

(+)-Camphor-derived tri- and tetradentate amino alcohols; synthesis and application as ligands in the nickel catalyzed enantioselective conjugate addition of diethylzinc

André H. M. de Vries, Rosalinde Imbos and Ben L. Feringa *

Department of Organic and Molecular Inorganic Chemistry, Groningen Center for Catalysis and Synthesis, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

Abstract: Several novel tri- and tetradentate amino alcohol ligands, all derived from (+)-camphor, have been synthesized by using specific *N*-alkylation procedures. The amino alcohols were employed as chiral ligands in the nickel catalyzed conjugate additions of diethylzinc to chalcone and cyclohexenone as model substrates. For the acyclic enone enantioselectivities up to 83% were achieved. © 1997 Elsevier Science Ltd

Introduction

The asymmetric conjugate addition reaction of carbon nucleophiles to α,β -unsaturated compounds is considered a highly attractive method for the synthesis of enantiomerically pure compounds.¹ However, such transformations using a *chiral catalyst* are less common and are mainly based on two approaches:² i) enantioselective conjugate addition reactions of stabilized carbon nucleophiles were successfully catalyzed by chiral amines^{1c,2} and crown ethers^{2,3} or chiral metal complexes^{2,4} and ii) copper and nickel catalyzed enantioselective conjugate addition reactions employing organometallic reagents, e.g. Grignard reagents,^{1e,2,5} organolithium compounds,^{2,6} and dialkylzinc reagents^{2,7} have been developed. Despite considerable progress catalytic approaches featuring broad scope and high selectivity are lacking. Herein we describe our results on the nickel catalyzed enantioselective conjugate addition of diethylzinc to enones employing multidentate chiral ligands.

Since the enantioselective version of the nickel catalyzed alkyl transfer from diethylzinc to chalcone was described by Soai and co-workers,⁸ Bolm and co-workers,⁹ our group,¹⁰ and others¹¹ have reported several modifications. Despite all these efforts the nickel catalyzed addition still shows enantioselectivity only for acyclic enones (chalcones). Stimulated by the observed nonlinear relationship between the e.e. of the chiral auxiliary and the e.e. of the 1,4-product,^{10,12} indicating the involvement of at least two chiral bidentate amino alcohol ligands in the catalytic process, we were interested in the behaviour of tri- and especially tetradentate amino alcohol ligands in the nickel catalyzed conjugate addition of diethylzinc to enones.

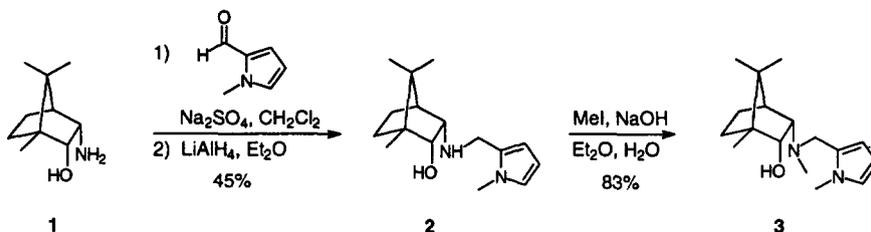
Results and discussion

Synthesis of the tridentate amino alcohols

The tridentate secondary amino alcohol ligand **2**, highly successful as chiral ligand in the conjugate addition of methyl lithium to a cyclic enone,⁶ was synthesized from *cis-endo*-3-aminoborneol **1**^{6,13} and subsequently *N*-methylated with an excess of methyl iodide to provide compound **3** (Scheme 1).

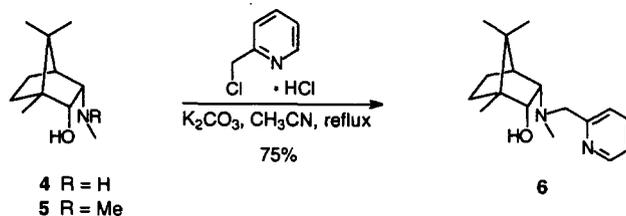
Since the electron pair on the nitrogen of the pyrrole group will be hardly accessible for metal complexation (due to the aromaticity of pyrrole) we attempted to synthesize the better coordinating pyridine substituted analogue **6** by employing pyridine-2-carboxaldehyde (conditions as in Scheme 1). However, the pyridine group was *N*-methylated as well in the last step. Fortunately, a route using *cis*-

* Corresponding author. Email: Feringa@chem.rug.nl



Scheme 1. Synthesis of amino alcohols 2 and 3.

