Pergamon

Tetrahedron 56 (2000) 2847–2855

TETRAHEDRON

Copper-Catalysed Asymmetric Conjugate Addition of Organometallic Reagents to Linear Enones

Simon M. W. Bennett,[a] Stephen M. Brown,[b] Anthony Cunningham,[c] Michael R. Dennis,[a] James P. Muxworthy,[b] Michael A. Oakley[a] and Simon Woodward[c,*]

[a]*Department of Chemistry, University of Hull, Hull HU6 7RX, UK*
[b]*Process Technology Department, Zeneca Limited, PO Box A38, Huddersfield HD2 1FF, UK*
[c]*School of Chemistry, Nottingham University, University Park, Nottingham NG7 2RD, UK*

Received 1 October 1999; revised 6 January 2000; accepted 13 January 2000

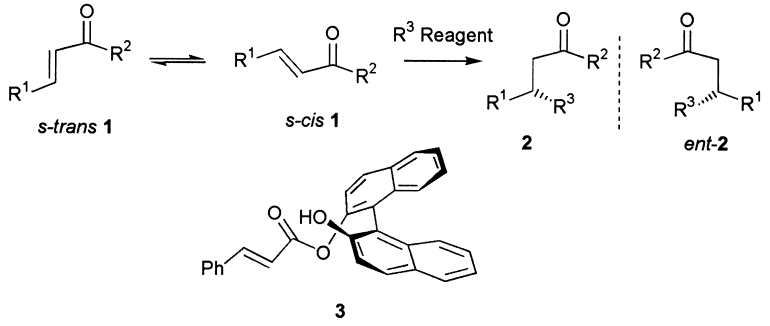
Abstract—Methods for enantioselective 1,4-addition of main-group organometallics to linear enones are overviewed. Thiourethane and thioether 1,1′-binaphthyl-based ligands are effective for copper-catalysed 1,4-addition of $ZnEt_2$ and AlR_3 (R=Me, Et) to *trans*-alkyl-3-en-2-ones; enantioselectivities of up to 72% e.e. are attained. In comparison 1,4-addition of $ZnEt_2$ to 2-cyclohexenone proceeds in up to 77% e.e. with the same ligand family. © 2000 Elsevier Science Ltd. All rights reserved.

Introduction

Enantioselective 1,4-addition of carbanions to linear enones **1** is an interesting challenge. Few efficient methods exist for these transformations (Scheme 1), yet the products **2** are versatile synthons for asymmetric synthesis.[1,2] It is the presence of *s-trans* and *s-cis* conformers in **1** that complicates the enantiofacial selectivity issues in this chemistry.

The binding of $LiCuMe_2$ by the BINOL-bound α,β-unsaturated acid **3** (giving up to 87% e.e.) is a typical auxiliary approach to the preparation of **2**.[3] However, the limitations of auxiliary-based syntheses (the necessity for extra steps) have lead to development of catalytic reagents for the transformation **1**→**2** over the last decade and a half. Chalcone (**1** R^1,R^2=Ph,Ph), benzylideneacetone (**1** R^1,R^2=Ph,Me), and *trans*-alkyl-3-en-2-ones (**1** R^1,R^2=Alkyl,Me) have served as model enones in these copper-promoted transformations whose recent evolution is charted in Table 1.[2] (For developments up to 1991 Rossiter's comprehensive review should be consulted.)[2] Thus far, the current generation of ligands (Table 1) have, unlike auxiliary **3**, largely excluded additional alkoxide donor atoms aimed at coordinating cuprate counter cations (Li, Mg, Zn, Al, etc.).

Aside from the transformations of Table 1 Sewald's additions of $ZnEt_2$ to nitroalkenes (also using BINOL-phosphoramidites and giving up to 86% e.e.) should be mentioned.[10] Since 1991, additional asymmetric catalytic 1,4-additions using other metals have been reported.[2] Nickel-catalysed addition of organozinc reagents to **1** (R^1,R^2=Ar,Ar) proceeds with good levels of stereoinduction (70−80+% e.e.).

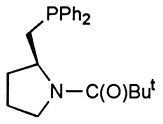
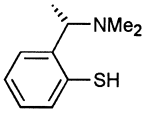
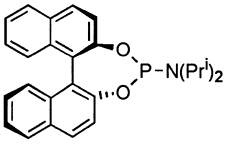
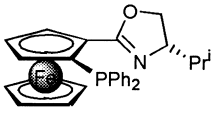
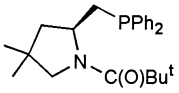
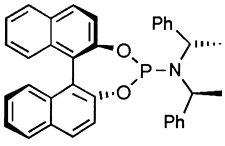
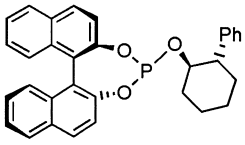


Scheme 1.

Keywords: asymmetric synthesis; enones; thiocarbonyl compounds; thioethers.
* Corresponding author. Tel.: +44-115-951-3541; fax: +44-115-951-3564; e-mail: simon.woodward@nottingham.ac.uk

0040–4020/00/$ - see front matter © 2000 Elsevier Science Ltd. All rights reserved.
PII: S0040-4020(00)00140-X

Table 1. Recent copper-promoted asymmetric conjugate addition reactions to enones **1**

Year [Ref.]	R^1	R^2	R^3	Ligand	Loading (mol%)[a]	e.e. (c.y) (%)
1992[4]	Ph	Ph	Me		148	84 (79)
1994[5]	Ph	Me	Me		9	76 (97)
1996[6]	4-ClPh	Ph	Et		4	90 (84)
1997[7]	Ph	Me	Et		12	81 (61)
1999[8]	Ph	Ph	Et		160	90 (99)
1999[9]	Ph	Ph	Et		2	71 (93)
1999[9]	$C_5H_{11}^n$	Me	Et		2	67 (97)

[a] Based on chiral ligand used.

Bolm's 2-pyridinyl *sec*-alcohols (used at 20 mol%)[11] and Ikeda's oxazolines (used at 10 mol%)[12] are particularly effective as the catalyst loadings are lower than those required with older $Ni(acac)_2$-based systems.[2] The rubidium salt of (L)-proline (20 mol%) catalyses the Michael addition of $CH_2(CO_2Bu^t)_2$ to **1** (R^1,R^2=Me,Me) in 88% e.e.[13] Finally, Hayashi has reported an exceptional Rh/(*S*)-BINAP catalyst (3 mol%) for the 1,4-addition of $PhB(OH)_2$ to the demanding substrates **1** (R^1,R^2=Alkyl,Me) in >92% e.e.[14]

