# Asymmetric catalysts

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## 1 Introduction

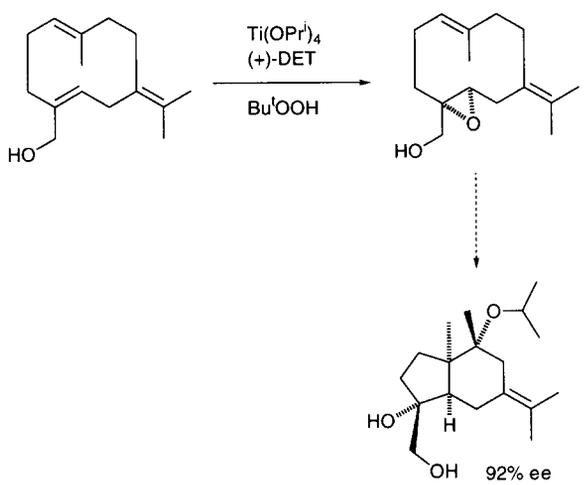
This review covers developments in asymmetric catalysis during the calendar year 1997. As in past years this area has continued to grow at a dramatic rate, in view of which the reviewers have had to be very selective in their coverage of the subject. Once again we have attempted to focus on significant new developments rather than attempting to include comprehensively every example.

## 2 Synthetic organic catalysts

### 2.1 Oxidations

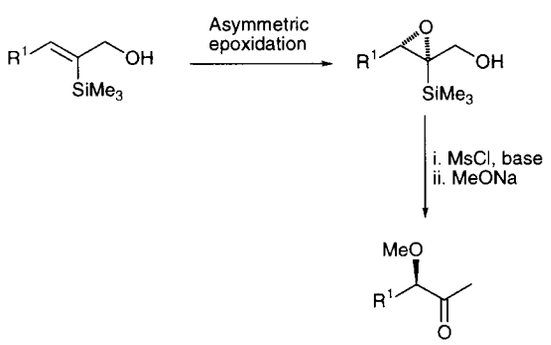
#### 2.1.1 Epoxidation and aziridination

Widespread acceptance of a given asymmetric transformation provides, without doubt, the best possible proof of its value and dependability. In this respect the Sharpless asymmetric epoxidation of allylic alcohols is an outstanding example. Despite its venerability, an astonishing number of total syntheses of complex natural products rely on this transformation in a pivotal step, not all of which can be referenced here.[1] Whilst in one sense the need for an alcohol to be present in the starting material can be seen as a limitation, it can be a beneficial feature, since selective directed epoxidation of only one double bond within a polyene can be achieved.[2] In the selected example (Scheme 1), asymmetric epoxidation of a cyclic triene establishes the correct reactivity, substitution pattern and absolute




**Scheme 1**

stereochemistry for a subsequent transannular ring closure.[3] The asymmetric epoxidation of trialkylsilyl substituted substrates provides some interesting opportunities.[4,5] When the substrate is 3-trimethylsilyl substituted, the products may be substituted with acyl groups whilst maintaining the stereochemical integrity of the epoxide.[4] Conversely 2-trimethylsilyl substituted allylic alcohols give products which may be converted, through ring-opening and Peterson elimination, into α-alkoxy ketones (Scheme 2).[5] Such products may also be prepared through asymmetric epoxidation of the enol (formed *in situ*) from 3-hydroxy ketones.[6]



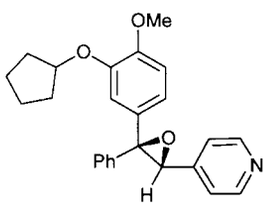

**Scheme 2**

The ability of the Sharpless epoxidation system to be used as a method for the kinetic resolution of a racemate has long been recognised. Matching of the natural directing effect of the substrate to that of the catalyst provides a very powerful method for the synthesis of complex building blocks, such as those found in the azinomycins.[7] When two allylic double bonds are present (relative to the same alcohol) then sequential use of two Sharpless systems can be employed to good effect.[8] In a detailed kinetic study it has been demonstrated that the coupling of kinetic resolution to asymmetric epoxidation in a molecule containing two remote allylic alcohol groups can be employed to give products of very high diastereo- and enantiopurity.[8b] In the

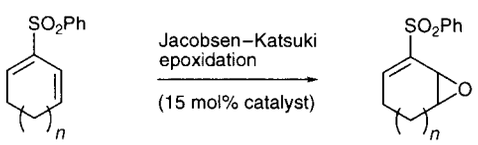
latter case, as is to be expected, high selectivity is achieved at the cost of yield, therefore the method is of highest value when inexpensive starting materials are available.

An effective polymer supported version of the Sharpless allylic epoxidation has been reported.[9] Key to the success of this is the use of the ester groups of tartaric diesters as sites for crosslinking.

Despite numerous detailed and careful mechanistic studies, the mechanism of the Mn–salen catalysed asymmetric epoxidation reaction is still the subject of ongoing investigations.[10] Few can doubt the value of this remarkable method, which in 1997 headlined in the asymmetric synthesis of the well known anticancer molecule CC-1065[11] and phosphodiesterase inhibitor CDP840.[12] The latter example serves to illustrate the vital importance of substrate structure; whilst **1** was formed in 89% ee from the alkene, the isomeric substrate gave a product of only 48% ee. The asymmetric epoxidation of cyclic dienes bearing sulfone groups provides a very useful method for the preparation of some otherwise highly challenging targets (Scheme 3).[13]




**1**, 89% ee




*n* = 1, 72% yields, 99% ee
*n* = 2, 80% yield, 99% ee

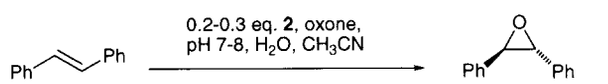
**Scheme 3**

Variations recently reported upon the Katsuki–Jacobsen epoxidation include the combination of the method with a selective product hydrolysis step to optimise the selectivity[14] and the combination of an *achiral* salen catalyst with (−)-sparteine.[15] In this base-resolved system, chromenes were oxidised in up to 73% enantiomeric excess. The importance of this reagent class has been underlined by the studies of Imanishi and Katsuki, who have reported some dramatic solvent effects in the Cr(III)·salen asymmetric epoxidation of chromenes.[15b] Changing from toluene to acetonitrile in one process not only results in an ee increase from 46 to 98%, but the absolute sense of asymmetric induction is actually reversed! Asymmetric chromene oxidation has also been achieved, although in slightly lower ee (up to 40%), through the combination of a trimeric amino alcohol with Mn(II) salts.[16]

As with many other catalytic systems, efforts are ongoing towards the preparation of supported Katsuki–Jacobsen catalysts; examples have been reported this year of the use of siloxy membranes[17] and zeolites[18] in this capacity. Whilst some success has been achieved, one should be careful to ensure that the catalyst, which is known to slowly decompose under normal solution phase conditions, is actually recoverable and reusable. In many ways, increasing the stability in these systems is perhaps a more important objective than high ee.

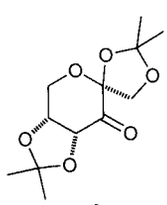
Despite their complexity and lengthy preparation, porphyrins remain the subject of studies by a number of groups.[19] Whilst overshadowed by Mn–salens in recent years, this group of potential catalysts do benefit from very high activity and turnover numbers. With ees now routinely in the '70–80's' it will be interesting to see what developments are forthcoming in the next 5 years or so.

Whilst research in the area has been 'bubbling under' for quite a number of years, it is only recently that chiral dioxiranes have come to the fore as practical reagents for the asymmetric epoxidation of isolated double bonds. The secret appears to be in the careful design of the electronic, as well as steric, structure of the ketone precursor. Whilst a catalytic mechanism is achievable, the major problem has been identified as the accompanying decomposition of dioxirane through a Baeyer–Villiger type process. In the extremely elegant work of Shi and co-workers,[20] the ketone **2** has been demonstrated to be a highly effective controller of asymmetric epoxidation at the 20–30 mol% level (Scheme 4). It should be noted that the control of pH is absolutely critical to the success of this process. This is an extremely versatile reaction, and many substrate examples are described in the comprehensive and detailed publications referenced.




75% yield, 97% ee

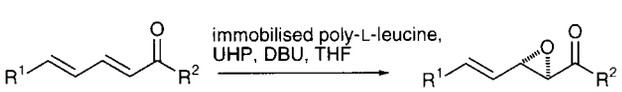
**Scheme 4**




**2**

Although **2** is perhaps the best catalyst reported to date, a number of other systems, notably those of a $C_2$ symmetric structure, have been employed to good effect in the asymmetric epoxidation of simple alkenes.[21]

For reasons which are still not fully understood, polymeric α-amino acids remain remarkable catalysts for the asymmetric epoxidation of electron poor double bonds, particularly those closely related to the chalcone structure. For a restricted range of substrates, the process has been refined by Roberts *et al.* into a very reliable process which gives products of high ee (Scheme 5).[22]




$R^1$ = Ph, $CO_2Me$, $CO_2Bu^t$, Cl
$R^2$ = Ph, Np

$R^1$ = Ph, $R^2$ = Np, 96% ee

**Scheme 5**

This method for enone epoxidation now faces formidable competition however. In reports by no less than three groups this year[23–25] new systems consisting of an organometallic complex of either a diol or amino alcohol have been reported to give extremely impressive yields and enantioselectivities for this type of process (Scheme 6). Whilst the Jackson system appears to be the most readily accessible and inexpensive, the Enders system benefits from the highest enantioselectivities and versatility.


Jackson[23] system: 0.1 eq. $MgBu^n_2$, 0.11 eq. (+)-DET, $Bu^tOOH$, up to 94% ee
Enders[24] system: $ZnEt_2$, (1*R*,2*R*)-*N*-methylpseudoephedrine, $O_2$, up to 98% ee
Shibasaki[25] system: 5 mol% Ln•BINOL catalyst, ROOH, 91% ee

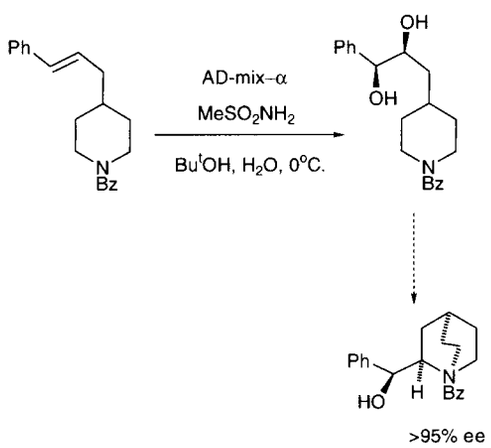
**Scheme 6**

Finally in this section the reader's attention is drawn to the report of the use of a chiral arenesulfonimidoylimidazole as a catalyst for the asymmetric epoxidation of allylic alcohols in ees of up to 42%.[26]

### 2.1.2 Dihydroxylations

The Sharpless dihydroxylation is now firmly established as a staple of the synthetic chemists' asymmetric armoury. Despite all the applications which have been reported, the mechanism still remains controversial. However it would appear that evidence in support of the traditional [3+2] mechanism seems to be mounting, although the electronic nature of the substrate is recognised to be important to the exact mechanism in any given case.[27]

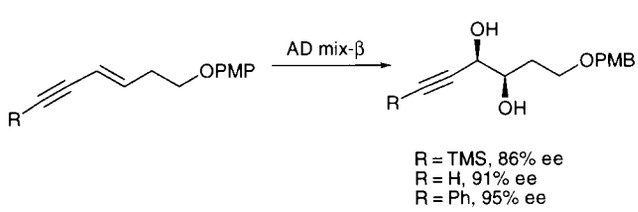
The sheer range of asymmetric dihydroxylation applications is expanding at breathtaking speed. In the simplest examples, the method provides a very concise access to enantiopure targets such as alkaloids[28] and heterocyclic natural products such as flavanols.[29] In the example illustrated in Scheme 7, an asymmetric dihydroxylation serves to set up all the stereochemical information needed for the synthesis of chiral dihydroxypiperidine derivatives.[28a] In fact using this method it is possible to prepare individually all four possible product stereoisomers. Asymmetric dihydroxylation works well in the presence of an azide group, providing a potential access to alkaloids.[28b]



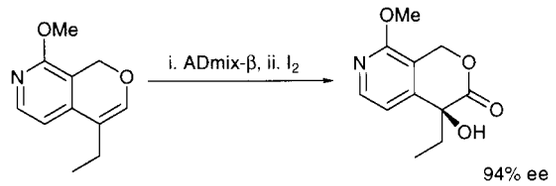

**Scheme 7**

Asymmetric dihydroxylation of trichloro- or trifluoromethyl substituted alkenes gives extremely valuable products in moderate to good ees (63–86%), which are somewhat dependent on the exact structure of the oxidising agent.[30] Enantiopure 2-arylpropionic acids have been prepared through the rearrangement of the diol formed from 2-arylpropene precursors.[31]

One of the most outstanding features of the Sharpless dihydroxylation reaction is its remarkable double-bond selectivity. This feature manifests itself usefully in several respects. In the first featured example, the preference for the reaction of a double bond in the presence of a triple bond, the latter of which is untouched in the process, is highlighted.[32] The example shown in Scheme 8 also serves to illustrate the dramatic effect which changes in the substrate can have on selectivity.[32a] The dihydroxylation reaction is remarkably tolerant of changes in the electronic nature of substrates. Unsaturated esters, for example, have been demonstrated to be of value in the synthesis of monomers for the synthesis of dendrimers through asymmetric dihydroxylation,[33] whilst electron rich enol ethers have proved to be useful precursors of α-hydroxy lactones (Scheme 9).[34]

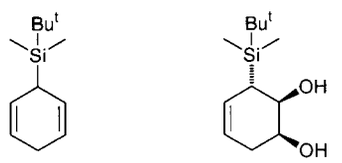



**Scheme 8**




**Scheme 9**

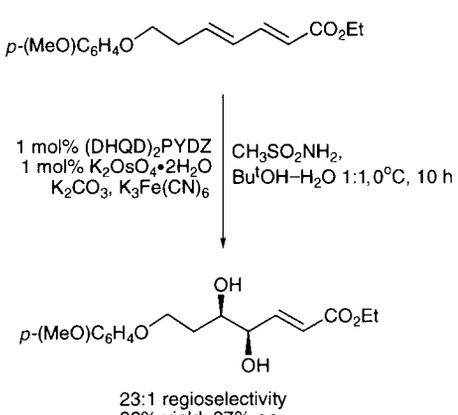
Given a choice of double bonds within a symmetrical substrate, the asymmetric dihydroxylation can in certain circumstances generate an additional chiral centre to those arising directly from the reaction.[35] A good example of this is the conversion of diene **3** into the diol **4** in greater than 98% de and 71% ee.[35a]