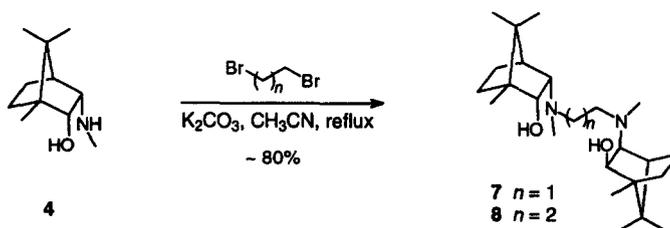
endo-N-methyl-3-aminoborneol ((+)-MAB, **4**)¹³ and 2-picolyl chloride hydrochloride furnished the desired tridentate ligand **6** (Scheme 2).



Scheme 2.

Synthesis of tetradentate amino alcohols

Several attempts to synthesize alkyl bridged aminoisoborneols by straightforward coupling of *cis-exo-N*-methyl-3-aminoisoborneol with 1,3-dibromopropane or 1,4-dibromobutane in refluxing ethanol, ethyl acetate, or DMF under basic conditions failed, probably due to steric hindrance. When the primary aminoalcohol *cis-exo*-3-amino-isoborneol and dibromoalkanes were used only the corresponding tertiary aminoalcohols were obtained as a result of a favoured intramolecular *N*-alkylation.¹⁰ More promising results were achieved when stereoisomer (+)-MAB **4** was used as nucleophile in the coupling reaction with dibromoalkanes. Apparently, the *endo* isomer is somewhat less sterically demanding and therefore better accessible for alkyl halides. In refluxing acetonitrile and in the presence of one equivalent K_2CO_3 , tetradentate amino alcohols **7** and **8** were synthesized and isolated in remarkable high yields (ca. 80%, Scheme 3). This substitution reaction was not successful with 1,4-dibromobutane as alkylating reagent. Probably the nucleophilic substitution in the former cases is assisted by the neighboring group.



Scheme 3. Synthesis of tetradentate amino alcohols 7 and 8.

Application of 2, 3, 6–8 as chiral ligand in the nickel catalyzed addition of diethylzinc to enones

First the effect of additional coordinating groups in the chiral ligand on the enantioselectivity in the nickel catalyzed addition of diethylzinc to chalcone **9** was examined. The results are summarized in Table 1. When the secondary amino alcohol **2** was employed as chiral ligand a relatively high

Table 1. Ligands **2**, **3**, **6–8** in the nickel catalyzed addition of diethylzinc to chalcone^a

| entry | chiral ligand (mol%) | yield (%) ^b | e.e. (%) ^c | abs. conf. ^d |
|-------|----------------------|------------------------|-----------------------|-------------------------|
| 1 | 2 (11) | 75 | 57 | <i>S</i> |
| 2 | 3 (11) | 91 | 80 | <i>S</i> |
| 3 | 3 (7) | 78 | 65 | <i>S</i> |
| 4 | 3 (16) | 83 | 83 | <i>S</i> |
| 5 | 6 (16) | 67 | ~ 0 | |
| 6 | 7 (8) | 72 | 21 | <i>S</i> |
| 7 | 8 (8) | 88 | 69 | <i>S</i> |

^aReactions at -25°C in 2 ml of acetonitrile using an *in situ* prepared catalyst from 7 mol% $\text{Ni}(\text{acac})_2$ and given amount of chiral ligand. 1.5 Equivalent of diethylzinc in toluene (1.1 M) was used. Reaction time 16 h. ^bIsolated yield of the 1,4-product. ^cDetermined by HPLC analysis. ^dComparison of HPLC-retention times of **10** with known data gave the absolute configuration.^{9b}

enantioselectivity (57% e.e.) was observed for 1,4-product **10**. Primary and secondary amino alcohols, like **4**, did hardly show any enantioselectivity in our earlier study (e.e. <5%).¹⁰ In spite of the proposed structure, responsible for the highly enantioselective alkyl lithium conjugate addition reported by Tanaka and co-workers,⁶ where coordination of the pyrrole group is ignored, a role of the pyrrole group in this alkyl transfer can not be excluded. However, it is also possible that only steric effects of the pyrrole group are responsible for the enantioselectivity found.