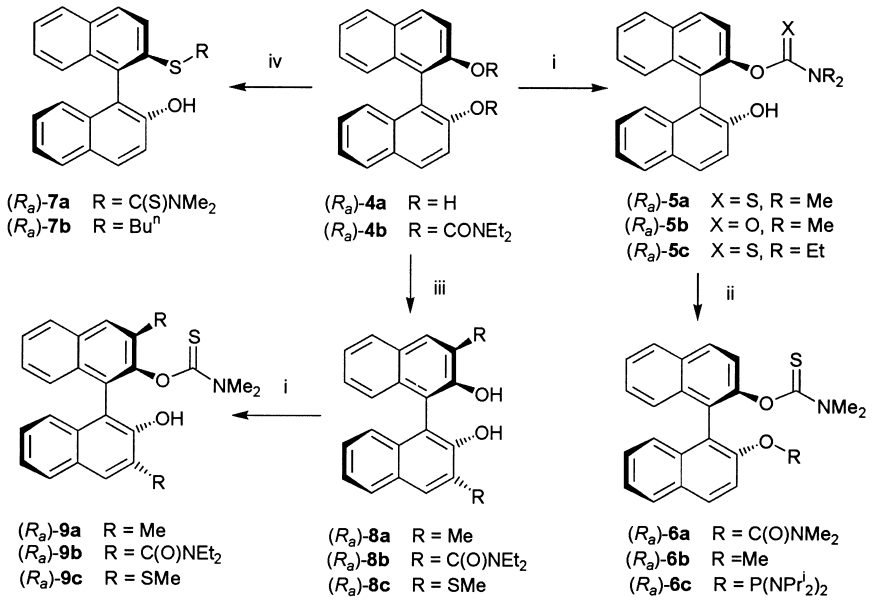
Some time ago we set ourselves the challenge of finding chiral ligands for efficient asymmetric 1,4-addition of *alkyl* organometallics onto *trans*-3-alkylen-2-ones (**1** R^1,R^2=Alkyl,Me). The fragment **2** (R^1,R^2,R^3=Alkyl) is an attractive synthon for the preparation of a number of natural products and currently no high e.e. copper-based methodology is available. Full details of our initial investigations are described here of which some elements have been communicated.[15]

Results and Discussion

We thought to synthesise ligands combining a directing ArOH group, as in auxiliary **3**, with a *soft*[16] donor capable of binding cuprates, $[CuR_2]^-$. The compounds used in this study are available through literature procedures or by simple procedures. The synthetic sequence, shown for simplicity in the (R_a) configuration, is summarised in Scheme 2.

Routine screening results had revealed that ligands containing the thiourethane (thiocarbamate) donors, especially **5a**, were effective in promoting 1,4-additions of organometallics to linear enones.[15] In particular, $AlMe_3$ and $[Cu(MeCN)_4]BF_4$ appeared to be the most efficient terminal organometallic and catalytic copper(I) sources, respectively. As initial goals the effect of changing the terminal organometallic on the catalytic system was investigated. The results for the 1,4-addition of various organometallics to nonenone **1** (R^1,R^2=$C_5H_{11}^n$, Me) in the presence of $[Cu(MeCN)_4]BF_4$ (10 mol%) and ligand **5a** (20 mol%) are shown in Table 2.

In reactions carried out at 91 mM initial ligand concentration triorganoaluminiums were confirmed as the optimal reagents. The use of AlR_3 reagents in copper-catalysed conjugate enone additions was popularised by Westermann[20]



Scheme 2. Reagents: (i) $R_2NC(=X)Cl$ (R=Me, Et; X=O, S), NEt_3, DMAP catalysis on **4a**[17] or **8a–c**; (ii) $Me_2NC(=O)Cl$ (for **6a**), or MeI (for **6b**), or $(Pr^i_2N)_2PCl$ (for **6c**) with appropriate bases; (iii) Lithiation of **4b** followed by MeI and deprotection (for **8a**),[18] lithiation and rearrangement (for **8b**),[18] lithiation followed by Me_2S_2 (for **8c**); (iv) Monothiobinaphthol (MTB)[17] preparation followed by $Bu^nLi/Me_2NC(=S)Cl$ (for **7a**) or Bu^nLi/Bu^nBr (**7b**).[17]

Table 2. Enantioselective 1,4-additions to *trans*-3-nonen-2-one (**1** R^1,R^2=$C_5H^n_{11}$, Me) catalysed by $[Cu(MeCN)_4]BF_4$ (10 mol%) and (R_a)-**5a** (20 mol%) as a function of organometallic type

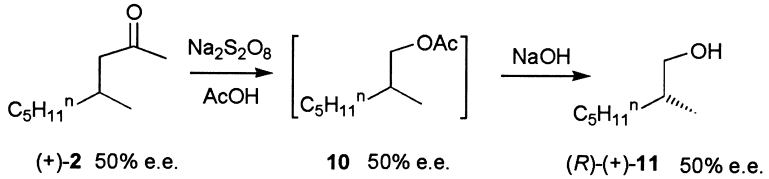
Run	Organometallic	Conversion (%)	1,4-Yield (%)	e.e. (%) (hand)
1	MeMgBr	>99	81	0
2	$ZnEt_2$	81	66	35 (+)
3	$AlMe_3$	95	80–90+	**49–52** (+)
4	$AlClMe_2$	95	<1	–
5	$MeTi(OPr^i)_3$	22	12	3 (+)
6	BEt_3	0	0	–

and Kabara[21] but asymmetric variants are rare.[15] In runs 2–3 (R_a)-**5a** fashions (+)-**2** (R^1,R^2,R^3=$C_5H^n_{11}$, Me, Me) as the major enantiomer. Even at −20°C one of the catalyst components is unstable and a black precipitate is always formed during the course of the reaction. However, this decomposition does not appear to affect the chemical yields or e.e. values of the product **2** and the systems are highly reproducible. In the case of $ZnEt_2$ and $AlMe_3$ the mass balance is good and normally only small amounts of starting enone contaminated the product. For the Grignard and titanium reagents some **1** is consumed as non-eluting oligomeric material. In no case is 1,2-addition observed. The absolute configuration of the addition was determined by the degradation shown in Scheme 3.

A sample of (+)-**2** (R^1,R^2,R^3=$C_5H^n_{11}$,Me,Me) derived from several repetitions of run 3 was treated with $Na_2S_2O_8$ leading to a single new species whose formation could be followed to completion by chiral GC. The crude ^1H NMR spectrum of this material was consistent with the expected Baeyer–Villiger product **10**.[22] Compound **10** was hydrolysed directly to afford (*R*)-(+)-**11** based on polarimetric comparison with literature values for (*S*)-(−)-**11**.[23,24]

The necessity for the presence of both a hydroxy function and an appropriate thio-donor in the ligand structure was investigated in the reaction of $AlMe_3$ with *trans*-3-nonen-2-one (**1** R^1,R^2=$C_5H^n_{11}$, Me) and is summarised in Table 3. The requirement for the 2-naphtholic directing group is confirmed by the poor performance of ligands **6a–c** (run 1 vs. runs 4–6). For effective stereoinduction the presence of a *soft* ligation site is also mandatory; the carbamate **5b** affords only low yields of racemic material whereas the other *hard–soft* ligands **5a**, **5c**, and **7a–b** give a range of interesting inductions (runs 1, 3, 7, 8).

Our previous attempts to optimise the enantioselectivity shown by the system (R_a)-**5**/Cu^I/$AlMe_3$ by changing solvents or including stoichiometic amounts of enone activating electrophiles (TMSCl or $BF_3{\cdot}OEt_2$) did not prove effective.[15] This lack of response left only the ligand structure and the use of compounds expected to change the catalyst structure as the major variables. The results of representative modifications are summarised in Table 4.



Scheme 3.

Table 3. Addition of $AlMe_3$ to *trans*-3-nonen-2-one (**1** R^1,R^2=$C_5H_{11}^n$, Me) in the presence of $[Cu(MeCN)_4]BF_4$ (10 mol%) and ligands (R_a)-**5**, (R_a)-**6** and (R_a)-**7a**,**b** (20 mol%).

