biphenyl analogue (45)[35] ($\Delta G^{\ddagger}$ 125.3 kJ mol^{-1} at 383 K) shows that the barrier in the binaphthalene is slightly higher. Compounds (19), (34) and (40) did not racemize at 394 K. Comparison of (30) and (40) demonstrates the effect of buttressing of a methyl group remote from the biaryl linkage.

Table 3. Free energy barriers and rates of racemization for 2,2′-binaphthalenes determined in tetrachloroethene at 394 K

Cpd	k (s^{-1})	$\Delta G^{\ddagger}$ (kJ mol^{-1})
(15)[A]	$(1.15 \pm 0.04)10^{-5}$	101.2 ± 0.1
(16)	$(5.33 \pm 0.18)10^{-5}$	129.6 ± 0.1
(18)	$(1.61 \pm 0.05)10^{-5}$	133.6 ± 0.1
(21)	$(4.04 \pm 0.21)10^{-5}$	130.6 ± 0.2
(23)	$(1.45 \pm 0.05)10^{-5}$	133.9 ± 0.1
(25)	$(1.28 \pm 0.12)10^{-5}$	134.3 ± 0.3
(30)	$(9.32 \pm 0.70)10^{-7}$	142.9 ± 0.2

[A] Determined in $CHCl_3$ at 298 K.

Experimental

Unless stated otherwise reactions were worked up by dilution with water and extracted with ethyl acetate, followed by washing with water and with saturated brine and then drying over anhydrous sodium or magnesium sulfate. Flash chromatography was performed on BDH silica gel (40–63 μm) and radial chromatography was performed on a Harrison Research Chromatotron by using plates coated with Merck Kieselgel 60 PF_{254}. Melting points were recorded on a Kofler hot-stage

apparatus. Optical rotations were measured for solutions in chloroform on a Perkin–Elmer 141 polarimeter with a 10 cm micro cell. Electronic spectra were determined for solutions in methanol by using a GBC 918 u.v./visible spectrophotometer. C.d. spectra were recorded for solutions in acetonitrile with a JASCO J-710 spectropolarimeter. ^{1}H, ^{19}F and ^{13}C n.m.r. spectra were recorded for solutions in deuteriochloroform, unless stated otherwise, on a Bruker ARX-500 instrument. Variable-temperature ^{1}H n.m.r. spectra were recorded on a Bruker ARX-500 instrument and the data in Table 2 were obtained by using a Gemini 200 instrument. Mass spectra were recorded with a VG Autospec spectrometer at 70 eV. The data recorded in Table 3 were determined by the method of Meyers and Himmelsbach.[35] The errors represent the 90% confidence limit from the least-squares analysis.

(–)-(4S)-4-Isopropyl-2-(2-methoxynaphthalen-1-yl)-4,5-dihydrooxazole (4)

A mixture of 2-methoxy-1-naphthoic acid (8.5 g, 48 mmol), oxalyl chloride (8.0 ml, 95 mmol) and 3 drops of dimethylformamide were stirred in anhydrous dichloromethane for 18 h under argon. The solvent and excess oxalyl chloride were removed under reduced pressure and the residue was dissolved in dichloromethane (40 ml) and added dropwise to a stirred solution of triethylamine (7.6 ml, 55 mmol) and (*S*)-valinol (4.76 g, 47 mmol) in dichloromethane (110 ml) at 0º under argon. The solution was stirred at room temperature for 18 h. The solution was cooled to 0º and water was added. Work-up of the organic layer in the usual way gave the crude hydroxy amide which was dissolved in dichloromethane (100 ml) and benzene (80 ml). The solution was stirred and cooled to 0º and thionyl chloride (13.0 ml, 182 mmol) was added dropwise and the solution was next stirred under argon at room temperature for 18 h. The solvents and excess thionyl chloride were removed under reduced pressure and ether and 5% aqueous sodium hydroxide were added. The usual work-up gave a crude product to which was added acetonitrile (100 ml), water (10 ml) and potassium carbonate (15 g) and the whole was heated under reflux for 24 h. The cooled mixture was filtered and the acetonitrile was removed under reduced pressure. The crude product was isolated by extraction with ether and was purified by flash chromatography with 10–30% ethyl acetate/light petroleum as eluent. The *oxazoline* (4) (7.7 g, 60%) was obtained as a viscous oil (Found: C, 75.3, H, 6.9; N, 5.0%; $M^{+\bullet}$, 269.1407. $C_{17}H_{19}NO_2$ requires C, 75.8; H, 7.1; N, 5.2%. $^{12}C_{17}{}^{1}H_{19}{}^{14}N^{16}O_2$ requires $M^{+\bullet}$, 269.1416). $[\alpha]_D^{23}$ –40.0º (*c*, 3.4). δ_H 1.05 and 1.11, each d, *J* 6.8 Hz, CH(C**H**$_3$)$_2$; 1.98, m, **H**CMe$_2$; 3.88, s, OMe; 4.21, dd, $J_{5,5} = J_{5,4}$ = 8.1 Hz, CH**H**5; 4.29, ddd, *J* 6.8, $J_{4,5}$ 8.1, $J_{4,5}$ 9.6 Hz, H4; 4.49, dd, $J_{5,5}$ 8.1, $J_{5,4}$ 9.6 Hz, C**H**H5; 7.20, d, $J_{3,4}$ 9.1 Hz, H3; 7.33, m, H6 or 7; 7.48, m, H7 or 6; 7.74, d, *J* 8.2 Hz, H5 or 8; 7.83, d, $J_{4,3}$ 9.1 Hz, H4; 7.89, dd, *J* 0.7, *J* 8.5 Hz, H8 or 5. δ_C 18.13 and 18.59, each Me; 32.44, H**C**Me$_2$; 56.33, OMe; 69.71, C5; 72.77, C4; 112.28, CAr; 112.69, 123.59, 123.79, 127.05 and 127.67, each CHAr; 128.23, CAr; 131.39, CHAr; 132.29, CAr; 155.43, ArC2; 161.05, C2. *m/z* 269 (M^+, 59%), 227 (58), 226 (100), 198 (30), 185 (22), 184 (12), 183 (32), 182 (22), 171 (48), 169 (14), 141 (11), 140 (20), 127 (12), 114 (15).

1-Bromo-2,3-dimethoxynaphthalene

A solution of *N*-bromosuccinimide (15.0 g, 84 mmol) in anhydrous dimethylformamide (100 ml) was added dropwise to a stirred solution of 2,3-dimethoxynaphthalene (16.0 g, 85 mmol) in anhydrous dimethylformamide (100 ml) at room temperature, and the solution was stirred for a further 24 h. The mixture was poured into saturated brine (500 ml) and extracted with dichloromethane. The crude product was chromatographed over a short column of silica gel with 5% ethyl acetate/light petroleum as eluent. The *bromo compound* crystallized from light petroleum as prisms (17.3 g, 77%), m.p. 46–48° (Found: $M^{+\bullet}$, 265.9931. $^{12}C_{12}{}^{1}H_{11}{}^{79}Br^{16}O_2$ requires $M^{+\bullet}$, 265.9942). δ_H 3.98, s, 2 × OMe; 7.14, s, H4; 7.42–7.47, m, H6,7; 7.68–7.77, m, H5; 8.15–8.17, m, H8. δ_C 55.76, 3-OMe; 60.61, 2-OMe; 106.77, C4; 116.23, C1; 125.01, 125.91, 126.52, 126.64, C5,6,7,8; 127.68 and 131.41, C4a,8a; 147.02, 152.28, C2,3. *m/z* 268 (M^+, 97%), 267 (13), 266 (M^+, 100), 253 (11), 251 (11), 225 (25), 223 (28), 210 (11), 208 (12), 182 (13), 180 (13), 172 (31), 157 (10), 144 (14), 127 (17), 126 (13), 115 (11), 113 (12), 101 (23).

2,3-Dimethoxynaphthalene-1-carboxylic Acid

The Grignard reagent was prepared from the foregoing bromo compound (15.9 g, 59.6 mmol), anhydrous thf (120 ml) and magnesium (1.5 g, 62 matom) in the usual way. The cooled solution was poured cautiously on to solid carbon dioxide (500 g) and the whole was stirred for 12 h. An excess of dilute hydrochloric acid was added and the crude product was isolated by extraction with ether. Further purification was effected by extraction into dilute aqueous sodium hydroxide in the usual way. The crude product crystallized from ethyl acetate as prisms (12.0 g, 87%), m.p. 150–152° (lit.[24] 153–155º).

(–)-(4S)-4-Isopropyl-2-(2,3-dimethoxynaphthalen-1-yl)-4,5-dihydroxazole (5)

This was prepared from the foregoing carboxylic acid in a manner similar to that described for compound (4). It was obtained as a viscous oil (86%) (Found: $M^{+\bullet}$, 299.1520. $^{12}C_{18}{}^{1}H_{21}{}^{14}N^{16}O_3$ requires $M^{+\bullet}$ 299.1521). $[\alpha]_D^{25}$ –33.4° (*c*, 2.5). δ_H 1.04 and 1.10, each d, *J* 6.8 Hz, CH(C**H**$_3$)$_2$; 1.96, m, **H**CMe$_2$; 3.89 and 3.96, each s, OMe; 4.22, dd, *J* 8.0, 9.0 Hz; C**H**H5; 4.27, ddd, *J* 6.8, 8.0, 9.4 Hz, CH4; 4.49, dd, *J* 8.0, 9.4 Hz, CH**H**5; 7.18, s, H4; 7.35, m, 2 × ArH; 7.36, m, 2 × ArH; 7.66, m, ArH; 7.85, m, ArH. δ_C 18.20 and 18.55, each Me; 32.48, H**C**Me$_2$; 55.41, 3-OMe; 61.57, 2-OMe; 69.63, C5; 72.88, C4; 108.89, CHAr; 119.62, CAr; 124.21, 124.48, 125.26 and 126.36, each CHAr; 126.83 and 130.78, each CAr; 141.81 and 151.42, C2,3; 160.70, C2. *m/z* 299 (M^+, 76%), 298 (12), 270 (18), 257 (35), 256 (100), 228 (14), 215 (28), 214 (16), 213 (47), 212 (33), 201 (52), 199 (18), 198 (27), 171 (10), 170 (15), 127 (19), 115 (13).

General Method for Coupling of Grignard Reagents with Oxazolines

The Grignard reagent was generated from the bromo compound (25.4 mmol) and magnesium (25.5 matom) in anhydrous thf (40 ml) under argon. The reaction was completed by heating the solution under reflux for 3 h. The cooled Grignard reagent was then added dropwise at room temperature to a stirred solution of the oxazoline (15 mmol) in thf (40 ml) under argon and the solution was stirred for 18 h and then poured into saturated aqueous ammonium chloride. The crude product was isolated by extraction with ethyl acetate and purified by flash chromatography with ethyl acetate/light petroleum as eluent.

General Method for Methylation of Oxazolines

Iodomethane (1.6 ml, 25 mmol), the oxazoline (10 mmol) and nitromethane (40 ml) were stirred together at 50° (bath) for 24 h, whereupon the solvents were removed under reduced pressure. The residue was dissolved in dichloromethane and washed with aqueous sodium thiosulfate solution. The usual work-up gave the crude oxazoline.

General Method for Conversion of N-Methyloxazolinium Iodides into 2,2′-Binaphthalene-1-carbaldehydes

The methiodide (5 mmol) was dissolved in thf/methanol (4 : 1 v/v, 25 ml) and stirred under argon and cooled to 0°. A solution of sodium borohydride (12.5 mmol) in thf/methanol (4 : 1 v/v, 15 ml) was added dropwise and stirring was continued at 0° for 2 h. Saturated aqueous ammonium chloride and ether were added and the mixture was worked up in the usual way. A solution of the crude product in thf/water (4 : 1 v/v, 15 ml) was stirred and treated with oxalic acid dihydrate (6.5 mmol) during 3 h. The usual work-up gave the crude product, which was purified by flash chromatography over silica gel with ethyl acetate/light petroleum as eluent.

General Method for Conversion of 2,2′-Binaphthalene-1-carbaldehydes into 2,2′-Binaphthalene-1-methanols

A solution of sodium borohydride (3 mmol) in aqueous sodium hydroxide (5%, 10 ml) was added at 0° to a stirred solution of the aldehyde (2 mmol) in thf (10 ml). The solution was stirred at room

temperature for 2 h and then diluted with water and extracted with ether. The crude product was purified by radial chromatography with ethyl acetate/light petroleum as eluent.

General Method for Conversion of 2,2′-Binaphthalene-1-methanols into 1-Methyl-2,2′-binaphthalenes

A solution of methanesulfonyl chloride (3.5 mmol) in anhydrous dichloromethane (4 ml) was added dropwise under argon to a stirred solution of the alcohol (0.5 mmol) and triethylamine (5 drops) in dichloromethane (4 ml). The solution was diluted with dichloromethane and washed in turn with dilute sodium hydroxide, dilute hydrochloric acid, water and saturated brine. The crude product was dissolved in anhydrous thf (4 ml) and added to lithium aluminium hydride (1.3 mmol) in thf (4 ml) at 0°. The solution was stirred at room temperature for 18 h and then diluted with ethyl acetate and treated with dilute hydrochloric acid. The usual work-up gave the crude product, which was purified by radial chromatography with ethyl acetate/light petroleum as eluent.