With the tertiary amine ligand **3**, enantioselectivities for **10** were observed which are comparable with those found for (+)-*cis-endo-N,N*-dimethyl-3-aminoborneol **5**¹⁰ (entries 2–4). An interesting feature of **3** is, in contrast to previous studies,^{8–11b–d} that even with a ligand-to-nickel ratio of 1 a significant e.e. value of 65% was found, indicating a role of the pyrrole moiety (*vide supra*). Rather to our surprise the pyridine substituted ligand **6** furnished the 1,4-product with no enantioselectivity at all (entry 5). Most probably, only the pyridine group is involved as a coordinating group in the *in situ* preparation of the catalyst, resulting in a complex or aggregate with the chiral backbone too far away from the active center.

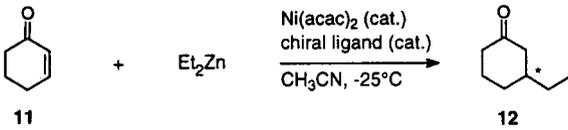
With the alkyl bridged ligands **7** and **8** alternating e.e. values for **10** were obtained, compared to the e.e. value found with two equivalents of the corresponding bidentate ligand **5** (e.e. 82%, reference 10). Probably somewhat different aggregates are formed in solution, especially with ligand **7**, resulting in less enantioselective alkyl transfer. Compounds **7** and **8** prohibit *trans* coordination of both amino alcohol moieties to nickel due to the alkyl bridge, which may be another explanation for the observed decrease in enantioselectivity.

All novel tri- and tetradentate amino alcohols furnished the same enantiomer of **10** in excess as compared to the results found for the analogous bidentate ligands,¹⁰ indicating that the direction of asymmetric induction is not influenced by introducing additional coordinating and/or sterically demanding entities.

In order to investigate whether this enantioselective alkyl transfer to chalcone can also be achieved with cyclic substrates, compounds **2**, **3**, **6–8** were examined as chiral ligand in the conjugate addition of diethylzinc to cyclohexenone (**11**). The results are summarized in Table 2.

In all cases the 1,4-product **12** was isolated in good yields (>70%). However, tridentate ligands **2** and **3** were not able to induce selectivity exceeding 12% e.e. (for ligand **3**) and with tetradentate

Table 2. Ligands **2**, **3**, **6–8** in the nickel catalyzed addition of diethylzinc to cyclohexenone^a

|  | | | |
|---|----------------------|------------------------------------|-------------------------|
| entry | chiral ligand (mol%) | e.e. of 12 (%) ^b | abs. conf. ^c |
| 1 | 2 (16) | 7 | <i>S</i> |
| 2 | 3 (16) | 12 | <i>S</i> |
| 3 | 6 (16) | 0 | - |
| 4 | 7 (8) | 0 | - |
| 5 | 8 (8) | 0 | - |

^aReactions at -25°C in 2 ml of acetonitrile using an *in situ* prepared catalyst from 7 mol% $\text{Ni}(\text{acac})_2$ and given amount of chiral ligand. 1.5 Equivalent of diethylzinc in toluene (1.1 M) was used. Reaction time 16 h. Conversion to the 1,4-product $>90\%$ as determined by GC analysis. Isolated yields of 3-ethylcyclohexanone (**12**) $>70\%$. ^bEnantiomeric excess of **12** was determined by derivatization with enantiomerically pure 1,2-diphenylethylene diamine.¹⁴ ^cComparison of the optical rotation of **12** with known data gave the absolute configuration.¹⁵

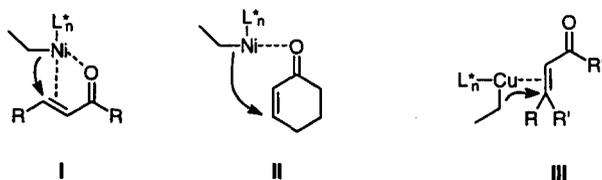


Figure 1. Possible intermediates in the nickel catalyzed alkyl transfer to acyclic (I) and cyclic enone (II) and the corresponding copper catalyzed reaction (III).

ligands **7** and **8** no enantioselectivity was observed. The pyridine substituted tridentate ligand **6** did not result in optically active **12** either. Remarkably, the ligands **2** and **3** furnished the *S* enantiomer of **12** in slight excess. Thus the same absolute configuration is obtained as in the reaction with chalcone (*s-cis* enone), indicating that with cyclohexenone (*s-trans* enone) another aggregate, present in solution, is responsible for this slightly enantioselective alkyl transfer.