Run	Ligand	X	R	Conversion (%)	1,4-Yield (%)	e.e. (%) (hand)
1	(R_a)-**5a**	S	–	95	80+	**50 (*R*)**
2	(R_a)-**5b**	O	–	36	13	2 (*R*)
3	(R_a)-**5c**	S	–	93	75	40 (*R*)
4	(R_a)-**6a**	–	$C(O)NMe_2$	46	23	15 (*S*)
5	(R_a)-**6b**	–	Me	69	31	12 (*R*)
6	(R_a)-**6c**	–	$P(NPr^i_2)_2$	90	63	8 (*R*)
7	(R_a)-**7a**	–	$C(S)NMe_2$	95	70	42 (*R*)
8	(R_a)-**7b**	–	Bu^n	88	79	**71 (*R*)**

The results of a non-linear effect[25] study, using ligand **5a**, are reported in Fig. 1. Together these data shed some light on the reaction mechanism. Benchmark results under standard conditions are given in Table 4, entries 1–3, for comparison. As both enone and organometallic are added during the course of the reaction the catalyst concentration falls during the reaction. For comparison between runs it is useful to note the initial copper(I) and ligand L concentrations, normally 46 mM $[Cu(MeCN)_4]BF_4$ (10 mol%) and (R_a)-**5** 91 mM (20 mol%) under standard conditions. The use of CuBr, $Cu(OTf)_2$, CuCN gives inferior systems (runs 4–6). In general, we have noted that the presence of halide anions can be very detrimental to the enantioselectivity in this reaction. Modification of the Lewis acid site in the catalyst to nominal ArO–$Al(OMe)_2$ (by addition of MeOH) did not affect the catalyst (run 7). However, nominal ArO–AlMeCl preparation (by use of 0.2 equivalents of Me_2AlCl) caused a large suppression of the e.e. (run 8).

Of the four ligand structures screened the sterically buttressed dimethylbinaphthalene ligand (R_a)-**9a** was the most successful (run 10) while the introduction of alternative binding sites lowered the selectivity (runs 9, 11, 12). In the case of the 3,3′-diamido ligand (R_a)-**9b** the sense of the enantioselection was reversed.

Lowering the reaction concentration proved to be the simplest way of improving the enantioselection of the (R_a)-**5**/$[Cu(MeCN)_4]BF_4$ (20/10 mol%) system (Table 4, runs 2 vs. 13–15). Thus, one explanation of the small apparent NLE in Fig. 1 is that a mononuclear catalyst is involved and that the slight deviation observed is due to competing dimeric catalysts. The catalytic manifold is

Table 4. Optimisation of asymmetric conjugate additions of organometallics (R^3M) to *trans*-3-nonen-2-one (**1** R^1,R^2=$C_5H_{11}^n$, Me) and comparison with 2-cyclohexenone

Run	Ligand (L)	R^3M	Conditions/Variations	Con.[a] (%)	1,4-Yield[a] (%)	e.e.[a] (%) (hand)
1	(R_a)-**5a**	$ZnEt_2$	*Standard conditions*	81	66	35 (*R*)
2	(R_a)-**5a**	$AlMe_3$	20 mol% L, 10 mol%, Kubas-Cu^{I},[b] 45 mM	95	94	**50 (*R*)**
3	(R_a)-**5a**	$AlEt_3$	Initial catalyst concentration *Variations*[c]	63	40	32 (*R*)
4	(R_a)-**5a**	$AlMe_3$	CuBr, 10 mol%	95	83	0
5	(R_a)-**5a**	$AlMe_3$	$Cu(OTf)_2$, 10 mol%	51	23	7 (*R*)
6	(R_a)-**5a**	$AlMe_3$	CuCN, 10 mol%	92	71	33 (*R*)
7	(R_a)-**5a**	$AlMe_3$	Added MeOH, 40 mol% to catalyst	94	85	**52 (*R*)**
8	(R_a)-**5a**	$AlMe_3$	Catalyst prepared with $AlClMe_2$, 20 mol%	97	97	23 (*R*)
9	(R_a)-**8c**	$AlMe_3$	3,3′-di-SMe BINOL	96	80	33 (*R*)
10	(R_a)-**9a**	$AlMe_3$	3,3′-di-Me thiocarbamate	79	55	**62 (*R*)**
11	(R_a)-**9b**	$AlMe_3$	3,3′-di-$C(O)NEt_2$ thiocarbamate	85	61	17 (*S*)
12	(R_a)-**9c**	$AlMe_3$	3,3′-di-SMe thiocarbamate	95	92	3 (*S*)
13	(R_a)-**5a**	$AlMe_3$	L 145 mM, Kubas-Cu^{I},[b] 72 mM	98	83	42 (*R*)
14	(R_a)-**5a**	$AlMe_3$	L 46 mM, Kubas-Cu^{I},[b] 23 mM	93	89	**56 (*R*)**
15	(R_a)-**5a**	$AlMe_3$	L 23 mM, Kubas-Cu^{I},[b] 11 mM	79	79	**61 (*R*)**
16	(R_a)-**5a**	$AlMe_3$	No Cu^{I} present, 20 mol% L	0	0	-
17	-	$AlMe_3$	No L, 10 mol% Kubas-Cu^{I},[b] 46 mM	49	33	0
18	(R_a)-**8c**	$ZnEt_2$	L 46 mM, Kubas-Cu^{I},[b] 23 mM	100	>95	**72 (*R*)**
19	(R_a)-**8c**	$ZnEt_2$	5 mol% L/2.5 mol% Kubas-Cu^{I},[b] 23 mM	71	71	**68 (*R*)**
20	(R_a)-**8c**	$ZnEt_2$	L 46 mM, Kubas-Cu^{I},[b] 23 mM, cyclohex[d]	100	78	**77 (*R*)**

[a] Conversion, yield, and e.e. by GC.
[b] Kubas-Cu^{I} is $[Cu(MeCN)_4]BF_4$ at initial concentration given.
[c] Unless stated otherwise all other reagents and conditions are as runs 1–3.
[d] 2-cyclohexenone used.

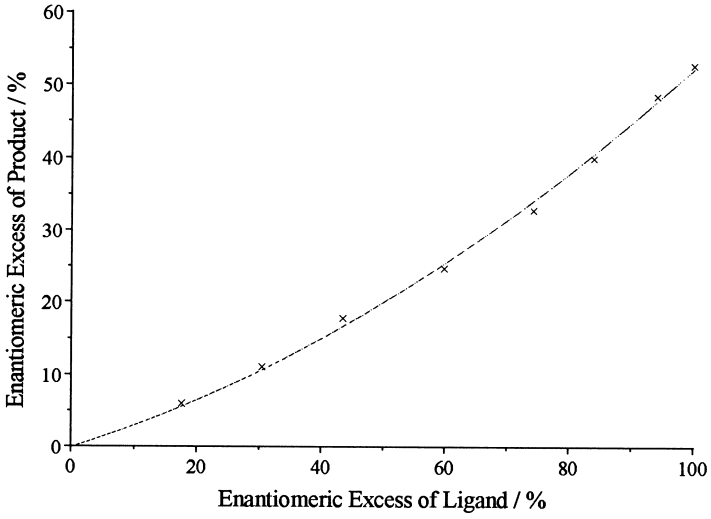


Figure 1. Non-linear effect (NLE) study of the reaction of $AlMe_3$ with to *trans*-3-nonen-2-one (**1** R^1,R^2=$C_5H_{11}^n$, Me) catalysed by $[Cu(MeCN)_4]BF_4$ (10 mol%; initial conc. 46 mM) in the presence of **5a** (20 mol%; initial conc. 91 mM).

complicated by the presence of achiral catalysts derived from $[Cu(MeCN)_4]BF_4/AlMe_3$ alone that are partially active (runs 16 and 17). Finally, we note that by changing the organometallic source with ligand (R_a)-**8c** a reasonably selective catalyst is formed which retains its potency at low catalyst loading and seems to recognise both acyclic and cyclic enones (runs 18–20). Attempts to realise highly enantioselective catalysts with related ligands are underway in our laboratory.

