Atropisomer-selective ligand-coupling reactions of sulfoxides.[1] X-Ray molecular and crystal structures for 2-({2-(4-chlorophenyl)naphtho-[1,2-*b*]thiophen-3-yl}amino)-2-methylpropan-1-ol, 2-(2-hydroxy-1,1-dimethylethyl)-2,3-dihydronaphtho[2,1-*d*]isothiazol-3-one and (*R*)-(+)-2-bromo-1-(*tert*-butylsulfinyl)naphthalene

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1-(Alkyl- or aryl-sulfinyl)naphthalenes activated by electron-withdrawing substituents at the 2-position undergo substitution reactions on treatment with Grignard reagents. Evidence suggesting that these transformations proceed through ligand-coupling reactions of σ-sulfuranes is presented. The ligand-coupling reaction of homochiral sulfoxides with 1-naphthylmagnesium bromide furnishes atropisomeric 1,1′-binaphthyls in 60–95% ee. Single-crystal X-ray structure determinations have been carried out on 2-({2-(4-chlorophenyl)naphtho[1,2-*b*]thiophen-3-yl}amino)-2-methylpropan-1-ol **18** and 2-(2-hydroxy-1,1-dimethylethyl)-2,3-dihydronaphtho[2,1-*d*]isothiazol-3-one **22**, compounds formed through intramolecular nucleophilic and electrophilic attack, respectively, on a neighbouring oxazoline group. The absolute configuration of (*R*)-(+)-1-(*tert*-butylsulfinyl)naphthalene **27** was determined by a single-crystal X-ray study of the 2-bromo derivative **28**.

Introduction

Since the report by Christie and Kenner[2] in 1922 of the resolution of 6,6′-dinitro-2,2′-diphenic acid the study of the atropisomerism of biaryls has burgeoned. By the time of the Adams review in 1933[3] the Kaufler controversy was defunct and the subject was already placed on a firm theoretical and experimental base. Since that time a number of natural products belonging to this class have been discovered[4,5] and although the preparation of enantiomerically pure atropisomeric biaryls is still often accomplished by resolution, a few atropisomer-selective synthetic methods have been developed.[4]

Atropisomeric 1,1′-binaphthyls have been used widely in the construction of chiral catalysts and auxiliaries for asymmetric synthesis.[6] The displacement of a methoxy group *ortho* to a chiral oxazoline entity by nucleophilic aromatic substitution (S_NAr) by an aryl Grignard reagent has afforded 2-substituted and 2,2′-disubstituted-1,1′-binaphthyls[7] and 2,2′,6-trisubstituted biphenyls[8,9] in good optical yields. In a similar way a chiral alkoxy group *ortho* to an achiral oxazoline[10] or hindered ester[11] will behave as a nucleofuge and such reactions have also provided 1,1′-binaphthyls in high chemical and optical yields.

Smiles and co-workers,[12] in examples of his eponymous rearrangement, demonstrated that the sulfinyl group will act as a nucleofuge in S_NAr reactions when activated by an *ortho* electron-withdrawing group. It was therefore of some interest to examine the behaviour of homochiral 1-naphthyl sulfoxides activated by electron-withdrawing substituents at the 2-position towards 1-naphthyl Grignard reagents. If an S_NAr reaction were to ensue then the presence of the chiral sulfur atom attached directly to the point of attack by the Grignard reagent might be expected to lead to asymmetric induction at the 1,1′-binaphthyl axis. Indeed, Fuji *et al.*[13] have described an addition–elimination strategy for asymmetric induction of carbon-centred chirality using a sulfoxide as chiral nucleofuge; reaction of a β-nitro-α,β-unsaturated sulfoxide with lactam enolates afforded products with enantiomeric excesses (ees) of 33–99%. The only other work of a similar nature, of which we are aware, is due to Furukawa and co-workers.[14] They have described the diastereoselective formation of an atropisomeric 2-pyridyl-1-naphthyl system by a ligand-coupling reaction of a 2-pyridyl sulfoxide, containing a chiral 3-substituent, with a 1-naphthyl Grignard reagent. However, it is not apparent whether the stereoselectivity in this reaction is dependent on the carbon-centred chirality of the 3-substituent on the pyridyl nucleus or the chirality of the sulfoxide. Given the high chiral induction demonstrated in the S_NAr reactions discussed above, with chiral elements equidistant[10,11] or more remote[7–9] from the reaction site, compared with Furakawa's case, the role of the carbon-centred chirality is likely to be significant. In the proposed study there would be no ambiguity as to the origin of the asymmetric induction.

The behaviour of aralkyl and heteroaralkyl sulfoxides towards Grignard reagents has been extensively studied by Oae and Furukawa and their co-workers.[15,16] 2-Pyridyl sulfoxides have been shown to undergo two types of reactions with Grignard reagents: ligand-exchange reaction, which occurs through an S_N2 process, generating a new sulfoxide with an inverted configuration at sulfur and a 2-pyridyl Grignard reagent; and ligand-coupling reaction, which can give rise to apparent S_NAr-type products. In the ligand-coupling reaction nucleophilic attack by the Grignard reagent is considered to occur on sulfur along an axial trajectory, generating a hypervalent σ-sulfurane intermediate. Subsequent ligand coupling can occur, in a concerted manner, between the axial Grignard-derived ligand and the 2-pyridyl ligand in an equatorial position, providing an apparent S_NAr-type product and a sulfenic acid salt. Rearrangement of the initially formed σ-sulfurane may also occur through pseudorotation, resulting in coupling between the 2-pyridyl ligand, again in an equatorial position, and the other ligand derived from the original sulfoxide, when in an axial position. This outcome is

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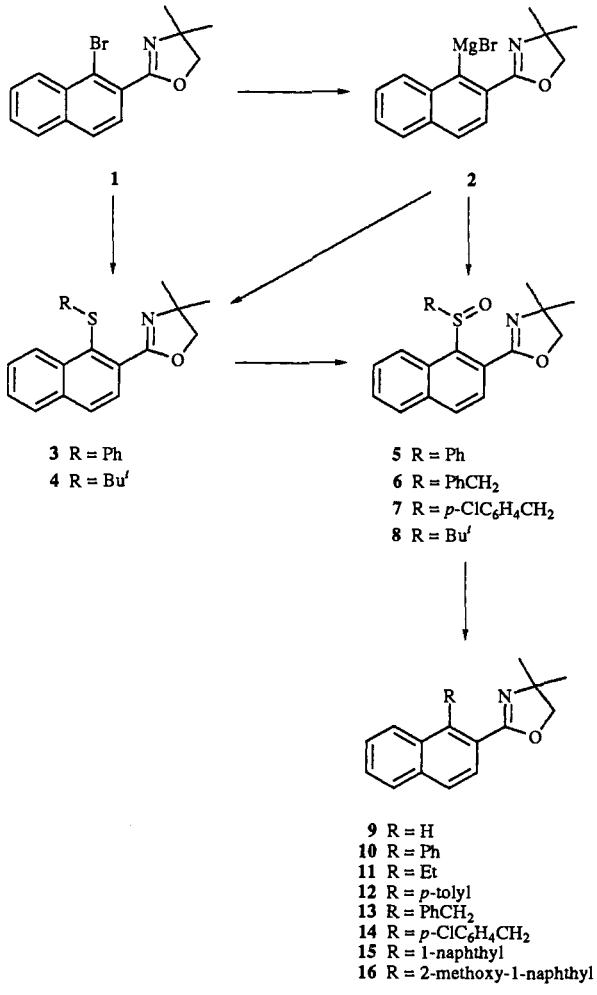
particularly facile if the 2-pyridyl sulfoxide contains an apicophilic ligand such as benzyl, allyl or vinyl. Similar behaviour has been demonstrated in the reactions of *p*-(phenylsulfonyl)phenyl sulfoxides with Grignard reagents. Hence, in our planned approach to the enantioselective synthesis of 1,1'-binaphthyls, there was a strong possibility that the displacement of the sulfinyl substituent might occur through a ligand-coupling reaction rather than through a direct S_NAr route.

Results and discussion

The racemic phenylsulfinyl oxazoline **5** was prepared by reaction of the Grignard reagent **2** (derived from the known bromo oxazoline **1**[10]) with diphenyl disulfide, followed by oxidation of the product **3** with *m*-chloroperbenzoic acid (MCPBA), in 64% overall yield (Scheme 1). The behaviour of

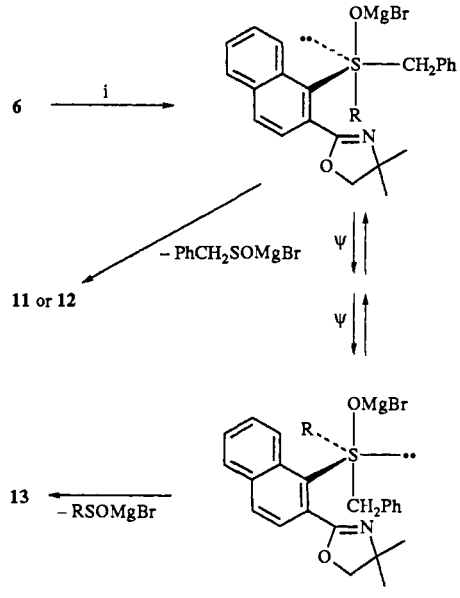


Scheme 1

this sulfoxide towards Grignard reagents was now investigated.

When the sulfoxide **5** was treated with 2 mol equiv. of phenylmagnesium bromide in tetrahydrofuran (THF) solution at −20 °C for 7 h the products were the phenylnaphthalene **10** (35%) and the desulfurised product **9** (44%). Also isolated from the reaction mixture was diphenyl sulfoxide (39%), generated through the ligand-exchange reaction which gave rise to the desulfurised product **9**, and a 2:1 mixture of diphenyl disulfide and phenyl benzenethiosulfonate (~40% combined yield), which arose from disproportionation of the benzenesulfenic acid generated on work-up. When the reaction was carried out at room temperature for 15 min the yield of the phenylnaphthalene **10** was 72%, accompanied by a 19% yield of the monosubstituted naphthalene **9**. The reaction of compound **5** with an excess of ethylmagnesium bromide in THF solution at room temperature proceeded at a significantly reduced rate compared with the reaction using phenylmagnesium bromide; after 4 h the yield of the ethylnaphthalene **11** was 19%, accompanied by a 36% yield of compound **9**.

Next we sought to obtain evidence regarding the mechanism of formation of the substitution products. As outlined above, evidence for the operation of a ligand-coupling mechanism involving σ-sulfurane intermediates is the occurrence of coupling between the ligands initially attached to the sulfoxide on treatment with Grignard reagents, an outcome that is particularly easily attained if the sulfoxide contains an apicophilic ligand such as benzyl. Accordingly, toluene-α-sulfinyl chloride was prepared from dibenzyl disulfide by the procedure of Youn and Herrmann,[17] and allowed to react with the Grignard reagent **2** in cyclohexane–THF solution at room temperature during 10 min, to provide the racemic benzylsulfinyl oxazoline **6** in 43% yield. When compound **6** was allowed to react with an excess of *p*-tolylmagnesium bromide in THF during 75 min the *p*-tolylnaphthalene **12** was obtained in 65% yield accompanied by the ligand-exchange product **9** in 10% yield. None of the benzyl-substituted naphthalene **13** was isolated. This result may be interpreted as indicating that the substitution reaction proceeds through a direct S_NAr mechanism. An alternative explanation is that the rate of the ligand-coupling reaction for the initially formed σ-sulfurane may be significantly greater than the rates of pseudorotation and subsequent ligand coupling involving the benzyl substituent (Scheme 2). Since the phenyl sulfoxide **5** was shown



Scheme 2 *Reagent:* i, RMgBr, R = Et or *p*-tolyl

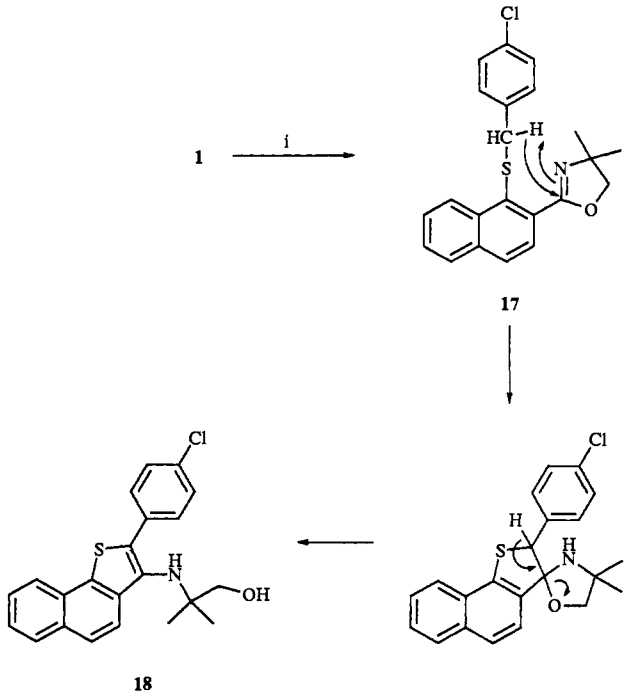
to couple more slowly with ethylmagnesium bromide compared with phenylmagnesium bromide, the benzyl sulfoxide **6** was allowed to react with an excess of ethylmagnesium bromide in THF during 2 h, to provide the ethylnaphthalene **11** in 69% yield accompanied by the benzylnaphthalene **13** (13%) and the ligand-exchange product **9** (10%), substantiating the second proposal. Oae and co-workers[18] reported that *p*-chlorine substitution on the benzylic group of 2-pyridyl or *p*-(phenylsulfonyl)phenyl benzyl sulfoxides enhances the extent of coupling of the original sulfoxide ligands on reaction with

benzylic Grignard reagents. This result was interpreted in terms of the electron-withdrawing chlorine substituent enhancing both the rate of pseudorotation of the initially formed σ-sulfurane intermediate and the rate of ligand coupling involving the chlorine-substituted benzyl group. The reaction of the *p*-chlorobenzylsulfinyl oxazoline **7** (prepared analogously to compound **6** in 53% overall yield) with ethylmagnesium bromide resulted in an increase in the yield of the benzyl-substitution product (compound **14** in this case) to 26% (accompanied by yields of 62% for **11** and 4% for **9**), further substantiating the proposal that these substitution reactions proceed through a ligand-coupling reaction of σ-sulfurane intermediates, rather than through a direct S_NAr reaction.