Concluding remarks

In conclusion, this paper describes the synthesis of new tri- and tetradentate ligands and the successful application in the nickel catalyzed enantioselective conjugate addition of diethylzinc to chalcone. Especially the relatively high e.e.'s observed with the secondary amino alcohol **2** and the low ligand-to-metal ratio for chiral ligand **3** are important features. However, the goal to develop a catalytic system, capable of enantioselective conjugate addition of diethylzinc to *both* cyclic and acyclic substrates, failed. Apparently, in the nickel catalyzed alkyl transfer a chiral alkyl-nickel species is formed with affinity for the carbonyl oxygen resulting in an enantioselective alkyl transfer for *s-cis* enones, *i.e.* chalcone, as is shown in Figure 1 (I). For cyclohexenone, probably intermediate II will be formed with the chiral alkyl-nickel species too far away from the β -position and therefore not able to introduce any asymmetry in the conjugate addition. Alkyl-copper species, on the other hand probably coordinate to the carbon-carbon double bond of the enone,¹⁶ furnishing intermediates like III, with possibilities for enantioselective alkyl transfer to both cyclic and acyclic enones (*i.e.* *s-trans* and *s-cis* enones).⁷ Our future studies will focus among other metals on copper catalyzed conjugate addition reactions.

Experimental section

General

¹H and ¹³C NMR spectra were recorded on a Varian Gemini 200 (at 200 and 50.3 MHz respectively) or a Varian VXR-300 (300 and 75.5 MHz) spectrometer; solvent CDCl₃. The chemical shifts are denoted in δ units (ppm) relative to TMS (δ=0.00) for protons or CDCl₃ (δ=76.91) for carbon atoms. Splitting patterns for ¹H: s (singlet), bs (broad singlet), d (doublet), dd (double doublet), t (triplet), q (quartet), m (multiplet) and for ¹³C determined with the APT pulse sequence: q (quartet, CH₃), t (triplet, CH₂), d (doublet, CH), s (singlet, C). Optical rotations were measured on a Perkin–Elmer 241 MC (at RT). High Resolution Mass Spectra (HRMS) were obtained on an AEI MS-902 mass spectrometer by Mr A. Kiewiet in our laboratories. GC analysis was carried out using a Hewlett–Packard 5890 II gas chromatograph (column: HP-1) equipped with a Hewlett–Packard series II integrator. HPLC analysis was performed on a Waters 480 with a LC spectrophotometer or a Waters 600E system controller with a Waters 991 photodiode array detector; Millenium™ 2010 as software.

(+)-cis-endo-N-[(1-Methylpyrrol-2-yl)methyl]-N-methyl-3-aminoborneol 3

Secondary amino alcohol **2** (0.80 g, 3.07 mmol), MeI (1.5 ml, excess), NaOH (4.0 g, excess) and 1 ml of H₂O were successively added to 25 ml of diethyl ether. The mixture was stirred for 16 h and an additional 1 ml of MeI was added. After another 24 h the mixture was poured into 50 ml of H₂O. The two layers were separated and the water phase was extracted with diethyl ether (3×30 ml). The combined organic layers were washed with brine (50 ml) and dried (Na₂SO₄). Filtration and evaporation of the solvent gave 0.73 g of a crude yellow solid. This material was recrystallised from 15 ml of hexane/ethyl acetate (10:1) yielding pure **3** as a white solid (0.70 g, 2.55 mmol, 83%); mp 54.9–56.4°C. [α]_D²⁰ +61.4 (c 2.01, CH₂Cl₂). ¹H NMR δ 0.91 (s, 3H), 0.92 (s, 3H), 0.93 (s, 3H), 1.16–1.29 (m, 1H), 1.49–1.59 (m, 2H), 1.78–1.94 (m, 2H), 2.09 (s, 3H), 2.64 (dd, *J*=8.6 Hz, *J*=3.3 Hz, 1H), 3.33 (d, *J*=13.6 Hz, AB system, 1H), 3.56 (d, *J*=13.6 Hz, AB system, 1H), 3.66 (s, 3H), 3.75 (d, *J*=8.6 Hz, 1H), 6.05 (m, 2H), 6.59 (m, 1H); ¹³C NMR δ 14.23 (q), 18.73 (q), 18.98 (t) 19.82 (q), 26.18 (t), 34.11 (q), 40.79 (q), 45.25 (s), 48.12 (d) 50.12 (s), 52.45 (t), 65.48 (d), 73.86 (d), 106.39 (d), 109.94 (d), 122.47 (d), 128.93 (s). HRMS calcd for C₁₇H₂₈N₂O: 276.220, found 276.220.

