Catalytic conjugate addition promoted by the copper(I)–monothiobinaphthol system. Part 2.[1] Optimal ligand synthesis and initial catalytic results

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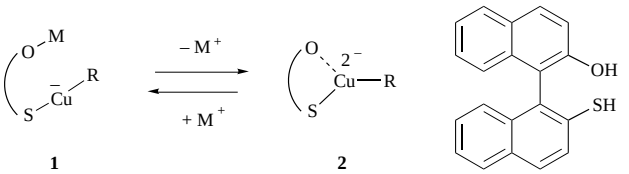
Both racemic and (R_a)-1,1′-bi-2-naphthol react with Bu_2SnO to provide an *O*,*O*-stannylene acetal which opens with $Me_2NC(S)Cl$ or RC(O)Cl [R = Ph, CCl_3, OPr, 1-$C_{10}H_7$, 2-$C_{10}H_7$, SMe, CH_2Cl and (−)-menthyl] to fashion monoacylated derivatives. Two of the products, 2-(*N*,*N*-dimethylthiocarbamoyloxy)-2′-hydroxy-1,1′-binaphthyl 6 and 2-hydroxy-2′-[(1*R*,3*S*,5*R*)-menthylcarbonyloxy]-1,1′-binaphthyl 14, have been crystallographically characterised. The former is converted to 2-(*N*,*N*-dimethylcarbamoyloxy)-2′-(*N*,*N*-dimethylthiocarbamoyloxy)-1,1′-binaphthyl 15 with $Me_2NC(O)Cl$. This compound is directly available from 1,1′-bi-2-naphthol *via* a one-pot sequential reaction with $Me_2NC(S)Cl$ and $Me_2NC(O)Cl$ under NEt_3–DMAP catalysis. Thermolysis of 15 followed by hydrolysis provides an efficient preparation of 2-hydroxy-2′-mercapto-1,1′-binaphthyl 3 (monothiobinaphthol). In the presence of $[Cu(MeCN)_4]BF_4$, 3 leads to a highly efficient catalyst for the 1,4-addition of BuLi and RMgX (R = Me, Bu, Ph; X = Cl, Br) to cyclic enones.

Introduction

Catalytic conjugate additions of organometallics (RM) to enones often use *neutral* copper(I) complexes as catalytic precursors. Viewed from the metal's standpoint such a choice is rather odd. Extensive structural modification is expected on addition of the catalyst to the richly *anionic* catalytic mixture (R^- and enolates are present in excess) resulting in conversion of the L_nCuX pre-catalysts to active copper 'ate' species. While it is not always necessary to worry about such effects, these problems can be acute in asymmetric catalysis where the enantioselectivity can become unpredictably dependent on slight variations in reaction conditions. In seeking to mediate such outcomes we considered the anionic structural motifs **1** and **2** where the S–O backbone is derived from **3**. These species have several interesting features. Firstly, while the Cu–S bond is robust the alkoxide can in principle serve three roles: (*i*) a binding site for Lewis acidic M, (*ii*) a leaving group in transmetallations with RM, and (*iii*) as a surrogate ligand after loss of catalyst-bound enolate products. Secondly, **2** is formally an analogue of the reactive higher order cyanocuprates[2] (whatever their structure). The recent reports on the chemistry of **3** and related compounds[3,4] lead us to disclose the full details of our initial investigation into catalysts based on **1** and **2** by use of monothiobinaphthol (MTB) **3**, parts of this work have been communicated.[1]



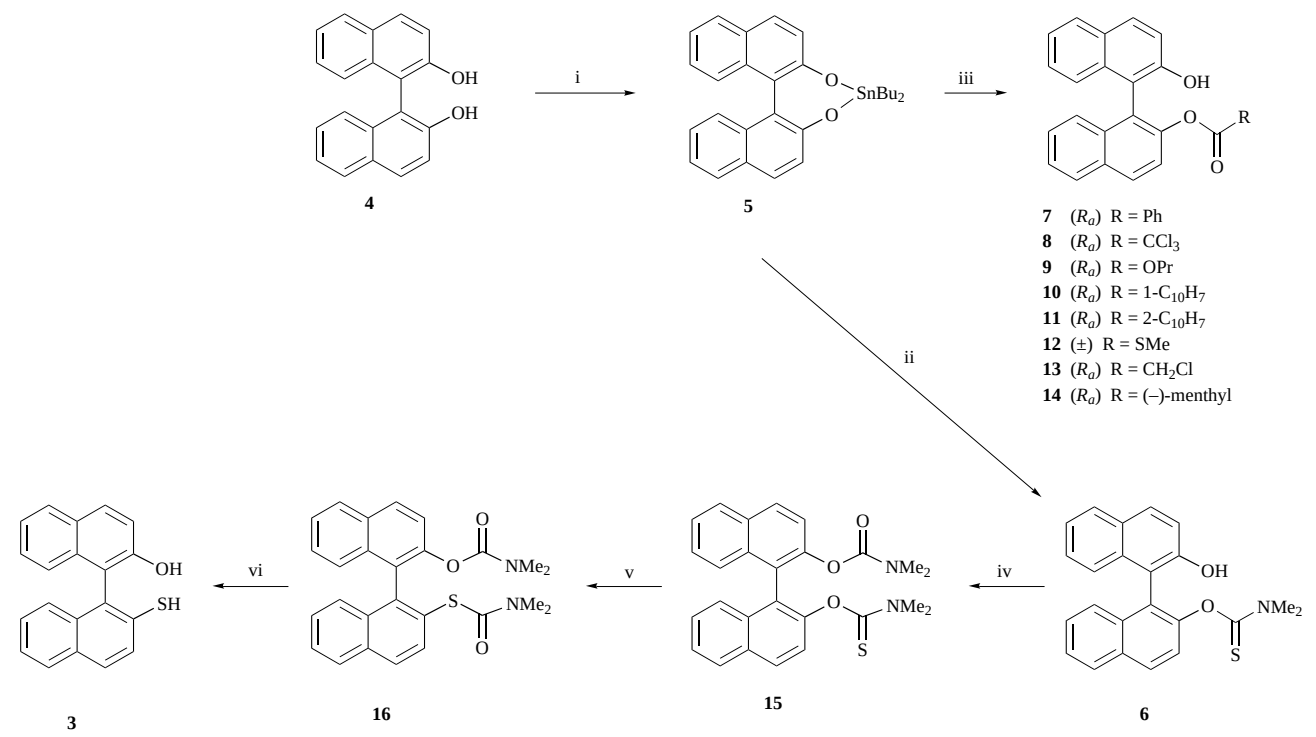
1 **2** **3**

Results and discussion

Ligand synthesis

Although a literature preparation[5] of **3** (MTB) quickly allowed us to confirm the potency of organocopper(I) catalysts derived from it this approach proved inappropriate to scale up. Requiring large quantities of **3** we determined to develop a 5–10 g scale route without chromatography. In fact we have developed two such approaches. Stannylene acetal chemistry, based on **5** (Scheme 1), offers one such approach and this compound is easily prepared in quantitative yield from either racemic or enantiomerically pure 1,1′-bi-2-naphthol **4**. The stannylene acetal **5** may either be isolated or reacted directly. Reaction with dimethylthiocarbamoyl chloride affords **6** after protonolysis with HCl in dioxane. Apparently few other applications of stannylene acetals featuring aromatic alcohols have appeared. The only contamination of **6** is by Bu_2SnCl_2 and small variable amounts of recovered 1,1′-bi-2-naphthol **4**. Fortunately, **6** is rather crystalline and both impurities may be removed by a single crystallisation from hot PhCl–heptane or preferably ethanol. Recrystallisation of **6** is strongly recommended, especially on a large scale, as the subsequent acylation products **15** and **16** are not easily separated from the bis(dimethylcarbamate) of **4**. In order to provide a comparison against the hydrogen bonding effects observed in the carbonate **14** (see later) an X-ray structural analysis of (±)-**6** was carried out. Two molecules are present in the unit cell and one of these is shown in Fig. 1. Interestingly, one of the two independent molecules shows a very weak hydrogen bond [O(1)–S(1) = 3.169(4) Å] while this is absent in its partner [equivalent distance, O(3)–S(2) = 3.304(4) Å].