Experimental

General

N,*N*-Dimethylthiocarbamoyl chloride was recrystallised from pentane. *trans*-3-Alkylen-2-ones (**1** R^1,R^2=Alkyl, Me) and 2-cyclohexenone were distilled under atmospheric pressure and then stored over 4 Å molecular sieves. THF was distilled from Na-benzophenone under a nitrogen atmosphere, diethyl ether and hexane were dried over sodium wire, dichloromethane was distilled from CaH_2. Catalytic reactions were carried out under argon using standard Schlenk techniques. Column chromatography and TLC analyses were performed on silica gel, Rhône Poulenc Sorbsil and Merck Kieselgel 60 $F_{254+366}$, respectively. Proton, ^{13}C and ^{31}P NMR spectra were recorded on either a JEOL JNMGX270 or JNMLA400. IR spectra were recorded on either a Perkin–Elmer 983G or a Perkin–Elmer 882 spectrometer. Mass Spectra were recorded on a Finnigan-MAT 1020 (electron impact ionisation, EI) machine (Hull) 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. Optical rotations were measured on an Optical Activity AA-10 instrument in units of $10^{-1}\,^{\circ}\,cm^{-2}\,g^{-1}$ (c in g/100 ml). Chemical yield (c.y.) and enantiomeric excess (e.e.) analysis of the catalysis was carried out on a Varian 3380 gas chromatograph using either LIPODEX A or *octakis*-(6-*O*-methyl-2,3-di-*O*-pentyl)-γ-cyclodextrin (γ-CD) columns as described previously.[19] All compounds **4a**,[26] **4b**,[18] **5a,b**,[17] **6a**,[17] **7b**,[19] **8a,b**,[18] $[Cu(MeCN)_4]BF_4$[27] and $MeTi(OPr^i)_3$[28] were prepared by literature methods. All other reagents were commercial products.

(R_a)-2-(*N*,*N*-Diethyliminothiocarbamoyloxy)-2′-hydroxy-1,1′-binaphthalene 5c. To a stirred solution of (R_a)-(+)-**4a** (6.6 g, 22.93 mmol) in dry dichloromethane (100 ml) under a nitrogen atmosphere, was added 4-*N*,*N*-dimethylaminopyridine (700 mg, 4.73 mmol), triethylamine (2.90 g, 4.00 ml, 28.67 mmol) and *N*,*N*-diethylthiocarbamoyl chloride (**TOXIC**! 4.00 g, 26.37 mmol). The mixture was stirred for 72 h at ambient temperature. When the reaction was complete (TLC) the solution was quenched with saturated aqueous NH_4Cl solution, washed with water (2×10 ml), dilute hydrochloric acid (2×10 ml), and saturated brine (1×10 ml). The dichloromethane layer was collected, dried (Na_2SO_4) and the solvent removed to give a yellow oil. This oil solidified on treatment with petroleum spirit to yield a pale yellow powder **5c** (6.65 g, 73%), mp 142–143°C; $[\alpha]_D^{24}$=+297 (*c*=5.0 in $CHCl_3$); (Found: C, 74.4; H, 5.95; N, 3.7; S, 7.5. $C_{25}H_{23}NO_2S$ requires C, 74.8; H, 5.8; N, 3.5; S, 7.9%); ν_{max}(KBr disc)/cm^{-1} 3280br, 3060w, 2990w, 2940w, 1522s, 1215s, 819s, 753s; δ_H NMR (400 MHz, $CDCl_3$) 0.47 (3H, t, *J*=7.3 Hz, Me), 1.06 (3H, t, *J*=7.0 Hz, Me), 2.83–2.93 (1H, m, CH_2Me), 3.13–3.23 (1H, m, CH_2Me), 3.56–3.72 (2H, m, CH_2Me), 5.93 (1H, s, OH), 7.10 (1H, d, *J*=8.3 Hz, $C_{8,8'}$–H), 7.22 (1H, d, *J*=8.1 Hz, $C_{8,8'}$–H), 7.32–7.22 (3H, m, $C_{6,6',7'7'}$–H), 7.33 (1H, d, *J*=8.8 Hz, $C_{3,3'}$–H), 7.43 (1H, d, *J*=8.8 Hz, $C_{3,3'}$–H), 7.49 (1H, apparent ddd, *J*=8.4, 1.5 Hz, $C_{6,6',7,7'}$–H), 7.82 (1H, d, *J*=7.8 Hz, $C_{4,4'}$–H), 7.86 (1H, d, *J*=8.8 Hz, $C_{5,5'}$–H), 7.97 (1H, d, *J*=8.1 Hz, $C_{4,4'}$–H), 8.06 (1H, d, *J*=8.8 Hz, $C_{5,5'}$–H); δ_C NMR (67.8 MHz, $CDCl_3$) 11.6, 12.1, 43.7, 48.1, 115.0, 119.4, 123.1, 124.1, 124.7, 125.8, 126.2, 126.5, 127.3, 127.9, 129.1, 130.0, 132.1, 133.6, 133.9, 151.2, 152.5, 186.3; *m*/*z* (EI) 401 (M^+, 26%).

(R_a)-2-(*N*,*N*-Dimethyliminothiocarbamoyloxy)-2′-methoxy-1,1′-binaphthalene, 6b. Sodium hydride (80 mg, 134 mg 60% w/w dispersion in mineral oil, 3.348 mmol)

was washed with dry petroleum (3×5 ml) and evacuated to dryness. Dry THF (10 ml) was added under an inert atmosphere and the suspension cooled to 0°C. A solution of **5a** (1.00 g, 2.68 mmol) in dry THF (10 ml) was added dropwise over ca 5 min causing the mixture to turn yellow and effervesced gently. This solution was then stirred at this temperature for 0.5 h. Methyl iodide (**TOXIC**! 475 mg, 208 μl, 3.35 mmol) was added and the solution allowed to warm to ambient temperature and stir overnight. The mixture was quenched with dilute aqueous NH_3 solution and washed with dilute hydrochloric acid (2×10 ml) saturated aqueous NaCl solution (1×10 ml), dried over $MgSO_4$ and filtered. Evaporation of the solution in vacuo yielded a white fluffy solid which was crystallised from hot ethanol to yield long, colourless needles of **6b**. (0.88 g, 85%), mp 161–164°C; $[\alpha]_D^{24}=+95$ (c=5.0 in $CHCl_3$); (Found: C, 74.05; H, 5.5; N, 3.7; S, 8.0. $C_{24}H_{21}NO_2S$ requires C, 74.4; H, 5.5; N, 3.6; S, 8.3%); ν_{max}(KBr disc)/cm^{-1} 3038w, 3005w, 2978w, 2856w, 2825w, 1539s, 1518s, 1290s, 1271s, 1220s, 1141s, 818m, 755m; δ_H NMR (400 MHz, $CDCl_3$) 2.50 (3H, s, NMe), 3.07 (3H, s, NMe), 3.75 (3H, s, OMe), 7.19–7.33 (5H, m, Ar), 7.40 (1H, d, J=9.0 Hz, Ar), 7.41–7.46 (1H, m, Ar), 7.57 (1H, d, J=9.0 Hz, Ar), 7.82 (1H, m, J=8.0 Hz, Ar), 7.93–8.02 (3H, apparent dt, J=9.5, 9.0 Hz, Ar); δ_C NMR (67.8 MHz, $CDCl_3$) 37.6, 42.7, 56.7, 113.6, 117.8, 123.5, 123.7, 125.5, 125.5, 126.0, 126.3, 126.3, 126.4, 127.6, 128.2, 128.3, 139.8, 129.8, 131.8, 133.6, 133.9, 149.6, 155.1, 186.6; m/z (EI) 387 (M$^+$, 91%).