(+)-cis-endo-N-[2-Pyridylmethyl]-N-methyl-3-aminoborneol 6

A mixture of secondary amino alcohol **4** (1.00 g, 5.50 mmol), picolyl chloride hydrochloride (0.90 g, 5.50 mmol) and K₂CO₃ (1.66 g, 12.0 mmol) in 50 ml of acetonitrile was stirred and refluxed for 4 days. The reaction mixture was poured into 50 ml of H₂O and extracted with diethyl ether (2×50 ml). The combined organic layers were washed with brine (50 ml) and dried (Na₂SO₄). Filtration and evaporation of the solvent gave 0.73 g of a crude yellow oil. Column chromatography (SiO₂, CH₂Cl₂/methanol (5:1)) afforded compound **6** as a light yellow oil, which solidified upon standing. Yield 73%; mp 90.2–91.5°C. [α]_D²⁰ +66.1 (c 2.24, CH₂Cl₂). ¹H NMR δ 0.88 (s, 3H), 0.89 (s, 3H), 0.92 (s, 3H), 1.12–1.29 (m, 1H), 1.48–1.63 (m, 2H), 1.78 (t, *J*=4.0, 1H) 1.82–1.96 (m, 1H), 2.12 (s, 3H), 2.82 (dd, *J*=8.8 Hz, *J*=4.0 Hz, 1H), 3.43 (d, *J*=13.8 Hz, AB system, 1H), 3.74 (d, *J*=8.8 Hz, 1H), 3.76 (d, *J*=13.8 Hz, AB system, 1H), 7.11–7.17 (m, 1H), 7.39 (d, *J*=7.8 Hz, 1H), 7.62 (dt, *J*=7.8 Hz, *J*=1.9 Hz, 1H), 8.53 (m, 1H); ¹³C NMR δ 14.23 (q), 18.65 (t) 19.81 (q), 26.18 (t), 41.15 (q), 45.05 (s), 48.11 (d) 50.22 (s), 62.69 (t), 64.54 (d), 73.93 (d), 121.89 (d), 122.40 (d), 136.36 (d), 149.07 (d) 159.10 (s). HRMS calcd for C₁₇H₂₆N₂O: 274.205, found 274.204.

(-)-N,N'-Bis[3-cis-endo-borneol]-N,N'-dimethyl-1,*n*-alkane 7 and 8

General procedure for the synthesis of compounds **7** and **8**. A mixture of *cis-endo-N*-monomethyl-3-aminoborneol ((+)-MAB) **4** (1.00 g, 5.46 mmol), 1,*n*-dibromoalkane (2.78 mmol) and K₂CO₃ (0.75 g, 5.46 mmol) in 50 ml of acetonitrile was stirred and refluxed for 16 h. The mixture was poured into 100 ml of H₂O and extracted with diethyl ether (3×50 ml). The combined organic layers were washed with brine (50 ml) and dried (Na₂SO₄). Filtration and evaporation of the solvent gave the crude

product, which was purified by column chromatography (SiO₂, CH₂Cl₂/methanol (10:1)) resulting in colourless oils which solidified upon standing. The physical data for compounds **7** and **8** are as follows:

(-)-N,N'-Bis[3-cis-endo-borneol]-N,N'-dimethyl-1,2-ethane **7**

Yield 69%. [α]_D²⁰ +42.6 (c 0.5, CH₂Cl₂). ¹H NMR δ 0.84 (s, 6H), 0.87 (s, 12H), 1.08–1.22 (m, 2H), 1.35–1.75 (m, 4H), 1.87–2.12 (m, 4H), 1.9–2.4 (broad signal 4H), 2.17 (s, 6H) 2.74–2.81 (m, 2H), 2.93–2.98 (m, 2H), 3.79 (dd, *J*=8.9 Hz, *J*=1.3 Hz, 2H); ¹³C NMR δ 13.75 (q), 18.32 (q), 18.57 (t) 19.59 (q), 25.65 (t), 41.40 (q) 48.18 (s), 48.56 (d) 50.24 (s), 55.00 (t), 65.02 (d), 74.00 (d). HRMS calcd for C₂₄H₄₄N₂O₂: 392.340, found 392.340.