(4S)-4-Isopropyl-2-(3-methoxy-2,2′-binaphthalen-1-yl)-4,5-dihydrooxazole (11)

This was prepared from 2-bromonaphthalene and the oxazoline (5). Flash chromatography of the crude product over silica gel with 5–25% ethyl acetate/light petroleum as eluent gave the *binaphthalene* (11) (95%) as 1 : 1 mixture of diastereomers, which crystallized from ethyl acetate/light petroleum as prisms, m.p. 143–145º (Found: $M^{+\bullet}$, 395.1881. $^{12}C_{27}{}^{1}H_{25}{}^{14}N^{16}O_2$ requires $M^{+\bullet}$, 395.1885). $[\alpha]_D{}^{32}$ –20.9° (*c*, 5.6). *m/z* 395 (M^+, 78%), 394 (100), 352 (33), 295 (19), 252 (12). δ_H (($^2H_8$)toluene, 233 K) 0.49, 0.54, 0.72 and 0.89, each d, *J* 6.7 Hz, CH(C**H**$_3$)$_2$; 1.25 and 1.35, each m, C**H**Me$_2$; 3.15, br m, oxazoline H; 3.17 and 3.18, each s, OMe; 3.38, m, oxazoline H; 3.51–3.63, m, 4 × oxazoline H; 6.927 and 6.933, each s, ArH; 7.24–7.28, m, 4 × ArH; 7.36–7.40, m, 4 × ArH; 7.60–7.69, m, 8 × ArH; 7.73–7.77, m, 2 × ArH; 7.97 and 8.02, each s, ArH; 8.39–8.41, m, ArH; 8.47, br d, *J* 7.6 Hz, ArH. δ_C (300 K) 18.52, 2 × Me; 32.39, **C**HMe$_2$; 55.73, OMe; 70.26, C5; 73.14, C4; 107.37, 124.67, 125.31, 125.76, 125.82, 126.63 and 126.72, each CHAr; 126.73, 2 × CAr; 126.87, CAr; 127.57, 128.02, 128.50 and 128.74, each CHAr, 132.60, 132.84, 133.97, and 134.08, each CAr; 154.80, C3; 162.20, C2. One CHAr was not located.

(4S)-Isopropyl-2-(1′-methoxy-2,2′-binaphthalen-1-yl)-4,5-dihydrooxazole (12)

This was prepared as a 1 : 1 mixture of diastereomers from 2-bromo-1-methoxynaphthalene (6) and the oxazoline (4). Flash chromatography of the crude product over silica gel with 5–20% ethyl acetate/light petroleum as eluent gave the *binaphthalene* (12) (91%) as a gum which slowly decomposed on standing (Found: $M^{+\bullet}$+1, 396.1949. $^{12}C_{27}{}^{1}H_{26}{}^{14}N^{16}O_2$ requires $M^{+\bullet}$+1, 396.1964). $[\alpha]_D{}^{20}$ –38.3º (*c*, 0.76). δ_H (($^2H_4$)methanol, 223 K) 0.51, 0.67, 0.717 and 0.722, each d, *J* 6.5 Hz, CH(C**H**$_3$)$_2$; 1.43 and 1.51, each m, **H**CMe$_2$; 3.43 and 3.51, each s, OMe; 3.80–3.95, 4.02, 4.22 and 4.39, each m, oxazoline H; 7.43, d, *J* 8.4 Hz, ArH; 7.50, d, *J* 8.4 Hz, ArH; 7.52–7.63, m, 10 × ArH; 7.65, d, *J* 8.5 Hz, ArH; 6.90, d, *J* 5.0 Hz, ArH; 7.88–7.91, m, 2 × ArH; 7.96, d, *J* 7.8 Hz, 2 × ArH; 7.99, d, *J* 8.5 Hz, ArH; 8.02, d, *J* 8.5 Hz, ArH; 8.09, d, *J* 8.2 Hz, ArH; 8.12, d, *J* 8.3 Hz, ArH; 8.15–8.17, m, ArH; 8.18–8.21, m, ArH. δ_C (300 K) 18.68 and 19.06, each Me; 32.67, H**C**Me$_2$; 61.33, OMe; 70.32, C5; 73.36, C4; 122.50, 122.83, 125.51 and 125.90, each ArH; 126.03, CAr; 126.22, 2 × CHAr; 127.00, 127.70 and 128.01, each CHAr; 128.33, CAr; 128.58 and 128.86, each CHAr; 129.16, CAr; 129.41, CHAr; 131.66, 132.48, 134.45 and 137.13, each CAr; 153.29, C1′; 162.63, C2.

(4S)-4-Isopropyl-2-(1′,3-dimethoxy-2,2′-binaphthalen-1-yl)-4,5-dihydrooxazole

This was prepared as a diastereomeric mixture from the oxazoline (5) and 2-bromo-1-methoxynaphthalene (6) and it was obtained by flash chromatography with 5–10% ethyl acetate/light petroleum as eluent as a solid (91%, 56.8% d.e.) which crystallized from dichloromethane/light petroleum as needles of the *oxazoline*, m.p. 113–115° (Found: C, 79.3; H, 6.4; N, 3.1%. $M^{+\bullet}$, 425.1985. $C_{28}H_{27}NO_3$ requires C, 79.0; H, 6.4; N, 3.3%. $^{12}C_{28}{}^{1}H_{27}{}^{14}N^{16}O_3$ requires $M^{+\bullet}$, 425.1991). $[\alpha]_D{}^{29}$ –93.5° (*c*, 2.5). λ_{max} 234.5, 322, 333.5 nm (log ε 5.09, 3.91, 3.94). C.d. λ_{max} nm/Δε 205.5 (+6), 223 (+15), 240 (–23), 280 (+5), 302 (–9), 336.5 (+3). λ_{min} nm/Δε 214.5 (+4.5). *m/z* 395 (M^+, 30%), 394 (100), 326 (20), 293 (10), 149 (38).

The major (*S*)-diastereometer (13) had δ_H 0.74 and 0.78, each d, *J* 6.7 Hz, CH(C**H**$_3$)$_2$; 1.46, m, C**H**Me$_2$; 3.72, dd, *J* 8.3, 8.3 Hz, C**H**H5, 3.73 and 3.87 each, s, OMe; 3.92, ddd, *J* 6.7, 8.3, 9.7 Hz, H4; 4.21, dd, *J* 8.3, 9.7, CH**H**5; 7.38, s, H4; 7.46–7.49, ArH; 7.49, d, $J_{3',4'}$ 8.4 Hz, H3′; 7.52–7.57, m, 3 × ArH; 7.68, d, $J_{4',3'}$ 8.4 Hz, H4′; 7.86, dd, *J* 0.7, 8.1 Hz, H5 or 8; 7.92, m, H5′ or 8′; 8.07, br d, *J* 8.1 Hz, H8 or 5; 8.29, m, H8′ or 5′. δ_C 18.49 and 18.89, each Me; 32.49, **C**HMe$_2$; 55.74, 3-OMe; 61.20, 1′-OMe; 70.24, C5; 73.20, C4; 107.28, ArC4; 122.33 and 122.53, each CHAr; 124.37, CAr; 124.49, 125.40, 125.44, 125.90, 126.56 and 126.66, each CHAr; 126.84, CAr; 127.70, CHAr; 127.83 and 128.54, each CAr; 129.61, CHAr; 130.24, 134.09 and 134.59, each CAr; 153.91 and 155.07, each COMe; 161.92, C2.

The n.m.r. spectrum of minor (*R*)-diastereomer included δ_H 0.67 and 0.69, each d, *J* 6.7 Hz, CH(C**H**$_3$)$_2$; 1.40, m, C**H**Me$_2$; 3.79, s, OMe; 3.82, dd, *J* 8.3, 8.3 Hz; C**H**H5; 3.87, s, OMe; 4.15, dd, *J* 8.3, 9.7, CH**H**5; 7.37, s, H4, 7.44, d, $J_{3',4'}$ 8.4, H3′; 7.67, d, $J_{4',3'}$ 8.4 Hz; 8.02, br d, *J* 8.3 Hz, ArH. δ_C 18.26 and 18.47, each Me, 32.31, **C**HMe$_2$; 55.77, 3-OMe; 61.11, 1′-OMe; 69.97, C5; 73.00, C4; 107.13, ArC4; 122.44 and 122.57, each CHAr; 124.38, CAr; 124.49, 125.24, 125.47, 125.90, 126.56 and 126.66; each CHAr; 126.84. CAr; 127.64, CHAr; 127.83 and 128.63, each CAr; 129.00 CHAr; 130.40, 134.09 and 134.61, each CAr; 154.09 and 155.13, each COMe; 161.89, C2.

(4S)-4-Isopropyl-2-(1′,3-dimethoxy-2,2′-binaphthalen-1-yl)-3-methyl-4,5-dihydrooxazolium Iodide

The foregoing mixture of oxazolines was methylated at 50º for 28 h, which gave the crude methiode as a solid (95%). Fractional crystallization of the mixture from acetone/dichloromethane gave the major *(R)-diastereomer* (14) as clusters of needles, m.p. 172–174° (Found: $M^{+\bullet}$, 567.1289. $^{12}C_{29}{}^{1}H_{30}{}^{127}I^{14}N^{16}O_3$ requires $M^{+\bullet}$, 567.1270). $[\alpha]_D{}^{26}$ +85.2° (*c*, 2.2). λ_{max} 227, 338.5 nm (log ε 4.98, 3.85). C.d. λ_{max} nm/Δε 215.5 (–67), 229 (+55). *m/z* 567 (M^+, 57%), 441 (17), 440 (52), 342 (25), 341 (100), 340 (46), 327 (13), 326 (52), 311 (18), 310 (28), 255 (12), 239 (11), 226 (12), 128 (23), 127 (24). δ_H 0.04 and 0.66, each d, *J* 6.6 Hz, CH(C**H**$_3$)$_2$; 2.11, m, **C**HMe$_2$; 3.32, s, Me; 3.63 and 3.88, each s, OMe; 4.01, br m, H4; 5.33 and 5.85, each br m, H$_2$C5; 7.21, br d, *J* 8.4 Hz, ArH; 7.26–760, m, 4 × ArH; 7.66–7.69, m, 2 × ArH; 7.87–7.93, m, 2 × ArH; 8.00–8.01, br m, ArH, 8.27, br m, ArH. δ_C 13.23 and 17.67, each Me; 25.81, **C**HMe$_2$; 34.21, 3-Me; 56.01, 3-OMe; 61.69, 1′-OMe; 68.37, C4; 72.84, C5, 111.07, CHAr, 119.20, CAr; 122.08, CHAr; 122.59 and 123.50, CAr; 124.06, 124.82, 126.55, 127.11 and 127.36, CHAr; 127.64, CAr; 127.75, 127.98, 128.09 and 128.29, CHAr; 130.73, 133.78 and 134.98, each CAr, 153.35 and 154.23, COMe; 173.12, C2.

The n.m.r. spectrum of the minor (*S*)-diastereomer included δ_H –0.10 and 0.45, each d, *J* 6.9 Hz, CH(C**H**$_3$)$_2$; 1.84, m, C**H**Me$_2$; 3.01, s, Me, 3.48 and 3.93, each s, OMe; 4.59, m, H4; 5.51, m, **H**HC5; 5.67, dd, *J* 9.5, 10.8 Hz, H**H**C5.

(+)-(R)-1′,3-Dimethoxy-2,2′-binaphthalene-1-carbaldehyde (15)

Reduction of the (*R*)-diastereomer (14) at 0° and work-up at 5º gave a crude product which was rapidly purified by radial chromatography over silica gel with 1–10% ethyl acetate/light petroleum as eluent. The *aldehyde* (15) was obtained as a solid (50%), a portion of which crystallized from acetone as prisms, m.p. 154–156° (Found: C, 80.8; H, 5.1%. $M^{+\bullet}$, 342.1253. $C_{23}H_{18}O_3$ requires C, 80.7; H, 5.3%. $^{12}C_{23}{}^{1}H_{18}{}^{16}O_3$ requires $M^{+\bullet}$, 342.1256). $[\alpha]_D{}^{25}$ +182.7° (*c*, 2.0). *m/z* 342 (M^+, 35%), 312 (27), 311 (100), 296 (11), 268 (22), 239 (12), 113 (10). δ_H 3.57 and 3.91, each s, OMe; 7.37, d, $J_{3',4'}$ 8.4 Hz, H3′; 7.53, s, H4, 7.56–7.60, m, H6,6′,7,7′; 7.72, d, $J_{4',3'}$ 8.4 Hz, H4; 7.86–7.88, 7.92–7.94 and 8.22–8.24, each 1 × ArH; 9.19–9.21, m, H8; 10.11, s, CHO. δ_C 55.92, 3-OMe; 61.09, 1′-OMe; 111.72, CHAr; 122.13, CAr;

122.60 and 123.24, each CHAr; 125.72, CAr; 125.80, 126.32, 126.58, 126.77, 126.89 and 127.19, each CHAr; 127.81, CAr; 127.96 and 129.15, each CHAr, 130.24, 134.41, 134.94 and 137.05, each CAr; 154.28 and 154.63, each COMe; 194.50, CHO.