The reaction of the stannylene acetal **5** with acid chlorides constitutes a general reaction both in the enantiomerically pure and racemic series (Scheme 1). The stannylene acetal **5** is atropisomerically robust as reaction of (R_a)-**5** with benzoyl chloride gives (R_a)-**7** without loss of enantiomeric purity as assessed by formation of the MTPA ester of **7**. Formation of the compounds **8**–**13** proceeds similarly. Of particular interest is the reaction of racemic stannylene acetal (±)-**5** with (1*R*,2*S*,5*R*)-(−)-menthyl chloroformate. Although two diastereomeric esters are formed one of these is very much more crystalline and hence easily isolated. An X-ray structural analysis was carried out revealing this compound to be (R_a)-(1*R*,2*S*,5*R*)-**14**. An ORTEP view of **14** is shown in Fig. 2. The crystallographic



Scheme 1 *Reagents and conditions*: i, Bu_2SnO, 1,2-dichloroethane, azeotrope, 3 h; ii, $Me_2NC(S)Cl$, 22 °C, 24 h, then HCl in dioxane; iii, RC(O)Cl, 22 °C, 1–4 days, then HCl in dioxane; iv, $Me_2NC(O)Cl$, NEt_3, DMAP catalysis, 22 °C, 24 h; v, 250 °C, 5 h; vi, KOH, H_2O–methanol, reflux, 24 h

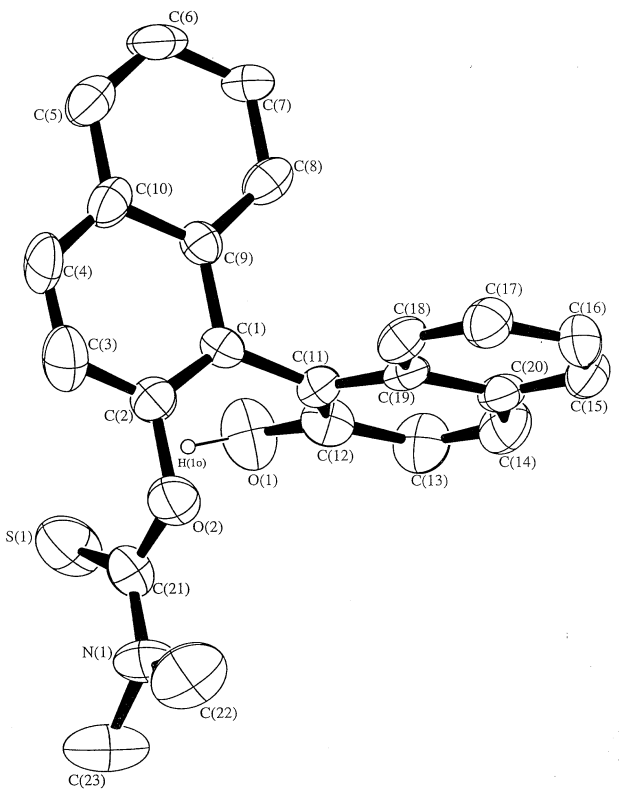


Fig. 1 An ORTEP view of one of the two molecules of **6** present in the unit cell. Only the weakly hydrogen bonded H(1o) is shown; O(1)–S(1) = 3.169(4) Å.

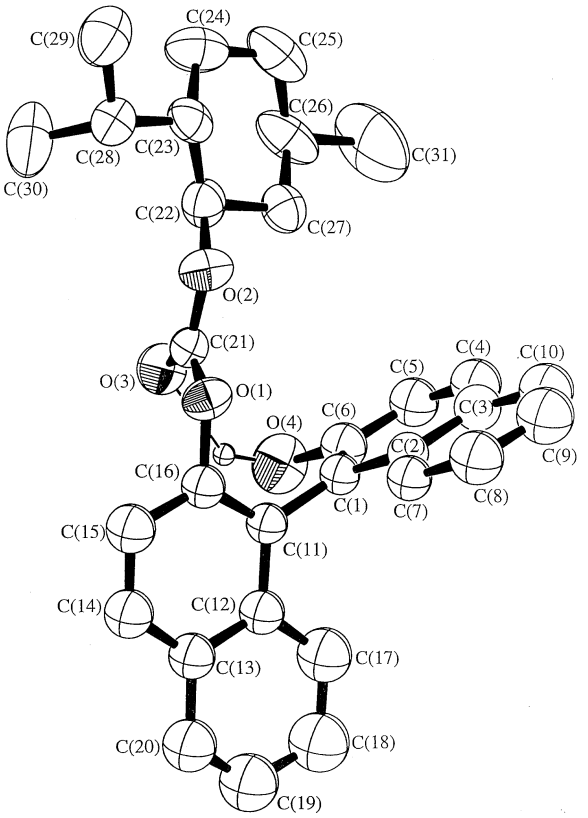


Fig. 2 An ORTEP view of (R_a)-**14**. Only hydrogen bonded H(O4) is shown; O(3)–O(4) = 2.872(7) Å.

study also showed the presence of a hydrogen bond between the naphtholic OH and the carbonate carbonyl. The hydrogen bonding patterns observed in the two molecules of (±)-**6** and (R_a)-**14** are summarised in Fig. 3 **A**–**C**. Based on the similarity of the IR spectra of **7**–**14** hydrogen bonding is probably present in all of these compounds.

As the presence of protonic functions within molecules often severely interferes with Newmann–Kwart rearrangements we chose to protect the OH in **6** as the carbamate **15** before transformation to **16.** This protection is best carried out under simple DMAP catalysis. Remarkably, despite the forcing conditions (250 °C, 5 h) the Newmann rearrangement of (R_a)-**15** may be carried out with only slight racemisation. Typically the crude (R_a)-**16** is isolated in 94% ee. A single recrystallisation from

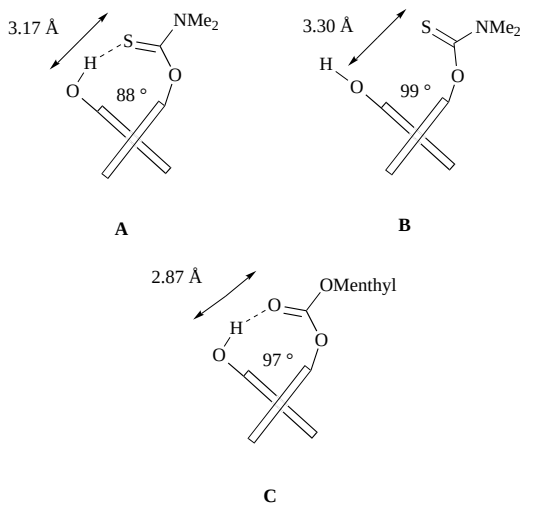
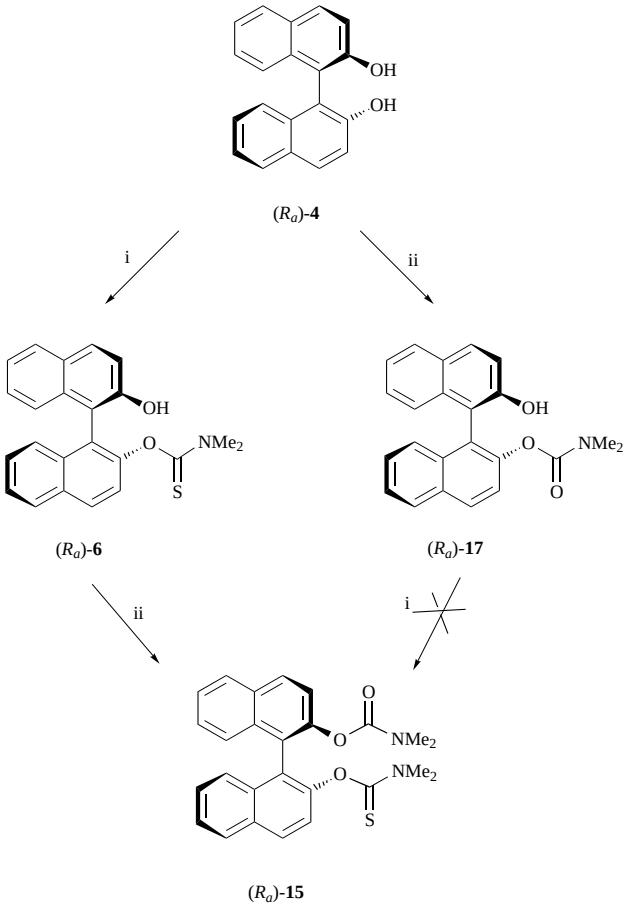