In an alternative approach to the synthesis of the *p*-chlorobenzylsulfinyl oxazoline **7**, the bromo oxazoline **1** was allowed to react with sodium 4-chlorophenylmethanethiolate in *N*,*N*-dimethylformamide (DMF) solution at 70 °C during 23 h. The high-resolution mass spectrum (HRMS) of the product, isolated in 96% yield, indicated the molecular formula $C_{22}H_{20}ClNOS$, consistent with the structure of the expected product **17** (Scheme 3). However, the other spectral characteristics of the new compound were not in keeping with this formulation. In particular, signals for the benzylic methylene group were absent from both the ^1H and ^{13}C NMR spectra. In the mass spectrum, the molecular ion lost CH_2OH and C_4H_8O, which is consistent with structure **18**. Further evidence for this structure is the presence of a broad band at 3360 cm^{-1} in the IR spectrum and a broad 2 H signal at δ_H 3.05 in the ^1H NMR spectrum, which are ascribed to the OH and NH groups. The latter spectrum also revealed the presence of two equivalent methyl groups (δ_H 0.93) and a hydroxymethyl group (δ_H 3.35). The presence of these features in the molecule was confirmed by the ^{13}C NMR spectrum. This revealed a signal at δ_C 70.6 for a CH_2OH group and the presence of a quaternary carbon bearing two methyl groups was indicated by signals at δ_C 58.8 and 24.7. These data are consistent with structure **18**, which was confirmed by single-crystal X-ray analysis (Fig. 1). Intermolecular addition of benzylmagnesium chloride[19] and organolithium reagents[20] to the imine of an oxazoline group has been previously observed to lead to the formation of oxazolidines. The formation of compound **18** presumably occurs through base-catalysed intramolecular addition of the benzylic methylene of compound **17** to the imine of the oxazoline, generating a spirooxazolidine intermediate, which then undergoes aromatisation concomitant with ring opening and prototropic shift (Scheme 3).

When the racemic phenylsulfinyl oxazoline **5** was allowed to react with an excess of 1-naphthylmagnesium bromide in THF solution at room temperature during 3.5 h the racemic 1,1'-binaphthyl **15** was obtained in 67% yield, accompanied by a 9% yield of the ligand-exchange product **9**.

The non-racemic sulfoxide **19** was synthesized by the Andersen method[21] by treatment of the Grignard reagent **2** with (1*R*)-menthyl (*S*)-toluene-*p*-sulfinate (Scheme 4). The best results were obtained by preparing the Grignard reagent in THF in the usual way and then replacing the THF by toluene. This was followed by rapid addition of the solid sulfinate ester followed by work-up after 10–15 min, which resulted in an 82–89% yield of the sulfoxide **19** in 85–95% ee. Longer reaction times resulted in a product of lower optical purity, presumably because the product **19** is then subject to ligand exchange by the Grignard reagent **2** and consequent racemisation.[22] The optical purity of the product could be further improved by trituration with hexane. The racemate, which is a solid, is less soluble in hexane and its removal allows the sulfoxide to be obtained in 95–97% ee. The optical purity of the sulfoxide **19** was determined by HPLC using a covalent (*R*)-(−)-*N*-(3,5-dinitrobenzoyl)phenylglycine Pirkle column. The absolute



Scheme 3 *Reagent:* i, *p*-$ClC_6H_4CH_2SNa$

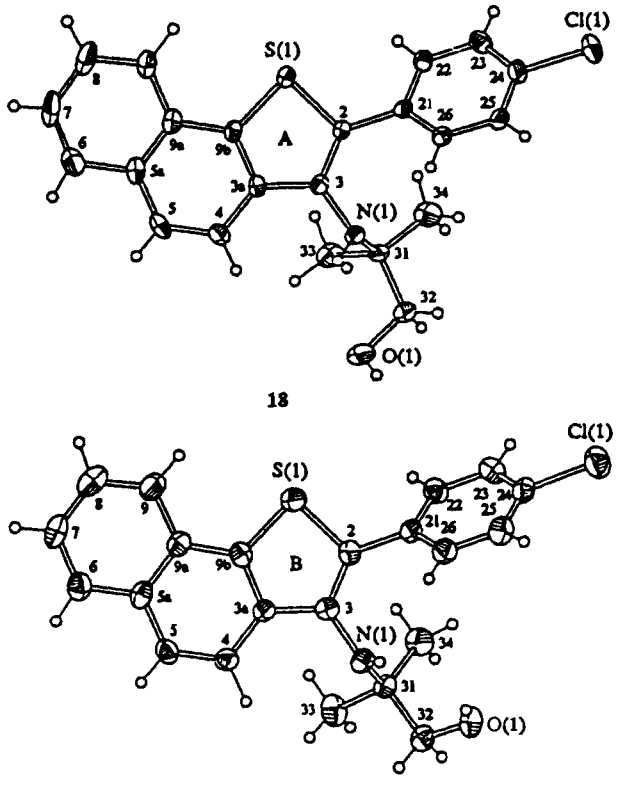
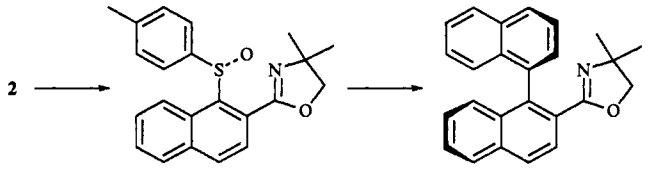


Fig. 1 Molecular projections of compound **18** normal to the aromatic planes; labelling and 20% thermal ellipsoids for the non-hydrogen atoms are shown, hydrogen atoms having arbitrary radii of 0.1 Å

configuration at the sulfur centre in the sulfoxide **19** is assumed to be *S* since it is known that inversion of configuration accompanies nucleophilic attack by Grignard reagents on (1*R*)-menthyl (*S*)-toluene-*p*-sulfinate.[23,24]



Scheme 4

Reaction of the sulfoxide **19** with 1-naphthylmagnesium bromide for 3.5 h at room temperature furnished the optically active (*S*)-1,1'-binaphthyl **20** in 62% yield and 60% ee, accompanied by 10% of the ligand-exchange product **9**. The absolute configuration and ee of product **20** were determined by comparison with the previously reported[10] optical rotation, and the ee confirmed by ^{1}H NMR spectroscopy using the chiral shift reagent tris-[3-(heptafluoropropylhydroxymethylene)-(+)-camphorato]europium(III) [Eu(hfc)$_3$]. The recovered starting sulfoxide **19** (13%) from this reaction was found to have partially racemised (~60% ee estimated by optical rotation). This observation can be accounted for by initial ligand-exchange reaction generating the Grignard reagent **2**, which is then able to racemise compound **19** through further ligand-exchange reactions, as discussed previously. Quenching of the reaction after 1.5 h provided the starting sulfoxide **19** (27% recovery) in ~85% ee; after 30 min compound **19** (64%) was isolated in *ca.* 95% ee. In neither case was the ee of the product **20** significantly different from that in the original experiment, as estimated by optical rotation, confirming that the rate of racemisation is substantially lower than the rate of ligand coupling for the major part of the reaction.

The sulfoxide **19** failed to undergo a coupling reaction with 2-methoxy-1-naphthylmagnesium bromide, only the ligand-exchange product **9** being isolated after several hours at room temperature. The added steric demands of the 2-methoxy group presumably prevent coupling, and ligand exchange becomes the favoured reaction pathway. Oae and Furukawa and their co-workers[15] have reported that 2-(*tert*-butylsulfinyl)pyridine fails to undergo ligand-exchange reactions with Grignard reagents, since this reaction can be likened to an S_N2 reaction at a neopentyl centre. Employing a *tert*-butyl sulfoxide in the coupling reaction could therefore prevent the competitive reaction pathways of ligand exchange and subsequent sulfoxide racemisation. We therefore treated the bromo oxazoline **1** with sodium 1,1-dimethylethanethiolate in DMF at 100 °C during 15 h. The resultant *tert*-butylsulfanyl oxazoline **4** was oxidised with MCPBA and provided the crude sulfoxide **8** in 87% overall yield. Repeated chromatography of compound **8** failed to separate an unidentified impurity, present in ~10% by high-field ^{1}H NMR analysis. Attempts at further purification through crystallisation were complicated by the instability of the compound (see below). Also evident in the ^{1}H NMR spectrum of compound **8** was the presence of an isomer resulting from hindered rotation about the naphthyl–sulfur bond. Atropisomerism in hindered 1-naphthyl sulfoxides has recently been described by Casarini *et al.*[25] For example, 1-(*tert*-butylsulfinyl)-2-methylnaphthalene has two rotameric forms in the ratio *Z*:*E* 64:36 at 25 °C in C_2Cl_4 solution. In the ^{1}H NMR spectrum of this compound 8-H in the *Z* atropisomer is significantly deshielded with respect to 8-H in the *E* atropisomer—δ_H 9.45 and 8.35, respectively, in $CDCl_3$ solution. In the case of compound **8** the *Z*:*E* ratio was *ca.* 1:10, with 8-H appearing at δ_H 8.24 and 9.49, respectively, in $CDCl_3$ solution, and δ_H 7.84 and 10.02 in [$^2H_8$]toluene solution (note that the change in substituent priorities reverses the terms for comparable isomers).‡ That the signal at δ_H 7.84 in [$^2H_8$]toluene solution was indeed due to a minor rotamer was confirmed by a saturation transfer experiment.[26] Thus, irradiation of the signal at δ_H 7.84 led to a 34% reduction in the intensity of the signal at δ_H 10.02 at 30 °C.

On attempted crystallisation of the sulfoxide **8** from light petroleum it was discovered that the compound decomposed to give a crystalline compound that HRMS indicated had the molecular formula $C_{15}H_{15}NO_2S$ so that the sulfoxide had lost the elements of isobutene. This was in keeping with both the ^{1}H and ^{13}C NMR spectra. The former spectrum revealed the presence of two equivalent methyl groups (δ_H 1.68) and an isolated hydroxymethyl group since there was a 2 H doublet at δ_H 4.03 assigned to the methylene protons and a 1 H triplet at δ_H 5.53. The ^{13}C NMR spectrum revealed the absence of the *tert*-butyl group and that the oxazoline entity had undergone rearrangement since the imine carbon atom was replaced by a carbonyl group (δ_C 167.1). The presence of a CH_2OH group was indicated by a signal at δ_C 69.7 and the presence of a quaternary carbon atom bearing two methyl groups was indicated by appropriate signals at δ_C 64.1 and 25.1. In the mass spectrum the molecular ion lost CH_2O and C_4H_8O as indicated by high resolution of the peaks at *m*/*z* 242 and 201. This evidence suggested that the attachment of the aliphatic side chain was on nitrogen. The IR spectrum confirmed the presence of a hydroxy group (ν_{max} 3415 cm^{-1}) and a carbonyl group (ν_{max} 1618 cm^{-1}). These data are in keeping with the isothiazolone structure **22** which was confirmed by a single-crystal X-ray analysis (Fig. 2).

It has been known for some time that sulfoxides having at least one alkyl substituent with a hydrogen atom attached to the β-carbon atom can undergo thermal decomposition to yield alkenes and sulfenic acids which normally undergo intermolecular disproportionation. Strong evidence has been adduced for a concerted mechanism involving *cis*-elimination *via* a cyclic five-membered transition state,[27] the E_i mechanism. When di-*tert*-butyl sulfoxide is heated at 80 °C the 1,1-dimethylethylsulfenic acid produced by the elimination of isobutene has been detected spectroscopically and it can be trapped by ethyl acrylate or methyl propiolate when these compounds are used as the reaction solvents.[28] Methanesulfenic acid has also been detected spectroscopically during the flash vacuum pyrolysis of *tert*-butyl methyl sulfoxide.[29] The intervention of sulfenic acids has also been put forward as an explanation for the specific incorporation of deuterium into penicillin sulfoxides.[30] The sulfoxide **8**, on account of the large number of available β-hydrogens and in order to relieve strain, undergoes thermal elimination of isobutene at quite low temperature, and the sulfenic acid **21** results (Scheme 5).

The fate of sulfenic acids resulting from the elimination of a cyclic sulfoxide may take two intramolecular courses depending on the substituents attached to the resultant olefin. For unactivated olefins the pathway is *cis*-addition as encountered in penicillin sulfoxides.[31] If the olefin is substituted with a heteroatom, self-catalysed electrophilic addition occurs with the loss of water.[32,33] It is plausible, then, that the sulfenic acid **21** is trapped by intramolecular electrophilic addition followed by addition of water to the iminium double bond; ring opening and prototropic shift then yields the isothiazolone **22**.

The sulfoxide **8** underwent reaction with an excess of 2-methoxy-1-naphthylmagnesium bromide at room temperature during 120 h and yielded the 1,1'-binaphthyl **16** in 44% yield. We have unsuccessfully explored a number of methods for

‡ The rotamer of 1-(*tert*-butylsulfinyl)-2-methylnaphthalene which is designated *E* has the sulfoxide oxygen *cis* to the methyl group on the naphthalene ring. The rotamer of **8** which is designated *E* has the sulfoxide oxygen *trans* to the oxazoline group on the naphthalene ring.