(R_a)-2-(N,N-Dimethyliminothiocarbamoyloxy)-2′-[bis-(diisoproylamino)phosphite)]-1,1′-binaphthalene, 6c. Under an inert atmosphere *N*-methyl-2-pyrrolidinone (776 μl, 8.03 mmol), triethylamine (450 μl, 3.214 mmol), and bis(diisopropylamino)chlorophosphine (**TOXIC**! 857 mg, 3.214 mmol) were added to a solution of **5a** (1.00 g, 2.77 mmol) in dichloromethane (40 ml) and the mixture stirred for up to 72 h. When complete [TLC (3:1 hexane/ethyl acetate)] the reaction was quenched with saturated $NH_4Cl_{(aq)}$ solution, washed with saturated $NH_4Cl_{(aq)}$ solution (2×10 ml), saturated brine (1×20 ml), dried over $MgSO_4$ and filtered. This solution was then left to evaporate overnight to give white crystals of **6c** on washing with petroleum spirit (480 mg, 30%), $[\alpha]_D^{24}=+126$ (c=3.54 in $CHCl_3$); (Found: C, 69.3; H, 7.8; N, 6.9 $C_{35}H_{46}N_3O_2PS$ requires C, 69.6; H, 7.7; N, 7.0%); ν_{max}(KBr disc)/cm^{-1} 3055w, 2970w, 2929w, 2865w, 1540m, 1221m, 1195m, 1158m, 1148m, 954m, 809s, 751s, 749s; δ_H NMR (400 MHz, $CDCl_3$) 0.74 (6H, d, J=6.6 Hz, CHMe_2), 0.81 (6H, d, J=6.6 Hz, CHMe_2), 0.96 (6H, d, J=6.6 Hz, CHMe_2), 1.02 (6H, d, J=6.6 Hz, CHMe_2), 2.46 (3H, s, NMe), 3.00 (3H, s, NMe), 3.18–3.28 (4H, m, CHMe$_2$), 7.14–7.27 (3H, m, $C_{6,6'7,7'}$–H), 7.29 (1H, d, J=7.8 Hz, $C_{8,8'}$–H), 7.32 (1H, d, J=8.6 Hz, $C_{8,8'}$–H), 7.39 (1H, dt, J=7.8, 1.2 Hz, $C_{6,6',7,7'}$–H), 7.64 (1H, d, J=8.8 Hz, C_3–H), 7.68 (1H, dd, J=8.8 Hz, J_{PH}=3.9 Hz, $C_{3'}$–H), 7.76 (1H, d, J=7.8 Hz, $C_{5,5'}$–H), 7.83 (1H, d, J=9.0 Hz, $C_{4,4'}$–H), 7.87 (1H, d, J=8.0 Hz, $C_{5,5'}$–H), 7.88 (1H, d, J=9.0 Hz, $C_{4,4'}$–H); δ_C NMR (100.4 MHz, $CDCl_3$) 23.5, 23.55, 23.6, 23.65, 23.85, 23.9, 23.95, 24.0, 37.9, 42.6, 44.6, 44.75, 44.8, 44.95, 117.5, 117.9, 118.1, 118.15, 123.3, 124.15, 125.3, 125.6, 125.9, 126.0, 126.4, 126.6 (d, J_{PC}=12.2 Hz),127.2, 127.4, 127.8, 128.5, 128.9, 128.9 (d, J_{PC}=3.1 Hz), 131.95, 133.8 (d, J_{PC}=4.9 Hz), 149.6, 151.75 (d, J_{PC}=7.4 Hz), 186.4, some signals overlap; δ_P NMR (162.0 MHz, $CDCl_3$) 113.4; m/z (EI) 604 (M$^+$, 5%).

(R_a)-2-(N,N-Dimethyliminothiocarbamoylthio)-2′-hydroxy-1,1′-binaphthalene 7a. A standard solution of Bu^{n}Li (0.53 ml of 1.08 M hexane solution was added to a cold (−78°C) solution of (R_a)-monothiobinaphthol (MTB)[17] (160 mg, 0.53 mmol) in THF (3.0 ml) under an argon atmosphere to give a dark solution. A sample of *N*,*N*-dimethylthiocarbamoylchloride (**TOXIC**! 74 mg, 0.60 mmol) dissolved in THF (2.0 ml) was added by syringe and the solution allowed to come to room temperature overnight. The solvent was evaporated and the residue partitioned between dichloromethane and $NH_4Cl_{(aq)}$. The organic layer was washed with dilute $HCl_{(aq)}$ and brine, dried ($MgSO_4$), and the solvent removed. The compound was purified by chromatography (dichloromethane/hexane) (121 mg 59%) mp 209–210°C; $[\alpha]_D^{23}=+724$ (c=5.1 in $CHCl_3$); ν_{max}(KBr disc)/cm^{-1} 3296br, w, 3062w, 2962w, 2938w, 1621m, 1597m, 1512s, 1383s, 1251s, 1215s, 1143s, 980s, 819s, 752s; δ_H NMR (270 MHz, $CDCl_3$) 3.35 (3H, s, NMe), 3.51 (3H, s, NMe), 6.41 (1H, s, OH), 6.87 (1H, d, J=8.2 Hz, $C_{8,8'}$–H), 7.15 (1H, d, J=8.5 Hz, $C_{8,8'}$–H), 7.19 (1H, ddd, J=1.3, 7.0, 8.5 Hz, $C_{6,6',7,7'}$–H), 7.26–7.33 (2H, m, $C_{6,6',7,7'}$–H), 7.34 (1H, d, J=9.0 Hz, $C_{3,3'}$–H), 7.54 (1H, ddd, J=1.2, 6.9, 8.2 Hz, $C_{6,6',7,7'}$–H), 7.69 (1H, d, J=8.8 Hz, $C_{3,3'}$–H), 7.85 (1H, d, J=8.0 Hz, $C_{5,5'}$–H), 7.88 (1H, d, J=8.8 Hz, $C_{4,4'}$–H), 7.96 (1H, d, J=8.0 Hz, $C_{5,5'}$–H), 8.05 (1H, d, J=8.8 Hz, $C_{4,4'}$–H); δ_C NMR (67.8 MHz, $CDCl_3$) 42.5, 45.7, 118.0, 119.3, 123.3, 124.6, 126.6, 127.1, 127.2, 127.8, 128.0, 128.2, 128.7, 129.8 (2C), 132.35, 133.7, 134.1, 134.4 (2C), 139.5, 153.1, 198.3; m/z (EI) 389 (M$^+$, 18%) [found (EI HRMS) M$^+$ 389.0909. $C_{23}H_{19}NOS_2$ requires 389.0908].