Fig. 3

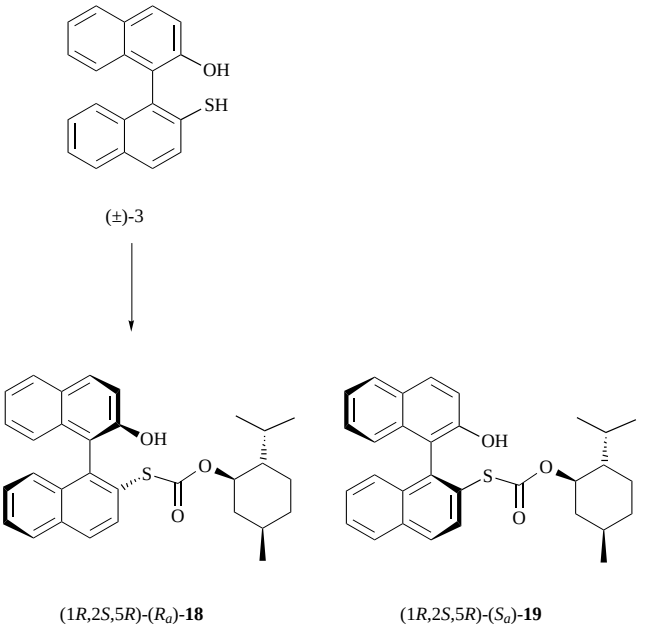
ethanol affords enantiomerically pure material. After purification **16** is hydrolysed to **3** under standard conditions, however, due to the air sensitivity of the thiol the work-up is best carried out in nitrogen-flushed glassware. In terms of its overall performance the tin-based route affords an overall 40–55% yield for the four step synthesis from either racemic or enantiomerically pure **4**.

Although the stannylene acetal **5** offers an effective route to the key compound **6** we were anxious to produce a more environmentally friendly preparation of **3** in fewer steps improving the accessibility of **3**. Although most bases will deprotonate **4** to fashion at least some **6**, after addition of dimethylthiocarbamoyl chloride, the problem is to accomplish this highly selectively avoiding the presence of both starting material and diacylated products. We find that the best solution to this problem is using DMAP catalysis under controlled conditions (Scheme 2). Addition of $Me_2NC(S)Cl$ to 1,1′-bi-2-naphthol **4** allows the isolation of essentially chemically and enantiomerically pure **6.** In fact the reaction is so selective that $Me_2NC(O)Cl$ may be added directly to the reaction mixture after the formation of **6** in a one-pot synthesis in which **15** is isolated enantiomerically pure and in high yield. The crude **15** may be used directly in the thermal Newmann rearrangement and this is most conveniently carried out in standard commercial Kugelrohr apparatus. After a simple recrystallisation (to ensure enantiomeric purity) **16** may be hydrolysed as normal to yield **3**. The three step transformation of **4** to **3** constitutes our currently preferred synthesis of the chiral monothiobinaphthol (MTB) ligand. It is interesting to note that the preparation of **15** by changing the order of the reagents is not viable under the conditions employed (Scheme 2). While the carbamate **17** is easily prepared the final acylation with $Me_2NC(S)Cl$ fails. We suspect that strong hydrogen bonding in **17** (akin to that in **14**) is the origin of the change of reactivity. Selective monofunctionalisations of 1,1-binaphthol with electrophiles are rare[3,6] and it seems that the acylation strategies developed here offer attractive routes to molecules with C_1 1,1′-binaphthyl cores.

As an alternative approach to asymmetric synthesis of **3** we have investigated its resolution *via* chemical derivitisation with (1*R*,2*S*,5*R*)-(−)-menthyl chloroformate. As compound **14** had proved so crystalline we selected the diastereomeric monothiocarbonates **18** and **19** as appropriate targets (Scheme 3). To obtain these selectively it proved necessary to use stoichiometric amounts of DMAP and even under these conditions some dimenthylated products were formed. While the diastereomers **18** and **19** were not separated by crystallisation they have rather different R_fs and are easily separated by chromatography. By comparison with samples that were prepared by asymmetric



Scheme 2 *Reagents and conditions*: i, $Me_2NC(S)Cl$, NEt_3, DMAP catalysis, 25 °C, 48 h; ii, $Me_2NC(O)Cl$, NEt_3, DMAP catalysis, 25 °C, 48 h



Scheme 3 *Reagents and conditions*: (−)-menthyl chloroformate, stoichiometric DMAP, 22 °C, 4 h

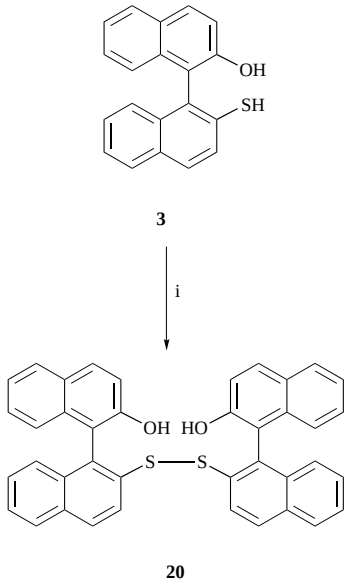
synthesis from (R_a)-1,1′-bi-2-naphthol **4** it is apparent that the first eluted diastereomer is (R_a)-(1*R*,2*S*,5*R*)-**18** followed by (S_a)-(1*R*,2*S*,5*R*)-**19**. The two diastereomers may be hydrolysed directly to yield (−)-(R_a)-**3** and (+)-(S_a)-**3** respectively. This approach is complimentary to asymmetric syntheses of **3** and to a recent resolution involving fractional crystallisation of the dimenthyl carbonates of **3**.[4] We have devised a simple procedure

Table 1 Catalytic additions of BuLi to cyclohex-2-en-1-one **21** using **3**

Run	Cu-source	Cu (mol%)/ **3** (mol%)	Conditions		1,4-Yield (%)[a]	1,2-Yield (%)[a]
			Solvent	*T*/°C		
1	None	0/0	Et_2O	−20	3	91
2	CuCl	5/6	Et_2O	−20	6	93
3	CuBr	5/6	Et_2O	−20	37	61
4	CuBr·SMe_2	5/6	Et_2O	−20	52	46
5	CuI	5/6	Et_2O	−20	47	52
6	$[Cu(MeCN)_4]BF_4$	5/6	Et_2O	−20	62	34
7	$[Cu(MeCN)_4]BF_4$	5/6	Et_2O	0	44	4
8	$[Cu(MeCN)_4]BF_4$	10/12	Et_2O	−20	78	0
9	$[Cu(MeCN)_4]BF_4$	10/12	Et_2O	0	57	0
10	$[Cu(MeCN)_4]BF_4$	10/24	Et_2O	0	75	13
11	$[Cu(MeCN)_4]BF_4$	10/12	THF	0	86	3
12	$[Cu(MeCN)_4]BF_4$	10/12	THF	−20	66	0

[a] Determined by GC; the mass balance is starting material.

based on iodine oxidation of **3** to its disulfide **20** to assay the enantiomeric purity of **3** (Scheme 4). While oxidation of



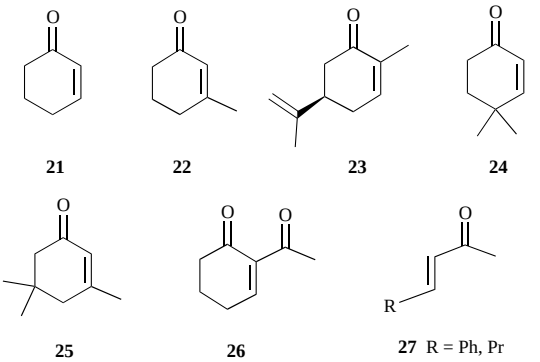
Scheme 4 *Reagents and conditions*: i, I_2, NEt_3, 0 °C, 1 h

enantiomerically pure **3** affords a single *rac*-diastereoisomer the oxidation of (±)-**3** leads to the presence of a 1:1 *rac–meso* pair. Thus, this simple derivatisation provides a quick assay on the enantiomeric purity of **3** without recourse to chiral HPLC or formation of MTPA esters. The ^{1}H NMR signals of the two diastereoisomers of **20** are sufficiently resolved at 600 MHz to allow simple integration. Alternatively, on lower field instruments two ^{13}C NMR signals (δ_C 136.8 and 136.6) provide a convenient handle for ee determination. Using these techniques the enantiomeric purity of the (R_a)-**3** prepared by either of our routes is >99%.