(-)-N,N'-Bis[3-cis-endo-borneol]-N,N'-dimethyl-1,3-propane **8**

Yield 85%. [α]_D²⁰ +53.8 (c 0.4, CH₂Cl₂). ¹H NMR δ 0.86 (s, 6H), 0.90 (s, 12H), 1.12–1.29 (m, 2H), 1.45–1.58 (m, 4H), 1.70–1.76 (m, 2H), 1.79–1.95 (m, 4H), 2.2–2.3 (bs, 2×3H, 2H), 2.45–2.55 (broad signal, 2H) 2.57 (dd, *J*=8.7 Hz, *J*=4.0 Hz, 2H), 3.66 (d, *J*=8.7 Hz, 2H); ¹³C NMR δ 14.50 (q), 18.88 (q), 18.95 (t) 20.06 (q), 25.13 (t), 26.44 (t), 40.62 (q) 45.29 (s), 48.20 (d) 50.20 (s), 54.65 (t), 65.31 (d), 73.94 (d). HRMS calcd for C₂₅H₄₆N₂O₂: 406.356, found 406.356.

Conjugate addition of diethylzinc to chalcone (9) or cyclohexenone (11) using catalytic amounts of Ni(acac)₂ and chiral amino alcohols

This procedure is typical for all conjugate addition reactions described in this paper. A solution of Ni(acac)₂ (0.07 mmol) and chiral ligand (amounts, see Tables 1 and 2) in 2 ml of acetonitrile was stirred and refluxed for 1 h under nitrogen. In general this results in a clear green solution. Substrate was added (1.0–2.0 mmol), the mixture was cooled to –30°C and diethylzinc in toluene (1.1 M) (1.5 equivalent) was added. Stirring was continued at –25°C for 16 h. An aliquot of the solution (0.1 ml) was taken and quenched with 1 ml of aqueous 1 N HCl. After extraction with 1 ml of diethyl ether the conversion was determined by GC analysis. Retention times: 1,3-diphenyl-2-propenone **9**, 5.66 min; 1,3-diphenylpentan-1-one **10**, 4.93 min (oven temperature 225°C, flow 101 ml/min He); cyclo-2-hexen-1-one **11**, 2.87 min; 3-ethylcyclohexan-1-one **12**, 5.88 min (oven temperature 100°C, flow 101 ml/min He). If complete conversion was achieved, the mixture was poured into 25 ml of aqueous 1 N HCl and extracted with diethyl ether (3×20 ml). The combined organic layers were washed with brine (25 ml), dried (MgSO₄), filtered and evaporated to give the crude 1,4-products. (**Caution**: compound **12** is volatile and long evaporation times should be avoided.) After purification by column chromatography (SiO₂, hexane:diethyl ether 5:1) the e.e.'s were determined. 1,3-Diphenylpentan-1-one **10**: HPLC analysis;^{8–10} 3-ethylcyclohexan-1-one **12**: derivatization with enantiomerically pure 1,2-diphenylethylene diamine followed by ¹³C NMR analysis.¹⁴

Acknowledgements

We thank Mr A. Arnold for performing some experiments. Mr M. Suijkerbuijk is acknowledged for assistance with the e.e. determinations of **10** and Mr W. Kruizinga and Dr J. Herrema for the e.e. determinations of **12**.