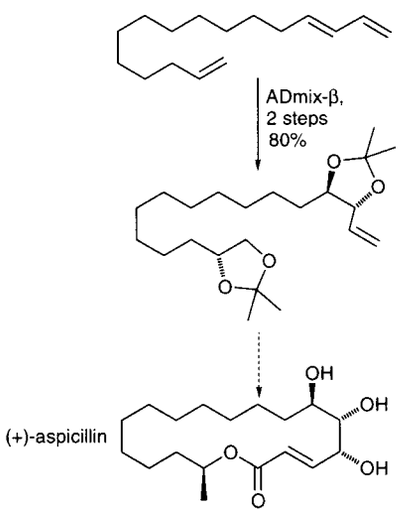

**3** **4** >98% de, 71% ee

One particular class of transformation which has received a great deal of attention is the dihydroxylation of ester-conjugated dienes, a process which appears to occur exclusively, and usefully, on the remote double bond.[36] This particular process has proved extremely valuable in the asymmetric synthesis of carbohydrate molecules. In the example illustrated in Scheme 10,[36a] the initial product is subjected, after protection, to a second, either matched or mismatched, dihydroxylation to complete the introduction of four stereogenic centres in a fully controlled manner. This preference for favourable dihydroxylation of the more electron-rich alkene in a given substrate appears to be quite general and has also been used to good effect in synthetic applications.[37] In situations where more than one dihydroxylation is carried out,[38] careful control of conditions can open the door to a very efficient process, as demonstrated by a recent synthesis of (+)-aspicillin (Scheme 11).[38a] The same synthetic target has been prepared from a substrate in which a furan ring is tolerated during the key asymmetric dihydroxylation.[39] Imidazoles are also stable to dihydroxylation processes at adjacent positions.[40]

As was discussed in some detail in the last review, the modification of the chiral ligands for asymmetric dihydroxylation through the attachment of an extended ethylene glycol chain




**Scheme 10**



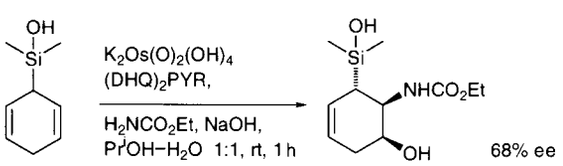

**Scheme 11**

delivers a reagent which works as well as the parent in solution yet may be conveniently removed from the reaction mixture through precipitation in ether.[41] Further examples of this process, which combines the advantages of a soluble reagent with a supported system, have been reported this year. More conventionally supported ligands, *i.e.* attached to crosslinked polystyrene beads, have also been developed,[42] but still suffer from the drawback of a competitive uncatalysed reaction pathway. Attachment of the catalysts to a silica support gives rather more effective supported reagents which have proven to be recoverable and reusable without significant loss of efficiency and selectivity.[43] In a sequence that turns the 'supported-reagent' concept on its head, Janda and Han have reported the asymmetric dihydroxylations of a polymer-supported substrate using a solution phase catalyst.[44] Tentagel proved rather better as the support than Merrifield resin in this application, which delivered the same advantages in terms of experimental simplicity and practicality.

Finally in this section, one should not overlook the fact that whilst the Sharpless method is usually the method of choice for asymmetric dihydroxylations, a number of other ligands including $C_2$ symmetric diamines, have been successfully applied to this process.[45]

### 2.1.3 Sulfoxidations, allylic oxidations and other oxidations

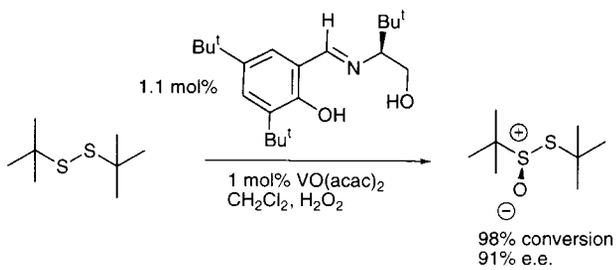
Moving to this section from a discussion of dihydroxylation leads conveniently into a discussion of the closely related aminohydroxylation process, also pioneered by Sharpless.[46,47] Whilst one group has reported an attractive asymmetric aminohydroxylation/desymmetrisation process (Scheme 12),[46] optimisation of the system has delivered a process capable of generating products in up to 99% ee in certain cases![47]




**Scheme 12**

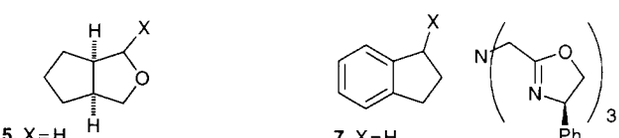
Asymmetric sulfoxidation may be catalysed by a remarkable variety of different reagents. Simple $C_2$-symmetric diols in conjunction with titanium(IV) are the original materials for this process and probably remain the most widely used.[48,49] In one example enantiomeric excesses of up to 84% have been achieved using chiral BINOLS as the diols.[49] An interesting observation in this case was the complete reversal in enantioselectivity upon introduction of nitro groups to the positions adjacent to each hydroxy on the BINOL ligand. Phosphorus derivatives are much less popular in sulfoxidation catalysis, presumably because they are prone to oxidation, although there has been one report this year of a BINOL-derived phosphite capable of generating modest ees in this application.[50]

Mono-oxidation of symmetric disulfides provides a useful variation on this theme, as well as access to some useful intermediates (Scheme 13).[51] The other extension of this process involves the synthesis of chiral sulfimides from sulfides using a combination of a bisoxazoline and copper(I) with a suitable nitrene precursor, such as PhINTs. This process was described in some detail in the last report and has now been developed further; in the best cases products of up to 80% ee may be prepared.[52]

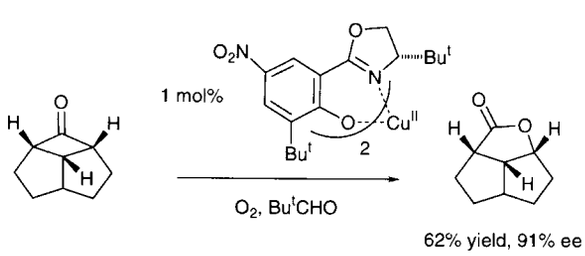



**Scheme 13**

As mentioned above, chiral bisoxazolines are very versatile and effective ligands for a range of asymmetric reactions, notably oxidation processes. For example, the conversion of a cyclic diene to the allylic acetate is one process where recent years have seen a high level of development.[53] Direct introduction of a hydroxy group stereoselectively adjacent to the oxygen atom of a cyclic *meso* or prochiral ether such as **5** may be achieved using a Mn salen complex and PhIO.[54] In the example cited, the product **6** was formed in up to 82% ee. A closely related process, the conversion of **7** into **8**, has been achieved successfully, but with rather lower enantioselectivity and conversion (up to 28% ee).[55] In the latter process the ligand of choice, which is used in conjunction with a Cu(II) salt, is the $C_3$ symmetric chiral tris(oxazoline)† **9**. Whilst selectivities and conversions are at present low, the potential as a reaction of the future is clear.



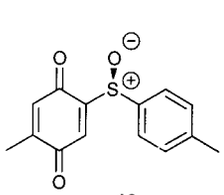

Asymmetric catalysis of the Baeyer–Villiger reaction has been a popular subject in recent years. Of the methods described this year, Bolm's system is an excellent one (Scheme 14).[56] The system is also a good one for asymmetric sulfoxidation.[56b]



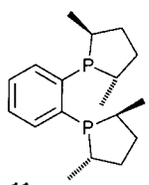

**Scheme 14**

† The IUPAC preferred name for oxazoline is 4,5-dihydrooxazole.

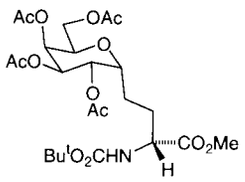
Despite their obvious potential, there are few examples of chiral sulfoxide ligands which have been employed in asymmetric catalysis. One notable exception is ligand **10**, which



**10**



**11**



**12**

has proved effective in directing the asymmetric conversion of cyclohexa-1,3-dienes into 1,4-diacetates in a palladium catalysed process; products of up to 45% ee were formed.[57]

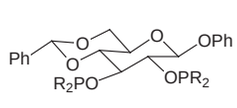
Finally, in this section, by running what is more commonly seen as a reduction reaction in reverse (see Section 2.2.3), it is possible to achieve a very effective kinetic resolution of racemic alcohols.[58] In the example cited only 0.2 mol% of a ruthenium(II) complex of a homochiral monotosylated diamine was required for excellent results. Using racemic 1-phenylethanol as substrate, and acetone as solvent and hydrogen acceptor, the remaining alcohol was recovered in 51% yield and 94% ee.

## 2.2 Hydrogenation

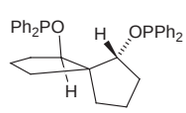
### 2.2.1 Hydrogenation

Asymmetric hydrogenation continues to be a major research area. Whilst this review is concerned in the main with *synthetic* applications of asymmetric catalysts, certain key structures, such as that of the partially hydrogenated reduction intermediate of a ruthenium catalyst, are most noteworthy.[59]

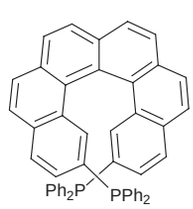
α-Acylaminoacrylates, popular precursors of α-amino acids, continue to provide useful test materials for new and established asymmetric hydrogenation catalysts. Rhodium(I) catalysts of the versatile DuPhos ligand **11** have been employed in a reduction of carbohydrate-functionalised acrylates, providing a direct entry to functionalised amino acids **12** with des of >95% for both galactose and mannose derivatives.[60] In the case of **12** the selectivity comes predominantly from the catalyst, which overrides the inherent control provided by the relatively distant carbohydrate. This catalyst-domination also appears to operate in the reduction of bis(acylaminoacrylates), where the distance between the two units is reasonably large.[61]



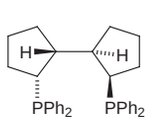
**13**



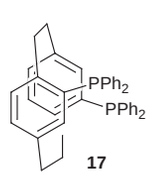
**14**



**15**



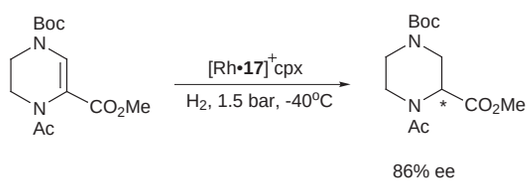
**16**



**17**

Ligands containing diarylphosphinates, such as those derived from carbohydrates **13**, benefit from ease of preparation as well as the ability for the user to fine-tune the properties of the ligands towards a particular application through variation of the electronic charge density and steric properties of the aryl rings on the phosphorus atoms.[62] In many cases even apparently small changes can make a large difference to the observed selectivity. In addition, of course, the ability of a glucopyranoside to mimic a $C_2$ symmetric system also provides certain advantages; where 2,3-diphosphine systems give *S* configuration products, the corresponding 3,4-substituted diphosphines give *R* configuration products, and *vice-versa*.

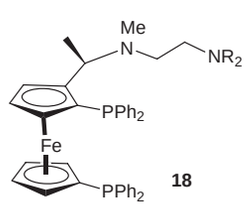
Actual $C_2$ symmetry is a clear design feature of the spiro diphenylphosphite ligand **14**,[63] which is capable of asymmetric inductions in acylaminoacrylate reductions of up to 99% in certain cases, and routinely 95–97% ee in conjunction with rhodium(I). $C_2$ Symmetry is also a key feature of the new *phosphine* ligands **15**–**17**, all of which have been reported this year.[64–67] The extraordinary helicene material **15** acts, in a rhodium(I) complex, as an effective catalyst for acrylic acid reductions in up to 39% ee.[64] Although selectivities are modest in this case, no doubt we shall see more applications of this novel ligand in the future. Diphosphine **16** gives products of acylaminoacrylate reduction in up to 97% ee,[65] and **17** achieves the same in up to about 98% ee (at this level the intention is to note, rather than compare).[66] Rather more interestingly, however, is the application of a rhodium complex of **17** to the hydrogenation of a cyclic substrate which is known to be a sluggish substrate (Scheme 15).[66] In the example shown the reaction using 1.5 bar of dihydrogen proceeds at temperatures as low as −40 °C!



**Scheme 15**

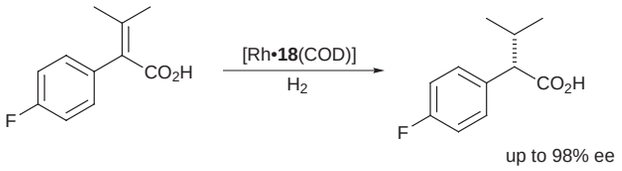
Asymmetric hydrogenation may be achieved using a zeolite-anchored rhodium complex of a chiral amide derived from prolinamide.[68] In another interesting development an ionic liquid has been demonstrated to be a satisfactory medium for asymmetric reduction of 2-arylacrylic acids in up to 80% ee using a ruthenium(II)–BINAP system.[69] Ionic liquids are currently the subject of a resurgence of research interest and benefit from very low vapour pressure, reusability and ease of separation from reagents and products.

In the last example, 2-arylpropionic acids were the targets. These are important targets because of their use as antiinflammatory compounds, and many methods have been developed for the reduction reaction which affords them. Introduction of further substituents in the substrates makes the reaction more challenging. However even highly functionalised substrates may be usefully employed in conjunction with the rhodium complex of the ferrocene derived ligand **18** (Scheme 16).[70]



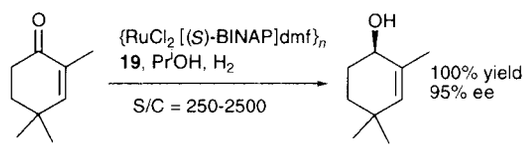
**18**

Moving on to the asymmetric reduction of ketones; a new method for the optimisation of reduction by the Ru(II)–BINAP system, key to which is the use of small amounts of a strong acid, has been reported.[71] A rather more dramatic effect however, is achieved through the addition of an equivalent of chiral diamine **19** (relative to catalyst) to the reduction mixture.[72] Under these modified conditions, simple ketones,

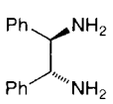



**Scheme 16**

notably enones, may be reduced in quantitative yield and very high enantioselectivity (Scheme 17) at very low catalyst loadings.

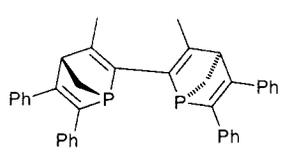



**Scheme 17**

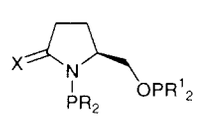



**19**

Whilst most ligands for asymmetric hydrogenation are well established, the occasional interesting newcomer is always welcome. In this respect the $C_2$ symmetric diphosphine **20** represents an interesting variation; a ruthenium(II) complex of this ligand reduces aryl/alkyl ketones in up to 95% ee and also appears to be applicable to unfunctionalised ketones[73] (*i.e.* those lacking a nearby coordinating group to direct the reduction).