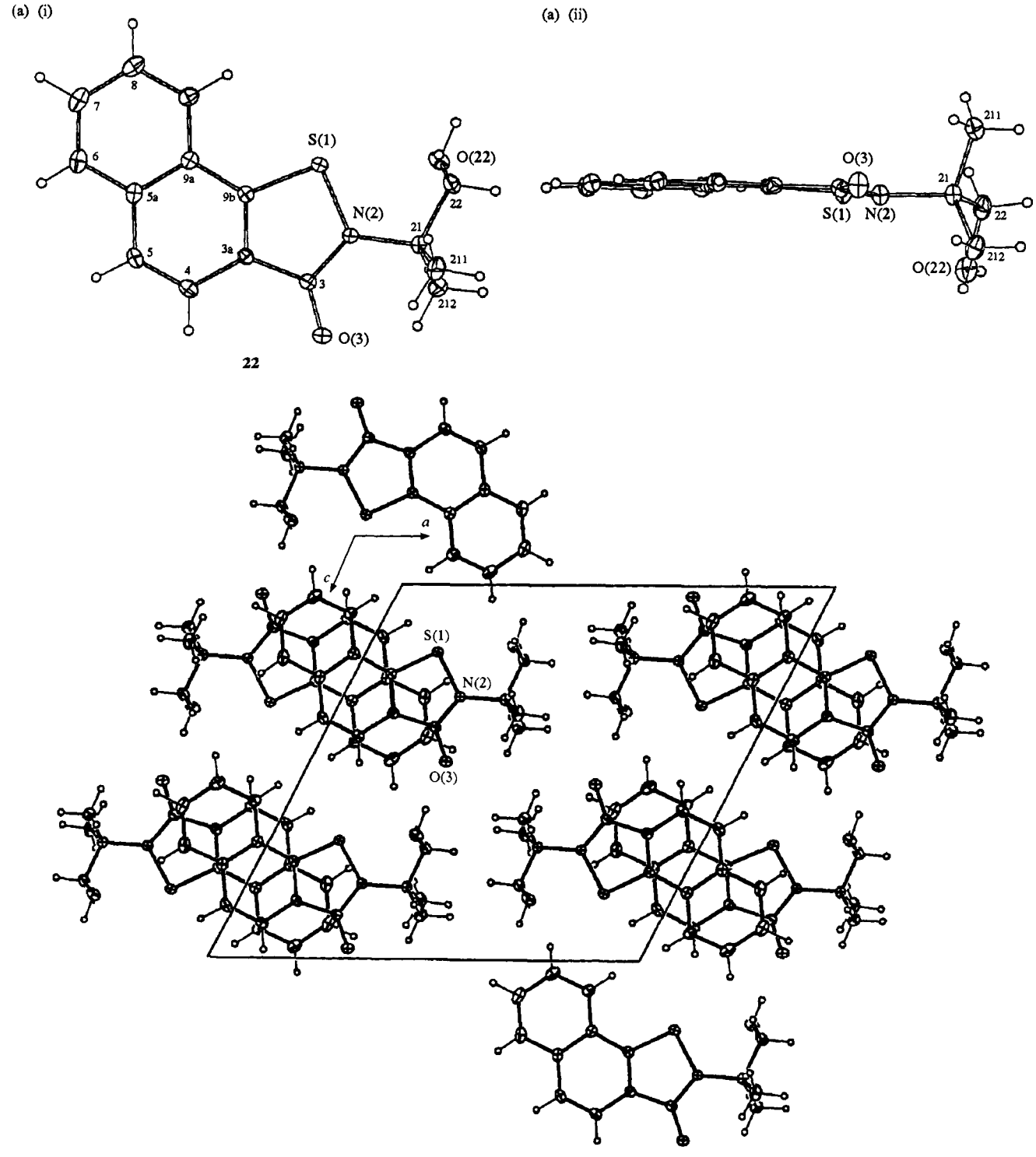
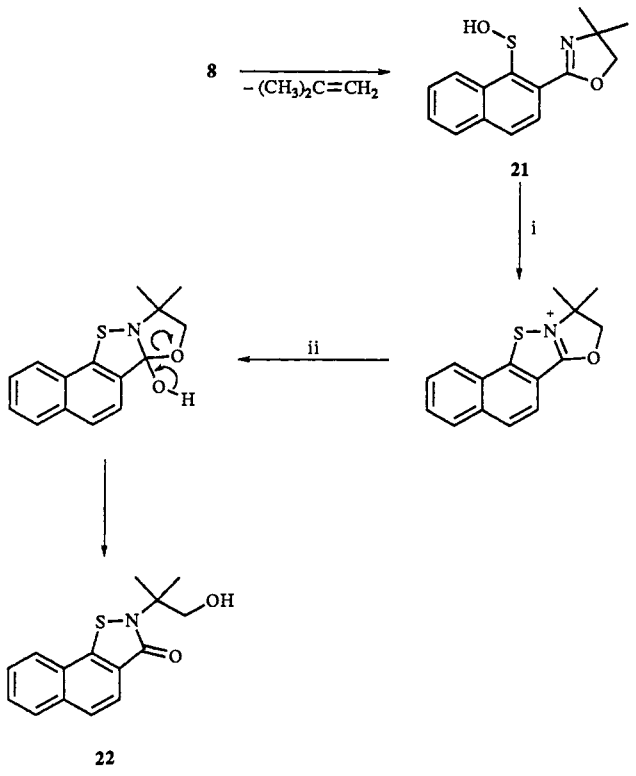


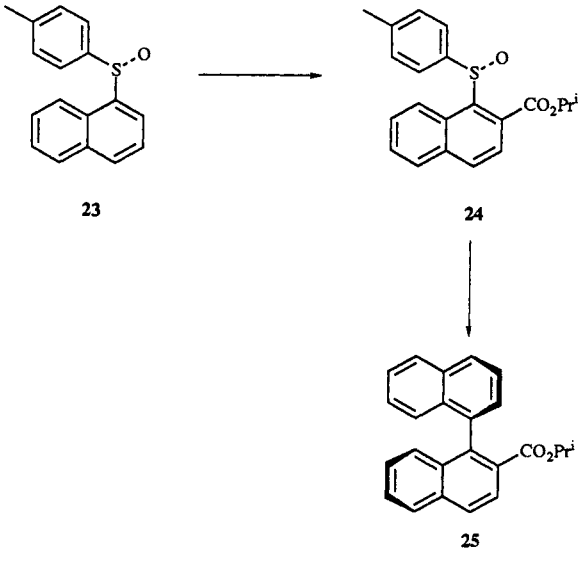
Fig. 2 (*a*) Molecular projection of compound **22** (i) normal to, and (ii) through the aromatic plane. (*b*) Unit-cell contents of compound **22** projected down *b*.

obtaining the sulfoxide **8** in non-racemic form, including the methods of Kagan,[34] and Evans[35] and their co-workers. Approaches based on the asymmetric oxidation of the sulfide **4** are currently being investigated.

Our attention next turned to the coupling reactions of 1-naphthyl sulfoxides containing alternative electron-withdrawing 2-substituents to an oxazoline. As mentioned previously, Miyano and co-workers[11] have demonstrated the enantioselective formation of 1,1′-binaphthyls through the S_NAr displacement of a chiral 1-alkoxy substituent from hindered naphthalene-2-carboxylic esters by 1-naphthyl Grignard reagents. An isopropyl ester was found to be sufficiently hindered adequately to suppress attack by the Grignard reagent at the ester carbonyl carbon. Ogawa and Furukawa[36] have demonstrated the directed *ortho*-metallation of optically active diaryl sulfoxides using lithium diisopropylamide (LDA) as the metallating reagent. Care must be taken in these reactions to avoid employing an excess of butyllithium (BuLi) in the generation of LDA, since it has been shown[22] that BuLi may initiate ligand exchange and racemisation of diaryl sulfoxides. When the known[23] (*S*)-1-(*p*-tolylsulfinyl)naphthalene **23** (Scheme 6) was treated with LDA in THF solution at −78 °C,



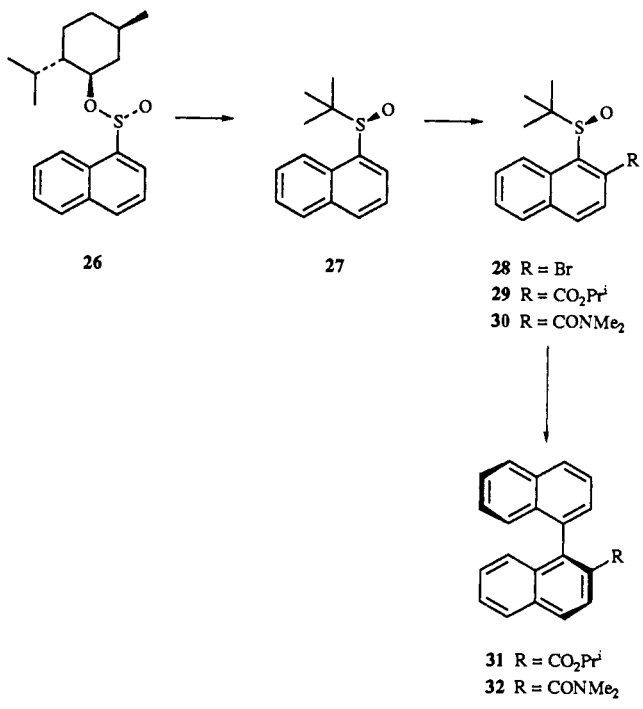
Scheme 5 *Reagents:* i, H^+ ($-H_2O$); ii, H_2O ($-H^+$)



Scheme 6

for 20 min, followed by inverse addition of the anion to a solution of isopropyl chloroformate in THF at −78 °C, the 2-isopropoxycarbonyl sulfoxide **24** was obtained in 36% yield and >99% ee, as determined by HPLC analysis. Regioisomeric products were not evident by TLC analysis. The sulfoxide **24** on reaction with an excess of 1-naphthylmagnesium bromide in THF solution at room temperature during 30 min gave the known[11] (*S*)-(−)-1,1′-binaphthyl **25** in 78% yield and 82% ee, as estimated by ^1H NMR spectroscopy using $Eu(hfc)_3$.

The directed *ortho*-metallation strategy has also provided access to optically active 1-(*tert*-butylsulfinyl)naphthalenes with electron-withdrawing 2-substituents. The known[23] (1*R*)-menthyl (*S*)-naphthalene-1-sulfinate **26** (Scheme 7) was readily prepared from naphthalene-1-sulfonyl chloride by the procedure of Klunder and Sharpless,[37] and was allowed to react with *tert*-butylmagnesium chloride in toluene solution at 0 °C during 45 min, to afford (*R*)-1-(*tert*-butylsulfinyl)naphthalene **27** in 78% yield and 90% ee, as determined by HPLC analysis. Sulfoxide **27** is a low melting solid and, although its optical purity could be improved through crystallisation, the recovery was poor. The material of 90% ee was, therefore, usually employed in subsequent transformations, since the products could be efficiently recrystallised to optical purity. Assignment of the *R* configuration to compound **27** was initially made by assuming that inversion of configuration accompanies nucleophilic attack by the Grignard reagent on sulfinate **26**.[23,24] However, Drabowicz *et al.*[38] have reported that in the reactions of either non-branched alkanesulfinates with hindered organometallic reagents or sulfinates containing sterically demanding substituents at the sulfur centre with non-hindered organometallic reagents, retention of configuration is observed. However, it has been found that the reaction between the sterically demanding *tert*-butyl Grignard reagent and diacetone-glucosyl methanesulfinates occurs with complete inversion of configuration at sulfur.[39] Given the large steric demand for the reaction of sulfinate **26** with *tert*-butylmagnesium chloride, we sought definitive evidence for the absolute configuration of product **27**. Metallation of sulfoxide **27** was very slow with LDA as the base. However, Snieckus and co-workers[40] have reported the directed *ortho*-metallation of racemic *tert*-butyl phenyl sulfoxide when using BuLi. It was not anticipated in this instance that the use of BuLi as metallating agent would initiate either ligand exchange or racemisation of compound **27**, based on the precedent of reactions of 2-(*tert*-butylsulfinyl)pyridine with Grignard reagents discussed previously. Treatment of compound **27**, of >99% ee, with BuLi in THF solution at −78 °C for 10 min, followed by inverse addition to 1,2-dibromotetrafluoroethane in THF at −78 °C, furnished the 2-bromo sulfoxide **28** in 46% yield. Again, regioisomeric products were not evident by TLC analysis. Single-crystal X-ray crystallographic analysis of sulfoxide **28** has confirmed the *R* absolute configuration (Fig. 3). Besides the stereogenic centre at sulfur, the molecule possesses a conformational stereogenic axis along the naphthyl-sulfur bond. In the crystal structure of compound **28** the



Scheme 7

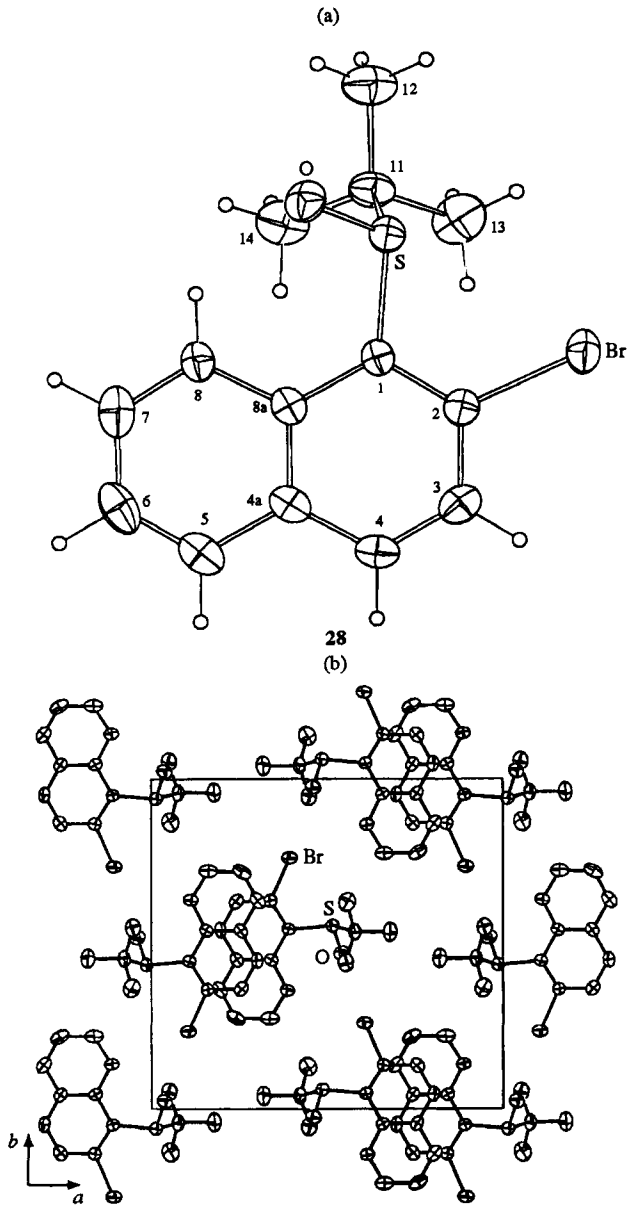


Fig. 3 (*a*) Molecular projection of compound **28** normal to the aromatic plane. (*b*) Unit-cell contents of compound **28** projected down *a*

molecule exists exclusively as one rotamer which has the *E*-conformation. Similarly, there are no signals apparent for the *Z*-rotamer in solution in the ^{1}H NMR spectrum of compound **28**.