Scope of the catalyst

In order to quickly assess the activity of our catalytic system towards a number of different enone systems and organometallic reagents initial reactions were carried out using racemic **3**. Cyclohex-2-en-1-one **21** is a popular test substrate for catalytic conjugate addition reaction chemistry. The ratio of the 1,4- to 1,2-addition products is often taken as a measure of the catalyst efficiency. Whilst this criterion is useful, care must be taken to carry out appropriate control reactions. Some organometallic reagents (especially Grignard reagents) have a tendency to add in a 1,4 sense to cyclohex-2-en-1-one **21** even in the absence of added catalysts. No such problems are encountered with BuLi and this was used in initial trials (Table 1). The most effective copper(I) source tried (runs 2–6) is the complex $[Cu(MeCN)_4]BF_4$, introduced by Kubas.[7] Repeating reactions also indicated that formation of the active catalyst from $[Cu(MeCN)_4]BF_4$, **3** and the organometallic is slow below −20 °C so this temperature was set as a lower limit. By increasing the catalyst loading to 10 mol% it proved possible to reach synthetically useful chemical yields and regioselectivities (runs 8 and 11). While changing the ligand–copper(I) ratio had little effect on the catalytic activity the highest temperature the catalyst can be used at is 0° C (decomposition is observed at room temperature). Aside from **3**–$[Cu(MeCN)_4]BF_4$ few other systems for promoting copper(I) catalysed 1,4-addition reactions of organolithiums (as opposed to stoichiometric $LiCuR_2$) have been reported.[8]

Moderate to high yields of 1,4-addition products may be realised using Grignard reagents and catalysts derived from $[Cu(MeCN)_4]BF_4$ and **3** (Table 2). Care must be taken when comparing catalytic runs carried out in THF as in some cases significant amounts of 1,4-products can be formed even in the absence of copper(I) catalysts. Cyclohex-2-en-1-one **21** represents the worst case (compare runs 1–3). Full data on the effects of addition mode, solvent and temperature on the 1,4-addition selectivity of BuMgCl to cyclohexen-2-en-1-one **21** are available.[9] For enones **22**–**27** control reactions showed that non-



copper(I) promoted 1,4-addition product yields amounted to no more than 5–25% depending on the choice of Grignard and conditions.[1] The catalyst system is active in both Et_2O and THF and, although generally the latter is preferred, dramatic changes in reactivity are observed in Et_2O (compare runs 4 and 5). The catalytic activity is in large part due to the ligand **3** and the system is still potent even at low catalyst loadings (runs 4–6). Synthetically useful conditions for the synthesis of 3-substituted cyclohexanones could be developed (runs 6–10). The catalyst is tolerant of both 2- and 3-disubstitution on the enone and to a degree to α and β branching patterns on the carbocycle (compare runs 11–16). We have only just started to probe the factors leading to enantioselectivity in this system and note for the present that these non-optimised results show

Table 2 Catalytic additions of Grignard reagents to various enones using **3**

Run	Enone	Grignard	Cu (mol%)/ **3** (mol%)	Conditions: Solvent	Conditions: *T*/°C	1,4-Yield (%)[a]	1,2-Yield (%)[a]
1	**21**	BuMgCl	0/0	Et_2O	−20	1	99
2	**21**	BuMgCl	0/0	THF	−20	52	47
3	**21**	BuMgCl	5/6	Et_2O	−20	98[b]	1
4	**21**	BuMgCl	1/1	Et_2O	−20	93	6
5	**21**	BuMgCl	1/0	Et_2O	−20	5	95
6	**21**	BuMgCl	3/4	THF	−20	100	0
7	**21**	BuMgCl	10/12	THF	−20	100 (85)[c,d]	0
8	**21**	MeMgBr	5/6	THF	−20	82 (78)[c]	6
9	**21**	EtMgBr	5/6	THF	−20	86 (73)[c]	5
10	**21**	PhMgBr	5/6	THF	−20	78 (67)[c]	8
11	**22**	BuMgCl	10/12	THF	−20	83 (77)[c]	2
12	**22**	MeMgBr	10/12	THF	−20	57	5
13	**23**	BuMgCl	10/12	Et_2O	−20	85	9
14	**23**	PhMgBr	10/12	THF	−20	70	25
15	**24**	BuMgCl	10/12	Et_2O	−20	66[e]	19[e]
16	**24**	MeMgBr	10/12	THF	−20	44[e]	5[e]

[a] Determined by GC; the mass balance is starting material. [b] (*R*)-product, 3% ee, using (R_a)-**3**. [c] Isolated yield in parentheses. [d] (*R*)-product, 23% ee, using (R_a)-**3**. [e] Combined yield of all diastereomers.

the beginnings of some stereoselection (runs 3 and 7). There are some limitations to the copper(I) catalyst derived from **3**. The hindered enone isophorone **25** did not participate in the catalysis, similarly enones possessing electron withdrawing functions such as 2-acetyl cyclohex-2-en-1-one **26** and benzylideneacetone **27** (R = Ph) give negligible yields. We believe that electronic rather than steric factors are the cause of the lack of reactivity as **27** (R = Pr) gives a near quantitative yield of 1,4-product with BuMgCl.[10]

Conclusions

New routes to the monothiobinaphthol **3** have been developed which allow succinct access to this interesting chiral auxiliary in significant amounts in both racemic and enantiomerically pure forms. The scope of the active catalyst formed between **3**, copper(I) sources and organometallic reagents is fairly broad for synthetically useful conjugate addition reactions. Further studies are now in hand to improve the enantioselectivities shown by the catalyst, to isolate the inorganic complexes responsible for the catalysis (or models thereof), and to effect easy modifications of **3** to seek for useful levels of stereoselection in catalysis by these derivatives.

Experimental

General

Procedures involving moisture sensitive intermediates were carried out under nitrogen atmospheres using standard Schlenk techniques. 1,2-Dichloroethane was distilled from CaH_2, tetrahydrofuran (THF) from sodium–benzophenone immediately prior to use, while diethyl ether was dried over sodium wire. All enones were commercial products (Aldrich) distilled or dried over 4 Å molecular sieves as appropriate. *N*,*N*-Dimethylthiocarbamoyl chloride must be recrystallised from pentane, all other reagents were used as supplied. Specific rotations were measured using an Optical Activity AA-10 automatic polarimeter at ambient conditions and are given in 10^{-1} deg cm^2 g^{-1}; *c* is in g 100 cm^{-3} of solvent. Column chromatography and TLC analyses were performed on silica gel, Rhône Poulenc Sorbsil and Merck Kieselgel 60 $F_{254+366}$ respectively. Infrared spectra were recorded using a Perkin-Elmer 983 G infrared spectrophotometer and a Perkin-Elmer 882 infrared spectrophotometer. Proton and ^{13}C NMR spectra were recorded on a JEOL JNM-GX270, a Bruker WH-400 or a Bruker VXR600S spectrometer using tetramethylsilane as standard; *J* values are given in Hz. Melting points were determined using a Gallenkamp melting point apparatus and are uncorrected. Mass spectra were obtained on a Finnigan-MAT 1020 (electron impact ionisation, EI) machine and a VG-ZAB (fast atom bombardment ionisation, FAB) machine (EPSRC Service, Swansea). Elemental analyses were performed using a Fisons Instruments EA 1108 CHN elemental analyser. Analysis by gas chromatograph was carried out using a Perkin-Elmer 8310 gas chromatograph and a Summit integrator using a BP-20 column with nitrogen as the carrier gas. A split ratio of 1:40 was used with an injection volume of 2 μl. Light petroleum refers to the fraction boiling in the range 40–60 °C. The following compounds were obtained by literature procedures: (±)-1,1′-bi-2-naphthol **4**,[11] (R_a) or (S_a)-1,1′-bi-2-naphthol **4**,[12] [Cu(MeCN)$_4$]-BF$_4$.[7]

(4,4-Dibutyldinaphtho[2,1-*d*: 1′,2′-*f*][1,3,2]dioxastannepine 5

A suspension of Bu_2SnO (26.10 g, 105.00 mmol) and 1,1′-bi-2-naphthol **4** (30.00 g, 105.00 mmol) in 1,2-dichloroethane was refluxed for 3 h with intermittent removal of water azeotrope. The resulting solution was used directly or evaporated to give a quantitative yield of near analytically pure **5** which could be stored for at least four weeks and used as required; mp 164–166 °C (from 1,2-dichloroethane) [Found: C, 64.4; H, 5.9%; M$^+$, 517 (Sn-isotope pattern). $C_{28}H_{30}O_2Sn$ requires C, 65.0; H, 5.9%; *M*, 517]; ν_{max}(KBr disc)/cm^{-1} 1350s, 1330s, 1267s, 1232s, 1215s; δ_H(270 MHz; $CDCl_3$) 0.56 (6 H, t, J 7.4, Me), 1.60-1.70 (12 H, m, CH_2), 7.03–7.33 (8 H, m, Ar), 7.73 (4 H, m, Ar) [Found (HRMS): 518.1270. $C_{28}H_{30}O_2Sn$ requires 518.1270 (based on ^{119}Sn)].