**20**



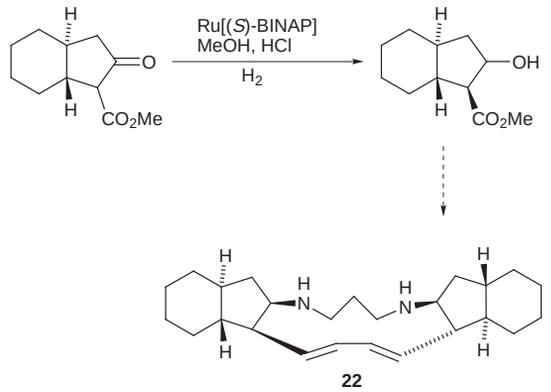

**21** X = O, $H_2$
R, R$^1$ = Ph, Cy

Mixed diarylphosphinite/aminophosphine complexes such as **21** have enjoyed an extended period of investigations over recent years.[74] An attractive feature of these complexes is that the catalyst structure may be tuned towards each particular application through variation of the groups on *each* phosphorus atom, and the use of either an amine or amide scaffold. Excellent results have notably been achieved in the use of rhodium and ruthenium complexes of such ligands in reductions of α-diketones (up to 63% ee), α-keto esters (pantolactone up to 98% ee) and amino-substituted ketones (1-, 2- and 3-substituted in up to 93, 96 and 97% ee respectively).

The asymmeric reduction of β-keto esters has been well studied, and the contemporary emphasis is on applications development rather than new ligands, since nothing really competes effectively with Ru–BINAP[75] or its close analogues.[76] This system is extremely versatile and dependable, with a directing effect that usefully overrides any internal substrate stereocontrol.[75a] Perhaps most notable about the method is the potential for *dynamic* kinetic resolution of α-substituted substrates, as demonstrated in a concise synthesis of (−)-halichonadiamine **22** (Scheme 18).[77]

Closely related to the above, reduction of α-ketophosphates[78] and β-ketosulfides[78,79] has also been employed to good effect in highly selective asymmetric hydrogenations, to give useful chiral building block products.

So far our discussions have been limited to homogeneous catalysis. With the exception of supported reagents, heterogeneous processes have not been addressed. In the arena of

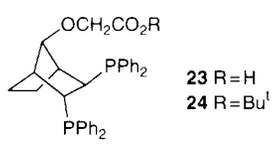



**22**

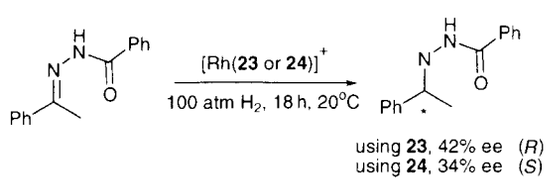
**Scheme 18**

ketone reduction there are two key mainstay processes; α-ketoester reduction by Pt/alumina modified by cinchona alkaloids[80] and β-keto ester reduction by tartaric acid–NaBr modified Raney nickel.[81] Both of these are very well established now, but the great potential for use of very small quantities of catalysts continues to fuel ongoing research. Given the intense level of work in each area, one wonders at the potential of heterogeneous systems which remain yet to be discovered. No doubt it is very considerable indeed. Evidence of this is the reduction of prochiral acrylates using the cinchonidine-modified palladium system, a process which gives products in excellent turnovers, but rather modest ees at present.[82]

Asymmetric reduction of C=N bonds serves to round off this section. A very attractive imine reduction may be achieved using the iridium(I) complex of chiral phosphino-oxazoles, although some work is still needed to improve the ees (57–76% in a typical range) to the level of other processes.[83] Finally, the reduction of hydrazones with two complexes of norphos-related ligands **23** and **24** reveals an interesting long range effect (Scheme 19).[84]



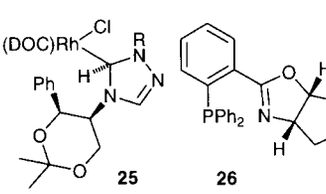

**23** R = H
**24** R = Bu$^t$




**Scheme 19**

### 2.2.2 Hydrosilylation

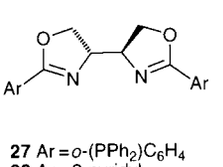
Although a long established reaction and closely related to hydrogenation, hydrosilylation of ketones has proven to be a rather more challenging system for the achievement of consistently high enantioinductions. Enantiomerically pure BINOL works very well, giving products of up to 93% ee when trialkoxysilanes are used as the reducing agents.[85] Ruthenium complexes of combined pyridine–diphosphines work reasonably well,[86] and a rather unorthodox rhodium complex **25** has been reported for this application by Enders *et al.*[87] In the latter case hydrosilylation products of up to 44% ee were obtained.




**25**



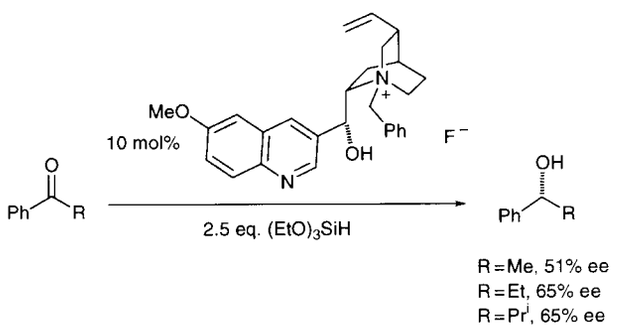

**26**




**27** Ar = *o*-(PPh$_2$)C$_6$H$_4$
**28** Ar = 2-pyridyl

Of the other complexes applied to this reaction, rhodium(I) complexes of chiral oxazoles dominate.[88–90] Chiral phosphinooxazoles such as **26** give reduction products in up to 94% ee[88] (aryl/alkyl ketones are the best substrates) whilst dimers of similar compounds, *i.e.* **27**, have been reported to achieve hydrosilylation of acetophenone in up to 97% ee.[89] The closely related pyridine substituted ligand **28** also works well, but products of somewhat lower ee are formed.[90]

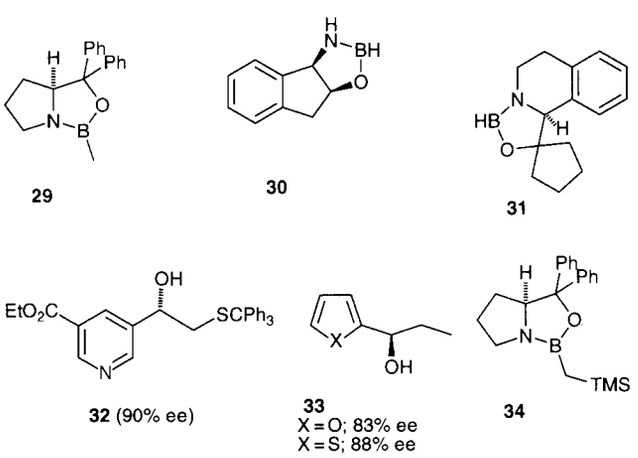
However, perhaps the most interesting variation to appear on the theme of hydrosilylation this year has been a non-organometallic method.[91] Specifically the use of salt derivatives of 10 mol% cinchonidine alkaloids with triethoxysilane (or the polymeric analogue) gives products of up to 65% ee after acid workup (Scheme 20). What this method marginally lacks in selectivity compared to other methods it certainly compensates for in terms of originality and (particularly in the polymeric silane variant) practical utility.




**Scheme 20**

### 2.2.3 Other reductions

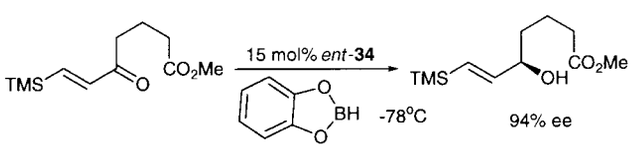
The sheer scope and versatility of oxazaborolidines such as the prolinol derived **29** is quite breathtaking, with numerous new applications and modifications being reported every year. The use of the diethylphenylamine complex of borane provides a convenient alternative to the more popular but reactive borane–THF complex.[92] Also by way of modification, it has been demonstrated that the problems of water-sensitivity of **29** can be circumvented by using a convenient *in situ* method for the preparation of a close analogue which is achieved by combination of the parent amino alcohol with tri(methoxy)borane.[93]




A modified solid supported version of **29**, mounted on a silica backbone, has been reported to be capable of the generation of up to 98% ee in prototype reductions.[94] Following a surge of development of new catalysts related to **29** in recent years, activity in this area has slowed somewhat with the emphasis turning again to applications development. However noteworthy 'alternative' oxazaborolidines which have been studied this year include the *cis*-aminoindanol derived **30**,[95] cyclopentyl derived **31**[96] and reagents which contain additional sulfur containing groups.[97]

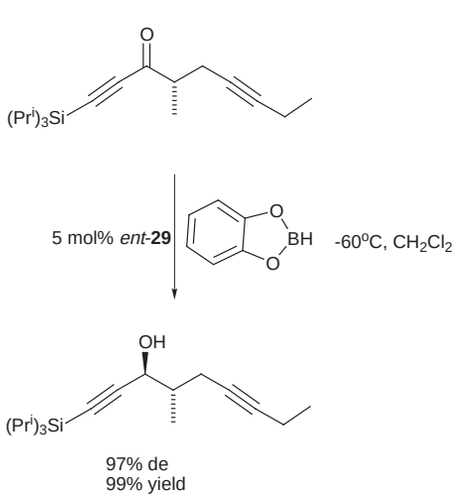
Compound **30** has proven to be a first rate catalyst for the reduction of highly functionalised α-bromoacetophenone derivatives, important precursors of epoxides and thereafter pharmaceutical products.[95] Diphenylprolinol derived **29** has already been employed in similar applications, and has further been reported to be applicable to a series of reductions of useful heterocyclic substrates.[98,99] In one of these reports, for example, the reduction of a 2-pyridyl substituted ketone gives the pharmaceutical precursor **32** in 90% ee without undue interference from the pyridyl ring.[98] In another example, furan and thiophene substituted alcohols **33** were prepared by direct reduction of the precursor ketones in the ees shown.[99]

Oxazaborolidine catalysts have been employed for the asymmetric reduction of ketones adjacent to oximes (up to 98% ee).[100] The oxime is not reduced in this application. A particular strength of oxazaborolidines is their ability to reduce enones and related materials without concommitant double bond reduction.[101–105] The trimethylsilyl substituted catalyst **34**, at the 15 mol% level, directs the reduction shown in Scheme 21 in 94% ee.[103] The structure of the substrate is important here; without the silyl group on the enone the reduction proceeds in much lower yield and only 74% ee. Reduction of symmetrical diketones using similar methods is reported to be a versatile reaction proceeding in up to 99% ee using a similar system.[104] Whilst enone reductions generally work in good selectivity with typically 10 mol% catalyst, it is in some cases necessary to add stoichiometric quantities for best results.[102]

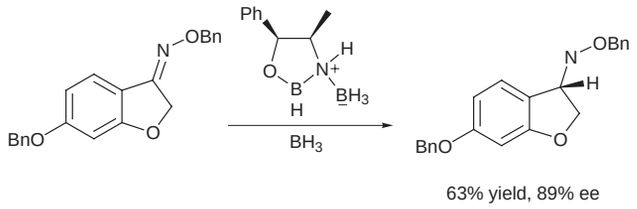



**Scheme 21**

Propargylic ketone (propynyl ketone) reduction also works well.[106,107] In the example given in Scheme 22 the directing effect of the catalyst is dominant over that of the stereogenic centre adjacent to the ketone; reduction with the other enantiomer of the catalyst gives the opposite product diastereoisomer in 96% de and 99% yield.[106] Although reported slightly earlier than ketone reduction, the use of oxazaborolidines in imine reduction is slightly less well developed in terms of enantioselectivity.[108,109] The oxime ether reduction (Scheme 23) is a useful one that has been applied to 5-lipoxygenase inhibitor synthesis.[108] Although this worked well in terms of selectivity, problems of work up prevented its transfer to the large scale.

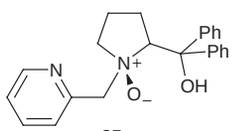



**Scheme 22**



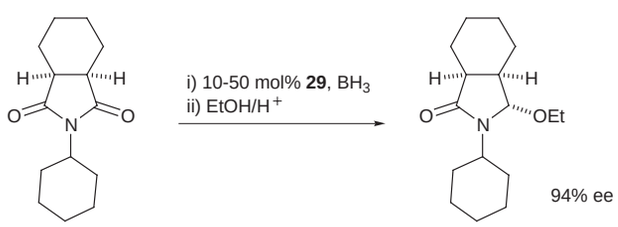

**Scheme 23**

Chiral phosphinamides have been employed to catalyse the reduction of ketones by borane.[110] These can be improved in terms of selectivity through incorporation of an asymmetric centre at the phosphorus atom, however selectivities still lag somewhat behind those of other reduction catalysts. An interesting reagent reported this year is the *N*-oxide **35**, which, at the 5 mol% level, directs reduction of α-chloroacetophenone by borane in up to 96% ee.[111] An interesting feature of this reagent is that the best results are obtained in THF at reflux. A titanium complex of a chiral diol has been successfully used in the asymmetric catalysis of ketone reduction by catecholborane in up to 97% ee.[112]




**35**

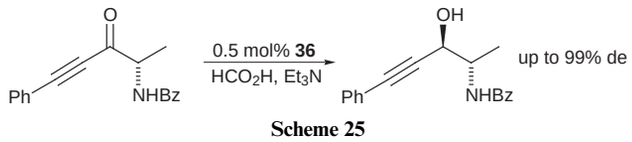
Reduction of racemic binaphthyl lactones using chiral oxazaborolidine catalysis results, in optimised cases, in reduction of one enantiomer to the diol in high selectivity, leaving the other unreduced.[113] Reduction of cyclic *meso*-imides followed by aminal formation gives the amide product in up to 94% ee (Scheme 24).[114]



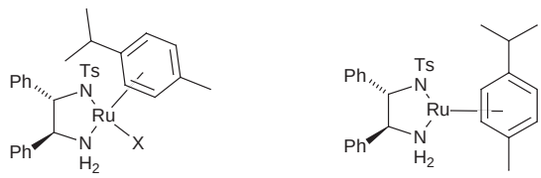

**Scheme 24**

Arguably the most significant development in carbonyl reduction over recent years, however, is the use of asymmetric transfer hydrogenation methodology. Without doubt the leading figure in the field at present is Noyori, who has recently published X-ray crystal structures of three key intermediate complexes in the remarkable ruthenium(II)–monotosylated diamine reduction system.[115] The precursor complex **36** initially eliminates HCl and the reduced *active* complex **37** is hydrogenated by formic acid or propan-2-ol to give **38** which participates in the catalytic cycle. With these results it has been possible to formulate a full mechanism for this highly practical and versatile reduction process. A new application of the above system is in the asymmetric reduction of propargylic ketones using remarkably low levels of catalyst (Scheme 25).[116] As was the case for the oxazaborolidine, it is the enantiodirecting effect of the catalyst which is dominant; use of the other enantiomer gives the other diastereoisomer of product in equally high diastereoselectivity.