(S_a)-2,2′-Dihydroxy-3,3′-dimethylthio-1,1′-binaphthalene 8c. *A. (S_a)-3,3′-Dimethylthio-2,2′-bis(N,N-diethylcarbamoyloxy)-1,1′-binaphthalene.* Bu^{s}Li in hexanes (1.3 M; 8.7 ml) was added dropwise over 9 min to a stirred solution of (S_a)-**4b** (2.5 g, 5.16 mmol) and TMEDA (1.54 ml, 10.3 mmol) in THF at −78°C. The reaction was stirred for a further 5 min after then methyl disulfide (1.02 ml, 11.4 mmol) was added and the reaction allowed to warm slowly to −50°C. The mixture was then brought to ambient temperature and quenched with saturated aqueous NH_4Cl solution, the volatiles removed by high vacuum, extracted into dichloromethane, the layers separated and the organic layer dried ($MgSO_4$). The solvent was removed and the product crystallised from EtOH to give white crystals of the 3,3′-di-SMe-bis-carbamate (2.01 g, 76%), mp 164–165°C; $[\alpha]_D^{29}=+84$ (c=5.0 in $CHCl_3$); ν_{max}(KBr disc)/cm^{-1} 3080w, 2940w, 1730s, 1410s, 1280, 1220s, 1160s, 1060, 965, 850, 755; δ_H (400 MHz, $CDCl_3$) 0.40–0.70 (6H, v br, CH_2Me), 1.0 (6H, v br, CH_2Me), 2.58 (6H, s, SMe), 2.7–3.3 (8H, v br, CH_2Me), 7.2–7.3 (4H, v br, Ar), 7.38 (2H, br t, J=7.8 Hz, Ar), 7.68 (2H, br s, $C_{4,4'}$–H), 7.77 (2H, br d, J=7.8 Hz, $C_{5,5'}$–H); δ_C (100.4 MHz, $CDCl_3$) 12.4, 13.7, 15.1, 41.75, 42.0, 124.4, 125.1, 125.4, 125.8, 126.2, 127.3, 131.1, 131.9, 132.5, 145.0, 152.2; m/z (EI) 576 (M$^+$, 41%) [found (EI HRMS) M$^+$ 576.2113. $C_{32}H_{36}N_2S_2O_4$ requires 576.2117].

B. Deprotection of (S_a)-3,3′-Dimethylthio-2,2′-bis(N,N-diethylcarbamoyloxy)-1,1′-binaphthalene. $LiAlH_4$ (0.33 g, 8.65 mmol) was added to a stirred solution of bis-carbamate prepared above (1.00 g, 1.73 mmol) in THF (12 ml) and the mixture refluxed for 16 h. After cooling, the excess $LiAlH_4$ was destroyed by cautious addition of ethyl acetate (12 ml) followed by 2 M $HCl_{(aq)}$. The layers were separated and the aqueous extracted twice with further ethyl acetate. The combined organic layer was dried ($MgSO_4$) and the solvent removed to give a white powder which was crystallised from EtOH to give white crystals of (S_a)-**8c** (0.51 g, 78%); mp 159–160°C; $[\alpha]_D^{29}=-87$ (c=2.0 in $CHCl_3$); ν_{max}(KBr disc)/cm^{-1} 3415br, 3070w, 2925w, 1580, 1500, 1435s, 1210, 1145s, 880, 850, 755; δ_H (400 MHz, $CDCl_3$) 2.56 (6H, s, SCH_3), 6.05 (2H, s, OH), 7.10 (2H, d, J=8.6 Hz, C_8–H), 7.24 (2H, ddd, J=1.3, 6.8, 8.6 Hz, C_7–H), 7.35 (2H, ddd, J=1.2, 6.8, 8.0 Hz, C_6–H), 7.82 (2H, d, J=8.0 Hz, C_5–H), 7.95 (2H, s, C_4–H); δ_C (100.4 MHz, $CDCl_3$) 17.34, 112.68, 124.31, 124.54, 126.45, 126.92, 127.48, 129.45, 129.91, 132.53, 150.11; *m/z* (EI) 378 (M^+, 100%) [found (EI HRMS) M^+ 378.0750. $C_{22}H_{18}S_2O_2$ requires 378.0748].

(R_a)-2′-Hydroxy-2-(*N*,*N*-dimethylthiocarbamoyloxy)-3,3′-dimethyl-1,1′-binaphthalene 9a. Compound **8a** (0.50 g, 1.59 mmol), DMAP (39 mg, 0.32 mmol) and *N*,*N*-dimethylthiocarbamoyl chloride (**TOXIC**!, 0.21 g, 1.67 mmol) were dissolved in dichloromethane (40 ml). NEt_3 (231 μl, 1.67 mmol) was added and the solution stirred for 15 days at ambient temperature. Some dichloromethane was then removed, the reaction warmed to 40°C and stirring continued for a further 4 days. The reaction was quenched with saturated $NH_4Cl_{(aq)}$ and the organic layer washed with $NH_{3(aq)}$, 2 M HCl (×2), H_2O, brine and dried ($MgSO_4$). The solvent was removed and the crude product purified by column chromatography (diethyl ether-light petroleum) to give a white powder (46%); mp 86–88°C; $[\alpha]_D^{29}=+363$ (c=1.0 in $CHCl_3$); (Found: C, 74.9; H, 6.05; N, 3.3; S, 7.6. $C_{25}H_{23}NSO_2$ requires C, 74.8; H, 5.8; N, 3.5; S, 8.0%); ν_{max}(KBr disc)/cm^{-1} 3310br, 3070w, 2930, 1545s, 1400s, 1290s, 1235s, 1135s, 885, 750s; δ_H (400 MHz, $CDCl_3$) 2.48 (6H, s, $C_{3,3'}$–Me), 2.50 (3H, s, NMe), 3.15 (3H, s, NMe), 5.84 (1H, s, OH), 7.05 (1H, d, J=8.6 Hz, Ar), 7.16 (1H, t, J=7.6 Hz, Ar), 7.20–7.28 (3H, m, Ar), 7.44 (1H, t, J=7.4 Hz, Ar), 7.71 (1H, s, $C_{4,4'}$–H), 7.74 (1H, d, J=7.8 Hz, $C_{5,5'}$–H), 7.85–7.89 (2H, m, Ar); δ_C (100.4 MHz, $CDCl_3$) 17.2, 17.5, 37.8, 43.0, 115.1, 123.3, 124.4, 124.55, 125.3, 125.6, 126.01, 126.35, 127.0, 127.5, 128.6, 129.0, 129.3, 130.3, 130.7, 132.2, 132.3, 132.5, 151.2, 151.5, 186.7; *m/z* (EI) 401 (M^+, 56%) [found (HRMS) M^+ 401.1452. $C_{25}H_{23}NSO_2$ requires 401.1450].