Treatment of sulfoxide **27** of ~90% ee, with BuLi in THF solution at −78 °C for 10 min, followed by inverse addition to isopropyl chloroformate in THF at −78 °C, furnished the 2-isopropoxycarbonyl sulfoxide **29** in 39% yield. After a single crystallisation the ester **29** was of >99% ee, as determined by HPLC analysis. As in the case of compound **8**, the ^{1}H NMR spectrum of ester **29** revealed the presence of two rotameric forms in the ratio $Z:E \approx 1:2.5$, with 8-H appearing at δ_H 7.86 and 10.02, respectively, in [$^2H_8$]toluene solution. When the sulfoxide **29** was treated with an excess of 1-naphthylmagnesium bromide in THF solution at room temperature during 35 min, the (*R*)-1,1′-binaphthyl **31** was obtained in 90% yield and 95% ee, as estimated by ^{1}H NMR spectroscopy using Eu(hfc)$_3$.

The 2-lithio derivative of sulfoxide **27** (~90% ee) was caused to react with *N*,*N*-dimethylcarbamoyl chloride in THF

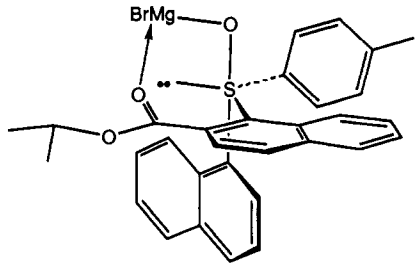


Fig. 4 Reaction of 1-naphthylmagnesium bromide with *p*-tolyl sulfoxide **24**

solution containing tetramethylethylenediamine (TMEDA) at −78 °C for 18 h, and furnished the 2-(*N*,*N*-dimethylcarbamoyl) sulfoxide **30** in 36% yield. After a single crystallisation, product **30** had ≥95% ee, as evident from its subsequent reaction with 1-naphthylmagnesium bromide [the enantiomers were not separable by HPLC on a Pirkle column and, in the presence of Eu(hfc)$_3$, the ^{1}H NMR spectrum was excessively broadened]. The ^{1}H NMR spectrum of compound **30** revealed the presence of two rotameric forms in the ratio $Z:E \approx 1:3$, with 8-H appearing at δ_H 8.07 and 9.80, respectively, in [$^2H_8$]toluene solution. The sulfoxide **30** on treatment with an excess of 1-naphthylmagnesium bromide in THF solution at room temperature during 25 h gave the (*R*)-1,1′-binaphthyl **32** in 65% yield and 95% ee, as determined by HPLC analysis. The absolute configuration of compound **32** was determined by conversion of the ester **31** into the amide **32**. The ^{1}H and ^{13}C NMR spectra of compound **32** at 20 °C contained very broad signals due to hindered rotation about the naphthalene–C(O) bond.[41] At −25 °C signals for two rotamers in the ratio ~2.5:1 were observed. It should be noted that the ^{1}H and ^{13}C NMR spectra of the sulfoxide **30** do not display broadening or additional signals due to hindered rotation about the naphthalene–C(O) bond.

A plausible rationalisation of the sense of asymmetric coupling is illustrated in Figs. 4 and 5. Based on the work of Oae and Furukawa[15,16] it is proposed that initial attack of 1-naphthylmagnesium bromide on the *p*-tolyl sulfoxides (*e.g.*, **24**) occurs axially from the side opposite the oxygen ligand, leading to a σ-sulfurane with the oxymagnesium bromide ligand in an apical position (Fig. 4). The equatorial 2-isopropoxycarbonyl-1-naphthyl ligand may then be oriented with the isopropoxycarbonyl group *syn* or *anti* to the *p*-tolyl group on sulfur, chelation of the magnesium to the carbonyl oxygen atom being possible for either orientation. The *syn* orientation should be sterically disfavoured over the *anti* provided the isopropoxycarbonyl group is coplanar with the naphthalene ring (required for activation of the coupling reaction). Unfavourable steric interactions between the *p*-tolyl group and Mg and associated ligands are also avoided with the *anti* orientation. The orientation of the axial 1-naphthyl ligand is such that non-bonded repulsions are minimised and this governs the configuration of the new asymmetric element created by subsequent ligand-coupling reaction.

For the *tert*-butyl sulfoxides (*e.g.*, **29**) it is proposed that initial attack of 1-naphthylmagnesium bromide occurs axially from the side opposite the *tert*-butyl ligand, avoiding non-bonding repulsions with the bulky *tert*-butyl group. The resulting σ-sulfurane has the oxymagnesium bromide ligand in an equatorial position (Fig. 5), so that chelation of the magnesium to the carbonyl oxygen atom of the isopropoxycarbonyl group fixes the orientation of the equatorial 2-isopropoxycarbonyl-1-naphthyl ligand. The orientation of the axial 1-naphthyl ligand is again such that non-bonded repulsions are minimised.

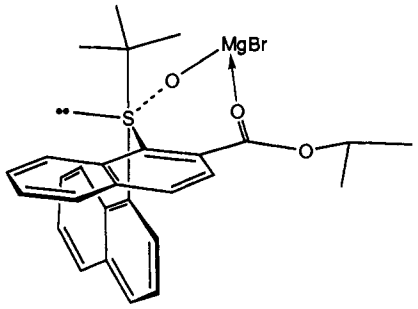


Fig. 5 Reaction of 1-naphthylmagnesium bromide with *tert*-butyl sulfoxide **29**

The sulfoxides **28**, **29** and **30** all failed to undergo a clean ligand-coupling reaction with the more hindered Grignard reagent, 2-methoxy-1-naphthylmagnesium bromide. Thus, there appears to be a well defined limit to the steric crowding about sulfur that can be accommodated, limiting the scope of the methodology for 1,1′-binaphthyl synthesis. We are currently exploring further applications of ligand-coupling reactions of sulfoxides for the enantioselective synthesis of other atropisomeric chiral systems.

Experimental

Mps were determined on a Kofler block and are uncorrected. All experiments involving the use of organometallic species were conducted under dry argon using the Schlenk technique. All organic extracts were dried over anhydrous sodium sulfate prior to evaporation under reduced pressure. Light petroleum was a hexane fraction. Radial chromatography was performed on a Harrison Research Chromatotron using plates coated with Merck kieselgel 60 PF_{254}. Unless otherwise stated ^1H NMR (300 MHz) and ^{13}C NMR (75.5 MHz) spectra were determined for solutions in deuteriochloroform on a Bruker AM300 instrument, with *J*-values given in Hz. ^1H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra were determined on a Bruker AMR500 instrument. The assignment of ^{13}C NMR spectra was assisted by use of the distortionless enhancement by polarisation transfer (DEPT) technique. IR spectra were determined for thin films or KBr discs using a Digilab FTS40 FTIR spectrophotometer. Mass spectra were recorded using a Hewlett-Packard 5986 GC-MS instrument. Optical rotations were determined on a Perkin-Elmer 141 polarimeter using a 10 cm microcell, and $[\alpha]_D$-values are reported in units of 10^{-1} deg cm^2 g^{-1}.

HPLC determinations of optical purity were carried out using an ICI LC1500 solvent-delivery system, an ICI Kortec K95 variable-wavelength absorbance detector operating at 254 nm, and a 25 cm × 4.6 mm ID covalent (*R*)-(−)-*N*-(3,5-dinitrobenzoyl)phenylglycine Pirkle column (E. S. Industries) eluted with the indicated mobile phase at a flow rate of 1.0 cm^3 min^{-1}.

4,4-Dimethyl-2-[1-(phenylsulfanyl)naphthalen-2-yl]-4,5-dihydrooxazole 3

A solution of the bromide **1**[10] (1.047 g, 3.44 mmol) in anhydrous THF (10 cm^3) containing magnesium turnings (100 mg, 4.1 mg-atom) and a trace of iodine was heated until the iodine colour disappeared and was then stirred at room temperature for 17 h. The resulting dark red solution was cooled to 0 °C, solid diphenyl disulfide (653 mg, 3.11 mmol) was added, and the mixture was stirred at room temperature for 23 h. An excess of 5% aq. ammonium chloride was added followed by dichloromethane. The separated organic layer was washed in turn with dil. aq. sodium hydroxide, water, and finally with saturated brine. The crude product was purified by radial chromatography with 10% ethyl acetate–light petroleum as eluent. The *sulfide* **3** (778 mg, 68%) was crystallised from dichloromethane–light petroleum as needles, mp 107–108 °C (Found: C, 75.55; H, 5.85; N, 4.2; S, 9.55. $C_{21}H_{19}NOS$ requires C, 75.65; H, 5.75; N, 4.2; S, 9.6%); δ_H 1.33 (6 H, s, 2 × Me), 4.08 (2 H, s, CH_2), 7.03–7.26 (5 H, m, Ph), 7.51–7.56 (2 H, m, 6- and 7-H), 7.71 and 7.95 (2 H, AB, $J_{3,4}$ 8.5, 3- and 4-H), 7.86–7.89 (1 H, m, 5-H) and 8.51–8.54 (1 H, m, 8-H); δ_C 163.0, 138.0, 134.7, 134.4, 133.9 and 130.0 (each C), 129.9 (CH), 128.7 (2 × CH), 128.4 and 127.5 (each CH), 127.4 (2 × CH), 127.2, 126.8, 126.5 and 125.3 (each CH), 79.4 (CH_2), 67.8 (C) and 27.3 (Me); ν_{max}(KBr)/cm^{-1} 1660 (C=N) and 1085 (C–O); *m*/*z* 333 (M^+, 100%), 260 (23), 256 (97), 247 (33), 234 (44), 202 (40) and 140 (48).

4,4-Dimethyl-2-[1-(phenylsulfinyl)naphthalen-2-yl]-4,5-dihydrooxazole 5

A solution of the foregoing sulfide **3** (510 mg, 1.53 mmol) in chloroform (20 cm^3) was stirred at 0 °C and MCPBA (93% by iodometry; 287 mg, 1.55 mmol) was added in one portion. The solution was stirred at 0 °C for 10 min and then was diluted with dichloromethane and washed in turn with saturated aq. sodium hydrogen carbonate, water, and finally with saturated brine. The crude product was crystallised from dichloromethane–light petroleum as pale yellow prisms of the *sulfoxide* **5** (433 mg, 78%), mp 151–152 °C (Found: C, 71.85; H, 5.75; N, 4.0; S, 9.5. $C_{21}H_{19}NO_2S$ requires C, 72.2; H, 5.5; N, 4.0; S, 9.15%); δ_H 1.43 and 1.46 (each 3 H, s, Me), 4.19 and 4.24 (2 H, AB, *J* 7.8, CH_2), 7.36–7.52 (5 H, m, Ph), 7.73 and 8.00 (2 H, AB, $J_{3,4}$ 8.4, 3- and 4-H), 7.84–7.87 (3 H, m, 5-, 6- and 7-H) and 8.71 (1 H, br d, 8-H); δ_C 160.9, 144.4, 139.2 and 135.2 (each C), 132.6 and 129.6 (each CH), 129.4 and 129.3 (each C), 128.8 (CH), 128.6 (2 × CH), 127.6, 127.5 and 125.1 (each CH), 125.0 (2 × CH), 124.8 (CH), 79.8 (CH_2), 68.8 (C) and 28.2 and 28.0 (each Me); ν_{max}(KBr)/cm^{-1} 1652 (C=N), 1084 (C–O) and 1045 (S=O); *m*/*z* 349 (M^+, 100%), 272 (33), 234 (28), 202 (42), 200 (28), 146 (25) and 140 (34).

4,4-Dimethyl-2-[1-(benzylsulfinyl)naphthalen-2-yl]-4,5-dihydrooxazole 6

The Grignard reagent was prepared from the bromide **1** (1.022 g, 3.36 mmol), magnesium (90 mg, 3.5 mg-atom) and anhydrous THF (10 cm^3) as described above. The mixture was added dropwise at room temperature to a stirred solution of phenylmethanesulfinyl chloride[17] (700 mg, 4.0 mmol) in cyclohexane (20 cm^3). Work-up after 10 min in the usual way gave a crude product, which was purified by radial chromatography with 30% ethyl acetate–light petroleum as eluent. The *sulfoxide* **6** (520 mg, 43%) was crystallised from light petroleum as prisms, mp 101–103 °C (Found: C, 72.85; H, 6.05; N, 3.7; S, 8.7. $C_{22}H_{21}NO_2S$ requires C, 72.7; H, 5.8; N, 3.85; S, 8.8%); δ_H 1.43 and 1.47 (each 3 H, s, Me), 4.15 and 4.21 (2 H, AB, *J* 8.0, CH_2), 4.66 and 4.85 (2 H, AB, *J* 12.5, PhCH_2), 7.26–7.38 (3 H, m, ArH), 7.45–7.48 (2 H, m, ArH), 7.58–7.62 (2 H, m, ArH), 7.72 and 7.98 (2 H, AB, $J_{3,4}$ 8.4, 3- and 4-H), 7.90–7.94 (1 H, m, ArH) and 9.36 (1 H, m, 8-H); δ_C 160.0, 139.7, 134.9 and 132.3 (each C), 131.6 (CH), 130.6 (C), 130.3 (2 × CH), 128.9 (CH), 128.6 (2 × CH), 128.1, 127.6 and 127.3 (each CH), 126.6 (C), 124.9 and 124.6 (each CH), 79.4 and 60.2 (each CH_2) and 28.5 and 28.2 (each Me); ν_{max}(KBr)/cm^{-1} 1638 (C=N) and 1050 (S=O); *m*/*z* 363 (M^+, 1%), 272 (35), 256 (30), 202 (22), 200 (20) and 91 (100).

2-{1-[(4-Chlorobenzyl)sulfinyl]naphthalen-2-yl}-4,4-dimethyl-4,5-dihydrooxazole 7

The Grignard reagent was prepared from the bromide **1** (2.55 g, 8.4 mmol), magnesium (220 mg, 9.2 mg-atom) and anhydrous THF (15 cm^3). The mixture was added dropwise to a stirred

solution of 4-chlorophenylmethanesulfinyl chloride, prepared[17] from bis-(4-chlorobenzyl) disulfide (1.518 g, 4.82 mmol), in cyclohexane (50 cm^3). Work-up after 15 min gave a crude product, which was passed through a short column of basic alumina and then crystallised from dichloromethane–light petroleum whereupon it was obtained as yellow prisms (1.4 g, 42%) of the *sulfoxide* **7**, mp 147–148 °C (Found: M^+, 397.0902. $^{12}C_{22}{}^{1}H_{20}{}^{35}Cl^{14}N^{16}O_2{}^{32}S$ requires M, 397.0903); δ_H 1.40 and 1.46 (each 3 H, s, Me), 4.13 and 4.19 (2 H, AB, J 8.0, CH_2), 4.60 and 4.79 (2 H, AB, J 12.6, PhCH_2), 7.31–7.41 (4 H, m, benzyl ArH), 7.55–7.60 (2 H, m, 6- and 7-H), 7.74 and 7.96 (2 H, AB, $J_{3,4}$ 8.4, 3- and 4-H), 7.89–7.92 (1 H, m, 5-H) and 9.31 (1 H, br, 8-H); δ_C 159.8, 139.5, 135.0 and 134.3 (each C), 131.7 (CH), 131.6 (2 × CH), 130.9 and 130.6 (each C), 129.0 (CH), 128.8 (2 × CH), 127.7 and 127.3 (each CH), 126.5 (C), 124.8 and 124.5 (each CH), 79.4 (CH_2), 69.1 (C), 59.6 (CH_2) and 28.6 and 28.2 (each Me); ν_{max}(KBr)/cm^{-1} 1647 (C=C) and 1043 (S=O); m/z 397 (M^+, 2%), 256 (39), 202 (20), 158 (18), 125 (100) and 55 (87).