(+)-(R)-1,3′-Dimethoxy-2,2′-binaphthalene-1-methanol (16)

Reduction of the foregoing aldehyde (15), $[\alpha]_D^{28}$ +170.2° (*c*, 2.0), gave, after radial chromatography of the crude product over silica gel with 2–20% ethyl acetate/light petroleum as eluent, the *alcohol* (16) (92%, 91.7% e.e) as a solid, which precipitated from ethyl acetate/light petroleum in amorphous form, m.p. 133–135° (Found: $M^{+\bullet}$, 344.1407. $^{12}C_{23}{}^{1}H_{20}{}^{16}O_3$ requires $M^{+\bullet}$, 344.1412). $[\alpha]_D^{25}$ +71.0° (*c*, 2.1). λ_{max} 234.5, 320.5, 332 nm (log ε 5.03, 3.62, 3.65). C.d. λ_{max} nm/Δε 205.5 (–22), 221 (–57), 237 (+45), 276 (–6), 295.5 (+17). λ_{min} nm/Δε 211 (–21). *m/z* 344 (M^+, 81%), 328 (13), 313 (29), 312 (100), 311 (52), 298 (11), 297 (21), 269 (35), 295 (17), 284 (11), 282 (17), 281 (57), 269 (20), 268 (31), 255 (14), 253 (22), 252 (31), 241 (10), 240 (11), 239 (32), 226 (14), 159 (10), 158 (79), 156 (13), 149 (19), 148 (15), 134 (23), 126 (22), 120 (13), 119 (23), 113 (13). δ_H 3.54 and 3.88, each s, OMe, 4.49 and 5.00, each d, *J* 12.1 Hz, C**H**$_2$OH; 7.31, s, H4; 7.35, d, $J_{3',4'}$ 8.4 Hz, H3′; 7.50–7.53, m, H7; 7.54–7.59, m, H6,6′,7′; 7.73, d, $J_{4',3'}$ 8.4 Hz, H4′; 7.86–7.88, m, H5; 7.93–7.95, m, H5′; 8.22–8.24, m, H8′; 8.33, br d, *J* 8.2 Hz, H8. δ_C 55.57, 3-OMe; 60.39, CH_2; 61.33, 1′-OMe; 106.01, 122.33, 123.61, 124.54 and 124.91, each CHAr; 125.90, CAr; 126.18, 126.45, 126.57 and 127.11, each CHAr; 127.74, CAr; 127.91, CHAr; 127.96 and 128.07, each CAr; 129.62, CHAr; 134.50, 134.70 and 136.63, each CAr; 153.30 and 155.09, each COMe.

The e.e. was estimated by ^{1}H n.m.r. spectroscopy in $CDCl_3$ in presence of 1.24 mol equiv. of (+)-(*S*)-1-(anthracen-9-yl)-2,2,2-trifluoroethanol. The major enantiomer had δ_H 3.47 and 3.87, each s, OMe; 4.43 and 4.94, each d, *J* 12.2 Hz, C**H**$_2$OH; 7.30, s, H4, 7.32, d, $J_{3',4'}$ 8.4 Hz, H3′; 7.40–7.59, m, 4 × ArH; 7.71, d, $J_{4',3'}$ 8.4 Hz, H4′; 7.86, dd, *J* 8.6, 8.1 Hz, H5; 7.92–7.95, m, H5′; 8.12–8.21, m, H8′; 8.24, d, *J* 8.4 Hz, H8. The n.m.r. spectrum of minor enantiomer included δ_H 3.52 and 3.87, each s, OMe.

(4S)-4-Isopropyl-2-(3-methoxy-1′-methyl-2,2′-binaphthalen-1-yl)-4,5-dihydrooxazole

This was prepared as a mixture of diastereomers from the oxazoline (5) and 2-bromo-1-methylnaphthalene (7) and it was purified by flash chromatography over silica gel with 1–20% ethyl acetate/light petroleum as eluent. The *oxazoline* was obtained as a solid (92%, 73.3% d.e.) which precipitated from acetone/light petroleum in amorphous form, m.p. 122–125° (Found: $M^{+\bullet}$, 409.2045. $^{12}C_{28}{}^{1}H_{27}{}^{14}N^{16}O_2$ requires M^+, 409.2042). $[\alpha]_D^{33}$ –44.6° (*c*, 4.3) λ_{max} 233.5, 319, 332 nm (log ε 5.08, 3.69, 3.78). C.d. λ_{max}/Δε 205.5 (+4), 222 (+15), 236.5 (–18), 269.5 (+1), 280.5 (+2), 302 (–5). λ_{min} nm/Δε 210 (+3), 273 (+0.8). *m/z* 409 (M^+, 36%), 395 (11), 394 (37), 297 (24), 296 (100), 265 (13), 253 (11), 158 (15), 149 (17), 114 (28).

The major (*S*)-diastereomer (17) had δ_H 0.65 and 0.73, each d, *J* 6.7 Hz, HC(C**H**$_3$)$_2$; 1.38, m, C**H**Me$_2$; 2.43, s, Me; 3.56, dd, *J* 8.5, 8.5 Hz, C**H**H5; 3.83, s, OMe; 3.86, ddd, *J* 6.7, 8.5, 9.7 Hz, H4; 4.05, dd, *J* 8.5, 9.7 Hz, CH**H**5; 7.33, br s, H4; 7.40, d, $J_{3',4'}$ 8.4 Hz, H3′; 7.43, m, ArH; 7.49–7.57, m, 3 × ArH; 7.73, d, $J_{4',3'}$ 8.4 Hz, H4′; 7.83, br d, *J* 8.2 Hz, ArH; 7.88, br d, *J* 8.0 Hz, ArH, 7.96, br d, *J* 8.4 Hz, ArH; 8.10, br d, *J* 8.5 Hz, ArH. δ_C 16.08, 18.29 and 18.82, each Me; 32.23, **C**HMe$_2$; 55.63, OMe; 69.98, C5; 72.93, C4; 106.99, 124.32, 124.60 and 124.97, each CHAr; 125.21, 2 × CHAr; 125.56, 126.55 and 126.69, each CHAr; 126.76 and 128.24, each CAr; 128.37 and 128.59, each CHAr; 132.45, 132.89, 132.98, 133.24, 133.34 and 133.99, each CAr; 154.92, COMe; 162.12, C2.

The minor (*R*)-diastereomer had δ_H 0.56 and 0.57, each d, *J* 6.7 Hz, CH(C**H**$_3$)$_2$; 1.16, m, C**H**Me$_2$; 2.45, s, Me; 3.64, dd, *J* 8.5, 8.5 Hz, C**H**H5; 3.84, s, OMe. The ^{13}C n.m.r. spectrum included δ_C 16.10, 18.22 and 18.45, each Me, 32.30, **C**HMe$_2$; 55.63, OMe, 70.05, C5; 72.85, C4; 107.15, 124.94, 125.59, 128.07 and 128.28, each CHAr; 128.33, 133.00 and 133.93, each CAr; 154.90, COMe; 162.06, C2.

(–)-(S)-3-Methoxy-1′-methyl-2,2′-binaphthalene-1-carbaldehyde (18)

The foregoing mixture of diastereomers was converted into the methiodide (96%) and a portion of this was reduced to the *aldehyde* (18) (55%) which was purified by radial chromatography with 1–10% ethyl acetate/light petroleum as eluent and which crystallized from ethyl acetate as prisms, m.p. 190–192° (Found: $M^{+\bullet}$, 326.1296. $^{12}C_{23}{}^{1}H_{18}{}^{16}O_2$ requires $M^{+\bullet}$, 326.1307). $[\alpha]_D^{25}$ –29.5° (*c*, 2.0). λ_{max} 229.5, 269, 354 nm (log ε 5.19, 4.56, 4.04). C.d. λ_{max} nm/Δε 218 (+12.5), 231 (–13.5). *m/z* 326 (M^+, 94%), 312 (23), 311 (100), 268 (26), 267 (14), 266 (11), 265 (27), 253 (11), 252 (21), 239 (17), 154 (14), 149 (18), 134 (13), 126 (20), 119 (14). δ_H 2.45, s, Me; 3.87, s, OMe; 7.34, d, *J* 8.4 Hz, H3′; 7.51, s, H4; 7.57–7.64, m, H6,6′,7,7′; 7.82, d, $J_{4',3'}$ 8.4 Hz, H4′; 7.85–7.87, m, ArH; 7.94, br d, *J* 8.0 Hz, ArH; 8.13, br d, *J* 8.6 Hz, ArH; 9.19–9.21, m, ArH; 10.01, s, CHO. δ_C 16.26, Me; 55.88, OMe; 111.70 and 124.33, each CHAr; 125.68, CAr; 125.69, 125.77, 125.97, 126.46, 126.67, 126.93, 127.13, 128.37 and 128.64, each CHAr; 130.40, 130.58, 132.46, 133.17, 133.40, 134.28 and 141.21, each CAr; 154.59, COMe; 194.40, CHO.

(–)-(S)-3-Methoxy-1′-methyl-2,2′-binaphthalene-1-methanol (19)

The foregoing aldehyde (18) was reduced to the *alcohol* (19) (87%, 57.7% e.e) which was purified by radial chromatography with 5–30% ethyl acetate/light petroleum as eluent and which crystallized from dichloromethane/light petroleum as prisms, m.p. 163–166° (Found: $M^{+\bullet}$, 328.1460. $^{12}C_{23}{}^{1}H_{20}{}^{16}O_2$ requires $M^{+\bullet}$, 328.1463). $[\alpha]_D^{20}$ –29.2° (*c*, 2.0). λ_{max} 234.5, 317, 331 nm (log ε 5.39, 3.89, 3.97). C.d. λ_{max}/Δε 222.5 (+44), 238 (–44.5). *m/z* 328 (M^+, 80), 311 (100), 309 (16), 295 (29), 281 (12), 279 (27), 278 (17), 267 (16), 266 (13), 265 (30), 253 (19), 252 (38), 239 (12), 148 (14), 133 (18), 126 (19), 120 (15). δ_H 2.42, s, Me; 3.83, s, OMe; 4.72 and 4.86, each d, *J* 11.7 Hz, C**H**$_2$OH; 7.28, s, H4; 7.31, d, $J_{3',4'}$ 8.3 Hz, H3′; 7.50, m, ArH; 7.54–7.63, m, 3 × ArH; 7.81, d, $J_{4',3'}$ 8.3 Hz, H4′; 7.88, br d, *J* 8.1 Hz, ArH; 7.94, br d, *J* 8.5 Hz, ArH; 8.14, br d, *J* 8.1 Hz, ArH; 8.26, br d, *J* 8.1 Hz, ArH. δ_C 15.97, Me; 55.60, OMe, 59.52, CH_2; 105.88, 124.35, 124.42, 124.56, 125.49, 125.81, 126.07, 126.32, 127.27, 128.12 and 128.57, each CHAr; 127.56, CAr; 132.66, 2 × CAr; 132.97, 133.12, 133.40, 134.56 and 135.08, each CAr; 155.21, COMe.

The e.e. was estimated by ^{1}H n.m.r. spectroscopy in $CDCl_3$ in the presence of 0.36 mol equiv. of europium(III) tris[3-(hepta-fluoropropylhydroxymethylene)-(+)-camphorate]. The major enantiomer had δ_H 3.14, s, Me; 4.20, s, OMe; 7.46–7.60, m, 3 × ArH; 7.67–7.70, m, ArH; 7.85, s, H4; 7.92, d, *J* 8.2 Hz, ArH; 8.04, d, *J* 8.4 Hz, ArH; 8.23, d, *J* 7.8 Hz, m, ArH; 8.29, d, *J* 8.6 Hz, ArH; 8.71, d, *J* 7.9 Hz, ArH; 9.03–9.16, br m, C**H**$_2$OH; 10.68, br s, ArH. The n.m.r. spectrum of the minor enantiomer included δ_H 4.19, s, OMe; 8.54, d, *J* 8.0 Hz, ArH; 10.88, br s, ArH.

(–)-(S)-1,1′-Dimethyl-3-methoxy-2,2′-binaphthalene (20)

This was prepared from the foregoing alcohol and was purified by radial chromatography with 1–5% ethyl acetate/light petroleum as eluent. The *binaphthalene* (20) (85%) was obtained as a solid which crystallized from acetone as prisms, m.p. 168–170° (Found: $M^{+\bullet}$, 312.1504. $^{12}C_{23}{}^{1}H_{20}{}^{16}O$ requires $M^{+\bullet}$, 312.1514). $[\alpha]_D^{28}$ –46.4° (*c*, 2.7). λ_{max} 236, 281, 317, 331 nm (log ε 5.01, 4.12, 3.34, 3.40). C.d. λ_{max} nm/Δε 222 (+58.5), 237 (–42), 296 (–9.5). *m/z* 312 (M^+, 100), 297 (31), 282 (22), 281 (19), 266 (16), 265 (25), 253 (12), 252 (15), 149 (17), 141 (16), 132 (11), 126 (20). δ_H 2.36 and 2.41, each s, Me; 3.82, s, OMe; 7.17, s, H4; 7.29, d, *J* 8.3 Hz, ArH; 7.44–7.61, m, 4 × ArH; 7.81, d, *J* 8.3 Hz, ArH; 7.85, d, *J* 8.0 Hz, ArH; 7.93, d, *J* 8.0 Hz, ArH; 8.04, d, *J* 8.3 Hz, ArH; 8.14, d, *J* 8.4 Hz, ArH. δ_C 15.57 and 15.96, each Me; 55.48, OMe; 103.52 and 123.66, each CHAr; 124.41, 2 × CHAr; 125.25, 125.67, 125.79, 125.99 and 127.20, each CHAr; 128.36, CAr; 128.50 and 128.54, each CHAr; 132.09, 132.43, 132.80, 132.86, 133.74, 134.04 and 134.86, each CAr; 155.66, COMe.