Equivalent reactions using (R_a)-**4** led to the isolation of (R_a)-**5** showing $[a]_D$ −70 (*c* 4.70, $CHCl_3$).

2-(*N*,*N*-Dimethylthiocarbamoyloxy)-2′-hydroxy-1,1′-binaphthyl 6

A suspension of Bu_2SnO (26.10 g, 0.11 mol) and (±)-1,1′-bi-2-naphthol **4** (30.00 g, 0.11 mol) in 1,2-dichloroethane (600 cm^3) was refluxed 3 h with intermittent removal of the water azeotrope. The resulting solution was cooled to room temperature and dimethylthiocarbamoyl chloride (15.55 g, 0.13 mol) added. After stirring (24 h), standard HCl solution (30 cm^3 of 3.48 M dioxane solution) was added. The solvent was removed and the oily residue stirred mechanically with light petroleum (400 cm^3, 16 h) to yield crude **6** (32.90 g, 84%) which was recrystallised from either PhCl–heptane or ethanol; mp 143–144 °C (from PhCl–heptane) (Found: C, 73.8; H, 5.1; N, 3.7%; M$^+$, 373. $C_{23}H_{19}NO_2S$ requires C, 74.0; H, 5.1; N, 3.8%; *M*, 373); ν_{max}-(KBr disc)/cm^{-1} 3313m, 3229m (2 × OH), 1210s (C=S);

δ_H(270 MHz; $CDCl_3$) 2.67 (3 H, s, Me), 3.37 (3 H, s, Me), 5.62 (1 H, s, OH), 7.12 (1 H, dd, *J* 8.3, 1.5, Ar), 7.33–7.20 (5 H, m, Ar), 7.42 (1 H, d, *J* 8.3, Ar), 7.49 (1 H, m, Ar), 7.83 (1 H, d, *J* 8.3, Ar), 7.88 (1 H, d, *J* 8.8, Ar), 7.97 (1 H, d, *J* 8.3, Ar), 8.06 (1 H, d, *J* 8.8, Ar)

Reaction of (R_a)-**4** with Bu_2SnO fashioned (R_a)-**6** with $[\alpha]_D$ +347 (*c* 2.02, $CHCl_3$) after recrystallisation from hot PhCl–heptane.

Representative reaction of the stannylene acetal (±)-5 or (R_a)-5 with acid chlorides; (R_a)-2-benzoyloxy-2′-hydroxy-1,1′-binaphthyl (R_a)-7

Neat benzoyl chloride (130 μl, 0.16 g, 1.12 mmol) was added to a solution of (R_a)-**5** (0.50 g, 0.97 mmol) in CH_2Cl_2 (5 cm^3) under an inert atmosphere. The reaction was stirred until complete by TLC analysis and then treated with a standard solution of HCl (0.6 cm^3 of 1.74 M dioxane solution, 0.97 mmol). The solvent was removed and the residue stirred with hexane to yield quantitative amounts of a powder, pure by ^{1}H NMR spectroscopy, which was recrystallised from CH_2Cl_2–hexane to give pure (R_a)-**7** (0.33 g, 88%); mp 174–175 °C; $[\alpha]_D$ +52 (*c* 0.92, $CHCl_3$) (Found: C, 83.1; H, 4.5%; M^+, 390. $C_{27}H_{18}O_3$ requires C, 83.1; H, 4.7%; *M*, 390); ν_{max}(KBr disc)/cm^{-1} 3427s (OH), 1702s (C=O); δ_H(270 MHz; $CDCl_3$) 5.30 (1 H, s, OH), 7.14 (1 H, m, Ar), 7.22–7.37 (6 H, m, Ar), 7.40–7.57 (4 H, m, Ar), 7.67 (2 H, m, Ar), 7.79 (2 H, m, Ar), 8.01 (1 H, d, *J* 8.3, Ar), 8.12 (1 H, d, *J* 8.8, Ar).

The (*S*)-(−)-(α)-MTPA esters of (R_a)-**7** and (±)-**7** were prepared by standard methods.[13,14] For (*S*)-(R_a)-**7**; δ_H(270 MHz; $CDCl_3$) 3.00 (apparent d, 3 H, $J_{apparent}$ 1.0, OMe), 7.13–7.51 (m, 15 H, Ar), 7.56 (1 H, d, *J* 9.0, Ar), 7.61 (2 H, m, Ar), 7.87 (1 H, d, *J* 8.0, Ar), 7.94 (1 H, d, *J* 8.0, Ar), 7.95 (1 H, d, *J* 8.5, Ar), 8.02 (1 H, d, *J* 8.8, Ar). The methoxy signal of (*S*)-(S_a)-**7** resonated at δ_H 2.97. Using this chemical shift the enantiomeric purity of the (R_a)-**7** was determined to be >98%.

(R_a)-2-Hydroxy-2′-(trichloroacetoxy)-1,1′-binaphthyl (R_a)-8. Yield 0.17 g (43%); mp 132–133 °C; $[\alpha]_D$ +8 (*c* 0.80, $CHCl_3$) [Found: C, 61.2; H, 2.9%; M^+, 430 (Cl_3-isotope pattern). $C_{22}H_{13}Cl_3O_3$ requires C, 61.2; H, 3.0%; *M*, 430]; ν_{max}(KBr disc)/cm^{-1} 3420m (OH), 1779s (C=O), 1512w, 1342w, 1218s, 984w, 816s; δ_H(270 MHz; $CDCl_3$) 4.90 (1 H, s, OH), 7.05 (1 H, d, *J* 8.1, Ar), 7.21–7.35 (3 H, m, Ar), 7.41–7.47 (2 H, m, Ar), 7.52 (1 H, d, *J* 8.9, Ar), 7.56–7.61 (1 H, m, Ar), 7.91 (1 H, d, *J* 8.1, Ar), 7.98 (1 H, d, *J* 8.8, Ar), 8.05 (1 H, d, *J* 8.1 , Ar), 8.18 (1 H, d, *J* 8.9, Ar).

(R_a)-2-Hydroxy-2′-propoxycarbonyloxy-1,1′-binaphthyl (R_a)-9. Yield 0.32 g (90%); mp 119–120 °C; $[\alpha]_D$ +43 (*c* 1.90, $CHCl_3$) (Found: C, 77.3; H, 5.5%; M^+, 372. $C_{24}H_{20}O_4$ requires C, 77.4; H, 5.4%; *M*, 372.); ν_{max}(KBr disc)/cm^{-1} 3471m (OH), 1724s (C=O), 1508w, 1342w, 1270s, 808w; δ_H (270 MHz; $CDCl_3$) 0.69 (3 H, t, *J* 7.4 , Me), 1.44 (2 H, sextet, *J* 7.4 , CH_2), 3.88–4.03 (2 H, m, CH_2), 5.24 (1 H, s, OH), 7.02 (1 H, d, *J* 8.8, Ar), 7.21–7.38 (5 H, m, Ar), 7.48 (1 H, d, *J* 8.8 , Ar), 7.51 (1 H, dd, *J* 6.6, 1.3, Ar), 7.84 (1 H, d, *J* 7.3, Ar), 7.90 (1 H, d, *J* 9.0, Ar), 7.98 (1 H, d, *J* 8.3, Ar), 8.08 (1 H, d, *J* 8.8, Ar).