4,4-Dimethyl-2-(1-phenylnaphthalen-2-yl)-4,5-dihydrooxazole 10

Phenylmagnesium bromide (1.0 mol dm^{-3}; 1.1 mmol) as a solution in THF (1.1 cm^3) was added dropwise at −20 °C to a stirred solution of the sulfoxide **5** (200 mg, 0.57 mmol) in anhydrous THF (10 cm^3). After 7 h at −20 °C the reaction was quenched by the addition of an excess of 5% aq. ammonium chloride and the mixture was extracted with dichloromethane. The extract was washed successively with water and saturated brine. The products were separated by radial chromatography with 10% ethyl acetate–light petroleum as eluent. The first fraction contained a 2:1 mixture of diphenyl disulfide and phenyl benzenethiosulfonate (29 mg, ~40% combined yield), based on GC-MS analysis.[42]

The second fraction furnished the ligand-exchange product 4,4-dimethyl-2-(naphthalen-2-yl)-4,5-dihydrooxazole **9** (57 mg, 44%) as an oil, which was identified by its ^1H NMR spectrum.[43]

The third fraction furnished the *phenylnaphthalene* **10** (60 mg, 35%) as an oil (Found: C, 83.4; H, 6.75; N, 4.95. $C_{21}H_{19}NO$ requires C, 83.7; H, 6.35; N, 4.65%); δ_H 1.20 (6 H, s, 2 × Me), 3.72 (2 H, s, CH_2), 7.35–7.54 (7 H, m, 6- and 7-H and Ph), 7.66 (1 H, br d, 8-H), 7.78 (1 H, A of AB, $J_{3,4}$ 8.5, 3-H) and 7.87–7.90 (2 H, m, 4- and 5-H); δ_C 163.6, 140.0, 138.6, 134.2 and 132.1 (each C), 130.0 (2 × CH), 127.9 (CH), 127.6 (2 × CH), 127.5, 127.2, 127.0, 126.7 and 126.3 (each CH), 126.0 (C), 125.9 (CH), 79.2 (CH_2), 67.3 (C) and 27.9 (2 × Me); ν_{max}(film)/cm^{-1} 1658 (C=N); m/z 301 (M^+, 18%), 300 (53), 230 (29), 228 (27), 216 (23), 215 (100), 202 (49) and 201 (20).

A fourth fraction contained diphenyl sulfoxide (45 mg, 39%), identified by GC-MS analysis.[42]

When the same reaction was carried out at room temperature for 15 min the yields of products **9** and **10** were 19% and 72%, respectively.

2-(1-Ethylnaphthalen-2-yl)-4,4-dimethyl-4,5-dihydrooxazole 11

A solution of ethylmagnesium bromide (0.53 mol dm^{-3}; 1.9 mmol) in THF (3.5 cm^3) was added dropwise at room temperature to a stirred solution of the sulfoxide **5** (215 mg, 0.62 mmol) in anhydrous THF (10 cm^3). After 4 h at room temperature the reaction mixture was quenched by the addition of an excess of 5% aq. ammonium chloride and extracted with dichloromethane. The extract was washed successively with water and saturated brine. The products were separated by radial chromatography with 10% ethyl acetate–light petroleum as eluent. The *ethylnaphthalene* **11** (29 mg, 19%) was eluted first and was obtained as an oil (Found: M^+, 253.1467. $^{12}C_{17}{}^{1}H_{19}{}^{14}N^{16}O$ requires M, 253.1467); δ_H 1.35 (3 H, t, J 7.4, $MeCH_2$), 1.44 (6 H, s, 2 × Me), 3.38 (2 H, q, J 7.4, MeCH_2), 4.15 (2 H, s, CH_2), 7.49–7.57 (2 H, m, 6- and 7-H), 7.70 (2 H, apparent s, 3- and 4-H), 7.82–7.85 (1 H, m, 5-H) and 8.14–8.18 (1 H, m, 8-H); δ_C 163.5 and 141.4 (each C), 134.5 (2 × C), 131.6 (C), 128.6 (CH), 126.4 (2 × CH), 126.2, 126.1 and 124.8 (each CH), 78.9 (CH_2), 67.8 (C), 28.4 (2 × Me), 22.7 (CH_2) and 15.7 (Me); ν_{max}(film)/cm^{-1} 1643 (C=N); m/z 253 (M^+, 93%), 252 (53), 198 (24), 182 (100), 167 (40), 154 (84), 153 (39), 152 (26) and 125 (28).

A second fraction furnished the ligand-exchange product **9** (50 mg, 36%).

4,4-Dimethyl-2-[1-(4-methylphenyl)naphthalen-2-yl]-4,5-dihydrooxazole 12

A solution of *p*-tolylmagnesium bromide (0.8 mol dm^{-3}; 1.5 mmol) in THF (1.9 cm^3) was added dropwise at room temperature to a stirred solution of the sulfoxide **6** (201 mg, 0.55 mmol) in anhydrous THF (10 cm^3). After 75 min at room temperature the reaction was quenched by the addition of an excess of 5% aq. ammonium chloride and extracted with dichloromethane. The extract was washed successively with water and saturated brine. The products were separated by radial chromatography with 10% ethyl acetate–light petroleum as eluent. The ligand-exchange product **9** (13 mg, 10%) was eluted first.

A second fraction furnished the p-*tolylnaphthalene* **12** (114 mg, 65%) as an oil (Found: C, 83.55; H, 6.6; N, 4.75. $C_{22}H_{21}NO$ requires C, 83.8; H, 6.7; N, 4.45%); δ_H 1.23 (6 H, s, 2 × Me), 2.45 (3 H, s, Ar*Me*), 3.74 (2 H, s, CH_2), 7.26 (4 H, s, ArH), 7.37–7.54 (2 H, m, ArH) and 7.68–7.90 (4 H, m, ArH); δ_C 163.8 and 140.0 (each C), 136.8 (2 × C), 135.6, 134.3 and 132.3 (each C), 129.9 and 128.4 (each 2 × CH), 127.9, 127.4, 127.2, 126.7, 126.3 and 126.0 (each CH), 79.3 (CH_2), 67.3 (C), 28.0 (2 × Me) and 21.3 (Me); ν_{max}(film)/cm^{-1} 1653 (C=N); m/z 315 (M^+, 99%), 259 (34), 244 (23), 242 (21), 230 (30), 229 (100), 227 (31) and 202 (34).

2-(1-Benzylnaphthalen-2-yl)-4,4-dimethyl-4,5-dihydrooxazole 13

A solution of ethylmagnesium bromide (0.54 mol dm^{-3}; 4.2 mmol) in THF (7.8 cm^3) was added dropwise at room temperature to a stirred solution of the sulfoxide **6** (510 mg, 1.4 mmol) in anhydrous THF (10 cm^3). After 2 h at room temperature the reaction mixture was quenched by the addition of an excess of 5% aq. ammonium chloride and extracted with dichloromethane. The extract was washed successively with water and saturated brine. The products were separated by radial chromatography with 10% ethyl acetate–light petroleum as eluent. The first fraction was the ethylnaphthalene **11** (246 mg, 69%).

The second fraction was the *benzylnaphthalene* **13** (56 mg, 13%). It formed prisms from light petroleum, mp 101–103 °C (Found: M^+, 315.1634. $^{12}C_{22}{}^{1}H_{21}{}^{14}N^{16}O$ requires M, 315.1623); δ_H 1.35 (6 H, s, 2 × Me), 4.07 (2 H, s, CH_2), 4.87 (2 H, s, PhCH_2), 7.10–7.23 (5 H, m, Ph), 7.40–7.50 (2 H, m, ArH), 7.80–7.85 (3 H, m, ArH) and 8.05 (1 H, dd, $J_{8,6}$ 1.5, $J_{8,7}$ 9.0, 8-H); δ_C 163.5, 141.1 and 136.9 (each C), 134.6 (2 × C), 132.5 (C), 128.5 (CH), 128.3 and 128.2 (each 2 × CH), 127.1, 126.6, 126.51, 126.47, 125.62 and 125.58 (each CH), 79.0 (CH_2), 67.8 (C), 34.9 (CH_2) and 28.3 (2 × Me); ν_{max}(KBr)/cm^{-1} 2971 (CH), 1633 (C=N), 1493, 1257 and 1111; m/z 315 (M^+, 80%), 260 (32), 259 (54), 258 (28), 244 (22), 243 (27), 231 (21), 230 (45), 215 (75), 182 (24), 155 (24) and 154 (100).

A third fraction was the ligand-exchange product **9** (33 mg, 10%).

2-[1-(4-Chlorobenzyl)naphthalen-2-yl]-4,4-dimethyl-4,5-dihydrooxazole 14

A solution of ethylmagnesium bromide (1.1 mol dm^{-3}; 2.9 mmol) in THF (2.6 cm^3) was added dropwise at room

temperature to a stirred solution of the sulfoxide **7** (275 mg, 0.69 mmol) in anhydrous THF (10 cm^3). After 30 min at room temperature the reaction mixture was quenched by the addition of an excess of 5% aq. ammonium chloride and extracted with dichloromethane. The extract was washed successively with water and saturated brine. The products were separated by radial chromatography with 10% ethyl acetate–light petroleum as eluent. The first fraction was the ethylnaphthalene **11** (109 mg, 62%).

The second fraction was the p-(*chlorobenzyl*)*naphthalene* **14** (63 mg, 26%). It formed prisms from light–petroleum, mp 90–91 °C (Found: Cl, 10.15. $C_{22}H_{20}ClNO$ requires Cl, 10.15%; Found: M^+, 349.1234. $^{12}C_{22}{}^{1}H_{20}{}^{35}Cl^{14}N^{16}O$ requires M, 349.1233); δ_H 1.35 (6 H, s, 2 × Me), 4.06 (2 H, s, CH_2), 4.84 (2 H, s, ArCH_2), 7.04 and 7.15 (4 H, AA'BB', benzyl ArH), 7.40–7.50 (2 H, m, 6- and 7-H), 7.78–7.85 (3 H, m, 3-, 4- and 5-H) and 7.97 (1 H, br d, 8-H); δ_C 163.2, 139.62, 139.56, 136.5, 134.7 and 131.35 (each C), 129.6 (2 × CH), 128.6 (CH), 128.3 (2 × CH), 127.3, 126.8, 126.7 and 126.5 (each CH), 126.4 (C), 125.4 (CH), 79.0 (CH_2), 67.9 (C), 34.3 (CH_2) and 28.3 (2 × Me); ν_{max}(KBr)/cm^{-1} 1625 (C=N); *m/z* 349 (M^+, 46%), 215 (36) and 154 (100).

A third fraction was the ligand-exchange product **9** (7 mg, 4%).

2-({2-(4-Chlorophenyl)naphtho[1,2-*b*]thiophen-3-yl}amino)-2-dimethylpropan-1-ol 18

4-(Chlorophenyl)methanethiol (0.50 cm^3, 3.8 mmol) was added dropwise at 0 °C to a stirred suspension of sodium hydride (55% mineral dispersion washed three times with pentane; 165 mg, 3.8 mmol) in anhydrous DMF (10 cm^3). The bromide **1**[10] (1.00 g, 3.3 mmol) was added in one portion and the bath temperature was increased to 70 °C. After 23 h the cooled solution was partitioned between diethyl ether and aq. sodium hydroxide (2 mol dm^{-3}). The organic layer was washed in turn with water, saturated aq. copper sulfate, water and finally with saturated brine. The crude product was passed through a short column of alumina with 1:1 dichloromethane–light petroleum as eluent. The *thiophene* **18** (1.21 g, 96%) was crystallised from dichloromethane–light petroleum as prisms, mp 123–126 °C (Found: M^+, 381.0953. $^{12}C_{22}{}^{1}H_{20}{}^{35}Cl^{14}N^{16}O^{32}S$ requires M, 381.0954); δ_H(500 MHz) 0.93 (6 H, s, 2 × Me), 3.05 (2 H, br s, NH and OH), 3.35 (2 H, s, CH_2), 7.45 and 7.69 (4 H, AA'BB', ArH), 7.51–7.60 (2 H, m, 7- and 8-H), 7.77 (1 H, d, $J_{4,5}$ 8.8, 4-H), 7.89 (1 H, br d, $J_{5,4}$ 8.8, 5-H), 7.92 (1 H, br d, $J_{6,7}$ 7.4, 6-H) and 8.09 (1 H, br d, $J_{9,8}$ 7.8, 9-H); δ_C(125 MHz) 136.7, 135.5, 134.5, 133.7, 133.4, 131.6 and 131.0 (each C), 130.6 and 128.9 (each 2 × CH), 128.8 (CH), 128.6 (C), 126.7, 125.9, 125.2, 122.9 and 120.7 (each CH), 70.6 (CH_2), 58.8 (C) and 24.7 (2 × Me); ν_{max}(KBr)/cm^{-1} 3360; *m/z* 383 (M^+, 3%), 381 (M^+, 19), 352 (44), 351 (24), 350 (100), 311 (9), 309 (37), 273 (20) and 150 (38).

Racemic 2-(1,1'-binaphthyl-2-yl)-4,4-dimethyl-4,5-dihydrooxazole 15

A solution of 1-naphthylmagnesium bromide (1.2 mol dm^{-3}; 1.2 mmol) in THF (1.0 cm^3) was added dropwise at room temperature to a stirred solution of the sulfoxide **5** (100 mg, 0.29 mmol) in anhydrous THF (5 cm^3). After 3.5 h at room temperature the reaction mixture was quenched by the addition of an excess of 5% aq. ammonium chloride and extracted with dichloromethane. The extract was washed successively with water and saturated brine. The products were separated by radial chromatography with 10% ethyl acetate–light petroleum as eluent. The first fraction furnished the binaphthyl **15** (67 mg, 67%) as an oil, which was identified by its ^1H NMR spectrum.[10]

A second fraction was the ligand-exchange product **9** (6 mg, 9%).