(–)-(S)-3-Methoxy-1′-methyl-2,2′-binaphthalene-1-carbonitrile (21)

Hydroxylamine hydrochloride (180 mg, 2.6 mmol) and the aldehyde (18) (600 mg, 1.84 mmol) in pyridine (4.5 ml) and water (0.5 ml) were stirred at room temperature for 1.5 h and then copper(II) sulfate pentahydrate (150 mg, 0.6 mmol) was added. The mixture was sequentially treated with solutions of triethylamine (0.6 ml, 4.3 mmol) in dichloromethane (1 ml) and dicyclohexylcarbodiimide (510 mg, 2.5 mmol) in dichloromethane (3 ml) and the whole was stirred for

17 h. Formic acid (5 drops) was added and the dicyclohexylurea was separated by filtration. The filtrate was diluted with dichloromethane and washed in turn with dilute hydrochloric acid, saturated aqueous sodium hydrogen carbonate, water and saturated brine. Radial chromatography of the crude product with 10–50% ethyl acetate/light petroleum as eluent gave the *nitrile* (21) as a solid (570 mg, 96%) which crystallized from acetone as prisms, m.p. 210–212° (Found: C, 85.7; H, 5.2; N, 4.1%. $M^{+\bullet}$, 323.1299. $C_{23}H_{17}NO$ requires C, 85.4; H, 5.3; N, 4.3%. $^{12}C_{23}{}^{1}H_{17}{}^{14}N^{16}O$ requires $M^{+\bullet}$, 323.1310). $[\alpha]_D^{20}$ –67.6° (*c*, 2.0). λ_{max} 228, 251, 346 nm (log ε 4.86, 4.65, 3.94). C.d. $\lambda_{max}/\Delta\varepsilon$ 202 (+14.5), 216.5 (+27.5), 233 (–19), 246.5 (–14.5), 285.5 (+4). $\lambda_{min}/\Delta\varepsilon$ 209 (+10.5), 239 (–11). *m/z* 323 (M^+,100), 322 (39), 307 (11), 293 (20), 292 (10), 291 (11) 290 (13), 280 (10), 146 (13). δ_H 2.51, s, Me; 3.88, s, OMe; 7.38, d, $J_{3',4'}$ 8.4 Hz, H3′; 7.49, s, H4; 7.55–7.64, m, H6,6′7,7′; 7.86, d, $J_{4',3'}$ 8.4 Hz, H4′; 7.91, br d, *J* 8.3 Hz, ArH; 7.93, br d, *J* 8.6 Hz, ArH; 8.15, d, *J* 8.4 Hz, ArH; 8.26, br d, *J* 8.0 Hz, ArH. δ_C 16.03, Me, 55.94, OMe; 110.52, C4; 112.08, C1; 116.39, CN; 124.55, 125.55, 126.01, 126.19, 126.22, 126.25, 127.14, 127.25 and 127.75, each CHAr; 127.89, CAr; 128.63, CHAr; 131.40, 132.67, 133.08, 133.50, 133.62 and 139.70, each CAr; 154.83, COMe.

(–)-(S,1S)-N-[2-Hydroxy-1-(isopropyl)ethyl]-3-methoxy-1′,N-dimethyl-2,2′-binaphthalene-1-carboxamide (22)

The foregoing methiodides (2.0 g, 3.6 mmol) and potassium hydroxide (2.0 g, 35.6 mmol) were stirred and heated at 60° (bath) in methanol/thf/water (1 : 4 : 1 v/v, 30 ml). The cooled mixture was acidified with dilute hydrochloric acid and extracted with ethyl acetate and the crude product was subjected to radial chromatography with 5–50% ethyl acetate/light petroleum as eluent. A mixture of diastereomeric amides (*S* : *R*, 2.1 : 1) (428 mg, 27%) was eluted first and this was followed by the *(*S,*1*S*)-diastereomer* (22) (554 mg, 35%) which crystallized from acetone/chloroform/light petroleum as plates, m.p. 184–186° (Found: C, 78.4; H, 7.5; N, 2.9%. $M^{+\bullet}$, 441.2316. $C_{29}H_{31}NO_3$ requires C, 78.9; H, 7.1; N, 3.1%. $^{12}C_{29}{}^{1}H_{31}{}^{14}N^{16}O_3$ requires $M^{+\bullet}$, 441.2304). $[\alpha]_D^{32}$ –79.9° (*c*, 2.3). λ_{max} 234.5, 319, 333.5 nm (log ε 4.91, 3.52, 3.59). λ_{infl} 221, 247 nm (log ε 4.60, 4.63). C.d. λ_{max} nm/$\Delta\varepsilon$ 203 (+50), 222 (+22), 238.5 (–46), 275.5 (+12), 298.5 (–24.5), 312 (+6.5). λ_{min} nm/$\Delta\varepsilon$ 217 (+3). *m/z* 441 (M^+, 12%), 356 (14), 325 (100), 324 (23), 310 (18), 265 (11), 252 (10), 149 (41). δ_H –0.29 and 0.71, each d, *J* 6.6 Hz, CH(C**H**$_3$)$_2$; 1.51, m, C**H**Me$_2$; 2.50, s, Me; 2.53, s, NMe; 3.50, dd, *J* 9.8, 11.6 Hz, C**H**OH; 3.76, dd, *J* 3.5, 11.6 Hz, CH**H**OH; 3.84, s, OMe; 4.04, m, CHN; 7.27, s, H4; 7.40, m, ArH; 7.48–7.56, m, 3 × ArH; 7.58, d, $J_{3',4'}$ 8.4 Hz; H3′; 7.76, d, *J* 8.4 Hz, ArH; 7.84, m, 2 × ArH; 8.00, d, *J* 8.4 Hz, ArH; 8.06, d, *J* 8.4 Hz, ArH. δ_C 16.37, 18.00 and 19.72, each Me; 26.04, **C**HMe$_2$; 31.69, NMe; 55.60, OMe; 61.63, CH$_2$; 61.94, CHN; 105.62, 123.94 and 125.01, each CHAr; 125.06, CAr; 125.40, 125.47, 125.72, 125.94, 126.70, 126.82 and 128.48, each CHAr; 128.58, CAr; 129.18, CHAr; 131.94, 132.36, 132.65, 133.21, 134.29 and 136.45, each CAr; 155.17, COMe; 171.38, CO.

(–)-(S)-3-Methoxy-1′,N-dimethyl-2,2′-binaphthalene-1-carboxamide (23)

A solution of the (*S*)-carboxamide (22) (300 mg, 0.68 mmol) in thf (6 ml) and water (35 µl) was stirred under reflux with potassium t-butoxide (640 mg, 5.7 mmol) for 31 h. The cooled mixture was acidified with dilute hydrochloric acid and extracted with dichloromethane. The crude product was purified by radial chromatography with 5–40% ethyl acetate/light petroleum as eluent, which gave the *amide* (23) (180 mg, 75%) as a foam (Found: $M^{+\bullet}$, 355.1571. $^{12}C_{24}{}^{1}H_{21}{}^{14}N^{16}O_2$ requires $M^{+\bullet}$, 355.1572). $[\alpha]_D^{33}$ –76.9° (*c*, 1.9). λ_{max} 234.5, 318, 332 nm (log ε 5.09, 3.68, 3.74). C.d. λ_{max} nm/$\Delta\varepsilon$ 222 (+75.5), 237 (–50.5), 278 (+4), 298 (–10). *m/z* 355 (M^+, 72%), 340 (17), 325 (47), 324 (100), 310 (12), 297 (24), 296 (22), 282 (10), 281 (16), 266 (10), 265 (26), 253 (23), 252 (27), 239 (13), 149 (28), 126 (22). δ_H 2.46, s, Me; 2.52, d, *J* 4.9 Hz, NMe; 3.82, s, OMe; 5.46, br q, *J* 4.9 Hz, NH; 7.28, s, H4; 7.33, d, $J_{3',4'}$ H3′; 7.41–7.44, m, ArH, 7.50–7.58, m, 3 × ArH; 7.75, d, $J_{4',3'}$ 8.4 Hz, H4′; 7.83, d, *J* 8.1 Hz, ArH; 7.88, br d, *J* 8.2 Hz, ArH; 7.93, d, *J* 8.4 Hz, ArH; 8.10, d, *J* 8.4 Hz, ArH. δ_C 16.17, Me; 26.24, NMe; 55.67, OMe; 106.39, 124.42, 124.68, 125.41, 125.49, 125.71, 125.88, 126.68; 126.74; 127.81 and 128.49, each CHAr; 129.98, 132.43, 132.55, 132.75, 132.96, 134.17 and 136.34, each CAr; 154.87, COMe; 168.91, CO. One CAr was not located.

(4S)-4-Isopropyl-2-(3-methoxy-1′,4′-dimethyl-2,2′-binaphthalen-1-yl)-4,5-dihydroxazole

This diastereomeric mixture of *oxazolines* was prepared from 2-bromo-1,4-dimethylnaphthalene (9) and the oxazoline (5) and was obtained by flash chromatography with 5–30% ethyl acetate/light petroleum as eluent as a gum (96%, 56.6% d.e.) (Found: $M^{+\bullet}$, 423.2194. $^{12}C_{29}{}^{1}H_{29}{}^{14}N^{16}O_2$ requires $M^{+\bullet}$, 423.2198). $[\alpha]_D^{31}$ –20.6° (*c*, 2.0). λ_{max} 238.5, 277, 316.5, 322 nm (log ε 5.02, 4.17, 3.75, 3.76). λ_{infl} 226 nm (log ε 4.91). C.d. $\lambda_{max}/\Delta\varepsilon$ 224.5 (+32), 241 (–26), 282.5 (+4), 302.5 (–7). $\lambda_{infl}/\Delta\varepsilon$ 210 (+11). *m/z* 423 (M^+, 24%), 409 (12), 408 (37), 311 (25), 310 (100), 295 (14), 252 (11), 114 (24).

The (*S*)-diastereomer (24) had δ_H 0.65 and 0.74, each d, *J* 6.8 Hz, CH(C**H**$_3$)$_2$; 1.30, m, C**H**Me$_2$; 2.42 and 2.68, each s, Me; 3.49, dd, *J* 8.4, 8.4 Hz, C**H**H5; 3.84, s, OMe; 3.91, ddd, *J* 6.8, 8.4, 9.7 Hz, H4; 4.09, dd, *J* 8.4, 9.7 Hz, CH**H**5; 7.28 and 7.33, each s, ArH; 7.42–7.45 and 7.50–7.53, each m, ArH; 7.56–7.58, m, 2 × ArH; 7.83, dd, *J* 0.5, 8.2 Hz, ArH; 7.97, dd, *J* 8.3 Hz, ArH; 8.04–8.06 and 8.12–8.14, each m, ArH. δ_C 16.03 and 18.39, CH(**C**H$_3$)$_2$; 18.78 and 19.22, each MeAr; 32.37, **C**HMe$_2$; 55.70, OMe; 70.10, C5; 73.04, C4; 107.09, 124.51, 124.59, 124.89 and 125.03, each CHAr; 125.21, 2 × CHAr; 126.52 and 126.69, each CHAr; 126.84, CAr; 129.28, CHAr; 130.77, 131.09, 132.25, 132.55, 132.59, 133.34 and 133.99, each CAr; 154.97, COMe; 162.12, C2. One CAr was not located.

The n.m.r. spectra of the (*R*)-diastereomer included δ_H 0.56 and 0.58, each d, *J* 6.8 Hz, CH(C**H**$_3$)$_2$; 1.18, m, C**H**Me$_2$; 2.44 and 2.70, each s, Me; 3.66, dd, *J* 8.4, 8.4 Hz, C**H**H5; 3.85, s, OMe; 4.06, dd, *J* 8.4, 9.7 Hz, CH**H**5. δ_C 16.08 and 18.26, CH(**C**H$_3$)$_2$; 18.46 and 19.19, each MeAr; 55.70, OMe; 70.13, C5; 72.97, C4; 106.97, 124.39, 124.56, 125.17, 125.23 and 128.74, each CHAr.