A number of other ligands have been reported for the transfer hydrogenation process, usually (and generally providing the best results) with ruthenium(II)[117–124] but often iridium(I)[119,125,126] or rhodium(I)[117,118] and in one case cobalt(II).[126] Some of the key ligands are featured in Fig. 1. Although there is clearly something very special about *monotosylate* diamines,




**Scheme 25**




**36** X = Cl
**38** X = H

**37**

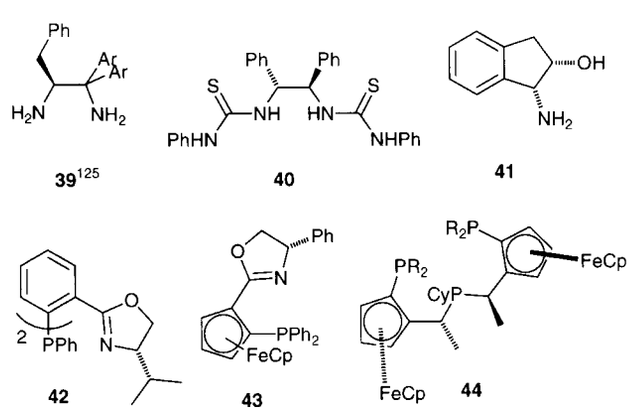
certain diamines such as **39** are reported to work well.[125,126] In an example featuring an iridium(I) complex of **39**, reduction products in the range of 76–83% ee were consistently formed.[125] Diamines functionalised as thioimidates, for example **40**, represent interesting variants which work well with ruthenium or rhodium, giving products with ees in excess of 90% in some cases. Amino alcohols have been used before in this application, however ligand **41**, which benefits from a high degree of stereochemical rigidity, gives particularly excellent results in combination with ruthenium(II).[120] It is noteworthy that the less rigid but analogous phenylalaninol acts as a catalyst, but gives products of much lower ee.

Ligands containing a phosphine and oxazoline in chelating positions such as **42**[121] and **43**[123] have given excellent results when applied to transfer hydrogenation. In the case of **43**, an unexpected observation was that triphenylphosphine was required as a co-additive for best results. This was actually released from the ruthenium complex which acted as a precursor to the active catalyst, but when deliberately removed from solution a dramatic decrease in enantioselectivity was observed. Triphosphines, for example **44** ("Pigiphos"), have also been applied to this reaction.[124]

A polymer bound version of the ligand precursor to **36** has been obtained through emulsion polymerisation of an alkene-functionalised precursor.[119] This material works well and is reusable, either with ruthenium or iridium, although it is not quite as selective as the homogeneous variant. Although propan-2-ol or formic acid are most commonly employed as hydrogen source, at least one paper has described the use of diphenylsilane for this purpose.[127]

Reduction of C=N bonds using transfer hydrogenation is relatively underdeveloped, however the formation of sultams by this method is a very attractive application (Scheme 26).[128]

In the last review a cobalt(II) complex (general structure **45**) of a $C_2$-symmetric diamine derivative was described as an excellent catalyst for ketone reduction using a modified sodium




**39**[125] **40** **41**

**42** **43** **44**

**Fig. 1** Ligands used in asymmetric transfer hydrogenation reactions.

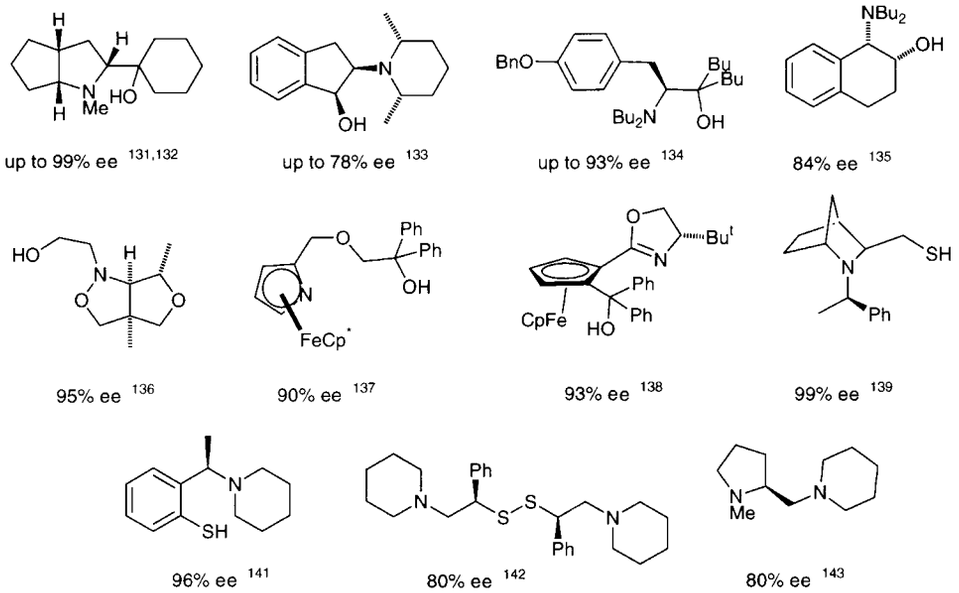
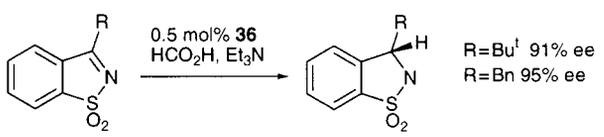
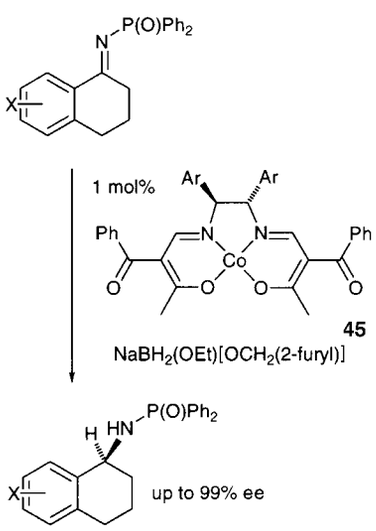



**Fig. 2** Ligands employed for the catalysis of the reaction of $Et_2Zn$ with benzaldehyde.




**Scheme 26**

borohydride system. The compound has been used in a remarkable imine reduction process, key to which is the use of a phosphinamide protecting group (Scheme 27).[129]




**Scheme 27**

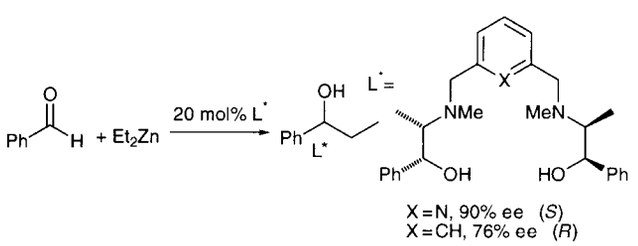
Finally, in this section, some of the latest results on catalytic, reductive ring opening of bicyclic dihydrofuran derivatives are featured.[130] Using the combination of catalytic Ni(cycloocta-15-diene)$_2$ with BINAP and DIBAL-H,[130a] tetrahydronaphthalenes were formed with enantioselectivities of up to 98% ee!

### 2.3 Carbon–carbon bond forming reactions

#### 2.3.1 Additions of carbon nucleophiles to C=O and C=N bonds

Interest in the addition of dialkylzinc reagents to aldehydes has continued unabated. As in previous years the focus has principally been on amino alcohol and related bidentate ligand accelerated addition of diethylzinc to benzaldehyde.[131–152] Fig. 2 illustrates some of the new ligands employed and compares their performance in terms of the degree of enantioselectivity achieved.

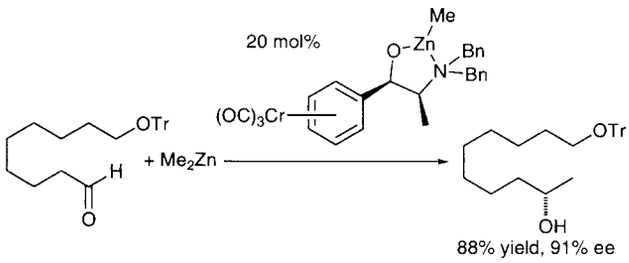
A dramatic example of how a minor change in the coordination properties of a ligand can affect the sense of chiral induction in the diethylzinc addition to benzaldehyde has been demonstrated using a pair of $C_2$ symmetric ligands derived from ephedrine[144] (Scheme 28). Simply changing the aromatic linker unit from a pyridine to a benzene caused a change in the enantioselectivity from 90% (*S*) to 76% (*R*)!




**Scheme 28**

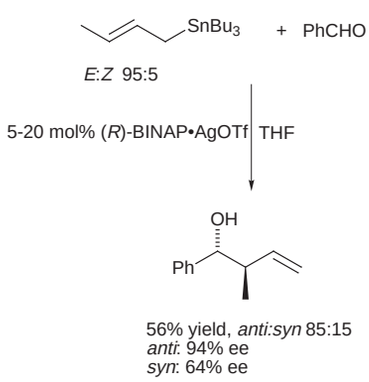
Work has continued on the Ti(IV) catalysed addition of dialkylzincs to aldehydes although to a somewhat lesser extent than in previous years.[153–158] However, the scope of the reaction has been extended to include long chain aliphatic aldehydes resulting in the formation of *sec*-alcohols with moderate to good enantioselectivities.[157] The addition of dialkylzincs to aldehydes has also been extended to more complex substrates containing a range of functional groups. Addition of dimethylzinc to a functionalised aliphatic aldehyde using an ephedrine derived chromium tricarbonyl ligand proceeded with excellent enantioselectivity to provide a key intermediate in a macrolide synthesis (Scheme 29).[159] Knochel and co-workers have also used a range of functionalised dialkylzinc reagents in additions to aromatic and allylic aldehydes with good success.[160–162] An example of the closely related triethylaluminium addition to benzaldehyde using a partially hydrogenated BINOL–titanium complex has been reported, giving a product of 96% ee when 20 mol% of catalyst was employed.[163] The addition of dialkylzincs has not been restricted to C=O species alone. For example, Ukaji and co-workers have reported a highly successful addition of diethylzinc to a nitrone catalysed by a dicyclopentyl tartrate complex.[164]

Another reaction which has seen some progress over the past



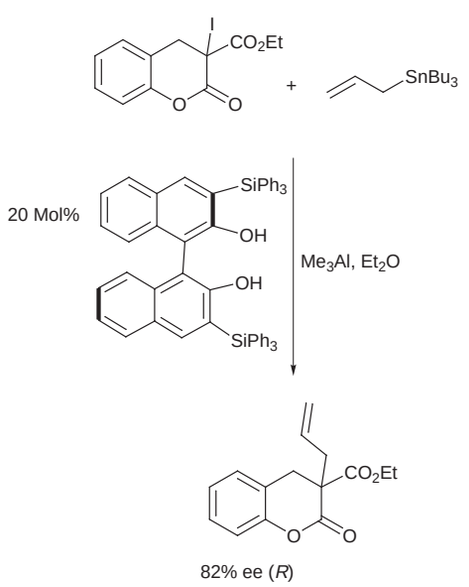

**Scheme 29**

year is the addition of allylstannanes to aldehydes.[165–169] Yu and co-workers reported a BINOL–Ti catalysed reaction in which trimethyl borate was employed as an "accelerator" giving improved yields and enantioselectivities.[165] The procedure also works well for the addition of allenylstannanes giving propargyl alcohols in up to 97% ee. Danishefsky and co-workers have successfully incorporated an asymmetric addition of allylstannane to an aldehyde in their synthesis of epothilone, demonstrating the increasing versatility of catalytic asymmetric reactions.[166] The addition of methallyl and crotylstannanes to aldehydes catalysed by an Ag(I)–BINAP complex led to the formation of allylic alcohols in high ee, however the reaction gave rather puzzling diastereoselectivity with the same *syn*:*anti* ratio of products being formed regardless of the initial *E*:*Z* ratio of the stannane employed (Scheme 30).[169]



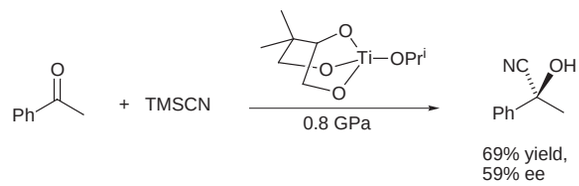

**Scheme 30**

Allylstannanes have also been employed in an interesting asymmetric radical reaction involving the use of an Al(III)–BINOL complex to generate a quaternary stereogenic centre with up to 82% ee (Scheme 31).[170]



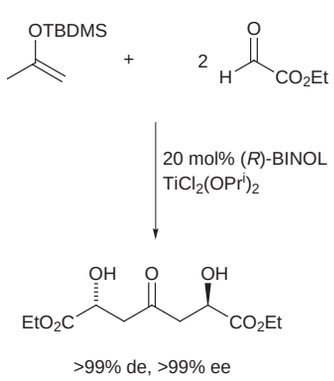

**Scheme 31**

1997 has seen increasing interest in the addition of TMSCN to carbonyl groups.[171–176] Most examples focused on addition to aldehydes (principally benzaldehyde) however one example demonstrated that the reaction is also applicable to ketones giving a yield of 69 and 59% ee for the expected product when the reaction was carried out under high pressure conditions (Scheme 32).[176]