(R_a)-2-Hydroxy-2′-(1-naphthoyloxy)-1,1′-binaphthyl (R_a)-10. Yield 0.41 g (96%); mp 126–127 °C; $[\alpha]_D$ +79 (*c* 1.90, $CHCl_3$) (Found: C, 84.2; H, 4.5%; M^+, 440. $C_{31}H_{20}O_3$ requires C, 84.5; H, 4.5%; *M*, 440); ν_{max}(KBr disc)/cm^{-1} 3449s (OH), 1705s, (C=O), 1620w, 1505w, 1270m, 1195s, 1140w, 815w, 778s; δ_H(270 MHz; $CDCl_3$) 5.31 (1 H, s, OH), 7.18–7.27 (3 H, m, Ar), 7.30–7.46 (5 H, m, Ar), 7.51–7.67 (4 H, m, Ar), 7.74–7.94 (4 H, m, Ar), 8.03 (1 H, d, *J* 8.9, Ar), 8.14 (1 H, d, *J* 8.1, Ar), 8.36 (1 H, d, *J* 8.8, Ar).

(R_a)-2-Hydroxy-2′-(2-naphthoyloxy)–1,1′-binaphthyl (R_a)-11. Yield 0.41 g (97%); mp 142–143 °C; $[\alpha]_D$ +75 (*c* 2.10, $CHCl_3$) (Found: C, 84.4; H, 4.65; M^+, 440. $C_{31}H_{20}O_3$ requires C, 84.5; H, 4.6%; M, 440); ν_{max}(KBr disc)/cm^{-1} 3452s (OH), 1714s, (C=O), 1612w, 1505w, 1296s, 1208s, 1145w, 724w; δ_H(270 MHz; $CDCl_3$) 5.37 (1 H, s, OH), 7.18–7.26 (3 H, m, Ar), 7.32–7.47 (5 H, m, Ar), 7.49–7.61 (4 H, m, Ar), 7.63–7.82 (4 H, m, Ar), 8.05 (1 H, d, *J* 8.4, Ar), 8.12 (1 H, d, *J* 8.2, Ar), 8.20 (1 H, d, *J* 8.6, Ar).

2-Hydroxy-2′-[(methylthio)carbonyloxy]-1,1′-binaphthyl 12. Yield 0.64 g (96%); mp 76–78 °C (Found: C, 73.1; H, 4.3%; M^+, 360. $C_{22}H_{16}O_4$ requires C, 73.3; H, 4.5%; *M*, 360); ν_{max}(KBr disc)/cm^{-1} 3468s (OH), 1702s, (C=O), 1645w, 1510w, 1320w, 1200m, 1115s; δ_H(270 MHz; $CDCl_3$) 2.13 (3 H, s, Me), 5.08 (1 H, s, OH), 7.01 (1 H, d, *J* 8.3, Ar), 7.21–7.39 (5 H, m, Ar), 7.47 (1 H, d, *J* 9.0, Ar), 7.52 (1 H, dd, *J* 6.6, 1.5, Ar), 7.86 (1 H, d, *J* 7.6, Ar), 7.92 (1 H, d, *J* 8.8, Ar), 7.98 (1 H, d, *J* 8.3, Ar), 8.07 (1 H, d, *J* 9.0, Ar).

(R_a)-2-(Chloroacetoxy)-2′-hydroxy-1,1′-binaphthyl (R_a)-13. Yield 0.20 g (57%); mp 117–118 °C; $[\alpha]_D$ +21 (*c* 0.81, $CHCl_3$) [Found: C, 72.8; H, 4.2%; M^+, 362 (Cl-isotope pattern). $C_{22}H_{15}ClO_3$ requires C, 72.8; H, 4.2%; *M*, 362]; ν_{max}(KBr disc)/cm^{-1} 3461m (OH), 1737s (C=O), 1500w, 1296m, 1204s, 968m, 810m; δ_H(270 MHz; $CDCl_3$) 3.76 (2 H, AB doublet, J_{AB} 14.8, CH_2), 4.98 (1 H, s, OH), 7.02 (1 H, d, *J* 8.0, Ar), 7.22–7.39 (5 H, m, Ar), 7.44 (1 H, d, *J* 9.0, Ar), 7.54 (1 H, dd, *J* 6.8, 1.3, Ar), 7.85 (1 H, d, *J* 8.4, Ar), 7.92 (1 H, d, *J* 9.0, Ar), 8.00 (1 H, d, *J* 8.3, Ar), 8.11 (1 H, d, *J* 9.0, Ar).

(R_a)-2-Hydroxy-2′-[(1*R*,3*S*,5*R*)-menthylcarbonyloxy]-1,1′-binaphthyl (R_a)-14. Prepared from (±)-**5**, yield 0.21 g (46%); mp 188–189 °C; $[\alpha]_D$ −35 (*c* 1.15, $CHCl_3$); ν_{max}(KBr disc)/cm^{-1} 3488m (OH), 2975w, 1735s (C=O), 1380w, 1215s, 820w; δ_H(270 MHz; $CDCl_3$) 0.53 (3 H, d, *J* 7.1, Me), 0.60–0.98 (4 H, m, menthyl) overlapped by 0.73 (3 H, d, *J* 7.1, Me) and 0.53 (3 H, d, *J* 6.4, Me), 1.15–1.48 (2 H, m, menthyl), 1.53–1.68 (4 H, m, menthyl), 4.32 (1 H, dt, *J* 11.0, 4.6, C*H*O-menthyl), 5.25 (1 H, s, OH), 7.03 (1 H, d, *J* 8.5, Ar), 7.20–7.38 (5 H, m, Ar), 7.50 (1 H, d, *J* 9.0 , Ar), 7.52 (1 H, dd, *J* 6.8, 1.3, Ar), 7.84 (1 H, d, *J* 8.6, Ar), 7.89 (1 H, d, *J* 9.0, Ar), 7.98 (1 H, d, *J* 8.3 , Ar), 8.08 (1 H, 9.0, Ar); *m/z* (EI): 468 (M^+, 8%), 286 (100), 83 (54), 69 (38), 55 (78) [Found (HRMS): M^+, 468.2301. $C_{31}H_{32}O_4$ requires *M*, 468.2301].

2-(*N*,*N*-Dimethylcarbamoyloxy)-2′-(*N*,*N*-dimethylthiocarbamoyloxy)-1,1′-binaphthyl 15

Neat *N*,*N*-dimethylcarbamoyl chloride (5.4 cm^3, 59.0 mmol) was added to a solution of **6** (20.0 g, 50.0 mmol) in dichloromethane (300 cm^3) containing NEt_3 (8.4 cm^3, 60.0 mmol) and 4-dimethylaminopyridine (0.61 g, 10 mol%). A standard work-up procedure and recrystallisation from dichloromethane–light petroleum or ethanol gave the product (19.30 g, 87%); mp 123–125 °C (from dichloromethane–light petroleum) (Found: C, 69.9; H, 5.4; N, 6.4%; M^+, 444. $C_{26}H_{24}N_2O_3S$ requires C, 70.3; H, 5.4; N, 6.3%; *M*, 444); ν_{max}(KBr disc)/cm^{-1} 1713s (C=O), 1212s (C=S); δ_H(270 MHz; $CDCl_3$) 2.22 (3 H, s, Me), 2.47 (3 H, s, Me), 2.68 (3 H, s, Me), 3.07 (3 H, s, Me), 7.24–7.34 (3 H, m, Ar), 7.38–7.48 (3 H, m, Ar), 7.60 (2 H, apparent t, *J* 8.5, Ar), 7.86–8.00 (4 H, m, Ar); δ_C(67.8 MHz; $CDCl_3$) 35.8, 36.3, 37.7, 42.7, 122.6, 123.0, 123.7, 125.4, 125.6, 125.7, 126.1, 126.3, 126.5, 126.6, 126.8, 127.7, 127.9, 128.3, 128.9, 131.1, 131.6, 133.4, 146.7, 149.6, 154.1, 186.4.

Reaction of (R_a)-**6** yielded (R_a)-**15** in 85% yield with $[\alpha]_D$ +140 (*c* 1.98, $CHCl_3$) after recrystallisation from dichloromethane–hexane. Further recrystallisation did not improve this optical rotation.