(–)-(S)-3-Methoxy-1′,4′-dimethyl-2,2′-binaphthalene-1-carbaldehyde (25)

The foregoing diastereomeric mixture of oxazolines was methylated (98%). Reduction of the methiodide and hydrolysis gave the *aldehyde* (25) as a solid (57%) which crystallized from dichloromethane/light petroleum as needles, m.p. 220–223° (Found: C, 84.8; H, 5.9%. $M^{+\bullet}$, 340.1459. $C_{24}H_{20}O_2$ requires C, 84.7; H, 5.9%. $^{12}C_{24}{}^{1}H_{20}{}^{16}O_2$ requires $M^{+\bullet}$, 340.1463). $[\alpha]_D^{30}$ –7.0° (*c*, 2.3). λ_{max} 232, 269, 355 nm (log ε 5.26, 4.69, 4.20). *m/z* 340 (M^+, 92%), 326 (26), 325 (100), 311 (13), 310 (13), 282 (24), 265 (25), 252 (24), 162 (27), 149 (30), 141 (29), 132 (18), 127 (20), 126 (37), 125 (20), 119 (20), 111 (26). δ_H 2.43 and 2.73, each s, Me; 3.88, s, OMe; 7.20, s, H3′; 7.51, s, H4; 7.58–7.64, m, 4 × ArH; 7.87–7.89, m, ArH, 8.10–8.16, m, 2 × ArH; 9.19–9.21, m, ArH; 10.02, s, CHO. δ_C 16.16 and 19.36, each Me; 55.90, OMe; 111.64, 124.77, 124.86 and 125.68, each CHAr; 125.69, CAr; 125.76, 126.08, 126.63, 126.91, 127.07, 129.08, each CHAr; 130.18, 130.36, 131.47, 131.80, 132.47, 132.56, 134.23 and 141.44, each CAr; 154.63, COMe; 194.59, CHO.

(–)-(S)-3-Methoxy-1′,4′-dimethyl-2,2′-binaphthalene-1-methanol (26)

Reduction of the aldehyde (25) gave, after radial chromatography with 5–20% ethyl acetate/light petroleum as eluent, the *alcohol* (26) as a solid (93%, 58.0% e.e) which precipitated from light petroleum/ethyl acetate in amorphous form, m.p. 150–152° (Found: $M^{+\bullet}$, 342.1610. $^{12}C_{24}{}^{1}H_{22}{}^{16}O_2$ requires $M^{+\bullet}$, 342.1620). $[\alpha]_D^{33}$ –9.9° (*c*, 2.0). λ_{max} 238.5, 278, 331 nm (log ε 5.14, 4.23, 3.71). C.d. λ_{max} nm/$\Delta\varepsilon$ 232.5 (+47), 241 (–36), 274.5 (+2.5), 298 (–7). *m/z* 342 (M^+, 25%), 326 (21), 325 (30), 311 (16), 310 (33), 309 (100), 295 (11), 294 (18), 293 (11), 281 (24), 279 (13), 278 (20), 277 (11), 276 (11), 266 (25), 265 (35), 263 (11), 252 (18), 154 (13), 147 (11), 139 (10), 133 (15), 132 (18), 131 (10), 126 (13). δ_H 2.39 and 2.73, each s, Me; 3.83, s, OMe; 4.74 and 4.86, each d, *J* 11.8 Hz, C**H**$_2$OH; 7.16, s, H3′; 7.27, s, H4; 7.42–7.68, m, H6,6′,7,7′; 7.87, br d, *J* 8.1 Hz, ArH; 8.09–8.15, m, 2 × ArH; 8.26, br d, *J* 8.0 Hz, ArH. δ_C 15.88 and 19.44, each Me; 55.60, OMe, 59.61, CH$_2$; 105.88, 124.39,

124.59, 124.71, 124.90, 125.31, 125.71, 126.28 and 127.26, each CHAr; 127.61, CAr; 128.76, CHAr; 130.72, 131.75, 132.28, 132.80, 133.06, 133.27, 134.56 and 135.13, each CAr; 155.31, COMe.

The e.e. was estimated by ^{1}H n.m.r. spectroscopy in $CDCl_3$ solution in presence of 1.27 mol equiv. of (+)-(*S*)-1-(anthracen-9-yl)-2,2,2-trifluoroethanol. For the (*R*)-diastereomer: δ_H 2.36 and 2.70, each s, Me; 3.81, s, OMe; 4.68 and 4.82, each d, *J* 11.8 Hz, C**H**$_2$OH; 7.10, s, H3′; 7.24, s, H4; 7.44–7.63, m, 4 × ArH; 7.85, d, *J* 8.2 Hz, ArH; 8.07–8.15, m, 2 × ArH; 8.20, d, *J* 8.3 Hz, ArH. The n.m.r. spectrum of the (*S*)-diastereomer included δ_H 2.35 and 2.70, each s, Me; 3.81, s, OMe; 4.70, d, *J* 11.6 Hz, C**H**HOH; 7.13, s, H3′; 7.25, s, H4.

(–)-(S)-3-Methoxy-1′,4′-dimethyl-2,2′-binaphthalene-1-carbonitrile (27)

Prepared from the aldehyde (25) by a manner similar to that employed for compound (21), it was purified by radial chromatography with 5% ethyl acetate/light petroleum as eluent, which gave the *nitrile* (27) (88%) as a solid which crystallized from ethyl acetate/light petroleum as needles, m.p. 236–238° (Found: $M^{+\bullet}$, 337.1461. $^{12}C_{24}{}^1H_{19}{}^{14}N^{16}O$ requires $M^{+\bullet}$, 337.1467). $[\alpha]_D{}^{30}$ –55.4° (*c*, 2.4). λ_{max} nm/Δε 229.5, 287, 346 nm (log ε 4.80, 3.96, 3.83). λ_{infl} 252 nm (log ε 4.55). C.d. λ_{max} nm/Δε 205.5 (+15), 220.5 (+34.5), 242.5 (–20), 293.5 (+7.5), 313 (–10). λ_{min}/Δε 211 (+13). *m/z* 337 (M^+, 100%), 336 (32), 322 (23), 321 (12), 307 (19), 306 (22), 290 (11), 153 (18), 139 (10). δ_H 2.47 and 2.74, each s, Me; 3.88, s, OMe; 7.22, s, H3′; 7.48, s, H4; 7.58–7.64, m, 4 × ArH; 7.89–7.91, 8.08–8.10, 8.15–8.17 and 8.24–8.26, each m, ArH. δ_C 15.96 and 19.43, each Me; 55.97, OMe; 110.45, CHAr; 112.03, C1; 116.44, CN; 124.74, 125.09, 125.24, 125.80, 125.81, 126.22, 127.12, 127.69 and 127.80, each CHAr; 127.89, 131.02, 131.09, 132.18, 132.77, 132.81, 133.56 and 139.86, each CAr; 154.87, COMe.

(4S)-4-Isopropyl-2-(1′,3′-dimethyl-2,2′-binaphthalen-1-yl)-4,5-dihydrooxazole

This diasteromeric mixture of oxazolines was prepared from 2-bromo-1,3-dimethylnaphthalene (8) and the oxazoline (4) in the usual way except that the reactants were stirred and heated under reflux for 60 h. Flash chromatography with 1–20% ethyl acetate/light petroleum as eluent gave the product as a solid (76%, 39.9% d.e.). The *(*R*)-diastereomer* (28) was separated by fractional crystallization from dichloromethane/light petroleum, the purity of fractions being monitored by ^{1}H n.m.r. spectroscopy, whereupon it was obtained as needles, m.p. 133–136° (Found: $M^{+\bullet}$, 393.2100. $^{12}C_{28}{}^1H_{27}{}^{14}N^{16}O$ requires $M^{+\bullet}$, 393.2093). $[\alpha]_D{}^{27}$ –195.4° (*c*, 1.0). λ_{max} 233.5, 275.5 nm (log ε 4.81, 3.78). C.d. λ_{max} nm/Δε 222 (+135), 234.5 (–137). *m/z* 393 (M^+, 31%), 378 (11), 281 (26), 280 (100), 279 (13), 266 (12), 265 (41), 149 (12), 114 (15). δ_H 0.62 and 0.68, each d, *J* 6.7 Hz, CH(C**H**$_3$)$_2$; 1.32, m, C**H**Me$_2$; 2.24 and 2.39, each s, Me; 3.63, dd, *J* 8.2, 8.2 Hz, C**H**H5; 3.89–3.95, m, H4; 4.04, dd, *J* 8.2, 9.6 Hz, CH**H**5; 7.33, d, $J_{3,4}$ 8.3 Hz, H3; 7.49–7.52, m, 2 × ArH; 7.61, br s, H4′; 7.56–7.63, m, 2 × ArH; 7.81–7.85, m, ArH; 7.95, br d, *J* 8.2 Hz, ArH; 8.01, d, *J* 8.5 Hz, ArH; 8.04–8.10, m, ArH; 8.12, br d, *J* 8.0 Hz, ArH. δ_C 16.52, 18.21, 18.49 and 21.71, each Me; 32.40, **C**HMe$_2$; 69.86, C5; 72.96, C4; 124.29 and 124.89, each CHAr; 125.37, 2 × CHAr; 125.47 and 126.10, each CHAr; 126.39, CAr; 127.11, 127.22, 127.61, 128.01 and 129.94, each CHAr; 131.00, 131.55 and 131.86, each CAr; 132.33, CAr; 133.14, 135.17, 138.44 and 139.50, each CAr; 162.46, C2.

The n.m.r. spectra of the minor (*S*)-diastereomer included δ_H 0.58 and 0.61, each d, *J* 6.7 Hz, CH(C**H**$_3$)$_2$; 1.25, m, C**H**Me$_2$; 2.20 and 2.42, each s, Me; 3.54, dd, *J* 8.4, 8.4 Hz, C**H**H5; 3.89–3.95, m, H4; 4.10, dd, *J* 8.4, 9.6 Hz, CH**H**5; 7.35, d, $J_{3,4}$ 8.3 Hz, H3; 8.11, br d, *J* 7.8 Hz, ArH. δ_C 16.68, 18.14, 18.49 and 21.53, each Me; 32.32, **C**HMe$_2$; 69.89, C5; 73.05, C4; 124.32, 124.92, 125.30 and 127.52, each CHAr; 131.09, 131.57, 132.29, 133.06, 134.83, 138.31 and 139.52, each CAr; 162.38, C2.

(–)-(R,4S)-4-Isopropyl-3-methyl-(1′,3′-dimethyl-2,2′-binaphthalen-1-yl)-4,5-dihydrooxazolium Iodide (29)

Methylation of the (*R*)-oxazoline (28) gave the *methiodide* (29) (83%) which crystallized from acetone/dichloromethane as prisms, m.p. 208–210° (Found: C, 65.2; H, 5.6; N, 2.5. $C_{29}H_{30}INO$ requires C, 65.0; H, 5.6; N, 2.6%). $[\alpha]_D{}^{25}$ –102.7° (*c*, 1.8). λ_{max} 232, 277, 341 (log ε 4.97, 4.03, 2.90). C.d. λ_{max} nm/Δε 217 (+63), 233.5 (–66.5). δ_H –0.21 and 0.66, each d, *J* 6.9 Hz, HC(C**H**$_3$)$_2$; 1.99–2.03; m; C**H**Me$_2$; 2.17, d, *J* 0.8 Hz, Me; 2.34, s, Me; 3.27, s, NMe; 4.31, dd, *J* 7.7, 9.7 Hz, C**H**H5; 5.55, dd, *J* 9.7, 11.1 Hz, CH**H**5; 5.83, m, H4; 7.44–7.47, m, ArH; 7.53–7.58, m, 2 × ArH; 7.65, br s, H4′; 7.75, ddd, *J* 1.0, 7.0, 8.1 Hz, ArH; 7.78–7.81, m, ArH; 7.93–8.03, m, 2 × ArH; 8.05, br d, *J* 8.3 Hz, ArH; 8.27, d, *J* 8.2 Hz, ArH; 8.55, dd, *J* 8.5 Hz, ArH. δ_C 12.81, 17.44, 17.55 and 21.59, each Me; 26.31, **C**HMe$_2$; 34.56, NMe; 68.97, C4; 73.28, C5; 116.75, CAr; 124.31, 125.83, 126.44, 126.95, 127.18, 127.26, 127.79, 128.40 and 128.60, each CHAr; 129.20, CAr; 130.85, CHAr; 131.21, 131.87, 132.78, 133.46 and 133.76, each CAr; 134.12. CHAr; 134.34 and 140.77, each CAr; 174.27, C2.

(–)-(R)-1′,3′-Dimethyl-2,2′-binaphthalene-1-carbaldehyde (30)

Reduction and hydrolysis of the (*R*)-methiodide (29) gave a crude product which was subjected to radial chromatography with 1–20% ethyl acetate/light petroleum as eluent. The *aldehyde* (30) was obtained as a solid (50%) which crystallized from acetone as prisms, m.p. 172–174° (Found: C, 89.3; H, 6.0%. $M^{+\bullet}$, 310.1351. $C_{23}H_8O_{12}$ requires C, 89.0; H, 5.8%. $^{12}C_{23}{}^1H_{18}{}^{16}O$ requires $M^{+\bullet}$, 310.1358). $[\alpha]_D{}^{31}$ –144.2° (*c*, 2.2). λ_{max} 231, 248.5, 254, 287, 319, 313 nm (log ε 5.07, 4.82, 4.84, 4.09, 4.12, 4.05). λ_{infl} 216 nm (log ε 4.84). C.d. λ_{max} nm/Δε 213 (+36), 228.5 (+17.4), 251 (–35.2). λ_{min}/Δε 196 (+1.4), 222 (+13.5). *m/z* 310 (M^+, 100%), 296 (24), 295 (100), 293 (13), 282 (12), 281 (23), 280 (11), 278 (13), 267 (26), 266 (28), 265 (47), 263 (12), 252 (27), 147 (11), 133 (19), 132 (24), 131 (11), 126 (18). δ_H 2.17, d, *J* 0.6 Hz, Me; 2.39, s, Me; 7.34, d, *J* 8.3 Hz, H3; 7.55–7.58, m, 2 × ArH; 7.65, ddd, *J* 1.1, 6.9, 8.1 Hz, ArH; 7.70, br s, H4′; 7.76, ddd, *J* 1.4, 6.9, 8.4 Hz, ArH; 7.86–7.89, m, ArH; 7.99, br d, *J* 8.1 Hz, ArH; 8.05–8.08, m, ArH; 8.17, d, *J* 8.3 Hz, H4; 9.41, dd, *J* 0.6, 8.5 Hz, ArH; 10.11, s, CHO. δ_C 16.74 and 21.94, each Me; 124.21, 125.77, 125.97, 126.08, 126.33, 126.81, 127.86, 128.08 and 128.34, each CHAr; 128.51, CAr; 128.38, CHAr; 130.52, 131.03, 132.21, 133.18, 133.24 and 133.70, each CAr; 134.96, CHAr; 136.35 and 148.68, CAr; 194.26, CHO.