**Scheme 32**

A wide variety of catalytic asymmetric aldol reactions have been reported.[177–189] Evans and co-workers have extended their methodology based on bisoxazoline ligands to include α-keto esters[180] and glyoxalate and pyruvate esters[181] as substrates. High levels of enantio- and diastereoselectivity were observed in all cases. Shibasaki reported an air and moisture stable Pd(II)–BINAP complex which gave enantioselectivities of up to 87% in the addition of silyl enol ethers to aldehydes.[182] Denmark and co-workers have continued their study of the phosphoramide catalysed addition of silyl enol ethers to aldehydes noting that the nature of the silyl group can have a dramatic effect on the enantio- and diastereoselectivity of the reaction, with $SiMe_3$ tending to favour *syn* aldol products and $SiCl_3$ favouring *anti* aldol products in some cases.[183,184] A remarkable two directional, tandem Mukaiyama aldol reaction was reported by Mikami and co-workers.[185] The high level of selectivity resulted from a chiral amplification process increasing the ee from 98.5% after the mono-aldol addition to greater than 99% after the bis-aldol reaction (Scheme 33). Yamamoto has reported the first enantioselective aldol reaction of a tin enolate catalysed by an Ag(I)–BINAP complex.[186] The diastereoselectivity of the reaction was shown to be very dependent on the geometry of the tin enolate, with *Z* enolates giving almost exclusively the *syn* product whilst *E* enolates favoured the *anti* product. The aldol reaction between ketones and aldehydes catalysed by an amphoteric lithium–lanthanide–BINOL complex (LLB) which acts both as a base and a Lewis acid has been demonstrated to give enantioselectivities of up to 94%.[187] LLB catalysts have also been successfully employed in an asymmetric nitroaldol reaction as part of the synthesis of (*R*)-arbutamine.[188] Shibasaki has also extended the use of LLB catalysts to tandem nitroaldol reactions providing bicyclic adducts with up to 65% ee (Scheme 34).[189]

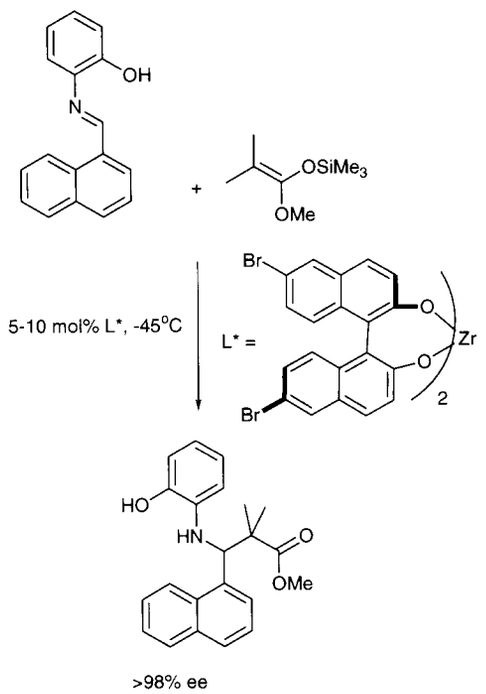



**Scheme 33**

The first example of a catalytic asymmetric Mannich reaction was reported by Kobayashi and co-workers.[190] The reaction between a silyl ketene acetal and an imine catalysed by a Zr–BINOL complex gave the resultant β-amino ester with 98% ee

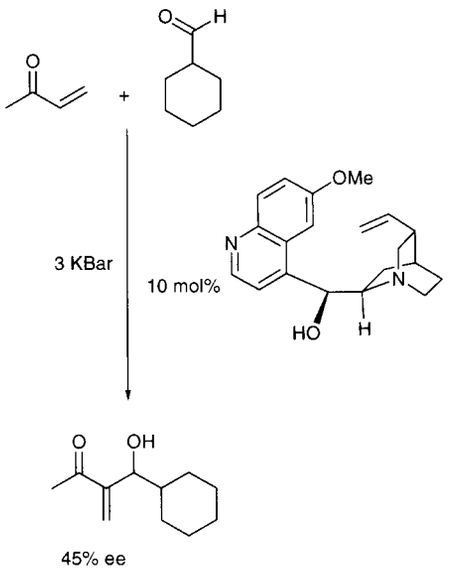

**Scheme 34**

(Scheme 35), the *o*-phenol group being essential for good enantioselectivity in the reaction. A related addition of lithium ester enolates to imines catalysed by a $C_2$ symmetric diether resulted in the formation of β-lactams with up to 75% ee.[191] The addition of diethylzinc to phosphinamide protected imines in the presence of 5 mol% of dendrimer bound chiral amino alcohols has been reported to give amines with up to 92% ee.[192]




**Scheme 35**

Finally, within this section, we shall mention two reactions which exist in categories of their own. Mikami has further studied the Ti(IV) catalysed carbonyl–ene reaction reporting one example where a combination of chiral ligands was successfully employed in the ene reaction between a styrene derivative and a glyoxalate ester giving a product with 97% ee.[193] Marko and co-workers have reported a noteworthy example of an asymmetric Baylis–Hillman reaction (Scheme 36).[194] The use of high pressure along with 10 mol% of quinidine gave the product vinyl alcohol with 45% ee, a result which will no doubt be improved by optimisation studies.



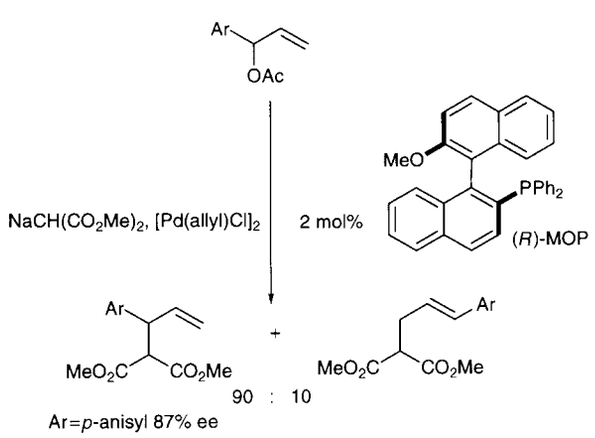

**Scheme 36**

### 2.3.2 Palladium-catalysed allylic substitution

As in previous years there remains great interest in the Pd-catalysed allylic substitution reaction, the most popular transformation being the reaction of the dimethyl malonate anion with 1,3-diphenylallylic substrates.[195–211] The large number of examples precludes any possibility of an in depth discussion of this reaction, however the new ligands employed are shown in Fig. 3. It should be noted that the reaction conditions are not the same in each case and the reader should refer to the original references for more details.

Although technically not a C–C bond forming reaction the related allylic amination reaction will be included at this point. Sudo and Saigo have reported a new P–N ligand (Fig. 4) specifically designed for the addition of amine nucleophiles to 1,3-diphenylallylic substrates giving allylic amines with up to 99% ee.[212] Togni and co-workers have studied the effect of hard and soft counterions in the allylic amination reaction catalysed by his P–N ferrocenyl ligand.[213] He notes that the addition of tetrabutylammonium salts can have a dramatic effect on the enantioselectivity of the reaction depending on the nature of the counterion. Hard $F^-$ ions giving 99% ee whilst soft $PF_6^-$ ions give only 10% ee under otherwise identical conditions.

Not all allylic substitution reactions employ 1,3-diphenylallylic compounds as substrates. Hayashi and co-workers reported the alkylation of 1-phenyl-1-acetoxyprop-2-ene using the MOP ligand to give the 1-substituted product in 90% yield and 87% ee, with only 10% of the unwanted terminally substituted compound being formed (Scheme 37).[214] Trost and Ariza have reported new applications of their $C_2$ symmetric bisphosphine ligand in reactions with cyclic allylic acetates and carbonates. The first example is a reaction of azalactone derived nucleophiles in the synthesis of α-alkylated amino acids with up to 95% ee.[215] The second example involves the addition of tetralone enolate derivatives to a cyclohexyl allylic carbonate with 99% ee.[216] The product, containing a quaternary chiral centre, was then elaborated to the natural product (−)-nitramine. Thirdly an example of a desymmetrisation of a *meso*-allylic ester is the key step in the synthesis of (−)-nephanocin and its 2,3-di-epi-isomer.[217]




**Scheme 37**

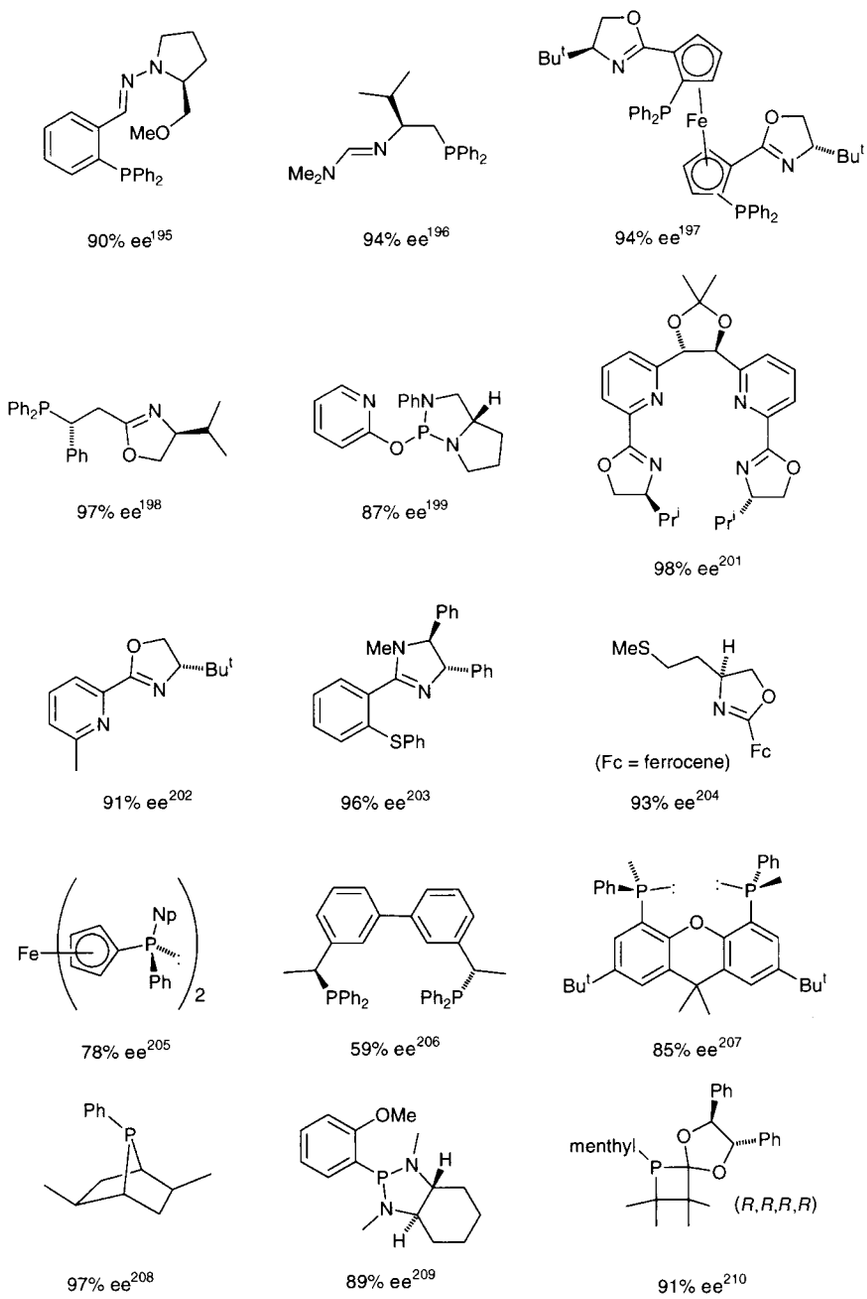



**Fig. 3** Ligands used in the asymmetric catalysis of allylic substitution reactions.

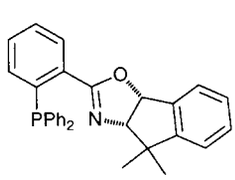
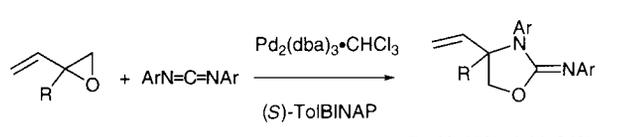


**Fig. 4**



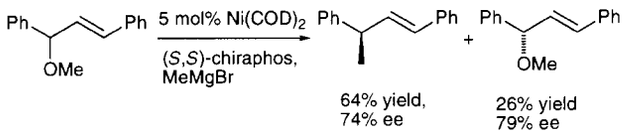

**Scheme 38**

A more complex example of an allylic amination step which forms part of a cycloaddition reaction to form vinyloxazolidine derivatives has been reported by Larksarp and Alper.[218] The reaction involves the Pd–(*S*)-Tol–BINAP catalysed addition of an aryldiimide to a vinyloxirane initially forming a palladium–allyl species which then cyclises to form the desired vinyloxazolidine derivative in 95% yield and up to 94% ee (Scheme 38).

A closely related nickel-catalysed allylic substitution reaction will be included at this point. Nomura and co-workers have reported a kinetic resolution of methyl 1,3-diphenylallyl ether employing the Ni(0)-(*S*,*S*)-Chiraphos catalysed addition of methylmagnesium bromide.[219] Unreacted methyl ether is recovered with a yield of 26% and 79% ee along with 64% yield of the methyl substituted compound with 74% ee (Scheme 39).

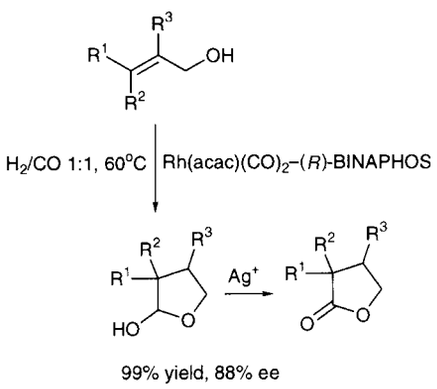
### 2.3.3 Hydroformylation, Heck and related reactions

The catalytic asymmetric hydroformylation reaction has received an increasing degree of attention over the past year.[220–224] Of particular interest is the use of a Pt–Sn–diphosphine complex (as opposed to the more usual Pd or Rh catalysts) in the hydroformylation of styrene derivatives.[221,222] Whilst the degree of enantioselectivity is high for such catalytic systems, they do suffer from a reduced level of regioselectivity and competing hydrogenation of the substrate. Nozaki and co-

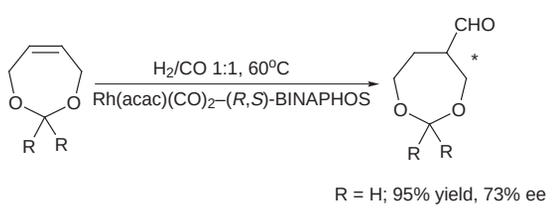



**Scheme 39**

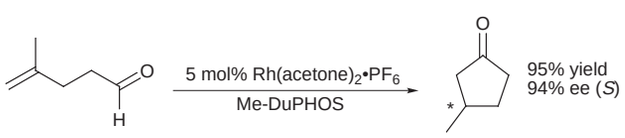
workers have reported an interesting example of hydroformylation of allylic alcohols using a Rh–BINAPHOS catalyst.[223] The initial product of the reaction is a lactol formed with up to 88% ee which is then converted into the corresponding lactone by use of an Ag(I) salt (Scheme 40). Nozaki has also reported the hydroformylation of *meso*-heterocyclic olefins using the same catalyst system giving rise to products with up to 73% ee (Scheme 41).[224] Some variations on the hydroformylation reaction including a hydrocyanation of norbornene,[225] an intramolecular hydroacylation reaction[226,227] (Scheme 42) and a Pd catalysed alkoxy carbonylation reaction[228] have also been reported.