References

1. Reviews: a) Perlmutter, P. *Conjugate Addition Reactions in Organic Synthesis*; Tetrahedron Organic Chemistry Series, No. 9; Pergamon: Oxford, 1992. b) Schmalz, H.-G. in *Comprehensive Organic Synthesis*; Trost, B.M.; Fleming, I., Eds.; Pergamon: Oxford, 1991; Vol 4, Chapter 1.5. c) Wynberg, H. in *Topics in Stereochemistry*; Eliel, E.L.; Wilen, S., Eds.; Wiley-Interscience: New York, 1986; Vol. 16, p 87. d) Tomioka, K.; Koga, K. in *Asymmetric Synthesis*; Morrison, J.D., Ed.; Academic: New York, 1983; Vol. 2, p 201. e) Rossiter, B.E.; Swingle, N.M. *Chem. Rev.* 1992, 92, 771.
2. For a recent review, see: Feringa, B.L.; de Vries, A.H.M. in *Advances in Catalytic Processes, Vol 1: Asymmetric Chemical Transformations*; Doyle, M.P., Ed.; JAI Press, Connecticut, 1995, p. 151.

3. Only leading references are shown: a) Cram, D.J.; Sogah, D.Y. *J. Chem. Soc., Chem. Commun.* **1981**, 625. b) Cram, D.J.; Sogah, D.Y. *J. Am. Chem. Soc.* **1985**, *107*, 8301.
4. Only leading references are shown: a) Brunner, H.; Hammer, B. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 312. b) Yamaguchi, M.; Shiraishi, T.; Hirama, M. *J. Org. Chem.* **1996**, *61*, 3520. c) Arai, T.; Sasai, H.; Aoe, K.; Okamura, K.; Date, T.; Shibasaki, M. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 104.
5. a) Zhou, Q.-L.; Pfaltz, A. *Tetrahedron* **1994**, *50*, 4467. b) Kanai, M.; Tomioka, K. *Tetrahedron Lett.* **1995**, *36*, 4275 and references therein.
6. Tanaka, K.; Matsui, J.; Suzuki, H. *J. Chem. Soc., Perkin Trans. I* **1993**, 153.
7. a) de Vries, A.H.M.; Meetsma, A.; Feringa, B.L. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2374. b) Alexakis A.; Frutos, J.; Mangeney, P. *Tetrahedron: Asymmetry* **1993**, *4*, 2427.
8. a) Soai, K.; Hayasaka, T.; Ugajin, S.; Yokoyama, S. *Chem. Lett.* **1988**, 1571. b) Soai, K.; Yokoyama, S.; Hayasaka, T.; Ebihara, K. *J. Org. Chem.* **1988**, *53*, 4148. c) Soai, K.; Hayasaka, T.; Ugajin, S. *J. Chem. Soc., Chem. Commun.* **1989**, 516.
9. a) Bolm, C.; Ewald, M. *Tetrahedron Lett.* **1990**, *31*, 5011. b) Bolm, C.; Ewald, M.; Felder, M. *Chem. Ber.* **1992**, *125*, 1205. c) Bolm, C.; Felder, M.; Müller, J. *Synlett* **1992**, 439.
10. de Vries, A.H.M.; Jansen, J.F.G.A.; Feringa, B.L. *Tetrahedron* **1994**, *50*, 4479.
11. a) Corma, A.; Iglesias, M.; Martín, V.; Rubio, J.; Sánchez, F. *Tetrahedron: Asymmetry* **1992**, *3*, 845. b) Uemura, M.; Miyake, R.; Nakayama, K.; Hayashi, Y. *Tetrahedron: Asymmetry* **1992**, *3*, 713. c) Asami, M.; Usui, K.; Higuchi, S.; Inoue, S. *Chem. Lett.* **1994**, 297. d) Fujisawa, T.; Itoh, S.; Shimizu, M. *Chem. Lett.* **1994**, 297.
12. Bolm, C. *Tetrahedron: Asymmetry* **1991**, *2*, 701.
13. Tanaka, K.; Ushio, H.; Kawabata, Y.; Suzuki, H. *J. Chem. Soc. Perkin Trans. I* **1991**, 1445.
14. A. Alexakis, J. C. Frutos, P. Mangeney, *Tetrahedron: Asymmetry* **1993**, *4*, 2431.
15. Posner, G.H.; Frye, L.L. *Isr. J. Chem.* **1984**, *24*, 88.
16. a) Ullenius, C.; Christenson, B. *Pure Appl. Chem.* **1988**, *60*, 57. b) Krause, N.; Wagner, R.; Gerold, A. *J. Am. Chem. Soc.* **1994**, *116*, 381.

(Received in UK 19 February 1997; accepted 25 March 1997)