(–)-(R)-1′,3′-Dimethyl-2,2′-binaphthalene-1-methanol (31)

Reduction of the (*R*)-aldehyde (30) gave a crude product which was purified by radial chromatography with 1–10% ethyl acetate/light petroleum as eluent to give the *alcohol* (31) as a solid (96%) which crystallized from ethyl acetate/light petroleum as prisms, m.p. 197–200º (Found: C, 88.3; H, 6.6%. $M^{+\bullet}$, 312.503. $C_{23}H_{20}O$ requires C, 88.4; H, 6.4%. $^{12}C_{23}{}^1H_{20}{}^{16}O$ requires $M^{+\bullet}$, 312.1514). $[\alpha]_D{}^{30}$ –122.1° (*c*, 2.4). λ_{max} 232, 273, 282 nm (log ε 5.08, 4.21, 4.20). C.d. λ_{max} nm/Δε 220.5 (+163), 234.5 (–147). *m/z* 312 (M^+, 16%), 296 (11), 295 (26), 294 (84), 281 (11), 280 (27), 279 (100), 278 (27), 277 (16), 276 (20), 266 (11), 265 (20), 149 (26), 139 (27), 138 (14), 126 (11). δ_H 2.15, d, *J* 0.8 Hz, Me; 2.39, s, Me; 4.77 and 4.85, each d, *J* 11.6 Hz, C**H**$_2$OH; 7.28, d, *J* 8.3 Hz, H3; 7.56-7.62, m, 3 × Ar; 7.67, ddd, *J* 1.4, 6.9, 8.3 Hz, ArH; 7.71, br s, H4′; 7.88–7.91, m, ArH; 7.95, d, *J* 8.3 Hz, H4; 7.99, br d, *J* 8.1 Hz, ArH; 8.08–8.11, m, ArH; 8.37, d, *J* 8.5 Hz, ArH. δ_C 16.62 and 21.92, each Me; 59.67, CH_2; 124.30, 124.62, 125.36, 125.65, 125.71, 126.06, 126.77, 127.54, 127.77, 128.58 and 128.90, each CHAr; 131.19, 131.63, 132.34, 132.79, 133.04, 133.28 and 134.34, each CAr; 138.77, 2 × CAr.

When the ^{1}H n.m.r. spectrum was determined in $CDCl_3$ in the presence of 1.92 mol equiv. of (+)-(*S*)-1-(anthracen-9-yl)-2,2,2-trifluoroethanol no signals due to the (*S*)-enantiomer could be detected. Enantio-enriched alcohol was prepared from the enantio-enriched oxazoline (39.9% d.e.), via the enantio-enriched aldehyde, $[\alpha]_D{}^{32}$ 32.0° (*c*, 2.6); the alcohol had $[\alpha]_D{}^{32}$ –30.0° (*c*, 1.0) and the e.e. was determined to be 22.8% by the ^{1}H n.m.r. method. Under these conditions the (*R*)-enantiomer (31) had δ_H 2.07 and 2.33, each s, Me; 4.73 and 4.81, each d, *J* 11.6 Hz, C**H**$_2$OH; 7.24, d, *J* 8.3 Hz, ArH; 7.47–7.63, m, 4 × ArH; 7.65, s, H4′; 7.84–7.86, m, ArH; 7.92, d, *J* 8.3 Hz, ArH; 7.95, br d, *J* 8.5 Hz, ArH; 8.01–8.03, br m, ArH; 8.29, d, *J* 8.3 Hz, ArH. The n.m.r. spectrum of the minor (*S*)-enantiomer included δ_H 2.09 and 2.31, each s, Me; 4.72 and 4.83, each d, *J* 11.6 Hz, C**H**$_2$OH.

(–)-(R)-1,1′,3′-Trimethyl-2,2′-binaphthalene (32)

This was prepared from the (*R*)-alcohol (31) and was purified by radial chromatography with light petroleum as eluent, which gave the *hydrocarbon* (32) as a solid (76%) that crystallized from ethyl acetate/light petroleum as prisms, m.p. 165–167° (Found: C, 93.0; H, 6.8%. $M^{+\bullet}$, 296.1559. $C_{23}H_{20}$ requires C, 93.2; H, 6.8%. $^{12}C_{23}{}^{1}H_{20}$ requires $M^{+\bullet}$, 296.1565). $[\alpha]_D^{32}$ –126.2° (*c*, 2.1). λ_{max} (C_6H_{12}) 236, 274.5, 284.5 nm (log ε 5.09, 4.15, 4.13). C.d. λ_{max} nm/Δε 221 (+135), 235.5 (–120). *m/z* 296 (M^+, 100%), 282 (15), 281 (64), 267 (12), 266 (52), 265 (50), 139 (12), 133 (20), 132 (21). δ_H 2.14, 2.38 and 2.40, each s, Me; 7.27, d, $J_{3,4}$ 8.3 Hz, H3; 7.53–7.65, m, 4 × ArH; 7.71, s, H4′; 7.84, d, *J* 8.3 Hz, H4; 7.87–7.90, m, ArH; 7.97, d, *J* 8.0 Hz, ArH; 8.09–8.10, m, ArH; 8.16, d, *J* 8.0 Hz, ArH. δ_C 15.25, 16.04 and 21.59, each Me; 124.34, 124.37, 125.17, 125.33, 125.44, 125.93, 126.00, 126.28, 127.73, 127.77 and 128.56, each CHAr; 131.35, 131.39, 131.49, 132.79, 132.91, 132.97, 134.60, 138.80 and 140.01, each CAr.

(4S)-4-Isopropyl-2-(3-methoxy-1′,3′-dimethyl-2,2′-binaphthalen-1-yl)-4,5-dihydrooxazole

This diastereomeric mixture of oxazolines was prepared from 2-bromo-1,3-dimethyl-naphthalene (8) and the oxazoline (5) in the usual way except that the reactants were stirred and heated under reflux for 19 h. Flash chromatography with 2–20% ethyl acetate/light petroleum as eluent gave the *binaphthalene* as a foam (82%, 37.0% d.e.) (Found: $M^{+\bullet}$, 423.2209. $^{12}C_{29}{}^{1}H_{29}{}^{14}N^{16}O_2$ requires $M^{+\bullet}$, 423.2198). $[\alpha]_D^{32}$ –52.4° (*c*, 3.0). λ_{max} 236, 268, 277, 318, 332 nm (log ε 5.23, 4.30, 4.30, 3.85, 3.92). C.d. λ_{max} nm/Δε 224 (+48), 237 (–36).

The major (*S*)-diastereomer (33) had: δ_H 0.58 and 0.67, each d, *J* 6.7 Hz, CH(C**H**$_3$)$_2$; 1.19, m, C**H**Me$_2$; 2.21, d, *J* 0.8 Hz, Me; 2.37, s, Me; 3.56, dd, *J* 8.2, 8.2 Hz, C**H**H5; 3.81-3.89, m, H4; 3.84, s, OMe; 3.98, dd, *J* 8.2, 9.7 Hz, CH**H**5; 7.36, s, H4′; 7.42–7.54, m, H6,6′,7,7′; 7.59, s, H4; 7.79–7.82, m, ArH; 7.85, br d, *J* 8.2 Hz, ArH; 7.94–7.96 and 8.02–8.05, each m, ArH. δ_C 16.36, 18.23, 18.69 and 21.14, each Me; 32.39, **C**HMe$_2$; 55.68, OMe, 69.94, C4; 72.91, C5; 107.12, 124.26 and 124.59, each CHAr; 125.23, 2 × CHAr; 126.56 and 126.74, each CHAr; 126.98, CAr; 127.64, CHAr; 128.28, 131.05, 132.22, 132.45, 133.32, 134.08, 134.28 and 135.77, each CAr; 154.84, COMe; 162.02, C2. Two CHAr were not located.

The n.m.r. spectra of the (*R*)-diastereomer included δ_H 0.53 and 0.59, each d, *J* 6.7 Hz, CH(C**H**$_3$)$_2$; 2.23, m, C**H**Me$_2$; 2.17, d, *J* 0.8 Hz, Me; 2.40, s, Me; 3.44, dd, *J* 8.5, 8.5 Hz, C**H**H5; 3.81–3.89, m, H4; 3.84, s, OMe; 4.06, dd, *J* 8.5, 9.7 Hz, CH**H**5. δ_C 16.44, 18.16, 18.63 and 21.02, each Me; 32.29, **C**HMe$_2$; 55.68, OMe; 69.98, C5; 73.04, C4; 124.32, 124.61 and 125.03, each CHAr; 127.01, CAr; 127.55, CHAr; 128.26, CAr; 131.14, 132.90, 133.23 and 135.44, each CAr; 154.84, COMe; 161.93, C2.

(–)-(S)-3-Methoxy-1′,3′-dimethyl-2,2′-binaphthalene-1-carbaldehyde (34)

The diastereomeric mixture of oxazolines was converted into the methiodide and this was reduced and hydrolysed. Radial chromatography of the crude product with 1–10% ethyl acetate/light petroleum as eluent gave the product as a solid (56%) which precipitated from acetone in amorphous form, m.p. 180–182° (Found: C, 84.4; H, 6.1%. $M^{+\bullet}$, 340.1465. $C_{24}H_{20}O_2$ requires C, 84.7; H, 5.9%. $^{12}C_{24}{}^{1}H_{20}{}^{16}O_2$ requires $M^{+\bullet}$, 340.1463). $[\alpha]_D^{25}$ –34.5° (*c*, 2.0). λ_{max} 232, 268, 329.5, 352.5 nm (log ε 5.14, 4.39, 3.88, 3.94). C.d. λ_{max} nm/Δε 220 (+19), 231 (–11). *m/z* 340 (M^+, 68%), 325 (36), 282 (13), 281 (22), 266 (11), 265 (17), 252 (13), 126 (14), 86 (64), 84 (100), 83 (11). δ_H 2.16 and 2.37, each s, Me; 3.88, s, OMe; 7.54–7.63, m, 4 × ArH; 7.56 and 7.70, each s, ArH; 7.87–7.92, 2 × ArH; 8.05–8.07 and 9.22–9.24, each m, ArH; 9.98, s, CHO. δ_C 16.45 and 21.39, each Me; 55.87, OMe; 111.96, 124.20, 125.46 and 125.74, each CHAr; 125.84, CAr; 125.93, 126.05, 126.63, 126.96, 127.11 and 127.88, each CHAr; 129.97, 131.02, 131.84, 133.00, 133.38, 134.30, 134.37 and 140.56, each CAr; 154.45, COMe; 194.29, CHO.

(–)-(S)-3-Methoxy-1′,3′-dimethyl-2,2′-binaphthalene-1-methanol (35)

Reduction of the aldehyde (34) yielded a crude product which was purified by radial chromatography with 5–20% ethyl acetate/light petroleum as eluent to give the alcohol (35) (93%, 35.5% e.e.) which precipitated from ethyl acetate/light petroleum in amorphous form, m.p. 150–152° (Found: C, 84.3; H, 6.7%. $M^{+\bullet}$, 342.1626. $C_{24}H_{22}O_2$ requires C, 84.2; H, 6.5%. $^{12}C_{24}{}^{1}H_{22}{}^{16}O_2$ requires $M^{+\bullet}$, 342.1620). $[\alpha]_D^{24}$ –26.2° (*c*, 2.3). λ_{max} 236, 266.5, 277, 316.5, 331 nm (log ε 5.06, 4.08, 4.07, 3.50, 3.58). C.d. λ_{max} nm/Δε 224 (+50), 239 (–40). *m/z* 342 (M^+, 55%), 326 (19), 325 (30), 324 (100), 310 (12), 309 (35), 295 (12), 294 (13), 281 (12), 279 (17), 278 (17), 266 (18), 265 (27), 253 (10), 252 (18), 171 (19), 149 (25), 133 (12), 129 (11), 127 (14), 126 (15), 113 (10). δ_H 2.09, d, *J* 0.8 Hz, Me; 2.34, s, Me; 3.82, s, OMe; 4.68 and 4.76, each d, *J* 11.6 Hz, C**H**$_2$OH; 7.30, s, ArH; 7.49–7.56, m, 4 × ArH; 7.68, s, ArH; 7.84–7.90, m, 2 × ArH; 8.04–8.07, m, ArH; 8.23–8.27, br d, *J* 8.7 Hz, ArH. δ_C 16.28 and 21.34, each Me; 55.63, OMe; 59.55, CH_2; 106.07, 124.23, 124.57, 125.10, 125.52; 125.91; 126.27 and 127.33, each CHAr; 127.77, CAr; 127.85, CHAr; 131.25, 131.83, 132.20, 133.23, 134.62, 134.68 and 134.87, each CAr; 155.09, COMe. One CHAr and one CAr were not located.