**Scheme 40**




**Scheme 41**

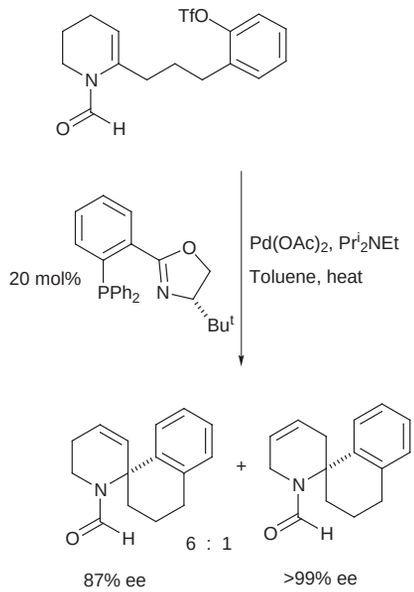



**Scheme 42**

A few new examples of catalytic, asymmetric Heck reactions have appeared.[229,230] Ripa and Halberg have applied Pfaltz's oxazoline–phosphine ligand to an intramolecular Heck reaction between an enamide and a triflate to give spiroamide products in up to 99% ee (Scheme 43).[229] Shibasaki and co-workers have prepared an arsine derivative of BINAP (BINAS) which they employed in an intramolecular Heck reaction to give products of up to 83% ee.[230]

### 2.3.4 Cyclopropanations

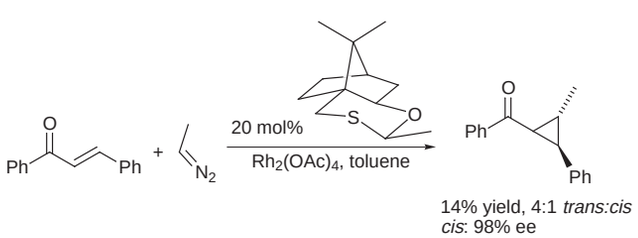
The area of catalytic asymmetric cyclopropanation is still largely dominated by Cu and Rh complexes. A few new examples of oxazoline and bis-oxazoline derived ligands for the Cu(I) catalysed cyclopropanation of styrene derivatives with alkyl diazo carboxylates have been reported,[231–235] however most systems provide good enantioselectivity at the expense of




**Scheme 43**

*cis–trans* selectivity. In cases where the *cis–trans* selectivity has been good the enantiomeric ratio of the products is generally lower, although this can be improved to some extent by using a menthyl-derived diazo carboxylate.[235] The use of olefin substrates other than styrene is less common. One example reported by Schumacher employs silyl enol ethers resulting in the formation of cyclopropyl alcohols of up to 77% ee. However the *cis–trans* selectivity is again rather poor; only 41 : 59 in this case.[236]

Some new examples of Rh complexes have also been reported to catalyse the cyclopropanation of styrene,[237–239] but none improve upon the levels of selectivity that Doyle and co-workers have reported in previous years. One significantly new approach to the Rh catalysed reaction is that reported by Aggarwal and co-workers who employed a chiral sulfide in the cyclopropanation of electron deficient olefins (Scheme 44).[240] Very high levels of enantioselectivity can be achieved when using either stoichiometric amounts of the sulfide or as little as 20 mol%. The only problem is the low activity of the catalytic system which affords only 14% conversion when 20 mol% of the sulfide is used. However, one must consider that these are only preliminary results and are bound to be improved upon further study.




**Scheme 44**

A new type of cyclopropanation reaction has entered onto the scene during 1997, namely the Ru–porphyrin catalysed cyclopropanation of styrene again with diazo carboxylates.[241–243] Three groups have reported chiral porphyrin derived catalysts with varying success. The best results have been achieved by Frauenkorn and Berkessel who achieved a *trans–cis* ratio of 95 : 5 and an enantioselectivity of 91% for the *trans* isomer (Fig. 5).[243] Several examples employing chiral bis-sulfonamide ligands in a Simmons–Smith cyclopropanation of a range of allylic alcohols have been reported.[148,149,244] Enantioselectivities of up to 85% can be achieved when 10 mol% of a chiral ligand is employed (Scheme 45).[244]

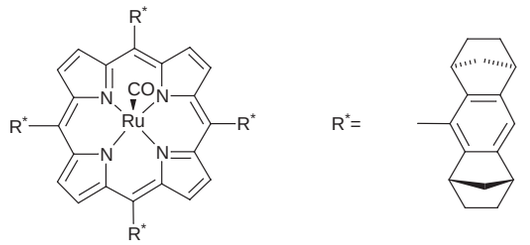
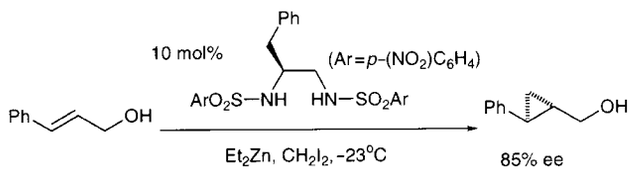


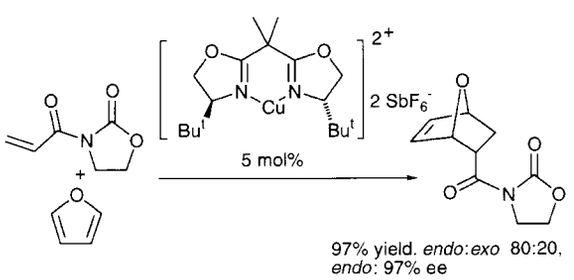
Fig. 5



Scheme 45

### 2.3.5 Cycloaddition reactions

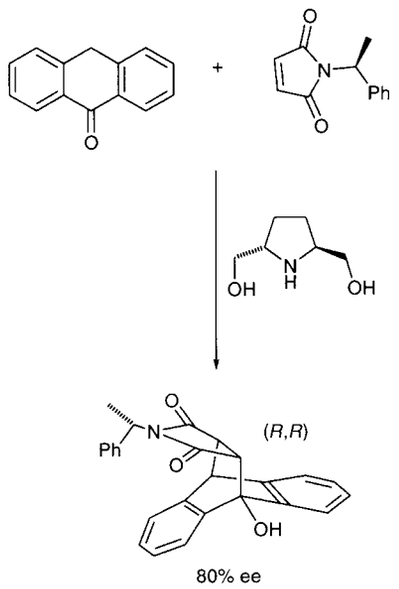
The Diels–Alder reaction between cyclopentadiene and a variety of electron deficient alkenes catalysed by oxazoline or bisoxazoline complexes of Cu, Mg, Ni, Zn or Rh has remained a popular area for investigation.[245–251] However, some more exotic examples of Diels–Alder reactions have somewhat stolen the limelight for 1997. Evans and Barnes have reported the first example of a furan Diels–Alder reaction using his Cu–bis-oxazoline catalyst providing 7-oxabicyclo[2.2.1]heptene derivatives in up to 97% ee (Scheme 46).[252] Corey[253] and Yamamoto[254] and their co-workers have demonstrated the reaction of electron deficient acetylenes with cyclopentadiene to give bicyclodienes in good to excellent ee. A rather unusual chiral base catalysed [4+2] cycloaddition between anthrone and *N*-substituted maleimides gave products with up to 80% ee when a chiral protecting group was present on the maleimide fragment (Scheme 47).[255]



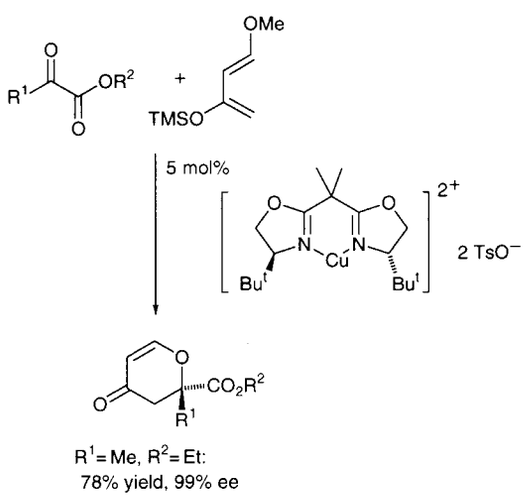
Scheme 46

Several examples of hetero Diels–Alder reactions employing Danishefsky's diene (DD) have been published.[256–259] Matsukawa and Mikami reported a Ti(IV) mixed BINOL catalyst system for the reaction of DD with glyoxalates with up to 84% ee.[256] A similar reaction of DD with aldehydes using a BINOL derived Yb(III) phosphate gave up to 93% ee.[257] Jorgensen and co-workers reported the first example of the related hetero Diels–Alder reaction of ketones catalysed by a Cu–bis-oxazoline complex with up to 99% ee (Scheme 48).[258] Reaction of a thio enone as the diene in a hetero [4+2] reaction catalysed by a $C_2$ symmetric Schiff base–Cu catalyst gave good *exo* to *endo* selectivity with up to 65% ee for the *endo* isomer.[260]

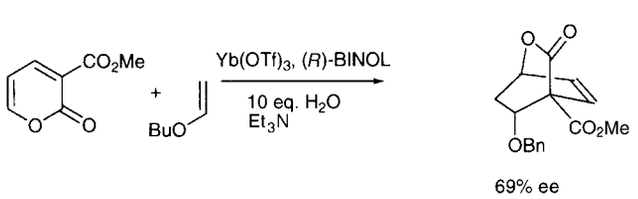
Marko and co-workers have reported an inverse electron demand Diels–Alder reaction of 3-methoxycarbonyl-2-pyrone in the presence of a Yb(III)–BINOL complex. Interestingly the addition of 10 equiv. of water to the reaction leads to an increase in ee from 30 to 69%, a similar result is achieved by the inclusion of THF in the solvent mixture (Scheme 49).[261]



Scheme 47

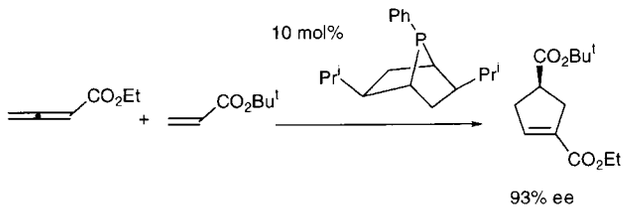


Scheme 48

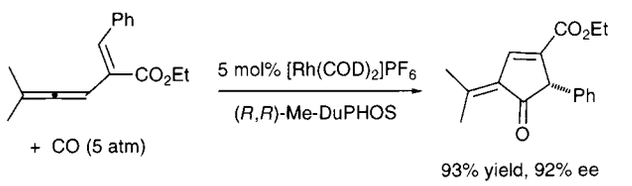


Scheme 49

Other cycloaddition reactions which have attracted interest include 1,3-dipolar cycloadditions.[262–265] Jorgensen reported two examples of cycloadditions of nitrones to oxazolidinone derivatised olefins, one employing a Yb(III)–pybox catalyst[262] and the other a TADDOL–Ti–bis-tosylate[264] which gave excellent *exo–endo* selectivity and good enantioselectivity. [3+2] Cycloaddition of an allene with an electron poor olefin catalysed by 10 mol% of a $C_2$ symmetric phosphabicyclo[2.2.1]-heptane gave rise to cyclopentenes with complete regioselectivity and up to 93% ee (Scheme 50).[266] Finally an unusual [4+1] cycloaddition reaction was reported by Ito and co-workers.[267] The Rh–DUPHOS catalysed reaction between CO and a vinyl allene proceeded with up to 92% ee (Scheme 51), although poorer selectivity was observed for allene substrates which did not contain an ester group.



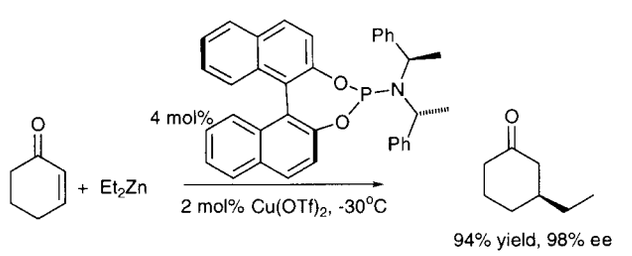

**Scheme 50**



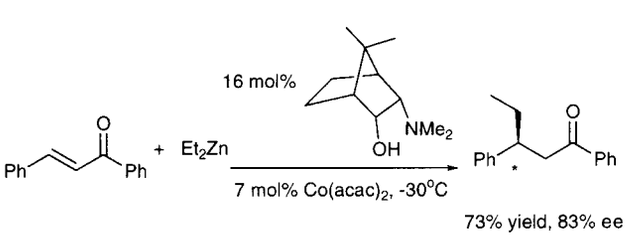

**Scheme 51**

### 2.3.6 Addition of carbon nucleophiles to C=C bonds

The catalytic asymmetric Michael addition reaction finally entered onto the scene in 1997. Several examples have been published, principally of the Cu catalysed addition of $Et_2Zn$ to enones.[268–272] Feringa and co-workers have produced perhaps the most impressive result employing a mono-dentate amino phosphite ligand in the Cu catalysed addition of $Et_2Zn$ to cyclohexenone in up to 98% ee using only 4 mol% of ligand (Scheme 52).[268] It is interesting to note that although a Cu(II) source is utilised in the reaction it is believed that Cu(I) is the active catalyst, but the mechanism for the conversion to Cu(I) is as yet unexplained. Other successful ligands giving moderate to good enantioselectivities for the 1,4-addition of dialkylzincs to cyclohexenone include a mono-dentate phosphite,[270] diphosphines,[271] a pyridyl thiazolidinone[272] and a phosphite-oxazoline.[273] However, all systems only seem to work well for cyclic enones and give dramatically reduced enantioselectivity for linear enones such as chalcone. Feringa and co-workers have tackled the problem of linear enones by employing chiral amino alcohols as ligands for Ni(II) and Co(II) in the addition of $Et_2Zn$ to *trans*-chalcone giving products of up to 83% ee using 7 mol% of catalyst (Scheme 53).[274,275]