(R_a)-3,3′-Bis(*N*,*N*-diethylcarbamoyl)-2′-hydroxy-2-(*N*,*N*-dimethylthiocarbamoyloxy)-1,1′-binaphthalene 9b. Prepared in a similar manner to **9a**. Purified by chromatography (EtOAc) to give a white powder (73%); mp 122–126°C; $[\alpha]_D^{25}=+266$ (c=2.0 in $CHCl_3$); ν_{max}(KBr disc)/cm^{-1} 3240br, 3075w, 2985, 2950, 1640vs, 1545, 1460, 1400, 1290, 1225, 1140, 755; δ_H (400 MHz, $CDCl_3$) 1.16 (9H, br t, J 7.0, 3×CH_2*Me*), 1.27 (3H, br t, J=6.8 Hz, CH_2*Me*), 2.79 (3H, br s, NMe), 3.12 (3H, s, NMe), 3.1–3.9 (8H, br m, 4×C*H*$_2$Me), 6.54 (1H, br s, OH), 7.19–7.37 (5H, m, Ar), 7.51 (1H, dt, J=1.0, 6.8 Hz, Ar), 7.78 (1H, d, J=8.5 Hz, $C_{5,5'}$–H), 7.90 (1H, s, $C_{4,4'}$–H), 7.93 (1H, d, $C_{5,5'}$–H), 7.94 (1H, s, $C_{4,4'}$–H); δ_C (67.8 MHz, $CDCl_3$) 12.0, 13.6, 14.1 (2C), 38.5, 38.9 (2C), 42.9 (2C), 43.9, 116.35, 124.2, 124.9, 125.8, 125.9, 126.1, 126.3, 126.8, 127.2, 127.4, 128.0, 128.2, 128.3, 128.4, 128.6, 130.2, 131.0, 133.4, 133.7, 148.6, 166.9, 168.4, 186.2; *m/z* (EI) 571 (M^+, 97%) [found (HRMS) M^+ 571.2511. $C_{33}H_{37}N_3SO_4$ requires 571.2505].

(S_a)-2′-Hydroxy-2-(*N*,*N*-dimethylthiocarbamoyloxy)-3,3′-dimethylthio-1,1′-binaphthalene 9c. Prepared in a similar manner to **9a**. Purified by crystallisation from dichloromethane–pentane to give pale yellow crystals (37%); mp 244–247°C (discolouration prior to melting); $[\alpha]_D^{25}=-345$ (c=1.0 in $CHCl_3$); ν_{max}(KBr disc)/cm^{-1} 3280br, 3070w, 2920w, 1585s, 1400s, 1290, 1220s, 1135s, 850, 755; δ_H (400 MHz; $CDCl_3$/d^6-DMSO) 2.58 (3H, s, Me), 2.65 (3H, s, Me), 2.72 (3H, s, Me), 3.20 (3H, s, Me), 6.60 (1H, s, OH), 7.05 (1H, d, J=8.3 Hz, $C_{8,8'}$–H), 7.14–7.20 (1H, m, Ar), 7.25 (1H, t, J=7.1 Hz, Ar), 7.31 (1H, t, J=7.4 Hz, Ar), 7.47 (1H, t, J=7.6 Hz, Ar), 7.65 (1H, s, $C_{4,4'}$–H), 7.78 (1H, d, J=8.6 Hz, $C_{5,5'}$–H), 7.79 (1H, s, $C_{4,4'}$–H), 7.87 (1H, d, J=8.1 Hz, $C_{5,5'}$–H); δ_C (400 MHz; $CDCl_3$-d^6DMSO) 14.6, 15.1, 37.95, 42.9, 115.2, 123.8, 124.1, 124.3, 125.1, 125.2, 125.3, 125.4, 126.1, 126.4, 126.5, 126.7, 129.1, 130.0, 130.6, 131.1, 132.1, 132.2, 148.2, 149.05, 1856.0; *m/z* (EI) 465 (M^+, 4%) [found (HRMS) M^+ 465.0887. $C_{25}H_{23}NS_3O_2$ requires 465.0891].

Representative copper-catalysed conjugate addition method

A solution of Me_3Al in hexanes (2.0 M; 0.43 ml, 0.85 mmol) was diluted with hexane to a volume of 0.8 ml in a syringe, rocking the syringe to affect mixing. An aliquot of this solution (0.1 ml, 0.11 mmol) was added to a stirred solution of ligand (**5a–c**, **6a–c**, **7a–b**, **8c**, and **9a–c**, 0.1 mmol) and $[Cu(MeCN)_4]BF_4$ (15.7 mg, 0.05 mmol) in THF (1.0 ml) at −20°C and the mixture stirred for approximately 1 min.

Using a syringe, THF (0.5 ml) was added to 3-nonen-2-one **1** (R^1,R^2=$C_5H_{11}^n$,Me) (83 μl, 0.5 mmol) and the solution mixed. The resulting solution was drawn back up into the syringe affording 0.7 ml of enone solution. This solution of **1** and the remaining Me_3Al solution (0.7 ml, generated above) were added simultaneously to the stirred catalyst solution (−20°C) over 20 min using a syringe pump. After addition was complete the mixture was stirred for a further 20 min at −20°C. Dilute HCl (2 M, 2.5 ml) was added cautiously and the mixture allowed to warm to room temperature. Internal standard (undecane, 50 μl) and diethyl ether were added, the layers separated and the organic fraction filtered through silica. Typical GC analysis[19] of the liquid showed that it contained only undecane (rt 11.0 min), 4-methyl-2-nonanone (rt 21.2 and 22.8 min for the (−) and (+) enantiomers, respectively, 0–71% e.e.) and a trace of 3-nonen-2-one (rt 29.0 min.). Distillation was carried out in some cases to confirm the presence of isolable **2**. Additions using other enones, organometallic sources, and ligands were carried out in an analogous manner.

Additions using manual sequential drop-wise additions of organometallic and enone gave essentially identical results.

4-Methyl-2-nonanone **2** *(R^1,R^2,R^3=$C_5H^n_{11}$,Me,Me).* δ_H (400 MHz; $CDCl_3$) 0.81–0.90 (6H, m, 2×Me), 1.26 (8H, m, 4×CH_2), 1.97 (1H, m, CH), 2.13 (3H, s, C(O)Me), 2.18–2.43 (2H, m, CH_2C(O)Me); *m/z* (EI) 156 (M^+, 1%), 141 (3), 127 (3), 109 (18), 101 (25), 91 (12), 85 (28), 69 (16), 58 (65), 43 (100).

4-Ethyl-2-nonanone **2** *(R^1,R^2,R^3=$C_5H^n_{11}$,Me,Et).* δ_H NMR (400 MHz, $CDCl_3$) 0.94–0.79 (6H, m, 2×Me), 1.40–1.15 (10H, m, alkyl C-*H*), 1.91-1.79 (1H, m, CH), 2.13 (3H, s, C(O)Me), 2.33 (2H, m, CH_2C(O)Me).

4-Ethyl-5-methyl hexane-2-one **2** *(R^1,R^2,R^3=Pr^i,Me,Et).* δ_H NMR (400 MHz, $CDCl_3$) 0.90–0.78 (9H, m, 3×Me), 1.26–1.13 (1H, m, CH), 1.42–1.28 (1H, m, CH), 1.82–1.65 (2H, m, C_4–CH_2Me), 2.15 (3H, s, C(O)Me), 2.26 (2H, m, CH_2C(O)Me).