The enantio-enriched alcohol (13.7 mg, 40 μmol) and (+)-(*S*)-Mosher acid chloride (15 μl, 88 μmol) were stirred together in anhydrous dichloromethane (3 drops) and pyridine (3 drops) under argon for 18 h. The solution was diluted with dichloromethane and washed in turn with dilute hydrochloric acid, saturated aqueous sodium hydrogen carbonate and saturated brine. The product was purified by radial chromatography with 5–10% ethyl acetate/light petroleum to give the diastereomeric α-trifluoromethyl-α-methoxyphenylacetates as a solid (18.3 mg, 35.5% d.e.).

For the major (*S,R*)-diastereomer the n.m.r. spectra included δ_H 1.97, d, *J* 0.7 Hz, Me; 2.09, s, Me; 3.40, m, OMe; 3.79, s, OMe; 5.34 and 5.37, each d, *J* 11.8 Hz, CH_2. δ_F –72.558. For the (*R,R*)-diastereomer the n.m.r. spectra included δ_H 1.84, d, *J* 0.7 Hz, Me; 2.20, s, Me. δ_F –72.558.

(–)-(S)-3-Methoxy-1,1′,3′-trimethyl-2,2′-binaphthalene (36)

This was prepared from the foregoing enantio-enriched alcohol (35) and the crude product was purified by radial chromatography with 1–5% ethyl acetate/light petroleum as eluent which gave the *hydrocarbon* (36) (79%) as a solid which precipitated from ethyl acetate/light petroleum in amorphous form (Found: C, 87.9; H, 6.9%. $M^{+\bullet}$, 326.1663. $C_{24}H_{22}O$ requires C, 88.3; H, 6.8%. $^{12}C_{24}{}^{1}H_{22}{}^{16}O$ requires $M^{+\bullet}$, 362.1671). $[\alpha]_D^{28}$ –26.9° (*c*, 1.2). λ_{max} 237, 277, 315.5, 329.5 nm (log ε 5.15, 4.33, 3.66, 3.71). C.d. λ_{max} nm/Δε 223 (+45), 235 (infl.) (–10), 241 (–20). *m/z* 326 (M^+, 100%), 311 (24), 296 (20), 295 (10), 279 (13), 265 (13), 252 (11), 149 (12), 148 (13), 133 (12), 126 (11). δ_H (300 MHz) 2.09, d, *J* 0.7 Hz, Me; 2.29 and 2.34, each s, Me; 3.81, s, OMe; 7.19, s, H4′; 7.43–7.56, m, 4 × ArH; 7.68, s, H4; 7.84–7.88, m, 2 × ArH; 8.03–8.09, m, 2 × ArH. δ_C 15.35, 15.77 and 21.14, each Me; 55.56, OMe; 103.66, 123.63, 124.42, 124.47, 124.95, 125.34, 125.85, 126.01, 127.35 and 127.91, each CHAr; 128.61, 131.05, 131.48, 132.10, 133.22, 133.53, 134.26, 135.14 and 136.08, each CAr; 155.55, OMe.

(4S)-4-Isopropyl-2-(1′,3′,4′-trimethyl-2,2′-binaphthalen-1-yl)-4,5-dihydrooxazole

This diastereomeric mixture of oxazolines was prepared from 2-bromo-1,3,4-trimethylnaphthalene (10) and the oxazoline (4). Flash chromatography with 1–20% ethyl acetate/light petroleum as eluent gave the *binaphthalene* as a solid (82%, 30.8% d.e.) which crystallized from acetone/light petroleum as plates, m.p. 125–130° (Found: $M^{+\bullet}$, 407.2239. $^{12}C_{29}{}^{1}H_{29}{}^{14}N^{16}O$ requires $M^{+\bullet}$, 407.2249). $[\alpha]_D^{32}$ –22.7° (*c*, 2.8). *m/z* 407 (M^+, 40%), 295 (32), 294 (100), 280 (15), 279 (54), 278 (14), 114 (68).

The major (*R*)-diastereomer (37) had δ_H 0.57 and 0.60, each d, *J* 6.7 Hz, CH(C**H**$_3$)$_2$; 1.19, m, C**H**Me$_2$; 2.19, 2.33 and 2.66, each s, Me; 3.56, dd, *J* 8.2, 8.2 Hz, C**H**H5; 3.91, ddd, *J* 6.7, 8.2, 9.7 Hz, H4; 4.06, dd, *J* 8.2, 9.7 Hz, m, CH**H**5; 7.33, d, $J_{3,4}$ 8.3 Hz, H3; 7.48–7.61, m, 4 × ArH; 7.94, dd, *J* 0.8, 7.3 Hz, ArH; 8.00, d, $J_{4,3}$ 8.3, H4; 8.05–8.09, m, 2 × ArH; 8.13, dd, *J* 1.1, 8.4 Hz, ArH. δ_C 14.90, 16.80, 18.16, 18.32 and 18.85, each Me; 32.28, **C**HMe$_2$; 69.89, C5; 72.88, C4; 124.15, 124.46, 124.78, 125.23; 125.34 and 126.05, each CHAr; 126.33, CAr; 127.13, 127.38 and 128.01, each CHAr; 128.82 and 129.65, each CAr;

129.86, CHAr; 130.95, 131.53, 132.25, 132.32, 132.72, 138.47 and 140.59, each CAr; and 162.58, C2.

The n.m.r. spectra of the (*S*)-diastereomer included δ_H 0.54 and 0.57, each d, *J* 6.7 Hz, CH(C**H**$_3$)$_2$; 1.24, m, C**H**Me$_2$; 2.14, 2.37 and 2.67, each s, Me; 3.53, dd, *J* 8.4, 8.4 Hz, C**H**H5; 4.08, dd, *J* 8.4, 9.7 Hz, CH**H**5. δ_C 14.95, 16.95, 18.04, 18.42 and 18.71, each Me; 32.23, **C**HMe$_2$; 69.81, C5; 72.94, C4; 124.04, 124.48, 124.85 and 125.39, each CHAr; 126.27, CAr; 127.44, CHAr; 128.64, CAr; 129.98, CHAr; 131.06, 131.55, 132.35, 138.39 and 140.64, each CAr; 162.48, C2.

(R,4S)-(38) and (S,4S)-4-Isopropyl-3-methyl-2-(1′,3′,4′-trimethyl-2,2′-binaphthalen-1-yl)-4,5-dihydrooxazolium Iodide (39)

Methylation of the diastereomeric mixture of oxazolines gave the methiodides as a foam (97%) which was fractionally crystallized from acetone/dichloromethane to afford the pure diastereomers.

The major *(*R*)-diastereomer* (38) crystallized as prisms, m.p. 204–207º (Found: C, 65.4; H, 5.8; N, 2.4%. $M^{+\bullet}$, 549.1528. $C_{30}H_{32}INO$ requires C, 65.5; H, 5.8, N, 2.5%. $^{12}C_{30}{}^{1}H_{32}{}^{127}I^{14}N^{16}O$ requires $M^{+\bullet}$, 549.1529). $[\alpha]_D^{27}$ –71.7º (*c*, 2.8). λ_{max} 236, 284.5 nm (log ε 5.10, 4.16). C.d. λ_{max} nm/Δε 223 (+81.5), 238 (–78). *m/z* 549 (M^+, 19%), 446 (22), 423 (19), 377 (58), 362 (9), 324 (23), 323 (90), 322 (27), 308 (24), 256 (22), 213 (22), 199 (38), 185 (30), 171 (60), 157 (20), 153 (21), 152 (16), 129 (59), 128 (32), 127 (36); 126 (11), 115 (21). 101 (15). δ_H –0.28 and 0.58, each d, *J* 6.8 Hz, CH(C**H**$_3$)$_2$; 1.98–2.02, m, **C**HMe$_2$; 2.08, 2.23 and 2.58, each s, Me; 3.20, s, NMe; 4.19, dd, *J* 7.8, 9.6 Hz, C**H**H5; 5.48, dd, *J* 9.6, 11.1 Hz, CH**H**5; 5.78, m, H4; 7.39, d, $J_{3,4}$ 8.4 Hz, H3; 7.50–7.57, m, 2 × ArH; 7.65, ddd, *J* 0.9, 7.0, 8.1 Hz, ArH; 7.85, ddd, *J* 1.2, 7.0, 8.3 Hz, ArH; 7.97–8.00, m, 2 × ArH; 8.05, d, *J* 8.3 Hz, ArH; 8.22, d, *J* 8.3 Hz, ArH; 8.52, dd, *J* 0.7, 8.4 Hz, ArH. δ_C 12.25, 17.24, 17.39, 17.42 and 19.02, each Me; 25.89, **C**HMe$_2$; 34.31, NMe; 68.47, C4; 72.93, C5; 116.48, CAr; 124.02, 124.58, 125.55, 125.69, 126.49, 127.22, 127.90 and 128.43, each CHAr; 128.80 and 129.66, each CAr; 130.27, CHAr, 130.79, 130.89, 131.06, 131.52, 132.43, each CAr; 133.80, CHAr; 134.14 and 141.75, each CAr; 173.88, C2.

The *(*S*)-diastereomer* (39) crystallized as prisms, m.p. 232–235º (Found: $M^{+\bullet}$, 549.1507. $^{12}C_{30}{}^{1}H_{32}{}^{127}I^{14}N^{16}O$ requires $M^{+\bullet}$, 549.1529). $[\alpha]_D^{27}$ +133.0º (*c*, 2.9). C.d. λ_{max} nm/Δε 218 (–86), 238 (+77). *m/z* 549 (M^+, 24%), 423 (22), 422 (66), 353 (12), 324 (25), 323 (100), 322 (30), 308 (29), 294 (15), 265 (10), 236 (16), 171 (21), 139 (15), 128 (25), 127 (31), 111 (16). δ_H –0.30 and 0.62, each d, *J* 6.8 Hz, CH(C**H**$_3$)$_2$; 1.97–2.03, m, C**H**Me$_2$; 2.03, 2.31 and 2.63, each s, Me; 3.23, s, NMe; 4.22–4.26, m, C**H**H5; 5.50, br dd, *J* 10.0, 10.0 Hz, CH**H**5; 5.87, m, H4; 7.42, d, *J* 8.4 Hz, ArH; 7.50–7.59, m, 2 × ArH; 7.69, br dd, *J* 7.6, 7.6 Hz, ArH; 7.89–7.95, m, 2 × ArH; 8.02, br d, *J* 8.2 Hz, ArH; 8.09, br d, *J* 8.4 Hz, ArH; 8.25, d, *J* 8.4 Hz, ArH; 8.59, d, *J* 8.4 Hz, ArH. δ_C 12.39, 14.99, 17.44, 17.45 and 18.86, each Me; 25.86, **C**HMe$_2$; 34.28, NMe; 68.62, C4; 72.97, C5; 116.48, CAr; 124.22, 124.36, 125.70, 125.76, 126.55, 127.25, 128.04 and 128.53, each CHAr; 128.89 and 129.19, each CAr; 130.56, CHAr; 130.70, 130.75, 131.55, 131.64 and 132.60, each CAr; 134.04, CHAr; 134.96 and 141.97, each CAr; 173.88, C2.

(–)-(R)-1′,3′,4′-Trimethyl-2,2′-binaphthalene-1-carbaldehyde (40)

Reduction and subsequent hydrolysis of the (*R*,4*S*)-methiodide (38) yielded the *aldehyde* (40) as a solid (56%) which crystallized from acetone as prisms, m.p. 199–202º (Found: $M^{+\bullet}$, 324.1499. $^{12}C_{24}{}^{1}H_{20}O$ requires $M^{+\bullet}$, 324.1514). $[\alpha]_D^{28}$ –118.6º (*c*, 2.4). λ_{max} 214, 233.5, 282, 293.5 nm (log ε 4.64, 4.83, 3.90, 3.91). C.d. λ_{max} nm/Δε 215.5 (+21), 231 (+32), 252.5 (–37.5). λ_{min} nm/Δε 221 (+19). *m/z* 324 (M^+, 100%), 310 (18), 309 (77), 285 (11), 294 (14), 281 (14), 279 (13), 260 (20), 265 (37), 155 (11), 149 (14), 133 (14). δ_H 2.12, 2.33 and 2.69, each Me; 7.33, d, *J* 3,4 8.3 Hz, H3; 7.54–7.65, m, 3 × ArH; 7.74, ddd, *J* 1.3, 6.9, 8.4 Hz, ArH; 7.97, br d, *J* 8.1 Hz, ArH; 8.07, br d, *J* 8.3 Hz, ArH; 8.15–8.18, 2 × m, ArH; 9.37, d, *J* 8.6 Hz, ArH; 10.07, s, CHO. δ_C 15.10, 17.05 and 19.04, each Me; 124.43, 124.73, 125.34; 125.93, 126.00, 126.78, 128.33 and 128.37, each CHAr; 128.62, CAr; 129.40, CHAr; 129.93, 130.02, 130.54, 130.96, 131.40, 132.50 and 133.13, CAr; 134.88, CHAr; 136.49 and 149.91, each CAr; 194.48, CHO.