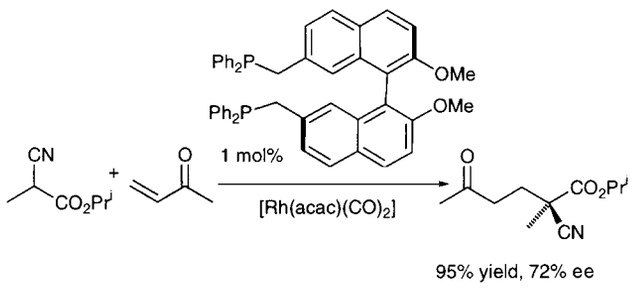



**Scheme 52**



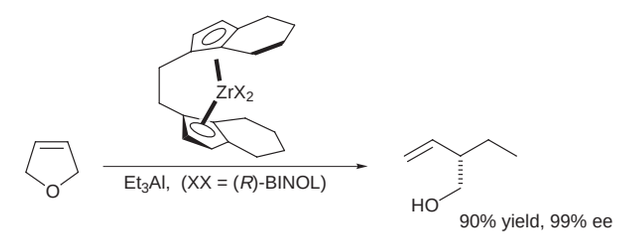

**Scheme 53**

The Michael addition of a variety of soft nucleophiles to linear enones has also been tackled with some success in the past year.[276–280] Takaya and co-workers have developed a large bite angle bis-phosphine for the Rh(I) catalysed addition of α-cyano esters to enones giving products of up to 72% ee (Scheme 54).[277] Feringa and co-workers have also been active in this area reporting an Li–Al–BINOL catalyst for the addition of α-nitro esters with up to 80% ee when 5–10 mol% of catalyst was used.[278] A somewhat different approach has been reported by Bako and co-workers who used a chiral phase transfer catalyst for the NaO$^t$Bu mediated addition of 2-nitropropane to *trans*-chalcone with an impressive 90% ee.[279] An interesting reaction between electron rich furans and butenyl-1,3-oxazolidin-2-ones has been carried out using either Sc(III)–BINOL or Cu(II)–bisoxazoline catalysts in up to 95% ee and with moderate to good diastereoselectivity.[280] The Michael addition of a carbon radical species in the presence of 10–30 mol% of a bis-oxazoline–Mg complex has been reported to give products of up to 97% ee at −78 °C and 93% ee at room temperature.[281]




**Scheme 54**

Finally, Whitby and co-workers have reported an asymmetric carbometallation reaction using Britzinger's catalyst.[282] The reaction of triethylaluminium with an endocyclic olefin resulted in the formation of a vinylic *sec*-alcohol of 99% ee (Scheme 55).




**Scheme 55**

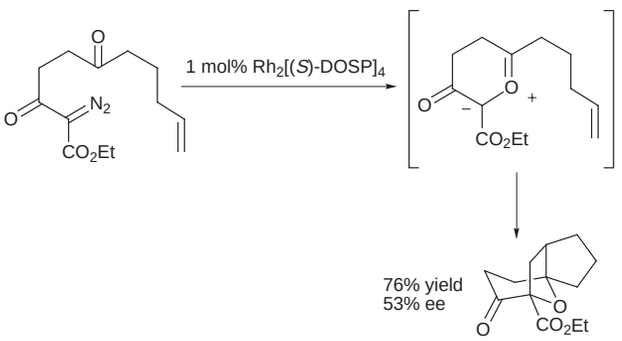
### 2.3.7 Other C–C bond forming reactions

This section deals with a number of different reactions which do not fit readily into any of the above sections. A Zr catalysed diene cyclisation reaction to form nitrogen heterocycles employed Britzinger's catalyst to good effect providing products of up to 95% ee although with poor diastereoselectivity.[283] Two examples of Ni catalysed Grignard cross coupling reactions were reported. The first by Nagel and Nedden using a pyrrolidine–phosphine ligand to couple vinyl halides with α-methyl benzyl Grignard gave a product of up to 88% ee.[284] The second example, coupling a similar Grignard with bromostyrene catalysed by an amino phosphine gave a product of up to 94% ee.[285] A more unusual cross coupling between an allylic alcohol and a terminal acetylene to give an allylic ketone was reported by Takei and co-workers.[286] The reaction catalysed by an Ru complex is thought to proceed *via* an Ru–vinylidene species although the overall mechanism has not been fully elucidated.

Two groups have reported the use of alkaloid derived chiral phase transfer catalysts for the synthesis of amino acid derivatives. The reaction involves the formation of a glycine enolate which is then trapped with a variety of alkyl halides to give amino acid derivatives in up to 90% ee.[287,288]

Carbene insertion into C–H bonds continues to be an area of some interest.[289–291] An example of an intermolecular reaction was reported by Davies and Hansen who used $Rh_2$[(*S*)-DOSP]$_4$ {DOSP = *N*-[(4-dodecylphenyl)sulfonyl]proline} to catalyse the

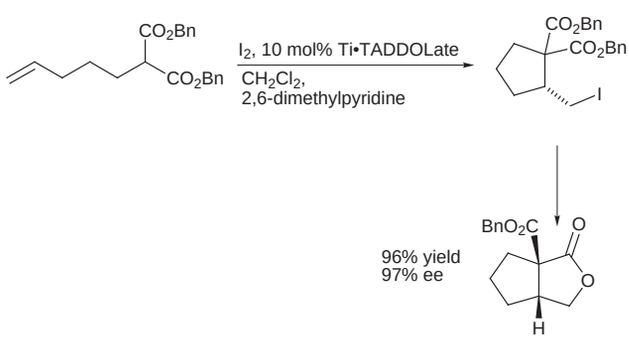
reaction between cyclohexane and a diazo ester in up to 83% ee and moderate yield.[289] Hodgson and co-workers have reported a particularly interesting example of an intramolecular carbene insertion to give a complex tricyclic product (Scheme 56).[291] The reaction involves an unusual tandem carbonyl ylide formation and cycloaddition reaction. Although the enantioselectivity is only modest (53%) this represents a promising entry into previously uncharted territory for catalytic asymmetric reactions. A related tandem intramolecular oxonium ylide formation, a [2,3]-sigmatropic rearrangement reaction using a *tert*-leucine derived Rh(II) carboxylate as catalyst has been reported by McKervey and co-workers.[292]




**Scheme 56**

The stereoselective [2,3]-sigmatropic rearrangement of sulfur ylides generated by reaction of a sulfide with a diazoacetate in the presence of catalytic quantities of a Co(III)–Salen complex have been reported to proceed in up to 74% ee when the menthyl derived diazoacetate is employed.[293] A Pd(II) catalysed rearrangement of allylic imidates to allylic amides has been reported to give products with up to 55% ee when 5 mol% of a chiral diamine ligand was employed.[294]

Finally two examples of enantiotopic differentiating reactions are worth noting.[295,296] Jadhav and May have reported the reaction of a Yb–bis-oxazoline catalysed reaction in which enantiotopic differentiation of two $sp^3$ chlorides was achieved with up to 88% enantioselectivity.[295] Taguchi and co-workers have developed an asymmetric iodo carbocyclisation reaction of alk-4-enyl malonates catalysed by a Ti-TADDOLate (Scheme 57).[296] The lactone product is produced with an impressive 97% ee when 2,6-dimethylpyridine is added as an HI scavenger.




**Scheme 57**

## 2.4 Miscellaneous applications of synthetic asymmetric catalysts

Catalytic asymmetric ring opening of *meso* (usually cyclic) epoxides may be achieved through the use of a number of nucleophilic reagents.[297–302] These include azide,[297–299] carboxylic acids,[300] thiols[301] and cyanide anion.[302] Using a chromium–salen complex as catalyst, 1,2-epoxycyclohex-4-ene may be ring opened in 93% yield and 92% ee to yield a key intermediate in the synthesis of balanol.[297] Other notable catalysts which have been employed in related reactions include

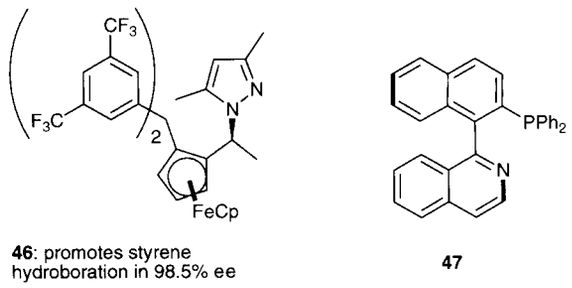
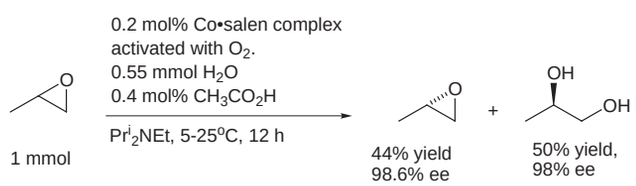



**Fig. 6**

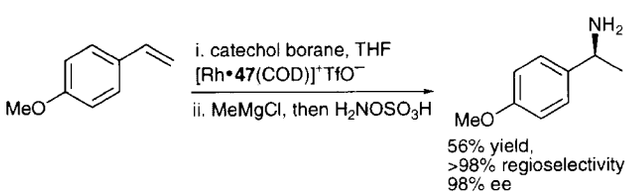
gallium–BINOL complexes[301] and titanium–diol complexes derived from spiroketals.[298] In addition further results of the ingenious combinatorial-modification approach to the optimisation of a titanium(IV) complex for this application have been reported.[302]

Kinetic resolution of racemic epoxides using asymmetric catalysis is a known process, however the use of only 0.2 mol% of a salen–cobalt complex serves to provide an excellent catalysis for the almost perfectly enantioselective ring opening of epoxypropene to a diol (Scheme 58).[303]




**Scheme 58**

Methods for the organometallic catalysis of asymmetric hydroboration of styrene and its derivatives have been known for some years now, however the development of new and improved ligands continues. The presence of the bis(trifluoromethyl)aryl groups in **46** (Fig. 6) is essential for high selectivity (only 5% ee is achieved if these are replaced by *p*-methoxyphenyl groups).[304] The mixed-donor ligand **47** is equally efficient, but an interesting variant on this process is the conversion of the initial hydroborated material into an amine (Scheme 59) in a one-pot process.[305,306] The result is a new efficient process for the electrophilic amination of styrenes. Amination of prochiral alkenes may also be achieved, in up to 95% ee, through the use of phenylamine coupled to an iridium–BINAP complex.[307]

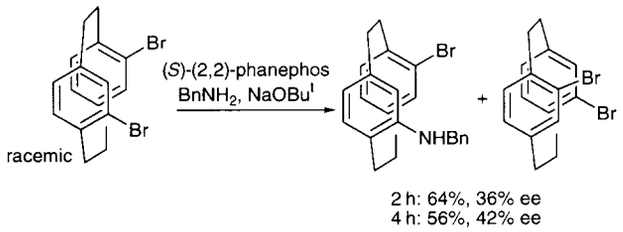



**Scheme 59**

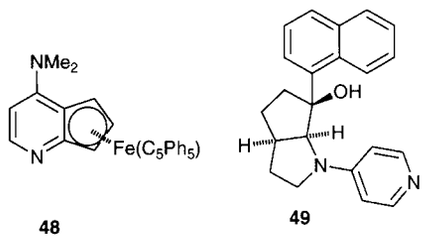
In an alternative approach to asymmetric amination, (*S*)-2,2-phanephos **17** proved to be an excellent ligand for the asymmetric kinetic resolution of a racemic dibromide using the popular Buchwald–Hartwig amination methodology.[308] This transformation is depicted in Scheme 60.

Some interesting new ligands **48**,[309] and **49**,[310] have been employed for the asymmetric catalysis of alcohol esterification. Acting upon racemic 1-(naphthyl)ethanol, the *S*-enantiomer is recovered in 99% ee at 63% conversion (a calculated *S* factor of 22) using **48**. Using **49** for the kinetic resolution of racemic monoesterified cyclohexane-1,2-diol derivatives, starting materials of up to 99% ee were recovered at 72% conversion.

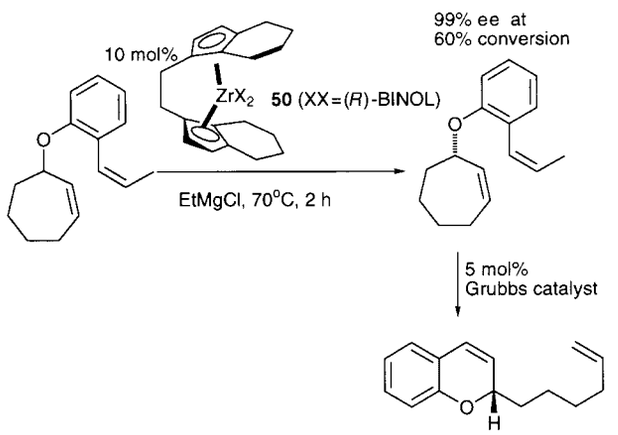
Highly efficient kinetic resolution of racemic *O*-aryl deriv-




**Scheme 60**




atives of cyclic allylic alcohols may be achieved by an asymmetric carbometallation process followed by a metathesis reaction (Scheme 61) using an enantiomerically pure catalyst **50**.[311]



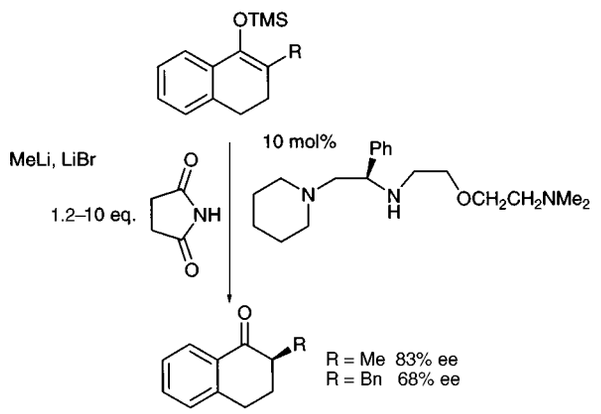

**Scheme 61**

Asymmetric insertions of carbenes into Si–H bonds may be catalysed by chiral dirhodium complexes.[312] Asymmetric intramolecular addition of a silicon–silicon bond across an alkene has been catalysed in up to 59% ee through the use of a palladium–isonitrile complex.[313]

Asymmetric catalysis of the addition of phosphinate esters to aldehydes using a combination of 10 mol% of a lanthanide–BINOL complex gives α-hydroxy phosphates in up to a remarkable 95% ee.[314,315] Although a venerable reaction by the timescale of developments in asymmetric catalysis, the asymmetric isomerisation of certain prochiral bis-silylated *meso*-allylic diols using rhodium–BINAP is reported to proceed in a remarkable 98% ee.[316]

Asymmetric copolymerisation has been the subject of increasing attention in recent years. Using a combined phosphine/phosphonite ligand within a palladium complex the copolymerisation of carbon monoxide and propene may be controlled with an unprecedented degree of enantioinduction.[317]

The reaction of a prochiral epoxide (usually cyclic) with an enantiopure base is known to be a highly controlled process in which high enantioinductions may be achieved. In recent years careful control of the reaction conditions has resulted in the development of *catalytic* variants of these processes, in which as little as 20 mol% of chiral base is required.[318,319] Very much the same is true of asymmetric protonation methodology, which has also been rendered catalytic with respect to chiral directing agents through careful control of reaction conditions (Scheme 62).[320] In the example shown the product was obtained in 91% ee using a stoichiometric amount of chiral ligand. An equally effective system based on a combination of palladium(II) and BINAP with silver(I) salts as additives, has also been reported.[321]




**Scheme 62**

## 3 Enzymes and antibodies

Nature's own asymmetric catalysts continue to find prolific applications in organic synthesis. Through the dual strategy of substrate engineering (finding the best substrate for an enzyme) and genetic engineering of the enzyme, biocatalysis has already achieved widespread acceptance throughout the synthetic community. In particular the extraordinary ability of enzymatic systems to effect *deracemisation* is one area in which biotransformations dominate.[322] As in past years, the volume of work in this area makes comprehensive coverage impossible, therefore the emphasis will be on what is perceived to be highly significant new developments in the area.