(*S*)-4,4-Dimethyl-2-{1-[(4-methylphenyl)sulfinyl]naphthalen-2-yl}-4,5-dihydrooxazole 19

The Grignard reagent **2** was prepared from the bromide **1**[10] (2.59 g, 8.52 mmol), magnesium (223 mg, 9.18 mg-atom) and anhydrous THF (15 cm^3). The resulting solution was diluted with anhydrous toluene (50 cm^3) and the volume of the solution was reduced to 35 cm^3 by distillation under reduced pressure. Solid (1*R*)-menthyl (*S*)-toluene-*p*-sulfinate (1.26 g, 4.28 mmol) was then added to the stirred solution in one portion. Work-up after 15 min in the usual way gave a crude product, which was purified by radial chromatography with 30% ethyl acetate–light petroleum as eluent. This afforded the *sulfoxide* **19** as a pale yellow oil (1.36 g, 88%) (Found: C, 72.9; H, 6.15; N, 3.6; S, 8.8. $C_{22}H_{21}NO_2S$ requires C, 72.7; H, 5.8; N, 3.85; S, 8.8%); $[\alpha]_D$ −132 (*c* 1.1, toluene). The enantiomeric excess could be raised to 95–97%, $[\alpha]_D$ −150 (*c* 1.3, toluene), by causing the racemate to precipitate by trituration with light petroleum. Enantiomeric excess was determined by HPLC: mobile phase, 10% propan-2-ol–hexane; t_R(*S*) 50 min, t_R (*R*) 64 min; δ_H 1.42 and 1.46 (each 3 H, s, Me), 2.34 (3 H, s, Ar*Me*), 4.19 and 4.23 (2 H, AB, *J* 8.0, CH_2), 7.21 and 7.72 (4 H, AA'**BB'**, tolyl ArH), 7.41–7.53 (2 H, m, 6- and 7-H), 7.71–7.73 (1 H, obscured, 3-H), 7.85 (1 H, br d, $J_{5,6}$ 7.8, 5-H), 7.99 (1 H, d, $J_{4,3}$ 8.5, 4-H) and 8.73 (1 H, br d, $J_{8,7}$ 8.2, 8-H); δ_C 161.0, 141.1, 139.8, 139.4 and 135.3 (each C), 132.5 (CH), 129.4 (2 × CH), 129.3 (C), 128.8, 127.6, 127.5 and 125.2 (each CH), 124.94 (2 × CH), 124.88 (CH), 79.8 (CH_2), 68.8 (C), 28.2, 28.0 and 21.1 (each Me); ν_{max}(film)/cm^{-1} 1653 (C=N), 1079 (C–O) and 1047 (S=O); *m/z* 363 (M^+, 100%), 234 (23), 202 (36), 160 (27), 153 (22), 146 (81), 140 (38), 133 (21), 132 (50), 126 (23), 118 (66), 106 (31) and 105 (71).

(*S*)-2-(1,1'-Binaphthyl-2-yl)-4,4-dimethyl-4,5-dihydrooxazole 20

A solution of 1-naphthylmagnesium bromide (0.43 mol dm^{-3}; 2.2 mmol) in THF (5.0 cm^3) was added dropwise at room temperature to a stirred solution of the sulfoxide **19** (208 mg, 0.57 mmol) in anhydrous THF (5 cm^3). After 3.5 h at room temperature the reaction mixture was quenched by the addition of an excess of 5% aq. ammonium chloride and extracted with dichloromethane. The extract was washed successively with water and saturated brine. The products were separated by radial chromatography with 10% ethyl acetate–light petroleum as eluent. The (*S*)-binaphthyl **20** (124 mg, 62%), $[\alpha]_{578}$ +70 (*c* 2.3, THF) {lit.,[10] extrapolated $[\alpha]_{578}$ +118 (*c* 2.6, THF)}, 60% ee, was eluted first.

A second fraction was the ligand-exchange product **9** (13 mg, 10%).

A third fraction contained the starting sulfoxide **19** (27 mg, 13% recovery), $[\alpha]_D$ −85 (*c* 1.0, toluene). The enantiomeric excess of compound **20** was estimated by ^1H NMR spectroscopy: $CDCl_3$ solution with 0.30 mol equiv. Eu(hfc)$_3$ separated the diastereotopic oxazoline Me signals; δ_H 1.56 and 1.68 for (*S*), δ_H 1.51 and 1.76 for (*R*).

When the same reaction was carried out at room temperature for 1.5 h the products were: compounds **20** {56%, $[\alpha]_{578}$ +67 (*c* 2.3, THF)}, **9** (12%) and **19** {27% recovery, $[\alpha]_D$ −130 (*c* 1.0, toluene)}. When the same reaction was carried out at room temperature for 30 min the products were: compounds **20** {29%, $[\alpha]_{578}$ +67 (*c* 1.3, THF)}, **9** (6%) and **19** {64% recovery, $[\alpha]_D$ −145 (*c* 1.0, toluene)}.

2-[1-(*tert*-Butylsulfanyl)naphthalen-2-yl]-4,4-dimethyl-4,5-dihydrooxazole 4

Solid sodium *tert*-butyl sulfide (873 mg, 7.8 mmol) was added in one portion to a stirred solution of the bromide **1** (2.405 g, 7.9 mmol) in anhydrous DMF (15 cm^3) and the bath temperature was increased to 100 °C. After 14.5 h the cooled solution was diluted with water and extracted twice with dichloromethane. The extract was washed in turn with water, saturated aq. copper

sulfate, water and finally with saturated brine. The crude product was passed through a short column of alumina with dichloromethane as eluent. The *sulfide* **4** (2.37 g, 97%) was crystallised from light petroleum as plates, mp 56–58 °C (Found: C, 72.6; H, 7.45; N, 4.3; S, 10.2. $C_{19}H_{23}NOS$ requires C, 72.8; H, 7.4; N, 4.45; S, 10.2%); δ_H 1.24 (9 H, s, 3 × Me), 1.46 (6 H, s, 2 × Me), 4.20 (2 H, s, CH_2), 7.56 (2 H, m, 6- and 7-H), 7.66 and 7.89 (2 H, AB, $J_{3,4}$ 8.4, 3- and 4-H) and 7.84 and 8.87 (each 1 H, br d, 5- and 8-H); δ_C 164.0, 136.9, 135.8, 134.3 and 131.3 (each C), 129.4, 128.5, 127.9, 126.8, 126.5 and 126.4 (each CH), 79.4 (CH_2), 67.8 and 49.6 (each C) and 31.8 and 28.1 (each Me); ν_{max}(film)/cm^{-1} 1666 (C=N) and 1087 (S=O); *m/z* 313 (M^+, 0.5%), 256 (71) and 185 (100).

2-[1-(*tert*-Butylsulfinyl)naphthalen-2-yl]-4,4-dimethyl-4,5-dihydrooxazole 8

Oxidation of the foregoing sulfide **4** (477 mg, 1.8 mmol) with MCPBA (93% by iodometry; 333 mg, 1.8 mmol) in chloroform (20 cm^3) at 0 °C during 1 h by a method similar to that described above gave the sulfoxide **8** (450 mg, 90%), mp 98 °C (decomp.), which was purified by radial chromatography with 30% ethyl acetate–light petroleum as eluent [Found: ($M^+ - C_4H_8$), 273.0823. $^{12}C_{15}{}^1H_{15}{}^{14}N^{16}O_2{}^{32}S$ requires *m/z*, 273.0824]. The ^{1}H NMR spectrum of this material indicated the presence of an unidentified impurity, present in ~10%, which was not separable, and signals for a rotamer of compound **8**, the ratio of the two forms being ~10:1 (# denotes signals for the impurity, *denotes signals for the minor rotamer); δ_H(500 MHz) 1.25 (9 H, s, 3 × Me*), 1.29 (9 H, s, 3 × Me), 1.36 (9 H, s, 3 × Me#), 1.42 and 1.43 (each 3 H, s, Me and Me#), 1.47 and 1.48 (each 3 H, s, Me*), 4.16 (2 H, s, CH_2), 7.55–7.60 (3 H, m, 3-, 6- and 7-H), 7.85–7.88 (1 H, m, 5-H), 7.95 (1 H, d, $J_{4,3}$ 8.4, 4-H), 8.12 (1 H, d, $J_{4,3}$ 8.3, 4-H#), 8.24 (1 H, br d, $J_{8,7}$ 8.4, 8-H*), 9.23–9.25 (1 H, m, 8-H#) and 9.48–9.50 (1 H, m, 8-H); δ_C(125 MHz, major component only) 162.0, 135.2, 134.8 and 132.6 (each C), 132.0 (CH), 130.2 (C), 128.3 and 127.7 (each CH), 127.2 (2 × CH), 125.6 (CH), 79.6 (CH_2), 68.6 and 60.6 (each C), 28.2 and 28.1 (each Me) and 25.6 (3 × Me); ν_{max}(KBr)/cm^{-1} 1664 (C=O) and 1048 (S=O); *m/z* 273 (M − C_4H_8, 42.5%), 256 (83) and 201 (100).

2-(2-Hydroxy-1,1-dimethylethyl)-2,3-dihydronaphtho[2,1-*d*]-isothiazol-3-one 22

A solution of the foregoing sulfoxide **8** (100 mg, 0.30 mmol) in light petroleum (15 cm^3) was heated under reflux for 2 h. The solution was cooled, and evaporated to dryness under reduced pressure. The crude product was purified by radial chromatography with 30% ethyl acetate–light petroleum as eluent and then by crystallisation from dichloromethane–light petroleum which gave the *isothiazolone* **22** (19 mg, 23%) as needles, mp 157–158 °C (Found: M^+, 273.0823. $^{12}C_{15}{}^1H_{15}{}^{14}N^{16}O_2{}^{32}S$ requires M, 273.0824); δ_H 1.68 (6 H, s, Me), 4.03 (2 H, d, *J* 6.8, CH_2), 5.53 (1 H, t, *J* 6.8, OH) and 7.51–7.88 (6 H, m, ArH); δ_C 167.1, 140.5, 134.4 and 131.5 (each C), 129.1, 128.6, 127.1 and 126.4 (each CH), 125.3 (C), 123.0 and 121.7 (each CH), 69.7 (CH_2), 64.1 (C) and 25.1 (2 × Me); ν_{max}(KBr)/cm^{-1} 1633 (C=O) and 1618; *m/z* 273 (M^+, 7.8%), 242 (14), 201 (100), 186 (20), 185 (32) and 158 (27).

Racemic 2-(2′-methoxy-1,1′-binaphthyl-2-yl)-4,4-dimethyl-4,5-dihydrooxazole 16

A solution of 2-methoxy-1-naphthylmagnesium bromide (0.55 mol dm^{-3}; 2.75 mmol) in THF (5.0 cm^3) was added dropwise at room temperature to a stirred solution of the sulfoxide **8** (188 mg, 0.57 mmol) in anhydrous THF (5 cm^3). After 121 h at room temperature the reaction mixture was quenched by the addition of an excess of 5% aq. ammonium chloride and extracted with dichloromethane. The extract was washed successively with water and saturated brine. Radial chromatography with 10% ethyl acetate–light petroleum as eluent furnished the binaphthyl **16** (96 mg, 44%) as a pale yellow oil which was identified by its ^{1}H NMR spectrum.[10]

Isopropyl (*S*)-(−)-1-[(4-methylphenyl)sulfinyl]naphthalene-2-carboxylate 24

Butyllithium (1.92 mol dm^{-3}; 2.6 mmol) in hexane (1.35 cm^3) was added at 0 °C to a stirred solution of diisopropylamine (289 mg, 2.86 mmol) in anhydrous THF (2 cm^3). After 15 min the solution was added *via* cannula to a stirred solution of (*S*)-(−)-1-[(4-methylphenyl)sulfinyl]naphthalene **23**[23] (628 mg, 2.36 mmol) in anhydrous THF (20 cm^3) at −78 °C. After 20 min at −78 °C the dark green solution was added rapidly *via* cannula to a stirred solution of isopropyl chloroformate (1.0 mol dm^{-3}) in toluene (2.6 cm^3) containing anhydrous THF (5 cm^3) at −78 °C. The solution was stirred 45 min longer and then an excess of 5% aq. ammonium chloride was added followed by dichloromethane. The separated organic layer was washed with brine and the crude product was purified by radial chromatography with 30% ethyl acetate–light petroleum as eluent which gave, besides the starting sulfoxide **23** (171 mg, 27% recovery), the *sulfoxide* **24** (295 mg, 36%) as an oil; $[\alpha]_D$ −94 (*c* 1.0, toluene), >99% ee (Found: M^+, 352.1134. $^{12}C_{21}{}^1H_{20}{}^{16}O_3{}^{32}S$ requires M, 352.1133). Enantiomeric excess was determined by HPLC: mobile phase, 5% propan-2-ol–hexane; t_R(*S*) 49 min, t_R(*R*) 69 min; δ_H 1.40 and 1.42 (each 3 H, d, *J* 5.0, Me), 2.34 (3 H, s, Ar*Me*), 5.35 (1 H, septet, *J* 5.0, CH), 7.24 and 7.70 (4 H, AA′BB′, tolyl ArH), 7.42–7.55 (2 H, m, 6- and 7-H), 7.74 and 8.00 (2 H, AB, $J_{3,4}$ 8.5, 3- and 4-H), 7.87 (1 H, br d, $J_{5,6}$ 8.1, 5-H) and 8.75 (1 H, br d, $J_{8,7}$ 8.6, 8-H); δ_C 166.5, 140.9, 140.1, 139.2, 135.4 and 133.1 (each C), 132.5 (CH), 129.5 (2 × CH), 129.2 (C), 128.8, 127.8, 127.7 and 125.5 (each CH), 125.0 (2 × CH), 123.9 and 70.5 (each CH), 21.7 (2 × Me) and 21.1 (Me); ν_{max}(film)/cm^{-1} 1733 (C=O) and 1049 (S=O); *m/z* 352 (M^+, 14%), 245 (22), 203 (100) and 115 (25).