(+)-(S)-1′,3′,4′-Trimethyl-2,2′-binaphthalene-1-carbaldehyde (41)

This was prepared in the same way as its enantiomer from the (*S*,4*S*)-methiodide (39). The aldehyde crystallized from acetone as prisms, m.p. 199–201°. $[\alpha]_D^{25}$ +117.7° (*c*, 1.4). C.d. λ_{max} nm/Δε 217 (–24), 231 (–35), 252 (+34). λ_{min} nm/Δε 222 (–21).

(–)-(R)-1′,3′,4′-Trimethyl-2,2′-binaphthalene-1-methanol (42)

Reduction of the (*R*)-aldehyde (40) gave a crude product which was purified by radial chromatography with 5–30% ethyl acetate/light petroleum as eluent. This gave the *alcohol* (42) as a solid (93%) which crystallized from ethyl acetate/light petroleum as clusters of needles, m.p. 99–101°C (Found: $M^{+\bullet}$, 326.1682. $^{12}C_{24}{}^{1}H_{22}{}^{16}O$ requires $M^{+\bullet}$ 326.1671). $[\alpha]_D^{30}$ –89.2° (*c*, 1.6). λ_{max} 237, 273, 282 nm (log ε 4.73, 3.74, 3.75). C.d. λ_{max} nm/Δε 224 (+150), 239 (–113). *m/z* 326 (M^+, 13%), 310 (11), 309 (17), 308 (56), 294 (26), 293 (100), 279 (19), 278 (53), 277 (13), 276 (16), 265 (11), 155 (14), 139 (16), 138 (11), 127 (24). δ_H 2.10, 2.33 and 2.70, each s, Me; 4.79 and 4.85, each d, *J* 11.7 Hz, C**H**$_2$OH; 7.25, d, $J_{3,4}$ 8.4 Hz, H3; 7.54–7.67, m, H6,6′,7,7′; 7.93, d, $J_{4,3}$ 8.4 Hz, H4; 7.97, dd, *J* 0.6, 8.1 Hz, ArH; 8.09, br d, *J* 8.0 Hz, ArH; 8.18, br d, *J* 8.4 Hz, ArH; 8.36, d, *J* 8.4 Hz, ArH. δ_C 15.16, 16.90 and 18.83, each Me; 59.77, CH$_2$; 124.34, 126.63, 124.80, 124.97, 125.53, 125,70, 126.84, 127.80, 128.62 and 128.88, each CHAr; 129.34, 129.66, 131.13, 131.89, 132.28, 132.36, 132.83, 133.26, 138.86 and 139.96, each CAr.

This alcohol was converted into the (*R,R*)-Mosher ester (98.7% e.e) by treatment with (+)-(*S*)-Mosher acid chloride. Its n.m.r. spectra included δ_H 1.97, 2.05 and 2.66, each s, Me; 3.41, br d, *J* 0.9 Hz, OMe; 5.39 and 5.51, each d, *J* 11.9 Hz, CH$_2$. δ_F –72.75.

(+)-(S)-1′,3′,4′-Trimethyl-2,2′-binaphthalene-1-methanol (43)

This was prepared in an analogous manner to its enantiomer from the (*S*)-aldehyde (41). $[\alpha]_D^{28}$ +88.5° (*c*, 2.1). C.d. λ_{max} nm/Δε 222.5 (–120), 238 (+82).

The diastereomeric mixture of methiodides (38) and (39) was converted sequentially, as above, into the enantiomeric mixture of alcohols (42) and (43), and finally into the derived Mosher esters. The n.m.r. spectra of the (*S,R*)-Mosher ester included δ_H 1.90, 2.18 and 2.61, each s, Me; 3.39, br d, *J* 1.0 Hz, OMe; 5.43 and 5.49, each d, *J* 11.9 Hz, CH$_2$. δ_F –72.75.

(4S)-4-Isopropyl-2-(3-methoxy-1′,3′,4′-trimethyl-2,2′-binaphthalenen-1-yl)-4,5-dihydrooxazole

This was prepared as a mixture of diastereomers from the oxazoline (5) and 2-bromo-1,3,4-trimethylnaphthalene (10) in the usual way except that the reactants were stirred and heated under reflux for 18 h. Radial chromatography with 5–20% ethyl acetate/light petroleum as eluent gave the *binaphthalene* as a foam (23%, 20.8% d.e.) (Found: $M^{+\bullet}$, 437.2345. $^{12}C_{30}{}^{1}H_{31}{}^{14}N^{16}O_2$ requires $M^{+\bullet}$, 437.2355). $[\alpha]_D^{26}$ –0.9° (*c*, 4.8). λ_{max} 239.5, 279.5, 316.5, 332 nm (log ε 5.20, 4.20, 3.82, 3.86). C.d. λ_{max} nm/Δε 227 (+33), 241 (–24). *m/z* 437 (M^+, 14%), 351 (10), 325 (28), 324 (100), 310 (11), 309 (36), 114 (39).

The major (*S*)-diastereomer (44) had δ_H 0.62 and 0.70, each d, *J* 6.7 Hz, CH(C**H**$_3$)$_2$; 1.17, m, C**H**Me$_2$; 2.29, 2.44 and 2.74, each s, Me; 3.54, dd, *J* 8.3, 8.3 Hz, C**H**H5; 3.88, s, OMe; 3.89–3.94, m, CH**H**5; 4.09, ddd, *J* 6.7, 8.3, 9.7 Hz, H4; 7.42, s, H4; 7.50–7.62, m, 4 × ArH; 7.92, d, *J* 8.1 Hz, ArH; 8.03, br d, *J* 8.3 Hz, ArH; 8.16, br d, *J* 8.2 Hz, ArH; 8.20, d, *J* 8.5 Hz, ArH. δ_C 14.84 and 16.54, each Me; 18.16, 2 × MeAr; 18.37, MeAr; 32.34, **C**HMe$_2$; 55.54, OMe, 69.87, C4; 72.81, C5; 106.92, CHAr, 124.09, 2 × CHAr; 124.48, 124.62, 125.01, 125.12, 126.41 and 126.65, each CHAr; 126.92, 128.18, 128.32, 130.13, 130.95, 132.45, 133.13, 133.23, 133.93 and 134.22, each CAr; 154.89, C3; 161.95, C2.

The n.m.r. spectra of the (*R*)-diastereomer included δ_H 0.59 and 0.65, each d, *J* 6.7 Hz, CH(C**H**$_3$)$_2$; 2.25, 2.48 and 2.76, each Me; 3.48, dd, *J* 8.3, 8.3 Hz, C**H**H5; 3.88, s, OMe; 3.89–3.94, m, CH**H**5; 4.09, ddd, *J* 6.7, 8.3, 9.7 Hz, H4; 8.05, br d, *J* 8.3Hz, ArH; 8.16, br d, *J* 8.5 Hz, ArH. δ_C 14.86 and 16.60, each Me; 18.04, 18.11, 18.46, each MeAr; 32.15, **C**HMe$_2$; 55.54, OMe; 69.79, C4; 72.90, C5; 106.94, 123.98, 124.50, 124.72, 125.00 and 125.17, each CHAr; 126.94, 128.11, 128.12, 129.43, 131.07, 132.37, 133.27, 133.95 and 134.09, each CAr; 154.89, C3; 161.85, C2.

Structure Determinations, (38), (38).2S and (22).0.5S (S = $(H_3C)_2CO$)

Unique room-temperature single-counter diffractometer data sets, together with 'Friedel pairs', were measured ($2\theta/\theta$ scan mode, $2\theta_{max}$ 50º; monochromatic Mo $K\alpha$ radiation, λ 0.7107_3 Å; *T c.* 295 K), for *N hkl*, N_o with $I > n\sigma(I)$ being considered ´observed' and used in the full-matrix least-squares refinements on $|F|$, with anisotropic thermal parameters forms refined C, N, O, I and $(x, y, z, U_{iso})_H$ constrained at estimated values, after gaussian absorption correction. Conventional residuals R ($= \Sigma\Delta/\Sigma|F_o|$), R_w ($=\Sigma w\Delta^2/\Sigma wF_o^2)^{1/2}$) on $|F|$ are quoted at convergence, statistical weights being derivative of $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0004\sigma^4(I_{diff})$. Neutral atom complex scattering factors were employed within the XTL 3.4 program system.[38] Atomic parameters are deposited. Copies are available, until 31 December 2005, on application to the Australian Journal of Chemistry, P.O. Box 1139, Collingwood, Vic. 3066, or the Cambridge Crystallographic Data Centre, deposition numbers 000000. All compounds are orthorhombic, space group $P2_12_12_1$ (D_2^4, No. 19).

Crystal/Refinement Data

(38). $C_{30}H_{22}INO$, *M* 549.5. *a* 21.666(8), *b* 13.971(5), *c* 8.705(3) Å, *V* 2635 Å^3. D_c ($Z = 4$) 1.38_5 g cm^{-3}. μ_{Mo} 12.4 cm^{-1}; specimen: $0.45 \times 0.52 \times 0.80$ mm; $T_{min,max}$ 0.55, 0.61. *N* 2647, N_o ($n = 2$) 2398; *R* 0.040, R_w 0.051. $|\Delta\rho_{max}| = 0.79$ (3) e Å^{-3}. x_{abs} –0.01(1).

(38).2S. $C_{36}H_{44}INO_3$, *M* 665.7. *a* 18.365(4), *b* 17.365(4), *c* 10.723(5) Å, *V* 3419 Å^3. D_c ($Z = 4$) 1.29_1 g cm^{-3}. μ_{Mo} 9.7 cm^{-1}; specimen: $0.18 \times 0.18 \times 0.58$ mm (capillary); $T_{min,max}$ 0.83, 0.85. *N* 3383, N_o ($n = 3$) 1742; *R* 0.057, R_w 0.064; $|\Delta\rho_{max}|$ 0.92 (3) e Å^{-3}. x_{abs} –0.01 (6).

The latter structure determination of (38).2S, derivative of rather weak data, was ultimately followed by the determination of the unsolvated form (38), as a precautionary corroboration of the absolute configuration; the two determinations are consistent.

(22).0.5S. $C_{30.5}H_{34}NO_{3.5}$, *M* 470.6. *a* 12.127(2), *b* 16.919(2), *c* 25.065(3) Å, *V* 5143 Å^3. D_c ($Z = 8$) 1.21_5 g cm^{-3}; *F* (000) 2016. μ_{Mo} 0.8 cm^{-1}; specimen: $0.4 \times 0.24 \times 0.16$ mm (no correction). *R* 0.053, R_w 0.054. $|\Delta\rho_{max}|$ 0.29 (3) e Å^{-3}

Variata.—For this compound only, a full sphere of CCD area detector data was measured on a somewhat twinned specimen (Bruker AXS instrument, *T c.* 153 K, ω-scan, $2\theta_{max}$ 58º) yielding 51234 total reflections merging (inclusive of 'Friedel pairs' since no significant anomalous scatterer was present) to 7391 unique (R_{int} 0.063), 5306 with $F > 4\sigma(F)$ used in the refinement. Chirality was set according to the internal reference (C(15)). Difference map residues were modelled in terms of a fully populated ordered acetone, for which all hydrogen atoms were located in difference maps.

Comment.—The results of the room-temperature single-crystal X-ray studies are consistent with the formulation of (38) in both cases in terms of stoichiometry, stereochemistry, connectivity *and* absolute configurations as given above; in each case, one molecule, devoid of crystallographic or intrinsic symmetry, comprises the asymmetric unit of the structure, (38).2S solvated with two molecules of acetone. Substituent dispositions are similar in both, dihedral angles between peripheral and central naphthyl (n_p/n_c) and oxazole planes (o_p) being, respectively, for (38), (38).2S: n_c/n_p 68.5(2), 88.5(5)°; o_p/n_c 85.5(2), 74.6(5)°; o_p/n_p 59.7(2), 59.1(6)°, the variation in n_c/n_p inclination perhaps accompanied by a concomitant variation N(1)–C(5)–C(51)–C(52) torsion (57.1(7), 62.2(2)º). In both cases, the iodide anion approaches the oxazole plane with closest contacts to H(8´, 4B) at 3.1_8, 3.2_7 (est.) (38), 3.1_5, 3.2_0 (est.) ((38).2S), suggestive of an ´electrostatic' interaction between the anion and the charged region of the cation substituent rather than with the aromatic charge-transfer implications.

In (22).0.5S, the dihedral angles between the pairs of naphthalene planes are 85.06(8) and77.39(8)º, the C.CO.N planes lying at 77.96(9), 80.9(1)º, to their associated central planes. H(14) hydrogen bonds to O(13) ($x - ½, 1½ - y, 2 - z$) 1.8_8 Å and H(24) to O(23) ($½ + x, ½ - y, 2 - z$) both 1.9 Å, so that molecules 1 and 2 form distinct strings generated by 2_1 screw axes parallel to *c*.

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