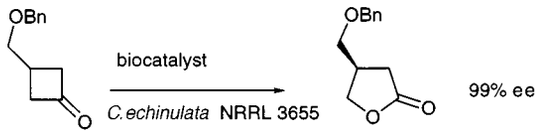
### 3.1 Reductions and oxidations

Methane mono-oxygenase (MMO) is an enzyme which performs probably the simplest oxidative process one can envisage, however its potential for asymmetric catalysis, whilst obvious, remains somewhat underdeveloped at present.[323] Whilst MMO is capable of asymmetric epoxidations of low molecular weight alkenes, the related chloroperoxidase is highly effective at asymmetric epoxidation of a variety of functionalised substrates with impressive selectivity.[324]

Kinetic resolution, through selective oxidation, of racemic α-hydroxy acids using glycolate oxidase (from spinach) is a remarkable process, delivering a product of 99% ee at 50% conversion![325] Enantioselective oxidation of one hydroxy group within a symmetrical diol is an ever popular '*meso*-trick' which can be coupled to a transition metal complex to assist with catalyst regeneration and turnover.[326]

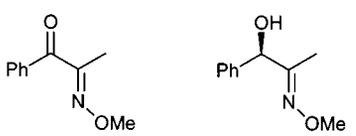
Baeyer–Villiger oxidations of prochiral cyclic substrates may be catalysed in an asymmetric sense with excellent stereocontrol.[327–329] This may be achieved through the use of whole cell systems (*e.g.* Scheme 63)[327] or by the coupling of a mono-oxygenase with a formate dehydrogenase; the latter mediating regeneration of the former.[329] Microbacterial methods for the asymmetric dihydroxylation of aromatic rings continue to be extended to more and more varied substrates.[330] Both established and modified strains of whole cell cultures are serving to extend considerably the versatility of this reaction, which often proceeds with total enantiocontrol. The same is very much true of asymmetric sulfoxidation reactions, which continue to be developed apace.[331]

Asymmetric reduction of ketones is without doubt one of the most valuable and versatile of all biotransformations. Whilst




**Scheme 63**

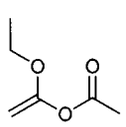
many new applications are reported each year, new modifications and developments of the basic process are continually being reported.[332] Many functional groups are compatible with asymmetric ketone reduction, including nitriles,[333] carboxylic acids,[334] sulfones[335,336] and halides.[336,337] In some cases reduction may be carried out together with ester hydrolysis, thus combining two useful processes into one step.[338] The reduction of ketone **51** containing an adjacent oxime ether, gives the corresponding alcohol **52** in 97% ee when Bakers' yeast was used.[339] Diastereoselective chemical reduction of the ketone completed a useful synthesis of β-amino alcohols. Reduction of both carbonyl groups of an α-diketone may be achieved through the use of *Bacillus steareothermophilis*.[340] Reduction of butanedione gave a diol product of >98% ee, whilst (*S*,*S*)-cyclohexane-1,2-diol was available through a similar process in up to 95% ee. Dynamic kinetic resolution of α-substituted β-keto esters, which are known to racemise rapidly, is a useful technique for the creation of two stereogenic centres in a single asymmetric process.[341]




**51** **52** 97% ee

### 3.2 Lipases

Kinetic resolution of alcohols or carboxylic acids through the action of lipases has been long established. This method is made considerably more amenable to the wide synthetic community through the use of commercially available cross linked enzyme crystals or 'CLEC' reagents.[342] These robust materials which may be used in either aqueous or mixed organic–aqueous environments for numerous amide and ester hydrolysis processes. Kinetic resolution of alcohols usually requires the use of a suitable acylating source, such as vinyl acetate. Modified reagents are available for this application, including **53** which avoids the sometimes troublesome formation of acetaldehyde as a side product.[343]

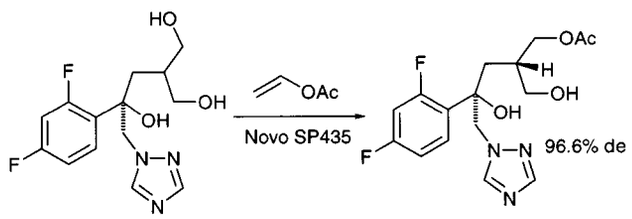



**53**

In any kinetic resolution process, it is a difference in the rate of hydrolysis or acylation which determines the product ee. The measurement of these rates can be laborious however using a newly developed process in which the rate of formation of a strongly UV-active phenol from the substrate under study is directly compared with a known hydrolysis process simultaneously taking place in the same reaction vessel. Since the rate of the latter hydrolysis is known, the rate of the unknown can be directly determined.[344]

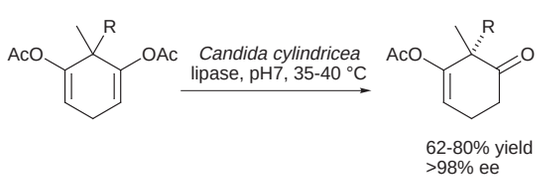
The versatility of kinetic resolution processes is quite remarkable, and new applications are constantly being reported. Fig. 7 illustrates some representative examples of alcohols which have been subjected to a kinetic resolution process this year.[345–352] In all the previous cases, the resolution was achieved through an acylation process which can also be applied to nonsymmetric diols.[353–355] Where there is a clear reactivity difference (*i.e.* tertiary *versus* primary) then the resolution process generally follows a sterically directed path.[353,354] The situation becomes a little more complex when two alcohols within a molecule are of similar reactivity, but may still be turned to the advantage of the synthetic chemist through careful planning.[355]

Acetylation of prochiral diols is of course an excellent method for the synthesis of enantiomerically pure compounds in both high ee and conversion, since all of the starting material may theoretically be converted into product.[356–358] The example shown in Scheme 64 gave a product of almost 97% de which was used in the synthesis of an orally active antifungal compound.[356]

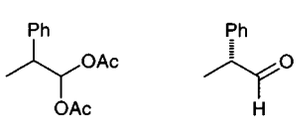



**Scheme 64**

Essentially equally efficient resolutions may be achieved through the hydrolysis of racemic acetates or prochiral diacetates of diols.[359–362] Prochiral enol ether hydrolysis provides an effective method for the asymmetric synthesis of compounds containing quaternary centres (Scheme 65).[363] In an interesting variation selective hydrolysis of one enantiomer of **54** resulted in conversion into an aldehyde **55** in 72% ee.[364] The opposite configuration of unreacted diacetate was recovered in 62% ee. Asymmetric hydrolysis of the carbonate of a 1,2-diol has also been reported to proceed with high selectivity.[365] Although the above discussion has focussed on the alcohol component, asymmetric hydrolysis processes may also be applied to the resolution of the carboxylic acid component as well.[366]




**Scheme 65**




**54** **55**

Enzymes have been employed for deracemisation processes for some years. In contrast to the '*meso* tricks' or conversions of prochiral compounds, which are not racemic to begin with, desymmetrisation involves coupling a rapid racemisation process to an enzymic transformation. This approach is in theory applicable to the hydrolysis of acetylated hemithioacetals,[367] and works well for the conversion of racemic **56** into **57** in 76% ee at >99% conversion.[368] A rapid racemisation of alcohol **58** catalysed by ruthenium complex **59** coupled to Novo-435 catalysed acylation gives acetate **60** in an extraordinary 100% yield and >99.5% ee.[369] A particular feature of this remarkable reaction is the requirement for the use of *p*-chlorophenyl acetate as the acetate source together with an equivalent of

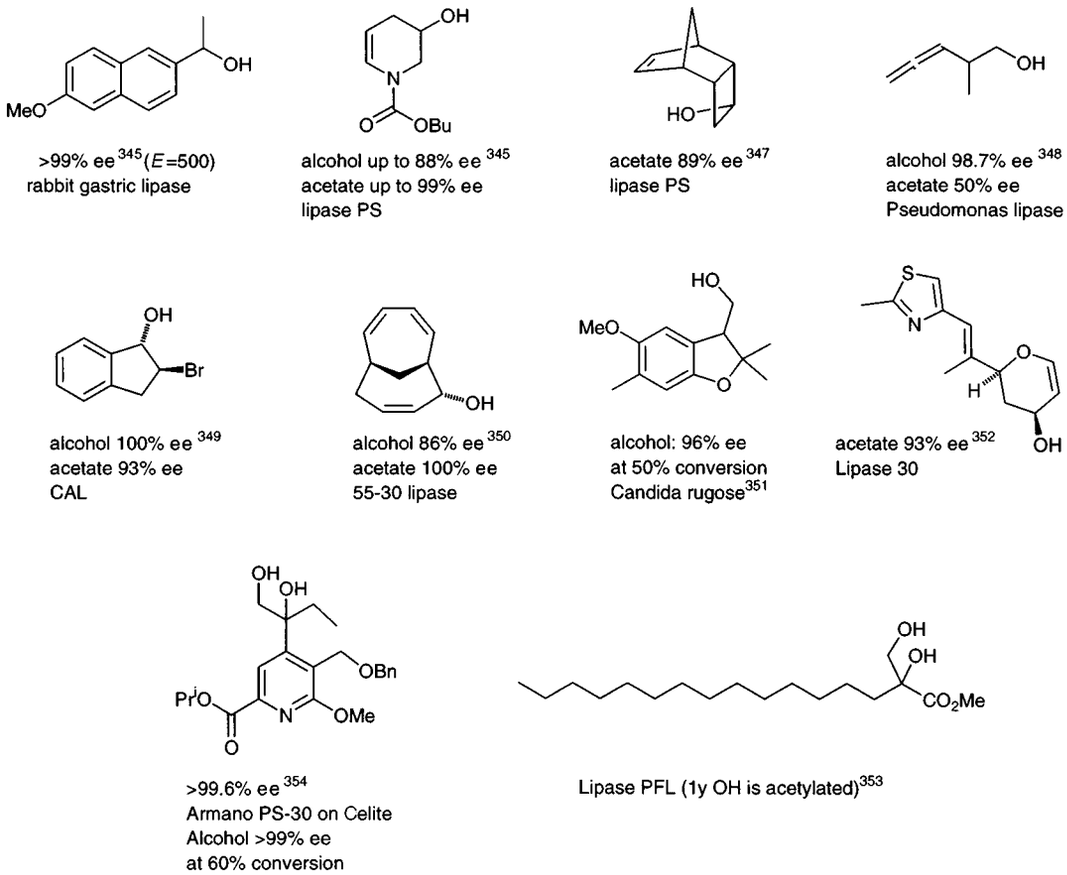
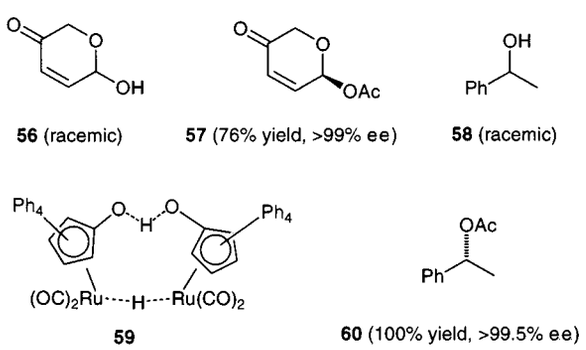



**Fig. 7** Representative substrates used in kinetic resolution of racemic alcohols.

acetophenone to act as the hydride acceptor in the racemisation process, which takes place *via* an oxidation–reduction sequence. Under these conditions vinyl acetate would release acetone, which would compete in the reduction process.

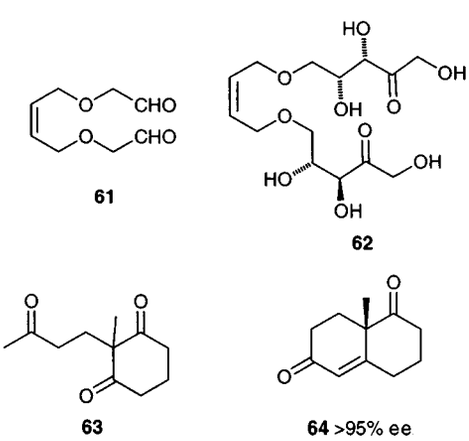



Antibodies are still relatively rare in synthetic applications, despite the relatively high level of research interest in them.[370,371] Asymmetric ester hydrolysis is one of their particular strengths and an antibody catalysed process for the hydrolysis of naproxen esters was reported to proceed with an *E* value of up to 123, which is competitive with levels achieved by enzymes.[370] In this application, as is usually the popular option, the hapten to which antibodies were raised was based on a phosphate ester structure.

### 3.3 Miscellaneous biotransformations

Although long established, valuable improved methods for miscellaneous transformations such as the oxynitrilase catalysed asymmetric addition of HCN to aldehydes,[372] hydrationase promoted ring opening to give *N*-urea derivatives of amino acids[373] and enantioselective epoxide opening[374–377] continue to be reported. Coupling a genetically engineered *E. coli* strain containing a modified transaminase with butyrate decarboxylase results in a system for the very efficient synthesis of modified amino acids from the prerequisite α-keto acids.[378]

Aldolases have now been developed to a high level of complexity by a number of groups, but perhaps most notably by that of Wong.[379,380] A simple enzyme system permits the conversion, for example, of dialdehyde **61** into highly complex productions such as **62** with a remarkably high level of enantiocontrol.[379] Antibodies have also been developed for intramolecular aldol reactions.[381] One example is the conversion of **63** into **64** in >95% ee using an antibody in which the amine of a lysine group is believed specifically to be responsible for directing the cyclisation process. This may be through the formation of an enamine intermediate, as has been demonstrated for the same reaction when catalysed by an enantiomerically pure amine.



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