Isopropyl (*S*)-(−)-1,1′-binaphthyl-2-carboxylate 25

A solution of 1-naphthylmagnesium bromide (0.74 mol dm^{-3}; 1.6 mmol) in THF (2.1 cm^3) was added dropwise at room temperature to a stirred solution of the sulfoxide **24** (188 mg, 0.53 mmol) in anhydrous THF (5 cm^3). After 35 min at room temperature the reaction mixture was quenched by the addition of an excess of 5% aq. ammonium chloride and extracted with dichloromethane. The extract was washed successively with water and saturated brine. The products were separated by radial chromatography with 2.5% ethyl acetate–light petroleum as eluent. The (*S*)-binaphthyl **25** (142 mg, 78%) was obtained as an oil and identified by its ^{1}H NMR spectrum;[11] $[\alpha]_D$ −11.0 (*c* 2.0, toluene), 82% ee. The enantiomeric excess of product **25** was estimated by ^{1}H NMR spectroscopy: C_6D_6 solution, with 0.30 mol equiv. Eu(hfc)$_3$, allowed separation of the diastereotopic isopropyl Me signals; δ_H 1.06 and 1.15 (each d, *J* 5.8) for (*S*), δ_H 1.15 and 1.20 (each d, *J* 5.8) for (*R*).

A sample of compound **25** with $[\alpha]_D$ −12.7 (*c* 1.45, toluene) had a corresponding rotation: $[\alpha]_D$ −8.5 (*c* 1.15, $CHCl_3$) [lit.,[11] $[\alpha]_D$ −6.8 (*c* 1.03, $CHCl_3$) for compound **25** of 80% ee].

(1*R*)-Menthyl (*S*)-naphthalene-1-sulfinate 26

Technical grade sodium naphthalene-1-sulfinate (80%; 20 g, 70 mmol), DMF (three drops) and thionyl dichloride (60 cm^3) were heated under reflux for 3.5 h. The cooled mixture was filtered through a bed of Celite and the excess of thionyl chloride was removed from the filtrate by evaporation under reduced pressure. The last traces of thionyl chloride were removed by azeotropic distillation with anhydrous benzene under reduced pressure. A solution of the crude sulfinyl chloride, (−)-menthol (9.2 g, 59 mmol) and triethylamine (12

cm^3, 86 mmol) was stirred in dichloromethane (200 cm^3) during the dropwise addition of trimethyl phosphite (13.5 cm^3, 114 mmol), and the mixture was then stirred and heated under reflux in nitrogen for 21 h. The cooled reaction mixture was diluted with dichloromethane and washed with 1 mol dm^{-3} hydrochloric acid. The extract was washed in turn with sodium hydrogen carbonate and saturated brine. The crude oily product was crystallised from aq. acetone and then was recrystallised from acetone to afford the sulfinate **26** (4.5 g, 23%) as needles, mp 118–119 °C (lit.,[23] 118–119 °C); $[\alpha]_D$ −424 (*c* 2.2, acetone) {lit.,[23] $[\alpha]_D$ −433 (*c* 2.07, acetone)}.

(*R*)-(+)-1-(*tert*-Butylsulfinyl)naphthalene 27

A solution of *tert*-butylmagnesium chloride (0.3 mol dm^{-3} in THF; 40 cm^3, 1.2 mmol) was diluted with anhydrous toluene (50 cm^3) and the volume was reduced to 40 cm^3 by distillation under reduced pressure. The stirred solution was cooled to 0 °C and the sulfinate **26** (1.99 g, 6 mmol) was added in one portion. After 45 min the reaction was quenched by the addition of 10% aq. ammonium chloride and the mixture was then extracted with dichloromethane. The crude product was purified by radial chromatography with 30% ethyl acetate–light petroleum as eluent which afforded the *sulfoxide* **27** (1.09 g, 78%) as a waxy solid (Found: M^+, 232.0923. $^{12}C_{14}{}^1H_{16}{}^{16}O^{32}S$ requires M, 232.0923); $[\alpha]_D$ +305 (*c* 1.7, toluene). The enantiomeric excess could be raised to >99% after several crystallisations from diethyl ether–light petroleum; $[\alpha]_D$ +333 (*c* 1.1, toluene), mp 61–63 °C (decomp.). Enantiomeric excess was determined by HPLC: mobile phase, 2.5% propan-2-ol–hexane; $t_R(S)$ 52.5 min, $t_R(R)$ 54.6 min; δ_H(500 MHz) 1.17 (9 H, s, 3 × Me), 7.46–7.51 (2 H, m, 6- and 7-H), 7.60 (1 H, dd, $J_{3,2}$ 7.3, $J_{3,4}$ 8.1, 3-H), 7.83–7.86 (1 H, m, 5-H), 7.92 (1 H, br d, $J_{4,3}$ 8.1, 4-H), 8.06 (1 H, dd, $J_{2,3}$ 7.3, $J_{2,4}$ 1.2, 2-H) and 8.16–8.19 (1 H, m, 8-H); δ_C(125 MHz) 136.8, 133.0 and 131.5 (each C), 131.3, 128.5, 126.5, 126.2, 125.5, 124.9 and 123.2 (each CH), 57.9 (C) and 23.2 (3 × Me); ν_{max}(KBr)/cm^{-1} 1043 (S=O); *m/z* 232 (M^+, 2.6%), 177 (32), 176 (100), 129 (25), 128 (100), 127 (28), 115 (43) and 57 (60).

(*R*)-(+)-2-Bromo-1-(*tert*-butylsulfinyl)naphthalene 28

A solution of butyllithium (0.83 mmol; 2.08 mol dm^{-3}) in hexane (0.4 cm^3) was added dropwise at −78 °C to a stirred solution of the sulfoxide **27** (>99% ee; 171 mg, 0.74 mmol) in anhydrous THF (10 cm^3). After 10 min at −78 °C the dark orange solution was added *via* cannula to a stirred solution of 1,2-dibromotetrafluoroethane (210 mg, 0.81 mmol) in THF (10 cm^3) at −78 °C. After 10 min at −78 °C the reaction mixture was quenched by the addition of 10% aq. ammonium chloride and extracted with dichloromethane. The crude product was purified by radial chromatography with 10% ethyl acetate–light petroleum as eluent. The sulfoxide **28** (106 mg, 46%) was crystallised from diethyl ether–light petroleum as prisms, mp 79–80 °C; $[\alpha]_D$ +124 (*c* 0.69, toluene) [Found: (M^+ − C_4H_8), 253.9401. $^{12}C_{10}{}^1H_7{}^{79}Br^{16}O^{32}S$ requires *m/z* 253.9401]; δ_H 1.41 (9 H, s, 3 × Me), 7.52–7.56 (2 H, m, 6- and 7-H), 7.58 and 7.74 (2 H, AB, $J_{3,4}$ 8.7, 3- and 4-H), 7.80–7.83 (1 H, m, 5-H) and 9.47–9.51 (1 H, m, 8-H); δ_C 134.1, 133.6 and 133.2 (each C), 133.0, 130.3, 128.5, 127.1, 126.9 and 125.0 (each CH), 124.2 and 61.9 (each C) and 25.3 (3 × Me); ν_{max}(KBr)/cm^{-1} 1042 (S=O); *m/z* 256 (M − C_4H_8, 100%), 254 (96), 208 (26), 206 (24), 175 (19), 174 (25), 158 (21), 126 (27) and 57 (60).

Isopropyl (*R*)-(+)-1-(*tert*-butylsulfinyl)naphthalene-2-carboxylate 29

A solution of butyllithium (2.07 mol dm^{-3}; 6 mmol) in hexane (2.9 cm^3) was added dropwise at −78 °C to a stirred solution of the sulfoxide **27** (~90% ee; 1.25 g, 5.4 mmol) in anhydrous THF (25 cm^3). After being stirred for 10 min after the addition the resulting dark orange solution was transferred rapidly *via* cannula to a stirred solution of isopropyl chloroformate (1.0 mol dm^{-3}; 5.4 mmol) in toluene (5.4 cm^3) dissolved in THF (15 cm^3) at −78 °C. The solution was stirred for 10 min at −78 °C and then an excess of 10% aq. ammonium chloride and dichloromethane were added. The separated organic layer was washed with brine and the crude product was separated by radial chromatography with 20% ethyl acetate–light petroleum as eluent. This yielded, besides the starting material **27** (128 mg, 10% recovery), the sulfoxide **29** (660 mg, 39%). Crystallisation from diethyl ether–light petroleum furnished pale yellow prisms, mp 100–101 °C; $[\alpha]_D$ +129 (*c* 1.3, toluene), >99% ee [Found: (M^+ − C_4H_8), 262.0663. $^{12}C_{14}{}^1H_{14}{}^{16}O_3{}^{32}S$ requires *m/z*, 262.0664]. Enantiomeric excess was determined by HPLC: mobile phase, 5% propan-2-ol–hexane; $t_R(S)$ 30.1 min, $t_R(R)$ 33.5 min. The ^1H and ^{13}C NMR spectra of compound **29** contain signals for two rotameric forms in the ratio ~2.5:1 (*denotes signals for the minor rotamer); δ_H([$^2H_8$]toluene) 1.08 (9 H, s, 3 × Me*), 1.10 and 1.16 (each 3 H, d, *J* 6.3, Me), 1.19 (9 H, s, 3 × Me), 1.30 and 1.44 (each 3 H, d, *J* 6.3, Me*), 5.14 (1 H, septet, *J* 6.3, CH), 5.47 (1 H, septet, *J* 6.3, CH*), 6.98–7.48 (6 H, m, ArH and ArH*), 7.86 (1 H, br d, $J_{8,7}$ 8.7, 8-H*) and 10.02 (1 H, br d, $J_{8,7}$ 9.0, 8-H); δ_C 169.1*, 167.1, 134.8, 134.4, 133.7*, 133.6*, 133.0* and 132.6 (each C), 132.1 (CH), 131.2* (C), 131.0*, 128.4, 127.9, 127.3, 127.2*, 127.1, 126.9*, 125.7*, 124.8*, 124.1, 70.1 and 69.4* (each CH), 61.6* and 60.5 (each C), 25.4 and 25.1* (each 3 × Me) and 21.9, 21.8* and 21.7 (each Me); ν_{max}(KBr)/cm^{-1} 1715 (C=O) and 1035 (S=O); *m/z* 262 (M − C_4H_8, 16%), 203 (56), 202 (100), 146 (22) and 57 (23).

Isopropyl (*R*)-(+)-1,1′-binaphthyl-2-carboxylate 31

A solution of 1-naphthylmagnesium bromide (0.49 mol dm^{-3}; 0.74 mmol) in THF (1.5 cm^3) was added dropwise at room temperature to a stirred solution of the sulfoxide **29** (107 mg, 0.34 mmol) in anhydrous THF (10 cm^3). After 30 min at room temperature the reaction mixture was quenched by the addition of an excess of 5% aq. ammonium chloride and extracted with dichloromethane. The extract was washed successively with water and saturated brine. The products were separated by radial chromatography with 10% ethyl acetate–light petroleum as eluent. The (*R*)-binaphthyl **31** (103 mg, 90%) was obtained as an oil; $[\alpha]_D$ +12.8 (*c* 1.7, toluene), 95% ee. The enantiomeric excess was determined as described previously.

(*R*)-(+)-1-(*tert*-Butylsulfinyl)-*N*,*N*-dimethylnaphthalene-2-carboxamide 30

A solution of butyllithium (2.01 mol dm^{-3}; 3 mmol) in hexane (1.5 cm^3) was added dropwise at −78 °C to a stirred solution of the sulfoxide **27** (~90% ee; 640 mg, 2.8 mmol) in anhydrous THF (10 cm^3). After being stirred for 10 min after the addition the resulting dark orange solution was added rapidly *via* a cannula to a solution of *N*,*N*-dimethylcarbamoyl chloride (1.0 mol dm^{-3}; 5.7 mmol) in toluene (2.4 cm^3) and TMEDA (1.85 g, 15.9 mmol) dissolved in THF (5 cm^3) at −78 °C. The reaction mixture was stirred at −78 °C for 18 h and then quenched by the addition of an excess of 10% aq. ammonium chloride followed by dichloromethane. The separated organic layer was washed with brine and the crude product was purified by radial chromatography. This yielded, besides the starting material **27** (176 mg, 28% recovery), the sulfoxide **30** (285 mg, 36%), which was crystallised from diethyl ether–light petroleum as prisms, mp 120 °C (decomp.); $[\alpha]_D$ +109 (*c* 0.38, toluene) [Found: (M^+ − C_4H_8), 247.0668. $^{12}C_{13}{}^1H_{13}{}^{14}N^{16}O_2{}^{32}S$ requires *m/z*, 247.0667]. The ^1H and ^{13}C NMR spectra of product **30** contain signals for two rotameric forms in the ratio ~3:1 (* denotes signals for the minor rotamer); δ_H([$^2H_8$]toluene) 1.17 (9 H, s, 3 × Me*), 1.23 (9 H, s, 3 × Me), 2.31 (3 H, s, Me), 2.35 (3 H, s, Me*), 2.77 (3 H, s, Me), 2.98 (3 H, s, Me*), 6.98–7.49 (6 H, m,

ArH and ArH*), 8.05–8.08 (1 H, m, 8-H*) and 9.80 (1 H, dd, $J_{8,7}$ 8.7, $J_{8,6}$ 0.6, 8-H); δ_C 170.7*, 169.1, 137.9, 136.2* and 134.1 (each C), 133.2 (CH), 132.9*, 132.8* and 132.0 (each C), 131.5* (CH), 131.4* and 130.9 (each C), 128.5, 127.4, 127.2, 127.0, 126.9*, 126.8*, 126.2*, 124.7* and 123.4 (each CH), 61.7* and 60.9 (each C), 38.8* and 38.6 (each Me), 34.9 (Me and Me*) and 25.6 and 25.3* (each 3 × Me); ν_{max}(KBr)/cm^{-1} 1627 (C=O) and 1040 (S=O); *m/z* 247 (M − C_4H_8, 37%), 203 (40), 202 (100), 158 (24), 146 (31), 115 (24), 45 (46) and 44 (23).