Alternative one-pot synthesis of 15 from (R_a)-1,1′-bi-2-naphthol 4

Neat dimethylthiocarbamoyl chloride (2.99 g, 24.2 mmol) was added to a solution of **4** (6.00 g, 21.0 mmol) in dichloromethane (200 cm^3) containing NEt_3 (3.5 cm^3, 25.2 mmol) and 4-dimethylaminopyridine (0.64 g, 25 mol%) under an inert atmosphere. The mixture was stirred under nitrogen at 20–25 °C for 48 h. To the resulting darkened solution fresh 4-dimethylaminopyridine (256 mg, 10 mol%), NEt_3 (3.5 cm^3, 23.1 mmol) and dimethylcarbamoyl chloride (213 μl, 23.1 mmol) were added. The reac-

tion was stirred for a further 48 h at 20–25 °C. A standard work-up typically gave crude **15** (7.50 g, 81%), containing at worst trace quantities of binaphthol **4**.

2-(*N*,*N*-dimethylcarbamoyloxy)-2′-(*N*,*N*-dimethylcarbamoylthio)-1,1-binaphthyl 16

Mechanically stirred **15** (15.0 g, 34.0 mmol) was thermalised (5 h at 250 °C) under nitrogen in a previously equilibrated heater. (This transformation could also be conveniently carried out in commercial Kugelrohr apparatus under N_2 at atmospheric pressure.) The sample was removed from the heat source and allowed to cool. The dark mass was extracted with dichloromethane, stirred with excess charcoal, filtered and crystallised from dichloromethane–light petroleum or ethanol to give the product (14.1 g, 93%); mp 169–171 °C (Found: C, 69.9; H, 5.5; N, 6.3%; M^+, 444. $C_{26}H_{24}N_2O_3S$ requires C, 70.3; H, 5.4; N, 6.3%; *M*, 444); ν_{max}(KBr disc)/cm^{-1} 1710s (C=O), 1652 (C=O); δ_H(270 MHz; $CDCl_3$) 2.18 (3 H, s, Me), 2.65 (3 H, s, Me), 2.79 (6 H, br s, Me), 7.15–7.32 (4 H, m, Ar), 7.39–7.51 (2 H, m, Ar), 7.60 (1 H, d, *J* 8.5, Ar), 7.79 (1 H, d, *J* 8.5, Ar), 7.88–8.02 (4 H, m, Ar).

Thermolysis of (R_a)-**15** (100% ee) gave crude (R_a)-**16** showing $[\alpha]_D$ +135 (*c* 2.00, $CHCl_3$). One recrystallisation from PhCl–heptane afforded material with $[\alpha]_D$ +144 (*c* 2.00, $CHCl_3$) (100% ee).

(R_a)-2-(*N*,*N*-dimethylcarbamoyloxy)-2′-hydroxy-1,1′-binaphthyl (R_a)-17

Neat dimethylcarbamoyl chloride (1.7 cm^3, 19.1 mmol) was added slowly to a solution of (R_a)-**4** (4.98 g, 17.4 mmol) in dichloromethane (200 cm^3) containing NEt_3 (2.9 cm^3, 20.9 mmol) and 4-dimethylaminopyridine (0.21 g, 9.8 mol%). The mixture was stirred under an inert atmosphere at 20–25 °C. Standard work-up procedures followed by recrystallisation from dichloromethane–hexane yielded the product (4.15 g, 67%); mp 184–185 °C; $[\alpha]_D$ +169 (*c* 1.61, $CHCl_3$); ν_{max}(KBr disc)/cm^{-1} 3278m (OH), 1691s (C=O), 1392m, 1220s, 812m, 804m; δ_H(270 MHz; $CDCl_3$) 2.43 (3 H, s, Me), 2.74 (3 H, s, Me), 5.92 (1 H, s, OH), 7.05 (1 H, d, *J* 8.3, Ar), 7.20–7.37 (5 H, m, Ar), 7.45 (1 H, d, *J* 8.8, Ar), 7.48 (1 H, dd, *J* 6.6, 1.3, Ar), 7.84 (1 H, d, *J* 8.9, Ar), 7.89 (1 H, d, *J* 8.8, Ar), 7.95 (1 H, d, *J* 8.1, Ar), 8.04 (1 H, d, *J* 8.8, Ar); *m/z* (EI) 357 (M^+, 24%), 268 (12), 72 (100) [Found (HRMS): M^+, 357.1365. $C_{23}H_{19}NO_3$requires *M*, 357.1365].

2-Hydroxy-2′-mercapto-1,1′-binaphthyl 3

Compound **17** (10.0 g, 23.0 mmol) was refluxed (24 h) under nitrogen in methanol–water (4:1, 440 cm^3) containing KOH (15.5 g, 276.0 mmol). Evaporation to dryness under reduced pressure yielded a solid which was dissolved in deoxygenated water (400 cm^3). Washing with CH_2Cl_2 (2 × 150 cm^3), acidification with concentrated HCl (30 cm^3), re-extraction into CH_2Cl_2 (2 × 150 cm^3), drying (Na_2SO_4) and evaporation to dryness yielded slightly air sensitive **3** (4.93 g, 71%); mp 154–155 °C (lit.,[5] 65–66 °C); ν_{max}(KBr disc)/cm^{-1} 3420s, br (OH), 2565w (SH); δ_H(270 MHz; $CDCl_3$) 4.57 (1 H, br s, SH), 5.05 (1 H, br s, OH), 7.01 (1 H, br dd, *J* 8.4, 1.5 plus unresolved long range couplings, Ar), 7.16 (1 H, br dd, *J* 8.4, 1.5 plus unresolved long range couplings, Ar), 7.24–7.47 (5 H, m, Ar), 7.59 (1 H, d, *J* 8.9, Ar), 7.90 (1 H, d, *J* 8.9, Ar), 7.91 (1 H, d, *J* 8.9, Ar), 7.97 (1 H, d, *J* 8.5, Ar), 7.99 (1 H, d, *J* 8.4, Ar); *m/z* (EI) 302 (M^+, 2%), 170 (63), 141 (40), 119 (100) [Found (HRMS): M^+, 302.0783. $C_{20}H_{14}OS$ requires *M*, 302.0765]. The air sensitivity of **3** prevented accurate elemental analysis.

Hydrolysis of (R_a)-**16** yielded (R_a)-**3** with $[\alpha]_D$ −32 (*c* 0.50, THF) identical to that obtained *via* resolution.

Resolution of 2-hydroxy-2′-mercapto-1,1′-binaphthyl (R_a)-3

A solution of racemic monothiobinaphthol (±)-**3** (0.50 g, 1.64 mmol) in dichloromethane (10 cm^3) was added dropwise to a solution of (−)-menthyl chloroformate (0.36 g, 1.64 mmol) and 4-dimethylaminopyridine (0.20 g, 1.64 mmol) in dichloromethane (10 cm^3). The resulting light yellow solution was stirred under nitrogen at room temperature for 4 h and acidified with dilute hydrochloric acid. Extraction into dichloromethane and drying (sodium sulfate) gave, after removal of the solvent, a light yellow crystalline mixture of the two diastereomers **18** and **19** in 90% yield. The diastereomers were separated using flash silica with 1:1 dichloromethane–light petroleum as eluent. Hydrolysis of the first eluted diastereomer [(1*R*,2*S*,5*R*)-(R_a)-**18**] using a 20-fold excess of KOH (2.40 g, 32.80 mmol) in 4:1 ethanol–deoxygenated water (25 cm^3) and evaporation to dryness under reduced pressure yielded a solid which was dissolved in deoxygenated water (50 cm^3). Washing with CH_2Cl_2 (2 × 15 cm^3), acidification with concentrated HCl (3 cm^3), extraction into CH_2Cl_2 (2 × 15 cm^3), drying (Na_2SO_4) and evaporation to dryness yielded (R_a)-**3** (0.20 g, 80%) with identical optical properties to a sample prepared by asymmetric synthesis; $[\alpha]_D$ −32 (*c* 0.50, THF).