Baeyer–Villiger oxidation of conjugate addition product, preparation of 2-methyl-1-heptanol acetate 10. A sample of (+)-4-methyl-2-nonanone (+)-**2** (R^1,R^2, R^3=$C_5H^n_{11}$,Me,Me) (119 μl ca. 50% e.e.) isolated from a combination of catalytic runs (and therefore containing some undecane) was slurried with acetic acid (1.3 ml) and water (0.7 ml). $Na_2S_2O_8$ (0.6 g) was added and the mixture stirred at room temperature. The reaction was followed by GC and worked up after 10 days by extraction into dichloromethane, drying ($MgSO_4$) and removing the solvent (by careful rotary evaporation) to give 112 mg yellow oil whose partial ^{1}H NMR spectrum was consistent with formation of **10**. δ_H (400 MHz, $CDCl_3$; signals due to starting material and undecane not given) 0.88–0.93 (6H, m, 2×Me), 1.26 (8H, br m, 4×CH_2), 2.10 (3 H, s, C(O)Me), 1.97 (1H, m, CH), 3.83–3.97 (2H, m, diastereotopic CH_2). GC analysis (γ-CD) of the product showed the presence of undecane, a small amount of ketone **2** and two new partially resolved peaks (rt 24.0 (small) and 26.1 (large) min; 1:3 ratio) assigned to **10**. The presence of 3-nonen-2-one **1** could no longer be detected. The conversion was approximately 85%.

Preparation of (*R*)-(+)-2-methyl-1-heptanol (*R*)-(+)-11 via hydrolysis of 10. The sample of **10** (112 mg, containing some undecane) isolated from the oxidation above was added to excess potassium hydroxide (2 g) in methanol (4.5 ml) and water (0.5 ml) and stirred at 50°C (16 h). The material was extracted into dichloromethane, dried ($MgSO_4$) and the solvent removed by careful rotary evaporation to give 102 mg of a yellow oil assigned structure (*R*)-(+)-**11** by comparison with literature data; $[\alpha]_D$ (c=3.4 in $CHCl_3$, 28°C) +3.2 [lit.[23,24] (*S*)-2-methyl-1-heptanol −13.1 (c=1.15 in $CHCl_3$, 20°C)]; δ_H (270 MHz, $CDCl_3$; signals due to undecane are not given) 0.86–0.93 (6H, m, 2×Me), 1.26 (8H, br m, 4×CH_2), 3.40–3.53 (2H, m, diastereotopic CH_2); δ_C (67.8 MHz, $CDCl_3$) 16.6, 20.7, 22.7, 26.65, 32.0, 33.1, 35.74, 68.44. GC analysis (γ-CD) of the product showed the complete disappearance of the ester with new peaks at 26.4 (small) and 27.8 (large) min, not totally resolved but in the same ratio as the starting material **2**.

Acknowledgements

We are grateful to EPSRC (grant GR/K52263 and access to the Mass Spectrometry Service at Swansea) and Zeneca (CASE award to SWMB). We thank the COST-D12 programme for additional support and Prof. D.G. Blackmond (University of Hull) for advice on non-linear effect interpretation.

References

1. Krause, N. *Angew. Chem. Int. Ed. Engl.* **1998**, *37*, 283–285; Taylor, R. J. K., Ed. *Organocopper Reagents, A Practical Approach*; Oxford University Press: Oxford, 1994; Perlmutter, P. *Conjugate Addition Reactions in Organic Synthesis*; Pergamon: Oxford, 1992.
2. For coverage of reactions prior to 1992 see: Rossiter, B. E.; Swingle, N. E. *Chem. Rev.* **1992**, *92*, 771–806 (especially Section III). Very recently, Zhang has reported highly enantioselective copper-catalysed additions of $ZnEt_2$ to **1** (R^1,R^2=Aryl; and R^1=*i*−Pr, R^2=Me); see: Hu, X.; Chen, H; Zhang, X. *Angew. Chem. Int. Ed. Engl.* **1999**, *38*, 3518–3521.
3. Fuji, K.; Tanaka, F.; Node, M. *Tetrahedron Lett.* **1991**, *32*, 7281–7282.
4. Kanai, M.; Koga, K.; Tomioka, K. *Tetrahedron Lett.* **1992**, *33*, 7193–7196.
5. van Klaveran, M.; Lambert, F.; Eijkelkamp, D. J. F. M.; Grove, D. M.; van Koten, G. *Tetrahedron Lett.* **1994**, *35*, 6135–6138.
6. de Vries, A. H. M.; Meetsma, A.; Feringa, B. L. *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2374–2430.
7. Strangeland, E. L.; Sammakai, T. *Tetrahedron* **1997**, *53*, 16503–16510.
8. Kanai, M.; Nakagawa, Y.; Tomioka, K. *Tetrahedron* **1999**, *55*, 3831–3842.
9. Alexakis, A.; Benhaïm, C.; Fournioux, X.; van der Heuvel, A.; Levêque, J.-M.; March, S.; Rosset, S. *Synlett* **1999**, 1811–1813.
10. Sewald, N.; Wendisch, V. *Tetrahedron: Asymmetry* **1998**, *9*, 1341–1344.
11. Bolm, C.; Ewald, M.; Felder, M. *Chem. Ber.* **1992**, *125*, 1205–1215.
12. Ikeda, S.-I.; Cui, D.-M.; Sato, Y. *J. Am. Chem. Soc.* **1999**, *121*, 4712–4713.
13. Yamaguchi, M.; Shiraishi, T.; Hirama, M. *J. Org. Chem.* **1996**, *61*, 3520–3530.
14. Takaya, Y.; Ogasawara, M.; Hayashi, T.; Sakai, M.; Miyaura, N. *J. Am. Chem. Soc.* **1998**, *120*, 5579–5580.
15. Bennett, S. M. W.; Brown, S. M.; Muxworthy, J. P.; Woodward, S. *Tetrahedron Lett.* **1999**, *40*, 1767–1770.
16. Pearson, R. G. *Coord. Chem. Rev.* **1990**, *100*, 403–425.
17. Azad, S. M.; Bennett, S. M. W.; Brown, S. M.; Green, J.; Sinn, E.; Topping, C. M.; Woodward, S. *J. Chem. Soc., Perkin Trans. 1* **1997**, 687–694.
18. Dennis, M. R.; Woodward, S. *J. Chem. Soc., Perkin Trans. 1* **1998**, 1081–1085.
19. Bennett, S. M. W.; Dennis, M. R.; Fraser, P. K.; Topping, C. M.; Woodward, S.; Brown, S. M.; Radojevic, S.; Conole, G.; McPartlin, M. *J. Chem. Soc., Perkin Trans. 1* **1999**, 3127–3132.
20. Westermann, J.; Nickisch, K. *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1368–1369.
21. Kabbara, J.; Flemming, S.; Nickisch, K.; Neh, H.; Westermann, J. *Tetrahedron* **1995**, *51*, 743–754.

22. Zheng, T.-C.; Richardson, C. *Tetrahedron Lett.* **1995**, *36*, 833–836.
23. Oppolzer, W.; Moretti, R.; Thomi, S. *Tetrahedron Lett.* **1989**, *30*, 5603–5606.
24. Högberg, H.-E.; Hendenström, E.; Fägerhag, J. *J. Org. Chem.* **1992**, *57*, 2052–2059.
25. Girard, C.; Kagan, H. B. *Angew. Chem. Int. Ed. Engl.* **1998**, *37*, 2922–2959.
26. Cai, D.; Hughes, D. L.; Verhoeven, T. R.; Reider, P. *Org. Synth.* **1999**, *76*, 1–5.
27. Kubas, G. *J. Inorg. Synth.* **1990**, *28*, 68–70.
28. Weidman, B.; Seebach, D. *Helv. Chim. Acta* **1980**, *63*, 2451–2454.