(*R*)-(+)-*N*,*N*-Dimethyl-1,1′-binaphthyl-2-carboxamide 32

A solution of 1-naphthylmagnesium bromide (0.44 mol dm^{-3}; 1.1 mmol) in THF (2.4 cm^3) was added dropwise at room temperature to a stirred solution of the sulfoxide **30** (91 mg, 0.30 mmol) in anhydrous THF (5 cm^3). After 25 h at room temperature the reaction mixture was quenched by the addition of an excess of 5% aq. ammonium chloride and extracted with dichloromethane. The extract was washed successively with water and saturated brine. The products were separated by radial chromatography with 50% ethyl acetate–light petroleum as eluent. The (R)-*binaphthyl* **32** (63 mg, 65%) was obtained as a solid, mp 147–149 °C; $[\alpha]_D$ +86 (*c* 0.9, toluene), 95% ee (Found: M$^+$, 325.1468. $^{12}C_{23}{}^1H_{19}{}^{14}N^{16}O$ requires M, 325.1467). Enantiomeric excess was determined by HPLC: mobile phase, 5% propan-2-ol–hexane; $t_R(S)$ 53 min, $t_R(R)$ 40 min. The ^{1}H and ^{13}C NMR spectra of product **32** in $CDCl_3$ solution at −25 °C contain signals for two rotameric forms in the ratio ~2.5:1 (*denotes signals for the minor rotamer); δ_H 2.36 and 2.65 (each 3 H, s, Me), 2.72 and 2.88 (each 3 H, s, Me*) and 7.26–8.04 (13 H, m, ArH and ArH*); δ_C 170.6, 170.4*, 135.1*, 134.6, 134.3, 134.0, 133.7, 133.0*, 132.9, 132.8*, 132.7, 132.6*, 132.1 and 131.5 (each C), 128.74, 128.68, 128.4, 128.3, 127.9, 127.8*, 127.7*, 126.8, 126.6, 126.3, 126.2, 126.0*, 125.6, 125.4, 124.5*, 123.5 and 123.1* (each CH), 38.9* and 38.7 (each Me) and 34.0 (Me and Me*); ν_{max}(KBr)/cm^{-1} 1630 (C=O); *m/z* 325 (M$^+$, 26%), 282 (24), 281 (100) and 252 (49).

Conversion of ester (*R*)-(+)-31 into amide (*R*)-(+)-32

Aq. sodium hydroxide (1 mol dm^{-3}; 10 cm^3) was added to a solution of ester (*R*)-(+)-**31** (103 mg, 0.30 mmol) in freshly distilled 1,4-dioxane (10 cm^3) and the mixture was stirred at 80 °C for 5 h. The cooled mixture was partitioned between dil. aq. sodium hydroxide and dichloromethane. The aqueous layer was then acidified with conc. hydrochloric acid and extracted with dichloromethane. The separated organic layer was washed with brine and the crude product was separated by radial chromatography with methanol as eluent to afford the carboxylic acid (66 mg, 73%) as a solid.

To a stirred solution of anhydrous DMF (12.5 mm^3, 0.16 mmol) in anhydrous dichloromethane (10 cm^3) at 0 °C was added dropwise oxalyl dichloride (14 mm^3, 0.16 mmol). After 10 min the aforementioned carboxylic acid (44 mg, 0.15 mmol) was added and the solution was stirred for a further 10 min. Aq. dimethylamine (26%; 4 cm^3) was then added and the mixture was vigorously stirred at room temperature for 30 min before being partitioned between water and dichloromethane. The separated organic layer was washed with brine and the crude product was separated by radial chromatography with 50% ethyl acetate–light petroleum as eluent to afford the amide **32** (11 mg, 23%) as a solid. HPLC analysis confirmed that the absolute configuration of this material was identical with that prepared through the coupling reaction of sulfoxide **30**.

Structure determinations

Unique room-temperature diffractometer data sets ($T \approx 295$ K; monochromatic Mo-Kα radiation, λ = 0.7107 Å; $2\theta/\theta$ scan mode) were measured, yielding N independent reflections, N_o with $I > 3\sigma(I)$ being considered 'observed' and used in the full matrix/large-block least-squares refinements without absorption correction. Anisotropic thermal parameters were refined for the non-hydrogen atoms; $(x, y, z, U_{iso})_H$ were also refined. Conventional residuals R, R_w on $|F|$ are quoted; statistical weights derivative of $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0004\,\sigma^4(I_{diff})$ were used. Neutral-atom complex scattering factors were employed; computation used the XTAL 3.2 program system,[44] implemented by S. R. Hall. Pertinent results are deposited‡ (atom coordinates and thermal parameters, full non-hydrogen atom geometries, and structure factor amplitudes) except for those presented in the Figures and Tables 1–3. For compound **28**, 'Friedel pairs' (*hkl*) were also measured. Fig. 3 shows the absolute configuration as established by refinement of the structure with coordinates (*x*, *y*, *z*) and their inverse; Flack's '*x*' was also refined. For $(h\bar{k}l)$ N was 1220, N_o 938, R 0.034, R_w 0.034; and for $(\bar{h}k\bar{l})$ they were 1218, 929, 0.034 and 0.033, respectively; for the alternative chirality, for (*hkl*) R was 0.056 and R_w 0.059, and for $(\bar{h}k\bar{l})$ these two were 0.053 and 0.056. For the total data set, x refined to −0.01(2).

Crystal/refinement data. Compound **18**. $C_{22}H_{20}ClNOS$, M = 387.0. Triclinic, space group $P\bar{1}$ (C_i^1, No. 2), a = 11.799(6), b = 13.289(2), c = 13.614(3) Å, α = 109.23(1), β = 101.93(3), γ = 97.45(3) °, V = 1926 Å^3. D_c (Z = 4) = 1.32 g cm^{-3}; F(000) = 800. μ_{Mo} = 3.1 cm^{-1}; specimen: 0.15 × 0.15 × 0.35 mm. $2\theta_{max}$ = 50 °; N = 6733, N_o = 2623; R = 0.047, R_w = 0.028.

Compound **22**. $C_{15}H_{15}NO_2S$, M = 273.4. Monoclinic, space group $P2_1/c$ (C_{2h}^5, No. 14), a = 14.599(7), b = 6.922(9), c = 14.462(4) Å, β = 116.43(3) °, V = 1304 Å^3. D_c (Z = 4) = 1.79 g cm^{-3}; F(000) = 576. μ_{Mo} = 2.4 cm^{-1}; specimen: needle, 0.10 × 0.50 × 0.10 mm. $2\theta_{max}$ = 65 °; N = 4709, N_o = 2589; R = 0.048, R_w = 0.047.

Compound **28**. $C_{14}H_{15}BrOS$, M = 311.3. Orthorhombic, space group $P2_12_12_1$ (D_2^4, No. 19), a = 14.239(6), b = 13.493(3), c = 7.123(3) Å, V = 1369 Å^3. D_c (Z = 4) = 1.51 g cm^{-3}; F(000) = 632. μ_{Mo} = 31.4 cm^{-1}; specimen: 0.20 × 0.32 × 0.44 mm; $A^*_{min,max}$ = 1.80, 2.44. $2\theta_{max}$ = 47.5 °.

Structural commentary

The results of the single-crystal room-temperature X-ray studies are consistent with the stoichiometries and connectivities depicted above (Figs. 1–3); for compounds **18** and **22** the components crystallise in racemic space groups with two (**18**) and one (**22**) molecule(s) in the asymmetric unit. In compound **22** the molecules stack in quasi-parallel arrays generated by 2_1 screw axes and an interplanar spacing of ~$b/2$, and typical 'charge-transfer' overlaps. Molecular geometries are substantially as expected, values associated with the heterocyclic rings being given in Tables 1 and 2. The two independent molecules of compound **18** differ slightly in the dihedral angles between the phenyl and main $C_{12}S$ aromatic planes (Table 1), and, more conspicuously, the dispositions of the CH_2OH moieties in the $NHCMe_2$-CH_2OH components.

For compound **28**, a single molecule comprises the asymmetric unit of the structure, the results being consistent with the stoichiometry, connectivity and absolute configuration as given above. The molecules lie almost normal to *c*, in stacks with molecular overlaps and spacings of *c*/2 consistent with charge-transfer interactions; some interesting perturbations in molecular geometry are found, with alternant bondlengths at the aromatic periphery, C(1)–C(2), C(3)–C(4), C(5)–C(6), C(7)–C(8) consistently short, all being less than 1.38 Å, while the other distances all exceed 1.40 Å. Substantial distortions at the exocyclic angles are found at C(1) and C(2); at

‡ See Instructions for Authors, in the January issue.

Table 1 Selected geometries for compound **18**. Values for molecule 2 follow those for molecule 1

Atoms[a]	Distance (Å)	Atoms[a]	Angle (degrees)
S(1)–C(2)	1.750(5), 1.741(6)	C(2)–S(1)–C(9b)	92.1(3), 91.6(3)
S(1)–C(9b)	1.719(7), 1.719(8)	S(1)–C(2)–C(21)	117.6(4), 117.9(5)
C(2)–C(3)	1.363(9), 1.36(1)	C(3)–C(2)–C(21)	131.0(4), 130.0(5)
C(3)–C(3a)	1.437(8), 1.437(9)	S(1)–C(2)–C(3)	111.4(4), 112.1(5)
C(3a)–C(9b)	1.394(8), 1.38(1)	C(2)–C(3)–C(3a)	112.7(5), 112.1(6)
C(3)–N(1)	1.423(7), 1.431(9)	C(2)–C(3)–N(1)	123.6(5), 126.0(6)
C(2)–C(21)	1.477(8), 1.482(9)	C(3a)–C(3)–N(1)	123.7(6), 121.8(7)
		C(3)–C(3a)–C(9b)	112.5(6), 112.7(7)
		C(3a)–C(9b)–S(1)	111.2(4), 111.4(5)
		C(3)–C(3a)–C(4)	129.3(5), 127.8(6)
		S(1)–C(9b)–C(9a)	126.5(5), 125.6(6)
		C(3)–N(1)–C(31)	117.8(5), 118.1(6)

[a] Crystallographic numbering scheme used (see Fig. 1). χ^2 for the $C_{12}S$ aromatic skeletal planes are 101, 224 with deviations of N(1) 0.071(7), 0.046(9) Å and C(21) −0.089(7), 0.221(8) Å. Torsion angles C(2)–C(3)–N(1)–C(31) are −82.1, −89.5, C(3)–N(1)–C(31)–C(32) are −171.0, 175.8 and N(1)–C(31)–C(32)–O(1) are 62.8, −61.4 °. Dihedral angles between the $C_{12}S$ plane and the associated aromatic ring are 43.7(2), 55.4(2) °

Table 2 Selected geometries for compound **22**

Atoms[a]	Distance (Å)	Atoms[a]	Angle (degrees)
C(21)–N(2)	1.502(3)	C(21)–N(2)–S(1)	120.8(2)
N(2)–C(3)	1.375(3)	C(21)–N(2)–C(3)	124.2(1)
N(2)–S(1)	1.707(1)	S(1)–N(2)–C(3)	114.4(1)
S(1)–C(9b)	1.724(3)	N(2)–S(1)–C(9b)	91.2(1)
C(3)–O(3)	1.232(2)	S(1)–C(9b)–C(3a)	111.9(2)
C(3)–C(3a)	1.458(3)	C(9b)–C(3a)–C(3)	113.1(2)
C(3a)–C(9b)	1.368(3)	N(2)–C(3)–O(3)	123.4(2)
		N(2)–C(3)–C(3a)	109.3(2)
		O(3)–C(3)–C(3a)	127.3(2)

[a] Crystallographic numbering scheme used (see Fig. 2). For the C_{10} aromatic bicyclic system, χ^2 is 258, no defining atom deviating by more than 0.024(4) Å [C(7)]; atoms S(1), N(2), C(3), O(3), C(21) are substantially coplanar with deviations 0.065(3), 0.151(3), 0.061(3), 0.016(3), 0.111(4) Å. Torsion angles C(211)–C(21)–N(2)–C(3), S(1) are −65.2(3), 105.0(2) °.

Table 3 Selected molecular geometries for compound **28**

Atoms[a]	Distance (Å)	Atoms[a]	Angle (degrees)
C(1)–C(2)	1.380(9)	C(11)–S–O	108.0(7)
C(1)–C(8a)	1.436(9)	C(11)–S–C(1)	103.0(3)
C(1)–S	1.811(7)	O–S–C(1)	108.8(3)
S–O	1.487(5)	S–C(1)–C(2)	116.7(5)
S–C(11)	1.862(8)	S–C(1)–C(8a)	123.1(5)
C(2)–C(3)	1.41(1)	C(2)–C(1)–C(8a)	119.3(6)
C(2)–Br	1.894(7)	C(1)–C(2)–Br	123.5(5)
C(3)–C(4)	1.34(1)	C(1)–C(2)–C(3)	120.6(6)
C(4)–C(4a)	1.40(1)	Br–C(2)–C(3)	115.9(5)
C(4a)–C(5)	1.42(1)	C(2)–C(3)–C(4)	120.8(7)
C(4a)–C(8a)	1.43(1)	C(3)–C(4)–C(4a)	121.3(7)
C(5)–C(6)	1.33(1)	C(4)–C(4a)–C(5)	121.3(7)
C(6)–C(7)	1.40(2)	C(4)–C(4a)–C(8a)	119.6(7)
C(7)–C(8)	1.36(1)	C(5)–C(4a)–C(8a)	119.1(7)
C(8)–C(8a)	1.411(9)	C(4a)–C(5)–C(6)	120.6(8)
		C(5)–C(6)–C(7)	121.1(8)
H(8)···O	2.2_3(est.)[b]	C(6)–C(7)–C(8)	120.3(7)
		C(7)–C(8)–C(8a)	121.0(7)
		C(1)–C(8a)–C(4a)	118.3(6)
		C(1)–C(8a)–C(8)	123.9(6)
		C(4a)–C(8a)–C(8)	117.8(6)

Intermolecular contact: O···Br $(1-x, y-\frac{1}{2}, \frac{1}{2}-z)$ 3.112(5). [a] Crystallographic numbering scheme used (see Fig. 3). [b] Estimated value. For the aromatic C_{10} skeleton, $\chi^2 = 25$, maximum defining atom deviation 0.025(8) Å [C(2)]; other atom deviations are [δS, O, Br, C(11)] − 0.189(8), −1.00(1), −0.123(7), 1.54(1) Å.

C(1) S–C(1)–C(2), C(8a) are 116.7(5), 123.1(5) °, while at C(2) Br–C(2)–C(1), C(3) are 123.5(5), 115.9(5) °. Possible factors influencing these are (i) the intermolecular contact O···Br $(1-x, y-\frac{1}{2}, \frac{1}{2}-z)$, 3.112(5) Å; (ii) intramolecular H(8)···O 2.2_3 Å. The latter is probably the more relevant, the atoms presumably held in proximity by an obligate disposition of methyls 13 and 14 *vis-à-vis* the ring plane; note that S deviates appreciably from the aromatic plane by 0.123(7) Å, but on the opposite side to C(11).

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