Preparation of bis(2′-hydroxy-1,1′-binaphthyl-2-yl) disulfide 20

Solid iodine (295 mg, 1.16 mmol) was added to a solution of **3** (0.70 g, 2.32 mmol) in acetonitrile (20 cm^3) containing NEt_3 (323 μl, 2.32 mmol) at 0 °C under an inert atmosphere. The reaction mixture was stirred for 1 h at 0 °C, allowed to warm to ambient temperature, and evaporated under reduced pressure. The crude product was extracted with dichloromethane and washed with $Na_2S_2O_3$ (three times, 0.2 M), dilute Na_2CO_3, water and finally brine. Drying (Na_2SO_4) and evaporation yielded **20** as a 1:1 mixture of *rac*- and *meso*-diastereomers (0.65 g, 93%); mp 178 °C (decomp.); ν_{max}(KBr disc)/cm^{-1} 3495br, 3415br (2 × OH), 2960m (CH), 1259s, 1093s, 1020s, 803s; δ_H(270 MHz; $CDCl_3$) 4.66 (1 H, br s, OH *meso*), 4.77 (1 H, br s, OH *rac*), 6.91–6.98 (1 H, m, Ar), 7.16–7.48 (6 H, m, Ar), 7.75–8.00 (5 H, m, Ar); *m/z* (FAB) 602 (M^+, 75%), 301 (44), 268 (71), 147 (100) [Found (HRMS): M^+, 602.1386. $C_{40}H_{26}O_2S$ requires *M*, 602.1374]. Fractional recrystallisation led to a first crop of mostly *rac*-**20**; δ_H(600 MHz; $CDCl_3$) 4.71 (1 H, br s, OH *rac*), 6.915 (1 H, m, *J* 8.4, 1.1, plus long range couplings, Ar), 7.193 (1 H, m, *J* 8.5, 1.1, plus long range couplings, Ar), 7.237 (1 H, apparent ddd, *J* 8.1, 6.8, 1.3, Ar), 7.298 (1 H, apparent ddd, *J* 8.1, 6.8, 1.3, Ar), 7.351 (1 H, apparent ddd, *J* 8.1, 6.8, 1.2, Ar), 7.363 (1 H, d, *J* 8.9, Ar), 7.444 (1 H, apparent ddd, *J* 8.1, 6.8, 1.2, Ar), 7.815–7.905 (4 H, m, Ar), 7.971 (1 H, d, *J* 8.7, Ar); δ_C(67.8 MHz; $CDCl_3$) 115.5, 117.7, 123.7, 124.2, 124.4, 125.1, 126.4, 127.0, 127.6, 128.3, 128.35, 128.5, 129.2, 130.0, 130.9, 132.6, 133.1, 133.4, 136.8, 151.35. Subsequent crops were mixtures enriched in *meso*-**20**; δ_H(600 MHz; $CDCl_3$) 4.69 (1 H, s, br, OH *meso*), 6.948 (1 H, m, *J* 8.4, 1.0, plus long range couplings, Ar), 7.177 (1 H, m, *J* 8.4, 1.0, plus long range couplings, Ar), 7.215–7.250 (1 H, m, Ar overlapped by *rac*-**20**), 7.258 (1 H, apparent ddd, *J* 8.1, 6.7, 1.3, Ar), 7.295 (1 H, d, *J* 9.0, Ar), 7.290–7.365 (1 H, m, Ar overlapped by *rac*-**20**), 7.518 (1 H, apparent ddd, *J* 8.1, 6.9, 1.3, Ar), 7.797 (1 H, d, *J* 8.9, Ar), 7.865–7.890 (1 H, m, Ar overlapped by *rac*-**20**), 7.947–7.976 (2 H, m, Ar overlapped by *rac*-**20**), 8.110 (1 H, dd, *J* 8.8, 0.6, Ar); δ_C(67.8 MHz; $CDCl_3$) 115.25, 117.6, 123.55, 123.7, 124.3 (2 C overlapped by *rac*-**20**), 124.9, 126.3, 127.65, 128.0, 128.3 (2 C overlapped by *rac*-**20**), 129.1, 130.1, 130.9, 132.5, 133.0, 133.3, 136.6, 151.3.

Oxidation of enantiomerically pure (R_a)-**3** afforded (R_a,R_a)-**20** with $[\alpha]_D$ +86 (*c* 1.55, $CHCl_3$).

Representative catalytic run—conjugate addition of either BuLi or BuMgCl to cyclohex-2-en-1-one 21

In typical catalytic runs a solution of monothiobinaphthol **3** (14.5 mg, 0.05 mmol, 6 mol%) and [$Cu(NCMe)_4BF_4$] (12.6 mg, 0.04 mmol, 5 mol%) in THF or Et_2O (2 cm^3) was treated with BuMgCl or BuLi (0.10 mmol) at −20 °C. Double deprotonation of the ligand **3** and formation of the active catalyst was

found to be slow below this temperature. At the required reaction temperature, BuMgCl or BuLi (0.80 mmol) and cyclohexen-2-en-1-one **21** (77 μl, 0.80 mmol in 0.5 cm^3 of THF or Et_2O) were added simultaneously over a period of 20 min with constant stirring and the reaction stirred for a further 20 min. The reaction was then quenched at once with a few drops of dilute HCl and the yield of the addition products determined by GC (BP-20, 100 °C) using a pentadecane (100 μl) internal standard. The sense and degree of optical induction in the 1,4-product was determined by the method of Alexakis.[15]

X-ray crystallography†

Crystal data for 2-(*N*,*N*-dimethylthiocarbamoyloxy)-2′-hydroxy-1,1′-binaphthyl (±)-6. $C_{23}H_{19}NO_2S$, $M = 373.5$. Monoclinic, $a = 10.144(3)$, $b = 25.702(6)$, $c = 15.156(2)$ Å, $\beta = 104.31(2)°$, $V = 3829(3)$ $Å^3$ (by least-squares refinement on diffractometer angles for 23 carefully centred reflections in the range $17.8 < 2\theta < 23.4°$), space group $P2_1/n$, $Z = 8$, $D_c = 1.30$ g cm^{-3}. Colourless blocks from dichloromethane–hexane, crystal dimensions 0.70 × 0.59 × 0.40 mm, μ(Mo-Kα) = 1.77 cm^{-1}.

Data collection and processing. All measurements were made as previously described[16] using a Rigaku AFC6S diffractometer with graphite monochromated Mo-Kα radiation. Scans (ω–2θ) of (1.05 + 0.30 tan θ)° were made at a speed of 8.0° min^{-1}. Of the 8626 reflections collected, 8164 were unique ($R_{int.} = 0.100$); equivalent reflections were averaged. Of these 3038 reflections had $F_o^2 > 3\sigma(F_o^2)$, where $\sigma(F_o^2)$ was estimated from the counting statistics.[16,17] Lorentz-polarisation corrections were applied. The intensity of three standard reflections measured after every 150 reflections declined by 1.0%; a linear correction factor was applied to account for this.

Structure analysis and refinement. The structure was solved by direct methods.[18] All non-hydrogen atoms were refined anisotropically. Full-matrix least-squares refinement was carried out as previously described[16] using the TEXRAY[19] program set giving $R = 0.056$ and $R_w = 0.056$ (for 3038 reflections and 487 variables). The weighting scheme was based on counting statistics and included a factor ($p = 0.04$) to downweight intense reflections.

Crystal data for (R_a)-2-hydroxy-2′-[(1*R*,3*S*,5*R*)-menthylcarbonyloxy]-1,1′-binaphthyl (R_a)-14. $C_{31}H_{32}O_4$, $M = 468.6$. Monoclinic, $a = 9.121(4)$, $b = 12.562(4)$, $c = 11.733(4)$ Å, $\beta = 104.20(3)°$, $V = 1303(1)$ $Å^3$ (by least-squares refinement on diffractometer angles for 25 carefully centred reflections), space group $P2_1$, $Z = 2$, $D_c = 1.19$ g cm^{-3}. Colourless blocks from dichloromethane–hexane, crystal dimensions 0.35 × 0.33 × 0.20 mm, μ(Mo-Kα) = 0.73 cm^{-1}.

Data collection and processing. Data were collected in an identical manner to compound (±)-**6**. Of the 4509 reflections collected, 2660 were unique ($R_{int} = 0.087$); equivalent reflections were averaged. Of these 1429 reflections had $F_o^2 > 3\sigma(F_o^2)$, where $\sigma(F_o^2)$ was estimated from the counting statistics.[16,17] Lorentz-polarisation corrections were applied. The intensities of three standard reflections measured after every 150 reflections varied no more than expected from Poisson statistics.

Structure analysis and refinement. The structure was solved using the same approach as for (±)-**6** except the factor to downweight intense reflections in the weighting scheme had a lower value ($p = 0.03$). All oxygen atoms, and C(21)–C(31) were refined anisotropically. The remaining atoms were refined isotropically. The full least-squares refinement converged at $R = 0.043$, $R_w = 0.041$ (for 2660 reflections and 215 variables). The assignment of the 1,1′-binaphthyl configuration was based on the known configuration of the (−)-menthyl group

† Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Perkin Trans. 1*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 207/82.

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